THE SYNTHESIS AND ELECTRICAL PROPERTIES OF FUNCTIONAL POLYMER NANOCOMPOSITES

by

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Submitted in partial fulfillment of the requirements
For the degree of Doctor of Philosophy

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Dedication

To my beloved parents, Yongjin Zhang and Mingqin Wu, and all best friends in my life
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>III</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>IV</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>V</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>XII</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>XV</td>
</tr>
<tr>
<td>CHAPTER 1: Introduction</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 2: Interfacial Polarization-induced Loss Mechanisms in Polypropylene/BaTiO₃ nanocomposite dielectrics</td>
<td>54</td>
</tr>
<tr>
<td>CHAPTER 3: The Role of Field Electron Emission in Polypropylene/Aluminum Nanodielectrics Under High Electric Fields</td>
<td>93</td>
</tr>
<tr>
<td>CHAPTER 4: Thermally stable metallic nanoparticles prepared via core-crosslinked block copolymer micellar nanoreactors</td>
<td>126</td>
</tr>
<tr>
<td>CHAPTER 5: Conclusions and future work</td>
<td>151</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>156</td>
</tr>
</tbody>
</table>
LIST of TABLES

Chapter 1
1.1 Dielectric constants for various common inorganic nanofillers..........................26

Chapter 3
3.1 Fitting parameters in hopping and Fowler-Nordheim tunneling models.......114

Chapter 4
4.1 Block composition and polydispersity of five PS-\textit{b}-P4VP BCPs.................138
LIST of SCHEMES

Chapter 2
2.1 (A) Synthesis of the POSS(PA)$_2$ ligand and (B) Procedure of surface modification of 70 nm BT NPs with POSS(PA)$_2$ and preparation of PP/BT@POSS nanocomposites via sequential solution- and melt-blending methods..................................................61
2.2 Proposed mechanism of interfacial polarization-induced internal AC conduction loss due to large permittivity and conductivity contrasts between BT NPs and the PP matrix........................................................................................................80

Chapter 3
3.1 (A) Synthesis of the PEB-PA ligand and (B) Procedure of surface modification of 18 and 100 nm nAl NPs with PEB-PA and preparation of PP/nAl@PEB-PA nanocomposites via sequential solution- and melt-blending methods...........102
3.2 Schematics of (a) series bilayer, (b) Maxwell-Garnet, (c) Bruggeman, and (d) the proposed charge-injection models. The white arrows in (b) and (c) represent the dipole moments of the NPs.................................................................109
3.3 Proposed schematic of internal electronic conduction. (A) When the nAl NPs are far away from each other, electrons tunnel into the PP matrix. (B) When the nAl NPs are close, electrons tunnel from one NP into a neighboring NP. Under a bipolar poling, electrons can tunnel back and forth. Under a unipolar poling, electrons only tunnel into one direction.................................................................122

Chapter 4
4.1 Schematic of preparing gold hairy NPs via PS-b-P4VP block copolymer micellar nanoreactors with either crosslinked or non-crosslinked P4VP cores........132
LIST of FIGURES

Chapter 1

1.1 Different types of polarization as a function of frequency for dielectric polymers. \( P_{\text{elect}} \) - electronic polarization, \( P_{\text{vib}} \) - atomic (or vibrational) polarization, \( P_{\text{dip}} \) - orientational (or dipolar) polarization, \( P_{\text{ion}} \) - ionic polarization, and \( P_{\text{int}} \) - interfacial polarization. The top panel shows the molar polarization (or the real part of permittivity) and the bottom panel shows the dissipation factor (or the imaginary part of permittivity)….7

1.2 (A) Ten connectivity patterns for two-phase composites; (B) Schematics illustrating five types of composites, their spatial arrangements and their representative volume elements. (a) particulate (0–3) composites with particulates arranged at the vertices of a cube in space; (b) short-fiber (0–3) composites with short-fibers arranged at the vertices of a cube in space; (c) long-fiber (1–3) composites with long circular fibers arranged in a square array; (d) laminate (2–2) composites with the interface perpendicular to the 1-axis; and (e) networked (3–3) composites with non-intersecting fibers arranged along three mutually perpendicular directions with fibers arranged in a square array on each face.…..11

1.3 Three-dimensional distribution of the local field \( E_L(r) \) in a polymer nanodielectric with the filler volume fraction \( (\eta) \) of 0.2. (A) and (B) Initial field distribution \( E_L/E_0 \) without and with loop correction for a random composite, respectively. (C) Initial field distribution \( E_L/E_0 \) with loop correction for a body-centered cubic (bcc) composite with \( \eta = 0.2 \). The color of the spherical particles is set to black to help visualization. The applied electric field is along the \( z \) direction. The particle size \( (\sigma_p) \) is 100 nm, and the applied field is 50 MV/m. The permittivities of the matrix and particles are \( \varepsilon_m = 3 \) and \( \varepsilon_p = 1,000 \), respectively. (D) Loop correction term \( \langle \mu \rangle_L \) for the dipole moment of the inclusions as a function of \( \eta \) for the random and bcc composites. The \( \sigma_p \) is 100 nm(2um), and the applied field is 50 MV/m. The permittivities of the matrix and particles are \( \varepsilon_m = 3 \) and \( \varepsilon_p = 100 \), respectively. (E) Loop correction term \( \langle \mu \rangle_L \) for the dipole moment of the inclusions as a function of \( \sigma_p \) for the random and bcc composites. The applied field is 50 MV/m. The matrix and particle permittivities are \( \varepsilon_m = 2 \) and \( \varepsilon_p = 100 \), respectively. (F) Dependence of \( \varepsilon_{\text{eff}} \) on the \( \eta \) in a random composite. The experimental \( \varepsilon_{\text{eff}} \) data are taken from literature. Litchtenecker, Maxwell-Garnett, and Bruggeman fittings are also shown for comparison. The applied field is 100 MV/m. The particle diameter is 50 nm. The permittivities of the polymer matrix and particles are \( \varepsilon_m = 4.3 \) and \( \varepsilon_p = 150 \), respectively. The inset shows schematic illustration for the octahedral cage to probe the local field \( E_L(r) \) in the composite. The green particle at the center is the probe to
measure the $E_l(r)$. Only dipoles of the case-forming particles are shown……….15

1.4 Electrical layers of extended $ab$ interface. Phase A is a semi-insulator with charged surface states, and phase B contains mobile ions. An adsorbed layer exists on A. The outer Helmholtz plane is the nearest approach of mobile ions to A…19

1.5 (A) Schematic illustration of the preparation of three- and two-phase P(VDF-HFP)/BaTiO$_3$ nanocomposites, respectively. (B) Chemical structure of the TMPc-Br atom transfer radical polymerization (ATRP) initiator. (C) Calculated apparent permittivity ($\varepsilon_r$) as a function of filler volume fraction for the three-phase nanocomposites based on theoretical prediction by Vo and Shi. Experimental permittivities at 1 kHz and room temperature for uniaxially stretched P(VDF-HFP)/BT@TMPc-PMMA and P(VDF-HFP)/BT@R2-PMMA nanocomposite films are shown for comparison with the theoretical predictions….23

1.6 (A) Bruggeman-corrected $\varepsilon_r$ as a function of particle size of BaTiO$_3$. Data are taken from the literature. (B) Schematic illustration of the crystalline grain and ferroelectric domain structures in a single BaTiO$_3$ particle. There may exist a finite surface layer with random dipole orientation (green arrows). (a) Single particle with multiple crystalline grains. In each crystalline grain, there are 90° and 180° ferroelectric domains. (b) Single particle and single crystal with both 90° and 180° ferroelectric domains. (c) Single particle and single crystal with only 180° ferroelectric domains. (d) Single particle, single crystal, and single domain. (e) Single particle, single crystal, but no ferroelectric domain any more. Thick blue lines define the crystalline grains. The red lines define the 90° ferroelectric domains. The red dashed lines define 180° ferroelectric domains. Black arrows show the direction of ferroelectric domains…………………………………….28

1.7 (A) Percent cumulative distribution function (% probability of device failure) of each nanocomposite as a function of applied electric field; (B) the Eb (failure probability: 63.2%) at each volume fraction as determined from the Weibull analysis; and (C) Two-dimensional (2D) simulated electric field distributions for 100 particles with permittivity ratio of (a, b) 100:1 and (c, d) 1.5:1, with respect to the matrix. For each, two cases reflect randomly distributed particles with and without grafted chains. For chain grafting, the minimum particle separation is greater than one radius (panels (b) and (d)), whereas without grafting, the particle–particle separation may be less than one radius (panels (a) and (c)). Colors correspond to the normalized field intensity (E/E$_0$). White regions observed in panel (a) are areas where E/E$_0 >$3…………………………………..33
1.8 (A) synthesis of the phosphonic-acid terminated P(VDF-CTFE) and grafting P(VDF-CTFE) onto the \( \text{ZrO}_2 \) NP surface (top). Dielectric permittivity and \( \tan \delta \) of P(VDF-CTFE) and the nanocomposites measured at 1 kHz and room temperature. Stars are the effective \( \varepsilon_r \) of the composites calculated from the Lichtenecker law (bottom left). Dependence of maximum-electric displacement on the \( \text{ZrO}_2 \) content in the nanocomposites measured at 225 MV/m (bottom right). (B) Repetitious coating of \( \text{Al}_2\text{O}_3 \) shell on nanofiller surface and immobilization of metallocene catalyst to in-situ polymerize propylene (top). Electric field-polarization loops for \( \text{BaTiO}_3-\text{Al}_2\text{O}_3(n)\)-isoPP nanocomposites, \( n=1, 3, 5 \). The volume fraction of \( \text{BaTiO}_3 \) are 0.05, 0.08 and 0.09 for \( n=1, 3, \) and 5, respectively (bottom left). Comparison of dielectric loss for capacitors fabricated from \( \text{BaTiO}_3-\text{Al}_2\text{O}_3(n)\)-isoPP nanocomposites \( n=1, 3, 5 \) \( \text{Al}_2\text{O}_3 \) layers at low and high field. The volume fraction of \( \text{BaTiO}_3 \) are 0.05, 0.08 and 0.09 for \( n=1, 3, \) and 5, respectively (bottom right).

1.9 (A) Preparation of \( \text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3 \) nanowire embedded PVDF nanocomposite for ultrahigh energy density capacitor (left), energy density of the nanocomposite with different volume fraction as a function of the electric field calculated from D−E loops (right); (B) a, Schematic of the preparation of c-BCB/BNNS films. b, c, Transmission electron microscopy (TEM) images of BNNSs exfoliated from h-BN powders. Inset to c is an electron-diffraction pattern of BNNSs, showing its hexagonal symmetry. d, Chemical structure of the BCB monomer. e, The repeating unit of c-BCB. f, Photographs of a 10-µm-thick c-BCB/BNNS film wrapped around a glass tube with diameter 4 mm. g, A bent 10-µm-thick c-BCB/BNNS film. h, The photopatterned c-BCB/BNNS on a Si wafer. i, j, Optical microscopic images of the patterned films; the dark regions correspond to c-BCB/BNNS. 

1.10 (a, b) SEM images of the cut surface of a sample of QTC™ (elongated by 32±2%). White scale bars denote: (a) 50 µm and (b) 2 µm; (c) current-voltage characteristic of an undeformed sample of QTC™. Data are shown for increasing and decreasing voltage; (d) current-voltage characteristic of a sample of QTC™ uniaxially compressed to a resistance of \( \sim 0.17 \Omega \) (70±0.5% compression, residual circuit resistance 0.02 Ω). Data are shown for increasing and decreasing voltage; (e) open circuit in unstressed state of QTC, behaving as an insulator; (f) closed circuit in compressed state of QTC, behaving as a conductor.

Chapter 2
2.1 (A) FTIR spectra of the 70 nm BT and BT@POSS NPs and the POSS(PA)2 ligand. (B) XRD profiles for the 70 nm BT, BT@POSS, and BT@TiO2(50-cycle)@POSS NPs at room temperature. Reflections for the cubic phase are indexed. (C) and (D) show extracted real part permittivity, $\varepsilon_r'$ for the 70 nm BT and BT@POSS NPs using the Bruggeman equation.

2.2 Bright-field TEM micrographs of thin sections of (A-C) PP/BT and (D-E) PP/BT@POSS nanocomposites with (A, D) 10 vol %, (B, E) 20 vol %, and (C, F) 30 vol % BT NPs.

2.3 Temperature-scan BDS results of $\varepsilon_r'$ at 1 kHz for PP/BT and PP/BT@POSS nanocomposites with (A) 10 vol %, (B) 20 vol %, and (C) 30 vol % NPs. (D) $\varepsilon_r'$ for PP/BT, PP/BT@POSS, and PP/BT@TiO2@POSS 80/20 nanocomposites as a function of volume fraction of BT NPs measured at 1 kHz and RT. Fitting curves using the Maxwell–Wagner, Bruggeman, and Lichtenecker equations are also shown.

2.4 Weibull distributions of electric breakdown strength at room temperature for hot-pressed films of (A) PP and PP/BT and PP/BT@POSS nanocomposites with (B) 10 vol %, (C) 20 vol %, and (D) 30 vol % BT NPs. The film thicknesses are 20–30 μm, and the test area is 5.15 mm².

2.5 Computer simulation of three-dimensional (3D) local electric field ($E_l/E_0$) distributions for a random nanocomposite with (A) 10, (B) 20, and (C) 30 vol % of 70 nm nanoparticles. The relative permittivities of the matrix and nanoparticles are 2.25 and 120, respectively. The applied field $E_0$ is along the $+z$ direction. The electric field inside nanoparticles is weak (i.e., close to zero), and the color is set to black for better visualization.

2.6 (A) Bipolar D-E loops (10 Hz) for the PP/BT@POSS 80/20 nanocomposite film at room temperature. (B) Discharged energy densities ($U_e$, solid symbols) and discharge efficiencies (open symbols) for the PP control film and various PP/BT@POSS nanocomposite films. (C) Unipolar D-E loops (20 Hz) for the PP/BT@POSS 80/20 nanocomposite film at room temperature. The starting points of the second to fourth loops are shifted down to the origin. (D) Comparison of discharge efficiencies for the bipolar and the first and the fourth unipolar loops for the PP/BT@POSS 80/20 nanocomposite film under various test frequencies.

2.7 Bright-field TEM micrographs for BT@TiO2 50-cycle NPs at (A) low and (B and C) high magnifications. (D) The corresponding PP nanocomposite at 20 vol % filler content.
2.8 Bipolar D-E loops (10 Hz) for the PP/BT@TiO$_2$(50c)@POSS 80/20 nanocomposite film at RT. (B) Discharged energy densities (Ue, solid symbols) and discharge efficiencies (open symbols) for the PP/BT@POSS 80/20 and the PP/BT@TiO$_2$(50c)@POSS 80/20 nanocomposite films. (C) Unipolar D-E loops (20 Hz) for the PP/BT@TiO$_2$(50c)@POSS 80/20 nanocomposite film at RT. The starting points of the second to fourth loops are shifted to the origin. (D) Comparison of discharge efficiencies for the bipolar, the first, and the fourth unipolar loops for the PP/BT@TiO$_2$(50c)@POSS 80/20 nanocomposite film under various frequencies………………………………………………………85

Chapter 3

3.1 TEM micrographs of (A) 100 nm nAl NPs, (B) 100 nm nAl@PEB-PA NPs, (C) 18 nm nAl NPs, and (D) 18 nm nAl@PEB-PA NPs. Insets in (A) and (C) show histograms of spherical particle diameters. (E) Powder XRD profiles for 100 nm nAl NPs, 100 nm nAl@PEB-PA NPs, PP/100 nm nAl@PEB-PA nanocomposite, 18 nm nAl NPs, and 18 nm nAl@PEB-PA NPs. (F) Transmittance FTIR spectra of 100 nm nAl NPs, 100 nm nAl@PEB-PA NPs, 18 nm nAl NPs, 18 nm nAl@PEB-PA NPs, and PEB-PA……………………………………………..101

3.2 TGA results for (A) PP/100 nm nAl and (B) PP/18 nm nAl nanocomposites with different filler contents…………………………………………………………………105

3.3 TEM micrographs of thin sections of the PP/100 nm nAl nanocomposites with (A) 5.3 vol.%, (B) 10.8 vol.%, (C) 18.3 vol.%, and (D) 25.0 vol.% NPs, and PP/18 nAl nanocomposites with (E) 5.3 vol.% and (F) 10.5 vol.% NPs…………….106

3.4 (A) Temperature- (at 1 kHz) and (B) frequency-scan (at room temperature) BDS results for PP/100 nm nAl and PP/18 nAl nanocomposites with a ~10 vol.% filler ratio. (C) Dielectric constant (ε’) of PP/100 nm nAl and PP/18 nm nAl nanocomposites as a function of the filler ratio measured at 1 kHz and room temperature. Fitting curves using the bilayer, Maxwell-Garnett, Vo-Shi core-shell, and Bruggeman models are also shown………………………………………..107

3.5 Weibull plots of dielectric breakdown strengths for (A) PP/100 nm nAl and (B) PP/18 nm nAl nanocomposites. (C) Weibull characteristic $E_b$ ($\alpha_w$) and (D) Weibull modulus ($\beta_w$) for PP/100 nm nAl and PP/18 nm nAl nanocomposites as a function of the volume fraction of nAl NPs………………………………….112

3.6 (A) Leakage current density and (B) electrical conductivity as a function of the applied electric field for the PP/100 nm nAl nanocomposites with 10.8, 18.3 and 25.0 vol.% NPs and the PP/18 nm nAl nanocomposite with 10.5 vol.% NPs.
Schematics of (C) hopping conduction and (D) Fowler-Nordheim field emission mechanisms for the PP/nAl nanocomposites.............................................................114

3.7 Five continuous bipolar D-E loops (10 Hz) for (A) the PP/18 nm nAl nanocomposite with 10.5 vol.% nAl NPs and (B) the PP/100 nm nAl nanocomposite with 18.3 vol.% nAl NPs at room temperature. The blue dash lines are AC conduction loops with the magnification indicated. Discharged energy densities ($U_e$) and discharge efficiencies for the PP control film and (C) PP/18 nm nAl and (D) PP/100 nm nAl nanocomposite films..............................................118

3.8 Four continuous unipolar D-E loops (10 Hz and room temperature) for (A) the PP/18 nm nAl(10.5%) at 240 MV/m and the PP/100 nm nAl nanocomposites with (B) 10.8 vol.% and (C) 18.3 vol.% NPs at 150 and 70 MV/m, respectively. The start points for the 2nd, 3rd, and 4th loops are shifted to the origin. (D) Hysteresis losses for the above nanocomposite films obtained from the corresponding unipolar D-E loops.................................................................121

Chapter 4

4.1 TEM micrographs of PS-b-P4VP micelles cast from toluene: (A) PS$_{132}$-P4VP$_{104}$, (B) PS$_{132}$-P4VP$_{215}$, (C) PS$_{37}$-P4VP$_{66}$-PS$_{37}$, (D) PS$_{135}$-P4VP$_{154}$-PS$_{135}$, (E) PS$_{418}$-P4VP$_{123}$. (G) R$_{Hs}$ distribution of the micelles formed by sample A, E, and their mixture in toluene.................................................................139

4.2 (A) FTIR spectra for non-crosslinked, crosslinked micelles, and micelles loaded with Au, Pd, or Ag precursor ions. (B) Color of micelle solutions due to solvation of metal ions in the P4VP cores. (C) Proposed interaction/chelation modes between pyridine units and different metal ions..................................................141

4.3 TEM micrographs of PS$_{135}$-P4VP$_{154}$-PS$_{135}$ micelles loaded with (A) HAuCl$_4$ (4VP:Au = 2:1), (B) Pd(OAc)$_2$ (4VP:Pd = 2:1), (C) AgNO$_3$ (4VP:Ag=2:1), (D) crosslinked PS$_{135}$-P4VP$_{154}$-PS$_{135}$ micelles (4VP:DBB = 2:1), (E) crosslinked PS$_{135}$-P4VP$_{154}$-PS$_{135}$ micelles loaded with HAuCl$_4$ (4VP:DBB = 1:1, 4VP:Au = 2:1), and (F) crosslinked PS$_{135}$-P4VP$_{154}$-PS$_{135}$ micelles loaded with HAuCl$_4$ (4VP:DBB = 1:1, 4VP:Au = 4:1).................................................................................142

4.4 TEM micrographs of reduced Au NPs inside the non-crosslinked PS$_{135}$-P4VP$_{154}$-PS$_{135}$ micelles (A) without and (B) with HCl (g) scavenger. (C and D) show reduced Au NPs inside the non-crosslinked (C) PS$_{37}$-P4VP$_{66}$-PS$_{37}$ and (D) PS$_{418}$-P4VP$_{123}$ micelles with HCl (g) scavenger.........................................................144

4.5 TEM micrograph of anhydrous hydrazine-reduced (A) Au NPs, (B) Ag NPs, and (C) Pd NPs inside the crosslinked PS$_{135}$-P4VP$_{154}$-PS$_{135}$ micelles............................................146
4.6 TEM micrographs of (A) Au NPs reduced by triethyilsilane in non-crosslinked micelles, (B) Au NPs reduced by triethyilsilane in crosslinked micelles, and Au NPs reduced by triethyilsilane with (C) 3% ethanol and (D) 5% ethanol inside crosslinked micelles. The BCP used is PS_{132}-P4VP_{104}.

4.7 TEM micrographs of crosslinked Au NPs (A) before heating, and after heating in toluene at 110 °C for (B) 18 h and (C) 40 h. Insets show the MNP size histograms. (D) UV-Vis spectra of crosslinked Au NPs being heated at 110 °C for 0, 18 and 40 h, respectively. The UV-Vis spectrum of Au@PS NPs is also shown for comparison.
ACKNOWLEDGMENTS

First, I would like to give my deep respects and sincere thanks to my advisor, Prof. Lei Zhu, for his guidance, support, encouragement and patience throughout my entire Ph.D. study. To me, he is not only our researcher advisor who instructed us how to do research in a critical think and detail-oriented way, but also a person who holds his values, standards, uprightness, diligence, curiosity and enthusiasm to his life, his research, his surroundings, and his truly believed “the greatest truth” - God. We are subtly being changed and doing better ourselves during the time working with him and learning from him.

I also want to give my thanks to a lot of people for their assistance in the past five years during my Ph.D. study. Without their help, I will not be able to finish this dissertation. Thank to Prof. Michael Hore, Prof. Alex. Jamieson, Prof. Kenneth Singer at Case Western Reserve University (CWRU) for being my dissertation committee. Thank to Prof. Rigoberto Advincula, Prof. Stuart Rowan, and Prof. Jon Pokorski at CWRU for informative discussions on my research and teaching me how to incubate ideas and turn them into scientific proposals. I would like to thank to Dr. Jonathan Cowen at Swagelok center for surface analysis of materials at CWRU for his help on X-ray diffraction measurements, Dr. Heather Holdaway and Dr. Sudheer Molugu at Cleveland center for membrane and structural biology at CWRU for their help on transmission electron microscopy (TEM), Dr. Ina Martin at MORE center for her help on thermal evaporation and deposition, Prof. Tianbo Liu and Student Lang Hu and Jiancheng Luo at University of Akron for their help on dynamic light scattering measurements, Prof. Kevin A. Cavicchi and student Mo Yang for their help on the use of Haake minilab compounding, Prof. Kenneth Singer, Prof. Jie Shan and Dr. Cory Christenson at Department of Physics at Akron.
CWRU for their constructive comments and suggestions on optical data storage projects, Dr. Tawfik Khattab at Kent State University for providing us the DCDHF dye sample, Prof. Gabriel Caruntu at Central Michigan University for supply of BaTiO₃ nanocube samples, and Prof. Liming Dai and student Min Wang at CWRU for their help on Raman characterization. I would like to give my special thanks to Prof. Eric Baer at CWRU for one-year supervision on multilayer project. I appreciate your generous support during the transition time when I switched my research group.

It is really my pleasure to work with every past and present group members. To me you are not just colleague but good friends for life. It is the efforts from all of you that makes our group more like a family, a heartwarming, cozy, happy and energetic place to work. I am so cherishing every moments that I spend with my dear colleagues and friends during my study at CWRU. I believe this piece of memory will be remembered for the rest of my life. I would give my most sincere thanks to all of you whom I used to work and play with: Dr. Elshad Allakhyarov for your help on dielectric simulations, Prof. Longxiang Tang, Dr. Daxuan Dong and Daniel Brannum for your help on BaTiO₃/iPP project, Dr. Saide Tang for your help on teaching me how to do microtome and TEM, Mr. Jung-Kai Tseng, Dr. Lianyun Yang and Dr. Imre Treufeld for your help on dielectric measurements, Prof. Aixiang Li for your help on optical data storage project, Prof. Yuanming Zhang, Prof. Jun Lei, Dr. Guo Yao, Dr. Bing Qin, Prof. Guo Jiang, Prof. Haiquan Wang, Prof. Huili Ding, Prof. Zaijun Lv, Prof. Juan Chen, Prof. Ruifang Guan, Dr. Yufeng Zhu, Zhongbo Zhang, Xinyue Chen, Qiong Li, Zhongqiang Zhao, Minghuan Wang, Yanfei Huang, Huadong Huang, Leipeng Liu, Peng Peng, Qingmeng Tang, Yuan Yao, Zhe Liu, Dr. Jianchuan Wang, Dr. Junji Wei, Nasly Jimenez, Michelle Song, Xiaozhou Shen, Dr.
Sangjin Lee, Karl Kodweis, Rhett D. Thompson, Emanuel Zlibut, and other group members.

I also want to thank all my friends outside our research groups who helped me with my research work and life: Dr. Jia Liu, Dr. Pengfei Cao, Dr. Qiong Wu, Dr. Min Wang, Dr. Kezhen Yin, Dr. Shanzuo Ji, Dr. Jian Han, Dr. Zhenghao Mao, Dr. Bin Liu, Dr. Longhe Zhang, Dr. Rongzhi Huang, Dr. Jia Wang, Dr. Zheng Zhou, Dr. Hongbing Chen, Dr. Feng Du.

Last but not the least, I owe my deepest gratitude to my parents and my lovely girlfriend, Yue Li. Without their kind understanding and support, I can never go this far.
The Synthesis and Electrical Properties of Functional Polymer Nanocomposites

Abstract

by

GUOQIANG ZHANG

The marriage between organic polymers and inorganic nanoparticles (NPs) is believed to give birth to polymer nanocomposites that feature both their merits. Sometimes, polymer nanocomposites can even exhibit novel structures, properties, functionalities and applications which are not observed in neither polymers nor inorganic NPs. Specifically, polymer nanodielectrics have attracted intense interests in recent years for the search of high-performance energy storage materials, because they are anticipated to combine high permittivity ($\varepsilon_r$) from inorganic NPs, and high breakdown strength ($E_b$), low dielectric loss from the polymer matrix. Although the apparent $\varepsilon_r$ and total energy density have so far been sufficiently improved in nanodielectrics, their relatively large dielectric losses limit real applications. More importantly, the underlying mechanisms are somehow overlooked.

In the first part of this dissertation, a large AC dielectric loss and decreased $E_b$s observed in a common ceramics/polymer nanocomposite dielectrics were systematically studied. The composite dielectrics were prepared by uniformly embedding 70 nm polyhedral oligomeric silsesquioxane (POSS)-modified BaTiO$_3$ NPs in polypropylene linear dielectric polymer. We found that a large dielectric contrast between high-$\kappa$ semiconducting nanofiller and low-$\kappa$ insulating polymer would result in the local field enhancement and generate interfacial charge carriers at the nanofiller/polymer interface.
Therefore, a deteriorated dielectric performance was observed because of the formation of extended conduction pathway and substantial AC internal current. By employing a medium-$\kappa$ TiO$_2$ as a buffer layer between nanofiller and polymer, unfavorable interfacial polarization could, to some extent, be mitigated to give better performance.

In the second part, the dielectric loss/conduction mechanism in conductor-polymer system was addressed. Two series of PP/aluminum (Al) composites were prepared and investigated regarding their $\varepsilon_r$, $E_b$, and energy storage performance. Three conduction regimes were identified as applied electric field increased. The field electron emission could happen at much lower field, and accounted for significantly decreased $E_b$. Therefore, conductor-insulator composites was believed not appropriate for energy storage applications.

During nanocomposite manufacturing or in real applications, the stability of nanoparticles was deemed very important, otherwise compromised properties and/or unwanted degradation might occur. By combining block copolymer micellar nanoreactors and core-crosslinking, we demonstrated a facile and effective way to substantially improve the thermal stability of metallic NPs in organic solvents, as given in the final part of this dissertation.
CHAPTER I

Introduction
1. Introduction to Polymer Nanodielectrics

1.1. The Need for Next Generation Polymer Film Capacitors

Advanced energy technologies in the 21st century (e.g. pulsed power, power conditioning, power electronics in hybrid/electric vehicles, and medical/consumer electronics), create an urgent need for light-weight, compact, and cost-efficient energy conversion and storage components such as capacitors, which feature high energy density ($U_e$), high power density, broad operating temperature range, as well as good environmental stability.\textsuperscript{1,2} Among various technologies, polymer film capacitors have gained importance in applications that require high power density and high $U_e$, fast charge/discharge rates, high voltage and tolerance to high ripple currents, because their power density is the highest compared to other types of capacitors such as ceramic and electrolytic capacitors. Unlike batteries, electrochemical capacitors, and fuel cells, energy storage using electrostatic capacitors is purely a physical process based on separation of opposite static charges under an applied electric field. Therefore, stable capacitance over a wide temperature range and a long cycle lifetime is a unique feature for linear dielectric film capacitors.

Ideally, a high-performance dielectric material should qualify the following factors, including large permittivity or dielectric constant ($\varepsilon_r$), high dielectric breakdown strength ($E_b$), high discharge efficiency ($\eta$), high resistivity, and broad operating temperature window. However, barely any currently available material is able to perform well in all aspects. For example, there are a few short-comings for current state-of-the-art polymer film capacitors. First, they have a lower $U_e$ than electrolytic and ceramic capacitors because of their low $\varepsilon_r$ (typically 2-5). This limits the miniaturization and often results in large
form factor and low energy-to-weight ratio (~0.01-0.1 kWh/kg) for film capacitors. Second, the temperature rating for current state-of-the-art biaxially oriented polypropylene (BOPP) film capacitors is limited at 85 °C. This is primarily attributed to the defect initiation and growth in BOPP at elevated temperatures. As a result, \( E_b \) and lifetime will substantially decrease compared to those at room temperatures. Current research focuses on enhancing the \( U_e \) and temperature tolerance, while keeping ultralow losses for dielectric polymers.\(^3\,^4\)

The overall performance of an electrostatic capacitor is largely determined by the dielectric material placed between two metal electrodes. For linear dielectrics, the \( U_e \) has a linear relationship with the relative permittivity \( \varepsilon_r \), and a square relationship with the \( E_b \) of the dielectric material: \( U_e = 0.5\varepsilon_r\varepsilon_0 E_b^2 \). To increase the \( U_e \), one can increase either the \( \varepsilon_r \) or the \( E_b \). From the first glance, it seems that increasing the \( E_b \) is more attractive because the power dependence is square for the \( E_b \) rather than one as for the \( \varepsilon_r \). However, polymer \( E_b \) can often reach as high as 700-800 MV/m for a 2 cm\(^2\) test area, which is close to the record \( E_b \) among all dielectric materials, i.e., \( \sim 2 \) GV/m for diamond.\(^5\) The room for further improving \( E_b \) of polymers is rather limited. Given the low \( \varepsilon_r \) of 2-5 for polymers, the room for further improvement can be large. For example, alkyl amides have a \( \varepsilon_r \) of 180\(^6\) and water has a \( \varepsilon_r \) of 80\(^7\) at room temperature. In a recent perspective article, we have discussed viable approaches for neat polymers to increase their \( \varepsilon_r \)s close to that of water.\(^3\) The basic idea is to utilize molecular dipoles to increase the overall polarization and thus \( \varepsilon_r \). Nonetheless, dielectric loss has to be kept low as the polarization and \( \varepsilon_r \) increase. Details should refer to that perspective article, and we will not elaborate here.
1.2. Proposal of Polymer Nanodielectrics for Electric Energy Storage

Inorganic ceramics [e.g., type I: titanium dioxide (TiO₂)-based and type II: barium titanate (BaTiO₃)-based] have been utilized as dielectric materials in capacitors for decades due to their high $\varepsilon_r$ (>$30$ for type I and >$1,000$ for type II), low-cost, and excellent temperature tolerance. However, ceramic capacitors usually suffer from low $E_b$ (<$50$ MV/m), brittleness (the lead connections can easily fall off), and high density/heaviness. Besides, its manufacturing involves high-temperature sintering processes. All these inherently limit their applications in future flexible, miniaturized, high-performance devices for power electronics. Electrolytic capacitors such as aluminum electrolytic capacitors are easy to fabricate and have a higher $U_e$ than BOPP film capacitors. Depending on the manufacturing, aluminum electrolytic capacitors can operate up to 600 V. Because Al₂O₃ is the dielectric material, fairly low dielectric loss is obtained. However, aluminum electrolytic capacitors are not suitable for high voltage and high temperature applications such as DC-link capacitors for electric vehicles, because they tend to dry up at high temperature. Also, aluminum electrolytic capacitors cannot tolerate high ripple currents in electric drives.

Recently, an interdisciplinary “composite” idea has emerged. The simple wish is to combine the high $\varepsilon_r$ property from inorganic ceramics and the high $E_b$ and low loss properties from organic polymers. Soon, nanocomposite dielectrics have become a hot research topic in the field of dielectric materials, and have gained intense research efforts. The essence of composites is not to create new polymeric materials, but to innovate advanced properties/functions based on combining known materials with appropriate structures and well-documented properties. However, it is important to make the
composites behave in a synergistic way, structurally, morphologically, and functionally. How to achieve this synergistic performance? It is not to mention that properties of each component in the composite should be carefully tailored. This has to do with the basic knowledge established in both ceramic and polymer fields. Moreover, the way by which ceramics and polymers are combined also matters, sometimes even more important. First, it has always been a challenge to achieve uniform dispersion of inorganic fillers in an organic polymer. Two dissimilar components thermodynamically tend to phase separate from each other and minor phase tend to form large aggregates/domains. This will greatly increase heterogeneity and adversely affect the overall properties. Homogeneous particle dispersion has to overcome a huge surface energy penalty by creating new contact areas between fillers and the polymer matrix. Second, properties of new contact areas (interfaces) are usually not just a compositional sum of the properties from each component. On the contrary, interface behaves so differently from either fillers or the matrix. Without considering interface as a new component, theories and simulations derived from biphasic systems can largely deviate from experimental observations.

For the past decade, numerous reports focus on enhancing $\varepsilon_r$ and $U_e$. However, there are great challenges and issues in this field, which need attention from researchers. First, for insulating ceramic fillers, as their particle sizes become smaller and smaller, their dielectric permittivities also significantly decrease, often many times lower than those of their bulk materials (i.e., $\varepsilon_r \sim 180$ for 70 nm BaTiO$_3$, and $\varepsilon_r \sim 5,000$ for bulk BaTiO$_3$). In fact, the apparent $\varepsilon_r$ of nanocomposites will not substantially increase until the filler content reaches near the percolation threshold. However, this usually accompanies a significant decrease in $E_b$ and deteriorated mechanical properties. Conductive metallic and
carbonaceous fillers or fillers with large aspect ratios tend to effectively increase the apparent $\varepsilon_r$ of the composite at a lower filler content. However, the percolation thresholds in these composites would also decrease, and the dielectric properties in the vicinity of percolation will drastically change. Extra research efforts have to be taken to precisely control the composition in order to avoid the percolation of nanofillers. This may limit the processing window to a very narrow composition range. Second, the electric field distribution is non-uniform in multicomponent polymer nanodielectrics, especially for those impregnated with high permittivity nanofillers and/or at high filler contents. Namely, the local field in high permittivity fillers is weak, whereas the field in the low permittivity polymer matrix is high (a few to several tens times larger than the applied electric field), resulting in reduced $E_b$. For conductive fillers, local field inside the particles is zero and field will be only applied to the polymer matrix, which results in early dielectric breakdown. Besides, the electron tunneling effect in conductive fillers much likely introduce conduction pathways even before they are in physical contact. This will make $E_b$ even lower. Third, large permittivity and conductivity contrasts between fillers and the polymer matrix will cause significant Maxwell-Wagner-Sillars (MWS) interfacial polarization, which is ubiquitous in all dielectrically heterogeneous systems. Whether the MWS interfacial polarization will enhance or deteriorate the dielectric properties needs to be carefully studied.

In the following, we will review most of the important aspects of polymer nanodielectrics, from fundamental polarization theories to interfacial models, from effective mixing laws to basic dielectric properties (i.e., $\varepsilon_r$, $E_b$, $U_e$, dielectric loss, etc.),
from insulating ceramic fillers to conductive fillers. Hopefully, this introduction will be informative and insightful for the fundamental science of polymer nanodielectrics.

2. Polymer Nanodielectrics – Theory and Modeling

2.1. Mechanisms of Polarization

Before directly jumping into the topic of polymer nanodielectrics, we had better go through some fundamental concepts in dielectrics. When an ideal linear dielectric is placed two electrodes and under an applied electric field $E$, it responds to the external stimulus with an electric polarization: \[ P = \epsilon_0 \chi E \] (1.1)

Figure 1.1 Different types of polarization as a function of frequency for dielectric polymers. $P_{\text{elec}}$ - electronic polarization, $P_{\text{vib}}$ - atomic (or vibrational) polarization, $P_{\text{dip}}$ - orientational (or dipolar) polarization, $P_{\text{ion}}$ - ionic polarization, and $P_{\text{int}}$ - interfacial polarization. The top panel shows the molar polarization (or the real part of permittivity) and the bottom panel shows the dissipation factor (or the imaginary part of permittivity). Reproduced with permission from ref 3. Copyright 2014 American Chemical Society.
where $\varepsilon_0$ is the permittivity of free space (vacuum), and $\chi_e$ is the susceptibility of the dielectrics. The electric displacement $D$ is related to electric polarization $P$ with the relationship:

$$D = \varepsilon_0 E + P = \varepsilon_0 \varepsilon_r E$$  \hspace{1cm} (1.2)

where $\varepsilon_r$ is the relative permittivity (or $\varepsilon_r$) of the dielectrics. Due to the complex nature in the measurement of complex permittivity ($\varepsilon_r^* = \varepsilon_r' - i \varepsilon_r''$, where $\varepsilon_r'$ and $\varepsilon_r''$ are real and imaginary parts of the relative permittivity), $D$ lags behind $E$ with a phase angle of $\delta$, which defines the linear dielectric loss: $\tan \delta = \varepsilon_r'' / \varepsilon_r'$. The linear dielectric properties, i.e., $\varepsilon_r'$, $\varepsilon_r''$, and $\tan \delta$, can be measured by broadband dielectric spectroscopy (BDS) at low electric fields (typically around 0.1 MV/m).

Dielectric polarization consists of various mechanisms. As shown in Figure 1.1, there are fundamentally four types of polarization for dielectric materials. They are electronic, atomic (or vibrational), orientational (or dipolar), and space charge (i.e., ions and electrons/holes) polarizations. Each type of polarization is associated with its own dielectric loss at a specific frequency range. These four types of polarization can be divided into two regimes, namely, resonance and relaxation regimes. The resonance regime includes electronic and atomic polarizations, because their permittivity will diverge at the resonance frequency. Electronic polarization is induced by a slight shift of the outer electron cloud of an atom with respect to the positive nucleus under an external electric field. Electronic polarization takes place in the optical frequency region of $10^{15}$-$10^{18}$ Hz. Atomic polarization is caused by vibration and/or distortion of molecular bonds in the infrared range ($10^{12}$-$10^{15}$ Hz). These two types of polarization are ubiquitous in all dielectric materials, no matter inorganic or organic. They are mostly desired for power and
radio frequency applications because their losses are located at very high frequencies. The ε_r from electronic polarization has an inverse relationship with the band gap for organic polymers,\textsuperscript{11} and its maximum value is about 3.6 when the band gap is as low as 4 eV (note that below 4 eV, the material can be considered as a wide band gap semiconductor). The ε_r from atomic polarization is usually 10-25% of the ε_r from electronic polarization.\textsuperscript{11,12} As a result, if we set the lower limit to band gap of 4 eV for insulating polymers, the maximum total ε_r from resonance polarizations is about 5. This is the reason why polymers usually exhibit relatively low ε_rs of 2-5. However, the situation is different for inorganic materials, where the atomic polarization (or ionic polarization as called in the inorganic ceramic field) can reach very high. For example, in the tetragonal phase of perovskite BaTiO_3, the displacement of the Ti^{4+} ion along the c-axis is about 0.06-0.08 Å.\textsuperscript{13} The displacement of the Ti^{4+} ions in the tetragonal phase can result in a spontaneous polarization of 0.27 C/m^2 and also a high ε_r >1,000. Similarly, CaCu_3Ti_4O_{12} (CCTO) and related materials can exhibit a colossal ε_r of >10,000, which is nearly temperature-independent in the range of 200-300 K.\textsuperscript{14} It is considered that atomic polarization in the grain boundaries, rather than in the ferroelectric domains, accounts for the ultrahigh ε_r in ferroelectric inorganic ceramics.\textsuperscript{15}

The relaxation regime includes orientational and space charge polarizations. For polar organics and polymers, orientational polarization is caused by rotation of permanent molecular dipoles along the direction of external electric field. Depending on the molecular dynamics, orientational relaxation usually takes place approximately between a fraction of 1 Hz and 20 GHz. For example, water molecules relax at 20 GHz with a ε_r of ca. 80 at 25 °C. For polar polymers such as amorphous PVDF, the dipolar switching is much slower (below 100 MHz) and the ε_r from dipolar polarization is usually around 10.\textsuperscript{3,16,17} Space
charge polarization sometimes is also called interfacial polarization, which involves polarization of ions and electrons/holes. The polarization of ions involves physical transport of ionic species over nanometers of distance in dielectric solids or liquids, and it is the working mechanism of electric double layer (EDL). Because of the short Debye screening length (\(\lambda\)) or the thickness of the EDL (about 1-2 nm), the capacitance of EDL capacitors (\(C_{\text{EDL}} \sim \kappa \varepsilon_0 / \lambda\), where \(\kappa\) is the permittivity of the EDL) are at least 1,000 times that (\(C_{\text{film}} = \kappa \varepsilon_0 A/d\), where \(\kappa\) is the permittivity of bulk film, \(A\) is the area, and \(d\) is the thickness of film) of a typical dielectric polymer film such as BOPP. Due to the physical transport of ions over a few nanometers, the relaxation frequency of ions is limited at \(10^4\) Hz. Ionic polarization is suitable for applications such as supercapacitors. For dielectric polymers, ionic polarization of a residual amount of ionic impurities is the major cause of dielectric loss, especially at elevated temperature when the ion mobility is high enough. Finally, polarization of electrons/holes in multicomponent systems and at surfaces produces MWS interfacial polarization. For example, PP nonwoven fiber electrets with stable surface charges can be used for air filtration. Triboelectric charges can be used to generate electricity. It also plays an important role in polymer nanodielectrics, and this will be discussed later.

2.2 Theoretical Models for Dielectric Composites

Before discussing detailed theoretical models, the composite nomenclature should be introduced. Fabricating a composite requires both proper constituent phases and optimum spatial connectivity. Based on the connectivity patterns of the constituent phases, formation of quasi-composites, orientation and transitions as a result of external variables, both
biphasic and triphasic composites are named precisely to reflect their internal connectivity, order, and symmetry. For example, biphasic composites can be defined as (0-0), (0-1), (0-2), (0-3), (1-1), (2-1), (2-2), (2-3), (1-3), and (3-3), totally ten families (seen in Figure 1.2). The 0/1/2/3 represents the number of dimension in continuity for each constituent phase within a composite. The first number is the connectivity of the filler and the second number is the connectivity of the polymer matrix. Normally, most of polymer nanodielectrics can be categorized as the (0-3) composites, i.e., spherical fillers randomly embedded in a three dimensionally connected polymer matrix.

**Figure 1.2.** (A) Ten connectivity patterns for two-phase composites; (B) Schematics illustrating five types of composites, their spatial arrangements and their representative volume elements. (a) particulate (0–3) composites with particulates arranged at the vertices of a cube in space; (b) short-fiber (0–3) composites with short-fibers arranged at the vertices of a cube in space; (c) long-fiber (1–3) composites with long circular fibers arranged in a square array; (d) laminate (2–2) composites with the interface perpendicular to the 1-axis; and (e) networked (3–3) composites with non-intersecting fibers arranged along three mutually perpendicular directions with fibers arranged in a square array on each face. Reproduced with permission from Ref. 23. Copyright 2012 Elsevier

Once the spatial arrangement of substituent phases in the composites is known, we want to study whether the overall properties of a composite could be described and predicted
based on the properties of each component. van Suchtelen has defined two types of effects in biphasic composites - sum and product properties. Young’s modulus and \( \varepsilon_r \) of composites are sum properties, which means that the overall property is the result of an “average” of a physical property of both constituent phases. As we know, \( \varepsilon_r \) is an important factor to evaluate dielectric properties of a dielectric. Accurately predicting the dielectric response of a composite can greatly help us design and fine-tune nanodielectrics by properly selecting good pairs of polymer and fillers. The key point is how to unveil the underlying mixing rule with the correct mathematic expression. Is the mixing rule based on i) unique property possessed primarily by only one phase, ii) desired property coefficient in a shared property, iii) the tensor order of coefficient or property? To answer these questions, people have proposed a variety of models and mixing rules to predict the effective dielectric properties of nanocomposites.

### 2.2.1 Model 1: Logarithmic Mixing Law

Begin with two extreme models, namely, the parallel and series models. In reality, None of 0-3 composites will arrange in these two ways. However, it is believed that \( \varepsilon_r \) of a real composite should fall between values calculated based on these two models. In other words, these two models estimate the upper and lower limits for a real composite (Wiener bounds):

\[
(\varphi_m \varepsilon_m^{-1} + \varphi_f \varepsilon_f^{-1})^{-1} \leq \varepsilon_c \leq (\varphi_m \varepsilon_m + \varphi_f \varepsilon_f)
\]  
(1.3)

where \( \varepsilon_m \) and \( \varepsilon_f \) represent \( \varepsilon_c \)s of polymer matrix and inorganic filler, and \( \varphi_m \) and \( \varphi_f \) are the volume fractions of polymer matrix and inorganic fillers, respectively. The dielectric constant \( \varepsilon_c \) of a composite can be rewritten in an index formula as:

\[
\varepsilon_c^n = \varphi_m \varepsilon_m^n + \varphi_f \varepsilon_f^n,
\]
and the $n$ is either 1 for the parallel model or -1 for the series model. If the approximation of $\varepsilon^n = 1 + n \ln \varepsilon$ is used when $n$ approaches zero or the dielectric constant is close to 1, the above expression will become the well-known Lichtenecker’s logarithmic mixing law:\textsuperscript{26}

$$\lg \varepsilon_c = \phi_m \lg \varepsilon_m + \phi_f \lg \varepsilon_f \text{ or } \varepsilon_c = \varepsilon_m^{\phi_m} \varepsilon_f^{\phi_f}$$  \hspace{1cm} (1.4)

Supposedly, Lichtenecker’s mixing law should only work in the case that both $\varepsilon$s of filler and matrix are very close to 1, corresponding to infinite dilute composites. Recently, Lichtenecker’s mixing law has also been derived by using the Maxwell’s equation with an assumption that particle shape and orientation of each constituent is statistically random. The theoretical derivation corroborated the general validity of Lichtenecker’s mixing law in predicting $\varepsilon_r$ of composites with a broad range of filler contents.

\textbf{2.2.2 Model 2: Effective Medium Theory}

Different from the logarithmic mixing law, Maxwell-Wagner (or Maxwell-Garnett) equation mathematically treats the whole composite as a core-shell structured dielectric sphere, in which the core was made of the filler and the shell is made of the matrix. The following equation is obtained using the Clausius-Mossotti relationship, where $\phi$ always stands for the composition of filler:\textsuperscript{27-30}

$$\varepsilon_c = \varepsilon_m \left[ 1 + \frac{3 \phi_f (\varepsilon_f - \varepsilon_m)}{(1 - \phi_f)(\varepsilon_f - \varepsilon_m) + 3 \varepsilon_m} \right]$$  \hspace{1cm} (1.5)

Maxwell-Wagner equation has also been widely used for predicting the $\varepsilon_r$ of 0-3 composites. This equation was firstly derived under a static field. Later, it was also derived using effective medium theory assuming spherical fillers dispersing in a continuous matrix.
at infinite dilution. Therefore, it will become more and more inaccurate as filler contents
are no longer considered dilute. In order to predicting $\varepsilon_r$ of more concentrated composites.
Bruggman further developed a symmetric equation based on effective medium theory:31,32
\[
\varphi \left( \frac{\varepsilon_f - \varepsilon_c}{\varepsilon_f + 2\varepsilon_c} \right) + (1 - \varphi) \left( \frac{\varepsilon_m - \varepsilon_c}{\varepsilon_m + 2\varepsilon_c} \right) = 0
\]
(1.6)
In this derivation, it is assumed that a composite is composed of two phases with similar
morphologies and are distributed randomly throughout the entire composite. Under this
assumption, the imaginary biphasic system is more likely a 0-0 composite rather than a
common 0-3 composite. Later on, Hanai brought up an asymmetrical Bruggeman equation
with a hypothesis that Wagner relationship holds for the infinitesimal process, so every
time, an infinitesimally small quantity of the disperse phase added to the dispersion
system.33,34
\[
1 - \varphi = \left( \frac{\varepsilon_f - \varepsilon_c}{\varepsilon_f - \varepsilon_m} \right) \left( \frac{\varepsilon_m}{\varepsilon_c} \right)^{1/3}
\]
(1.7)
Hanai took a step further to introduce infinitesimal process, making Maxwell-Wagner
relationship applicable to deal with composite systems with higher filler contents.
Compared to Bruggeman equation, which considered filler and matrix interchangeably,
Hanai equation treated matrix and filler differently. In order to further address factors such
as filler shape, orientation and percolation, Maxwell equation was modified by introducing
new parameters to more accurately represent experimental data. For example, when fillers
are non-spherical, it is revised as:35
\[
\varepsilon_c = \varepsilon_m \left[ 1 + \frac{\varphi_f (\varepsilon_f - \varepsilon_m)}{u(1-\varphi_f)(\varepsilon_f - \varepsilon_m) + \varepsilon_m} \right] \text{ for } \varphi_f < 0.1
\]
(1.8)
where depolarization factor $u$ is introduced to give the geometry information of the filler;
e.g., for spherical fillers, $u$ is 1/3.
Figure 1.3. Three-dimensional distribution of the local field $E_L(r)$ in a polymer nanodielectric with the filler volume fraction ($\eta$) of 0.2. (A) and (B) Initial field distribution $E_L/E_0$ without and with loop correction for a random composite, respectively. (C) Initial field distribution $E_L/E_0$ with loop correction for a body-centered cubic (bcc) composite with $\eta = 0.2$. The color of the spherical particles is set to black to help visualization. The applied electric field is along the $z$ direction. The particle size ($\sigma_p$) is 100 nm, and the applied field is 50 MV/m. The permittivities of the matrix and particles are $\varepsilon_m = 3$ and $\varepsilon_p = 1,000$, respectively. (D) Loop correction term $\langle \mu \rangle_L$ for the dipole moment of the inclusions as a function of $\eta$ for the random and bcc composites. The $\sigma_p$ is 100 nm (2 um), and the applied field is 50 MV/m. The permittivities of the matrix and particles are $\varepsilon_m = 3$ and $\varepsilon_p = 100$, respectively. (E) Loop correction term $\langle \mu \rangle_L$ for the dipole moment of the inclusions as a function of $\sigma_p$ for the random and bcc composites. The applied field is 50 MV/m. The matrix and particle permittivities are $\varepsilon_m = 2$ and $\varepsilon_p = 100$, respectively. (F) Dependence of $\varepsilon_{\text{eff}}$ on the $\eta$ in a random composite. The experimental $\varepsilon_{\text{eff}}$ data are taken from literature.$^{36}$ Lichteneker, Maxwell-Garnett, and Bruggeman fittings are also shown for comparison. The applied field is 100 MV/m. The particle diameter is 50 nm. The permittivities of the polymer matrix and particles are $\varepsilon_m = 4.3$ and $\varepsilon_p = 150$, respectively. The inset shows schematic illustration for the octahedral cage to probe the local field $E_L(r)$ in the composite. The green particle at the center is the probe to measure the $E_L(r)$. Only dipoles of the case-forming particles are shown. Reproduced with permission from Royal Society of Chemistry.$^{37}$

2.2.3 Model 3: Numerical Simulations

In the past, it is nearly impossible to directly solve Maxwell equation without making any approximation to simplify the calculation. Nowadays, the prevalence of high-performance
computers as well as breakthroughs on computing algorithms enable to perform numerical simulation on dielectric composites. Sareni et al. combined the boundary integral equation method with finite element method (FEM) to investigate the dielectric behavior of a two-phase system with fillers either in a periodic lattice or in a random distribution. They outlined that the numerical simulation can handle systems with a high concentration of fillers and/or with a high filler/matrix dielectric contrast, where mean-field approximation failed to consider inclusion interaction. In another report, FEM method was carried to compare the frequency dependent dielectric properties of the ordered and disordered 2D binary composites. Results showed that the dielectric relaxation characters due to MWS interfacial polarization changed drastically by changing the conductivity ratio of two phases, as well as their topologies.

In a recent simulation, Zhu and coworkers used coarse-grained molecular dynamics to study the effect of dipole correlation on local field and effective $\varepsilon_r$ in polymer nanodielectrics. The basic model was comprised of nanoparticles (NPs) connected to the nearest neighbors by elastic springs. The spatial organization can be either random or ordered such as body-center cubic (bcc). Upon electric poling, the NPs would be polarized and can be abstract into individual dipoles with a dipole moment of $\mu_0$. Depending on the spatial arrangement of the NPs, dipole-dipole coupling would take place through the change of local electric field, $E_L(r)$. As a result, the actual dipole moment of the NPs would increase. The permittivities of the polymer matrix and the NPs were $\varepsilon_m = 3$ and $\varepsilon_p = 1,000$, respectively. The applied electric field was 50 MV/m. The particle diameter was 100 nm. Figures 1.3A and B showed the $E_L(r)$ distributions for a random nanocomposite without and with dipole-dipole correlation, respectively. As one can see, without dipole-dipole
coupling (Figure 1.3A), the $E_L(r)$, especially around the NPs, appeared to be weaker than the situation with dipole-dipole coupling (Figure 1.3B). Meanwhile, the enhancement of $E_L(r)$ near the particles appeared to be different for random and bcc nanocomposites. As shown in Figure 1.3B, the $E_L(r)$ can be significantly increased when more than 3 particles chain in the direction of electric field. For example, the $E_L/E_0$ can reach as high as $10^{-12}$ between chained particles, serving as hot-spots for early breakdown. However, the enhancement of $E_L(r)$ was significantly suppressed in a bcc crystalline structure (Figure 1.3C). Therefore, ordered crystalline structure such as bcc was desired to avoid early breakdown in polymer nanodielectrics. The dipole correlation term can be defined as $\langle \mu \rangle_L = \mu/\mu_0 - 1$. When the poling field was $50 \text{ MV/m}$, particle size ($\sigma_p$) was $100 \text{ nm}$, and $\varepsilon_m = 3$ and $\varepsilon_p = 100$, the $\langle \mu \rangle_L$ result was shown in Figure 1.3D. As one can see, the $\langle \mu \rangle_L$ increased significantly as a function of the $\eta$ for the random composite, whereas it remained very small for the bcc composite. Similarly, the dipole correlation term was also particle size dependent, especially for the random composites (Figure 1.3E). The larger the particle size, the higher the $\langle \mu \rangle_L$ and hence the stronger the enhancement of the local field. This was consistent with experimental observations, where nanocomposites behaved better than micro-composites in $E_b$.

To derive the effective $\varepsilon_r$ for the nanodielectric, an octahedral cage with a center particle was designed in the inset of Figure 1.3F. In this cage, the additive fields from the eight corners canceled each other, and thus can be placed inside the nanodielectrics to probe the local field. The effective $\varepsilon_r$ was defined as:\textsuperscript{40}

$$\varepsilon_{eff} = \langle \varepsilon(r)E^2(r) \rangle_\Omega / \langle E(r) \rangle^2_\Omega$$  \hspace{1cm} (1.9)
where $\varepsilon(r)$ was the local permittivity. It was $\varepsilon(r) = \varepsilon_m$ for the polymer matrix and $\varepsilon_p$ in the NPs. To compare with the experimental result from a reference $^{36}$, the author changed the system parameter: $E_0 = 100$ MV/m, $\varepsilon_m = 4.3$, $\varepsilon_p = 150$, and NP size was 50 nm. The simulation results were shown in Figure 1.3F, where the simulated results fitted with the experimental results reasonably well. It can be seen that the Lichtenecker model overestimated the $\varepsilon_r$ of the composite. This was possibly due to the empirical nature of the model to fit between the parallel and series capacitor models. The Maxwell-Garnett model underestimated the $\varepsilon_r$ of the composite, because in the Maxwell-Garnett (or most FEM) model, no dipole-dipole coupling was taken into account. The Bruggeman model generally fitted our simulation result reasonably well, except at very high volume fractions. This was because Bruggeman model took into account of the local field perturbation from both the matrix and NPs. Therefore, Bruggeman model was often used to estimate the effective $\varepsilon_r$ for polymer nanodielectrics containing spherical particles. The apparent $\varepsilon_r$ of polymer nanodielectrics would further increase because that particle aggregation could enhance dipole-dipole interaction. In the future, theory and modeling should be carried out to deal with nanocomposites containing nanorods and nanoplatelets.
2.2.4 Filler/Polymer Interfaces

Interfaces and related interfacial phenomena are important features of polymer nanodielectrics. The volume fraction of interface, $f$, is strongly dependent on the filler size. Assuming a core-shell model, where a spherical filler in diameter $d$ and an interfacial shell in thickness $t$, $f$ can be calculated using the following formula:

$$f = 3 \left(\frac{2t}{d}\right) \left[1 - \left(\frac{2t}{d}\right) + \frac{1}{3} \left(\frac{2t}{d}\right)^2\right]$$  \hspace{1cm} (1.10)

The inverse relation between $f$ and $d$ makes the interfacial phenomenon more prominent in nanocomposites than it is in mico-composites. It is possible that eventually bulk properties of the filler and matrix will be gone, leaving the whole composite as an pure “interfacial” material when the filler size is below a certain critical point. Then, it is the interfaces that dictate the overall properties of a nanocomposite. Therefore, establishing certain interfacial theories or models to help understand what polymer/filler interfaces look like and how
interfacial behavior works are considered essential in polymer nanodielectrics. Initially, the concept of EDL is borrowed from heterogeneous fluid-based systems to explain the interfacial phenomenon in nanodielectrics. As shown in Figure 1.4, the surface of nanofiller A will be charged either owing to ionization of surface groups as a result of equalization of Fermi level or chemical potential, or absorption of space charges (electron/holes and impurity ions) from the polymer matrix B. The buildup of immobile electric surface charge layer on A/B interface will create a local electric field to affect nearby space charges inside B. There is a charge screening layer, starting from the A surface, across the interface into B, in order to make the system electrically neutral. This screening layer has two parts, one is the Stern layer and the other is the Gouy-Chapman diffuse layer. The Stern layer with a few nm thickness comprises small molecules (if any), specific absorbed ions, and solvated ions. They are firmly attracted by the surface charge layer of A and cannot move freely. Beyond the Stern layer is the so-called Gouy-Chapman diffuse layer. This layer contains a great number of loosely attracted counter ions, which are conductive and can move freely in response to the local field change. Depending on the ion concentration and conductivity of B, the Debye length \( \lambda \), which defines the extent of the exponential decay of the diffuse layer, can vary from 10 to 100 nm. This layer, like the space charge depletion zone in the p-n junction, is considered to potentially work as the “interaction zone” to affect the polarization and \( E_b \) of nanodielectrics. The above-mentioned “coupling effect” between the filler and matrix is likely to interact throughout the diffuse layer. Overlap of the Gouy-Chapman diffuse layer between neighboring filler particles might result in some collective effects. For example, if interparticle distance is on the same length scale as the diffuse layer thickness, ion percolation pathway might form through the overlapped area, and thus free
charges can move over a long distance, resulting in much higher leakage current and lower $E_b$. From the above discussion, local field enhancement and percolation of ionic pathways in polymer nanodielectric could be the reasons to cause early dielectric breakdown at a high enough filler content.\textsuperscript{37} Research are currently underway to solve this problem.

Based on the conventional EDL theory, Tanaka et al. proposed a multilayered core-shell model to specifically understand various properties and phenomena that polymer nanocomposites exhibit in electrical insulation applications.\textsuperscript{43} From their point of view, the interface between nanofiller and polymer matrix consists of a first bonded layer, a second bound layer, and a loose layer and an EDL that overlaps with all three these three layers. The 1 nm-thick bonded layer corresponds to a coupling agent layer tightly bonded to both inorganic and organic substances through ionic, covalent, or hydrogen bonds, or van der Waals force. The second layer is made of a layer of polymer chains strongly bound and/or interacted to the first layer and the surface of particle. It is also not thick, usually in the range of 2-9 nm. The third loose layer is a much thicker polymer layer loosely coupling and interacting with the bound layer. In this layer, the chain conformation, mobility, and even free volume or crystallinity will be different from polymer matrix. This theory illustrates that tight bonding will favor a good interface in the second and third layers. The multilayer core-shell model was used to successfully explain partial discharge resistance of polyamide/layered silicate nanocomposites. However, it is a highly hypothetical theory given the difficulty to detect and visualize their multilayered interface structure. In future, more experimental evidence needs to be collected to further evaluate the validity of their hypothesis, as well as this field also calls for new understanding and theories.
In 2002, Vo and Shi introduced a phenomenological interfacial layer model to mathematically describe the properties of filler/matrix interface. According to the Vo-Shi model, the $\varepsilon_r$ of composite was not only a function of filler content $\phi$, $\varepsilon_r$s of filler and matrix, which is already included in Maxwell or Bruggeman equation, but also has to do with the interphase volume constant $k$, and interphase permittivity $\varepsilon_{r,int}$. The size-dependent $k$ is used to assess the interaction strength between filler and matrix. The value of $k$ and $\varepsilon_{r,int}$, and the thickness of interface can be obtained by fitting experimental data using Vo-Shi Model. From the Vo-Shi theory, it suggests that the $\varepsilon_r$ of composite can also be enhanced by increasing the $\varepsilon_{r,int}$, even keeping other conditions the same. That is to say, $\varepsilon_r$ of composite might be further increased by carefully designing interface and/or engineering filler/matrix interaction. Murugaraj et al. showed that the Vo-Shi theory fitted well to their experimental observations in PI/alumina and PI/silica nanodielectrics. The fitting $\varepsilon_{r,int}$ and $k$ were 280, 3.24 for the PI/alumina composite, and the interphase layer was assumed to be about 4 nm. This PI/alumina system exhibited a condition of $\varepsilon_{r,pol} < \varepsilon_{r,int} < \varepsilon_{r,par}$. As a comparison, fitting of a 900 nm lead magnesium niobate-lead titanate (PMN-PT)/epoxy system gave $\varepsilon_{r,int} = 6,070$ and $k = 0.72$, showing a relationship of $\varepsilon_{r,pol} < \varepsilon_{r,int} < \varepsilon_{r,par}$. The author attributed this difference to the fact that the 10 nm alumina fillers had an interphase volume fraction about three orders of magnitude larger than that of the 900 nm PMN-PT filler in nanocomposites, as well as a better filler/matrix interaction strength. Inspired by the Vo-Shi model, a number of novel polymer nanocomposites based on core/shell nanofillers or interfacially engineered nanofillers have been designed to enhance the apparent $\varepsilon_r$. Thin layers of metal ($\varepsilon_r = \infty$), brookite TiO$_2$, carbon or CuPc ($\varepsilon_r \sim 10^4$-$10^5$) were coated on BaTiO$_3$ surface to aggrandize interfacial contribution, the apparent $\varepsilon_r$ of
the three-phase polymer nanodielectrics can be effectively enhanced at a filler ratio of only 5-10 vol.%. This is drastically different from the two-phase polymer nanodielectrics, whose apparent εrs only increase when the filler concentration is close to the percolation threshold (i.e., ~ 35 vol.% for spherical NPs).

![Figure 1.5](image)

**Figure 1.5.** (A) Schematic illustration of the preparation of three- and two-phase P(VDF-HFP)/BaTiO3 nanocomposites, respectively. (B) Chemical structure of the TMPc-Br atom transfer radical polymerization (ATRP) initiator. (C) Calculated apparent permittivity (εr) as a function of filler volume fraction for the three-phase nanocomposites based on theoretical prediction by Vo and Shi.44 Experimental permittivities at 1 kHz and room temperature for uniaxially stretched P(VDF-HFP)/BT@TMPc-PMMA and P(VDF-HFP)/BT@R2-PMMA nanocomposite films are shown for comparison with the theoretical predictions. Reproduced with permission from Wiley.46

An example is shown in Figure 1.5.46 Two-phase P(VDF-HFP)/BT@R2-PMMA [poly(methyl methacrylate)] and three-phase P(VDF-HFP)/BT@TMPc-PMMA nanocomposites were prepared by surface-initiated ATRP of MMA from 70 nm BaTiO3
NPs, followed by solution-blending with P(VDF-HFP). Various NP compositions were prepared, ranging from 0.5 to 5 vol.%. In the two-phase nanocomposite, the surface initiator was the R2 ligand (Figure 1.5A). In the three-phase nanocomposite, the surface initiator was tetrameric Cu-phthalocyanine (TMPc, Figure 1.5B), a high permittivity oligomer.47 After solution-blending, nanocomposite films were prepared by hot-pressing above the melting temperature (ca. 155 °C) of P(VDF-HFP). The apparent \( \varepsilon_{rs} \) of both two-phase and three-phase nanocomposites were studied by BDS, and the \( \varepsilon'_r \) at 1 kHz and room temperature are shown in Figure 1.5C. Obviously, the three-phase nanocomposite exhibited a higher \( \varepsilon_r \) than the two-phase nanocomposite. Compared with the Vo-Shi prediction, the three-phase nanocomposite fits with the interface ratio \([(b-a)/c]\) of 0.20, when the \( \varepsilon_{is} \) of P(VDF-HFP), BaTiO\(_3\), and TMPc were taken as 11.2, 300, and 10,000, respectively. Clearly, the high permittivity TMPc interfacial layer effectively enhanced the apparent \( \varepsilon_r \) of the P(VDF-HFP)/BaTiO\(_3\) nanocomposites at a filler ratio even less than 5 vol.%.

3. Polymer Nanodielectrics – Experimental Achievements

3.1 Dielectric Constants of Ceramic NPs and Polymers

Unlike bulk materials, it is fairly difficult to accurately determine \( \varepsilon_{is} \) of inorganic NPs, because NPs are usually small powder with poor film-forming properties. Instead, people have proposed some indirect ways to measure it. In the most straightforward way, one can use a hydraulic press to compress the powder of NPs at ambient temperature into pellets with a uniform thickness.48,49 Sometimes, a small amount (<0.5 wt.%) of polymer adhesives can be used as the binder.50 However, to avoid the interference of solvents
(especially water) and ionic impurities, it is better not to use any polymer binder for the compressed pellets. The packing volume fraction (between 55 and 65 vol.% depending on the hydraulic pressure) can be obtained by comparing the apparent density of the pellet to the actual density of the bulk material. Using the mask with known area, silver paste can be applied to both sides of the pellets as electrodes. The $\varepsilon_r$ can be directly measured using BDS. The $\varepsilon_r$ of NP can be extracted using Bruggeman equation, if packing volume fraction and $\varepsilon_r$ of pellets are determined. The $\varepsilon_r$ of pellet obtained after sintering at high temperature is misleading. The sintering alters grain boundary structure and helps domain growth. What measured is no longer a dielectric property of NP but that of bulk material.$^{15}$

Researchers also prepared nanofiller slurries or suspensions in certain dielectric solvents and then studied the $\varepsilon_r$ of filler using an impedance analyzer. Wada and coworkers synthesized a group of defect-free, high purity BaTiO$_3$ crystallites with particles sizes between 17 and 100 nm.$^{51}$ The $\varepsilon_r$s were obtained by measuring capacitance of BaTiO$_3$ suspensions of several NP contents in propylene carbonate. Results were then fitted using FEM and an optimized model, which assumed that semi-sphere BaTiO$_3$ NPs made of numerous tetrahedrons were homogeneously surrounded by propylene carbonate tetrahedrons. Their study revealed that BaTiO$_3$ particles with a size around 70 nm exhibited the highest permittivity among particles from 0 to 600 nm, and are most desirable for capacitor applications. Dogan and coworkers further developed this slurry method for dielectric studies of different micron- and nano-sized ceramic particles.$^{52}$ Micron-sized particle slurry showed two distinctive dielectric relaxation semi-circles in the impedance spectrum, which was equivalent to a circuit containing two RC elements connected in series. As long as a large dielectric contrast existed between particles and solvents, $\varepsilon_r$ of
particles could be determined by impedance circuit deconvolution analysis. Because of the large surface to volume ratio and surface conductivity, \( \varepsilon_r \) of NPs cannot be accurately measured using this method, unless a monolayer of small molecule ligands was chemically coated onto the particle surface to mitigate surface conduction.

Adam and coworkers applied an electrical polarization measurement to a series of cyanoethyl cellulose composites that contains as-synthesized or commercial BaTiO\(_3\) particles with sizes between 10 nm and 0.8 \( \mu \)m, to study the size effect on \( \varepsilon_r \) of particles\(^{53}\). They found that three intrinsic and size-dependent properties, namely, tetragonality, \( \varepsilon_r \), and the individual switching fields, would influence the ferroelectric polarizability of composites made with these particles.

<table>
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<tr>
<th>Fillers</th>
<th>Size/Phase</th>
<th>Surface Modification</th>
<th>Permittivity</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>np-BaTiO(_3)</td>
<td>70 nm/cubic</td>
<td>unmodified</td>
<td>185</td>
<td>54</td>
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<tr>
<td>np-BaTiO(_3)</td>
<td>70 nm/cubic</td>
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<td>54</td>
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<td>50</td>
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<tr>
<td>np-BaTiO(_3)</td>
<td>6 nm/cubic</td>
<td>( n )-hexylphosphonic acid</td>
<td>25</td>
<td>50</td>
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<tr>
<td>np-BaTiO(_3)</td>
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<tr>
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<td>300 (11 nm); 450 (27 nm)</td>
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<tr>
<td>mp-SrTiO(_3)</td>
<td>&lt;5 ( \mu )m</td>
<td>unmodified</td>
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<td>np-Ba(<em>{0.7})Ti(</em>{0.3})O(_3)</td>
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<td>65,66</td>
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<td>66</td>
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<td>-</td>
<td>980</td>
<td>68</td>
</tr>
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</table>

| CuPc           |      |      | ~10⁴-10⁵ | 69   |

Abbreviations: b - bulk; p - particles; f - film; m - micron-sized; n - nano-sized.

Table 1.1 summarizes $\varepsilon_r$s of a number of common inorganic particles (mostly non-sintered) used for polymer nanodielectrics. Barium titanate (BaTiO₃) is the most widely used ferroelectric ceramics, and can be synthesized in various forms, including spheres and rods/whiskers. Bulk BaTiO₃ exhibits four crystalline phases depending on temperature, the rhombohedral phase transforms into the orthorhombic phase around -90 °C, the orthorhombic phase transforms into the tetragonal phase around 5 °C, and finally the tetragonal phase transforms into the cubic phase around 125 °C. The cubic phase is a paraelectric phase, whereas the rest three phases are ferroelectric phases. Therefore, 125 °C is the ferroelectric - paraelectric Curie transition temperature ($T_C$). At room temperature, bulk BaTiO₃ exhibits very high $\varepsilon_r$ up to several thousand, depending on the sintering temperature, density, and grain size, and grain boundaries. Because of the $T_C$ around 125 °C, its $\varepsilon_r$ is strongly dependent upon temperature and a peak in $\varepsilon_r$ appears around the $T_C$.

However, micro- and nano-sized spherical BaTiO₃ particles does not show $\varepsilon_r$ as high as that of bulk BaTiO₃. As shown in Figure 1.6A, the Bruggeman-corrected $\varepsilon_r$ of BaTiO₃ particles gradually decreases with decreasing the particle size. The $\varepsilon_r$s are measured using
the method of compressed pellets from particle powder, followed by correction using the Bruggeman mixing model. When the particle size decreases from 130 µm to 10 µm, the \( \varepsilon_r \) quickly decreases from around 800 to about 300. Below 10 µm, the \( \varepsilon_r \) decreases slowly to ca. 185 at a particle size of 70 nm.

**Figure 1.6.** (A) Bruggeman-corrected \( \varepsilon_r \) as a function of particle size of BaTiO\(_3\). Data are taken from the literature. (B) Schematic illustration of the crystalline grain and ferroelectric domain structures in a single BaTiO\(_3\) particle. There may exist a finite surface layer with random dipole orientation (green arrows). (a) Single particle with multiple crystalline grains. In each crystalline grain, there are 90° and 180° ferroelectric domains. (b) Single particle and single crystal with both 90° and 180° ferroelectric domains. (c) Single particle and single crystal with only 180° ferroelectric domains. (d) Single particle, single crystal, and single domain. (e) Single particle, single crystal, but no ferroelectric domain any more. Thick blue lines define the crystalline grains. The red lines define the 90° ferroelectric domains. The red dashed lines define 180° ferroelectric domains. Black arrows show the direction of ferroelectric domains.

Initially, the particle size-dependent \( \varepsilon_r \) of BaTiO\(_3\) is considered as a pure size effect. Actually, it should not be simply attributed to the size effect, but an effect of the ferroelectric domain structure in BaTiO\(_3\) particles (see Figure 1.6B). When the particle size is large (e.g., > 10 µm, Figure 1.6B-a), a single particle contains multiple crystalline grains (divided by thick blue lines) and each grain contains multiple ferroelectric domains, i.e., 90° domains (divided by thick red lines) and 180° domains (divided by red dashed lines).
In addition, there may exist a finite surface layer with much decreased ferroelectricity (or tetragonality) because of the surface dangling bonds and defects. This is supported by the evidence that the electric displacement - electric field (D-E) loops for the compressed BaTiO₃ pellets do not exhibit any hysteresis and become linear in loop shape.⁴⁸ Because of this weakly ferroelectric surface layer, the εᵣ of BaTiO₃ particles becomes lower than the bulk BaTiO₃. The high permittivity for ferroelectric ceramics originates from the high mobility of Ba²⁺ ions in the domain walls. In other words, the εᵣ inside the ferroelectric domains is not very high. Note that the 90° domain walls are more electrically active than the 180° domains. When the particle size decreases to about 1 µm (Figure 1.6B-b), it may become a single particle single crystal, together with both 90° and 180° domains. As the particle further decreases to about 200 nm (Figure 1.6B-c), 90° domains disappear, resulting further decrease in εᵣ. When the particle size decreases to about 50 nm (Figure 1.6B-d), the single particle single crystal may contain a single domain. Because of the lacking of domain walls, the εᵣ again decreases. Finally, when the particle is smaller than 20 nm, the surface defects destabilize the tetragonal phase. The particle becomes single crystal cubic phase, and the εᵣ is the lowest. The above situation is a rough description for ball-milled and sol-gel synthesized BaTiO₃ particles, depending on the synthesis and domain structures. If multiple ferroelectric domains can be stabilized in BaTiO₃ NPs, the εᵣ can be enhanced. For example, in a recent study, 11-27 nm BaTiO₃ NPs are synthesized using a unimolecular star-block copolymer containing poly(acrylic acid) (PAA) in the core and polystyrene (PS) in the shell (i.e., a nanoreactor approach).⁵⁶,⁷⁰ The Bruggeman-corrected εᵣs are about 270 for 11 nm particles and 420 for 27 nm particles (10⁴ Hz).⁵⁶ Only when the particle size decreases below 6 nm, the tetragonality disappears. In addition,
surface charges can also affect the stability and structure of ferroelectric domains in BaTiO$_3$ NPs. For example, as the defective BaTiO$_3$ surface is passivated by nonpolar organic ligands, the ferroelectric domains are destabilized and the permittivity can decrease.$^{50,54}$ Therefore, there are many factors affecting the apparent $\varepsilon_r$ of BaTiO$_3$ NPs.

In addition to BaTiO$_3$, researchers also expand their choices for nanofillers to a variety of high-$\kappa$ ferroelectric NPs, such as Ba$_x$Sr$_{1-x}$TiO$_3$ (BST),$^{71}$ lead magnesium niobate-lead titanate (PMN-PT),$^{72}$ and lead lanthanum zirconium titanate (PLZT).$^{73}$

Other than high permittivity semiconducting NPs, conducting nanofillers are also used to prepare high-$\kappa$ nanocomposites. These conducting nanofillers include metallic NPs (e.g., Ni, Ag, Al, and Cu)$^{74-77}$ and carbonaceous nanomaterials (e.g., carbon black, carbon nanotubes, and graphene/graphite).$^{78-80}$ The $\varepsilon_r$ of these conducting NPs are considered as infinity. Sometimes, conductive polymers (e.g. polyaniline, PANi)$^{81}$ and oligomers (e.g., copper phthalocyanine, CuPc)$^{47}$ are also used as fillers, and high $\varepsilon_r$s are reported for their nanocomposites when filler content is around percolation threshold.

As the major phase in nanodielectrics, the $\varepsilon_r$ of polymer plays an important role in determining final $\varepsilon_r$ of nanocomposites. In general, $\varepsilon_r$s of linear dielectric polymers are relatively low, often between 2 and 5.$^3$ This is attributed to the relatively low electronic and atomic polarizations in nonpolar polymers, as discussed in section 2.1. Examples of linear dielectric polymers include PP ($\varepsilon_r = 2.25$), PS ($\varepsilon_r = 2.8$), polycarbonate (PC, $\varepsilon_r = 2.8-3.0$), polyimide (PI, $\varepsilon_r = 2.8-3.2$), epoxy ($\varepsilon_r = 2.5-4$), and many others. The advantage of using linear dielectric polymers as the matrix lies in the fact that dielectric losses from impurity ions, electronic conductivity, and ferroelectricity (if any) can be largely suppressed. Therefore, they are suitable for the study of dielectric loss mechanisms in
nanodielectrics, which will be discussed later. The disadvantage is that due to their low permittivity, the apparent $\varepsilon_r$ of the nanocomposite is difficult to reach above 10 even at a composition close to the percolation threshold, which is ca. 30-35 vol.% for spherical NPs.\textsuperscript{82,83} Strongly dipolar polymers, e.g., ferroelectric and relaxor ferroelectric polymers, appear to be more attractive, because they exhibit high $\varepsilon_r$s between 10 and 70.\textsuperscript{3} Examples include PVDF and its random copolymers [e.g., P(VDF-HFP), P(VDF-CTFE), and P(VDF-TrFE)]; here, HFP is hexafluoropropylene, CTFE is chlorotrifluoroethylene, TrFE is trifluoroethylene], and P(VDF-TrFE-X) [X is 1,1-chlororfluoroethylene (CFE) or CTFE] random terpolymers. Here, PVDF and its random copolymers are ferroelectric. Their ferroelectricity at high poling electric fields significantly decreases the discharge efficiency, even though their permittivity can be as high as 10-15. Therefore, ferroelectric PVDF and its copolymers are not suitable for electric energy storage applications. P(VDF-TrFE-X) terpolymers are relaxor ferroelectric with narrow hysteresis loops. They appear to be fairly appealing for certain applications. Nonetheless, PVDF-based polymers can easily undergo electrochemical reactions and release HF under high electric field and high temperature conditions.\textsuperscript{17,84} Meanwhile, high electronic (and ionic) conductivity at high temperatures (about 3 orders of magnitude higher than that of linear dielectric polymers) is another shortcoming for relaxor ferroelectric fluoropolymers,\textsuperscript{17} and this should be taken into account when directly using polar fluoropolymers for high-field electrical applications.

### 3.2 Nanocomposite Breakdown Strength
Weibull statistical analysis is widely used to evaluate dielectric breakdown strength for insulating materials. The two-parameter Weibull cumulative distribution function $F$, is defined as:\(^85\)

\[
F(E_b) = 1 - \exp \left( -\frac{E_b}{\alpha} \right)^\beta
\]

(1.11)

where $E_b$ is the measured breakdown electric field. The scale parameter, $\alpha$, is the characteristic electric field, where 63.2% failure probability occurs. The shape parameter, $\beta$, is the Weibull modulus evaluating the width of distribution. The breakdown profile of a series of BaTiO$_3$/P(VDF-HFP) nanocomposites was given in Figure 1.7A. Kim et al. observed a monotonic decrease in $E_b$ as the filler content increased, as plotted in Figure 1.7B.\(^86\) For example, $E_b$ around 380 MV/m for neat P(VDF-HFP) decreased to 210 MV/m for the 50 vol.% nanocomposite. Li et al. analyzed the permittivity, $E_b$ and $U_e$ for dielectric nanocomposites using an effective medium approximation.\(^87\) In the double-inclusion method, a nanocomposite was considered as a three-phase material. Simulation showed that an increase in $\varepsilon_r$ would inevitably result in a decrease in $E_b$, and interfacial interaction shifted the “percolation” threshold to lower filler content. As a result, the potential gain in $U_e$ might be negative, unless the microstructure of nanocomposites were carefully controlled. Two-dimensional (2D) simulations of local electric field distribution for randomly distributed NPs with and without grafting chains were shown in Figure 1.7C by Grabowski et al.\(^88\) For low dielectric contrast nanocomposites ($\varepsilon_{\text{particle}}/\varepsilon_{\text{polymer}} = 1.5$, e.g., silica NPs in PMMA), almost no local field enhancement can be observed. The interfacial effects was fairly negligible and $E_b$ was only slightly lower than that of neat polymer. However, for nanocomposites with a high dielectric contrast, ($\varepsilon_{\text{particle}}/\varepsilon_{\text{polymer}} = 100$, e.g., BaTiO$_3$ NPs in PMMA), filler without effective separation (no grafted polymer brushes)
easily form aggregated chains and clusters. Their interfacial “interaction zones” could overlap, resulting in extended conduction pathway and numerous hot pots, especially for the region near two poles of individual NPs along the direction of external field. The local field might reach values tens of times greater than the external applied field. Matrix-free nanocomposites with ordered particle arrangement might, to some extent, mitigate local field enhancement by not forming particle chains or clusters, and thus no overlapped “interaction zones”. However, local field around NPs could still be several times higher than applied field owing to large dielectric contrast. In short, large dielectric contrast is the main reason to account for early breakdown in polymer nanodielectrics.

**Figure 1.7.** (A) Percent cumulative distribution function (% probability of device failure) of each nanocomposite as a function of applied electric field; (B) the Eb (failure probability: 63.2%) at each volume fraction as determined from the Weibull analysis; and (C) Two-dimensional (2D) simulated electric field distributions for 100 particles with permittivity ratio of (a, b) 100:1 and (c, d) 1.5:1, with respect to the matrix. For each, two cases reflect randomly distributed particles with and without grafted chains. For chain grafting, the minimum particle separation is greater than one radius (panels (b) and (d)), whereas without grafting, the particle–particle separation may be less than one radius (panels (a) and (c)). Colors correspond to the normalized field intensity (E/E₀). White regions observed in panel (a) are areas where E/E₀ >3. Reproduced with permission from American Chemical Society. 86,88

Whether inclusion of NP in polymer definitely lower Eb is still in debate. Some researchers argued that adding a small fraction of NP could be beneficial to the Eb of polymer. For example, improved EbS were observed for lightly crosslinked PE (XLPE, used in high voltage cables) nanocomposites filled with silica, alumina and titania NPs
compared to that of base resin (usually $E_b$ of base resins is below 200 MV/m).\textsuperscript{89} It was proposed that enrichment of interfacial area in nanocomposites created “interaction zones”, which may give the following benefits to enhance dielectric properties in nanocomposites than either base resin or micro-composites:\textsuperscript{89} 1) NPs serve as scattering centers and increase the tortuosity of the breakdown pathway. 2) NPs can influence properties of polymer by changing its morphology, chain mobility, crystallinity and so on. 3) NPs are able to change the space charge distribution in the sample. 4) NPs rather than micro-particles might reduce the local field enhancement. As a result, the $E_b$ for these nanocomposites behaved better. Grabowski et al. also studied the impact of the polymer-NP interaction on the $E_b$ of nanocomposites.\textsuperscript{90} They found that for high $E_b$, amorphous polymers (e.g., PMMA and PI), incorporation of silica NPs always reduced the $E_b$ at all compositions. On the contrary, for low $E_b$ polymers [e.g., PS and poly(4-vinyl pyridine) (P4VP)] with comparable NP dispersion, their nanocomposites showed equal or even better $E_b$ at relatively low filler contents between 7.5 and 15 vol.\% than of neat polymers. The $E_b$ would eventually decrease when filler content was above 20 vol.\%. Regarding what researchers discovered with different nanocomposites, it looks like that two effects are competing with each other. One is the decreasing effect from electric field concentration in the polymer matrix, and the other is the increasing effect from trapped space charges by NPs. The competition will eventually determine the final $E_b$ of polymer nanocomposites. However, the decreasing effect is more significant especially at high electric fields. Therefore, for most polymer nanocomposites containing spherical or rod-like NPs, the $E_b$ tends to decrease with increasing the filler content.
To enhance the $E_b$ for polymer nanocomposites, nanoplatelets with insulating properties can be used. For example, organic-modified montmorillonite (oMMT) with a layered structure can increase the $E_b$ of poly(vinyl butyrate) (PVB) from 100 MV/m (neat film) to 130 MV/m (10 vol.% oMMT).\textsuperscript{91} Recently, boron nitride nanosheets (BNNS, $\kappa = 4.6$) nanocomposites were reported.\textsuperscript{92} When BNNS was employed as the filler, it was able to function as a robust scaffold to hamper the onset of electromechanical failure at high temperatures, and as an efficient insulating barrier against electrical conduction. At 12 vol.% filler content, it could increase the $E_b$ of P(VDF-TrFE-CTFE) terpolymer by 20% and 44% enhancement in overall $U_e$. Basically, the above nanoplatelets have low permittivities and high electrical resistivities. Mitigation of both permittivity and conductivity contrasts between the polymer matrix and nanoplatelets minimizes the interfacial polarization. In turn, less inhomogeneous and distorted electric field distribution is resulted, and thus the $E_b$ can be increased. Alternatively, instead of using discrete nanofillers, multilayer films with high permittivity contrast can be beneficial. However, it has been difficult, if not impossible, to multilayer organic polymers with inorganic ceramics. Therefore, research in this area has been focused on polymer multilayer films.\textsuperscript{93-96} High $U_e$, high $E_b$, and low dielectric loss can be achieved simultaneously.

### 3.3 NP Dispersion in Polymer Matrix

Other than simply using physical force such as sonication, ball-milling, agitation, and twin-screw mixing to break up NP aggregates during nanocomposite preparation. Sometimes, researchers also add a small amount of organic compatibilizer to make NP more miscible with polymer. However, compatibilizers may compromise dielectric
properties due to possible degradation under high electrical field. Chemical modification of NP surface serves as an important supplementary way to help improve interfacial adhesion and NP dispersion. Both small molecules and polymer brushes are grafted onto NP and make NP more compatible with polymer. Kim et al. found that organic phosphonic acids could form robust surface coating on BaTiO$_3$ NPs through either metal-oxygen coordination or condensation with surface -OH groups$^{86}$ The phosphonic acid monolayer on BaTiO$_3$ surface guaranteed a good NP dispersion within composite film, and thus a high $\varepsilon_r$ with a reasonable $E_b$ was achieved for this nanocomposite. Dang et al. used a commercial silane coupling agent (KH-550) to modify BaTiO$_3$ NP surface.$^{97}$ Amine groups of KH-550 were able to form hydrogen bonds with fluorines in PVDF. Besides, KH-550 treatment also help to increase the tetragonality of BaTiO$_3$ and enable a higher dielectric polarization. They also used peroxide to treat BaTiO$_3$, which increased the density of surface hydroxyl groups and favored forming more hydrogen bonds between NP and PVDF, as well as a better NP dispersion.$^{98,99,100}$ Later, dopamine, titanate coupling agent, and hydantoin were reported to improve NP dispersion.$^{101}$ Although these small molecules do help with dispersion, particle flocculates with a few NPs clustering together can still be observed in most nanocomposites, due to the dry-brush scenario.$^{102}$ When the molecular weight of surface ligand is much smaller than that of the polymer matrix, polymer chain cannot sneak in and wet NP surface, which leads to NP flocculates and aggregates.

To avoid the dry-brush scenario, researchers proposed to graft the same polymer chains as the polymer matrix with equal or higher molecular weights onto NP surface. Then the obtained hairy NPs can be uniformly dispersed in the polymer matrix without flocculates. Related studies were reported as early as 2005 by Maliakal,$^{103}$ who synthesized phosphonic
acid-tethered PS and attached it to anatase TiO$_2$ NPs via a ligand exchange reaction to replace the former oleic acid ligands. Tchoul et al. implemented a combination of phosphonate coupling and “click” chemistry to make macroscopic assemblies of hybrid NPs composed of a TiO$_2$ core surrounded by covalently attached PS corona.$^{104}$ Different from the graft-to method, Jiang and coworkers recently demonstrated a number of successful examples using atomic transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT) polymerization to prepare core-shell high-κ PMMA@BaTiO$_3$ and PS@BaTiO$_3$ NPs, respectively.$^{105}$ In their reports, fine tuning the polymerization parameters and kinetics resulted in control of the molecular weight of polymer brushes, thus nanocomposites with a broad range of filler contents and tailored filler/polymer interface can be obtained. The ε$_{rs}$ as high as 14.6 and 24, and tanδ as low as 0.037 and 0.013 were reached in PMMA@BaTiO$_3$ (32 vol.%) and PS@BaTiO$_3$ (48 vol.%) nanocomposites, respectively. Similarly, Tang and coworkers employed RAFT polymerization to grow acrylic polymer brushes with terthiophene side groups (PTTEMA) from BaTiO$_3$ NPs. Embedding these hairy NPs in PTTEMA homopolymer afforded well-dispersed, high-κ nanodielectrics.$^{106}$ However, it is difficult to grow very long polymer brushes (e.g., >100 kDa) from inorganic NPs using surface-initiated polymerization. Recently, hairy NPs with bimodal polymer brushes, namely, a combination of a majority of short polymer brushes and a minority of long polymer brushes, were prepared to overcome the dry-brush scenario.$^{107}$ To have truly aggregates-free, ordered nanocomposites, researchers even abandoned mixing hairy NPs with a matrix polymer, instead, hairy NPs alone formed so-called matrix-free nanocomposites. Paniagua and coworkers claimed that a matrix-free BaTiO$_3$@PMMA nanocomposite outperformed the
BaTiO₃/PMMA blend almost in every dielectric properties regarding dispersion, polarization, Eₜ, Uₑ and discharged efficiency.³⁶ This is how matrix-free nanocomposites behaves better than their blends in high dielectric contrast system, while in low contrast system, Grabowski and coworkers also observed 50% and 100% improvement of Uₑ in SiO₂@PMMA and SiO₂@PS matrix-free nanocomposites, respectively, as compared to that of normal nanocomposites.⁸⁸ This was attributed to higher discharge efficiencies at high fields and better morphology for the matrix-free hairy particle nanocomposites. If neat hairy NPs can self-assemble into ordered colloidal crystals, decrease of Eₜ can be largely avoided, as suggested from simulation result in Figure 1.7C-(b) and (d). However, surface-initiated polymerization is not suitable for commercialization, and this limits the further development of the matrix-free hairy NP approach. Other approaches, such as nanoreactors,¹⁰⁸ should be explored to synthesize, in large scale, hairy NP polymer dielectrics.

3.4 High Energy Storage in Polymer Nanodielectrics

3.4.1 The 0-3 Nanocomposites

In the beginning, high-κ perovskite fillers gained intense interests in polymer nanodielectrics. Li et al. reported that addition of 30 vol.% diamine-modified BaTiO₃ NPs into P(VDF-TrFE-CTFE) increased Uₑ from 3.2 J cm⁻³ to 7 J cm⁻³ at 150 MV/m.¹⁰⁹ Soon, researchers realized that field distribution inside nanocomposites was highly unbalanced. Most electric field was applied on polymer with fairly small field on filler due to a high permittivity contrast between them. Increase in apparent εₑ came from enhanced local field on polymer at the expense of significantly lowering Eₜ of polymer, not the contribution
from high-κ filler. Later, more resistive and moderate-κ NPs was chosen as nanofillers due to a less dielectric contrast. ZrO₂ and TiO₂, whose permittivities are close to those of PVDF copolymers or terpolymers were exploited by Wang and coworkers.⁶¹,¹¹⁰ With only 10 vol.% TiO₂ fillers, enhanced electric displacement from 6.3 mC/m² of the neat polymer to 7.6 mC/m², total Uₑ of 6.9 J/cm³, and Eₑ over 200 MV/m were accomplished. The author attributed enhanced dielectric performance to the interfacial coupling effect, which reached maximum at 10 vol.%. In another work (see Figure 1.8A), P(VDF-TrFE) was grafted onto ZrO₂ and ZrO₂/P(VDF-TrFE) nanocomposites was prepared, achieving total Uₑ as high as 11.2 J cm⁻³ with Eₑ comparable to that of neat polymer. Although matching εᵣ of the filler and polymer seems promising, the limitation is also obvious. The apparent εᵣ of nanocomposites would not be very much increased even at high filler content. In order to further improve nanodielectrics, researchers started to use core-shell or multicore nanofillers. The shell acted as a dielectric buffer layer between high-κ core and polymer matrix. The εᵣ from core to shell, and to polymer gradually decreased, meanwhile high-κ core can still raise εᵣ of nanocomposite. Marks and coworkers executed this “interfacial engineering” idea and prepared a series of matrix-free PP nanocomposites filled with different Al₂O₃ coated nanofillers, including BaTiO₃, ZrO₂, MgO, SrTiO₃, TiO₂, Ba₀.₅Sr₀.₅TiO₃, and yttria-stabilized zirconia (as shown in Figure 1.8B).¹¹¹ Nanofillers were treated with methylaluminoxane precursor followed by oxidation to form Al₂O₃ shell. By repeatedly performing this process, shell thickness can be varied up to 10 nm. Afterwards, single-site metallocene catalyst was immobilized on coated nanofillers to in-situ polymerize propylene. They found that high-field dielectric loss was proportional to NP
interfacial area, regardless of the constituent NP type. Moreover, increasing the thickness of Al₂O₃ shell dramatically suppressed dielectric loss.

**Figure 1.8.** (A) synthesis of the phosphonic-acid terminated P(VDF-CTFE) and grafting P(VDF-CTFE) onto the ZrO₂ NP surface (top). Dielectric permittivity and tanδ of P(VDF-CTFE) and the nanocomposites measured at 1 kHz and room temperature. Stars are the effective εₑ of the composites calculated from the Lichtenecker law (bottom left). Dependence of maximum-electric displacement on the ZrO₂ content in the nanocomposites measured at 225 MV/m (bottom right). (B) Repetitious coating of Al₂O₃ shell on nanofiller surface and immobilization of metallocene catalyst to in-situ polymerize propylene (top). Electric field-polarization loops for BaTiO₃-Al₂O₃(n)-isoPP nanocomposites, n=1, 3, 5. The volume fraction of BaTiO₃ are 0.05, 0.08 and 0.09 for n=1, 3, and 5, respectively (bottom left). Comparison of dielectric loss for capacitors fabricated from BaTiO₃-Al₂O₃(n)-isoPP nanocomposites n=1, 3, 5 Al₂O₃ layers at low and high field. The volume fraction of BaTiO₃ are 0.05, 0.08 and 0.09 for n=1, 3, and 5, respectively (bottom right). Reproduced with permission from American Chemical Society 110, 112

### 3.4.2 The 1-3 and 2-3 Nanocomposites

Prolate nanofillers with large aspect ratios are more advantageous than spherical nanofillers in enhancing dielectric properties. They usually exhibit much lower percolation threshold but higher and anisotropic polarization response under electric field. [e.g., at an aspect ratio of 3, the percolation threshold decreases from ca. 35 vol.% for a spherical NP composites to 18 vol.% for a prolate NP composite.]⁸³ Fillers in forms of nanotubes, nanorods, nanowires, and oriented nanospheres were used in the design of new polymer nanodielectrics. With less amount of nanofiller inclusion, prolate NPs might be able to achieve better dielectric performance without compromising too much processability and
flexibility of polymer. In Figure 1.9A, Tang et al. synthesized high-aspect-ratio paraelectric Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ (BST) nanowires (NWs) via two-step hydrothermal reaction and blended them into PVDF to prepare BST/γ-PVDF nanocomposites.\textsuperscript{113} Those nanocomposites were able to deliver a maximum $U_e$ of 14.9 J cm$^3$ at 450 MV/m. The key to achieve such high performance was attributed to induce formation of high polarizable γ-phase PVDF during nanocomposite preparation, plus employing high-$\kappa$ BST NWs. Later, they conducted an exhaustive studies on PVDF and P(VDF-TrFE-CFE) nanocomposites with a series of NW inclusions, such as PZT, BaTiO$_3$, CCTO, and TiO$_2$.\textsuperscript{114-117} Similarly, high energy densities were also observed in those nanocomposites, which seems proving that NWs behaved overall much better than spherical NPs when employed in nanodielectrics. Wang et al. evaluated four types of high-$\kappa$ NWs, namely, nonferroelectric Na$_2$Ti$_3$O$_7$ and TiO$_2$, ferroelectric BaTiO$_3$, and paraelectric SrTiO$_3$ in P(VDF-HFP) nanocomposites.\textsuperscript{118} He found that BaTiO$_3$ is the best while Na$_2$Ti$_3$O$_7$ is the worst at the same test conditions, probably due to their different resistivities. The idea of using multicore nanofillers was also extended to prepare 1-3 nanocomposites. Core/shell structured BaTiO$_3$/TiO$_2$ nanofibers (NFs) were made by coaxial electrospinning followed by high-temperature calcination and blending with PVDF polymer.\textsuperscript{119} The additional interfacial polarization induced by charge shifting at the BaTiO$_3$/TiO$_2$ interface was believed the reason to greatly increase the polarization of polymer nanocomposite. Meanwhile, high $E_b$ was still maintained because charge shifting was strictly confined within the interfacial zone. As a result, $U_e$ as high as 10.94 J/cm$^3$ at 360 MV/m was obtained at only 3 vol.% NF inclusion. Other than inorganic fillers, organic fillers with large aspect ratio were also considered as potential candidates. PANi NFs doped by protonic acids exhibited good dispersion in ferroelectric polymers and
gave rise to a 50-fold $\varepsilon_r$ increase compared to that of P(VDF-TrFE), much lower percolation threshold, and suppressed leakage current at low frequencies. Intriguingly, addition of these NFs could reduce the coercive field required to switch P(VDF-TrFE) dipoles, which makes its nanocomposites suitable for electrostrictive applications.

Two-dimensional (2D) nanosheets (NS), nanoplatelets, and nanoflakes are considered as the thinnest functional nanomaterials because they possess only molecular thickness, and infinite planar dimension. The in-plane properties of 2D nanomaterials will be wholly different from their out-of-plane properties, such as the electron transport in 2D graphene nanosheets. Note that highly conductive 2D nanomaterials such as graphene should be avoided for high field dielectric applications. Insulating 2D clay nanoplatelets are much preferred in nanodielectrics to reinforce electrical insulation. Tomer and coworkers investigated the effect of spatial arrangement of 2D clay fillers in PE on the final electrical properties of nanocomposites. Their results clearly proved that oriented layered silicates were able to serve as scattering centers or traps and resist electric tree formation. The $E_b$ of nanocomposites at high field was markedly improved, although random and oriented nanocomposites behaved almost no difference at low field. Overall, total $U_c$ and discharge efficiency were also improved in oriented nanocomposites. Recently, Li et al. published their seminal work in *Nature* by bringing boron nitride (BN) nanosheets into thermoset polymer for energy storage (as shown in Figure 1.9B). The nanocomposite could retain high $E_b$ of 403 MV/m, and deliver a discharged $U_c$ of 1.8 J cm$^3$ at 250 °C, making it competitive to or even better than high-performance polyimide films. This extraordinary high-temperature performance was attributed to high thermal conductivity of BN nanosheets, which facile the heat dissipation in nanocomposites. Their highlighted work
greatly extends the operating temperature window of polymer nanodielectrics. The above examples suggested that dielectric anisotropy could be engineered to benefit electrical properties of polymer nanodielectrics.

Figure 1.9. (A) Preparation of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ nanowire embedded PVDF nanocomposite for ultrahigh energy density capacitor (left), energy density of the nanocomposite with different volume fraction as a function of the electric field calculated from D–E loops (right); (B) a, Schematic of the preparation of c-BCB/BNNS films. b, c, Transmission electron microscopy (TEM) images of BNNSs exfoliated from h-BN powders. Inset to c is an electron-diffraction pattern of BNNSs, showing its hexagonal symmetry. d, Chemical structure of the BCB monomer. e, The repeating unit of c-BCB. f, Photographs of a 10-μm-thick c-BCB/BNNS film wrapped around a glass tube with diameter 4 mm. g, A bent 10-μm-thick c-BCB/BNNS film. h, The photopatterned c-BCB/BNNS on a Si wafer. i, j, Optical microscopic images of the patterned films; the dark regions correspond to c-BCB/BNNS. Reproduced with permission from American Chemical Society$^{109}$ and Nature Publishing Group.$^{117}$
3.4.3 Ternary Nanocomposites and Nanocomposites with Complex Architectures

Nanodielectrics are mostly binary systems composed of a single type of filler and a polymer matrix. In fact, it is nearly impossible to find one perfect type of filler that qualifies all expected merits, i.e. high-κ, high resistivity, low dielectric loss, low cost, good compatibility with the polymer matrix, and good temperature stability. Instead, the proposal of exploiting ternary systems and building up hierarchical structures is believed that can overcome limitation in binary system. By introducing more variables in composition, morphology, geometry and structure, a combination of two different fillers might cooperatively behave as one single perfect filler. Li et al. designed a ternary nanocomposites based on dual fillers, BaTiO$_3$ and BNNS, and P(VDF-CTFE) for concurrently enhancing $E_b$ and $\varepsilon_r$.\textsuperscript{123} Highly insulating, a few nanometer-thick 2D BNNS was responsible for improving $E_b$, while 100 nm, high-κ BaTiO$_3$ can effectively increase $\varepsilon_r$. The obtained nanocomposite exhibited a 68% enhancement in $E_b$ from 387 MV/m of P(VDF-CTFE) to 649 MV/m of its nanocomposite. The $\varepsilon_r$ varied from 8.0 to 15.3 depending on filler contents of BaTiO$_3$ and BNNS. Overall $U_e$ of 21 J cm$^3$, $\varepsilon_r$ of 12, $E_b$ of 552 MV/m, and discharge efficiency above 80% were achieved at 12 wt.% BNNS and 15 wt.% BaTiO$_3$ inclusion. To solve a dilemma that increase in $\varepsilon_r$ was usually accompanied with a substantially decreased $E_b$, Nan and coworkers incorporated large aspect ratio TiO$_2$ NFs into ferroelectric fluoropolymers and BaTiO$_3$ NPs were embedded inside NFs (BTO@TO$_2$ NFs), which created a new interface between BaTiO$_3$ NP and TiO$_2$ NF.\textsuperscript{124,125} Incredibly high $U_e$ of 20 and 31.2 J/cm$^3$ with $E_{bs}$ as high as 650 and 800 MV/m were achieved at only 3 vol.% BTO@TO$_2$ NFs loading in PVDF and P(VDF-HFP), respectively. The P(VDF-HFP) nanocomposite is by far the world record with the highest $U_e$ ever
documented in nanodielectrics. At the same loading, BTO@TO_NFs exhibited larger polarization than either BaTiO$_3$ NPs or TiO$_2$ NF alone, which was ascribed to mutual occupation of Ba$^{2+}$ and Ti$^{4+}$ cations at the interfacial region as well as the expansion of BaTiO$_3$ lattice, offering additional dipoles or larger dipole moments. Hu et al. tried to develop multilayered nanodielectrics to break up the reverse relationship between increasing $\varepsilon_r$ and decreasing $E_b$. These topologically engineered composites were made by placing a central PVDF/2 vol.% BaTiO$_3$ NF layers in between two PVDF/10 vol.% BaTiO$_3$ NF layers. From his results, it showed that at this specific NF and NP contents, both $E_b$ and $\varepsilon_r$ were optimized to maximal values. The position of layer boundary with respect to the central layer thickness was investigated. The enhancement of $E_b$ was related to only incomplete breakdown can occur in two outer layers. The incomplete breakdown was able to release dielectric stress and delay or prevent complete film breakdown. As a result, these three-layered nanodielectrics can deliver a maximal $U_e$ as high as 9.7 J cm$^3$ with a $E_b$ of 453 MV/m. Wang and coworkers modified Hu’s design by replacing the central PVDF/2 vol.% BaTiO$_3$ NF layer with 1 vol.% PVDF/BaTiO$_3$ NP layer. Again, significantly enhanced $E_b$ and even higher $U_e$ of 18.8 J/cm$^3$ were achieved. Using finite element analysis, they figured that a small amount of fillers can act as scattering centers to suppress inside electric tree formation and propagation during breakdown. Recently, Nan and coworkers even combine multicomponent and multilayer ideas and prepare nanodielectrics composed of a central PVDF/TiO$_2$-coated graphene oxide NS (G layer)
sandwiched between two PVDF/BST NF layers, or vice versa. An ultrahigh \( U_e \) of \( \sim 14.6 \) J/cm\(^3\) was achieved in these BGB three-layered nanocomposites.

### 3.4.4 Polymer Nanodielectrics Containing Conductive Fillers

The apparent \( \varepsilon_r \) of metallic NPs is assumed to be infinity. Therefore, it is perceived that metallic NPs may enhance \( \varepsilon_r \) of nanodielectrics more effectively than ceramic NPs do. Dang et al. prepared PVDF/5 µm nickel (Ni) composites using powder blending and compression molding.\(^7^4\) The \( \varepsilon_r \) could reach nearly 400 when filler content was close to the percolation threshold, with weak temperature and frequency dependence. Such high-\( \kappa \) composites might be useful for embedded capacitor technology. Qi et al. considered that percolation probability was related to the ratio of filler size to film thickness.\(^1^2^9\) This meant that in practical applications (20-100 µm for the composite films), nanofiller would be more suitable than micro-sized filler. They reported a silver/epoxy nanocomposite with \( \varepsilon_r \) higher than 300 and dissipation factor as low as 0.05. The mercaptosuccinic acid coating on Ag surface was believed to result in several intriguing phenomena that were not observed in classical metal-polymer composites. Another advantage for nanofiller is that small metallic NPs might exhibit so-called Coulomb blockade effect. Feng et al. reported that the \( E_b \) of Ag (20-30 nm) /poly(vinyl alcohol) (PVA) nanocomposites doubled compared to that of neat PVA film because of this effect.\(^1^3^0\) Later, Wong and coworkers prepared three-component nanocomposites based on carbon black, epoxy and \textit{in-situ} formed small Ag NPs.\(^7^7\) The presence of Ag NPs reduced the overall conduction loss at 10 and 100 kHz. In 2013, a pulsed power capacitor was fabricated using a percolative aluminum (Al) NPs/PP nanocomposites by Marks and coworkers. It was able to reversibly
store/release an Ue as high as 14.4 J cm$^{-3}$, though E$_b$ of nanocomposites decreased to 100 MV/m.$^{75,131}$ Moreover, the 10.4 vol.% nanocomposite can keep permittivity >6 even at frequency of 7 GHz, which might be good for making coaxial resonators or dielectric resonator filters. Maxwell-Wagner-Sillars theory was applied to explain the loss at high frequencies (MHz to THz), and simulation provided insights into how Al volume fraction was correlated to the high frequency response.

Things are never perfect, there are also concerns about metal-polymer nanodielectrics. First, high ε$_r$ can only be achieved when filler content approaches the percolation threshold ($f_c$) due to abrupt changes in both permittivity and conductivity near this critical point. Above $f_c$, metal-polymer nanocomposite will be no longer an dielectric insulator but an electrical conductor, and hence no energy can be stored. According to Rao’s report,$^{132}$ ε$_r$ of nanocomposites can be varied from 200 to 2000 when filler content changes by only 0.4 vol.% from 11.03 to 11.43 vol.%. At 11.52 vol.%, the nanocomposite just became a conductor. Therefore, it needs precaution to watch out composition fluctuation during preparation, a small variation can result in dramatic change of overall electrical properties.

Second, the electric field inside metallic NPs, theoretically, should be zero, because it is totally conductive and has no voltage drop. Therefore, energy storage cannot be relied on the contribution from NP. On the contrary, field inside polymer matrix could be greatly enhanced, and the local field enhancement may be more dramatic than that of ceramics/polymer composites. High local field might trigger field-dependent conduction in metal-polymer composites. During an investigation of discovering novel organic electric switches, IBM researchers experimentally observed that in an Au/poly(tetrafluoroethylene) (PTFE) nanocomposites, field emission effect can occur at a fairly small electric field,
resulting in a transition between high conduction and high resistance states. What they discovered poses a question mark on whether metal-polymer or even broadly, conductive filler/polymer nanocomposites is appropriate to be used for energy storage purpose, if field electron emission is an universal phenomena in those composites.

On the other hand, metal-polymer nanocomposites under a name of quantum tunneling composites (QTC) were developed and commercialized by Peratech as novel mechanical sensors, artificial skins and electrical switches. Using polymer elastomers or rubbers as polymer matrix, interparticle distance can be altered easily by applying force on QTC film. If the distance happens to be within the interaction range of field emission, the film resistance can be substantially change. For example (Figure 1.10), spiky Ni particles were uniformly dispersed in poly(dimethylsiloxane) (PDMS). In the non-deformed state, the QTC has a resistance greater than $10^{12} \Omega$. Upon finger-touching, the resistance can quickly drop to less than 1 $\Omega$. This process is completely reversible with little or no hysteresis for thousands of times. The spiky morphology of Ni particles helps with buildup of high concentration electrons at spike tips and decreases the width of the potential barrier to facilitate electron tunneling. In pristine state, Ni particles stay well isolated in silicone rubber to avoid electrical contact. Under pressure, the rubber layer between two adjacent particles can be squeezed to shorten their distance and electron tunneling probability greatly increases owing to shorter distance, the QTC becomes less resistive.
Graphene, as we mentioned, might not be good for dielectric applications due to its excellent electron conductivity. Some researchers hope graphene can behave super high-$\kappa$ to boost $\varepsilon_r$ of their nanocomposites. Fan and coworkers investigated a PVDF/graphite nanoplatelets (xGnP) nanocomposites on their electrical properties. The xGnP fillers of 0.5-25 $\mu$m in diameter and 20-60 nm in thickness were obtained by acidic intercalation and exfoliation. Apparent $\varepsilon_r$s more than 200 and 2,700 were obtained at 1000 and 100 Hz, respectively. The nanocomposites had a very low $f_c$ ($\sim 1.01$ vol.%). The author attributed the colossal permittivity to 1) a huge number of micro-capacitors made of two parallel xGnPs and the polymer between them; 2) the MWS effect. Yousefi et al. studied the electric properties of a nanocomposite based on self-aligned reduced graphene oxides (rGO) in epoxy. He thought that the macroscopic rGO/epoxy nanocomposite can be equivalent to a series of microscopic nanocapacitors composed of nearly parallel rGO sheets together. 

**Figure 1.10.** (a, b) SEM images of the cut surface of a sample of QTC™ (elongated by 32%±2%). White scale bars denote: (a) 50 $\mu$m and (b) 2 $\mu$m; (c) current-voltage characteristic of an undeformed sample of QTC™. Data are shown for increasing and decreasing voltage; (d) current-voltage characteristic of a sample of QTC™ uniaxially compressed to a resistance of $\sim 0.17$ $\Omega$ (70%±0.5% compression, residual circuit resistance 0.02 $\Omega$). Data are shown for increasing and decreasing voltage; (e) open circuit in unstressed state of QTC, behaving as an insulator; (f) closed circuit in compressed state of QTC, behaving as a conductor. Reproduced with permission from American Institute of Physics.
with the interleaved epoxy thin film. That was how ultra-high $\varepsilon_r$ over 14,000 came from at only 3 wt.% rGO loading. As contradictorily as in the case of metal-polymer nanocomposites, researchers also observed that Zener effect, the field emission in semiconductor, also occurred in graphite/polymer nanocomposites,\textsuperscript{136} which might be detrimental by causing high leakage current and early breakdown.

In sum, nanodielectrics based on conductive fillers below the physical percolation threshold often exhibit extremely high $\varepsilon_r$s with reasonable dielectric losses at low fields ($< 0.1$ MV/m). Whether this low field properties can also be true at high field condition might not be taken for granted, and should be under close scrutiny and proved by more experimental data points.

4. Dissertation Overview and Scientific Novelty

    The quest for high $\kappa$, high $E_b$, low dielectric loss and temperature-stable dielectric materials to boost future energy storage motivates researchers to seek every bit for possible solutions. Instead of creating new materials, researchers have been fascinated with the idea of “nanodielectrics”, which originated from making a hybrid of known inorganic materials and organic polymers. People believed that when high $\kappa$ inorganic fillers met high $E_b$ of organic polymers, their marriage revolutionized. Till now, from a point of increasing the apparent $\varepsilon_r$s, polymer nanocomposite dielectrics with $\varepsilon_r$s of several hundred or even a couple thousand were reported using different types, compositions, sizes, shapes, surface modifications of nanofillers, film capacitor geometries and structures. Nevertheless, dielectric loss, especially at high electric field which is the common scenario for real applications, has still been less studied. High dielectric loss usually leads to a waste of
stored energy. More importantly, energy loss will dissipate in the form of heat and speed up thermal degradation and electrical failure. For film capacitor, dielectric loss even as low as 1% is not acceptable for applications. In this regard, this dissertation aims to answer the question of what causes the dielectric loss in polymer nanodielectrics under high field and how to reduce such dielectric loss.

The dissertation comprised five chapters. A detailed research background was given in chapter 1 to introduce the “nanodielectrics” idea. Goals, fundamental concepts, mechanisms, theories, scientific achievements and current issues will be all included.

An universal dielectric loss mechanism in common ceramics/polymer nanodielectrics was discussed in Chapter 2, using a BaTiO3/iPP nanocomposite as a model. For the first time, we discussed some important issues, which cannot be overlooked in the development of viable polymer nanodielectrics. These included decreased electrical $E_b$ of the nanocomposite and internal AC conduction loss associated with the embedded nanoparticles. On the basis of Weibull breakdown analysis, and both bipolar and unipolar D-E loop studies, the fundamental reason for these issue was attributed to the interfacial polarization induced by permittivity and conductivity contrasts in multicomponent polymer nanodielectrics. From this understanding, we proposed that nanoparticles with high resistivity and moderate permittivity, and a low filler ratio should be used to develop viable polymer nanodielectrics for electric energy storage applications.

In chapter 3, we talked about the field electron emission effect under high electric field for conductive metallic filler/polymer nanodielectrics. The conductive filler/polymer nanocomposites have attracted substantial research efforts because they sometimes exhibit colossal $\varepsilon_r$ just below percolation threshold, though it is a low-field dielectric property.
How these nanocomposites behave under high field is still not very clear. A broad range of capacitor performance was reported in previous studies, some being capable of delivering extraordinary high discharged energy density (>15 J/cm³), while some showing substantially decreased $E_b$ with very poor dielectric properties. In this study, PP/aluminum nanocomposites exhibited three electronic conduction regimes, namely, the ohmic conduction at low fields, the hopping conduction at intermediate fields, and the Fowler-Nordheim field electron emission at high fields. It was the field electron emission that substantially increased the electronic conduction and thus decreased $E_b$ for the PP/nAl nanodielectrics. Meanwhile, the internal electronic conduction due to field electron emission significantly increased the dielectric nonlinearity. From this study, we concluded that polymer/metallc NP composites were not suitable for high-field film capacitor applications. Instead, they might be appropriate for electrical switches and piezoelectric sensors.

Nanofiller properties played an important role in determining final performance of nanocomposites. During nanocomposite manufacturing, processing conditions might inevitably alter the original properties belonging to nanofillers due to high temperature, pressure, force, irradiation or addition of chemicals. Therefore, obtaining environmentally stable NPs which could remain insusceptible even at harsh conditions became crucial toward nanocomposite manufacturing and utilization. In chapter 4, we demonstrated using crosslinked PS-$b$-P4VP block copolymer micelles as the 3D constrained nanoreactors to make metallic NPs, which could result in a morphology of one particle per micelle, as well as the excellent thermal stability. Key factors such as the block length, the reducing agent, polymer/metal ion chelation and micelle crosslinking were discussed. We believe that this
facile method could be extended to the synthesis of a broad range of NPs, which served as robust nanofillers in making high-performance nanocomposites.

At the end, a summary including important conclusions for each chapter was provided. Additionally, an overlook for future research opportunities in nanodielectrics based on findings of this dissertation was also briefly discussed.
CHAPTER II

Interfacial Polarization-Induced Loss Mechanism in Polypropylene/BaTiO$_3$ Nanocomposite Dielectrics
ABSTRACT

Polymer/inorganic particle nanocomposites (or nanodielectrics) have attracted pronounced attention for electric energy storage applications, based on a hypothesis that polymer nanodielectrics could combine the high permittivity of nanoparticles and the high electrical breakdown strength of the polymer matrix for enhanced dielectric performance. Although higher discharged energy densities have been reported for numerous polymer nanodielectrics, the dielectric loss mechanisms, which are extremely important for eventual applications, are rarely discussed. In this work, we intend to address the intrinsic dielectric loss mechanisms associated with polymer nanodielectrics using a model system comprised of 70 nm BaTiO$_3$ nanoparticles (BT NPs) in an isotactic polypropylene (PP) matrix. The effect of space charge-induced interfacial polarization on dielectric losses was investigated using bipolar and unipolar electric displacement – electric field (D-E) hysteresis loops. Since the bipolar D-E loops always exhibited greater nonlinearity than the unipolar loops, the dielectric loss was attributed to the internal AC conduction loss from space charges (i.e., electrons and holes) in the BT NPs, including boundary layer and bulk conductions. To mitigate the internal conduction along the PP/BT interface, atomic layer deposition of a nanolayer (5 nm) of amorphous TiO$_2$ was applied to the BT NPs. Due to a higher resistivity, the coated amorphous TiO$_2$ effectively reduced the boundary layer conduction loss. Nonetheless, the bulk conduction loss in BT NPs still needed to be reduced. This study suggests that more insulating high permittivity NPs are desired for polymer nanodielectrics to enhance the dielectric performance.
KEYWORDS: Nanodielectrics, interfacial polarization, BaTiO$_3$ nanoparticles, polypropylene, internal AC conduction
Introduction

The fast-growing energy markets in portable electronics, biomedical devices, electric and hybrid electric vehicles, stationary power conditioning and pulsed power applications demands for high-performance dielectric materials featuring low cost, light weight, reduced volume, high energy density, and high temperature capability. Compared to ceramic and electrolytic dielectrics, dielectric polymers have gained importance in the above mentioned applications due to the ease of processing, high breakdown voltage, long lifetime, ultralow loss, high ripple current, and self-clearing ability.\textsuperscript{1,2} Current state-of-the-art polymer film capacitors utilize biaxially oriented polypropylene (BOPP) film because of its ultralow loss (dissipation factor, $\tan \delta \sim 0.0003$), high breakdown strength ($\sim$730 MV/m at room temperature, RT), and thin film thickness ($\sim$2.5 µm) for high capacitance.\textsuperscript{137,138} However, the drawback of BOPP is its low permittivity ($\varepsilon_r = 2.25$) and thus low energy density ($\sim$5.3 J/cm$^3$ at breakdown). Meanwhile, its temperature rating is limited at 85 °C due to significantly reduced lifetime at elevated temperatures. Therefore, current research focuses on enhancing permittivity/energy density and high temperature tolerance while maintaining low loss for dielectric polymers.\textsuperscript{3,4,11}

In addition to the neat polymer approaches, polymer nanocomposite dielectrics (or nanodielectrics) have gained significant attention with a hypothesis that inorganic nanofillers in a polymer matrix could improve the overall dielectric properties by combining high permittivity from nanofillers and high breakdown strength from the polymer matrix.\textsuperscript{42,139,140} Numerous theoretical/computer simulations and experimental results have been reported, covering a broad range of material design parameters: i) linear dielectric polymer matrices\textsuperscript{75,111,131} versus ferroelectric/relaxor ferroelectric polymer
matrices,\textsuperscript{61,141-143} ii) different inorganic nanoparticles (NPs) with various permittivities (e.g., ZrO\textsubscript{2}: $\varepsilon_r \sim 25$,\textsuperscript{144} anatase TiO\textsubscript{2}: $\varepsilon_r \sim 40$,\textsuperscript{61} BaTiO\textsubscript{3} or Ba\textsubscript{x}Sr\textsubscript{(1-x)}TiO\textsubscript{3}: $\varepsilon_r \sim 200$),\textsuperscript{71,111,113,123,141,142} and metals/carbons (nanotubes and graphenes; $\varepsilon_r \sim \infty$),\textsuperscript{75,80,131} iii) NPs with different aspect ratios (i.e., spheres, nanowires, and nanoplatelets),\textsuperscript{80,113,118,122,145} iv) surface modification of nanofillers with small molecule ligands or polymer brushes for better dispersion,\textsuperscript{75,110,111,131,141,142,145} v) matrix-free hairy particle composites,\textsuperscript{36,88,103} and vi) multicomponent systems with complex architectures.\textsuperscript{123,124,126}

Although the above reports showed enhanced apparent dielectric constant and increased discharge energy density, the fundamental understanding of dielectric loss mechanisms in polymer nanodielectrics is still lacking. First, the electric field distribution is non-uniform in multicomponent polymer nanodielectrics, especially for those impregnated with high permittivity nanofillers.\textsuperscript{10,39,83,87} Namely, the local field in high permittivity fillers is weak (or zero for conducting particles), whereas the average field in the low permittivity polymer matrix is enhanced (a few times that of the applied electric field), resulting in reduced apparent breakdown strength, especially when the polymer matrix itself exhibits a high breakdown strength.\textsuperscript{87,90,142} Note that when the polymer matrix has a low breakdown strength, the polymer nanodielectrics may exhibit somewhat enhanced breakdown strengths,\textsuperscript{90,146} which is related to the improved polymer/NP interfaces\textsuperscript{146} and accumulated interfacial polarization at the interfaces.\textsuperscript{147} To mitigate the effect of non-uniform electric field distribution on decreased breakdown strengths, it has been proposed to reduce the permittivity contrast by utilizing a high permittivity polymer matrix and moderate permittivity nanofillers.\textsuperscript{61,144}
Second, Maxwell-Wagner-Sills (MWS) interfacial polarization is ubiquitous for polymer nanodielectrics. There are two sources for the MWS interfacial polarization, namely, permittivity contrast and conductivity contrast between nanofillers and the polymer matrix. A large permittivity contrast between nanofillers and the polymer matrix results in dipolar-type interfacial charges, especially at the two poles of the NP along the electric field direction. When NPs are aligned along the field direction, the local electric field between the NPs will be enhanced due to superposition of the fields from these interfacial charges, as proposed in a recent perspective article. On the basis of a recent two-dimensional (2D) computer simulation, this local field enhancement is clearly seen when the permittivity contrast is large. In addition, different concentrations of space charges (i.e., electrons/holes and ions) in the NPs and the polymer matrix will cause a large contrast in conductivity. Due to the high permittivity, the concentration of space charges is usually higher in NPs compared to the polymer matrix. Under an applied electric field, the space charges tend to accumulate at the vicinity of the two poles of the NP, further enhancing the local field between neighboring NPs aligned along the field direction. As a result of all these local field additions, the apparent breakdown strength tends to decrease, which becomes more pronounced with increasing the filler content.

Despite the above disadvantages, the interfacial charges may provide some advantages. First, the interfacial charges may serve as effective traps in multicomponent dielectrics. For example, polarized interfacial charges in multilayer polymer films can effectively increase the breakdown strength at various compositions. Second, the MWS interfacial polarization can increase the overall polarization of the sample and thus its apparent dielectric constant. According to an empirical theory developed by Vo and Shi,
a finite interface/interphase having a high permittivity could significantly enhance the apparent dielectric constant at a low filling ratio due to the MWS interfacial polarization. Following this phenomenological prediction, various interfacial nanocomposites have been designed to enhance the apparent dielectric constant. For example, coating the surface of BaTiO$_3$ NPs with a thin layer of metal ($\varepsilon_r = \infty$)\textsuperscript{149}, brookite TiO$_2$\textsuperscript{150} or oligomeric metallophthalocyanine ($\varepsilon_r \sim 10^4$-10$^5$),\textsuperscript{46} the apparently dielectric constant of the three-phase polymer nanodielectrics can be effectively enhanced at a filler ratio of only 5-10 vol.%. This is drastically different from the two-phase polymer nanodielectrics, whose apparent dielectric constant only increases when the filler concentration is close to the percolation threshold (i.e., $\sim 35$ vol.% for spherical NPs).\textsuperscript{82,83}

Whether a polymer nanodielectric will exhibit enhanced or reduced overall dielectric properties depends intimately on the delicate balance of the above factors. Although the advantages such as enhanced apparent dielectric constant and discharged energy density have been repeatedly reported for polymer nanodielectrics, the loss mechanisms in polymer nanodielectrics have not been well-understood. Utilizing a nanocomposite system of surface-modified 70 nm BaTiO$_3$ NPs in an isotactic polypropylene (PP) matrix, this work aims to unravel the effects of uniform NP dispersion and the MWS interfacial polarization on dielectric breakdown strength and nonlinear dielectric losses in polymer nanodielectrics. The choice of a linear dielectric polymer, PP, rather than a ferroelectric polymer [poly(vinylidene fluoride) (PVDF)] as the polymer matrix, is to avoid the interference of nonlinear dielectric behavior from ferroelectric PVDF crystals.
Scheme 2.1. (A) Synthesis of the POSS(PA)$_2$ ligand. (B) Procedure of surface modification of 70 nm BT NPs with POSS(PA)$_2$ and preparation of PP/BT@POSS nanocomposites via sequential solution- and melt-blending methods.
RESULTS

Synthesis of POSS(PA)$_2$-Modified BT NPs and Linear Dielectric Properties.

To achieve uniform dispersion of BT NPs in the PP matrix, a polyhedral oligomeric silsesquioxane (POSS) ligand containing seven isobutyl and two phosphonic acid groups, POSS(PA)$_2$ (Scheme 2.1A), was used. The isobutyl side groups favored hydrophobic interaction increasing compatibility with PP.$^{151}$ It is well-known that phosphonic acid reacts with the surface hydroxyl groups to form strong covalent bonding on the surface of metal oxides.$^{141,152}$ The choice of two adjacent phosphonic acid groups, rather than one phosphonic acid group, is to enhance the conjugation. The synthesis of POSS(PA)$_2$ is shown in Scheme 2.1A. 1,2-Propanediol isobutyl POSS (POSSdiol) was first esterified with diethyl phosphonoacetic acid by a Steglich esterification reaction using dicyclohexylcarbodiimide (DCC)/4-dimethylaminopyridine (DMAP) to obtain bis(phosphonate ester)-terminated POSS, POSS (PE)$_2$. This intermediate was then converted to POSS(PA)$_2$ using trimethylsilyl bromide (TMSBr) as the dealkylation agent. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectroscopy were used to characterize both POSS(PE)$_2$ and POSS(PA)$_2$, and results are shown in Figures S2.1-S2.3 in the Appendix A.

The average size of the commercial BT NPs was 70 nm as determined by particle analysis using transmission electron microscopy (TEM).$^{46}$ The product contained certain ionic impurities, which were detrimental to the dielectric performance of polymer nanocomposites. To eliminate the interference from ionic impurities, repeated washing with deionized water followed by stringent dialysis were performed on the commercial BT
NPs. The purified BT NPs were pre-dispersed in 1:1 (vol./vol.) xylene/ethanol mixture using an ultrasonic bath (1 h) and a homogenizer probe (15 min), and reacted with 10 eq. POSS(PA)$_2$ under refluxing condition (140 °C) for 24 h. Excess (ca. 10 eq.) POSS(PA)$_2$ was important to maximize surface coverage on BT NPs. After surface modification, about 50% of the BT particles could be dispersed individually in organic solvents (see dynamic light scattering and TEM results in Figure 2.4A in the Appendix A), and large aggregates were removed by low-speed centrifugation at 3,000 rpm. Excess and physisorbed POSS(PA)$_2$ impurities were removed by repeated washing (with 1:1 xylene/ethanol) and centrifugation (at 7,500 rpm) cycles. From the TGA result (Figure S2.4B in the Appendix A), POSS(PA)$_2$ ligands formed a double layer on the BT NPs (see Figure 2.4C in the Appendix A).
Figure 2.1. (A) FTIR spectra of the 70 nm BT and BT@POSS NPs, and the POSS(PA)$_2$ ligand. (B) XRD profiles for the 70 nm BT, BT@POSS, and BT@TiO$_2$@POSS 50-cycle NPs at room temperature. Reflections for the cubic phase are indexed. (C) and (D) show extracted real part permittivity, $\varepsilon'_r$, for the 70 nm BT and BT@POSS NPs using the Bruggeman equation.

The surface modification of BT NPs using POSS(PA)$_2$ was confirmed by Fourier transform infrared (FTIR) spectroscopy (Figure 2.1A). Neat BT NPs showed a strong characteristic Ti-O vibrational band at 594 cm$^{-1}$, and POSS(PA)$_2$ exhibited several characteristic peaks from the inorganic -Si-O-Si- framework, alkyl, ester, and phosphonic acid groups. BT@POSS NPs inherited IR absorption bands from both BT and POSS(PA)$_2$, namely, Ti-O band at 594 cm$^{-1}$, at methyl/methylene bands at 2800-3000 cm$^{-1}$, C=O band at 1745 cm$^{-1}$, P=O band at 1230 cm$^{-1}$, and Si-O-Si band at 1110 cm$^{-1}$. From literature reports, the P(=O)-OH should form strong covalent bonding with the surface -OH groups on the BT surface.\textsuperscript{141,152}
The crystalline structures of the BT and BT@POSS NPs were studied by X-ray diffraction (XRD, see Figure 2.1B). For the 70 nm BT NPs, overlapped peaks were identified around the scattering angle \(2\theta = 45.25^\circ\) (see inset of Figure 2.1B). This could be attributed to the coexistence of the cubic [(200)c] and tetragonal [(200)t and (002)t] crystal structures, consistent with a previous report.\(^{153}\) From peak deconvolution (see inset of Figure 2.1B), the content of the tetragonal phase was estimated to be ca. 20% for the BT NPs. After coating with POSS(PA)\(_2\), the peak at 45.25° became more symmetric, and the estimated content of the tetragonal phase decreased to ca. 9% for the BT@POSS NPs. Raman spectroscopy was also used to confirm the tetragonality in BT NPs (Figure S2.5A in the Appendix A). In addition to absorption bands of the cubic phase, BT NPs exhibited a weak absorption band at 306 cm\(^{-1}\) from the tetragonal phase. Differential scanning calorimetry (DSC) was used to study the Curie transition of BT and BT@POSS NPs (Figure S2.5B in the Appendix A). Compared with 2 \(\mu\)m BT NPs, the 70 nm BT NPs showed a lower Curie transition around 50 °C, and it was even less for the BT@POSS NPs.

The linear dielectric properties of purified BT and BT@POSS NPs were studied by broadband dielectric spectroscopy (BDS). Currently, there is no direct way to measure permittivity for ceramic NPs. Instead, empirical fitting using various models for two-phase composites are often used, e.g., Maxwell-Wagner, Bruggeman, and Lichteenecker mixing rules.\(^{23}\) Among these, the Bruggeman effective approximation appears to be more reasonable for spherical particle composites at relatively low concentrations. Following existing literature reports,\(^{50,56}\) compressed disks of BT and BT@POSS NPs were prepared at a pressure of \(~500\text{ MPa}\) using an IR press. The complex permittivity of the NP disks was studied by BDS (raw data are shown in Figure S6 in the Appendix A). By comparing
the density of the pellets to the bulk density of BaTiO$_3$ (i.e., 6.02 g/cm$^3$), the volume fractions for the BT and BT@POSS NPs in the IR-pressed disks were estimated to be 56.8% and 46%, respectively. The extracted real part permittivities ($\varepsilon_r'$) for the BT and BT@POSS NPs using the Bruggeman equation are shown in Figures 2.1C/D, respectively. Compared with BT NPs ($\varepsilon_r' = 185$ at RT and 1 kHz), BT@POSS exhibited a lower permittivity around 123 at RT and 1 kHz. Meanwhile, the Curie transition for the BT NPs was observed around 50-60 °C at 1 kHz, and this transition became much weaker for the BT@POSS NPs, consistent with the DSC results in Figure S2.5B in the Appendix A. Above 100 °C, higher $\varepsilon_r'$ was observed for both particles at low frequencies. This could be attributed to the migrational loss from ionic impurities at elevated temperatures (note that even sub-ppm level of ionic impurities could cause significant loss in BDS at high temperatures and low frequencies$^{94,154}$). The higher permittivity for the BT NPs could be attributed to a higher ferroelectric content than that in the BT@POSS NPs. The dielectric constant (123) for the BT@POSS NPs was close to the value ($\varepsilon_r \sim 135$) reported for organophosphate surface-passivated 30-50 nm BaTiO$_3$ NPs determined by impedance spectroscopy analysis.$^{52}$

There are inconsistent reports for the ferroelectricity in BaTiO$_3$ NPs with particle sizes ranging from 5 nm to ca. 1 µm. A common sense attributes the ferroelectricity in BaTiO$_3$ NPs to a simple size effect. Namely, there is a critical particle size for BaTiO$_3$ NPs, below which the ferroelectric tetragonal phase becomes unstable and the BaTiO$_3$ NPs have a paraelectric cubic structure. Consequently, the permittivity of BaTiO$_3$ NPs should decrease with decreasing particle size. For example, this critical size was reported to be around 100-120 nm,$^{155,156}$ followed by another reported value of 30 nm.$^{157}$ Later, the
ferroelectric tetragonal structure was observed to coexist with the cubic phase in BaTiO$_3$ NPs with the particle size greater than 26 nm. Recently, it was considered that the critical size should be around 10 nm. Based on the contradicting views above, a comprehensive view for the ferroelectricity in BaTiO$_3$ NPs is needed. Actually, it should not be simply attributed to the size effect, but an effect of the ferroelectric domain structure in BaTiO$_3$ NPs. For neat BaTiO$_3$ NPs, both $90^\circ$ and $180^\circ$ ferroelectric domains exist in large (>500 nm) particles. The high permittivity for these large NPs actually originates from the high mobility of Ba$^{2+}$ and Ti$^{4+}$ ions in the domain walls. As the particle size decreases (ca. 500-100 nm), $90^\circ$ domains disappear first and the $180^\circ$ domains tend to result in a nonpolar overall structure. As a result, the permittivity decreases. When the particle size decreases to below 20 nm, the ferroelectric tetragonal phase becomes completely unstable and the BaTiO$_3$ NPs transform into pure paraelectric cubic structure. In between 20 and 100 nm, tetragonal and cubic phases coexist and the composition could depend on different synthesis methods. In addition, surface charges can also affect the stability and structure of ferroelectric domains in BaTiO$_3$ NPs. For example, as the defective BaTiO$_3$ surface is passivated by nonpolar organic ligands, the ferroelectric domains are destabilized and the permittivity further decreases. This is exactly observed in a recent study and our results in Figures 2.1B-D.
Morphology of Nanocomposites and Their Linear Dielectric Properties. To ensure good dispersion of BT@POSS NPs in the PP matrix, sequential solution- and melt-blending processes were employed. First, BT@POSS NPs were mixed with PP in hot xylene at 140 °C, followed by quick precipitation in cold hexane to obtain a premix. It was observed that solution-blending alone could not generate uniform particle dispersion. In the next step, a Haake™ Minilab micro-compounder was used to further homogenize the BT@POSS NPs in the PP matrix (Scheme 2.1B). Computer simulation results indicated that the percolation threshold for spherical particles in a polymer matrix should be around 35 vol.%. To avoid NP percolation and thus forming conductive pathways, nanocomposites with 10, 20, and 30 vol.% of BT@POSS were prepared. Nanocomposite controls with purified BT NPs were also prepared by melt-blending using the Minilab
micro-compounder. The actual volume fraction of each nanocomposite was determined by thermogravimetric analysis (TGA, Figure S2.7 in the Appendix A). Melt-blended nanocomposites were hot-pressed at 200-220 °C into 20-30 μm films for dielectric studies.

Figure 2.3. Temperature-scan BDS results of \( \varepsilon'_r \) at 1 kHz for PP/BT and PP/BT@POSS nanocomposites with (A) 10 vol.%, (B) 20 vol.%, and (C) 30 vol.% NPs. (D) \( \varepsilon'_r \) for PP/BT, PP/BT@POSS, and PP/BT@TiO₂@POSS 80/20 nanocomposites as a function of volume fraction of BT NPs measured at 1 kHz and RT. Fitting curves using the Maxwell-Wagner, Bruggeman, and Lichtenecker equations are also shown.

The morphology and NP dispersion of the nanocomposites were studied by TEM on ~100 nm thin sections obtained by cryomicrotome at -30 °C using a diamond knife. For the PP/BT nanocomposites (Figures 2.2A-C), large micron-sized agglomerates of unmodified BT NPs were observed, regardless of different volume fractions. In addition, some individual NPs were observed. After surface modification with POSS(PA)_2 and low-
speed centrifugation at 3,000 rpm, micron-sized aggregates were removed, as shown in the TEM micrographs for the PP/BT@POSS nanocomposites (Figures 2.2D-F). A significant amount of NPs were individually dispersed in the PP matrix, together with some flocculates containing ~10-20 NPs. Even at 10 vol.%, these flocculates still remained, because the molecular weight of POSS(PA)₂ was lower than that of the PP matrix, suggesting a dry-brush scenario. Increasing the filler content to ≥20 vol.%, BT NPs started to form chains and clusters.

Linear dielectric properties of these nanocomposites with different volume fractions of BT NPs were studied by BDS. Temperature-scan BDS results at 1 kHz for the PP/BT and PP/BT@POSS nanocomposites with various volume fractions of BT NPs are shown in Figures 2.3A-C, respectively. The complete BDS results, including both temperature and frequency scans, for PP, PP/BT, and PP/BT@POSS are shown in Figures S2.8-S2.12 in the Appendix A. As expected, inclusion of high permittivity BT NPs increased the apparent dielectric constant ($\varepsilon_r$) of the nanocomposites. For example, the $\varepsilon_r'$ at 1 kHz and 25 °C increased from 2.25 for PP to 11.7 and 8.92 for the PP/BT and PP/BT@POSS nanocomposites with ca. 30 vol.% BT NPs. In general, the PP/BT nanocomposites exhibited higher $\varepsilon_r'$ than the PP/BT@POSS nanocomposites for all compositions. This observation is consistent with a previous report by McCarthy, et al. Namely, permittivity, AC conductivity, and dielectric loss for SEBS nanocomposites filled with octylsilane-modified rutile TiO₂ NPs were lower than those without any modification. Meanwhile, a higher loss permittivity, $\varepsilon_r''$, was observed for the PP/BT nanocomposites. From the $\varepsilon_r''$ results, the glass transition temperature ($T_g$) of the PP matrix at 1 kHz was observed at 15 °C.
The higher $\varepsilon_r'$ for the PP/BT nanocomposites compared to the PP/BT@POSS nanocomposites could be attributed to BT’s higher permittivity ($\varepsilon_r' = 185$) than the BT@POSS NPs ($\varepsilon_r' = 123$) at 1 kHz and RT. To determine if this is the case, experimental $\varepsilon_r'$ values at 1 kHz and RT are compared with those predicted by the Maxwell-Wagner, Bruggeman, and Lichteneker mixing models (Figure 2.3D). In general, the Maxwell-Wagner model underestimated whereas the Lichteneker model overestimated the apparent dielectric constants of the nanocomposites. The Bruggeman model fit better to the experimental data. Indeed, at ca. 30 vol.%, the experimental $\varepsilon_r'$ values of both nanocomposites fit the Bruggeman model reasonably well, and the higher $\varepsilon_r'$ for the PP/BT nanocomposite was primarily due to the higher $\varepsilon_r'$ of the BT NPs. At ca. 10 and 20 vol.%, both experimental $\varepsilon_r'$ values were higher than the Bruggeman prediction. However, the deviation from the Bruggeman prediction was higher for the PP/BT nanocomposites than for the PP/BT@POSS nanocomposites. The difference is attributed to the NP dispersion in the PP matrix for PP/BT and PP/BT@POSS nanocomposites (see Figure 2.2). It is known that the dipole-dipole coupling interaction among many bodies increases with decreasing the interparticle distance, which in turn increases the dipole moment of individual dipoles (note that each NP could be considered as a mesoscale dipole in this case). Therefore, nanocomposites with significant aggregation of BT NPs tend to show a higher apparent dielectric constant than those with less or no aggregation. At ca. 30 vol.%, which is close to the percolation threshold at 35 vol.%, the concentration of NPs becomes so high that their dispersion is close to the case of aggregation. As a result, the experimental $\varepsilon_r'$ values for both PP/BT and PP/BT@POSS nanocomposites fit well with
the Bruggeman predictions. However, for 10 and 20 vol.% nanocomposites, aggregation of BT NPs increases the apparent dielectric constant.

**Electric Breakdown Strength of Nanocomposites.** From the above linear dielectric property study, it is noticed that embedding high permittivity NPs in a low permittivity polymer matrix is not effective in promoting the apparent dielectric constant of nanocomposites below the percolation threshold. This is because of the high permittivity contrast between the ceramic NPs and the polymer matrix, which leads to a low local field in the NPs. Above the percolation threshold, the local field in the NPs effectively increases. As a result, high permittivity NPs are only effective in raising the apparent dielectric constant of nanocomposites above the percolation threshold. Nonetheless, as we mentioned before, percolation of NPs should be avoided for high voltage applications because the interconnected interfaces can provide a conduction pathway for injected hot electrons from the negative electrode, thus lowering the electric breakdown strength (and lifetime). To effectively enhance the apparent dielectric constant while preventing NP percolation for potential conduction, one strategy is to implement nanocomposites with the NP content just below the percolation threshold. To investigate whether this is viable, electric breakdown studies were carried out and results are shown below.

Parallel plate capacitor geometry with an electrode area of 5.15 mm$^2$ was used to study the breakdown strength of PP/BT and PP/BT@POSS nanocomposites. Experimental data (ca. 30 for each sample) was analyzed using two-parameter Weibull statistics. The Weibull cumulative distribution function, $F$, is defined as:

$$F(E_b) = 1 - \exp \left[ - \left( \frac{E_b}{\alpha} \right)^\beta \right]$$

(1)
where $E_b$ is the measured breakdown electric field. The scale parameter, $\alpha$, is the characteristic electric field, at which 63.2% of capacitors fail the breakdown test. The shape parameter, $\beta$, is the Weibull modulus evaluating the width of distribution. The Weibull statistical analysis results for hot-pressed films of PP, PP/BT, and PP/BT@POSS are shown in Figure 2.4. As a control, the hot-pressed PP film exhibited a characteristic $E_b$ (or $\alpha$) of 622 MV/m with a Weibull slope of 11.4. All hot-pressed films of PP/BT and PP/BT@POSS nanocomposites exhibited lower $E_b$ and $\beta$ values than those for the PP film. This observation is consistent with prior reports for nanodielectrics with high breakdown strength polymer matrices. The effect of

Figure 2.4. Weibull distributions of electric breakdown strength at room temperature for hot-pressed films of (A) PP, and PP/BT and PP/BT@POSS nanocomposites with (B) 10 vol.%, (C) 20 vol.%, and (D) 30 vol.% BT NPs. The film thicknesses are 20-30 μm and the test area is 5.15 mm².
BT NP dispersion in the PP matrix can be seen from Figures 2.4B-D. Namely, the PP/BT@POSS nanocomposites with better NP dispersion exhibited higher breakdown strength than the PP/BT nanocomposites. For the PP/BT nanocomposites, the $E_b$ was nearly independent of the volume fraction of BT NPs, suggesting that the electric breakdown is caused by extrinsic reasons, rather than the intrinsic property of the nanocomposite. From Figures 2.2A-C, micron-sized aggregates (sometimes ~10 µms) of BT NPs were observed for the PP/BT nanocomposites. Considering the total film thickness of 20-30 µm, it should be the macroscopic defects from these large aggregates that caused the low $E_b$ values, which were nearly independent of the BT content. For the PP/BT@POSS nanocomposites, the characteristic $E_b$ slightly decreased with increased volume fraction of nanofillers. This is closely related to the enhanced local electric field in the polymer matrix when the interparticle distance gradually decreased as the volume fraction of BT NPs increased. Since there is no direct way to accurately measure local electric field in polymer nanocomposites, computer simulation using coarse-grain molecular dynamics is used to understand the lowered breakdown strengths observed above (see Section 7 in the Appendix A).

![Figure 2.5](image)

**Figure 2.5.** Computer simulation of three-dimensional (3D) local electric field ($E_l/E_0$) distributions for a random nanocomposite with (A) 10, (B) 20, and (C) 30 vol.% of 70 nm nanoparticles. The relative permittivities of the matrix and nanoparticles are 2.25 and 120,
respectively. The applied field $E_0$ is along the $+z$ direction. The electric field inside nanoparticles is weak (i.e., close to zero) and the color is set to black for better visualization.

In the simulation, local field enhancement ($E_L/E_0$, where $E_L$ is local field and $E_0$ is applied field) was obtained by considering the permittivity contrast between the NP and the matrix, leaving out the effects of space charges in the system. The parameters in simulation were adapted from the experimental data. Figures 2.5A-C show simulated local field enhancement for nanocomposites with 10, 20, and 30 vol.% NPs, respectively. For all compositions, the local field near the two poles of an isolate particle along the field direction was the most enhanced, as compared to the field in the polymer matrix far away. The local field inside the NPs was weak (close to zero). This was attributed to the interfacial polarization due to the large permittivity contrast between particles and the polymer matrix.\textsuperscript{39,83} For example, the local field enhancement, $E_L/E_0$, near the two poles of an isolated particle in the 10, 20, and 30 vol.% nanocomposites was as high as 4, 6, and 8, respectively. For the 10 vol.% nanocomposite (Figure 2.5A), most particles were isolated. For the 20 and 30 vol.% nanocomposites in Figures 2.5B and C, some particles were chained or clustered together along the field direction due to the increased NP concentration. Consequently, the local field between these chained or clustered particles was further enhanced (e.g., $E_L/E_0 \sim 18$ for the 20 vol.% nanocomposite and 40 for the 30 vol.% nanocomposite), creating “hot spots” for electrical breakdown. Note that the local field enhancement between neighboring particles in a chain of less than 3 particles appeared to be fairly weak (e.g., see the $yz$ planes of Figures 2.5B and C). This is because of the large color scale used in Figure 2.5. If the color scale is reduced, local field enhancement will be visualized (see Figure S2.13 in the Appendix A). According to our
simulations, for the composite parameters discussed in the manuscript, at least 5 particles should arrange into a chain along the applied field with small interparticle spacing in order to show large field localization.

From this simulation, we conclude that local field enhancement due to interfacial polarization, especially between chained or clustered particles, is the reason for decreased breakdown strength for polymer nanocomposites filled with high permittivity particles, as observed in Figure 2.4. On the basis of this understanding, nanocomposites with pre-existing large aggregates or above the percolation threshold should be avoided. Even with a uniform particle distribution, high volume fraction should also be avoided, because certain particles could chain or cluster together along the field direction, as seen in Figures 2.5B and C.

**Effect of Interfacial Polarization from Space Charges in BT NPs.** As we have mentioned above, besides the permittivity contrast, conductivity contrast can also induce interfacial polarization, i.e., the accumulation of space charges (including electrons/holes and ions) at interfaces in a multicomponent system under an applied electric field due to electrical conduction.\(^{10}\) From literature report,\(^{161}\) the bulk conductivity (\(\sigma\)) of BaTiO\(_3\) films is around \(10^{-10} \text{ S/m}\). Typical \(\sigma\) of PP is as low as \(10^{-17} \text{ S/m}\). At room temperature, the ion mobility is very low for PP nanocomposites, and thus interfacial polarization from impurity ions can be ignored. However, free electrons (and holes) in BT NPs could still induce interfacial polarization in polymer nanocomposites.
Figure 2.6. (A) Bipolar D-E loops (10 Hz) for the PP/BT@POSS 80/20 nanocomposite film at room temperature. (B) Discharged energy densities ($U_e$, solid symbols) and discharge efficiencies (open symbols) for the PP control film and various PP/BT@POSS nanocomposite films. (C) Unipolar D-E loops (20 Hz) for the PP/BT@POSS 80/20 nanocomposite film at room temperature. The starting points of the second to fourth loops are shifted down to the origin. (D) Comparison of discharge efficiencies for the bipolar, the first and the fourth unipolar loops for the PP/BT@POSS 80/20 nanocomposite film under various test frequencies.

Discharged energy densities ($U_e$) and discharge efficiencies for PP/BT@POSS and PP/BT nanocomposites were studied by electric displacement - electric field hysteresis loop (D-E loop) measurements using a Radiant ferroelectric tester with the modified Sawyer-Tower circuit. First, continuous bipolar poling was performed by applying sinusoidal voltage waves at 10 Hz on metal-coated films. Representative continuous bipolar D-E loop for the PP/BT@POSS 80/20 film are shown in Figure 2.6A. All other
bipolar D-E loop results for the PP control and the PP/BT nanocomposite films can be found in Figure S2.14 in the Appendix A. Here, continuous bipolar loops are used to minimize the effect of remanent polarization from previous D-E loop runs.\textsuperscript{154} Assuming negligible remanent polarization, the upshift of the top part of the bipolar loop with respect to the E-axis could be used to estimate the external DC (electronic) conduction.\textsuperscript{113} Figure 2.6A (and Figures S2.14B-G in the Appendix A) shows significant dielectric nonlinearity with elliptical shaped bipolar loops for both PP/BT@POSS and PP/BT nanocomposites, especially at high enough poling electric fields. These results are drastically different from the linear dielectric behavior of the PP matrix (Figure S2.14A in the Appendix A). As we recently reported,\textsuperscript{162} nonlinear D-E loops can result in significant dielectric losses, thus undesired for electric energy storage applications. This was clearly seen from the discharge efficiencies of various PP/BT@POSS nanocomposites compared to those of PP in Figure 2.6B. Although the discharged $U_e$ for the PP/BT@POSS nanocomposites appeared to be higher than that for PP at the same poling field, the discharge efficiencies for the PP/BT@POSS nanocomposites were much lower; the higher the BT@POSS content, the lower the discharge efficiency. Meanwhile, their ultimate $U_e$s at breakdown were also significantly lower than that of the neat PP.

To minimize the dielectric loss, it is important to understand the major causes for the nonlinearity in polymer nanodielectrics. There are several possible reasons for dielectric nonlinearity of polymers.\textsuperscript{162} First, normal ferroelectricity can cause significant dielectric nonlinearity. However, the nonlinear D-E loops in Figure 2.6A appeared to be different from typical ferroelectric switching of dipoles, because there was no obvious saturation at the end of the charging cycle. As shown in Figure 2.1, the content of the
ferroelectric phase in the BT@POSS NPs is fairly low, only ca. 9%. It is unlikely that weak ferroelectricity in BT@POSS NPs can cause significant nonlinearity in the bipolar D-E loops. To further support this idea, bipolar D-E loops were measured at temperatures up to 130 °C (Figure S2.15 in the Appendix A), which is higher than the Curie temperature (121 °C) for 2 µm BaTiO₃ particles (see Figure S2.5B in the Appendix A). With increasing temperature, the dielectric nonlinearity in the bipolar D-E loops did not decrease. Instead, it became more significant. Therefore, the dielectric nonlinearity in the nanocomposites should not originate from the weak ferroelectricity in the BT@POSS NPs. Second, DC conduction of the sample can cause significant loop-broadening and upshift of bipolar D-E loops. However, there is negligible DC conduction for the PP/BT@POSS 80/20 film at room temperature, because there is no upshift of the bipolar D-E loops in Figure 2.6A. In addition, the bulk conductivity (σ) for the PP/BT@POSS 80/20 film was studied by leakage current measurements, and the value was as low as 5×10⁻¹⁵ S/m (Figure S2.16 in the Appendix A). Therefore, external DC conduction (or leakage) is not a major reason for the dielectric nonlinearity of the nanocomposites at RT.

To further identify the major cause of dielectric nonlinearity for the above polymer nanodielectrics, continuous unipolar D-E loops were measured at 20 Hz at RT, and results (after shifting the starting points of the second to fourth loops down to the origin) are shown in Figure 2.6C (other unipolar D-E loops at different poling frequencies are shown in Figure S2.17 in the Appendix A). Note that a unipolar loop is exactly half of the bipolar loop if the test frequency doubles (i.e., both are 50 ms in poling time). Intriguingly, the second to fourth unipolar loops became much slimmer as compared with the first unipolar loop. The discharge efficiencies from the bipolar, and the first and fourth unipolar loops
for the PP/BT@POSS 80/20 film at 150 MV/m and various frequencies are shown in Figure 2.6D. The efficiencies for the first unipolar loops were similar to those for the bipolar loops; however, the efficiencies for the fourth loops were much higher. With decreasing poling frequency, all discharge efficiencies gradually decreased.

**Scheme 2.2.** Proposed mechanism of interfacial polarization-induced internal AC conduction loss due to large permittivity and conductivity contrasts between BT NPs and the PP matrix. There are two conduction pathways: (I) boundary layer conduction and (II) bulk conduction. The orange circles with negative and positive signs represent free space charges (i.e., electrons and holes) in the BT NPs.

Considering the higher bulk conductivity ($\sigma \sim 10^{-10} \text{ S/m}$) of BT NPs than that ($\sigma \sim 10^{-17} \text{ S/m}$) of the PP matrix, the dielectric nonlinearity in bipolar electric poling can be related to the internal AC conduction of free space charges (e.g., electrons) within BT NPs (see Scheme 2). Given the wide band gap of BaTiO$_3$ (ca. 3.2 eV), we consider that the free electrons should be thermally activated, and the holes (or positive ions) are immobile in the crystal (see Figure S2.18 in the Appendix A). Therefore, the net effect of electric polarization can be represented as in Scheme 2. Upon the first poling, space charges in BT
NPs will be polarized to the two poles along the electric field direction. Upon the reverse poling, these polarized space charges in BT NPs will swap the polarity. Because the resistivity of the BT NPs was still relatively high (~$10^{10}$ $\Omega\cdot$m) compared to semiconductors or conductors, a significant AC conduction loss is observed. Therefore, it should be the internal AC conduction of space charges that causes the significant dielectric nonlinearity for the polymer nanodielectrics. Similar round or elliptical (i.e., nonlinear) D-E loops were also reported for ferroelectric ceramic (BaTiO$_3$)-glass nanocomposites. However, switching of these interfacial space charges will be absent during continuous unipolar poling cycles, because the polarized interfacial charges do not swap the polarity. Therefore, after the first unipolar loop, later unipolar loops appear slimmer.

The space charge density ($n_0$) could be estimated from fitting the bipolar D-E loop at 150 MV/m in Figure 2.6A by assuming the electron mobility ($\mu$) in BaTiO$_3$ of $1.0\times10^{-4}$ m$^2$·V$^{-1}$·s$^{-1}$. Detailed theoretical fitting of the D-E loop is shown in section 9 in the Appendix A. The space charge density $n_0$ is estimated to be $1.5\times10^{15}$/m$^3$. This value is much lower than the density of photorefractive charge carriers in single crystal BaTiO$_3$ ($10^{22}$ /m$^3$). Using equation for conductivity: $\sigma = e\mu n_0$ ($e$ is the charge of an electron, $1.602\times10^{-19}$ C), the conductivity of the BT NPs is about $2.4\times10^{-8}$ S/m. Note that this value is slightly higher than that ($10^{-10}$ S/m) of bulk BaTiO$_3$. However, considering the large amount of surface defects in BT NPs, this conductivity value should be reasonable.

**Mitigation of Internal AC Conduction by Coating BT NPs with a Nanolayer of TiO$_2$.** There are two possible internal conduction pathways in BaTiO$_3$ NPs: (I) boundary layer conduction$^{166}$ and (II) bulk conduction, as shown in Scheme 2. Compared with the PP/BT nanocomposites (see Figure 2.6B and Figures S2.14I in the Appendix A), the
PP/BT@POSS nanocomposites exhibited higher discharge efficiencies at low poling fields (<80 MV/m). It is known that electronic conductivity is closely related to the defect density in ceramic crystals. It is likely that the surface of BT NPs contains more defects (i.e., vacancies) than the bulk, and is therefore more conductive. After coating with POSS(PA)$_2$, certain surface defects are passivated by forming certain covalent bonds with phosphonic acid groups. Therefore, the boundary layer conduction (pathway I in Scheme 2) are reduced. This also explains the lower loss permittivity for the PP/BT@POSS composites observed in the BDS results in Figure 2.3. However, the discharge efficiencies for the PP/BT@POSS nanocomposites became similar to those of PP/BT nanocomposites at >100 MV/m, suggesting that passivation from POSS(PA)$_2$ became less effective at high electric fields.

Another method to passivate the defective BT NP surface is to coat it with a relatively insulating ceramic, such as Al$_2$O$_3$ or SiO$_2$ ($\sigma \sim 10^{-12} - 10^{-14}$ S/m under dry condition). For example, using in-situ polymerization of propylene on Al$_2$O$_3$-coated BT NPs, nanodielectrics were prepared. Nanocomposites with 1 layer of Al$_2$O$_3$ coating (2 nm) still exhibited lossy D-E hysteresis loops, even at a filler content as low as 5 vol.%. After 5 layers (10 nm) of Al$_2$O$_3$ coating, the nanocomposites started to show a slimmer loop with a moderate loss. Wang, et al., reported PVDF nanocomposites with surface-treated BT NPs having a 7 nm SiO$_2$ layer. A reduction of remnant polarization and thus hysteresis loop loss was observed. However, the permittivity of Al$_2$O$_3$ ($\varepsilon_r \sim 10$) and SiO$_2$ ($\varepsilon_r \sim 4$) are relatively low. Coating a relatively thick layer of these low permittivity materials on BT NPs can decrease the apparent dielectric constant of the nanodielectrics.
In this study, atomic layer deposition (ALD)\textsuperscript{169} of relatively high permittivity TiO\textsubscript{2} is used to passivate the defective surface of BT NPs (refer to Section 10 in the Appendix A for detailed experimental procedure of ALD). In general, the permittivities of amorphous, anatase, and rutile TiO\textsubscript{2} films have been reported to be around 33, 40, and 115, respectively.\textsuperscript{170,171} For ALD TiO\textsubscript{2} films, the electrical conductivity decreases in the order of (rutile), anatase, and amorphous phases.\textsuperscript{172,173} Therefore, it will be interesting to compare different forms of ALD TiO\textsubscript{2} as the passivation coating for BT NPs.

![Figure 2.7. Bright-field TEM micrographs for BT@TiO\textsubscript{2} 50-cycle NPs at (A) low and (B and C) high magnifications. (D) The corresponding PP nanocomposite at 20 vol.% filler content.](image)

First, BT@TiO\textsubscript{2} NPs with 50 cycles (50c) of ALD TiO\textsubscript{2} were prepared, and example bright-field TEM micrographs are shown in Figures 2.7A-C. From these images, a layer of amorphous TiO\textsubscript{2} (~5 nm thick) was obtained at a reaction temperature of 200 °C with a deposition rate of ~0.1 nm/cycle. Under high magnifications (Figures 2.7B and C), the \(d\)\textsubscript{100} (~0.4 nm) was identified for the cubic BaTiO\textsubscript{3} crystals. Occasionally, some anatase TiO\textsubscript{2} domains (\(d\)\textsubscript{200} of ~0.2 nm) were found near the TiO\textsubscript{2}/BaTiO\textsubscript{3} interface (see inset of Figure 2.7C). The small fraction of the anatase phase was confirmed by the Raman result in Figure S2.5A in the Appendix A, where two weak absorption bands at 398 and 640 cm\textsuperscript{-1}. }
and a strong band at 145 cm$^{-1}$ from the anatase phase were seen for the BT@TiO$_2$ 50c NPs. Note that amorphous TiO$_2$ does not exhibit distinct Raman absorption in the frequency range studied.\textsuperscript{174} It was possible that during 50 cycles of ALD at 200 °C, the anatase phase started to grow on the BaTiO$_3$ substrate in the amorphous TiO$_2$ layer.

After coating with POSS(PA)$_2$ (see characterization results in Figure S2.21 in the Appendix A), the BT@TiO$_2$@POSS 50c NPs exhibited primarily the cubic phase (94%, see the XRD result in Figure 2.1B). The corresponding PP/BT@TiO$_2$@POSS 80/20 50c nanocomposite had relatively uniform particle dispersion, as seen in the TEM micrograph in Figure 2.7D. From the BDS study (Figure S2.22 in the Appendix A), the $\varepsilon'$ was 5.67 at 1 kHz and RT, and the dissipation factor was as low as tanδ = 0.002.
Figure 2.8. (A) Bipolar D-E loops (10 Hz) for the PP/BT@TiO2@POSS 80/20 50c nanocomposite film at RT. (B) Discharged energy densities ($U_e$, solid symbols) and discharge efficiencies (open symbols) for the PP/BT@POSS 80/20 and the PP/BT@TiO2@POSS 80/20 50c nanocomposite films. (C) Unipolar D-E loops (20 Hz) for the PP/BT@TiO2@POSS 80/20 50c nanocomposite film at RT. The starting points of the second to fourth loops are shifted to the origin. (D) Comparison of discharge efficiencies for the bipolar, the first and the fourth unipolar loops for the PP/BT@TiO2@POSS 80/20 50c nanocomposite film under various frequencies.

Figure 2.8A shows the bipolar D-E loops for the PP/BT@TiO2@POSS 80/20 50c nanocomposite at room temperature. Compared with those for the PP/BT@POSS 80/20 nanocomposite in Figure 2.6A, the bipolar loops for the PP/BT@TiO2@POSS 80/20 50c film appeared slimmer with slightly decreased maximum D. The discharged $U_es$ in these bipolar D-E loops for both nanocomposites appeared to be similar; however, the PP/BT@TiO2@POSS 80/20 50c nanocomposite showed much higher discharge efficiencies (Figure 2.8B). To see if the ALD TiO2 coating reduced the boundary layer AC conduction in BT NPs, unipolar D-E loops were measured, and results are shown in Figure 2.8C. Compared with the results for the PP/BT@POSS 80/20 film in Figure 2.6C, the first unipolar loop for the PP/BT@TiO2@POSS 80/20 50c film appeared to be much slimmer. To quantify the results, discharge efficiencies for the bipolar loop, the first and fourth unipolar loops at 150 MV/m and various frequencies are compared in Figure 2.8D; the rest bipolar and unipolar loops are shown in Figure S2.23 in the Appendix A. Again, with decreasing poling frequency, the discharge efficiency decreased. Compared with the results for the PP/BT@POSS 80/20 sample in Figure 2.6D, the discharge efficiencies for the bipolar and the first unipolar loops of the PP/BT@TiO2@POSS 80/20 50c film were much higher. However, the discharge efficiencies for the fourth loops were similar for both samples. These results indicated that the boundary layer AC conduction of space
charges in the BT NPs was effectively reduced by 50 cycles ALD of amorphous TiO$_2$ (~5 nm). Nonetheless, certain bulk conduction still remained in the BT NPs, because the bipolar loops were significantly broader than the second to fourth unipolar loops (see Figure 2.8C and Figure S2.23 in the Appendix A).

Anatase TiO$_2$ coating can be obtained by raising the ALD temperature to 300 °C. However, when the coating is thin, it contains amorphous TiO$_2$. To ensure a pure anatase TiO$_2$ coating, 200 cycles of ALD is performed (see Section 13 in the Appendix A). Because the ALD anatase phase with certain oxygen vacancies is more conductive than the amorphous TiO$_2$, enhanced external electronic conduction is observed for the PP/BT@TiO$_2$@POSS 80/20 200c nanocomposite. As a result, a lower discharge efficiency is obtained for the PP/BT@TiO$_2$@POSS 80/20 200c nanocomposite, although the discharged energy density is similar to the PP/BT@TiO$_2$@POSS 80/20 50c nanocomposite.

**DISCUSSION**

From the above results, several designing rules should be discussed to implement viable polymer nanodielectrics for electric energy storage applications. First, to avoid internal AC conduction due to space charges, NPs with ultralow conductivity (i.e., comparable to that of the polymer matrix or below $10^{-13}$ S/m) are more desirable than high permittivity/high conductivity NPs such as ABO$_3$ perovskites. Possible examples include Ta$_2$O$_5$ ($\varepsilon_r \sim 22$), ZrO$_2$ ($\varepsilon_r \sim 25$), and amorphous TiO$_2$ ($\varepsilon_r \sim 33$). The conductivity of these metal oxides can reach as low as $10^{-14}$ S/m, depending on the synthesis and processing methods. However, their $\varepsilon_r$ values are too low to achieve high apparent dielectric constant
for polymer nanodielectrics. Ideally, the $\varepsilon_r$ of the fillers should be greater than 100. Nonetheless, such high $\varepsilon_r$ and low conductivity ceramic particles have yet to be discovered (see discussion in section 14 in the Appendix A). If the internal AC conduction cannot be effectively avoided, DC applications are more suitable for polymer nanodielectrics.

Second, there is a dilemma for polymer nanodielectrics. On one hand, high permittivity NPs and high NP content before percolation are desired to enhance the apparent dielectric constant. On the other hand, large permittivity contrast and high NP content can result in reduced breakdown strength, and thus these should be avoided. To avoid the decrease in breakdown strength, experimental work has proposed to match permittivity contrast for polymer nanodielectrics.\textsuperscript{61,88,90,144} However, this does not solve the dilemma. To solve the problem, it is desired to increase the apparently dielectric constant of nanocomposites at low volume fractions. One approach is to use rod- or wire-like materials rather than spherical NPs, and the apparent dielectric constant can be effectively increased at a volume fraction of ca. 7-10 vol.$\%$.\textsuperscript{113,145} However, one should note that the percolation threshold can decrease to 10-15 vol.$\%$, depending upon the aspect ratio of the nanowires. When the nanowire content is close to the percolation threshold, breakdown strength can still be reduced for nanocomposites because of enhanced electrical leakage. Alternatively, it has been proposed theoretically\textsuperscript{44} and later proved by experiments\textsuperscript{46,149,150} that adding a high permittivity interface/interphase (e.g., metals or conducting oligomers/polymers) between the NP and the dielectric polymer matrix could effectively enhance the apparent dielectric constant at a reduced filler volume fraction (e.g., ca. 5 vol.$\%$). However, there is a concern for adding conductive fillers in an insulating
dielectric, because conductive fillers tend to increase the dielectric loss by enhancing the leakage current via the electron tunneling or field electron emission mechanism.\textsuperscript{10}

Third, there should be a delicate balance between the advantages (enhanced polarization and effective electron traps) and disadvantages (enhanced local electric field in the polymer matrix and internal AC conduction) for the MWS interfacial polarization in polymer nanodielectrics. In recent reports on multilayer polymer films, the advantages from interfacial polarization can be promoted and the disadvantages can be minimized by utilizing the layered geometry, where layered interfacial charges serve as effective charge traps.\textsuperscript{3,95,148} Similar to the multilayer concept, experimental reports have demonstrated that nanoplatelets such as hexagonal boron nitride\textsuperscript{122,123} and nanoclay\textsuperscript{91} can reduce the leakage current for polymer nanodielectrics. In the future, it is desired to design hierarchically structured polymer nanodielectrics with low volume fractions of spherical NPs and certain nanoplatelets.

**CONCLUSIONS**

In summary, interfacial polarization played an important role in the failure and dielectric losses in polymer nanodielectrics. Two major sources for interfacial polarization were present in the multicomponent system, namely, large permittivity contrast and large conductivity contrast.\textsuperscript{10} The polarized interfacial charges in the dispersed BT NPs had significant influence on the dielectric performance of polymer nanodielectrics. First, polarized interfacial charges (including both polarized dipoles and space charges) effectively increased the local electric field in the polymer matrix, especially near two poles of the NP along the field direction. When high permittivity NPs chained, clustered, or even
aggregated together, this local field could be further enhanced due to the dipole-dipole coupling among neighboring particles, resulting in decreased electric breakdown strength. Second, due to the large conductivity contrast, the concentration of space charges (electrons and/or holes) in BT NPs was much higher than that in the PP matrix. Bipolar polarization of these space charges in BT NPs resulted in substantial internal AC conduction and thus dielectric nonlinearity, causing high dielectric losses. On the contrary, continuous unipolar poling could avoid the internal conduction from the free space charges. There are two internal conduction pathways: i) boundary layer and ii) bulk conductions. After ALD of a nanolayer (5 nm) of amorphous TiO₂ onto the BT NPs, the boundary layer AC conduction loss could be significantly suppressed. Nonetheless, the bulk conduction loss in BT NPs still needed to be reduced. This study suggests that more insulating high permittivity NPs are desired for polymer nanodielectrics in order to achieve better dielectric performance for electrical energy storage applications.

**EXPERIMENTAL METHODS**

**Materials.** POSS-diol was purchased from Hybrid Plastics, Inc. (Hattiesburg, MS). BaTiO₃ nanopowders (70 nm and 2 µm) were purchased from Aldrich (St Louis, MO), and purified by washing with acetone/water, and dialysis in deionized water. Diethylphosphonate acetic acid, DCC, DMAP, and TMSBr were purchased from Aldrich and used as received. All other solvents were purchased from Fisher Scientific (Pittsburgh, PA) and were used without purification. Syntheses of POSS(PE)₂ and POSS(PA)₂ are described in Sections 2 and 3 in the Appendix A.
Surface Modification of 70 nm BT NPs with POSS(PA)$_2$. In a 500 mL round-bottom flask with 150 mL xylene and 150 mL ethanol, 5 g of 70 nm BT particles were added and ultrasonicated for 4 h using a 300 W ultrasonication bath (Fisher Scientific). 1.0 g of POSS(PA)$_2$ in 40 mL of 1:1 (vol./vol.) xylene/ethanol was added into the BT suspension using a syringe pump under continued sonication within 1 h. Afterwards, the suspension was treated with an ultrasonic homogenizer (probe diameter 13 mm, Sonics & Materials, Inc., Newton, CT) for 15 min. The surface modification was then carried out by refluxing at 140 °C under rigorous stirring for 24 h. The suspension was then centrifuged at 3,000 rpm for 5 min to remove large aggregations. About 15 mL of the supernatant suspension was sampled and dried to calculate the solid content. Well-dispersed BT@POSS particles were obtained by further centrifugation at 7,500 rpm and washed with 1:1 xylene/ethanol thoroughly to remove impurities and physisorbed POSS(PA)$_2$. The yield of well-dispersed BT@POSS particles was ~50%. From TGA result (Figure S2.4 in the Appendix A), nearly a double layer of POSS(PA)$_2$ was coated on the BT NPs.

Blending BT NPs in PP Matrix and Film Preparation. After centrifugation at 7,500 rpm and repeated washing, the purified BT@POSS particles (2.0-2.5 g, calculated from the solid content) were redispersed in 100 mL of xylene with the help of ultrasonication. Meanwhile, predetermined amount of PP resin (Dow Chemical, H349-02) was dissolved in 60 mL of xylene at 140 °C and poured into the BT@POSS suspension. The mixture was stirred at 140 °C for 10 min to ensure a good mixing. The hot PP/BT@POSS suspension was poured into cold hexane (ca. -20 °C, cooled using an acetone/dry ice bath) under stirring. Finally, the co-precipitated PP/BT@POSS master batch was retrieved by centrifugation at 7,500 rpm for 20 min, followed by drying in a
vacuum oven at 80 °C for 2 d. The dried master batch was further melt-processed using a HAAKE™ MiniLab II Micro Compounder (Thermo Scientific, Waltham, MA) at 195 °C for 15 min to ensure uniform particle dispersion in the PP matrix. The BT content of the master-batch PP/BT@POSS was determined by TGA to be 29.2 vol.% (densities of BT particles and PP are taken as 6.08 and 0.90 g/cm³, respectively). The solution-blended master batch was then used to further melt-blend with PP resins (170-195 °C for 10-15 min) for nanocomposites with 10 and 20 vol.% BT@POSS NPs. From TGA results (Figure S2.7 in the Appendix A), the BT@POSS contents were 11.2 and 19.8 vol.%, respectively. The melt-compounded nanocomposites were weighed and put in between two Kapton films. One layer of aluminum foil (~25 µm) was used as spacer to control the sample thickness during compression molding. The hot-press temperature was set at 190-210 °C and 10 tons pressure was applied.

**BDS and Leakage Current Measurements.** BDS was performed on a Novocontrol Concept 80 broadband dielectric spectrometer with temperature control. The applied voltage was 1 Vrms (root-mean square voltage) with frequency ranging from 0.001 Hz to 1 MHz and temperature ranging from -55 to 110 °C. Silver electrodes (50 nm thick and area of 0.785 cm²) were evaporated on both sides of the film using a thermal evaporator (EvoVac Deposition System, Angstrom Engineering, Inc.). Leakage current measurements were performed also using the Novocontrol Concept 80 dielectric spectrometer equipped with a Keithley 6517B electrometer. To measure the permittivity of BT and BT@POSS NPs, the powder samples were isostatically pressed at ~500 MPa with a 13 mm IR die to prepare a cylindrical pellet. Silver paste was carefully spread on
each side of pellet as electrodes, and a mask with a circular hole of 0.785 cm² was used to control the electrode area.

**Breakdown Strength Measurement.** The breakdown strength of nanocomposite films were determined using a home-made fixture. Silver electrodes of 50 nm thickness and 5.15 mm² area were thermally deposited on both sides of the film. The voltage was supplied by a Quadtech (Marlborough, MA) Guardian 20-kV HiPot tester, and was ramped at a speed of 50 V/(s·μm) until dielectric breakdown. All breakdown tests were carried out in a silicone oil bath to reduce surface corona discharge. At least thirty repetitions were measured for each sample for Weibull statistical analysis.

**D-E Loop Measurement.** The D-E hysteresis loop measurements were carried out using a Premiere II ferroelectric tester (Radiant Technologies, Inc.) equipped with a Trek 10/10B-HS high voltage amplifier (0-10 kV AC). The applied voltage had either a bipolar or unipolar sinusoidal waveform ranging from 0.1 Hz to 1000 Hz (note that frequency doubled for unipolar loops in order to keep the same poling time). Most D-E loop tests were conducted under 10 Hz at RT. Samples were immersed in a silicone oil bath during tests, and the temperature was varied from RT to 130 °C using an IKA RCT temperature controller. Silver electrodes with 50 nm thickness and area of 5.15 mm² were used.
CHAPTER III

The Role of Field Electron Emission in Polypropylene/Aluminum Nanodielectrics

Under High Electric Fields
ABSTRACT

Polymer/metallic particle nanocomposites or nanodielectrics can exhibit colossal dielectric constants with a relatively low dissipation factor under low electric fields, and thus seem to be promising for high energy density dielectric capacitors. To study this possibility, this work focused on the dielectric performance and loss mechanisms in polypropylene (PP)/aluminum nanoparticle (nAl NP) composites under high electric fields. Phosphonic acid-terminated poly(ethylene-co-1-butene) was grafted to the Al₂O₃ surface layer on the nAl NPs in order to achieve reasonable dispersion in the PP matrix. The dielectric breakdown study showed that the breakdown strength decreased to nearly 1/20 that of the neat PP film as the nAl content increased to 25.0 vol.%. The leakage current study revealed three electronic conduction mechanisms in the PP/100 nm nAl nanocomposites, namely, ohmic conduction at low fields, hopping conduction at intermediate fields, and Fowler-Nordheim (FN) field electron emission above a critical field, depending on the filler content. Compared to the 100 nm nAl NPs, smaller (e.g., 18 nm) nAl NPs needed a much higher electric field to exhibit FN field electron emission. It was the FN electron tunneling that induced a substantial reduction in breakdown strength for the PP/nAl nanocomposites. Meanwhile, electron-tunneling injected space charges (electrons) from nAl NPs into the PP matrix, and internal electronic conduction led to significant dielectric nonlinearity at high poling fields. Although polymer/metallic NP composites are not suitable for high-field electric applications, they can be good candidates for electrical switches and quantum tunneling composites operated at relatively low electric fields.

KEYWORDS: Nanodielectrics, field electron emission, electron tunneling, aluminum nanoparticles, polypropylene
**Introduction**

Solid-state dielectric capacitors, including ceramic and polymer film capacitors, can deliver ultra-high power density, exhibit constant capacitance with little hysteresis, and are carefree for electrolyte-leaking or explosion. In addition to high power density, high energy density \( (U_e) \) for dielectric capacitors has drawn great interest in a variety of emerging electrical and power applications because of the need for low cost, light weight, miniaturization, flexibility, and high efficiency.\(^1,2\) The low dielectric constant \( (\varepsilon_r) \) of common dielectric polymers \( (\varepsilon_r = 2-5) \) is the bottleneck which holds back the development of high performance film capacitors.\(^{175} \) For examples, the state-of-the-art biaxially oriented polypropylene (BOPP) with an \( \varepsilon_r \) of 2.25 can only reach a maximum energy density of 5 J/cm\(^3\) at breakdown, lower than those for electrolytic and ceramic capacitors. In recent years, various strategies have been pursued to enhance the \( \varepsilon_r \) of polymers without drastically increase the dielectric loss.\(^{3,4,176,177} \) Inorganic ceramics usually possess notably high \( \varepsilon_r \) around several thousand as well as good temperature stability.\(^8\) However, they suffer from poor breakdown strength \( (E_b) \), usually around 50 MV/m. Inspired by the nanocomposite concept, it is attractive to achieve synergistic properties of polymers and inorganic ceramics, namely, high \( \varepsilon_r \)/high energy density from ceramics and high \( E_b \)/low dielectric loss from polymers.\(^{42,139,177,178} \) So far, numerous nanocomposite systems (or nanodielectrics) have been implemented, covering different combinations of polymers\(^{61,111,141,179} \) and inorganic fillers with varying shape and morphology,\(^{61,91,111,113,118,141,179} \) surface modification,\(^{110,111,141,145} \) matrix-free composites,\(^{36,88,103} \) and multicomponent and multilayered architectures.\(^{124,126,180} \) Intense efforts have been focused on enhancing the apparent \( \varepsilon_r \) of nanocomposites while
maintaining relatively high $E_b$, which leads to dramatically increased discharged energy density between 10 and 30 J/cm$^3$.

For practical capacitor applications, low dielectric loss is extremely important, rather than high energy density, because significant heat generation will lead to early thermal runaway of capacitors. Nonetheless, only a few reports discuss the dielectric loss mechanisms for polymer nanodielectrics. As revealed in our recent study on PP/BaTiO$_3$ nanocomposites, interfacial polarization could be resulted from large contrasts in permittivity and conductivity between the nanofillers and the polymer matrix. The interfacial charges at two poles of a nanoparticle (NP) in the field direction substantially increased the local electric field in the polymer matrix. When the NPs chain or aggregate together, the local field enhancement in the confined polymer matrix become more dramatic, inevitably leading to a decrease in the $E_b$. In addition, the interfacial space charges (i.e., free electrons) in more conductive BaTiO$_3$ NPs can be polarized back and forth upon high-field bipolar poling, resulting in significant dielectric loss from internal electronic conduction. Therefore, polymer/ceramic nanodielectrics are not appropriate for high-field AC electrical applications.

Compared to ceramic nanofillers, conductive NPs might be more advantageous due to the following reasons. First, the apparent $\varepsilon_r$ of conductive fillers, such as metallic NPs, can be considered as infinity. It is supposed that metallic NPs may enhance the apparent $\varepsilon_r$ of nanodielectrics more effectively than ceramic NPs. Second, the density of states of metallic NPs was discrete due to the quantum confinement. Single electron tunneling between two neighboring NPs could create a voltage buildup and disfavor the following electron-tunneling. This so-called Coulomb blockade effect can be observed for ultra-
small metallic NPs at room temperature.\textsuperscript{183} Third, different from ceramic NPs, metallic NPs are conductive and thus the internal electronic conduction should be negligible, and the corresponding loss will be low. Indeed, numerous polymer/metall ic NP composites have been reported to improve dielectric properties, especially the apparent $\varepsilon_r$. For example, neat micro-sized nickel and mercaptosuccinic acid functionalized silver NPs were simply blended with poly(vinylidene fluoride) (PVDF) and epoxy, respectively, for making embedded capacitors on printed circuit boards\textsuperscript{74,129}. High apparent $\varepsilon_r$s of 300-400 and relatively low dissipation factors with weak temperature and frequency dependence were achieved at the filler content close to the percolation threshold. Similar results were also discovered by Lu et al. through incorporating \textit{in-situ} reduced Ag NPs into carbon black/epoxy nanocomposites for exploiting the Coulomb blockade effect.\textsuperscript{77} It seems that nanocomposites filled with conductive fillers are promising, since extremely high $\varepsilon_r$ with reasonably low loss are often achieved at low electric fields (i.e., $<0.1$ MV/m).

In addition to the low-field studies, investigations on dielectric properties of polymer/metall ic NP composites under high fields are somewhat limited, although the high-field performance is more relevant to practical applications. Feng et al. demonstrated that the Coulomb blockade effect could be utilized to increase the resistivity and the $E_b$ of nanocomposite films.\textsuperscript{130} Recently, PP/nAl nanodielectrics were prepared by grafting metallocene catalyst on the native Al$_2$O$_3$ surfaces of nAl, followed by \textit{in-situ} polymerization of propylene.\textsuperscript{75} A 10.4 vol.\% nanocomposite exhibited a permittivity $>6$ for frequencies up to 7 GHz under low electric fields.\textsuperscript{131} From the bipolar D-E loop at a poling field of $\sim$120 MV/m, the apparent $\varepsilon_r$ was ca. 270, the discharged $U_e$ was 14.4 J/cm$^3$, and the discharge efficiency was 76\%.\textsuperscript{75} When the filler content increased to 12.4 vol.\%,
the apparent $\varepsilon_r$ was 1,729 at 47.8 MV/m. The discharged $U_e$ was as high as 16.7 J/cm$^3$ and the discharge efficiency was 95%. When the poling field increased to above 55 MV/m, the D-E loop became nonlinear with significant hysteresis losses. On the contrary, decreased dielectric properties were reported at high electric fields in other studies. For example, Qi et al. investigated epoxy/Ag NP composites. The $E_b$ decreased monotonically upon increasing the nanofiller content, from 25 MV/m for the neat epoxy finally to only 1.25 MV/m for the 25.2 vol.% nanocomposite. It was considered that the direct electrical contact of Ag NPs might be responsible for the drastic decrease in the $E_b$. To prevent direct electrical contact among Ag NPs, Shen et al. coated Ag NPs with an organic carbon shell (Ag@C). Nonetheless, a substantial decrease in the $E_b$ was still observed upon increasing the filler concentration, e.g., from ca. 30 MV/m for the neat epoxy to 0.6-1.0 MV/m for the epoxy/Ag@C nanocomposites with 20-30 vol.% NPs. Huang et al. studied the dielectric properties of polyethylene (PE)/nAl nanocomposites, and the electrical percolation seemed to depend on the applied field, above which the nanocomposites became fairly conductive and the $E_b$ substantially decreased. For example, the low-field dielectric spectroscopy and leakage current study suggested a percolation threshold of ca. 10 vol.%, whereas the breakdown study suggested a percolation threshold of only 5 vol.%. In a separate study to develop electrical switches based on ultrathin (15 nm) films of co-evaporated poly(tetrafluoroethylene) (PTFE)/Au nanocomposites, Laurent et al. observed bistable field dependent conductivity when the Au loading was above 10 vol.% but below the percolation threshold of 40 vol.%. The critical electric field to trigger the bistable switching was around 10 MV/m. Meanwhile, the Weibull $E_b$ decreased from 180 MV/m of the neat PTFE to about 100 MV/m for the
12.5 vol.% nanocomposite film. The field-induced bistable switching and decreased $E_b$ were attributed to the result of field-dependent electron tunneling.$^{187}$

Given the broad range of high-field dielectric properties reported for polymer/metallic NP composites, it is highly desirable to thoroughly understand the physics of the enhancement of dielectric constant and the decrease in the $E_b$ as the metallic filler content increases. In this work, we investigated both linear and nonlinear dielectric properties for PP/nAl nanocomposites using broadband dielectric spectroscopy (BDS), Weibull analysis of $E_b$, leakage current study, and electric displacement-electric field (D-E) loop tests. The nAl NPs are chosen because they have a thin, self-passivated oxide layer on the surface, which offers an insulating barrier to prevent direct electrical contact.$^{186}$ Low loss PP is chosen as the polymer matrix, rather than the high dielectric constant PVDF, because PVDF shows high ionic conduction and ferroelectricity under high electric fields.$^{17}$ Through a fundamental study of the loss mechanisms, the goal of this study is to address the question whether polymer/conductor nanocomposite is appropriate for the dielectric capacitor application.

Results and Discussion

Synthesis of Poly(ethylene-co-1,2-butylene) Biphosphonic Acid (PEB-PA)-Modified nAl NPs. Metals such as aluminum and zinc usually have a thin, self-passivated oxide layer on their surfaces. These surface oxide layers play an important role to prevent further oxidation and corrosion, and can be used for ligand modification. Especially for $\text{Al}_2\text{O}_3$, it can also act as an insulating dielectric layer in aluminum electrolytic capacitors.$^{175}$ In this work, the 100 nm nAl NPs were made by electrical explosion of Al wires. The
mean particle size \(d\) was 93±45.8 nm with a relatively broad size distribution (see inset of Figure 3.1A). The surface Al₂O₃ layer was clearly seen in transmission electron microscopy (TEM, Figure 3.1A), but no crystalline reflections were detectable from powder X-ray diffraction (XRD, Figure 3.1E). This indicated that the Al₂O₃ layer should be amorphous. From the TEM image in Figure 3.1A, the Al₂O₃ shell thickness (\(\zeta\)) was 4.8 nm. For the 18 nm particles made by laser ablation, rod-like particles were seen in addition to spherical NPs. The mean size \(d = 37±26\) nm) of the spherical particles was about twice the value (18 nm) specified by the manufacturer. The Al₂O₃ shell thickness was \(\zeta = 2.0\) nm. Besides four sharp crystalline reflections, i.e., (111), (200), (220), and (311) for the face-centered cubic (FCC) Al crystals, additional reflections for the γ-Al₂O₃ was observed from the XRD (Figure 3.1E). The rod-like particles were attributed to γ-Al₂O₃ for the 18 nm nAl sample by Mandilas et al.,¹⁸⁸ and the content was determined by energy dispersive spectrum (EDS) analysis to be around 30 wt.%.
Figure 3.1. TEM micrographs of (A) 100 nm nAl NPs, (B) 100 nm nAl@PEB-PA NPs, (C) 18 nm nAl NPs, and (D) 18 nm nAl@PEB-PA NPs. Insets in (A) and (C) show histograms of spherical particle diameters. (E) Powder XRD profiles for 100 nm nAl NPs, 100 nm nAl@PEB-PA NPs, PP/100 nm nAl@PEB-PA nanocomposite, 18 nm nAl NPs, and 18 nm nAl@PEB-PA NPs. (F) Transmittance FTIR spectra of 100 nm nAl NPs, 100 nm nAl@PEB-PA NPs, 18 nm nAl NPs, 18 nm nAl@PEB-PA NPs, and PEB-PA.

Poly(ethylene-co-1,2-butylene) mono-ol (PEB-OH) is the hydrogenated product of polybutadiene, which is miscible with the amorphous phase of isotactic polypropylene (PP). The PEB-OH had a number-average molecular weight (Mn) of 4,200 g/mol with 67% ethylene and 33% 1-butene units, and its molecular weight distribution was 1.06 as reported before. Crouse et al. found that the surface hydroxyl groups of the Al₂O₃ shell could form robust bonding with organic phosphonic acids. To achieve uniform dispersion of nAl NPs in the PP matrix, the hydroxyl chain ends in PEB-OH were functionalized into phosphonic acid groups via two-step reactions, yielding PEB-diphosphonic acid (PEB-PA, see Scheme 3.1). In the first step, PEB-diethylphosphonate ester (PEB-PE) was synthesized by N,N'-dicyclohexylcarbodiimide (DCC)-catalyzed esterification in the
presence of 4-dimethylaminopyridine (DMAP). In the second step reaction, bromotrimethylsilane (TMSBr) was used to hydrolyze the biphosphonate ester groups in the presence of methanol/water in tetrahydrofuran (THF), yielding PEB-PA. Detailed synthesis procedure and proton nuclear magnetic resonance (1H NMR) characterization of PEB-PE and PEB-PA are given in Figure S3.1 in the Appendix B.

Scheme 3.1. (A) Synthesis of the PEB-PA ligand. (B) Procedures of surface modification of 18 and 100 nm nAl NPs with PEB-PA and preparation of PP/nAl@PEB-PA nanocomposites via sequential solution- and melt-blending methods.

Surface modification of nAl NPs was conducted with two-fold excess of the PEB-PA polymer in toluene at 60 °C under N2 protection. Afterwards, large NP aggregates were removed by centrifugation at 1,500-3,000 rpm. Individually dispersed NPs could be retrieved by high-speed centrifugation at 8,000 rpm with repeated wash-centrifugation cycles to remove impurities and physisorbed PEB-PA polymers. The dried nAl@PEB-PA NPs could be easily re-dispersed in a nonpolar solvent such as toluene and n-hexane with no sediment for weeks. On the contrary, bare nAl NPs could not be dispersed in toluene even with rigorous sonication. Although polar solvents such as methanol and DMF could temporarily disperse bare nAl NPs, sedimentation took place within a few days. This result indicated that the grafted PEB-PA brushes greatly improved the dispersibility of nAl NPs.
in nonpolar solvents. The grafted PEB-PA layer on the 100 nm nAl NPs could be clearly seen in the TEM image in Figure 3.1B, and the brush layer was ca. 14.0 nm, excluding the Al₂O₃ layer. The PEB-PA layer thickness was only ca. 2.4 nm for the 18 nm nAl NPs, as seen in the TEM image in Figure 3.1D. The grafting densities of PEB-PA on 18 and 100 nm nAl NPs were determined from the thermogravimetric analysis (TGA) results (see Figure S3.2 and related discussion in the Appendix B). For the 100 and 18 nm nAl NPs, the PEB-PA grafting densities were 0.99 and 0.36 chains/nm², respectively. The lower PEB-PA grafting density was attributed to the steric effect when grafting the PEB-PA chains onto small-sized nAl NPs.

It was reported that nAl NPs could be corroded by acids such as phosphonic acid. However, no corrosion was observed for nAl@PEB-PA NPs, because the XRD for the surface-modified nAl NPs were identical to those of unmodified NPs (Figure 3.1E), suggesting that the PEB-PA brushes formed a protective layer to stabilize the NPs. The surface modification was also confirmed by Fourier transform infrared (FTIR) spectroscopy, as shown in Figure 3.1F. The presence of γ-Al₂O₃ phase for the 18 nm nAl NPs was evidenced by two discernable absorption bands at 840 and 588 cm⁻¹, which are assigned to ν-AlO₄ tetrahedral and ν-AlO₆ octahedral coordination, respectively. The Al-O absorption bands of the amorphous phase for the 100 nm nAl NPs was identified as an intense and broad peak centered at 915 cm⁻¹. After surface modification, nAl@PEB-PA NPs inherited the absorption bands from the bare nAl NPs and the PEB-PA polymer, namely, Al-O bands at 750-1,000 cm⁻¹, methyl and methylene C-H stretching at 2,750-3,000 cm⁻¹ and bending at 1,300-1,500 cm⁻¹, and C=O band at 1,735 cm⁻¹. Because of the low content of chain ends, it was difficult to observe any P(=O)-OH absorption bands in
nAl@PEB-PA NPs as well as their interaction with the surface hydroxyl groups on nAl NPs.

**Preparation and Morphology of PP/nAl Nanocomposites.** Because surface-modified nAl NPs were able to uniformly disperse in nonpolar solvents, it was possible to prepare a master batch (e.g., 30 vol.% nAl NPs) by solution-blending (Scheme 3.1B). The premix was prepared by mixing nAl@PEB-PA NPs with PP in hot xylene at 140 °C, followed by quick precipitation in cold methanol. After thorough vacuum-drying, the premix was further melt-blended using a descending temperature gradient (from 190 °C to 170 °C in ca. 12 min) in a mini-Haake compounder to ensure homogeneous particle dispersion (Scheme 3.1B). The high temperature, high pressure, and high shear rate during the melt-processing could densify the premix by removing air voids in the nanocomposite. The theoretical physical percolation threshold for spherical fillers was around 30-35 vol.%. Composites filled with conducting fillers were reported to show even lower electrical percolation thresholds (e.g., 12-15 vol.%) than the physical percolation threshold because of enhanced electrical conduction. To avoid NP percolation and thus conductive pathways, PP/nAl nanocomposites were prepared with no higher than 25 vol.% for the electrical studies. Nanocomposites with different nAl NP contents were prepared by diluting a melt-processed master batch with PP resins. This method was important to achieve high quality, pin hole-free composites with uniform particle dispersion. Otherwise, if the nanocomposite was directly prepared by melt-processing of the corresponding solution-blended premix (<20 vol.% nAl NPs), poor film quality (e.g., pin-holes) and poor particle dispersion were observed. As controls, 100 nm bare nAl NPs without any surface modification were also melt blended with PP resin to prepare nanocomposites.
Unfortunately, poorly dispersed nAl NPs and conductive nanocomposites were obtained even when the filler content was as low as 5-10 vol.%. It was clear that final electrical properties of nanocomposites were sensitive to the dispersion of conductive fillers. Therefore, no control nanocomposites were used in this study.

**Figure 3.2.** TGA results for (A) PP/100 nm nAl and (B) PP/18 nm nAl nanocomposites with different filler contents.

Thermogravimetric analysis (TGA) was used to determine the actual volume fractions of nAl NPs for each melt-blended nanocomposite (Figure 3.2). For the PP/100 nm nAl nanocomposites, four volume fractions were prepared: 5.3, 10.8, 18.3, and 25.0 vol.% of nAl NPs. For the PP/18 nm nAl nanocomposites, the solid contents were 4.8, 8.3, and 16.4 vol.%. Taking into account of 30 wt.% rod-like $\gamma$-Al$_2$O$_3$ particles, the actual nAl NP contents were corrected to 3.1, 5.3, and 10.5 vol.% Dielectric films of 25-40 $\mu$m were prepared by compression molding at 170 $^\circ$C for dielectric property studies later.
Figure 3.3. TEM micrographs of thin sections of the PP/100 nm nAl nanocomposites with (A) 5.3 vol.%, (B) 10.8 vol.%, (C) 18.3 vol.%, and (D) 25.0 vol.% NPs, and PP/18 nAl nanocomposites with (E) 5.3 vol.% and (F) 10.5 vol.% NPs.

The dispersion of nAl NPs in various nanocomposites was studied by TEM (see Figure 3.3). Compared to small molecule surface modifiers, such as polyhedral oligomeric silsesquioxane (POSS)\textsuperscript{54} and silane coupling agents,\textsuperscript{186} the low molecular weight (MW) PEB-PA polymer appeared to be more effective in dispersing nanofillers in the PP matrix. At low filling ratios (0-10 vol.%, see Figures 3.3A/B), a significant amount of 100 nm nAl NPs remained isolated in the PP matrix, although a small fraction of clusters and floculates containing 2-6 NPs was still seen because of the dry-brush scenario.\textsuperscript{158} Namely, when the polymer matrix MW is higher than that of the polymer brushes, nanoparticles tend to phase separate from the polymer matrix, because the high MW PP chains in the matrix are difficult to penetrate and swell the grafted short PEB-PA brushes. Increasing to higher
filling ratios such as 18.3 and 25.0 vol.%, the nAl NPs tended to form chains and aggregates (Figures 3.3C/D), which again could be attributed to the dry-brush scenario. From Figures 3.3E/F (also Figure S3.2D in the Appendix B), the 18 nm NPs were composed of mixed spherical (nAl), irregular, and nano-rod (γ-Al₂O₃) NPs. Compared to the PP/100 nm nAl nanocomposites, the 18 nm nAl NPs were more difficult to disperse uniformly in the PP matrix, probably due to the large surface-to-volume ratio and thus enthalpy compensation. Nonetheless, the dispersion of the 18 nm nAl@PEB-PA NPs was much better than the bare nAl NPs without any surface treatment because of the compatibility of the PEB-PA brushes with the PP matrix.

Figure 3.4. (A) Temperature- (at 1 kHz) and (B) frequency-scan (at room temperature) BDS results for PP/100 nm nAl and PP/18 nm nAl nanocomposites with a ~10 vol.% filler ratio. (C) Dielectric constant ($\varepsilon'$) of PP/100 nm nAl and PP/18 nm nAl nanocomposites as a function of the filler ratio measured at 1 kHz and room temperature. Fitting curves using the series bilayer, Maxwell-Garnett, Vo-Shi core-shell, and Bruggeman models are also shown.

Linear Dielectric Properties of PP/nAl Nanocomposites. Low-field, linear dielectric properties of both PP/nAl nanocomposites with different filler ratios were studied by BDS. Example temperature and frequency sweeps for the 18 and 100 nm PP/nAl nanocomposites with a filler ratio of ca. 10 vol.% are shown in Figures 3.3A and B, respectively. The complete BDS results, including temperature and frequency sweeps for
nanocomposites of all compositions, are shown in Figures S3.3-3.6 in the Appendix B. In the temperature-scan BDS plots in Figure 3.4A, the $\varepsilon'$ values were similar for both 18 and 100 nm nAl nanocomposites, which remained nearly constant below 10 °C and slightly decreased above 15 °C. A weak and broad peak was observed around 15 °C in the $\varepsilon''$ plot for the PP/100 nAl 10.8% nanocomposite, and it could also be seen around 200 Hz in the frequency-scan plot in Figure 3.4B. From the frequency-scan plots in Figure S3.6 in the Appendix B, this peak was nearly independent of temperature for all compositions. Therefore, it could not be assigned to the amorphous relaxation of PP. Instead, it should be attributed to the internal conduction loss from space charge (SC, i.e., free electrons) in the 100 nm nAl NPs. This is similar to the case reported for the PP/70 nm BaTiO$_3$ nanocomposites recently.$^{54}$ For the PP/18 nm nAl 10.3% nanocomposite, this SC peak became much weaker, and this could be attributed to the nanoconfinement effect on space charge transport in small NPs (note that a similar nanoconfinement effect was reported for impurity ion conduction loss in nano-layered multilayer films$^{193}$). Namely, when the nAl NPs were small, the internal conduction loss from free electrons would be low due to the limited distance that space charges could travel. On the contrary, when the nAl NPs were large, the internal conduction loss from free electrons would be high. Summarizing all the dielectric constant ($\varepsilon'$) at 1 kHz for both PP/nAl nanocomposites in Figures S3.3-3.6 in the Appendix B, Figure 3.4C shows the dielectric constant as a function of the nAl NP content ($\phi_p$). As expected, the $\varepsilon'$ of the PP/nAl nanocomposites gradually increased with increasing the filler content, and there was negligible difference in $\varepsilon'$ for both nanocomposites when the filler ratio was below 11 vol.%. Finally, the $\varepsilon'$ of the PP/100 nm nAl 25% nanocomposite increased from 2.24 of neat PP to 5.7 at 25 °C (1 kHz).
Scheme 3.2. Schematics of (a) series bilayer, (b) Maxwell-Garnett, (c) Bruggeman, and (d) the proposed charge-injection models. The white arrows in (b) and (c) represent the dipole moments of the NPs.

To understand the origin of this increase in $\varepsilon_r'$, predicted results using various mixing models, such as the series bilayer, Maxwell-Garnett, and Bruggeman models, are shown in Figure 3.4C. Here, the dielectric constant of the nAl NPs is taken as infinity. For the bilayer model (Scheme 3.2a), the nanocomposite is simplified as a macroscopic bilayer, which is comprised of a PP layer and a metallic (Al) layer in series. Because the Al layer is conductive, the apparent $\varepsilon_r'$ will be $\varepsilon_{r,m}/(1-\phi_p)$, where $\varepsilon_{r,m}$ is the dielectric constant (2.24) of the PP matrix. Obviously, the series bilayer model significantly underestimates the apparent $\varepsilon_r'$ for the PP/nAl nanocomposites (Figure 3.4C). In the Maxwell-Garnett model (Scheme 3.2b), the local field enhancement (near two poles of a particle along the field direction) is considered; however, the dipole-dipole interactions among neighboring particles are ignored because it mainly considers the situation of a low particle concentration.\textsuperscript{194,195} From Figure 3.4C, we can see that the Maxwell-Garnett model also underestimates the apparent $\varepsilon_r'$ for the PP/nAl nanocomposites due to the neglect of the dipole-dipole interactions, particularly at high filler contents. The Bruggeman model takes into account of the dipole-dipole interactions among neighboring particles in the
nanocomposite (Scheme 3.2c). Namely, the dipole moment of individual NPs will enhance when they get close to each other due to the reactive interactions. The increased dipole moment of NPs, in turn, will further enhance the local electric field in the polymer matrix, particularly between neighboring particles aligned along the electric field direction. As a result, the apparent $\varepsilon_r'$ will further increase. On the basis of our recent computer simulation, the Bruggeman model fits polymer nanodielectrics better than the Maxwell-Garnett model, and is often used to predict the dielectric constant of polymer nanocomposites.

In Figure 3.4C, the Bruggeman prediction however overestimated the apparent dielectric constant for the PP/nAl nanocomposites. It was surprising that the apparent dielectric constants for the PP/nAl nanocomposites were lower than those for the PP/70 nm BaTiO$_3$ nanocomposites, although the dielectric constant of metallic NPs was considered higher than that of ceramic NPs. The lower apparent $\varepsilon_r$ for the PP/nAl nanocomposites could be attributed to the insulating layer of Al$_2$O$_3$ on the nAl NPs, which had an $\varepsilon_r$ of ca. 10. By employing a modified core-shell model developed by Vo and Shi, the experiment $\varepsilon_r'$ data could fit reasonably well using the experimentally determined diameter of the Al core (97 nm) and the thickness of the Al$_2$O$_3$ shell (4.7 nm; see Figure 3.4C). The situation of the PP/nAl NP composites is different from other polymer nanocomposites with silver or gold NPs (no oxide layers), where high dielectric constants are reported. Actually, Huang et al. reported that 100 nm nAl NPs were not very conductive due to the thin Al$_2$O$_3$ layer, only in the range of $10^{-9}$-$10^{-8}$ S/cm.

For the PP nanocomposites with 18 nm nAl NPs, the actual volume fraction of the metallic Al needed to correct for the existence of 30 wt.% $\gamma$-Al$_2$O$_3$. After correction, the
\( \varepsilon_r \) values of the 18 nm nAl nanocomposites almost overlapped with those of the 100 nm nAl nanocomposites. Therefore, the apparent \( \varepsilon_r \) of the PP/nAl nanocomposites had little to do with the particle size, and this is consistent with our recent simulation results. However, the loss \( \varepsilon'' \) for the 18 nm nAl nanocomposites was lower than that for the 100 nm nAl nanocomposites (Figures 3.4A/B). In this sense, it is better to have smaller metallic NPs for the PP nanocomposites to lower the dielectric loss.

From our recent simulation results, the contribution of the electric field inside high \( \kappa \) NPs to the overall apparent \( \varepsilon_r \) is less than 3%, when the permittivity contrast \((\varepsilon_{r,p}/\varepsilon_{r,m})\) is >30. The enhanced dielectric constant for the nanocomposites should be a result of local field enhancement in the polymer matrix due to the interfacial polarization in the high \( \kappa \) ceramic or metallic NPs. Even with the local field enhancement, the dielectric constant of the nanocomposites should not significantly exceed the Bruggeman predictions. In the past, it has been reported that polymer nanocomposites with metallic (e.g., silver or gold) NPs, carbon nanostructures, and conducting polymers could exhibit apparent \( \varepsilon_r \) values as high as several hundreds or even a couple thousands at a high enough composition before percolation. According to the Bruggeman prediction in Figure 3.4C, it is difficult to increase the apparent \( \varepsilon_r \) of polymer nanocomposites beyond 30 for spherical NPs at ca. 30 vol.%. One possible reason for the reported colossal \( \varepsilon_r \) of the polymer/conductor nanocomposites is space charge injection from metal electrodes, as shown in Scheme 3.2d. In most reports, the conducting inclusions often flocculate or even aggregate in the polymer matrix because of the lack of surface modification. If the conducting aggregates are in direct contact with one electrode, but not the other one, space charges (homo-charges) will be injected into the nanocomposites, which can be considered as one type of electrode
polarization.\textsuperscript{196} As a result, the apparent $\varepsilon_r$ will substantially increase. Because there is no actual conduction, the dissipation factor may still remain relatively low, e.g., $\tan\delta \sim 0.01$-0.05.

![Figure 3.5](image)

**Figure 3.5.** Weibull plots of dielectric breakdown strengths for (A) PP/100 nm nAl and (B) PP/18 nm nAl nanocomposites. (C) Weibull characteristic $E_b$ ($\alpha_W$) and (D) Weibull modulus ($\beta_W$) for PP/100 nm nAl and PP/18 nm nAl nanocomposites as a function of the volume fraction of nAl NPs.

**Decreased Electric Breakdown Strength due to Field Electron Emission.** As discussed above, the dielectric constant increase for polymer nanodielectrics originates primarily from the local field enhancement in the polymer matrix, rather than the electric field inside the NPs. On the basis a recent report,\textsuperscript{54} the local field enhancement, especially
in areas between chained or aggregated NPs, is high and can cause the “hot spots” for early dielectric breakdown. To study whether this is also true for PP/nAl nanocomposites, Weibull analysis of dielectric breakdown strength is carried out.

At least 25 individual samples with a parallel plate capacitor geometry and an electrode area of 5.15 mm$^2$ were tested for each nanocomposite. Experiment data was analyzed using the two-parameter Weibull statistics (Figures 3.5A/B). The characteristic Weibull strength ($\alpha_w$) or $E_b$ at 63.2% failure probability and the Weibull modulus ($\beta$) are plotted in Figures 3.5C/D. The PP/100 nm nAl nanocomposites showed a dramatic decrease in $E_b$ as the composition of nAl NPs increased. For example, the PP/100 nm nAl(25%) nanocomposite exhibited an $E_b$ of only 37.5 MV/m, nearly one twentieth of that (622 MV/m) of the hot-pressed PP film. A slightly gentle decrease was seen for the PP/18 nm nAl nanocomposites. This could possibly be attributed to the existence of $\gamma$-Al$_2$O$_3$ NPs in the system, which modulated the local field enhancement between particles. The Weibull modulus represents the distribution of $E_b$. From Figure 3.5D, adding nAl NPs would decrease the $\beta_w$ value up to ca. 5 vol.% of nAl NPs. This could be attributed to the defects and hot-spots introduced by nAl NPs. Above 5 vol.%, the $\beta_w$ values started to increase for both nanocomposites. Note that this increase did not mean better dielectric performance, but consistently poorer performance of the nanocomposites. In other words, at high nAl contents the dielectric breakdown happened at an extremely low $E_b$ within a narrow distribution.
Figure 3.6. (A) Leakage current density and (B) electrical conductivity as a function of the applied electric field for the PP/100 nm nAl nanocomposites with 10.8, 18.3 and 25.0 vol.% NPs and the PP/18 nm nAl nanocomposite with 10.5 vol.% NPs. Schematics of (C) hopping conduction and (D) Fowler-Nordheim field emission mechanisms for the PP/nAl nanocomposites.

Table 3.1. Fitting Parameters in Hopping and Fowler-Nordheim (FN) Tunneling Models

<table>
<thead>
<tr>
<th>$d$ (nm)</th>
<th>$\phi$ (vol.%)</th>
<th>$\Delta_{sc}$ (nm)</th>
<th>$E_H$ (MV/m)</th>
<th>$A_H$ (A/m$^2$)</th>
<th>$B_H$ (m/V)</th>
<th>$\lambda$ (nm)</th>
<th>$E_{FN}$ (MV/m)</th>
<th>$A_{FN}$ (A/V$^2$)</th>
<th>$B_{FN}$ (MV/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>10.8</td>
<td>64.4</td>
<td>60-90</td>
<td>2.8×10$^{-6}$</td>
<td>5.2×10$^{-8}$</td>
<td>2.6</td>
<td>&gt;90</td>
<td>1.54×10$^{-17}$</td>
<td>606</td>
</tr>
<tr>
<td>18.3</td>
<td>39.0</td>
<td>20-38</td>
<td>7.9×10$^{-6}$</td>
<td>8.2×10$^{-8}$</td>
<td>4.2</td>
<td>&gt;40</td>
<td>2.1×10$^{-17}$</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>26.0</td>
<td>15-27</td>
<td>1.2×10$^{-5}$</td>
<td>1.8×10$^{-7}$</td>
<td>9.2</td>
<td>&gt;30</td>
<td>4.5×10$^{-17}$</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>10.5</td>
<td>26.2</td>
<td>&gt;50</td>
<td>5.6×10$^{-6}$</td>
<td>4.8×10$^{-8}$</td>
<td>2.4</td>
<td>-</td>
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</tr>
</tbody>
</table>

Compared to the PP/70 nm BaTiO$_3$ nanocomposites,$^{54}$ the decrease of $E_b$ as a function of the filler content for the PP/100 nm nAl nanocomposites appeared to be much more dramatic, and thus could not be simply attributed to the local field enhancement alone. To investigate the underlying mechanism, we performed leakage current studies by
stepwise increasing the applied electric field until dielectric breakdown. The current
density versus electric field (J-E) and conductivity versus electric field (σ-E) plots are
shown in Figures 3.6A/B, respectively. Three conduction mechanisms were identified for
the PP/100 nm nAl nanocomposites (Figure 3.6A). At low fields (<40 MV/m for the 10.8
vol.% nanocomposite and possibly <15 MV/m for the 18.3 and 25.0 vol.% nanocomposites),
the nanocomposites roughly followed the ohmic conduction mechanism
(i.e., J ∝ E). Under the intermedium fields (60-90 MV/m for the 10.8 vol.% nanocomposite,
20-38 MV/m for the 18.3 vol.% nanocomposite, and 15-27 MV/m), the current density for
both nanocomposites became nonlinear as a function of the electric field. From the data-
fitting, the hopping conduction (Figure 3.6C) can be identified.\textsuperscript{138}

\begin{equation}
J = A_H \sinh (B_H E)
\end{equation}

Here, $A_H$ is the prefactor and can be defined as $A_H = 2ne\lambda v \exp (-E_a/kT)$, where $n$ is the
carrier concentration, $e$ the electric charge of the carrier, $\lambda$ the hopping distance, $v$ the
attempt-to-escape frequency, $E_a$ the activation energy, $k$ the Boltzmann constant, $T$ the
absolute temperature, and $E$ the electric field. $B_H$ is defined as: $B_H = \lambda e/(2kT)$. From the
fitting results of $B_H$ in Table 3.1, the $\lambda$ values were determined to be 2.6, 4.2, and 9.2 nm
for the PP/100 nm nAl 10.8, 18.3, and 25.0 vol.% nanocomposites. Assuming a simple
cubic (SC) packing for the nAl NPs, the average distance ($a_{SC}$) between the surfaces of
neighboring particles could be calculated (see Table 3.1), i.e., 64.4, 39.0, and 26.0 nm for
the PP/100 nm nAl 10.8, 18.3, and 25.0 vol.% nanocomposites. Obviously, the $a_{SC}$ values
were much larger than the $\lambda$ values for the PP/100 nm nAl nanocomposites. It was unlikely
that only the nAl NPs served as charge traps. Instead, defects and impurities in the PP
matrix should still serve as effective traps for electrons (see Figure 3.6C). The direct
electron tunneling between trapped sites resulted in the hopping conduction. This is different from the thermionic detrapping in the Poole-Frenkel emission conduction.\textsuperscript{10,197} Note that the $\lambda$ values were similar to those (1.4-3.2 nm) reported for biaxially oriented PP (or BOPP),\textsuperscript{138} indicating that the $B_H$ values should be similar for both PP/nAl nanocomposites and BOPP. However, the $J$ values of the PP/nAl nanocomposites at room temperature were nearly four orders of magnitude higher than that ($10^{-8}$ A/m$^2$) of BOPP at 35 °C.\textsuperscript{138} Therefore, the much higher $J$ values must be attributed to the higher $A_H$ prefactor. At a similar temperature, the activation energy $E_a$ and the attempt-to-escape frequency $v$ should be similar for the PP matrix and BOPP.\textsuperscript{198} If this was the case, the much higher $A_H$ prefactor for the PP/nAl nanocomposites should be attributed to the much higher carrier concentration $n$. Then, the question is: where did the electrons come from in the PP matrix of the nanocomposites? Given the local field enhancement near two poles of the nAl NPs along the electric field direction (see Scheme 3.2b), it was likely that under high electric fields, electrons could tunnel through the thin Al$_2$O$_3$ layer and inject into the PP matrix to increase the carrier concentration (see the inset in Figure 3.6C). The mechanism of electron injection through tunneling can explain the higher conductivity of polymer/conductive particle nanocomposites than the neat polymer reported in the past.\textsuperscript{185,192} The high-field bulk conductivities for the PP/100 nm nAl nanocomposites were orders of magnitude higher than that ($10^{-16}$ S/m\textsuperscript{138}) of neat PP at 35 °C (Figure 3.6B).

Above a critical field (i.e., 90, 40, and 30 MV/m for the 10.8, 18.3, and 25.0 vol.% nanocomposites, see Table 3.1), the current density the PP/100 nm nAl nanocomposites increased even more rapidly than predicted by the hopping conduction. The high-field J-E curves could fit into the so-called Fowler-Nordheim (FN) tunneling equation:\textsuperscript{10,197}
\[ J = A_{FN} E^2 \exp(-B_{FN} / E) \]  

(3.2)

where \( A_{FN} \) is the prefactor and \( B_{FN} \) is a constant related to the FN barrier height, \( \varphi^{3/2} \). The fitting \( A_{FN} \) and \( B_{FN} \) parameters are given in Table 3.1. Conventionally, FN tunneling is considered as an electrode-limited conduction mechanism, and often happens at fairly high electric fields. \(^{197}\) For example, the FN tunneling was not observed for BOPP when the field was below 500 MV/m, \(^{138}\) and it only happened at ca. 1 GV/m for thermally grown gate SiO\(_2\) thin films (3.6-5.7 nm thick). \(^{199}\) The much lower \( E_{FN} \) values observed in the PP/100 nm nAl nanocomposites could not be explained by the electrode FN tunneling. A possible FN tunneling mechanism for PP/nAl nanocomposites is shown in Figure 3.6D. When the filler content is high, the distance between neighboring NPs is decreased, and the overlapped local field enhancement between aligned metallic NPs (e.g., Scheme 3.2c) can facilitate the FN field electron emission. In other words, each metallic NP behaves like a nanosized metal electrode. Consequently, a flux of electrons will be emitted from the surface of a nAl NP to the conduction bands of the Al\(_2\)O\(_3\) layer and the PP matrix, and then move along the external field direction into the neighboring nAl NPs. Eventually, a high level of FN field electron emission will lead to ultralow dielectric breakdown strengths (see Figure 3.5). The increased \( E_{FN} \) as the nAl content increased could be attributed to the interparticle distance effect; the larger the interparticle distance \( (a_{SC}) \), the higher the critical electric field \( (E_{FN}) \) for the FN field electron emission. Laurent et al. observed FN field electron emission at 11.2 MV/m for the 28.5 vol.% polytetrafluoroethylene (PTFE)/Au nanocomposite, which was consistent with theoretically predicted threshold of 7.8 MV/m. \(^{133}\) Compared with this low FN field emission threshold, our observed \( E_{FN} \) of 27 MV/m was higher. We speculate that the insulating Al\(_2\)O\(_3\) layer on the nAl NPs added an
extra energy barrier to the FN electron tunneling and postponed its emergence until a higher electric field.

For the PP/18 nm nAl 10.3 vol.% nanocomposite, the hopping conduction could fit the experimental data reasonably well, and no FN field emission was seen below 150 MV/m (Figure 3.6A). We speculate that the FN field emission should happen at an even higher field than 150 MV/m. Comparing the PP/18 nm and 100 nm nAl nanocomposites, the 100 nm nAl NPs were easier to undergo FN field emission than the 18 nm nAl NPs under high electric fields. This can be attributed to a size effect; the larger the nAl NPs, the easier the FN field electron emission.

Figure 3.7. Five continuous bipolar D-E loops (10 Hz) for (A) the PP/18 nm nAl nanocomposite with 10.5 vol.% nAl NPs and (B) the PP/100 nm nAl nanocomposite with 18.3 vol.% nAl NPs at room temperature. The blue dash lines are AC conduction loops
with the magnification indicated. Discharged energy densities ($U_e$) and discharge efficiencies for the PP control film and (C) PP/18 nm nAl and (D) PP/100 nm nAl nanocomposite films.

**Nonlinear Dielectric Properties of PP/nAl Nanocomposites.** Nonlinear dielectric property appears at elevated electric fields. Instead of measuring the nonlinear dielectric constants, $\varepsilon'_r$ discharged energy densities ($U_e$) and discharge efficiencies for the PP/nAl nanocomposites were studied by electric displacement - electric field hysteresis (D-E) loop measurement using a Radiant ferroelectric tester. Basically, the hysteresis loop represents the overall loss from both linear and nonlinear dielectric losses. A bipolar sinusoidal voltage waveform at 10 Hz was used as the input to test Ag-coated films at room temperature. Representative continuous D-E loops for the PP/100 nm nAl 18.3% and the PP/18 nm nAl 10.5% are shown in Figures 3.7A/B, respectively. All other bipolar D-E loop results for the rest nanocomposites are shown in Figure S3.7 in the Appendix B. The discharged $U_e$ and discharge efficiency results are shown in Figures 3.7C/D. For both nanocomposites, the $U_e$ data collapsed onto a master curve with an apparent dielectric constant of 3.4, almost regardless of different filler contents. Note that this result was different from the linear dielectric constant ($\varepsilon'_r$) results at low fields in Figure 3.3C, where the $\varepsilon'_r$ increased with the filler content. On the contrary, the charged $U_e$ of both nanocomposites increased with the filler content, as shown in Figure S3.8 in the Appendix B. Therefore, the master curve for the discharged $U_e$ in Figures 3.7A/B should be attributed to the dielectric nonlinearity at high electric fields, where electron injection from nAl NPs into the PP matrix played an important role.

Comparing the PP/18 nm nAl and the PP/100 nm nAl nanocomposites, the discharged $U_e$ results were similar, indicating that the discharged $U_e$ was not sensitive to
the size of the nAl NPs. Because of the higher high-fields dielectric constant of 3.4 for the PP/nAl nanocomposites, the discharged $U_e$ values improved moderately as compared to that of the neat PP film. For example, the discharged $U_e$ values for the PP/18 nm nAl nanocomposites were always about 1.5 times that of the neat PP film at the same poling field (Figure 3.7C). However, due to significantly decreased breakdown strengths, all the PP/nAl nanocomposites exhibited much lower discharged $U_e$ at breakdown than that (3.7 J/cm³ at 600 MV/m) of the neat PP film. In addition, the PP/nAl nanocomposites also exhibited much lower discharge efficiencies than the neat PP film, as seen in Figures 3.7C/D. Especially, the discharge efficiency decreased more dramatically with increasing the filler content or the poling field.

The above D-E loop results showed that the discharged $U_e$ for the nanocomposites was nearly independent of the filler content, whereas the discharge efficiency strongly depended on the filler content. In other words, the incorporation of nAl NPs in the PP matrix did not bring much benefit but lead to significant nonlinear dielectric loss. It would be interesting to find out the loss mechanism for the PP/nAl nanocomposites. As reported in our recent report, dielectric nonlinearity can originate from electronic conduction, ionic conduction, switching of dipolar groups near the glass transition temperature ($T_g$), and ferroelectricity from ferroelectric crystals. In the PP/nAl nanocomposites, there are no ferroelectric crystals nor dipolar groups. Meanwhile, the nAl NPs were thoroughly washed by solvents and there should be an extremely low level of impurity ions. The only possibility for the nonlinear dielectric behavior is electronic conduction, which could be divided into external and internal electronic conductions, as reported recently. In the
following, we discuss the major contribution to the nonlinear dielectric behavior in PP/nAl nanocomposites.

**Figure 3.8.** Four continuous unipolar D-E loops (10 Hz and room temperature) for (A) the PP/18 nm nAl 10.5% at 240 MV/m and the PP/100 nm nAl nanocomposites with (B) 10.8 vol.% and (C) 18.3 vol.% NPs at 150 and 70 MV/m, respectively. The start points for the 2nd, 3rd, and 4th loops are shifted to the origin. (D) Hysteresis losses for the above nanocomposite films obtained from the corresponding unipolar D-E loops.

To avoid interference of remanent polarization, five continuous bipolar loops were performed. Without any remanent polarization, the external electronic conduction could be obtained from the upshift in the upper part of the bipolar loop, as discussed in a recent report.\textsuperscript{154} From the bipolar loops in Figures 3.7A/B, the external electronic conduction was
negligibly small and had to be magnified 1,000 and 10 times for the PP/18 nm nAl(10.5%) and the PP/100 nm nAl(18.3%) nanocomposites, respectively, in order to be visible. In addition, continuous unipolar D-E loops were also conducted close to the breakdown electric fields for the PP/18 nm nAl 10.5%, and PP/100 nm nAl 10.8% and 18.3% nanocomposites (Figures 3.8A-C). If the electronic conduction was purely external (i.e., conduction from one electrode to the other electrode, which could be represented as a resistor in the equivalent circuit), each loop would have the same hysteresis loss. However, this was not the case, because the first loop had a much higher loss than the rest loops (Figure 3.8D). These bipolar and unipolar D-E loop results indicated that the external electronic conduction was not a major reason for the significant hysteresis loop loss, especially at high poling fields. Instead, the internal electronic conduction, which could be represented as a resistor and a capacitor in series in the equivalent circuit, should be the cause of high hysteresis losses in the bipolar and the first unipolar D-E loops.

Scheme 3.3. Proposed schematic of internal electronic conduction. (A) When the nAl NPs are far away from each other, electrons tunnel into the PP matrix. (B) When the nAl NPs are close, electrons tunnel from one NP into a neighboring NP. Under a bipolar poling, electrons can tunnel back and forth. Under a unipolar poling, electrons only tunnel into one direction.

For the PP/BaTiO₃ nanocomposites, the internal electronic conduction refers to the internal electronic current from interfacial charges inside each BaTiO₃ NP. Because of
relatively high resistivity of the BaTiO$_3$ NPs ($\sim 10^{10}$ Ω·m), the internal electronic conduction causes a significant nonlinear dielectric loss. This should not be the case for nAl NPs because Al is conductive with an extremely low resistivity. Here, we propose a possible mechanism for the internal electronic conduction, as shown in Scheme 3.3. When the nAl NPs are far away from each other, such as in the PP/100 nm nAl 10.8 vol.% and 18.3 vol.% nanocomposites (the interparticle distances, $a_{SC}$, are 64.4 and 39.0 nm, respectively; see Table 3.1), the tunneled electrons may not be able to reach neighboring nAl NPs (Scheme 3.3A). When the nAl NPs are close to each other, such as in the PP/18 nm nAl 10.5 vol.% nanocomposite ($a_{SC} = 26.0$ nm; see Table 3.1), the electrons can tunnel through the PP matrix and reach the neighboring NP (Scheme 3.3B). As the polarity of the poling electric field switches, electrons near the nAl NPs will be polarized back and forth in localized regions of the nanocomposites. As a result, significant internal conduction loss will be observed. During the unipolar poling, the electric polarity will be fixed. The first batch of tunneled electrons will make later electron tunneling more difficult, which is similar to the Coulomb blockade effect. Therefore, the hysteresis losses in the 2nd-4th unipolar loops become decreased. Upon continuous unipolar poling in Figure 3.8D, the decrease in hysteresis loop loss is significantly less for the PP/18 nm nAl(10.5%) nanocomposite than those for the PP/100 nm nAl nanocomposites with 10.8 and 18.3 vol.% NPs. This could be attributed to the closer interparticle distance (26.0 nm) in the PP/18 nm nAl 10.5% nanocomposite, where interparticle electron-tunneling is more significant than that in the PP/100 nm nAl 10.5% and 18.3% nanocomposites.

**Conclusions**
Compared to the PP/BaTiO$_3$ nanodielectrics, the PP/nAl nanodielectrics were originally thought to be more advantageous for electric energy storage, because the effective dielectric constant of nAl NPs can be considered as infinity due to the high conductivity. However, inferior dielectric properties were observed for the PP/nAl nanodielectrics, even though the nAl NPs were more or less uniformly dispersed in the PP matrix. Under low electric fields, moderate enhancement of $\varepsilon_r$ was observed for the PP/nAl nanocomposites due to the local field enhancement in the PP matrix from interfacial polarization. The linear dielectric constant was between the predictions by the Maxwell-Garnett and the Bruggeman models, and could fit with the Vo-Shi core-shell model with an insulating Al$_2$O$_3$ layer (2-5 nm) between the Al core and the PP matrix. Under high electric fields, hopping conduction with direct electron tunneling was observed for PP/nAl nanocomposites when the filler content was below 10 vol.%. For those with a high filler content (i.e., >18 vol.%), FN field electron emission was observed above a critical electric field, e.g., 40 MV/m for the 18.3 vol.% nanocomposite and 30 MV/m for the 25.0 vol.% nanocomposite, facilitated by the local field enhancement in the PP matrix. Consequently, substantially decreased $E_{bs}$ with a much narrower distribution were observed as the nAl filler content increased. Upon bipolar poling, the tunneled electrons from the nAl NPs into the PP matrix could be polarized back and forth, leading to high internal electronic conduction and thus nonlinear dielectric behavior. As a result, the hysteresis loop loss significantly increased with the poling field and the filler content, whereas the discharged energy densities remained almost the same for all nanocomposites with different filler contents.
In this sense, polymer/metallic NP composites may not be suitable for high-field insulation applications due to the field-induced electron emission. However, the electron-tunneling property can still be useful for other electrical applications. For example, when the nanocomposites have a high modulus, ultrathin films of polymer/metallic NP composites can be used for field-dependent electrical switches.\textsuperscript{133,201} When the polymer matrix is an elastomer, such as poly(dimethyl siloxane) (PDMS), deformation sensitive electrical conduction can be used for pseudo-piezoresistive sensors and wearable electronics.\textsuperscript{134,135,202} These elastomeric/metal nanocomposites are called quantum tunneling composites (QTCs). The working principal is to utilize spiky nickel NPs to enhance the field emission effect just below the electrical percolation. Upon a mechanical deformation, the resistivity of the nanocomposite can change from $10^{12} \ \Omega \cdot m$ of a non-deformed state to $\sim 1 \ \Omega \cdot m$ of a compressed state.
CHAPTER IV

Thermally stable metallic nanoparticles prepared via core-crosslinked block copolymer micellar nanoreactors
ABSTRACT

Thermally stable metallic nanoparticles (MNPs) are highly desirable for the melt-processing of polymer nanocomposites. However, due to the high surface energy penalty and decreased melting temperature, MNPs are easy to agglomerate and lose their unique properties if there is no protection or confinement layer. In this work, we report a facile and efficient way to synthesize thermally stable MNPs using core-crosslinked polystyrene-\(b\)-poly(4-vinyl pyridine) (PS-\(b\)-P4VP) reverse micelles as nanoreactors. From infrared results, gold, silver, and palladium ions exhibited distinctive coordination to the 4VP groups with varying chelation strengths. Compared to the non-crosslinked micelles, 1,4-dibromobutane (DBB)-crosslinking of the P4VP cores provided several advantages. First, it prevented severe swelling of the P4VP cores caused by the reducing agents and subsequent merger of swollen micelles. Second, the quaternized P4VP with hydrophilicity enhanced the uptake speed of precursor metal ions into the cores. Third, the crosslinked cores greatly stabilized the MNPs against the high temperature environment (e.g., 110 °C for 48 h in toluene). In addition, the solubility of the reducing agents also played an important role. Anhydrous hydrazine could swell the P4VP cores and concentric core-shell particle morphology was obtained. On the contrary, triethylsilane could not swell the P4VP cores and thus eccentric core-shell particle morphology was observed. Only the concentric core-shell MNPs exhibited good thermal stability, whereas the eccentric core-shell MNPs did not. This work suggested that these thermally stable MNPs could be good candidates for the melt-processing of functional polymer nanocomposites.
KEYWORDS: polystyrene-\(b\)-poly(4-vinyl pyridine), crosslinked micellar nanoreactor, thermal stability, metal nanoparticles
INTRODUCTION

Metallic nanoparticles (MNPs) represent a large and important family of nanomaterials, whose properties are distinct from bulk metals, and hence have drawn intense research interests and industrial significance in electrical, optical, magnetic, catalytic and biomedical applications. These intriguing properties are usually related to their large surface-to-volume ratio and the quantum size (or confinement) effect. For example, surface electrons with discrete energy states can oscillate freely under external photo-excitation and give rise to surface plasmon resonance (SPR), which has been widely used as the light-harvesting layer in organic photovoltaics and the sensing components in biosensors or bio-labeling. The catalytic efficacy of MNPs in organic reactions exclusively relies on the density of active surface dangling bonds or defects. The enrichment of surface/interface effects in MNPs sometimes could also be detrimental from a thermodynamic point of view, making them highly reactive. MNPs tend to form large aggregates to lower the surface energy during production, storage, and utilization. Once large clusters or aggregates of MNPs are formed, surface/interface characteristics and related catalytic, optical and electrical properties will be significantly compromised or even completely disappear. In addition, how to handle and process MNPs during manufacturing also relies on their stability. Thermoplastic processing of polymer nanocomposites and catalytic reactions in the presence of MNPs are usually accompanied with MNP degradation issues at elevated temperatures. Thus, it has been a persistent challenge to develop effective protocols to prevent the instability of MNPs.

Researchers have been using surface ligands to passivate MNPs and increase their stability for decades. A variety of surface ligands were employed such as long chain
thiols, amines, and carboxylic acids. The molecular head groups could strongly bind to the MNP surface and mitigate penalty from surface energy, while bulky alkyl tails endow steric repulsion to effectively reduce irreversible aggregation. It was demonstrated that monodentate surface ligands were able to keep MNPs stable at the ambient environment. When it comes to harsh conditions involving high temperature, shearing or long-time aging, monodentate ligands could possibly lose their efficacy in a form of degradation or desorption from the MNP surface. For example, the Au-S bond, which is widely used to construct thiol self-assembled monolayer, starts to break up above 60 °C. To enhance the binding between ligands and MNPs, researchers have proposed to utilize multidentate ligands based on the concept that the chance for all binded groups to detached from the MNP surface simultaneously would be much less than that with only one bind group. Enhanced colloidal stability for Au NPs against high temperature, high salt concentration, wide pH variation, and competing thiols, was reported using different biopolymers bearing multiple thiol groups. Other than polythiols, polymers appended with multidentate amine or hydroxyl anchoring groups were also used to build up multiple binding sites to the MNP surface. However, particle agglomeration might happen if one multidentate ligand at the same time binds to two or more MNPs or in the presence of precursor metal ions. Alternatively, forming a protective layer around each MNP without interfering their original, unique properties are believed to be a better idea. In 2008, Matyjaszewski and co-workers demonstrated a one-pot synthesis of thermally stable core/shell Au NPs via surface-initiated atom transfer radical polymerization (ATRP) of n-butyl acrylate and an acrylate crosslinker. Unlike this in-situ polymerization induced crosslinking, post-crosslinking was also adopted to form a
crosslinked layer wrapping the MNP. Disulfide monomers were used as ligands to make Au NPs, followed by crosslinking via either ring-opening metathesis polymerization or Michael addition of polyfunctional amines. Meanwhile, a number of thiol-terminated polymers equipped with crosslinkable fragments/blocks were designed and used for MNP stabilization, such as random copolymers and block copolymers (BCPs) containing poly(furfuryl glycidyl ether), azido-polystyrene, poly(allyl glycidyl ether), poly(4-chloromethylstyrene), and poly(1,2 and 3,4-isoprene). The presence of a small amount of unbound free polymers sometimes could result in unwanted interparticle crosslinking or gelation during final crosslinking step, despite a strict, repetitious purification was usually conducted. Similar as the organic shielding, inorganic shielding was also proposed and implemented, such as formation of a silica shell via the sol-gel process.

BCP micelles with metal ion-chelating groups have been explored as nanoreactors to make inorganic NPs since the late 1990s. Polystyrene-b-poly(2(or 4)-vinyl pyridine) (PS-b-P2(or 4)VP), polystyrene-b-poly(acrylic acid) (PS-b-PAA), and polystyrene-b-poly(ethylene oxide) (PS-b-PEO) are three common micelle-forming block copolymers in related research. By carefully choosing the length of each block, the type of metal ions and the way of reduction, MNPs with controllable size and morphology were readily synthesized inside the micellar core. Depositing metal ion-loaded micelle solutions onto a substrate followed by plasma, laser or radiation treatment was broadly used for generating highly ordered MNP arrays (nanopatterning). Besides, wet chemistry was used to obtain MNPs as high-performance catalysts for organic reactions, or functional nano-luminaphores. In 2014, Lennox and co-worker first reported BCP-
capped Au and Cu NPs with high thermal stability.\textsuperscript{250} In their method, PS-$b$-P4VP BCPs were used more as a capping agent rather than the micellar reactor.

In this work, combining the nanoreactor approach and core-crosslinking, robust and thermally stable MNPs (Au and Pd) were successfully prepared from PS-$b$-P4VP block copolymer micelles (Scheme 4.1). In brief, 1,4-dibromobutane (DBB) was used to crosslink the P4VP cores in toluene. Due to the enhanced polarity of the quaternized P4VP cores, the metal ion uptake was much faster than that for non-crosslinked micelles. Depending on the solubility of the reducing agent in the P4VP core, either concentric (i.e., one MNP in the center of the core, reduced by anhydrous hydrazine) or eccentric (i.e., one MNP at the boundary between the P4VP core and the PS corona, reduced by triethylsilane) NP morphology was observed. Compared to the in-situ reduction method in the presence of thiol-terminated diblock copolymers,\textsuperscript{238,239} this method had a higher efficacy because the tedious purification step of unbound diblock copolymer ligands could be avoided.

Scheme 4.1. Schematic of preparing gold hairy NPs via PS-$b$-P4VP block copolymer micellar nanoreactors with either crosslinked or non-crosslinked P4VP cores.

**Experimental Section**

132
**Materials.** Styrene (St) and 4-vinylpyridine (4VP) were purchased from Aldrich. St was washed with NaOH aqueous solution to remove the inhibitor, and was distilled under reduced pressure. 4VP was purified by passing through a column filled with basic alumina, followed by distillation under reduced pressure. Both monomers were stored in a freezer at -25 °C before use. Chain transfer agents (CTAs) were used for reversible addition-fragmentation chain-transfer (RAFT) polymerization. S,S-dibenzyl trithiocarbonate was kindly donated by Arkema, and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid was purchased from Aldrich. 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Aldrich and recrystallized twice before use. Metal precursors, chloroaurious acid (HAuCl₄), palladium (II) acetate [Pd(OAc)₂], and silver nitrate (AgNO₃), were purchased from Strem Chemicals, Inc. Reductants such as anhydrous hydrazine, hydrazine monohydrate, and triethylsilane were purchased from Aldrich and used as received.

**Characterization methods and instruments.** Proton nuclear magnetic resonance (¹H NMR) spectra were collected on a Varian Mercury 600 MHz spectrometer with CDCl₃ as the solvent and TMS as the internal reference. Fourier transform infrared (FTIR) spectra were recorded using a Bomen Michelson MB100 FTIR spectrometer at a resolution of 2 cm⁻¹. Solutions of pure block copolymers and block copolymer/metal precursor mixtures in toluene (5 mg/mL) were drop-cast onto a KBr crystal and dried in oven. The number-average molecular weight (Mₙ) and polydispersity (PDI) were measured on a size-exclusion chromatography (SEC) using a Water 515 HPLC pump and a Waters 2414 differential refractive index (RI) detector. For PS samples, THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. For PS-b-P4VP block copolymers, DMF with 0.05 M
lithium bromide was used as the eluent to minimize polymer/column filler interaction. Linear PS standards were employed for conventional calibration. UV-Vis spectra for samples in toluene was recorded using a PerkinElmer Lambda 1050 UV-Vis-NIR spectrometer. Imaging block copolymer micelles and metallic nanoparticles was performed using an FEI Technai 12 transmission electron microscope (TEM) at an accelerating voltage of 80 kV. Samples in toluene (~0.05-0.1 mg/mL) were drop-cast onto carbon-coated copper grids and dried for 24 h to evaporate the solvent. Dynamic light scattering (DLS) was measured using a Brookhaven Instrument BI-9000 AT multichannel digital correlator. The scattering angle was set to 90°, and samples were measured in toluene with an appropriate concentration. The scattering signal was analyzed by the CONTIN algorithm to extract the diffusion coefficient information from the correlation function data, and then convert the diffusion coefficient to the hydrodynamic radius using the Stokes-Einstein equation.

**RAFT polymerization of PS-b-P4VP block copolymers.** Styrene was polymerized in bulk to prepare PS-CTA macro-initiator first. Into a Schlenk flask with a magnetic stirrer, St, AIBN, and CTA were added all at once with pre-determined ratios. The whole system was degassed by performing three freeze-pump-thaw cycles and finally the flask was refilled with dry nitrogen. Afterwards, it was immersed into a silicone oil bath at 110 °C. After 18 h, the polymerization was quenched in liquid nitrogen. The PS-CTA macro-initiator was recovered by precipitation twice in methanol to remove unreacted monomer. Finally, the sample was dried at 60 °C in a vacuum oven for 2 d until constant weight.
The obtained PS-CTA macro-initiator ($M_n = 28.5$ kDa, $PDI=1.16$, 1.00 g, 0.0351 mmol CTA), 4-vinylpyridine (1.5 mL, 13.9 mmol), AIBN (2.3 mg, 0.014 mmol), and 6.5 mL THF were put into a Schlenk flask. After degassing through three freeze-pump-thaw cycles, the flask was transferred into a silicone oil bath at 90 °C. The polymerization process was monitored by SEC until a desire molecular weight was reached. The products were purified by precipitation twice in methanol and dried in a vacuum oven at 60 °C for 3 d. $^1$H NMR (600 MHz, CDCl$_3$) δ: 1.41 (broad, -C$_2$H$_2$CH-), 1.85 (broad, -CH$_2$CH-), 6.27-6.56, (broad, 2,6-StH), 7.03-7.25 (m, 3,4,5-StH and 2,6-4PyH), 8.32 (broad, 3,5-4PyH).

**Formation of reverse micelles in toluene and crosslinking of the P4VP core.** 50 mg PS-\textit{b}-P4VP block copolymer sample was dissolved in 10 mL of anhydrous toluene. The solution was heated at 90 °C overnight and cool down to room temperature to form non-crosslinked reverse micelles in toluene. To crosslink the P4VP core, a predetermined amount of 1,4-dibromobutane (DBB) was added together with the block copolymers before heating to 90 °C, followed by the same procedure as mentioned above.

**Loading of metal precursors in reverse micelles and subsequent reduction.** 0.5 eq. of metal precursors [HAuCl$_4$, Pd(OAc)$_2$, and AgNO$_3$] per 4VP units were directly added into 50 mL non-crosslinked or crosslinked reverse micelle solution. Solid metal salts, which were otherwise insoluble in toluene, were taken up into the P4VP cores within a few hours under mild stirring. The loading process was kept for 24 h to ensure a complete uptake of all salts. For reduction by triethylsilane, a small amount of ethanol was also added after the complete dissolution of the solid metal precursor salts. Then, 2.5 mL of metal-loaded micelle solution was poured into a small vial containing 10 eq. reductants in 0.5 mL of toluene. The color changed from orange red of HAuCl$_4$ to purple immediately.
after mixing with hydrazine, and became bordeaux red in a few minutes. Note that stirring during reduction is not necessary since it might destabilize micelles and facilitate their coalescence. Finally, hydrochloric acid (HCl) gas was bubbled into the micelle solution containing reduced MNPs to scavenge excessive hydrazine.

**Thermal stability at elevated temperatures.** Freshly synthesized PS-capped Au NPs [Au@PS-SH] and hydrazine-reduced crosslinked Au NPs [Au@XP4VP-PS] in toluene were diluted to 2.5 mg/mL. The vials were well capped and immersed into an oil bath at 110°C. The solutions were occasionally checked to see whether any color change or any insoluble precipitate was visible. UV-Vis spectroscopy was used to monitor the change in the plasmon absorption peak at high temperatures.

**RESULTS**

**Formation of reverse micelles and loading of metal precursors.** It is well-known that BCPs with immiscible blocks can self-assemble into either nano-sized micelles in a selective solvent or microdomain structures in the bulk state. Toluene is a good solvent for PS, but a poor solvent for P4VP. Thus, PS-b-P4VP could form reverse micelles in toluene with hydrophilic P4VP blocks inside as the core and hydrophobic PS blocks outside stabilizing the micelle. The lone pair electrons on the pyridine groups make the PS-b-P4VP micelles capable of forming coordination bonds with inorganic salts or hydrogen-bonding with polar small molecules. Therefore, PS-b-P4VP micelles have been employed as nano-sized containers for inorganic nanocrystal synthesis or encapsulation of dye molecules for coloration and electrochromic display. The micellar container provides a nanoscale, spatially restricted environment for nanocrystal growth or cargo.
molecule loading. It is interesting to first study the size of the P4VP core, a storage space for cargo. According to the light scattering results, Forster S. and co-workers found that the aggregation number (Z) of PS-\(b\)-P4VP micelles, namely, how many polymer chains form one individual micelle, exhibited a scaling relationship to the length of each substituent blocks \(N_{PS}\) and \(N_{P4VP}\): \(Z \sim N_{P4VP}^2 N_{PS}^{-0.8}\).\textsuperscript{252,253} The core radius (\(R_c\)) could be calculated from \(Z\) via the space filling condition:

\[
\frac{4}{3} \pi R_c^3 = Z N_{P4VP} v_0,
\]

where \(v_0\) was the molecular volume of each 4VP repeating units. Thus, the core diameter (\(d_c = 2R_c\)) was proportional to \(N_{P4VP}^{-8/3} N_{PS}^{-1/3}\). Three PS-\(b\)-P4VP diblock copolymers (samples A, B and E) and two triblock copolymers (samples C and D) were prepared via the RAFT polymerization. The \(N_{PS}, N_{P4VP},\) and PDI can be found in Table 4.1. Based on the scaling relationship, \(d_c\)'s of these micelles should follow the order of \(d_{c,C} < d_{c,E} < d_{c,D} < d_{c,A} < d_{c,B}\) at a ratio of 1: 1.55: 1.65: 1.78: 3.68. The actual micelle sizes were determined by transmission electron microscopy (TEM). In Figure 4.1, the micelle contour of samples D and E was not as sharp as that of the other samples, since they had lower P4VP compositions and hence lower \(Z\) values. Without staining, spherical P4VP cores showed enough contrast from the PS corona and was visualized under TEM. Note that these physical micelles without crosslinking were fragile in expose to the electron beam. Low dose was used to avoid fragmentation of them during imaging. The mean core size was in a range between 18 and 35.2 nm, and the histograms were given as insets in Figure 4.1. The core size showed an increasing order of \(d_{c,C} < d_{c,D} < d_{c,A} < d_{c,B}\) at a ratio of 1: 1.35: 1.41: 1.46: 2.0, which was semi-quantitatively consistent with the above theoretical prediction. The relatively large discrepancy between theoretical predication and experimental result of sample B could be attributed to the fact that when \(N_{P4VP} \geq N_{PS}\), the
$N_{P4VP}$ exponent of the scaling relationship, $Z \sim N_{P4VP}^2 N_{PS}^{-0.8}$, dropped to an intermediate number between 2 and 1.\textsuperscript{254} It was also interesting to see that sample B, unlike the other samples, formed anisometric cluster or aggregates. This agreed with what Calderara F. et al. discovered for PS-$b$-P4VP via light scattering that a transition from spherical micelles to non-spherical ones, such as coagulations or short cylinders, was identified when $f_{P4VP}$ is in the range of 60-70\%.\textsuperscript{254}

### Table 4.1. Block Composition and Polydispersity of Five PS-$b$-P4VP BCPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{P4VP}$ (by NMR)</th>
<th>$N_{PS}$ (by GPC)</th>
<th>$f_{P4VP}$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>104</td>
<td>132</td>
<td>0.44</td>
<td>1.27</td>
</tr>
<tr>
<td>B</td>
<td>215</td>
<td>132</td>
<td>0.62</td>
<td>1.35</td>
</tr>
<tr>
<td>C</td>
<td>66</td>
<td>74</td>
<td>0.47</td>
<td>1.51</td>
</tr>
<tr>
<td>D</td>
<td>154</td>
<td>270</td>
<td>0.36</td>
<td>1.31</td>
</tr>
<tr>
<td>E</td>
<td>123</td>
<td>418</td>
<td>0.23</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Mixed micelles with a single size population were obtained by physically mixing two different BCP micelles (samples A and E) at a molar ratio of 3:2. The TEM image of the mixed micelles is seen in Figure 4.1F, showing uniform P4VP core morphology. The hydrodynamic radius ($R_H = 33$ nm) of the mixed micelles determined by DLS was found between the $R_H$ of samples E ($R_H = 38$ nm) and A ($R_H = 28$ nm) with a relatively same polydispersity. Similar to previous studies,\textsuperscript{254,255} formation of mixed micelles could be useful to construct multi-disperse (different brush length) or multifunctional (different functional groups) micelles.
Figure 4.1. TEM micrographs of PS-6-P4VP micelles cast from toluene: (A) PS\textsubscript{132-P4VP\textsubscript{104}}, (B) PS\textsubscript{132-P4VP\textsubscript{215}}, (C) PS\textsubscript{37-P4VP\textsubscript{66}-PS\textsubscript{37}}, (D) PS\textsubscript{135-P4VP\textsubscript{154}-PS\textsubscript{135}}, (E) PS\textsubscript{418-P4VP\textsubscript{123}}, (G) R\textsubscript{HS} distribution of the micelles formed by sample A, E, and their mixture in toluene.

It took a few hours for BCP micelles to take up all the solid metal precursors, which were originally insoluble in toluene. Micelle solutions after the complete loading of metal precursors turned to colorful because of the solvated metal ions (Figure 4.2B). FTIR was used to study the crosslinking reaction and the loading of metal ions (Figure 4.2A). An intense peak at about 1597 cm\textsuperscript{-1} is the overlapped stretching vibrations of C=N bonds from 4VP and C=C bonds from St. After pyridine reacted with the DBB crosslinker, a new IR peak appeared at 1639 cm\textsuperscript{-1}, which was assigned to the C=N\textsuperscript{+} stretching of the quaternized pyridines. The degree of quaternization could not be accurately determined by simply using the relative intensities of two peaks at 1597 and 1639 cm\textsuperscript{-1} due to the presence of C=C bonds in St. Nor could \textsuperscript{1}H NMR determine the degree of quaternization because of the suppressed chain mobility in the cores, no matter the micelles were crosslinked, not crosslinked, or loaded with metal ions. The loading of different metal (Au, Ag and Pd) precursors revealed distinctive interactions between metal ions and 4VP. For HAuCl\textsubscript{4}, one of the two emerged IR peaks at 1636 cm\textsuperscript{-1} indicated the existence of pyridinium ions after
precursor loading. It suggested that 4VP units were protonated by HAuCl₄, and then formed ionic complexes. The AuCl₄⁻ ions acted as counter ions in the close proximity.²⁵⁶ The other new peak at 1616 cm⁻¹ was usually attributed to the formation of metal-ligand π-bonding between the pyridine and the metal ion.²⁵⁷ Its IR peak usually blue shifted by 15-20 wavenumbers compared to that of non-coordinated pyridines. We also observed an IR peak at the same position for Pd(OAc)₂-loaded micelles, with weak signal of protonation. The interaction between pyridines and Ag ions only broadened the C=N and C=C stretching peaks and shifted it from 1597 cm⁻¹ to 1608 cm⁻¹. The appearance of new IR peaks and their blue shift compared to that of C=N bonds was considered as a probe to detect the association strength between metal ions and pyridines. Our observation corroborated what Lin and co-workers discovered for PS-ₜₜ-P4VP/metal ions hybrids,²⁵⁸ which suggested that Au and Pd ions are able to form much stronger association with pyridine than Ag⁺. After quaternizing pyridines with an equal molar DBB, crosslinked micelles supposedly would no longer have any free pyridines to form protonation/coordination with metal ions. Interestingly, the uptake of metal ions proceeded even faster than those for non-crosslinked micelles. Clearly, the relative IR intensity ratio of the peak belonging to pyridinium at 1639 cm⁻¹ and the peak belonging to pyridine and styrene at 1597 cm⁻¹ (I₁₆₃₉/I₁₅₉₇) became almost twice as large as that before loading of HAuCl₄. This implied that insoluble AuCl₄⁻ ions could be quickly captured into the cores, replacing Br⁻ ions and serving as new counter ions. The highly polar and hydrophilic environment due to quaternization might account for this fast ion capture process. Zhang and Zhao observed similar effects using reverse surfactant micelles that had crosslinked triallylammonium head groups to efficiently extract AuCl₄⁻ from water to chloroform and
work as templates for the MNP growth. In reality, the DBB quaternization could not be 100%, leaving a certain amount of free 4Py units for chelation with metal ions.

**Figure 4.2.** (A) FTIR spectra for non-crosslinked, crosslinked micelles, and micelles loaded with Au, Pd, or Ag precursor ions. (B) Color of micelle solutions due to solvation of metal ions in the P4VP cores. (C) Proposed interaction/chelation modes between pyridine units and different metal ions.

The morphology of metal ion-loaded micelles were examined by TEM, as shown in Figure 4.3. The HAuCl4 loaded micelles exhibited a “raspberry” morphology with many black dots uniformly distributed inside the P4VP cores (Figure 4.3A). The black dots were fine Au NPs reduced by the electron beam radiation. The loading of metal ions seemed to make P4VP core more condensed, and hence a clear P4VP core contour with better contrast was seen. A notable core shrinkage from the diameter of 26.1 nm of non-crosslinked micelles to 18.3 nm after loading of metal ions was observed. Surprisingly, this core shrinkage was even more pronounced than that caused by DBB crosslinking, which only made the cores to slightly shrink from 26.1 nm to 24.4 nm (Figure 4.3D). No sign of inter-
micellar crosslinking was found because of the spatial repulsion from outer PS brushes. Reducing the molar ratio of HAuCl₄ to 4VP to 0.25:1 or lower just resulted in fewer AuCl₄⁻ ions inside the P4VP core without any empty micelles. The micelles loaded with AgNO₃ encapsulated fewer but larger Ag dots inside P4VP, probably due to a lower redox potential to reduce Ag⁺ than Au ions under radiation.²⁶⁰

Figure 4.3. TEM micrographs of PS₁₃₅-P4VP₁₅₄-PS₁₃₅ micelles loaded with (A) HAuCl₄ (4VP: Au = 2:1), (B) Pd(OAc)₂ (4VP: Pd = 2:1), (C) AgNO₃ (4VP: Ag = 2:1), (D) crosslinked PS₁₃₅-P4VP₁₅₄-PS₁₃₅ micelles (4VP: DBB = 2:1), (E) crosslinked PS₁₃₅-P4VP₁₅₄-PS₁₃₅ micelles loaded with HAuCl₄ (4VP: DBB = 1:1, 4VP: Au = 2:1), and (F) crosslinked PS₁₃₅-P4VP₁₅₄-PS₁₃₅ micelles loaded with HAuCl₄ (4VP: DBB = 1:1, 4VP: Au = 4:1).

Preparation of non-crosslinked and crosslinked MNPs. A variety of reductants can be used to reduce metal ions in the P4VP cores into MNPs. The strength of reductant could, to a large extent, affect the particle size and morphology. Strong reductants such as sodium borohydride (NaBH₄) usually lead to fast reduction, multiple nucleation sites, and
many fine particles per micelle (data not shown). Such reductants are good choices to make ultrafine MNPs with the “raspberry” morphology, which could be used as efficient noble metal catalysts. Nonetheless, it is not suitable for producing MNPs with the “cherry” morphology, i.e., one MNP per micelle. Hydrazine, as a milder reductant, is polar and hence can easily go inside the protonated P4VP core. In Figure 4.4A, Au NPs with an average size of 5.8 nm were obtained using anhydrous hydrazine. Supposedly, metal ions inside each micelle would be reduced into one MNP, presenting a well-defined, core-shell structure. After reduction by anhydrous hydrazine, individual MNPs were largely separated; however, the micelle morphology became diffuse with significant merger. Spatz et al. attributed this to both the swelling by anhydrous hydrazine and coalescence of micelles during reduction, because hydrazine could possibly destabilize P4VP(H+)−b-PS/AuCl4− micelles by de-protonation. When micelles merged, several MNPs would aggregate together. Upon extended waiting, no further changes in micelle morphology was observed compared to that in Figure 4.4A, suggesting that the micelle integrity was not compromised, although they were swollen (Figure S4.1A in the Appendix C). To scavenge excessive hydrazine and re-protonate P4VP, gaseous HCl was purged to react with unreacted hydrazine, similar to what Spatz suggested in their report. Hydrazinium chloride crystals were seen to precipitate from the toluene solution. The removal of hydrazine, to some extent, helped to prevent further swelling or disintegration of the P4VP cores (Figure 4.4B); however, it was not possible to restore the originally tight micelle morphology. We suspected that the tight ionic clusters were changed by swelling of hydrazine.
The addition of HAuCl₄ loaded micelles into the hydrazine/toluene solution is important, because the loaded metal ions were exposed to a large excess of reductant and thus could be quickly reduced all at once. Otherwise, partial reduction would happen if hydrazine was dropwise added to the micelle solution. Once the metal ions in some micelles got reduced and became nuclei, they would absorb additional metal ions from neighboring micelles, leaving them empty without any MNPs (see Figure S4.1B in the Appendix C). Compared to anhydrous hydrazine, hydrazine monohydrate also led to large MNPs with empty micelles. It was possible that water compete with hydrazine to swell the P4VP cores, decreasing the reduction speed and increasing the diffusion of metal ions. As a result, large MNPs were obtained with empty micelles (see Figure 4.1C in the Appendix C). Additionally, three BCPs with different PS and P4VP lengths were used as micellar reactors, as presented in Figure 4.4 B-D. It was first expected that Au NPs with various sizes could be obtained by tuning the size of the P4VP cores and the number of complexation/coordination sites. However, this effect was not significant enough, because the reduced Au NPs were all between 6 and 7 nm.

Figure 4.4. TEM micrographs of reduced Au NPs inside the non-crosslinked PS₁₃₅-P4VP₁₅₄-PS₁₃₅ micelles (A) without and (B) with HCl (g) scavenger. (C and D) show reduced Au NPs inside the non-crosslinked (C) PS₃₇-P4VP₆₆-PS₃₇ and (D) PS₄₁₈-P4VP₁₂₃ micelles with HCl (g) scavenger.
In order to prevent swelling of the micelle cores, covalently crosslinking the P4VP cores with DBB was performed. After quaternization, the P4VP core became ionic and hydrophilic, which was beneficial for uptake of the metal precursors in toluene. The instability caused by deprotonation of P4VP would no longer be problematic once the core was crosslinked. After reducing the Au ions, the excessive hydrazine could be scavenged by HBr, a byproduct from the complexation of quaternized P4VP and HAuCl₄. In Figure 4.5A, most reduced Au NPs stayed inside the crosslinked micelles despite not exactly located in the center. Different from the non-crosslinked micelles, the contour of P4VP cores was much sharper, though the shape of the P4VP cores became somewhat deformed. The crosslinking of the P4VP cores was much helpful to prevent swelling and coalescence of micelles. The crosslinked micellar reactors also worked well for producing Pd NPs (Figure 4.5C), which had even better core-shell morphology than that of Au NPs. For the Pd²⁺ ions, a stronger bonding with quaternized P4VP could confine the growth of NPs inside the micellar core. Unlike Au and Pd ions, Ag⁺ ions were weakly binded to the quaternized P4VP, as evidenced by FTIR (Figure 4.2A). Weakly bonded Ag⁺ ions could easily interdiffuse among neighboring micelles. As soon as anhydrous hydrazine reduced some Ag NPs, the existing Ag NPs would absorb additional Ag⁺ from neighboring micelles, leaving them empty. This was exactly seen in the TEM image in Figure 4.5B. The Ag NPs were relatively large and most micelles were empty.
Figure 4.5. TEM micrograph of anhydrous hydrazine-reduced (A) Au NPs, (B) Ag NPs, and (C) Pd NPs inside the crosslinked PS_{135}-P4VP_{154}-PS_{135} micelles.

Switching anhydrous hydrazine to another mild reductant, triethylsilane, resulted in different MNPs and micelle morphology. We first used triethylsilane to reduce Au ions loaded in non-crosslinked micelles. The TEM micrograph is shown in Figure 4.6A. Even though nonpolar triethylsilane was unlikely to swell the P4VP cores, micelles after reduction still looked like merging together, which was similar to what happened using anhydrous hydrazine for reduction. We speculate that the oxidized product of triethylsilane might be polar and was able to swell the P4VP cores. The core crosslinked micelles could keep their morphology after reduction with triethylsilane, as seen in Figure 4.6B. It was interesting to see that several Au NPs were formed either on the perimeter of individual cores or in the interstitial areas among connected micelles. Judging from this morphology, the Au NPs must be formed at the boundary between the P4VP core and the PS corona, and no particles were inside the cores. Since triethylsilane was compatible with PS but not P4VP, supposedly it could only reach the PS/P4VP boundary to reduce the metal ions. Most times several Au NPs were formed at the P4VP/PS boundary, and sometimes only one Au NP was seen for one micelle. Formation of multiple Au NPs per micelle could be
attributed to the slow diffusion of AlCl$_4^-$ ions in the crosslinked P4VP. After adding a small amount of ethanol (3 vol.%), the ion diffusion could be enhanced because of the ethanol-swelling of the P4VP cores. As shown in Figure 4.6C, most micelles only contained one NP at the PS/P4VP boundary. When increasing the ethanol content to 5 vol.%, the reduction became a similar situation as that for Ag$^+$ ions reduced by hydrazine (Figure 4.5B). Too much ethanol made the ion diffusion too fast to interdiffuse among neighboring micelles. As a result, a large number of micelles became empty after reduction and the final Au NPs could grow fairly large (Figure 4.6D).

Figure 4.6. TEM micrographs of (A) Au NPs reduced by triethylsilane in non-crosslinked micelles, (B) Au NPs reduced by triethylsilane in crosslinked micelles, and Au NPs reduced by triethylsilane with (C) 3% ethanol and (D) 5% ethanol inside crosslinked micelles. The BCP used is PS$_{132}$-P4VP$_{104}$.

Thermal Stability. One of the most important applications for MNPs is to act as active components in polymer nanocomposites. Inclusion of MNPs can provide polymers with a variety of functionalities to meet specific performance requirements for real applications. For example, highly conductive Ag, Al, or Cu NPs could be introduced into commercial polymers such as polyimide and poly(vinylene fluoride) (PVDF) to improve their electrical conductance, which needs NPs to be able to tolerate the internal joule heat generated by the current passing through without causing heat-induced agglomeration or degradation.$^{262}$ The mixing and compounding during nanocomposite manufacturing also
require MNPs to be thermally stable under a short time (less than hours), high temperature (160-230 °C), and high shear conditions. To promote the utilization of MNPs in the field of functional nanocomposites, we carried out thermal stability study of the synthesized MNPs. As discussed in the introduction, improvement in MNP’s thermal stability is of great importance to broaden the processing window and retain their distinct properties, no matter they are used alone (e.g., catalysts) or as an active component (e.g., in nanocomposites).

The thermal stability tests were performed for crosslinked Au NPs (reduced by hydrazine or triethylsilane) at 110 °C. One convenience for this micellar reactor approach is that no post-purification is needed, and the NP dispersion at the desirable concentration could be directly solution-mixed with commercial polymers. The thiolated PS-capped Au NPs (Au@PS-SH) were used as the control for comparison. As expected, the Au -S bond was not able to survive heating above 60 °C (Figure 4.7D). For crosslinked Au NPs reduced by triethylsilane (i.e., formed at the P4VP/PS boundary), large irreversible agglomerates were soon observed at the bottom of the vial. The color of the dispersion turned from bordeaux red to dark purple, and finally to nearly no color within a few hours. On the contrary, crosslinked Au NPs reduced by hydrazine remained the bordeaux red color throughout the entire test, confirming that the Au NPs resided inside the crosslinked P4VP cores and were very stable. The NP morphology before and after being heated at 110 °C for 18 and 40 h were examined with TEM. There were no notable differences in particle size and size distribution (see Figure 4.7A-C). The number of empty micelles slightly increased (Figure 4.7C), which might be associated to the oxidation or dissolution of Au NPs upon extended heating in air. The UV-Vis spectra are shown in Figure 4.7D.
The surface plasmon absorption of Au NPs initially found at 532 nm slightly redshifted by 8 nm to 540 nm after heating for 18 h, and remained unchanged afterwards. The peak intensity stayed almost the same with the peak width becoming slightly narrower. The redshift and peak width narrowing might be associated with particle ripening during heating in the first few hours.213

The self-assembled, crosslinked BCP micellar reactors provided a facile, autonomous protocol for synthesizing MNPs with excellent thermal stability. These MNPs were considered to be compatible with traditional polymer processing techniques such as melt extrusion. Meanwhile, the PS corona outside crosslinked cores could help the dispersion of MNPs in styrenic polymer matrices. Recently, researchers reported that bimodal brush-grafted hairy silica NPs was able to exhibit better dispersion than unimodal brush-grafted particles in a polymer matrix owing to favorable wetting of the long brushes and less entropy penalty.107 As we demonstrated before, mixed BCP micelles could be easily prepared at different compositions and have bimodal PS brushes. Following the same crosslinking, loading, and reduction procedure, stable MNPs inside crosslinked mixed BCP micelles can be obtained, which will show better dispersibility in polymer nanocomposites. Currently, experiments are being carried out to prepare these MNPs, and their dispersion in styrenic polymer nanocomposites will be reported in the future.
Figure 4.7. TEM micrographs of crosslinked Au NPs (A) before heating, and after heating in toluene at 110 °C for (B) 18 h and (C) 40 h. Insets show the MNP size histograms. (D) UV-Vis spectra of crosslinked Au NPs being heated at 110 °C for 0, 18 and 40 h, respectively. The UV-Vis spectrum of Au@PS NPs is also shown for comparison.

CONCLUSIONS

In summary, PS-\textit{b}-P4VP BCPs with different block lengths were synthesized via RAFT controlled radical polymerization, and later were employed as nanoreactors to prepare thermally stable MNPs. Without crosslinking of the P4VP cores, the micelles could be swollen by excessive anhydrous hydrazine and became easy to merge together, making them unstable when heated at high temperatures. By quaternization with DBB, the P4VP cores were crosslinked before loading precursor metal ions. The crosslinking and metal ion uptake were studied by FTIR, which revealed that both coordination and ionic interactions stabilized the metal ions in P4VP cores. As a result, the uptake of solid metal salts by the crosslinked micelles was speeded up. Both anhydrous hydrazine and triethylsilane were used as reducing agents to prepare MNPs. Because anhydrous hydrazine could swell the crosslinked P4VP cores, the MNPs were nucleated inside the core, forming the concentric core-shell morphology. On the contrary, triethylsilane could not diffuse into the P4VP cores, and the MNPs were nucleated at the P4VP/PS boundary, forming the eccentric core-shell morphology. Upon heating at 110 °C, the eccentric MNPs were not stable and tended to precipitate from the toluene solution. However, the concentric MNPs were stable in toluene up to 48 h at 110 °C. From this study, thermally stable MNPs are promising for future melt-processing of thermoplastic polymer nanocomposites.
CHAPTER V

Conclusions and Future Work
In summary, the first two chapters in this dissertation included a thorough dielectric loss/conduction and nonlinearity studies on two common nanodielectric systems, namely, semiconductor ceramics/polymer and conductive filler/polymer composites. In chapter 2, the interfacial polarization due to large permittivity and conductivity contrasts between high κ BaTiO₃ and iPP was found to be the main reason to result in significantly decreased E_b as well as substantial dielectric losses in D-E loop measurement. The three-dimensional molecular dynamic simulation showed that local field around two poles of NPs along the field direction was greatly enhanced. The overlapped, field-enhanced local area between aggregated/chained NPs could form “hot spots” and/or extended conduction pathways to trigger early, severe breakdown, which was supported by Weibull breakdown analysis. Meanwhile, a large bipolar loop loss was identified by a combination of unipolar and bipolar D-E loop measurements, suggesting loss came from the movement of generated interfacial charges under high AC field. To further determine whether the internal conduction pathway is through BaTiO₃ surface or bulk, TiO₂ layer was atomically deposited on BaTiO₃ surface to block surface conduction. The internal AC loss indeed became much smaller, and nanodielectric capacitor showed higher discharged efficiency. Considering this interfacial polarization induced E_b decrement and internal AC conduction it was concluded that nanocomposites composed of high κ nanofillers and polymers should be only used for DC energy storage under low to moderate field.

In chapter 3, self-passivated nAl NPs was chosen as nanofillers in iPP to avoid direct electrical contact between fillers. Moreover, conductive fillers were expected to show less internal AC conduction and higher apparent ε_r. In fact, the ε_r of these nAl/iPP nanocomposites did not increase as much as we expected. Meanwhile, the E_b decreased
even more abruptly than that of BaTiO3/iPP composites. Several dielectric mixing models were used to predict $\varepsilon_r$ and compare with experimental data, convincing that normally observed colossal $\varepsilon_r$s for conductive filler/polymer composites were presumably attributed to charge injection. The field inside NPs was nearly zero, but highly unbalanced local field was detected at filler/polymer interface, giving rise to charge injection even at low field. The presence of an insulating Al2O3 layer, to some extent, limited charge injection. Three conduction regimes, including ohmic, hopping and field-emission conduction were differentiated by leakage current study as gradually increasing field until breakdown occurred. Field emission conduction can be easily triggered at much lower field in nAl/iPP composites, which was believed the major reason explaining the breakdown observation. Depending on the interparticle distance and the field strength, electrons from nAl NPs can be back and forth polarized into either iPP matrix or neighboring nAl NPs, resulting in significant dielectric nonlinearity. In other words, conductive filler/polymer composites was not good for any energy storage applications, but might be useful as electrical switches.

In chapter 4, a facile yet efficient method based on crosslinked block copolymer micellar reactors was brought up to synthesize core/shell metallic NPs, which was later tested to be thermally robust at elevated temperature. To this end, a series of PS-b-P4VP block copolymers was prepared using RAFT polymerization and formed reverse micelles in toluene. The metal precursors were enriched inside the P4VP core due to the chelation between metal ions and pyridines. The ionic association, coordination or both with varied association strength were observed for Au, Ag, and Pd ions from FTIR. Crosslinked micelles were able to capture metal ions much faster than non-crosslinked micelles. Both metal ion-loaded non-crosslinked and crosslinked micelles were reduced using anhydrous
N₂H₄. The structural integrity can be preserved when micelle was crosslinked with DBB, which produced a concentric core/shell morphology of one metal NP per micelle. Switching to nonpolar triethylsilane reductant led to off-centered core/shell morphology that most particles were reduced at the PS/P4VP boundary. Finally, the thermal stability was tested at 110 °C in toluene, and crosslinked metal NPs reduced by N₂H₄ showed excellent morphological and spectroscopic robustness at least within 48 hours continuous heating in air. Our results indicated that these NPs were thermally stable to be engaged in occasions such as high temperature catalytic reactions or nanocomposite manufacturing.

As a continuity of this Ph. D. work, commercial star diblock copolymers namely, poly(t-butyl styrene)-b-poly(1, 2(4)-isoprene) star polymers, are chemically modified to convert double bonds of isoprene into carboxylic acid or other metal ion-chelating groups. The modified star polymers are able to form unimolecular micelles in selective solvents much like linear PS-b-P4VP block copolymers did in Chapter 4. The core of acid-modified polyisoprene will, for one purpose, act as a nanosized reactor to control the growth of NPs, and give birth to size-uniform, well-defined metallic or metal oxide NPs. More importantly, the molecular chain of modified polyisoprene might be trapped inside NPs as crystal boundary to induce formation of multiple dipole domains. This is the only viable way to achieve attractively high κ for NPs as comparable to that of their bulk materials. As known, εᵣ of NPs will dramatically decrease as the particle size decreases. The explanation for this abnormal size dependence is presumably owing to the fact that domain wall rather than domain is the key to result in high κ. The obtained matrix-free composites (star polymer/BaTiO₃) are able to assembly into ordered supercrystals, which will significantly mitigate the above-mentioned local field
enhancement, and hence a more balanced field distribution with much enhanced $E_b$ may be observed.

Nowadays, polymer nanocomposites dielectrics have attracted profound attention in research for the application of high electric energy storage (e.g. film capacitor). Most of researchers concentrated their efforts on how to solely increase the apparent $\varepsilon_r$ of polymer nanocomposites, which sometimes lead to an overlook of an even more important factor, dielectric loss. The dielectric loss mechanisms, which is extremely important for the eventual realization of the practical applications, is seldom discussed. The scientific contribution of this dissertation is that it embraced a thorough dielectric loss/conduction mechanism study on two well-studied nanodielectric systems: 1) semiconductor ceramics/polymer nanocomposites; 2) conductive filler/polymer nanocomposites. The key discoveries in here hopefully could help future researchers to notice and identify three intrinsic issues in polymer nanodielectrics, namely, local field enhancement in polymer matrices, interfacial polarization induced internal AC conduction and field electron emission. These issues needs to be carefully scrutinized and addressed in future design of novel nanodielectrics, as what we proposed in the future work. It is exactly how this “nanodielectric” idea evolves in the course of identification of new problems and proposal of new solutions.
Appendix A

for

Chapter 2: Interfacial Polarization-Induced Loss Mechanism in

Polypropylene/BaTiO$_3$ Nanocomposite Dielectrics
1. General Characterization Methods

$^1$H and $^{13}$C NMR spectra were collected on a Varian Mercury 600 MHz spectrometer with CDCl$_3$ as the solvent and TMS as the internal reference. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) study was carried out on a Bruker Autoflex™ III MALDI TOF/TOF mass spectrometer using dithranol as the matrix and silver trifluoroacetate, Ag(CF$_3$COO), as the doping salt. Fourier transform infrared (FTIR) spectra were recorded using a Bomen Michelson MB100 FTIR spectrometer at a resolution of 2 cm$^{-1}$. IR pellets were made by grinding solid samples with dry potassium bromide (KBr) powder and pressing with a hydraulic press at 4 tons (or 5 MPa). Fourier transform Raman spectra were recorded using a Raman spectrometer (Renishaw) with a 514 nm laser. Thermogravimetric analysis (TGA) was carried out on a TA instruments Q500 thermogravimetric analyzer at a heating rate of 10 °C/min under a dry nitrogen flow. Differential scanning calorimetry (DSC) was carried out on a TA Q2000 DSC under a dry nitrogen atmosphere. The sample amount was about 20 mg and the scanning rate was 10 °C/min. Powder X-ray diffraction (XRD) was performed on a Scintag X-1 advanced diffractometer using the Cu Kα radiation (wavelength of 0.15418 nm). Dynamic light scattering (DLS) was measured using a Brookhaven Instrument BI-9000AT multichannel digital correlator. The CONTIN analysis was used to convert correlation function data into hydrodynamic radius.

Nanocomposite films were embedded in the standard epoxy using a silicone rubber mold (Ted Pella, Inc., Redding, CA). The standard epoxy with nanocomposite films were cured at 50-60 °C in a gravity oven for overnight. The cured epoxy block was roughly trimmed using a razor blade, and then finely trimmed using a freshly cleaved glass knife.
to obtain a small block surface (less than 0.5×0.5 mm²) with the embedded nanocomposite films in the middle. The finely trimmed block were cut by a Pelco® diamond knife (Ted Pella, Inc.) at -80 °C using a Leica EM UC6 ultramicrotome equipped with a cryo FC6 unit (Leica Microsystems, Inc., Buffalo Grove, IL). Thin slices about 70-100 nm were floated onto the surface of a water trough and collected using 400-mesh copper grids. For characterization of neat nanoparticles, dilute dispersion was drop-cast onto carbon-coated transmission electron microscopy (TEM) grids. After solvent evaporation, the samples were dried using the house vacuum before TEM observation. Conventional TEM was performed on an FEI Tecnai 12 electron microscope at an accelerating voltage of 100 kV. High resolution TEM was carried out on an FEI Technai F30 electron microscope operated at 300 kV.

2. Synthesis of POSS(PE)₂

POSS-diol (C₃₄H₇₆O₁₅Si₈, 949.65 g/mol, 12 g, 12.64 mmol, 1 eq.) and 4-dimethylaminopyridine (DMAP, 122.17 g/mol, 0.36 g, 2.95 mmol, 0.1 eq.) were dissolved with 130 mL dry dichloromethane (DCM) in a 250 mL dry round-bottom flask, into which diethylphosphonate acetic acid (196 g/mol, density ρ = 1.22 g/mL, 5 mL, 6.1 g, 29.5 mmol, 2.33 eq.) in 10 mL DCM was added. The reaction mixture was cooled to 0 °C using an ice-water bath. N,N’-dicyclohexylcarbodiimide (DCC, 206.33 g/mol, 6.1 g, 29.5 mmol, 2.33 eq.) was dissolved in 10 mL DCM, and was dropwise added into the reaction mixture. When finished, the ice/water bath was removed and the reaction mixture was allowed to warm back to room temperature (RT). The reaction was run at RT for additional 24 h. After reaction, the by-product, dicyclohexylurea (DCU), was removed by filtration, and
DCM was evaporated. The raw product was re-dissolved in ethyl acetate and kept in a freezer (-20 °C) overnight to further crystallize the residual DCU, which was again removed by filtration. Finally, the product was purified by recrystallization in acetonitrile (MeCN) twice. Pale white powder was obtained after drying in a vacuum oven with a yield of 74%. The $^1$H and $^{13}$C NMR spectra are shown in Figures S2.1A and B, respectively. $^1$H NMR (600 MHz, CDCl$_3$) δ: 5.23 (m, 1H), 4.40 (dd, 2H, J = 3.6 Hz), 4.17 (m, 8H), 3.57 (dd, 2H, J = 2.8 Hz), 3.39 (d, 2H, J = 6.8 Hz), 3.02 (d, 2H, J = 2.8 Hz), 2.96 (d, 2H, J = 2.4 Hz), 1.84 (m, 7H), 1.61 (m, 2H), 1.34 (t, 12 H, J = 7.2 Hz), 0.95 (d, 42H, J = 6.8 Hz), 0.59 (m, 16H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 165.3-165.7, 74.0, 71.4, 68.6, 63.7, 62.8, 34.7-34.9, 33.8-34.0, 25.8, 24.0, 23.0, 22.7, 16.5, 8.4. MALDI-MS (matrix: dithranol, salt: CF$_3$COONa): m/z 1412.6 ([M]+Ag$^+$) and the spectrum is shown in Figure S2.3A.

Figure S2.1. (A) $^1$H and (B) $^{13}$C NMR spectra of POSS phosphonate ester, POSS(PE)$_2$. Solvent is CDCl$_3$. 
3. Synthesis of POSS(PA)$_2$

POSS(PE)$_2$ (1305.64 g/mol, 3 g, 2.3 mmol, 1 eq.) was dissolved in 40 mL dry DCM. The solution was cooled down to 0 °C using an ice/water bath under nitrogen protection. Trimethylsilyl bromide (TMSBr) (153.09 g/mol, $\rho = 1.16$ g/mL, 2.43 mL, 2.81 g, 18.38 mmol, 8 eq.) in 5 mL DCM was dropwise added into the reaction mixture, which was allowed to react at RT for 24 h. After reaction, solvent and excess TMSBr were removed by distillation, and 38 mL of methanol was added together with 30 mL DCM to convert trimethylsilyl phosphonate ester into phosphonic acid. After reaction for 2 h, all solvents were evaporated, and the obtained product was washed by acetonitrile several times. The final yield was 69%. The $^1$H and $^{13}$C NMR spectra are shown in Figures S2.2A and B, respectively. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 4.34 (m, 2H), $\delta$ 3.58 (m, 6H), $\delta$ 3.08 (m, 3H), $\delta$ 1.86 (m, 7H), $\delta$ 1.66 (m, 2H), 0.95 (d, 42H, $J = 6.8$ Hz), 0.59 (m, 16H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.1, 73.9-64.2, 35.6, 34.6, 25.7, 23.9, 22.5, 8.24. MALDI-MS (matrix: dithranol, salt: CF$_3$COONa): $m/z$ ([M]+Ag$^+$) 1300.6; $m/z$ ([M]+2Ag$^+$) 1406.5; $m/z$ ([M]+3Ag$^+$) 1514.3 and the spectrum is shown in Figure S2.3B.
From the above characterization results, POSS(PE)$_2$ had a high purity, whereas POSS(PA)$_2$ contained a small amount of impurities with lower molecular weights. Some POSS frameworks broke or lost parts during the mild hydrolysis with TMSBr. Because POSS(PA)$_2$ strongly adsorbed/reacted on silica gel and alumina, it could not be further purified using flash column chromatography. However, this did not cause any problem for the following surface modification of BT NPs because of the following reasons. First, the amount of impurities was small (~15% as estimated from $^1$H NMR) and the POSS(PA)$_2$ was in large excess during the surface modification reaction. Second, impurities and excess POSS(PA)$_2$ were effectively removed by repeated centrifugation and washing of the BT@POSS NPs using 1:1 (vol./vol.) xylene/ethanol mixed solvent.

Figure S2.3. MALDI-TOF mass spectra for (A) POSS(PE)$_2$ and (B) POSS(PA)$_2$.

Figure S2.4. (A) Dynamic light scattering (DLS) result for BT@POSS NPs dispersed in
toluene. The inset shows individual BT@POSS NPs drop-cast on carbon-coated TEM grid. 
(B) TGA result for BT and BT@POSS NPs in a dry N₂ atmosphere. The inset shows the TGA result for the POSS(PA)₂ ligand. The heating rate is 20 °C/min. (C) A bilayer model for the POSS(PA)₂ attached to the BaTiO₃ NP surface.

4. Characterization of BT@POSS NPs

From the DLS result in Figure S2.4A, the mean particle size for the BT@POSS in THF is about 112 nm (based on the CONTIN algorithm), indicating POSS(PA)₂ ligands are effective to disperse the 70 nm BT NPs into individual particles in dilute organic solvents (the inset shows TEM image for the drop-cast NPs from toluene). TGA results for BT and BT@POSS NPs are shown in Figure S2.4B. At 600 °C, the different between BT and BT@POSS NPs is ca. 1.94 wt.%. The grafting density of POSS(PA)₂ on BaTiO₃ can be obtained by using the following equation:

\[
\text{Grafting density} = \left( \frac{\text{wt.\%}}{100 - \text{wt.\%}} \right) \times \left( \frac{6.02 \times 10^{23}}{\text{MW} \times \text{SSA}} \right)
\]

(S2.1)

where MW and SSA are molecular weight of POSS(PA)₂ (1193.64 g/mol) and specific surface area of 70 nm BaTiO₃ NPs (14.3 m²/g based on calculation). Taking into account of the fact that weight loss for POSS(PA)₂ is about 37 wt.% at 600 °C due to inorganic Si and P residue, the grafting density can be calculated to be 1.14 POSS(PA)₂ molecules/nm². Assuming the radius of a POSS(PA)₂ molecule is about 0.8 nm (i.e., the same as in POSS crystals), the theoretical grafting density for a monolayer should be about 0.5 POSS molecule/nm². Therefore, the experimental grafting density is about 2 times that of the theoretical grafting density. Considering that we had washed away any physically adsorbed POSS(PA)₂ from the BT@POSS NPs, this result suggests that POSS(PA)₂ should form a bilayer, rather than a monolayer, structure on the BaTiO₃ surface, as shown in the schematic drawing in Figure S2.4C. The first layer of POSS(PA)₂ molecules could form a pseudo-
hexagonal packing, and the POSS(PA)$_2$ molecules in the second layer occupy the interstitial spaces of the first layer molecules, forming an AB stacking of pseudo-hexagonally packed POSS molecules.

**Figure S2.5.** (B) Raman spectra for 2 μm BaTiO$_3$, 70 nm BT, BT@TiO$_2$ 50-cycle, BT@TiO$_2$ 200-cycle, anatase TiO$_2$, POSS(PA)$_2$, BT@POSS, and BT@TiO$_2$@POSS 200-cycle NPs at room temperature. (A) Second heating DSC curves for 2 μm BaTiO$_3$, 70 nm BT, BT@POSS, BT@TiO$_2$ 200-cycle, and BT@TiO$_2$@POSS 200-cycle NPs.

For 2 μm BaTiO$_3$ particles, the Raman absorption band for the ferroelectric tetragonal phase [E(TO+LO), B1] is seen at 306 cm$^{-1}$. For the 70 nm BT NPs, the intensity of this absorption band is decreased, indicating decreased ferroelectric content. Note that additional Raman absorption bands are also observed at 145, 187, 395, and 640 cm$^{-1}$, which can be attributed to anatase TiO$_2$. It is likely that the 70 nm BT NPs are prepared from BaCO$_3$ and anatase TiO$_2$ NPs. $^{S2}$ After ALD coating with TiO$_2$, the BT@TiO$_2$ 50- and 200-
cycle NPs exhibit additional Raman bands at 145, 187, 395, and 640 cm\(^{-1}\), which again belong to anatase TiO\(_2\). However, after surface modification with the POSS(PA\(_2\)) ligand, no absorption bands could be observed for BT and BT@TiO\(_2\) NPs at all. This result suggests that POSS(PA\(_2\)) ligands have strong Raman absorption and thus block the signals emitted from BT and BT@TiO\(_2\) NPs.

For the 2 \(\mu\)m BaTiO\(_3\) particles (Figure S2.5B), the orthorhombic-to-tetragonal temperature (\(T_{OT}\)) is observed at \(\sim\)21 \(^\circ\)C and the Curie temperature (\(T_C\)) is seen at 121 \(^\circ\)C. For the 70 nm BT NPs, the Curie transition becomes weak and broad with the \(T_C\) decreasing to around 50 \(^\circ\)C, indicating a reduction in the domain size and ferroelectric content. For BT@POSS, BT@TiO\(_2\) 200c, and BT@TiO\(_2\)@POSS 200c, very weak Curie transitions are observed around 50 \(^\circ\)C. Obviously, the content of the ferroelectric phase is further reduced in these NPs.

Figure S2.6. Temperature-scan BDS results (raw data without correction using the Bruggeman equation), (A and D) \(\varepsilon'\), (B and E) \(\varepsilon''\), and (C and F) tan\(\delta\) for IR-pressed pellets.
of BT and BT@POSS NPs.

For the BT NPs, a weak and broad Curie transition is seen around 50 °C (see Figures S2.6A/B). For the BT@POSS NPs, this Curie transition becomes even weaker (Figures S2.6D/E).
5. Thermal Properties of Various PP Nanocomposites

Figure S2.7. TGA results for (A) PP/BT, (B) PP/BT@POSS, and (C) PP/BT@TiO$_2$@POSS nanocomposites in $N_2$. The heating rate is 20 °C/min.

6. Linear Dielectric Properties of Various PP Nanocomposites

Figure S2.8. (A-C) Temperature- and (D-E) frequency-scan BDS results for the hot-pressed PP film: (A and D) $\varepsilon'_r$, (B and E) $\varepsilon''_r$, and (C and F) tanδ.

The $T_g$ of PP is observed at 6, 10, 18, and 26 °C at $10^2$, $10^3$, $10^4$, and $10^5$ Hz, respectively. From the frequency-scan result at 100 °C, the upturn at low frequencies
(slope of -1 in the double logarithmic plot) is attributed to migrational loss of impurity ions in the hot-pressed PP film.

**Figure S2.9.** Temperature-scan BDS results for the hot-pressed PP/BT films with (A-C) 10 vol.%, (D-F) 20 vol.%, and (G-I) 30 vol.% BT NPs at various frequencies: (A, D, G) $\varepsilon_r'$, (B, E, H) $\varepsilon_r''$, and (C, F, I) tanδ.

For the PP/BT nanocomposites, the $T_g$ of the PP matrix is observed at 0, 6, 15, 24, 34, and 48 °C at $10^0$, $10^1$, $10^2$, $10^3$, $10^4$, and $10^5$ Hz, respectively.
Figure S2.10. Frequency-scan BDS results for the hot-pressed PP/BT films with (A-C) 10 vol.%., (D-F) 20 vol.%, and (G-I) 30 vol.% BT NPs at various temperatures: (A, D, G) $\varepsilon_r'$, (B, E, H) $\varepsilon_r''$, and (C, F, I) tan$\delta$.

In Figure 2.10, the increased $\varepsilon_r'$, $\varepsilon_r''$, and tan$\delta$ at high temperatures and low frequencies are attributed to migrational loss from impurity ions.
Figure S2.11. Temperature-scan BDS results for the hot-pressed PP/BT@POSS films with (A-C) 10 vol.%, (D-F) 20 vol.%, and (G-I) 30 vol.% BT@POSS NPs at various frequencies: (A, D, G) $\varepsilon'$, (B, E, H) $\varepsilon''$, and (C, F, I) $\tan\delta$.

For the PP/BT@POSS nanocomposites, the $T_g$ of the PP matrix is observed at -5, 3, 12, 20, 29, and 42 °C at $10^0$, $10^1$, $10^2$, $10^3$, $10^4$, and $10^5$ Hz, respectively.
In Figure 2.12, the increased $\varepsilon_r'$, $\varepsilon_r''$, and $\tan\delta$ at high temperatures and low frequencies are attributed to migrational loss from impurity ions.

7. Coarse-Grain Molecular Dynamics Simulation of Local Field in Nanocomposites

This coarse-grain molecular dynamics simulation is based on a previous publication. Briefly, the simulation model and procedure are described below. N spherical particles of volume $V_p = \frac{3}{4} \pi R^3$ and dielectric permittivity $\varepsilon_p$ are randomly distributed in a cubic box of size $L$, $\{\vec{r}_i\} = \text{rand}_i(L)$. An external field $\vec{E}_0$ is applied along
the z-direction of system. Due to the polarization effect, the inclusions gain an induced
dipole moment $\vec{\mu}_p^i$,

$$\vec{\mu}_p^i = \vec{\mu}_p^0(E_0) + \vec{\mu}_p(E_j) \quad (S2.2)$$

Here the first part $\vec{\mu}_p^0$ is the pure dipole moment of inclusion $i$ stemming from the external
field $E_0$:

$$\vec{\mu}_p^0 = V_p \frac{\epsilon_p - \epsilon_m}{\epsilon_m + (\epsilon_p - \epsilon_m)\alpha_p^z} \frac{1}{1 + (\epsilon_m - 1)\alpha_m^z} \epsilon_0 \epsilon_m \vec{E}_0 \quad (S2.3)$$

and the second part $\vec{\mu}_p(E_j)$ is the excess dipole moment of inclusion $i$ corresponding to the
cumulative sum of the fields created by other inclusions $j$ ($1 \leq j \leq N, j \neq i$) at the position
of the inclusion $i$,

$$\vec{\mu}_p(E_j) = V_p \frac{\epsilon_p - \epsilon_m}{\epsilon_m + (\epsilon_p - \epsilon_m)\alpha_p^z} \epsilon_0 \epsilon_m \sum_j \vec{E}_j \quad (S2.4)$$

Here, $\alpha_p^z$ and $\alpha_m^z$ are polarization factors for the particle and the host polymer. For the
experimental set-up, where the inclusions are spherical particles, and host polymer has a
slab shape, $\alpha_p^z=1/3$ and $\alpha_m^z=1$. Then Eqn. (S2.2) can be rewritten as:

$$\vec{\mu}_p^i = 4\pi \epsilon_0 \rho^3 \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \left( \vec{E}_0 + \sum_j \epsilon_m \vec{E}_j(\mu_j^i) \right) \quad (S2.5)$$

Note that $\vec{E}_j$ in Eqn. (S2.5) depends on the dipole moment of inclusion $j$, and thus the dipole
moment of each inclusion depends on the dipole moment of all other inclusions. In other
words, Eqn. (S2.5) should be solved using the iteration method for getting true dipole
moments $\vec{\mu}_p^i$ of inclusions. This issue is overlooked in most theoretical considerations.
Our simulations show that the number of iterative steps necessary for achieving a stabilized \( \vec{\mu}_p \) in Eqn. (S2.5) depends on the particle packing fraction, \( \eta \). The higher the \( \eta \), the larger is the number of iterations. During the iterations, the long-range interaction between the induced dipoles \( \vec{\mu}_p \) and \( \vec{\mu}_p \) is handled using Ewald’s summation technique.\(^{S4-S6}\) Direct summation of the dipolar interactions can also be speeded up using the dipole-(infinite) chain interaction potentials.\(^{S7}\) Once all dipoles \( \vec{\mu}_p \) in the system are stabilized, we create a mesh network \( \{ \vec{r}_i \} \) with 400 points per particle diameter in each direction, and calculate the components of local electric field \( \vec{E}_L (\vec{r}_i) \) at the mesh points \( \vec{r}_i \) as a sum of the dipolar fields \( \vec{E}_j \) of all inclusions \( j, j = 1, \ldots, N \). At this point,

\[
E_L(x_i) = \sum_j^N E_j(x_i) \quad E_L(y_i) = \sum_j^N E_j(y_i) \quad E_L(z_i) = \sum_j^N E_j(z_i) + E_0
\]  

(S2.6)

where \( x_i, y_i, \) and \( z_i \) are the coordinates of mesh points \( \vec{r}_i \). The amplitude of the local field at the mesh points \( \vec{r}_i \) is defined as:

\[
E_L(\vec{r}_i) = |\vec{E}_L(\vec{r}_i)| = \sqrt{E^2_L(x_i) + E^2_L(y_i) + E^2_L(z_i)}
\]  

(S2.7)

The simulation model for randomly distributed particles in a polymer matrix is described in detail in section 3 of ref. S3. Briefly, we consider \( N \) hard spherical inclusions randomly distributed in the bulk of the host matrix of volume. The random distribution of inclusions is created by their random insertion into the host polymer matrix. Each inclusion is connected by elastic springs to its \( n_b \) nearest neighbors (see Figure 2.2 in ref. S3). All springs are assumed to have the same elasticity constant \( \chi \). The lattice structure of the inclusion distribution is periodically extended in all three directions. When an external
field $E$ is applied along the $z$-axis, which coincides with the [001] direction of the lattice structures, the long-range interaction between the induced dipoles is handled using Ewald’s summation technique with a correction for the rectangular shape of the simulation cell. Test simulations with direct summations over the 100 neighboring image cells produced results similar to Ewald’s summation with a difference between these two methods less than 0.01%. Direct summation of the dipolar interactions can also be speeded up using the dipole-(infinite)chain and (infinite)chain-(infinite)chain interaction potentials.

We used the following system parameters for the simulation: particle diameter $\sigma = 2R = 70$ nm, particle number in the box $N = 600$, applied field strength $E_0 = 50$ MV/m, permittivity of the polymer matrix $\varepsilon_m = 2.34$, permittivity of the inclusions $\varepsilon_p = 120$. Three systems configurations were considered, $\eta = 0.1$ for $L = 13.80\sigma$, $\eta = 0.2$ for $L = 11.03\sigma$, and $\eta = 0.3$ for $L = 9.63\sigma$. Simulations show that about several dozen iterations for $\eta = 0.1$, and several hundred iterations for $\eta = 0.3$ were necessary for getting stable dipolar fields in the system.

Detailed analysis of Figure 2.5 shows that the local field enhancement effect, $E_L/E_0$, is strong at the particle poles, and weak in the bulk of the polymer matrix. The strength of the local field enhancement depends on the position of the inclusion. When the inclusion is not in a chained configuration along the $z$-axis (i.e., the field direction; referred here as a single inclusion), the local field enhancement effect at its poles will be less than when the particle belongs to a chained configuration (referred as a chained inclusion). For $\eta = 0.1, 0.2, \text{ and } 0.3$, the enhancement factor $E_L/E_0$ was about 4, 6, 8 for single inclusions, and about 9, 18, 40 for chained inclusions, correspondingly.
The proximity of two or even three particles does not guarantee the large field localization between them, as seen in Figures 2.5B and C. This is clearly seen in Figure S2.13, when we change the color scales for a slice at \( x = 150 \) nm in Figure 2.5C. According to our simulations, for the composite parameters discussed in the manuscript, at least 5 particles should arrange into a chain along the applied field with small interparticle spacing in order to show large field localization.

8. Nonlinear Dielectric Properties of Various Nanocomposites
Figure S2.14. Bipolar D-E loops for hot-pressed films of (A) PP, (B-D) PP/BT, (E-G) PP/BT@POSS, and (H) PP/BT@TiO$_2$@POSS 80/20 50c nanocomposites at room temperature. (I) Discharged energy density ($U_e$) and discharge efficiency for PP/BT (10, 20, and 30 vol.%) and PP/BT@TiO$_2$@POSS 80/20 50c nanocomposites. The poling frequency is 10 Hz with a sinusoidal wave function.

From Figure S2.14 I, the discharged $U_e$ values for the hot-pressed PP/BT 80/20 films are similar to those for the PP/BT@TiO$_2$@POSS 80/20 film at the same poling electric field. However, the discharge efficiencies for the PP/BT 80/20 film are lower than those for the PP/BT@TiO$_2$@POSS 80/20 film. In addition, the maximum discharged $U_e$ values at breakdown for the PP/BT nanocomposites are much lower than those the PP/BT@TiO$_2$@POSS 50c (and also the PP/BT@POSS; see Figure 2.6 in the main text) nanocomposites.
Figure S2.15. Continuous bipolar D-E loops for the hot-pressed PP/BT@POSS 80/20 film at various temperatures: (A) RT, (B) 70 °C, (C) 100 °C, and (D) 130 °C. Solid and dashed lines are the first and third runs, respectively. Each run contains 6 continuous bipolar loops at 30 (×2), 90 (×2), and 150 (×2) MV/m, respectively. The time interval between consecutive runs is ca. 20 s. The poling frequency is 10 Hz with a sinusoidal wave function.

At each temperature, three runs are performed with each run containing 6 loops. The first and second loops are both at 30 MV/m, the third and fourth loops are both at 90 MV/m, and the fifth and sixth loop are both at 150 MV/m. To avoid the transient effect, only the second, fourth, and sixth loops are shown in Figure S2.15. The time interval between consecutive runs is ca. 20 s. First, all loops in the third runs (dashed lines) shift up with respect to the E-axis, indicating the effect of remanent polarization from the
previous second runs. This remanent polarization disappears within the 20 s interval at temperatures above 100 °C. Second, D-E loops in the first runs at RT and 70 °C are symmetric with respect to the origin, indicating little DC conduction in the sample. At 100 and 130 °C, the upper parts of the loops in the first runs shift up, indicating certain DC conduction in the sample as temperature increases. Third, from RT to 70 °C and then to 100/130 °C, the loops in the first run become slimmer first and then broaden again. This could relate to the broad Curie transition peak around 50 °C for BT@POSS NPs in Figure 2.1D in the main text. Finally, even above the broad Curie transition, significant dielectric nonlinearity is still observed at 130 °C, indicating that the weak ferroelectricity should not be the cause of dielectric nonlinearity of the nanocomposites.

Figure S2.16. Bulk conductivities for hot-pressed PP, PP/BT@POSS (10, 20, and 30 vol.%), and PP/BT@TiO₂@POSS 80/20 (50 and 200 cycles) nanocomposites, as determined by the leakage current study at RT.
Figure S2.17. Continuous 4 unipolar D-E loops for the hot-pressed PP/BT@POSS 80/20 films at room temperature under various frequencies: (A) 2000 Hz, (B) 200 Hz, (C) 20 Hz, (D) 2 Hz, and (E) 0.4 Hz. (F) Continuous 4 unipolar loops measured at 130 °C and 20 Hz. The poling field is 150 MV/m with a sinusoidal wave function. Continuous 3 bipolar D-E loops at 30, 90, and 150 MV/m under poling frequencies of 1000, 100, 10, 1, and 0.2 Hz are shown for comparison. The double frequency for the unipolar loops makes sure that the poling time of each unipolar loop is the same as that of the first half bipolar loop, i.e., 50 ms.

As we can see, the first unipolar loop nearly overlaps with the first half of the bipolar loop. Subsequent unipolar loops become much slimmer. This is not only true at room temperature, but also at 130 °C (which is above the Tc of ~120 °C for bulk BaTiO3; see Figure S2.17F). These results are consistent with the proposed dielectric loss mechanism from internal conduction of free space charges (electrons and holes) in BT NPs in Scheme 2.2 in the main text. Namely, during the first unipolar loop, space charges in BaTiO3 NPs are polarized at two poles. Because of the unipolarity in the electric poling, these interfacial charges cannot relax or reverse. Therefore, subsequent unipolar loops become much slimmer. As the test frequency decreases, both internal conduction within BT NPs and external DC conduction through the film enhances, causing a higher dielectric...
loss (i.e., dielectric nonlinearity). From the slope of the charging part of the fourth unipolar D-E loop at low fields (<50 MV/m), the apparent dielectric constant can be obtained and the value is the same as those measured using BDS at 1 Vrms (i.e., $\varepsilon_r' \sim 6.2$, see Figures 2.3 and S2.11D).

9. Estimation of Space Charge Density and Conductivity in BT NPs

Since neat BaTiO$_3$ is a wide band gap material (3.2 eV), we consider that the space charge should be thermally activated free electrons, and the holes are immobile ions in the ionic crystal. Upon electric poling, only free electrons are polarized and the immobile holes are relatively uniformly distributed, as shown in Figure S2.18. The net effect of polarization can be abstract as that shown in Scheme 2.2 in the main text.

**Figure S2.18.** Schematic representation of polarization of space charges (i.e., free electrons) in electrically neutral BaTiO$_3$ nanoparticles. The left shows the polarization of free electrons, and the middle shows the uniform distribution of immobile holes (or ions). The net effect of electric polarization is equivalent to the one shown on the right in order to keep electrical neutrality.
Figure S2.19. (A) Abstraction of the PP/BT@POSS nanocomposite with 20 vol.% filler content into an ABA three-layer model. Layer thicknesses for the BT@POSS layer (orange) and each PP layer (blue) are $d_1$ (assuming 100 nm) and $d_2$ (assuming 200 nm), respectively. The total thickness is thus $d_1 + 2d_2$ (i.e., 500 nm) with the filler volume fraction of 20 vol.%. The applied voltage $V = E(d_1 + 2d_2)$, where $E$ is applied electric field to the entire layer (i.e., 150 MV/m in this case). The electric fields in BT@POSS and PP layers are $E_1$ and $E_2$, respectively. The relative permittivities of BT@POSS and PP are $\varepsilon_{r1}$ (125) and $\varepsilon_{r2}$ (2.25), respectively. The electric displacements for the BT@POSS layer and each PP layer are $D_1$ and $D_2$, respectively. (B) Schematic representation of the space charge (i.e., free electrons) migration in the BaTiO$_3$ layer under an alternating electric voltage $V_1(t) = V_1^0 e^{i\omega t}$, where $V_1^0 = E_1 d_1 = E_1 (2a)$. Here, $d_1 = 2a$. Within the BaTiO$_3$ layer, we consider that only free electrons migrate along the $x$ direction and the holes are immobile.

To fit the bipolar D-E loops shown in Figure 2.6A, we need to abstract the nanocomposite into an ABA three-layer model and obtain an analytical solution for the electric displacement as a function of the switching electric field. The three-layer model is shown in Figure S2.19A with all material parameters described in the figure caption. The electric displacements for the BT@POSS layer ($D_1$) and each PP layer ($D_2$) thus obey the following relationship:\(^8\)

$$D_1 = \varepsilon_{r1}\varepsilon_0 E_1 = D_2 = \varepsilon_{r2}\varepsilon_0 E_2$$

(S2.8)

where $\varepsilon_{r1}$ and $\varepsilon_{r2}$ are relative permittivities for BT@POSS and PP, $E_1$ and $E_2$ the electric fields in BT@POSS and PP layers, and $\varepsilon_0$ the vacuum permittivity. The voltage drop ($V$)
across the entire layer is: $V = \Delta \text{E}_1 \text{d}_1 + \Delta \text{E}_2 \text{d}_2 = \text{E}(\text{d}_1 + 2\text{d}_2)$. Here, $\text{E}$ is 150 MV/m. Therefore, the electric field in the BT@POSS layer ($\text{E}_1$) can be obtained:

$$E_1 = \frac{\varepsilon_2 (d_1 + 2d_2)E}{\varepsilon_2 d_1 + 2 \varepsilon_1 d_2} = 3.36 \text{ MV/m} \quad \text{(S2.9)}$$

In the following, we use the model shown in Figure S2.19B to retrieve the electric displacement as a function of the alternating electric voltage $V_1(t) = V_1^0 e^{i\omega t}$, where $V_1^0 = E_1 d_1 = E_1 (2a)^S$ for the BaTiO$_3$ layer. Here, $d_1 = 2a$, and the voltages at $+a$ and $-a$ are $+0.5 V_1^0 e^{i\omega t}$ and $-0.5 V_1^0 e^{i\omega t}$, respectively. The BaTiO$_3$ layer has a dielectric constant $\varepsilon_{r1} = 125$, and is held at $T = 300$ K. Within the BaTiO$_3$ layer, we consider that only free electrons migrate along the $x$ direction under the electric field, and the holes or positive ions are immobile.

In order to find the displacement $D$, which in the geometry of our set-up is the surface charge density of the plates, $D = \sigma$, and $[D] = \frac{C}{m^2}$. We use the following relationship:

$$\sigma(t) = \int_0^{t} j_{tot}(\tau) d\tau \quad \text{(S2.10)}$$

Here, $j_{tot}(t)$ is the total current density at the electrode surface ($x = a$),

$$I_{tot}/S = j_{tot}(t) = j_e(t) + j_{disp}(t) \quad \text{(S2.11)}$$

where $S$ is the electrode surface area, the first term $j_e(t)$ is the current density due to the diffusion of electrons and the gradient of their concentration. The second term $j_{disp}(t)$ is the displacement of the electronic current density because of the time changing of applied field. Below we separately calculate $j_e(t)$ and $j_{disp}(t)$ currents.

**Electronic Current.** The electronic current is defined as

$$j_e(x, t) = e j(x, t) \quad \text{(S2.12)}$$

Here, $j(x, t)$ is the electronic flux, whereas $e j(x, t)$ is the electronic current density. For
simplicity we call the current density as current (bearing in mind that the true current is $I_e = j_e(x, t) \times S$). The continuity equation for the electrons reads

$$\frac{\partial j_-(x, t)}{\partial x} = -\frac{\partial n_-(x, t)}{\partial t} \quad \text{(S2.13)}$$

where $n_-(x, t)$ is the distribution of electronic concentration in the membrane along the applied field $E$. The electronic current obeys the Nernst-Planck equation

$$j_-(x, t) = -D_e \frac{\partial n_-(x, t)}{\partial x} - \mu n_-(x, t) E_i(x, t) \quad \text{(S2.14)}$$

where $E_i(x, t)$ is the local electric field in the layer along the applied field $E$, and $\mu$ denotes the electronic mobility. $\mu$ is related to the diffusion coefficient $D_e$ through the Einstein equation

$$\mu = \frac{D_e e |e|}{k_B T} \quad \text{(S2.15)}$$

where $k_B$ is the Boltzmann constant. For the electronic concentration $n_-(x, t)$ and for the internal electric field $E_i(x, t)$, we use the macroscopic Poisson-Boltzmann (PB) equation

$$-\frac{\partial E_i(x, t)}{\partial x} = -\frac{e}{\varepsilon_r \varepsilon_0} n_-(x, t) \quad \text{(S2.16)}$$

By putting Eq. (S2.14) into Eq. (S2.13), we get

$$\frac{\partial j_-(x, t)}{\partial x} = -D_e \frac{\partial^2 n_-(x, t)}{\partial x^2} - \mu E_i(x, t) \frac{\partial n_-(x, t)}{\partial x} - \mu n_- \frac{\partial E_i}{\partial x} = -\frac{\partial n_-}{\partial t} \quad \text{(S2.17)}$$

This second order differential equation can be solved using a linear perturbation approach for the electronic density and assuming that $n_-$ does not deviate much from its equilibrium value:

$$n_- = n_0 + \delta_-(x, t), \quad \delta_-(x, t) = \eta_- (x) e^{i\omega t} \quad \text{(S2.18)}$$

Here, we also assume that the perturbation in the electronic density has the same periodicity as the internal electric field $E_i(x, t) = E_i(x) e^{i\omega t}$. Putting Eq. (S2.18) into Eq. (S2.14) leads to
\( j_-(x,t) = -D_e \frac{\partial \eta_-}{\partial x} e^{i\omega t} - \mu n_0 E_i(x) e^{i\omega t} \)  
\hspace{1cm} (S2.19)

Also, putting Eq. (S2.17) into Eq. (S2.16) we get
\[
\frac{\partial j_-(x,t)}{\partial x} = -D_e \frac{\partial^2 \eta_-}{\partial x^2} e^{i\omega t} - \mu n_0 \frac{\partial E_i(x)}{\partial x} e^{i\omega t} = -\eta_- (x) i \omega e^{i\omega t} \]
\hspace{1cm} (S2.20)

By dividing the left and right sides of Eq. (S2.20) by \( e^{i\omega t} \), we have
\[
-D_e \frac{\partial^2 \eta_-}{\partial x^2} - \mu n_0 \frac{\partial E_i(x)}{\partial x} = -\eta_- (x) i \omega \]
\hspace{1cm} (S2.21)

Here, the term \( \frac{\partial E_i(x)}{\partial x} \) can be taken from the PB equation Eq. (S2.16), which is now rewritten as
\[
\frac{\partial E_i(x,t)}{\partial x} = \frac{e}{\varepsilon_{r1} \varepsilon_0} (e \eta_- (x)) \]
\hspace{1cm} (S2.22)

Finally, the Eq. (S2.21) takes the form
\[
-D_e \frac{\partial^2 \eta_-}{\partial x^2} - \mu n_0 \frac{e}{\varepsilon_{r1} \varepsilon_0} \eta_- (x) + \eta_- (x) i \omega = 0 \]
\hspace{1cm} (S2.23)

Putting Eq. (S2.15) for the mobility \( \mu \) into Eq. (S2.23), and introducing Debye screening length \( \lambda^2 = \varepsilon_{r1} \varepsilon_0 k_B T / (2n_0 e^2) \), we have
\[
\frac{\partial^2 \eta_-}{\partial x^2} - \left( \frac{1}{2 \lambda^2} + \frac{i \omega}{D_e} \right) \eta_- (x) = 0 \]
\hspace{1cm} (S2.24)

The solution of this second order differential equation is sought in the form
\[
\eta_- (x) = B_1 e^{\beta_1} + B_2 e^{-\beta_1} + B_3 e^{\beta_2} + B_4 e^{-\beta_2} \]
\hspace{1cm} (S2.25)

Putting Eq. (S2.25) into Eq. (S2.24), and after simple mathematical manipulations we arrive at the following analytical formula for the density profiles
\[
\eta_- (x) / n_0 = A_0 \frac{\sinh(Bx)}{\sinh(Ba) + \frac{i \omega \lambda^2}{D_e} \cosh(Ba)} \]
\hspace{1cm} (S2.26)

Here, \( B = \frac{1}{\lambda} \sqrt{1 + i \omega \lambda^2 / D_e} \), and \( A_0 = -e V_0 (B \lambda)^2 / (2 k_B T) \). For the derivative of the electronic concentration profile we get
\[
\frac{1}{n_0} \frac{\partial \eta_0}{\partial x} = A_0 B \frac{\cosh(Bx)}{\sinh(Ba) + i \omega \lambda^2 D_e \cosh(Ba)}
\]  
(S2.27)

Now, putting Eq. (S2.26) into the PB equation (S2.22), we get, for the electric field \( E_i(x) \), the following relation
\[
E_i(x) = \frac{-e}{\varepsilon_r \varepsilon_0} \int (- \eta_0(\ell)) d\ell = - \frac{-e n_0 A_0 \cosh(Bx)}{\varepsilon_r \varepsilon_0 B \left( \sinh(Ba) + i \omega \lambda^2 D_e \cosh(Ba) \right)} - C
\]  
(S2.28)

where \( C \) is an integration constant, and can be deduced from the boundary condition
\[
- V_0 = \int_{-a}^{a} E_i(x) dx
\]  
(S2.29)

Finally, we obtain
\[
C = \frac{i \alpha B \lambda^2 V_0}{4 D_e} \frac{\cosh(Bx)}{\sinh(Ba) + i \omega \lambda^2 D_e \cosh(Ba)}
\]  
(S2.30)

Using \( \partial \phi / \partial x = -E_i \), where \( E_i \) is given by equation (S2.28), and taking into account Eq. (S2.27) for the derivative of the electronic concentration, we arrive at
\[
\frac{\partial \phi}{\partial x} = \frac{-e}{\varepsilon_r \varepsilon_0 B^2} \frac{\partial \eta_0}{\partial x} + C
\]  
(S2.31)

Now, we go back to Eqs. (S2.12), (S2.14), and (S2.19) for \( j_e(x, t) \) and \( j_i(x, t) \), and put there the expressions (S2.26) and (S2.27) for the electronic concentrations and their derivatives. Then, for \( j_e \) we have
\[
j_e(x, t) = -e D_e \eta_0'(x) + \mu n_0 E_i(x) e^{i \omega t}
\]  
(S2.32)

which can be rewritten as
\[
j_e(x, t) = -e D_e n_0 A_0 B \left( 1 - \frac{1}{(B \lambda)^2} \right) F(x) e^{i \omega t} - \varepsilon_r \varepsilon_0 \frac{D_e}{2 \lambda^2} C e^{i \omega t}
\]  
(S2.33)

where
\[
F(x) = \frac{\cosh(Bx)}{\sinh(Ba) + i \omega \lambda^2 D_e \cosh(Ba)}
\]  
(S2.34)
Finally, putting the value of $C$ from Eq. (S2.30) into Eq. (S2.33), for the electronic current we get

$$j_e(x, t) = -eD_e n_0 A_0 B \left(1 - \frac{1}{(B \lambda)^2}\right) F(x)e^{i\omega t} - \frac{1}{4} \varepsilon_{r1} \varepsilon_0 BV_0 i\omega F(a)e^{i\omega t}$$

(S2.35)

**Displacement Current.** The displacement current density is defined as

$$\frac{I_{disp}}{S} = j_{disp}(x, t) = \varepsilon_{r1} \varepsilon_0 \frac{\partial E(x,t)}{\partial t} = -\varepsilon_{r1} \varepsilon_0 \frac{\partial \phi(x)}{\partial x} i\omega e^{i\omega t}$$

(S2.36)

Taking the value of $\phi'_x$ from Eq. (S2.31), we have

$$j_{disp}(x, t) = -en_0 \frac{A_0}{B} \left[\frac{\omega^2 x^2}{D_e} F(a) - i\omega F(x)\right]e^{i\omega t}$$

(S2.37)

**Total Charge on the Metal Electrode Plates.** Total charge density on the metal electrode plates is

$$Q(t)/S = \sigma(t) = \int_t^\tau j_{tot}(x = a, \tau) d\tau = \frac{1}{i\omega} e^{i\omega t} (j_e(a, t) + j_{disp}(a, t))$$

(S2.38)
Figure S2.20. Calculated bipolar D-E loop using the analytical model in Figure S2.19 in order to fit the experimental bipolar D-E loop in Figure 2.6A at 150 MV/m and 10 Hz. The fitting parameters are: $\mu = 1 \times 10^{-4} \text{ m}^2/(\text{V} \cdot \text{s})$ and $n_0 = 1.5 \times 10^{15} /\text{m}^3$.

Using the above analytical solution, the bipolar D-E loop at $E = 150 \text{ MV/m}$ in Figure 2.6 can be fitted with $n_0 = 1.5 \times 10^{15}/\text{m}^3$. The result is shown in Figure S2.20. This $n_0$ value is much lower than the density of photorefractive charge carriers ($10^{22} /\text{m}^3$) reported for BaTiO$_3$ single crystals,$^{10}$ and is thus considered reasonable. Using equation: $\sigma = e\mu n_0$ ($e$ is the charge of an electron, $1.602 \times 10^{-19} \text{ C}$), the conductivity of the BT NPs is about $2.4 \times 10^{-8} \text{ S/m}$. Note that this value is slightly higher than that ($10^{-10} \text{ S/m}$) of bulk BaTiO$_3$. However, considering the large amount of surface defects in BT NPs, this conductivity value should be reasonable.

10. Atomic Layer Deposition of TiO$_2$ onto BT NPs

Atomic layer deposition (ALD) of TiO$_2$ (from TiCl$_4$ and H$_2$O) onto BT NPs was performed by ALD Nanosolutions, Inc. (Broomfield, CO). ALD is a dry, gas phase deposition process based on sequential and self-limiting surface reactions.$^{11}$ The 50-cycle sample was prepared at 200 °C in a 100 gram batch, and the 200-cycle sample was performed at 300 °C in a 2 kg batch. Both were carried out in a fluidized bed reactor. The experimental parameters were changed during the ALD process to keep growth rate of the TiO$_2$ layer at approximately 0.1 nm/cycle.
11. Characterization of BT@TiO\textsubscript{2}@POSS 50c and 200c NPs

FTIR results in Figure S2.21A show that POSS(PA)\textsubscript{2} ligand is successfully coated onto the BT@TiO\textsubscript{2} 200c NPs. TGA results in Figure S2.21B show that the weight losses of POSS(PA)\textsubscript{2} ligand are ca. 1.88 and 2.27 wt.% for the BT@TiO\textsubscript{2}@POSS 50c and 200c NPs, respectively. These weight losses are close to the value of 1.94 wt.% for the BT@POSS NPs. Similar to the BT@POSS NPs, a double layer of POSS(PA)\textsubscript{2} on the BT@TiO\textsubscript{2} 50c and 200c NPs can be assumed (see Figure S2.4C).

12. Dielectric Properties of the PP/BT@TiO\textsubscript{2}@POSS 80/20 50c Nanocomposite
Figure S2.22. (A-C) Temperature- and (D-E) frequency-scan BDS results for the hot-pressed PP/BT@TiO₂@POSS 80/20 50c film: (A and D) $\varepsilon_r'$, (B and E) $\varepsilon_r''$, and (C and F) $\tan\delta$.

For the PP/BT@TiO₂@POSS 50c nanocomposites, the $T_g$ of the PP matrix is observed at -2, 3.5, 10, 13, 18, and 25 °C at $10^0$, $10^1$, $10^2$, $10^3$, $10^4$, and $10^5$ Hz, respectively. The increased $\varepsilon_r'$, $\varepsilon_r''$, and $\tan\delta$ at high temperatures and low frequencies are attributed to migrational loss from impurity ions.
Figure S2.23. Continuous 4 unipolar D-E loops for the hot-pressed PP/BT@TiO2@POSS 80/20 50c films at room temperature under various frequencies: (A) 2000 Hz, (B) 200 Hz, (C) 20 Hz, and (D) 2 Hz. The poling field is 150 MV/m with a sinusoidal wave function. Continuous bipolar D-E loops at 30, 90, and 150 MV/m under poling frequencies of 1000, 100, 10, and 1 Hz are shown for comparison. The double frequency for the unipolar loops makes sure that the poling time of each unipolar loop is the same as that of the first half bipolar loop, i.e., 50 ms.

The first unipolar loop nearly overlaps with the first half bipolar loop for the PP/BT@TiO2@POSS 80/20 50c film. Subsequent unipolar loops become slimmer. These results are similar to those for the PP/BT@POSS 80/20 film; however, the 2nd-3rd unipolar loops are much slimmer for the PP/BT@TiO2@POSS 80/20 50c film. This suggests that the 50 cycles of amorphous TiO2 coating effectively blocked the boundary layer conduction from space charges. Nonetheless, there is still certain bulk conduction, which cannot be
fully eliminated by the TiO$_2$ coating. In the future, it is desired to search for much more insulating ceramic nanoparticles with high permittivity.

13. TEM Characterization of BT$@$TiO$_2$ 200c NPs and Dielectric Properties of the PP/BT$@$TiO$_2$@POSS 80/20 200c Nanocomposite

Figure S2.24. Bright-field TEM micrographs for BT$@$TiO$_2$ 200-cycle NPs at (A) low and (B) high magnifications. (C) The corresponding PP nanocomposites at 20 vol.% filler content.
After 200 cycles of ALD, the TiO$_2$ layer is about 20 nm thick on the BT NP (Figure S2.24A). Under high magnification (Figure S2.24B), most of the TiO$_2$ layer becomes crystalline. From the Raman result in Figure S2.5A, the crystalline TiO$_2$ is in the anatase phase. From the magnified box in Figure S2.24B, the $d_{100}$ (~0.4 nm) of the cubic BaTiO$_3$ and $d_{200}$ (~0.2 nm) of the anatase TiO$_2$ are seen. After coating with POSS(PA)$_2$ ligands (see Figure S2.21), the BT@TiO$_2$@POSS 200c NPs are relatively uniformed dispersed in the PP matrix (Figure S2.24C).
**Figure S2.25.** (A-C) Temperature- and (D-E) frequency-scan BDS results for the hot-pressed PP/BT@TiO$_2$@POSS 80/20 200c film: (A and D) $\varepsilon'$, (B and E) $\varepsilon''$, and (C and F) tan$\delta$.

**Figure S2.26.** Continuous four unipolar D-E loops for the hot-pressed PP/BT@POSS 80/20 200c films at room temperature under various frequencies: (A) 2000 Hz, (B) 200 Hz, (C) 20 Hz, (D) 2 Hz, and (E) 0.4 Hz. The poling field is 150 MV/m with a sinusoidal wave function. (F) Comparison of discharge efficiencies for the bipolar, the first unipolar, and the fourth unipolar loops for the PP/BT@TiO$_2$@POSS 80/20 200c film under various test frequencies. Continuous three bipolar D-E loops at 30, 90, and 150 MV/m under poling frequencies of 1000, 100, 10, 1, and 0.2 Hz are shown for comparison. The double
frequency for the unipolar loops makes sure that the poling time of each unipolar loop is the same as that of the first half bipolar loop (50 ms).

In order to differentiate whether this internal conduction is a surface electrode phenomenon because of charge injection or a truly bulk property. We dip coated both sides of the BT@POSS/PP (80/20) composite film with thin polystyrene (PS) layers to block the possible charge injection from electrodes. The D-E loops are shown in Figure S2.27. We can still observe the similar unipolar/bipolar difference and huge AC dielectric loss as the film without PS blocking layer shows from previous D-E loops. It indicates that the AC dielectric loss should be attributed to bulk interfacial effect, not a electrode charge injection.

![Figure S2.27](image)

**Figure S2.27.** (A) Continuous four bipolar D-E loops for the PS dip-coated PP/BT@POSS 80/20 film at room temperature under 10 Hz poling frequency (100 ms); (B) unipolar D-E loops for the PS dip-coated PP/BT@POSS 80/20 film at room temperature under 20 Hz poling frequency (50 ms).

In addition, 200 cycles of ALD coating of TiO$_2$ was applied to BT NPs, and the corresponding TEM micrographs are shown in Figures S2.24A/B. Crystalline TiO$_2$ domains are observed on the BT NP surface, and are approved to be the anatase phase (see the Raman result in Figure S2.5A). After coating with POSS(PA)$_2$, again a double layer of POSS molecules was obtained for the BT@TiO$_2$@POSS 200c NPs (see the FTIR and TGA results in Figure S2.21). Using these NPs, the PP/BT@TiO$_2$@POSS 80/20 200c
nanocomposite was prepared, and the corresponding TEM micrograph in Figure S2.24C shows relatively uniform dispersion of NPs. The nanocomposite exhibited an apparent dielectric constant of 5.86 with a reasonably low dissipation factor of \(\tan\delta = 0.0036\) at 1000 Hz and RT (see Figure S2.25). The high field dielectric performance of this nanocomposite is studied by both bipolar and unipolar D-E loops (see Figure S2.26), and the discharge efficiency results are summarized in Figure S2.26F. Compared to the PP/BT@POSS 80/20 nanocomposite (Figure 2.6D), the discharge efficiencies for both bipolar and the fourth unipolar loops were higher for the PP/BT@TiO@POSS 80/20 200c nanocomposite, when the poling frequency is above 10 Hz, indicating that the ALD of 200 cycles of anatase TiO\(_2\) was effective in reducing the internal AC conduction loss at high frequencies. However, at lower frequencies (<10 Hz), significant nonlinearity in the bipolar and unipolar D-E loops was observed (Figures S2.26D and E), resulting in even lower discharge efficiency (Figure S2.26F). Judging from the upshift in the upper part of the bipolar D-E loops, there must exist significant external DC conduction at low poling frequencies. This is confirmed by the leakage current result in Figure S2.16. Namely, the PP/BT@TiO@POSS 80/20 200c nanocomposite exhibited the highest conductivity among all samples studied. This can be attributed to the ALD anatase TiO\(_2\) with certain oxygen vacancies\(^\text{S12,S13}\), resulting a higher conductivity than the amorphous TiO\(_2\).

### 14. Search for High Permittivity and Low Conductivity Ceramic Particles

**Table S2.1.** Permittivity, Highest Bulk Resistivity, and Band Gap for Various Ceramic Particles.

<table>
<thead>
<tr>
<th>Ceramics/Polymers</th>
<th>Permittivity ((\varepsilon_r))</th>
<th>Highest bulk Resistivity ((\Omega \cdot m))</th>
<th>Bandgap ((eV))</th>
<th>Refs.</th>
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<td>BN</td>
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2. [http://accuratus.com/boron.html](http://accuratus.com/boron.html)


To avoid internal AC conduction, much more insulating (ideally, $\rho > 10^{13} \, \Omega \cdot m$ or comparable to that of insulating polymers) ceramic particles with a high dielectric constant (at least $\varepsilon_r > 100$) should be useful for viable polymer nanodielectrics. However, to the best of our knowledge, such ceramic particles have not been found or even produced. Fundamentally, high permittivity and low conductivity often do not work together because of the mechanism of space charge-limited conduction current. The current density $J$ is proportional to the permittivity $\varepsilon$. This means the higher the permittivity, the higher the concentration of space charges and thus the higher the bulk conductivity. Here, we list the permittivity, resistivity, and band gap for a number of ceramics and polymers in Table S2.1.
From Table S2.1, a rough inverse trend of high permittivity and low bulk resistivity is seen for various ceramics, regardless of the band gaps. Actually, TiO$_2$-based ceramics are used commercially for Class 1 ceramic capacitors because of their high resistivity. However, the permittivity and thus the volume efficiency are low. BaTiO$_3$-based ceramics are used commercially for Class 2 ceramic capacitors because of their high permittivity and thus high volume efficiency. However, the resistivity is relatively low and the permittivity is temperature sensitive. Currently, no ceramics with both high permittivity and high resistivity have been found for ceramic capacitors.

Given this said, we currently do not have a viable candidate particle to be embedded in the polymer matrix. However, we expect future development of these high $\varepsilon_r$ and low conductivity ceramic particles in nanoscience to be used for future polymer nanodielectrics.

References


Appendix B

For

The Role of Field Electron Emission in Polypropylene/Aluminum Nanodielectrics under High Electric Fields
1. Experimental Section

1.1. Materials. Aluminum nanoparticles (nAl NPs, 18 nm, laser synthesized, specific surface area (SSA) >60 m²/g; 100 nm, electrical explosion synthesized, SSA ~ 10-20 m²/g) were purchased from U.S. Research Nanomaterials, Inc. The nAl NPs were stored in a glove box and used directly for surface modification without further purification. Poly(ethylene-co-1,2-butylene) mono-ol (PEB-OH, \(M_n=4,200\) g/mol, PDI=1.07) was purchased from Sigma Aldrich. The ethylene and 1-butylene contents were determined by \(^1\)H NMR to be 0.67 and 0.33, respectively. Diethylphosphonate acetic acid (DEPA), N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and bromotrimethylsilane (TMSBr) were also purchased from Aldrich and used as received. All solvents were purchased from Fisher Scientific (Pittsburgh, PA) and used without purification.

1.2. Synthesis of PEB-Diethylphosphonate Ester (PEB-PE). Dichloromethane (DCM) was dried with CaH₂ powder overnight and distilled before use. An oven-dried (80 °C) three-necked round-bottom flask charged with a stirring bar was cooled down under a nitrogen stream. PEB-OH (1 eq., 1.5 g, 0.36 mmol), DMAP (0.2 eq., 8.8 mg, 0.072 mmol), and DEPA (1.5 eq, 0.106 g, 0.54 mmol) were dissolved with 25 mL anhydrous DCM. The mixture was stirred and purged with N₂ for 30 min. Then, DCC (1.5 eq. 0.11 mg, 0.54 mmol) in 5 mL DCM was dropwise added into the mixture at 0 °C (cooled using an ice/water bath). Soon, white precipitation was seen and the system became light yellowish. The reaction was held for 48 h in order to increase the yield of chain-end functionalization. After filtering out white byproduct, dicyclohexylurea (DCU), the solution was concentrated by evaporation of the solvent using a rotary evaporator. The concentrated oily raw product was re-dissolved in \(n\)-hexane and put in a refrigerator (-20 °C) overnight to further crystallize the residue DCU. The crystallized DCU was filtered and the \(n\)-hexane was evaporated again. The raw product was dissolved in toluene and precipitated into methanol (MeOH). This dissolution-precipitation process was repeated twice. Then, the relatively pure product was subjected to fumed silica column chromatography using \(n\)-hexane:ethyl acetate (1:1 v/v) as the eluent and iodine as the staining indicator.

1.3. Synthesis of PEB-Diphosphonic Acid (PEB-PA). 0.36 mmol of thoroughly dried PEB-PA in 25 mL of anhydrous DCM were cooled with an ice/water bath to 0 °C under nitrogen. 1.44 mmol of TMSBr was dropwise added into the mixture. Then, the ice/water bath was removed to let the mixture warm up to room temperature. The reaction last 24 h. Afterwards, volatiles were evaporated using a rotary evaporator to yield a light yellow oil. The raw product was re-dissolved in a tetrahydrofuran (THF)/MeOH/water ternary solvent to convert the trimethylsilyl groups into the hydroxyl groups. The mixture was stirred for 3-4 h at room temperature. Thereafter, all solvents were removed by rotary evaporation to give a yellow, viscous oil. The final product was purified by repeated precipitation in excess MeOH.

The \(^1\)H-NMR spectra of PEB-OH, PEB-PE and PEB-PA are given in Figure S3.1. The reaction could be monitored by noticing the chemical shift of the methine proton (a, CH) adjacent to the chain end -OH group. After esterification of the -OH groups with DEPA, the original proton signal at about 3.68 ppm would downshift to 4.18 ppm. Meanwhile, the triplet peak from the -CH₃ protons of the ethoxyl groups of DEPA (d), doublet peak from the -CH₂- protons directly linked to phosphorus atom (e) appeared at 1.35 and 2.9-
3.0 ppm, respectively. The peak from the -CH₂- protons of the ethoxyl groups of DEPA (b) added up to the peak from a, making it a multiplet peak. Compared to the NMR spectrum of the intermediate PEB-PE, that of the final hydrolyzed product PEB-PA showed little position change on protons a and c, but the disappearance of the peak from proton d. The two protons on phosphoric acid were difficult to observe due to deuterium exchange with CDCl₃. The common hydrolysis condition (MeOH/CH₂Cl₂) was less efficient to completely convert the esters to phosphonic acids. Therefore, we added water and THF in MeOH to completely convert the esters to phosphonic acids. As seen in Figure S3.1, the peak from proton d totally disappeared.

![Figure S3.1. ¹H NMR spectra of (A) PEB-OH, (B) PEB-PE and (C) PEB-PA hydrolyzed using a MeOH/H₂O/THF mixture solvent. (D) is the PEB-PA obtained by hydrolysis in the methanol/methylene chloride mixture solvent. The solvent is CDCl₃.](image)

1.4. Surface Modification of nAl NPs with PEB-PA. 2.5 g of nAl NPs (100 nm or 18 nm) were weighed and transferred into a 250 mL round-bottom flask in a glove box. 4 g of PEBPA was dissolved into 200 mL of anhydrous toluene. The solution was purged with N₂ for 40 min and transferred into the flask containing nAl NPs via a cannula. The mixture was sonicated using a 300 W ultrasonicication bath (Fisher Scientific, FS30) for 2 h, and then treated with an ultrasonic homogenizer probe (diameter 13 mm, Sonics & Materials, Inc., Newton, CT) for a total of 9 min. Afterwards, the suspension was purged with N₂ for 30 min and immersed into a silicon oil bath at 60 °C under rigorous stirring for 24 h. The large nAl aggregates were removed by centrifugation at 1,500 rpm for 6 min (3,000 rpm for 18 nm). Well-dispersed nAl@PEB-PA particles were obtained by further centrifugation at 7,500 rpm for 30 min and washed with toluene thoroughly to remove
impurities and physisorbed PEB-PA. The yields of well-dispersed nAl@PEB-PA particles were about 70% for the 100 nm nAl NPs and 50% for the 18 nm nAl NPs.

1.5. Nanocomposite and Film Preparation. After centrifugation at 7,500 rpm and repeated washing, the purified nAl@PEB-PA particles (~1.8 g) were re-dispersed in 100 mL of xylene with the help of ultrasonication. Meanwhile, a predetermined amount of PP resin (Dow Chemical, H349-02, melt flow index of 2 g/10 min) was dissolved in 60 mL of xylene at 140 °C and poured into the nAl@PEB-PA suspension. The mixture was stirred at 140 °C for 5 min to ensure a good mixing. The hot PP/nAl@PEB-PA suspension was poured into cold methanol (cooled using an acetone/dry ice bath at -78 °C) under stirring. Finally, the co-precipitated nAl@PEB-PA master batch was retrieved by centrifugation at 6,000 rpm for 5 min. The pre-mix was first dried in a fume hood for overnight, followed by cutting into small pieces and drying in a vacuum oven at 80 °C for 3 d. The dried master batch was further melt-processed using a HAAKE™ MiniLab II Micro Compounder (Thermo Scientific, Waltham, MA). To ensure uniform particle dispersion in the PP matrix, the temperature of the minilab was gradually decreased from 192 °C to 170 °C during the compounding process to maintain suitable melt viscosity. The concentrated master batch was further diluted with neat PP resin using minilab compounding to obtain nanocomposites with lower filler contents of 2.5-18 vol.%. Thermogravimetric analysis (TGA) measurements were performed to determine accurate volume fractions of nAl NPs in the nanocomposites, assuming densities of nAl particles and PP are 2.7 and 0.90 g/cm³, respectively. The melt-compounded nanocomposites were weighed and put in between two Kapton films. One layer of aluminum foil (~27 µm) was used as spacer to control the sample thickness during compression molding. The hot-press temperature was set at 172 °C and a 10-ton pressure was applied. The final hot-pressed film thicknesses were between 25 to 40 µm.

1.6. General Characterization. ¹H and ¹³C NMR spectra were collected on a Varian Mercury 600 MHz spectrometer with CDCl₃ as the solvent and trimethylsilane (TMS) as the internal reference. Fourier transform infrared (FTIR) spectra were recorded using a Bomen Michelson MB100 infrared spectrometer at a resolution of 2 cm⁻¹. IR pellets were made by grinding solid samples with dry potassium bromide (KBr) powder and pressed with a hydrodaulic press at 4 tons (or 5 MPa). TGA was carried out on a TA instruments Q500 thermogravimetric analyzer at a heating rate of 10 °C/min under a dry nitrogen flow. Powder X-ray diffraction (XRD) was performed on a Bruker diffractometer using the Cu Kα radiation (wavelength of 0.15418 nm).

1.7. Transmission Electron Microscopy (TEM) Characterization. Nanocomposite films were embedded in the standard epoxy using a silicone rubber mold (Ted Pella, Inc., Redding, CA). The standard epoxy with nanocomposite films were cured at 80 °C in a gravity oven for overnight. The cured epoxy block was roughly trimmed using a razor blade, and then finely trimmed using a freshly cleaved glass knife to obtain a small block surface (less than 0.5×0.5 mm²) with the embedded nanocomposite films in the middle. The finely trimmed block were cut by a Pelco® diamond knife (Ted Pella, Inc.) at -30 °C using a Leica EM UC6 ultramicrotome equipped with a cryo FC6 unit (Leica Microsystems, Inc., Buffalo Grove, IL). Thin slices about 70-100 nm were floated onto the surface of a trough filled with a dimethylsulfoxide (DMSO)/water 1:1 solution and collected using 400-mesh copper TEM grids. For characterization of neat nanoparticles, dilute dispersion was
drop-cast onto carbon-coated TEM grids. After solvent evaporation, the samples were dried using the house vacuum before TEM observation. Conventional TEM was performed on an FEI Technai 12 electron microscope operated at an accelerating voltage of 100 kV. A bottom-mounted Gatan CCD camera was used to record the digital images.

1.8. Broadband Dielectric Spectroscopy (BDS) Measurements. BDS was performed on a Novocontrol Concept 80 broadband dielectric spectrometer with temperature control. The applied voltage was $1 V_{\text{rms}}$ (root-mean square voltage) with frequencies ranging from 0.002 Hz to 1 MHz and temperatures ranging from -55 to 110 °C. Silver electrodes (50 nm thick and area of 0.785 cm$^2$) were evaporated on both sides of the film using a thermal evaporator (EvoVac Deposition System, Angstrom Engineering, Inc.).

1.9. Breakdown Strength Measurement. The breakdown strength of nanocomposite films was determined using a home-made fixture. Silver electrodes of 50 nm thickness and 5.15 mm$^2$ area were thermally deposited on both sides of the film. The voltage was supplied by a Quadtech (Marlborough, MA) Guardian 20-kV HiPot tester, and was ramped at a speed of $50 \text{V/(s \cdot \mu m)}$ until dielectric breakdown. All breakdown tests were carried out in a silicone oil bath to reduce surface corona discharge. At least twenty-five repetitions were measured for each sample for Weibull statistical analysis.

1.10. Electric Displacement-Electric Field (D-E) Loop and Leakage Current Measurements. The D-E hysteresis loop measurements were carried out using a Premiere II ferroelectric tester (Radiant Technologies, Inc.) equipped with a Trek 10/10B-HS high voltage amplifier (0-10 kV AC). The applied voltage had a bipolar sinusoidal waveform at 10 Hz. Tests were performed in silicon oil bath at room temperature. Silver with 50 nm thickness and area of 5.15 mm$^2$ were coated as electrodes on both sides of the film. The leakage current studies were also measured using the Premiere II ferroelectric tester. A period of 21 s was used as both the soaking and measurement times to lower the transient current and avoid breakdown during test.
Figure S3.2. TGA curves for (A) 18 nm nAl NPs and nAl@PEB-PA NPs, and (B) 100 nm nAl NPs and nAl@PEB-PA NPs. (C) TGA curves for 18 nm nAl@MPS and nAl@PEB NPs synthesized via thiol-ene click reaction. (D) TEM micrograph of a thin section of the PP/18 nm nAl nanocomposite with 3.1 vol.% NPs.

2. Determination of PEB-PA Grafting Densities on 18 and 100 nm nAl NPs

As we known, Al can react with air and nitrogen to produce Al₂O₃ and AlN byproducts, respectively. Therefore, TGA experiments need to be performed in an argon atmosphere. It was interesting to see that bare nAl NPs gradually gained weight above 300-350 °C, making TGA curves going up after the major weight loss around 400 °C (Figures S3.2A-C). This weight-gaining TGA result was also reported by Arranz-Andrés et al. for their PP/Al nanocomposites in an inert atmosphere (Ar). Since argon is highly inert and will not react with nAl, it is reasonable to propose the following reason. Argon molecules must have diffused into the interstitial sites of FCC Al crystals at elevated temperatures, which is similar to helium diffusion into Al crystals and nitrogen diffusion into Ti crystals. The adsorbed Ar molecules accounted for the gained weight for nAl NPs. Above the PEB-PA degradation between 350-450 °C, surface modified nAl@PEB-PA NPs also exhibited the weight-gaining TGA curves (Figures S3.2A-C). The grafting density (σ) of the PEB-PA brushes can be calculated using the following equation:

\[
\sigma = \left( \frac{\Delta \text{wt.\%}}{100 - \Delta \text{wt.\%}} \right) \times \left( \frac{6.02 \times 10^{23}}{M\text{W} \times \text{SSA}} \right)
\]

(S3.1)

where Δwt.% is the weight loss due to PEB-PA degradation compared between the bare nAl NPs and surface-modified nAl@PEB-PA NPs, and MW is the molecular weight of the polymer. At 455 °C, 98.5 wt.% of PEB-PA thermally decomposed (Figure S3.2A).
corrected Δwt.% values for the 18 nm and 100 nm nAl@PEB-PA NPs were 7.4 wt.% and 7.7 wt.% respectively. The SSA values for the 18 and 100 nm nAl NPs based on the particle size distribution data obtained from TEM were 30 m²/g (32 m²/g from BET measurement) and 12 m²/g, respectively. Accordingly, the grafting density (σ) for the 18 nm and 100 nm nAl NPs were calculated to be 0.36 and 0.99 chain/nm², respectively.

**Scheme S3.1.** Grafting PEB-SH polymers onto nAl NPs via the thiol-ene click reaction.

The thiol-ene click reaction was also performed in order to compare the efficiency of condensation grafting of PEB-PA. First, the chain end of PEB-OH was thiolated with 3-mercaptopropionic acid to yield PEB-SH. The 18 nm nAl NPs were treated with 3-(trimethoxysilyl)propyl methacrylate (3-MPS) to attach vinyl groups, yielding nAl@MPS NPs. Reaction of nAl@MPS NPs with PEB-SH in the presence of azobisisobutyronitrile (AIBN) yielded nAl@PEB-SH. The grafting densities of 3-MPS and thiolated PEB determined by TGA were 1.9 and 0.38 chain/nm², respectively. The result of thiol-ene click grafting reaction was close to that of the condensation grafting reaction, suggesting that the steric hindrance prevented a dense grafting of PEB brushes onto the surface of the 18 nm nAl NPs. Therefore, it seemed that the grafting density could not be further increased more than 0.36-0.38 chains/nm² for the small 18 nm nAl NPs. Particles with too low grafting density should be avoided, because sparse polymer brushes were unable to prevent NPs from aggregating together.
Figure S3.3. Temperature-scan BDS results of PP/18 nm nAl nanocomposites with (A-C) 3.1 vol.%, (D-F) 5.3 vol.%, and (G-I) 10.5 vol.% 18 nm nAl NPs at various frequencies: (A,D,G) $\varepsilon'$, (B,E,H) $\varepsilon''$, and (C,F,I) $\tan\delta$. 
Figure S3.4. Frequency-scan BDS results of PP/18 nm nAl nanocomposites with (A-C) 3.1 vol.%, (D-F) 5.3 vol.%, and (G-I) 10.5 vol.% 18 nm nAl NPs at different temperatures: (A,D,G) $\epsilon'$, (B,E,H) $\epsilon''$, and (C,F,I) tan\(\delta\).
Figure S3.5. Temperature-scan BDS results of PP/100 nm nAl nanocomposites with (A-C) 5.3 vol.%, (D-F) 10.8 vol.%,(G-I) 18.3 vol.%, and (J-L) 25.0 vol.% 100 nm nAl NPs at various frequencies: (A,D,G,J) $\varepsilon_r'$, (B,E,H,K) $\varepsilon_r''$, and (C,F,I,L) tan$\delta$. 
Figure S3.6. Frequency-scan BDS results of PP/100 nm nAl nanocomposites with (A-C) 5.3 vol.%, (D-F) 10.8 vol.%, (G-I) 18.3 vol.%, and (J-L) 25.0 vol.% 100 nm nAl NPs at different temperatures: (A,D,G,J) $\varepsilon'$, (B,E,H,K) $\varepsilon''$, and (C,F,I,L) $\tan\delta$. 
Figure S3.7. Five continuous bipolar D-E loops (10 Hz) for the PP/100 nm nAl nanocomposites with (A) 5.3 vol.%, (B) 10.8 vol.%, and (C) 25.0 vol.% nAl NPs, and the PP/18 nm nAl nanocomposites with (D) 3.1 vol.% and (E) 5.3 vol.% nAl NPs.

Figure S3.8. (A) Charged energy densities ($U_e$) for PP and various PP/18 nm nAl nanocomposites. (B) Charged $U_e$s for various PP/100 nm nAl nanocomposites. Results obtained from the D-E loops measured at room temperature.

References
Appendix C

For

Thermally stable metallic nanoparticles prepared via core-crosslinked block copolymer micellar nanoreactors
**Figure S4.1.** TEM micrographs of (A) non-crosslinked PS$_{135}$-P4VP$_{154}$-PS$_{135}$ micelles swollen by anhydrous hydrazine, (B) reduction of Au NPs by dropwise adding anhydrous hydrazine into the micelle solution, and (C) reduction of Au NPs by hydrazine monohydrate.
Reference:


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