GLASS FORMATION BEHAVIOR OF MODEL IONOMERS

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Dihui Ruan

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ABSTRACT

Ionomers – polymers with bonded ionic groups – are important because of their wide applications in various fields. The glass formation behavior of ionomers has direct impact on their properties and performance, and therefore demands a deeper understanding. The ionic groups collapse into distributed ionic aggregates in the ionomers. The region surrounding the aggregates shows dynamic suppression among uncharged polymer chains, and the size of this region is correlated to chains’ persistence length. This phenomenon is a consequence of the fact that there is bond connectivity between aggregates and polymers, which differs from materials with only non-bonded interfaces, like composites. Here, we perform molecular dynamics simulations of model ionomers to test this conventional view and propose a fundamental reconsideration of grafted micro-phase materials like ionomers. Based on our results, the covalent grafts are not the central factor determining linear segmental dynamics and glass formation. Instead, we find that they are equivalent to strong physical attractions, as in ungrafted nanocomposites and nanoconfined glass-formers, where near-interface mobility suppression is mediated by cooperative rearrangements intrinsic to glass-forming liquids, rather than by a unique covalent ‘tethering effect’. This conclusion indicates the need for a revised understanding of glass formation and segmental dynamics in materials incorporating covalent grafting.
DEDICATION

To
My Family
AKNOWLEDGEMENTS

I would like to thank my advisor, Dr. David S. Simmons, for his patience and friendliness in leading me not only on the path of my research but also on other parts of my life and career. Also, I’m thankful to my other committee members: Dr. Kevin A. Cavicchi for discussion on the structure of ionic aggregates, and Dr. Robert A. Weiss for suggestions on the manuscript. Finally, I would like to thank all my colleagues, friends, and family for supporting my research.
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CHAPTER I
INTRODUCTION

Ionomers – ion-containing polymers – have received attentions from academics and industry for decades because they are widely applied in the fields of elastomers\textsuperscript{1,2}, dental composites\textsuperscript{3–7}, electrolytes\textsuperscript{8,9}, fuel cells\textsuperscript{10,11}, and golf balls\textsuperscript{12,13}. Throughout the ionomer, ionic groups mixed with neutralizers undergo aggregation via a micro-phase separation driven by the polar ions and nonpolar polymers, and also balanced by the electrostatic force of ions and elastic force from polymer chains.\textsuperscript{14–17} The ionomer’s glass formation, reflecting its linear-regime segmental dynamics, has a huge impact on the properties and performance of the material, such as transport\textsuperscript{18–20} and mechanical\textsuperscript{21–23} properties that are central to most applications. Since polymer chains are connected to aggregates via covalent bonds, the glass formation behavior of ionomers also raises profound questions regarding the physical origin of glass-forming dynamics in soft materials with micro-phase grafts, such as grafted nanoparticle composites, substrate-bonded films, and semi-crystalline polymers or copolymers.

The existence of ionic aggregates, formed by the collapse of the bonded ionic groups and neutralizers, are directly shown by small-angle x-ray scattering (SAXS), where there is a peak located at a small scattering angle.\textsuperscript{24} This peak is therefore called the ‘ionomer peak’ as a common feature of ionomers, illustrating the long-distance inter-
aggregate spacing correlation\textsuperscript{14–16}. As is postulated by Eisenberg\textsuperscript{25}, the ionic groups can collapse into ionic aggregates either including or excluding polymer chains, investigated under dielectric\textsuperscript{26}, infrared\textsuperscript{27,28} and Raman\textsuperscript{29} measurements. Both the interpretation of the ‘ionomer peak’ and the existence of polymer-included aggregation are validated by a famous hard-sphere model modified by Yarusso and Cooper\textsuperscript{30}, based on the core-shell model established by Macknight \textit{et al.}\textsuperscript{31}, that any two spherical ion-rich domains are separated by surrounding shells composed of uncharged polymer chains. However, the intra-aggregate structure is less clear, partly as a result of the small size of aggregates (1~150nm)\textsuperscript{32,33}, which are constrained by the balance among ion interaction, steric hindrance from polymer chains, interfacial tension or interaction, and possible crystallinity.\textsuperscript{34} It is worth noting that a lamellar model\textsuperscript{24}, deviating from the commonly-believed spherical shape of ionic aggregates and including a short-range intra-aggregate correlation, has been originally proposed by Macknight’s group to track the features in SAXS. Both the structure and the size of these ionic aggregates are sensitive to the polymer backbond, the placement and randomness of the ionic groups in the polymer chain, the type of the ionic group and neutralizer, and the degree of neutralization.\textsuperscript{4,22,35–37}

With respect to computational studies on ionomers, ionic aggregates, including only ions, have been investigated as an extended, unordered stringy structure at relatively high temperature within both coarse-grained and atomistic molecular dynamics (MD) simulations\textsuperscript{38–42}; additionally, Goswami and his coworkers\textsuperscript{43} have reported that ionic aggregates self-assemble into a condensed, well-ordered plane with two layers at low temperature. This structure can be understood as a planar model with a small lateral
extent with uncharged polymer chains located above and below, modified from the lamellar model of Macknight et al.\textsuperscript{24}

The ionic aggregates collapse into a condensed, well-ordered structure from a relatively extended, disordered one via a self-assembly transition, observed by a high-temperature relaxation process within the simulation by Goswami et al.\textsuperscript{43} and termed as a ‘second $T_g$’. However, in physical experiments, the high temperature of an additional relaxation, investigated by a broad peak within mechanical response\textsuperscript{44–46}, is interpreted as the $T_g$ for those polymer chains whose dynamics are reduced by ionic aggregates. The introduction of ionic aggregates into the polymer matrix yields an enhancement in ionomers’ glass transition temperature $T_g$\textsuperscript{18,22,44–47} via a strong spatial gradient in suppressed dynamics approaching aggregates\textsuperscript{45,48,49}. The $T_g$ of ionomers is more greatly enhanced with increasing ion concentration\textsuperscript{44,45,50}, with an increase in the range of 1.2–5.9°C per mole of ionic groups\textsuperscript{48}. This suppression in segmental dynamics has often been attributed to the crosslinking role played by ionic aggregates.\textsuperscript{14,51–53} This crosslinking effect is emphasized by Eisenberg, Hird, and Moore\textsuperscript{17}, who suggest that the range of the restricted-mobility region surrounding the ionic aggregates is correlated with the stiffness of the polymer chains, characterized by the persistence length. This EHM model has since become a predominant view of the structure and dynamics of ionomers. Since the persistence length is nearly temperature independent, we note that this view also implies that the size of the reduced-dynamics domain around aggregates should be insensitive to temperature.
The above view represents a significant difference from the behavior of materials near non-bonded interfaces. In these systems, similar alterations in glass transition temperature and the spatial gradient in dynamics have also been also found in nanoconfined materials, such as thin films\textsuperscript{54–56} and nanoparticle composites\textsuperscript{57–59}. According to simulations done by Betancourt et al.\textsuperscript{59}, $T_g$ is enhanced in nanoparticle polymer composites with attractive interfaces, induced by a gradient in dynamics around the nanoparticle with respect to the bulk polymer. The comparability of the gradient in dynamics between ionomers and nanoconfined materials is explained by their similar morphology as heterogeneous systems, according to Tsagaropoulos and Eisenberg\textsuperscript{44,46}. In contrast, for these nanoconfined materials, the effective range of the dynamics gradient has been found in simulation to exhibit a roughly Arrhenius dependence on temperature, and is correlated to the size of cooperatively rearranging regions (CRRs) underpinning dynamics in fragile (non-Arrhenius) glass-forming liquids.\textsuperscript{57,59–61} These CRRs are defined as subsets of correlated moving particles whose arrangement is independent of the surroundings. It has been predicted by Adam and Gibbs\textsuperscript{62} that relaxation depends on temperature via the size of CRRs determined by the configurational entropy, as shown in the following equation:

$$
\tau_\alpha = \tau_0 \exp\left(\frac{z\Delta\mu}{k_BT}\right), \ (1.1)
$$

where $\tau_\alpha$ is segmental relaxation time, $\tau_0$ is vibrational relaxation time, $\Delta\mu$ is the limiting activation free energy, and $z$ is the size of CRRs evaluated as the average number of particles included in CRRs. Adam and Gibbs have not given a specific definition for the shape of the cooperatively rearranging regions (CRRs), leading to the difficulty in direct
characterization of the CRRs’ size. While in simulations\textsuperscript{46,61,63–65}, a string-like cooperative motion has been observed in simulations of glass formers, such that mobile particles in a string-shaped group move by replacing their former one’s position. The size of the ‘strings’ in this model, which captures most of the features of CRRs relevant to the dynamics, is computed by the mean string length, defined as the average number of particles included in the same string-like motion.\textsuperscript{63}

In nanoconfined materials, the chains’ stiffness, as characterized by the persistence length, is not central to the glass-forming dynamics, but it is a factor of the kinetic fragility, defined as the slope of an Arrhenius plot of relaxation time versus temperature at $T_g$ in an Angell plot:

$$m = \left[ \frac{d \log \tau_\alpha}{d \left( T_g / T \right)} \right]_{T=T_g}, \quad (1.2)$$

where $\tau_\alpha$ is the segmental relaxation time. It indicates how rapidly the relaxation is slowed down around $T_g$. For example, the fragility as well as the glass transition temperature $T_g$ of polymers generally grows with increasing stiffness of the backbond, as predicted in the generalized entropy theory\textsuperscript{66} of glass formation, which is an extension of the Adam-Gibbs theory\textsuperscript{62}.

With respect to the similar trends in dynamics within ionomers and nanoconfined materials, do covalent attachments fundamentally transform the physics by which an interface alters nearby segmental dynamics and glass formation, or are they essentially indistinguishable from strong physical adsorption for these purposes? A recent study by Papon and coworkers\textsuperscript{67} have reported that the existence of covalent bonds connecting the
polymers with the fillers is not essential to the dynamic gradient, with similar results in filler-grafted elastomers by Berriot\textsuperscript{68}. These results imply that the covalent bonds are, instead of central to the physical origin, equal to an adhesion to the surface of ionic aggregates in ionomers for the purpose of glass-forming dynamics. Is this really the case? If near-interface dynamics propagate \textit{via} intra-chain bond correlations, their size should mirror the typically weak temperature dependence of the chain persistence length, accompanied with a huge leap as a consequence of increasing stiffness; if the ‘cooperativity’ model dominates, their size should exhibit a strong, roughly Arrhenius, growth upon cooling instead.

To understand the nature of the impact of covalent grafting on the glass transition in ionomers, we perform molecular dynamics (MD) simulations on model ionomers with the ionic groups placed either on the end or the side of the uncharged backbond with varying the chain stiffness. Our discussions begin with a consistency check of the morphology of ionic aggregates compared with the results in previous experiments and simulations. We test the bond-centric view of the EHM model\textsuperscript{17} by comparing overall $T_g$ and spatial $T_g$ gradient among systems, accompanied with more general interfacial length scales defined from structural relaxation and vibration dynamics. Additionally, the size of CRRs is characterized by the mean string length \textit{via} a well-established protocol developed in the string model\textsuperscript{69,65,70} and is then compared with the interfacial length scales. Finally, a test on Adam-Gibbs theory is performed in terms of the mean string length and the interfacial length scale. These results prove that the chain connectivity between the polymer chains and the ionic aggregates is not critical for the purpose of
glass formation in ionomers; rather, the glass formation of ionomers is consistent with that of nanoconfined materials.
CHAPTER II

METHODOLOGY

Simulation Model

We perform molecular dynamics (MD) simulations of coarse-grained bead-spring model ionomers within the LAMMPS\textsuperscript{17,27,31} (Large-scale Atomic/Molecular Massively Parallel Simulator) environment, in order to study (pendant/semi-telechelic) ionomers’ glass formation.

Figure 2.1 Schematics of the pendant (a) and the semi-telechelic (b) ionomer models including neutral monomer beads (blue), anion beads (light grey), and free cation beads (black).

As shown in Figure 2.1, model ionomers are composed of 20 neutral beads on each backbond, designed to compare with 20-bead linear homopolymers. To make the pendant and semi-telechelic ionomers, an anion bead (-1e) is bonded to either the 10\textsuperscript{th} or the 20\textsuperscript{th} uncharged bead on each chain. Within (either pendant or semi-telechelic) ionomer simulations, 100 ionomer chains are 100% neutralized by cation beads (+1e), while a
50/50 pendant ionomer/homopolymer blend is additionally simulated for the purpose of a dilute ionomer system.

Interactions among beads are computed in Lenard-Jones (LJ) non-dimension units\textsuperscript{71} based on an attractive extension of the Kremer-Grest model\textsuperscript{72} commonly employed to study polymers’ glass formation. Within these models, bonded beads interact \textit{via} a standard finitely extensible nonlinear elastic (FENE) potential\textsuperscript{71,72}:

\[
E_{\text{bond}} = -0.5K_{\text{bond}}R_0^2 \ln \left[1 - \left(\frac{r}{R_0}\right)^2\right], \quad (2.1)
\]

where spring constant \(K_{\text{bond}}\) is \(30\varepsilon / \sigma^2\), maximum extent of the bond \(R_0\) is \(1.5\sigma\), and \(r\) is distance. Bonds’ angles are computed \textit{via} a cosine angular potential\textsuperscript{71}:

\[
E_{\theta} = K_\theta \left[1 + \cos(\theta)\right], \quad (2.2)
\]

where bending coefficient \(K_\theta\) is set as 0, \(1.5\varepsilon\), and \(3\varepsilon\) for different bond stiffnesses\textsuperscript{73}. Non-bonded beads interact \textit{via} a 12/6 Lenard-Jones (LJ) potential\textsuperscript{71}:

\[
E_{\text{LJ}} = 4\varepsilon_{\text{LJ}} \left[\left(\frac{\sigma_{\text{LJ}}}{r}\right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r}\right)^6\right] \text{ for } r \leq R_c, \quad (2.3)
\]

where, \(\sigma_{\text{LJ}}\) sets the diameter with a cutoff distance \(R_c\) as \(2.5\sigma\). Charged beads additionally interact \textit{via} a Coulombic interaction potential\textsuperscript{71}, directly calculated within cutoff \(R_c = 8\sigma\) as:

\[
E_{\text{coul}} = \frac{q_i q_j \varepsilon_r}{4\pi\varepsilon_0 \varepsilon_r r} \text{ for } r < R_c, \quad (2.4)
\]

where \(q_i\) and \(q_j\) are charges of ion pairs, \(\varepsilon_0\) is vacuum permittivity, and \(\varepsilon_r (=4.0)\) is the dielectric constant. Longer-range Coulombic interactions beyond the cutoff \(R_c\) are
computed via a particle-particle particle-mesh (pppm) solver\textsuperscript{74}, with further optimization applied for the reason that most particles are uncharged in systems.

Based on the model based on poly(ethylene-co-acrylic acid) (PEAA) fully neutralized with sodium (Na\textsuperscript{+}) established by Hall \textit{et al.}\textsuperscript{38}, each neutral polymer bead is set as 1.0\(\sigma\) (\(\sigma \approx 0.4\text{nm}\)) in diameter, mapped to three CH\textsubscript{2} units (\(\sim 0.4\text{nm}\)) along a polyethylene backbond; the diameter of each monovalent anion and cation bead is scaled as 1.0\(\sigma\) and 0.5\(\sigma\) representing a COO\textsuperscript{–} group (\(\sim 0.4\text{nm}\)) and a Na\textsuperscript{+} (\(\sim 0.2\text{nm}\)). The masses of uncharged monomers, anions, and counterions are chosen to be 1.0, 1.0, 0.5 in LJ units respectively, based on their molar masses of 42, 44, and 23 g/mol. The time in LJ units \(\tau \approx 1\text{ps}\), and room temperature (300K) corresponds to \(T = 1.0\) in LJ units. By choosing the dielectric constant \(\varepsilon_r\) as 4.0, the fundamental electron charge \(e\) is converted into 11.80 in LJ units in order to obtain proper Coulombic and LJ interactions consistent with the properties of poly(ethylene-co-acrylic acid) (PEAA) fully neutralized with sodium (Na\textsuperscript{+}) for the purpose of glass formation.

We perform MD simulations on the pendant ionomer with \(K_\theta = 0\), a 50/50 blend of pendant ionomer with homopolymer with \(K_\theta = 0\), the semi-telechelic ionomer with \(K_\theta = 0\), the pendant ionomer with \(K_\theta = 1.5\), and the pendant ionomer with \(K_\theta = 3.0\), and in each case we compare results to simulations of the corresponding pure (charge-free) linear homopolymer with the same \(K_\theta\). For each system, four initial configurations are generated by Packmol\textsuperscript{75} (Packing Optimization for Molecular Dynamics Simulations) in a cubic simulation box. Simulations employ the Nose-Hoover thermostat and barostat\textsuperscript{71}.
within damping parameter 2.0 and a rRESPA\textsuperscript{76} integrator with a timestep of 0.005$\tau$ for non-bonded and 0.001$\tau$ for bonded interactions.

We begin each simulation with a $5\times10^4\tau$ run in the NPT ensemble at $T = 1.5$ and $P = 0$ for each configuration. The system is then quenched to a low temperature at a rate of $10^{-5}T/\tau$ and $P = 0$ with configurations saved at regular temperature intervals. For each saved configuration, an additional equilibration run is employed at $P = 0$ with the length of time varying from $10^4\tau$ for $1.0 < T \leq 1.5$ with selected $T$ interval 0.025 to $10^5\tau$ for $T < 1.0$ with selected $T$ interval 0.02. After that, the simulations boxes of four configurations at each temperature are deformed to an identical equilibrium density determined by the second half average of equilibration runs within $10^3\tau$, and then equilibrated for $10^3\tau$. Finally, data is collected in the NVT ensemble. This data is then analyzed via methods implemented in AMDAT\textsuperscript{77} (Amorphous Molecular Dynamics Analysis Toolkit), a MD analysis code written by Simmons’ Research Group.

Simulation Analysis

Average number of ions in an aggregate within simulated ionomer systems is calculated at each temperature as the total number of ions divided by the number of ion clusters, where a cluster is defined as a subset of ions within which the bonded anions (1.0$\sigma$) and the free cations (0.5$\sigma$) are continuously connected using a cutoff distance of 1.0$\sigma$ from one another, evaluated by a cluster computation implemented in LAMMPS\textsuperscript{71}.

Pair interaction energy among either ions or all the beads within each system is calculated based on thermodynamic data computed by LAMMPS\textsuperscript{71}, in order to track the calorimetry and investigate the transition upon cooling.
Static structure is quantified by the structure factor $S(q)$:\textsuperscript{78}

$$S(q) = \left(\frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-i q \cdot r_i) \exp(i q \cdot r_j)\right), \quad (2.5)$$

where $q$ is the wave vector and $r_i$ and $r_j$ are the positions of the $i^{th}$ and $j^{th}$ bead within the calculation among $N$ particles.

Free volume and vibrational dynamics are quantified by the Debye-Waller Factor $\left<u^2\right>$, defined as the length scale of a ‘cage’ within which particles rattle around. $\left<u^2\right>$ is calculated as the mean-squared displacement at a crossover time ($\sim 1\tau$) from ballistic to ‘cage’ limited motion, which is set as $0.99\tau$ in our systems\textsuperscript{79}. This important parameter has been proved as a measurement of free volume\textsuperscript{80} defined as the unoccupied volume in a system. A free volume theory relates this local packing into properties of glass formers, such as segmental relaxation given by:\textsuperscript{80}

$$\tau_\alpha \sim \exp\left[\left(\nu_c / \left<\nu_f\right>\right)^{2/3}\right], \quad (2.6)$$

where $\nu_c$ is a constant, $\left<\nu_f\right>$ is the free volume, and $\tau_\alpha$ is the segmental relaxation time.

Non-Gaussian behavior is quantified by the non-Gaussian parameter, calculated from the mean-squared displacement ($\left<r^2\right>$):

$$\text{non-Gaussian parameter} = \frac{3\left<r(t)^4\right>}{5\left<r(t)^3\right>^2} - 1, \quad (2.7)$$

the peak time of which is considered as the time when maximum cooperative motion takes place.\textsuperscript{70}
Segmental relaxation dynamics are quantified via the self-part of the intermediate scattering function $F_{\text{self}}(\mathbf{q}, t)$, which is comparable to characterization by time-resolved incoherent neutron scattering in experiments:

$$F_{\text{self}}(\mathbf{q}, t) = \frac{1}{N} \sum_{j} \left\{ \exp \left[ -i \mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)) \right] \right\}, \quad (2.8)$$

where $\mathbf{r}_j(t)$ and $\mathbf{r}_j(0)$ are the positions of particle $j$ at time $t$ and an initial time. Also, we employ wave number $q = 7.07$, comparable to the first peak in the structure factor of a standard FENE 20-bead linear homopolymer. The alpha segmental relaxation time $\tau_\alpha$ is defined as the time when $F_{\text{self}}(\mathbf{q}, t) = 0.2$, after employing a Kohlrausch-Williams-Watts (KWW) stretched exponential fit\textsuperscript{81,82} to smooth and interpolate the data after the fast beta relaxation (within 0.99$\tau$):

$$F_{\text{self}}(t)\big|_{q=7.07} = A \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right], \quad (2.9)$$

where $A$, $\tau$ and $\beta$ are fitting parameters.

The dynamic glass transition temperature $T_g$ is defined as the temperature threshold at which these simulations fall out of equilibrium within the timescale ($10^3 \tau$). In another word, the definition of $T_g$ in our study is the temperature at which the segmental relaxation time $\tau_\alpha = 10^3 \tau$. The $\tau_\alpha$ data, which is less than $10^3 \tau$, for temperatures less than 1.0 is fit to a Vogel-Fulcher-Tamman (VFT) form:\textsuperscript{83,84}

$$\ln \tau_\alpha = A + \left( \frac{DT_0}{T - T_0} \right), \quad (2.10)$$
where $A$, $D$, and $T_0$ are fitting parameters. The computational $T_g$ is then determined by a negligible extrapolation of this fit, since the data within the super-cooled region are considered as in-equilibrium from the simulations whose equilibration time is no less than $10^2\tau_a$ ($\tau_a \leq 10^3$ for $T \leq T_g$ ) within these systems at each temperature.

*The kinetic fragility index* $m$ is then defined as the slope on an Angell plot (Arrhenius) of $\tau_a$ at $T_g$:

$$m = \left[ \frac{d\log\tau_a}{dT_g/T} \right]_{T=T_g}.$$  \hspace{1cm} (2.11)

In order to compare some results in our simulation with physical experiments, we defined an extrapolated glass transition temperature ($T_g^{\text{EX}}$) by an extrapolation from the VFT functional form to a temperature at which $\tau_a = 10^{14}\tau$ ($\sim 10^2\tau$), which is comparable to the criterion in experiments to define the glass transition temperature. $T_g^{\text{EX}}$ is not usually used in our study, because the huge extrapolation involved can lead to aphysical trends. To keep the precision of our work, most of discussions are based on the computational $T_g$ defined above.

Additional local dynamics analyses on vibration and relaxation are performed on each subset of uncharged polymer beads by binning them as a function of the distance to their nearest ion at an initial time. For the purpose of discussion, we denote analyses only on bonded anion and counterion beads as ‘ion’ properties, while analyses on only uncharged polymer beads and all the particles within these systems are denoted as ‘monomer’ and ‘overall’ properties, respectively.
CHAPTER III
RESULTS AND DISCUSSIONS

Figure 3.1 (a): Plot of structure factor ($S_{\text{overall}}$) versus wave number ($q$) for all the particles in the systems at $T = 1.0$. (b): Plot of ion-ion structure factor ($S_{\text{ion-ion}}(q)$) versus wave number ($q$) from $q = 5$ to $q = 15$ for ions at $T = 1.3$ (dashed lines) and $T = 1.0$ (solid lines). The included systems are the pendant/homopolymer $K_\theta = 0$ (green), the semi-telechelic ionomer $K_\theta = 0$ (red), the pendant ionomer $K_\theta = 0$ (blue), the pendant ionomer $K_\theta = 1.5$ (purple), and the pendant ionomer $K_\theta = 3.0$ (grey).

Ionomer Morphology and Glass Transition

We perform MD simulations on ionomer systems with about 5mol% ionic groups bonded to the neutral backbone and an additional diluted system of the 50/50 pendant
ionomer/homopolymer blend with about 2.4mol% ionic groups for longer distance range among ionic aggregates, all fully neutralized with free counterions. The pendant ionomer and the semi-telechelic ionomer are employed to ascertain how the placement of ionic groups affects dynamics, while varying the bending coefficient ($K_\theta$) in the pendant model is aimed to clarify the correlation between chains’ stiffness and ionomers’ dynamics.

Figure 3.2 VMD snapshots for ionic aggregates at $T = 1.3$ (top) and $T = 1.0$ (bottom) in pure ionomer systems. Dark grey beads and silver beads represent for the bonded anions and the free cations respectively.
Figure 3.3 Snapshots of single ionic aggregates with grafted chains at $T = 1.0$ in the pendant ionomer (a) and the semi-telechelic ionomer (b) with polymer chains (colorful), bonded anions (silver), free cations (dark grey).

Figure 3.4 Plot of average number of ions in an ionic aggregate in the semi-telechelic ionomer $K_\theta = 0$ (●), the 50/50 pendant ionomer/homopolymer blend $K_\theta = 0$ (green ■), the pendant ionomer $K_\theta = 0$ (blue ■), the pendant ionomer $K_\theta = 1.5$ (▲), and the pendant ionomer $K_\theta = 3.0$ (♦).
The ‘ionomer peak’ around $q = 0.70/\sigma \sim 0.95/\sigma$ appears in all the systems with ionic groups in Figure 3.1(a), consistent with previous work on ionomers’ morphology\textsuperscript{14–16}. This peak at a low $q$ reflects the inter-aggregate correlations investigated by scattering data, which is a common feature of ionomers. Within these simulated systems, the mean distance among ionic aggregates is $6.6 \sim 8.8\sigma\left(2.6 \sim 3.5\text{nm}\right)$. The images made by the trajectories of ions in Figure 3.2 and the average number of ions in the aggregate from Figure 3.4 demonstrate that the size of ionic aggregates in the pendant ionomer with $K_\theta = 0$ is smaller compared with the other pure ionomer systems both at a higher $T$ and lower $T$. The formation of larger aggregates is attributed to the weakened entropy from polymer chains, caused by the reduction of chains bonded to each anion bead between the pendant ionomer (Figure 3.3(a)) and the semi-telechelic ionomer (Figure 3.3 (b)), as well as the increasing stiffness tuned by bending coefficient $K_\theta$. Also, these images and plots indicate an intriguing self-assembly transition at $T = 1.3 \sim 1.0$ in which relatively disordered extended ionic aggregates with changing sizes collapse into more ordered bilayer platelets with a more stable size upon cooling, found in the prior simulation by Goswami \textit{et al.}\textsuperscript{43} This high-temperature transition corresponds to a ‘peak-splitting’ behavior in the ion-ion structure factor at $q = 5/\sigma \sim 15/\sigma\left(0.17 \sim 0.50\text{nm}\right)$, in a wave number range reflecting the intra-aggregate correlation, as shown in Figure 3.1(b). As a sanity check, the heights of the two peaks corresponding to intra-aggregate correlation are evaluated in Figure 3.5 as an indirect characterization of the aggregate size. These results are consistent with the average number of ions in the aggregate as shown in Figure 3.4, in that the size of ionic aggregates is enhanced by reducing the number of chains bonded to
each anion and increasing the stiffness of polymer chains. The bilayer aggregates are ordered into two layers of a body-centered cubic (BCC) lattice, as shown by the two split peaks located at wave numbers with a ratio approximately $2^{1/2}$, even though the structure seems like an FCC lattice such as NaCl. This is because the structure factor $S(q)$ of the bonded anion beads and free cations is computed at the same time based on the two scatterers with the same scattering cross section. Thus, two FCC lattice of the two ions are cancelled into one BCC lattice such as KCl. The intra-aggregate correlation indicated by peaks’ splitting is difficult to capture both in the overall structure factor (Figure 3.1 (a)) within our simulations and in the ionomers’ scattering experiments, because of the small aggregate, whose mean length is $3 \sim 4.5\sigma$ (1.2 ~ 1.8 nm) in our simulations.

Figure 3.5 Plots of the peak value of ion-ion structure factor within wavenumber $q = 5$-9 (a) and $q = 9$-15 (b) at $T = 1.0$ for the semi-telechelic with $K_\theta =0$ (●), the 50/50 pendant ionomer/homopolymer blend with $K_\theta =0$ (green ■), the pendant ionomer with $K_\theta =0$ (blue ■), 1.5 (▲), 3 (♦).
according to the average number of ions in the aggregates (Figure 3.4), based on a bilayer square platelet model after the ordering transition as an estimation. Figure 3.6 shows that the existence of this transition is also supported by the feature observed in the ion-ion energy versus $T$ (a), corresponding to the high-$T$ feature in the overall energy (b), where the aggregate-ordering assembly shows increasing discontinuity in calorimetry from the flexible pendant ionomer to the stiff pendant ionomers to the flexible semi-telechelic ionomer, consistent with the sharpness of those split peaks in the ion-ion structure factor (Figure 3.1 (b)) and the two peak height values (Figure 3.5) at low $T$. The ordering transition within ionic aggregates, combined with glass transition among neutral monomers, is argued as the origin of two apparent glass transitions observed in the mechanical response of ionomers by a previous simulation.\textsuperscript{43}

Figure 3.6 Ion-ion pair-interaction energy (a) and overall pair-interaction energy (b) vs. temperature for the semi-telechelic ionomer $K_\theta = 0$ (●), the pendant ionomer $K_\theta = 0$ (■), the pendant ionomer $K_\theta = 1.5$ (▲), and the pendant ionomer $K_\theta = 3.0$ (♦).
Glass transition temperature $T_g$ of overall simulated systems is calculated based on the segmental relaxation time $\tau_\alpha$ by fit into a VFT function form as shown in Figure 3.7(a). There is no significant difference among the segmental relaxation time of ionomer systems normalized by the corresponding pure polymer with the same bending coefficient $K_\theta$ (Figure 3.7(b)), indicating that neither the chain connectivity with the aggregates nor the stiffness of chains is central to the suppression of the segment mobility as a result of the introduction of ionic aggregates into the polymer bulk. The enhancement of the glass transition temperature $T_g$ of uncharged monomers within these systems.

Figure 3.7 Monomer-part $\tau_\alpha$ versus $T$ (a) and monomer-part $\tau_\alpha$ normalized by the neat-state $\tau_\alpha$ versus $T$ normalized by the neat-state $T_g$ (b) for simulated systems: the semi-telechelic ionomer $K_\theta=0$ (●), the 50/50 pendant ionomer/homopolymer blend $K_\theta=0$ (green ■), the pendant ionomers with $K_\theta=0$ (blue ■), 1.5 (▲), and 3 (♦), and the pure systems with $K_\theta=0$ (×), 1.5 (-), and 3 (+).
systems relative to the corresponding pure polymer with the same bending coefficient \( K_\theta \) is consistent with experimental results. To note, the comparison in \( T_g \) between the ionomers and the corresponding pure polymer with the same stiffness is supported by \( T_g \) of all simulated systems increasing with \( K_\theta \), in agreement with predictions of the generalized entropy theory\(^{66}\) of glass formation. As shown in Table 3.1, \( T_g \) is enhanced by 7.0\% with respect to the neat polymer for the pure pendant ionomer and the semi-telechelic ionomer both with \( K_\theta = 0 \), indicating \( T_g \) enhancement is insensitive to the placement of the ionic group on the neutral polymer chain. Otherwise, based on the EHM model\(^{86}\), there would be weaker enhancement in \( T_g \) in the semi-telechelic ionomer compared with the pendant ionomer, because of the reduction in steric hindrance from two to only one chain covalently bonded to each anion in ionic aggregates (Figure 3.3).

Table 3.1 List of overall monomer-part \( T_g \) and \( m \) for the semi-telechelic ionomer \((K_\theta = 0)\), the 50/50 pendant ionomer/homopolymer blend \((K_\theta = 0)\), the pendant ionomer \((K_\theta = 0, 1.5, \text{and } 3.0)\) compared with the corresponding neat polymer.

<table>
<thead>
<tr>
<th>( K_\theta )</th>
<th>semi-telechelic</th>
<th>pendant/homo</th>
<th>pendant</th>
<th>pendant</th>
<th>pendant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_g )</td>
<td>0.476</td>
<td>0.459</td>
<td>0.476</td>
<td>0.545</td>
<td>0.650</td>
</tr>
<tr>
<td>( T_g^{\text{pure}} )</td>
<td>0.445</td>
<td>0.445</td>
<td>0.445</td>
<td>0.514</td>
<td>0.615</td>
</tr>
<tr>
<td>( T_g/T_g^{\text{pure}} - 1 )</td>
<td>7.0%</td>
<td>3.3%</td>
<td>7.0%</td>
<td>6.1%</td>
<td>5.8%</td>
</tr>
<tr>
<td>( m )</td>
<td>15.40</td>
<td>15.38</td>
<td>15.41</td>
<td>19.71</td>
<td>23.87</td>
</tr>
<tr>
<td>( m^{\text{pure}} )</td>
<td>15.87</td>
<td>15.87</td>
<td>15.87</td>
<td>21.54</td>
<td>27.59</td>
</tr>
<tr>
<td>( m/m^{\text{pure}} - 1 )</td>
<td>-2.9%</td>
<td>-3.0%</td>
<td>-2.9%</td>
<td>-8.5%</td>
<td>-13.5%</td>
</tr>
</tbody>
</table>
The 50/50 pendant ionomer/homopolymer blend exhibits a 3.3% enhancement in $T_g$, roughly consistent with the reduced concentration of ions in this system. If the stiffness of polymer chains increases mobility restriction by ionic aggregates as pointed out in the EHM model\textsuperscript{17}, the enhancement in $T_g$ would be much stronger relative to the pure polymer with the same $K_\theta$, with comparison to the flexible pendant ionomer. In contrast, the enhancement in $T_g$ of these stiff pendant ionomers is similar or even weaker with respect to the flexible one, indicating the contribution of ionic aggregates to $T_g$ enhancement is weakened by increasing chains’ stiffness. These results are consistent with a typical range of $T_g$ enhancement in experimental ionomers; a 1.2~1.4% $T_g$ enhancement per mole-percent ion observed in our simulations corresponds to an enhancement of approximately 2.8~3.3 K per mole-percent ion\textsuperscript{48}, as based on amorphous polyethylene with a $T_g$ of 237 K\textsuperscript{87}. As a result of the introduction of ionic groups into uncharged polymers, the enhancement in $T_g$ is irrelevant to the placement of the ionic group to the polymer chain, slightly weakened by the stiffness of chains, but sensitive to the ion concentration for a 100% neutralized ionomer system.

The kinetic fragility $m$ associated with those uncharged monomers in each system is suppressed with respect to the neat polymer with the same bending coefficient $K_\theta$, showing the similarity to nanoconfined polymers\textsuperscript{57,59} where the suppression of $m$ is commonly observed with respect to the pure state polymer. Also, this comparison in fragility $m$ between the ionomers and the pure polymers is supported by the growth of fragility $m$ with the increase in stiffness tuned by the bending coefficient $K_\theta$, consistent with the prediction by the generalized entropy theory\textsuperscript{66}. Intriguingly, the suppression of $m$
is insensitive to both the ion content and the chain connectivity to ionic aggregates on the uncharged polymer chain, shown (in Table 3.1) by a ~ 3.0% $m$ suppression with respect to the neat polymer in the semi-telechelic, the pendant ionomer/homopolymer blend, and the pendant ionomer system with $K_\theta = 0$. In contrast, the suppression in $m$ rises dramatically with increasing $K_\theta$, raised by $\geq 5\%$ for every 1.5 increase in $K_\theta$. The increasing contribution of ionic aggregates to fragility suppression of uncharged monomers is associated with a larger adjustment in packing as a result of more favorable formation of ionic aggregates in ionomers, and more loose packing in the neat polymer caused by increasing stiffness. This indicates that introducing ionic aggregates can tune the kinetic fragility $m$ (which characterizes the abruptness of the increase in segmental relaxation upon $T_g$), and this is meaningful for processing of polymers and is relevant to the glassy modulus.
Figure 3.8 Monomer-part $\tau_\alpha$ versus $T$ as a function of distance $r$ from the nearest ion for the pendant/homopolymer blend with $K_\theta = 0$ (b), the semi-telechelic ionomer with $K_\theta = 0$ (c), and the pendant ionomer with $K_\theta = 0$ (a), $K_\theta = 1.5$ (d), and $K_\theta = 0$ (e).
Near-aggregate Gradient in Dynamics

In order to quantify the effect of the ionic aggregates on local segmental dynamics of the polymer, we compute dynamics on monomers in bins with thickness $0.5\sigma$ measured by the distance from the nearest ion. As shown in Figure 3.8, the $T_g$ of the monomers is calculated after fitting the $\tau_\alpha$ data as a function of temperature in each bin to a VFT functional form; the figure shows that $\tau_\alpha$ of monomers is enhanced with decreasing distance from the nearest ion in each ionomer system. In Figure 3.9(a), the $T_g$ of uncharged monomers increases as the aggregates are approached, but remains above the

Figure 3.9 (a): $T_g$ (solid markers) and $m$ (hollow markers) normalized by their values in the neat homopolymer with the same $K_\theta$, as a function of distance from the nearest ion for the semi-telechelic ionomer $K_\theta=0$ (●), the 50/50 pendant ionomer/homopolymer blend $K_\theta=0$ (green ■), the pendant ionomer $K_\theta=0$ (blue ■), the pendant ionomer $K_\theta=1.5$ (▲), and the pendant ionomer $K_\theta=3$ (♦). (b) Data for the same properties plotted versus distance from an attractive nanoparticle surface, with different markers representing different nanoparticle concentrations.59
value in the neat homopolymer at all distances within our computed range \( 3.75 \sim 5.25\sigma \) (1.5~2.1nm), as a result of lacking sufficient distance between aggregates. This result is consistent with the trend of \( T_g \) decaying with increasing distance from the aggregates as reported in the experimental study by Miwa et al.\(^49\) They interpret the gradient in \( T_g \) in their study as supporting the EHM model’s ‘crosslinking’ view\(^17\) because the extrapolated distance at which \( T_g \) enhancement vanishes is comparable to the persistence length of the neat polymer. In contrast, the effective length range of \( T_g \) enhancement is considerably greater than the chains’ persistence length in our simulations, for example, which is approximately \( 0.7\sigma \) in those systems with bending coefficient \( K_\theta = 0 \).

Additionally, the gradient of \( T_g \) enhancement by distance is similar in both shape and magnitude for the pendant ionomers with different \( K_\theta \), and hence, different persistence lengths. If the effective region size of the suppressed dynamics around the ionic aggregates is correlated to the chains’ stiffness, the \( T_g \) enhancement and \( m \) suppression should be greater with increasing bending coefficient \( K_\theta \) at longer distance. Thus, the results in Figure 3.9(a) is inconsistent with the ‘restricted-mobility’ region around ionic aggregates which grows proportionally with the neat polymer’s persistence length, as stated in the EHM model\(^17\).

The trends in both \( T_g \) and \( m \) in Figure 3.9(a)&(b) resemble each other significantly, mostly with a quantitative consistence in the near-nanoparticle behavior of \( T_g \) and \( m \), which are observed in simulations of the same model polymer employed in our study, but in the presence of attractive (non-grafted) crystalline nanoparticles\(^59\). Specifically, the two studies exhibit excellent agreement in the extent of near-surface enhancement in \( T_g \).
near-surface suppression in $m$, and long-distance enhancement of $m$, as well as the location of a crossover from $m$-suppression to $m$-enhancement. We emphasize that no effort has been made to design the present model to achieve this correspondence. Instead, the interface effect involved is apparently sufficiently universal that nearly the same results are obtained when these distinct interfaces are introduced to the same model polymer even with the difference between the size of aggregates ($3 \sim 4.5\sigma$) and nanoparticles ($\sim 10.7\sigma$). This observation strongly suggests that covalent crosslinking between the chains and the ionic aggregate is no different than a strong non-covalent surface attraction and does not otherwise play a significant role in the physics of near-aggregate segmental mobility and $T_g$, which is also observed in the grafted-nanoparticle polymer$^{58,67}$ in experiments.
Figure 3.10 Plots of $\tau_a$ normalized by the corresponding pure-polymer value versus distance from the nearest ion at $T = 1.2$ (●), $T = 0.8$ (▲), and $T = 0.6$ (■). Solid and dashed lines are fits to equ (3.3) and the criterion for $\xi$ in equ (3.1).
Figure 3.11 Plots of $\langle u^2 \rangle$ normalized by pure-state value versus distance from the nearest ion at $T = 1.2$ (●), $T = 0.8$ (▲), and $T = 0.6$ (■). Solid and dashed lines are fits to equ (3.4) and the criterion for $\xi_{u^2}$ in equ (3.2).
In addition to the important characteristic temperature in dynamics \( (T_g) \), more general analyses are demanded to further study the physical origins of the dynamics gradient near ionic aggregates in ionomers. Thus, a length scale is defined below in order to test the persistence length dependence of the range over which the mobility of polymer chains is restricted by ionic aggregates as proposed in the EHM model\(^\text{17} \). This defined length scale and the persistence length should exhibit the same temperature dependence and scale with each other by a factor, if the gradient in dynamics is indeed dominated by the chain’s persistence length.

We employ the data characterizing the structural relaxation \((\tau_\alpha)\) and the vibrational dynamics \(\langle u^2 \rangle\) as a function of distance from the nearest ion \((r)\) from the binned analysis at each \(T\). In Figure 3.10, \(\tau_\alpha\) is enhanced approaching the aggregate, but decays towards a pure-state value with increasing distance from the aggregate; while in Figure 3.11, \(\langle u^2 \rangle\) is suppressed closer to the aggregate and resumes the pure-state value at a sufficient distance from the aggregate. According to prior simulation work examining dynamics near interfaces\(^88 \), we define an interfacial length scale \(\xi\) as a distance at which dynamics have sufficiently recovered pure-state dynamics, in order to characterize the effectivity of the gradient in dynamics in terms of \(\tau_\alpha\) and \(\langle u^2 \rangle\), based on the criteria:

\[
\frac{\tau_\alpha}{\tau_{\alpha\text{pure}}} = 1.2, \quad (3.1)
\]

\[
\frac{\langle u^2 \rangle}{\langle u^2 \rangle_{\text{pure}}} = 0.8, \quad (3.2)
\]

after smoothing \(\tau_\alpha\) and \(\langle u^2 \rangle\) as a function of distance \(r\) by using the functional form:
\ln \left( \frac{\tau_a(r)}{\tau_a^{\text{pure}}} \right) = A r^B + C \, , \quad (3.3) \\
\ln \left( \frac{\langle u^2 \rangle(r)}{\langle u^2 \rangle^{\text{pure}}} \right) = A r^B + C \, , \quad (3.4)

where \( A, B, C \) are fitting parameters, as illustrated in Figure 3.10 for \( \tau_a \) and in Figure 3.11 for \( \langle u^2 \rangle \). According to the previous work in polymer films, the specific criteria and the fitting function do not have a qualitative impact on the results.\textsuperscript{54,88}

\( \xi_t \) grows by a factor of 2.5\textasciitilde3 cooling from \( T \approx 2.2 T_g^{\text{pure}} \), the corresponding neat polymer \( T_g \), down close to \( T_g^{\text{pure}} \) in these systems with \( K_\theta = 0 \) shown in Figure 3.12(a), with an Arrhenius behavior on temperature dependence shown in Figure 3.13(b). In Figure 3.13(a), the persistence length of polymer chains, as investigated by the Kuhn length \( b \), grows by a factor of 1\textasciitilde1.5 upon cooling within the same temperature range, which is much less dependent on \( T \) as compared to the growth of \( \xi_t \) with \( T \). This mismatch between \( \xi_t \) and persistence length from our results is inconsistent with a correlation between the restriction range on mobility and the persistence length postulated in the EHM model\textsuperscript{17}. To associate \( \xi_t \) with some results in physical experiments, we employ an Arrhenius extrapolation of \( \xi_t \) to an extreme value at the extrapolated \( T_g^{\text{EX}} \) defined as the temperature at which \( \tau_a = 10^{14} \tau(\sim 100s) \), comparable with physical experiments. This size of the dynamics suppression described by \( \xi_t \) ranges from 9 \textasciitilde 14\( \sigma \), scaling as 3.6\textasciitilde5.6nm in real units, comparable to the range of the dynamics alterations near the interfaces of polymer thin films and nanocomposites in simulations\textsuperscript{60,88\textendash92}. With respect to these pendant ionomers without any simple
dependence of $\xi_\tau$ on $T$, we do not observe a significant enhancement of either $\xi_\tau$ at the same $T$ ratio relative to the pure-state $T_g$ in Figure 3.12(b) or of the altered-mobility range extrapolated at $T_g^{EX}$, even though their persistence length is raised, as shown by the Kuhn length $b$ increasing by a factor of $\sim 3$ tuned by $K_\theta$ from 0 to 3 in Figure 3.13. If the range over which the dynamics of polymer chains are suppressed by ionic aggregates is proportional to the chains’ persistence length, there will be an observable leap in both $\xi_\tau$ at each normalized $T$ and the extrapolated $\xi_\tau$ at $T_g^{EX}$ with increasing $K_\theta$ varying chains’ stiffness. Clearly, the persistence length of polymer chains is not central to determining the size of the restricted mobility region in our simulations.

Debye-Waller Factor $<u^2>$ is a length scale of particles rattling within a ‘cage’ at a short time$^{79}$, and is a practical measure of free volume. $<u^2>$ can also be used to calculate $kT/<u^2>$, which is proportional to the local modulus at high frequency$^{66}$. Accordingly, the interfacial length scale $\xi_{u^2}$ characterizes the gradient in dynamics, caused by the introduction of ionic aggregates into the homopolymer, in terms of free volume. The weak temperature dependence of $\xi_{u^2}$, ranging from 1~1.5$\sigma$ in Figure 3.12, as compared to the $T_g$ and $m$ gradient in Figure 3.9, rules out the possibility of free volume dominating the origin of glass formation of ionomers, consistent with results near non-grafted interfaces$^{59,88}$.

As is studied in those nanoconfined systems, $\xi_\tau$ is associated with the length scale of cooperatively rearranging regions (CRRs) as developed in the Adam-Gibbs theory$^{85}$ in the glass-forming liquid. Due to the similarities between the simulated ionomer systems and the nanoconfined systems demonstrated above, it is interesting whether this
correlation holds here, tested by calculating a mean number of segments $L$ participating in the cooperative rearrangements via a protocol well-established and widely employed in the literature.\textsuperscript{69,65,70} The string analysis is computed on the mobile particles, defined as the particles moving farther than an Gaussian approximation at a time. The correlated moving particles consisting a ‘string’ are determined based on a criterion that one particle replace other particle within a radius of $0.6\sigma_c$, where $\sigma_c$ is the kissing distance between the centers of two beads. Then the mean string length $L$ is calculated as the average number of segments participating in the same ‘string-like’ collective motion. Here, the mean string length $L$ is only computed at the peak time (less than the segmental relaxation time $\tau_\alpha$) of the non-Gaussian parameter (Figure 3.14), corresponding to the
time of peak participation of particles in cooperative motion. As the bending coefficient $K_\theta$ goes up (Figure 3.14 (b)&(c)), the peak time within $\tau_a$ gets harder to capture both in the pendant ionomer systems and the pure polymer systems due to the extra non-Gaussian behavior invoked by chains’ stiffness. Thus, the string analyses are only performed on the flexible systems to deliver further discussion on cooperative motion.

Figure 3.13 (a): Plot of Kuhn length $b$ versus $T$ for the pure systems with $K_\theta = 0 \times$, 1.5 (.), and 3 (+). (b): Arrhenius plot of $\xi_T$ versus $T$, where solid lines are an Arrhenius extrapolation, and dashed lines indicate extrapolated $\xi_T$ at an extrapolated experimental monomer $T_g^{EX}$; inset shows linear correlation between $\xi_T$ and $L$ for the flexible systems: the pendant ionomer (blue ■), the 50/50 pendant ionomer/homopolymer blend (green ■), and the semi-telechelic ionomer (●).

Figure 3.12(a) demonstrates the similar growth of $\xi_T$ and $L$ with $T$; additionally, the inset in Figure 3.13(b) shows that $\xi_T$ is linearly correlated to $L$ over the entire range of glass formation in the flexible systems. This correspondence indicates that the size of
Figure 3.14 Plots of non-Gaussian parameter versus time $t$ at $T = 1.5$ (dashed line) and $T = 0.7$ (solid line) for (a): the pendant ionomer (blue), the 50/50 pendant ionomer/homopolymer blend (green), and the semi-telechelic ionomer (red) with $K_\theta = 0$; (b): the pendant ionomer with $K_\theta = 0$ (blue), 1.5 (purple), 3 (grey); (c): the pure polymer with $K_\theta = 0$ (orange), 1.5 (pink), 3 (aqua).
suppressed-mobility regions in ionomers is determined by the scale of cooperative rearrangements inherent to supercooled liquid dynamics rather than by chain connectivity effects.

Figure 3.15 (a): Illustration for Arrhenius correlation between $\tau_\alpha$ and $T$, where $\tau_\alpha$ has an Arrhenius dependence on $T$ when $T \ln(\tau_\alpha / \tau_\lambda) / E_a$ on the y axis equals 1. (b): Plot of enthalpy-entropy compensation, the slope of which is the compensation temperature. The solid line indicates a linear relation. Including systems are the pendant ionomer (blue ■), the 50/50 pendant ionomer/homopolymer blend (green ■), and the semi-telechelic ionomer (●) with $K_\theta = 0$; (b): the pendant ionomer with $K_\theta = 0$ (■), 1.5 (▲), 3 (♦); (c): the pure polymer with $K_\theta = 0$ (×), 1.5 ( JTextField ), 3 (+).

Test of the Adam-Gibbs Theory of Glass Formation in Ionomers

Finally, we test the proposition that segmental relaxation dynamics during glass formation in these ionomers are determined by the scale of cooperative rearrangements, characterized by mean string length $L$ in this thesis. A dependence of segmental
relaxation time $\tau_\alpha$ on the size of cooperatively rearranging regions (CRRs) is established by Adams and Gibbs$^{62}$. Recent work has indicated that, if Adam-Gibbs theory holds for a given system, $\tau_\alpha$ should be correlated with $L$ via the equation$^{59,60,70}$

$$
\tau_\alpha (T) = \tau_\alpha \exp \left[ \frac{L(T) \Delta \mu}{L_A k_B T} \right], \quad (3.5)
$$

where $k_B$ is the Boltzmann constant (equal to 1 in LJ units), $\tau_\alpha$ is the high temperature relaxation time that is treated as a fitting parameter, $\Delta \mu$ is the high temperature activation energy, and $L_A$ is the CRR size at the high-temperature onset of glass formation $T_A$. After fitting $\tau_\alpha$ and $T$ from $T = 1.5$ to 1.0 to an Arrhenius functional form:

$$
\tau_\alpha (T) = \tau_A \exp \left( \frac{E_a}{k_B T} \right), \quad (3.6)
$$

where $\tau_A$ and $E_a$ are fitting parameters, $T_A$ is determined as the $T$ at which $\tau_\alpha$ deviates ~10% from this fit. It is illustrated in Figure 3.15(a) that $\tau_\alpha$ has an Arrhenius dependence on $T$ when $T \ln (\tau_\alpha / \tau_A) / E_a$ is equal to 1, and this quantity gets larger than 1 as $\tau_\alpha$ deviates from this Arrhenius correlation with $T$. In equation (3.5), the high-temperature activation energy $\Delta \mu = \Delta H - T \Delta S$, where $\Delta H$ and $\Delta S$ are the high temperature activation enthalpy and entropy, respectively. $\Delta H$ is equal to the fitting parameter $E_a$ in the above Arrhenius function form, and $\Delta S$ is evaluated via $\Delta S = -k_B \ln (\tau_A / \tau_0)$, where $\tau_A$ is also a fitting parameter from the Arrhenius fit above and $\tau_0$ is the vibrational relaxation time, taken to be 0.1$\tau$ in LJ units, consistent with prior work$^{60,70}$. It is reported that there is a linear compensation between $\Delta H$ and $\Delta S$,$^{60}$ which is also true in our simulation for all the systems as shown in Figure 3.15(b). Accordingly, a compensation $T$ is defined as the
slope of the linear relation, which is \( T_{\text{comp}} = 1.74 \), roughly \( 3 \sim 3.5 T_g \) of all the systems. This extremely high \( T_{\text{comp}} \), based on the ionomers and pure polymers with bending coefficient \( K_\theta = 0 \sim 3 \), is different than the low \( T_{\text{comp}} = 0.18 \) characterized in the nanofilms\(^6\); this discrepancy shows that the mechanism behind this \( T_{\text{comp}} \) is still an open question.

Based on the relation in equation (3.5), if \( \ln \left( \frac{\tau_a}{\tau_\infty} \right) \) is plotted against \( \frac{L}{L_A} \frac{\Delta \mu}{k_B T} \), all glass-forming materials obeying these physics should collapse to a line of slope 1. Moreover, Hanakata et al. have pointed out that \( \xi_r \) and \( L \) should be related as\(^6\)

\[
\frac{L}{L_A} - 1 = A \left( \frac{\xi_r}{\xi_A} - 1 \right), \tag{3.7}
\]

where \( \xi_A \) is the value of \( \xi_r \) at the onset temperature \( T_A \) and \( A \) is a fitting parameter. Inserting this equality into the Adam-Gibbs relation suggests that, if the size of the restricted mobility region is indeed determined by the CRR size, then the relaxation time in the system should be related to \( \xi_r \) as\(^6\)

\[
\tau_a(T) = \tau_\infty \exp \left[ A \frac{\xi_r(T)}{\xi_A} + 1 - A \right] \frac{\Delta \mu}{k_B T}, \tag{3.8}
\]

where the high-\( T \) relaxation time \( \tau_\infty \) is determined by the fit in equation (3.5) without refitting, \( \Delta \mu \) is also the same as in equation (3.5), and \( \xi_A \) is the interfacial length scale \( \xi_r \) at \( T_A \). If the Adam-Gibbs theory holds in our systems, it should collapse into a linear line with a slope of 1 when plotting \( \ln \left( \frac{\tau_a}{\tau_\infty} \right) \) versus \( A \frac{\xi_r(T)}{\xi_A} + 1 - A \frac{\Delta \mu}{k_B T} \).

As shown in Figure 3.16, the collapses corresponding to equations (3.5) and (3.8) are both successful in all systems considered in this study. This success provides
additional evidence that glass formation in these ionomers is driven by cooperative motion associated with universal glass physics and not with persistence length or crosslinking considerations particular to these systems. Furthermore, these results indicate that the Adam-Gibbs entropy theory of glass formation is an excellent candidate for describing the glass transition of ionomers.

Figure 3.16 Test of Adam Gibbs theory based on equ (3.5) and (3.8) for the pendant ionomer (blue ■), the 50/50 pendant ionomer/homopolymer blend (green ■), the semi-telechelic ionomer (●) and the pure polymer (×) with $K_0 = 0$. 
CHAPTER IV
CONCLUSIONS

We study glass formation behavior of ionomers by means of coarse-grained molecular dynamics simulations on model semi-telechelic and pendant ionomers. Simulations exhibit the presence of reduced-mobility regions surrounding ionic aggregates, the sizes of which grow in a nearly Arrhenius manner on cooling. Our results are inconsistent with the prediction in the EHM model\textsuperscript{17} that the range over which the dynamics of polymer chains are suppressed around ionic aggregates is correlated with the persistence length as a parameter characterizing chains’ stiffness. These conclusions are supported by the fact that the temperature dependences of the suppressed-dynamics range and the persistence length are not equal, accompanied with the invariance in the size of these regions when quantified in ionomers over a broad range of persistence lengths.

Like previously studied filler-grafted composites\textsuperscript{67,68}, bond connectivity between polymers and interfaces does not qualitatively transform the physical origin of glass formation in ionomers. Specifically, ionomers behave like nanoconfined materials in that their dynamics are determined by the size of CRRs, which grow upon cooling. These findings have practical implications for grafted micro-phase materials and their glass forming dynamics, for example, semi-crystalline polymers and brush copolymers.
More broadly, the consistency of glass formation among ionomers, filler-grafted materials and those materials without a grafted micro-phase, such as nanoparticle composites\textsuperscript{57–59} and thin films\textsuperscript{54–56}, tends to merge the superficially different dynamical behaviors in various materials into a unified intuition. In this thesis, the success of the test of the Adam-Gibbs theory\textsuperscript{62} via a string-like cooperative motion model\textsuperscript{60,70} takes us one step closer to such an idealized goal.
Further work will involve studies on the self-assembly of ionic aggregates as a tool to generate super molecules. Due to electrostatic interaction among ions, the morphology of ionic aggregates can be controlled by employing either an electric or magnetic field. The structural control into a percolated or networked morphology will bring about improvement in ionomers’ transportation properties.

Theoretical work on glass forming dynamics can help to uncover the factors affecting the dependence of fragility on polymer chains’ stiffness in ionomers. Also, the ionic aggregates do not participate in cooperative motion with polymer chains as a consequence of huge difference on timescale for segmental relaxation. In addition to ionomers, it would be interesting to study other systems, like polymers with additives, within which different components compose cooperatively rearranging regions.
REFERENCES


15. Weiss, R. A. et al. in Coulombic Interactions in Macromolecular Systems 302, 2–19


77. AMDAT: Amorphous Molecular Dynamics Analysis Toolkit.


APPENDIX A

CALCULATION OF DEBYE-WALLER FACTOR FOR FLEXIBLE IONOMERS

\[
\text{MSD}_{\text{pendant (}} K_\theta = 0) \\
\text{MSD}_{\text{pen/homo (}} K_\theta = 0) \\
\text{MSD}_{\text{semi (}} K_\theta = 0)
\]
APPENDIX B

CALCULATION OF DEBYE-WALLER FACTOR FOR PENDANT IONOMERS

![Graphs showing MSD dependencies on time for different temperatures and Debye-Waller factors.](image-url)
APPENDIX C

CALCULATION OF DEBYE-WALLER FACTOR FOR PURE POLYMERS

![Graphs showing MSD vs. t for different values of $K_\theta$ and $T$.]
APPENDIX D

CALCULATION OF SEGMENTAL RELAXATION FOR FLEXIBLE IONOMERS

\[ F_{\text{self}}(t) |_{q=7.07} \text{ in Pendant with } K_\theta = 0 \]

\[ F_{\text{self}}(t) |_{q=7.07} \text{ in Pen/homo with } K_\theta = 0 \]

\[ F_{\text{self}}(t) |_{q=7.07} \text{ in Semi with } K_\theta = 0 \]

\[ \tau_a \]

\[ t \]

\[ T=1.5 \quad T=1.1 \quad T=0.8 \quad T=0.5 \]
APPENDIX E

CALCULATION OF SEGMENTAL RELAXATION FOR PENDANT IONOMERS
APPENDIX F

CALCULATION OF SEGMENTAL RELAXATION FOR PURE POLYMERS

\[ F_{\text{self}}(t) \mid q = 7.07 \text{ in Pure with } K_\theta = 0 \]

\[ F_{\text{self}}(t) \mid q = 7.07 \text{ in Pure with } K_\theta = 1.5 \]

\[ F_{\text{self}}(t) \mid q = 7.07 \text{ in Pure with } K_\theta = 3 \]
## APPENDIX G

OVERALL EXTRAPOLATED GLASS TRANSITION TEMPERATURES

![Graph showing extrapolated glass transition temperatures](image)

<table>
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<th></th>
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<th>pendant</th>
<th>pendant</th>
<th>pendant</th>
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</thead>
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<td>0.0</td>
<td>1.5</td>
<td>3.0</td>
</tr>
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<td>0.376</td>
<td>0.390</td>
<td>0.468</td>
<td>0.572</td>
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<tr>
<td>$T_g^{\text{EX}}</td>
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<td>0.367</td>
<td>0.367</td>
<td>0.449</td>
</tr>
<tr>
<td>$T_g^{\text{EX}}/T_g^{\text{EX}}</td>
<td>_{\text{pure}}-1$</td>
<td>6.1%</td>
<td>2.4%</td>
<td>6.1%</td>
<td>4.4%</td>
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<td>208</td>
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<tr>
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<td>-2.9%</td>
<td>-8.5%</td>
</tr>
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</table>
APPENDIX H

VFT EXTRAPOLATION IN BINNED ANALYSES FOR FLEXIBLE IONOMERS
APPENDIX I

VFT EXTRAPOLATION IN BINNED ANALYSES FOR PENDANT IONOMERS
APPENDIX J

BINNED EXTRAPOLATED GLASS TRANSITION TEMPERATURE

![Graph a](image)

![Graph b](image)