CONTROL AND CHARACTERIZATION OF TEXTURED, HYDROPHOBIC IONOMER SURFACES

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CONTROL AND CHARACTERIZATION OF TEXTURED, HYDROPHOBIC IONOMER SURFACES

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ABSTRACT

Polymer thin films are of increasing interest in many industrial and technological applications. Superhydrophobic, self-cleaning surfaces have attracted a lot of attention for their application in self-cleaning, anti-sticking coatings, stain resistance, or anti-contamination surfaces in diverse technologies, including medical, transportation, textiles, electronics and paints. This thesis focuses on the preparation of nanometer to micrometer-size particle textured surfaces which are desirable for super water repellency.

Textured surfaces consisting of nanometer to micrometer-sized lightly sulfonated polystyrene ionomer (SPS) particles were prepared by rapid evaporation of the solvent from a dilute polymer solution cast onto silica. The effect of the solvent used to spin coat the film, the molecular weight of the ionomer, and the rate of solvent evaporation were investigated. The nano-particle or micron-particle textured ionomer surfaces were prepared by either spin coating or solution casting ionomer solutions at controlled evaporation rates. The surface morphologies were consistent with a spinodal decomposition mechanism where the surface first existed as a percolated-like structure and then ripened into droplets if molecular mobility was retained for sufficient time. The SPS particles or particle aggregates were robust and resisted deformation even after annealing at 120°C for one week. The water contact angles on as-prepared surfaces were relatively low, ~90° since the polar groups in ionomer reduce the surface hydrophobicity.
After chemical vapor deposition of 1H,1H,2H,2H-perfluoroctyltrichlorosilane, the surface contact angles increased to ~109° on smooth surfaces and ~140° on the textured surfaces. Water droplets stuck to these surfaces even when tilted 90 degrees.

Superhydrophobic surfaces were prepared by spraying coating ionomer solutions and Chemical Vapor Deposition (CVD) of 1H,1H,2H,2H-perfluoroctyltrichlorosilane onto textured surfaces. The surfaces after CVD of silane exhibited water contact angle of 152° and the water droplet stuck to the surfaces without falling even when tilted upside down. This kind of sticky superhydrophobic surface would have potential applications in no-loss transport of liquid, and cleaning robots.
DEDICATION

To my wife, Wen, for your undivided support and love.
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CHAPTER I
INTRODUCTION

1.1 Polymer Film Wetting/Dewetting

Polymer thin films are of increasing interest in many industrial and technological applications. Modern coating technologies require thinner films, e.g., optical coating for electronic packaging. The ability to reduce film thickness while improving film properties depends on the wettability and adhesion of the polymer film to the substrate [1, 2]. Controlling wettability of thin films plays an important role in many biological and industrial applications. Good wetting is required in many emerging technologies, e.g., decorative or protective coatings, adhesives, functional or smart coatings, electronic devices, dielectric layers, electric packaging and biocompatibility [3]. Control of film wetting properties is vital for these applications since “dewetting” leads to rupture of a thin film and deteriorates the film properties [4]. Furthermore, dewetting may produce surface defects and roughness that comprises the film performance [5].

Thick polymer films remain stable due to gravity, while thin films may undergo dewetting when the film is thinner than a critical thickness. The dewetting tendency of a thin polymer film is characterized by the spreading coefficient S, [3, 6]

\[ S = \gamma_s - (\gamma_c + \gamma_{cs}) \]  \hspace{1cm} (1.1)
where $\gamma_s$ is the surface energy of the substrate, $\gamma_c$ is the surface energy of film and $\gamma_{sr}$ is the film/substrate interfacial energy. Thin polymer films may undergo dewetting when the spreading coefficient, $S < 0$.

Many studies have been performed on the mechanism and kinetics of dewetting [7-29]. Dewetting can be initiated by capillary forces [7-23] and residual stresses [24-29] inside the film. It has been shown that polymer film dewetting can happen in two different ways: spinodal decomposition or nucleation and growth. Nonwetting (S<0) ultrathin films may break up via a spinodal decomposition mechanism (i.e., thermal amplification of capillary waves) [30], while nonwetting ultrathick films dewet through nucleation and growth mechanism [8].

The kinetics of dewetting has been well studied by numerous researchers [9-11, 31-36]. Reiter and co-workers studied the dewetting dynamics of spin coated thin polystyrene films on silica substrates [11-16]. Three stages of dewetting in thin polystyrene films thinner than 60 nm were observed: 1) rupture of film, 2) expansion and coalescence of dewetted holes to form a network, and finally 3) breakup of network system into droplets.

Stabilization of polymer films from dewetting has drawn a lot of attention recently. Strategies to prevent film dewetting include modification of polymers by introducing ionic groups to polymer backbone, modification of substrate and addition of nanoparticles or fillers to the film [5, 37-41]. Kinetic stabilization of polymer film could also be achieved by using an entangled, high molecular weight polymer film to inhibit dewetting. Feng et al. reported that randomly sulfonated polystyrene (SPS) ionomers were much more resistant to dewetting than unmodified PS [5]. Weiss et al. reported that
spin-coating provided a facile method for preparing rough surfaces with submicrometer-scale roughness [42]. A nano-particle-textured surface with particle diameters of ~200 nm was produced by spin-coating a lightly sulfonated polystyrene (SPS) ionomer from THF or THF/methanol solutions onto a silica substrate. The particle-textured surface was attributed to spinodal decomposition at the liquid/vapor interface of the drying film.

1.2 Superhydrophobic Surfaces

Wettability of liquid to polymer surfaces plays an important role in many biological and industrial applications. Good wetting is required in many emerging technologies, i.e. electronic packaging, adhesives, composite materials and biocompatibility [43]. Non-wettable surfaces, or superhydrophobic surfaces, also have important applications, for example in self-cleaning, anti-sticking coatings, stain resistance, or anti-contamination surfaces in diverse technologies, including medical, transportation, textiles, electronics and paints [44-45]. Superhydrophilic surfaces where water completely wets the surface are also useful, for example, to design fog-free windows [46]. Superhydrophobic surfaces are generally considered those with water contact angles of $\theta > 150^\circ$, and superhydrophilic surfaces have water contact angles $\theta < 5^\circ$. Since the early work of Wenzel [47] and Cassie and Baxter [48], it has been known that the wetting properties of surfaces are dependent on their surface structure and chemical composition.

Contemporary development of superhydrophobic surfaces has involved designing surface textures that mimic natural plants or animals. Many plant surfaces i.e. lotus leaf and rose petal, animal furs, spider legs, gecko feet, butterfly wings are superhydrophobic (with water contact angle $> 150^\circ$) and exhibit super water repellency. This is achieved by
a combination of surface roughness and low-surface energy coating (i.e. wax on the lotus
leaf surface). The roughness usually consists of micro- or nano-size structures or
hierarchical structures that enhance the hydrophobic properties of the surface.

Synthetic superhydrophobic surfaces have been prepared either by top-down or
bottom-up approaches [44]. The top-down approach involves lithographic and template
based techniques, in many cases using the naturally occurring textured surfaces of plants
and animals as templates. The bottom-up approaches rely on molecular self-assembly to
create substrates with designed patterns. A review of literature is provided in Chapter II.

As described earlier in this chapter, nano-particle textured surfaces were prepared
by spin coating SPS ionomer solutions and the mechanism is believed to be spinodal
decomposition during the solvent evaporation process [42]. In this research, the
parameters controlling surface morphology were investigated and high adhesion
superhydrophobic surfaces using various coating techniques were prepared.

Chapter II focuses on the literature review on the basic concepts of polymer film
dewetting, methods to prevent dewetting, and the application of ionomers to inhibit
dewetting and fabricate textured surfaces. Chapter II also introduces the research progress
on superhydrophobic surfaces, methods to prepare textured surfaces, advantage and
disadvantage of these techniques. Motivation and objectives of this research are discussed
in Chapter II.

Lightly sulfonated SPS ionomers were synthesized and neutralized to lithium salt
and then spin cast onto silica substrates under different conditions. The surface
morphology and roughness was characterized with atomic force microscopy (AFM) and
scanning electron microscopy (SEM). Surface water contact angle was characterized with
Ramé-Hart Model 500 goniometer. The effect of solvent properties, polymer molecular weight, and solution concentration on spin coated SPS ionomer morphology are described in Chapter III. The experimental and instrumental techniques employed in the present study are also discussed in Chapter III. Ammonium-ended telechelic polystyrene ionomer was also used to evaluate if nano-particle textured surface formation mechanism is applicable to other ionomer/solvent systems.

Chapter IV presents the effect of solvent evaporation rates on the surface morphology and the surface hydrophobicity. By carefully adjusting the solvent evaporation rates, structures characteristic of different stages of spinodal decomposition were captured when the film is dry.

Chapter V describes a simple spray coating method to prepare sticky superhydrophobic surfaces. The effect of solution concentration, polymer molecular weight on the surface morphology and hydrophobicity were investigated. An operation diagram that predicts the structure formed at given concentration and polymer molecular weight was constructed. Sticky superhydrophobic surfaces with a water contact angle of 152° were prepared and the water droplet adhered to the surface even when tilted upside down. The ability to hold water droplets was characterized by tilting stage measurement.

The concluding Chapter VI is devoted to the overall summary and recommended work for the future.
CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Polymer Film Wetting/Dewetting

Polymer thin films on solid substrates are widely used in many industrial and technological applications, e. g. decorative or protective coatings, lubricants, sensors, active layers in devices such as organic solar cells and organic light-emitting diodes, smart coatings and biocompatibility [49-53]. Modern coating technologies require thinner films, e. g. optical coating for electronic packaging. Defect-free, stable and nano-meter thickness polymer thin films are desired for such applications. It is well known that polymer thin films are vulnerable to dewetting when the film is thinner than a critical thickness [7-30]. Dewetting exposes the substrate and produces surface defects and roughness that compromises the film performance [5].

2.1.1 Dewetting Mechanism

Figure 2.1 shows the effective interface potential $\varphi(h)$ (the excess free energy per unit area when bringing the polymer film and the solid substrate from infinity to within a certain distance, $h$ ) dependence on the film thickness, $h$. When $\varphi(h) > 0$ and the global minimum of interface potential energy lies at infinite film thickness, the film is stable, as
shown in curve (1). If the second derivative of $\varphi(h)$ with respect to thickness is negative, $\varphi''(h) < 0$, the system is considered unstable (curve (2)) [53]. The film will dewet via “spinodal dewetting” (i.e. thermal amplification of capillary waves) [30]. In curve (3), the film is unstable for thin films where $\varphi'(h) < 0$, and metastable for thick films $\varphi'(h) > 0$. In the metastable region, the system need to overcome an energy barrier in order to reach its minimum energy at $h = h^*$. Dewetting must be externally induced, e.g. by nuclei (dust particles or defects) or nucleating a hole in the film [8]. In addition, thin films could also dewet through “thermal nucleation (TN)” or “homogenous nucleation” where the nucleation was initiated by thermal activation [54] or residual stress accumulated during sample preparation [24-29]. For example, thin films prepared by spin coating will induce polymer chains in non-equilibrium state since there is not enough time for the polymer chains to rearrange themselves, which introduces residual stresses into the film. The release of the residual stress may form holes in the film and induce dewetting.

The dewetting tendency of a thin polymer film is characterized by the spreading coefficient $S$, [3, 6]

$$S = \gamma_s - (\gamma_c + \gamma_{cs})$$  \hspace{1cm} (2.1)

where $\gamma_s$ is the surface energy of the substrate, $\gamma_c$ is the surface energy of film and $\gamma_{cs}$ is the film/substrate interfacial energy. After holes are formed in the film, negative spreading coefficient ($S$) will act as the driving force for the hole growth. These holes
keep growing until they reach each other, then the dewetted materials coalesce to form polygons and finally the polygons breakup into droplets [11-16].

Figure 2.1 Effective interface potential $\varphi(h)$ as a function of the film thickness ($h$) for stable (1), unstable (2), and metastable (3) films [redraw from ref. 54 with permission].

2.1.2 Method to Prevent Dewetting

There have been many studies on suppression of dewetting of polymer thin films. Parameters including molecular weight, film thickness and substrate interaction influence
the dewetting of polymer thin films. The stabilization of films may be thermodynamic or kinetic. Strategies to prevent film dewetting can be divided into two main categories: (1) modification of interfacial tension and interaction between the film and substrate and (2) reduction of mobility of polymer chains by chemical modification or adding nanoparticles and fillers [5, 37-41]. Kinetic stabilization of polymer films can also be achieved by using an entangled, high molecular weight polymer film to inhibit dewetting.

**Modification of Substrates** Most studies on preventing dewetting use a surface treatment to modify substrates, either chemically or physically. The main purpose of modification is to change the surface energy of the substrate and make the spreading coefficient (S) positive. Inhibition of dewetting could be achieved by modifying the substrate with HF passivation [55], or by using grafted homopolymer [56], or random copolymer [57], or increasing surface roughness [58]. Recently, a method involving using functionalized self-assembly monolayer (SAM) has been developed [59], which allows varying the surface functionality continuously. Ashley et al. [60] constructed a library of PS film cast onto substrates with temperature and surface energy gradients and observed the wetting and dewetting transition line over a range of polymer molecular weights (1800 – 35,000 g/mol) and film thickness $h$ (30 – 40 nm). The transition line was found to coincide with the apparent polymer surface energy, which is dependent on the film thickness [61]. Modification of silica substrates with other materials could also inhibit dewetting of PS films. For example, Choi *et al.* [62] used cross-linked 3-amino-
propyltriethoxysilane (APTES) network to modify the substrate and it could completely suppress dewetting of PS films.

**Modification of Polymers** In contrast to substrate modification methods, there have been far fewer studies involving modification of polymers to improve their wetting properties. Modification of polymers with randomly distributed ionic groups or end-functional groups has been found to suppress dewetting [5, 56]. The modification introduces electrostatic or dipolar interactions into the polymer chain and enhances the interaction between polymer film and substrates. Feng *et al.* reported that randomly sulfonated polystyrene (SPS) ionomers were much more resistant to dewetting than unmodified PS [5]. In 2.3LiSPS films, dewetting was strongly suppressed and no dewetting was observed when the sulfonation level was higher than 7 mol%. No dewetting was observed in ZnSPS films even at low sulfonation level. Henn *et al.* used end-functionalized polystyrene (ω -barium sulfonated polystyrenes, M_w = 3000 g/mol) to form a densely packed brush layer on the silica surface. Retardation of dewetting was achieved when the polymer molecular weight was large enough to form entanglement between the adsorbed and unadsorbed polymer chains [56]. The modification of the polymer backbone heterogeneous segments (copolymer) was also used to improve the polymer wettability [63].

**Cross-linking of Polymers** Crosslinking polymer films increases the viscosity of the film and inhibits the dewetting process. Crosslinking reduces the mobility of polymers
chains, thus stabilizing polymer films by eliminating hole formation. Crosslinking via irradiation [64] and photoinduced crosslinking [65] has been demonstrated to prevent polymer film dewetting. Long polymer chains and high degree of crosslinking are desirable for suppressing dewetting.

Addition of Nano Particles or Fillers Recent studies revealed that some organic or inorganic additives in polymer thin films could suppress the dewetting process [38, 66-72]. Many kinds of additives have been used including fullerene nanoparticles (C60) [38, 66], quantum dots [66, 68], carbon nanotubes [69, 70], dendrimers [71]. The presence of nano-size additives in the polymer films severely suppresses dewetting and it appears that this is a general phenomenon for a variety of polymers [72]. The segregation of nanofillers toward the substrate interface has been proposed to explain the suppression of dewetting. The interfacial roughness leads to contact line pinning and change in film wettability. Kropka et al. [73] studied the effect of interaction between additives (tetramethylethylene polycarbonate (TMPC)) and the substrates with the dewetting of PS films. The TMPC nanodroplets covered the substrates due to the interaction of TMPC chains with the substrates and the PS chains. The coverage of TMPC nanodroplets changed the surface energy and spreading coefficient (S), which improved the film stability and suppressed dewetting of the PS films.
2.2 Superhydrophobic Surfaces

2.2.1 Definition of Superhydrophobic Surfaces

Wettability of liquid to polymer surfaces is important in many biological and industrial applications. Water droplets can interact with a surface in a variety ways ranging from superhydrophilic to superhydrophobic behaviors. Non-wettable surfaces, or superhydrophobic surfaces, have recently attracted more and more attention for their application in self-cleaning, anti-sticking coatings, stain resistance, or anti-contamination surfaces in diverse technologies, including medical, transportation, textiles, electronics and paints [74-87].

Superhydrophobic surfaces are generally defined as surfaces with water contact angle higher than 150° and are commonly observed in nature, such as lotus leaves, butterfly wings, water spider foot etc. The research of superhydrophobic surface and the related phenomenon of super water repellency started a long time ago. Ollivier observed water contact angles close to 180° on surfaces coated with soot, lyco-podium powder and arsenic trioxide in 1907 [88-90]. Coghill and co-workers observed contact angle of nearly 160° on galena surfaces after deposition of stearic acids [91-95]. Based on these experimental data, Wenzel and Cassie-Baxter models were proposed to explain the relationship of water contact angle and the surface roughness [47, 48].

Contact angle hysteresis (difference between advancing and receding contact angle) is another important factor in describing surface property. Superhydrophobic
surface can be slippery (low contact angle hysteresis, lotus leaf), or sticky (high contact angle hysteresis, rose petal). Slippery surfaces have low contact angle hysteresis and the droplet would easily fall off the surface and remove the dust particles, which is the origin of self-cleaning effect. Sticky surfaces, on the other hand, show high contact angle hysteresis and are observed in nature as rose petal, gecko foot.

2.2.2 Lotus Effect

The lotus leaf remains totally clean although growing in dirty water and has been treated as a symbol of purity. The water CA of a lotus leaf is $161 \pm 2.7^\circ$ with CA hysteresis of $2^\circ$ [96, 97]. The rolling of the water droplets and cleaning of dust and contaminates is called the lotus effect, or self-cleaning effect. The mechanism of lotus effect was unclear until Neinhuis and Barthlott studied the surfaces of lotus leaves with SEM in 1997 [98, 99]. The epidermis of the lotus leaf possesses a combination of two-scale roughness: papillae with diameter in the range of 3–15 μm and nanohair around 100 nm on the top of each papilla, as shown in Figure 2.2. The micro-papillae and nano-hair hierarchical structures together with hydrophobic epicuticular wax crystalloids lead to superhydrophobicity of lotus leaf. The hydrophobic wax itself has a water contact angle of $110^\circ$ [44], while the lotus leaf shows a superhydrophobic surface of $161 \pm 2.7^\circ$ [96, 97].

The self-cleaning mechanism has been thoroughly studied [99]. The contact of the fluid on the surface is minimized for rough superhydrophobic surfaces. The nonslip
boundary condition dominates at the interface of the liquid droplet and the solid substrate [100]. When the droplet rolls off a lotus leaf, it behaves as an elastic ball instead of a viscous fluid due to the high contact angle, as shown in Figure 2.3 (minimized contact between the water droplet and the surface). On a normal hydrophobic surface, the water droplets will collect the dust particles and the dust particles are mainly displaced to the sides of the droplet and re-deposited behind the droplet (Figure 2.3 left) [79]. In the case of superhydrophobic surfaces, the contact between water droplet and the substrate is minimized due to high contact angle. The almost spherical water droplet would collect the dust particles from the surface when it rolls off (Figure 2.3 left). The lotus leaf therefore remains clean, which is called “lotus effect” or “self-cleaning effect”.

![Figure 2.2 SEM images of the lotus leaf surface: (a) valleys surrounded with multipapillae; (b) higher magnification of a papilla with nanohairs [80].](image)

2.2.3 Petal Effect and Gecko Effect

In contrast to low-adhesion, slippery superhydrophobic surfaces, researchers also reported high-adhesion, sticky superhydrophobic surfaces where the water droplets pinned to the surfaces at any tilted angles [101-115]. Rose petal, for example, is a kind of sticky superhydrophobic surfaces. When raindrops fall on rose petals, they form almost spherical droplets but stick to the flowers even when tilted upside down [80, 101, 102] (Shown in Figure 2.4). Geckos and many insects such as beetles and spiders have extraordinary climbing abilities. The remarkable adhesive ability of gecko foot has been attributed to the van der Waals forces coupled with the millions of nanoscale foot hairs
on its toe [102, 103]. These bio-adhesion systems have attracted a lot attention recently [104-115]. The high adhesive surfaces could be used in non-loss transport of small volume liquids, cleaning robots, or inside coating of aircraft to reduce the falling of condensed water [116-121].

Two kinds of biomimetic approaches were proposed to prepare stick superhydrophobic surfaces, which have been inspired from gecko foot and rose petal. The first approach is to mimic the nanoscale tube structures of gecko foot. Jiang et al. [122, 123] fabricated a high adhesion superhydrophobic surface with polystyrene (PS) nanotubes mimicking the gecko’s foot. The surface is composed of more than 6,000,000 aligned nanotubes per square millimeter, similar to gecko foot. The water contact angle was 162.0±1.7 ° and the water droplet stay stayed pinned to the surface even when tilted vertically or upside down. The maximum adhesive force between the droplet and the surface was about 59.8 μN measured by a high-sensitivity microelectro-mechanical balance system. The high adhesive force arises from the capillary forces and capillarity-induced negative pressure in the nanotubes. This surface has been used as a “mechanical hand” in no-loss transport of a super-paramagnetic microdroplet [122].

The other approach is inspired by rose petals. Raindrops stick to rose petals and the almost spherical droplets resist rolling off the flower, which is believed to help attract insects for pollination [80]. The surface of rose petal exhibits a periodic array of micropapillae and nano-scale cuticular folds on the top of the micropapillae, as shown in
Figure 2.4. A water droplet on the petal’s surface is believed to partially penetrate into the microscale grooves, but air gaps still exist in the nanoscale folds, thus forming a partial Wenzel state [102]. The water penetrates into micropapillae, causes a strong adhesion, while the air trapped in nanoscale folds enhances the water contact angle. Jiang *et al.* fabricated high adhesion superhydrophobic surfaces by replicating the microstructures of rose petal using polydimethylsiloxane (PDMS) [124]. Poly(vinyl alcohol) (PVA) was used as negative template to duplicate the petal surface and then peeled off, PDMS was cast onto the negative PVA template and solidified and peeled off. The resulting PDMS surface copied the microstructures of rose petal with high fidelity and exhibited a water CA of 154.3±1.8°. The as-prepared surface showed superhydrophobic properties in the pH range of 1-14.

![SEM images](image_url)

Figure 2.4 SEM images showing the structures of a rose petal at low (A) and high magnifications (B), and the inset shows the shape of water on the petal’s surface when it turned upside down. [Reprinted from reference 80 with permission]
2.2.4 Other Natural Superhydrophobic Surfaces

Other examples of superhydrophobicity observed in nature include water spider legs, butterfly wings, taro (*Colocasia Esculenta*) leaf, rice leaf and so on. The water spider has the ability to stand and move quickly on the water surfaces and it is found that their legs have hierarchical micro- and nano-structures [125]. The maximum supporting force of a strider leg is about 15 times of the weight of the insect due to the super water repellency. Butterflies can keep their wings uncontaminated by removing dust particles employing a directional rolling of water away from the body. The superhydrophobicity is caused by the microstructures on the wings [126]. The anisotropic liquid-solid adhesion is ascribed to the direction-dependent arrangement and orientation of the micro- and nano-structures of the wings [127]. Cicadae wings also exhibit superhydrophobicity, and the wing is comprised of aligned nano-columns with diameters around 70 nm [128].

2.2.5 Theoretic Background

The wettability of a flat surface, expressed by the contact angle, is given by Young’s equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$ (2.1)

where $\gamma_{SV}$, $\gamma_{SL}$, and $\gamma_{LV}$ refer to interfacial surface tensions with S, L and V as solid, liquid and gas respectively. Young’s equation results from thermodynamic equilibrium of the free energy at the solid-liquid-vapor interphase.
The behavior of a water drop on a rough surface is schematically shown in Figure 2.5. The water droplet can either penetrate into the rough surface or suspend above the asperities. These two situations are named the Wenzel state [47] and the Cassie-Baxter state [48].

The contact angle of surface in Wenzel state is predicted by Wenzel’s equation,
\[ \cos \theta_e^w = \gamma \cos \theta_e \]  
(2.2)
Where \( \gamma > 1 \) is the roughness factor, or the ratio of the contact surface area divided by the projection area and \( \theta_e \) is the contact angle on a smooth surface, \( \theta_e^w \) is the contact angle on a rough surface. Wenzel’s equation predicts that if \( \theta_e > 90^\circ \), then surface roughness makes it more hydrophobic; when \( \theta_e < 90^\circ \), rough surface makes it more hydrophilic.

The Cassie-Baxter model, on the other hand, describes the liquid suspends on the rough surface, in other words, the droplet sits on a composite surface of solid material and air gaps between materials. The contact angle is then given by a weighted average of the cosine values of the contact angles of the solid material and the air,
\[ \cos \theta_e^C = \phi_s (\cos \theta_e) + (1- \phi_s) \cos \theta_{air} \]  
(2.3),
Where \( \phi_s < 1 \) is the fraction of solid material in contact with the droplet and \( (1- \phi_s) \) corresponds to the fraction of air. \( \theta_{air} \) is \( 180^\circ \) and this equation can be rewritten as,
\[ \cos \theta_e^C = \phi_s (\cos \theta_e) + \phi_s - 1 \]  
(2.4)
Figure 2.5. A liquid droplet sits on a rough surface. Left: liquid penetrates into the rough surface (Wenzel state); right: liquid sits on the surface (Cassie-Baxter state).

In a Wenzel state, the water droplet penetrates into the surface and leads to a high contact angle hysteresis, while the hysteresis is low in Cassie-Baxter state. It has been reported that transition from Cassie to Wenzel state when the liquid droplet is pressed with external forces [129-131]. The rolling-off and sliding behavior of water droplets on solid substrates are also important in characterization of surface properties. Wenzel’s surface does not allow droplets rolling off easily due to large CAH. The relationship between CAH and sliding angle is described in equation 2.5 [132]

\[ mg\sin(\alpha) / R = \gamma_\mu (\cos \theta_r - \cos \theta_a) \] (2.5)

Where m and R are the mass and width of the droplet, \( \alpha \) is the tilting angle, \( \theta_r \) and \( \theta_a \) are the receding and advancing angles, \( \gamma_\mu \) is the surface energy of the droplet. Equation 2.4 shows that surface with smaller CAH will allow the droplet to roll off at a smaller tilting angle \( \alpha \) as expected. The surface roughness was found to affect the CAH [133]. Johnson et al. [134] found that contact mode switched from Wenzel to Cassie modes with increasing surface roughness and the CAH was dramatically reduced.

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2.3 Techniques to Prepare Superhydrophobic Surfaces

The topic of superhydrophobic surfaces has drawn more and more attention in recent years. Figure 2.6 shows the number of papers published recently by searching key word “superhydrophobic” in the ISI Web of Science.

Research on the surfaces of plant leaves and insects revealed the importance of surface roughness and the chemical composition for surface superhydrophobicity. Based on this, various approaches have been used to prepare superhydrophobic surfaces, which can be categorized into two categories: top-down or bottom-up approaches [44]. The top-down approaches utilize lithography, template based techniques and plasma treatment, in many cases using the naturally occurring textured surfaces of plants and animals as templates. The bottom-up approaches rely on molecular self-assembly to create substrates with designed patterns, layer-by-layer (LBL) deposition, colloidal assembly, chemical deposition, electrospinning, phase separation and so on.

2.3.1 Top-down Approaches

Top-down approach refers to the fabrication of surfaces by molding, carving, or machining bulk materials with laser, plasma or other tools. Template [135, 136] and lithography approaches [137-139], and plasma treatments [140] have been used to prepare superhydrophobic surfaces. These techniques can be used independently, or as a combination to generate superhydrophobic surfaces.
Figure 2.6 Number of publications indexed in ISI web of science by the key word “superhydrophobic”.

**Template Synthesis** Generally speaking, the template process involves preparing a featured template master, then molding the replica and finally removing or dissolving the templates. Many materials have been used as templates including plant leaves, insect wings and filter paper. One typical process is the fabrication of superhydrophobic surfaces by templating the lotus leaf. Sun *et al.* [97] used PDMS to replicate the structures of lotus leaf and the positive replica showed similar micro-papillae hills and fine nano-textures between the hills. The replica exhibited the same superhydrophobicity as the natural lotus leaf with a water contact angle of 160°. Nanoporous anodic aluminum oxide (AAO) has been widely used for pressure-driven imprint processes. For example,
superhydrophobic surfaces mimicking the nano-tube structure of gecko foot using hard-
PDMS was fabricated by using nanoporous AAO membranes as templates [135]. The
aluminum substrate was anodized to produce a nanoporous AAO template with
cylindrical pore channels. Then hard poly(dimethylsiloxane) (h-PDMS) precursors were
spin cast onto the AAO template, the sample was cured and the molded h-PDMS film
was peeled off from the template. The length of the cylinders of AAO templates can be
adjusted by the processing time, and superhydrophobic surfaces can be produced.
Template-based methods are effective in replicating regular surface patterns. However,
templates with micro- and nano-scaled structures are delicate and require careful
handling to avoid damage to the templates.

Lithography Lithographic technique has been widely used in making patterned
surfaces, and can be divided into the following categories depending on the light source:
photolithography (X-ray or e-beam depending on the light source), soft lithography,
nanoimprint lithography, capillary lithography, and colloidal lithography. Generally
speaking, the lithography technique includes copying of information from a master, and
then transferring it to a replica. Surface patterns prepared by lithography method are well-
ordered and easy to characterize, so they are widely used in surface modeling. Martines et
al. [141] created nanopillars and nanopits structures on silicon wafers using e-beam
lithography. The samples were post modified with octadecyltrichlorosilane (OTS) to
enhance the surface hydrophobicity. Both sticky and slippery surfaces were prepared with
different surface morphology and the Wenzel and Cassie-Baxter states were ascribed to
different aspect ratio (h/d). Increasing the aspect ratio can stabilize the Cassie-Baxter
regime.

Plasma Treatment Plasma treatment has also been used to prepare surface patterns
desired for superhydrophobic surfaces. Reactive atoms or ions are generated in a gas
discharge to etch the surface. Depending on the type of gas, ammonia, argon or oxygen,
different elements can be introduced into the surface and provide additional functions.
Fresnais et al. [142] used plasma etching to prepare superhydrophobic surfaces based on
low-density polyethylene (LDPE). Surfaces after plasma treatment had a roughness in the
range of 20 to 400 nm. Sequential treatment of LDPE with oxygen and CF4 plasma
yielded a surface with CA of 170 and low hysteresis (<5°). A variety of materials
including poly(ethyleneterephthalate) (PET) [143], poly(tetrafluoroethylene) (PTFE)
[144], poly(dimethylsiloxane) (PDMS) [145] have been used for the generation of
superhydrophobic surfaces. Plasma treatment can be used to produce textured
superhydrophobic surfaces on various substrates and materials. It can be used alone and
with other techniques such as lithography, templating method to create desired surface
patterns. The source gas has to react well with the material and the reaction condition
needs to be precisely controlled, which limits its large scale application to produce
extremely complex surface patterns.
2.3.2 Bottom up Approaches

Bottom up approaches, on the other hand, involve building larger objects by integration of smaller building units or components. Self-assembly [146], layer-by-layer (LBL) depositions [147-151], colloidal assembly [152-156], sol-gel method [157] have been employed to fabricate superhydrophobic surfaces.

**Self Assembly** Lee *et al.* [158] reported a raspberry-like particulate superhydrophobic film using self-assembly of silica particles. Silica particles with 0.5 μm in diameter were used to prepare a surface with microscale roughness, then nanosized silica particles were assembled on the particulate film to construct a finer structure. The surface was then modified with dodecyltrichlorosilane to enhance the hydrophobicity. The advancing and receding contact angles of water on the dual-sized structured surface were 169° and 165°.

**Layer-by-Layer Deposition** LBL deposition uses the electrostatic charge interaction between the different layers and has the advantage of facile structure and thickness control. Nanoparticles are often incorporated during the LBL process to increase the surface roughness. Cohen and co-workers [149-153] have produced transparent superhydrophobic surfaces using LBL. Poly(allylamine hydrochloride) (PAH) was used as the cationic solution and poly(sodium 4-styrenesulfonate) (SPS) as the anionic solution for the adhesion layer, while the body layer was an anionic water solution containing 20 nm silica particles. The obtained multilayered transparent film has
the contact angle of 160° with CAH around 10°. Polyelectrolytes are commonly used in the LBL process, and they are hydrophilic. Post chemical modification using low surface energy materials is necessary to render the surface hydrophobic.

**Colloidal Assembly** Monodispersed particles can self-assembly themselves onto surfaces by van der Waals interactions. The assembly particles provide roughness to the substrates and following treatments, such as plasma etching, can be used to enhance the roughness. For example, monodispersed polystyrene (PS) beads were used to form closely packed superhydrophobic surface by spin coating [159]. Oxygen plasma etching was used after assembly to adjust the solid fraction and increase the surface roughness. Plasma etching reduced the bead size and the bead size was found to affect the apparent water contact angles. After modification with gold and SAM formation, the surface exhibited a water CA of 156°.

**Sol-gel Method** Sol-gel methods has been used to prepare superhydrophobic surfaces from a variety of materials [160-162]. A sol is usually prepared by hydrolysis of corresponding oxide, for example, silica sols are prepared by hydrolysis of orthosilicate. The sol is then applied to form a gel, and nano-particles can be used in the gel formation process to enhance the surface structure. The final surface property can be adjusted with the method of preparation of the sol and the surface chemistry of the gel. Shang et al. [157] reported transparent superhydrophobic silica-based films made by a sol-gel method. Surface structures and roughness was controlled by the hydrolysis and condensation
reaction of various silica precursors and the surface was post modified with a monolayer through surface condensation reaction. The surface showed optical transparency higher than 90% and the surface had advancing and receding angles of 165 and 115°.

Bottom up approaches provide precise control of the surface pattern, molecular composition and thickness of the products. However, the hydrophobic properties of the products are often unknown until the last step.

2.3.3 Other Approaches

Combinations of top down and bottom up approaches have also been used in preparing superhydrophobic surfaces, i.e. electrospinning [163-165], phase separation [166,167], and combination methods based on chemical vapor deposition (CVD) [168].

**Electrospinning** has been widely used in preparation of polymer nanofibers. Asmatulu *et al.* [165] fabricated superhydrophobic surfaces by electrospinning polystyrene and polyvinyl chloride (PVC) fibers. The water repellency depended on the diameter of the fibers and the morphology. The morphology of electrospun films can be controlled from beads to fibers by increasing the solution viscosity.

**Phase Separation** during membrane casting can also form superhydrophobic surfaces. Phase separation occurs when a polymer solution is submerged in non-solvents or during heat treatment. The polymer phase separate into a polymer-rich phase and a polymer-poor phase. The polymer-poor phase will form pores when the solvents evaporate. Erbil *et al.* [166] used isotactic polypropylene (i-PP) to prepare phase
separated structures using various nonsolvents and drying temperature. For industrial applications, fabrication of structured surfaces on large scale at low cost is vital and phase separation provides a good solution.

Methods based on CVD processes have been commonly used in the preparation of superhydrophobic surfaces and it is usually used in combination with other techniques such as LBL deposition, self-assembly. CVD of carbon nanotubes (CNT) to produce superhydrophobic surfaces was reported by Zhu et al [168], who grew CNT arrays using CVD. The micro-scale roughness determined the apparent water CA and nano-scale roughness drastically decreased the water CAH.

2.4 Ionomers

Ionomers refer to polymers containing a small amount of ionic groups (usually less than 15 mol %) [169]. Ionomers can be classified into random ionomers or telechelic ionomers depending on the distribution of ionic groups. Random ionomers denote ionomers in which the ionic groups are randomly distributed along the polymer chain, while telechelic ionomers have the ionic groups attached at one end or both ends. These materials may be viewed as random copolymers and are prepared by either direct copolymerization methods or post-polymerization modification of a polymer. In contrast to the relatively weak interactions in non-ionic polymers, such as hydrogen bonding, the ionic groups in ionomers tend to aggregate into ionic clusters and serve as physical crosslinking, which will dramatically change the structures and properties. Commercial
applications for ionomers are golf ball covers, proton exchange membranes, shape
memory materials, and thermoplastic elastomers etc. Sulfonated polystyrene ionomers
suppress film dewetting and improve adhesion to polar substrates such silica [5].

The behavior of ionomer solutions depends on the solvent polarity and has been
moderately studied [170-175]. In solvents with low polarity, ionomers show aggregation
behavior and the ionic species tend to associate to form dipoles and the dipoles associate
with each other to form aggregates. In polar solvents, ionic groups tend to dissociate to
form polyions and free counterions in polar solvents. Ionomers can show polyelectrolyte-
like behavior insolution.

2.4.1 Aggregation behavior

In relatively non-polar solvents, the ionic groups tend to aggregate due to
attraction between the ion-pair dipoles. Many experimental methods including dilute
solution viscometry, viscoelasticity, static and dynamic light scattering, neutron
scattering have been used to study the aggregation behavior. Lundberg et al. [170]
observed that the reduced viscosity of sodium sulfonated polystyrene (NaSPS) in THF, or
p-dioxane was lower than that of unmodified polystyrene. With an increase of
concentration, a cross-over in the viscosity occurred at a critical concentration. The lower
viscosity at low ionomer concentration was due to single-chain collapse caused by the
intra-molecular association, and the higher reduced viscosity above the crossover
concentration was due to the inter-molecular association to form multi-chain aggregates.
2.4.2 Polyelectrolyte behavior

Lundberg and Phillips [170] also found that solutions of NaSPS ionomers in solvents with high polarity, such as dimethylformamide (DMF) and dimethysulfoxide (DMSO) showed “polyelectrolyte behavior”. The reduced viscosity had an upturn at very low concentrations and decreased with increasing concentrations. This is due to the repulsion of ions fixed to the backbone with the same charge. As the polymer concentration decreases, the chain expands to larger size due to intramolecular repulsion, and this is manifest as a higher viscosity. Addition of salt shields the bare ions and eliminates the polyelectrolyte effect [173, 174].

2.4.3 Ionomer Phase Diagram

Theoretical studies of ionomer solution phase behavior are very limited. Joanny [176] proposed that random ionomer solutions exhibit two phase transitions: demixing and gelation (Figure 2.7). Phase demixing follows Flory’s theory when the temperature is below the theta temperature of the unmodified parent polymer and the solution concentration is low. Randomly distributed ionic groups affect the second virial coefficient \(A_2\) and it was renormalized to take into account the effect of dipolar interactions:

\[
\hat{A}_2 = \hat{A}_2' + f^2 \hat{A}_2 \\
\]

where \(\hat{A}_2\) is the term describing the attraction of the ionic dipoles and is always negative, \(f\) is the percent of dipoles on the polymer backbone. Joanny’s theory predicts a gelation
curve at high concentration and temperature. The gelation concentration, $C_{gel}$, will decreases with an increase of the ion pair concentration.

![Diagram](image)

Figure 2.7. Theoretical temperature concentration phase diagram of random ionomer solutions. $T_k$ and $C_k$ are the critical temperature and concentration, respectively. $C_0$ is the point where the gelation line and the coexistence curve meets. (Reprinted with permission from reference 176)

Experimental measurement of the ionomer phase diagram has been limited so far. Chakrabarty et al. [177] studied the phase diagram of lightly sulfonated polystyrene acid (HSPS) solution in decalin and found that it exhibits UCST phase behavior. At low polymer concentration, the solution goes from one phase to phase separation as the
solution is cooled. At higher concentration, gelation occurs before phase separation when the solution is cooled. The results followed Joanny’s theory pretty well.

2.5 Phase Separation during Solvent Evaporation

2.5.1 Spinodal Decomposition

Nano-structured surfaces have attracted increasing attention these years in the field of biomimetic applications and surface coatings. Industrial applications require methods to prepare large-scale rough surface with reproducible, uniform structures at low cost. Phase separation provides an easy solution to prepare well-controlled micro- and nano-scale patterns.

Phase separation in polymer systems is of technological as well as fundamental interest and has been extensively studied [179, 180]. The initial process of phase separation usually occurs via either nucleation and growth (NG) or spinodal decomposition (SD) mechanisms. NG occurs in the metastable region of the phase diagram (area between the bimodal and spinodal), while SD occurs in the unstable region of the phase diagram (inside the spinodal curve) (Figure 2.8). Spinodal decomposition is initiated by small-amplitude composition fluctuations which increase with time and the kinetics has been extensively studied.
2.5.2 Kinetics of Spinodal Decomposition

Phase separation dynamics is a subject of increasing interest [81-186]. The commercial product quality depends on the morphology of the system and the structure and size of domains obtained by the phase separation. The phase separation process in the liquid/melt state can be stopped at any stage by rapid vitrification of the separating mixture and the captured structure determines the product properties.

Research on the phase separation kinetics of spinodal decomposition has been focused on polymer blends melts. The spinodal decomposition process is generally divided into three regimes: (1) a percolation regime where a bicontinuous structure is formed, (2) a percolation-to-cluster transition (PCT) regime where the polymer fibrils
break up into discrete domains and (3) a cluster regime where the domains grow [182-189]. Hashimoto et al. [182] studied the time evolution of spinodal decomposition for the mixtures of poly(styrene-ran-butadiene) (SBR) and polybutadiene (PB) or SBR and polyisoprene (PI). It was found that phase separation in polymer blends with higher molecular weights stopped during the phase separation. According to them, the transport of polymer chains across the interface is necessary for droplet domain growth and the energy barrier of transportation of polymer chains, which is proportional to the degree of polymerization, $N$. Therefore, the spinodal decomposition of higher molecular weight polymer blend will be stopped at PCT, and no cluster structure was formed. Takeno et al. [187] studied the crossover of the domain growth behavior for PCT transition in phase separation of polymer blend of polybutadiene (PB) and polyisoprene (PI) using time-resolved light scattering. Holyste et al. [188] also reported network breaking and domain growth in phase separation in binary mixture of polymer and liquid crystal.

In contrast, relatively little work has been done on the phase separation dynamics of polymer solution. Tan et al. [189] prepared a slippery superhydrophobic surfaces by solution-casting polystyrene ($M_w = 8.9 \times 10^6$ g/mol) from DMF solution onto glass slides. The morphology formation mechanism was attributed to the spinodal decomposition of polymer films during solvent evaporation. A major problem with polystyrene surfaces, however, is that the adhesion of polystyrene film to most substrates, and especially polar substrates, is generally poor. A cast film of polystyrene onto glass or silicon is relatively
easy to peel off, or it spontaneously delaminates from the substrate when immersed in water.

Weiss et al. [42] reported that spin-coating provided a facile method for preparing rough surfaces with submicrometer-scale roughness, as shown in Figure 2.9. A particle-textured surface with particle diameters of ~200 nm was produced by spin-coating a lightly sulfonated polystyrene (SPS) ionomer from THF or THF/methanol solutions onto a silica substrate. The particle-textured surface was attributed to spinodal decomposition at the liquid/vapor interface of the drying film. The incorporation of a small amount of ionic functionality into the polystyrene significantly improved its resistance to dewetting [190].
2.6 Characterization of Polymer Films

This research required characterization of the structure and morphology of ionomer films and surface hydrophobicity. The ability to characterize the film morphology is vital in this research. The characterization techniques used in this research including AFM, SEM, and contact angle will be briefly discussed here.

2.6.1 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was developed in 1986 by Binning, Quate and Gerber and has been widely used in the characterization of solid surfaces and polymer films [191]. AFM has the advantage of imaging non-conductive surfaces and operating under ambient conditions without vacuum. AFM offers lateral and vertical resolutions up to the atomic scale and 3-D imaging ability. AFM measures the forces between the tip and the surface. AFM can be operated in contact mode or non-contact mode. In contact mode, a constant force is applied between the tip and the surface during scanning and the tip deflection is maintained constant. In non-contact mode, or tapping mode, the cantilever does not contact the sample surface, but it oscillates at a constant frequency. Dynamic force mode or tapping mode is also used, because it eliminates the lateral force and reduces the damage to the sample and tip in the contact mode. The cantilever is oscillated closer to the sample and in larger amplitude (typically 100–200 nm) compared with non-contact mode (<10 nm).
2.6.2 Scanning Electron Microscopy (SEM)

SEM was first developed in early 1930’s and first marketed in 1965 [192-194]. Since its development, it has been widely used in characterization of surfaces in physical, medical and chemical science. SEM uses a focused beam of high-energy electrons to scan the sample surfaces and produce signals containing information about the surface topography and chemical composition.

A beam of electrons is produced at the top by an electron gun and then accelerated through the magnetic field. When the beam hits the sample, electrons and X-rays are emitted from the sample. Scattered electrons, secondary electrons and X-rays signals are collected by the detector and converted into the computer to produce the image. The advantage of SEM is that it provides fast date acquisition, covers a wide range of magnifications, from about 10 times to more than 500,000 times, and it measures the surface chemical composition (Energy-dispersive X-ray spectroscopy, EDX) together with the topography. On the other hand, the sample size is limited to the dimension of the microscope chamber (usually less than 5 by 5 cm) and SEM requires high vacuum in the order of $10^{-5}$ to $10^{-6}$ torr. In addition, SEM only works with conductive samples and non-conductive samples need to be coated with a conductive metal layer.
2.6.3 Contact Angle Measurement

The contact angle of a liquid droplet on a solid surface is determined by the interfacial tensions between liquid and solid surrounded by vapor, and is given by the Young’s equation,

$$\cos \theta = \frac{\gamma_{SL} - \gamma_{SV}}{\gamma_{LV}}$$  \hfill (2.1)

where $\gamma_{SL}$, $\gamma_{LV}$ and $\gamma_{SV}$ are the interfacial energy between the solid, liquid and vapor interface as denoted. The contact angle gives information about the surface roughness and chemical composition of the sample.

The most common method to measure static contact angle is to place a small liquid droplet onto the solid surface and measure the angle of the tangent to the liquid at the three-phase boundary line and the horizontal plane of the surface. The dynamic contact angle, including the advancing and receding contact angle is measured by continuously adding or withdrawing liquid from the droplet. Contact angle hysteresis, which is the difference between the advancing and receding angle, is important in determining the droplet sliding on the surfaces, and has been the subject of recent literature [195, 196].

Contact angle hysteresis results in a retentive force describing the ability of the surface to retain the droplet. The retentive force, $F_r$, which results from the contact angle hysteresis, is given by

$$F_r = k \gamma R (\cos \theta_r - \cos \theta_a)$$  \hfill (2.7)
where \( k \) is a numerical constant depending on the droplet shape, \( \gamma \) is the surface tension of the liquid and \( R \) is radius of the droplet [197]. The maximum droplet volume that can adhere to the films can be characterized for different tilt angles. Tilting the film applies a force, \( F_g \), to the droplet parallel to the surface,

\[
F_g = \rho g V \sin \alpha
\]

(2.8)

where \( \rho \) is density of water, \( g \) is the gravitational acceleration constant, and \( V \) is the drop volume [198]. The droplet starts rolling when \( F_g \geq F_r \), which occurs when the volume of the droplet becomes too large.

2.7 Objectives and Approaches

As described earlier in this chapter, nano-particle textured surfaces were prepared by spin coating ionomer solutions and the mechanism is believed to be spinodal decomposition during the solvent evaporation process [42]. This research seeks to develop a more complete understanding of the process, specifically to delineate the mechanism of the surface texture formation, to investigate the parameters controlling surface morphology during spin coating and solution casting process, to explore other polymer/solvent pairs can be used in this process and how superhydrophobic surfaces may be developed with the textured surfaces.

This thesis involved the study of SPS ionomer surfaces with different structures, how to control those surfaces by varying the processing parameters. I further the application of textured surface to mimic the sticky superhydrophobic surfaces, or the so
called “petal effect”. The effect of solvent properties, polymer molecular weights, solution concentrations, solvent evaporation rates on the surface structures on surface morphology was studied. The structure-property relationship of surface morphology and the hydrophobicity was investigated. High adhesion superhydrophobic surfaces were prepared by spray coating ionomer solutions. The preparation of textured, hydrophobic surfaces with high adhesion provides a low-cost method for large-scale fabrication of sticky superhydrophobic surfaces.
CHAPTER III

NANO-PARTICLE TEXTURED SURFACES FROM SPIN COATING

3.1 Introduction

Spin-coating is a widely-used technique of preparing highly uniform, thin polymer films [199-204]. It has wide application in industry for making thin films of semiconducting polymers for light-emitting diodes and photovoltaic cells, photoresists, sol-gel glasses. Polymer solution is deposited onto the substrate, which is rotated at a set speed to produce uniform thin films. The quick evaporation of solvent and solution spreading over the substrate as consequence of centripetal force generates a very thin film. The film thickness is controlled by the coating speed, solution concentration and viscosity, and polymer molecular weight. During spin coating process, the viscosity of polymer solution rises rapidly because of the fast evaporation of the solvent. At the same time, the film undergoes thinning as a result of the solvent evaporation and spreading over the substrate [203].

The majority of the work which is related to the morphology of spin coated polymer films focuses on immiscible polymer blends to study the phase separated structures. PMMA and PS blend is a good example of an immiscible polymer blend. Li et al. [206] studied the effect of polymer molecular weight morphology and
stability of spin coated PMMA and PS blend using AFM and X-ray photoelectron spectroscopy (XPS). Three type of surface morphologies were observed when the $M_w$ of PS varied from 2.9 to 129 kg/mol: (1) a nanophase separated morphology, (2) a PMMA cellular or network-like morphology whose meshes are filled with PS, (3) a sea-island like morphology. The results showed that the surface morphology of polymer blend film can be controlled by varying of the molecular weight of one polymer.

In contrast to polymer blend systems, the surface morphology for homopolymer films has been rarely studied. Spangler et al. [202] studied the effect of solvent on the spin cast film thickness and topography. It was found that both solvent volatility and solvent quality affect the surface thickness and topography. Use of highly volatile solvents and high molecular weights polymers tends to create thicker films. For dilute solutions, “poor” solvents and highly volatile solvents created waves on the surfaces, which is due to the conformation of polymer coils in the poor solvent or the rapid increase of viscosity as a result of the fast evaporation of volatile solvents. Good solvents with low volatilities produce uniform polymer films. Muller-Buschbaum et al. [206] investigated the surface morphology and roughness using polystyrene and brominated polystyrene in various solvents for spin coating. The relationship between the solvent vapor pressure to the film thickness of the spin-cast polystyrene film was reported. Solvents with low vapor pressure as well as solvents with high vapor pressure generated smooth polymer surfaces. However, rough surfaces were created when solvents with intermediate vapor pressure were chosen.
Weiss et al. recently reported a facile, one-step method for preparing rough surfaces with nano-scale roughness [42]. A particle-textured surface with particle diameters of ~200 nm was produced by spin coating a lightly sulfonated polystyrene (SPS) ionomer from THF or THF/methanol solutions onto a silica substrate. The particle-textured surface was attributed to spinodal decomposition at the liquid/vapor interface of the drying film. The incorporation of the small amount of ionic functionality into the polystyrene significantly improved its adhesion to polar substrates and resistance to dewetting [190].

This chapter presents the preparation and characterization of lightly sulfonated polystyrene SPS ionomers spin coating films. The effect of solvent, molecular weight of the ionomer, solution concentration and choice of cation on the surface morphology was investigated. Furthermore, mono-functional ammonium-ended telechelic polystyrene (PS-1-NH₃⁺Cl⁻) ionomer was synthesized and film morphology from spin coating PS-1-NH₃⁺Cl⁻ ionomer was characterized. The hydrophobic nature of the surfaces was characterized by contact angle measurements and the effect of a post-casting chemical modification of the surface on the hydrophobicity was assessed.

3.2 Experimental Details

3.2.1 Materials and Solvents

Toluene (99.9%, Aldrich), 1,2-dicholorethane (reagent grade, Fisher Scientific Co.), acetic anhydride (reagent grade, Aldrich), sulfuric acid (reagent grade, Aldrich), chloroform (99.9%, Aldrich), dichloromethane (99.9%, Fisher Scientific Co.), 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%, Acros Organics), 2-
aminoethanethiol hydrochloride (98%, Acros Organics), and 1H,1H,2H,2H-perfluoroocetyltrichlorosilane (Fisher Scientific Co.) were used as received. Benzene (Certified ACS, EM Science), tetrahydrofuran (THF, Certified ACS, EM Science), and styrene (99%, Aldrich) were purified as previously reported [207, 208]. Benzene and THF were distilled as needed from poly(styryl)lithium into the polymerization reactors. Methanol (Fisher Scientific, reagent grade) was degassed on the vacuum line before distillation into ampules and flame-sealed. 4-Pentenyllithium was prepared according to the literature procedure [209] and used after double titration with allyl bromide [210, 211].

3.2.2 Synthesis of Sulfonated Polystyrene Ionomers

Two narrow molecular weight distribution polystyrenes (PS) were obtained from Pressure Chemicals with weight average molecular weights of 4.0 kg/mol and 13.5 kg/mol with PDI<1.06. These are denoted as PS-4 and PS-13.5, respectively. These molecular weights are below the chain entanglement molecular weight (M_n) of PS, 16.6 kg/mol [212]. PS was sulfonated at 50°C in 1,2-dichloroethane to 2.5 mol% using acetyl sulfate, prepared by the reaction of concentrated sulfuric acid (Fisher Scientific Co., 95%) with acetic anhydride (Andrich Chemical Co, reagent grade) at 0°C, as the sulfonating agent according to the procedure of Makowski et al. [213], as shown in Figure 3.1. The sulfonic acid derivative of the sulfonated polystyrene ionomer (HSPS) was recovered by flashing the solvent in boiling water, washing with D.I. water and then drying under vacuum at 120°C. HSPS was neutralized to the lithium (Li⁺) salt ionomers (LiSPS) and Tetraoctyl ammonium (TOA⁺) ionomer salt
(TOA-SPS) using LiOH and TOA-OH (Figure 3.2). TOA-OH was prepared by passing a solution of Tetraoctyl ammonium bromide (TOAB) (20 g/L) in a mixed solvent of water and methanol (30/70 g/g) through a packed column of a hydroxide-exchange resin (Figure 3.3). Methanol was used because TOAB is not soluble in water. The addition of a small amount of water increased the ion-exchange. The extent of ion exchange was 90–95%, as determined by titration with 0.01 N HCl [214].

The sulfonation procedure randomly sulfonates the styrl ring, primarily at the para- position. The sulfonation level was characterized by elemental analysis (Galbraith Laboratories) and titration with sodium hydroxide solution in toluene/methanol (v/v=95/5) solution. During titration, nitrogen gas was bubbled into the solution to remove any carbon dioxide dissolved in the solution. Each sample was titrated three times to get the average sulfonation level. The nomenclature used for the ionomers was 2.5 MSPS-z, where M is the type of cation, and z is the molecular weight of the parent PS in kg/mol. The characteristics of the ionomers and the polystyrenes are summarized in Table 3.1. The glass transition temperatures (T_g) of the polymers were determined with a differential scanning calorimeter (DSC), TA2920, TA Instruments, using a heating rate of 20°C/min.
Figure 3.1 Synthesis procedures of randomly sulfonated polystyrene ionomers.

Figure 3.2 Schematic draw of tetraoctyl ammonium bromide (TOAB) structure.

Figure 3.3 Schematic of ion exchange and neutralization reaction of HSPS acid to form TOA salt.
Table 3.1 SPS Ionomer Characteristics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfonation (mol%)(^a)</th>
<th>(M_w) kg/mol</th>
<th>(M_w/M_n)</th>
<th>(N)(^b)</th>
<th>(T_g (\degree C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-4</td>
<td>0</td>
<td>4</td>
<td>&lt;1.06</td>
<td>39</td>
<td>82</td>
</tr>
<tr>
<td>PS-13.5</td>
<td>0</td>
<td>13.5</td>
<td>&lt;1.06</td>
<td>130</td>
<td>98</td>
</tr>
<tr>
<td>2.5LiSPS-4(^c)</td>
<td>2.5</td>
<td>4.2</td>
<td>&lt;1.06</td>
<td>39</td>
<td>87</td>
</tr>
<tr>
<td>2.5LiSPS-13.5</td>
<td>2.5</td>
<td>13.5</td>
<td>&lt;1.06</td>
<td>130</td>
<td>104</td>
</tr>
<tr>
<td>2.5TOASPS-13.5</td>
<td>2.5</td>
<td>13.5</td>
<td>&lt;1.06</td>
<td>130</td>
<td>107</td>
</tr>
</tbody>
</table>

\(^a\) number of sulfonate groups per 100 repeat units

\(^b\) N = degree of polymerization.

\(^c\) assuming that sulfonation does not affect the chain length of PS

3.2.3 Synthesis of ammonium-ended telechelic polystyrene ionomer (PS-1-NH\(_3^+\)Cl\(^-\))

Monochain-end-functionalized polystyrene ionomer was synthesized by Yiwen Li using thiol-ene chemistry with 4-pentenyllithium as the initiator, following the procedure by Li et al. [210, 211]. Specifically, 4-pentenyllithium was first used as a functional initiator to prepare \(\alpha\)-vinyl-functionalized poly(styryl)-lithium (vinyl-PS-Li) [211], then the resulting \(\alpha\)-vinyl-PS can react with various functional thiols to prepare the desired \(\alpha\)-functionalized PS (PS-1-NH\(_3^+\)Cl\(^-\)), as shown in Figure 3.4. The PS-1-NH\(_3^+\)Cl\(^-\) ionomer was characterized by \(^1\)HNMR, \(^13\)C NMR, and MALDI-TOF mass spectrometry to characterize their chemical structures and chain-end functionality. The results clearly indicate the cleanness of the reaction, the precisely defined
structure, and the high degree of functionalization (~100%). The polymers thus synthesized serve as important model compounds in the study of their bulk properties as well as nano-particle formation behavior in spin coating process.

3.2.4 Film Preparation

Atomically smooth silicon wafers with \{100\} orientation and one side polished were obtained from Wafer World, Inc. The silicon wafers were washed in an ultrasonic bath for 10 minutes followed by immersion in a “piranha” solution (30% concentrated hydrogen peroxide and 70% concentrated sulfuric acid) bath for 30 minutes to remove any organic contamination and to oxidize the surface to silica. After the “piranha” treatment, the samples were rinsed thoroughly with deionized water and dried with compressed nitrogen gas.

Ionomer films were prepared by spin-coating polymer solutions onto silica substrates. 2.5LiSPS-4, 2.5LiSPS-13.5, 2.5 TOASPS-13.5 and PS-1-NH$_3^+$Cl$^-$ solutions (1 wt%) were spin coated onto the silicon wafers with a SCS Corp., model P6700, spin coater using a rotor speed of 3000 rpm. Four solvents and two solvent mixtures were used (Table 3.2). The solubility parameters, dielectric constants, and vapor pressure values of the mixtures are calculated using a volume average of the individual components. 2.5LiSPS-4 surfaces were spin cast from 1 wt% and 5 wt% THF solutions to study the effect of concentration on the surface morphology.

3.2.5 Characterization

Intrinsic viscosities of the SPS ionomers in solution at 25 °C were measured with a Ubbelohde viscometer (Fisher Scientific Co, model-1). The surface
morphology of the ionomer was imaged with an Asylum Research, Inc., MFP-3D, atomic force microscope (AFM) using the tapping mode. Silicon tips (tip curvature radii \( \sim 5-10 \) nm) with a spring constant of about 2.5 N/m were used. The root mean square roughness of the surface was calculated using the AFM instruments software. Scanning electron micrographs were obtained with a JEOL-6335F field-emission scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV. The specimens were sputter coated with silver to prevent arcing. Water contact angles (CAs) were measured using a Ramé-Hart Model 500 Advanced Goniometer equipped with a rotating stage. Water droplets (5.0 \( \mu \)L) were carefully placed on the surface

\[
\text{4-Pentenyllithium} \quad \text{Vinyl-PS-Li}
\]

\[
\text{Vinyl-PS-Li} + \text{CH}_2\text{OH} \quad \text{DMPA, R}_F\text{SH} \quad \text{hv, 15min} \quad \text{FG-PS}
\]

\[
\text{R}_{FG} = \text{CH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-
\]

Figure 3.4 Synthesis procedure of mono-telechelic polystyrene using combination of living anionic polymerization and thiol-ene chemistry. [Reprinted with permission from reference 210].

using the Ramé-Hart automated dispensing system and the images were taken and analyzed with DropImage Advanced v2.4 software. Static CAs were calculated as the
average of five measurements made at different positions on the surface. Dynamic CAs were measured by placing a water droplet on the surface and then rotating the stage 90° and measuring the advancing and receding angles. The as-cast films were

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility parameter (MPa)$^{1/2}$</th>
<th>Dielectric Constant</th>
<th>Vapor Pressure (kPa @ 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>19.8</td>
<td>9.1</td>
<td>45.7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>19.0</td>
<td>4.8</td>
<td>23.5</td>
</tr>
<tr>
<td>Chloroform/Methanol* 4/1 (v/v)</td>
<td>21.1</td>
<td>10.4</td>
<td>22.2</td>
</tr>
<tr>
<td>Methanol</td>
<td>29.7</td>
<td>33</td>
<td>16.8</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>18.6</td>
<td>7.6</td>
<td>21.5</td>
</tr>
<tr>
<td>THF/Methanol* 9/1 (v/v)</td>
<td>19.7</td>
<td>10.1</td>
<td>21.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.2</td>
<td>2.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

* Solvent mixture properties were calculated from a volume-weighted average

*Solubility parameter values were taken from reference 215, dielectric constant and vapor pressure values are from reference 216.

also modified with (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1- trichlorosilane by chemical vapor deposition. The as-cast polymer film was placed on the top of a vial containing a few drops of silane at the bottom with the film side facing the silane, so
that there was no direct contact between the polymer film and the silane. The vial was placed in a vacuum oven at 60°C for 1 h to allow the silane vaporize and condense on the polymer surface. Finally, the film was placed in an oven at 80°C for another 0.5 h to evaporate excess silane.

3.3 Results and Discussion

3.3.1 Sulfonation Distribution

The sulfonation process is a random reaction and the distribution of sulfonate groups on each chain is not uniform. The average sulfonation level was characterized by titration of the acid form and elemental analysis of the sulfur content. A binomial distribution was often used to calculate the probability, P(x), that a chain with a degree of polymerization, N, has x sulfonate groups on a chain where p is the probability of a monomer being sulfonated (equation 3.1) [190]. Note that p is the mole fraction of substituted styrene units = mol % of sulfonation divided by 100.

\[
P(x) = \frac{N!}{(N-x)!x!} p^x (1-p)^{(N-x)}
\]

(3.1)

Figure 3.5 shows the distribution function \(P(x)\) for the two ionomers studied. Although the average sulfonation level is 2.5 mol %, the distribution shows that each sample has a finite amount of chains with no sulfonation and more sulfonate groups than average. This is particularly important when it comes to solution behavior in the high concentration regime. Even in the sample with an average of one sulfonate group per chain \((x = 1)\), there will also be a finite concentration of multiple substituted chains. Since the ion-pairs phase separates from the non-polar styrene backbone, ionic
aggregate are commonly observed in ionomers [217]. Polymer chains with one or two sulfonate groups only produce chain extension of the oligomers. When \( x > 2 \), network formation is possible. According to the distributions \( P(x) \) for the different ionomers, one might reasonably expect that network formation is possible for all the ionomers studied here, since both ionomers contain certain number of chains with \( x > 2 \).

![Graph](image_url)

**Figure 3.5** Probability \( P(x) \) distribution as a function of the number of sulfonate groups per chain, \( x \), for SPS ionomers with molecular weights of 4.0 and 13.5 kg/mol and sulfonation level 2.5mol%.

3.3.2 Parameters Controlling Film Morphology during Spin Coating of SPS Ionomers

**Effect of Solvent.** Spin-coating is a simple method for preparing thin polymer films. The quick evaporation of solvent and solution spreading over the substrate as a consequence of centripetal forces produces thin films. Muller-Buschbaum *et al.* [206] reported that the surface of spin-cast PS films was smooth when solvents were used
with either high (i.e. chloroform ~ 26.2 kPa) or low (i.e. toluene~3.79kPa, 1,2 dichloroethane~10.6kPa) vapor pressures. However, rough surfaces were produced with solvents having intermediate vapor pressures (i.e. THF~21.5kPa).

The effect of solvent properties on the film morphology of spin coated SPS ionomers was investigated with a number of solvents and solvent mixtures, varying the solubility parameter, vapor pressure, and dielectric constant, Table 3.2. For 2.5LiSPS-4, spin-coating from the solvents dichloromethane, chloroform, and toluene produced films with smooth and featureless surfaces. In contrast, the use of THF and mixed solvents of THF/methanol and chloroform/methanol produced unusual morphology composed of submicron particles, Figure 3.6, which is believed to result from a spinodal decomposition of the surface during film drying [42]. Unlike the PS particle morphologies reported before, which do not adhere well to a surface, the ionomer particles were well adhered to the silica surface.

The evaporation rate of the solvent is expected to scale with the solvent vapor pressure, $p^o$. Figure 3.6 shows that when $p^o = 3.4$ or greater than 22.2 a smooth film was produced, while when $p^o \sim 21 – 22$, the particle morphology resulted (note that methanol, which is listed in Table 3.2, was not a solvent for the ionomer). These results are similar to those reported for Muller-Buschbaum et al. [206], and it suggests that there is characteristic time for which the particle morphology is formed during drying the film.

Based on the spinodal decomposition model proposed by Zhai and Weiss [190], the characterization time at which this morphology occurs is determined from a
balance of the energy of viscous dissipation in the film and the energy gained per unit time from film undulation. That balance results in the characteristic time given by the following equation,

\[ \tau \propto \xi^4 \eta / h^3 \gamma \]  \hspace{1cm} (3.2)

where \( \tau \) is the characteristic time, \( \gamma \) is the surface energy of the polymer/air interface, \( \eta \) is the solution viscosity and \( h \) is the film thickness. \( \xi \) is the healing length, which means when the surface fluctuation exceeds the healing length, the film becomes wrinkled and breaks into particles,

\[ \xi \approx h^3 \sqrt{2 \pi \gamma / |A_{\text{eff}}|} \]  \hspace{1cm} (3.3)

\( A_{\text{eff}} = A + 0.9 k_B T \) is the effective Hamaker constant that has contributions from the long-range van der Waals attraction [218] and polymer confinement [219], \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature.

A rough surface is produced only when the solvent evaporation time, \( t \), is of the order of the characteristic time. When the solvent evaporates rapidly, i.e., \( t \gg \tau \), there is insufficient time for structure formation to occur and a smooth films is produced. At the other extreme, \( t \ll \tau \), phase separation occurs during drying, but the particle phase retains sufficient mobility to spread and form a uniform surface before vitrification occurs. That explanation is supported by the observation made by Zhai and Weiss [190] that when the particle morphology was annealed above \( T_g \) for a long time, the particles coalesced and formed a smooth film. It is noteworthy that the coalescence of the particle morphology into a film took up to 10 days at 30 degrees
above $T_g$, which indicates that the particle morphology once formed is relatively robust.

![AFM micrographs of films spin cast from 1wt % 2.5 LiSPS-4 at 3000 rpm from solvents listed in Table 3.2. The solvent used and its vapor pressure $p^0$ at 25°C is indicated below each micrograph. The root mean square roughness, $r$, in $\text{nm}$ is indicated on the micrograph.](image-url)

Solvent polarity affects the ionomer conformation in solution, which can also affect the spin coated film morphology. The ionic groups of SPS ionomers tend to associate in relatively non-polar solvents due to the low solubility of the polar...
sulfonate groups, which decreases the coil size of the chains [172]. Polar solvents solvate the dipolar interactions of the ionic groups and the chain conformation is similar to that of PS in a good solvent [172].

![Image](image.png)

**Figure 3.7** SEM images of films spin cast from 1 wt% 2.5LiSPS-4 in chloroform and chloroform/methanol (v/v=4/1) solutions at 3000 rpm and room temperature.

Figure 3.7 compares the surface morphology of films spin cast from chloroform and chloroform/methanol mixture (v/v = 4/1). The differences in the dielectric constants (4.8 and 10.4) and solubility parameters (19.0 and 21.1(MPa)$^{1/2}$) indicated that the mixture was more polar and a better solvent for the sulfonate groups. This is supported by the intrinsic viscosity data given in Table 3.3. The higher intrinsic viscosity for chloroform/methanol (v/v=4/1) mixture indicates that the ionomer chain in the solution is more expanded. Although the vapor pressures were similar, the particle texture was only formed when the more polar solvent was used. Although vapor pressure is important for determining whether a particle texture forms, it is not a sufficient criterion. A relatively polar solvent is needed.
Table 3.3 Intrinsic viscosity of 2.5LiSPS-4 Ionomer at 25°C

<table>
<thead>
<tr>
<th>Ionomer</th>
<th>THF</th>
<th>THF/MeOH (9/1)</th>
<th>Toluene</th>
<th>Chloroform</th>
<th>Chloroform/MeOH (4/1)</th>
<th>Methylene Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5LiSPS-4</td>
<td>8.55</td>
<td>8.85</td>
<td>4.72</td>
<td>5.89</td>
<td>8.32</td>
<td>8.22</td>
</tr>
</tbody>
</table>

Effect of Polymer Molecular Weight. Figure 3.8 shows the effect of the ionomer molecular weight on the morphology of the films spin cast at room temperature from THF at 3000 rpm. The 2.5LiSPS-4 sample exhibited a surface morphology of mostly discrete particles, while the 2.5LiSPS-13.5 ionomer film had a structure composed of chain-like, multiple particle aggregates. The difference in the two morphologies is consistent with the progression of phase separation by a spinodal decomposition mechanism. As the solvent evaporates during spin coating, the morphology can change until the sample vitrifies, which occurs when the T_g of the solvent-swollen polymer reaches the temperature at which spin-coated is performed. The T_g of 2.5LiSPS-13.5 was 17°C higher than 2.5LiSPS-4, Table 3.1, so for similar evaporation rates of the solvent, the higher molecular weight sample is expected to vitrify at shorter drying time. As such, the morphology of that sample will reflect a shorter time of the phase separation than the lower molecular weight sample.
Figure 3.8 SEM micrographs of films spin cast from 1wt% 2.5 LiSPS ionomer/THF solutions at room temperature and 3000 rpm rotor speed: (a) 2.5LiSPS-4; (b) 2.5LiSPS-13.5.

The spinodal decomposition process is generally divided into three regimes: (i) a percolation regime, (ii) a percolation-to-cluster transition regime and (iii) a cluster regime [188-189, 220]. Different structures are observed in each regime and the kinetics of the process is influenced by the degree of polymerization of the polymer. The structure of a polymer with a higher degree of polymerization will be frozen at an earlier stage than a polymer with lower degree of polymerization. The percolation regime, which is accessed at short times, is characterized by a bi-continuous network structure, and the percolation-to-cluster transition represents the breakup of the bi-continuous phase into discrete droplets. The morphology for 2.5LiSPS-13.5, Figure 3.8 (a), is similar to that of a bicontinuous network of polymer and solvent, but instead of continuous polymer filaments, the morphology of the polymer phase is composed of chains of discrete sub-micrometer particles. This picture is believed to have caught the early stage of the percolation-to-cluster transition, where the polymer filaments break up into discrete droplets. In contrast, the micrograph for 2.5LiSPS-4, Figure 3.8
(b) captured the later stages of the percolation-to-cluster transition. Here, the sample is mostly in the cluster regime, but some evidence of particle break-up is still observed, see the particles identified by the arrows in Figure 3.8 (b).

The morphology difference between these two samples has a significant effect on the nature of the surface. The inter-connected structure shown in Figure 3.8 (a) was very hydrophobic as evidenced by a water contact angle (CA) of 135°, while the film in Figure 3.8 (b) was less hydrophobic, CA = 120°. The difference is believed to be a consequence of the interconnected structure which can trap air and promote water-air contacts that have lower surface energy than water-polymer contacts.

**Effect of Concentration.** Increasing the polymer concentration in the drying solution increases its viscosity (Figure 3.9), which affects the dynamics of the phase separation process during spin coating. Higher concentrations are expected to slow down the drying kinetic and, all else the same, should allow access to later times of the phase separation before vitrification occurs. That hypothesis is supported by the film morphologies shown in Figure 3.10, produced by spin coating two different solution concentrations, 1 and 5 wt%, of 2.5LiSPS-4. The morphology of the 1 wt% solution, Figure 3.10 (a) shows discrete particles characteristic and some coalesced particles, but Figure 3.10 (b) shows a smooth, featureless film.
Figure 3.9 Solution viscosity of 2.5 LiSPS-4/THF as a function of concentration measured by a Ubbelohde viscometer.

Figure 3.10 SEM micrographs of 2.5 LiSPS4 spin cast at room temperature and 3000 rpm from THF solutions with: (a) 1wt% polymer concentration; (b) 5% concentration.

The latter result is a consequence of the slower drying kinetics that allows the polymer in the particles to relax and flow into a film before vitrification occurs. That
explanation is consistent with a spin coating mechanism where first the polymer precipitates from solution and then the solvent-swollen, i.e., plasticized polymer, flows and coalesces into a film. Another way to look at this is that the higher viscosity slows down the evaporation rate and effectively increases the characteristic time scale for structure formation. As a result, the experimental timeframe, \( \tau \), of the process wherein the film structure is formed and frozen is smaller than \( \tau \), the characteristic time given by Equation (3.2), which allows for sufficient mobility of the solvent-swollen polymer following phase separation to form a film. The work of Zhai and Weiss [190] showed that the particle morphology is a metastable state and a smooth film is the stable state, and it can be formed from the particle morphology by annealing at elevated temperature for a long time.

Effect of Cation Zhai and Weiss [190] studied the effect of cation on the surface morphology of spin cast SPS ionomer films and found that not all cations are suitable for formation of nano-particle textured surface. In this research, we neutralized SPS ionomer to tetraoctyl ammonium (TOA) salt to alter the hydrophobicity of the ionomer and to see if it could enhance the water contact angle of spin cast films.

Figure 3.11 shows the surface morphology of spin cast TOA-SPS films and found that the surface is comprised of bi-continuous structures, which is characteristic of initial stage of spinodal decomposition. The long alkyl chain in the TOA cation would expand and increase the hydrodynamic volume of the polymer chain in a non-polar solvent, like THF. The mobility of the polymer chain during spin coating
reduced and slowed down the phase separation kinetics. Thus with the same time of film drying, the phase separation is stopped at earlier stage of structure formation. In other words, the surface is vitrified and loses mobility to advance into latter stage of spinodal decomposition. The surface shows a contact angle of 125° after CVD of silane.

![SEM micrographs of 2.5TOASPS-13.5 spin cast at room temperature and 3000 rpm from 1wt% THF solutions.](image)

**Figure 3.11**

3.3.3 Characterization of PS-1-NH$_3^+$Cl$^-$ Ionomer and Film Morphology

**Polymer Characterization** One objective of this research was to find other polymer/solvent pairs suitable for preparing textured surfaces. The PS-1-NH$_3^+$Cl$^-$ telechelic ionomer was synthesized to study if similar nano-particle textured morphology could be achieved as the SPS ionomers.

The mono-functional ammonium-ended polystyrene ionomer (PS-1-NH$_3^+$Cl$^-$) was synthesized using living anionic polymerization combined with thiol-ene “click”
chemistry [211]. Figure 3.12 shows the $^1$HNMR spectra of vinyl-PS prepolymer (a) and PS-1-NH$_3^+$Cl$^-$ ionomer (b). The characteristic alkene proton peaks at δ 5.7 and 4.9 ppm, with an integration ratio of 1: 2 indicated α-vinyl-functionalized polystyrene (vinyl-PS) was successfully prepared. PS-1-NH$_3$ was prepared by thiol-ene “click” process by reacting 2-aminoethanethiol hydrochloride with vinyl-PS and the photoinitiator, DMPA, in solution and irradiating for 15 min. Figure 3.12 b shows the $^1$HNMR of PS-1-NH$_3^+$Cl$^-$ and the peaks characteristic of alkene protons (a and b) completely disappeared. The two methylene protons from the α-chain end can be clearly seen at δ 3.2 ppm for –NCH- (c), and δ 2.9 ppm for –NCH$_2$CH$_2$S- (d) respectively. MALDI-TOF mass spectrum (Figure 3.13) shows one single, narrow distribution of molecular weight for PS-1-NH$_3^+$Cl$^-$ sample and the molecular weight characterization results were listed in Table 3.4. Experimentally measured $m/z$ values agree well with the calculated molar masses and no unfunctional polymer residue (vinyl-PS) was observed. Therefore, the PS-1-NH$_3^+$Cl$^-$ sample has 100% functionality.

Table 3.4 Summary of Molecular Weight Characterization Results for PS-1-NH$_3^+$Cl$^-$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular Formula</th>
<th>M (calcd) (Da)</th>
<th>$m$/z (obsd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vinyl-PS</td>
<td>C$<em>{181}$H$</em>{186}$Ag$^+$</td>
<td>2466.4</td>
<td>2466.5</td>
</tr>
<tr>
<td>PS-1-NH$_3^+$Cl$^-$</td>
<td>C$<em>{183}$H$</em>{194}$NSAg$^+$</td>
<td>2544.4</td>
<td>2543.9</td>
</tr>
</tbody>
</table>

*Calculated monoisotopic molecular weight of vinyl-PS, PS-1-NH$_3^+$Cl$^-$

*Experimentally observed m/z are based on 22-mers of vinyl-PS, PS-1-NH$_3^+$Cl$^-$ with a silver ion (MAg$^+$).
Figure 3.12 $^1$HNMR of Vinyl-PS and PS-1-NH$_3^+$Cl$^-$ showing the chemical shift of proton a-d.

Figure 3.13 MALDI-TOF Mass Spectrum of PS-1-NH$_3^+$Cl$^-$ sample.

Figure 3.14 shows the film morphology of spin cast PS-1-NH$_3^+$Cl$^-$ ionomer at room temperature from THF/methanol (V/V=9/1) at 3000 rpm. The spin cast film exhibited a surface morphology of nano-particle aggregate structure, and the particle
diameter is around 200-400 nm. This morphology is similar to the nano-particle textured surface prepared from spin casting SPS ionomers. The surface hydrophobicity was tested after modification with silane. The textured rough surface showed a water CA of 120° and the water droplet stuck to the surfaces at any tilting angle. Figure 3.14 b showed the image of a 5 μL water droplet when the surface was tilted vertically. The water droplet stayed pinned on the surface with a high contact angle hysteresis.

The similar morphology of amine-ended telechelic polystyrene ionomer (M_w~2.5 kg/mol) and SPS ionomers ((M_w~4 kg/mol) might reveal the spinodal decomposition of ionomer solution during the spin coating process is a facile method to prepare nano-particle textured surfaces and this process is applicable to other ionomer systems. The technique is suitable for the preparation of high adhesion surfaces, which has potential applications in no-loss transport of microdroplets [117, 118], wall-climbing robots [118, 119], or coatings to prevent falling of condensed water droplets, e.g., in aircraft [101]. A more systematical study of the effect of ammonium content, the interaction between the functional group with the substrates should be carried out to better understand the process.
3.4 Conclusions

Nano-particle textured surfaces can be easily produced by a spin-coating process. The surface of the film undergoes spinodal decomposition (SD), and the roughness of the surface can be controlled by the rate of evaporation of solvent, which determines what stage of SD is frozen in the vitrified film. Relatively high or relatively low vapor pressure solvents favor the formation of smooth films. Intermediate vapor pressure solvents produce particle-textured surfaces, but a relatively polar solvent is also required.

Preparing films from dilute solutions produced textured surface morphologies, while high solution concentrations favored smooth film formation. Those observations were consistent with the SD mechanism in that freezing polymer mobility early in the film formation process produced particle textures at the surface, while retaining polymer mobility longer in the drying process allowed the phase-
separated particles to coalesce and condense into a smooth film. Increasing the polymer molecular weight or the evaporation rate allows access to morphologies typical of early stages of spinodal decomposition and lowering those variables was conducive to freezing in morphologies characteristic of latter stages of SD.

The use of a lightly sulfonated polystyrene ionomer provides good adhesion to a silica surface, in contrast to neutral polystyrene, which has poor adhesive properties. That distinguishes the surfaces described herein from the literature on superhydrophobic surfaces prepared from polystyrene. Superhydrophobicity (CA > 150°), however, was not achieved by the films prepared in this study. Although the ionomer surface itself is not hydrophobic, when coated with a silane, the rough surfaces produced from the solvent evaporation process can approach superhydrophobicity.

The achievement of a superhydrophobic surface requires sufficient contact area of the droplet with trapped air. In that regard, the surfaces described in this paper were not rough enough to create the trapped void space required. Most of the experiments used an ionomer with a molecular weight of 4 kg/mol. However, surface morphology results shown for a higher molecular weight ionomer, 13.5 kg/mol, indicated that much finer particle morphology was possible with the higher molecular weight. Thus, using higher molecular weight ionomers may allow for the achievement of higher CAs and CAHs.

Mono-functional ammonium-ended telechelic polystyrene ionomer was also found to produce similar morphology when spin cast from THF/methanol (V/V=9/1)
solutions. The film is consisting of nano-particle aggregates and this indicates that the particle formation mechanism is applicable to many other similar systems.

The hydrophobic films produced here also exhibited large contact angle hysteresis, which produced sticky surfaces, rather than the slippery surfaces observed with most hydrophobic films. The much larger drop size required for slippage of a water droplet on an inclined surface for the rough SPS films compared with smooth films and the adhesion of the droplets at high inclined angles and even when the surface was turned 180° indicate that the water droplets were in a Wenzel state on these surfaces.

Sticky, hydrophobic surfaces have been proposed for applications such as no-loss transport of microdroplets [117, 118], wall-climbing robots [119], or coatings to prevent dripping of condensed water, e.g., in aircraft [101]. The method described in this paper for preparing a sticky, hydrophobic surface may provide a facile means for developing such applications.
CHAPTER IV

SOLUTION CASTING IONOMER UNDER CONTROLLED EVAPORATION

4.1 Introduction

Solution casting is a common method to prepare thick polymer films. A polymer solution with known concentrations is cast onto a solid substrate and the solvent slowly evaporates to form a film. The film morphology depends on the evaporation of the solvent, the properties of the solvent, the property of the substrate and the spreading of the solution.

Characterization and measurement of evaporation process is a difficult task [221-227]. The evaporation rates of a solvent depend on the surface area, solvent vapor pressure, temperature, and convection. Researchers have used chambers with temperature control either using a hot plate [221] or water bath [222] and gravimetric methods [223-225], quartz crystal microbalances [226, 227] to control and measure the evaporation rates of water and polymer solutions. Cakmak et al. [228] recently reported an automated real-time measurement instrument that can track the mass, temperature, and thickness coupled with in- and out-of-plane birefringence measurement while subjecting a sample to convective heating.
Phase separation processes are widely observed in various systems and recent research focuses on controlling the morphology of a product by controlling the kinetics of phase separation. There are typically four types of phase separation related to polymer film preparation: thermally induced phase separation (TIPS), air casting, non-solvent induced phase separation (NIPS), and immersion precipitation [229, 231]. TIPS is when the solvent quality decreases when the temperature decreases and phase separation occurs. Air-casting of a polymer solution, where a polymer is dissolved in a volatile solvent and as the solvent evaporates, polymer concentration increases and phase separation occurs. Non-solvent induced phase separation (NIPS) is when the polymer solution is brought into contact with non-solvent vapor and the polymer precipitates. Immersion precipitation is when a cast film is immersed into a non-solvent bath and precipitation occurs. Phase diagrams can predict if a polymer solution of certain concentration is thermally stable and when phase separation will occur. However, the kinetics of phase separation processes determine whether the phase separation will occur and at to what extent, and if the final product is in equilibrium or non-equilibrium state.

In general, two mechanisms are well known for phase separation of polymer solutions: nucleation and growth (NG) and spinodal decomposition (SD). It is widely accepted that NG occurs when the polymer system enters the metastable region which is located between the binodal and spinodal lines in phase diagram. Once a system enters this region, dispersed nuclei are formed spontaneously and grow slowly to droplets. On
the other hand, SD occurs when the system enters the unstable region in the phase diagram. In this region the amplitude of concentration fluctuations grows with time, which results in a bi-continuous morphology with a characteristic length scale that eventually coalesces into droplets.

The spinodal decomposition process has been the subject of extensive research projects, both theoretically and experimentally, in many different systems, i.e. polymer blends, binary liquids, polymer solution [182-189]. Research on the phase separation kinetics of spinodal decomposition has been focused on polymer blends melts. The spinodal decomposition process is generally divided into three regimes: (1) a percolation regime where a bicontinuous structure is formed, (2) a percolation-to-cluster transition (PCT) regime where the polymer fibrils break up into discrete domains and (3) a cluster regime where the domains grow [182-189]. Hashimoto et al. [182] studied the time evolution of spinodal decomposition for the mixtures of poly(styrene-ran-butadiene) (SBR) and polybutadiene (PB) or SBR and polyisoprene (PI). It was found that phase separation in polymer blends with higher molecular weights stopped during the phase separation. According to them, the transport of polymer chains across the interface is necessary for droplet domain growth and the energy barrier of transportation of polymer chains, which is proportional to the degree of polymerization, \( N \). Therefore, the spinodal decomposition of higher molecular weight polymer blend will be stopped at PCT, and no cluster structure was formed.
On the other hand, relatively little work has been done on the phase separation in polymer solutions during solvent evaporation. Weiss et al. recently reported a facile method for preparing nano-particle textured surfaces [42]. A rough surface with particle diameters of ~200 nm was produced by spin coating a lightly sulfonated polystyrene (SPS) ionomer from THF or THF/methanol solutions onto a silica substrate. The particle-textured surface was attributed to spinodal decomposition at the liquid/vapor interface of the drying film. Tan et al. [189] prepared a slippery superhydrophobic surface by solution-casting PS from dimethylformamide (DMF) solution onto glass slides under ambient atmosphere. The morphology formation mechanism is attributed to the spinodal decomposition of polymer films during solvent evaporation. The film morphology was bi-continuous percolated structures when the polymer molecular weight is high ($\text{M}_w = 8.9 \times 10^6$ g/mol), and the morphology was spherical droplet for low molecular weights PS ($\text{M}_w = 8.0 \times 10^4$ g/mol), which is due to the breakup of network structures in the PTC regime.

During the solution casting process, the solvent evaporates and the polymer solution goes from a one-phase region to two-phase region and phase separate occurs, as shown in Figure 4.1. The final film structure depends on the kinetics of phase separation and the time scale of film drying, in other words, the solvent evaporation rate. Thus, by adjusting the solvent evaporation rate, one can study the film morphology at different stages of phase separation. For a spinodal decomposition process, the phase separated
structures are frozen at earlier stage and the characteristic morphology is interconnected or percolated structure at high evaporation rates. The phase separated structures would breakup and coalesce into discrete particles if allowing longer times, i.e., at low evaporation rates. 

In chapter III, the effect of solvent property, polymer molecular weight, solution concentration on the morphology of spin cast ionomer films was investigated. The solvent vapor pressure was found to control the nano-particle textured film formation. In this chapter, the effect of solvent evaporation rate of THF solvent on the solution casting SPS ionomer films under controlled evaporation. The evaporation rate was controlled by
the convection and temperature and the film morphology was characterized at different evaporation rates.

4.2 Experimental Details

4.2.1 Materials

Tetrahydrofuran (THF 99.9%) and 1H,1H,2H,2H-perfluoroctyltrichloro-silane were obtained from Fisher Scientific Co. and used as received. Lightly sulfonated polystyrene ionomers were synthesized following procedures in Chapter III and denoted as 2.5 LiSPS-4, where 2.5 is the sulfonation level in mol%, and 4 is the molecular weight of parent polystyrene in kg/mol.

Fisherfinest* Premium Plain Glass Microscope Slides (3 inch × 1inch) were purchased from Fisher Scientific Co. The glass slides were washed in an ultrasonic bath for 10 minutes followed by immersion in a “piranha” solution (30% concentrated hydrogen peroxide and 70% concentrated sulfuric acid) bath for 30 minutes to remove any organic contamination. After the “piranha” treatment, the samples were rinsed thoroughly with deionized water and dried with compressed nitrogen gas.

4.2.2 Film Preparation

Ionomer films were prepared by solution casting ionomer solutions onto glass substrates under controlled evaporation rates. In this research, we used a custom setup
with controlled evaporation rates under pre-set temperatures and wind speeds, as shown in Figure 4.2 [228]. The custom built evaporation system consisted of a platform on a balance (Sartorius LA-6200S, 0.01 g precision) placed inside an insulation chamber with an adjustable speed hot air supply (Model TSK-52HT, Type 3200-17C-025Y-LB-HT eclectic hot-air generator) to a wind tunnel. The air velocity and temperatures were controlled and measured with an air flow meter (Kanomax anemomaster model 6162) at the entrance to the sample chamber and four pyrometers (Micro-epsilon thermometer 0.1°C precision) placed around the sample. Two lasers (Keyence LK-G 152 laser sensors) were mounted above the sample to record the film thickness change during evaporation. All control and measuring components were controlled by a LabView-based software.

Figure 4.2 Experimental setup for controlling and measuring the solvent evaporation rate during casting of polymer solutions.
The rate of evaporation of the solvent was determined by measuring the kinetics of mass loss of solvent after the polymer solution was cast onto a substrate on top of the sample platform. The sample substrate was preheated until it reached the desired temperature (~ 5 min). 500 µL of 0.5 wt% 2.5LiSPS-4/THF solution was then cast onto the substrate using a plastic syringe (MSH, 1mL). Different evaporation rates were achieved by varying the temperature of the substrate from 25 to 45°C.

4.2.3 Characterization

The morphology of solution casting ionomer surfaces was imaged with a JEOL-6335F field-emission scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV. The specimens were sputter coated with silver to prevent arcing. Water contact angles (CAs) were measured using a Ramé-Hart Model 500 Advanced Goniometer equipped with a rotating stage. Water droplets (5.0 µL) were carefully placed on the surface using the Ramé-Hart automated dispensing system and the images were taken and analyzed with Dropimage Advanced v2.4 software. Static CAs were calculated as the average of five measurements made at different position of the surface. Dynamic CAs were measured by placing a water droplet of 5.0 µL on the surface and then rotating the stage 90° and measuring the advancing and receding angles. The contact angle hysteresis was calculated as the difference of the advancing and receding angles. The as-cast films were also modified with (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1-
trichlorosilane by chemical vapor deposition. The as-cast polymer film was placed on the top of a vial containing a few drops of silane at the bottom with the film side facing the silane, so that there was no direct contact between the polymer film and the silane. The vial was placed in a vacuum oven at 60°C for 1 h to allow the silane vaporize and condense on the polymer surface. Finally, the film was placed in an oven at 80°C for another 0.5 h to evaporate excess silane [232].

4.3 Results and Discussions

4.3.1 Characterization of Evaporation Rates during Solution Casting Process

The film morphologies discussed in Chapter III were achieved by spin-coating, where solvent evaporation is rapid. This section discusses the results of casting a solution onto a silica substrate and allowing the solvent to evaporate by convection. Depending on the vapor pressure of the solvent and its temperature, this can be a slow process (e.g., at low solvent vapor pressure) or a rapid one (high solvent vapor pressure). Also, the evaporation rate is not necessarily constant, since as the solvent evaporates, the film viscosity increase, which decreases the diffusion of the solvent through the swollen film.

Solvent casting experiments using THF solutions were carried out under controlled evaporation rates, and the rate of evaporation of THF was varied by controlling the air speed and temperature in the drying chamber. Figure 4.3 shows the time-resolved evaporation data for 2.5LiSPS-4 for three temperatures (25°C, 30°C and 35
°C) at constant air speed. Figure 4.4 shows the evaporation curve for 2.5 LiSPS-4 at
different air speeds. All of the graphs were linear till the film was almost dry, which
indicated that the evaporation rates, i.e., the slopes of the plots in Figure 4.3 and 4.4, were
constant. The evaporation rates, calculated from the slope of a linear least squares fit of
the data. As expected, the evaporation rates increase when the temperatures increase at
constant wind speed, or the wind speeds increase at the same temperature. The
evaporation rate data was summarized in Table 4.1. It varied from 2.5 to 14.3 mg/s as the
air speed was varied from 0.31 m/s to 1.53m/s and temperature was varied from 25 °C to
45°C.

![Graph showing evaporation rate data](image.png)

**Figure 4.3** Time-resolved evaporation data for 2.5LiSPS-4 films cast from
THF solution as a function of temperatures at constant wind
speed of 0.31 m/s.
In general, the drying time of the film is inversely proportional to the solvent evaporation rate, and the time before the film vitrifies and freezes in the morphology is expected to be proportional to the solvent evaporation rate. Thus, with respect to the hypothesis of the texture formation of the ionomer films being due to spinodal decomposition, rapid solvent evaporation should arrest spinodal decomposition at an earlier stage and slower evaporation should be conducive to discrete particle formation.
4.3.2 Effect of Evaporation Rates on Surface Morphology

The effect of the THF evaporation rate on the surface morphology of 2.5LiSPS4 is shown in Figure 4.5. When the evaporation was relatively slow ($E_v = 2.5$ mg/s), a uniform structure of particles with diameters $\sim$1 $\mu$m was formed, Figure 4.5 a. When the evaporation was increased to 3.8 or 5 mg/s, Figures 4.5 b and c, deformed droplets were found that appeared to have been captured immediately after rupture of the chain-like morphology observed in Figure 4.5 d ($E_v \sim$7.8 mg/s). The latter is similar to what would be expected from early stage spinodal decomposition.

When the evaporation rate was increased to 14.3 mg/s, the surface was smooth and featureless, Figure 4.5 e. In that case, the solvent was essentially flashed and the evaporation rate was so fast that phase separation was completely suppressed. The morphology sequence shown in Figures 4.5 d to 4.5 a are consistent with a spinodal decomposition mechanism, where an interconnected or percolated structure is formed at early stages (faster evaporation rate) and as structure evolves (slower evaporation rate), the fibrils of the percolation structure breakup into droplets, as expected in the percolation to cluster stage (Figure 4.5 c, b). At longer times (slowest evaporation rate), droplets (clusters) coalesce and coarsens into discrete particles (Figure 4.5 a).

Similar morphologies were reported for PS by Tan et al. [189], who also attributed the structure formation to a spinodal decomposition mechanism. Whereas a textured PS has little, if any, adhesion to silica substrate, the SPS textured surfaces were
much more robust and resisted deformation and dewetting even after annealing at 120°C for 1 week, during which the water contact angle remained unchanged. Zhai and Weiss [190] showed that longer annealing eventually coalesce the particle into a smooth film.

Table 4.1 Solution evaporation rates under different conditions

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Speed Set on the fan</th>
<th>Wind Speed (m / s)</th>
<th>Evaporation Rate (mg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Minimum</td>
<td>0.307</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.727</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.132</td>
<td>3.9</td>
</tr>
<tr>
<td>30</td>
<td>Minimum</td>
<td>0.307</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.727</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.868</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.952</td>
<td>6.7</td>
</tr>
<tr>
<td>35</td>
<td>Minimum</td>
<td>0.307</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.868</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.132</td>
<td>7.8</td>
</tr>
<tr>
<td>40</td>
<td>3</td>
<td>0.868</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.132</td>
<td>10</td>
</tr>
<tr>
<td>45</td>
<td>3</td>
<td>0.868</td>
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<tr>
<td></td>
<td>5</td>
<td>1.132</td>
<td>14.3</td>
</tr>
</tbody>
</table>
Figure 4.5 SEM images of 2.5 LiSPS-4 films solution cast onto silica from 0.5 wt% THF solutions. The number indicated on the figure is the evaporation rate in [mg/s], see Table 4.1. The shapes of a water droplet and contact angle are shown in the inset to each micrograph.

4.3.3 Effect of Surface Morphology on Hydrophobicity

The water contact angles on the as-prepared surfaces were relatively low (~ 90°) for all the films shown in Figure 4.5, the samples prepared at the five evaporation rates, which is probably a consequence of the polar groups in ionomer. However, modification
of the surfaces with 1H,1H,2H,2H-perfluoroctyltrichlorosilane rendered them more hydrophobic and the hydrophobicity increased from 120° to 140° as the surface morphology changed from discrete particles to a percolated structure (Figure 4.5 a-d). The bi-continuous structures greatly reduce the contact area between the water droplet and surface, and would help to trap air inside the holes, like the rose petal. The profiles of water drops on the smooth surface (Figure 4.5 e) and textured surfaces (Figures 4.5 a-d) of 2.5LiSPS-4 after modification with silane are shown in the insets of Figure 4.6.

![Profiles of water droplets](image)

Figure 4.6 Profiles of a 5.0 μL water droplet on film tilted 90° (a-e) and 180° (f). The contact angle hysteresis (CAH) is the difference of the advancing and receding angles (a-e correspond to the surfaces in Figure 4.5). Sample f is sample d tilted at 180°.

The smooth silane-treated surface prepared using the fastest evaporation rate (14.3 mg/s) had the lowest contact angle, ~106° and the lowest contact angle hysteresis 16°, sample c in Figure 4.6. Both the water contact angle and contact angle hysteresis increase with evaporation rates for the textured surfaces, Figure 4.6. For the textured surfaces, the CA and the CAH increased with evaporation rates, i.e., as the textured progressed from discrete particles to a percolated structure.
The SPS films had good adhesion to the silica substrate, and remained attached even after immersion in water for 1 week, as opposed to polystyrene films prepared in the same manner that did delaminate when immersed in water. Although the surfaces were hydrophobic and the silane-coated surface prepared from the sample shown in Figure 4.5d approached superhydrophobic behavior, water droplets did not roll off the surface. Instead, the water droplets stuck to these surfaces even when the surface was tilted 90 degrees, see Figure 4.6.

The CAH of the droplet in Figure 4.6 d is \( \approx 50^\circ \) and indicates the surface is in a Wenzel state, which explains why the droplet stuck to the surface even when it was turned 180\(^\circ\) (Figure 4.6 f). Both the water contact angle and CAH increased with increasing evaporation rates for the textured surfaces, as shown in Figure 4.7. The surface texture corresponding to the data points in Figure 4.5 progressed from discrete particles to a percolated structure as \( E_\nu \) increased from 2.5 to 8.5 mg/s, but above an evaporation rate of 10.0 mg/s, the film surfaces were smooth. The CA and the CAH increased as the film surface became rougher, but for the faster evaporation rates, when the film surface was smooth, the CA and CAH dropped to 106\(^\circ\) and 16\(^\circ\), respectively, independent of the magnitude of the evaporation rate. Such sticky hydrophobic surfaces have potential application where high adhesive forces are required, such as no-loss transport of micro-droplet without sliding, and the inside coating of aircraft to prevent the falling of condensed water.
The maximum droplet volume that can adhere to the films was characterized at different tilt angles. Tilting the film at an angle induces a downward gravitational force $F_g$

$$F_g = \rho g V \sin \alpha$$  \hspace{1cm} (4.1)

where $\rho$ is water density, $g$ is the gravitational acceleration constant, and $V$ is the drop volume [117]. The retentive force $F_r$, which results from the contact angle hysteresis, is given by

$$F_r = k \gamma R (\cos \theta_r - \cos \theta_a)$$  \hspace{1cm} (4.2)

Figure 4.7 Water contact angle and contact angle hysteresis for 2.5LiSPS-4 samples solution cast from THF as a function of the solvent evaporation rate, $E_v$ (mg/s).
where k is a numerical constant depending on the droplet shape, $\gamma$ is the surface tension of the liquid and R is radius of the droplet [197]. The droplet starts rolling off when $F_g \geq F_r$, which occurs when the volume of the droplet becomes too large than the critical droplet volume. Figure 4.8 compares the critical droplet volumes of percolated surface 4.5 d and smooth surface 4.5 e. The activation energy required for a droplet to move on a textured surface is higher than that of a smooth surface, thus the textured surface suppresses motion of much larger droplets than a smooth surface due to contact line pinning by microscopic surface irregularities, as was explained by Gao and McCarthy [233].

![Graph showing critical drop volume as a function of sample tilt angles for percolated surface (sample 4.5d) and smooth surface (sample 4.5e).]
4.4 Conclusions

Textured ionomer surfaces can be easily produced by evaporation of a solvent from a solvent-cast film. The surface of the film undergoes a spinodal decomposition (SD) process, and the roughness of the surface can be controlled by the rate of evaporation of solvent, which determines what stage of SD is frozen in the vitrified film.

The use of a lightly sulfonated polystyrene ionomer provides good adhesion to a silica surface, in contrast to neutral polystyrene, which has poor adhesive properties. That distinguishes the surfaces described herein from the literature on superhydrophobic surfaces prepared from polystyrene. Superhydrophobicity (CA > 150°), however, was not achieved by the films prepared in this study. Although the ionomer surface itself is not hydrophobic, when coated with a silane, the rough surfaces produced from the solvent evaporation process can approach superhydrophobicity. Extrapolation of the line in Figure 4.7, i.e., CA vs E_v, suggests that, perhaps, a higher evaporation rate between 8.5 and 10.0 mg/s might produce a film surface that is superhydrophobic. However, that may be an unstable processing condition to work with in a real process, since the evaporation rate will be too close to the transition where the surface goes from rough to smooth. Thus, small fluctuations in the evaporation rate could prove disastrous with regard to reproducing a surface structure.

The achievement of a superhydrophobic surface requires sufficient contact area of the droplet with trapped air. In that regard, the surfaces described in this paper were not
rough enough to create the trapped void space required. Most of the experiments used an ionomer with a molecular weight of 4 kg/mol. However, surface morphology results shown for a higher molecular weight ionomer, 13.5 kg/mol, indicated that a much finer particle morphology was possible with the higher molecular weight. Thus, using higher molecular weight ionomers may allow for the achievement of higher CAs and CAHs.

The hydrophobic films produced here also exhibited large contact angle hysteresis, which produced sticky surfaces, rather than the slippery surfaces observed with most hydrophobic films. The much larger drop size required for slippage of a water droplet on an inclined surface for the rough SPS films compared with smooth films and the adhesion of the droplets at high inclined angles and even when the surface was turned 180° indicate that the water droplets were in a Wenzel state on these surfaces.

Sticky, hydrophobic surfaces have been proposed for applications such as no-loss transport of microdroplets [117, 118], wall-climbing robots [119]. The method described in this chapter for preparing a sticky, hydrophobic surface with controlled surface morphology and hydrophobicity, which may provide a facile method for preparing such applications.
CHAPTER V

SUPERHYDROPHOBIC IONOMER SURFACES FROM SPARYING COATING

5.1 Introduction

5.1.1 Superhydrophobic Surfaces

The wettability of surfaces plays an important role in industrial, biological and environmental applications. [44, 45, 74-81] Superhydrophobic surfaces, for example, are surfaces with super water repellency (water contact angle>150°). They can be divided into two different categories based on the contact angle hysteresis (CAH), i.e. slippery superhydrophobic surface (with small CAH), and sticky superhydrophobic surface (with large CAH). Both types of superhydrophobic surfaces have been observed in nature. The lotus leaf, for example, is a typical type of slippery superhydrophobic surface with water CA ~ 160° and tilting angle less than 5° [96, 97]. The rolling of water droplets and cleaning of dust and contaminates is called the lotus effect, or self-cleaning effect. The mechanism of the lotus effect has been well documented [98, 99]. Micro-papillae and nano-hair hierarchical surfaces combined with a low surface energy wax coating leads to the superhydrophobicity of the lotus leaf. On the other hand, gecko feet and rose petals are examples of sticky superhydrophobic surfaces and water droplets stick to the rose

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petal even when it is tilted upside down. Those bio-adhesion systems have attracted much attention for applications such as non-loss transport of small volume liquids, and inside coatings of aircraft [110-115]. Two kinds of biomimetic approaches have been proposed for preparing stick superhydrophobic surfaces. The first approach is to mimic the nanoscale tube structures of gecko feet. The other approach is inspired by rose petals. Raindrops stick to rose petals and the almost spherical droplets resist rolling off the flower, which is believed to help attract insects for pollination [80]. The surface of the rose petal exhibits a periodic array of micropapillae and nano-scale cuticular folds on the top of the micropapillae. A water droplet on the petal’s surface is believed to partially penetrate into the microscale grooves, but air gaps still exist in the nanoscale folds, thus forming a partial Wenzel state [102]. The water penetrated into micropapillae causes strong adhesion while the air trapped in nanoscale folds increase the water contact angle.

The difference between advancing and receding angles is the contact angle hysteresis (CAH), and it has been widely studied because of the recent interest in superhydrophobic surfaces. While the contact angle of water has been commonly used as a criterion for hydrophobicity, the sliding angles of water droplet are also important in characterizing surface properties. Surfaces with high water contact angle do not always exhibit a low contact angle hysteresis, or sliding angle. For example, the gecko foot and rose petal show superhydrophobic behavior with high CAH.

When a liquid droplet resting on a solid surface is tilted, the droplet leans in the tilted direction. For a droplet to move, the droplet must advance on the downhill
side and recede on the uphill side. The CAH originates from the contact line pinning. Bikerman studied the effect of surface roughness of stainless steel plates on sliding of water droplets [234]. It was found that surface roughness provides resistance for the sliding of water droplets. Miwa et al. [133] studied sliding angles of water droplets on various superhydrophobic surfaces and found that sliding angles decreased with increasing contact angles in the highly hydrophobic region. Microstructures that can trap air are important for preparation of low-sliding-angle surfaces. Johnson et al. [134] investigated the effect of surface roughness on the hysteresis and found that CAH on hydrophobic surfaces increases with increasing surface roughness in the low-roughness region, but decreases when the roughness exceeds the critical value.

The contact angle hysteresis affects the properties of maximum droplet the surface can hold at different tilting angles. Extrand et al. studied the relationship between the droplet motion and contact angle hysteresis and derived an equation describing the retentive force [197]. The maximum droplet volume that can adhere to a film was characterized at different tilt angles. Tilting the film at an angle induces a downward gravitational force $F_g$

$$F_g = \rho g V \sin \alpha$$  \hspace{1cm} (5.1)

where $\rho$ is water density, $g$ is the gravitational acceleration constant, and $V$ is the drop volume. The retentive force $F_r$, which results from the contact angle hysteresis, is given by

$$F_r = k \gamma R (\cos \theta_r - \cos \theta_d)$$  \hspace{1cm} (5.2)
where k is a numerical constant depending on the droplet shape, \( \gamma \) is the surface tension of the liquid and R is radius of the droplet. The droplet starts rolling off when \( F_g \geq F_r \), which occurs when the volume of the droplet becomes too large than the critical droplet volume. In chapter IV, textured hydrophobic ionomers surfaces were found to suppress the motion of much larger droplets than smooth surfaces due to contact line pinning.

5.1.2 Spray Coating

Superhydrophobic surfaces can be prepared by various methods such as, template [135, 136], photolithography [137-139], plasma etching [140], self assembly [146], electrospinning [163-165] etc. These techniques are too complicated, time-consuming and expensive for large scale industrial applications.

Air spray coating is a well-established technique for painting, industrial coating, and arts. This simple process is applicable for preparation of large-scale painting or coatings on a variety of substrates at a low cost. The morphology of spray coated surfaces depends mostly on the solution concentration and viscosity. At high concentration or viscosity, the morphology is mostly fiber, but at low concentration or viscosity, the fibers are not able to hold their structure and break into particle or bead structures.

Srinivasan et al. developed superhydrophobic and superoleophobic surfaces by spraying coating a blend of poly(methyl methacrylate) (PMMA) and the low surface energy fluorodecyl-POSS (\( \gamma_{sv} \sim 10 \text{ mN/m} \)) [235]. The surface structure can be
controlled systematically by controlling the solution concentration and molecular weight of the polymer. The coil overlap concentration was the critical condition for the structure transition from spherical beads to fibrous structures. An operation diagram predicting the structure transition was constructed by calculating the solution overlap concentration dependence on polymer molecular weight. The microbead and nanofiber complex textured morphology possessed re-entrant curvature and holes that can trap air and was desirable for liquid repellency. The surfaces showed superomniphobic (both superhydrophobic and superoleophobic) behavior for liquids with a wide range of surface tensions, including water, ethanol, decane and rapeseed oil.

Tu et al. [236] spray coated polystyrene (Mₐ=181,000 g/mol) solutions in tetrahydrofuran (THF) at different concentrations and fabricated superhydrophobic/superoleophilic surfaces without any chemical modification. The surface was comprised of micro-beads and nano-fibers. Spray coated surfaces morphology progressed from micro-beads to bead-on-string, then to nano-fibers with increasing of solution concentration. Airbrushed films made from a 4wt% solution showed a water contact angle of 155° with a bead-on-string morphology. H

Yang et al. [237] fabricated superhydrophobic multiwall carbon nanotubes (MWNT) films using poly(acrylic acid)-block-polystyrene (PAA-b-PS) and studied the transition from slippery to sticky behaviors by adjusting the distribution of PAA chains on the surface. They found that transition from rollable to pinned surfaces
happened by immersing spray coated surfaces into water because of the movement of PAA chains to the surface due to the strong interaction between hydrophilic carboxyl of PAA domains with water. Upon annealing above the $T_g$ of the PS domains, the hydrophobic PS chains would move to the surface and cover the hydrophilic PAA groups, thus the surface recovers to a slippery state. Microscope study showed that the air trapped inside the textured surface was reduced when the transition occurred from a slippery to a sticky region.

Bhushan et al. [238] reported a method to prepare mechanically durable carbon nanotube-composite structures with superhydrophobicity, self-cleaning, and low-drag ability. They sprayed a suspension of carbon nanotubes (CNT), epoxy resin in acetone to prepare nanostructured surfaces. To improve the adhesion between CNT and silica substrates, the surface was annealed at 120 °, above the melting temperature of the epoxy resin to allow epoxy moved into the interface between CNT and the substrate. The epoxy improved the bonding of the CNT and the substrate and the mechanical stability of spray coated structures. The superhydrophobic surface remains stable not only from long-term exposure to water, but also high water pressure. However, the adding of epoxy resin is undesirable for many industrial applications because it may change the product properties.

Lightly sulfonated polystyrene (SPS) ionomers improved the wettability and adhesion of the polymer film to silica substrates by the incorporation of a small amount of ionic groups. In chapter III and IV, we have demonstrated the textured
surfaces prepared by spin coating and solution casting SPS ionomer solutions exhibit high water contact angles and improved adhesion compared with unmodified PS. In this chapter, a simple, low-cost method to prepare superhydrophobic ionomer surfaces by spray coating is reported. The effect of solution concentration, viscosity, polymer molecular weight on surface morphology was studied.

5.2 Experimental Details

5.2.1 Material and Sample Preparation

Materials used in this research include lightly sulfonated polystyrene ionomers (lithium salt) with different molecular weights and sulfonation levels synthesized according to the procedure of Makowski et al. [171] as listed in Table 5.1. The solution viscosity of these solutions was measured with a Ubbelohde viscometer (Fisher Scientific Co, model-1) at 25 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution Viscosity in THF at 25°C (10^3 Pa*s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mg/mL</td>
</tr>
<tr>
<td>2.5 LiSPS-13.5</td>
<td>N/A</td>
</tr>
<tr>
<td>1.9 LiSPS-135</td>
<td>1.0</td>
</tr>
<tr>
<td>0.4 LiSPS-335</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The glass slides were washed in an ultrasonic bath for 10 minutes followed by immersion in a “piranha” solution (30% concentrated hydrogen peroxide and 70% concentrated sulfuric acid) bath for 30 minutes to remove any organic contamination.
After the “piranha” treatment, the samples were rinsed thoroughly with deionized water and dried with compressed nitrogen gas before coating.

LiSPS samples were dissolved in THF solvent at various concentrations of 10, 20, 40 and 100 mg/mL. The polymer solution was fed into a receptacle of an airbrush (McMaster-Carr), and then sprayed evenly on a glass slide (75 * 25 mm) with dry compressed nitrogen (100 kPa). The distance between the nozzle and substrate was set at 150 mm and the time of spraying was varied to coat the same amount of polymer onto the substrate at the different concentrations.

5.2.2 Characterization

The morphology of the spray coated surface was characterized with a JEOL-6335F field-emission scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV. The specimens were sputter coated with silver to prevent arcing. Water contact angles (CAs) were measured using a Rame Hart Model 500 Advanced Goniometer equipped with a rotating stage. Water droplets (5.0 μL) were carefully placed on the surface using the Ramé-Hart automated dispensing system and the images were taken and analyzed with Dropimage Advanced v2.4 software. Static CAs were calculated as the average of five measurements made at different position of the surface. Dynamic CAs were measured by placing a water droplet on the surface and then rotating the stage 90° and measuring the advancing and receding angles. The maximum water droplet size for adhesion to the surface was measured for tilt angles ranging from 20° to 90°. The tilt angle was fixed and then the water droplet volume

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was slowly increased until it began to roll off the surface. The measurements were repeated twice at different locations on the polymer surface.

The as-cast films were also modified with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane by chemical vapor deposition. The as-cast polymer film was placed on the top of a vial containing a few drops of silane at the bottom with the film side facing the silane, so that there was no direct contact between the polymer film and the silane. The vial was placed in a vacuum oven at 60°C for 1 h to allow the silane vaporize and condense on the polymer surface. Finally, the film was placed in an oven at 80°C for another 0.5 h to evaporate excess silane.

5.3 Results and Discussions

The solution concentration and molecular weight of the dissolved polymer are critical in controlling the morphology of spray coated surfaces since they affect the solution viscosity. To demonstrate this, three different lightly sulfonated polystyrene ionomer in THF solutions were used with solution concentrations of 10, 20, 40, 100 mg/mL, and the duration of spraying coating was adjusted to keep the total mass of polymer delivered to the substrate the same for different concentrations.

5.3.1 Effect of Molecular Weight on Spray Coating Morphology

Molecular weight of the polymer affects the viscosity of the solution, thus it was important to study the effect of molecular weight on the morphology of spray coating surfaces. A series of polymer solutions were sprayed at a constant concentration of 40 mg/mL at a distance of 15 cm under a pressure of 100 kPa. The solution viscosities are given in Table 5.1.
The morphology of spray coated surfaces depends on the solution concentration and viscosity. At high concentration or viscosity, the morphology is mostly fiber, but at low concentration or viscosity, the fibers are not able to hold their structure and break into particle or bead structures. A transition of morphology from spherical beads to fibers would be observed with the increase of polymer solution viscosity in spray coating. Figure 5.1 shows the transition from a corpuscular morphology \((M_w = 13,500 \text{ g/mol})\) to a bead-on-string morphology \((M_w = 135,000 \text{ g/mol})\) then to a nano-fiber morphology \((M_w = 335,000 \text{ g/mol})\). The solution viscosity increased from \(6.9 \times 10^{-4} \text{ Pa*s}\) to \(2.49 \times 10^{-3} \text{ Pa*s}\) then to \(6.58 \times 10^{-3} \text{ Pa*s}\) as shown in Table 5.1 as expected. For the lowest molecular weight (Figure 5.1 a), the low viscosity of the solution resulted in insufficient solution viscosity to hold the fiber structures and the morphology was disk shape. The sprayed solution breakup into droplets and when the droplets contacted the surface, they deformed into disks either by wetting or by the high pressure force. The water contact angle was 115° for the sample in Figure 5.1 a, which is close to the smooth surface of the same material \((\text{CA}=109°)\). When the molecular weight increased to 135 kg/mol, the viscosity increased up to \(2.49 \times 10^{-3} \text{ Pa*s}\) and the morphology was mostly bead-on-string with micrometer-size beads, and the water contact angle increased to 135°. At the highest molecular weight (Figure 5.1 c), \(M_w = 335,000 \text{ g/mol}\), and the solution viscosity was \(6.58 \times 10^{-3} \text{ Pa*s}\). The structure was mostly nano-fibers, because of the high viscosity suppressed the breakup of the polymer solution jet during the spraying process. The water contact angle was 124°, lower than the surface comprised of bead-on-string
morphology, which is consistent with previous work by Ma et al. [239] and Tuteja et al. [240] who reported higher contact angles for electrospun bead-on-string structures compared with pure fiber structures [235].

![Image of SEM micrographs](image)

Figure 5.1 SEM micrographs of spraying coating 40mg/mL LiSPS/THF ionomer samples. a) 2.5-LiSPS-13.5 b) 1.9-LiSPS135 c) 0.4-LiSPS-335

5.3.2 Effect of Molecular Weight on Spray Coating Morphology

For the same molecular weight, concentration is also important for controlling the surface structure. The effect of concentration on spray coating morphology using 1.9LiSPS-135/THF with different concentrations, 10mg/mL, 40 mg/mL and 100 mg/mL was studied. The duration of the spraying process was adjusted to ensure the total mass delivered to the substrates was the same. For the lowest solution concentration (10mg/mL), the solution viscosity was $10^{-3}$ Pa*s and the surface morphology was mainly micro-beads or disk shape. That surface showed a water contact angle of 116°. When the solution concentration increased to 40mg/mL, the viscosity increased to $2.5 \times 10^{-3}$ Pa*s and the surface structure was a mixture of beads and fibers. The bead-on-string morphology is beneficial to trap air inside, thus the
static water contact angle increased to 135°. When the concentration was 100mg/mL, the viscosity was 7.5 × 10⁻³ Pa·s and the morphology was still bead-on-string structure with mostly fibers and polymer domains. The water contact angle was 142°. One might expect that if keeping increasing the solution concentration of spray coating, the surface morphology may eventually transform to pure nano-fibers. However, due to the limit of polymer samples, spray coating at concentrations higher than 100 mg/mL was not carried out.

![SEM micrographs of spraying coating 1.9-LiSPS135 ionomer samples at different concentrations. a) 10 mg/mL b) 40 mg/mL c) 100 mg/mL. The insets are the images of a 5 μL water droplet on the surfaces.](image)

5.3.3 Operation Diagram

Shenoy et al. [241] developed an equation that predicts fiber formation in electrospinning due to the increase of polymer molecular weight and concentration. Chain entanglement in polymer solutions with good solvents plays an important role in fiber formation during electrospinning process. Srinivasan et al. [235] applied this principle to the spray coating process and developed an operation diagram that can estimate the fiber formation with the polymer molecular weight and solution concentration. The operation curve was estimated using the Mark-Houwink-Sakurada
equation to calculate the relationship between the critical overlap concentration $c^*$ and the polymer molecular weight $M_w$. A transition from corpuscular to fiber-containing structures was observed when the solution concentration $c \approx c^*$.

An analogous operating diagram was constructed for the spray coating of the lightly sulfonated polystyrene ionomer described in this chapter. The measurement of intrinsic viscosities of SPS ionomers with different sulfonation levels and molecular weight requires lots of work and it not feasible for industrial applications. Furthermore, the samples used here are mostly lightly sulfonated with low sulfur content (less than 2.5 mol%), the intrinsic viscosity of unmodified PS/THF was taken from the polymer handbook based on the Mark-Houwink equation \([216]\) and used to estimate the $c^*$ dependence on $M_w$.

\[
[\eta] = K M^\alpha \tag{5.1}
\]

where $[\eta]$ is the intrinsic viscosity, $K=0.011$ mL/g and $\alpha = 0.725$ are parameters taken from polymer handbook. The polydispersity was low in this research and $M \approx M_w$.

\[
c^* = \frac{1}{[\eta]} \tag{5.2}
\]

The critical overlap concentration was calculated as the reciprocal of the intrinsic viscosity. A Combination of equations 5.1 and 5.2 provides the relationship between overlap concentration $c^*$ and molecular weight $M_w$.

\[
c^* = 9.09 \times 10^4 M_w^{-0.725} \tag{5.3}
\]
The dotted line in Figure 5.3 represents the relationship between critical overlap concentration $c^*$ and the polymer molecular weight $M_w$ as shown in equation 5.3. The circles are the morphology observed during spray coating of LiSPS in THF at the specific molecular weight and concentration. Since the intrinsic viscosity of unmodified PS/THF was used for the calculation, the operation curve is probably only qualitative.

**Operation Diagram for Spray Coating**

![Operation Diagram for Spray Coating](image)

**Figure 5.3** Operation diagram for spray coating lightly sulfonated polystyrene ionomer/THF system. The dotted line represents equation (5.3), which describes the estimated overlap concentration $c^*$ for unmodified polystyrene as a function of $M_w$.

The intrinsic viscosity of lightly sulfonated polystyrene ionomer in non-polar solvents, such as THF, is lower than the unmodified polystyrene due to the
intramolecular associations of the ion pairs at low concentration. The intrinsic viscosity of SPS ionomers decreases with increasing ionic concentration and polymer molecular weight [172]. The critical overlap concentration c* of SPS ionomer is higher than the unmodified polystyrene. This operation curve predicted by equation 5.3 still provides a good estimation of structure change from corpuscular to fiber-containing structures and could be useful in industrial applications.

5.3.4 High Adhesion Superhydrophobic Surface from Spray Coating

The effect of solution concentration and polymer molecular weight on the spray coating structures was studied in part 5.3.1 and 5.3.2. It was demonstrated that the surface morphology and hydrophobicity was successfully manipulated by varying the spray coating parameters. The surfaces prepared exhibited high water contact angle up to 142° and approached superhydrophobicity after surface modification with (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1-trichlorosilane. Bead-on-string morphology is desirable for preparing superhydrophobic surfaces compared with pure nano-fibers or beads only structures because the hybrid structure could help trap air inside and enhance the surface hydrophobicity.

Superhydrophobic surface was prepared by spraying coating 20 mg/mL 0.4LiSPS-335/THF solution and the surface was modified with CVD of (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1- trichlorosilane. The surface morphology is a mixture of beads and fibers as shown in Figure 5.4 and the surface water contact angle is 152°. Although the surface exhibit super water repellency, water droplet sticks the surface even when tilted upside down. The inset of Figure 5.4 b shows a 10
uL water droplet sticks to the superhydrophobic surface when the sample is rotated upside down.

![SEM images](image)

**Figure 5.4** SEM images of spraying coating 20mg/mL 0.4LiSPS-335, b is enlarged image of the square area of sample a. The water droplet image is shown in a, while the insets of sample b is the droplet image when the sample is rotated upside down.

The adhesion of coating to glass substrate was assessed by immersing the sample in a beaker with D.I. water to see if the surface delaminates from the substrate. The control sample was prepared by spraying coating 20mg/mL PS ($M_w = 200k$) under the same condition (operation distance 15 cm and air pressure 100 kPa). The surface morphology was bead-on-string structure (Figure 5.5) and the water contact angle was $\sim 150^\circ$. The surface exhibited superhydrophobic behavior due to the rough surface and the hydrophobic property of polystyrene backbone. However, the adhesion of the glass substrate is poor. Upon storage in water, the polystyrene film delaminated from the substrate after several hours and the ionomer coating adhered to the substrate for at least two weeks. This demonstrates the better adhesion of ionomer
films to glass substrates due to the strong interaction between the ionic groups and the glass slides.

![SEM image](image)  

**Figure 5.5** SEM images of spraying coating 20mg/mL PS-200k. The water droplet image is shown in the inset.

The sliding behavior of the sample c is summarized in Figure 5.6. The maximum droplet volume before rolling increases a lot compared with the spin coating flat surface, which is probably due to contact line pinning as explained by Gao and McCarthy [233]. This result was similar to the results in chapter IV where percolated structures suppressed the motion of water droplets.

This kind of sticky superhydrophobic surface or coating is very useful in wall-climbing robots and the inside coating of spacecraft [117-119]. This facile method to
prepare sticky superhydrophobic surfaces would make it suitable for large scale industrial applications.

![Graph showing critical drop volume as a function of sample tilt angles for sticky superhydrophobic surface (sample 5.4) and smooth surface (from spin coating).](image)

**Figure 5.6** Critical drop volume as a function of sample tilt angles for sticky superhydrophobic surface (sample 5.4) and smooth surface (from spin coating).

5.4 Conclusion

A simple, low-cost method to prepare micro- and nano-textured surfaces by spraying polymer solutions was demonstrated in this chapter. The effect of polymer molecular weight and solution concentration on the spray coating film morphology was studied. The surface morphology ranged from corpuscular structures and micro-beads to nano-fibers was controlled by the polymer molecular weight and solution concentration. As the polymer weight increases, the spray coating structure changes
from beads or round disk bumps to bead-on-string, then to nano-fibers. Solution concentration increase shows similar trends on the spray coating structures.

Coil overlap concentration (c*) provides a quick method to estimate the structure formation during spraying coating. At give polymer molecular weight, solution with concentration above c* gives fiber structures, while corpuscular structures dominate when the solution concentration is lower than c*.

The post-modification using (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane improved the surface hydrophobicity and sticky superhydrophobic surface was produced by spray coating. The surface structure is a mixture of micro-size beads and nano-size fibers. The hybrid structure enhances the surface hydrophobicity, and the water droplet keeps stuck in the surface. Surface adhesion to the substrate is good compared with PS. The textured surface could hold much larger volume of water droplet compared with smooth surface. This kind of high adhesion superhydrophobic surface could find application in no-loss transport of microdroplets [117, 118] coatings to prevent dripping of condensed water, e.g., in aircraft [101] and wall-climbing robots [119]. The spray coating method described in this chapter could be useful for producing large-scale textured surface at a relatively low-cost. This makes it suitable for industrial applications for developing high adhesion hydrophobic surfaces.
CHAPTER VI

SUMMARY AND FUTURE WORK RECOMMENDATIONS

Superhydrophobic surface is attracting more and more attentions for its application in self-cleaning coatings, non-loss transport of small volume liquids, biommetics etc. Typical examples of superhydrophobic surfaces include lotus leaf, gecko foot, rose petal etc. The surface roughness and chemical composition are two parameters affect the surface hydrophobicity. Many techniques have been used in preparing superhydrophobic surfaces; however, these techniques are either time-consuming, or too expensive, which limits the large scale applications. The research in this dissertation explored the development of textured surfaces and control of surface morphology to prepare superhydrophobic surfaces. The material used was lightly sulfonated polystyrene ionomer and it showed better wettability and adhesion to polar substrates. Various coating methods including spin coating, solution casting and spray coatings were chosen, and the mechanism of structure formation during solvent evaporation was investigated. By controlling the parameters in spin coating and the evaporation rates in solution casting, the structure formation mechanism follows a spinodal decomposition process. A facile method to prepare stick, high adhesion superhydrophobic surfaces was developed and the
operation diagram was produced. Chapter III described the fabrication of nano-particle textured surfaces via spin coating of ionomer solutions onto silica substrates. The effect of solvent property, polymer molecular weight, solution concentration on the film morphology was evaluated. The nano-particles textured films consisting of particles with diameters around 200–300 nm and the particles resisted annealing for over a week above $T_g$. The nano-particles formation is believed to be a result of spinodal decomposition of the polymer film during the solvent evaporation. The choice of solvent controls the morphology and it was found nano-particle textured surface was only formed from solvents with medium vapor pressure. Either the solvent vapor pressure is too high or too low, the surface is smooth. Solvent polarity also controls the surface structures and rough surface was formed when the solvent is polar. High concentration will suppress the phase separation, and gives smooth film. High molecular weight will slow the phase separation process and the resultant morphology is interconnected structures compared with discrete particles at low molecular weight. Nano-particles textured surface were also prepared from other ionomer system, such as amine-ended polystyrene ionomer. Large cation, such as $\text{TOA}^+$, could slow down the phase separation and the surface structure is characteristic of initial stage of spinodal decomposition.

The effect of solvent evaporation on the film morphology was studied by a controlled evaporation setup, where the solvent evaporation rate is adjusted by the convection and temperature inside a chamber. Faster evaporation freezes the phase separation at earlier stage and the film vitrifies at interconnected structures, while
slower evaporation rates will allow longer time for the phase separation to proceed and the interconnected structures will break up into discrete particles. The particle size of solution casting is about one magnitude higher than spin coating nano-particles and this is due to the initial film thickness difference. The interconnected structures exhibited a high contact angle of \( \sim 142^\circ \) and the water droplet stick to the surface even when tilted upside down. The textured surface also holds larger volume of water droplet compared with smooth surface since the high contact angle hysteresis will generate larger retentive force and suppress the particle motion.

In Chapter V, superhydrophobic surfaces with high adhesion to water droplets were prepared by a facile spray coating method. The surface exhibited a water contact angle of \( 152^\circ \) while water droplet pinned to the surface at any tilt angles. The surface morphology can be easily tuned by the choice of polymer molecular weight and solution concentration. The critical overlap concentration was found to control the surface structure transition from corpuscular to fibers. An operation diagram was constructed based on overlap concentration dependence of molecular weight of unmodified polystyrene. The curve predicts the structure during spraying coating qualitatively. This kind of high adhesion, superhydrophobic surfaces would be used in applications such as non-loss transport of small volume liquids, wall-climbing cleaning robots, inside coating of aircraft etc.

Significance of Research

This research demonstrates a facile method to prepare micro- and nano-particle or nano-fiber textured surface which could be useful for a large variety of
applications. This provides a low-cost alternative to current methods for preparing superhydrophobic surfaces and the incorporation of SPS ionomers proves better adhesion and wettability to polar substrates. This preparation method does not require tedious synthesis or special equipments, which make it suitable for large scale industrial applications. The formation mechanism of surface texture was also investigated and it helps us to understand to phase separation dynamics, especially in the process of solvent evaporation. Little work has been done in the field of phase separation dynamics of polymer solution, and this is the first report of the spinodal decomposition structure formation of this system.

Future Work Recommendations

1. Construction of phase diagram using light scattering techniques. The phase diagram of SPS ionomer in THF was not reported before and construction of the whole phase diagram could help us understand the phase boundary, especially useful in the modeling process. The phase diagram combined with the evaporation rate data could give us information such as when will the phase separation start.

2. Time-resolved light scattering study of phase separation kinetics. The time-resolved light scattering data could help us better know the separation dynamics, such as how is the structure size grow with time and how the scattering factor will shift according to the phase separation mechanism. The difficulty with this research could be that the surface thickness is changing
during the evaporation process, thus the scattering intensity could be fluctuating with time.

Computer simulation of the structure formation process. With all the information from this research and all the recommend future work, we would expect a following work to simulate the structure formation dynamics using computer simulation, which would interesting for polymer physicist to better understand the process of phase separation. Furthermore, the kinetics of phase separation and structure change would be additional information that could be useful addition to the theory of Spinodal decomposition.
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