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Relaxation of Thin Films of Polystyrene Floating on Ionic Liquid Surface

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ABSTRACT: We have investigated the dynamics of polymer films, free of physical constraints, floating on the surface of an ionic liquid (IL) to minimize substrate−polymer interactions and constraints arising from the adhesion of the polymer to the substrate. ILs, which have a negligible vapor pressure, were used to support polystyrene (PS) thin films to investigate the relaxation behavior and glass transition temperature (T_g) of thin polymer films. Freely floating films relaxed when heated to the temperatures above the bulk T_g, resulting in a thickening of the film and a concomitant shrinkage in the lateral dimensions of the film. The relaxation behavior depended on the temperature, film thickness, and molecular weight of the polymer. Completely relaxed films showed T_g values similar to that in the bulk, independent of the initial thicknesses, molecular weight, and cooling rate.

Introduction

During the past two decades, the dynamics of confined, amorphous polymers have attracted increasing interest among researchers.[1,2] Most studies have focused on supported ultrathin polymer films. In 1991, Jackson and McKenna observed a reduced glass transition temperature (T_g) when they confined the glass-forming liquids into controlled pore glasses.[3] Subsequently, the glass transition in thin films of polystyrene (PS) supported on hydrogen passivated Si(111) wafers was investigated by Keddie et al. where they found that T_g for films thinner than 40 nm was much lower than that observed in the bulk.[4] Since then, a great number of studies have shown that the T_g of polymer films supported on a substrate decreases with decreasing film thickness, provided that there are no strong attractive interactions between the polymer and substrate.[5−9] A much larger decrease in T_g has been reported in suspended PS films.[10−13] There is a growing consensus that the T_g depression arises from the presence of a free-surface layer that has an enhanced mobility and a reduced T_g relative to the interior of the film.[8,14−16] Enhanced mobility at the free surface was also adopted in several theoretical models. For example, de Gennes[17] argued that the chain loops coming in contact with the free interface exhibit an enhanced mobility which played a key role in the pronounced T_g depression for the suspended PS films.[18] Later studies showed that the T_g of thin films was counterbalanced by the free surface effect and the interfacial effect, that is, the depressed mobility at the interface coupled with the enhanced mobility induced by the presence of the surface.[19,20]

There are, however, some reports that counter this viewpoint, where a reduction in T_g with film thickness was not observed.[21−23] By studying the relaxation of PS segments at the free surface as a function of temperature, Russell and co-workers did not find a significantly enhanced chain mobility of the polymer chains at the free surface.[24] Weber et al. also came to a similar conclusion in a study on embedding metal nanocolloids into a surface of PS films by using X-ray reflectometry.[25] In addition, recent publications suggested that water vapor or ambient air was found to change the molecular dynamics and reduce the T_g of polymer films due to a degradation or plasticization of the polymer surface.[26−28] Using nulling ellipsometry, Forrest et al. recently provided strong reinforcement to the idea that the reduction in T_g is an intrinsic property of confined materials, independent of the measurement environment.[29] The time scale of the measurement and cooling rates have also been considered to be an issue leading to the observed differences in glass transition dynamics in thin polymer films.[30,31] The cooling rate was found to influence the magnitude of T_g depression, with T_g of the ultrathin films approaching that of bulk at a cooling rate of 130 K/min in supported PS thin films.[30]

In addition, spin-coated thin polymer films represent a "highly metastable" state of matter,[32] and large "residual stresses" persist[33,34] after their preparation, as spin-coating can lead to oriented, nonequilibrium conformations of the polymer chains.[35] Torkelson and co-workers used intrinsic fluorescence to characterize the structural relaxation from residual stresses in thin polymer films, showing that, while partial stress relaxation occurred upon heating in the glassy state, the full relaxation of local conformations could only be achieved by heating to well above T_g for time scales that were long relative to average relaxation times for cooperative segmental mobility.[36] However, the constraints arising from the substrate or sample holder in supported and suspended films might suppress the stress relaxation of polymer chain conformations.

So, the dynamics of thin polymer films is still a controversial topic, with no unambiguous answer emerging from the growing body of experimental results. To avoid the influence of substrate−polymer interactions or constraints on the relaxation and glass transition dynamics, we investigated the dynamics of polystyrene thin films floating on a liquid surface, free of constraints. Bodiguel and Fretigny previously investigated the viscoelastic dewetting behavior of unconstrained films floating on a liquid surface in the vicinity of the glass transition.[37−39] They used glycerol as the substrate and studied the global deformation of the film. In the present work, we have studied the relaxation and glass transition dynamics of PS thin films floating on the surface of an ionic liquid (IL). Owing to their extremely low vapor pressure and excellent chemical and thermal stability, ILs, used as a "green solvent" industrially,[40,41] serve as a unique, unrestricting support for polymer films. By heating the IL and, consequently, the floating films to temperatures greater than the bulk T_g and measuring film thickness as a function of temperature and time, the relaxation behavior of PS films was investigated. Studies were

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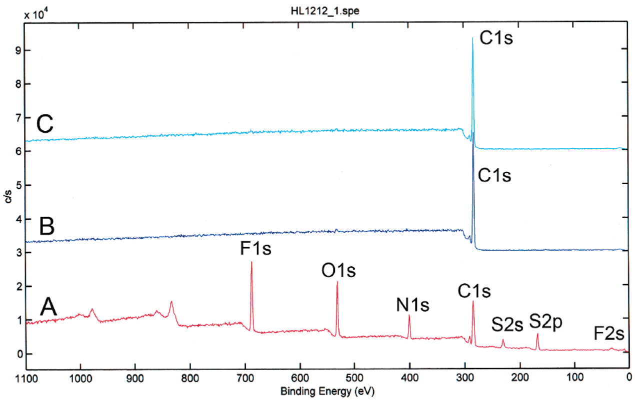


Figure 1. X-ray photoelectron spectra of (A) pure [BMIM][CF_3SO_3], (B) PS film, and (C) PS film which has been annealed with [BMIM]-[CF_3SO_3] on the surface at 130 °C for 48 h followed by washing and drying.

performed as a function of the film thickness and molecular weight of the PS. The T_g values of the thin PS films were determined during cooling from temperatures well above the T_g of bulk PS.

Experimental Section

1. Materials. Atactic polystyrene (PS) of three different molecular weights (M_w = 105 kg/mol, PDI = 1.06, denoted as PS_{105K}; M_w = 654 kg/mol, PDI = 1.09, denoted as PS_{654K}; M_w = 1650 kg/mol, PDI = 1.10, denoted as PS_{1650K}) was used as received from Polymer Source Inc. 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][CF_3SO_3]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]), 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]), 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][$MeSO_4$]), and dioctyl phthalate were purchased from Sigma-Aldrich Co. Toluene (ACS grade) was obtained from Fisher Scientific Inc.

2. Film Preparation. PS films were spin-coated onto clean Si⟨100⟩ wafers with a 250 nm SiO_2 layer (International Wafer Service Inc.) from toluene solutions at 3000 rpm. After annealing under high vacuum (10^{-6} mbar) at 150 °C (for PS_{654K} and PS_{1650K} films) or 120 °C (for PS_{105K} films) for 96 h, the SiO_2 layer was etched with a 5% aqueous solution of hydrogen fluoride, and the film was floated onto the solution surface. The film was then transferred onto the surface of a pool of pure water and, subsequently, the ionic liquid (Scheme 1 in the Supporting Information). The PS film floating on the surface of the ionic liquid was stored in a desiccator prior to use.

1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM]-[CF_3SO_3]), an air- and water-stable hydrophilic room temperature ionic liquid, was used in all experiments, unless otherwise stated. [BMIM][CF_3SO_3] has a relatively low viscosity at room temperature,[42−44] which made the film transfer easy. In addition, PS is insoluble in [BMIM][CF_3SO_3] as confirmed by gel permeation chromatography and infrared spectroscopy at room temperature and at temperatures as high as 150 °C over extended periods of time. In addition, PS films were not swollen by [BMIM][CF_3SO_3] even if the floating film was heated to 130 °C for 48 h, as evidenced by X-ray photoelectron spectroscopy measurements (Figure 1).

The bulk $T_g$values of polystyrene with different molecular weights were measured by differential scanning calorimetry (DSC) with a DSC 2910 of DuPont Instrument under a nitrogen gas flow (50 cm^3/min). The samples were cycled at a ramp rate of 10, 20, 30, and 40 °C/min between 20 and 240 °C; the first cycle was used to erase thermal history, and the second cycle was used to determine T_g values from the heating curves. The T_g values thus obtained were plotted as a function of heating rate, and the equilibrium thermodynamic T_g was obtained by extrapolating the plot to heating rate of 0, showing T_g values of 105.7, 107.7, and 106.5 °C for PS_{105K}, PS_{654K}, and PS_{1650K}, respectively.

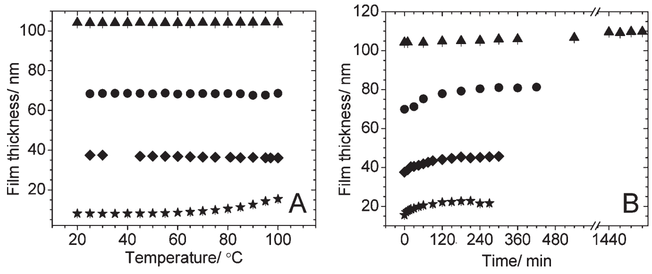


Figure 2. Thickness of PS_{654K} films (A) as a function of temperature during the initial heating and (B) as a function of time at 100 °C. Different symbols indicated films with different initial thicknesses: (★) 8, (◆) 37, (●) 68, and (▲) 100 nm.

3. Apparatus. Film thickness measurements were performed with a Filmetrics F20-UV thin film measurement system (Filmetrics Inc.) with a regulated deuterium and tungsten−halogen high-power UV−vis fiber light source (Hamamatsu Inc.) over a wavelength range from 200 to 1100 nm with the incident light normal to the sample surface. The data were fit using a single layer model to obtain the film thickness.

Measurements of film thickness as a function of temperature were performed in a custom-designed brass chamber with a quartz window cover. The entire chamber was heated uniformly with Kapton-insulated flexible heaters (Omega Engineering Inc.) mounted on both the bottom and the cover of brass chamber. The Eurotherm 905S EPC temperature controller was utilized to control the temperature under a helium atmosphere, a good thermal conductor to avoid the generation of thermal gradient in the experimental process. The whole experimental setup was also isolated by an external Teflon box from ambient environment (Scheme 2 in the Supporting Information).

The film thicknesses measured by F20-UV at room temperature were consistent with the results of X-ray reflectivity, which was employed on a PANalytical X′Pert X-ray diffractometer in the W. M. Keck Nanostructure Laboratory (a NSF-MRSEC Shared Experimental Facility) at the University of Massachusetts-Amherst. Considering the data collection by the F20-UV was much faster, the thicknesses of PS film upon heating and cooling were mainly obtained from the F20-UV.

Optical microscopic images were captured in reflection using an Olympus model BX60 microscope. The surface tensions of ILs were measured using pendant tensiometry on an OCA20 interfacial tension measuring device (Future Digital Scientific Co.), with a drop of IL as the minor phase and air as the major phase.

Results

1. Film Relaxation. A PS film floating on the surface of [BMIM][CF_3SO_3] was heated from 20 to 100 °C and held at 100 °C for several hours. The lateral dimensions of the film decreased with time, but the shape was not altered during the contraction. This is similar to the lateral shrinking of films floating on a glycerol surface studied by Bodiguel et al., where they concluded that this behavior could be attributed to a viscoelastic dewetting of the film.[37] In our studies, the film thickness was monitored as a function of temperature and time, as shown in parts A and B of Figure 2, respectively. The thickness of an 8 nm film began to increase at ~60 °C. However, thicker films did not show an obvious thickness increase in the temperature range from 20 to 100 °C. When the samples were held at a certain temperature, the film thickness increased with time, suggesting a relaxation of the film. The time-dependent thickness reached a plateau after a time that depended on the film thickness. Thicker films

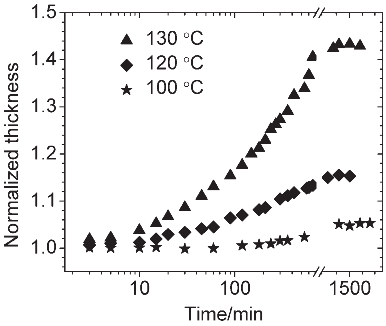


Figure 3. Normalized film thickness as a function of time at different temperatures: (▲) 130, (◆) 120, and (★) 100 °C for PS_{654K} films with an initial thickness of 100 nm. The thicknesses were normalized to the onset thicknesses at different temperatures.

relaxed more slowly, requiring a longer time to achieve a plateau value.

If the films were heated to higher temperatures, e.g. 120 °C, as shown the "thickness-temperature" profile (Supporting Information Figure S1) a "kink" is seen at ~107 °C for a 37 nm thick film, while for 68 and 100 nm thick films, the "kink" is seen at higher temperatures. The time dependence of film thickness showed similar trends to that observed at 100 °C, but for the films with thicknesses of 8 and 37 nm, a dewetting of the films on the IL surface was observed when the films were heated to 120 °C for an extended period of time. At 130 °C, only the 100 nm thick film reached a plateau in the film thickness, while for the thinner films, the thickness increased rapidly and then dewetted (Figure S2 in the Supporting Information). The thinner the film was, the more rapidly it reached a plateau value in the film thickness and the more rapidly dewetting occurred. Once dewetting occurred, reliable measurements of the film thickness could not be obtained. The dewetting of PS films on the IL surface was observed by optical microscopy after cooling the system to room temperature (Figure S3 in the Supporting Information). The interference colors of the film became nonuniform, and the holes with diameters on the micrometer size scale were evident.

As shown in Figure 3, the film thickness showed a logarithmic dependence on the relaxation time initially, but depending on the film thickness, deviations from this behavior were observed with the film thickness increasing more rapidly and, ultimately, achieving a time-independent thickness. The higher the temperature, the more rapid were deviations observed.

2. Influence of Molecular Weight. Films of PS_{1650K} and PS_{105K} also showed similar behavior after being heated to 130 °C. At 130 °C, PS_{1650K} films, 104 and 152 nm in thickness, reached a plateau value after 4 and 9 h, respectively (Figure S4A in the Supporting Information). However, the 66 nm thick PS_{1650K} film was found to dewet after ~3 h, and as the film thickness was decreased to 29 and 6 nm, dewetting occurred even more rapidly. However, for PS_{105K} films with thickness from 10 to 166 nm, dewetting occurred immediately after the temperature reached 130 °C (Figure S4B in the Supporting Information). In addition, the rate of film thickness increase and subsequent dewetting were enhanced with decreasing film thickness, similar to that observed in the films of PS with higher molecular weights (Figure 2 and Figure S4A in the Supporting Information).

The relaxation behavior of the PS films with different molecular weights is compared in Figure 4. Below 105 °C, there were no differences between the films. In contrast to PS_{654K} and PS_{1650K} films, the thickness of PS_{105K} increased more rapidly above 110 °C, and upon heating the films to 130 °C, the increase in the thickness was greatly accelerated (Figure 4B). The trend of thickness change had no significant differences between PS_{654K} and PS_{1650K} films.

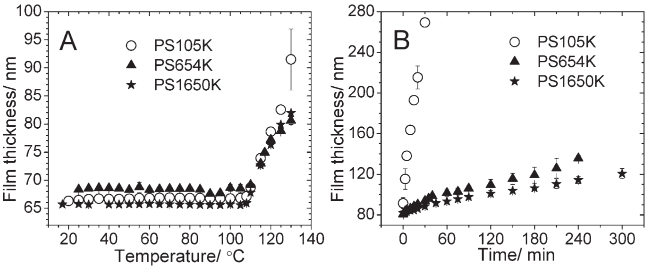


Figure 4. Film thickness (A) as a function of temperature during the initial heating and (B) as a function of time annealed at 130 °C for 66 nm thick (○) PS_{105K}, (▲) PS_{654K}, and (★) PS_{1650K} films.

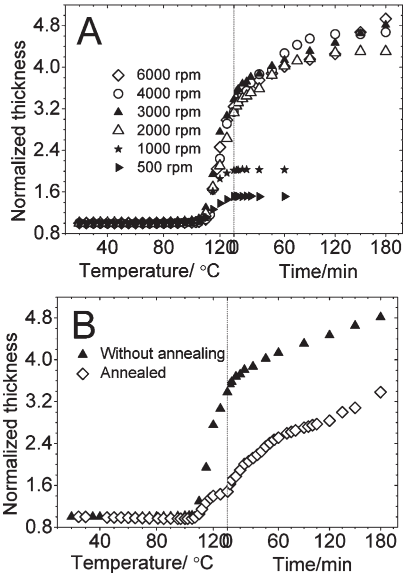
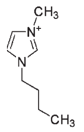
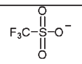
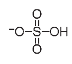
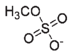


Figure 5. (A) Normalized film thickness as a function of temperature during the initial heating and as a function of time upon annealing at 130 °C for PS_{654K} films with an initial thickness of 25 nm, which were prepared by different spin-coating rates: (tilted ▲) 500, (★) 1000, (△) 2000, (▲) 3000, (○) 4000, and (◇) 6000 rpm. All the films were transferred onto [BMIM][CF_3SO_3] surface after spin-coating without preannealing. (B) Normalized film thickness as a function of temperature during the initial heating and as a function of time upon annealing at 130 °C for PS_{654K} films with an initial thickness of 25 nm, which were prepared by spin-coating at 3000 rpm (◇) followed by annealing and (▲) followed by transferring without annealing.

All of the three PS films with the same initial thickness (~66 nm) but different molecular weights dewetted on the ionic liquid surface at 130 °C, with the lower M_w sample dewetting much more quickly. Such a behavior is understandable on the basis of chain mobility.

3. Influence of Film Preparation Process. If the film was directly transferred onto the IL surface without preannealing, the conditions of film preparation, like the speed of spin-coating, significantly influenced the relaxation behavior of floating films (Figure 5A). Films prepared at higher spinning speeds relaxed more rapidly, as evidenced by the more rapid increase in film thickness. This behavior can be attributed to highly oriented and stretched polymer chains as a consequence of high-speed spin-coating. The higher the spinning speed is, the greater is the chain orientation and the more rapid and greater will be the relaxation of the films. In the case of spinning speeds greater than 3000 rpm, no significant changes were observed.

Table 1. Properties of ILs Used in the Experiments

Logogram of ILs	Cation	Anion	M_p (°C)	Viscosity (cP)	Water Solubility	Surface tension (mN/m)
[BMIM][CF_3SO_3]		 $\mathrm{F_3C{-}\overset{O}{\underset{O}{S}}{-}O^-}$	16	90	Yes	33
[BMIM][BF_4]		BF_4^-	-71	233	Yes	42
[BMIM][HSO_4]		 $\mathrm{{}^-O{-}\overset{O}{\underset{O}{S}}{-}OH}$	28	3383	Yes	53
[BMIM][$MeSO_4$]			25	350	No	32

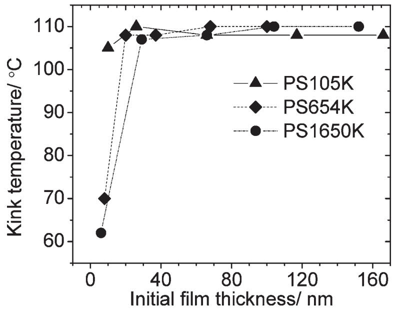


Figure 6. "Kink" temperature as a function of initial film thicknesses for (▲) PS_{105K}, (◆) PS_{654K}, and (●) PS_{1650K} films.

If the spin-coated films are annealed on a rigid substrate well above the T_g of bulk PS, the orientation of the chains will decrease, but there still exists a residual stress in the films. Shown in Figure 5B is a "temperature−time" plot for 25 nm thick PS_{654K} films spin-coated at 3000 rpm with and without annealing prior to the transfer to the IL surface. Significant differences between the two are seen, with the extent of change in the film thickness being much greater for the film transferred without annealing. Nonetheless, even the annealed film showed significant changes.

4. Influence of Ionic Liquid. Different ILs were used in this study as the floating bath for PS films and their properties are listed in Table 1. PS films with an initial thickness of 37 nm were successfully floated onto the surface of these ILs using the method described above. The high surface tension and viscosity of [BMIM][HSO_4] made the thickness measurements rather difficult at low temperatures, since the floating PS film was not flat and uniform. But above 110 °C, the thickness of the films increased on these four IL surfaces (Figure S5 in the Supporting Information). When the temperature was held at 130 °C, the thickness increased with time and the films dewetted in a few minutes, which was confirmed by optical microscopy. No significant differences in the relaxation or dewetting behavior of the films on surfaces of these four ILs were observed, though the PS films relaxed slightly more rapidly on [BMIM][CF_3SO_3] and [BMIM][$MeSO_4$] than those on [BMIM][BF_4] or [BMIM][HSO_4]. This may arise from the differences in surface tension for these ILs, which will be discussed later.

5. Measurements of T_g. During the initial heating, the increased film thickness as a function of temperature showed a distinct jump at a well-defined temperature, termed "kink" temperature (Figures 2A, 4A, and 5). This temperature depended on the film thickness and molecular weight, as shown in Figure 6. For films thinner than the radius of gyration (R_g) of PS, such as the 6 nm thick PS_{1650K} and 8 nm thick PS_{654K} films, the "kink" temperature was much lower than bulk T_g. This "kink" temperature, though, cannot be taken as the T_g of the thin film, since stress relaxation is occurring during this heating process.

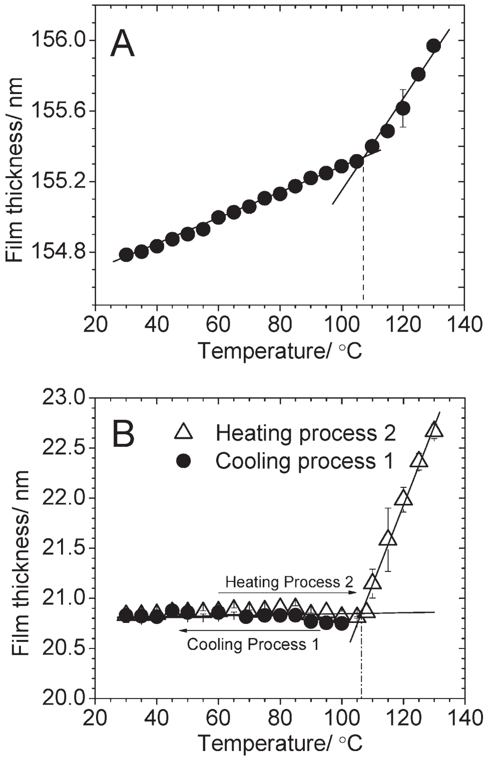


Figure 7. (A) Temperature-dependent film thickness for a PS_{654K} film with an initial thickness of 100 nm during the cooling after annealing at 130 °C for 26 h. (B) Temperature-dependent film thickness during the first cooling (●) and the second heating (△) for a PS_{654K} film with an initial thickness of 8 nm after annealing at 100 °C for 4 h.

In addition, T_g can only be obtained when the glass-forming material is cooled from the fully relaxed, equilibrium melt state. Figure 7A shows the temperature dependence of film thickness upon cooling from 130 °C for a 100 nm thick PS_{654K} film. Initially, the thickness decreased with decreasing temperature, and at ~107 °C, the rate of contraction markedly slowed. The temperature at which the change in the rate of contraction occurred was taken as the T_g of the film. The linear thermal expansion coefficient determined from the slopes of the lines were 1.4×10^{-4} and 4.8×10^{-5} K^{-1} in the higher and lower temperature range, respectively. These values are close to but slightly lower than those for bulk polystyrene ($(6-8) \times 10^{-5}$ K^{-1} for glassy state).[45]

For films with an initial thickness less than 100 nm, dewetting of the film occurred on the IL surface at 130 °C. In lieu of this, the films were heated to 100 °C for an extended period of time to relax the polymer chains. Subsequently, the film thickness was measured upon cooling and no "kink" was observed, suggesting that T_g was at least 100 °C. When the film was reheated to 130 °C, the thickness increased with increasing temperature, showing a "kink" at ~107 °C, which was taken as the T_g of this film. Figure 7B shows the temperature-dependent film thickness for an 8 nm thick film during the first cooling and second heating. No depression in the T_g relative to bulk PS was observed.

According to the methods described above, we measured T_g values of the PS films with different thicknesses and molecular weights. All the films studied showed T_g values at ~107 °C, close to that of bulk PS.

Discussion

The principal finding of this study is the observation of a notable relaxation process of PS films floating on the surface of an IL even though the films have been annealed on Si substrates for several days (Figure 2) and no observable depression in the T_g relative to the bulk polymer for the relaxed films. Both the rate and the extent of the relaxation depended critically on the heating temperature, film thickness, and polymer molecular weight (Figures 2−4, Supporting Information Figures S1, S2, and S4).

The relaxation of volume (or thickness) in thin films of glass-forming polymers has been observed in neat polymers and polymers containing residual solvent.[46−49] In these previous experiments, the thickness was measured as a function of increasing temperature, and it was observed that the change in volume or thickness due to relaxation occurred simultaneously with a change resulting from thermal expansion. Kanaya and coworkers investigated annealing effects on thickness of deuterated PS thin films supported on a Si substrate using neutron reflectivity and found that the contraction of thickness with temperature in the glassy state originated from an unrelaxed structure,[47] and in a subsequent study, they observed the contraction and re-expansion normal to the film surface if the thickness was below 10 nm after annealing.[48] Using ellipsometry, Beaucage et al. observed the time dependence of film thickness and the in-plane lateral dimension of the film, indicating that relaxations in thin films occurred over many hours.[46]

The structural relaxation of polymer films is attributed to the nonequilibrium state or residual stresses within the film. For films prepared by spin-coating, the polymer chains are stretched in and oriented parallel to the plane of the film. This chain conformation and orientation will affect the value of T_g measured. While some stresses can be relaxed during heating, full relaxation appears to occur only when the film is annealed near the bulk T_g. It has been argued that full relaxation of a supported film could only be achieved by annealing the sample at ~15−20 °C above T_g.[36]

In the present study, we annealed the films spin-coated onto Si substrates at 150 °C for 96 h before transferring to the IL surface. The film thickness on Si wafer did not show obvious changes before and after annealing within the precision of the thickness measurement. If full relaxation or equilibrium state was reached after such a long-time-annealing process, then the film thickness should not have increased with increasing temperature or annealing time on the IL surface. In our studies, the complete relaxation of films could not be achieved when the films remained on the solid substrate. Even extended thermal annealing of the films on a Si wafer at 150 °C did not relax the film completely (Figure 5B). On the IL surface, on the other hand, although the film is not physically attached to a solid substrate, there is an in-plane force arising from the three phase contact line at the edge of film.[37]

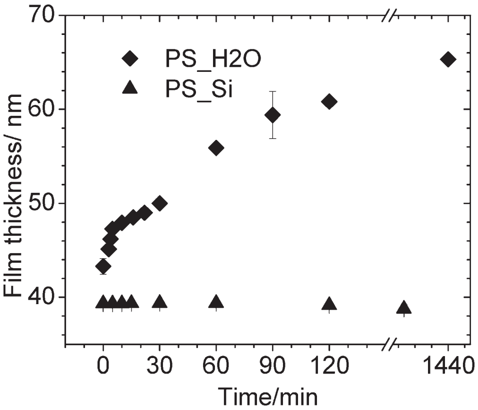


Figure 8. Time dependence of film thickness for a 39 nm thick PS_{105K} film (plasticized with 30% dioctyl phthalate) (▲) supported on Si wafer and (◆) floating on water surface at room temperature.

According to Bodiguel and Fretigny,[37] the stress arising from surface tensions, which acts on a film floating on a liquid surface, could be described as $\sigma = (\gamma_f + \gamma_{f/l} - \gamma_l)/h$, where γ_f and γ_l are the surface tensions of polymer film and liquid substrate, respectively, $\gamma_{f/l}$ is the interfacial tension between polymer film and liquid, and h is the film thickness. Since the viscosity of polymer film is typically 100 times more than that of the liquid, mechanical interactions with the substrate were neglected. In addition, the surface tension of [BMIM][CF_3SO_3] (~33 mN/m) is quite close to that of PS (~33−35 mN/m).[45] Thus, the in-plane stress, in our case, should be very small. When the film is heated to a temperature above T_g, polymer chains are mobile and should be able to relax toward their equilibrium state rapidly. With relaxation, the planar dimensions of the film should decrease and the film thickness should increase with increasing temperature. When the films are fully relaxed, large dimensional changes of the film should cease and only thermal expansion should dictate changes in the film dimensions. Similar relaxation behavior was also observed on the surface of other ILs with different surface tensions (Figure S5 in the Supporting Information).

In addition, relaxation of PS films was observed on the surface of water. Spin-coated PS film plasticized by dioctyl phthalate exhibited an increase in thickness after being transferred from Si substrate onto H_2O. On the water surface, the thickness of plasticized PS film increased with time at room temperature, while the supported plasticized PS film did not show obvious change in thickness with time (Figure 8). Doped with the plasticizer, the T_g of the PS film is decreased so that a rapid relaxation can occur on water surface even at room temperature. These results also indicated that the freely floating films could relax when brought above the T_g, whereas the relaxation of supported plasticized film is suppressed by the solid substrate.

In our studies, it was noted that the thinner the film, the faster the film relaxed upon heating (Figure 2 and Figures S1, S2, and S4 in the Supporting Information). This result is perfectly understandable, since the orientation of the polymer chains in the plane of the film will increase with decreasing film thickness. In some cases, the film thickness increased to several times its initial value. For example, a PS_{654K} film with the initial thickness of 37 nm, less than $2R_g$, after annealing at 130 °C for 3 h, increased to 127 nm before dewetting. In fact, in all cases studied, it was impossible for a floating film to have a thickness less than $2R_g$ at elevated temperatures, unlike films constrained by a substrate. Consequently, we are forced to conclude that it is not possible to obtain a fully relaxed film on a solid substrate which, in our opinion, can markedly affect the value of T_g measured by any technique.

As mentioned previously, the time scale of the measurement or the cooling rate has been shown to influence the magnitude of the

T_g depression. Both Forrest and Simon's works[30,31] showed that the cooling rate greatly influenced the measured T_g values, and they used this point to explain why no discernible T_g depressions were found in some studies for PS films as thin as 3 nm. However, in our experiments, we found that the measured T_g values for relaxed films were not influenced by the cooling rate we could achieve (Figure S6 in the Supporting Information).

To better understand the reason for the absence of T_g depression for the ultrathin floating films relative to the bulk polymer, the T_g values for supported PS_{654K} films were also measured using the same method in our experiment. A 10 nm thick film on Si substrate showed a T_g value at ~85 °C, about 22 °C below that of bulk value, which is consistent with many studies in the literature. In addition, the thickness did not show any obvious increase with time when the film was annealed at 130 °C, which further suggests that the adhesion of polymer to the substrate constrained the relaxation of the film. We also tried to suspend a PS film on an aluminum holder with a 6 mm hole in the center. Then the Al frame with the suspended film was placed on the surface of an ionic liquid, with the IL entering into the hole and contacting the lower surface of the film (Figure S7A in the Supporting Information). For the PS_{654K} films with thicknesses in 10−100 nm, hole formation and nonuniform thickening were observed in all these films when they were heated to 130 °C (Figure S7B in the Supporting Information). This phenomenon was different from that of the freely floating films where the 100 nm thick film could completely relax without dewetting and the surface would remain quite uniform after being heated to 130 °C for 26 h. Hole formation and growth were also observed in conventionally suspended PS films near or above the bulk glass transition temperature, with surface tension being considered to act as the driving force.[50−53]

The above results reinforced the idea that constraints from the substrate or sample holder exist in both supported and suspended films. Because of these constraints, the polymer film cannot fully relax, causing the film to be in a metastable state during the T_g measurements. This may offer the possibility to observe a noticeable shift in T_g for ultrathin films relative to bulk. Thus, it is difficult, if not impossible, to achieve the true T_g for a thin polymer film on a solid substrate.

Conclusion

In the present work, the relaxation and glass transition dynamics of polystyrene thin films, floating on an IL surface, have been investigated. By taking advantage of the negligible volatility and rather low surface tension of ILs, we have shown that the floating PS films will relax when heated to the temperature above bulk T_g, with a thickness increasing and a concomitant lateral contraction. The relaxation behavior, manifested by the change of temperature- or time-dependent thickness, was significantly influenced by the film thickness and molecular weight of the polymers. Ultrathin films or low molecular weight PS films would dewet after annealing at 130 °C for a certain time. By measuring the thickness as a function of temperature during the cooling for a completely relaxed film, the true T_g of the film was obtained, close to that of bulk polymer. Compared with conventional supported and suspended thin polymer films, the absence of the strong substrate−polymer interactions or constraints in freely floating films makes the investigation of polymer dynamics more straightforward, since perturbations to the polymer chains are minimized. It is clearly found that glass transition dynamics in the thin polymer films is close to those of the bulk state.

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Supporting Information Available: Film preparation, the representation of custom-designed experimental setup, relaxation behaviors of PS_{654K} films at 120 and 130 °C, optical microscopy images of PS films on IL surface, relaxation behaviors of PS_{1650K} and PS_{105K} films, the influence of ILs on the relaxation of PS films, the effects of the heating and cooling rates, and schematic representation and optical microscopy image of suspended films. This material is available free of charge via the Internet at http://pubs.acs.org.

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