

Sub-Glass-Transition Temperature Interface Formation Between an Immiscible Glass Rubber Pair

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ABSTRACT: We used neutron reflectivity to measure the interfacial width in the immiscible system polystyrene/poly(*n*-butyl methacrylate) (PS/*P**n*BMA). Measurements were made on the same samples at temperatures ranging from below the glass-transition temperature (T_g) of PS to slightly above. We observed significant broadening of the interface at temperatures below the T_g of PS, indicating chain mobility below the bulk T_g value. The interfacial width exhibited a plateau at a value of 20 Å in the temperature range of 365 K < T < 377 K. A control experiment involving hydrogenated and deuterated PS films (hPS/dPS) showed no such broadening over the same temperature region. The results are consistent with a reduction of the T_g of PS in the interfacial region of ~20 K. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part B: Polym Phys* 39: 2664–2670, 2001

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INTRODUCTION

It is becoming increasingly obvious that the properties of polymers in thin films may not always be the same as they are in bulk samples. One example that has attracted significant attention is the dynamics in polymer films as measured by the glass-transition temperature (T_g),^{1,2} structural relaxation,³ or polymer chain mobility.⁴ It is interesting that studies of T_g have suggested faster dynamics, but very similar systems reveal decreases in chain mobility. The origin of this discrepancy has yet to be satisfactorily resolved, but it has been noted¹ that because no measurements

of the temperature dependence of chain diffusion have been made, direct comparisons between chain diffusion and segmental motion are not possible. It has been suggested^{5–7} that lower T_g values and faster dynamics in thin polymer films may result from an enhanced mobility at the polymer free surface. The results of computer simulations also support the idea of enhanced mobility at the polymer surface.⁸ Recent experiments have been performed to directly measure the dynamics of the polymer surface. The results of these studies have not been conclusive, and claims of enhanced mobility⁹ as well as unaffected mobility¹⁰ have both been reported. One idea that has been suggested is that the interface between highly immiscible systems forms a model to investigate how excess free volume can lower the T_g near an interface with a lower T_g component. For the case of lower T_g 's in block copolymer microstructures, excess free volume in the interfacial mixing layer was suggested to be the origin of an observed

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lowering of the T_g of glassy microphases embedded into a rubbery phase.¹¹

Enhanced mobility at polymer surfaces or interfaces should affect other aspects of surface properties—among the most important of these is adhesion. For instance, if there is sufficient chain mobility at the interface between two polymer layers, then interface formation will increase the adhesive strength. In this sense, the ability to promote adhesion with sub- T_g annealing can serve as a probe of enhanced chain mobility at the interface. Experiments using a double cantilever beam geometry to measure interfacial strength have revealed interfacial strengths more than an order of magnitude greater than the thermodynamic work of adhesion for polystyrene/poly(methyl methacrylate) (PS/PMMA) welded at 15 K below the T_g values.¹² Experiments using a lap-shear geometry for both polydisperse as well as monodisperse samples of PS have revealed the onset of significant adhesive strength even when annealed below the bulk T_g value.¹³ The time dependence of the interfacial strength was used to suggest that reptative motion of chains across the interface during the annealing process was responsible for the adhesive strength. This interfacial strength should be observed as interface formation below T_g , and direct correlation between the two quantities is expected.

Reflectivity techniques have proven to be powerful tools for the study of interfacial growth in polymer systems. For the case of neutron reflectivity, the power of the technique is increased further by utilizing the fact that H and D atoms, although essentially chemically identical, have a large difference in the neutron scattering cross section. The net result of this is that two layers of nearly chemically identical materials have a different effective index of refraction for the neutrons, and there will be significant scattering from the interface. This allows one to label a species by deuteration without significantly affecting the chemical properties of the polymer. Neutron reflectivity techniques have been applied to look at interface formation in immiscible¹⁴ as well as highly miscible¹⁵ polymer layer systems, but surprisingly little work has been done on highly immiscible systems with different T_g values. Freitas Siquera et al.¹⁶ have recently looked at interface formation between poly(*n*-butyl methacrylate) (P*n*BMA) and PS, but these experiments were done for only two temperatures, both well above the T_g of PS.

Experiments aimed at observing interface formation below the bulk T_g of PS have been performed and have been unable to discern any interface formation below T_g (bulk).¹⁷ The inability of experiments to observe such sub- T_g growth is seemingly in contradiction with the observation of enhanced interfacial strength. One possible explanation for the discrepancy concerns the difference in sample type for the two experiments. Samples prepared for adhesion studies are microscopically rough, and there must be a substantial amount of free surface as a result of surface asperities. Samples prepared for neutron reflectivity experiments, on the other hand, are spin cast and smooth on a sub-nanometer level. When a multilayer sample is made by a water-transfer technique, the surface forces between the spin cast films are strong enough to ensure intimate contact. In an attempt to test the validity of this idea, one might try to replace the real free surface found in the samples used for adhesion with rubbery samples where there might be expected to be significant free volume. The use of miscible polymers would result in substantial plasticization of the glassy phase, and to best mimic the situation of pure PS surrounded by free volume, a highly immiscible polymer pair is required.

EXPERIMENTAL

In choosing appropriate polymer pairs for this study, it is important to find polymers that are both highly immiscible and have sufficiently dissimilar T_g values that one can see an interfacial T_g reduction. This turns out to be a rather restrictive constraint because in many such cases the low T_g component will simply dewet from the other component. We did some initial studies with PS/polyisobutylene systems, but they were found to dewet at elevated temperatures. To provide the opportunity to make reasonable quantitative comparisons with other investigations we chose the PS/P*n*BMA systems studied in ref. 16. The P*n*BMA used in these experiments has a T_g of 298 K, and PS has a T_g of 370 K.

The samples used for these studies are of two types. All polymers were obtained from Polymer Source Inc. The first sample type is a trilayer with P*n*BMA and *d*-polystyrene (*d*PS), and is shown schematically in Figure 1. The sample configuration is Si/P*n*BMA/*d*PS/P*n*BMA. The trilayer configuration (rather than a simple bilayer) was chosen to provide an indication of the effects of the

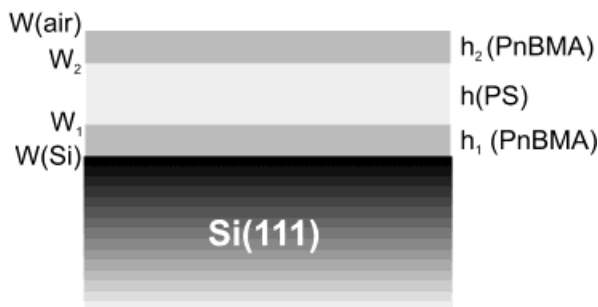


Figure 1. Diagram of sample geometry showing trilayer polymer films used in the neutron reflectivity experiments.

substrate. Polymer diffusion can be significantly affected by the substrate, and monitoring two interfaces at different distances from the substrate allows us to rule out substrate-induced effects.¹⁸ The second set of samples represents a control group and are *h*-polystyrene (*h*PS)/*d*PS with a configuration Si/*h*PS/*d*PS/*h*PS. The *h*PS used had a number-average molecular weight (M_n) of 115,000 with a polydispersity (M_w/M_n) of 1.05. Samples were prepared using spin-coating techniques. The initial *Pn*BMA ($M_n = 173,900$, $M_w/M_n = 1.05$) layer was spin cast directly onto a 25-mm-diameter Si(111) wafer with the native oxide coating intact. The 25-mm-diameter wafers were used instead of the more standard (for reflectivity experiments) 50–75 mm diameter wafers because it was found that spin-cast samples had a much greater thickness uniformity throughout the lateral dimension of the sample for the smaller diameter samples. These films were then annealed at 325 K [T_g (*Pn*BMA) + 27 K] for 10–12 h to remove solvent and relax the polymer chains. After cooling to room temperature the single *Pn*BMA films were measured with ellipsometry for film-thickness determination. All of these samples had a thickness, $h \sim 800$ Å, and showed a thickness variation of less than 1 nm over the dimension of the sample. The *d*PS ($M_n = 209,000$, $M_w/M_n = 1.04$) layers were spin cast onto a mica substrate, annealed at 385 K [T_g (PS) + 15 K] for 10–12 h, and then slowly cooled to room temperature. These films were then water transferred onto the *Pn*BMA films to prepare a bilayer. Thickness determination of the *d*PS layers was done by ellipsometric measurements of the bilayers and then compared to calculations made using a multilayer technique as well as by floating some of the PS films directly onto Si. The *d*PS films had a thickness $h \sim 1700$ Å. The bilayers were then

dried in vacuum at room temperature. The final *Pn*BMA layers were spin cast onto clean glass slides and then, after the same annealing treatment as the first *Pn*BMA film, were water transferred onto the bilayer to make the final sample. It is important to reiterate that although each trilayer sample was never heated above room temperature before the reflectivity experiment, each individual polymer layer had been fully annealed above its bulk T_g for times longer than the reptation time to minimize any residual chain orientation as a result of the spin coating. The samples were of excellent optical quality being uniform in color with no observable scattering and the presence of only a few small cracks from the water-transfer procedure. The final samples were studied with optical microscopy and ellipsometry to investigate lateral uniformity, and the most uniform samples were used for the neutron reflectivity experiment. To ensure that the samples would not dewet during the experiment we subjected one of the *Pn*BMA containing samples to an annealing of 425 K (~ 50 K higher than the highest temperature to be used in the reflectivity experiments) for 3 h (the same as the *in situ* annealing time). This sample was investigated with optical microscopy after this aggressive thermal treatment and showed no signs of dewetting. This is consistent with the observation of Freitas Siqueria et al.¹⁶ where neutron reflectivity was used to measure interfacial roughness in the same systems at temperatures as high as 449 K.

Neutron reflectivity data were acquired using the CRISP reflectometer at the ISIS spallation source at Rutherford Appleton Lab, Didcot, U.K. To avoid the difficulties associated with variation among the different samples, we made all of the heating measurements *in situ* in a sample hot stage. Each sample was held for 3 h at one of the predetermined annealing temperatures, and the reflectivity profile was then measured, which required an additional 3 h. Data were acquired after annealing at temperatures of 321.5, 352.7, 358, 363, 368.1, and 377.1 K. The temperature was calibrated by a fine gauge (40 awg) thermocouple wire glued to a Si wafer and controlled to within 0.5 K. We estimated the absolute error in the temperature to be ± 2 K. Reflectivity profiles were taken with incident angles of 0.25, 0.65, and 1.5°. This range allowed for sufficient overlap to accurately and unambiguously combine the data sets.

Detailed analysis of all the reflectivity data (such as that shown in Fig. 2) was accomplished using the Parrat program.¹⁹ To obtain the most

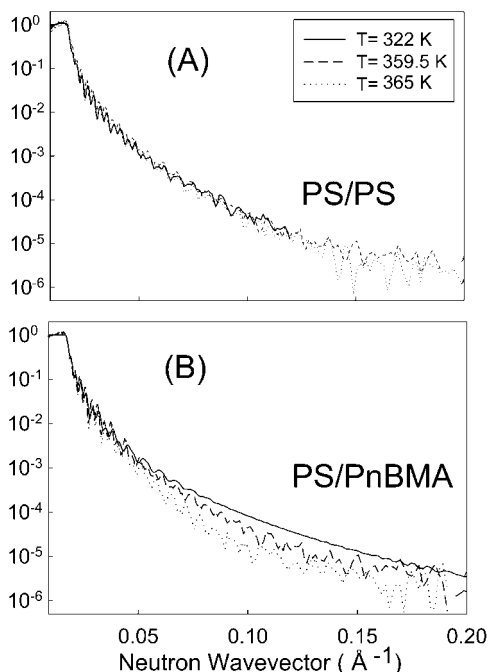


Figure 2. Neutron reflectivity profiles for PS/PS trilayer system (A) and the PS/PnBMA trilayer system (B). The profiles are given at temperatures of 322, 359.5, and 365 K. All three temperatures are below the bulk T_g value of PS.

reliable values for the interfacial width, we developed a self-consistent fitting process. In this process, we first fixed the film thicknesses of the constituent layers to those determined using ellipsometry and the top surface and Si roughness to values determined by an initial free fit. We then performed the fit allowing only the width of the PnBMA-dPS interface to vary. The fit values from this initial procedure were used as constants, and the film thicknesses and scattering cross sections were fit again (making sure that the latter varied by only the amounts expected by the thermal expansion). These new values for the

film thickness were fixed, and the interfacial widths were fitted a final time. This procedure resulted in uniform variation of the film thickness, scattering cross sections, and interfacial width with all parameters being properly bound by the known constraints as determined by ellipsometry. This procedure was also found to lead to good agreement between the two similar interfaces, a constraint not forced upon the system (see Table I). Free fitting with all seven parameters invariably led to inconsistent results.

RESULTS AND DISCUSSIONS

Figure 2(A,B) illustrates a series of reflectivity profiles for the (*d*PS/*h*PS, PnBMA/*d*PS) system at temperatures of 322, 359.5, and 365 K. All of these temperatures are below the T_g value of bulk PS. Considering first the *h*PS/*d*PS system, Figure 2 shows that in the entire temperature range covered between 322 and 365 K there is no obvious indication of significant interfacial width in the *h*PS/*d*PS system in the 3–6 h of total time at the experimental temperature. Such increased interfacial width would result in smaller values of the reflectivity at higher values of the neutron wavevector. In contrast, we can also see that for the *d*PS/PnBMA system the reflectivity at large neutron wavevector values is smaller for the data acquired at high temperatures than it is for that at lower temperatures, even for temperatures below the bulk T_g of PS. This is an obvious indication of larger effective roughness as a result of interfacial growth.

Figure 3 depicts a typical data set with the model profile leading to the best fit shown in the inset. We have good agreement between the fit and the experimental data for the five orders of magnitude in reflectivity over which we have obtained data. To present the results, we average

Table I. Interfacial Widths Obtained by Fitting the Experimental Reflectivity Profiles. The Estimated Uncertainty in the Width Values is ± 3 Å

Temperature (K)	W_1 (PS) (Å)	W_2 (PS) (Å)	W_1 (PnBMA) (Å)	W_2 (PnBMA) (Å)
321.5	6.3	6.1	4.7	4.6
352.7	8.9	8.7	9.0	8.8
358.0	7.7	7.4	10.4	10.8
363.0	8.9	9.4	25.1	13.2
368.1	11.1	11.7	21.6	17.5
377.0	14.5	14.1	24.24	17.8

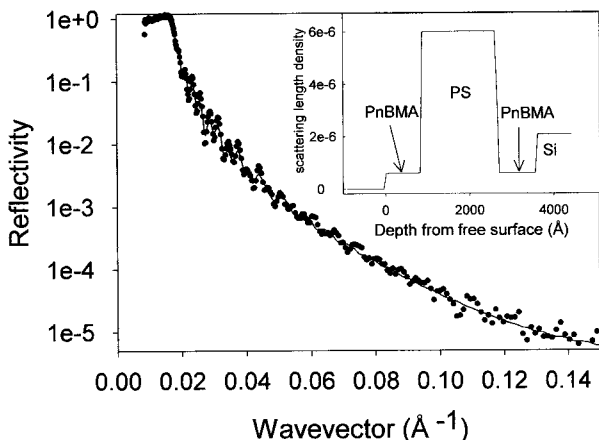


Figure 3. Example of data fitting to model profile. The symbols are a typical data set, and the solid curve is the model fit to the experimental data. The inset is the scattering cross-section profile that gives the fit curve.

the two interfacial widths of interest and plot the result as a function of temperature in Figure 4. By doing simulations with different values of the PS interfacial width, we estimate that we can determine the PS interfacial width to about 3 Å.

Interfacial strength is an obvious consequence of interdiffusion of chains across the interface. Boiko and Prud'homme observed increased interfacial shear strength for PS layers after annealing for 6 h at a temperature of $T = 365$ K. This value is ~ 5 – 10% that the strength of the same interface annealed at 382–391 K. Previous work on interfacial strength between PS and poly(methyl styrene) shows that interfacial strength grows linearly with interfacial width,²⁰ and for the case of PS annealed at 393 K for 24 h we expect an interfacial width of ~ 100 Å. Comparing this to the interfacial strengths observed in the literature¹³ suggests that one would expect to observe an increase in interfacial width of about 5–10 Å at $T = 365$ K. This is within our quoted resolution, and thus the results in Figure 4 for the PS/PS interface appear to disagree with the reported results.¹³ However, we should stress that the PS/PS interface in this experiment is done as a control and is not meant to be used in such a detailed comparison. If that were the goal, the obvious experiment would be to use a single sample and perform reflectivity experiments with sub- T_g annealing over a much larger time range.

The procedure previously described was also used to extract the width of the *d*PS/*Pn*BMA interface, and these results are shown by the open

symbols in Figure 4. These data show that the interfacial widths at the lowest temperature $T = 322$ K are the same for the *d*PS/PS and *d*PS/*Pn*BMA layers. This simply indicates that the initial roughness of the films (probably the result of the capillary wave contribution during spin coating) is the same for both systems. The data show indication of increased roughness below the T_g of bulk PS, and the detailed analysis reveals quantitatively that the interface grows rapidly at temperatures below the bulk T_g of PS and appears fully developed by 365 K. The 'plateau' value of 20 Å is in good agreement with the interfacial widths between PS and other *n*-alkyl methacrylate systems¹⁴ (suggesting we may be near the equilibrium width). In principle, the interfacial width of PS/*Pn*BMA can be used to estimate the value of the Flory–Huggins interaction parameter χ (as was done in ref. 16). In this study, we do not make this connection for two reasons. First, for such small interfacial widths, there is a substantial contribution to the equilibrium width because of thermally excited capillary waves,²¹ and the measured interfacial width cannot be compared accurately without considering this contribution. Second, and perhaps more importantly, we have not taken care to anneal the samples to the point where the equilibrium width is achieved. Instead we chose the width at a fixed annealing time to be an indication of the mutual diffusion coefficient, and we want to study the temperature dependence of this quantity. The

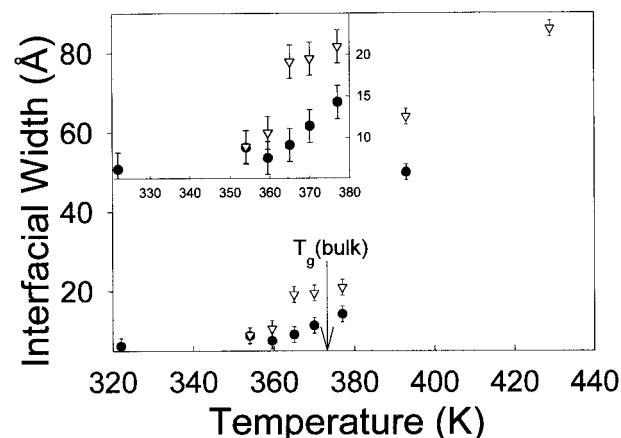


Figure 4. Temperature dependence of the interfacial width in both *d*PS/*h*PS (solid) and *d*PS/*Pn*BMA (open) systems. All data for temperatures below 390 K are from the present study. For the *d*PS/*Pn*BMA system, the higher temperature data points are from ref. 16. For the PS/PS system, the data are from ref. 14.

measure of chain diffusion provided by the growth of interfacial width certainly suggests that the T_g of PS in the interfacial region is reduced below the bulk value.

To further quantify the reduction of the T_g of PS in the interfacial region, we can make a comparison to interfacial growth in the *d*PS/*h*PS system (keeping in mind that the measured quantity in these experiments is the interfacial width after a fixed annealing time of 3 h). For the *d*PS/*h*PS system, the T_g value of each component is the same at 370 K. We can correlate this with interfacial growth by using data found in the literature.²⁰ For 3 h of annealing time at $T_g + 20$ K, the interfacial width (for comparable values of M_w) is ~ 50 Å (also shown in Fig. 4). From our own data on the PS/PS system we can see that at the bulk T_g value we have an interfacial width of about 10 Å. Because this is very far from the equilibrium width, we can neglect the difference in the equilibrium widths of the two systems and suggest that at the T_g , after 3 h of annealing time the interfacial width is $\sim 20\%$ of the value it has at $T_g + 20$ K. Applying this analogy to the *d*PS/*Pn*BMA system suggests an interfacial T_g of less than 343–353 K, but certainly greater than 322 K. This corresponds to a reduction in the T_g of PS in the interfacial region of at least 20–30 K. An additional aspect of the data (see Table I) concerns the symmetry of the interfaces. For all of the profiles with 321 K $< T < 358$ K (below the T_g of bulk PS), both of the *d*PS/*Pn*BMA interfaces have the same values within the uncertainty of the experiment. For 363 K $< T < 377$ K (near and above the bulk T_g of PS), the two interfacial widths no longer have the same value, and in fact the width of the interface nearest the substrate has the larger value. In contrast, both of the PS/PS interfaces have the same value over the entire temperature range studied. We do not have a detailed explanation for this asymmetry in the *Pn*BMA/PS system near the bulk T_g , although this may be due to the onset of a van der Waals instability at the PS/*Pn*BMA interface that would eventually lead to dewetting.

Also shown in Figure 4 are two data points from the literature¹⁶ for $T > 380$ K. That study used the same polymers with comparable constituent layer thickness, annealing times, and *Pn*BMA M_w value as this investigation (the largest difference in the experimental parameters between our study and that of ref. 16 is their PS has $M_w = 720,000$, whereas we used PS with $M_n = 209,000$). This similarity between the polymer

types and annealing times allows us to make reasonably direct comparisons between the results. The collective data for the *Pn*BMA/PS system display an interesting behavior. For $T < T_g$ bulk (PS) we do see interface formation to some small extent. Of course the limit to which the interface can grow is limited because the chain segments near the interface have a very high probability of being part of chains that also have chain segments much more interior in the film. In this way, the mobile segments near the interface will act like a polymer brush that is grafted to a glassy PS layer. This is expected to lead to the plateau behavior observed in Figure 4. Once the bulk T_g is reached, then this constraint on chain motion disappears and the interfacial width may increase again. Of course in analyzing the reflectivity data, it is not easy to separate the contribution of intrinsic interfacial width from that of capillary wave roughness,²¹ and it is possible that the additional width at the higher temperatures ($T > 380$ K)¹⁶ is due to capillary roughness driven by van der Waals forces. In either case, the onset of the additional growth is indicative of whole chain motion in the PS layer.

The data for the *d*PS/*Pn*BMA system show evidence for two distinct T_g values as probed by the chain mobility. There is an interfacial T_g that is reduced from the bulk value by at least 20–30 K, and there is the bulk T_g that is the determining factor in whole chain motion. It is worth giving some consideration to how one might rationalize the decreased interfacial T_g . There are two very simple arguments that may be used to explain the reduction of the T_g of the PS in the interfacial region. One way to consider the properties near the interface is to use a simple free-volume model and calculate the available free volume in the interfacial region and how this can plasticize PS. This can then be used to estimate what the T_g of PS in the interfacial region will be. This simple argument leads to a relation $T_g = \phi T_{g,1} + (1 - \phi)T_{g,2}$, where ϕ is the volume fraction of the component with $T_{g,1}$. This approach predicts a T_g at the interface (using the fact that $\phi = 0.5$ at the interface) of 335 K. An alternative way of thinking is to consider PS/*Pn*BMA as a miscible system (because in the interfacial region they do mix and so may not be distinguished from miscible systems). For such systems there is a well known mixing rule $1/T_g = \phi/T_{g,1} + (1 - \phi)/T_{g,2}$. This relation can be used to predict an interfacial T_g of 330 K. These two values are too close to allow any distinction between the two approaches, but both

approaches provide a way of qualitatively describing the observation of reduced T_g at the interface between these immiscible layers.

SUMMARY

In conclusion we have measured the onset of interfacial width formation in the immiscible system *Pn*BMA/PS as well as the miscible system PS/PS. In both cases, interfacial widths were obtained at temperatures below to slightly above the T_g value of the bulk PS. For the PS/PS system we observe a slight monotonic increase in the interfacial width with insignificant growth below the bulk T_g value. For the *d*PS/*Pn*BMA systems we observed a significant increase in the interfacial width below the bulk T_g value for PS. Our measurements revealed a leveling off of the interfacial width for $365\text{ K} < T < 377\text{ K}$. Comparison of our data with that of previous work on a similar system PS/PMMA suggests that the interfacial width achieved by the sub- T_g annealing is near the thermodynamic equilibrium value.

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