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Interfacial Broadening and Self-Adhesion of Segmented Block Copolymers Studied by Neutron Reflection

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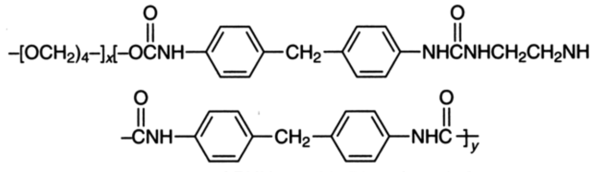
It is generally accepted that chain interdiffusion is necessary for strong self-adhesion in high molecular weight polymers.[1,2] In some cases, such as multilayer film lamination or thermal bonding, rapid increases in the level of adhesion are desired. In other instances, especially the handling of low glass transition temperature (T_g) polymers, low interparticle adhesion is desired. The self-adhesion process has been studied for interfaces of polymers using a number of techniques. We present a mechanistic study of such a phenomenon in a more complicated system, namely, a biphasic poly(urethane−urea) (PUU) elastomer.

The PUU studied here is a segmented block copolymer consisting of 85% by volume poly(tetramethylene oxide) (PTMeO) soft segments and 15% aromatic urethane−urea-linked hard segments.[3,4] It is one of the sephadex family of elastomers.



structure of PUU, x = 20–50 and y = 1–3

For our studies, a deuterium-labeled PUU was also prepared by substituting perdeuterated poly(tetramethylene oxide) (d-PTMeO) for PTMeO. The urethane−urea hard segments consist of diphenylmethane diisocyanate (MDI) and ethylenediamine. Molecular weights of the two materials were matched to ca. 10%.

Our PUU is microphase-separated, which is typical of this type of segmented poly(urethane−urea).[5−7] Studies of related polyurethanes show hard-segment domains on the order of 2 × 10 nm.[8] A DSC trace for a dried film of PUU is shown in Figure 1, showing the glass transition of the PTMeO phase at −65 °C, a small PTMeO crystallization exotherm immediately after T_g, and a melting endotherm of the partially crystallized PTMeO which ends at 15 °C. This is evidence for microphase separation in that T_g and T_m are comparable to those for a pure homopolymer PTMeO of this MW. No clear glass or melting transitions are observed for the hard-segment domains up to 250 °C. Mechanical tests show that these remain at least partially intact well past the nominal degradation region, which begins near 200 °C.

Specular neutron reflectivity (NR) was applied to probe the extent of interdiffusion in bilayer films. This technique affords very high resolution for concentration profiles normal to the plane of the interface and is nondestructive.[9] Few NR experiments have been performed on semicrystalline[10,11] or microphase-separated films. This is because films for specular reflectivity must be optically flat, and with many phase-separated polymers it is difficult to obtain the high-quality thin films needed. In addition, any neutron scattering losses reduce the ability to interpret data.

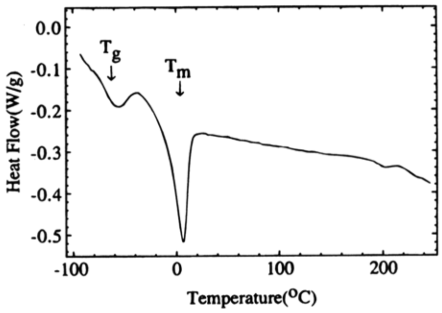


Figure 1. DSC heat flow vs temperature for PUU at a heating rate of 10 °C/min. The glass transition and melting points of the PTMeO phase can be seen in the data. No thermal events due to the hard-segment phase are evident up to 250 °C (see text).

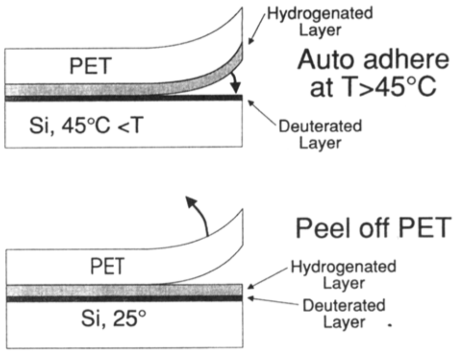


Figure 2. Schematic of self-adhesion or bonding of deuterated and hydrogenated PUU layers together at elevated temperature (top) for preparation of bilayers for reflectivity. Removal of the PET cover sheet at room temperature (bottom) is facilitated by weak adhesion of PUU to untreated PET.

The following conditions were found to give films and bilayers of acceptable quality. Individual d-PUU films (0.7 μm thick by ellipsometry) were spun at 45 °C onto 2-in.-diameter silicon wafers from a ca. 7% by weight solution in *N,N*-dimethylacetamide (DMAc). At lower spinning temperatures, the polymer precipitated during DMAc evaporation.[12] h-PUU films (ca. 1 μm thick) were prepared by solution coating onto poly(ethylene terephthalate) (PET; Mylar film) at $T > 45$ °C. Bilayers were produced by pressing the PET/h-PUU film onto the d-PUU film and running a wedge across the PET surface to remove air bubbles at $T > 40$ °C and then peeling off the PET film at room temperature, as shown in Figure 2. This procedure produced films of sufficient quality for neutron reflectivity, as evidenced by low surface roughness (ca. 12 Å). It was also found that bulk scattering losses due to the microphase-separated nature of d-PUU were negligible (see below).

For peel tests, a similar procedure was used with two h-PUU films. In these experiments, the stiff PET backing sheet was not removed in order to negate the large mechanical contribution due to elongation of the elastomer. Glass slides were used as substrates for the other side of the bilayer. PUU adhesion to the surface of the PET film was improved by corona treating the PET to make the surface more hydrophilic, which enabled the bilayer interface to be fractured without

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Table 1. Interfacial Widths (in nm) as a Function of Thermal History

PUU-A (Single Layer of d-PUU)	
as prepared, 45 °C	1.2 ± 0.5
+15 min, 80 °C	1.2 ± 0.5
+10 min, 120 °C	1.2 ± 0.5
PUU-B (Bilayer "Bonded" at 60 °C for 1 min)[a]	
+3 days, 23 °C	6.6 ± 0.3
+15 min, 80 °C	6.6 ± 0.3
+25 min, 120 °C	8.0 ± 0.5
PUU-C (Bilayer "Bonded" at 45 °C for 1 min)[a]	
+4 days, 23 °C	13.0 ± 1.0[b]
+15 min, 120 °C	9.0 ± 0.5
PUU-D (Bilayer "Bonded" at 65 °C for 1 min)[a]	
+5 days, 23 °C	7.0 ± 0.5
PUU-E (Bilayer "Bonded" at 70 °C for 1 min)[a]	
+5 days, 23 °C	9.0 ± 1.0

[a] The samples were bonded at the indicated temperature and then remained at room temperature for 3−5 days before the reflectivity data were obtained (see text). [b] A significant fraction of this large interface width may be due to roughness due to the rather low (45 °C) bonding temperature used. Apparently, this roughness was removed by subsequent higher temperature annealing.

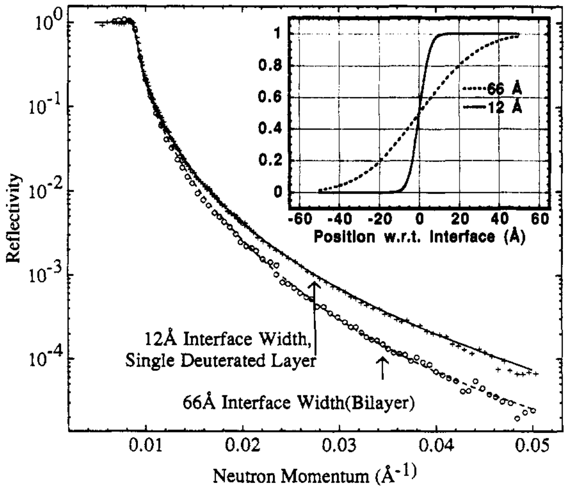

Figure 3. Comparison of the reflectivity vs momentum transfer from a single d-PUU layer and a d-PUU/h-PUU bilayer, both on a Si wafer. The interfacial broadening of the bilayer is indicative of substantial chain interdiffusion caused by annealing at 60 °C for 1 min plus 3 days at 23 °C (Table 1). Inset: Schematic of compositional profiles normal to the interface for air/d-PUU and d-PUU/h-PUU.

debonding at the PET/h-PUU interface. Measurements of the 90° peel force were obtained on strips 2 cm wide by 10 cm long on an Instron tensile tester at a rate of 0.3 mm/s. These were performed at room temperature after various annealing times and temperatures.

Four d-PUU/h-PUU bilayers were fabricated for neutron reflection experiments (Table 1). These were performed using the POSY-II spectrometer at the Intense Pulsed Neutron Source of Argonne National Laboratory. The reflected intensity is measured as a function of neutron momentum transfer ($q = 2\pi \sin \theta/\lambda$), where θ is the grazing angle and λ is the neutron wavelength. All films are effectively infinite in thickness for reflectivity purposes, and only the interfacial width and neutron scattering cross sections of the layers are important. The interface widths reported here are full widths defined in terms of a linear gradient profile,[13] with the precision in the interfacial widths of better than 0.5 nm. In Figure 3 the experimental and model results are compared for a single layer of d-PUU and a h-PUU/d-PUU bilayer, with schematics of the corresponding interfacial profiles shown in the inset. For the single d-PUU layer, the air/polymer interface has a sharp interface width of 1.2 ± 0.5 nm typical of a single layer of amorphous polymer on a Si wafer.[9,13] The interface of the bilayer prepared by "bonding" at 60 °C for 1 min with a subsequent 3-day anneal at 23 °C, broadened to 6.6 ± 0.3 nm, indicating that there is significant interpenetration of d- and h-chains across the interface (inset Figure 3). Figure 4 shows three simulated curves for the bilayer system in order to illustrate the sensitivity of the reflectivity data to the d-PUU/h-PUU interface width. The data illustrate the very high resolution achievable with this technique. Results are presented in Table 1 for bilayers originally "bonded" at temperatures between 45 and 70 °C and then further annealed for 3 days at 23 °C. The bilayers have interface widths of 7.0 ± 1.5 nm, which does not change significantly with further annealing for short times at temperatures below 80 °C. Figure 5 and Table 1 show that annealing at 120 °C increases the interface width only slightly, eg., 20%, which indicates that there may be additional mechanisms leading to the broadening under extreme conditions. In general, interpenetration seems to be strongly limited because of the constraining effect of the phase-separated hard-segment domains.

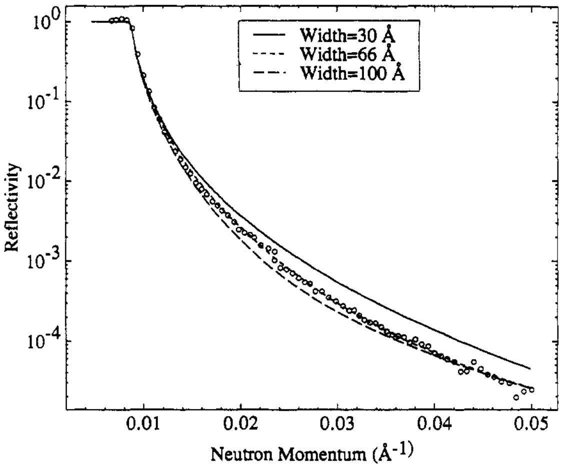

Figure 4. Reflectivity data and selected simulated data. The experimental points are the same as the bilayer data shown in Figure 3. The different interface widths used in the simulations are indicated on the plot.

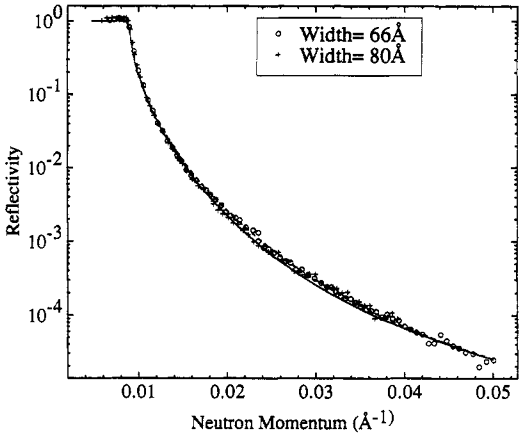

Figure 5. Reflectivity data for PUU-B annealed at 60 °C for 1 min plus 3 days at 23 °C (O) and then further annealed for 25 min at 120 °C (x) showing a slight interfacial broadening due to the 120 °C anneal (see Table 1).

We note that the high quality of the data was to a certain extent surprising because of the microphase-separated nature of PUU. For example, the labeled d-PUU material consists of 85% by volume deuterated PTMeO segments with a scattering length density of $b/v = 6.4 \times 10^{-10}$ cm^{-2} and 15% nondeuterated hard segment with a substantially lower value of b/v of 2.0×10^{-10} cm^{-2}. Assuming a homogeneous system, the average b/v for d-PUU is calculated to be 5.8×10^{-10} cm^{-2}. This is in reasonable agreement with our value of $(6.2 \pm 0.1) \times 10^{-10}$ cm^{-2} determined from fitting the reflectivity profiles. This fitted value is quite precise because the critical angle is very sensitive to b/v of the deuterated layer. Assuming a homogeneous material, the calculated b/v for h-PUU is 0.45×10^{-10} cm^{-2} which compares reasonably well with the experimentally determined value of $(0.8 \pm 0.3) \times 10^{-10}$ cm^{-2}. The larger error for the value of b/v for h-PUU is due to the much lower precision of the data because of the insensitivity of the reflectivity experiment. In both cases there is also contrast between hard- and soft-segment domains because of the microphase-separated morphology. This must cause some extraneous bulk scattering. However, we observed no significant off-specular scattering, and the results were effected to a negligible extent, possibly because of the limited extent of microphase separation in these materials or the small size of the hard segment in at least one dimension.

Further insight into the nature of interdiffusion was obtained by peel tests. Peel tests of self-adhesion of elastomers are inherently difficult because of the problem of separating viscoelastic contributions from the actual interface strength. With the rigid PET backing on the PUU film and a sample geometry similar to that shown in Figure 2, extension of the PUU layer was minimized and reproducible peel test results were obtained. Peel energy release rates (G) were calculated from

$$G = \mathbf{F}/w \tag{1}$$

where **F** is the peel force and w is the width of the peel strip. The measured values of G were 15, 54, and 186 J/m^2 after 10, 90, and 1320 min anneals at 23 °C, respectively. These values qualitatively follow the $t^{1/2}$ dependence expected for an interdiffusion process of high-MW polymers.[14] G was found to plateau near 200–300 J/m^2 at longer annealing times or higher temperatures. At these high values cohesive failure of the PUU or debonding from the substrates began to occur. The rate of increase in peel strength with time was also found to increase about 1 order of magnitude at 45 °C relative to 23 °C and was even faster at higher temperatures.

These results raise a number of intriguing questions. The measured interfacial width maximizes at 7 nm, consistent with idea that the hard-segment domains limit the interpenetration of the mobile soft segments to this extent. The interface half-width is slightly larger than the radius of gyration (R_g) of the PTMeO soft-segment block, which we have estimated to be ca. 3 nm. Since the majority of the soft-segment "loops" are anchored at both ends by hard segments, we must ask how interdiffusion to lengths greater than R_g is possible and whether diffusion of these loops with fixed ends would lead to significant buildup of interface strength. One possibility is that the hard segments are not completely phase segregated, resulting in some fraction of mobile segments, substantially larger than a single soft segment, which could migrate across the interface. A dynamic character of the hard-segment domains would also allow center of mass mobility of the chains. However, it is known from thermal and mechanical analysis that these domains are thermally stable up to at least 150 °C, so this migration appears unlikely. Exchange chemistry such as transurethanification would also appear to be unlikely at the low temperatures utilized here.[15,16]

It is also likely that chain end diffusion contributes substantially to the interface broadening and the increase in interface strength. Extensive studies of cross-linked elastomers with dangling chain segments have shown large increases in bond strengths due to interdiffusion.[2] The observed $t^{1/2}$ dependence of G in bilayers of PUU is reminiscent of that seen for high-MW homopolymer interdiffusion[14,17,18] and could be consistent with a chain end diffusion mechanism. Soft-segment chain ends comprise an appreciable fraction of each PUU chain and would have a significantly greater ability to interpenetrate than soft-segment chain centers.[17,18] While the precise knowledge of how the soft segments migrate remains elusive, it does appear clear that this mixing governs the formation of strong interfaces even with constraints imposed by the hard-segment domains.

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