Effects of a Diblock Copolymer on Adhesion between Immiscible Polymers. 2. PS-PMMA Copolymer between PPO and PMMA

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ABSTRACT: Measurements have been made on the effects of a thin layer of polystyrene-poly(methyl methacrylate) diblock copolymer on the toughness of the interface between poly(methyl methacrylate) and poly(phenylene oxide). For a wide range of copolymer molecular weights, provided the interface is not saturated with copolymer, the interfacial toughness is a function of just the areal density Σ of the copolymer molecules, independent of their molecular weight. The toughness was found to vary with Σ^2 in accordance with the predictions of a recent model of crazing failure where it is assumed that G is a measure of the energy to form the crack tip craze and the craze fails when the force per molecule at the crack tip (in the craze) equals the molecular scission force. SIMS experiments confirmed that the diblock copolymer organizes at the interface and that interface fracture breaks the copolymer molecules near their junction points. The highest obtainable toughness for any given molecular weight diblock was found to itself exhibit a maximum when considered as a function of molecular weight. This maximum occurred at a molecular weight of about 80 K. The obtainable toughness decreased as the copolymer molecular weight was increased from 80K because the saturation value of Σ decreased with increasing molecular weight. As the molecular weight was decreased from 80K, both pull-out and crowding effects become more evident, so again the toughness decreases from the value at 80K.

1. Introduction

There is considerable interest in the use of block copolymers as coupling agents between immiscible polymer phases. The phases can be two components in a blend[1-3] or two actual components made of different materials. A series of recent studies have shown that a thin layer of a block copolymer can cause a considerable increase of the adhesion between immiscible polymers.[4-10] The diblock copolymer needs to be chosen so that each block is miscible or nearly miscible[11] with one of the bulk phases. Much of the recent work, including the work presented here, is concerned with the situation where all of the materials are glassy at the test temperature. There has however been some work on systems where at least one of the phases is rubbery.[12,13]

The mechanism of the enhancement of interfacial adhesion between glassy polymers depends on the molecular weight and state of organization of the copolymer. In a companion paper we consider situations where the copolymer is not well organized at the interface, in this paper we are mainly concerned with well organized copolymer layers. It has been shown that short copolymer chains can pull out of the interface, causing little adhesion enhancement.[10] Long copolymer chains have been shown to break near their junction points when their density Σ is relatively low.[5] The toughness of the interface is profoundly affected by the bulk failure mode, in particular the existence of crazing at the interface.[10,14] The bulk failure mode has been shown to be a function of both the molecular weight and amount (normally measured as areal density of chains, Σ) of copolymer present, as it is controlled by the stress across the interface. This stress is the product of the force per chain to cause failure and the chain areal density. The maximum force across the interface per chain is the force to pull out or to break the chain, whichever is lower. If the stress on the interface is sufficient to cause crazing, the interface tends to be significantly tougher than when there is no crazing.[10]

The relation between Σ, the force to break or pull out a chain, f, and the joint toughness has been explored in a recent model of crazing failure.[8] This model is based on the realization that craze fibrils are interconnected, and so a stress concentration that increases with craze width may be expected at the crack tip in the craze. The fracture energy is the energy to grow the craze and is much larger than chain pull-out or scission energies. The model predicts that the toughness of the interface, G, will vary as $(\Sigma f)^2$ and gives reasonable values for the force to break a chain. A better mechanical solution which gives a more accurate value for the constant A has recently been proposed.[15] The model has also been extended to explain polymer welding and the molecular weight dependence of bulk toughness.[16] One of the aims of the work described here is to test the predictions of this model in the situation where the copolymer chains are long enough to break rather than pull out.

The measurement of the toughness of an interface can be distinctly more problematic than the measurement of bulk toughness because cracks in bulk homogeneous materials always propagate in pure opening mode but shear mode can often occur when cracks propagate at interfaces.[17] The ratio of the opening to shear mode at the crack tip is normally described by the mixity where a zero mixity refers to pure opening mode. In glassy polymers that craze, a relatively small mixity with a shear component that pushes the crack toward the material with lower craze resistance can have the effect of generating a large bundle of crazes at the crack up and hence a high measured toughness.[18] The use of a simple asymmetric double cantilever beam test has been proposed to alleviate this problem.[19] For materials such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) or PMMA and PPO (poly(phenylene oxide)), as are used here, the fracture results are not very dependent on the mixing as long as it is sufficient to suppress any multiple crazing in the lower crazing stress material. For materials such as PS and poly(2-vinylpyridine) (PVP) the mixity of the test has to be chosen with considerable care, as the crazing stress of PVP is not very much larger than that of PS, so multiple crazes could be formed in either material.[10]

The experimental system we have chosen in this study consists of PPO and PMMA homopolymers that were coupled by thin layers of PS-PMMA diblock copolymers. This system has two main advantages over the system

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where the same copolymers are used to join PS and PMMA homopolymers. The adhesion between PMMA and PPO is very weak in the absence of copolymer, presumably because PMMA and PPO are strongly immiscible in a thermodynamic sense. PPO and PS are quite miscible so that the Flory interaction parameter χ is significantly negative, implying a favorable enthalpy of interaction.[20] This favorable enthalpic interaction helps to drive the diblock copolymer to organize at the interface as the PS block is "sucked" into PPO. It also causes the PS block of the copolymer to be stretched in PPO[6] to form a PS brush near the interface. One disadvantage of the system is that the glass transition temperature T_g of PPO is higher than the decomposition temperatue of PMMA, so the joining temperature has to be below the T_g of PPO (~216 °C). The PS block plasticizes the PPO and so permits interdiffusion, but there is no possibility of obtaining interfaces that are at at local equilibrium structure.

2. Experimental Techniques

2.1. Materials. The nearly symmetric polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymers used in this study were purchased from Polymer Laboratories, Inc. These polymers were prepared by sequential anionic polymerization, and the residual PS prepolymer was removed by successive extractions in cyclohexane. Molecular weights of the diblock copolymer range from 53 000 to 900 000. For dynamic SIMS analysis (to study the organization of the diblock copolymer at polymer interfaces), either the PS or the PMMA block was perdeuterated giving contrast for that block. d-PS-*b*-h-PMMA denotes perdeuteration of the PS block with the PMMA block hydrogenated. The molecular weights of d-PS-*b*-h-PMMA and h-PS-*b*-d-PMMA were both approximately 300 000. A PS-PMMA random copolymer, denoted as PS-*r*-PMMA, was purchased from Polysciences, Inc. The ratio of PS segments to PMMA segments was 70:30 by weight. The weight average molecular weight M_w was 270 000, and the material was polydisperse. Detailed characteristics of the copolymers are given in Table I of the companion paper.[21]

Homopolymers used in this study were fairly polydisperse in molecular weight: Poly(phenylene oxide) (PPO) was obtained from General Electric (646-111). M_w was 55 000 and M_w/M_n was about 2.4. The PMMA homopolymer, which was purchased from DuPont (Elvacite 2021), had an M_w of approximately 118 000. Toluene, which was used to dissolve the PS-*b*-PMMA copolymer and PMMA, and chlorobenzene, which was a solvent for PPO, were both spectroscopic grade and used without further purification.

2.2. Samples for Fracture Mechanical Test. Homopolymer (PMMA and PPO) sheets with dimensions 50 mm × 64 mm × 1.7 mm were compression molded above the glass transition temperature (T_g) of each polymer: T_g (PMMA) ~ 110 °C and T_g (PPO) ~ 216 °C. Two different techniques were used to place the diblock layer at the interface. Normally, the diblock copolymer, dissolved in toluene, was spun on the PMMA sheet and then dried at 60 °C for more than 3 h to remove residual toluene. Direct spinning on the PMMA sheet was the only technique used for very thin films, as such films are difficult to handle. For diblock copolymer thickness larger than 25 nm, the copolymer was initially spin coated onto a 75-mm × 125-mm glass slide. The edges of the slide were scored with a razor blade, and the copolymer film was floated from the slide onto deionized water. The floating diblock copolymer film was then picked up onto the PMMA sheet, and the specimen was allowed to air dry and was placed onto a hot plate at 60 °C for 20 min for final drying. The comparison of interface toughness results obtained from samples prepared by two methods will be discussed later. To check if any organization of the as-spun-on-glass copolymer has an effect on the interfacial toughness, a comparison was made between samples where the copolymer was floated onto the PPO sheets and those where it was floated onto the PMMA sheets. No difference was found.

In this study the thickness of the copolymer layer before annealing was varied between 5 and 100 nm. The film thicknesses reported here were obtained by ellipsometry on copolymer films that were spun on silicon wafers using the same spinning conditions that were used for films spun on glass or PMMA.

Table I. Effect of Diblock Copolymer Spun Side on Fracture Energies of PMMA-PPO Interfaces (PS-*b*-PMMA (84K), Copolymer Thickness 27 nm, Joined at 190 °C for 2 h)

	fracture energy (J/m²)
spun on PPO	7
spun on PMMA	410

The two homopolymer sheets were typically joined in a press at 190 °C for 2 h. The applied pressure was just low enough to facilitate the wetting between the two homopolymers. The reason for joining the samples at 190 °C is that this temperature is about the maximum that can be used without the bulk PMMA degrading and forming bubbles. The joined samples were fractured using an asymmetric fracture toughness test[19] that drives the crack along the interface; the PMMA side was glued down to an aluminum sheet with a cyanoacrylate adhesive, and a razor blade was then inserted along the polymer interface to propagate the crack. The crack was allowed 24 h to grow after razor insertion, and then the final crack length was measured with an optical microscope. The interfacial toughness was obtained from the sample dimensions and crack length using the standard relationships.[19]

2.3. Samples for Dynamic SIMS. Specimens for the dynamic SIMS study were prepared as follows: The PPO homopolymer was first spin coated at 2000 rpm from a chlorobenzene solution (5 wt %) onto an optically smooth 1-in. quartz wafer. The thickness of the first layer was approximately 320 nm. This film was annealed overnight near the glass transition temperature to remove any residual solvent and to allow the PPO chains to relax. A thin layer of diblock copolymer of molecular weight 300 000 was spin coated from toluene solution (1 wt %) at 4000 rpm onto a glass slide producing a film thickness of 24 nm, a value which is less than half of the long period of the bulk ordered copolymer (~36 nm). The diblock film was then floated off the glass onto deionized water and picked up on a quartz substrate coated with the PPO layer. The bilayer film was allowed to air dry and was then placed on a hot plate at 60 °C for 20 min. Finally, a film of PMMA of thickness approximately 250 nm was spin coated onto a glass slide, floated onto deionized water, and placed on top of the bilayer substrate. The trilayer specimen was then allowed to dry in air and placed in a vacuum oven for annealing at 190 °C for 2–4 h.

SIMS samples were analyzed with a Perkin-Elmer 6300 secondary ion mass spectrometer using oxygen as a primary ion source. Details of the instrument can be found elsewhere.[22] In our experiment, negative secondary ion intensity was monitored as a function of etch time. We found that the detection of negative secondary ions is much more effective than that of positive ions in terms of the dynamic range as well as the capability to distinguish deuterium signals from H^+_2 signals which might be especially important for the PMMA homopolymer. The raw data was converted to secondary ion intensity vs depth using the results from standard samples which enabled us to calculate the etch rate for each homopolymer. The etch rate for PPO was 3.5 Å/s, while that for PMMA was 6.3 Å/s.

2.4. Effects of the Diblock Deposition Technique. Preliminary experiments were undertaken to examine the effects of different possible techniques for deposition of the diblock copolymer layer at the interface. Three different techniques were compared: direct spinning of the diblock copolymer onto the PPO and PMMA homopolymer sheets and floating the diblock copolymer film onto water and transferring it to the PMMA homopolymer sheet, as already described.

Table I compares results from samples where the copolymer was spun on PMMA to those from samples where the copolymer was spun on PPO. A much lower fracture energy was found when the copolymer was spun on PPO. This effect was also observed for different molecular weight copolymers. The reason for this result was made clear by some dynamic SIMS observations on the fracture samples.

In order to use SIMS to examine the diblock copolymer distribution close to the surface of the fractured specimen, the

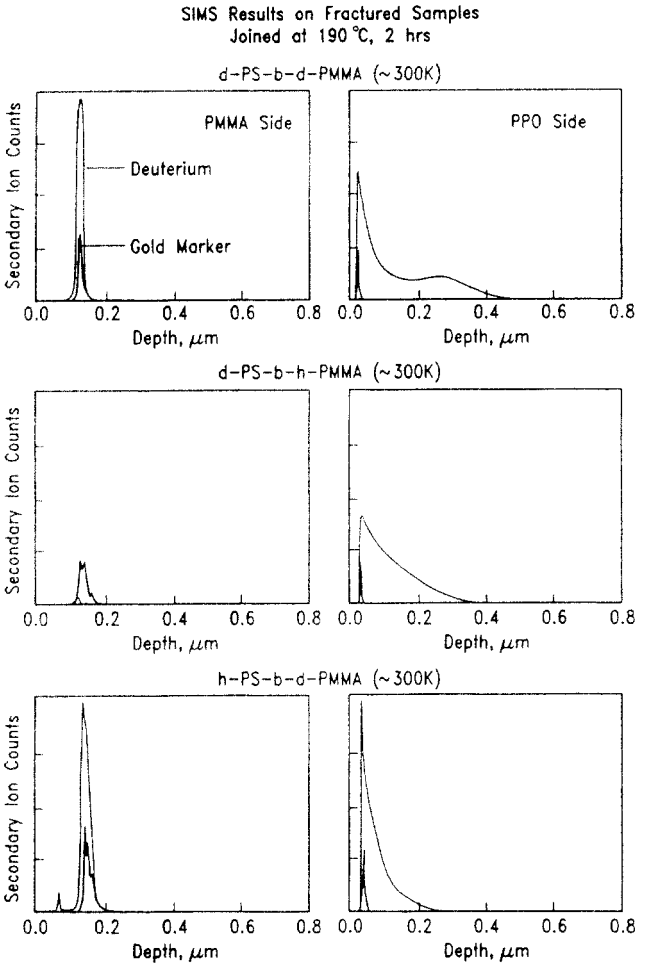

Figure 1. SIMS depth profiles under the fracture surfaces of samples where the diblock copolymer was spun onto PPO. Clearly, a considerable portion of both parts of the diblock is to be found deep in PPO.

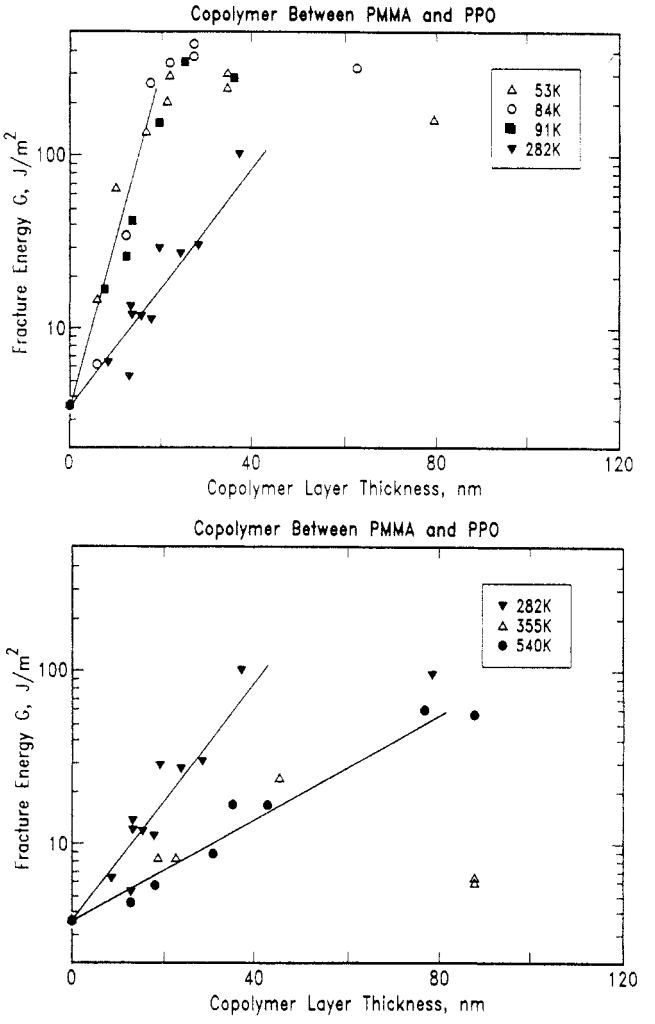

Figure 2. Variation of the fracture energy with thickness of the PS–PMMA diblock layer for (a, top) the lower molecular weight diblocks and (b, bottom) the higher molecular weight diblocks.

fractured polymer sheet was first covered with a thin (5-nm) layer of gold, serving as a marker for the fracture surface, and then a PS homopolymer layer of thickness 50 nm was placed on top of the gold layer to serve as a buffer layer to stabilize the initial sputtering process.

Figure 1 shows the distribution of each block on both the PMMA and PPO homopolymer sheets using the series of three PS-*b*-PMMA copolymers where respectively the PMMA block, the PS block, and both blocks are perdeuterated. In the fabrication of these samples the diblock copolymer, dissolved in toluene, was spun on the PPO sheet and then dried overnight at 80 °C. In these samples a large proportion of the PMMA block, as well as the PS block, is still embedded in the PPO homopolymer after fracture, as can be clearly seen from the case when only the PMMA block is perdeuterated (Figure 1 (bottom)). This result is presumably caused by the rapid swelling of PPO by the toluene, a separate qualitative experiment showed that toluene swells PPO faster than its swells PMMA. A consequence of this swelling is that the diblock penetrates PPO fairly deeply (about 300–400 nm) and low mobility of the diblock in the PPO at 190 °C (the joining temperature) means that the diblock cannot migrate back to the interface during the joining time. Hence the interfaces were weak.

Table II shows the comparison of the fracture energies of the PPO–PMMA interface between the samples made by direct spinning of the diblock on PMMA and samples made by floating the diblock layer onto PMMA. Except for the 31K symmetric diblock copolymer, the difference in fracture energy between samples prepared by the two different methods is within the experimental error of the fracture test. There is, however, a systematic trend that the fracture energy of the samples prepared by the floating technique is slightly higher than that of the samples obtained by the spinning technique. The reason for this difference is unclear.

Table II. Comparison of Fracture Energies between PPO and PMMA with Diblock Copolymers Spun or Floated onto the Interface (Join Condition: 190 °C, 2 h)

mol wt of PS-*b*-PMMA (thickness (nm))	fracture energy (J/m^2)	
	spun	floated
31K (t = 23.5)	161	91
53K (t = 34.4)	280	365
84K (t = 27)	426	543
282K (t = 28)	29	37

3. Results

3.1. Fracture Behavior. Figure 2 shows the fracture energy (defined as the energy dissipated per unit area of crack formed) at the interface between two immiscible polymers as a function of the amount and molecular weight of PS–PMMA diblock copolymer. The first point to notice from the figure is that the diblock copolymer is very effective in increasing the toughness of the interface between PPO and PMMA; for example, the interfacial toughness was increased about 60 times over that for a bare interface by using a 20-nm layer thickness of a diblock copolymer of molecular weight 53K. Secondly, the shorter diblock copolymer is much more effective in increasing the interfacial strength than the longer diblock copolymer at a given copolymer thickness: the interfacial fracture energy increases more rapidly as a function of the copolymer thickness for a shorter diblock copolymer than for a longer (higher molecular weight) copolymer. Thirdly, the interfacial toughness, when considered as a function of the amount of copolymer at the interface, levels off at

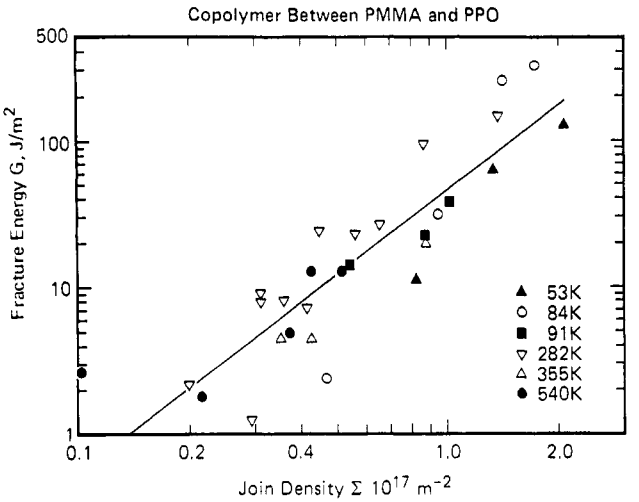

Figure 3. Results of Figure 2 plotted to show the variation of fracture energy with copolymer areal density, Σ.

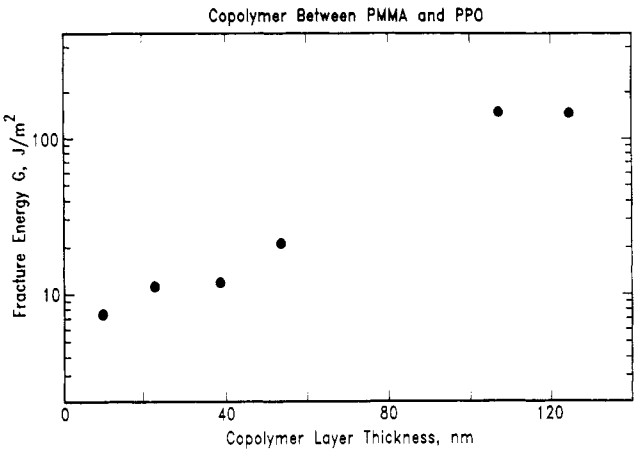

Figure 4. Fracture energy obtained using the 900K copolymer.

a certain diblock layer thickness that depends on the molecular weight of the diblock copolymer: the saturation copolymer layer thickness increases with the increase in copolymer molecular weight. For copolymer layer thicknesses greater than the saturation level there is evidence that the fracture energy decreases slightly. This decrease is particularly noticeable for 355K diblock copolymer, as shown in Figure 2b. Fourth, the maximum obtainable fracture energy is higher for a lower molecular weight diblock copolymer than for a higher molecular weight copolymer. These results for the PMMA–PPO interface clearly contrast with the results on the PMMA/PS system given in the companion paper[21] where, for a given adhesion condition, the interfacial toughness saturates at a certain value that is independent of the molecular weight of the PS–PMMA diblock copolymer.

It is known that a symmetric diblock copolymer has, when microphase separated, a lamellar morphology that is characterized by a long period (L).[23] Half the long period ($L/2$) is the thickness that corresponds to a single interface and thus is a good estimate of the amount of copolymer that will saturate the interface. $L/2$ is experimentally known for the diblock copolymers used in this study,[24] so it is reasonable to try to superpose all the fracture data obtained with different molecular weight copolymers for layer thicknesses up to $L/2$ for each block copolymer. For these copolymers L scales as N^{α} where α is about 0.65.[24] If we assume that the diblock copolymer as well organized at the PPO–PMMA interface, as will be demonstrated later (i.e. the PMMA block is mixed with the PMMA homopolymer and separate from the PS block which is mixed with the PPO), then we can convert the copolymer

Table III. Effect of Join Time on Fracture Energies of PPO and PMMA Interfaces Joined by PS-*b*-PMMA (900K) (Join Temperature, 190 °C; Copolymer Thickness, 100–126 nm)

join time (h)	fracture energy (J/m²)
2	150
20	55

layer thickness (or copolymer amount at the interface) to joint density Σ, since it is assumed that one diblock polymer chain contributes only one joint across the interface due to the well organized structure near the interface.[5] Hence

$$\Sigma = \rho t N_A / M \quad (1)$$

where t is the thickness of the diblock copolymer, ρ is the density of the copolymer, N_A is Avogardro's number, and M is the molecular weight of the copolymer.

Figure 3 shows the results of Figure 2 in semilogarthmic scale when replotted as described above. All the fracture energy data points collapse fairly well into a single line drawn in the figure. Using linear regression the facture energy G is found to scale with Σ as follows:

$$G \equiv \Sigma^{\beta} \quad \text{where} \quad \beta = 2.0 \pm 0.2 \quad (2)$$

for diblocks in the molecular weight range from 53K to 540K. The interpretation of the scaling exponent β in eq 2 will be discussed later.

Figure 4 shows the variation of the fracture energy with the copolymer layer thickness for the nearly symmetric 900K PS–PMMA copolymer using the same joining condition (190 °C, 2 h) as that used to obtain the data given in Figure 2. Note that the fracture energy at a copolymer thickness greater than $L/2$ (~65 nm) is higher than the saturation fracture energy for the 355K and 540K diblock copolymers. In order to check if the increase in fracture energy for the 900K copolymer is related to the degree of the organization of the diblock polymer at the interface, the joining time was increased about 10-fold. As shown in Table III, this increase in the joining time reduced the fracture energy by about a factor of 3. This result, when taken with the results on the PS–PMMA interface described in the companion paper, implies that the typical joining condition (190 °C, 2 h) for shorter diblock copolymers (53K–540K) is not enough to organize completely the 900K diblock copolymer at the PPO–PMMA interface. This interpretation is discussed in more detail in the PS–PMMA paper.

There is good evidence in the system where PMMA and PS are the homopolymers that the degree of organization of the diblock can have a considerable effect on the interfacial toughness and that a random copolymer can be quite effective in toughening the interface. Experiments were done to find if a random copolymer is also effective in toughening the interface when the homopolymers are PMMA and PPO. The fracture energy was measured as a function of copolymer film thickness, as shown in Figure 5, when the polydisperse PS-*r*-PMMA copolymer with an M_w of 270K is placed between PPO and PMMA. Comparison of the results in Figure 5 with the adhesion data (Figure 2) obtained with the diblock copolymer of comparable molecular weight (282K) shows that the random copolymer is not as effective as the diblock copolymer in toughening the interface at layer thicknesses of 20 nm and above. However a 10-nm layer of random copolymer was more effective than the equivalent thickness of 282K diblock.

3.2. Dynamic SIMS on Fractured Specimens. Figure 6 shows results similar to those of Figure 1 but for the case where the diblock dissolved in toluene was spun on the PMMA side and then dried overnight at 70 °C. It

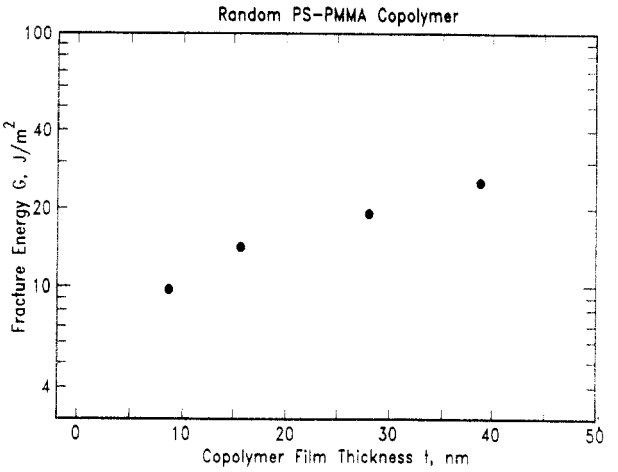

Figure 5. Fracture energy obtained using the random copolymer.

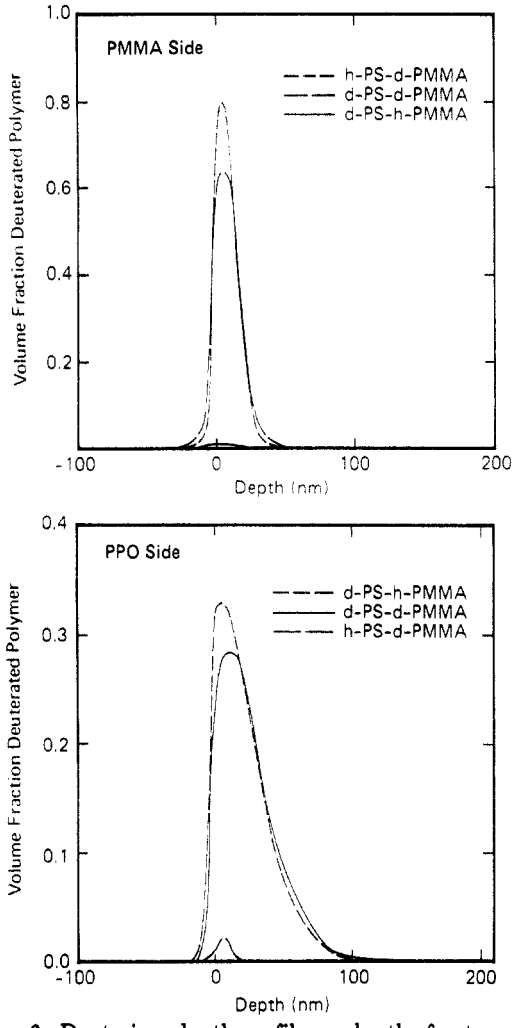

Figure 6. Deuterium depth profiles under the fracture surface similar to Figure 1 but obtained on samples where the diblock copolymer was spun on the PMMA sheet:[5] (a, top) PMMA side; (b, bottom) PPO side.

is evident that the crack propagates near the junction point between the PS and PMMA blocks, a result which implies that the diblock copolymer organizes at the PPO–PMMA interface fairly well with each block diffused to the relevant homopolymer. The detailed analysis of the fracture position[5] reveals that the mean fracture position (center of the Gaussian distribution) was 0.7% of the 300K diblock chain into the PMMA block from the junction point. A second observation from the results of Figure 6 is that the PS block is more stretched into the PPO homopolymer than the PMMA block is stretched into the PMMA homopolymer. This stretching is due to the more favorable

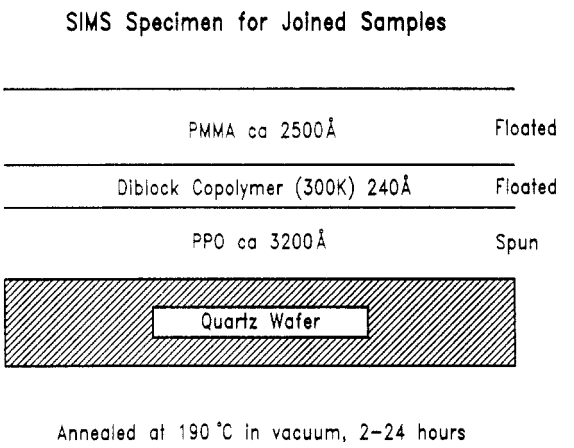

Figure 7. Diagram of the trilayer sample used in the SIMS experiments.

interaction between PS and PPO than the athermal interaction among the PMMA segments. More detailed analysis of the PS block profile in PPO will be discussed in the context of the results from dynamic SIMS on thin polymeric films given below.

3.3. Dynamic SIMS on Thin Trilayer Polymer Films. Information about the distribution of each block near the interface is best obtained from thin trilayer polymer films which consist of a known amount of diblock placed between two different homopolymers. Pairs of samples can be made with PS block-deuterated and PMMA block-deuterated diblock copolymers of the same molecular weights, respectively. Once the position of the PMMA–PPO interface is located, we can obtain the distribution of each block near the interface by overlapping the two profiles from the two differently labeled diblock copolymers.

A schematic of the trilayer polymer film for the dynamic SIMS experiment is given in Figure 7. The first layer was, as described in the Experimental Techniques, spin coated on a 1-in. quartz water and then the other layers were placed on top by the floating technique. The total thickness of the polymeric film was controlled below 0.6 μm to optimize the efficiency of the dynamic SIMS depth profiling.

Figure 8 illustrates the raw SIMS data on two trilayer films with a middle diblock copolymer layer of h-PS-*b*-d-PMMA and d-PS-*b*-h-PMMA, respectively. The middle diblock layer has a molecular weight of 300K and a thickness of 24 nm. The trilayer specimen was annealed in vacuum at 190 °C for 2 h, which is the same as the anneal used in the adhesion experiment. The secondary ion counts for different masses ^{1}H, ^{2}D, ^{12}C, ^{16}O, and ^{26}CN are plotted against time in seconds in semilogarithmic fashion. The ^{12}C signal was used to monitor the stability of the etch process. Note that the etching through the PMMA layer is rather unstable compared to etching through PPO. Such unstable etching is often seen with PMMA. The ^{16}O signal is used to detect when the primary ion hits the substrate (quartz). Since the contrast between PS and PMMA blocks is the perdeuteration, the ^{1}H and ^{2}D signals were monitored. Note that the dynamic range of the ^{2}D signal was nearly 3 decades. The ^{26}CN signal is used to locate the PMMA and PPO interface since it is known that a nitrogen containing catalyst was employed for the polymerization of PPO.

It was necessary to convert the etch time into a depth scale to transform the raw SIMS data into a form which can be compared with any existing theories of block copolymer organization (i.e. volume fraction vs distance). This conversion was done by preparing a series of

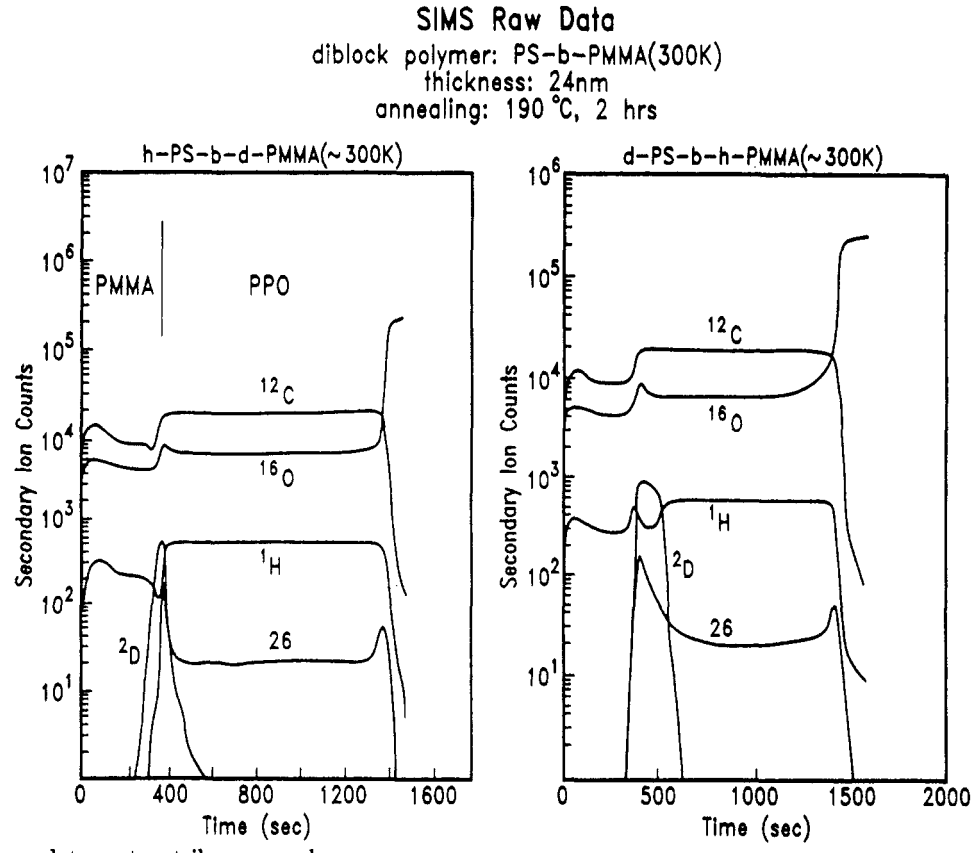

Figure 8. SIMS raw data on two trilayer samples.

calibration samples of PMMA, PPO, and PS with thicknesses determined by ellipsometry and then etching through the samples with the same sputtering condition as were used for the trilayer samples. Hence we obtained the etch rate for each material. The etch rates for PPO, PS, and PMMA are 4, 4, and 7 Å/s. Figure 9 shows the results of superposing the data of Figure 8 to obtain deuterium profiles for each block across the PMMA and PPO interface plotted in linear fashion after converting the raw SIMS data.

There are a few things to notice from the profile shown in Figure 9. Firstly, the blocks are fairly well separated across the interface in spite of the short joining time (2 h at 190 °C). This rapid organization of the diblocks across the interface is presumably due to the favorable interaction between the PS and PPO segments ($\chi_{PPO-PS} < 0$).[20] Secondly, it is clear that the PS block is significantly stretched into PPO. This stretching is in contrast to the case of PS-*b*-PMMA between PS and PMMA homopolymer sheets where the distribution of each block on the relevant side (*i.e.* the PS block in the PS homopolymer) is almost symmetric since the interaction between the PS block and PS homopolymer segments is athermal. The profile of the PMMA block in the PMMA homopolymer given in Figure 9 shows the typical profile associated with the athermal interaction. The stretching of the PS block in PPO is, like the rapid organization, due to the favorable enthalpic interaction between the PS and PPO segments. We have already described this observation of the "enthalpy driven swelling of the PS brush in PPO" in a previous communication[6] where the profile is compared to a predicted profile thickness obtained using a modification of de Gennes' brush model. Thirdly, since the etch rate in the PMMA phase is rather fast (7 Å/s) and the etching process is less stable than in PS and PPO, as can be noticed from the ^{12}C profile in the PMMA phase (Figure 8), the depth resolution of the profile of the PMMA block in the PMMA homopolymer is not as high as that

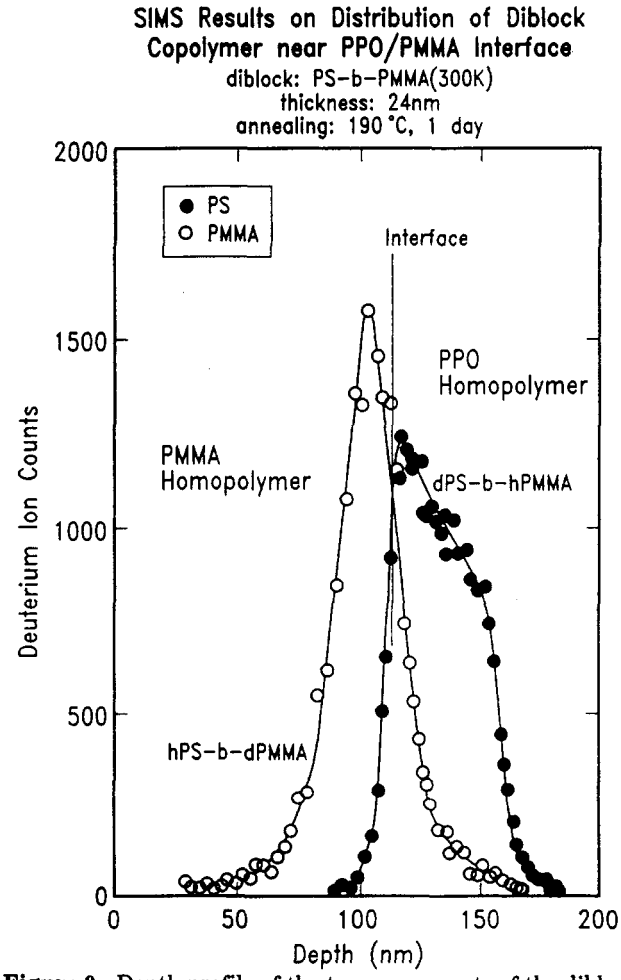

Figure 9. Depth profile of the two components of the diblock at the PMMA–PPO interface.[6]

of the PS block in PPO. Thus, the observed PMMA block profile is broader than expected. Comparison of the

PMMA profile with theory would be better done using an experimental profile obtained by neutron reflectivity.

Discussion

The results shown in Figure 1 demonstrate that the toughness of the interface G_c is a function of the areal density of copolymer chains, Σ, but independent of the length of the chains for molecular weights between 53K and 540K. Very long chains (M_n of 900 000) yielded tougher interfaces than might be expected from this rule. The SIMS results show that, at least in some circumstances, the diblock copolymer is organized at the interface and fracture of the interface caused the copolymer chains to break near their junction points. The superposition of the results obtained with the different molecular weight copolymers shows that each diblock molecule provides a single "stitch" across the interface and the stitches fail at a force that is independent of the size of the molecule. The SIMS results confirm that the diblock molecules break rather than pull out from one side or the other of the interface. For each molecule to provide just a single stitch across the interface it is necessary that the diblock is organized so that the PS block is mixed with PPO while the PMMA block is mixed with the PMMA homopolymer. The rate of organization doubtless decreases with the diblock molecular weight, so it is not surprising that it is the highest molecular weight copolymer that does not fully organize during the standard joining process and so provides a stronger interface than expected from the superposition.

The interfacial toughness was found to vary within experimental error as Σ^2, a result that is very strong evidence for the validity of the recent model of crazing failure.[8,15] Estimates of the force to break a chain f_b have already been presented[8,9,15] and vary between 1.4 and 3.5 $\times 10^{-9}$ N depending on the precise assumptions of the model. When there is no diblock at the interface, the toughness of the PMMA–PPO interface is about 3 J/m^2 and the interface probably fails without crazing. As the amount of diblock at the surface is increased, the interface toughness increases and at some point the failure mode is expected to transform into crazing. Recent work[14] has demonstrated that this transition is sharp and probably occurs when the stress Σf across the interface equals the stress at a craze boundary σ_c.[10] As the craze stress is known for PMMA,[25] it is possible to estimate the minimum Σ_c for which crazing failure would be expected. Assuming values of 2.2 nN for f_b and 80 MPa for σ_c one obtains a value for Σ_c of 0.036 chains/nm^2. Very little of the data in Figure 3 is for values of Σ below this estimate of Σ_c, so it is reasonable to assume that the vast majority of the samples fail by crazing.

It is valuable to compare the results presented here with some recent data on the fracture of the PS/PVP system.[10] In the PS/PVP system it has been shown that, for samples with Σ large enough that the failure mode was well into the crazing regime, for diblock polymers of molecular weight 105K and 167K, only a small amount of the deuterated PS block remained on the PS fracture surface. This result shows that the copolymer did not break close to the junction point but rather broke well onto the PS side and perhaps partially pulled out of the PS homopolymer. It is worth noting that the transition with increasing Σ to a crazing failure mode may be separate from the transition from failure at the junction point to failure in the brush.[10] The results of SIMS on the fracture surfaces shown in Figure 6 shows that the 300K molecular weight PS–PMMA diblock with an areal density Σ of 0.053 chains/nm^2 broke very close to its junction point. The difference between the results in the two systems is striking. It could be argued that the areal density of PS–PMMA is not high enough to be truly in the crazing regime, particularly as the crazing stress of PMMA is significantly higher than that of PS. However, the toughness of 25 J/m^2 is fairly large and suggests that crazing is occurring. In fact the craze width v can be estimated to be about 0.3 μm from this value of G_c, assuming the craze can be described by the Dugdale model. It is worth noting that the PS–PMMA diblock is significantly larger than the PS–PVP diblock, particularly considering that the entanglement molecular weight of PMMA is about half that of PS. In addition, PS crazes have a finer fibril structure than PMMA crazes so the fibrillation process in PS will cause a greater decrease in the number of entangled strands than will occur in PMMA. Hence chain pull out in the craze is more to be expected in the PS/PVP system than in the PMMA/PPO system.

The results presented here for the copolymers between the PMMA and PPO system are strikingly different from the results presented in the companion paper for the same copolymers between PS and PMMA. However the differences are entirely consistent with the hypothesis presented here that the small χ between PS and PMMA gave little driving force to organize the high molecular weight diblocks and so the high molecular weight diblocks did not fully organize during the relatively short joining times. In addition, the small χ meant that a disorganized diblock molecule could form a number of stiches between the homopolymers and so was more effective than an organized molecule. A similar, though small, effect was seen here just with the very largest, 900K, diblock. The lower molecular weight diblocks were probably well organized. We know that the 300K diblock could organize in the standard joining condition between PMMA and PPO, as demonstrated clearly in Figure 9, but not between PS and PMMA. The results from the random copolymer show that a disorganized layer can only cause a small increase in the toughness between PMMA and PPO, doubtless because it is not capable of entangling well with the PPO.

The comparison of the results with the random copolymer with those from the equivalent molecular weight diblock deserves more consideration. The different regimes of interface toughening have been discussed in detail by Creton et al.[10] in the context of using block copolymers at interfaces. They show that, when the interface is not capable of sustaining a stress high enough to cause crazing, failure can occur by chain scission with very little energy loss or by chain pullout with some energy loss. The fact that the random copolymer was more effective than the diblock copolymer just at very low coverage suggests that the random copolymer was able to mix a little with the homopolymers and so form some loops that pulled out on failure. We know that the block copolymer failed by chain scission. The number of effective loops increased slowly with increasing random copolymer coverage probably because the χ between PPO and PMMA is fairly large. The adhesion between PPO and PMMA using the random copolymer shown in Figure 5 can also be compared with the adhesion between PS and PMMA using the same copolymer (Figure 4 in the PS–PMMA paper). For thin copolymer layers the fracture energy of the two systems is indistinguishable, but for thick layers the PS/PMMA system is much tougher. The χ between PS and PMMA is known to be smaller than the χ between PPO and PMMA, so it is reasonable that the random copolymer can form more mechanically effective loops in the former system.

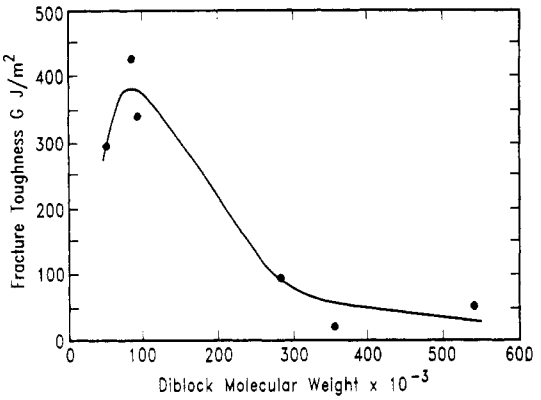

Figure 10. Variation of the highest obtainable toughness with the diblock copolymer molecular weight.

It is worth considering what the information presented here tells us about the optimum molecular weight of a diblock that might be used to couple two phases. Figure 10 shows a plot of the maximum toughness obtained as a function of the molecular weight of the diblock copolymer. Clearly, there is an optimum diblock molecular weight that, in this case, was about 80 000. If the diblock is to be added to a homopolymer rather than placed at an interface so that diffusion to an interface is also an issue, then the optimum molecular weight is probably lower than this, perhaps as low as 50K. Clearly, more data with small diblock copolymers are required to judge how rapidly the toughness decreases at the lower molecular weights. The form of the relation shown in Figure 10 is qualitatively explicable by a very simple model. As long as the interface is tough enough to fail by crazing, the maximum toughness obtainable varies as $(\Sigma_{sat}/f)^2$ where Σ_{sat} is the saturation value of the copolymer areal density and f is the force to pull out (f_p) or break (f_b) the copolymer chains.[8] Σ_{sat} is expected to vary as $M^{-0.4}$ as the long period varies as $M^{0.6}$. (In the companion paper we have assumed that the long period varies as $M^{0.5}$ where here we assume a slightly different index. The different index was chosen because the system considered in this paper has higher χ's though the quality of the data does not justify the discrimination.) Long copolymer chains fail by scission at a constant f_b, so the maximum toughness varies as $M^{-0.8}$. As the molecular weight to reduced, the simple assumption that all chains are fully entangled begins to fail. Eventually, at low molecular weights the chains pull out rather than break and the pull-out force f_p for molecular weights before M_c probably varies as M. Hence, in this low molecular weight regime one might expect the maximum toughness obtainable to vary as $M^{1.2}$ (Σ_{sat} varies as $M^{-0.4}$, f varies as M). An optimum molecular weight is therefore expected at a molecular weight around the transition from pull out to scission. This very simple model however misses one very important effect. At values of Σ near saturation a "dry brush" tends to form,[26] and so the mixing between the copolymer and homopolymer is limited.[10] Failure can then occur, not at the interface but between the brush and the homopolymer. This effect will reduce the toughness for low and medium molecular weight copolymers but probably not have much effect on the qualitative picture.

Conclusions

We have shown that the toughness of the interface between PMMA and PPO can be increased by the presence of a thin layer of PS-PMMA diblock copolymer. For a wide range of copolymer molecular weights, 50K-500K, provided the interface is not saturated with copolymer, the interface toughness is a function of just the areal density Σ of the copolymer molecules, independent of their molecular weight. This result, by itself, strongly suggests that the copolymer layer is organized so that it provides one stitch per molecule. Also each molecule provides a strength that is independent of its length and so, on interface fracture, the molecules must break and not pull out. The toughness was found to vary with Σ^2 in accordance with the predictions of a recent model of crazing failure where it is assumed that G is a measure of the energy to form the crack tip craze and the craze fails when the force per molecule at the crack tip (in the craze) equals the molecular scission force.

SIMS experiments on fractured samples and thin layer samples confirmed that the diblock copolymer does indeed organize at the interface and that interface fracture does break the copolymer molecules near their junction points. The remarkable difference between the mechanical results seen here and those found when the homopolymer PS is exchanged for PPO is caused by the much more rapid organization of the diblock here in the presence of the attractive mixing enthalpy between PS and PPO and the strong repulsion between PPO and PMMA. Only a diblock with a very high molecular weight, 900K, failed to organize in the joining time.

The highest obtainable toughness for any given molecular weight diblock was found to itself exhibit a maximum when considered as a function of molecular weight. This maximum occured at a molecular weight of about 80 K. The obtainable toughness decreased as the copolymer molecular weight was increased from 80K because the saturation value of Σ decreased with increasing molecular weight. As the molecular weight was decreased from 80K, both pull-out and crowding effects become more evident, so again the toughness decreases from the value found at 80K.

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