Segregation of a Random Copolymer from Miscible Blends

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ABSTRACT: Thin film bilayers of deuterated polystyrene (dPS) and blends of deuterated poly(methyl methacrylate) (dPMMA) with a compositionally symmetric random copolymer of styrene and methyl methacrylate (P[$S_{0.49}$-*ran*-MMA]) were investigated by neutron reflectivity. Copolymer segregation to the free surface occurs upon spin-coating blends onto silicon substrates. Annealing the bilayers to equilibrium at 150 °C increases the segregation of the copolymer from the blend layers to the interface with dPS. Blends containing 5 and 10 vol % copolymer both exhibit this segregation behavior. For these blend compositions the interfacial segregation of copolymer from the miscible blends is insufficient to form a discrete layer. These results suggest that this random copolymer would be an interfacial specific additive.

Introduction

Copolymers continue to be investigated as a method for reinforcing homopolymer blends and joints. To be a practical interfacial strengthening agent, a copolymer should synthesize easily and at low cost, strengthen the interface between phase-separated homopolymers, and segregate to the region of the interface. Much effort has been focused on investigating block copolymers for such strengthening applications, and block copolymer films of ~10-100 nm have been shown to increase the fracture toughness of joints between homopolymers.[1,2] Block copolymers do not, however, meet some of the other criteria for being preferred interfacial agents. They are relatively expensive to synthesize in commercial quantities and also may form low-energy states in blends such as micelles, bringing into question the ability of block copolymers to diffuse to interfaces in sufficient quantity for strengthening.[3,4]

One alternative polymer architecture under current investigation is the random copolymer. Random copolymers are relatively inexpensive to synthesize and offer a great extent of design flexibility. Also they do not form micelles in blends. Currently the strengthening abilities of random copolymers are not as well understood as those of their blocky counterparts, as fracture toughness experiments involving random copolymers at homopolymer joints currently provide inconclusive results. Kramer and co-workers[5] used the asymmetric double cantilever beam (ADCB) or "crack-opening" test and found that a compositionally symmetric random copolymer of styrene and 2-vinylpyridine strongly reinforces the interface between polystyrene (PS) and poly(2-vinylpyridine) homopolymers. The interfacial fracture toughness for this system decreases as the molar fraction of styrene in the copolymer varies from 0.5. Kulasekere, et al., used a static ADCB test to study the properties of poly(styrene-*co*-methyl methacrylate) random copolymer.[6] They report that as the thickness of the copolymer layer between PS and poly(methyl methacrylate) (PMMA) increases from ~8 to 380 nm, the interfacial fracture toughness increases. In addition, the maximum strengthening is found at a copolymer molar composition of ~0.68 styrene. However, these authors note that their test geometry was not optimal. In our own fracture toughness experiments using P[S_f-*ran*-MMA] between PS and PMMA, we found that a 50 nm film formed a discrete layer requiring consideration of two interfaces, namely copolymer/PS and copolymer/PMMA.[7] Using a dynamic ADCB experiment, carefully selecting the optimal geometry, and avoiding crack instability, we found that a copolymer composition of $f = 0.73$ gave a slightly stronger joint than $f = 0.49$. The increased strength was apparently from the formation of oblique crazes in the PS as determined by optical microscopy and FTIR analysis of the fractured specimens. Fracture always occurred at or near the copolymer/PS interface, so the role of the copolymer/PMMA interface in the strengthening of the joint is currently unresolved.

As an alternative to fracture toughness experiments the interfacial width has been studied to determine the ability of a random copolymer to reinforce an immiscible interface. Fracture toughness is expected to increase with interfacial width. We have used neutron reflectivity studies to determine the interfacial widths between deuterated poly(methyl methacrylate) (dPMMA) or deuterated polystyrene (dPS) with P[S_f-*ran*-MMA] copolymers as a function of copolymer composition.[8]

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Asymmetric behavior of a compositionally symmetric copolymer with the two homopolymers was observed, in that P[S$_{0.49}$-*ran*-MMA] exhibits a broader interface with dPMMA than with dPS. Kulasekere et al. found similar results in their neutron reflectivity experiments,[6] determining that the point of symmetry in the copolymer/deuterated homopolymer interfacial widths occurred when $f = 0.65$, closely corresponding to the maximum fracture toughness found when the copolymer had $f = 0.68$.

Of the criteria listed initially for determining the feasibility of copolymer blend additives, the issue which remains to be addressed is how well an AB-random copolymer can segregate from a miscible blend to the interface between two immiscible A- and B-type homopolymers. For example, if a miscible AB-copolymer/A-homopolymer blend is annealed while in contact with a B-type homopolymer phase, will the copolymer move to the interfacial region from the miscible blend and thereby reinforce the interface? Will a random copolymer form a discrete phase between the homopolymers?

Here, we have investigated whether the compositionally symmetric P[S-*ran*-MMA] copolymer can segregate from a miscible blend with dPMMA to the interface with dPS. From previous studies, we know that this random copolymer exhibits asymmetric miscibility with the two homopolymers for certain molecular weights, M_w.[9] TEM studies found that a P[S$_{0.48}$-*ran*-MMA] copolymer of M_w = 286K exhibits a wider range of miscibility with PMMA (M_w = 32K) than with PS (M_w = 22K). The copolymer was immiscible for the range 6−72 vol % copolymer blended with PMMA, but immiscible for the range 0−100 vol % copolymer when blended with PS. We refer to such behavior as “asymmetric miscibility” in copolymer/homopolymer blends, and it is the focus of further investigation. For our segregation studies presented here, a blend of dPMMA with either 5 or 10 vol % P[S$_{0.49}$-*ran*-MMA] was spin-coated into a thin film (~50 nm) on a silicon wafer and then topped with a thicker layer of dPS, ~200 nm. Neutron reflectivity studies were performed on these bilayers before annealing, after 4 h of annealing at 150 °C, and again after an additional 4 h of annealing at the same temperature. A significant degree of copolymer segregation to the free surface from the copolymer/dPMMA miscible blend occurs during the spin-coating, based on the reflectivity results of the unannealed bilayers. Four hours of annealing was found to be sufficient time to reach equilibrium conditions at 150 °C in these bilayers, with segregation occurring to the extent that the bulk of the blend layer contained only 1 vol % copolymer. For these low vol % copolymer blends, segregation to the interfacial region was insufficient to form a distinct copolymer phase.

Experimental Section

Polymer Synthesis. The P[S$_{0.49}$-*ran*-MMA] copolymer was synthesized via free radical copolymerization.[10] Purified styrene and methyl methacrylate monomers in benzene solution were reacted at 60 °C under a nitrogen atmosphere and with benzoyl peroxide as initiator. The reaction was carried out to no more than 5% conversion to ensure a product of narrow molecular weight polydispersity and avoid copolymer composition drift from the desired average $f = 0.5$. The reaction mixture was poured into excess methanol to precipitate the copolymer, which was redissolved in toluene and reprecipitated twice more before vacuum drying at temperatures near 150 °C to remove the remaining unreacted monomers and initiator. The average mol % MMA and styrene in the copolymer was determined by ^{1}H NMR. A comparable P[S$_{0.50}$-*ran*-MMA] copolymer investigated by Bovey[11] with ^{13}C NMR was found to be more alternating than blocky in sequence, with only 10% of triads occurring as homotriads. This is consistent with the published reactivity ratios for styrene and MMA.

Table 1. Materials Description

material	M_w^{a}	M_w/M_n^{a}	$(b/V) \times 10^{-6}$ (Å^{-2})
dPS	690 000	1.09	6.46
dPMMA	310 000	1.05	7.02
P[S$_{0.49}$-ran-MMA]	361 000	2.23	1.22

^{a} All molecular weights measured using size exclusion chromatography with four columns, THF solvent, and PS standards, except those for dPMMA, which are measured using PMMA standards.

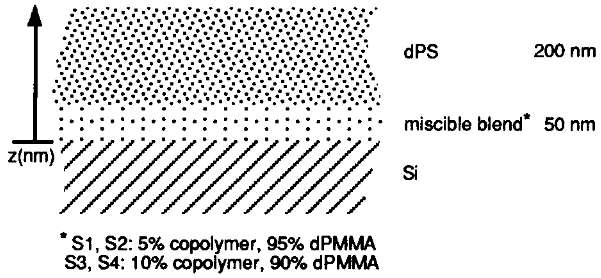

Figure 1. Sample geometry for neutron reflectivity measurements.

The dPMMA and dPS homopolymers were purchased from Polymer Laboratories. The molecular weights and dispersities of all materials were characterized by size exclusion chromatography (SEC), using four mixed columns in series and THF as the solvent at room temperature. PS homopolymer standards were used for molecular weight calibration for the copolymer. The properties of the polymers are summarized in Table 1.

Sample Preparation. Silicon wafers 5 or 7.5 cm in diameter were used as substrates for the polymer bilayers. Wafers were cleaned with alternating toluene and acetone rinses on a spin coater, then placed in a UV oven for 5 min. The wafers were not treated to remove the native SiO$_2$ on their surface. The dPMMA/copolymer blend film, ~50 nm thick, was spin-coated from toluene solution onto the cleaned silicon wafer. The wafer was air-dried and then vacuum-dried overnight at room temperature. The dPS film, ~200 nm thick, was spin-coated from toluene solution onto a clean glass slide. The film was scored on all sides with a razor blade and floated carefully off onto a water bath. This film was then retrieved onto the Si wafer. The completed bilayers were vacuum dried overnight at room temperature. Four samples were prepared to this stage, S1−S4, with their geometries illustrated in Figure 1. S1 and S2 both contain 5 vol % P[S$_{0.49}$-*ran*-MMA] in the blend layer and S3 and S4 contain 10 vol.% P[S$_{0.49}$−*ran*-MMA] in the blend layer. S2 and S4 were annealed for 4 h under vacuum at 150 °C and then quickly quenched in liquid nitrogen. S1 and S3 were left unannealed. Samples were examined under a light microscope to check the quality of the films and to ensure annealing had not resulted in dewetting. Films appeared adequately smooth and defect-free for the reflectivity experiments. The 50 nm/200 nm layer thickness geometry was chosen based on the results of previous neutron reflectivity experiments.[8] Using asymmetric layer thickness was found to aid in the reflectivity data fitting. The use of a thick top layer helped discourage dewetting.

Neutron Reflectivity. The neutron reflectivity experiments were performed on the NG7 neutron reflectometer at NIST. Reflectivity scans were run by traversing the incident neutron beam through the silicon wafer, reflecting the beam off the Si/polymer, polymer/polymer, and polymer/air interfaces, and traversing the reflected beam again through the silicon wafer. This improved the data quality by having the neutron beam first pass through the Si/polymer interface, which is smoother and therefore results in less surface scattering than the polymer/air interface. After all four

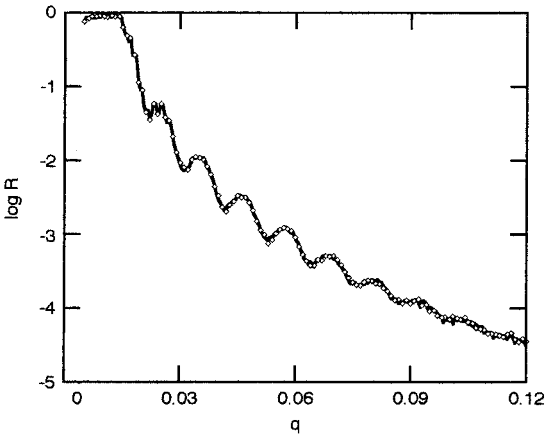

Figure 2. Neutron reflectivity profiles for sample S2 (Si/(5 vol % P[$S_{0.49}$-*ran*-MMA] + 95% dPMMA)/dPS). Solid line is reflectivity after a 4 h anneal at 150 °C; open diamonds are reflectivity after an additional 4 h of annealing at 150 °C.

samples were run once, they were annealed for 4 h under a vacuum at 150 °C, quenched in liquid nitrogen, and reanalyzed.

Experimental results were fitted to algorithm-generated reflectivity curves. In our profile-generating algorithm, constant slit size smearing was used, with $\Delta\theta = 1 \times 10^{-6}$ and $\Delta\lambda = 0.035$. Each simulated curve was created from a model profile of scattering length density, (b/V), as a function of sample depth, z (taking $z = 0$ as the silicon/polymer interface). Hyperbolic tangent profiles were used at interfaces. Through trial and error, the best fit for each reflectivity curve was found. Surface roughnesses were estimated for the silicon/polymer and polymer/air interfaces; values fell between 5 and 15 Å for these samples.

Results and Discussion

Establishing the annealing time necessary for reaching equilibrium at 150 °C was our first objective. The reflectivity curves of sample S2 after both the 4 and 8 h total annealing times are compared in Figure 2. There is no significant change in the results after the additional 4 h of annealing, and similar results were observed for sample S4. We can conclude that the bilayers are under equilibrium conditions after 4 h. Thus we will limit our discussion to samples S1 and S3 both prior to annealing and after the 4 h anneal.

We will now examine the results for sample S1, the bilayer of Si/(5% P[$S_{0.49}$-*ran*-MMA] + 95% dPMMA)/dPS. Interestingly, this sample exhibits significant copolymer segregation to the free surface of the miscible blend during spin coating, before adding the dPS film and annealing. This can be observed in Figure 3a, which shows the reflectivity data of sample S1 before annealing, and fitted with a reflectivity profile assuming no copolymer segregation had occurred. The reflectivity profile was calculated by using the scattering length density model shown in the inset. Note that the scattering length densities of dPS and the miscible copolymer/dPMMA blend are very similar, 6.46×10^{-6} and 6.61×10^{-6} Å^2, respectively. Furthermore, a 15 Å thick dPMMA layer was included at the Si/polymer interface, due to the known favorable interaction between PMMA and the oxide layer that forms on the silicon surface,[12] and this is incorporated into this and all other (b/V) profiles. Consequently, without segregation, the scattering length density model is nearly uniform and produces a simulation in which the oscillations in the reflectivity curve dampen out very quickly. Clearly this simulation disagrees with the reflectivity data. Taking into account a small degree of copolymer segregation into the simulated (b/V) profiles leads to much more acceptable data fitting, as seen in Figure 3b, where the same unannealed reflectivity results are fitted with a new model profile. The P[$S_{0.49}$-*ran*-MMA] copolymer has a (b/V) of 1.22×10^{-6} Å^{-2}, which causes the contrast that allows us to determine where the copolymer is primarily located in the bilayers. Based

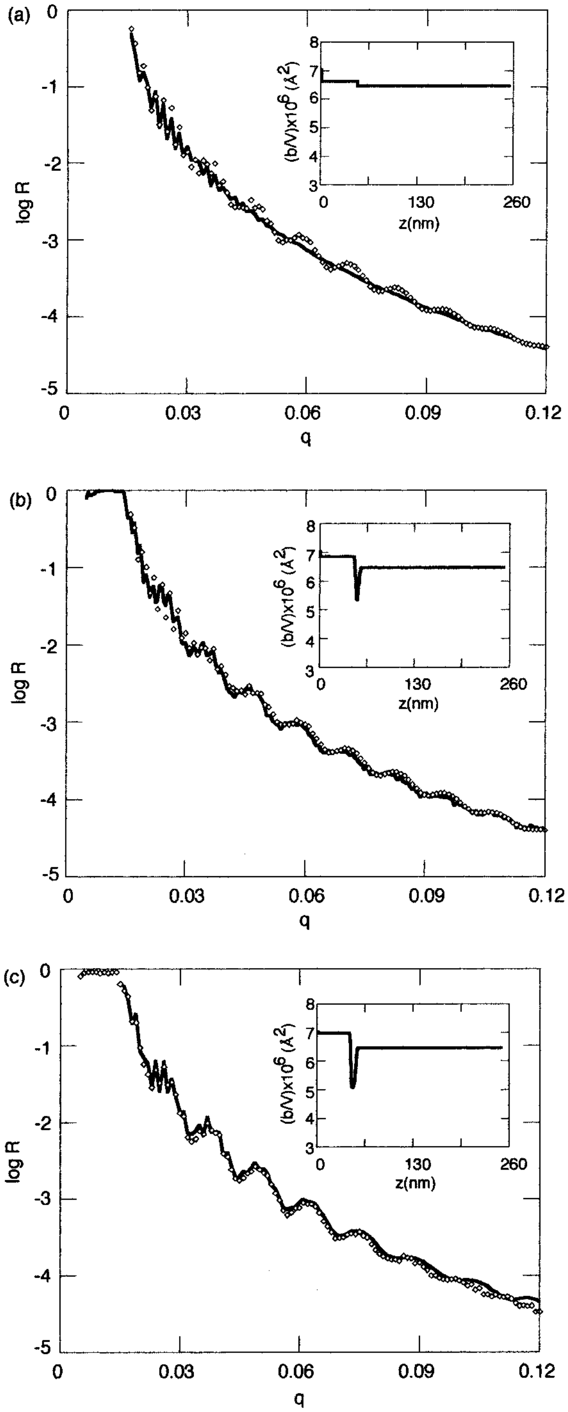

Figure 3. Neutron reflectivity data for sample S1, Si/(5 vol % P[$S_{0.49}$-*ran*-MMA] + 95% dPMMA)/dPS, shown as open diamonds. The solid curves are the calculated reflectivity profiles corresponding to the scattering length densities shown in the insets. The silicon/polymer blend interface corresponds to $z = 0$ nm. Key: (a) sample before annealing, fitted with a profile having no copolymer segregation in the model; (b) sample before annealing, fitted with a profile which includes copolymer segregation; (c) sample after 4 h of annealing at 150 °C, fitted with a profile which includes greater copolymer segregation.

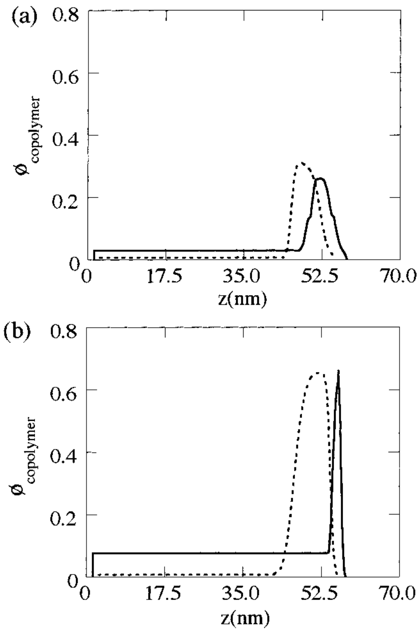

Figure 4. Estimated copolymer composition, ϕ_c, as a function of depth for (a) sample S1, Si/(5 vol % P[$S_{0.49}$-*ran*-MMA] + 95% dPMMA)/dPS, and (b) sample S3, Si/(10 vol % P[$S_{0.49}$-*ran*-MMA] + 90% dPMMA)/dPS. Solid and dashed lines are copolymer volume fractions before and after annealing, respectively.

on the simulation fit in Figure 3b, the bulk composition of the blend film is 97 vol % dPMMA, in contrast to the overall blend composition of 95 vol %. The interfacial region of enriched copolymer content is on the order of 10 nm in width. This type of surface segregation during spin-coating has been observed in other systems involving a partially miscible blend,[13] so it is not an unprecedented behavior. Estimation of the copolymer vol % at the interface for this sample and all other samples will be described in conjunction with Figure 4.

The reflectivity results of sample S1 and after 4 h of annealing at 150 °C are shown in Figure 3c. After annealing, more copolymer moves from the blend layer to the area of the interface with dPS, resulting in a layer composition of 99 vol.% dPMMA and a slightly broader interface. The dPS top layer remains essentially unaffected by the copolymer segregation.

Similar results were found for sample S3 (10% P[$S_{0.49}$-*ran*-MMA] + 90% dPMMA/dPS), before and after 4 h of annealing at 150 °C. Again a significant degree of copolymer segregation is observed in the unannealed sample, with the composition of the blend layer at 92 vol % dPMMA. The scattering length density in the interfacial region is lower than in the 5% copolymer sample, indicative of a higher concentration of the hydrogenated copolymer, although the width of the region is narrower, only ~4 nm. Annealing for 4 h at 150 °C results in further segregation of the copolymer to the interface, until again the concentration within the blend layer is 99 vol % dPMMA. The interfacial region is broadened as well to 14 nm. Table 2 summarizes the layer thickness and composition changes observed in samples S1 and S3 with annealing.

Table 2. Results of Neutron Reflectivity Modeling

sample	thickness of blend layer (nm)	vol % dPMMA in blend layer	width of interfacial region (nm)	thickness of dPS layer (nm)
S1, as prepared	48 ± 0.2	97	11 ± 1	194 ± 1
S1, 4 h, 150 °C	44 ± 0.2	99	13 ± 1	193 ± 1
S3, as prepared	53 ± 0.5	92	4 ± 1	222 ± 1
S3, 4 h, 150 °C	42 ± 0.5	99	14 ± 1	222 ± 1

The volume fraction profiles of the copolymer in the interfacial region for both samples S1 and S3 as prepared and after annealing were estimated from the scattering length density profiles and are shown in parts a and b of Figure 4, respectively. There are three components present in the interfacial region of these samples, P[$S_{0.49}$-*ran*-MMA], dPMMA, and dPS, so the scattering length densities used in the models are combinations of values for these individual components. For a simple approximation of the copolymer content in the bilayer as a function of *z*, the deuterated component contribution to (b/V), or $(b/V)_d$, is taken as a combination of $(b/V)_{dPMMA}$ and $(b/V)_{dPS}$. A linear gradient from 7.02×10^{-6} to 6.46×10^{-6} Å^{-2} is used for $(b/V)_d$ over the width of the interface from the dPMMA-rich phase to the dPS-rich phase. Given this simplification we can describe the scattering length density of our model, $(b/V)_m$, at each position (z) as a weighted summation of contributions from the copolymer and the deuterated components, or

$$(b/V)_m = \phi_d(b/V)_d + \phi_c(b/V)_c \tag{1}$$

where ϕ_d is the volume fraction of deuterated component at z, ϕ_c is the volume fraction of copolymer at z, and $(b/V)_c$ is the scattering length density of the copolymer, 1.22×10^{-6} Å^{-2}. Rearranging the above, the copolymer volume fraction is given as

$$\phi_c = \frac{(b/V)_d - (b/V)_m}{(b/V)_d - (b/V)_c} \tag{2}$$

and shown in Figure 4. While this model of the interface is very simplistic, the overall shape and maxima of the ϕ_c peaks were not radically changed when more complex estimation methods were attempted, because the difference between $(b/V)_{dPMMA}$ and $(b/V)_{dPS}$ is much smaller than the difference between either deuterated polymer $(b/V)_d$ and $(b/V)_c$. The area under a ϕ_c peak corresponds to the amount of copolymer in the interfacial region and increases by >400% upon annealing either sample. In contrast the maximum of the ϕ_c peak at the interface did not change significantly upon annealing for either sample, occurring at ~0.30 for the 5% blend and ~0.70 for the 10% blend. Thus, the increase in copolymer excess at the interface is accomplished predominantly by forming a thicker interfacial region, which is consistent with the neutron reflectivity model (see Table 2).

Finally, note that both before and after annealing the area of the peak is on the order of four times greater for the 10% blend sample as compared to the 5% blend. The greater the copolymer concentration is in the miscible blend, the more copolymer is available to segregate to the interface. In our TEM studies performed in conjunction with the fracture toughness measurements, the P[$S_{0.49}$-*ran*-MMA] copolymer formed a distinct phase at the joint between hydrogenated polystyrene (hPS) and hydrogenated poly(methyl methacrylate) (hPMMA) when the copolymer layer was greater than 50 nm thick.[7] Distinct interfaces with both homopolymer phases were observed, with negligible diffusion of the copolymer into the hPMMA and hPS phases. These current neutron reflectivity results indicate that thin layers of a miscible blend of low copolymer concentration (5 or 10 vol %) contain insufficient copolymer to form a distinct copolymer layer.

The ease with which the random copolymer segregates to the interface between the immiscible layers in these samples is a promising result for industrial polymer blend applications. This paper supports an alternative scheme to adding an interfacial specific agent to a polymer blend. A miscible system of a random copolymer and a homopolymer containing a low copolymer concentration is premixed. This homogeneous compound is then mixed with a second homopolymer which is immiscible with the first homopolymer. During this second mixing stage the random copolymer is sufficiently mobile to segregate to the interface in order to promote interfacial adhesion and to limit phase coalescence. The important parameters in this scheme include the miscibility of the random copolymer and one of the homopolymer components, the copolymer concentration in the premixed miscible blend, and the kinetics of segregation during the second mixing stage. This approach to interfacial modification may be considered as an alternative to in situ reactions to form copolymers at interfaces. This alternative scheme has also been suggested by the groundbreaking work of Genzer et al.[14,15]

Conclusions

Our neutron reflectivity results show the feasibility of using random copolymers as interfacial specific agents in homopolymer systems. P[$S_{0.49}$-*ran*-MMA] segregates from a miscible blend with dPMMA to the free surface during spin coating of the blend and to the immiscible dPMMA/dPS interface upon annealing. At the low copolymer concentrations used, the copolymer concentration at the interface is <70 vol %. The segregation of random copolymer to the boundary between immisible homopolymers as shown in this paper should broaden the interface and thereby increase the interfacial fracture toughness and reduce phase coalescence.

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