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Functionalizing polymer surfaces by surface migration of copolymer additives: role of additive molecular weight

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Abstract

Surface migration of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymer additives in polystyrene (PS) hosts was investigated using a series of narrow molecular weight distribution polystyrenes ($5 \times 10^3 < M_{PS} < 2 \times 10^7$ g mol^{-1}). Dynamic contact angle (DCA) analysis and attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy measurements were used to characterize the surface chemical make-up of polymer/additive blends created by solvent casting, precipitation, and melt annealing processes. Selective surface enrichment of methyl methacrylate (MMA) groups was observed at the air/polymer interface for PS hosts with molecular weights substantially larger than that of the PS-*b*-PMMA additives. Surfaces of PS/PS-*b*-PMMA blends containing high molecular weight copolymer were, on the contrary, found to be depleted of MMA groups. An approximate relationship between surface excess concentration of PMMA $\Delta\Phi_{PMMA}$ and polystyrene molecular weight M_{PS}, $\Delta\Phi_{PMMA} \sim M_{PS}^{0.8\pm0.04}$ for $M_{PS} \leq 10^5$ g mol^{-1}, could be defined in blends containing PS-*b*-PMMA additives of fixed molecular weight M_a and concentration. A somewhat different scaling form $\Delta\Phi_{PMMA} \sim M_a^{-0.53\pm0.05}$ was found to describe the effect of PS-*b*-PMMA additive molecular weight on PMMA surface excess in PS/PS-*b*-PMMA blends with fixed M_{PS}. These results are discussed in terms of surface migration mechanisms based on entropic driving forces and the molecular-weight dependence of the mutual diffusion coefficient of PS-*b*-PMMA in PS. © 2002 Published by Elsevier Science Ltd.

Keywords: Polymer surface functionalization; Additive migration; Polymer/copolymer blends

1. Introduction

There is a longstanding need for low-cost, reliable methods for functionalizing polymer surfaces. Migration of functionalized additives dispersed in a host polymer to the host polymer's surface has long been recognized as a potential solution to this problem [1–3]. The premise is that if a surface active additive with desirable functional groups is blended in small amounts with a host polymer melt or solution, physical processes such as diffusion, spontaneous surface segregation, and shear might be used to transport the additive to the host polymer's surface during normal polymer processing. Despite the method's appeal, there has been surprisingly little fundamental research conducted to establish principles for additive selection and for optimizing processing conditions to enhance the transport of surface functionalizing additives in polymeric hosts.

In a recent article Lee and Archer [4] investigated surface migration of polystyrene-*b*-poly(dimethyl siloxane) (PS-*b*-PDMS) copolymer additives in polystyrene hosts using attenuated total reflectance (ATR) infrared spectroscopy and dynamic contact angle (DCA) measurements. These authors reported that migration of the copolymer to the polymer/air interface was driven primarily by the large difference in surface tension ($\Delta\gamma \sim 25$ mN m^{-1}) of polystyrene and poly(dimethyl siloxane) [5,6]. Nonetheless, for PS-*b*-PDMS additives of fixed molecular weight and bulk composition Φ_b in the blends, the authors found that the surface excess of dimethyl siloxane groups could be decreased by reducing the host PS molecular weight M_{PS}. Lee and Archer [4] also reported that low surface energy DMS groups could even be induced to migrate to rigid high energy aluminum substrates if the molecular weight of the PS matrix is sufficiently high, $M_{PS} > 10^5$ g mol^{-1}.

The objective of the present study is to investigate surface migration of copolymer additives in polymer hosts where surface energy differences are small. Our goal is to use these systems to investigate the effect of host and additive molecular weight on migration. For this purpose, we investigate migration of (polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) additives in narrow molecular weight distribution PS hosts over a wide range of molecular weights.

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This material provides several advantages for investigating additive migration in polymers. First, the surface energies of pure polystyrene and poly(methyl methacrylate) (PMMA) are quite similar for comparable molecular weight materials, $\gamma_{PS} \approx (32–38)$ mN m^{-1} and $\gamma_{PMMA} \approx (34–41)$ mN m^{-1}, at 20 °C [5,6], thus the energetic preference for either material at the surface is weak. The interfacial tension of PS and PMMA is also small (approximately 1.1 mN m^{-1} at 180 °C (3.2 mN m^{-1} at 20 °C), and the Flory–Huggins interaction parameter $\chi \approx 0.04$ at 180 °C [5]. Finally, a recent analysis of surface segregation in conformationally asymmetric incompressible A/B polymer blends near rigid substrates by Donley et al. [7], suggests that the sign of surface enrichment is determined by $\kappa = B_1((b_A/b_B)^2 - 1) + B_2\chi(\Delta\rho/\bar{\rho})$, for materials with the same bulk compressibility. Here, $\kappa > 0$ implies that component B will segregate to the blend surface, b_A and b_B are statistical segment lengths of A and B components, $\Delta\rho$ is the difference in monomer densities of A and B, and the B_i are constants of order 1. The statistical chain lengths of PS and PMMA can be estimated from C_∞ values provided by Fetters et al. [8] to be 6.75 and 6.58 Å, respectively. The monomer densities of the two materials are 0.906 and 0.944 g ml^{-1} [9], respectively. It is therefore apparent that for the system PS/PS-*b*-PMMA conformational asymmetry is not likely to be an important factor in surface migration.

At least three different entropic free energy contributions can drive migration in the PS/PS-*b*-PMMA system. First, a so-called *purely entropic* effect can be derived from the fact that higher molecular weight polymer species in blends experience greater entropic penalty for residing near a phase interface [6]. In the absence of large offsetting enthalpic contributions, this effect favors preferential enrichment of lower molecular weight materials at phase interfaces. Second, the number of chain ends per unit volume of polymer at an interface increases as polymer molecular weight decreases. The added mobility of chain ends enhances molecular configurational freedom near interfaces [10–12], and therefore favors surface enrichment of lower molecular weight species. Finally, for PS-*b*-PMMA bulk compositions above the critical micelle concentration, blends with high molecular weight PS result in formation of micelles in bulk that are only weakly penetrated by the surrounding matrix material. The free energy of this system is minimized when micelles segregate to the surface [13].

Several experimental and theoretical studies reveal strong connections between polymer molecular weight, configurational freedom, and blend composition near phase interfaces [14–24]. Bucknall et al. [14], for example, used neutron reflectivity to measure the near-surface composition profile of thermally annealed two-layer films consisting of thin deuterated PS-*b*-PMMA copolymer ($M_w = 2.84 \times 10^4$ g mol^{-1}, $w_{PS} = 0.47$) and entangled PMMA ($M_w = 1.2 \times 10^5$ g mol^{-1}) sheets stacked one on top of the other and supported on optically polished glass substrates. In either configuration (glass/PS-*b*-PMMA/PMMA/air or glass/PMMA/PS-*b*-PMMA/air) the authors observed selective enrichment of the lower molecular weight copolymer within a distance of order 1.5–3 polymer radii of gyration from the polymer/air interface. Tanaka et al. [15], reported that lower molecular weight PMMA chains segregate to the air-side interface of binary blends with high molecular weight PS ($M_{PS} = 1450$ kg mol^{-1}). Surface PMMA compositions Φ_{PPMA} observed by the authors support a scaling relationship $\Phi_{PMMA} \sim M_{PMMA}^{-0.5}$ between PMMA surface composition and molecular weight, for high molecular weight PMMA materials. Watternberger et al. [17] used a two-dimensional lattice model simulation to determine how the number of available conformations, Z, for small polymer molecules (degree of polymerization $N = 16$) changed with distance from a surface. They found that Z increases with distance away from the surface and that more compact structures such as helices and sheets are favored by molecules within a few molecular diameters away from a wall. The same authors also reported conformational free energy losses of order 7 kT when the center of mass of a chain is moved from a bulk polymer to an interface.

2. Experiment

2.1. Materials and sample preparation

Narrow molecular weight distribution PS and PS-*b*-PMMA diblock copolymers were used in the study. Molecular weight and other pertinent information about these materials are summarized in Table 1. PS/PS-*b*-PMMA blends were prepared by solvent casting from

Table 1
Molecular weights and other information about polymers used in the study

Polymer	M_n	M_w/M_n	Source
Polystyrene	5000	1.22	Polymer Source Inc.
	8300	1.22	Polymer Source Inc.
	13,000	1.02	Polymer Laboratories
	19,000	1.22	Polymer Source Inc.
	44,000	1.02	Polymer Source Inc.
	75,700	1.22	Polymer Source Inc.
	90,000	1.04	Pressure Chemical Co.
	142,000	1.22	Polymer Source Inc.
	223,000	1.22	Polymer Source Inc.
	393,000	1.22	Polymer Source Inc.
	550,000	1.22	Polymer Source Inc.
	935,000	1.05	Aldrich Chemical Co.
	1,880,000	1.05	Aldrich Chemical Co.
	2,000,000	1.2	Pressure Chemical Co.
	5,480,000	1.15	Tosoh Haas
	6,680,000	1.22	Polymer Source Inc.
	8,000,000	1.15	Tosoh Haas
	8,990,000	1.22	Polymer Source Inc.
	20,000,000	1.15	Tosoh Haas
PS13K-*b*-PMMA13K	26,000	1.05	Polymer Source Inc.
PS32K-*b*-PMMA12K	44,000	1.05	Dexco
PS328K-*b*-PMMA173K	501,000	1.09	Polymer Source Inc.
PS128K-*b*-PMMA1M	1,127,000	1.3	Polymer Source Inc.

toluene at room temperature or by precipitation from toluene solutions using methanol. Details of these procedures can be found in Ref. [4]. The solvent casting procedure yields polymer films with controlled thicknesses in the range of 40–50 μm and diameters ranging from 12.5 to 50 mm. Following room temperature drying for 1–2 days, residual traces of solvent were removed by vacuum evaporation at approximately 25.4 °C for 24 h. The effectiveness of the vacuum evaporation protocol for removing toluene was determined by weighing sample specimen at 3 h intervals, until constant weight was recorded. The weight fraction of copolymer in all blends was maintained at 0.1 and bulk PMMA weight fraction was adjusted from 0.02 to 0.08 by varying the PMMA content in PS-*b*-PMMA copolymer.

2.2. Surface analysis

Surface composition of PS/PS-*b*-PMMA blends were analyzed using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy and DCA measurements. ATR-FTIR measurements were performed at room temperature (ca. 24.5 °C) and fixed angle of incidence (45°) using a Nicolet ATR-FTIR spectrometer outfitted with a germanium crystal. In this configuration, ATR-FTIR measurements were used to obtain quantitative information about the composition of polymer mixtures within a characteristic penetration depth of around 0.5 μm [25]. ATR-FTIR absorbance spectra for pure PS, PMMA, and PS-*b*-PMMA copolymer are shown in Fig. 1. The infrared absorption band at ca. 1735 cm^{-1} is assigned to asymmetric C=O stretching modes in PMMA chain segments. The band at ca. 1600 cm^{-1} is assigned to aromatic stretch of C=C groups in PS segments. Since the composition of styrene segments in the blends is very large compared to MMA segments, the infrared absorption strength of the 1600 cm^{-1} band is insensitive to changes in blend surface composition. Infrared peak height ratios of 1735 and 1600 cm^{-1} bands were therefore used to determine PMMA surface composition of the blends. In addition to the obvious simplicity of using infrared peak heights versus peak areas, for quantifying MMA surface composition, this choice was motivated by several considerations. The bands in question are reasonably

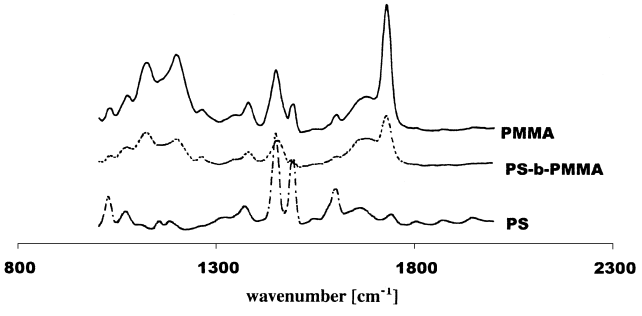

Fig. 1. ATR-FTIR spectra of pure PMMA, PS-*b*-PMMA, and PS.

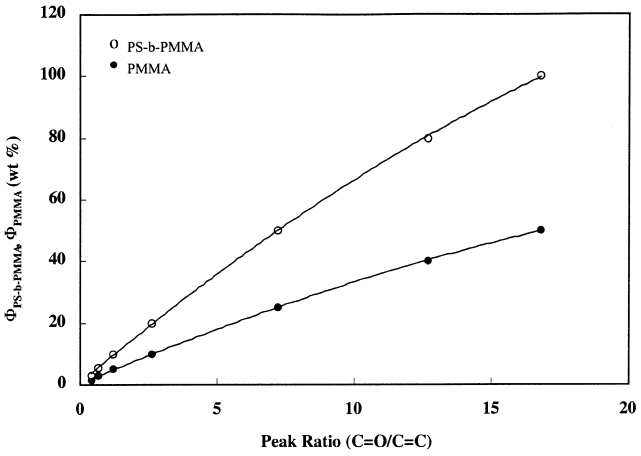

Fig. 2. ATR-FTIR calibration curves based on total PS-*b*-PMMA copolymer weight fraction and PMMA weight fraction at the surface of polymer/additive blends. The calibration curves were obtained using separate ATR-FTIR measurements on solutions containing known concentrations of copolymer and PMMA in toluene.

well resolved, possess symmetric shapes, and clear base lines can be identified.

As discussed in the previous paper [4], quantitative surface composition information can be obtained from such ratiometric measurements provided the instrument is calibrated in the ATR mode using MMA/toluene solutions of known concentration. Calibration curves based on ATR-FTIR data for PMMA and a symmetric PS-*b*-PMMA diblock copolymer are shown in Fig. 2. Best-fit polynomial curves to the data are also provided in the figure (solid lines). It is apparent from the results that approximately twice as much copolymer is needed to obtain the same infrared peak ratio as a pure PMMA specimen in toluene solution. This result is expected for the symmetric PS-*b*-PMMA copolymer used in the calibration, and validates the calibration procedure.

DCA analysis was performed at 25 °C using a DCA 315 (Cahn Instruments Inc.), by the Wilhelmy method. Measurements using this method are sensitive to chemical changes within the first 5 Å of a material's surface. Samples for DCA analysis were prepared by dip coating polymer solution onto glass substrates. DCAs were determined from a simple force balance equation, $F_m = mg + p\gamma_L \cos(\theta) - F_b$ where mg is sample weight, $p\gamma_L \cos(\theta)$ is the surface tension force acting on the meniscus, and F_b is a buoyancy force [26]. The surface tension γ_L for all samples were calculated from advancing contact angles (θ) in distilled water and ethylene glycol [27].

3. Results and discussion

3.1. Effect of molecular weight on migration

The main results of the article are shown in Figs. 3(a)–(c) and 4(a),(b). These figures summarize the effect of PS

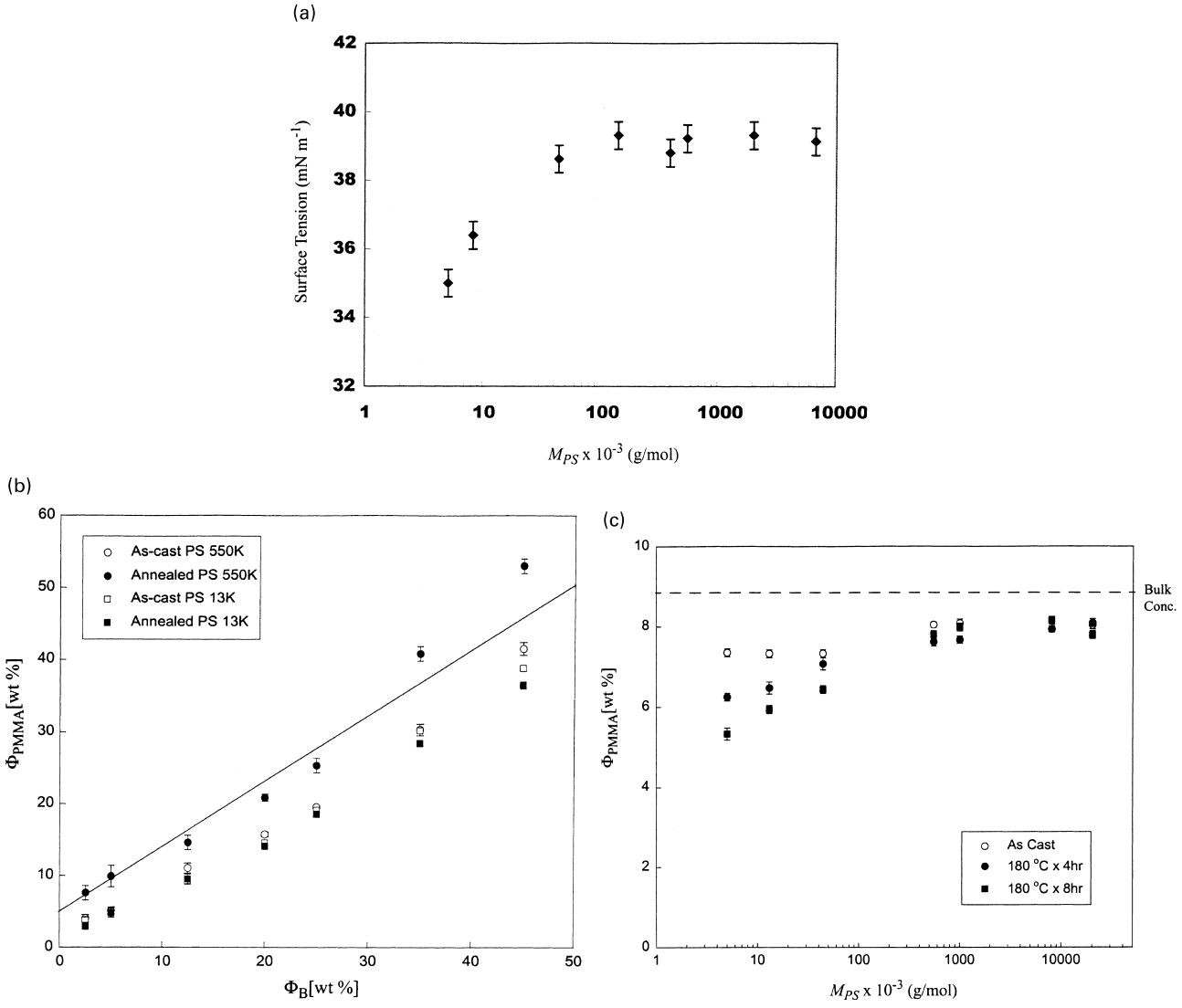

Fig. 3. (a) Surface tension of film cast PS/PS32K-*b*-PMMA12K blends containing 10 wt% copolymer as a function of PS molecular weight. (b) Surface PMMA concentration versus bulk PMMA concentration of PS13K/PS13K-*b*-13K and PS550K/PS13K-*b*-13K blends. Blend films were prepared by casting from toluene and dried at room temperature or annealed at 210 °C for 5 h. The straight line in the plot represents expectations if no surface migration occurs. (c) Concentration of PMMA at the surface of PS/PS128K-*b*-PMMA1M blends containing 10 wt% copolymer, at various matrix PS molecular weights. Polymer blend films were cast from toluene, evaporated for 24 h, and subsequently annealed at 180 °C under the high vacuum conditions for 8 h.

matrix molecular weight on PMMA surface composition of blends containing 10 wt% PS-*b*-PMMA with variable PMMA molecular weight. Polymer samples used for the measurements were prepared by film casting (Figs. 3(a)–(c) and 4(a)) and precipitation (Fig. 4(b)) procedures discussed earlier. Some samples were subjected to high temperature ($T \gg T_{g,PS}$) annealing under high vacuum conditions for periods ranging from 0.5 to 12 h. In all cases annealing conditions were limited by concerns about sample degradation.

Results from DCA surface tension measurements using unannealed PS/PS32K-*b*-PMMA12K blends comprising 2.7 wt% PMMA are shown in Fig. 3(a) for a range of PS molecular weights. These results were found to be unaffected by thermal annealing for periods ranging from 0.5 to 8 h at temperatures as high as 180 °C. Surface tension data for pure PS measured by the same DCA procedure are available in Ref. [4]. Comparison of the two sets of results indicate that despite the small concentration of PMMA in bulk, the concentration of MMA groups at the surface is quite large. Specifically, the surface tension of the PS/PS32K-*b*-PMMA12K blends are generally larger than those of pure PS of comparable molecular weight by as much as 4 mN m^{-1}. This range of difference is in fact nearly identical to the difference in surface tension of pure PS and PMMA of comparable molecular weight. It is also apparent from the results that unlike PS-*b*-PMMA copolymers and PS/PS-*b*-PDMS blends where surface migration to the

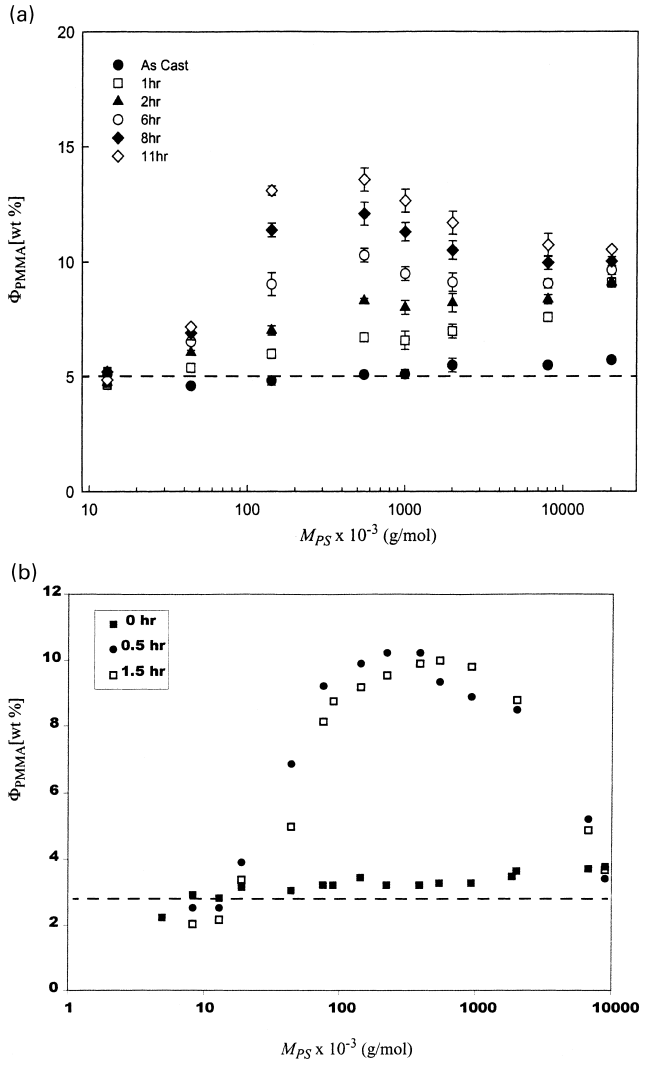

Fig. 4. (a) Surface concentration of PMMA groups determined from ATR-FTIR measurements using toluene-cast PS/PS328K-*b*-PMMA173K blends containing 10 wt% copolymer. Blend samples studied cover a wide range of PS molecular weight and thermal annealing conditions. (b) Concentration of PMMA at the surface of PS/PS32K-*b*-PMMA12K blends containing 10 wt% copolymer as a function of matrix PS molecular weight. Blend samples were precipitated from toluene solutions using methanol and subsequently annealed at 180 °C under the high vacuum conditions.

polymer/air interface lowers the polymer surface energy, migration in PS/PS-*b*-PMMA produces higher surface energy materials. The migration mechanism in the PS/PS-*b*-PMMA systems is therefore anticipated to be quite different from PS/PS-*b*-PDMS.

Fig. 3(b) more clearly shows the effect of polystyrene molecular weight and annealing conditions on PS/PS-*b*-PMMA blend surface chemical make-up. This figure summarizes ATR-FTIR PMMA surface composition data for film cast blends comprising a low molecular weight symmetric PS-*b*-PMMA copolymer (PS13K-*b*-PMMA13K) at various bulk compositions Φ_B in low and high molecular weight polystyrenes. The solid line in the plot depicts the expected blend PMMA surface composition in the absence of migration. Contrary to the surface tension results, this data suggests only a slight excess of lower energy PS groups at the surface of unannealed blends. This apparent discrepancy between DCA and ATR-FTIR results for unannealed materials is known [4], and results from the large difference in 'surface' length-scale (5–10 Å for DCA versus (5,000–10,000) Å for ATR-FTIR spectroscopy) probed by the two techniques. Nonetheless, after thermal annealing at 210 °C for 5 h, blends formulated using the higher molecular weight polystyrenes are clearly enriched in MMA groups, in agreement with DCA data supporting PS-*b*-PMMA surface migration in higher molecular weight PS.

The apparent absence of surface migration in materials where the PS matrix molecular weight is comparable or lower than that of the copolymer additive provides powerful evidence in support of a surface migration mechanism based on differences in polymer configurational entropy in bulk and at phase interfaces. The observation is, for example, consistent with expectations based on the idea that the configurational entropy penalty for residence near a phase interface is larger for higher molecular weight molecules [6]. Segregation of lower molecular weight species polymer/additive is also consistent with expectations from Shull's SCF analysis [13]. Specifically, since the concentration of copolymer in the blends is well above the critical micelle concentration, PS corona should be well penetrated by the surrounding PS chains in blends with lower or comparable molecular weight PS molecules. In this situation, the entropy penalty for existence of micelles in bulk is small and the driving force for surface migration is weak. On the other hand, substantially higher molecular weight PS molecules in the blends are excluded from the corona, yielding a large molecular-weight dependent entropy penalty in bulk; promoting surface segregation of the copolymer micelles.

Additional insight into the surface migration mechanism in PS/PS-*b*-PMMA systems is provided by Fig. 3(c). This figure summarizes PMMA surface composition in PS/PS128K-*b*-PMMA1M blends containing 8.9 wt% PMMA and variable M_{PS}. These blends were prepared by solvent casting from toluene. The dashed line in the figure again depicts expected blend surface PMMA composition for homogeneous materials. A clear trend from surfaces depleted in PMMA (at low M_{PS}) to PMMA surface compositions approaching the average bulk value is apparent for all three annealing conditions considered. This trend becomes more distinct, however, as the duration and temperature of annealing increases. The figure also shows that PMMA surface concentration most closely approaches the bulk value when M_{PS} is of order 10^6 g mol^{-1}, which is about an order of magnitude higher than $M_D \approx 10^5$ g mol^{-1} where γ_{PS} becomes independent of molecular weight [4] and about the same order higher than the PS molecular weight in the PS128K-*b*-PMMA1M copolymer additive. Notice, however, that the PS molecular weight at which surface migration appears to be arrested is comparable to

the overall molecular weight of the copolymer additive. This finding points either to the difference between the corona and the surrounding polymer molecular weight as the driving force for migration (i.e. the degree to which surrounding A or B molecules penetrate A/B copolymer micelles), or suggests that the larger entropy penalty incurred when higher molecular weight polymer resides near the surface is the most important driving force for surface migration in the systems studied here. At very high M_{PS} there is evidence of a slight down-turn in Φ_{MMA} with increasing host polymer molecular weight. This result is inconsistent with either surface migration mechanism, but is later shown to be caused by slowing-down of copolymer diffusion in high molar mass PS hosts.

Surface migration in systems where the copolymer additive molecular weight is substantially lower than that of the polystyrene host (PS/PS13K-*b*-PMMA13K blends with $\Phi_{PMMA} \approx 5$ wt%, in bulk) provide the clearest insight into the surface migration mechanism. Blend samples were prepared by solvent casting from toluene and annealed at 180 °C for variable time. PMMA surface concentrations measured by ATR-FTIR spectroscopy are shown in Fig. 4(a) for a range of M_{PS}. The dashed line depicts the expected PMMA surface composition in the absence of migration. Except for the unannealed materials and lowest molecular weight PS matrix, elevated levels of PMMA are apparent for all PS matrices and annealing conditions. The dramatic effect of annealing conditions on surface migration is also clearly evident from the data. For the symmetric case PS13K/PS13K-*b*-PMMA13K, PMMA surface compositions nearly identical to the bulk are observed, regardless of annealing conditions. In blends with higher M_{PS}, the surface composition of MMA groups initially increases as a progressively stronger function of host polymer molecular weight, as annealing time increases. In fact, for the most extensively annealed blends, Φ_{PMMA} is observed to increase nearly in proportion to M_{PS} up to $M_{PS} \approx 0.5 \times 10^6$ g mol^{-1}. These changes in polymer surface concentration with increasing PS matrix molecular weight are substantially stronger than those reported in Ref. [4] for migration of PS-*b*-PDMS copolymers through PS matrices, where differences in surface energy of the two components provided the major driving force for migration. The greater effect of host polymer and additive molecular weight on migration in the PS/PS-*b*-PMMA system is in fact expected for a surface migration process driven primarily by entropic forces.

Surface PMMA concentration for PS/PS32K-*b*-PMMA12K blends comprising 10 wt% copolymer in bulk are provided for a range of PS molecular weights in Fig. 4(b). In this case blend samples were prepared by precipitation from toluene solutions using methanol. Except for the more rapid approach to steady state surface compositions, the trends are similar to those seen for the film cast PS/PS13K-*b*-PMMA13K materials. Specifically, both sets of results show: (a) that the driving force for surface migration exist well after the solvent has been removed and that the concentration of PMMA groups at the blend surface is a strong function of annealing conditions; (b) above a PS molecular weight approximately one half that of the PS-*b*-PMMA copolymer the concentration of PMMA groups at the surface increases nearly linearly with M_{PS} ($\Delta\Phi_{PMMA} \sim M_{PS}^{0.8\pm0.04}$), up to $M_{PS} \approx 3.5 \times 10^5$ g mol^{-1}. This trend is again much stronger than observed in Ref. [4] for surface tension-driven migration; (c) beyond a PS matrix molecular weight $M_D \approx 5.5 \times 10^5$ g mol^{-1} the surface excess MMA $\Delta\Phi_{PMMA} = \Phi_{PMMA,S} - \Phi_{PMMA,B}$ remains positive, but decreases rather sharply with increasing M_{PS}. Here, $\Phi_{PMMA,S} = \Phi_{PMMA}$ is the weight fraction of PMMA at the surface and $\Phi_{PMMA,B} = \Phi_B$ is PMMA weight fraction in bulk.

Faster transport of PS-*b*-PMMA copolymer to the surface of precipitated blends is consistent with the greater initial porosity of these materials. The absence of appreciable surface migration in unannealed blends prepared by precipitation underscores the utility of the method for preserving bulk compositions at blend surfaces when desired. The dramatic sensitivity of the surface compositions to annealing conditions is obviously desirable in situations where surface functionalization by spontaneous copolymer migration is desired after polymers shaping processing steps are complete. An initial linear dependence of excess PMMA surface concentration $\Delta\Phi_{PMMA}$ with M_{PS} can be rationalized by either of the two entropic mechanisms discussed in Section 1. However, the DCA results (Fig. 3(a)) indicate that the effect saturates at $M_{PS} \approx 10^5$ g mol^{-1}, which is similar to the molecular weight at which the contribution of chain end entropy to the surface tension of pure polymers saturate. This last observation leads us to the tentative conclusion that migration in the PS/PS-*b*-PMMA system is most likely driven by gradients in chain end entropy. Furthermore, if the surface excess PMMA measured using materials with fixed M_{PS} and MMA composition in bulk, but variable copolymer additive molecular weight M_a, a relationship $\Delta\Phi_{PMMA} \sim M_a^{-0.53\pm0.05}$ is apparent from the data. This trend is nearly identical to that deduced from surface composition data reported by Tanaka et al. [15] ($\Phi_{PMMA} \sim M_{PMMA}^{-0.5}$) from studies of PMMA migration in incompatible PS/PMMA blends, suggesting that the migration mechanism in the two systems are similar. More detailed measurements of the near-surface concentration profile are needed to permit more rigorous comparisons to theory and to facilitate firmer conclusions about the surface migration mechanism in the system PS/PS-*b*-PMMA. We have recently begun work using Rutherford backscattering (RBS) spectroscopy and neutron reflectivity measurements with this precise goal in mind. This work will be the subject of a forthcoming publication.

The down-turn in $\Delta\Phi_{PMMA}$ with $M_{PS} \geq 5.5 \times 10^5$ g mol^{-1} shown in Fig. 4(a),(b) is inconsistent with all of the proposed mechanisms for surface migration in PS/PS-*b*-PMMA identified in Section 1. The onset molecular weight for the down-turn is sensitive to annealing conditions,

suggesting that slower PS-*b*-PMMA transport through high molecular weight PS hosts is very likely the source of this behavior. Consider the surface excess PMMA $\Delta\Phi_{PMMA}$ produced by transport of a PS-*b*-PMMA additive in a semi-infinite PS/PS-*b*-PMMA blend of thickness H. At short times and thin diffusion films, the surface excess PMMA should satisfy

$$\Delta\Phi_{PMMA} \approx \frac{2}{\delta}\sqrt{\frac{D_M t}{\pi}},$$

where δ is the thickness of the surface layer in which concentration is measured ($\delta/H \approx 0.01$) and we have implicitly assumed that the driving force for transport is sufficiently weak that it can be approximated as a linear function of the composition difference. The mutual diffusion coefficient D_M can therefore be estimated from the slope of a plot of $\Delta\Phi_{PMMA}$ versus $\sqrt{t}$.

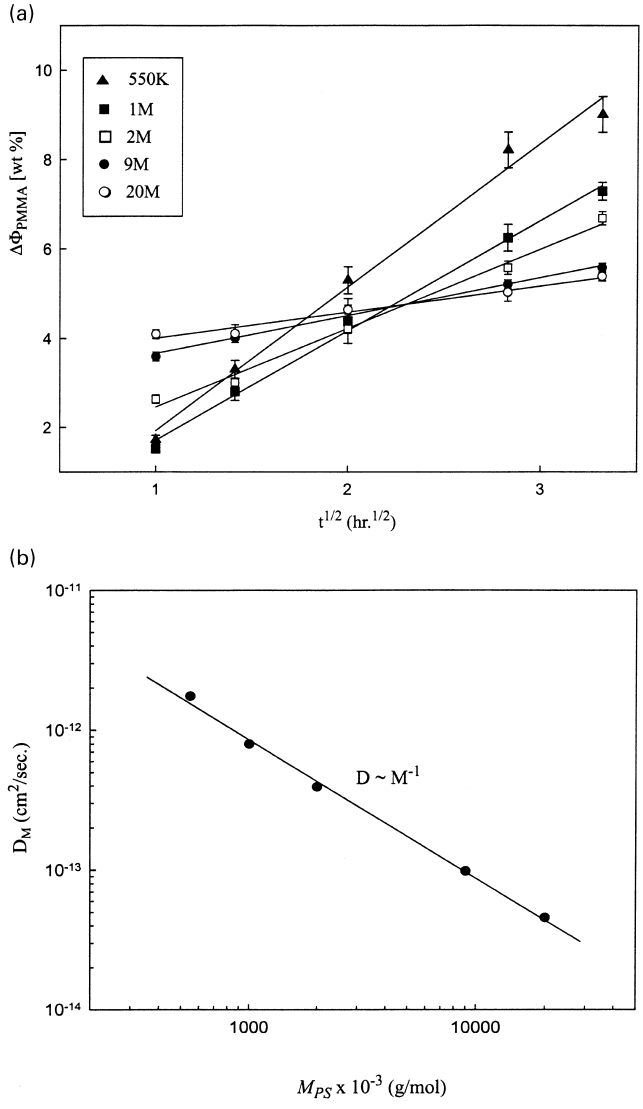

Fig. 5. (a) Surface excess PMMA concentration of PS/PS13k-*b*-PMMA13K blends versus $\sqrt{t}$ after onset of annealing at 180 °C under high vacuum conditions. Blend samples containing 10 wt% copolymer were prepared by solvent casting from toluene. (b) Mutual diffusion coefficient of PS13K-*b*-PMMA13K in PS as a function of matrix PS molecular weight.

Time-dependent surface excess PMMA measured using ATR-FTIR spectroscopy in various high molecular weight PS/PS13K-*b*-PMMA13K blends are shown in Fig. 5(a). Blends were annealed at 180 °C for variable times prior to the ATR measurements. The experimental results clearly show the $\sqrt{t}$ scaling expected for short-time Fickian transport through a semi-infinite slab, confirming our previous assertion that the measured blend surface concentrations at high M_{PS} were non-equilibrium values. Mutual diffusion coefficients deduced from the line slopes in Fig. 5(a) are shown in Fig. 5(b) for various M_{PS}. The figure shows that the experimental results are well described by the relation $D_M = K/M_{PS}$, which disagrees with expectations for transport of unentangled Rouse chains through a fixed polymer network. More careful diffusion coefficient measurements using RBS and forward recoil spectroscopy measurements are underway in our group to determine the source of this behavior. We suspect that micelles created by phase segregation of PS-*b*-PMMA chains in the host PS are in some way responsible for the observed dependence of D_M on matrix polymer molecular weight. A simple analysis of diffusion of a short star-arm through an entangled linear polymer matrix [4] does not predict the effect, however, clearly justifying the need for additional study.

When the experimental data in Fig. 4(a),(b) are reconsidered in light of the observed strong dependence of PS-*b*-PMMA transport coefficient on M_{PS}, $\Delta\Phi_{PMMA}$ is anticipated to either display a plateau or slowly increase with M_{PS} at high polystyrene molecular weights, in agreement with the surface tension data. The contribution of chain end entropy to the total free energy is negligible for high molecular weight polymers. A weaker dependence of surface excess MMA on M_{PS} is therefore consistent with a surface migration mechanism based on differences in chain end entropy. If surface migration is driven instead by the free energy cost of expelling host polymer molecules from copolymer micelles in bulk, one would anticipate a similar saturation of $\Delta\Phi_{PMMA}$ at high M_{PS} on purely physical grounds. However, analyses presented in Refs. [13,28] indicate that the saturation molecular weight should be a stronger function of copolymer molecular weight than observed in our experiments.

4. Conclusions

Surface migration of PS-*b*-PMMA block copolymer additives in polystyrene (PS) hosts was investigated by DCA and ATR-FTIR spectroscopy measurements. Selective surface enrichment of methyl methacrylate (MMA) groups was observed at the air/polymer interface of blends comprising PS host with molecular weights M_{PS} substantially higher than the copolymer additive M_a. The opposite result was observed in blends for which $M_{PS} < M_a$. Surfaces of these

latter blends were found to be depleted of MMA groups. A relationship between surface excess concentration of PMMA $\Delta\Phi_{PMMA}$ and polystyrene molecular weight M_{PS}, $\Delta\Phi_{PMMA} \sim M_{PS}^{0.8\pm0.04}$ for $M_{PS} \leq M_D$, can be defined in blends containing PS-*b*-PMMA of fixed molecular weight M_a and concentration. A somewhat different trend ($\Delta\Phi_{PMMA} \sim M_a^{-0.53\pm0.05}$) approximately describes the effect of PS-*b*-PMMA additive molecular weight M_a on PMMA surface excess in PS/PS-*b*-PMMA blends with fixed M_{PS}.

Using time-dependent ATR-FTIR measurements we have determined that slower transport of PS-*b*-PMMA in PS hosts with progressively higher molecular weight is at least partly responsible for the 'cut-off molecular weight' M_D apparent from migration experiments. Surface tension measurements using film cast PS/PS-*b*-PMMA blends indicate that the driving force for migration saturates at M_{PS} values comparable to the critical molecular weight where chain end contributions to surface tension reaches a plateau in pure polystyrene. This last observation along with the weak dependence of M_D of PS-*b*-PMMA copolymer molecular weight suggests that a migration mechanism based on differences in chain end entropy is quite likely the source of our observations. More detailed studies are needed to determine what role, if any, is played by copolymer micelles on surface migration in homopolymer/block copolymer blends, when the surface tension of the two components are similar.

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