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Functionalizing Polymer Surfaces by Field-Induced Migration of Copolymer Additives. 1. Role of Surface Energy Gradients

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ABSTRACT: Field-induced migration of low surface tension polystyrene-*b*-poly(dimethyl siloxane) (PS-*b*-PDMS) block copolymer additives in a polystyrene (PS) host was investigated using a series of narrow molecular weight distribution polystyrenes ($5 \times 10^3 < M_{\mathrm{w,PS}} < 2 \times 10^7$ g/mol). Dynamic contact angle analysis (DCA) 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. For all host PS molecular weights investigated, selective dimethyl siloxane (DMS) enrichment of the air/polymer interface was observed. Near saturation levels of DMS surface coverage were found in PS/PS-*b*-PDMS blends with bulk copolymer additive compositions as low as 2 wt %. The surface excess concentration of DMS groups $\Delta\phi_{\mathrm{DMS}}$ in these blends could be manipulated, however, by careful selection of the host PS and PS-*b*-PDMS additive molecular weight, annealing conditions, and physicochemical properties of materials comprising the bounding interfaces. The effect of the first two factors on $\Delta\phi_{\mathrm{DMS}}$ can be summarized by an approximate scaling relation, $\Delta\phi_{\mathrm{DMS}} \sim M_{\mathrm{wPS}}{}^{\alpha}$, where the scaling exponent α is a function of annealing conditions. For unannealed PS/PS-*b*-PDMS blend samples, $\alpha \approx -0.5$, whereas for samples annealed for prolonged periods at elevated temperatures α values in the range 0.1−0.15 were found. Surprisingly, PS/PS-*b*-PDMS blend samples annealed at elevated temperatures near high-energy aluminum substrates also manifested enhanced DMS concentration at the polymer/metal interface. These observations are discussed in terms of the molecular weight dependence of diffusivity, surface tension, and configurational entropy of the host polystyrene.

1. Introduction

Surface functionalization of polymers is used to impart specific properties to a polymer's surface that are not present in bulk. Many desirable polymer surface characteristics, such as wettability, paintability, adhesion susceptibility, and biocompatibility, are known to be determined by the chemical make-up of molecules within the first one to five molecular layers from the surface. These properties often demand different polymer physiochemical characteristics than those responsible for bulk mechanical performance, which generally makes it difficult to achieve acceptable surface and bulk properties using a single homopolymer material.

Conventionally, polymer surface functionalization is achieved using chemical or physical processes (e.g., plasma or flame treatment, chemical reaction, surface grafting, and surface coating of finished articles), designed to change polymer surface characteristics without producing substantial changes in bulk material properties.[1] The surface of polyethylene films, for example, can be functionalized with sulfonyl or carbonyl groups using chemical reaction of the virgin polymer with sulfuric acid and with chromic acid, respectively.[2,3] Ketones may be introduced by subjecting the polymer to a plasma discharge in an oxygen environment.[4] These surface functionalization approaches are difficult to implement on a large scale for a number of reasons: (a) they invariably require specialized equipment to implement; (b) new synthetic steps must be added to already expensive polymer processing operations; and (c) complete surface functionalization cannot always be achieved, especially when used to modify surface properties of intricately molded articles. In addition, the task of removing trace amounts of chemicals inevitably left behind by these processes is expensive.

There is a longstanding need for alternative 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.[1−5] The premise here is that if a surface active additive with desirable functional groups is blended in small amounts with the 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. This approach for surface modification is attractive for several reasons: (i) The bulk properties of polymer products are not substantially changed since a small amount of additives (1−2 wt %) is believed sufficient to achieve the desired surface modification. (ii) The process relies on physical forces to maintain additive molecules at the host polymer's surface; it is therefore not limited by the ability to control chemical reactions on a mobile polymer surface. (iii) The surface modification process can be integrated into conventional polymer processing operations, such as solution casting or melt extrusion, and therefore requires no new equipment.[1,5] (iv) Provided that the additive can be made to migrate to the host polymer's surface, any functional group or perhaps even combinations of desirable functional groups can be presented at the host polymers surface.

The objective of this study is two-fold. First, to determine the basic principles that govern surface migration of copolymer additives in a homopolymer

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matrix, and second, to develop fundamentally based general procedures for modifying polymer surfaces based on copolymer migration in a host polymer melt or solution. We are particularly interested in systems where the majority component in the copolymer additive is chemically identical to the host and where both host and copolymer additives can be synthesized with narrow molecular weight distributions and well-defined architectures. These systems are advantageous because interactions (topological and/or secondary bonds) between additive and host polymer provides desirable long-term durability of surface coatings produced by migration.[6] Complexities associated with separate effects arising from polydispersity, branching, etc., can also be avoided.

This paper, the first in a series of three, considers selective enrichment of polystyrene (PS) by poly(dimethyl siloxane) (PDMS) in melt and solution blends of PS/PS-*b*-PDMS. Because the surface energies of PS and PDMS are quite dissimilar ($\gamma_{PS} \approx 30-34$ mN m^{-1}, $\gamma_{PDMS} \approx 15-19$ mN m^{-1}),[7,8] migration in this system is anticipated to be driven by the surface energy difference between additive and host polymer. In the second paper, we study surface migration in the system PS/PS-*b*-PMMA ($\gamma_{PMMA} \approx 31-41$ mN m^{-1})[8] and in oligomeric PS/high molecular weight PS homopolymer blends. In these two systems differences in surface energy are too small to drive migration. Differences in host polymer and additive molecular weight are therefore believed to be the main cause of additive surface migration. Finally, in the third paper we investigate the effect of shear on migration in a Poiseuille flow geometry. In that study we determine the role played by stress gradients and normal stresses in promoting (or suppressing) surface migration in polymers.

2. Background

There are numerous examples of polymer systems where additives of one type or another spontaneously migrate to a host polymer's surface. *Blooming* of small-molecule additives such as plasticizers and antioxidants in poly(vinyl chloride) (PVC),[9] and surface segregation of fatty acid *slip agents* in polyolefins processing to reduce mechanical work,[10] have long been identified and studied. There is also a large body of experimental[11-18] and theoretical[19-25] research concerning preferential surface enrichment by one component of two-component homopolymer blends. The physical processes responsible for surface migration in polymers, particularly in systems where migration can occur by multiple mechanisms, are the focus of this study.

One school of thought is that migration is driven by surface free energy differences between the host polymer and additive $F_\gamma \sim \Delta\gamma$.[12-14,16] The fact that the system's (polymer/additive mixture) free energy is minimized by a higher concentration of additive at the host polymer surface is thought to provide the thermodynamic driving force for migration. This mechanism has been used, for example, by Thomas et al.[26] to explain selective enrichment of polystyrene in PS-*b*-PEO diblock copolymer films cast from different solvents. Likewise, differences between the surface tension of polystyrene and poly(vinyl methyl ether) (PVME) have been credited for surface enrichment of PVME in miscible polystyrene/poly(vinyl methyl ether) (PS/PVME) blends.[16] The same mechanism is believed responsible for surface segregation of PDMS in immiscible polystyrene/poly(dimethyl siloxane).[18-21]

Surface migration in response to a surface tension gradient is not however limited to additive/polymer systems where chemical dissimilarities are the source of surface tension differences. In fact, the surface tension of a homopolymer is well-known to follow a simple scaling relationship,[29,30] $\gamma = \gamma_\infty - k_0/(M_n)^\alpha$, where γ_∞ is the surface tension in the limit of infinite polymer molecular weight and k_0 a constant. Jalbert et al.[29] contend that depending on the surface energy of polymer chain ends and chain backbone the constant k_0 could be positive, negative, or even zero. Thus, for PDMS terminated with hydrophilic end groups, $k_0 \approx 0$, and no dependence on molecular weight is expected. In the opposite case (PDMS terminated by hydrophobic groups), k_0 is positive and $\alpha \approx {}^2/_3$, indicating a strong increase in interfacial tension should occur as polymer molecular weight increases. De Gennes[30] proposed that α itself reflects changes in interaction strength between polymer chain end groups and a surface ($\alpha \approx 1$ for repulsive interactions and $\alpha \approx 0.5$ for attractive ones). For positive k_0, γ should therefore always increase with increasing polymer molecular weight.

A second school of thought contends that the configurational entropy per segment of polymer chains near rigid surfaces is substantially lower than in bulk polymer systems.[31,32] Thus, the highest molecular weight polymer component in a mixture experiences a large entropy penalty for residence near the surface. In homopolymer systems, it has been suggested that this should result in greater concentration of polymer chain ends at surfaces.[8] In a polydisperse melt, the polymer layer near the surface would therefore be expected to be depleted in high molecular weight polymer components and enriched in lower molecular weight ones. Thus, even in systems where no substantial difference exists between additive and polymer surface energetics, surface migration could be made to occur by selecting additives with molecular weights significantly lower than that of the host polymer.[23] In polymer solutions, the depletion polymer layer near a phase interface may be filled with low molecular weight solvent molecules, producing a low-viscosity fluid layer at the surface. This last possibility has in fact been cited as one cause of apparent slip violations in polymer solutions sheared between metallic substrates.[33,34]

Finally, in polymer systems subject to flow fields, stress gradients have long been thought to produce migration.[35-39] The argument in this case is fundamentally similar to that used to support the existence of a polymer depletion zone near a surface. The main difference is that in flow fields, such as Poiseuille flow down tubes or through slits, stresses are largest near the conduit walls; the configurational entropy of macromolecular units is therefore lowest near walls. Migration of high molecular weight material away from the wall follows from the much greater degree of configurational freedom possible in the bulk. In a rectilinear flow (e.g., Poiseuille or plane-Couette shear) two of the three normal stresses by definition act perpendicular to flow lines. Large normal stresses at high flow rates could therefore provide an additional driving force for cross-streamline migration of a low-viscosity additive in a polymer host.

3. Experiment

3.1. Materials and Sample Preparation. This study focuses on migration of narrow molecular weight distribution

Table 1. Characteristics of Polymers Used in the Study

polymer	M_w	M_w/M_n	source
PS1(polystyrene)	13 000	<1.02	Polymer Labratories
PS2(polystyrene)	90 000	<1.04	Pressure Chemical Co.
PS3(polystyrene)	935 000	<1.05	Aldrich Chemical Co.
PS4(polystyrene)	1 880 000	<1.05	Aldrich Chemical Co.
PS5(polystyrene)	2 000 000	<1.2	Pressure Chemical Co.
PS6(polystyrene)	5 480 000	<1.15	Tosoh Co.
PS7(polystyrene)	6 680 000	<1.22	Polymer Source Inc.
PS8(polystyrene)	8 990 000	<1.22	Polymer Source Inc.
PS58K-*b*-PDMS7K	65 000	<1.05	Polymer Source Inc.
PS193K-*b*-PDMS39K	232 000	<1.08	Polymer Source Inc.

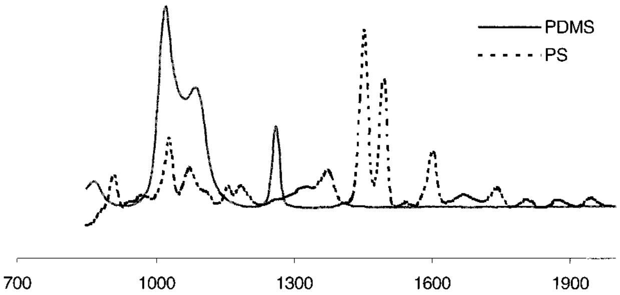

Figure 1. Attenuated total reflectance Fourier transform infrared (ATR−FTIR) spectra of pure polystyrene (PS) and poly(dimethyl siloxane) (PDMS).

PS-*b*-PDMS diblock copolymers in host polystyrenes covering a broad range of molecular weights. PDMS content in the copolymers range from 0.04 to 16 wt %. Molecular weight and other pertinent information about all polymers used in the study are provided in Table 1. All but one of the polystyrenes (PS 1) are of sufficiently high molecular weight that entanglement constraints can be assumed to dominate long-time dynamics. PS/PS-*b*-PDMS blend samples were prepared using two techniques, solution casting and precipitation. Solution cast samples were obtained by dissolving polymer components in the desired ratio in toluene at room temperature, to create solutions containing 2 wt % polymer. Subsequent evaporation of the toluene at 30 °C over a 24 h period yielded sample films with controlled thickness in the range 40−50 μm. Because the block copolymer systems used in the study are dominantly polystyrene (Table 1), selective surface enrichment due to differential miscibility of the polymer components in toluene is minimized during casting.

Precipitated samples were obtained using a simple two-step procedure. In the first step, a large quantity of methanol was injected into the PS/PS−PDMS/toluene blend solution and the mixture agitated vigorously. The polymer precipitate produced was carefully separated from the supernatant liquid by decantation. Subsequent evaporation of the remaining methanol and toluene over a 24 h period at room temperature yielded polymer/additive blends suitable for further study. To eliminate the effect of solvent and sample preparation history, polymer samples prepared by both methods were thermally annealed at 185 °C for periods ranging from 0.5 to 15 h under a nitrogen blanket prior to measuring their surface composition. Thermal annealing at even higher temperatures and for longer periods of time was prohibited by sample degradation.

3.2. Surface Analysis. Dimethyl siloxane (DMS) surface composition was analyzed using ATR−FTIR and dynamic contact angle (DCA) measurements. ATR−FTIR spectra were acquired at a fixed incident angle (45°), using a Nicolet ATR−FTIR spectrometer equipped with a germanium crystal. Infrared-active vibration modes associated with the Si−C asymmetric stretch (1250 cm^{-1}) and the aromatic C=C stretch (1600 cm^{-1}) (see Figure 1) were used to determine DMS surface concentration. The penetration depth d_p in the ATR measurements can be estimated to be 0.53 μm at 1250 cm^{-1}, using the formula $d_p = \lambda/[2\pi n_c(\sin^2\theta - (n_s/n^c)^2)^{1/2}]$.[40] Here $n_c = 4.0$ and $n_s = 1.5$ are the refractive indices of the ATR crystal and polymer sample, respectively. A new calibration method based on ATR−FTIR measurement of PS−PDMS solutions of known concentration in toluene was used to quantify surface concentrations (see Figure 2). This calibration procedure is attractive because it removes measurement uncertainties that arise from known differences in transmittance and attenuated total internal reflectance infrared spectra.[40]

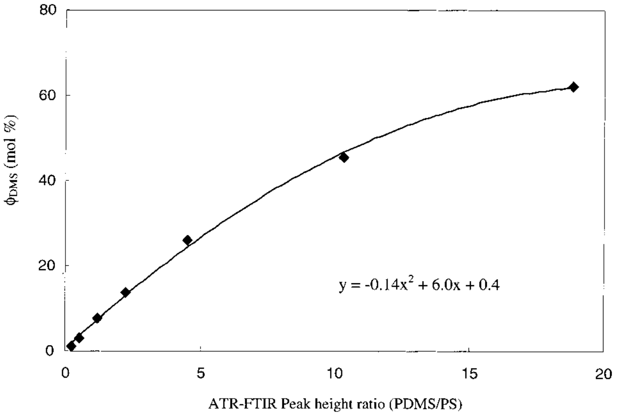

Figure 2. Calibration curve for surface DMS concentration vs ATR peak ratio. A calibration procedure based on ATR−FTIR measurements using standard solutions of PS-*b*-PDMS in toluene was used. ATR−FTIR maximum absorbance ratios corresponding to the asymmetric Si−CH$_3$ stretch for PDMS and the aromatic C=C stretching vibration in PS were used in the calibration.

Dynamic contact angle analysis was performed by a Cahn Intruments Inc. DCA315 device, using the Wilhelmy plate method. This method facilitates surface tension measurements of solids and is 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 to create thin, uniform films of polymer on the substrate. The force generated when the polymer-coated glass substrate enters a test liquid, such as water, or, when it just breaks free from the liquid, can be used to compute the surface tension γ_L of the liquid.[41] Once γ_L is determined from a first contact or pull-out experiment, the force measured when the probe advances slowly through the test liquid can be used to determine the equilibrium advancing contact angle of the liquid on the solid. Measurements of advancing contact angles in liquids with dissimilar polarities (e.g., water and ethylene glycol) can be used to estimate the surface tension γ_s of the polymer film.[42]

4. Results and Discussion

4.1. Effect of Concentration and Preparation Method on Migration. ATR−FTIR absorbance spectra of pure PS and PMMA are shown in Figure 1. As evident from the figure, the infrared absorption band at ca. 1250 cm^{-1} is unique to PDMS, while the band at 1600 cm^{-1} is a characteristic feature of PS units. The 1250 cm^{-1} infrared peak results from the asymmetric stretching vibration mode of Si−C groups present in DMS, and the 1600 cm^{-1} peak results from aromatic C=C vibrations in polystyrene. Since the PS/PS-*b*-PDMS blend samples used in the present study are dominantly styrene, little change in the 1600 cm^{-1} infrared band is anticipated to accompany changes in copolymer surface concentration. The ratio of the 1250 cm^{-1} to the 1600 cm^{-1} absorption intensities should therefore be quite sensitive to DMS composition within the first 0.5−1 μm of the blend surface.

Pure PDMS is known to possess much lower surface energy than polystyrene ($\gamma_{PDMS} \approx 15$ mN m^{-1}; cf. $\gamma_{PS} \approx 36$ mN m^{-1}). In the absence of strong attractive PS/substrate interactions or repulsive PDMS/substrate

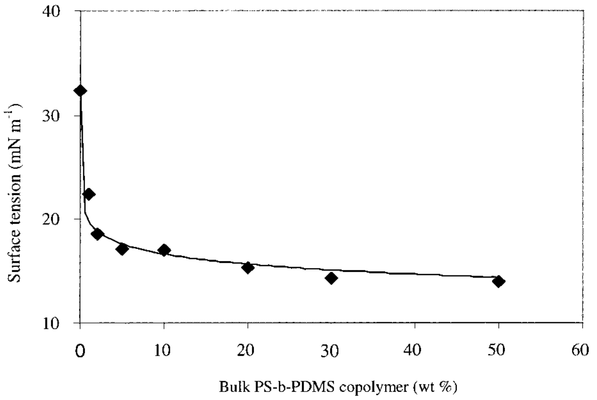

Figure 3. Surface tension of PS193K-*b*-PDMS39K/PS393K as a function of PS-*b*-PDMS copolymer concentration. Surface tensions of solid films of the polymers deposited on glass slides were estimated using dynamic contact angle analysis (DCA) in ethylene glycol and deionized water.

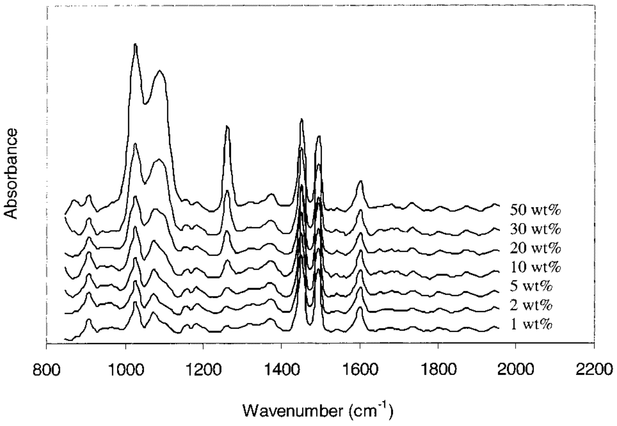

Figure 4. ATR−FTIR absorbance spectra for PS193K-*b*-PDMS39K/ PS393K blends cast from toluene at room temperature with varying copolymer concentrations.

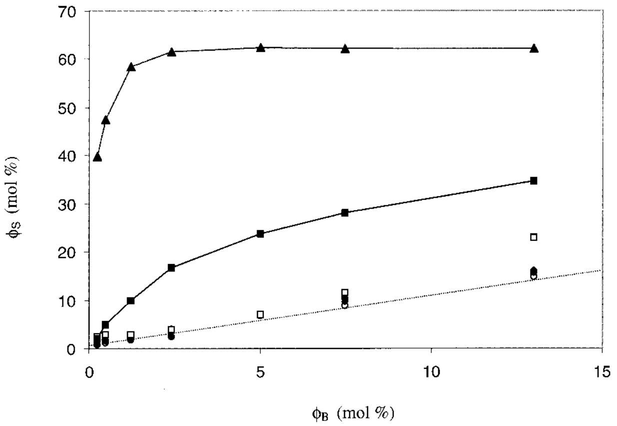

Figure 5. Surface dimethyl siloxane (DMS) concentration vs bulk concentration for PS390K/PS193K-*b*-PDMS39K blends subjected to a wide range of annealing and preparation conditions. Filled circles, air-side precipitated sample at 25 °C; filled diamonds, air-side cast sample at 25 °C; open circles, aluminum-side precipitated sample, 185 °C × 5 h annealing; open squares, air-side cast sample, 145 °C × 5 h annealing; filled squares, air-side cast film, 185 °C × 5 h annealing; filled triangle, air-side precipitated sample, 185 °C × 5 h annealing. Straight solid line represents expected result for $\phi_S = \phi_B$.

interactions, the surface free energy of a PS/PDMS mixture is minimized by a larger concentration of DMS groups at the mixture surface. Figure 3 summarizes dynamic contact angle results for a PS/PS-*b*-PDMS blend ($M_{w,PS} = 3.9 \times 10^5$ g/mol and $M_{w,PS-b-PDMS} = 1.93 \times 10^5$ g/mol-*b*-3.9×10^4 g/mol) for a range of copolymer concentrations in bulk. This blend was cast at room temperature from toluene solution onto a glass DCA probe substrate. It is immediately evident from the data that, even at copolymer concentrations as low as 1%, DMS groups dominate surface energetics of the blend. At higher bulk copolymer concentrations, the surface tension decrease follows a weak single-exponential function of copolymer concentration, approaching the surface tension of pure PDMS at concentrations above ca. 20 wt %. It is also clear from the data that a PS surface almost completely functionalized with DMS groups can be achieved at bulk copolymer concentrations as low as 2 wt %.

ATR−FTIR spectra obtained using PS/ PS-*b*-PDMS blend films cast at room temperature are provided in Figure 4. Data for various bulk copolymer concentrations have been offset by a fixed constant for clarity. Molecular weights of the PS matrix and PS-*b*-PDMS copolymer additive are the same as those used for the DCA experiments. Surface DMS concentrations computed with the help of the ATR−FTIR calibration curve (Figure 2) are provided in Figure 5 for polymer film samples prepared under a variety of postcasting thermal annealing conditions. Surface composition data for samples prepared by precipitation are also provided for comparison. The straight line through the data represents expectations for a homogeneous blend.

Very little change in surface composition is evident from ATR−FTIR measurements on polymer blend samples (cast or precipitated) annealed at room temperature. This result might at first seem surprising, because DCA measurements on similar materials (see Figure 3) indicate near-saturation levels of DMS surface coverage at bulk blend concentrations as low as 2 wt % (i.e., approximately 3.2 mol % DMS). Consideration of the gross differences in surface depth scales probed by the two methods (~5 Å for DCA and >0.5 μm for ATR−FTIR) provides an explanation for the difference. Namely, that the ATR−FTIR experiments are averaged over a much greater thickness of blend material and, as a result, provide a more pessimistic estimate of additive concentration at the host polymer surface. Quantitative correspondence between surface compositions reported by FTIR−ATR and DCA analysis of PS/PS-*b*-PDMS blends is in fact only expected when the surface PDMS layer thickness becomes sufficiently large to mask the PS-rich underlayer in the ATR−FTIR average. This last is precisely what is observed for polymer films annealed at elevated temperatures (see Figure 5).

The fact that thermal annealing enhances DMS surface coverage is significant because it indicates that the driving force for preferential DMS surface segregation exists well after the solvent has been removed. Thus, enhanced DMS surface concentration produced by differences in solubility of PS and PDMS in the casting solvent is ruled out as the cause of the observed DMS surface enrichment. Additional support for this point is apparent from data obtained using precipitated PS/PS-*b*-PDMS blends (Figure 5), which show that even higher levels of DMS surface coverage are possible in samples annealed under the same conditions as the cast samples. Figure 5 in fact suggests that DMS surface coverages approaching 60 mol % are possible in precipitated blend samples when as little as 2 mol % DMS groups are present in bulk. We believe that the larger

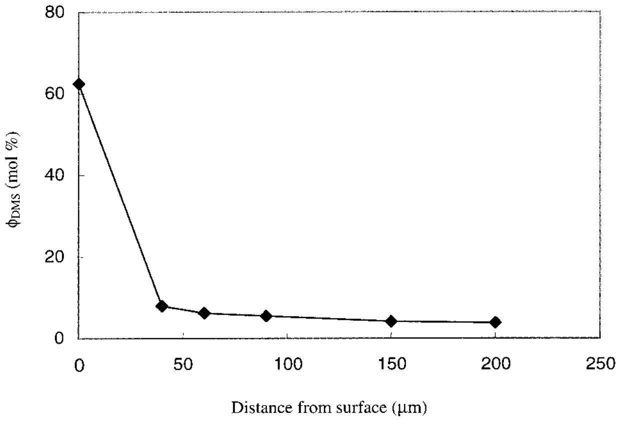

Figure 6. DMS concentration as a function of distance from the surface in μm. Blend samples were created by precipitating a 10 wt %/90 wt % (10/90) blend of PS193K-*b*-PDMS39K/PS2M in toluene using excess methanol. Precipitated samples were annealed for 5 h at 185 °C.

excess DMS surface concentration ($\Delta\phi_{DMS,surface} = \phi_{DMS,surface} - \phi_{DMS,bulk}$) in the precipitated blends results from a combination of faster initial transport (see section 4.2) and larger volume/surface ratio of these materials.

PS/PS-*b*-PDMS blend samples prepared using the precipitation technique are of sufficiently large thickness that physical, noncryogenic microtomy methods could be used to section the materials into several ca. 25 μm layers, along the surface normal. Using this approach, the surface selectivity of PS functionalization by PS-*b*-PDMS can be evaluated further. Figure 6, for example, summarizes the depth dependence of DMS surface concentration. The figure shows that at a depth of around 50 μm from the surface DMS concentration quickly falls below 5% of the surface value. Optical microscopy measurements of thermally annealed sample specimen reveal large nonuniform droplets of PS-*b*-PDMS on the host polymer surface. Similar observations have been reported by Shull et al., in block copolymer compatibilized blends of polystyrene and poly(vinylpyridine) (PVP), where entire PS−PVP copolymer micelles were found to localize at the PS/PVP blend interface.[43] The average size of the PS-*b*-PDMS droplets was generally larger for precipitated blends than for solvent cast ones annealed under comparable conditions. Droplet sizes were also found to increase rapidly with annealing time at fixed temperature. These results suggest that even higher DMS surface coverage could be achieved if longer annealing times and blend samples with larger volume/surface ratios were used.

4.2. Effect of Polystyrene Matrix Molecular Weight. Figure 7 summarizes surface tension results for several blend samples of PS/PS-*b*-PDMS with fixed copolymer molecular weight and composition in the blend (10 wt %) but variable PS matrix molecular weight, M_{wPS}. Samples were prepared by film casting polymer/copolymer blends from toluene at room temperature. For low M_{wPS}, the surface tension of the blends are close to values expected for pure PDMS. At higher matrix PS molecular weights, however, a weak increase in surface tension is apparent. A similar observation can be made from ATR−FTIR results obtained using the same blend systems annealed at 185 °C for short times (Figure 8). For short annealing times (ca. 30 min), the excess DMS surface composition ($\Delta\phi_{DMS}$) decreases with increasing M_{wPS} ($\Delta\phi \sim M_{wPS}{}^{-0.5}$), in qualitative agreement with the surface tension results. Samples annealed for much longer times, however, reveal an almost opposite trend ($\Delta\phi \sim M_{wPS}{}^{0.13}$). Materials annealed for intermediate times show changes in excess DMS surface composition with M_{wPS} intermediate between the two extremes. Although these results appear to point to a diffusion-limited process for DMS transport to the host PS surface, the implicit dependence of the transport coefficient on matrix polymer molecular weight is unexpected.

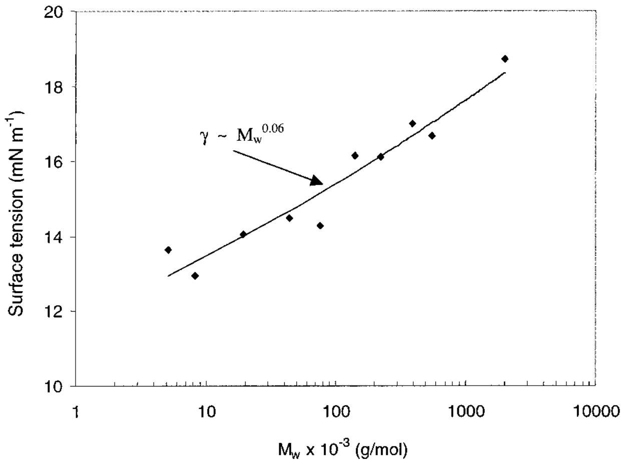

Figure 7. Surface tension of PS/PS193K-*b*-PDMS39K blend as a function of matrix PS molecular weight. Surface tensions were measured using dynamic contact angle analysis.

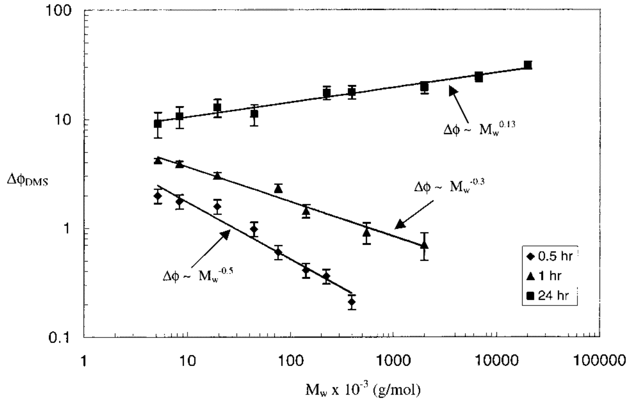

Figure 8. Surface excess DMS concentration for several 10 wt % PS193K-*b*-PDMS39K/PS blend samples at various PS molecular weights. Samples were cast from toluene, evaporated for 24 h at 25 °C, and subsequently annealed at 185 °C.

To explore this point further, time-dependent changes in DMS surface composition for a few selected values of M_{wPS} were studied in detail. Figure 9a presents results for two film cast materials with PS matrix molecular weights $M_w = 6.7 \times 10^4$ g/mol and $M_w = 2.0 \times 10^6$ g/mol. Curve fits to the experimental data indicate that a weakly non-Fickian diffusive transport process could describe DMS surface migration in the blends. Similar results are seen for the precipitated PS/PS-*b*-PDMS blends, except the deviations from Fickian diffusive transport are greater and the effective transport coefficients substantially larger (see Figure 9a,b). This difference is believed to be caused by higher porosity of the precipitated samples. Both sets of results do, however, suggest that DMS compositions of PS/PS-*b*-PDMS blends annealed at temperatures below the effective glass transition temperature of the blend, $\approx T_{g,PS}$, or annealed for short times at temperatures above $T_{g,PS}$ are not equilibrium concentrations.

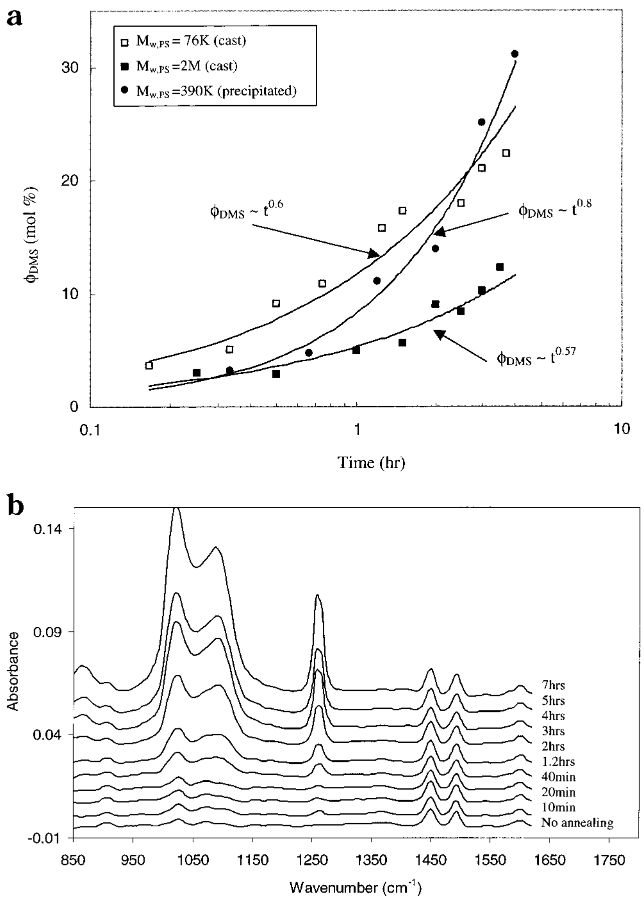

Figure 9. (a) Time-dependent surface DMS concentration following onset of annealing at 185 °C for two film cast materials with PS matrix molecular weights $M_w = 6.7 \times 10^4$ g/mol and $M_w = 2.0 \times 10^6$ g/mol containing 10 wt % PS193K-*b*-PDMS39K copolymer and for a 5/95 PS193K-*b*-PDMS39K/PS390K blend sample prepared by precipitation. (b) Time-dependent ATR−FTIR spectra following onset annealing at 185 °C for a precipitated 5/95 PS193K-*b*-PDMS39K/PS390K polymer blend sample.

Figures 9a indicates that slower transport of PS-*b*-PDMS through a higher molecular weight PS matrix reduces nonequilibrium $\Delta\phi_{\mathrm{DMS,surface}}$ as the host PS molecular weight increases. This result is surprising because conventional thinking holds that the diffusivity of a short linear polymer tracer through a high molecular weight entangled polymer network consisting of chemically identical chains is independent of the network polymer molecular weight.[44,46] Considering the dominance of PS in PS/PS-*b*-PDMS blends studied here and that the annealing temperature is well above $T_{\mathrm{g,PS}}$, the dependence of $\Delta\phi_{\mathrm{DMS,surface}}$ on M_{wPS} seen at short and intermediate annealing times (Figure 8) is inconsistent with expectations based on this viewpoint. A related observation was reported by Green et al.[12] from measurements of tracer diffusion of deuterated polystyrenes (d-PS) in PS-*b*-PMMA copolymers. These authors found that the tracer diffusion coefficient for d-PS (D_{dPS}) decreased with increasing matrix copolymer molecular weight (M_{C}), roughly as $D_{\mathrm{dPS}} \sim M_{\mathrm{C}}^{-0.55}$. The authors were unable to rationalize their observations in terms of molecular weight dependent changes in morphology of the copolymer host. No such changes in morphology are anticipated in the system studied here, copolymer diffusing through a homopolymer host.

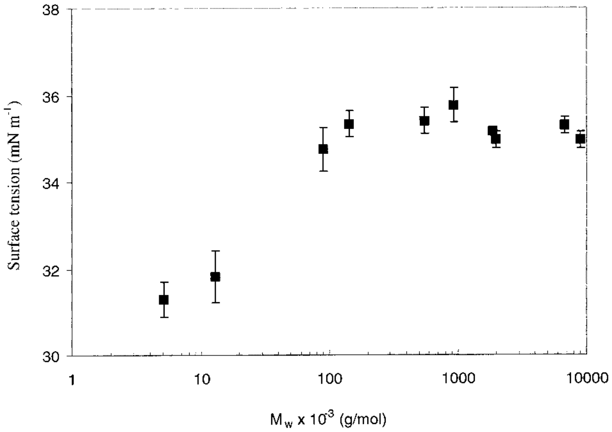

Figure 10. Surface tension of pure PS at 25 °C vs PS molecular weight.

A possible explanation for our observations can be obtained with the help of an analogy to diffusion of entangled starlike polymers in an entangled linear polymer matrix. This analogy is realized when (a) the probe is a diblock copolymer consisting of two immiscible blocks (e.g., PS−PDMS), (b) the copolymer probe volume fraction in the homopolymer matrix is large enough to induce micelle formation, and (c) the molecular weight of PDMS in the micelle core is sufficiently small that the core may be modeled as a point constraint on the entangled PS-block (arms) (see ref 6). Brochard-Wyart et al. have analyzed diffusion of star polymer molecules (Z-mer arms) in a medium of entangled linear chains (N-mers). They conclude that except for very short arms (Z less than around 5−10 times N_{e}), where arm retraction (AR) is the dominant transport mechanism for the star arms, constraint release (CR) of Z-mer arms by reptating N-mers dominates, regardless of the size of N.[48] The diffusion coefficient of the star molecule is therefore anticipated to show a N dependence ranging from $D_{\mathrm{S}} \sim N^{-3.0}$ to $D_{\mathrm{S}} \sim N^{-2.5}$, depending on the relative sizes of Z and N. An analysis by Mhetar and Archer for a Z-mer arm pulled by one end with a small force through a sea of chemically identical entangled N-mer chains, yields $D_{\mathrm{S}} \sim N^{-2}$.[33] Both scaling predictions are evidently much stronger than estimates from our experimental results, perhaps indicating that a combination of AR and CR diffusion may be present in the materials used in the experiments (e.g., for PS/PS193K-*b*-PDMS39K, $Z/N_{\mathrm{e,PS}} \approx 10$).

If the weak decrease of $\Delta\phi_{\mathrm{DMS,surface}}$ with M_{wPS} is of diffusive origin, the observed increases in $\Delta\phi_{\mathrm{DMS,surface}}$ with M_{wPS} for samples subjected to long periods of thermal annealing point to a matrix molecular weight-dependent thermodynamic driving force for PS-*b*-PDMS segregation to the blend surface. Since the dominant driving force for migration in the present system is the interfacial energy difference between copolymer additive and host polymer, the molecular weight dependence of γ_{PS} could be the source of this behavior. To address this point further, DCA measurements were performed on homopolymer polystyrenes covering a very broad range of molecular weights. Surface tensions determined from these measurements are provided in Figure 10. An equation of the form $\gamma = \gamma_\infty - k_0/(M_{\mathrm{n}})^{\alpha}$, with $\gamma_\infty \approx 36$ mN m^{-1}, $\alpha \approx 2/3$, and $k_0 \approx 1600$ mN m^{-1} (g/mol)$^{2/3}$, fairly approximates the experimental surface tension data for all but the highest molecular weight PS. The measured α is consistent with previous experimental results for

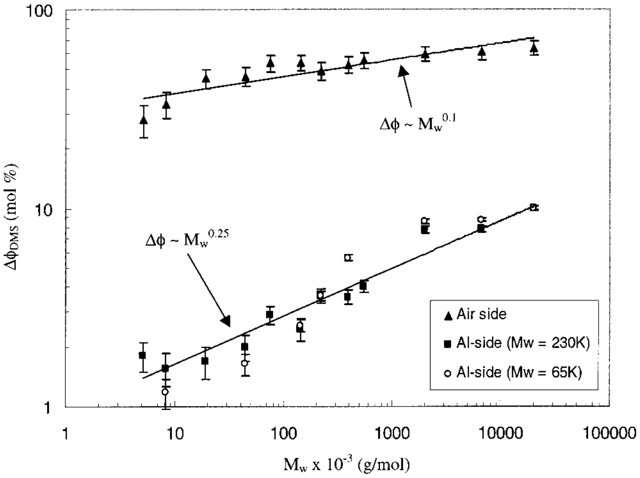

Figure 11. Surface excess DMS at low- and high-energy interfaces vs matrix PS molecular weight for precipitated 10/90 PS193K-*b*-PDMS39K/PS and 10/90 PS58K-*b*-PDMS7K/PS blend samples annealed for 5 h at 185 °C.

polystyrene, but the experimental k_0 value is different,[7] perhaps reflecting slight differences in polarity of the terminating groups used in the two studies. As the molecular weight of the PS matrix increases, the interfacial energy difference between the PS-*b*-PDMS copolymer additive and the host polymer should therefore become larger, enhancing the driving force for surface migration of the additive. This expectation though qualitatively consistent with the experimental observations yields an overall dependence of $\Delta\phi_{DMS,surface}$ on M_{wPS} that is about 5 times too strong. More careful scrutiny of Figure 10 does show however that γ_{PS} is nearly independent of M_{wPS} beyond a molecular weight of around 1×10^5 g/mol, which could explain the weaker dependence of $\Delta\phi_{DMS,surface}$ on M_{wPS} seen in the experimental results.

4.3. Surface Energetic Effects. Up to this point we have assumed that when a low surface energy additive migrates to the surface of a host polymer, it reduces the surface free energy of the system. There are, however, important practical situations where the host polymer is bounded by high-energy metallic substrates and the system free energy might be increased by migration of a lower surface energy additive to the interface. To investigate this issue further, PS/ PS-*b*-PDMS blends prepared by the precipitation method were annealed in laboratory aluminum weighing pans at elevated temperatures for periods ranging from 2 to 5 h. After annealing, DMS content at the polymer/aluminum and polymer/air interfaces was quantified. Figure 11 summarizes the experimental results for a wide range of matrix PS molecular weights and two PS-*b*-PDMS molecular weights. Very large differences in DMS content at the air/polymer and polymer/aluminum interfaces are clearly evident from the figure. This observation confirms that migration of low surface energy DMS groups to the lower energy polymer/air interface is preferred. Surprisingly, the experimental results also show a clear excess of DMS groups, particularly for large host polystyrene molecular weights, near the high-energy aluminum surface. This observation suggests that a second mechanism for surface migration might exist in these materials. Unlike the air−side surface excess DMS concentration data which manifests little if any dependence on M_w, beginning at a host PS molecular weight around 100 000 g/mol, the aluminum-side data show a much stronger dependence on matrix polymer molecular weight. Nearly identical results are observed for PS/PS-*b*-PDMS blends with lower copolymer molecular weight, except that the trend toward stronger dependence on host $M_{w,PS}$ is apparent even at lower $M_{w,PS}$.

Our findings suggest that migration of PS-*b*-PDMS to the high-energy interface may be driven by the molecular weight difference between copolymer additive and the polystyrene host. As discussed in the Introduction, high molecular weight chains are believed to experience greater configurational entropy penalties than low molecular weight ones for residence near impenetrable surfaces.[31,32] For Gaussian homopolymer chains, it has been suggested that the entropy penalty should yield an enhancement in the surface concentration of chain ends $\rho_s \sim M^{-0.5}$ (compared with $\rho \sim M^{-1}$, in bulk).[45] Thus, for a fixed copolymer molecular weight, one would anticipate the increase in copolymer surface concentration to scale roughly as $M^{0.5}$, which is about 2 times stronger than the observed molecular weight dependence. The trend toward higher levels of migration of low-energy DMS groups to the high energy aluminum surface with increasing matrix polymer molecular weight and decreasing copolymer molecular weight is, however, consistent with migration by this mechanism.

5. Conclusions

Surface migration of PS-*b*-PDMS copolymer additives in PS hosts with variable molecular weight was investigated using DCA and ATR−FTIR experiments. The two measurement techniques provide complementary information about the chemical make-up of the polymer material at the PS/PS-*b*-PDMS blend surface and in a thin subsurface layer (within 1 μm of the surface). Selective DMS enrichment of the air/polymer interface was observed, irrespective of the host polymer molecular weight. Near saturation levels of DMS surface coverage were in fact apparent at bulk copolymer compositions as low as 2 wt %. The excess surface concentration of DMS groups $\Delta\phi_{DMS}$ was however found to depend on the host polymer molecular weight and annealing conditions. Specifically, a simple scaling relation, $\Delta\phi_{DMS} \sim M_{wPS}{}^{\alpha}$, could be used to evaluate the data. For unannealed PS/PS-*b*-PDMS blend samples, the scaling exponent $\alpha \approx -0.5$. Polymer blend samples annealed at elevated temperatures, on the other hand, yielded α values in the range 0.25−0.3. A continuous transition between the two scaling regimes was observed when annealing conditions intermediate between the two extremes were imposed. Though the decrease in $\Delta\phi_{DMS}$ with increasing $M_{wPS}{}^{\alpha}$ can be explained in terms of slowing down of additive transport through a higher molecular weight matrix, the specific mechanism by which this occurs is unclear. An increase in PS-*b*-PDMS concentration with increasing $M_{wPS}{}^{\alpha}$ is qualitatively consistent with expectations from the molecular weight dependence of surface tension of the PS host. However, the scaling exponents observed experimentally are somewhat weaker than might be anticipated on the basis of enhanced additive surface migration due to an increase in host polymer surface energy. Finally, enhanced DMS migration at high-energy polymer/aluminum interfaces has also been reported. A mechanism based on reduction in the configurational entropy penalty of low molecular weight chains near surfaces fairly explains this last observation.

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