$Al(CH_3)_3$, and $Al(CH_3)_2F$ were introduced into the reaction flask and thermostated. Gaseous propene (30 mL) was condensed into the reactor while stirring, and finally the titanium compound was introduced, dissolved in 1 mL of toluene.

Polymerization runs at 0 and 25 °C were performed in a 100-mL glass autoclave equipped with magnetic stirrer and gas inlet. The metallocene compounds, $Al(CH_3)_2F$ and $Al(CH_3)_3$, were dissolved in toluene (30 mL) and introduced into the thermostated reactor. The system was evacuated and charged with propene at a constant pressure of 3.5 atm. Polymerization were stopped by introducing methanol, and the polymers were coagulated in acidified methanol, washed with fresh methanol, and dried in vacuo at 60 °C.

The stereoirregular fraction of sample 12 was separated from isotactic fraction by extraction with heptane at room temperature. Melting points were measured on previously melted and recrystallized samples by using a Du Pont 9000 DSC calorimeter with a rate of temperature increase of 5 °C/min. NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at a temperature of 393 K. The NMR samples were prepared by dissolving 80 mg of polymer in 0.4 mL of tetrachloro-1,2-dideuterioethane in a 5-mm-o.d. tube. Hexamethyldisiloxane (HMDS) was used as internal reference.

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Surface Interaction in Solvent-Cast Polystyrene/Poly(methyl methacrylate) Diblock Copolymers

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ABSTRACT: The relative surface coverage of components of a series of symmetric polystyrene/poly(methyl methacrylate) (PS/PMMA) diblock copolymers solution cast from toluene was studied by X-ray photoelectron spectroscopy. The copolymers, which ranged in total molecular weight from 27 000 to 535 000, are microphase separated into domains of pure PS and pure PMMA. The surface energy of PS is a fraction of a dyne per centimeter less than that of PMMA. The surface composition of PS, Φ_{PS}, was in excess of its bulk value of 50% and increased as the total molecular weight of the copolymer, N, increased. This dependence could be described by an equation of the form $\Phi_{PS} = a - bN^{-1/2}$ where a and b are constants.

Introduction

Block copolymers have received considerable attention in recent years.[1-6] Most of this work, however, has concentrated on the bulk morphology. These studies have shown that in a microphase-separated copolymer, under near equilibrium conditions, the volume fraction of each component dictates the morphology. If the average volume fraction of one of the blocks in the copolymer is between 0.4 and 0.6, then the structure is comprised of alternating lamellae of each component. When the volume fraction of one component is 0.2 or less, then this minor component forms spherical domains whose spatial arrangement exhibits a body-centered cubic symmetry in a matrix of the major component. At volume fractions between 0.2 and 0.4, cylindrical microdomains of the minor component are arranged in a hexagonally close-packed structure in a host of the major component. There is now strong evidence[6] that the cylindrically shaped microdomains arrange themselves in a structure which exhibits diamondlike symmetry at volume fractions which lie in the narrow regime between those which dictate the formation of the cylindrical and lamellar microdomains.

The equilibrium conformation of the chains located at a free surface should be different from that in the bulk since the surface free energy differs from the bulk free energy. The average composition near the surface of a block copolymer, which should reflect a minimization of the total free energy, will differ from the bulk composition. Contact angle measurements of copolymer melts suggest that the component with the lowest surface energy preferentially segregates to the free surface.[7] There have also been a number of X-ray photoelectron spectroscopy (XPS)[8-10] and electron microscopy (EM)[11,12] studies of solvent-cast films which also show that the lower surface energy component preferentially segregates to the free surface.

It is, however, clear from the literature describing surface measurements on copolymers[7-13] that it is not possible to predict the extent of surface coverage based solely on knowledge of the surface energies of both components. While some studies show that the lower surface energy component of the copolymer completely wets the surface, other studies, in which the surface energy difference of the constituents of the copolymer is comparable, show that both components are present at the surface. XPS and contact angle measurements of block copolymers comprised of poly(dimethylsiloxane) (PDMS) and polystyrene (PS) show that the surface of the copolymer is completely covered with the lower surface energy PDMS even in situations where the concentrations of PDMS is low.[7] Here, the surface energy difference between the constituents of the block copolymer at room temperature is about 20 dyn/cm (the surface energy of PS is γ = 40.7 dyn/cm[13]). EM studies of polystyrene/polyisoprene (PS/PI)[11] copolymers, solution cast from a nonselective solvent, which exhibit a lamellar morphology, show that the surface is completely covered by a layer of polyisoprene (γ = 30 dyn/cm) irrespective of the orientation of the lamellae. EM studies of polystyrene/polybutadiene (PS/PB) copolymers which exhibit varying morphologies also lead to the same conclusion; the lower surface energy component, PB (γ = 30–32 dyn/cm), wets the surface completely. An XPS study of the PS/poly(ethylene oxide) (PEO) copolymer, where the surface energies of both components differ by only 3 dyn/cm (γ of PEO is 42.9 dynes/cm), indicate that both components are present at the surface. The extent of coverage of the lower surface energy component, PS, increased as the volume fraction of PS in the copolymer increased. It is generally believed that the presence of both components at the surface resulted from the crystallization of the PEO where the kinetics of the crystallization and resultant morphology dominated the surface coverage. For copolymers of bisphenol A polycarbonate (PC) and PDMS, XPS measurements were combined with low-energy ion scattering spectroscopy (ISS)[9] measurements to show that both components appear on the surface yet the surface energies differ by 10 dyn/cm.

The presence of a free surface alters the thermodynamic interactions between the polymer segments in the vicinity of the surface. The differences in chemical potential, or indeed surface energy differences between the two constituents, result in one component exhibiting a preferential affinity for the free surface. It is clear from experiment that in polymer blends or block copolymers the lower surface energy component is preferentially adsorbed to the free surface. Other factors may affect the surface coverage in block copolymers that have been solvent cast. The nature of the solvent is important. Use of a solvent that has an affinity for one of the components will result in that component being preferentially adsorbed to the surface. The rate of solvent evaporation during the preparation process is also expected to be important, particularly in cases where a nonselective solvent is used. In addition, the relative length of the blocks in the copolymer and, to a somewhat lesser extent, the polydispersity of the individual components are crucial. Finally, the fact that the one component is crystallizable may be important, as is currently believed.

Table I
Characteristics of PS/PMMA Copolymers Investigated

copolymer	N_{PS}	N_{PMMA}	$f = N_{PS}(N_\alpha + N_{PMMA})^{-1}$
SMI	135	135	0.50
SMII	404	420	0.49
SMIII	567	560	0.50
SMIV	1510	1620	0.48
SMV	2644	2600	0.50

Table II
SAXS Long Period of PS/PMMA Diblock Copolymers

copolymer	long period, Å	copolymer	long period, Å
SMI	224	SMIV	755
SMII	388	SMV	977
SMIII	447		

In the present report, we address the influence of the solvent evaporation rate, the degree of compatibility, and surface energies of the constituents of the copolymer on the surface coverage. We have chosen a series of symmetric polystyrene/poly(methyl methacrylate) (PS/PMMA) diblock copolymers of varying total molecular weights. The surface energies of these components differ by only a fraction of a dyne per centimeter (γ_{PS} = 40.7 dyn/cm and γ_{PMMA} = 41.1 dyn/cm at 20 °C).[13] These copolymers have been well characterized by small-angle X-ray scattering (SAXS).[14,15]

Experimental Section

All the block copolymers were prepared by sequential anionic polymerization[16] of styrene and methyl methacrylate. The molecular weight of the PS block was determined by GPC. NMR was used to determine the composition of the copolymers, allowing the molecular weight of the PMMA by NMR to be calculated.[16] Five copolymers, which are identified as SMI, SMII, SMIII, SMIV, and SMV, were investigated. The molecular weights and the relative volume fractions of the components are listed in Table I. Samples were prepared by using three different procedures. In one series, solutions of 3% (wt/vol) of copolymer in toluene were prepared. The solution was cast onto a polished silicon wafer and the solvent was allowed to evaporate in air. When dried, the films were transferred to a vacuum for further drying in order to remove remaining solvent. Another series was prepared from 1.5% (wt/vol) solutions in toluene. In this case, the solvent was allowed to evaporate slowly over a period of a few hours in an environment where the vapor pressure of toluene was very high. The films were then placed under a vacuum to extract the remaining toluene. A third set was prepared by exposing one of the samples that was prepared by the rapid solvent evaporation procedure to an environment where the vapor pressure of toluene was high for a period of 24 h. Films of the PS and PMMA homopolymer were also prepared by casting from toluene solutions onto silicon wafers. The thickness of each of the films was approximately 5 μm.

All XPS spectra were obtained with a Kratos XSAM 800 spectrometer using a hemispherical analyzer with a high-resolution band pass energy of approximately 10 eV. The source, employing an nonmonochromatic Mg Kα radiation source with an energy of 1253.6 eV, was operated at 300 W (15 kV and 20 mA). The pressure in the analysis chamber was on the order of 10^{-8} Torr. Most of the spectra were recorded at electron take-off angles normal to the detector. Angle resolved measurements were also done on the lower molecular weight copolymers at take-off angles of 70° and 45°. No evidence of radiation damage was observed

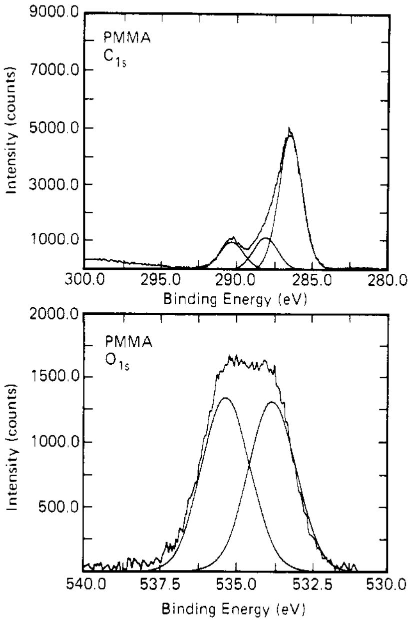

Figure 1. XPS spectrum of PMMA.

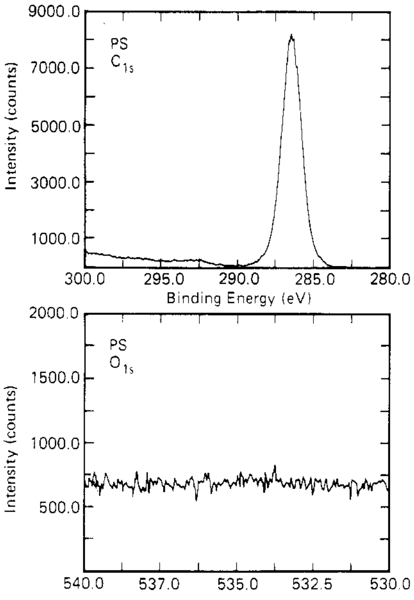

Figure 2. XPS spectrum of PS.

for time periods in excess of the time required to obtain a spectrum. The fwhm of the C_{1s} peaks was 1.6 eV.

Results

An analysis of the PS and PMMA homopolymers was important so as to determine unambiguously the relative surface composition of the copolymers. Figure 1 show the XPS spectrum of PMMA, and Figure 2, that of PS. Clear differences in the spectra of the two homopolymers are evident. In Figures 1, the single peak centered at a binding energy of approximately 534 eV results from the ionization of the O_{1s} core level in PMMA and is not present in PS. This peak is the sum of two peaks, one at a binding energy of 533.8 eV which is associated with the C=O bond and the other at 353.4 eV associated with the C—O—C bond. Peaks which result from the ionization of the C_{1s} core level that are associated with the C—H, C—O, and O—C=O bonding environments occur at binding energies of 286.4, 288.1, and 290.3 eV, respectively. For polystyrene, only two peaks are observed. One results from the ionization of the C_{1s} level bond (285 eV) and the other from the π–π^* shakeup transition at an energy of 292.2 eV. Clearly, there are a number of features which distinguish PS from PMMA. Consequently, the relative concentration of each component at the surface can be determined unambiguously. The analysis of the spectra entailed a nonlinear least-squares analysis of the peaks using Gaussian line shapes followed by integration of the area under the peaks. The areas were then converted to atomic percent. Care was taken to ensure that under these sample preparation conditions, the correct stoichiometric ratio of carbon to oxygen was obtained for PMMA. The surface coverage of PS and PMMA was determined by using the peaks which result from the ionization of both the O_{1s} and C_{1s} core levels. The use of the oxygen peaks was straightforward since PS does not contain oxygen. It was assumed that any signal arising from oxygen that was distributed evenly between the two appropriate binding energies was due solely to PMMA. The carbon peaks were also used. This was done by recognizing that the total amount of carbon associated with the C–H peak comes from both PS and PMMA, but the contribution of PS is approximately twice as much as that which comes from PMMA ($100f_{PS} + 50f_{PMMA} = \%\text{C–H}$ and $f_{PS} + f_{PMMA} = 1$, f_i is the fraction of species i on the surface). Figure 3 shows a typical profile of the copolymer. These two methods, using the O_{1s} and C_{1s}, gave the same results to within less than a few percent.

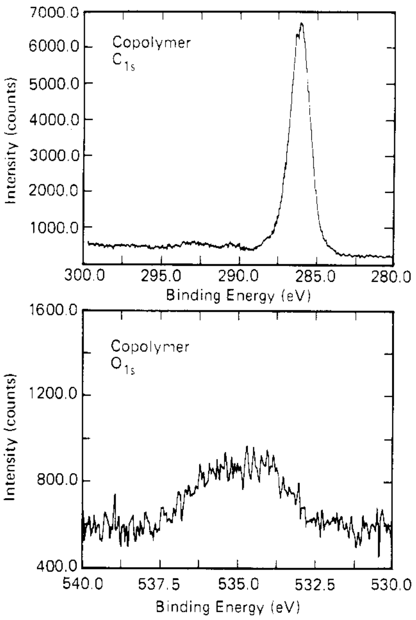

Figure 3. XPS profile of the copolymer.

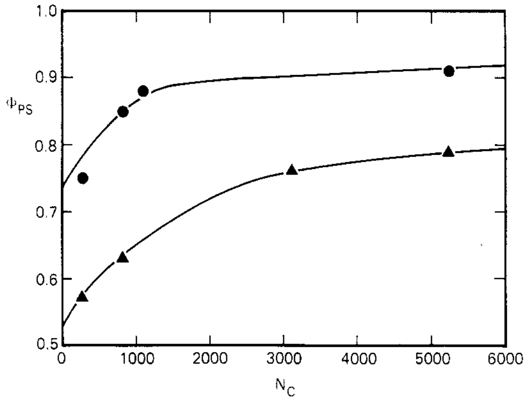

Figure 4. Surface coverage of PS as a function of the number of segments of the copolymer chain.

Shown in Figure 4 is a plot of the surface coverage of PS as a function of the number of segments of the copolymer chain. Three important observations may be made immediately from these data. The relative surface compositions differ from the bulk composition of 50%. There is a definite molecular weight dependence; i.e., as the total molecular weight of the copolymer increases, the relative PS coverage increases. In addition, the PS surface fraction of the copolymer films produced by rapid solvent casting is appreciably lower than that found for films prepared by slowly extracting the solvent. It is also found that by exposing the SMV copolymer films initially produced by rapidly extracting the solvent to toluene vapor for 24 h, the surface coverage of PS increased from 80% to 90%.

The experiments described above were performed at take-off angles normal to the detector where the depth of analysis is 50 Å. Angle-resolved measurements were also done at take-off angles of 70° and 45° so that shallower regions could be probed. To within 2%, the higher molecular weight copolymer samples showed no dependence of composition on depth. Only the shortest copolymer chain showed a depth dependence of the composition. Using the O_{1s} peaks of the SMI sample, the composition of PMMA at take-off angles of 90°, 40°, and 70° were found to be 0.25, 0.19, and 0.17, respectively. Based on the C_{1s} peaks, compositions of 0.24, 0.18, and 0.19 were determined, respectively.

Discussion

The equilibrium morphology of a symmetric diblock copolymer exhibiting microphase separation is lamellar. At the copolymer/air interface, the free energy is minimized when the lower surface energy component preferentially covers the surface and, consequently, the lamellae are oriented parallel to the surface. Preparation of copolymer films by solvent evaporation does not necessarily produce an equilibrium morphology. SAXS measurements[14,15] of the copolymers used in this study prepared by casting from toluene showed that these films are far from their equilibrium configurations. In these measurements, the microphase-separated domains were characterized by a short-range order and the domains were found to be randomly oriented with respect to the surface. The long period, which is the combined thickness of a PS and PMMA domain, scaled as $N^{1/2}$. The average dimension of each domain (shown in Table III) is on the order of a few hundred angstroms with a diffuse boundary of ca. of 50 Å. These results suggest that this copolymer is in the weak segregation limit. A complete description of the SAXS measurements and analysis is published in a separate paper.[15]

There is strong evidence from the electron microscopy studies of Hasegawa and Hashimoto[11] and Henkee et al.[12] that a thin layer of the lower surface energy component will completely cover the surface of the PS/PB and PS/PI symmetric copolymers, regardless of the domain orientation. The thickness of this overlayer is approximately one-half of the average thickness of the domains. Therefore, an important question arises regarding whether there is a thin PS overlayer in this system and, during the experiment, whether signals from deeper within the sample are observed. To address this question, angle-resolved measurements at 70° and 45° were done on a number of these samples so that one could sample shallower depths.

In the presence of an overlayer of thickness d, the intensity of a signal coming from a given core level can be expressed in terms of two basic equations for signal attenuation[10,17]

$$I_i^0 = f(\theta)F\alpha_i N_i k_i \lambda_i (1 - e^{-d/\lambda_i \cos\theta}) \qquad (1)$$

$$I_j^s = f_j(\theta)F\alpha_j N_i k_i \lambda_i e^{-d/\lambda_j \cos\theta} \qquad (2)$$

where I_i^0 is the signal arising from ionization of core levels in the overlayer, I_j^s is the signal arising from core levels beneath the overlayer, F is the incident X-ray flux, α is the photoionization cross section, N is the number of atoms per unit volume, k is the spectrometer factor of core levels, $f(\theta)$ is the signal intensity of the core levels as a function of the take-off angle θ, and λ is the mean free path of the electron. The electron mean free paths of C_{1s} and O_{1s} are comparable. If the sampling depth is large in comparison to d, then an exponential increase in I_i^0 and an exponential decrease in I_j^s would be expected. This is not seen for the copolymer studied here. On the other hand, if the sampling depth is much less than d, then I_i^0 would increase exponentially but I_j^s would be too heavily attenuated to be observable. Since the average sizes of the domains in the PS/PMMA copolymers are large in comparison to be sampling depth of 50 Å for XPS, this latter situation applies. However, signals from both PS and PMMA are observed and are found to be independent of take-off angle. Consequently, these results argue strongly against a surface overlayer.

Results of diffusion experiments corroborate the findings of the absence of an overlayer in these copolymers. When a thin layer of deuteriated polystyrene was placed on the surface of each of the copolymers, the labeled homopolymer was observed to diffuse readily into the copolymer at elevated temperatures. On the other hand, a PS-*d* film placed on the surface of high molecular weight PMMA encounters a diffusion barrier. Similar experiments were done for the diffusion of a thin film of deuteriated PMMA into the SMII, SMIII, and SMIV copolymers with similar results. A complete study of the diffusion of homopolymers into the copolymers is published elsewhere.[14]

The observation that the composition of PS at the surface, Φ_{PS}, is in excess of its bulk value is consistent with the findings of previous studies which show that when a nonpreferential solvent is used to prepare films the lower surface component is preferentially adsorbed to the surface. The extent of the surface coverage in the PS/PMMA system is somewhat surprising if one compares it with the findings of the PC/PDMS, PS/PI, and PS/PB systems where the surface energies between the components in each copolymer differed by approximately 10 dyn/cm.

The rate of solvent evaporation during the samples preparation affects Φ_{PS}, as illustrated by Figure 4. Samples produced from more concentrated solutions where the solvent was allowed to evaporate rapidly in air had a higher concentration of PMMA, the higher surface energy component, at the surface than those prepared by allowing the solvent to evaporate slowly. At the slower rates of evaporation, the copolymers more closely approximate an equilibrium morphology where the surface coverage of PS is expected to dominate. This is consistent with the findings that the PS coverage increased from 80% to 90% upon exposure of the SMV film to toluene vapor for 24 h after it was first prepared by a rapid solvent evaporation process. It is clear though that the solvent evaporation rates do not appear to have an appreciable affect on the general molecular weight dependence of both sets of data, suggesting that it is controlled by other factors.

As shown in Figure 4, both sets of data exhibit a monotonic decrease in Φ_{PS} with decreasing N. At lower N, the change in Φ_{PS} with N is more rapid than at large N where the dependence is weaker. One may attempt to rationalize this behavior by noting that as N increases and χN, where χ is the Flory–Huggins interactions parameter, increases, the system becomes more incompatible. It is well docu-

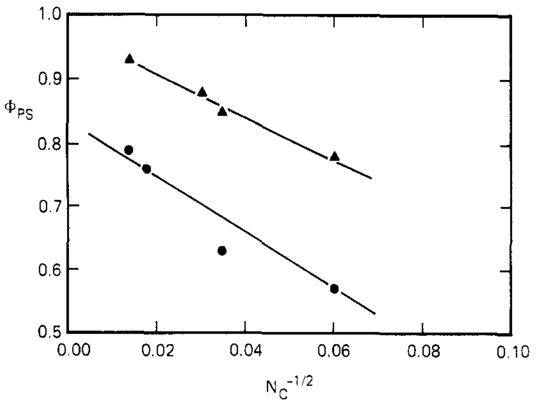

Figure 5. Data of Figure 4, replotted in a format where $\Phi_{PS} = a - bN^{-1/2}$.

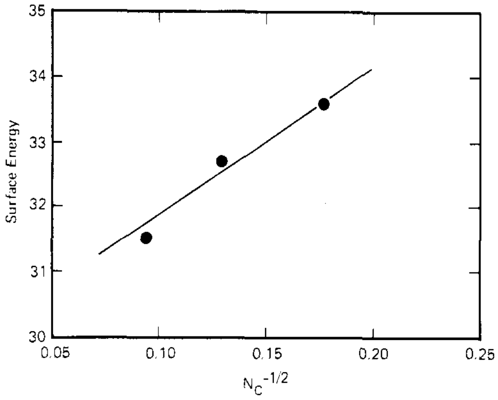

Figure 6. Surface energies of the copolymers as a function of $N^{-1/2}$.

mented that incompatible mixtures exhibit more surface activity that compatible ones.[13] The data have been replotted in Figure 5 in a format where the polystyrene coverage exhibits a curious power law dependence, where Φ_{PS} may be expressed by an equation of the form $\Phi_{PS} = a - bN^{-1/2}$ where a and b are constants. It is clear, however, that the correlation of the data obtained from the samples prepared by the slow solvent evaporation process is much better. This may suggest that one has to be sufficiently close to equilibrium to observe this power law behavior.

One may attempt to explain this behavior as follows. In a solution where the solvent does not preferentially solvate either block, the copolymer is effectively disordered. PS and PMMA are incompatible; as the solvent evaporates, a demixing process commences where the copolymer chains undergo a cooperative rearrangement process in order to assume a structure that minimizes the total free energy of the system, in this case, a series of alternating lamellae of PS and PMMA. Since a nonpreferential solvent is used, one may assume that the surface tension of each component plays an important role in determining the relative amounts of each component on the surface. Therefore, there should be a driving force that favors preferential coverage of the lower surface energy component appearing on the surface. The role should be comparable to that which would be expected in a melt since a mutual solvent is used. As the solvent evaporates, the rate at which the copolymer approaches its equilibrium structure decreases since in a highly viscous environment the cooperative diffusion process that is necessary to accommodate this becomes more difficult. If the solvent evaporation is slow, then the system can more closely approximate its equilibrium structure with an appropriate surface coverage. If the evaporation rate is fast, one finds that the structure is kinetically controlled where a nonequilibrium structure is "frozen in".

It is worthwhile to point out that the results of independent measurements of the surface energy of diblock copolymers are consistent with the observation made in this study that Φ_{PS} varies with $N^{-1/2}$. Rastogi and Pierre,[18] by means of a pendant drop method, determined the surface energies of a series of melts of ABA block copolymers comprised of poly(propylene oxide) (PPO) as the middle segment and poly(ethylene oxide) (PEO) as the end segments. After extrapolation of their data to 25 °C, the surface energies of the copolymers, where the composition of PPO and PEO was 50%, could be estimated. These data are shown in Figure 6 as a function of $N^{-1/2}$ where, although limited, a nearly linear behavior is found. It is evident, however, that as N increases, the surface energy of the copolymer approaches that of the lower surface energy component PPO in a manner which is similar to that in the PS/PMMA system, where as N increases, the surface coverage of the lower surface energy PS increases. It is important to point out that the surface energy of PPO is about 43 dyn/cm and that of PEO is about 33 dyn/cm, a difference of about 10 dyn/cm. These data suggest that at very large N, or more correctly large χN, the surfaces will be comprised of only the lower surface energy component. These observations underscore the fact that the surface energies alone are not enough to determine the surface coverage.

The molecular weight dependence of Φ_{PS} observed in this study may be rationalized on the basis of the work of Fredrickson.[20] Using a mean-field approach, the surface ordering of a symmetric, diblock copolymer ($f = {}^1/_2$) exhibiting a lamellar morphology in the weak segregation limit is considered. Due to a surface energy difference between the blocks in the copolymer, which is represented by a small "field" H_1 in the theory, one component shows a perferential affinity for the surface. This situation closely resembles that seen for PS/PMMA copolymers in that the surface energy difference between PS and PMMA is small, the copolymers exhibit lamellar morphologies, and they appear to be in the weak segregation limit. In a strict sense, however, the theory should be applicable to a system that is close to the microphase separation temperature (MST). In other words $\epsilon = (\bar{\chi} - \bar{\chi}_s)/\bar{\chi}_s$ is small where $\bar{\chi}_s = 3^{1/2}/[f(1-f)]^{3/2}$ is the value of the interaction parameter χ at the spinodal temperature. Here, $\bar{\chi}$ is related to the Flory–Huggins interaction parameter, χ, by the equation $\bar{\chi} = 2\chi N - 2\chi_s N + 3^{1/2}/[f(1-f)]^{3/2}$. It is not clear, however, how close the PS/PMMA system is to the MST under the present experimental conditions.

According to Fredrickson,[20] the excess surface concentration of the more strongly absorbing component (PS in this work) ψ_1 is given by

$$\psi_1 = \left[\frac{8\bar{\chi}_s\epsilon}{\Delta}\right]^{1/2} Q_1 \cos\phi \qquad (3)$$

where Δ is a constant which has a value of 156.56 for a perfectly symmetric diblock copolymer, Q_1 is surface amplitude factor, and ϕ is a phase angle which, at the critical point, is zero. In this equation, the molecular weight dependence of ψ_1 is embodied in Q_1 which is explicitly given as

$$Q_1 = \left[\frac{1}{2}(\gamma \tan\phi + \xi_-/\lambda)^2 + \frac{H_1\xi_-}{B\cos\phi}\left(\frac{\Delta}{4\bar{\chi}_s\epsilon}\right)^{1/2} + 1\right]^{1/2} - \frac{1}{2^{1/2}}(\gamma\tan\phi + \xi_-/\lambda) \qquad (4)$$

Here, ξ_-, the correlation length in the ordered phase, is given by $[4B/\epsilon\bar{\chi}_s]^{1/2}$, where $B = R_g^{\,2}/[2f(1-f)]$, and R_g is the radius of gyration of the unperturbed block of copolymer. $\gamma = q_0\xi_- = (2/\epsilon)^{1/2} \gg 1$ where q_0 is a wavenumber characteristic of the ordered phase in the copolymer, and $\lambda = B/a_1 > 0$ where a_1 is a measure of the surface effects on the strength of the A–B interactions in the system. For $a_1 > 0$, the local interaction parameter is less than in the bulk, whereas for $a_1 < 0$ it is greater than in the bulk. It is important to realize, however, that H_1 and a_1 were defined[20] such that they are both proportional to N.

The molecular weight dependence of Q_1 can be examined in a straightforward manner by defining the following constants which are independent of N, the number of statistical segment lengths:

$$K = \gamma \tan \phi$$

$$C = \left(\frac{H_1}{B\cos\phi}\right)\left(\frac{\Delta}{4\bar{\chi}_s\epsilon}\right)^{1/2}\left(\frac{4}{\bar{\chi}_s\epsilon}\right)^{1/2}\left(\frac{1}{12f(1-f)}\right)^{1/2} \qquad (5)$$

$$G = \frac{1}{\lambda}\left(\frac{4}{\epsilon\bar{\chi}_s}\right)^{1/2}\left(\frac{1}{12f(1-f)}\right)^{1/2}$$

By substitution, eq 4 reduces to

$$Q_1 = \frac{1}{2^{1/2}}(K + GN^{1/2})\left[1 + \frac{2CN^{1/2}}{(K+GN^{1/2})^2} + \frac{2}{(K+GN^{1/2})^2}\right]^{1/2} - \frac{1}{2^{1/2}}(K + GN^{1/2}) \qquad (6)$$

The sum of the second and third terms between the barckets is less than 1 since $G \sim \epsilon^{1/2}$ and $H_1 < N^{2/3}$. Therefore for large N and small ϵ one gets, by expanding the second and third terms, retaining terms greater than $1/N$, and recognozing that $\tan\Phi \sim \epsilon^{1/2} \ll 1$ which implies $\cos\Phi \sim 1$), an expression with the N dependence of the surface coverage of the more strongly adsorbing species:

$$\Psi_1 = \frac{H_1\lambda}{B} - 2.7\frac{H_1^{\,2}\lambda^3}{B^2}N^{-1/2} \qquad (7)$$

This equation adequately describes the trends in the experimental data. The constants $H_1\lambda/B$ and $2.7H_1^{\,2}\lambda^3/B^2$ are related to the constants a and b, respectively, that were used to describe the coverage of the polystyrene component, $\Phi_{PS} = a - bN^{-1/2}$. The magnitude of Ψ_1 (Φ_{PS}) depends on H_1 which may be related to the surface energy differences; it is also depends, indirectly, on a_1, the ability of the surface to modify the A–B interactions near the surface. The $N^{-1/2}$ dependence arises from the fact that the range of interactions between molecules vary as $N^{1/2}$ ($\xi_- \sim N^{1/2}$). This result suggests that Ψ_1, to first order, is not influenced by ϵ, the proximity the system to the MST.

Conclusion

It is clear from the foregoing discussion that the surface coverage of a copolymer film prepared from solution is controlled by a number of factors. These include the surface energy of the components, the rate of solvent extraction, assuming that a nonselective solvent is used, and χN, which defines the microphase separation of the copolymer. Based on the theory of Fredrickson,[20] it appears that the $N^{-1/2}$ dependence of Φ_{PS} results from the fact that the range of interactions in polymer systems varies as $N^{1/2}$. The behavior observed in the PS/PMMA copolymer system should be found in all copolymer systems. Henkee et al.[12] and Hasegawa and Hashimoto[11] may not have observed both components on the surface for two reasons. First, EM is not sensitive enough to determine if both components are on the surface, since the process relies on the staining of one component for contrast. Therefore, if one component is present in small concentrations at the surface, it may not be observable by EM. Henkee et al.[12] recognized this limitation in their work. Second, it is possible that χN for these copolymers may not be low enough to observe the behavior reported here, i.e., the systems are stongly segregated. Observations in the PC/PDMS system[9] are entirely reasonable since, as is the case for the PPO/PEO system,[18] very low molecular weights (small χN) were used. The crystallization kinetics which are generally believed to account for the observations of Thomas and O'Malley[10] may not be as important in view of the above findings.

It is conceivable, however, that other factors, such as the film thickness and the substrate, may be influential in cases where the films are below some critical thickness comparable to the dimensions of the microphase-separated domains. Presently, XPS studies of copolymer systems that have been annealed in order to avoid the uncertainties associated with solvent casting are being pursued. Preliminary results of measurements under equilibrium conditions at 175 °C show the $\Phi_{PS} = 1$ for the SMV copolymer and $\Phi_{PS} = 0.7$ in the SMI copolymer.

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