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Enhanced Segregation of a Diblock Copolymer Caused by Hydrogen Bonding

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ABSTRACT: Utilizing forward recoil spectrometry (FRES), we have determined the segregation isotherm which describes the interfacial excess z_i^* of diblock copolymers of poly(d_8-styrene-*b*-2-vinylpyridine) [dPS-PVP] at the interface between the PS/PVP, PS/poly(4-vinyl phenol) [PS/PVPh], and PS/poly(4-vinylbenzoic acid) [PS/PVBA] as a function of ϕ_∞, the volume fraction of diblock copolymer remaining in the host PS phase after annealing the specimens to reach the equilibrium segregation. A remarkable increase in the saturation z_i^* is observed at the PS/PVBA and the PS/PVPh interfaces as compared to that at the corresponding PS/PVP interface. This enhanced segregation is caused by an attraction due to the formation of hydrogen bonds of the PVP block with PVBA and PVPh homopolymers. The segment density profile of copolymer at the PS/PVBA interface determined by neutron reflectometry indicates that the interface is almost totally occupied by the copolymer and the copolymer chains at the interface are highly stretched. This result suggests that the interface is close to the "brush" structure as pictured by Leibler.

Introduction

The strong attraction between molecules resulting from hydrogen bonding has been found in numerous natural processes and has been utilized in various applications. For example, hydrogen bonding is the key function to establish the structure of proteins and furthermore is also believed to play an important role in the genetic mechanism.[1] The mesogenic structure necessary for liquid crystalline behavior can be built through hydrogen bonding.[2,3] Hydrogen bonding is also a specific interaction which can be used to enhance the miscibility of polymer blends.[4–6] These examples demonstrate that hydrogen bonding may be used to tailor the interaction between molecules.

It has been shown that the segregation of a A–B diblock copolymer can be used to improve the interfacial strength between homopolymers A and B.[7–11] The copolymer chains at the interface entangle with the respective homopolymers on each side of the interface which in turn allows these to be transferred across the interface from the homopolymer A to the homopolymer B. This mechanism serves to increase the fracture energy G_c of the interface. With increasing areal chain density of copolymer at the interface, G_c increases up to a value[9] which corresponds to a saturation of the diblock copolymer at the interface. Therefore, in general, achieving a high areal density of copolymer chains at the interface is an important way to improve interfacial adhesion. Shull et al.[12] have demonstrated that a high areal chain density can be achieved by introducing an attractive interaction between the homopolymer and the copolymer via hydrogen bonding. In this work, the segregation of a A–B diblock copolymer to the interface between homopolymers A and C where B can form hydrogen bonds with C is examined for two different C homopolymers.

Furthermore, knowledge of the copolymer structure at the interface is important for the interfacial modification on a molecular scale as well as to the understanding of the thermodynamics of segregation. To examine the copolymer structure at the interface,[13,14] we use a high-resolution technique, neutron reflectometry, to measure the segment density profile of the deuterium-labeled copolymer block.

Experimental Section

Materials. A diblock copolymer, poly(d_8-styrene-*b*-2-vinylpyridine) (dPS–PVP) was synthesized by anionic polymerization with cumyl potassium as the initiator.[15] A small amount of dPS precursor was sampled from the reactor prior to the addition of 2-vinylpyridine monomer. By using this precursor, the molecular weight of the dPS block was determined to be 66.9 × 10^3 (and thus the degree of polymerization to be 597) by size-exclusion chromatography (SEC). Forward recoil spectrometry (FRES)[16] was then used to evaluate the molar ratio between dPS and PVP which yields a molecular weight for the PVP block of 6.2 × 10^3 (and thus the degree of polymerization 59). The polydispersity index of the resulting block copolymer determined by SEC was less than 1.1.

A PS homopolymer of molecular weight of 233 × 10^3 with polydispersity less than 1.1 was purchased from Polyscience Inc. and used as received. The homopolymer PVP with molecular weight of ~210 × 10^3 (determined by SEC with PS standards as the reference) was synthesized by procedures similar to those used to prepare the block copolymer. The homopolymer poly(4-vinylbenzoic acid) (PVBA) of weight-averaged molecular weight (M_w) around 150 × 10^3 was prepared by free-radical polymerization of 4-vinylbenzoic acid.[17] The homopolymer poly(4-vinylphenol) (PVPh) with $M_w \approx 200 \times 10^3$ was obtained by thermally cleaving poly(*p*-*tert*-butoxycarbonyl)oxy]styrene) (PtBoc).[18] PtBoc was prepared in chlorobenzene at 65 °C using AIBN as a free-radical polymerization initiator.

Segregation Isotherm: Forward Recoil Spectrometry (FRES) The homopolymers PVP and PVBA were spun cast from pyridine

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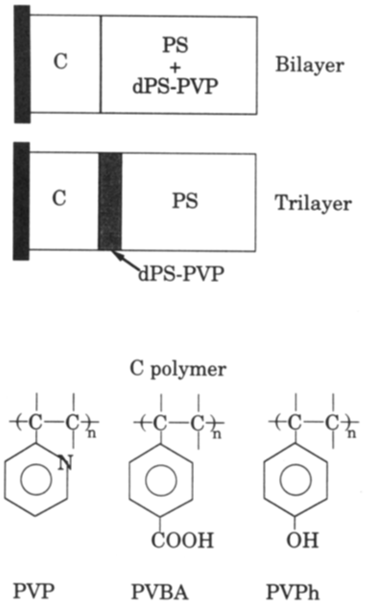

Figure 1. A schematic of the segregation specimens and the molecular formula of the homopolymers.

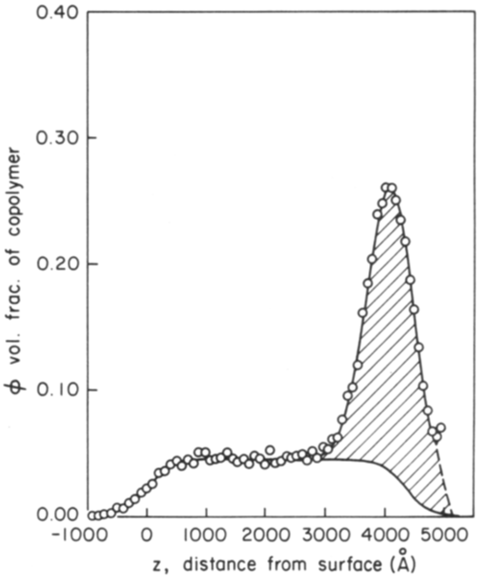

Figure 2. A volume fraction versus depth profile of the dPS–PVP copolymer segregating to the PS/PVBA interface measured by FRES where $\phi_\infty \approx 0.02$ and $z_i^* \approx 260$ Å where the z_i^* is indicated by the hatched area.

or tetrahydrofuran (THF) onto silicon wafers, respectively. It should be emphasized that these polymer-coated wafers were then dried at ~160 °C in vacuum. The PVPh layer was prepared by thermally hydrolyzing a PtBoc layer, spun cast on a silicon wafer from toluene. The details of the hydrolyzing process can be found elsewhere.[18] These homopolymer layers are typically 1000–2000 Å thick. A series of bilayer specimens were made by spin casting the blends of various proportions of the dPS–PVP copolymer with the PS homopolymer from toluene onto these homopolymer-coated wafers. A series of trilayer specimens were also made with the following procedures: A thin layer (thickness from 200 to 1000 Å) of the dPS–PVP copolymer was spun cast onto the homopolymer-coated wafer and a relatively thick layer of PS, floating on the water surface, was subsequently laid on top of the thin layer of copolymer. The geometries of these bilayer and trilayer specimens are shown in Figure 1. These specimens were then annealed at 178 °C in vacuum for at least 12 h. It should be noted the annealing temperature is well above the glass transition temperature of PS (T_g = 100 °C[19]) and PVP (T_g = 104 °C[19]), but lower than that of PVPh (T_g = 190 °C[20]) and PVBA (T_g = 250 °C[17]). The interfacial excess as a function of copolymer volume fraction in the host PS phase is measured by FRES.

Segment Density Profile: Neutron Reflectometry (NR). The bilayer specimens for the measurement of the copolymer segment density profile were prepared exactly as described above except that HF-stripped silicon wafers were used to avoid possible complication in data analysis caused by an additional layer (SiO_2) of high neutron scattering density.[14]

The NR experiments were performed on the POSYII beam line at the Intense Pulsed Neutron Source of the Argonne National Laboratory. Neutrons are generated upon impingement of a pulsed proton beam on a uranium target. The resulting incident neutrons possess a distribution of wavelength λ from 2.5 to 15 Å, peaked at 4 Å. The principles and the procedures of NR are briefly summarized in what follows; further details can be found in a recent review article.[13] The reflectivity (R) of the sample for neutrons is measured as a function of k_z, the perpendicular component of the incident wave vector defined as $k_z \equiv (2\pi/\lambda) \times \sin\theta$. Different incident angles θ are used to achieve overlapping ranges of k_z up to approximately 0.05 Å^{-1}. $R(k_z)$ is determined by the neutron scattering length density (b/V) profile of the specimen in the direction (z) normal to the interface. Selective isotope substitution of hydrogen by deuterium provides sufficient contrast to isolate the segment density profile of the deuterated PS block of the block copolymer. With use of a standard multilayer algorithm,[21] the reflectivity is calculated from an assumed neutron scattering length density profile approximated by a series of uniform layers; the number of layers was chosen to be large enough so that no difference in the calculated reflectivity is observed as a finer mesh is used. This calculated reflectivity is then compared with the measured reflectivity and this procedure is repeated until good agreement between the calculated and the measured reflectivities is reached. The final profile from this fitting procedure may be checked for consistency: the overall volume fraction of copolymer as well as the interfacial excess z_i^* may be calculated from the dPS segment density profile and compared to the actual volume fraction and the interfacial excess measured independently by FRES.

Results and Discussion

The interfacial excess of copolymer z_i^* and its corresponding copolymer volume fraction in the host PS homopolymer, ϕ_∞, after annealing are determined from the volume fraction of copolymer versus depth profile measured by FRES. z_i^* is defined in eq 1 as

$$z_i^* = \int [\phi(z) - \phi_\infty]\, dz \tag{1}$$

where $\phi(z)$ is the fraction of copolymer as a function of the distance from the interface in the z direction (perpendicular to the interface). An example of the depth profile of the dPS/PVP copolymer at the PS/PVBA interface is shown in Figure 2 and the z_i^* is indicated by the hatched area.

A qualitative approach proposed by Leibler[22] provides a basic understanding of the copolymer segregation at polymer–polymer interfaces. The segregation of a A–B block copolymer to the A/B interface from a host homopolymer A phase is mainly driven by the unfavorable interaction between B segments of the copolymer and A segments of the homopolymer as represented by the Flory interaction parameter χ. On the basis of Leibler's scheme, this unfavorable interaction is simply minimized by confining the copolymer joints at the interface to form a so-called "brush". In general, an apparent saturation of segregation will occur when (1) the chemical potential is pinned by the formation of micelles; or (2) the enthalpic gain by placing a copolymer chain at the interface equals the entropic loss due to the stretching and localization of the copolymer chain at the interface. Therefore, introducing an attractive interaction between the copolymer

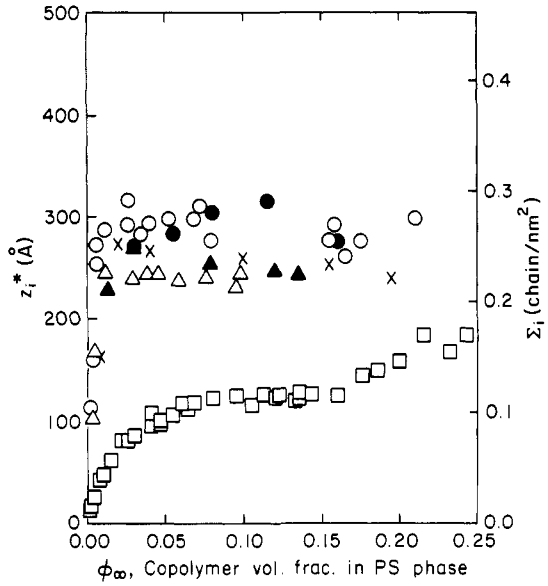

Figure 3. The segregation isotherm of dPS–PVP copolymer at PS/PVP (□), PS/PVBA (△, ▲) and PS/PVPh (○, ●) interfaces at 178 °C. The unfilled and filled symbols represent the results from bilayer and trilayer geometries, respectively; the symbol × represents the result where PVBA layer was spun cast from THF, whereas the rest of specimens were spun cast from pyridine.

and the homopolymer on the other side of the interface should provide an additional driving force for the segregation and in turn may allow a high interfacial excess to be achieved before the critical micelle concentration is reached. This additional driving force should also cause the copolymer chains at the interface to be more strongly stretched at saturation. To test these ideas, the segregation isotherms of the A–B copolymer to A/C interface were measured.

The segregation isotherms of the dPS–PVP diblock copolymer at the PS/PVP, PS/PVPh, and PS/PVBA interfaces are shown in Figure 3. The open circle, triangle, and square symbols represent the segregation isotherms at the PS/PVPh, PS/PVBA, and PS/PVP interfaces, respectively, obtained from bilayer specimens. The corresponding filled symbols represent the results obtained from the trilayer specimens. The symbol × represents the segregation isotherm at the PS/PVBA interface in which the PVBA layer was spun cast from THF, whereas the PVBA layers of the remaining specimens were spun cast from pyridine.

It should be noted that no significant differences in the saturation excesses between the two different specimen geometries (bilayer, trilayer) indicates that segregation is at, or at least close to, equilibrium. The interfacial excesses at the PS/PVBA and the PS/PVPh interfaces reach their saturation at $\phi_\infty < 0.01$ and the saturation value is maintained to $\phi_\infty = 0.2$. The saturation excesses at PS/PVBA, PS/PVPh, and PS/PVP are found to be around 260, 300, and 100 Å, respectively. As observed, the saturation excesses of the copolymer at the PS/PVBA and the PS/PVPh interfaces are nearly 2.5 to 3 times that at the PS/PVP interface. This remarkable increase in the interfacial excess is due to the attractive interaction between the PVP block and the PVBA and the PVPh homopolymers caused by the formation of hydrogen bonds. This result unambiguously illustrates that hydrogen bonding can indeed be used to enhance the segregation.

It has been demonstrated that the interfacial tension may vanish if a high enough interfacial excess can be achieved.[15] Such a phenomena is signaled by an abrupt increase in the interfacial excess due to the formation of an emulsified phase. It should be noted however that PVBA and PVPh are at their glassy states at the annealing temperature and thus no emulsified phase is likely to form in the PVBA or the PVPh phase. In any case, no such an abrupt increase in the interfacial excess at the PS/PVPh or the PS/PVBA interfaces is observed even for z_i^* as high as 300 Å and $\phi_\infty \approx 0.2$.

There may be solvent residues resulting from the film casting if the polymer can form hydrogen bonds with the solvent molecules. However, such a possible effect due to solvent uptake can be minimized by using a less polar solvent and annealing the film in vacuum during drying. THF was used instead of pyridine as an alternate solvent to prepare the PVBA films to minimize such solvent effect. Nevertheless, any residual THF in the PVBA film that is hydrogen bonded to PVBA should not prevent the formation of stronger hydrogen bonds between the PVP blocks and the PVBA during the annealing. Therefore, the segregation in the case of using THF as the solvent provides a reference state to examine the effect due to possible residual pyridine solvent. However, it needs to be emphasized that the cast films of PVBA were dried under vacuum at 160 °C for about 1 h and thus the residual solvent is expected to be a minimum.[23] As indicated by Figure 3, there is no significant difference in the segregation isotherms at the PS/PVBA interface between PVBA films cast from pyridine and those cast from THF. This fact indicates that neither solvent for PVBA affects the segregation of the copolymer to the interface, if the film is dried at high temperature in vacuum. It should be noted that residual solvent is not an issue for the PVPh case since it was converted from the PtBoc which is spun cast from toluene. In that case, no hydrogen bonds should be formed between the polymer and the solvent.

As observed in Figure 3, the interfacial excess of dPS–PVP at the PS/PVPh interface exhibits a higher saturation excess than that at the PS/PVBA interface which means the effective attractive interaction, described by the magnitude of the negative χ parameter between PVP and PVBA, is less than that between PVP and PVPh. This result seems to be contradictory to the idea that the hydrogen bonding between the carboxylic acid group and the nitrogen (i.e. PVBA and PVP) should be stronger than that between the phenolic OH and the nitrogen (i.e. PVPh and PVP).[24] However, it should be noted that χ_{BC} describes the excess free energy resulting from the exchange of the contacts between B and B, C and C, to B and C and thus is not solely determined by the interaction energy between B and C. This point is clearly illustrated in the following equation:

$$\chi_{BC} \propto \frac{1}{2}(\epsilon_{BB} + \epsilon_{CC}) - \epsilon_{BC} \qquad (2)$$

where ϵ_{BB}, ϵ_{CC}, and ϵ_{BC} are the "contact" energies between BB, CC, and BC, respectively.[4] It is commonly known that carboxylic acid forms cyclic dimers via hydrogen bonding through carboxyl groups.[1,24] Therefore, the self hydrogen bonding among PVBA segments reduces the energy gain resulting from the formation of hydrogen bonds between PVBA and PVP. This fact apparently leads to a smaller χ between PVP and PVBA than that between PVP and PVPh, and thus results in a lower saturation z_i^* at the PS/PVBA interface than that at the PS/PVPh interface.

It is known that the thermodynamics of polymer blends is further complicated by hydrogen bonding.[5,25] However, in this experiment, the hydrogen bonding occurs only in the vicinity of the interface and acts as a source of attraction of the copolymer PVP blocks to the glassy PVBA (or PVPh). A scaling argument based on the results from a self-consistent mean field theory of the segregation can thus be used to estimate the χ parameter between PVP and PVBA from the saturation excess. The apparent saturation occurs when the enthalpic gain from placing the copolymer chain at the interface, as described by the left hand side of eq 3, equals the entropic loss due to the chain stretching and localization at the interface, as described by the right hand side of eq 3.[26]

$$(\chi_{\mathrm{PS-PVP}} - \chi_{\mathrm{PVP-C}})N_{\mathrm{PVP}} \cong {}^{3}/_{4}(z_i^*/R_g)^2 + 1.1\ \ln(\delta/R_g) \quad (3)$$

where N_{PVP} is the degree of polymerization of the PVP block and C stands for either PVBA or PVPh corresponding to the interface in question, R_g is the radius of gyration of the copolymer at a corresponding state in the host phase,[27] and δ can be treated as the "effective range" for the interfacial interaction which can be taken as the statistical length (a) of the polymer in the case of inpenetrable interface and the interfacial width in the case of penetrable interface. However, since $\ln(\delta/R_g)$ is a weak function of δ/R_g, the exact value of δ/R_g is not important and thus δ is taken to be around 11 Å, as value between $a = 6.7$ Å of PS and an interfacial width (~17 Å) between immiscible polymer with $\chi = 0.1$ and $a = 6.7$ Å.[16] From the value of $\chi_{\mathrm{PS-PVP}} = 0.105$, the $\chi_{\mathrm{PVP-PVBA}}$ and $\chi_{\mathrm{PVP-PVPh}}$ are estimated to be on the order of -0.24 and -0.28, respectively. It should be noted that these values translate into an interaction energy $|\chi| k_{\mathrm{B}}T$ of around 1.5×10^{-21} J which is significantly less than the strength[24] of a single hydrogen bond, (~0.35–3.5) $\times 10^{-19}$ J. However, it should be noted that the hydrogen bonds can form only if the donor and the acceptor groups are at an appropriate distance and have an appropriate orientation from each other. Therefore, the steric restrictions arising from the bulky polymer chain may act to prevent the formation of all possible hydrogen bonds and consequently only a fraction of the PVP segments form hydrogen bonds with the PVBA or PVPh.

It is important to point out that the left hand side of eq 3 used to calculate the enthalpic gain for placing copolymer chains to the interface is only valid if the PVP blocks penetrate (and stretch) into the homopolymer PVBA or PVPh phase, in which case the enthalpic gain by placing the PVP block into the homopolymer phase is thus proportional to N_{PVP}. Evidence for the penetration of copolymer blocks into the homopolymer at an annealing temperature below the T_g of the homopolymer but above that of the copolymer has been observed in other systems, as described below. A large fracture toughness G_c of the poly(2,6-dimethyl-p-phenylene oxide)/poly(methyl methacrylate) (PPO/PMMA) interface reinforced by PS–PMMA diblock copolymer was observed by Brown et al.[28] after annealing at a temperature which was below the T_g of the PPO homopolymer but above that of PMMA and PS. Such a large G_c cannot be explained if the PS block did not stretch into the PPO homopolymer. In fact, the volume fraction versus depth profiles of the copolymer blocks at the interface measured using secondary ion mass spectrometry directly demonstrated that the PS block penetrated into the PPO homopolymer under such an annealing condition.[29]

Figure 4 shows the neutron reflectivity data as a plot of Rk_z^4 versus k_z. The NR data taken at different angles of incidence θ (each curve corresponds to a different θ) have different resolutions in k_z space due to the somewhat different relative angular divergences ($\Delta k_z/k_z$) of the incident neutrons at different incident angles. The inset represents the neutron scattering length density (b/V) profile used to generate the specific (best) fit to the reflectivity data shown as the solid line in which a different $\Delta k_z/k_z$ is used for each incident angle. The surface roughness used in the reflectivity calculation is 5–7 Å in all cases, which is known to be a typical roughness of a spun-cast polymer film on a silicon wafer.[30] The segment density profile of the dPS block determined from this (b/V) profile[31] using an approximate method described in a previous paper[14] is shown in Figure 5. For the purpose of comparison, a segment density profile of the dPS–PVP diblock copolymer at the corresponding PS/PVP inter-

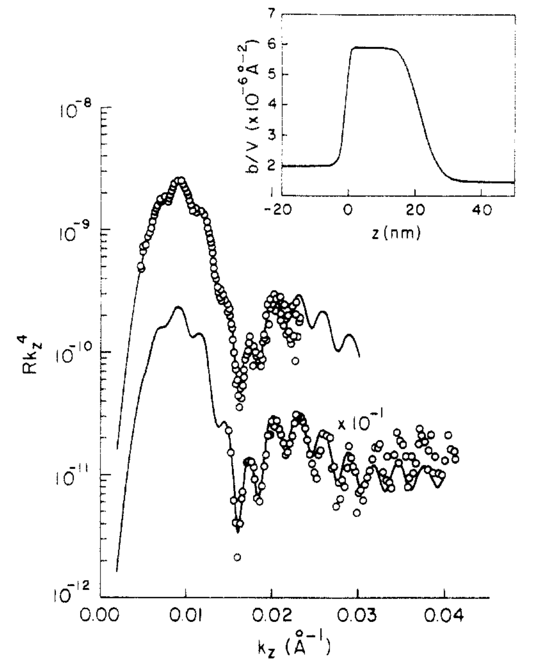

Figure 4. Neutron reflectivity data for the segregation specimens of dPS–PVP copolymer at a PS/PVBA interface. Different sets of data are obtained for different incident angles; the circles represent the experimental data; the solid line represents the calculated reflectivity using the (b/V) profile shown in the inset.

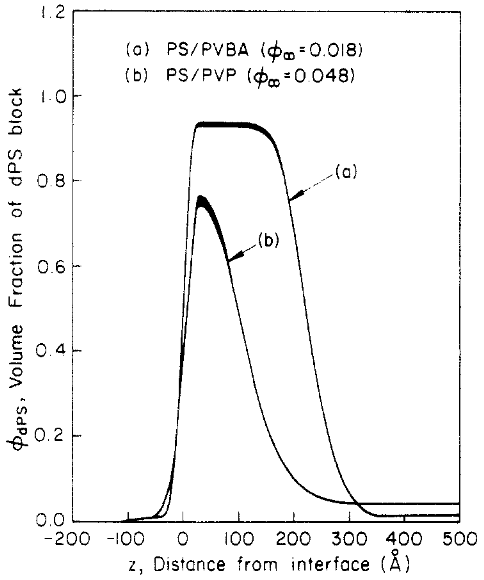

Figure 5. Volume fraction versus depth profile of dPS block in the dPS–PVP diblock copolymer, $\phi_{\mathrm{dPS}}(z)$, at the PS/PVBA interface (curve a) converted from reflectivity data as shown in Figure 4. The thickness of the lines indicates the uncertainty accompanying the conversion. A corresponding profile at a PS/PVP interface from ref 14 is also plotted for comparison (curve b).

face[14] is also plotted (curve b) in Figure 5. Both profiles correspond to z_i^* on the saturation plateau of the segregation isotherm in Figure 3. The width (full width half maximum) of the dPS block "brush" at the PS/PVBA interface is approximately $3R_g$ which is nearly two times larger than that at the PS/PVP interface. The interface between the stretched chains in the dPS brush and the PS host homopolymer is nearly as sharp as that at the PS/PVBA interface. Furthermore, the maximum volume fraction of dPS is very close to one for the PVBA case which leads us to conclude that the interface is almost totally occupied by the copolymer chains, i.e. only very few PS homopolymer chains penetrate to the interface. This distribution of copolymer is very close to the dry brush structure as pictured by Leibler.[22]

Conclusions

(1) A remarkable increase in the saturated interfacial excess of the dPS–PVP diblock copolymer is observed at the PS/PVBA and the PS/PVPh interface as compared to that at the corresponding PS/PVP interface. This enhanced segregation is believed to be caused by an attraction due to the formation of hydrogen bonds of the PVP block with the PVBA and the PVPh homopolymers.

(2) A lower saturation z_i^* is observed at the PS/PVBA interface than at the PS/PVPh interface which suggests $|\chi_{\mathrm{PVP-PVBA}}| < |\chi_{\mathrm{PVP-PVPh}}|$ although it is believed that the carboxyl group forms stronger hydrogen bonds than that of the phenol group. This result may be due to self hydrogen bonding between PVBA segments which reduces the magnitude of $\chi_{\mathrm{PVP-PVBA}}$.

(3) The segment density profile of copolymer at the PS/PVBA interface determined by neutron reflectometry indicates that the interface is almost totally occupied by the copolymer and the copolymer chains at the interface are highly stretched. This result suggests that the interface is close to the "brush" structure as pictured by Leibler.[22]

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