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Communications to the Editor

Enthalpy-Driven Swelling of a Polymer Brush

A system of polymer chains attached at their ends to a rigid, nonadsorbing wall is known as a polymer brush. There is a considerable amount of literature, both experimental[1,2] and theoretical,[3–6] on polymer brushes as they are good models for the way polymers are used in a number of practical situations such as colloid stabilization, wetting, and adhesion.

In many cases, if the polymer is in a moderate to good solvent, the chains are extended away from the rigid boundary so that the brush thickness varies linearly with the chain length N and as $\sigma^{1/3}$ where σ is the surface coverage. For moderately good solvents, the brush profile has been calculated by lattice mean-field techniques[7] and analytical self-consistent-field techniques[6] with good agreement between the two approaches. The results of such calculations agree well with recent experiments on the repulsive forces between mica sheets covered with terminally attached chains in a fairly good solvent.[2,8]

In the situations described above, the solvent has been of low molecular weight so that the driving force for the swelling of the brush has been entropic in nature and characterized by the excluded-volume parameter. In other words, the low molecular weight solvent does not screen the repulsive interactions between the tethered chains. However, that is not the only situation where a swollen brush can be found. Here we demonstrate that polymer brushes can be swollen in situations where the solvent is high molecular weight, so the mixing entropy is small and the long-range interactions between the tethered chains are screened. The brush is swollen when a favorable mixing enthalpy exists between the solvent and the attached chains. The experimental situation is a diblock A–B copolymer at the interface between two homopolymers, A and C, and where C and B have a favorable mixing enthalpy ($\chi < 0$). The interface can be considered as two brushes placed back-to-back with the A brush in an athermal situation and the B brush more likely to be swollen. The molecular weights of the copolymer and homopolymers are not grossly different. If the homopolymer molecular weight was much lower than that of the copolymer, then swelling might be expected for entropic reasons.

The swelling of a polymer coil, C, in dilute solution in a polymeric solvent, B, is well-known and is the basis for some measurements of χ. The linear swelling obtained for the polymer considered in this work is relatively small, about 10%,[9] because the solution must be dilute so there are not many C–C contacts to be reduced by swelling. No swelling is to be expected in concentrated solutions as the C coils overlap. The situation for a brush is quite different. The C coils are no longer dilute but can greatly reduce C–C contacts by swelling. Hence much larger swellings (perhaps 200%) are observed in the brush than in the dilute solution.

A polymer brush in a polymeric solvent has been examined with a simple Flory theory by de Gennes.[4] He considered just the athermal situation, but it is simple to extend this model to the case of a nonzero χ. The mixing free energy per brush chain is given by (eq III.6[4])

$$F_{\mathrm{mix}}/kT = (LD^2/a^3P)\phi_P \ln \phi_P + \chi N\phi_P \qquad (1)$$

where L is the brush thickness, D is the distance between attachment sites for the brush ($D = a\sigma^{-1/2}$), a is the monomer size, N and P are the degrees of polymerization of the brush and solvent chains, respectively, and ϕ_P is the volume fraction of solvent in the brush. The areal chain density, σ, is given in units of a^2. de Gennes assumed that the elastic energy that resists the brush stretching is of the form

$$F_{\mathrm{el}}/kT = (L^2/R_o^2 + R_o^2/L^2) \qquad (2)$$

where $R_o = N^{1/2}a$.

The brush thickness, L, can be obtained by minimizing the sum of $F_{\mathrm{el}} + F_{\mathrm{mix}}$ with the constraint that

$$\phi_N = 1 - \phi_P = Na^3/LD^2 \qquad (3)$$

The result has the form

$$\phi_N \ln(1 - \phi_N) + \phi_N^2 + \chi\phi_N^3 P = -2P\sigma^2[1 - (\phi_N^2/N\sigma^2)^2] \qquad (4)$$

which is just de Gennes' result with the addition of the term in χ. For a dilute brush (ϕ_N small) the result can be expanded as

$$[\chi P - {}^1/_2]\phi_N^3 = -2P\sigma^2[1 - (\phi_N^2/N\sigma^2)^2] = -2P\sigma^2[1 - (R_o/L)^4] \qquad (5)$$

For large solvent chains often $-\chi P \gg 1$ and for significant stretching $(R_o/L)^4 \ll 1$ so

$$L \simeq (-\chi/2)^{1/3}Na\sigma^{1/3} \qquad (6)$$

This result is very similar to that for swelling of chains in a moderately good solvent but in this case with $-\chi/2$ taking the place of the excluded-volume parameter.

We have observed enthalpy-driven brush swelling by using a series of deuterated polystyrene (PS)–poly(methyl methacrylate) (PMMA) symmetric diblock copolymers with a molecular weight of about 300 000 that were placed between PMMA and poly(2,6-dimethylphenylene oxide) (PPO) homopolymers. Three copolymers were used, a fully deuterated material, a polymer with just the PS half deuterated, and one with only the PMMA half deuterated. Two types of experiments were done to examine the conformation of the diblock at the interface. In the first, a known amount of diblock was spin coated onto a PMMA sheet and a layer of PPO was spin coated onto a PS sheet. After drying at 60 °C the two coated sheets were placed face to face in a mold and were heated at 190 °C for 2 h in a press. The sandwich was split along the interface at room temperature. The copolymer profiles under the fracture surfaces were obtained with the use of secondary ion mass spectrometry (SIMS) with quadrapole mass analysis and secondary ion detection to measure the deuterium depth profiles. This experiment has been described in a previous publication[10] where the results obtained from copolymers with one half deuterated were used to show that the copolymer fractured very close to its junction point. Hence, the deuterium

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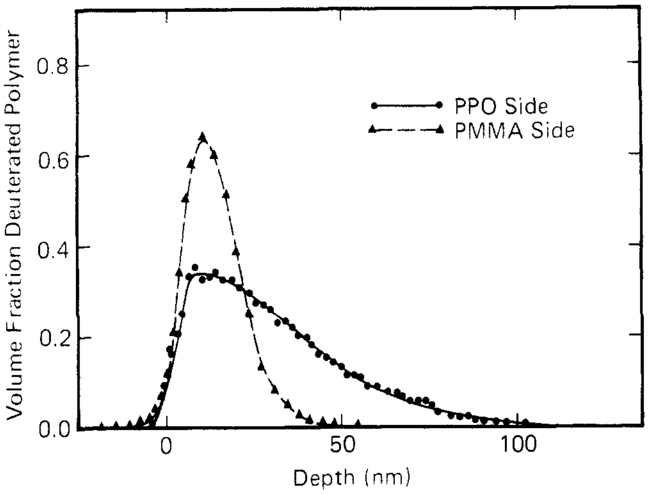

Figure 1. SIMS deuterium depth profiles under the PPO and PMMA fracture surfaces. The fracture surfaces were covered by a 50-nm layer of polystyrene to establish a constant etching rate.

profile on the PMMA side corresponds to the PMMA brush, and the profile on the PPO side, to the PS brush. The second type of experiment was fairly similar, but in this case the partially deuterated copolymers were spin coated onto glass, floated onto a water surface, and then placed between thin layers of the homopolymers on a quartz substrate. The samples were annealed at 190 °C for 2 h in a vacuum oven, and then SIMS was used to profile right through the interface. The presence (but not the concentration) of PPO could be detected by monitoring mass number 26, which showed a peak at the interface, as did carbon and oxygen, so the position of the interface was clearly evident in the depth profiles. Mass number 26, which corresponds to CN, is known to be very sensitive as a negative ion and presumably comes from catalyst residues or other impurities in the PPO that concentrate at the interface.

Figure 1 presents the depth profiles obtained from the fracture experiment for the PS and PMMA halves of the block shown on both linear and logarithmic scales. Equivalent results obtained by the second experiment are shown in Figure 2. SIMS has a depth resolution for polymers that depends on the experimental parameters but has been measured to be in the range of 12–15 nm[11,12] where the figure given is twice the standard deviation of the assumed Gaussian resolution function. The resolution of the current data, at least on the PPO side, was probably in the range of 8–10 nm. As the PMMA profile was the narrower of the two, the instrumental resolution had a larger effect on the PPMA profile than it had on the profile of the PS. The differences between the profiles obtained by using the two techniques could be a real effect caused by the presence of residual solvent in the thick fractured samples.

It is evident from the profiles that the PS side of the block copolymer is swollen by at least a factor of 2 with respect to the PMMA side. The swelling of the PS block in the PPO is a specific effect of enthalpic mixing of the PS with the PPO. The swelling could not be caused by the molecular weight of the PPO ($M_w \simeq 55\,000$) being much lower than the PS. The normal criterion[13] for mixing entropy-driven swelling in polymers is that $N > P^{3/2}$ where N and P are the degrees of polymerization of the swollen polymer and the solvent, respectively. This criterion shows that entropy-driven swelling would not be expected for the PS half of the diblock in the PPO.

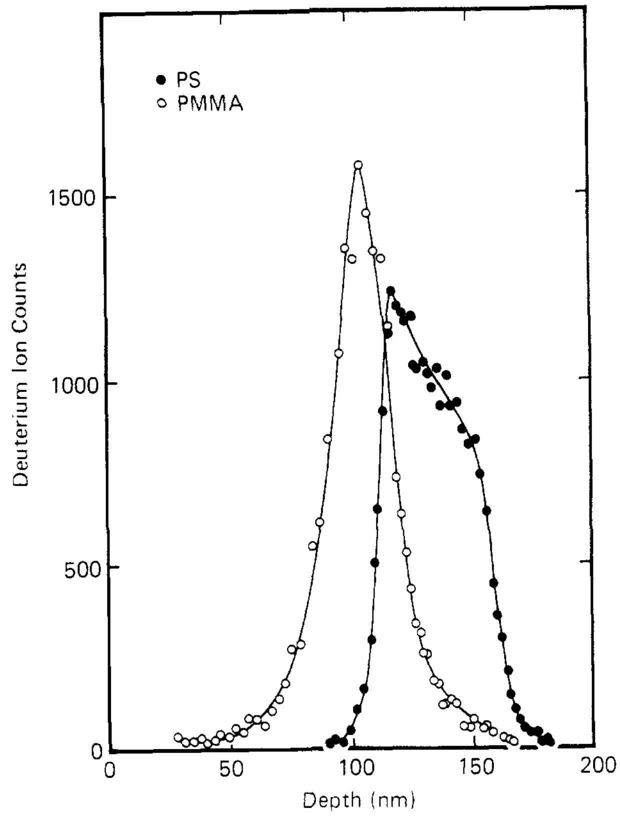

Figure 2. SIMS profiles obtained by etching through the interface for the two part deuterated copolymers. The profiles were superimposed by using mass number 26 as an interface marker as discussed in the text.

Composto et al.[14] have measured χ in the PS–PPO system by mutual diffusion and shown that their results agree well with previous measurements using neutron scattering. From their results, one can estimate that χ is −0.024 at 190 °C. If the monomer size a is assumed to be 0.6 nm, then for the experimental situation σ, the chain density, in units of a^2, was 0.017. Using these values for σ, a, and χ, one can estimate the brush thickness L from eq 6 to be 50 nm. This brush thickness is to be compared with the radius of gyration R_g of a 150 000 molecular weight PS chain which is 10.5 nm. The simple theory given above therefore suggests that significant swelling is to be expected.

It is tempting to compare the measured profiles in more detail with theoretical predictions, but that would be unwise as it is not clear that the system was at equilibrium. PPO has a glass transition temperature of about 215 °C, which is significantly above the joining temperature, so the diffusion of the PS into the PPO is expected to be slow (and non-Fickian). Subsidiary experiments have shown that a 12-nm layer of homopolymer PS of molecular weight 200K diffuses about 50 nm into the PPO in 2 h at 190 °C. The experimental conditions were chosen as the maximum time and temperature that the homopolymer PMMA could withstand in the press without forming many voids. Profiles obtained by using thin film samples do not change significantly with annealing times up to 24 h at 190 °C, but copolymer chain breakage was evident for longer times at 190 °C and after 12 h at 210 °C.

In conclusion, we have shown both experimentally and theoretically that a small favorable mixing enthalpy can cause significant swelling of a polymer brush in a polymeric solvent. Our profiles may not have been at equilibrium so we have not compared them with theoretical predictions of the form of the brush profile.

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Carbon-13 Nuclear Magnetic Resonance Study of Chain Conformation in the Solid Polymorphs of Syndiotactic Polystyrene

Ishihara et al.[1] have recently reported the synthesis of highly stereoregular, crystalline, syndiotactic polystyrene (s-PS), which was quickly confirmed and expanded upon by Zambelli et al.[2] X-ray[1,3] and electron[4] diffraction patterns obtained from oriented fibers and films yielded a chain axis repeat distance of 5.1 Å, which is consistent with a planar zigzag, all-trans conformation for the s-PS chains. These form I crystals melt at ca. 270 °C.

When s-PS is cast from dilute solution[5,6] in solvents such as chloroform or 1,2-dichlorobenzene or when melt-quenched, amorphous films or fibers are swollen[3,7] in chloroform, dichloromethane, 1,2-dibromo- or dichloroethane, or cyclohexane, a different crystalline polymorph is obtained. X-ray diffraction patterns observed[3] for the oriented, swollen form II fibers yielded a fiber repeat of 7.5 Å, which is consistent with a ...ttggttgg... chain conformation observed[8] previously for syndiotactic polypropylene (s-PP).

DSC[3,7] and IR[5,6] observations indicate that a solid–solid phase transition to form II crystals occurs at T = 190–200 °C. Once the thermal conversion of form II to form I s-PS is complete, it has not been possible to recover form II s-PS without melting or dissolving the form I crystals and reexposing them to the swelling solvents. X-ray diffraction patterns observed[7] on the swollen form II fibers suggest the formation of crystalline molecular compounds between the s-PS chains and the swelling solvent molecules, which was confirmed[3] by thermal gravimetric analysis (TGA).

In this paper we describe our initial efforts to study the conformations of s-PS chains in their form I and form II polymorphs. Our principal experimental probe is high-resolution, solid-state ^{13}C NMR spectroscopy, with emphasis placed on the chemical shift positions of the ^{13}C resonances observed in both polymorphs. Our motivation for this approach derives from the demonstrated[9] sensitivity of ^{13}C chemical shifts observed in solid-state polymer ^{13}C NMR spectra to their solid-state conformations.

s-PS was kindly provided by A. Zambelli. The sample was observed by ^{13}C NMR in solution to be highly syndiotactic (rr > 95%). Forms I and II of s-PS were obtained by bulk crystallization from the melt at room temperature or by annealing melt-quenched films at 200 °C and by exposing melt-quenched films to the vapors of chloroform or dichloromethane.

^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer at a static magnetic field of 4.7 T (50.3 MHz for ^{13}C). Magic-angle sample spinning (MAS) at speeds of ca. 3 kHz were achieved with a Doty Scientific probe, which utilizes a double air-bearing design. An 80-kHz radio frequency field strength was used for ^1H dipolar decoupling (DD), with a decoupling period of 200 ms. A 3-ms cross-polarization (CP) time was found to be optimum at room temperature where all spectra were recorded.

All s-PS samples were packed in aluminum oxide rotors with Kel-F [poly(chlorotrifluoroethylene)] end caps. The spectra were referenced to the resonance of poly(oxymethylene) (POM) at 89.1 ppm[10] from TMS recorded immediately prior to and after each s-PS spectrum.

All samples were also observed by DSC, TGA, and X-ray diffraction for the purpose of characterizing and monitoring their structures. These observations together with additional NMR results will be reported[11] upon their completion.

The CPMAS/DD ^{13}C NMR spectra of forms I and II of s-PS are presented in Figure 1. The aromatic C_1 carbons resonate at 146.1 (I) and 147.2 (II) ppm, while the remaining aromatic resonances appear at 129.8 (II) and 127.4 (II) ppm and at 128.3 (I) ppm. The methine carbons are observed to resonate at 41.3 (II) and 43.4 (I) ppm, where the shoulder at 41.4 ppm in the form I spectrum is produced by the amorphous methine carbons, as indicated by comparison to the CPMAS/DD spectrum (not shown) of a melt-quenched, amorphous sample of s-PS. A single CH_2 carbon resonance at 48.4 ppm is observed in the form I spectrum, while two CH_2 resonances at 49.1 and 38.1 ppm are seen in the form II spectrum. These resonance assignments are consistent with the spectrum of s-PS recorded in solution.[1,11]

The solid-state ^{13}C NMR spectra observed for forms I and II s-PS are consistent with those expected from γ-gauche shielding effects[12] if the chains adopt the planar zigzag, ...tttt... and 2_1 helical, ...ttggttgg... conformations, respectively. In the ...ttggttgg... conformation half of the CH_2 carbons are gauche to two γ substituents (CH's), while the remaining half are trans to both γ-CH substituents. We expect, as was observed[13] in the CPMAS/DD ^{13}C NMR spectrum of s-PP, to see two CH_2 resonances separated by two γ effects, or ca. (2)(5 ppm) = 10 ppm. The actual observed separation is 11 ppm. In the ...tttt... conformation of form I s-PS, all methylene carbons are in the trans arrangement with their γ substituents (CH's). We therefore expect to see and do observe a single CH_2 resonance in form I s-PS at nearly the same chemical shift position as the most downfield of the two CH_2 resonances observed for the form II polymorph.

Because of severe steric interactions in the $\bar{g}$ conformation illustrated in Figure 2, only the t and g bond con-

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