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Small Angle Neutron Scattering Studies on Ultrathin Films

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Small angle neutron scattering (SANS) has played a pivotal role in the characterization of natural and synthetic macromolecules in solution and in the condensed state. Isotopic substitution of hydrogens by deuterons provides a simple means of labeling macromolecular chains or specific portions of chains with minimal perturbation to the thermodynamics of the system. For example, SANS studies on mixtures of normal and perdeuterated polystyrene allowed Benoit and co-workers[1] to prove that amorphous polymers in the bulk exhibit unperturbed Gaussian coil conformations. Since then, the use of SANS has grown immensely and it is now an indispensable tool for probing the dynamic and thermodynamic properties of macromolecules.[2−4] For organic materials, the signal-to-noise ratio (S/N) is optimal with a sample thickness of ~1 mm. Consequently, most SANS studies on solids have focused on the bulk behavior of macromolecules. Pioneering studies using SANS to elucidate the structure of polymers adsorbed or grafted onto solid surfaces from solution[5,6] have been reported where an ensemble of particles are dispersed in the scattering volume. In those studies, density correlations of the grafted or adsorbed polymers can be proved by SANS effectively on a bulk sample. Here, however, SANS results are shown for single ultrathin polymer films, ~100 nm thick, which represents a breakthrough in the application of SANS for the study of confined samples or samples of limited quantity.

Symmetric diblock copolymers are comprised of two chemically distinct polymer chains of equal length covalently linked at one end. Such copolymers microphase separate into a periodic, lamellar morphology where, due to the connectivity of the chains, the period of the structure is comparable to molecular dimensions. If one block is labeled with deuterium, the SANS would show a peak characteristic of the periodic array. For a sample 1 mm in thickness, the signal-to-noise ratio (S/N) at the peak, based on experimental measurements, is $\sim 2.5 \times 10^3$. The signal, in this case, is composed of both incoherent and coherent scattering, whereas the noise arises from parasitic scattering and electronic noise. If the parasitic scattering is small, then this implies that the S/N of a 100 nm thick sample would be 0.25. This is unacceptably low and has prevented using SANS for the study of thin films. Since thin films are usually uniform over large areas laterally, the area illuminated by the incident beam and the solid angle defined by the detector elements can be increased by using larger apertures to define the beam. This does not result in a resolution loss but, rather, a reduction in the scattering vector range measured. However, one can gain a factor of 5 or better in the S/N, which makes SANS measurements on thin films possible without inordinate data accumulation times.

Table 1. Copolymer Characteristics[a]

designation	mol wt[b] (10^3 Daltons)	M_w/M_n[c]
29K	29	1.04
121K	121	1.03
289K	289	1.05
690K dPS	690	1.03
760K PS	760	1.04

[a] The methyl methacrylate block of the copolymer was labeled with deuterium. [b] Weight average molecular weight, M_w. [c] M_n is the number average molecular weight.

If the scattering volumes for the bulk and thin film cases are calculated, one finds that the sample mass is reduced from several tenths of a gram in the bulk case to several tens of micrograms for the thin film case, a reduction of at least 4 orders of magnitude. The results presented here on the ordering and orientation of diblock copolymers and on the demixing of homopolymers show conclusively that quantitative information can be obtained from such small samples using current neutron sources with relatively short data acquisition times. The studies described are only representative examples where very small scattering volumes are inherent to the problems under investigation. Other applications of SANS for the investigation of finite dimensional phenomena or of specimens of limited quantity should, also, be possible.

Copolymers of polystyrene, PS, and perdeuterated poly(methyl methacrylate), dPMMA, denoted P(S-*b*-d-MMA), and mixtures of PS and dPS homopolymers were investigated. The characteristics of the copolymers and homopolymers, purchased from Polymer Laboratories, are given in Table 1. All copolymers were approximately symmetric in composition. Homopolymer impurities, generated in the synthesis of the copolymer, were removed by Soxhlet extraction with cyclohexane prior to use. Ultrathin films of the copolymers and homopolymer mixtures were prepared by spin coating toluene solutions (~1 w/v) onto cleaned, 5 cm diameter (5 mm thick) silicon substrates. SANS experiments were performed on the as-cast films and after specific thermal treatments. For the copolymers, experiments were performed on films heated to 170 °C under vacuum for 15 min and 23 h. For the homopolymer mixtures, the films were heated to 130 °C for 15 h. SANS measurements were performed on the NG-7 and NG-3 spectrometers at the Cold Neutron Research Facility at the National Institute of Standards and Technology using neutrons with wavelengths of 0.5, 0.7, and 0.8 nm. The neutron beam entered the back side of the Si substrate at normal incidence and passed through the Si and then into the sample. This places the direction of the scattering vector in the plane of the film, so that SANS probes lateral correlations in the scattering length density. Details of the geometry of the facility can be found elsewhere.[7] To perform these studies, the sample aperture was increased from its usual size of 1.25 to 1.8 cm in diameter. Due to the larger beam size, a 10 cm diameter beam top on the 65×65 cm^2 detector was used which reduced the angular range measured by the detector. Typically, 2 h was allowed to record

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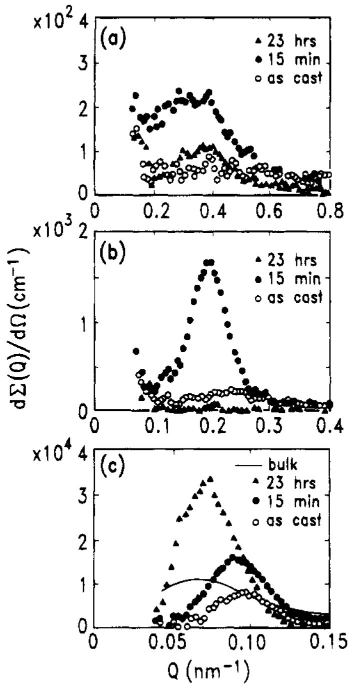

Figure 1. Absolute differential scattering cross section $d\Sigma/d\Omega$, as a function of the vector, Q, for P(S-*b*-d-MMA) copolymers on an Si substrate: (○) as-cast; (●) heated to 170 °C for 15 min; (△) heated to heated to 170 °C for 23 h. (a) is for a 70 nm film of the 29K copolymer, (b) is for a 100 nm film of the 121K copolymer, and (c) is for a 110 nm film of the 289 copolymer. The solid line in Figure 1c is the scattering measured for a bulk 289K copolymer.

the scattering profiles, though reasonable statistics were usually obtained within 30 min.

Shown in Figures 1a–1c are the SANS profiles for the 29K, 121K, and 289K P(S-*b*-d-MMA) films having thicknesses, measured ellipsometrically, of 70, 100, and 110 nm, respectively. The data are presented as the absolute neutron scattering cross section, $(d\Sigma/d\Omega)$ (Q) (in cm^{-1}), as a function of Q, the neutron momentum transfer or scattering vector ($Q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength and 2θ is the scattering angle). In each figure, scattering profiles of the as-cast films (○) and films heated to 170 °C for 15 min (●) and 23 h (△) are shown. Focusing first on the as-cast films, the scattering from the 29K copolymer is Q independent, whereas the scattering from the 121K and 289K copolymers clearly show a maximum in the profiles. For the 121K copolymer, a peak at $Q \simeq 0.25$ nm^{-1} is seen, which corresponds to a period of 25 nm, and for the 289K copolymer a maximum is found at $Q \simeq 0.095$ nm^{-1}, corresponding to a spacing of 66 nm. An important result is that the local segregation of the copolymer is clearly evident in the scattering from a *single, 100 nm thick film*. The results on the 121K copolymer, where the reflection is weak, suggest that the PS and dPMMA domains are highly disordered though spatially correlated. Recent electron microscopy studies[8] on the 121K copolymer clearly show a microphase separated morphology for the as-cast film in keeping with the SANS results. The reflection for the as-cast 289K copolymer is narrower and more intense, suggesting that the block domains are further advanced in their formation. In addition, the period is larger, as would be expected for a higher molecular weight copolymer. The weak scattering from the 29K copolymer suggests that the copolymer segments are intimately mixed. While a diffuse maximum in the scattering (orders of magnitude less intense than that for the microphase separated copolymers) would be expected,[9] it is, apparently, too weak to be observed in these experiments.

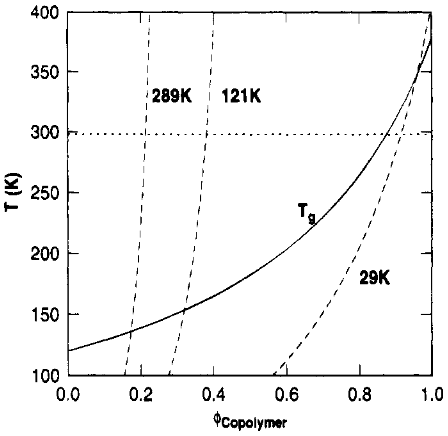

Figure 2. Schematic diagram of the glass transition temperature (solid line) and microphase separation temperature (dashed lines) as a function of volume fraction of copolymer, $\phi_{copolymer}$, during the spinning process. At room temperature as the solvent evaporates (proceeding from left to right on the dotted line) one crosses either a phase transition to a microphase separated state or encounters the glass transition freezing in a phase mixed morphology.

These results can be understood by recalling that symmetric diblock copolymers microphase separate into lamellar morphologies. For copolymer solutions there is a critical concentration of copolymer, ϕ_C, above which microphase separation occurs. ϕ_C was estimated theoretically[10] and is shown in Figure 2 for each copolymer (dashed lines). The glass transition temperature of the solution also increases with increasing copolymer concentration, as indicated by the solid line. Thus, as the solvent evaporates during the spinning process, one proceeds along the dotted horizontal line and either a phase mixed or a microphase separated glass will result. The extent of microphase separation will increase with increasing molecular weight, which is precisely what is observed experimentally.

After heating the films for 15 min at 170 °C, the SANS profiles change markedly. For the 121K and 289K copolymers, the interference maxima intensify, sharpen, and shift to smaller Q. Maxima centered at ~0.195 and 0.089 nm^{-1}, corresponding to periods of 32 and 71 nm, are seen for the 121K and 289K copolymers, respectively. Thus, a pronounced local segregation of the blocks has occurred which, for the 121K copolymer, is consistent with recent electron microscopy studies.[8] For the 29K copolymer, a diffuse reflection develops at 0.33 nm^{-1} corresponding to a period of 19 nm, which is effectively the bulk period of this copolymer.[11]

Annealing the specimens at 170 °C for 23 h produces substantial changes in the SANS profiles as shown in Figures 1a–1c. For both the 29K and 121K copolymers, the SANS is dramatically reduced. The specific interactions of the blocks of the copolymer with the surface and substrate interfaces orient the lamellae parallel to the surface.[12] Thus, lateral density correlations are suppressed. The peak in the scattering profile of the 289K copolymer continues to sharpen, increase in intensity, and shift to smaller Q of 0.072 nm^{-1} or a period of 87 nm, which corresponds closely to the bulk period.[11] Thus, after 23 h, the 289K copolymer is in a similar state as the 121K copolymer after annealing only 15 min, reflecting the slower orientation kinetics of the higher molecular weight copolymer. For comparison,

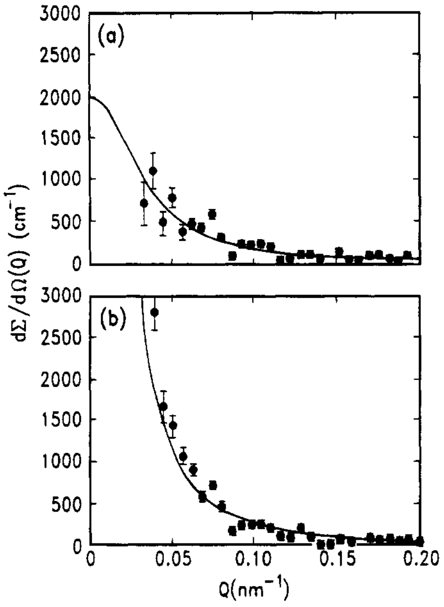

Figure 3. $d\Sigma/d\Omega$ as a function of Q for a mixture of PS-760K and dPS-690K (a) as-cast from a toluene solution and (b) heated to 130 °C for 15 h. The sample thickness is 170 nm. The solid lines are fits the scattering profiles using a Debye function.

the SANS profile for a bulk 289K copolymer is shown as the solid line in Figure 1c. The 97 nm period, corresponding to $Q = 0.065$ nm^{-1}, is 10% larger than that seen for the thin film. The bulk reflection, though, is much broader, suggesting that fewer defects are present in the thin film structure.

A key aspect of this study is that the scattering profiles were obtained from single films only ~100 nm in thickness. This was extended to films 40 nm thick with similar success. Since these results were so compelling, experiments were also performed on a 170 nm thick film of 50% mixture of 690K PS and 760K d-PS. SANS was measured for the as-cast film and after heating to 130 °C for 15 h. After 4 h each of acquisition time for the background and sample scattering, the SANS in excess of the background is shown in Figure 3a. Even though the SANS is distributed over a large Q range and the S/N ~0.1, quite reasonable statistics were obtained. The data was fit to a Debye scattering function (solid line) which yielded a radius of gyration, R_g, of 47 ± 5 nm with an intercept at $Q = 0, I(0)$, of $(2.0 \pm 0.5) \times 10^3$ cm^{-1}. For a homogeneous mixture of these two polymers with a segmental interaction parameter, χ_{HD}, between the protonated and deuterated segments, of 1.5×10^{-4}, an R_g of ~23 nm with an $I(0)$ of ~1.6×10^3 cm^{-1} would be expected. The deviation from the experimental results suggests either a demixing of the homopolymers or that the homopolymers are trapped in a nonequilibrium conformation during the spinning process. After annealing the mixture at 130 °C for 15 h, the SANS changes markedly as shown in Figure 3b. From a Debye scattering function fit to the data, $R_g = (1.9 \pm 0.5) \times 10^2$ nm and $I(0) = (5.4 \pm 0.9) \times 10^4$ cm^{-1}. Thus, both the radius of gyration and the $Q = 0$ intercept have increased markedly. In the bulk, isotopic mixtures of normal and deuterated polymers exhibit an upper critical solution temperature (UCST) behavior where, upon cooling, phase separation occurs.[13] The ultrathin film results indicate that, at 130 °C, the mixture is near the UCST. At 130 °C, the segmental interaction parameter between PS and dPS, χ_{HD}, is calculated[14] to be 2.1×10^{-4} at 130 °C. At the spinodal temperature, $\chi_{HD} = 2.9 \times 10^{-4}$. Thus, in the absence of finite size effects, the mixture would be homogeneous, but near the binodal which would give rise to the observed increase in the SANS upon heating.

In conclusion, it is possible to perform SANS measurements on ultrathin films of polymers and obtain, within a reasonable time period, scattering profiles with good signal-to-noise. It is apparent that the use of SANS to investigate ultrathin or exceptionally small samples is possible with current neutron sources. This represents a new and unconventional use of SANS and dispels previous concepts that SANS is restricted to bulk measurements.

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