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Solvent Retention in Thin Spin-Coated Polystyrene and Poly(methyl methacrylate) Homopolymer Films Studied By Neutron Reflectometry

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ABSTRACT: We utilize neutron reflectometry (NR) to probe the amount of residual solvent in thin polystyrene (PS) and poly(methyl methacrylate) (PMMA) films spin-coated from deuterated toluene solutions onto silicon substrates. The effect of thermal treatment at temperatures below and above the glass transition of PS and PMMA are examined to determine how these treatments affect the residual solvent. The parameters investigated include the total film thickness and molecular mass for PS and only thickness for PMMA. We find that the volume fraction of solvent in PMMA films is less than a few percentages, while no residual solvent was detected in PS films. The residual solvent content of the PMMA films had a slight dependence on thickness. These results are corroborated utilizing Fourier Transform infrared (FTIR) spectroscopy. We discuss these observations in the context of a large body of seemingly conflicting literature on residual solvent in polymer thin films.

Introduction

Polymer thin films are of significant interest because numerous technologies depend on thin and ultrathin polymer films, including optical coatings, next-generation data storage, high-resolution photoresists, and dielectric insulators.[1,2] The properties of thin films are very dependent on the amount of residual solvent, as it can influence substrate adhesion, molecular dynamics, and the glass-transition temperature, T_g.[3−8] The latter is found to be dependent on the film thickness and the polymer−substrate interfacial interaction. There are a number of reports[9] suggesting a large amount of residual solvent in thin films that depends on parameters including the polymer chemistry and molecular mass, solvent, and film thickness. Here we describe a systematic measurement using selectively labeled polymer/solvent combinations to quantify the amount of residual solvent as a function of molecular mass, thickness, and thermal history, for two commonly studied polymers: polystyrene (PS) and poly(methyl methacrylate) (PMMA) .

Spin-coating is a widely used technique for the preparation of thin polymer films on solid substrates, producing films with a uniform thickness and small surface roughness. Film thickness can be adjusted from just a few nanometers up to several micrometers. In this procedure, a polymer solution is first deposited on a substrate that is then rapidly spun. Owing to the centrifugal force, a film of the solution is formed after the excess liquid is ejected off the edge of the spinning substrate. The film continues to thin slowly until it reaches an equilibrium thickness or becomes solid-like due to a dramatic rise in viscosity resulting from the solvent evaporation. Although most of the solvent evaporates during the final stage of spin-coating, some solvent could remain trapped in the films at the end of the process.

Our group previously studied the effect of the ordering temperature (T) and film thickness (h_f) of the surface morphology of asymmetric cylinder-forming block PS-b-PMMA.[10] These results identified residual solvent as a possible factor in directing orientation in block-copolymer (BCP) films. However the measurement of residual solvent in multicomponent polymer films is ambiguous. In addition to the question of whether and how much solvent is retained, there is the issue of how solvent is distributed in the films. To address these questions, we investigate PS and PMMA homopolymer thin films with neutron reflectometry (NR) and focus on quantifying the total amount of residual solvent. Numerous studies of residual solvent in thin homopolymer and block-copolymer films have been conducted.[10−14] García-Turiel and Jérome studied solvent retention in thin PS (178 kg/mol) films by gas chromatography (GC)[11] and reported that the mass fraction of residual toluene in as-cast films increased from 2% to 35% with decreasing film thickness (500 to 15 nm). GC analysis gives quantitative information on the absolute amount of solvent. However, this technique requires redissolution of the thin films. In other words, GC analysis is destructive. There are some reports suggesting that solvent is retained even in dried films. In absorption/desorption experiments of toluene in several methacrylate polymer films, Saby-Dubreuil et al.[12] observed that some toluene remains trapped even after heating to 50 °C for 12 h. The presence of residual solvent in films has also been surmised through changes in the film properties.[13,14] Using mass loss, Croll measured the difference between a solution of known concentration and the dried polymer films to indirectly obtain the solvent loss and residual solvent in polymer film.[15] In solvent loss experiments, it is challenging to precisely measure the tiny amount of residual solvent. Clearly, a sensitive and nondestructive technique is needed to precisely and directly detect the amount of residual solvent in polymer films. Neutron interactions meet the desired needs of a nondestructive, direct, noncontact, and sensitive probe.[9,11,15,16] Perlich et al.[9] applied neutron reflectometry (NR) to determine the amount of residual solvent in PS samples with varying mass average relative molecular mass M_n and film thickness h. They suggest that a significant

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amount of solvent (9% to 15% volume fraction) remains in as-cast films and that the amount of residual solvent increases with both M_n and h. Their data indicate that the annealed films were only slightly thinner than the as-cast films, despite removal of a significant quantity of solvent. Further, based on the amplitude and decay of the fringes in their reflectivity data (which do not persist beyond $q \approx 0.06$ Å^{-1}), their PS films were very rough. This roughness constricts the q range they were able to use in data fitting, which could influence the fitting. The somewhat 'rounded' critical region seen in the data of ref 9 suggests film roughness and/or a slight misalignment of the sample with respect to the neutron beam, both of which make robust fitting more difficult. The critical edge, and nearby data, strongly affect the film densities obtained through fitting; thus errors in this region of the data can translate into substantial errors in predicted film composition (in this case, solvent content). However with careful alignment, NR is a powerful technique for measuring the residual solvent, in particular when there is a strong contrast in the scattering length density (SLD) of the solvent and polymer. This contrast is achieved in the present work by deuterium-labeling one of the components. This manuscript presents a quantification of the residual solvent in smooth thin PS and PMMA homopolymer films with very little roughness spin-coated from a deuterated toluene solution, as a function of film thickness in the range 40 to 200 nm and mass average relative molecular masses in the range 24 to 818 kg/mol.

Experimental Section

Sample Preparation. Protonated PMMA (M_n = 20 kg/mol, polydispersity = 1.06), protonated PS (M_n = 24 kg/mol, polydispersity = 1.03 and M_n = 97 kg/mol, polydispersity = 1.01), and deuterated PS (M_n = 52 kg/mol, polydispersity = 1.09, deuteration > 99%) were purchased from Polymer Source Inc.[17] The content of syndiotactic PMMA is more than 79% and thus the bulk T_g of PMMA materials used is ~116 °C. PS with M_n = 51 kg/mol, polydispersity = 1.01 and M_n = 818 kg/mol, polydispersity = 1.10 were purchased from Scientific Polymer Products Inc. and Pressure Chemical Company, respectively. The solvents used were protonated toluene (C_7H_8, J. T. Baker, purity > 99.9%) and deuterated toluene (C_7D_8, Sigma-Aldrich Inc., purity 99%). Different concentrations of homopolymer solution were selected to obtain the desired film thickness, which is dependent on the homopolymer molecular mass and the spin-coating parameters. Films were prepared by spinning the individual solutions for 60 s at speeds from 105 to 262 rad/s.

Three different sample series were prepared. The first series was composed of films with a fixed thickness of h = 150 nm and varying PS mass average relative molecular mass (M_n = 24, 51, 97, and 818 kg/mol). The second series was comprised of PS films with different thicknesses (h = 41, 91, 147, and 208 nm) and a fixed mass average relative molecular mass (51 kg/mol) and PMMA films with different thicknesses (h = 69, 121, 169, and 201 nm) and a fixed mass average relative molecular mass (20 kg/mol). All of the PS and PMMA samples were prepared using deuterated toluene as solvent. In a third series, PS (M_n = 51 kg/mol, polydispersity = 1.01) and dPS films with thickness h = 133 nm were cast from both protonated and deuterated toluene, giving rise to two complementary sample sets. The preparation of identical samples from protonated as well as deuterated solvent enables a direct comparison; any difference can then be ascribed to residual solvent. The samples were annealed at 93 °C for 15 h in a vacuum oven, which is below the PS and PMMA glass transition temperature (T_g for PS and PMMA are 100 and 116 °C, respectively). Films were then further annealed above T_g at 155 °C for 15 h.

Neutron Reflectivity (NR). The NR experiments were conducted at the Center for Neutron Research at the National Institute of Standards and Technology. The NG7 horizontal reflectometer utilized a 4.76 Å collimated neutron beam with a wavelength divergence of 0.18 Å. Scans were made over a wavevector magnitude (q) range from 0.05 Å^{-1} to 0.13 Å^{-1}. The angular divergence of the beam was varied through the reflectivity scan and this provided a relative q resolution dq/q of 0.04, where $q = 4\pi \sin(\theta)/\lambda$, and θ is the incident and reflection angle with respect to the surface of the film. The critical angle, α_c, increases as $\alpha_C = \lambda\sqrt{Nb/\pi}$ where Nb is the coherent scattering length density (SLD) step at the interface. NR measurements were taken on as-cast films, after annealing below T_g and after annealing above T_g. The standard uncertainty in fitting parameters, such as film thickness and residual solvent content, is included as error bars in the figures.

FTIR measurement. The Fourier transform infrared (FTIR) spectra were collected with a Bomem FTLA 2000 spectrometer in transmission mode. A resolution of 8 cm^{-1} is used, and 128 scans were averaged to improve the signal-to-noise ratio. The quantification of residual solvent is based on the strong IR band located at ~2275 cm^{-1}, which belongs to the stretching vibration of the carbon−deuterium bond in toluene-d_8. This band has very limited overlap with carbon dioxide or other signatures of the PS and PMMA films, providing a convenient method for identification and characterization of residual toluene. A calibration was conducted with a liquid cell containing a polymer solution of known concentration to deduce the mass ratio of the solvent to the polymer from the area ratio of their FTIR bands.

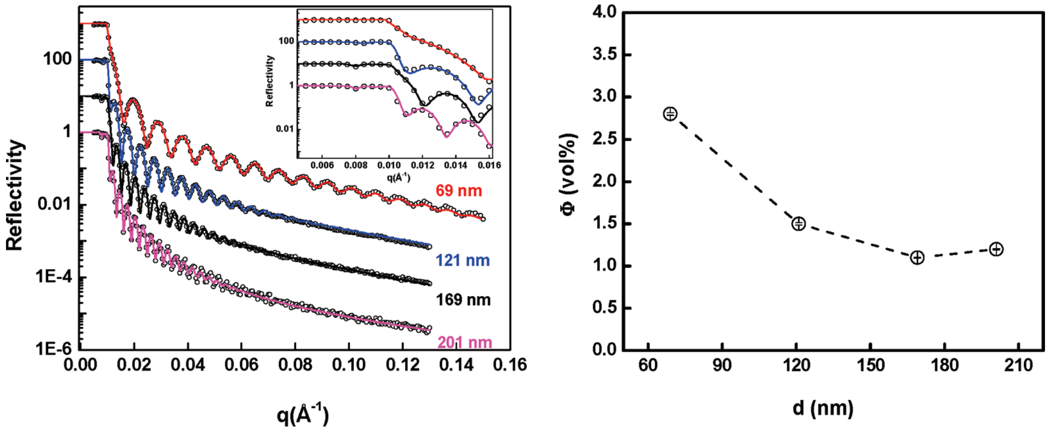
Results and Discussion

Our intent in the present work is to quantify the residual solvent in PMMA and PS homopolymer thin films, utilizing the high SLD contrast between the homopolymer and the deuterated solvent, toluene-d_8. For the deuterated toluene and the protonated homopolymers, $\mathrm{SLD_{tol\text{-}d8}}/\ \mathrm{SLD_{PMMA}} \approx 5$ and $\mathrm{SLD_{tol\text{-}d8}}/\mathrm{SLD_{PS}} \approx 4$. The SLD of the thin film is the most important fitting parameter, since it contains the desired information about the solvent content. We analyze the NR data using a single-layer model, representing the thin homopolymer film, on a very thin native Si oxide layer. The SLD of the thin film is adjusted to fit the data, and from this value we compute the volume fraction, Φ, of residual solvent using the relation

$$\Phi = \frac{\mathrm{SLD} - \mathrm{SLD_{polymer}}}{\mathrm{SLD_{tol\text{-}d_8}} - \mathrm{SLD_{polymer}}} \quad (1)$$

We note that $\mathrm{SLD_{polymer}}$ could, in principle, vary from its bulk equilibrium value in thin films and may change slightly with annealing history.

PMMA Film Thickness Effect. Figure 1 shows NR measurements on PMMA cast from deuterated toluene-d_8. Smooth films with very little roughness are used to obtain deep fringes up to high q, which make fits more accurate and reliable. In order to obtain the most quantitative information on the residual solvent in thin films we used a rigorous alignment procedure (double alignments), as can been seen from the sharp critical edges at low q in NR scans. The solid lines in this figure are best fits to our composition profile model; the low q region is highlighted in the inset of Figure 1a. Detailed information about the NR method is given elsewhere.[18] The oscillations evident in the data result from interferences between neutrons reflected at the substrate and air interfaces and are thus characteristic of the film thickness. The fits show good agreement with data. We also fit all of our data using multilayer models for the polymer film with interfacial roughness between polymer layers in order to consider nonuniform film profiles (which would include gradients in solvent concentration). Applying these multilayer models did not significantly improve the fit quality; the resulting models had only very slight changes



(a) (b)

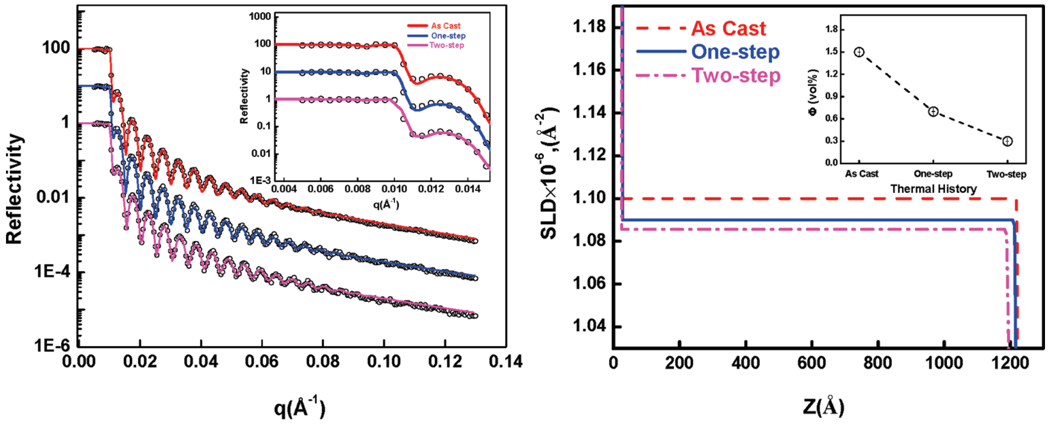
Figure 1. (a) NR scans (symbols) measured from as-cast PMMA films of different thicknesses at fixed molecular mass (20 kg/mol). The solid lines are the fits to the data for determining the total content of residual solvent. (b) The extracted total content of residual solvent, Φ, as a function of the film thickness. The dashed line is a guide to the eye. The error bars represent 1 standard deviation.

in SLD throughout the film (smaller than our estimated uncertainty in fitting a film SLD). We also used fitting procedures that allowed for a completely free-form SLD profile within the film region. However the best fits in these cases were worse than the simpler one-box model. In alternative multilayer models, we also varied the thickness of SiO_2, the roughness of the polymer layers, and the SLD of the (Si) substrate. However, the resulting best-fit model parameters were not physically reasonable. Thus in this manuscript we present the one-box fits, as this simple single-layer model is sufficient for describing the full NR curve and, in fact, provides the best fit.

From the fit to the NR data, the SLD, film thickness, and roughness can be extracted, and from the SLD, the total content of residual solvent inside the polymer films is calculated. To calculate Φ, a value for the scattering length density of the polymer film ($SLD_{polymer}$) must be assumed in eq 1. The simplest assumption is that the SLD of the polymer contribution is roughly equal to the SLD of bulk solvent-free PMMA (1.07×10^{-6} Å^{-2}). However this assumption is overly restrictive. In fact, we observe a decrease in thickness larger than can be accounted for by solvent loss alone. Instead, we solve the system of equations formed by applying eq 1 to the three measurement states (as-cast, one-step, two-step), with the additional constraint that the total scattering contribution of the polymer component is constant. In other words we assume that annealing removes solvent but does not change the amount of polymer. Moreover we assume that after annealing the polymer film approaches its bulk density. Using these criteria, the total content of residual solvent, Φ, is calculated (see Figure 1b). The volume fraction of residual solvent, Φ, slightly decreases from 2.8% ± 0.02% to 1.2% ± 0.01%, with increasing film thickness. Toluene-d_8 is a relatively poor solvent for PMMA[19] resulting in low chain mobility. During the spin-coating, the evaporation at the uppermost layer of the film produces a gradient of solvent that is the driving force for the diffusion of solvent molecules toward the polymer−air interface.[7] One explanation for the presence of residual solvent in PMMA films is the hindered diffusion of solvent escaping from the film during spin-coating due to the vitrification of PMMA chains. Additionally, the native oxide substrate has a strong interaction with PMMA and the solvent. This substrate effect also explains the greater relative solvent content in thinner films. The confining effect of a thinner film and/or the substrate interface could also restrict the mobility of PMMA, decreasing the diffusion coefficient of toluene and, thereby, trapping more solvent in the film. Another important effect is the relief of packing frustration in ultrathin films which is evidenced by a drop in the Debye−Waller factor and an overall broadening of the glass transition in thin polymer films. The drop of the Debye−Waller factor has been directly correlated with a drop in the diffusivity of diluents in polymer films,[20,21] an effect of some significance in the lithography of electronic materials. Thus both the chemical and confining effects of the substrate serve to limit solvent diffusion, trapping more solvent in the film during casting.

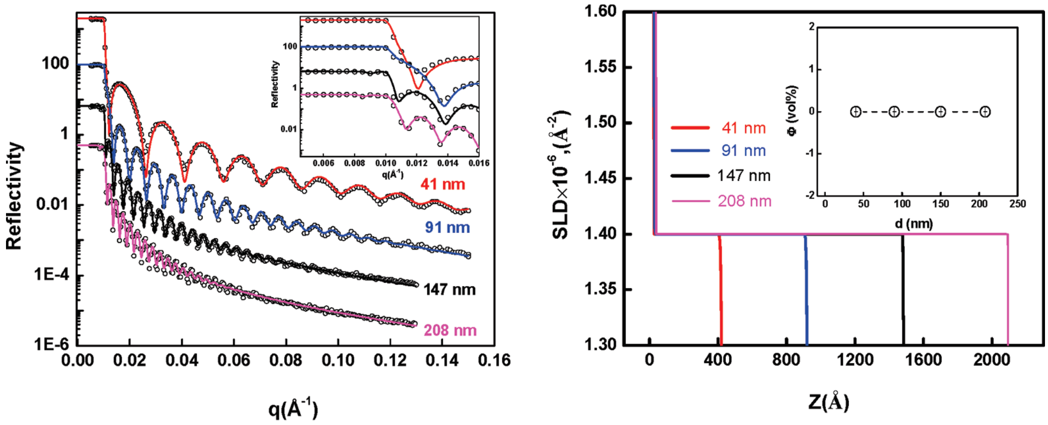
Freshly cast films loaded with residual solvent are in a nonequilibrium state. To address this, spin-coated PMMA films were subjected to different thermal treatments. The PMMA film is first annealed at 93 °C for 15 h (one-step annealing) and then heated to 155 °C for another 15 h (two-step annealing). NR measurements are performed on the as-cast films as well as after each annealing step (see Figure 2a). The as-cast PMMA film contains 1.5% by volume fraction residual solvent. Annealing at 93 °C (below the glass transition temperature of PMMA, 116 °C) leads to a decrease in the volume fraction of residual solvent by 0.8% (see inset in Figure 2b); the film is also 1 nm thinner than the as-cast state. For the two-step annealing, the total decrease in solvent volume fraction is 1.2%. Consistent with this loss of solvent is a reduction in the thickness by 3 nm, which is outside the error for film thickness determination and thus can be attributed to the annealing. The measured decrease in film thickness after thermal annealing arises from both solvent loss and an increase in the density of the PMMA component. The increase in PMMA density may arise from relaxation of a nonequilibrium low-density state after casting and/or the intrinsic effect of the solvent on the PMMA packing. We investigated the effect of annealing on the amount of residual solvent on films with film thicknesses 69, 169, and 201 nm (data not shown). In all cases, the effect is the same: the amount of residual solvent decreases with annealing.

PS Film Thickness Effect. To gain insight into the effect of polymer composition on residual solvent, we investigated films of pure homopolymer PS on Si substrates. Figure 3 shows the NR curves for PS films cast from deuterated toluene-d_8 which again provides a large neutron contrast. The best-fit SLD profiles, using a single-layer model as before, are shown in Figure 3b. Total residual solvent as a function of the PS film thickness is shown as an inset in



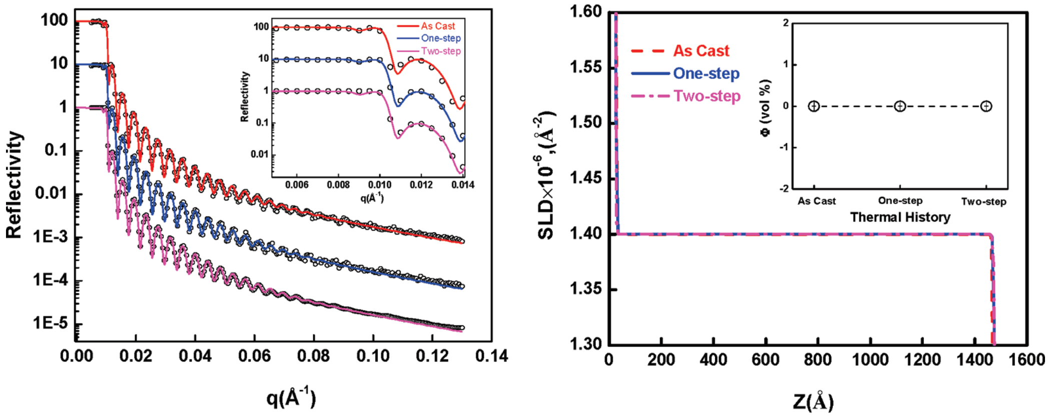
(a) (b)

Figure 2. (a) NR data (symbols) of as-cast, one-step (93 °C for 15 h), and two-step (93 °C for 15 h followed by 155 °C for another 15 h) annealed PMMA films with as-cast film thickness of 121 nm at fixed molecular mass (20 kg/mol). The solid lines are the fits to the data for determining the total content of residual solvent. (b) Best-fit SLD profiles based on the NR data. Shown in the inset is the residual solvent, Φ, as a function of the film thickness. The dashed line is a guide to the eye.



(a) (b)

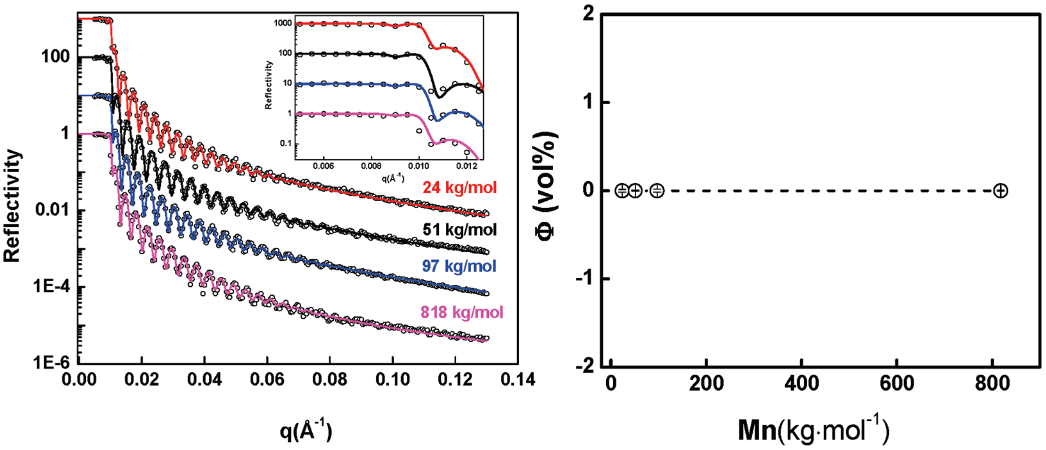
Figure 3. (a) NR scans (symbols) measured from the as-cast PS films of different thicknesses at fixed molecular mass (51 kg/mol). The solid lines are the fits to the data for determining the total content of residual solvent. (b) Best-fit SLD profiles based on the NR data. Shown in the inset is extracted total content of residual solvent, Φ, as a function of the film thickness. The dashed line is a guide to the eye.



(a) (b)

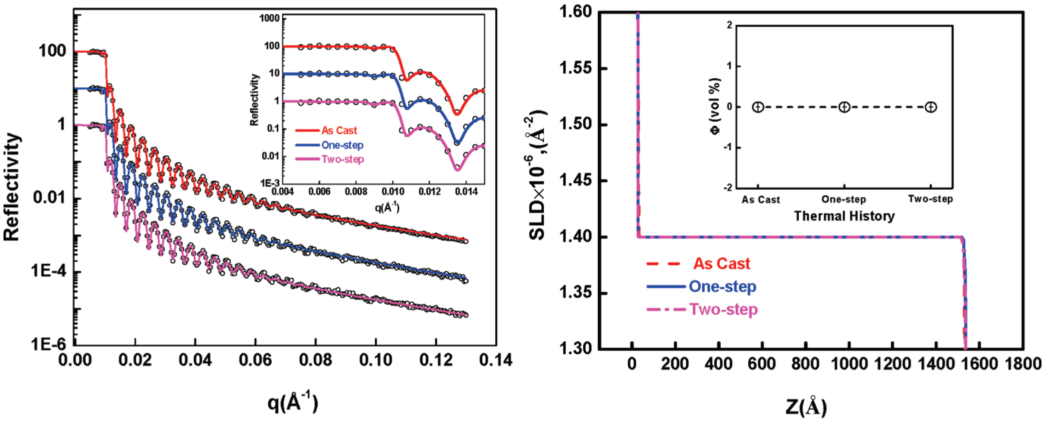
Figure 4. (a) NR data (symbols) of the as-cast, one-step and two-step annealed PS films with film thickness of 147 nm at fixed molecular mass (51 kg/mol). The solid lines are the fits to the data for determining the total content of residual solvent. (b) Best-fit SLD profiles based on the NR data. Inset shows extracted total content of residual solvent, Φ, as a function of the thermal history. The dashed line is a guide to the eye.

Figure 3b. For all samples, the SLD remains constant at $\sim 1.4 \times 10^{-6}$ Å^{-2}, the SLD of pure PS homopolymer. This result indicates that there is no residual solvent, which is supported by the fact that thickness does not vary with annealing. In fact, the NR data (Figure 4) are almost identical for before and after one-step and two-step annealing.



(a) (b)

Figure 5. (a) NR data (symbols) from the PS films with different molecular masses. The solid lines are the fits to the data for determining the total content of residual solvent. (b) Extracted total content of residual solvent, Φ, as a function of the PS molecular mass. The dashed line is a guide to the eye.



(a) (b)

Figure 6. (a) NR data (symbols) of as-cast, one-step, and two-step annealed PS films with the film thickness of 153 nm at fixed mass average relative molecular mass (97 kg/mol). The solid lines are the fits to the data. (b) Best-fit SLD profiles. Shown in the inset is extracted total content of residual solvent, Φ, as a function of the thermal history. Dash line is a guide to the eye.

PS Molecular Mass Effect. In addition to film thickness, the influence of the PS molecular mass (24 to 818 kg/mol) was addressed (see Figure 5). As before, the SLDs of the PS films are used to calculate the residual solvent (Figure 5b). The SLDs for all of the films remain constant at $\sim 1.4 \times 10^{-6}$ Å^{-2}, again indicating no detectable residual solvent. Annealing of the PS films over the one- and two-step procedures (Figure 6) leads to no changes within the uncertainty of the measurement.

Effect of Isotopic Labeling. Measurements on PS films cast from deuterated solvent indicate no measurable residual solvent. To confirm this conclusion and eliminate any isotopic bias, we performed a complementary series of measurements using the opposite contrast conditions. First, we compared PS films freshly prepared from protonated toluene and deuterated toluene, at a given molecular mass (51 kg/mol) and film thickness (133 nm). The NR profiles of the films prepared from the deuterated and the protonated solvents should be identical if no residual solvent is present in either film, whereas the presence of residual solvent should lead to a measurable difference between the two reflectivity curves. An example of such a pair is shown in Figure 7. NR data are almost identical suggesting that no residual solvent is present.

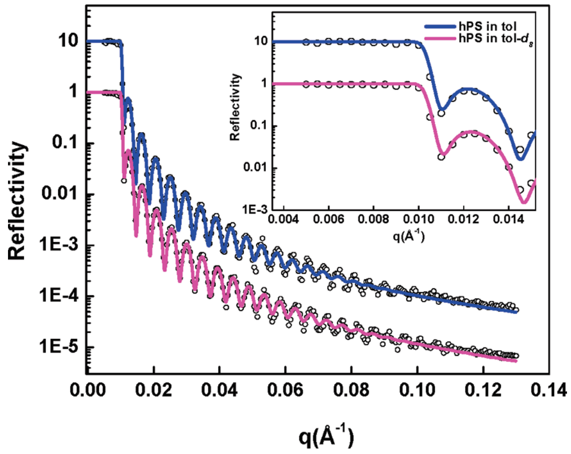


Figure 7. NR data (symbols) of as-cast PS films prepared from protonated toluene and deuterated toluene of a selected molecular mass (51 kg/mol) and film thickness (133 nm). The solid lines are the fits to the data.

For protonated PS films the critical edge of the film surface occurs at a lower q than the critical edge of the silicon oxide substrate. By deuterating the PS, the film critical edge is shifted to a q larger than the substrate crticial edge, which makes determination of the film SLD (and changes thereof)

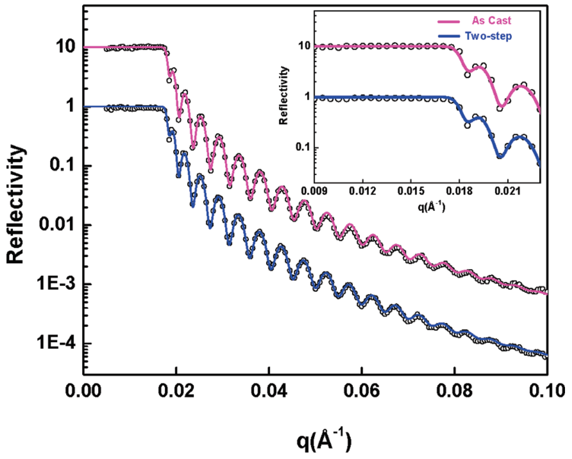


Figure 8. NR data (symbols) of as-cast and two-step annealed deuterated PS films prepared from protonated toluene of a selected molecular mass (52 kg/mol) and film thickness (120 nm). The solid lines are the fits to the data.

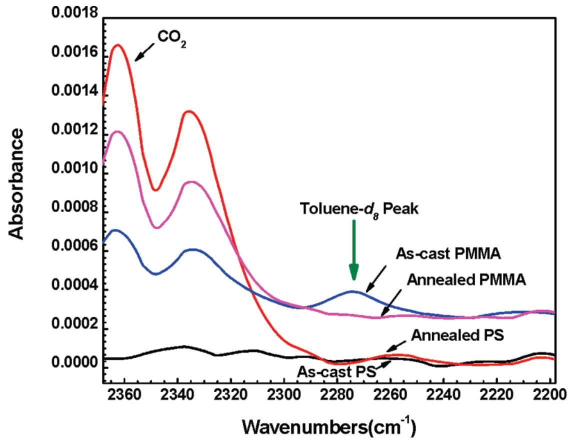


Figure 9. IR spectra of as-cast and two-step annealed PS (51 kg/mol) and PMMA (20 kg/mol) homopolymer films with a film thickness of 160 nm. The intensity of the CO_2 peaks (2300 cm^{-1} and below) vary based on the remaining CO_2 in the cell after purging but do not overlap with the peaks of interest.

more robust. Figure 8 shows NR data for annealing of dPS: Even after the full two-step annealing, there is no change in the position of the critical edge or the overall NR profile. Thus, within the uncertainty of the measurement, there is no change in film density or thickness. Based on the fitting of the NR data (not shown here), the SLDs of as-cast and annealed dPS films match the SLD value of pure dPS homopolymer ($\approx 6.2 \times 10^{-6}$ Å^{-2}). Thus, even when directly measuring the critical angle of the polymer film, the most sensitive means of determining composition, there is no measurable residual solvent in polystyrene films. PS has slightly higher solubility in toluene than PMMA. Compared with PMMA, PS chains dissolved in toluene are more swollen and more flexible. Tsige et al.[22] found the stiffness of polymer chains considerably influences the transport properties of solvents. In particular, small molecules diffuse more easily through a flexible polymer network. During spin-casting, solvent is rapidly evaporating and the polymer concentration rapidly increasing. The solvent molecules are experiencing a corresponding rapid decrease in their diffusion coefficients. During the casting of a PMMA film, the toluene diffusion will be comparatively slow, preventing the solvent from diffusing out of the film (and evaporating) before the film vitrifies and further diffusion is arrested. In other words, the relatively lower mobility of a PMMA matrix (for toluene) traps some solvent within the film during preparation. This solvent can be removed by heating the material, which induces mobility and enables relaxation.

FTIR Measurements. To complement the inverse-space reflectivity techniques employed above, we performed measurements of residual solvent concentration in similarly prepared films using Fourier transform infrared (FTIR) spectroscopy. Figure 9 shows an example of FTIR data from PS and PMMA films prepared from toluene-d_8 with a film thickness of ~160 nm. The stretching vibration of the C$-$D bond in toluene-d_8 occurs at ~2275 cm^{-1}, which has very limited overlap with spectra associated with atmospheric CO_2. As a result, the peak at 2275 cm^{-1} provides a reliable measure of residual solvent concentration. The as-cast PMMA film shows a peak at ~2275 cm^{-1}, indicating a measurable amount of residual toluene. After thermal annealing, the peak in the as-cast PMMA film disappears, a result consistent with the NR data above. For as-cast and annealed PS films, there are no peaks at ~2275 cm^{-1}. In order to estimate the mass fraction of residual solvent in the PMMA film, a calibration was conducted with a liquid cell with a known mass ratio of toluene and PMMA. Using this calibration and the area ratio of the solvent and polymer FTIR band, the mass fraction of residual solvent in the as-cast film was calculated to be $1.2\% \pm 0.2\%$. These results are all consistent with the NR data reported above.

Conclusions

We undertook a quantitative investigation of residual solvent content in homopolymer thin films, using neutron reflectivity and FTIR. Only a small amount of toluene solvent remains in as-cast PMMA films prepared at room temperature. However, the amount of residual solvent in PMMA films can conceivably be controlled by adjusting the casting temperature. The residual solvent in PMMA can be progressively removed with thermal treatment. There was no measurable quantity of residual toluene in PS for the range of molecular mass and thickness we investigated. This result was confirmed using all four protonated/deuterated contrast conditions for the polymer and solvent. Residual solvent within polymer films can greatly affect film properties: e.g., the solvent can facilitate ordering or reduce film brittleness. Neutron reflectivity proves a powerful measurement tool for studying this problem and better understanding the interplay between residual solvent and film properties.

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(17) Certain equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the NIST, nor does it imply the materials are necessarily the best available for the purpose.

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