Low-density polymer thin film formation in supercritical carbon dioxide

Tadanori Koga,[a),b)] Y.-S. Seo, J. L. Jerome, S. Ge, M. H. Rafailovich,[a),c)] J. C. Sokolov, and B. Chu
State University of New York at Stony Brook, Stony Brook, New York 11794

O. H. Seeck
FZ Juelich GmbH, Institut für Festkoerperforschung, 52425 Juelich, Germany

M. Tolan
Universitaet Dortmund, Experimentelle Physik I, Otto-Hahn-Strasse 4, D-44221 Dortmund, Germany

R. Kolb
ExxonMobil Research and Engineering Company, Annandale, New Jersey 08801

We report a method for producing stable low-density polymer films by using supercritical carbon dioxide ($scCO_2$). Two different molecular weight polystyrene films with various thicknesses were exposed to $scCO_2$ along the density fluctuation ridge in $P-T$ phase diagram. The swollen structures could be then frozen by flash evaporation of CO_2 without forming additional voids. X-ray reflectivity data clearly showed that exposure to $scCO_2$ could be used to produce uniform low-density films of about $2R_g$ thick or less, where R_g is radius of polymer gyration. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1629799]

Increased miniaturization in the electronics industry has produced a need for highly uniform ultrathin polymer coatings with well-controlled optical and dielectric properties. Often the thickness of these films is commensurate with a few radii of gyration (R_g) of the polymer, and tight clearances impose very strict tolerances on surface roughness. This high degree of confinement therefore makes it difficult to satisfy the stringent uniformity requirements if we modify the electronic properties by standard methods of gas foaming or blending with other polymers or inorganic additives. Here we show an approach for producing stable, uniform, low-density ultrathin polymer films by using supercritical carbon dioxide ($scCO_2$). We demonstrate that this method provides an efficient and environmentally safe mean for producing materials with variable index of refraction and dielectric constants for electronics applications.

$ScCO_2$ has long been known to be a "green" medium for polymer chemistry or material science.[1] Unfortunately, its potential benefits have not been fully exploited since only a limited class of polymers can be dissolved in $scCO_2$. Recently, using *in situ* neutron reflectivity, we have shown that a wide variety of polymer thin films can swell as much as $30\%-60\%$ when exposed to $scCO_2$ within a narrow temperature and pressure regime, known as the "density fluctuation ridge"[2–4] that defines the maximum density fluctuation amplitude in CO_2. Furthermore, we found that the *in situ* film quality, i.e., density, roughness, and film thickness, could be frozen by flash evaporation of CO_2. This process vitrifies the polymer without formation of micron-sized voids which are known to form in the bulk when $scCO_2$ is forced under high pressures into polymers with which it is immiscible.[5,6]

In this letter, we report x-ray reflectivity (XR) measurements where the density profile of the vitrified films is measured directly and correlated with other properties such as the dielectric constant, index of refraction, and surface glass transition.

Samples consisted of two kinds of hydrogenated polystyrene (PS) (PS1:$M_w = 2.0 \times 10^5$, PS2:$M_w = 6.5 \times 10^5$) with glass transition temperature, $T_g = 100\,°C$. Both polymers were obtained from Polymer Laboratories and their polydispersity indices were 1.05. Thin films were spun cast on HF etched Si substrates and annealed for 5 h in vacuum of 10^{-6} Torr at $T = 150\,°C > T_g$, in order to remove residual solvent and spin induced stress. The films were then placed in a high pressure chamber containing $scCO_2$ at $T = 36\,°C$ and $P = 8.2$ MPa for 2 h, and then quickly depressurized to atmospheric pressure within 10 s. This condition was chosen since they correspond to the density fluctuation ridge in the vicinity of the critical point and can be still tuned within the experimental resolution. The XR measurements have been carried out at the X10B beamline of the National Synchrotron Light Source, Brookhaven National Laboratory using photon energy of 11 keV, i.e., x-ray wavelength (λ) of 1.13 Å.

Figure 1 shows the representative XR profile for a PS1 thin film before and after exposure to $scCO_2$. In the figure we plot the scattering intensity, $I(q_z)$, as a function of the momentum transfer normal to the surface, $q_z = 4\pi \sin \theta/\lambda$ where θ is the glancing angle of incidence. The dashed line in the figure illustrates the shift of the Kiessig fringes to a higher frequency after exposure, which indicates that the layer has thickened. A three layer model used to obtain the solid line fits to the data is shown in the inset (a), where we plot the dispersion (δ) value in the x-ray refractive index corresponding to the silicon substrate and the native oxide and the PS layers. The dashed and solid lines correspond to the profiles before and after exposure, where we see that the

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[a)]Author to whom correspondence should be addressed.
[b)]Electronic mail: tkoga@notes.cc.sunysb.edu
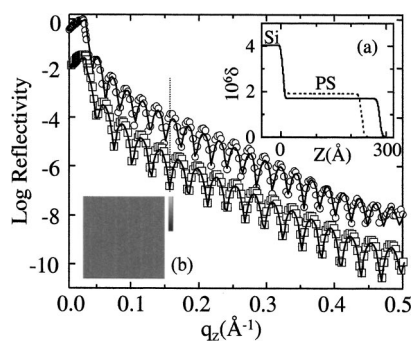[c)]Electronic mail: mrafailovich@notes.cc.sunysb.edu

FIG. 1. Measured XR before (□) and after (○) exposure. The solid lines correspond to the best-fit to the data using the dispersion profiles shown in the inset (a). The inset (b) shows AFM data (image size of 10 μm×10 μm, height scale of 0–5 nm) for the exposed film.

FIG. 2. (a) ρ vs L_0 for the exposed films: PS1 (○), PS2 (□). In the inset, L_0/R_g dependence of ρ is shown. (b) Measured XR (○) and refinement (solid line) of the thick frozen PS1 film. (c) FT of measured (○) and calculated (solid line) XRs. (d) δ profile used for the refinement. In the inset, ρ expanded near the surface area is shown.

initial thickness, $L_0 = 223$ Å has increased to $L = 275$ Å. This corresponds to a linear dilation, $S_f = (L-L_0)/L_0 = 0.23$ which is much larger than the bulk swelling of 0.07.[4] Examination of the data also shows that the dilation occurs without a significant damping of the Kiessig fringes. This is consistent with the fitting model where we found that the rms roughness (σ) between the polymer and air layers remain unchanged ($\sigma = 4.6 \pm 0.4$ Å) before and after exposure. This was further confirmed by measuring the x-ray diffuse scattering of the films where no change in intensity or deviation from the usual capillary power law decay[7] was observed before and after exposure. These results show that no lateral density inhomogeneity larger than the x-ray wavelength and less than the coherence length of the x-ray beam (1 μm) occurs due to exposure in scCO$_2$. In order to further check that large voids (>1 μm) were not present, the surface of the film was scanned with atomic force microscopy (AFM) in series of 100×100 μm scans across the entire sample surface. A typical scan is shown in the inset (b) where the surface appears flat and featureless with $\sigma = 5$ Å. Consequently, it is reasonable to conclude that the films exposed to CO$_2$ in the density fluctuating regime have an excessive amount of the free volume and can be used to produce uniform, low-density polymer films. In order to determine whether the decrease in density is a function of L_0 or molecular weight (M_w), we performed similar measurements on films of different thicknesses for PS1 and PS2. The results are plotted in Fig. 2(a) where we see that the density of PS films can be decreased from approximately 23% to 13% by varying the thickness of the film. It is interesting to note that the data can be collapsed on a universal curve when L_0 is scaled by R_g, expressed in terms of the polymerization index, N, as $R_g = 6.7$ Å$\times (N/6)^{1/2}$, as shown in the inset of Fig. 2(a). Hence, when confined as a thin film on a surface, thickness as well as molecular structure influence the density. The density obtained from the *in situ* S_f values[2,4] is plotted as a dashed line in the inset of Fig. 2(a), assumed that the polymer chains stretch only in the direction normal to the surfaceand the total mass is conserved.[8] The fact that the results from the differing experiments are in good agreement indicates that in the case of PS, rapid sublimation of the gas preserves the *in situ* dilation of the films.

We also exposed films that were much thicker than size of polymer chain ($2R_g$) in order to see whether dilation occurred in the absence of direct contacts with the surface. The
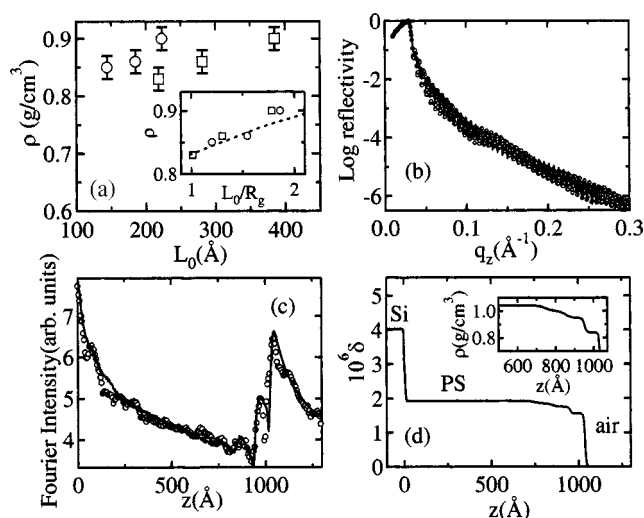
XR spectra for the PS1 film ($L_0 = 930$ Å, $S_f = 0.10$) are shown in Fig. 2(b) where we can see that the data shows a pronounced beating pattern. Since we can observe many Kiessig fringes, a Fourier transform (FT) analysis method[9] was used to analyze the profile. The FT profile of the spectra corresponding to the data in Fig. 2(b) is shown in Fig. 2(c).[10] In this technique the XR and FT data are fitted simultaneously using a dispersion model. The best fits [solid lines in Figs. 2(b) and 2(c)] were obtained with the model shown in Fig. 2(d) which consisted of six layers, silicon substrate, native oxide, and four different PS layers, based upon the number of the peaks in the FT profile. From the inset of Fig. 2(d) we can clearly see that a layer about 100 Å thick is formed at the polymer/air surface with a reduced density of $\rho = 0.83$ g/cm^3 and a relatively sharp interface of about 10 Å with the layers beneath. The subsequent layers also have reduced density, but these layers are more diffuse and decay over a region of approximately 200 Å towards a uniform layer with the bulk density. This behavior, which was independent of M_W, was observed in all films larger than $4-5R_g$, and for thickness of at least 200 nm, which are at the limit of our XR detection method. Hence, surface modification through exposure to scCO$_2$ appears to be a universal phenomenon for all the polymer films regardless of thickness. This effect had not been previously reported since it occurs on a nanometer scale and is difficult to detect when only bulk properties are measured.

The reduction in density has several consequences regarding the material properties of the films: (i) A decrease in the density of a film can be correlated to a decrease in its optical index of refraction (n_f) and dielectric constant. We therefore measured the corresponding changes in the electronic properties of the exposed films by using spectroscopic ellipsometry.[11] Figure 3 shows the refractive indices of the PS2 layers for the unexposed ($L_0 = 2R_g$) and two exposed films with $L_0 = 1.3R_g$ ($S_f = 0.21$) and $L_0 = 2R_g$ ($S_f = 0.16$). From the figure we can clearly see that the n_f values for the exposed films decreased with increasing the S_f values over
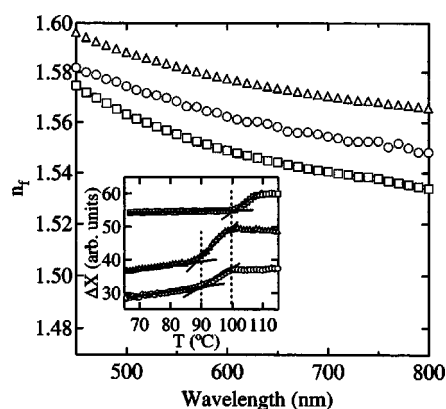
FIG. 3. Index of refraction for PS2: before (Δ) and after [$L_0 = 2R_g$ ($\bigcirc$) and $L_0 = 1.3R_g$ ($\square$)]. In the inset, ΔX vs T curves for PS2: exposed films $L_0 = 1R_g$ ($\bigcirc$) and $L_0 = 6.4R_g$ (Δ), and unexposed film ($\square$).

the wide wavelength range of 450–800 nm. Since dielectric constant of materials can be derived from a square of refractive index, we can therefore vary the dielectric constant for PS film from 2% to 4% in the same L_0, R_g parameter space.

(ii) A change in density is also associated with a change in free volume of the polymer. It is well known from the Flory–Fox theory[12] that a change in free volume will result in decreased T_g. In order to explore this hypothesis, T_g measurements were made using the shear modulation force microscopy (SMFM) technique using a Digital Instruments Dimension 3000 which was previously shown to be a simple and robust method for measuring the surface T_g with an accuracy of 2 °C.[13] In the inset of Fig. 3 we plot the modulation amplitude, ΔX, vs T for an unexposed PS2 film and two PS2 films exposed to scCO$_2$ one, $L_0 = 220$ Å or $1R_g$ thick, and another 1400 Å or $6.4R_g$ thick. From the figure we can see that the discontinuity in the plot, which corresponds to T_g, occurs at $T = 100$ °C or the bulk T_g for the unexposed film, as expected. The T_g value for the exposed film $1R_g$ thick ($S_f = 0.23$), decreases by 10 °C compared to that of the unexposed PS film. Similarly, for the film $6.4R_g$ thick shown by squares, we also find a T_g value of 90 °C. This result is consistent with the x-ray data which show a region of effective dilation, $S_f \sim 0.2$ near the surface, since SMFM is a surface sensitive technique it cannot detect the difference in the concentration profiles of the thick and thin films below the surface.

In conclusion we have found that exposure to scCO$_2$ in the P–T range corresponding to a density fluctuation regime, can be used to produce uniform low-density films of approximately $2R_g$ or less. For films $L_0 \gg 2R_g$, a region of low-density, about $3R_g$ thickness, is produced at the surface that then decays into the bulk. In this study we used PS, where the miscibility of scCO$_2$ is low and the dilation is enhanced only by a factor of 0.2 at the ridge. It is expected that much higher dilations can be achieved in polymers such as Teflon and the acrylates.[4] This technique can therefore be exploited to produce high quality films of low dielectric constants, variable index of refraction, and enhanced adhesion at lower temperatures to other surfaces.

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[8] As we already reported [T. Koga, Y.-S. Seo, X. Hu, K. Shin, Y. Zhang, M. H. Rafailovich, J. C. Sokolov, B. Chu, and S. K. Satija, Europhys. Lett. **60**, 559 (2003)] a roughly 20 Å decrease cannot be avoided in the quick evaporation process. We therefore estimated the "apparent" dilation for the films considering this change to calculate the density.

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[10] FT profile is related to the corresponding one-dimensional Patterson function, i.e.:
$F(d, q_1) = |\int_{q_1}^{q_2} q_z^4 I(q_z) \exp(iq_z d) dq_z|^2$, where q_1 is the lower q limit set as $q_1 = 0.052$ Å^{-1}, q_2 is the higher q limit set as $q_2 = 1.0$ Å^{-1} and d is the film thickness, respectively.

[11] A H-VASE spectroscopic ellipsometry (J. A. Woollam Co., Inc.) was used. In order to fit the data, the same three-layer model was used with the literature n_f values for native oxide and Si substrate and the film thicknesses determined by XR.

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