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# Reversible negative thermal expansion of polymer films

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A basic understanding of the properties of thin polymer films is of fundamental importance for developing applications in nanotechnology. Results of energy and angle dispersive x-ray reflectivity measurements on polymer thin films as a function of temperature exhibit reversible negative thermal expansion below the glass transition temperature $T_g$. Above $T_g$, the thickness expansion becomes almost equal to the expected bulk volume expansion. These results could be explained on the basis of evolution of disorder with temperature at the interfaces, chain entanglement and associated entropy changes.

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The physical properties of materials confined in nanometer length scale exhibit interesting deviation from the properties of the bulk materials. The utilization of organic materials in device fabrication [1] has generated a lot of research activities to understand properties of nanometer thick organic thin films [2]. These studies have provided us interesting insight about the growth mechanism and thermal properties of these ultrathin films [2–5]. Polymer films are particularly relevant for technological applications and are experimentally easy to control for developing fundamental knowledge regarding the effect of confinement (between film-air and film-substrate interfaces) on nanosoft materials. The thermal expansion of polymer films have been studied before [4–8], but to the best of our knowledge no systematic experimental measurement has been made to understand the negative thermal expansion (NTE) of polymer films and its reversibility as a function of temperature. Here we present results of energy (EDR) and angle (ADR) dispersive x-ray reflectivity studies of spin-coated polystyrene (PS) and polyacrylamide (PAM) films in the temperature range of 333 K – 433 K to study the reversibility of thermal expansion of polymer films. The NTE phenomena is observed in variety of materials and a thermodynamic relation between thermal expansion and disorder, $\alpha_V = K(dS/dV)_T$ with $K$ as volume compressibility, may be used to explain this behavior [9]. In conventional materials, as volume expands, disorder (or entropy) also increases giving rise to positive thermal expansion coefficient. But in some systems, the molecules may attain a more ordered state (negative $dS$) as the volume expands giving rise to NTE.

The two polymers studied here are of widely different nature, PAM being soluble in water and PS in nonaqueous medium. A 2 mg/ml solution of the PAM (BDH Chemicals, UK. $M_w > 5\,000\,000$) was prepared with water having 18.2 Mohm cm resistivity (Millipore, USA) which have been used to spin cast the PAM films on hydrophilic Si (100) substrates. A 6 mg/ml. solution of PS (Aldrich, USA. $M_w = 212\,400$) in toluene were used to prepare the PS films on similar substrates. We have carried out the reflectivity measurements by keeping the samples in vacuum ($10^{-2}$ mbar).

In x-ray reflectivity measurements [10], the intensity of the specularly reflected x-ray beam is measured as a function of wave-vector transfer $q_z (= 4\pi E \sin\theta/12.3986)$ by keeping the incident and exit angle $\theta$ equal. Here $q_z$ is in angstrom inverse and $E$ is in keV units. The ADR measurements were carried out by changing the angle $\theta$ in a laboratory setup [3] and the EDR measurements were performed at the EDR beamline [11,12] of the BESSY II synchrotron (Berlin, Germany) by keeping the angle $\theta$ constant (0.8° here).

One can extract the reflectivity profile $|r(q_z)|^2$ of a sample from the measured energy dispersive intensity profile $I(q_z)$ if the incident intensity distribution $I_0(E)$ is known [11,12], as $|r(q_z)|^2 = I(q_z)/I_0(E)$. However, to obtain more reliable thickness and roughness parameters as a function of temperature from the EDR measurements, we extracted $I_0(E)$ for EDR data by measuring both angle and energy dispersive intensity profiles of each sample at room temperature and noting that $I_0(E)$ for ADR is a constant. The $I_0(E)$ profile for EDR was extracted for each sample from these measurements and then this profile was used to normalize higher temperature intensity data for that sample. In Fig. 1, we have shown EDR and ADR profiles for both PS and PAM films at room temperature alongwith the raw energy dispersive intensity profiles.

Although EDR measurements provide reflectivity profile in a limited range of $q_z$ as compared to that obtained in ADR measurements, the entire profile can be collected within a minute. We collected EDR data at a fixed temperature of 434 K continuously for 20 min to confirm that no noticeable radiation damage occurs during the measurement time. All the normalized EDR and ADR data were analyzed [10] using a simple model having constant electron density of polymer film and two interfacial roughness profiles situated at polymer-air and polymer-substrate interfaces. Typical fits of PS and PAM reflectivity data are shown in the inset of Fig. 1. We have used here a simple model to reduce the uncertainty of thickness determination within ±0.5 Å. The thickness determination has to be accurate in this study as the expected change is only a few angstrom. Moreover, we measured film thickness continuously at small temperature steps to reduce this uncertainty further. The EDR is an ideal technique for this type of measurements. The earlier studies [6–8] relied

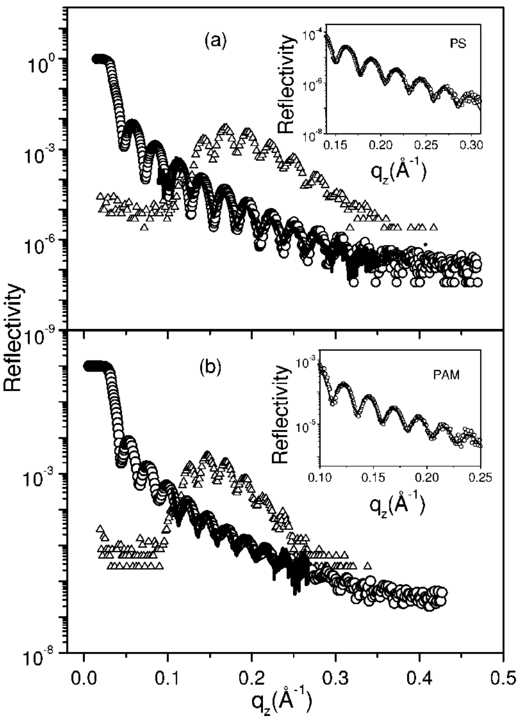

FIG. 1. Raw energy dispersive data (triangle) are shown as a function of $q_z$ for (a) PS and (b) PAM thin films with the ADR profiles (circles). The extracted EDR profiles (lines) are also shown. In the insets, typical fits of EDR profiles are shown.

only on ADR measurements and could not establish the reversibility of NTE of polymer films beyond doubt due to possible error in thickness determination.

To establish reversibility of thermal expansion below and above glass transition temperature ($T_g$) we have performed both EDR and ADR studies on several polymer films and results of four PS films and two PAM films will be presented here. In Fig. 2(a) we have presented typical thermal expansion behavior of PS films. This result was obtained by fitting large number of EDR profiles. Below the $T_g$ of PS ($\sim 375$ K) we observe 2-Å thickness reduction over about 40-K temperature range giving rise to a thermal expansion coefficient of $-2.5\times10^{-4}\ K^{-1}$. Above $T_g$ the thickness increases about 6 Å over about 60-K temperature range and the resultant expansion coefficient comes to be $4.7\times10^{-4}\ K^{-1}$. In Fig. 2(b) we have presented the obtained thickness variation of two PAM films having initial thicknesses 143 Å and 260 Å. As the temperature range used in these measurements was below $T_g$ of PAM ($\sim 438$ K), we could only observe negative thermal expansion here with the coefficient of $-6.8\times10^{-4}\ K^{-1}$ and $-1.0\times10^{-3}\ K^{-1}$, respectively for these two films. Our preliminary results above $T_g$ indicate positive thermal expansion of PAM films. We have investigated PS films in detail to understand reversibility and stability of NTE in polymer films as plenty of earlier results exists for this system starting from 1940s [13].

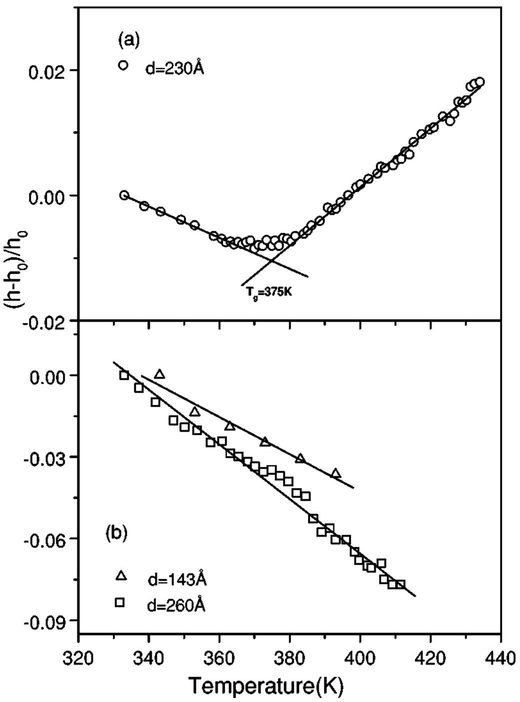

FIG. 2. The obtained thickness variations of (a) PS and (b) PAM films are shown as a function of temperature. Linear fits are used to extract $\alpha_N$ and $T_g$.

In Figs. 3(a) and 3(b) we have presented results of temperature cycles for two PS films having thicknesses 528 Å and 290 Å, respectively. We did not wait at each temperature for more than a minute, the time required by the temperature controller to stabilize a temperature, to avoid the effect of synchrotron beam damage. For the case of 528 Å film the first temperature cycle was done up to 363 K (below $T_g$) from 323 K and back. The film shows a NTE and the thickness reduction was about 6 Å. We also observe that lower thickness (522 Å) obtained at 363 K is retained by the film

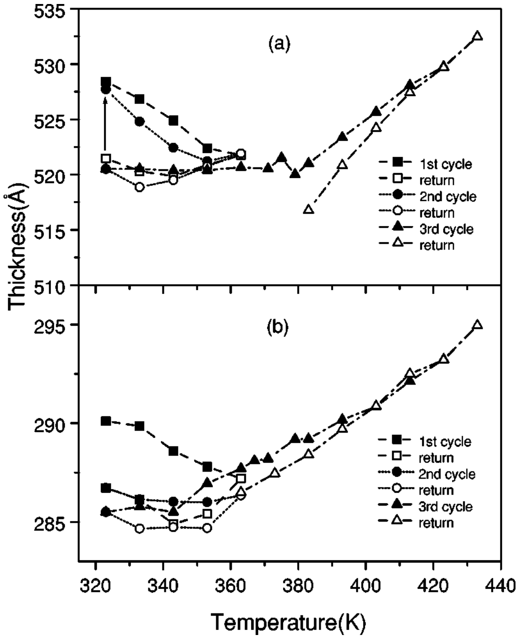

FIG. 3. The obtained thickness variations in three temperature cycles (heating and cooling) for the PS films of thicknesses (a) 528 Å and (b) 290 Å are presented as a function of temperaure.

after reaching back 323 K exibiting almost zero thermal expansion (ZTE) coefficient during this cooling. However, when we kept the film in vacuum for several hours by turning off x-ray beam, the film gained back its original thickness [refer to the arrow in Fig. 3(a)]. In the second temperature cycle, almost the first cycle is repeated that is NTE during heating cycle and ZTE during cooling cycle. At the end of second cycle, however, we started the third heating cycle immediately and went up to 433 K and back to 383 K. The film almost traces back (with the error bar of ±0.5 Å) the thickness observed during the first and second cooling cycle until the glass transition temperature, and beyond that temperature it exibits positive thermal expansion. During third cooling cycle, we get positive thermal expansion but we observe that thickness at a temperature during cooling cycle is less than that observed during heating. However, if the film is kept at any temperature during cooling cycle, it attains heating cycle thickness with a time delay. This delay is less at high temperature due to decrease in polymer viscosity [2]. For the PS film having 290 Å thickness, we observe almost same behavior [refer to Fig. 3(b)]. For this film the entire experiment was performed without any time delay between cycles and third cooling cycle was done up to 363 K.

We have performed ADR measurements at four temperatures over several thermal cycles to establish the reversibility in polymer thermal expansion, both negative and positive observed below and above $T_g$, respectively, beyond doubt. Before measuring ADR profiles, the film was kept at each temperature for couple of hours. In some cases we followed the increase in thickness as a function of time after reaching back 305 K in a temperature cycle. Our ADR measurements confirm the above mentioned EDR results that the film almost regains its original thickness at this temperature within 45 min. The measured ADR profiles and the corresponding fits as a function of temperature are shown in Fig. 4. The temperatures, top to bottom, indicate the thermal cycles and the corresponding film thicknesses, obtained by fitting (with an error bar of ±0.5 Å), are shown in the inset of Fig. 4. Dips of reflectivity profiles clearly show the thickness variation over cycles. In the first two cycles, starting from 305 K, this film of thickness 236 Å showed ~6 Å reduction in thickness at ~349 K and almost regains original thickness during cooling. Then the film was heated to 406 K in the third heating cycle and positive thermal expansion above $T_g$ was observed and the film again came back close to initial thickness at 305 K following the same path during this third cooling cycle. The next temperature cycle below $T_g$ also reflects the NTE behavior as obtained in first and second heating cycles. From these measurements, we conclude that with each temperature cycle the film thickness comes very close to (with a total spread in thickness $\Delta d \sim 1.4$ Å) initial film thickness, thereby proving nicely the reversible nature of polymer thermal expansion. We also note that in ADR measurements, where sufficient time is spent in each temperature, ZTE is not observed in cooling cycle.

In summary, we have observed three key points in the measurements of thermal expansion coefficient of polymer films normal to the substrate ($\alpha_N$), namely, below $T_g$ the EDR results show NTE and ZTE during heating and cooling cycles, respectively; at any temperature thickness obtained during heating is more than that obtained during cooling in a temperature cycle, and $\alpha_N$ obtained by ADR measurements are always greater than that obtained in EDR studies. We can explain all these observations by using the extensive results of earlier thermal expansion studies of oriented (ordered) polymer rods [13] and noting that thin films of polymer on solid substrate forms ordered structure exibiting a layering [14] that is related to the radius of gyration of the polymer [15]. By using these information we can write $\alpha_N$ as

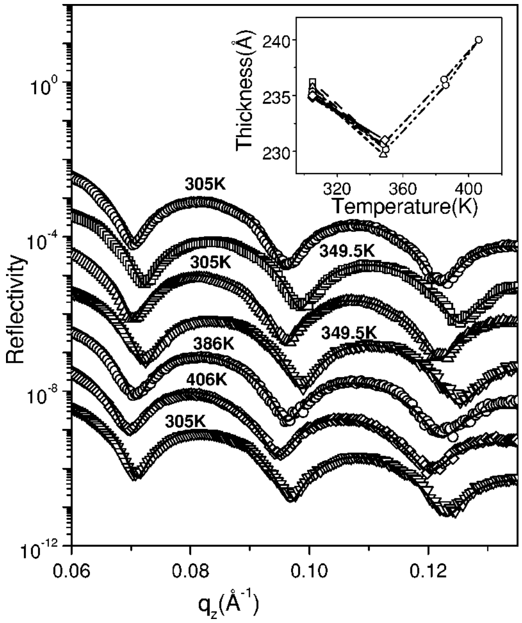

FIG. 4. The measured ADR profiles are presented with fits as a function of temperature for a PS film of thickness 236 Å. Inset shows thicknesses obtained in four temperature cycles.

$$\alpha_N = \frac{(1+\nu)}{3(1-\nu)}\alpha_V \equiv \frac{(1+\nu)}{3(1-\nu)}[\alpha_V^B + \alpha_V^I](1 - e^{-(t/\tau)}), \quad (1)$$

where $\nu$ is the Poisson ratio and $\alpha_V^B$ is the equibrium bulk volume expansion coefficient. The interfacial term can be expressed in terms of entropy change as $\alpha_V^I = K(dS/dV)_T$. This term is relevant as long as there is ordering (layering) at the polymer-substrate interface. At small $t$ ($t \rightarrow 0$), measured $\alpha_N$ accommodates the increase in average space occupied by each molecule, similar to that observed in conventional materials. The last term takes the measured expansion coefficient $\alpha_V$ to the equilibrium value ($\alpha_V^B + \alpha_V^I$) provided the time $t$ is sufficiently large compared to the relaxation time $\tau$, which reduces with reduction of viscosity hence with increasing temperature. This kinetics arises due to change in equilibrium position of molecule — sometimes referred to as the diffusion of *holes* into or out of polymer [4,13]. This is the main reason [13] of having different $\alpha_V$ of polymers below and above $T_g$ and for PS these values are 1.7–2.1 $\times 10^{-4}\ K^{-1}$ and 5.0–6.0$\times 10^{-4}\ K^{-1}$, respectively [16]. The EDR results on 230-Å, 528-Å, and 290-Å PS films above $T_g$ gives us $\alpha_N$ values of $4.7\times 10^{-4}\ K^{-1}$, $4.3\times 10^{-4}\ K^{-1}$, and $4.6\times 10^{-4}\ K^{-1}$, respectively. These values provide us a value of Poisson ratio $\nu$ almost equal to 0.5, indicating that there is almost no movement of molecules along the substrate surface. ADR result gives us $\alpha_N$ value of 7.3 $\times 10^{-4}\ K^{-1}$, which is higher than the value obtained in EDR studies as the measurement time $(t)$ here was much higher. The NTE observed below $T_g$ is arising due to interfacial entropy term. The polymer molecules move into disorder state (positive $dS$) with elevated temperature, the portion of the chain occupies *holes* created during layer formation and as a result the volume reduces (negative $dV$) giving rise to negative thermal expansion. However, during cooling cycle the polymer chains, which are entangled into these holes take longer time to recover back to the *ordered state*. The average NTE coefficient obtained in ADR and EDR measurements comes out to be about $-5.0 \times 10^{-4}\ K^{-1}$ and $-2.6 \times 10^{-4}\ K^{-1}$, respectively. This result and ZTE during cooling cycle indicate that the movement of polymer chain is involved in generating the entropy term. The observed fact that the thickness of polymer film during cooling is always less than that observed during heating confirms that the interfacial entropy term and hence the Eq. (1) is operative over the entire temperature range measured here. This observation indicates that the order through layering in polymer films having thickness close to radius of gyration ($\sim$126 Å for this PS) continues even in liquid state (above $T_g$), which is consistant with earlier observation [17] of layering in simple liquids.

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