

## Glass transition in ultrathin polymer films: A thermal expansion study

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(Received 5 April 2004; revised manuscript received 3 December 2004; published 4 April 2005)

The glass transition process gets affected in ultrathin films having thickness comparable to the size of the molecules. We observe systematic broadening of the glass transition temperature ( $T_g$ ) as the thickness of an ultrathin polymer film reduces below the radius of gyration but the change in the average  $T_g$  was found to be very small. The existence of reversible negative and positive thermal expansion below and above  $T_g$  increased the sensitivity of our thickness measurements performed using energy-dispersive x-ray reflectivity. A simple model of the  $T_g$  variation as a function of depth expected from sliding motion could explain the results.

DOI: 10.1103/PhysRevE.71.041801

PACS number(s): 61.41.+e, 61.10.Kw, 65.60.+a, 64.70.Pf

### I. INTRODUCTION

The phase transition process of noncrystalline materials from a glassy to molten state has remained an outstanding problem in condensed matter physics especially when these materials are confined in a nanometer length scale. This is a subject of intense research for macromolecules like polymers as the confinement effect becomes prominent even in films having thicknesses of tens of nanometers. The effect of nanoconfinement on the glass transition temperature ( $T_g$ ) of ultrathin polymer films is being studied extensively [1,2] as the results may influence our basic understanding about the glass transition mechanism in general [3,4] and the dynamics of polymer chains near the glass-melt transition, in particular [5,6]. These studies are also important for technological applications of nanometer-thick polymer films [7]. In most of these investigations the thicknesses of polymer films are measured using ellipsometry technique [8] as a function of temperature across glass-melt transition. The  $T_g$  in these measurements was defined [2,8] using temperatures at which thermal expansion deviates from linearity above ( $T_+$ ) and below ( $T_-$ ) the glass transition with  $T_g=0.5(T_++T_-)$ . In ellipsometry measurements,  $T_+$  was found to be constant and  $T_-$  exhibited a rapid reduction as the thicknesses of the polymer films approached 10 nm—a thickness below which  $T_g$  could not be determined from thickness measurements due to the contrast problem [2,3,8]. As  $T_+$  was constant, both broadening of the glass transition  $\Delta T (=T_+-T_-)$  and  $T_g$  itself were found to follow the variation of  $T_-$  with thickness in polystyrene thin films. It was assumed that for thin polymer films a top layer of thickness around 5 nm is in a molten state even at room temperature. The effect of the molten top free surface on the reduction of  $T_g$  has been confirmed by capping the polymer films by a metal layer [9]. The measurements were performed on primarily polystyrene films having thickness between 10 and 100 nm and the values of  $T_g$  thus obtained from various different measurements could be parameterized with an empirical relation

$$T_g^f = T_g^b [1 - (A/h)^\delta], \quad (1)$$

where  $T_g^b$  and  $T_g^f$  are glass transition temperatures for bulk polymer and for a film of thickness  $h$ , respectively [2,3,8].

This equation obviously indicates finite  $T_g$  above a thickness  $A$  and its value was found to be 3.2 nm. It is indeed very interesting to note that except for one data set [4], a large number of measurements [2,8,9] performed in different experimental conditions with a variety of surface treatments of silicon substrates, which were used for depositing polystyrene films of various molecular weights, followed this empirical relation with  $A=3.2$  nm and  $\delta=1.8$ . The implication of this intriguing result is that a film of 3.2 nm will not show finite  $T_g$  and even for an 8-nm film  $T_g^f$  will be below room temperature. Our results, however, exhibit evidence of a glass transition for films having even 4 nm thickness and the obtained value of  $T_g^f$  remains close to  $T_g^b$  though the transition becomes broad as the thickness is reduced. We also demonstrate that one has to use the concept of a distributed glass transition temperature [6] to explain the dramatic increase in  $\Delta T$  as the thickness becomes comparable to the radius of gyration ( $R_g$ ) of the polymer. In a recent calorimetric measurement, ultrathin (1–10 nm) polymer films exhibited [10] a pronounced glass transition temperature and this measurement also showed a minor change in  $T_g$  with thickness but confirmed the broadening of the glass transition with a reduction of the film thickness, which is in agreement with our findings. Moreover, the results presented here are consistent with earlier thickness measurement studies using conventional x-ray reflectivity and ellipsometry techniques except for films less than 20 nm for which the sensitivity of earlier thickness measurements was not satisfactory [2,3,8].

### II. EXPERIMENTAL STUDIES

#### A. Sample preparation

We have studied the thermal expansion behavior of spin-coated ultrathin polystyrene films in the thickness range of 4–31 nm. Polystyrene (Aldrich Chem. Co., Milwaukee, WI,  $M_w=212\,400$ , radius of gyration  $R_g \sim 12.6$  nm, and  $T_g^b=373$  K) thin films were deposited by spin coating solutions of the polymer in toluene at around 3000 rpm onto hydrophilic silicon (100) substrates prepared following RCA (Radio Corporation of America) cleaning procedure. In this chemical treatment, substrates were first heated with

30% ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution (1:1 volume ratio) for 10 min followed by a rinsing with acetone and alcohol and finally washed with purified water having 18.2 M $\Omega$  cm resistivity (Millipore Corp., Billerica, MA). The film thickness was controlled by changing the rotation speed and by choosing an appropriate concentration of the solution from 1 to 6.5 mg/ml of toluene.

### B. Sample characterization

It is known that any property of polymer films determined through thickness measurements is sensitive to dewetting phenomena and one has to be careful especially for ultrathin polymer films [5,11–13]. We present here the results of polymer films deposited on a hydrophilic silicon (100) substrate, which do not show any dewetting even after repeated thermal cycling. The polymer films were heated in a sample cell under vacuum ( $3 \times 10^{-2}$  mbar) at a temperature (403 K) above  $T_g^b$  of polystyrene (PS) and we have monitored the top surface of the film with an optical microscope. We have performed these measurements for both thick and ultrathin PS films down to the 4.3-nm range reported here. In Fig. 1(a), the obtained angle-dispersive x-ray reflectivity (ADR) profiles and corresponding fits are presented as a function of temperature for a 4.3-nm-thick polymer film. From our analysis, it is seen that the roughness values of this film of 4.3 nm thickness measured at 303 K and 403 K come out to be 2.8 Å and 3.3 Å, respectively [Fig. 1(a)] and we could get back the same parameter after repeated thermal cycling. Dewetting of the film would have increased the roughness drastically [5] and we could not have got back the same reflectivity profile after thermal cycling.

We have also performed energy-dispersive x-ray spectrometry measurements on a chemically treated silicon substrate and polymer films. In the inset of Fig. 1(a), part of the energy-dispersive x-ray spectra of a substrate and polymer film collected at 5 keV energy in a scanning electron microscope is shown to indicate that the film is free from other contaminants and our impression is that a clean environment should be used to avoid dewetting of the polystyrene films deposited on hydrophilic silicon substrates.

### C. Transverse x-ray diffuse scattering measurements

We have studied the in-plane correlation present in polymer films by measuring transverse x-ray diffuse scattering as a function of temperature at the X22C beamline of the National Synchrotron Light Source, Brookhaven National Laboratory. In Figs. 1(b) and 1(c) we have shown data collected at two temperatures as a function of  $q_x$  [ $= (2\pi/\lambda)(\cos \beta - \cos \alpha)$ ] at three fixed  $q_z$  [ $= (2\pi/\lambda)(\sin \alpha + \sin \beta)$ ] values, where  $\alpha$  and  $\beta$  are incidence and exit angles of x-rays of wavelength  $\lambda$ . Capillary waves are of particular importance in the case of soft matter interfaces and polymer films are known [11,13] to exhibit characteristics of capillary-wave correlation [11–15]. From the theory of capillary waves, the height-height correlation function can be expressed as

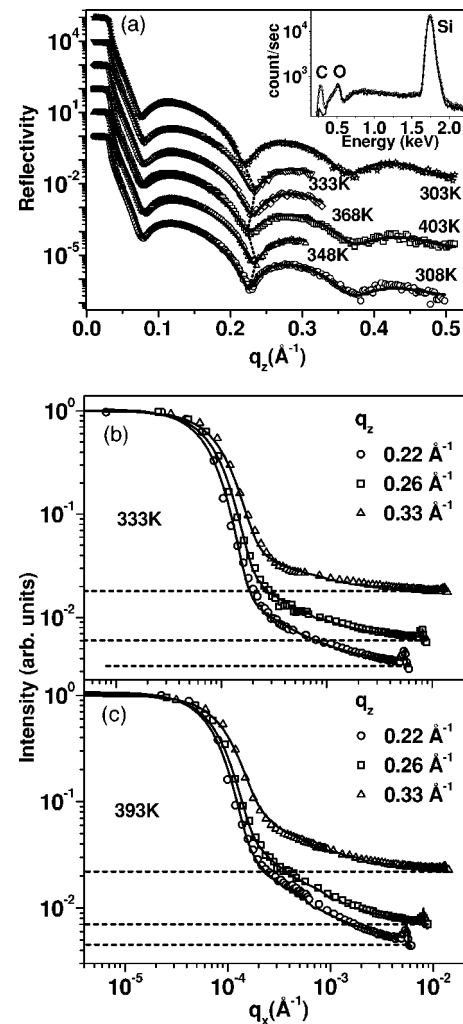


FIG. 1. (a) The measured ADR profiles (shifted vertically) of a 4.3-nm film with fits are shown as a function of temperature, top to bottom, for a thermal cycle. The shift of minima, marked by dashed lines, indicates the reversibility of the thermal expansion. In the inset, part of the energy-dispersive x-ray spectra collected from a silicon substrate (line) and an ultrathin polymer film (line+circle) is shown. In (b) and (c), log-log plots of transverse diffuse scattering intensities are presented along with the fitted curves [15] (solid lines) as a function of  $q_x$  at three values of  $q_z$  (with different symbols) at 333 K and 393 K, respectively. Also the backgrounds used for fitting are indicated by dashed lines.

$$C(R) = (B/2)K_0(\kappa R), \quad (2)$$

where  $K_0(\kappa R)$  is a modified Bessel function,  $\kappa$  is a low-wave-vector cutoff, and  $B = k_B T / (\pi \gamma)$  with  $\gamma$  as the surface tension at temperature  $T$  and  $k_B = 1.3806 \times 10^{-23}$  J/K is the Boltzmann constant. Within an experimentally accessible wave vector range,  $K_0(\kappa R)$  can be well approximated as  $[K_0(\kappa R) \approx -\ln(\kappa R/2) - \gamma_E]$ , where  $\gamma_E$  is the Euler constant. Inserting this type of logarithmic correlation into the scattering function calculation and considering an approximation of the transmission functions  $|T(\alpha)|^2 |T(\beta)|^2$  with that of the substrate the observed intensity can be obtained as [15]

$$I = I_0 \frac{R(q_z)q_z}{2k_0 \sin \alpha} \frac{1}{\sqrt{\pi}} \exp[-q_z^2 \sigma_e^2] \Gamma\left(\frac{1-\eta}{2}\right) \times {}_1F_1\left(\frac{1-\eta}{2}; \frac{1}{2}; \frac{q_x^2 L^2}{4\pi^2}\right) |T(\alpha)|^2 |T(\beta)|^2. \quad (3)$$

Here  ${}_1F_1(x; y; z)$  is the Kummer function and we could fit all the data using Eq. (3) self-consistently [15] [Figs. 1(b) and 1(c)] with this line shape. From our analysis, the values of  $B$  come out to be  $1.1 \text{ \AA}^2$  and  $2.1 \text{ \AA}^2$  for 333 K and 393 K, respectively. Dewetting of films would have generated different line shapes as observed earlier [13]. We find that the films retain this line shape through thermal cycling, confirming that dewetting is not taking place.

#### D. Thickness measurements through reflectivity

Thermal expansion studies of the polymer thin films were carried out in the temperature range of 308–433 K using both energy-dispersive x-ray reflectivity (EDR) and ADR techniques [16]. In specular condition, the intensity of reflected x-ray beam is measured as a function of wave vector transfer  $q_z$  [ $=4\pi E \sin \theta / (hc)$  with  $hc = 12.3986 \text{ keV \AA}$ ] where the incident and exit angles  $\theta$  are kept equal. The ADR experiments were performed by changing the angle  $\theta$  in a laboratory setup [12] and the EDR measurements were carried out at the EDR beamline [17] of the BESSY-II synchrotron (Berlin, Germany) by keeping the angle  $\theta$  constant ( $1^\circ$  here). All the reflectivity measurements both in angle- and energy-dispersive modes were carried out keeping the samples in vacuum ( $10^{-2}$  mbar).

We have already demonstrated [16] that the polymer films deposited on a hydrophilic Si(100) substrate exhibit reversible negative and positive thermal expansion below and above  $T_g^b$ , respectively. Our observation has been confirmed in an independent measurement and a predicted large relaxation time has also been measured [18]. Negative thermal expansion was also observed in polycarbonate ultrathin films while cooling the films below an apparent  $T_g$  [19]. The existence of positive and negative thermal expansion [16,18–20] coefficients above and below  $T_g$  improved the sensitivity of the measurement of the glass transition temperature. Moreover, we used here the EDR technique, which allowed us to collect a large number of reflectivity profiles around  $T_g^b$  in quick succession. The EDR technique is an ideal method to investigate small thermal expansion in thin polymer films. In Fig. 2 we have shown the measured ADR and EDR profiles collected from a polymer film at room temperature along with the fit giving us a thickness of 4.5 nm. The procedure of EDR data extraction and other experimental details of the EDR beamline of the BESSY-II synchrotron has been described earlier [16,21]. We have also shown some of the representative EDR profiles at three different temperatures along with the fitted curves in the inset of Fig. 2. The change in thickness is apparent in the shift of the minimum of the reflectivity curves itself. In the analysis [21] of normalized EDR and ADR data, we have used a model of a polymer film of constant electron density with two roughness profiles at film-air and film-substrate inter-

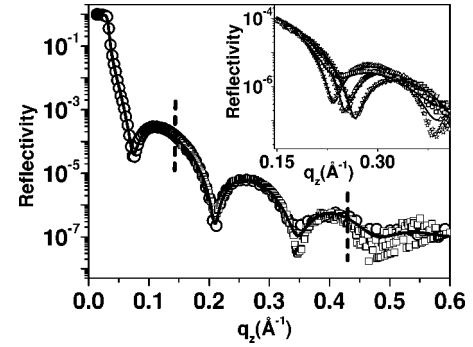


FIG. 2. The ADR (circle) and extracted [16] EDR (square) profiles at room temperature for another 4.5-nm PS film are shown along with the fitted line. Two dashed lines indicate the usable EDR data range. Typical EDR profiles for this film at temperatures 333 K (star), 373 K (up triangle), 429 K (square), and 321 K (down triangle) are also shown along with the fitted profiles in the inset.

faces. The obtained thickness as a function of temperature for this film is shown in Fig. 3(a). Initially, the 4.5-nm PS film showed negative thermal expansion with a coefficient of  $-3.7 \times 10^{-3} \text{ K}^{-1}$  over a  $\sim 30$ -K temperature range starting from 308 K. Near  $\sim 339$  K, negative thermal expansion decreases to give rise to a flat region up to  $\sim 408$  K in the thickness versus temperature curve. Above  $\sim 408$  K, the film thickness increases and the resultant expansion coefficient comes to be  $2.5 \times 10^{-3} \text{ K}^{-1}$ , much greater than that of bulk PS [16,21]. The temperatures  $T_+$  and  $T_-$  were determined by fitting two straight lines at the high- and low-temperature regions, respectively, as shown in Fig. 3(a). The calculated  $T_g^f$  obtained from  $0.5(T_+ + T_-)$  (indicated as  $T_m$ ) and from the intersection of the two fitted lines as shown in Fig. 3(a) were found to be very close for all the films. In Figs. 3(b) and 3(c) we have shown the results of the films having room-temperature thicknesses of 5.7 nm and 23.1 nm, respectively. We find that value of  $T_g^f$  remains very close to that for the bulk polymer  $T_g^b$  for all films but the broadening of the glass transition  $\Delta T (=T_+ - T_-)$  reduces as the film thickness increases.

### III. RESULTS AND DISCUSSIONS

It has been argued [6] that for ultrathin films one can expect two types of diffusion processes: the first one is standard motion controlled by the free volume and the second one is sliding (*reptation*) motion for chains having end points at the free surface. One can expect an increase in the sliding motion for molecules having a center of mass near the surface, giving rise to a decrease in  $T_g$  towards the free surface of a film. In a recent fluorescence measurement of multilayer polymer films, systematic reduction of  $T_g$  was observed for the molecules close to the free surface [22]. We have used this concept for explaining the observed thickness variation with temperature and large broadening ( $\Delta T$ ) of the glass transition. In our simple model, we have assumed that a film is composed of small pseudolayers of equal thickness having different glass transition temperatures ( $T_g$ ). Each of these pseudolayers continues to show negative thermal expansion

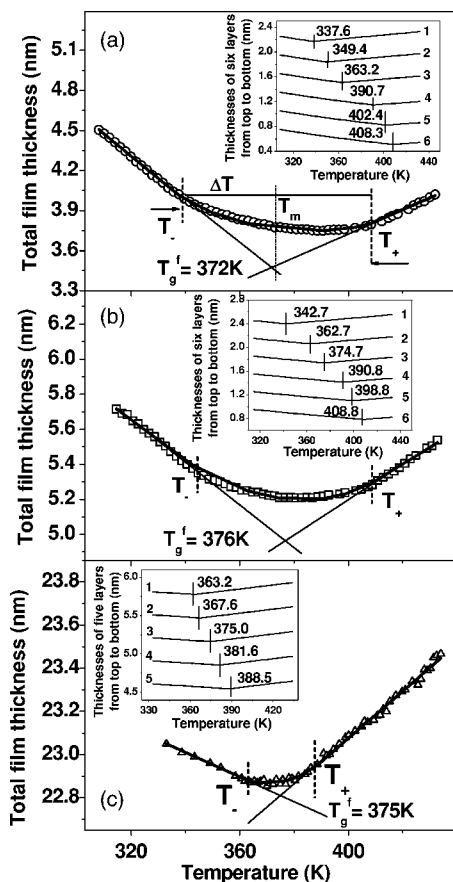


FIG. 3. (a) The obtained thickness variation for the 4.5-nm PS film is presented as a function of temperature for a heating cycle along with the generated curve obtained from our model. The temperatures  $T_-$ ,  $T_+$ ,  $T_m$ , and  $T_g^f$  are indicated and the broadening of the glass transition  $\Delta T$  is marked by straight dashed lines with arrows. Another straight dashed line is used to show that  $T_m$  and  $T_g^f$  are very close (refer to the text for details). In the inset of (a) the six straight lines are shown, indicating the  $T_g$ 's of six pseudolayers as obtained from our model (the profiles are vertically shifted for clarity). The results of a similar analysis is shown for films having room-temperature thicknesses of 5.7 nm (b) and 23.1 nm (c) (refer to the text for details).

up to the corresponding  $T_g$ , independent of other pseudolayers, and then expands, giving rise to a positive thermal expansion. The negative and positive thermal expansion coefficients in each of these pseudolayers were kept equal to that of the total film. The  $T_g$ 's, obtained from best fit of the measured curve corresponding to the  $T_g$  of six pseudolayers used here for the 4.5-nm and 5.7-nm PS films, are indicated in the inset of Figs. 3(a) and 3(b). The generated curve by adding all these six pairs of the straight line match quite well with the experimental data. The fit can be improved by using more numbers of pseudolayers but the basic feature is quite clear even in this simple model. In case of the 23.1-nm film [Fig. 3(c)] we used five pseudolayers instead of six as  $\Delta T$  has reduced significantly. The molecules near the surface have an enhanced probability of sliding motion and thereby a lower effective  $T_g$ . The effective  $T_g$  of pseudolayers progressively approach a bulk value  $T_g^b$  as the position of the pseudolayer

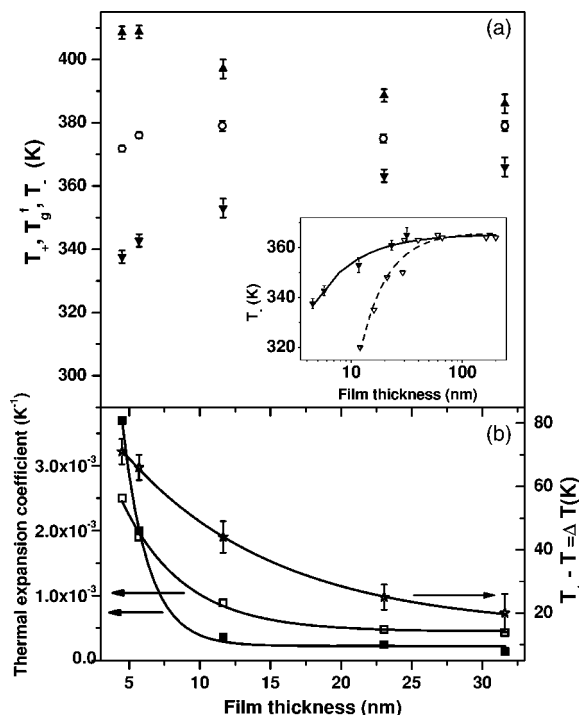


FIG. 4. (a)  $T_+$  (solid up triangle),  $T_g^f$  (open circle), and  $T_-$  (solid down triangle) are presented with the error bars as a function of film thickness for five PS films of thicknesses 4.5 nm, 5.7 nm, 11.6 nm, 23.1 nm, and 31.6 nm. In the inset of (a) the solid line represents the fit with Eq. (1) to the  $T_-$  data (solid down triangle) of our films and for the thicker films published earlier [2]. The inclusion of earlier published thinner film  $T_-$  values (open down triangle) clearly indicates a rapid reduction (dashed line) of  $T_-$  erroneously. (b) The obtained negative thermal expansion (solid square) and positive thermal expansion (open square) coefficients together with  $\Delta T$  (star) for the five PS films are presented with exponential fits (refer to the text for details).

lowers and this value becomes even more than  $T_g^b$  for the pseudolayer situated near the film substrate interface due to the strong interaction between polymer and substrate. In our model,  $T_-$  and  $T_+$  are the effective  $T_g$  of the top and bottom pseudolayers in each film. The calculated values of  $T_g^f$ ,  $T_+$ , and  $T_-$  for all films are shown in Fig. 4(a). In Fig. 4(b), we have presented obtained absolute value of the thermal expansion ( $|\alpha|$ ) both below and above  $T_g$  and the extracted  $\Delta T$  for the five PS films of different thicknesses. We note that the values of  $|\alpha|$  in these films decreases exponentially as the film thickness is increased, and from PS films that are  $\sim 2R_g$  thick, the thermal expansion above  $T_g$  becomes close to the volume expansion of bulk PS as observed earlier [16]. The broadening of the glass transition  $\Delta T$  also exhibits an exponential dependence and we could parametrize all the curves with a function  $a_1[\exp(-h/a_2)]+a_3$ . The values of the fitting parameters  $a_1$ ,  $a_2$ , and  $a_3$  for negative and positive thermal expansion coefficients come out to be  $4.1 \times 10^{-2} \text{ K}^{-1}$ , 1.8 nm,  $2.2 \times 10^{-4} \text{ K}^{-1}$  and  $5.6 \times 10^{-3} \text{ K}^{-1}$ , 4.4 nm,  $4.5 \times 10^{-4} \text{ K}^{-1}$  respectively. For the  $\Delta T$  data, we obtain these parameters as 85.46 K, 10.8 nm, and 15.1 K respectively.

In Fig. 4(a) we have also shown the variation of  $T_g^f$  with thickness and found that there is a reduction of 7 K as the



thickness of the film is reduced to 4 nm with an error bar around 3 K. Our results agree with the calorimetric results [10] which indicated no appreciable dependence of the glass transition temperature on film thickness. In fact, one averaged value of  $T_g$  for ultrathin films having a large  $\Delta T$  is an ill-defined parameter. Referring back to Eq. (1) and its remarkable success in explaining a large number of ellipsometry results, we note that this equation represents essentially a variation of  $T_-$  as  $T_+$  was found to be constant in ellipsometry measurements. We extracted the values of  $T_-$  as a function of thickness from the published values [2,8] of  $T_g^f$  knowing the constant values of  $T_+$  in those ellipsometry measurements. The extracted values of  $T_-$  are shown with the obtained values of  $T_-$  from our measurements in the inset of Fig. 4(a). Excluding the present data, one can indeed get respective values of  $A$  and  $\delta$  as  $3.76 \pm 0.88$  nm and  $1.76 \pm 0.35$ , by fitting (dashed line) Eq. (1) as reported [2,3,8]. For fitting the data set over the entire thickness range shown in the inset of Fig. 4(a) with Eq. (1) one has to ignore the earlier measured ellipsometry data below 20 nm, which had a problem of contrast [8]. We obtained the values of  $0.47 \pm 0.21$  nm and  $1.13 \pm 0.23$  for  $A$  and  $\delta$ , respectively, from this fitting (solid line). It may be noted that the obtained value of  $A$  here is close to the segment length of polystyrene 0.67 nm, indicating that a polymer film of finite thickness will always have finite  $T_-$ . Moreover, an increase in  $T_+$  for ultrathin films will keep  $T_g^f$  close to  $T_g^b$ .

#### IV. CONCLUSION

In conclusion, we have shown by measuring the thickness of ultrathin polystyrene films as a function of temperature

that a conventional glass transition takes place even for a 4.5-nm film and we do not observe an appreciable dependence of average  $T_g$  as a function of thickness. We find that a large broadening of the glass transition temperature occurs as the film thickness reduces below the radius of gyration. We could explain this broadening by invoking the continuous glass transition temperature as a function of depth arising due to a variation of the contribution of sliding motion in the diffusion process. The probability of having *ends* of a polymer chain at the free surface [23], the essential requirement for sliding motion, increases as the center of mass of the chain comes closer to the free surface [6], giving rise to a lowest but finite  $T_g$ , marked as  $T_-$  in a film. The reduction of the surface glass transition ( $T_-$  here) has also been discussed [24,25] for films having chain ends at the free surfaces without invoking sliding motion. It is quite clear that the effect of disentanglement in polymer thin films giving rise to a segregation of chain ends at the top surface [23] and the formation of layering [26] in the bulk of the film has a strong influence [27] in generating the distribution of the glass transition temperature. The results presented here will stimulate further theoretical and experimental investigations.

#### ACKNOWLEDGMENTS

The authors are grateful to Manabendra Mukherjee and Yves Bodenthin for valuable discussions. The authors are also thankful to Joydeep Basu and John Hill for their support in the NSLS experiment. This work was supported by a DST-DAAD India-Germany collaboration program.

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