

## Activated Physical Properties at Air-Polymer Interface

Tisato Kajiyama\*

Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received October 9, 2006; Revised October 31, 2006

**Abstract:** The surface molecular motion of monodisperse polystyrene (PS) films was examined using scanning viscoelasticity microscopy (SVM) in conjunction with lateral force microscopy (LFM). The dynamic storage modulus,  $E'$ , and loss tangent,  $\tan\delta$ , at a PS film surface with number-average molecular weights,  $M_n$ , smaller than 30 k were found to be smaller and larger than those for the bulk sample, even at room temperature, meaning that the PS surface is in a glass-rubber transition or fully rubbery state at this temperature when the  $M_n$  is small. In order to quantitatively elucidate the dynamics of the molecular motion at the PS surface, SVM and LFM measurements were performed at various temperatures. The glass transition temperature,  $T_g$ , at the surface was found to be markedly lower than the bulk  $T_g$ , and this discrepancy between the surface and bulk became larger with decreasing  $M_n$ . Such an intensive activation of the thermal molecular motion at the PS surfaces can be explained in terms of an excess free volume in the vicinity of the film surface induced by the preferential segregation of the chain end groups.

**Keywords:** air-polymer interface, polystyrene, scanning viscoelasticity microscopy, lateral force microscopy.

### Introduction

The physical properties at surfaces and interfaces of polymeric materials have received great recent attention and are of pivotal importance in many technological applications such as lubrication, adhesion, and biomaterials.<sup>1</sup> Hence, the systematical understanding of it, which can not be deduced by extrapolating its bulk ones, is crucial so that the performance of these materials is promisingly improved.

For a last decade, dynamics in thin films and at interfaces of amorphous polymers, mainly polystyrene (PS) and poly(methyl methacrylate) (PMMA), have been extensively studied owing to the manifestation of modern spectroscopic methods and microscopy. Restricted ourselves within the reports on PS for brevity, the consistent conclusion obtained thus far is that the glass transition temperature,  $T_g$ , in thin films differs markedly from that for bulk.<sup>2-7</sup> A depression of the  $T_g$  in thin films seems to be accounted for by the peculiar mobility of polymer chains existed in the vicinity of the outermost surface rather than the geometrical confinement effect of polymer chains.

Authors have embarked on surface molecular motion of PS films by a family of scanning force microscopy, e.g., scanning viscoelasticity<sup>8-11</sup> and lateral force microscopy<sup>12-14</sup> (SVM and LFM). The principle of SVM is briefly stated here. Under the condition that the sample surface is deformed by the indentation of a tip, the tip is sinusoidally modulated.

This leads to the sinusoidal modulation of the force acting between sample surface and cantilever tip if the modulation signal, stimulation strain, is imposed within the linear viscoelasticity region. Measuring the amplitude of the modulated deformation for the sample (response stress) and the phase lag between stimulation strain and response stress, the dynamic viscoelastic functions at the sample surface can be evaluated. LFM has been used as a powerful tool as well to investigate surface properties of various polymers.<sup>15,16</sup> In case of polymeric materials, lateral force between sample surface and a probe tip is postulated to come from the energy dissipation of molecular movement. Hence, it becomes possible to examine surface molecular motion based on the scanning rate dependence of lateral force, which corresponds well to the relation between measuring frequency and mechanical loss modulus.

Jean *et al.*, and De Maggio and co-workers, using positron-annihilation lifetime measurement, independently observed that the  $T_g$  in the thin surface layer of PS films was suppressed.<sup>17,18</sup> Lap-shear strength measurement clearly indicated that the strength at PS/PS interface can be developed due to interdiffusion of PS chains at a temperature below the bulk  $T_g$ , and concluded that the mobility at the free surface was highly enhanced in comparison with its bulk state.<sup>19</sup> In contrast, these conclusions are not in agreement with a recent report on surface relaxation of PS films with the number-average molecular weight,  $M_n$ , of 96 k based on the spectroscopy of near-edge X-ray absorption fine structure by Russell *et al.*<sup>20</sup> They have not observed at all any evidence of vigorous molecular motion on the PS film surface at temperature below

\*Corresponding Author. E-mail: kajiyama@cstf.kyushu-u.ac.jp

its bulk  $T_g$ . Hence, it seems that a consistent understanding about thermal molecular motion at film surface is far from clear for the moment.

The purpose of this study is to rationalize the thermal molecular motion at the surface of the monodisperse PS films, which are typical amorphous polymer, by SVM in conjunction with LFM measurements. Especially, our intent in this review article is to show how polymer chains at the film surface are thermally activated in comparison with its internal bulk phase.

## Experimental

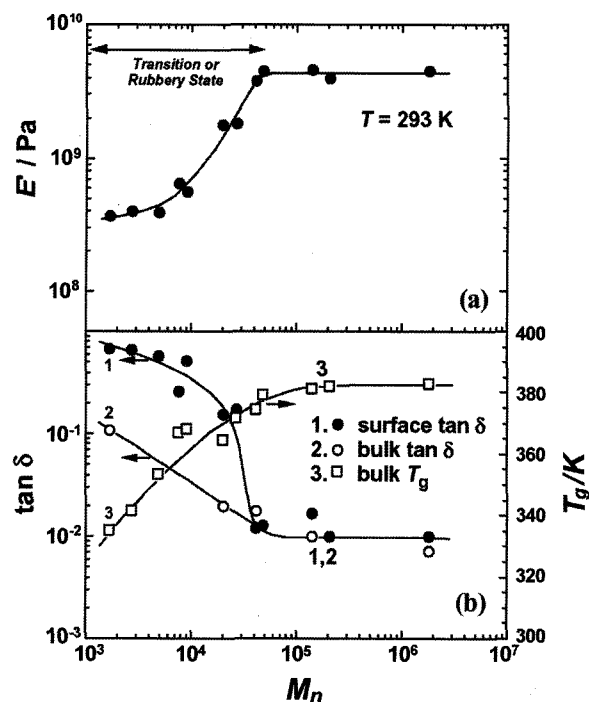
Monodisperse PSs with various  $M_n$ s were synthesized by a living anionic polymerization using *sec*-butyllithium and methanol as an initiator and a terminator, respectively. Hence, the chemical structures at both ends of a chain are composed of a *sec*-butyl group and a repeating unit terminated by proton. The PS film was coated from a toluene solution onto a cleaned silicon wafer by a spin-coating method. The film was dried at 296 K for more than 72 h and then annealed at 423 K for 24 h under vacuum. The film thickness evaluated by the ellipsometric measurement was approximately 200 nm, which did not show any ultra-thinning effects on the surface molecular motion.

The molecular motion at the PS surfaces was examined by using SVM and LFM (SPA 300 HV, Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. Both measurements were carried out at various temperatures in vacuo to avoid the surface oxidation and a capillary force effect induced by surface adsorbed water. A piezoscanner was thermally insulated from the heating stage. A cantilever with the bending spring constant of  $0.09 \text{ N} \cdot \text{m}^{-1}$ , of which both sides were coated by gold, was used. It was confirmed that the sample surface was not damaged at all by scanning the tip under the current experimental condition.

## Results and Discussion

### Surface Viscoelastic Functions at Room Temperature.

Parts (a) and (b) of Figure 1 show the molecular weight dependence of dynamic storage modulus,  $E'$ , and loss tangent,  $\tan \delta$ , at the monodisperse PS film surfaces at a controlled ambient temperature. The modulation frequency and amplitude at the supporting part of the cantilever for SVM measurement were 4 kHz and 1.0 nm, respectively. The bulk  $\tan \delta$  and  $T_g$  values, which were measured by Rheovibron and differential scanning calorimetry (DSC), respectively, are plotted in it to make a comparison with surface ones. Before starting to discuss surface molecular motion, of note is that the bulk  $T_g$ s of all PSs used are far above room temperature, that is, the internal bulk states of the PS films are glassy at room temperature, independent of  $M_n$ . In case of a PS with  $M_n$  larger than 40 k, the surface  $E'$  and surface  $\tan \delta$  were



**Figure 1.** Dependence of (a) storage modulus,  $E'$ , and loss tangent,  $\tan \delta$ , at the monodisperse PS surface on molecular weight,  $M_n$ . Bulk  $\tan \delta$  and glass transition temperature,  $T_g$ , are present in part (b) as well.

constant with regard to  $M_n$ , and their magnitudes were approximately 4.5 GPa and 0.01. Since these magnitudes of the surface  $E'$  and  $\tan \delta$  are typical values for glassy PS, it is clear that the surface is in a glassy state at 293 K for a PS film with  $M_n$  larger than 40 k. On the other hand, the surface  $E'$  and surface  $\tan \delta$  vary in the magnitude with  $M_n$  once  $M_n$  falls short of 30 k. That is, the surface  $E'$  and the surface  $\tan \delta$  decreases and increases with the decreasing  $M_n$ , respectively, as shown in Figure 1(a). Hence, it is plausible that while the internal phase of the PS film is in a glassy state, the surface of a PS film with  $M_n$  smaller than 30 k is in a glass-rubber transition state or rubbery one even at 293 K. The  $\tan \delta$  of the bulk PS sample was measured by the technique of dynamic spring analysis to compare with the surface one. At an  $M_n$  smaller than 30 k, the surface  $\tan \delta$  is much larger than the bulk  $\tan \delta$ . This implies once again that thermal molecular motion at the PS surface is activated in comparison with that for the bulk sample in this  $M_n$  range. It is worthwhile to note that the above-mentioned SVM results do not deny at all the possibility of peculiar molecular motion at the surface for a larger  $M_n$  PS. Even though the  $T_g$  at the surface,  $T_g^\sigma$ , is somewhat reduced from its bulk value, such a depression of the  $T_g$  can not be detected by SVM measurement at room temperature if the declined  $T_g^\sigma$  is higher than the measuring temperature, namely, room temperature. This issue will be discussed later in a quantitative way. Deffering

why the  $T_g$  must be reduced at the PS surface, the parallel experiment is carried out by another technique, LFM, to make an assurance.

#### Surface Relaxation Behaviors at Room Temperature.

Since the frictional behavior of polymeric solids is closely related to their viscoelastic properties,<sup>21</sup> it is possible to examine surface molecular motion of the polymeric solids by dragging a tip on surface with various speeds. Postulating that lateral force is arisen from the energy dissipation of molecular movement, the lateral force variation with measuring temperature and scanning rate can be regarded as the temperature and frequency dependences of dynamic loss modulus.<sup>10,15</sup> In either case that the surface is completely in a glassy or rubbery state, the magnitude of lateral force might be independent of the measuring temperature at a given scanning rate or the scanning rate at a given temperature. On the other hand, the lateral force varies with the temperature (or scanning rate) and a peak is observable on the lateral force-temperature (scanning rate) curve when the surface is in a glass-rubber transition state. Thus, it can be judged that the surface is in a glass-rubber transition state, if the magnitude of lateral force increases or decreases with the temperature (scanning rate). More detail interpretation of lateral force for polymeric materials has been published elsewhere.<sup>10</sup>

Figure 2 collects the plots of lateral force against the scanning rate as a function of  $M_n$  at room temperature. In the case of  $M_n$  of 140 k, the lateral force is independent of the scanning speed, meaning that the surface of this PS film is glassy at room temperature, whereas the lateral force for a PS film with  $M_n$  smaller than 40 k alters with the scanning rate. Of note is that this trend is in good agreement with our parallel experiment using SVM shown in Figure 1. Although in the case of  $M_n$  of 40 k, the lateral force is apparently constant against the sliding speed of the tip at the higher side, it is increased with a decrease in the scanning rate at the lower side. This result makes it clear that the state of molecular motion is strongly dependent on the sample deformation rate even at film surface as well, as extensively observed in molecular motion of bulk polymer samples, and the PS surface with this  $M_n$  is in a transition state and glassy one at lower and higher scanning rate regions, respectively. In contrast, the lateral force for the PS films with  $M_n$  of 27 and 20 k monotonically decreases with the increasing scanning rate in all range employed here. As the  $M_n$  becomes further smaller, e.g., 9 and 5 k, the peak is appeared on the lateral force-scanning rate curve, indicating that these surfaces are in fully rubbery state. Figure 3 shows the master curve drawn by horizontal and vertical arbitrary shifts of each curve in Figure 2. Since this master curve is very similar to the lateral force-temperature curve, which will be shortly shown, it can be considered that the fashion of lateral force against the scanning rate and the  $M_n$  reflects the successive change of the surface molecular motion from a glassy to a rubbery state via the glass-rubber transition even at room temperature. By

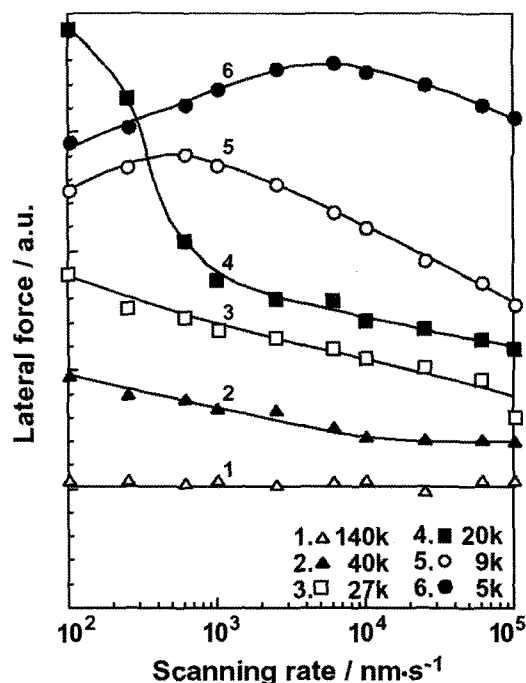


Figure 2. Lateral force alteration with scanning rate as a function of molecular weight,  $M_n$ , for the PS films. The measurement was carried out at a temperature of 293 K.

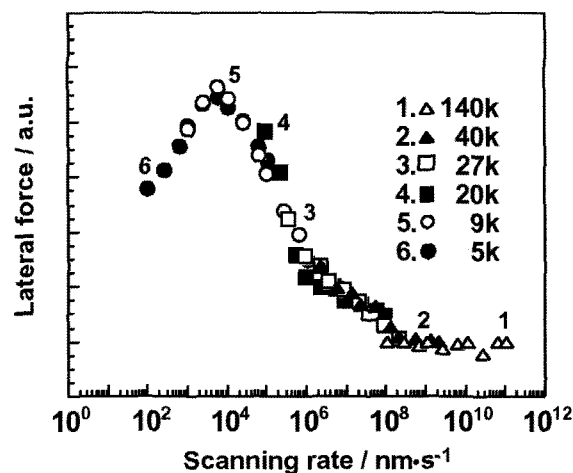


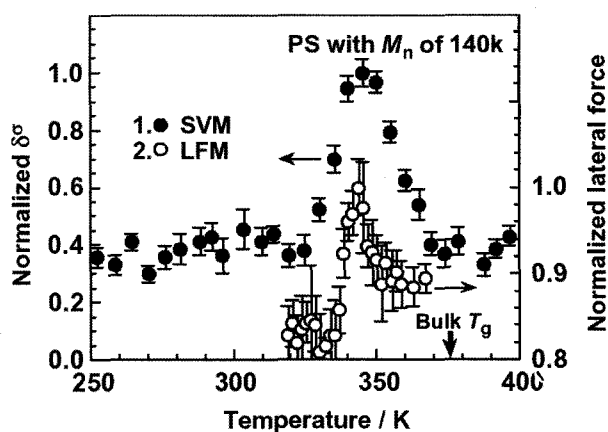
Figure 3. Master curve of the scanning rate-lateral force relationship for the PS films drawn from the each curve in Figure 2. The symbols are the same in Figure 2.

taking into account the facts that the internal phase of the PS film is in a glassy state, it seems reasonable to conclude that thermal molecular motion is intensively activated at the PS film surface compared with its bulk state.

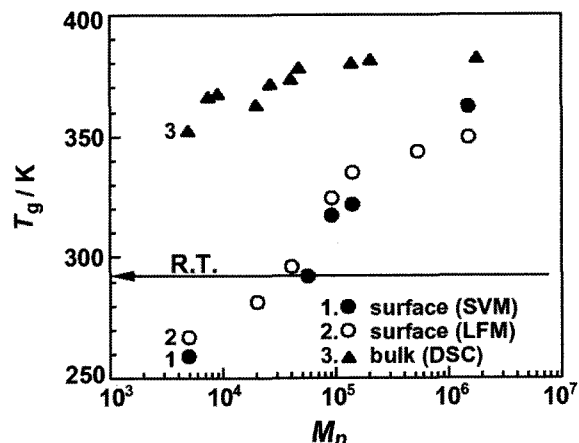
**Direct Evaluation of Surface Glass Transition Temperatures.** Thus far it has been qualitatively stated that the  $T_g^\sigma$  is lower than the bulk  $T_g$ . Therefore, the time is ripe to quantitatively show how peculiar the surface molecular

motion is. Here the  $T_g^\sigma$  is directly evaluated by SVM in conjunction with LFM at various temperatures. Figure 4 shows temperature dependence of surface phase lag,  $\delta^\sigma$ , between strain and stress, and lateral force for the PS films with  $M_n$  of 140 k. The shape factor related to how a cantilever tip contacts with the surface must be precisely determined so that the experimental  $\delta^\sigma$  is converted into the surface  $\tan \delta$ . At present, however, it is difficult to obtain this factor when the ambient temperature is kept changing such as a temperature-dependent measurement. Hence, the  $\delta^\sigma$  itself is used here as an index of molecular motion instead of the surface  $\tan \delta$ . Besides the lateral force variation with temperature is collected at a given scanning speed of  $10^3 \text{ nm} \cdot \text{s}^{-1}$ . The ordinates in Figure 4 are normalized by the maximum value of the  $\delta^\sigma$  and lateral force to show how these values vary with temperature around a transition region. The peaks on both curves are assigned to the  $\alpha_u$ -absorption corresponding to the micro-Brownian motion of polymeric chains at the PS surface.<sup>22</sup> While the bulk  $T_g$  of this PS is 376 K, the  $\delta^\sigma$  starts to increase at much lower temperature, as shown in Figure 4. Thus, it seems the most likely that the glass-rubber transition at the surface for the PS films with  $M_n$  of 140 k is present below its bulk  $T_g$  of 376 K.

An onset temperature on the  $\delta^\sigma$  or lateral force-temperature curve, i.e., the temperature at which the magnitude of lateral force starts to increase, can be empirically defined as  $T_g^{\sigma 23}$ . Figure 5 shows such temperatures as a function of  $M_n$ . The bulk  $T_g$ s are again plotted in it to make a comparison with the  $T_g^\sigma$ . The arrow beside the ordinate denotes room temperature, which is abbreviated as "R.T." in Figure 5. The results in Figure 5 make it clear that the  $T_g^\sigma$  has the stronger  $M_n$  dependence than the bulk  $T_g$ , that is, a decrement of the  $T_g^\sigma$  with a decrease in  $M_n$  is more remarkable in comparison with the bulk  $T_g$ . Even at ultra-high molecular weight,  $M_n$  of 1,450 k, the  $T_g^\sigma$  is definitely lower than the bulk  $T_g$  and also



**Figure 4.** Temperature dependence of surface phase lag,  $\delta^\sigma$ , (by SVM) and lateral force (by LFM) for the PS films with  $M_n$  of 140 k. The left- and right-hand ordinates stand for  $\delta^\sigma$  and lateral force, respectively. The bulk  $T_g$  of 376 K was measured by DSC.



**Figure 5.** Variation of surface and bulk glass transition temperatures,  $T_g$ , with molecular weight,  $M_n$ , for the PS films.

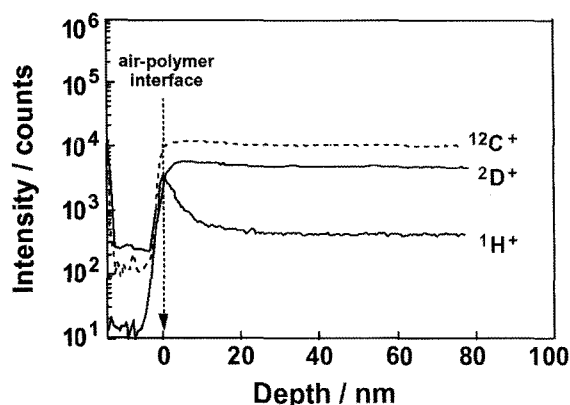
in case of a lower  $M_n$  smaller than approximately 30 k, the  $T_g^\sigma$  is below room temperature. These results strongly advocate our previous conclusion, which is guided by measurements at room temperature, that the PS film surface is in a glass-rubber transition or fully rubbery state even at room temperature if the  $M_n$  is smaller than 30 k.

**Surface Localization of Chain End Groups.** The physical meaning of the variation of  $M_n$  related to glass transition temperature is now discussed. According to Fox-Flory equation,<sup>24</sup> the dependence of bulk  $T_g$  on  $M_n$  is given by

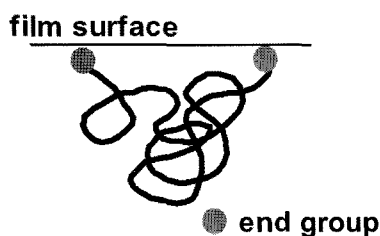
$$T_g = T_{g,\infty} - K/M_n \quad (1)$$

where  $T_{g,\infty}$  and  $K$  are the bulk  $T_g$  for the infinite longer PS and a material constant, respectively. The eq. (1) means that the bulk  $T_g$  declines with a decrease in  $M_n$  and this  $T_g$  variation has been interpreted based on the increasing the number density of chain end groups. It is clearly discerned that the effect of  $M_n$  on  $T_g$  is stronger at the film surface than the bulk sample, as shown in Figure 5. Thus, it seems reasonable to infer that the number density of chain end groups at the surface is larger compared with its internal phase.

In order to confirm whether such a situation, preferential surface segregation of chain end groups, becomes true, dynamic secondary ion mass spectroscopic (DSIMS) measurement is made using deuterated PS (dPS), of which chain end groups were labelled by protonated groups, as a sample. Figure 6 shows the typical SIMS depth profile of the end-labelled dPS film. The dashed vertical line depicts the air-polymer interface. The depth before reaching the film surface means the etching of the platinum layer to avoid charging up the specimen during the measurement. Since the intensity of carbon ion,  $C^+$ , is almost constant through the polymer film, it can be judged that the steady-state etching proceeds. Although the secondary ion efficiency of hydrogen atom is generally higher than that of heavy hydrogen atom, the stronger intensity of deuterium ion,  $D^+$ , is maintained through



**Figure 6.** Typical SIMS depth profile of proton, deuterium, and carbon ions for the end-labelled deuterated PS film.



**Figure 7.** Schematic representation of the most probable chain conformation of a PS at surface.

the polymer film. This is due to the larger fraction of heavy hydrogen atom in the end-labelled dPS film. At the air-polymer interface, an apparent increase in the  $H^+$  intensity and a decrease in  $D^+$  count are observed. All styrene units were deuterated, and protons were present only in both chain end portions. Thus, the SIMS depth profile indicates a remarkable enrichment of chain end groups at the film surface. Figure 7 displays a cartoon of the most plausible conformation of a PS chain at the film surface drawn on the basis of the DSIMS result. Since the localized chain ends at the surface might induce an excess free volume compared with its internal phase, it can be envisaged that the  $T_g$  is lowered at the film surface, resulting in that the thermal molecular motion at the film surface becomes active in comparison with the bulk sample. Another possible explanation why  $T_g$  must be depressed at the film surface is that the segmental density declines gradually to the outermost surface, as observed in simulation studies by Mattice *et al.*<sup>25</sup> A more conclusive work including this situation based on the apparent activation energy of micro-Brownian motion at the film surface will be reported soon with our temperature-dependent LFM.

## Conclusions

The SVM and LFM were applied to examine the surface relaxation processes of the monodisperse PS films with var-

ious  $M_n$ s. The  $T_g^\sigma$  was found to be much lower than the bulk  $T_g$  for the entire  $M_n$  range, and was strongly affected by the chain length of PS. Finally, the activation of the thermal molecular motion at the PS film surfaces was explained in terms of an excess free volume induced by the enriched chain end groups at the surface.

## References

- (1) F. Garbassi, M. Morra, and E. Occhiello, *Polymer Surfaces, from Physics to Technology*, Wiley, Chichester, 1994.
- (2) G. Beaucage, R. Composto, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **31**, 319 (1993).
- (3) G. Reiter, *Europhys. Lett.*, **23**, 579 (1993).
- (4) G. Reiter, *Macromolecules*, **27**, 3046 (1994).
- (5) J. L. Keddie, R. A. L. Jones, and R. A. Cory, *Europhys. Lett.*, **27**, 59 (1994).
- (6) J. A. Forrest, K. Dalnoki-Veress, J. R. Stevens, and J. R. Dutcher, *Phys. Rev. Lett.*, **77**, 2002 (1996).
- (7) J. A. Forrest, K. Dalnoki-Veress, and J. R. Dutcher, *Phys. Rev. E*, **58**, 6109 (1998).
- (8) T. Kajiyama, K. Tanaka, I. Ohki, S.-R. Ge, J.-S. Yoon, and A. Takahara, *Macromolecules*, **27**, 7932 (1994).
- (9) K. Tanaka, A. Taura, S.-R. Ge, A. Takahara, and T. Kajiyama, *Macromolecules*, **29**, 3040 (1996).
- (10) T. Kajiyama, K. Tanaka, and A. Takahara, *Macromolecules*, **30**, 280 (1997).
- (11) N. Satomi, A. Takahara, and T. Kajiyama, *Macromolecules*, **32**, 4474 (1999).
- (12) K. Tanaka, A. Takahara, and T. Kajiyama, *Macromolecules*, **30**, 6626 (1997).
- (13) K. Tanaka, X. Jiang, K. Nakamura, A. Takahara, T. Kajiyama, T. Ishizone, A. Hirao, and S. Nakahama, *Macromolecules*, **31**, 5148 (1998).
- (14) T. Kajiyama, K. Tanaka, N. Satomi, and A. Takahara, *Macromolecules*, **31**, 5150 (1998).
- (15) J. A. Hammerschmidt, B. Moasser, W. L. Gladfelter, G. Haugstad, and R. R. Jones, *Macromolecules*, **29**, 8996 (1996).
- (16) R. H. Schmidt, G. Haugstad, and W. L. Gladfelter, *Langmuir*, **15**, 317 (1999).
- (17) Y. C. Jean, R. W. Zhang, H. Cao, J. P. Yuan, C. M. Huang, B. Nielsen, and P. Asoka-Kumar, *Phys. Rev. B*, **56**, R8459 (1997).
- (18) G. B. DeMaggio, W. E. Frieze, D. W. Gidley, M. Zhu, H. A. Hristov, and A. F. Yee, *Phys. Rev. Lett.*, **78**, 1524 (1997).
- (19) Y. M. Boiko and R. E. Prud'homme, *J. Polym. Sci., Polym. Phys. Ed.*, **36**, 567 (1998).
- (20) Y. Liu, T. P. Russell, M. G. Samant, J. Stöhr, H. R. Brown, A. Cossy-Favre, and J. Diaz, *Macromolecules*, **30**, 7768 (1997).
- (21) K. Minato and T. Takemura, *Jpn. J. Appl. Phys.*, **6**, 719 (1967).
- (22) D. G. H. Ballard, G. D. Wignall, and J. Schelten, *Eur. Polym. J.*, **9**, 965 (1973).
- (23) N. Saito, K. Okano, S. Iwayanagi, and T. Hideshima, *Solid State Physics*, Academic Press, New York, 1963, Vol. 14.
- (24) T. Fox and P. Flory, *J. Polym. Sci.*, **14**, 315 (1954).
- (25) P. Doruker and W. L. Mattice, *J. Phys. Chem. B*, **103**, 178 (1999).