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Relaxation Mechanism of Polymer Melts†

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ABSTRACT: A centrally deuteriated triblock polystyrene was used to probe the mechanism of orientation relaxation of a step strained polymer melt. On the basis of the reptation model, the orientation of the chain should relax from the ends toward the center of the chain. Since the center block was deuteriated, the FT-IR dichroism method was ideally suited to simultaneously monitor both the orientation relaxation of the central segments and the protonated ends of the chain. The infrared results showed that the deuteriated center block loses little orientation initially and decays in a predictable exponential manner after some time. These observations strongly support the reptation model for melt dynamics. The data are discussed in terms of the fraction of the deuteriated center block remaining in the initial tube, while the entire chain executes a one-dimensional curvilinear diffusion with relaxation of entanglements.

1. Introduction

On the basis of the reptation model of polymer melts,[1-3] over a long time scale, the entire chain, on average, moves coherently back and forth along the contour of the chain and the orientation of the chain relaxes from the ends toward the center. To examine the reptation mechanism, we used a centrally deuteriated polystyrene (DPS) triblock copolymer to observe the relaxation process of deformed polymer melts. Since the infrared vibrational frequencies of the deuteriated group are different from that of the protonated group (Figure 1), the centrally deuteriated triblock copolymer has the ideal chemical structure to investigate such a relaxation mechanism.

Previously, we have used the infrared dichorism method to study both the uniaxially strained homopolymer melts[4] and matrix effects on the relaxation of labeled polymer chains.[5] The process of the orientation relaxation for a short chain in a long chain matrix was shown to be dominated by the reptation mechanism, whereas the long chain relaxation in a lower molecular weight matrix was dominated by contraint release. Therefore, the triblock copolymer was immersed in the protonated polystyrene (HPS) matrix of higher molecular weight to ensure the domination of the reptation mechanism.

The portion of the chain which escaped from its initial tube was described by the analysis of the one-dimensional random walk.[1-7] A portion of the chain was said to have relaxed its orientation when it had escaped from the initial deformed state. Thus, the measured normalized Hermans orientation function at time t is a measure of the fraction of the chain still trapped in the initial conformation at that time. Since the chain is moving back and forth at any given time, the relaxation could be assumed to be symmetrical with respect to the center of the chain; i.e., on the average, at a given time, the chain had relaxed fractions at both ends as described by the minor chain reptation model.[7]

Some recent stress-strain experiments have been done on centrally deuteriated triblock polystyrenes,[8] and the nonuniform relaxation of the chain segments has been observed at short times. The calculations[9] of the orientation function for the central and end segments have also been discussed. In this paper we focus on the dynamics of the long time relaxation processes of the central deuteriated block. In section 2, we present the calculation for the fraction and orientation of the center block remaining at time t, based on the minor chain reptation model.[7] In section 3, the experimental procedures are presented. In section 4, the results of experiment are compared with theory and discussed. The summary and conclusions are given in section 5.

2. Theoretical Considerations

Previously, the calculation of the orientation relaxation of step strained polymer melts was made by using the analysis of a one-dimensional random walk.[4] For a pure random walk, the probability of moving to the left should be the same as moving to the right. Thus, for a long enough walk, on the average, the number of steps to the left would be the same as the number of steps to the right. So, for a long chain, the orientation relaxation process is symmetrical with respect to the center of the chain. To compare with the experimental results, we made calculations using a one-third centrally labeled polymer chain (25 000 HPS-25 000 DPS-25 000 HPS), whose spectrum is shown in Figure 1.

The fraction of the chain, $F(t)$, still trapped in the initial tube at time t is given by[1]

$$F(t) = \frac{8}{\pi^2}\sum_{p=\mathrm{odd}} \frac{1}{p^2} \exp\left(-p^2 \frac{t}{T_r}\right) \qquad (1)$$

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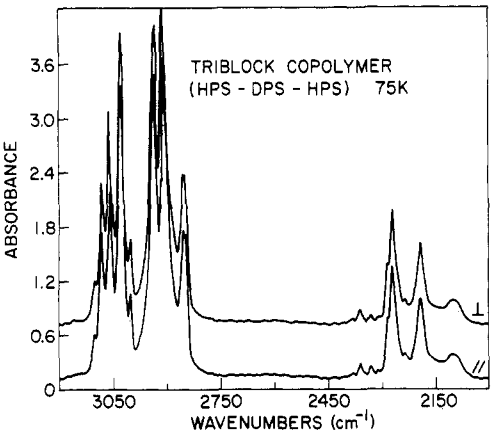

Figure 1. Polarized infrared spectra of the symmetric centrally deuteriated triblock 25 000 HPS–25 000 DPS–25 000 HPS. The CD_2 and CH_2 stretchings occur at 2195 and 2850 cm^{-1}, respectively.

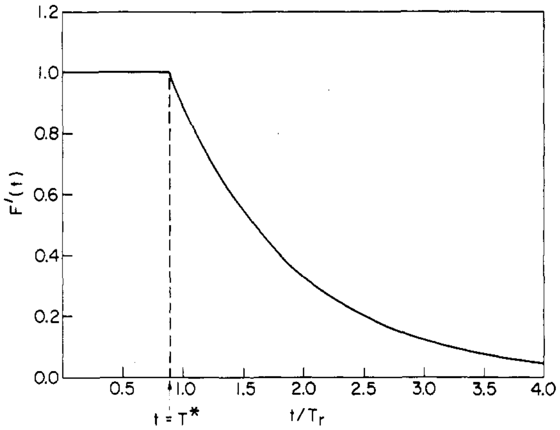

Figure 2. Fraction, $F'(t)$, of the labeled central one-third of the copolymer remaining in the initial tube at time t vs. the dimensionless time t/T_r. T_r is the characteristic relaxation time of the entire copolymer chain. T^* is the time needed for two-thirds of the unlabeled fraction to escape the initial tube.

where $T_r \equiv L^2/(\pi^2 D)$, L is the contour length of the chain, and D is the one-dimensional diffusion coefficient.

Since the chain relaxes from the ends toward the center, on the average, the central third of the chain remains oriented until the other two-thirds of the chain escapes from its initial oriented tube. The fraction of this one-third centrally labeled section $F'(t)$, which is still trapped in the initial tube at time t, is then given ideally by

$$F'(t) = \begin{cases} 1 & \text{for } t \leq T^* \quad \text{(2a)} \\ 3F(t) & \text{for } t > T^* \quad \text{(2b)} \end{cases}$$

where $F(t)$ is the fraction of the entire chain remaining and is the same as in eq 1 and T^* is the time in which only the center third of the entire chain remains in the initial tube, i.e., $F(T^*) = {}^1/_3$. $F'(t)$ vs. t/T_r is shown in Figure 2 according to eq 1 and 2. Note that in this case T^* is approximately equal to T_r since T^*/T_r is a little less than unity.

3. Experimental Procedure

A. Sample Preparation. The centrally deuteriated triblock polystyrene was synthesized by Dr. Hadziioannou's group at the IBM Almaden Research Center in San Jose, CA. The centrally deuteriated section had a molecular weight of 25 000 with two protonated ends each of molecular weight 25 000, resulting in a copolymer with a total molecular weight of 75 000. The polarized infrared spectra of the copolymer are shown in Figure 1.

Since the molecular weight of the sample was 75 000, it was very brittle and easily fractured. To avoid this and constraint release problems, we blend a 6% weight fraction of the copolymer in a protonated polystyrene matrix with molecular weight of 233 000. Since the chain was immersed in a long chain matrix, we know that the relaxation process of this copolymer is independent from the motion of the surroundings.[5] For comparison purposes, a fully deuteriated polystyrene sample with molecular weight of 83 000 was blended in another identical matrix. To ensure homogeneous consistency, both blends were dissolved in toluene for 3 days and magnetically stirred for an hour before casting on a glass surface. After a film was air-dried, it was then placed in a vacuum for 2 days at room temperature to further remove the solvent. The residual stress due to solvent casting and the remaining solvent were removed completely by heating the film at 100 °C in a vacuum for a day. The film was then cut into strips of length L = 2.5 in. and width W = 0.5 in. To provide for local measurement of the draw ratio, small successive equidistant ink marks were engraved on the edge of the sample perpendicular to the stretching direction.

The uniaxial stretching was performed by a tensile testing machine (MTS Model 820) equipped with a thermostatically controlled chamber set at a temperature of 115 ± 1 °C and an initial gauge length of 1.5 in. The samples were first allowed to equilibrate to the oven temperature and then stretched in pure extension at a constant strain rate of 0.1 s^{-1} to an overall draw ratio of about 3.5. The specimen was then quickly quenched to room temperature, effectively freezing the orientation of the uniaxially deformed polymer chains.

B. Orientation Relaxation. Rapid orientation relaxation of an amorphous polymer melt occurs only at a temperature above its glass transition temperature. Thus, the uniaxially deformed samples were held at a fixed strain on a sample holder and placed in an oven at a constant temperature of 115 ± 0.5 °C. At the end of each relaxation interval, the sample was quickly quenched to room temperature, effectively freezing the residual orientation of the polymer melt. The polarized FT-IR spectra were obtained in between each relaxation interval at room temperature.

C. Infrared Measurement. Polarized infrared spectra were collected with the Nicolet 170 SX FT-IR spectrometer equipped with a Perkin-Elmer gold wire grid polarizer. The number of scans of each spectrum for the centrally deuteriated triblock PS and protonated PS blend was 1000 scans; 300 scans were obtained for the fully deuteriated PS and protonated PS blend. The large number of scans was necessary to ensure that the reproducibility was 0.2% or better for the dichoric ratio, $R = A_{\parallel}/A_{\perp}$, of each vibrational frequency used in this study. $A_{\parallel}$ and $A_{\perp}$ are the total absorption intensity of the parallel and perpendicular polarized incident radiation with respect to the orientation direction, respectively.

The orientation of the polymer melt at the end of each relaxation interval was determined with the Hermans orientation function,[10] f_t. Similar to all our previous studies,[4] we normalized f_t with respect to the initial Hermans orientatio function, f_i. Thus, we obtained a normalized Hermans orientation function, $F(t)$,

$$F(t) = \frac{f_t}{f_i} = \frac{R_t - 1}{R_t + 2}\frac{R_i + 2}{R_i - 1} \tag{3}$$

where R_i and R_t were the measured dichoric ratios of the initial deformed state and relaxation state at time t later, respectively. This normalized Hermans orientation function is a direct measure of the fraction of the chain remaining oriented. Thus, when used for the deuteriated bands of the copolymer, it is a measure of $F'(t)$ calculated by the minor chain reptation model shown in eq 2.

4. Results and Discussions

The parallel and perpendicular polarized infrared spectra obtained for the centrally deuteriated PS/protonated PS blend are shown in Figure 3. The vibrational frequency of interest is that of the CD_2 asymmetric stretching mode at 2195 cm^{-1}. The normalized Hermans orientation function, $F(t)$, for each relaxation interval is obtained by using eq 3. In comparison with Figure 2, we plot $F(t)$ vs. time (two sets of data) as shown in Figure 4. Initially, the deuteriated fraction of the copolymer chains loses little orientation and then decays in an exponential

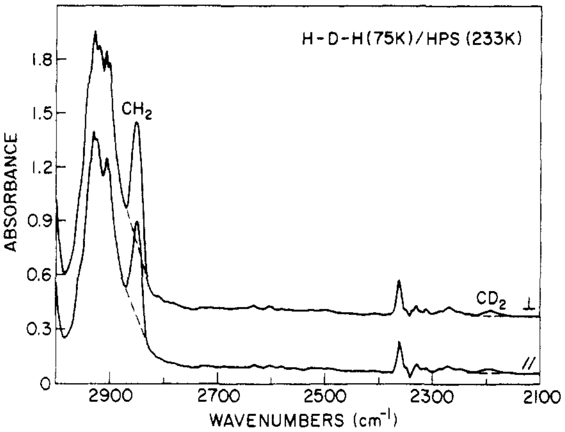

Figure 3. Polarized infrared spectra of the centrally deuteriated triblock polystyrene/protonated polystyrene blends after an initial uniaxial deformation.

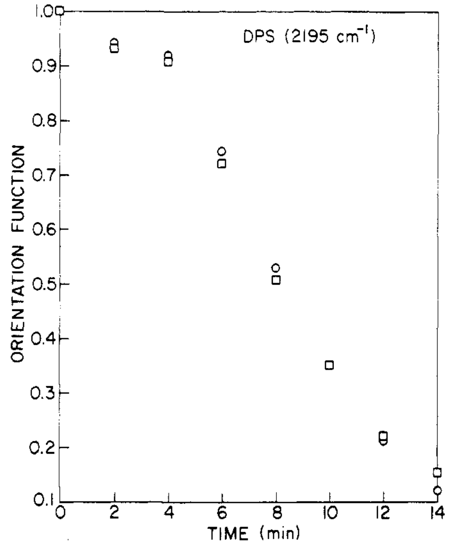

Figure 4. Normalized Hermans orientation function, $F(t)$, of the deuteriated fraction of the triblock polystyrene at 2195 cm^{-1} vs. time. The molecular weight of the centrally deuteriated triblock polystyrene is 75000 (25000–25000–25000). The molecular weight of the HPS matrix is 233000.

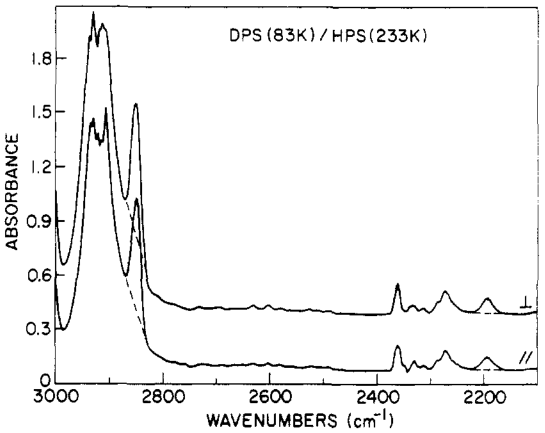

Figure 5. Polarized infrared spectra of the completely deuteriated polystyrene/protonated polystyrene blends after an initial uniaxial deformation.

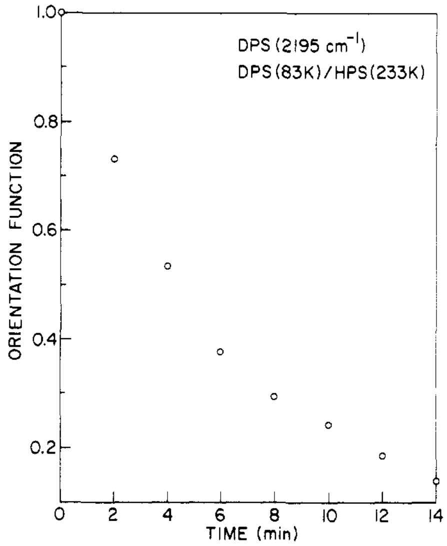

Figure 6. Normalized Hermans orientation function, $F(t)$, of the fully deuteriated DPS chain at 2195 cm^{-1} vs. time. The molecular weight of the DPS is 83000. The molecular weight of the HPS matrix is 233000.

predictable manner after some time. This observation clearly demonstrates that the orientation of the step strained polymer chain relaxes from the ends of the chain toward the central part of the chain, which is in agreement with the mechanism described by the reptation model.

To compare the rate of relaxation for the centrally deuteriated PS chains with its chain ends, we prepared a blend of the completely deuteriated PS in the same protonated PS matrix used for the triblock copolymer experiments. The parallel and perpendicular polarized infrared spectra of the blend are shown in Figure 5. The infrared vibrational frequency used again is the CD_2 asymmetric stretching band at 2195 cm^{-1}. The normalized Hermans orientation function, $F(t)$, for the entire chain obtained at each relaxation interval is shown in Figure 6 plotted linearly with respect to time. As compared to the triblock copolymer, the differences in the initial rate of the relaxation of the deuteriated chains is clear. Here, we have observed a continuous exponential decay in the orientation of the deuteriated PS as predicted by the one-dimensional random walk analysis for the reptation model.

For the central third of the labeled polymer chain, the relaxation time, T^*, required for the other two-thirds of the unlabeled fraction to relax completely is near the characteristic relaxation time, T_r, of the entire chain as shown in Figure 2. Since the experimental time scale used here is $t \geq T_r$, a useful approximation for eq 1[4] is used to determine T_r of the entire chain, as

$$F(t) = \frac{8}{\pi^2} \exp\left(-\frac{t}{T_r}\right) \tag{4}$$

where $F(t)$ is the fraction of the entire chain that is still trapped in its initial tube. By use of eq 2b, the labeled fraction of the copolymer chain, $F'(t)$, remaining in its initial orientation is then equal to

$$F'(t) = 3F(t) \tag{5a}$$

$$F'(t) = \frac{24}{\pi^2} \exp\left(-\frac{t}{T_r}\right) \tag{5b}$$

Thus, we plotted the normalized Hermans orientation function, $F(t)$, at 2195 cm^{-1} for the deuteriated fraction of the copolymer vs. time in a semilogarithmic manner as shown in Figure 7. T_r of the entire triblock copolymer is determined from the slope as $T_r = 5.1$ min; the intercept on the $F(t)$ axis is 2.4, which is close to the theoretical value of $24/\pi^2$. The value of T_r is also close to T^* as described in Figure 2.

In the completely deuteriated PS chain, since the molecular weight was close to the centrally deuteriated PS

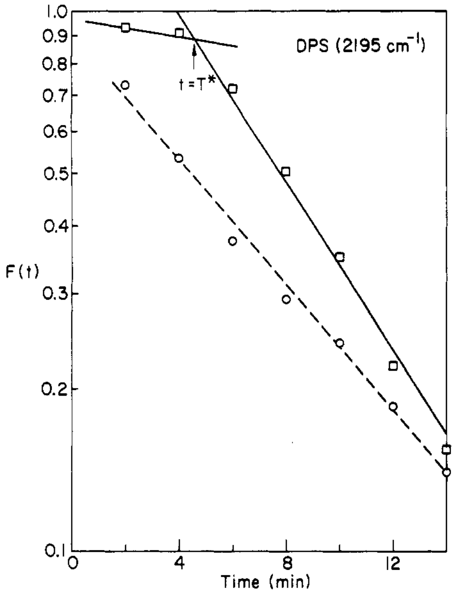

Figure 7. Normalized Hermans orientation function, $F(t)$, vs. the relaxation time t in a semilogarithmic plot for both the copolymer and DPS chain. The CD_2 2195-cm^{-1} band is examined for the triblock copolymer and completely deuteriated polystyrene. The slope of each curve gives the inverse of the charactristic relaxation time: (□) centrally deuteriated triblock polystyrene; (○) fully deuteriated polystyrene.

(83 000 vs. 75 000), we plotted the results in the same manner as shown together in Figure 7. For the fully deuteriated chain, we obtained T_r = 7.4 min, which is slightly greater than the triblock copolymer as would be expected from the molecular weight difference. Also, the $F(t)$ axis intercept of 0.9 was close to the theoretical value of $8/\pi^2$ and was smaller as expected when compared to the copolymer case.

T_r (M = 83 000) of the fully deuteriated PS can be compared with T_r values of other deuteriated PS obtained from our previous experiments;[5] T_r (M = 482 000) $\approx$ 1325 min and T_r (M = 250 000) $\approx$ 192 min. The molecular eight dependence of these relaxation times is consistent with $T_r \sim M^3$, as predicted by the reptation model.

5. Summary and Conclusions

In this paper, we have presented experimental support for the reptation mechanism of orientation relaxation in entangled polymer melts. Using the centrally labeled triblock copolymer coupled with the infrared dichroism method, we observed in a step strain experiment that the centrally labeled fraction loses little orientation initially and then decays in a predictable exponential manner. Thus, for the first time, we have experimental results to describe the molecular motion controlling the relaxation of step strained polymer melts. The orientation of a strained polymer chain relaxes from its ends toward the center. This observation of relaxation provides considerable support for the reptation model.

The experimental results not only agreed qualitatively with the mechanistic description of the reptation model, but they were also in agreement quantitatively with the analytical descriptions for the reptation model. The molecular weight dependence of $T_r \sim M^3$ was observed again, which added to the consistency needed for the support of the use of the infrared dichroism to monitor the molecular dynamics of entangled polymer melts.

To summarize this FT-IR study, we conclude that the following (1) the orientation of a strained polymer chain relaxes from its ends toward the center, as confirmed by the observation of the orientation relaxation of the deuteriated block in a centrally deuteriated triblock polystyrene. (2) Both the quantitative dynamic nature of the experimental results and the molecular weight dependence of T_r are in agreement with the reptation prediction.

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Registry No. (DPS)(HPS) (block copolymer), 108592-10-5.

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