Dielectric Relaxation in Lamellas of *trans*-1,4-Polyisoprene and a Block Copolymer Derivative

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ABSTRACT: The dielectric relaxation of mats of α-TPI solution crystallized lamellas, suspension-epoxidized lamellas, and solution-crystallized block copolymer lamellar structures was obtained in the 100–320 K range at frequencies from 0.01 to 10 000 Hz. Two relaxation processes were detected for each of the three samples and apparent activation energies obtained. Both of these processes are located in the fold surfaces for the TPI lamellas and suspension-epoxidized lamellas and in the folds and interlamellar traverses in the crystallized block copolymer. The most prominent of these processes in each sample is associated with the glass transition, but the subglass processes can be well characterized also.

Introduction

Precipitation of *trans*-1,4 polyisoprene, TPI, from solution by cooling yields semicrystalline single lamellas or lamellar structures in one of two different crystal modifications depending on the crystallization conditions.[1-7] Various properties of these preparations have been studied including the morphology,[1-7] crystallinity,[4,5,7-9] thermal behavior,[2,3,7] dynamic mechanical behavior,[10] and chemical reactivity in suspension using carbon-13 NMR.[8,11,12] Chemical modification in suspension leads to segmented block copolymers and supplies quantitative information regarding the crystalline stem length and the average fold length in the original TPI structures. Segmented block copolymers containing TPI and epoxidized TPI sections have been found from differential scanning calorimetry to crystallize from the melt[10] and from solution;[13] the morphology, crystallinity, and average crystalline and noncrystalline lengths of solution-crystallized segmented block copolymer samples have recently been studied.[13] Multilamellar structures with TPI crystal cores and a surface component containing both epoxidized TPI and TPI units result under the crystallization conditions used to date.

Three mechanical relaxations at 110 Hz were exhibited by pressed solution-grown lamellar TPI mats having a crystalline component in either the α or β form.[10] Upon epoxidation in suspension of α-form containing lamellas the mechanical relaxation process related to the glass transition was observed to shift by 55 deg to higher temperatures. To date dielectric relaxation measurements have not been reported for solution-grown TPI lamellas or segmental block copolymers of TPI. However, some dielectric results for lamellas from solution of lightly oxidized polyethylene[14] and for melt-crystallized segmented polyether/polyurethanes have appeared.[15] In the study of polyethylene lamellas a low-temperature relaxation associated with the folds was reported, and in the other investigation the crystallizing polyurethane segments were shown to affect the polyether chain mobility.

Due to the polarity of the epoxy group, dielectric measurements appear to be particularly appropriate for studying the behavior of epoxidized TPI. In the present work the dielectric relaxation of three solution crystallized samples was investigated. These were (1) α-TPI solution-crystallized lamellas, (2) suspension-epoxidized solution-crystallized α-TPI lamellas (from 1), and (3) solution-crystallized segmented block copolymer (from 2). The frequency/temperature behavior of the relaxation process associated with the glass transition depended on the sample; a secondary process was apparent for each of the three materials.

Experimental Section

Samples. Unfractionated synthetic TPI (Polysciences, Inc.) was used as received (M_n = 35 000, M_w/M_n = 4.8, trans content = 99%). The crystallization procedure involves dissolution in a hexane mixture (0.5% w/v) and filtration at 68 °C, precipitation at 0 °C, slow heating to the temperature of redissolution (34 °C), and isothermal crystallization at 20 °C. The characteristics of this single lamella preparation are given in the first line of Table I; details of the methods used and a discussion of the results for this particular sample were given previously.[7] A segmented block copolymer containing TPI and epoxidized TPI sections was prepared by reaction with an excess of *m*-chloroperbenzoic acid at 0 °C dissolved in 2-ethoxyethanol with the hexane-grown TPI lamellas in suspension for 20 days.[13] The reaction product was washed repeatedly with 2-ethoxyethanol and then with ethyl ether, filtered, and dried at 0 °C. The procedure used leads to lamellas with completely epoxidized TPI surfaces as evidenced by the agreement within experimental error of the fraction epoxidized from carbon-13 NMR measurements (0.41) and the amorphous fraction from infrared spectroscopy measurements (0.44) and by the complete disappearance of the infrared bands characteristic of amorphous TPI.[13] The segmented block copolymer was subsequently dissolved in 2-pentanone at about 44 °C, the solution filtered, and precipitation carried out at 0 °C. The characteristics of this preparation are shown on line 2 of Table I; these are discussed separately.[13]

All samples were first obtained as cylindrical filtered mats 1–2 mil in thickness. Specimens for dielectric measurements were prepared by pressing a stack of these mats together using a pressure of 2000–5000 psi giving an average thickness of 10–13 mil. After coating with gold, cylindrical samples of about 30-mm diameter were cut with a cork borer. A guard ring was scribed in the gold coating on one side.

Dielectric Measurements. The measurements were made isothermally in the time domain by using a dielectric spectrometer manufactured by the IMASS Co. of Hingham, MA. This instrument is closely based on an instrument designed at the National Institute of Standards and Technology by Mopsik.[16]

Table I
Sample Characteristics[7,13]

sample	cryst solv	T_c, °C	T_m, °C	cryst form	% crystallinity FTIR	% crystallinity density	% crystallinity NMR	$\langle A\rangle^b$	$\langle B\rangle^c$
TPI	hexane	20	56	α	56	54	59	14.$_5$	10
block coplym^a	2-pentanone	0	44	α	32		33	11	22

[a] Segmented block copolymer prepared by suspension epoxidation of TPI lamellas. [b] Average crystalline stem length in repeat units from epoxidation/carbon-13 solution NMR. [c] Average noncrystalline traverse length in repeat units from epoxidation/carbon-13 solution NMR.

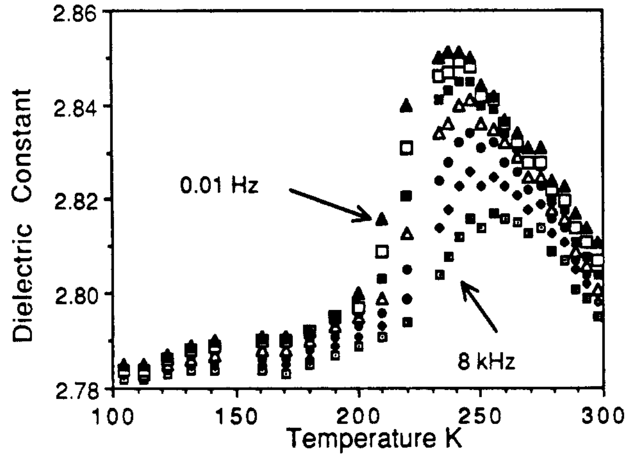

Figure 1. Dielectric constant versus temperature for α-TPI lamellas at six decade frequencies from 0.01 Hz to 1 kHz plus 8 kHz.

It measures the charging curve in response to a step voltage that then remains constant over the course of the measurement. Fourier transformation[17] of the charging curve to produce the frequency-dependent complex dielectric constant is carried out on a computer local to the instrument immediately on termination of accumulation of the charging curve. Attention has been given to the special characteristics of dielectric charging curves in the Fourier transformation algorithm,[17] and the resultant complex dielectric constant can be measured from a high frequency (10 kHz) dependent on the step voltage rise time to a low frequency dependent on the length of the charging process (up to 3000 s for 10^{-4} Hz). In the present work the charging was terminated at 30 s or ~0.01 Hz.

The sample was supported[18] by the measuring electrodes that had the form of two opposed small cylindrical rods normal to the sample surfaces. One of these is spring loaded and thus serves to hold the specimen. The guard ring connection was made by means of a small alligator clip on the edge of the specimen. The sample was housed in the controlled temperature chamber supplied with the instrument. The chamber is controlled by the instrument's computer, and a series of isothermal measurements at programmed temperatures was made.

Although the data were taken in isothermal mode and the transforms made, to give dielectric constant and loss output, at seven frequencies per decade, for display purposes in the present case, it is more informative to plot the data isochronally at various selected frequencies as a function of temperature.

Results

Plots of the dielectric constant and dielectric loss versus temperature at five frequencies from 0.1 to 1000 Hz are given in Figures 1 and 2 for the pressed α-TPI lamellar mat sample. Two loss processes are apparent. The dielectric constant at 100 K was 2.78 to 2.79, depending on the frequency; in conjunction with the process starting around 200 K, an increase in the dielectric constant with temperature to 2.81–2.85 and then a decrease to 2.80–2.81 was observed.

Dielectric results for the pressed mat of lamellas after surface epoxidation are given in Figures 3–5. Two dielectric processes are also observed for this specimen. However, the dielectric loss maxima for both processes are about an order of magnitude larger than those found for the TPI mat. A shift of the loss maximum for the more prominent process by about 70 deg and the secondary process by about 30 deg to higher temperatures is also seen. Following crystallization of the surface epoxidized material from 2-pentanone at 0 °C, dielectric measurements gave the results in Figures 6–8. Two processes are again evident in these data. Comparison of these results with those obtained from the suspension-epoxidized lamellas before crystallization show a shift of the more prominent process to lower temperatures by about 16 deg after crystallization and little change in the temperature position for the secondary process.

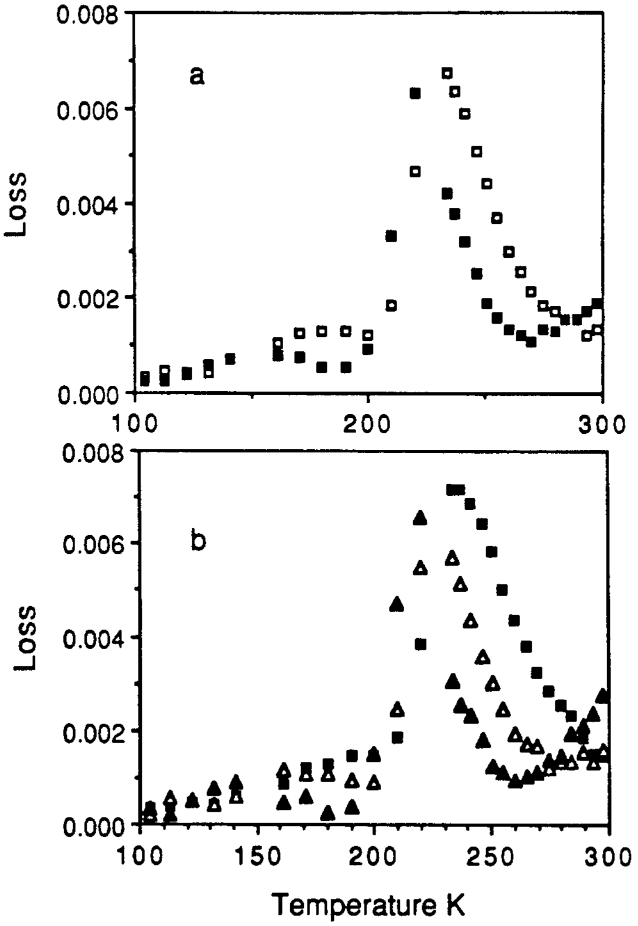

Figure 2. Dielectric loss versus temperature for α-TPI lamellas: (a) filled squares, 1 Hz; open squares, 100 Hz; (b) filled triangles, 0.1 Hz; open triangles, 10 Hz; filled squares, 1 kHz.

To aid in the interpretation, relaxation strengths and width parameters were determined for the primary processes in the surface-epoxidized α-TPI lamellas and surface-epoxidized α-TPI lamellas recrystallized from solution by fitting the Cole–Cole equation[19] to complex plane plots. In order to give a more complete arc, two nearby temperatures were used for each plot and it was assumed that over the small temperature interval the parameters

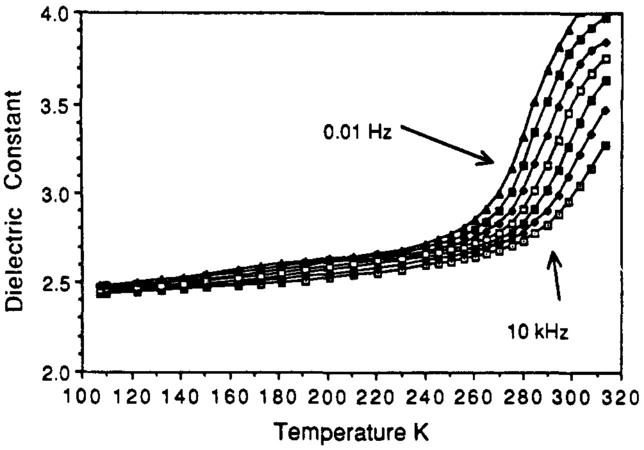

Figure 3. Dielectric constant versus temperature for surface-epoxidized α-TPI lamellas at 7 decade frequencies from 0.01 Hz to 10 kHz.

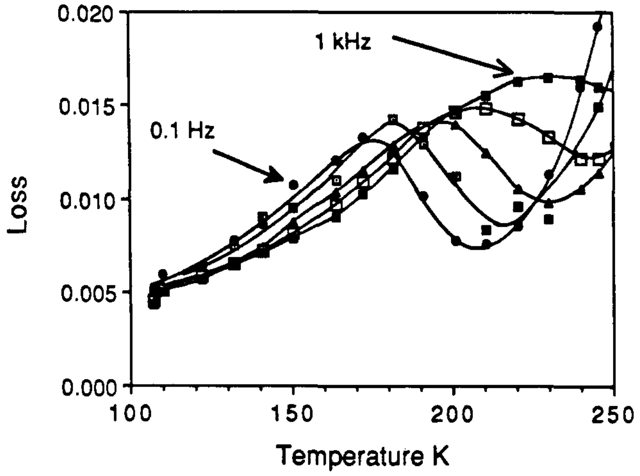

Figure 4. Dielectric loss versus temperature of the surface-epoxidized α-TPI lamellas of Figure 3 plotted in the secondary loss region. Shown are five decade frequencies from 0.1 Hz to 1 kHz.

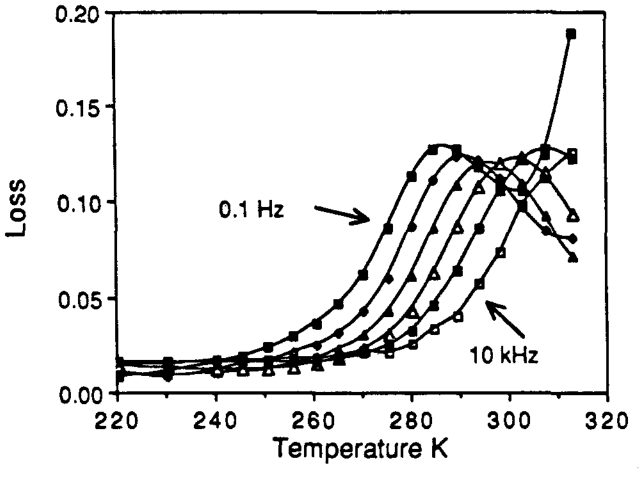

Figure 5. Dielectric loss versus temperature of the surface-epoxidized α-TPI lamellas of Figure 3 plotted in the primary loss region. Shown are six decade frequencies from 0.1 Hz to 10 kHz.

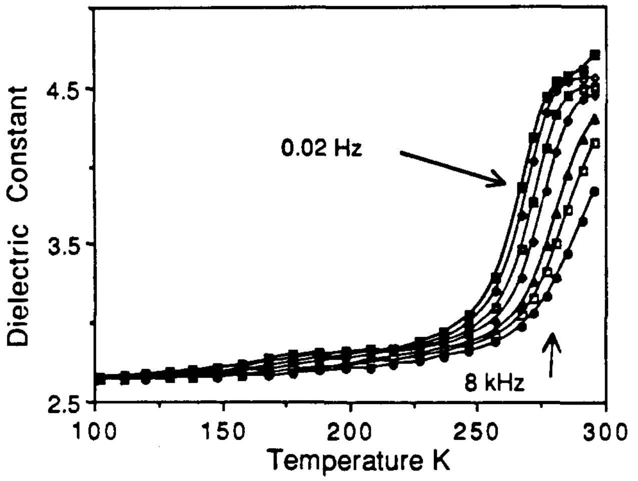

Figure 6. Dielectric constant versus temperature for surface-epoxidized α-TPI lamellas, subsequently crystallized from 2-pentanone at 0 °C, at 0.02, 0.1, 1, 10, 200, 1000, and 8000 Hz.

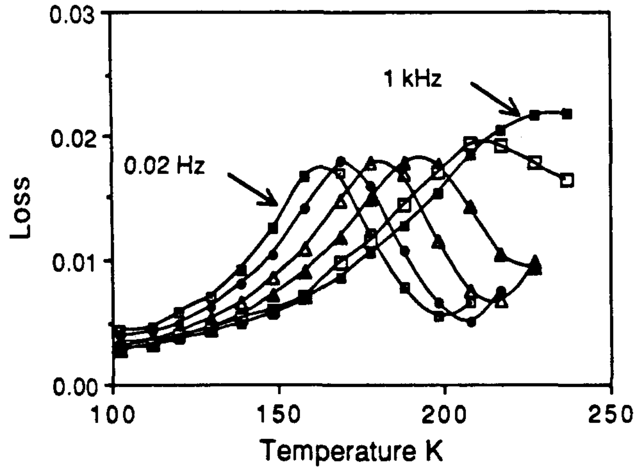

Figure 7. Dielectric loss versus temperature in the secondary loss region for the surface-epoxidized α-TPI lamellas, subsequently crystallized from 1-pentanone at 0 °C, of Figure 6 at 0.02, 0.1, 1, 10, 200, and 1000 Hz.

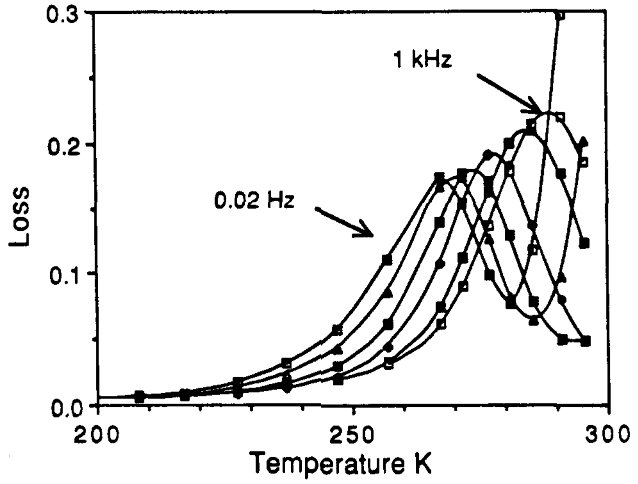

Figure 8. Dielectric loss versus temperature in the primary loss region for the surface-epoxidized α-TPI lamellas, subsequently crystallized from 1-pentanone at 0 °C, of Figure 6 at 0.02, 0.1, 1, 10, 200, and 1000 Hz.

could be considered as temperature independent. The fits are shown in Figures 9 and 10 along with the parameters determined.

Kirkwood–Onsager "g" factors[19] were calculated from the relaxation strengths in Figures 9 and 10. In accomplishing this, the specimen values reported in Figures 9 and 10 were used to calculate amorphous phase dielectric constants using mixture bounding equations for lamellar morphologies.[20] The crystal-phase dielectric constant was assumed to be the same as the unrelaxed dielectric constants of the specimens, and the degrees of

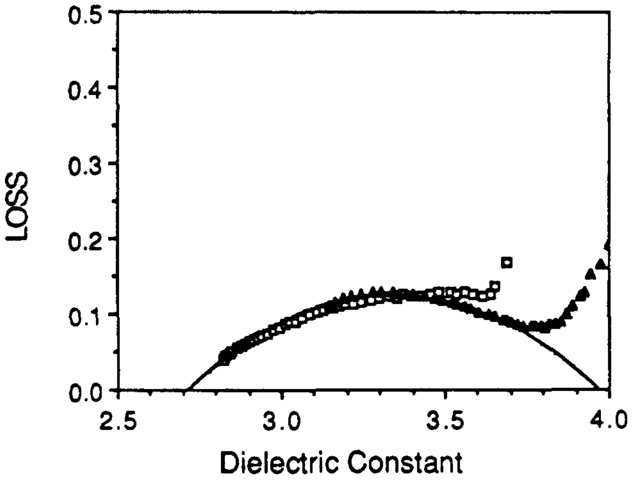

Figure 9. Complex plane plot of dielectric loss and constant in the primary loss region for surface-epoxidized α-TPI lamellas at 290 (open squares) and 310 K (filled triangles). The curve is calculated from the Cole–Cole width parameter, 0.251 (= 1, single relaxation time; ϵ_R = 3.97 and ϵ_U = 2.72.

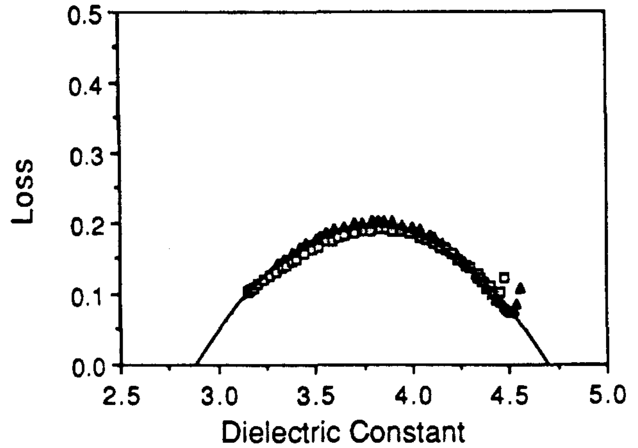

Figure 10. Complex plane plot of dielectric loss and constant in the primary loss region for surface-epoxidized α-TPI lamellas, subsequently crystallized from 2-pentanone at 0 °C, at 277 (open squares) and 281 K (filled triangles). The curve is calculated from the Cole–Cole width parameter, 0.270 (= 1, single relaxation time); ϵ_R = 4.70 and ϵ_U = 2.89.

crystallinity were taken from Table I. In this way, amorphous-phase relaxed dielectric constant values of 6.7 and 6.1 were determined for the epoxidized and solution-crystallized epoxidized materials, respectively, and used with low-temperature specimen values of 2.45 and 2.65, respectively, for the unrelaxed amorphous-phase constants. The density of the amorphous phase was estimated to be 1.1 g cm^{-3} by assuming no change in molar volume of TPI on epoxidation. The latter has an amorphous density of 0.905.[21] The zero change in volume seems reasonable as the change in molar volume of liquid propylene on epoxidation is slightly negative. A dipole moment of 1.95 D, derived from ethylene and propylene oxides,[22] was adopted. The above values in the Kirkwood–Onsager equation resulted in $g = 0.49$ at 300 K for the amorphous phase in epoxidized lamellas and $g = 0.37$ in the solution-crystallized epoxidized lamellas.

A composite plot of ln frequency versus the reciprocal of the temperature at the loss process maximum for the three samples investigated is given in Figure 11. Activation energies for the processes observed are given in Table II; the values for the block copolymer, before and after crystallization from 2-pentanone, are from 30 to 60% larger than those for unreacted TPI.

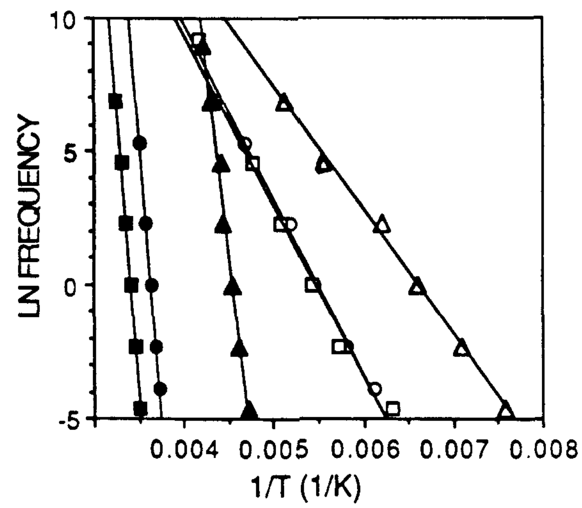

Figure 11. Loss map (ln f_{max} versus $1/T$) for α-TPI lamellas (filled triangles are primary process and open are secondary), surface-epoxidized α-TPI (filled squares are primary process and open are secondary), and surface-epoxidized α-TPI lamellas, subsequently crystallized from 2-pentanone at 0 °C (filled circles are primary process and open are secondary).

Table II
Activation Energies for Dielectric Processes

	E^*, kcal/mol	
sample	secondary	primary
TPI	10	50
block copolymer	15	84
recrystallized block copolymer	13	82

Discussion

Dielectric measurements were made on three related but different TPI containing preparations. The first of these is α-TPI lamellas crystallized from solution with a crystalline stem length of 14.$_5$ monomer units and an average fold length of 10 monomer units.[7] This average fold length suggests that at the lamellar surfaces a significant proportion of either loose adjacent reentry folding or of nearby nonadjacent reentry folding occurs.[8] The second sample was derived from the α-TPI lamellas by a surface reaction, retaining the morphology. It is known that segmented block copolymers are formed upon reaction of *m*-chloroperbenzoic acid in solution with suspended TPI lamellas.[8,11] A product in which the fold and lateral surfaces are epoxidized and the crystal core is unreacted, as shown by agreement between the fraction reacted from carbon-13 NMR and the noncrystalline fraction obtained before reaction by FTIR, can be obtained by careful choice of reaction conditions and post-reaction purification.[13] A third sample, having a different morphology and properties, is obtained by crystallization of the reacted lamellas. The crystallization procedure used yields multilamellar sheafs of folded chain lamellas in the α-TPI form with average stem lengths of 11 monomer units and average noncrystalline traverse lengths of 22 monomer units. The noncrystalline traverses are expected to include interlamellar tie chains as well as folds and chain ends. Agreement in the FTIR and carbon-13 solution NMR crystallinities show that all of the epoxidized blocks are rejected from the crystal core and that the noncrystalline traverses contain both TPI and epoxidized TPI units.[13] The increase in the average noncrystalline traverse length for the crystallized segmented block copolymer from that for the parent TPI lamellas cannot be explained only in terms of the decrease in the crystalline stem length since this would lead to a

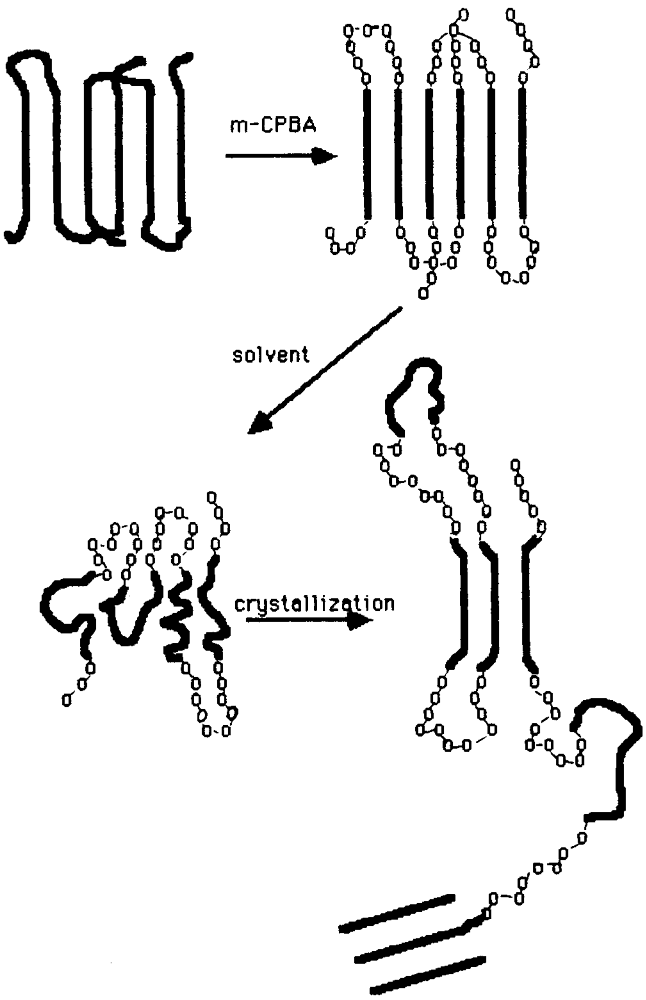

Figure 12. Schematic diagram of changes in α-TPI lamellas due to (a) epoxidation in suspension followed by (b) segmented block copolymer dissolution and (c) crystallization.

traverse length of only about 14 and a crystallity of about 44%. The measured values of 22 for the traverse length and 32–33% for the crystallinity suggest that some complete TPI blocks are present in the noncrystalline traverses of the crystallized block copolymers. Each complete TPI block present will be preceded and followed by an epoxidized TPI block giving an average length of about 39 monomer units for a traverse containing one complete TPI block. About a 50:50 mixture of traverses with lengths of 14 and 39 would correspond to an average of 22. However, traverses containing two or more TPI blocks could also occur. A diagram showing reaction at a lamellar surface, subsequent dissolution, and crystallization is given in Figure 12.

In the present work all preparations were subjected to pressures of 2000–5000 psi. It is known that pressures from small amounts up to 10 000 psi convert about 4–5% of the crystalline material to amorphous material in TPI and epoxidized TPI lamellas.[9] Therefore, the true crystallinity of the samples used can be as much as 5% lower than the values given in Table I.

Three dynamic mechanical processes at −118, −30, and 45 °C (110 Hz) have been reported for α-TPI lamellas;[10] the positions and relative strengths of the two relaxation processes below room temperature are in general agreement with the results of the dielectric measurements. A shift in the −30 °C dynamic mechanical process to about 20 °C is brought about by surface epoxidation of TPI lamellas; a similar effect on the analogous dielectric process was observed in the present study. Glass transition temperatures from DSC of −60 °C for melt-crystallized TPI (β-form) and 32 °C for ~100% epoxidized TPI were reported.[10] The relaxation process reported at 45 °C was not investigated in the present work.

From the ln frequency versus $1/T$ plots (Figure 11) and the general shape of the dielectric loss peaks it appears reasonable to assume a correlation of the secondary process exhibited by surface-epoxidized α-TPI lamellas with that for the TPI lamellas. A similar correlation of the primary processes can also be made. The 10-fold increase in the maximum relaxation strength for the secondary (lower temperature) process and the 20-fold increase for the primary (higher temperature) process in the surface-reacted lamellas over the values found for the unreacted lamellas are brought about by the addition of the dipolar epoxy groups. Due to this increase in relaxation strength, the location of both processes in the modified lamellas, and therefore in the α-TPI lamellas as well, is believed to be the fold surfaces. The primary dielectric processes for the α-TPI lamellas and for the surface epoxidized lamellas have the high activation energy (Table II) characteristic of glass transitions[19,20] and are roughly correlated with the glass transition temperatures for melt-crystallized β-TPI and ~100% solution-epoxidized TPI. The lower activation energies for the secondary processes suggests that the motion responsible is localized.

It is pertinent to note that the characteristics of the primary glass transition processes in both the epoxidized lamellas and the solution-crystallized epoxidized lamellas are similar to those in typical melt-crystallized semicrystalline polymers. In totally amorphous polymers, the glass transition process studied dielectrically has a loss peak or complex plane plot that is skewed toward high frequency but is otherwise relatively narrow. In contrast, in semicrystalline polymers, the process appears to be more symmetrical and much broader.[20] As may be seen in Figures 9 and 10, this is the case here. The Cole–Cole symmetrical circular arc fits well, and width parameters are quite small. The constraining effect of the crystal phase on the amorphous phase is often observed in the Kirkwood–Onsager correlation factor derived from the relaxation strength as well.[20] Its value for otherwise uncorrelated dipoles is often diminished from unity. This has been attributed to the connections to the crystal interfering with the ability of amorphous chain dipoles to relax completely spatially. In the case here, the g values of 0.49 and 0.37 found for the epoxidized lamellas and the solution-crystallized epoxidized lamellas are significantly less than one. Since there are three flexible bonds separating the dipoles, the intramolecular correlation should be modest and the small values for g may well reflect spatial hindrance.

It is of interest to compare the mechanical and dielectrical responses. For the primary or T_g process, in the dynamic mechanical case[10] the most prominent effect is the shift in location to higher temperature occasioned by the alteration of chemical structure of the surface chains. The effect on intensity is more subtle and is complicated by which descriptor to use mechanically as a measure of intensity. The dielectric investigations before and after surface reaction show the temperature shift with change in chemical structure but in addition show a dramatic increase in intensity due to the introduced groups being polar. With respect to the secondary process, it is worth noting that there has been considerable discussion in the literature concerning the morphological location of sub T_g relaxation processes in semicrystalline polymers[19,20] and whether assignment to the amorphous fraction is appropriate. The mechanical studies were not able to address this since the introduction of the epoxy groups had only a minor effect on the measured characteristics of the process. However, in the dielectric case, which responds specifically to the introduction of polar groups, the effect is pronounced. A subglass process that can be well characterized is now observed. In view of the fact that the epoxidation only alters the chemical structure of the surface and not its organization, at the very least it may be said that the amorphous overlayer in single-crystal lamellas is the location of a well-developed subglass relaxation process. This has not been an easy phenomenon to demonstrate experimentally, and the epoxidized specimens constitute an ideal system for accomplishing this.

Solution crystallization of the surface reacted lamellas under the conditions used in this work yields multilamellar structures with cores of α-TPI and noncrystalline traverses containing blocks of TPI and epoxidized TPI, as described above. The lengths of the noncrystalline traverses are distributed about two or more different values due to the exclusion of complete blocks of TPI or epoxidized TPI units from the crystal core. The change in morphology upon copolymer crystallization is accompanied by a shift of the primary dielectric process to lower temperatures without a significant change in the activation energy, suggesting some relaxation of restraints on the chain sections involved with little change in the energy barriers to motion. The secondary process for the segmented block copolymer appears to be less sensitive to the change in morphology which again suggests that a localized motion is involved for both preparations.[19]

Acknowledgment is made to the PSC/CUNY faculty research program for support of part of this research. F.L. and R.H.B. are grateful to the National Science Foundation Polymers Program for financial support (DMR 86-16565).

Registry No. TPI, 9003-31-0.

References and Notes

(1) Schlesinger, W.; Leeper, H. M. *J. Polym. Sci.* **1953**, *11*, 203.
(2) Keller, A.; Martuscelli, E. *Makromol. Chem.* **1972**, *151*, 189.
(3) Anandakumaran, K.; Kuo, C.-C.; Mukherji, S.; Woodward, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1669.
(4) Anandakumaran, K.; Herman, W.; Woodward, A. E. *Macromolecules* **1983**, *16*, 563.
(5) Kuo, C.-C.; Woodward, A. E. *Macromolecules* **1984**, *17*, 1034.
(6) Xu, J.; Woodward, A. E. *Macromolecules* **1986**, *19*, 1114.
(7) Corrigan, J. P.; Zemel, I. S.; Woodward, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 1135.
(8) Xu, J.; Woodward, A. E. *Macromolecules* **1988**, *21*, 83.
(9) Gavish, M.; Corrigan, J.; Woodward, A. E. *Macromolecules* **1988**, *21*, 2079.
(10) Anandakumaran, K.; St. John Manley, R. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 1425.
(11) Schilling, F. C.; Bovey, F. A.; Anandakumaran, K.; Woodward, A. E. *Macromolecules* **1985**, *18*, 2688.
(12) Tischler, F.; Woodward, A. E. *Macromolecules* **1986**, *19*, 1328.
(13) Zemel, I. S.; Corrigan, J. P.; Woodward, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2479.
(14) Kakizaki, M.; Hideshima, T. *J. Macromol. Sci., Phys.* **1973**, *B8*, 367.
(15) North, A. M.; Reid, J. C. *Eur. Polym. J.* **1972**, 8, 1129.
(16) Mopsik, F. I. *Rev. Sci. Instrum.* **1984**, *55*, 79.
(17) Mopsik, F. I. *IEEE Trans. Electr. Insul.* **1985**, *El-20*, 957.
(18) This configuration was suggested to us: Mopsik, R. I., private communication.
(19) McCrum, N. G.; Williams, G.; Read, B. E. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967.
(20) Boyd, R. H. *Polymer* **1985**, *26*, 323.
(21) Cooper, W.; Vaugh, G. *Polymer* **1963**, *4*, 329.
(22) Nelson, R. D., Jr.; Lide, D. R., Jr.; Maryott, A. A. *Natl. Stand. Ref. Data Series (U.S., Natl. Bur. Stand.)* **1967**, *NSRDS-NBS 10.*

Monte Carlo Studies of the Interface between Two Polymer Melts

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ABSTRACT: By use of pseudokinetic rearrangements, the interface between two polymer melts that are mutually repulsive but otherwise identical is simulated on a five-way cubic lattice at a total volume fraction of unity. The position of the interface, which has been deliberately located at $z = 0$, remains stable if the repulsion energy is large enough and if it is ensured in the algorithm that the ratio of the volume fractions of the two polymers is distributed sharply about unity. Conventional periodic boundary conditions were used in the x and y direction, while antiperiodic boundary conditions were introduced at $z = -l_z/2$ and $z = +l_z/2$ (l_z being the lattice dimension in the z direction). At such an antiperiodic boundary one kind of chain is continued as the other kind if the chain stretches across that boundary and nearest neighbors are counted as the same if they are different (and as different if they are the same), thus avoiding the need for a hard boundary. The interface appears to be thicker and local energies are lower than predicted by mean field theories. At the interface it is seen that chain ends and, in case of polydisperse polymers, smaller chains migrate preferentially into the opposite melt while chain dimensions perpendicular to the interface are decreased.

1. Introduction

Although there is considerable interest in the behavior of macromolecules at interfaces there have been only a few Monte Carlo studies on bulk polymers near interfaces. These investigations have recently been summarized by Madden[1] who simulated the melt–vapor interface of a polymer with a combination of pseudokinetic

0024-9297/90/2223-0224$02.50/0