tion. Finally, it is obvious that the mechanical behavior of the PS–PCL diblock copolymers changes dramatically when the phase inversion occurs, i.e., when the nature of the continuous phase changes. Nevertheless, the minor component does not form systematically dispersed microdomains, especially at compositions close to the phase inversion. When the minor component forms semicontinuous phases intermingled within the matrix of the major block, there is evidence of a strong dependence of the stress–strain curves on the two-phase morphology.

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Registry No. (S)(ϵ-CL) (block copolymer), 106107-55-5.

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Block Copolymers near the Microphase Separation Transition. 4. Dielectric Spectroscopy

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ABSTRACT: In this paper, we report evidence of local concentration fluctuations in thermodynamically homogeneous diblock copolymers near the microphase separation transition (MST). Dielectric spectroscopy has been used to probe the local structure of a series of 1,4-polybutadiene/1,2-polybutadiene diblock copolymers with morphologies that ranged from well-ordered to disordered. Four transitions, corresponding to the primary (glass) and secondary transitions of each block, are observed in the dielectric loss spectrum of each copolymer studied. Observation of a primary transition for each block provides evidence of local concentration heterogeneities, large enough to exhibit an apparent glass transition, even in samples that are homogeneous on the molecular length scales probed by small-angle neutron-scattering and rheological measurements. To characterize these heterogeneities, the dielectric loss data have been fit with four discrete transitions, representing each of the glass and secondary transitions. Model fits indicate that the disordered block copolymers are characterized by large-amplitude concentration fluctuations which diminish in magnitude with decreasing χN, where χ is the segment–segment interaction parameter and N is the degree of polymerization. These results are consistent with recent fluctuation corrections by Fredrickson and Helfand to Leibler's mean-field theory for diblock copolymers near the MST.

Introduction

Most of the thermodynamic properties characterizing polymer mixtures are determined by local (segment–segment) interactions. In general, the nature of these short-range interactions, which occur over length scales around the size of a polymer repeat unit, are inferred from experiments that probe length scales larger than the radius of gyration (R_g) of the polymer coils. Techniques such as differential scanning calorimetry (DSC), cloud-point measurements, dynamic mechanical spectroscopy, or zero-angle scattering using light, X-rays, or neutrons have been used to determine the phase diagrams of polymer mixtures from which χ, the Flory–Huggins segment–segment interaction parameter, can be obtained. The success of these macroscopic measurements in establishing χ derives from the mean-field nature of polymer–polymer phase behavior, which breaks down only very near the critical point where fluctuation effects are manifested.[1]

Diblock copolymers represent an alternative class of materials that may be used to study segment–segment interactions. The local interactions in block copolymers are, in principle, indistinguishable from those of binary polymer blends when both systems are in the homogeneous state. Whereas mean-field theories predict that polymer–polymer mixtures can macroscopically phase separate when the parameter χN exceeds 2 (ref 2; N is the degree

Table I
Molecular Characterization

sample	structure	$\Phi_{1,4}$[a]	$10^{-2}N$[b]	N_w/N_n
BB1	1,4/1,2 diblock	0.47	4.7	1.05
BB2	1,4/1,2 diblock	0.46	10.6	1.03
BB7	1,4/1,2 diblock	0.48	15.5	1.05
BB8	1,4/1,2 diblock	0.61	8.0	1.05
1,2	1,2 homopolymer	0	8.9	1.02
1,4	1,4 homopolymer	1	36	1.1

[a] Volume fraction of 1,4-polybutadiene block (89% *cis*- and *trans*-1,4-polybutadiene and 11% 1,2-polybutadiene isomer content. [b] Overall number-average degree of polymerization.

of polymerization), block copolymers are predicted to undergo a microphase separation transition (MST) to an ordered state only when χN exceeds a much higher value, e.g., 10.5 for symmetric diblock copolymers.[3] Thus, the homogeneous region of phase space is extended to considerably higher degrees of polymerization for block copolymers. In a series of recent papers,[4-7] various properties of 1,4-polybutadiene/1,2-polybutadiene diblock copolymers near the MST have been reported. By varying N and the 1,4-polybutadiene block composition $\Phi_{1,4}$, the degree of order of this diblock system has been varied from microphase separated ($\chi N \approx 15$) to thermodynamically homogeneous ($\chi N \approx 5$). The latter systems exhibit a single, albeit broad, glass transition as determined by DSC[4] and behave as simple fluids rheologically.[5] In addition, the small-angle neutron scattering (SANS) results[6,7] can be modeled by the homogeneous-state scattering function predicted by Leibler.[3] These results, which all reflect the long-range properties of these materials, firmly establish the macroscopic phase behavior for this diblock system.

In contrast with the techniques described above, dielectric spectroscopy is sensitive to the short-range structure of a polymer or a polymer mixture since the method can detect correlated motions of small groups of segments. Local heterogeneities are manifested as distinct dielectric transitions attributable to glass transitions of regions rich in each component. From these experiments, we have gained information concerning the interactions between the copolymer blocks at a local level. In this paper, we demonstrate the application of the dielectric technique to 1,4-polybutadiene/1,2-polybutadiene diblock copolymers near the microphase separation transition.

Experimental Section

Four 1,4-polybutadiene/1,2-polybutadiene diblock copolymers, along with corresponding 1,4-polybutadiene and 1,2-polybutadiene homopolymers, have been examined in this investigation. The synthesis and characterization of the materials have been described previously,[4] with the results summarized in Table I. The fraction of 1,4-polybutadiene isomers in the homopolymer and blocks designated as 1,4-polybutadiene is 0.89.

Diblock copolymer samples BB2 and BB7 are completely protonated, whereas samples BB1 and BB8 contain perdeuterated 1,4-polybutadiene blocks. The latter have been prepared for SANS studies described elsewhere.[6,7] The isotopic differences do not impact the present investigation (e.g., DSC analysis indicates no discernible differences in the glass transition behavior for perdeuterated and normal polybutadiene[4]) and therefore are not considered further.

The positions of the copolymers in phase space are given in Figure 1, which shows the combined parameter χN at room temperature as a function of $\Phi_{1,4}$, the volume fraction of 1,4-polybutadiene blocks. The solid curve in Figure 1 indicates the microphase separation transition, $(\chi N)_{\text{MST}}$, predicted by Leibler[3] as a function of $\Phi_{1,4}$ using the value of χ for sample BB1, as determined by SANS measurements.[6,7] For $\chi N > (\chi N)_{\text{MST}}$, the system is ordered at equilibrium, while for $\chi N < (\chi N)_{\text{MST}}$, the system is disordered. These states are also denoted as microphase separated and homogeneous, respectively. The dielectric loss ϵ'' was measured isothermally at 17 frequencies spaced logarithmically from 10 Hz to 100 kHz. A data acquisition adapter (Andeen Model No. CGA-83) controlled a modified GR 1615a capacitance bridge. The precision of the ϵ'' measurement was 0.0001, which was sufficient to allow determination of peak positions for peak heights as small as 0.001. The temperature was stepped between scans and was controlled from −160 to 50 °C. Measurements were taken after a 4-min thermal soak at each temperature.

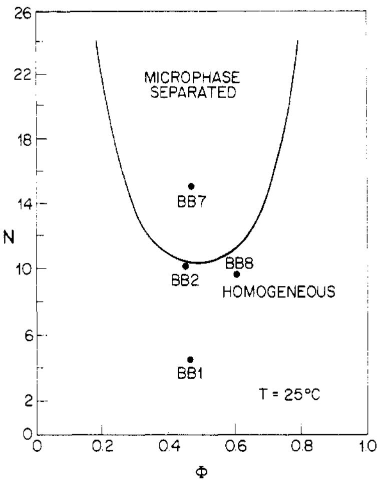

Figure 1. Room-temperature phase diagram for the 1,4-polybutadiene/1,2-polybutadiene diblock copolymer system.

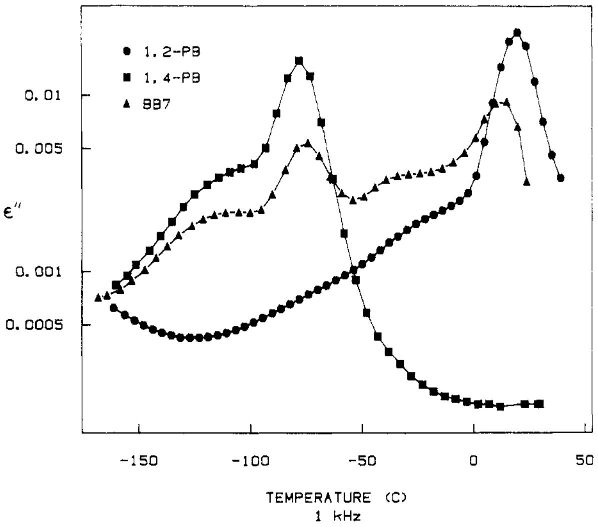

Figure 2. The 1-kHz dielectric loss data for homopolymers and diblock copolymer BB7 as a function of temperature.

Dielectric samples were contained between upper and lower metal plate electrodes within a confinement ring soldered to the lower plate. Approximately 250 mg of material, yielding a thickness of about 250 μm, was employed for dielectric measurements. Isolation of the electrodes was accomplished by using fluoropolymer spacers.

Results

Identification of Dielectric Relaxations. Most amorphous polymers show a primary (i.e., glass) transition associated with cooperative main-chain motion and one or more smaller transitions that occur at temperatures below the glass transition.[8] These secondary transitions are generally attributed to more limited motion of the main chain or to side-group motions. The homopolymers of 1,2- and 1,4-polybutadiene each show more than one transition, as seen in Figure 2 where $\epsilon''(T)$ has been extracted from the isothermal data for $f = 1$ kHz. The two transitions for 1,4-polybutadiene are well-defined, with a peak ($\alpha_{1,4}$) at −78 °C and a shoulder ($\beta_{1,4}$) at −109 °C when $f = 1$ kHz. Apparent activation energies of 34 and 8 kcal/mol, re-

Table II
Temperatures and Activation Energies of Copolymer Transitions ($f = 10^3$ Hz)

	$\alpha_{1,2}$		$\beta_{1,2}$		$\alpha_{1,4}$		$\beta_{1,4}$	
sample	ΔH, kcal/mol	$T_{\epsilon''_{max}}$, °C	ΔH, kcal/mol	$T_{\epsilon''_{max}}$, °C	ΔH, kcal/mol	$T_{\epsilon''_{max}}$, °C	ΔH, kcal/mol	$T_{\epsilon''_{max}}$, °C
1,2-polybutadiene	50	18	19	-26				
1,4-polybutadiene					34	-78	8	-109
BB7 diblock	60	13	16	-34	44	-75	8	-105

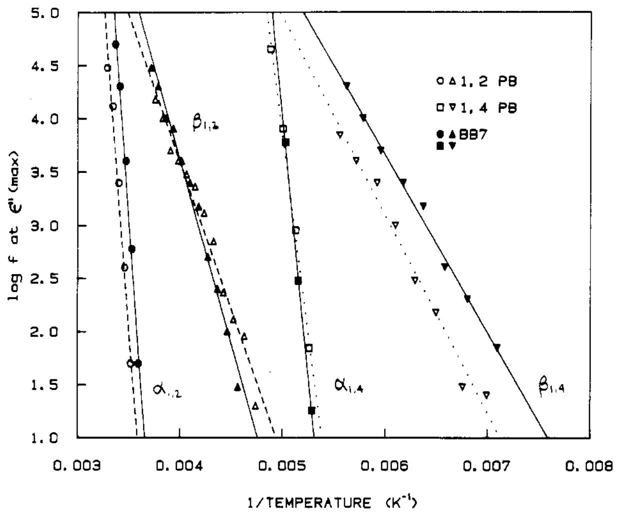

Figure 3. Transition map for homopolymers and diblock copolymer BB7.

spectively, can be obtained from an Arrhenius plot (Figure 3) of the frequency of the maximum in $\epsilon''(\omega)$ at each temperature, $f(\epsilon''_{max})$, versus reciprocal temperature. Uncertainty of the values obtained for the activation energy is approximately 10%. The primary transition of 1,2-polybutadiene, $\alpha_{1,2}$, has a well-defined peak at 19 °C at 1 kHz and an apparent activation energy of 50 kcal/mol. The secondary transition with a peak at approximately -26 °C, denoted $\beta_{1,2}$, is quite broad and weak, although an apparent activation energy of 18 kcal/mol can be estimated. The leading edge of a third transition for 1,2-polybutadiene homopolymer is evident below -150 °C in Figure 2, but the frequency and temperature ranges used in this work are insufficient to characterize this transition.

The apparent activation energies for the α-transitions of both homopolymers (Table II) are close in magnitude to literature values for the α (glass) transitions of other homopolymers.[8] The low-temperature transition of 1,4-polybutadiene, a linear polymer, occurs at a similar temperature and has about the same apparent activation energy as the γ-transition of polyethylene[8] which is attributed to local rotations (crankshaft type motions) of the main chain. The $\beta_{1,2}$ transition at -26 °C has an activation energy similar to the β-transitions observed in polymethacrylates and polyacrylates[8,9] which have been attributed to rotation of the side groups.

Transitions in Microphase Separated Samples. Figure 2 also shows $\epsilon''(T)$ at 1 kHz for diblock copolymer sample BB7, which has been independently shown to be microphase separated at all experimentally accessible temperatures[4,5] (see Figure 1). Four distinct transitions (Figures 2 and 3) are observed as a function of temperature for this diblock copolymer, each closely correlated with the glass transitions and secondary transitions of the corresponding homopolymers. Slight shifts in the glass transition temperatures for the copolymer relative to the homopolymers (Table II) suggest some degree of microphase mixing (Table III). Also, the apparent activation energies are slightly higher than those of the homopolymer α-transitions (Figure 3). Activation energies of the secondary transitions show similar agreement, although both of these transitions appear to be shifted to lower temperatures; this is due in part to the lack of resolution between the primary and secondary peaks. Finally, the secondary transition in BB7 associated with 1,2-polybutadiene microphases is considerably more distinct than that observed for 1,2-polybutadiene homopolymer.

Table III
Characterization of Composition Fluctuations from Modeling[a]

sample	$1 - F$	$\phi^{1,2}$	F	$\phi^{1,4}$
BB1	0.71	0.35	0.29 (0.24)	0.76
BB2	0.62	0.21	0.38 (0.34)	0.87
BB7	0.55	0.07	0.45 (0.41)	0.98
BB8	0.56	0.42	0.44 (0.40)	0.85

[a] F: Fraction of polymer partitioned into 1,4-polybutadiene-rich regions obtained by mass balance over the 1,4-polybutadiene segments. Values in parentheses have been calculated from: $A_4H_4/(A_2H_2 + A_4H_4)$, where the subscripts 2 and 4 refer to 1,2-polybutadiene and 1,4-polybutadiene, respectively, and A and H are the area and activation energy of each α-transition. $\phi^{1,2}$: 1,4-PB composition within 1,2-PB-rich regions. $\phi^{1,4}$: 1,4-PB composition within 1,4-PB-rich regions.

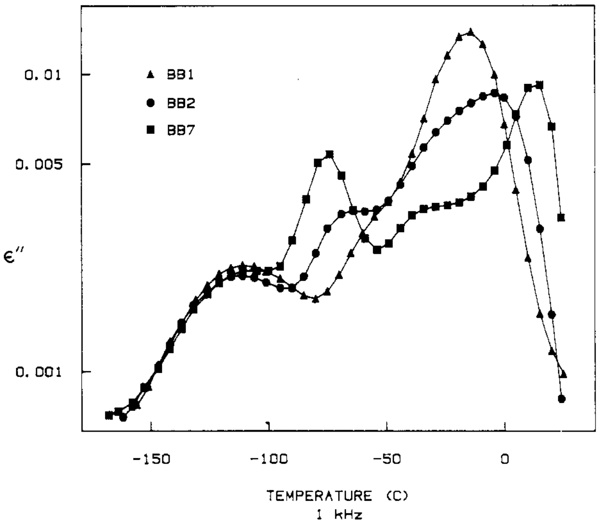

Figure 4. The 1-kHz dielectric loss data for diblock copolymers BB1, BB2, and BB7.

Effects of Microphase Mixing. In addition to sample BB7, two other polymers with $\Phi_{1,4} \approx 0.5$ but with lower molecular weights (samples BB2 and BB1) were measured dielectrically. The three copolymer samples are thermodynamically quite different since the parameter χN ranges from approximately 15 for BB7 to 5 for BB1. These values bracket the MST (Figure 1) such that BB7 is ordered, BB2 ($\chi N \approx 10$) is disordered but near the MST, and BB1 is disordered and well below the MST. $\epsilon''(T)$ at 1 kHz is plotted for copolymer samples BB7, BB2, and BB1 in Figure 4. The lowest temperature transition, the secondary transition associated with the 1,4-polybutadiene segments ($\beta_{1,4}$), is essentially unchanged in position and intensity for all three diblocks. A glass transition attributable to regions rich in 1,4-polybutadiene ($\alpha_{1,4}$) is seen in all three materials, although the dielectric loss intensity

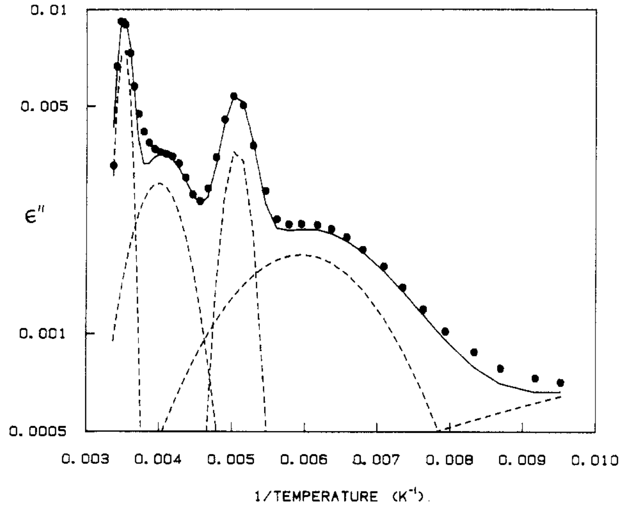

Figure 5. Model fit of 1-kHz dielectric loss data for diblock copolymer BB7. Dashed lines show four Gaussians and a linear base line.

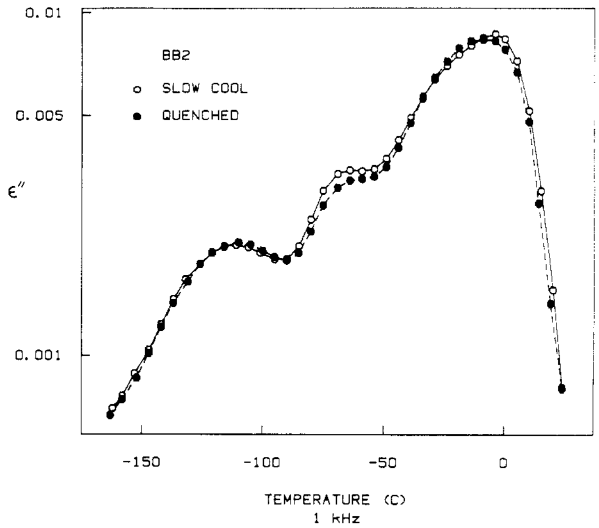

Figure 6. The 1-kHz dielectric loss data for diblock copolymer BB2 after quenching and after slowly cooling at 5 °C/10 min.

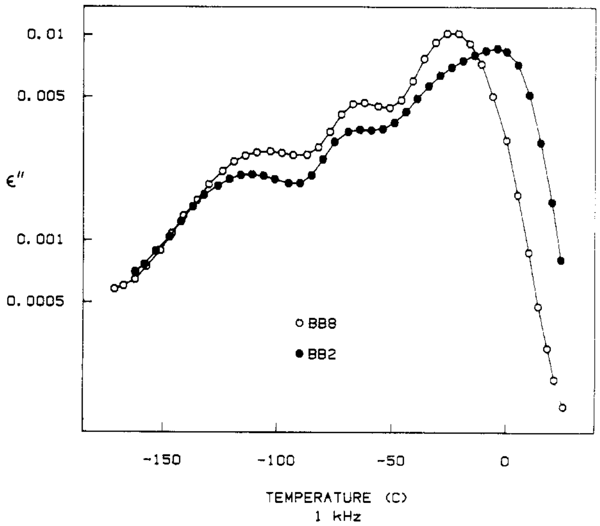

Figure 7. The 1-kHz dielectric loss data for diblock copolymers BB2 and BB8 as a function of temperature.

decreases and the glass transition is shifted to higher temperature as χN is decreased. Correspondingly, the high-temperature glass transition associated with regions rich in 1,2-polybutadiene ($\alpha_{1,2}$) shifts to lower temperature as χN decreases. This transition eventually merges with the secondary transition attributed to 1,2-polybutadiene ($\beta_{1,2}$) which does not appear to shift significantly.

The apparent degree of microphase separation can be estimated by fitting the dielectric loss data with four distinct transitions, arbitrarily assumed to be Gaussian in $1/T$. A small linear sample-independent base-line intensity was also included in the modeling. The positions and widths of the β-transitions are assumed to be similar for all of the block copolymer samples. The validity of this fitting procedure is discussed in the Appendix. Results of the analysis are summarized in Table III. Figure 5 shows a model fit of the 1-kHz data for sample BB7.

From the peak positions of the two α-transitions, the 1,4-polybutadiene composition within the 1,2-polybutadiene- and 1,4-polybutadiene-rich regions, $\phi^{1,2}$ and $\phi^{1,4}$, respectively, can be estimated. A linear combination of the glass transition temperatures of pure homopolymers has been used since this gives the best predictions for the glass transition temperatures of a series of homogeneous blends of 1,2-polybutadiene and 1,4-polybutadiene homopolymers and of several random copolymers of 1,2-polybutadiene and 1,4-polybutadiene.[10] The fraction of material partitioned into regions rich in 1,4-polybutadiene, F, is calculated from $\phi^{1,2}$, $\phi^{1,4}$, and $\Phi_{1,4}$. F has also been estimated from the areas of the glass transition peaks, weighted by the activation energies of each peak, since the number of dipoles contributing to a transition are proportional to the integral of ϵ'' with respect to $1/T$. Differences between the values obtained with these two calculation methods are small and give an indication of the uncertainty in this measurement.

Effects of Thermal History. Because sample BB2 lies close to the MST at room temperature, cooling during the measurement might induce microphase separation since the system is governed by an upper critical solution temperature (UCST).[5,7] From the temperature dependence of χ,[6] we calculate that the MST should lie at ≈−120 °C, well below the effective glass transition of −1 °C (the glass transition temperature of the 1,2-polybutadiene-rich phases at 1 kHz). However, to ensure that the results shown in Figure 4 for this sample were not a reflection of ordering, sample BB2 was examined during heating, following different cooling histories. A comparison of the dielectric results obtained by quenching to −160 °C at 50 °C/min and by slowly cooling at an average rate of −0.5 °C/min (−5 °C steps every 10 min) is given in Figure 6; the two scans are almost identical. If our expression for $\chi(T)$ were incorrect and the MST occurred between room temperature and the effective glass transition temperature of the system, we would anticipate a qualitative difference in these data due to differences in the microphase separation behavior.

The effects of thermal history can also be tested by examining the dielectric data for a sample that is known to be so far from the MST that it cannot microphase separate. Diblock copolymer BB8 (Table I) is characterized by nearly the same value of χN as sample BB2 but with a composition of $\Phi_{1,4} = 0.61$. SANS experiments[6,7] indicate that the MST temperature for this sample lies well below the glass transition temperature at ≈−200 °C. As illustrated in Figure 7, the dielectric loss spectrum obtained from BB8 at 1 kHz qualitatively resembles that for BB2; in particular, a distinct $\alpha_{1,4}$ transition is observed. The combined transition due to 1,2-polybutadiene segments is shifted to lower temperature due to the greater 1,4-polybutadiene content.

These experiments confirm that for sample BB2, which is close to the microphase separation transition, the results obtained under conditions of slow cooling are a reflection of the thermodynamically disordered state. Samples BB1 and BB8 are both much farther from $(\chi N)_{MST}$ than sample BB2 and thus also are not affected by the thermal histories used in this work.

Discussion

Origin of Dielectric Relaxations in Polybutadienes. Polybutadienes are often considered to be nonpolar molecules and, as such, are not expected to exhibit a significant dielectric response. However, our results show that transitions can be clearly resolved for both 1,4-polybutadiene and 1,2-polybutadiene segments and that these transitions correlate with the transitions observed by thermal techniques. We believe that the dielectric response of the butadiene polymers can be attributed to the weak dipole moments of the cis double bond in 1,4-polybutadiene and the vinyl side group in 1,2-polybutadiene. Rough calculations of dipole moments from the geometry of these chemical structures yield values that are comparable to those estimated from the measured intensity of the dielectric relaxation ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$). Observation of the same transitions in both homopolymers and block copolymers indicates that the same dipolar relaxation mechanism occurs for all of these polymers, and the spectra obtained for the block copolymers are not due to Maxwell–Wagner or other interfacial effects.[11,12]

Local Concentration Fluctuations. A number of workers previously have studied the properties of miscible mixtures of polymers. In general, miscibility has been defined by the observation of optical clarity or of a single glass transition,[4,12,13] while phase separation is manifested by a combination of the properties of the pure homopolymer components.[14-16] However, it has been recognized for some time that certain blends determined to be miscible by using one technique may appear to be heterogeneous when studied with another. Wetton et al.[12] observed broadened dielectric relaxation spectra for random copolymer/homopolymer blends that had a single DSC-determined glass transition, implying that there are local concentration fluctuations in these "miscible" systems. With use of NMR spectroscopy to probe extremely short-range interactions, local heterogeneities have also been observed in homogeneous blends of homopolymers.[17] In block copolymers quenched from the homogeneous state, evidence of residual mixed regions rich in the component with the lower glass transition temperature has been observed by using DSC,[18] although it has been suggested that this may be an effect of thermal history.

In this work, a distinct $\alpha_{1,4}$-transition is observed persistently in a set of diblock copolymers that range from strongly ordered to thermodynamically homogeneous. The microphase separation behavior of the 1,2/1,4-polybutadiene block copolymer system has been characterized extensively by using a number of independent techniques,[4-7] conclusively establishing the macroscopic phase state of these materials. Our identification of the $\alpha_{1,4}$-transition seems unambiguous when the data for the entire series of block copolymers are considered. The behavior of the most strongly microphase separated sample, BB7, is clearly a combination of the features of the two homopolymers (see Figure 2). When the temperatures of the $\alpha_{1,2}$- and $\alpha_{1,4}$-transitions are used to estimate the compositions of the microphases (Table III), it appears that they are almost pure, i.e., the block copolymer is strongly segregated. As χN and the degree of ordering are decreased, the $\alpha_{1,4}$-transition shifts to higher temperatures, as one would expect since the extent of microphase mixing increases; nonetheless, $\alpha_{1,4}$ remains distinct from the combined $\alpha_{1,2}$ and $\beta_{1,2}$ transitions. However, the fraction of material partitioned into the 1,4-polybutadiene-rich regions, F, decreases roughly linearly as χN is decreased, so the effect of the 1,4-polybutadiene-rich regions on the overall behavior of the block copolymer may be small. From Figures 6 and 7 it is clear that the observed peaks are not artifacts of the experimental procedure; i.e., the samples are not microphase separating during cooling.

$\phi^{1,4}$, the estimated 1,4-polybutadiene composition in the 1,4-polybutadiene-rich regions, decreases from 0.98 for sample BB7 to 0.76 for sample BB1. This indicates that these regions have relatively high concentrations of 1,4-polybutadiene, even for values of χN well below $(\chi N)_{MST}$. In other words, the amplitudes of the concentration fluctuations in homogeneous diblock copolymers are large, despite the usual mean-field assumption that they are infinitesimally small. In fact, within the context of mean-field theory,[3] all samples for which $\chi N < (\chi N)_{MST}$ should have the same dielectric behavior, which contradicts the results shown in Figure 4. The length scale of the 1,4-polybutadiene-rich heterogeneities must be less than the radius of gyration of the polymer chain since the samples appear to be thermodynamically homogeneous in both SANS[6,7] and rheological studies.[5]

Recent modifications of Leibler's theory by Fredrickson and Helfand[19] incorporate concentration fluctuation effects that diminish in magnitude with decreasing χN. This behavior is qualitatively consistent with our findings in Table III, although the magnitude of the concentration fluctuations appears to be higher and more strongly dependent on N than predicted.

Phase Mixing in High Glass-Transition Temperature Regions. Although the concentration fluctuations that lead to the 1,4-polybutadiene-rich regions vary with χN, the variation is small and the concentration of 1,4-polybutadiene within these regions remains relatively high. However, the degree of mixing within the 1,2-polybutadiene-rich regions, which have a higher glass transition temperature, is more dependent on χN; $\phi^{1,2}$ increases from 0.07 for sample BB7, which is strongly segregated, to 0.35 for BB1, which is disordered. The 1,2-polybutadiene-rich regions in the latter sample are highly mixed. Since the fraction of polymer incorporated in these regions increases to 0.71 for this sample, the properties of the block copolymer will be dominated by the microphase mixing in these regions. The greater sensitivity of the high glass-transition temperature regions to microphase mixing is not unique to this system; thermal analysis of a number of block copolymers and of a homopolymer blend has shown a pronounced broadening and shift of the upper glass transition at compositions where the lower transition remains almost unchanged.[20]

Enhancement of Side-Group Rotation. A separate result involves the $\beta_{1,2}$-transition, which is observed to be enhanced in the microphase separated block copolymer. A distinct peak is observed in the dielectric data for sample BB7, whereas the corresponding transition in the 1,2-polybutadiene homopolymer is extremely broad and weak. The low activation energy of the copolymer transition indicates that it is not simply the glass transition of a microphase of mixed composition such as an "interphase" as has been proposed to explain similar secondary peaks observed in dynamic mechanical analysis.[15] If the transition is attributed to local motion of the vinyl side group, similar to the β-transition observed for the polymethacrylates,[8,9] the enhancement may be due to plasticization of the matrix by incorporated 1,4-polybutadiene segments, allowing freer rotation of the side groups. Previous researchers have shown that low molecular weight plasticizers can impact the secondary transitions of a homopolymer matrix.[21]

Conclusions

A series of model diblock copolymers near the microphase separation transition (MST) has been investigated by using dielectric spectroscopy. Ordered and disordered specimens each exhibit two α- and β-transitions, attributable to primary and secondary relaxations, respectively, of the two polymer blocks. These results indicate the presence of local concentration heterogeneities which, on the basis of model fitting of the dielectric loss data, appear to scale in magnitude with the product χN. The recent fluctuation corrections by Fredrickson and Helfand[19] to Leibler's mean-field theory for the MST[3] are qualitatively consistent with these findings.

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Appendix

Use of Model Fits. Qualitatively, the conclusions discussed above can be drawn directly from the dielectric loss data. To estimate more quantitatively the composition of the apparent microphases, we decided to fit the data with four discrete transitions. This model is easily justified for sample BB7, shown in Figure 5, where the transitions are distinct. The choice of Gaussian line shapes may be inappropriate, especially for the β-transitions which are broad and asymmetric, but the effect of the assumption on the positions of the α-peaks and hence on the composition of the microphases is negligible. It must be stressed that the only information used from the model fits are the positions of the α-peaks, which can be obtained directly from the dielectric loss data for the homopolymers and for microphase separated samples such as BB7. For the homogeneous samples, the model fits are more arbitrary, since the $\alpha_{1,2}$ and $\beta_{1,2}$ transitions coalesce. However, by assuming that the motions giving rise to the $\beta_{1,2}$ relaxations are independent of the degree of mixing within the microphases, estimates of the $\alpha_{1,2}$ and $\alpha_{1,4}$ transition temperatures were obtained. The assumption did not have a major effect on the determination of the composition of the 1,2-polybutadiene-rich regions but did have a slightly larger effect on the determination of the $\alpha_{1,4}$-transition for sample BB1.

The partitioning of material into 1,4-polybutadiene-rich regions, F, can be estimated from the activation energies and the areas of the α-transition peaks. These values are similar to those obtained from a mass balance over the 1,4-polybutadiene segments but are consistently lower. The discrepancy may be due to regions of mixed composition, such as interfacial material, which would broaden the transitions asymmetrically and could modify the activation energies. In this case, the assumption of a Gaussian shape for the major transitions would be inappropriate. Thus, F was estimated by a total mass balance, assuming an equipartitioning of mixed material into 1,4-polybutadiene- and 1,2-polybutadiene-rich regions. In spite of the potential shortcomings of this modeling method, we believe the trends observed in Figure 4 are captured in Table III, i.e., that all samples exhibit large local composition fluctuations whose amplitudes scale with χN.

Registry No. Polybutadiene, 9003-17-2.

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