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Dielectric Relaxations of Homopolymer Blends

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ABSTRACT: Concentration heterogeneities have been observed dielectrically in 1,2-polybutadiene/1,4-polybutadiene homopolymer blends that are expected to be homogeneous from their low molecular weight and interaction parameter. The length scale of the heterogeneities is estimated to be on the order of 25 Å or less. Most of the material has a composition close to that of the bulk, but a small fraction of the blend has a composition quite rich in 1,4-polybutadiene. The asymmetry of the two populations is similar to that observed previously for the analogous diblock system, but the amplitudes of the concentration heterogeneities are smaller for the blends than for the diblock copolymers. In both cases, the asymmetry may be a consequence of the difference in conformer size of the two monomers.

In this work, we report the observation of large-amplitude concentration heterogeneities in low molecular weight homopolymer blends. These blends of 1,2-polybutadiene and 1,4-polybutadiene homopolymers are considered to be homogeneous since they exhibit a single glass transition when measured by bulk experimental techniques such as differential scanning calorimetry (DSC). However, our data show two distinct glass transitions from which we infer the existence of regions rich in each of the components at the length scale of dielectric measurements. These observations have important ramifications since many bulk properties are related to the local relaxations of the chains and hence to the local structure of the blends.

The homopolymers used in this study are described in Table I, with all polymers having a narrow molecular weight distribution. The blends listed in Table II were prepared by solvent-blending in dichloromethane. Estimated positions of the blends in phase space at room temperature are given in Figure 1, which shows the combined parameter χN as a function of $\Phi_{1,4}$, the overall volume fraction of 1,4-polybutadiene monomers. The Flory–Huggins interaction parameter, $\chi \sim 0.0115$, was set to the value determined at room temperature for the homogeneous diblock copolymer BB1 ($N \sim 500$, $\Phi_{1,4} \sim 0.5$) from small-angle neutron scattering measurements (SANS).[1] The number-average degree of polymerization, N, was determined by size exclusion chromatography and averaged for the homopolymers in each blend. As a guide to the phase state of each blend, the solid curve in Figure 1 indicates the spinodal estimated from the Flory–Huggins theory for binary blends[2] assuming equal homopolymer molecular weights. All blends showed a single glass transition in DSC, although an extremely broad transition, on the order of 50 °C, was observed for blend B50H,[3] which might be expected to be phase-separated from the estimated phase diagram. However, the dielectric loss, ϵ'', measured isothermally as described previously,[4] generally showed evidence of two glass transitions.

In a previous paper,[4] we discussed the dielectric characterization of a series of 1,2-polybutadiene/1,4-polybutadiene diblock copolymers which had been characterized extensively through DSC,[5] rheology,[6] and SANS.[1] The phase state of these materials ranged from well below the microphase separation transition (MST) where they are fully homogeneous to somewhat above the MST where they are strongly microphase-separated. A surprising result from this study was that in each case, regardless of the phase state of the block copolymer, evidence of two glass transitions was observed. These results imply that there are two distinct populations of polymer molecules, even in the nominally homogeneous samples. The higher temperature transition corresponded to regions rich in 1,2-polybutadiene, while the lower temperature transition corresponded to regions rich in 1,4-polybutadiene. Quantitative determination of the partitioning of material between the two populations was accomplished by modeling the position and intensity of each transition independently.

Table I
Molecular Characterization of Homopolymers

polymer[a]	N_n[b]	PDI[b]
B1: 1,4-PB	230	1.1
B2: 1,2-PB	250	1.0
B3: 1,4-PB[d]	40, 44[c]	1.1
B4: 1,2-PB[d]	50	1.2
B5: 1,4-PB[d]	30	1.2
B6: 1,2-PB[d]	20	1.2

[a] From ^{1}H NMR in deuteriochloroform; each homopolymer consists of approximately 90% of the named isomer. [b] From size exclusion chromatography in toluene at 50 °C using universal calibration from 1,4-polybutadiene standards; PDI = polydispersity. [c] From vapor phase osmometry in toluene at 50 °C. [d] From Polysciences (Warrington, PA).

Table II
Composition Heterogeneities from Modeling the Dielectric Loss Data Taken at 1 kHz[a]

blend	components	$\Phi_{1,4}$	$\phi^{1,2}$	$1 - F$	$\phi^{1,4}$	F
B25L	B5/B6	0.24	0.19	0.85	0.50	0.15
B50L	B5/B6	0.50	0.36	0.52	0.65	0.48
B75L	B5/B6	0.74	0.53	0.38	0.87	0.62
B25M	B3/B4	0.25	0.22	0.91	0.55	0.09
B50M	B3/B4	0.50	0.41	0.70	0.72	0.30
B60M	B3/B4	0.60	0.44	0.55	0.79	0.45
B25H	B1/B2	0.22	0.21	0.98	0.65	0.02
B50H	B1/B2	0.48	0.40	0.80	0.80	0.20
B50Hb	B1/B2	0.50	0.39	0.74	0.83	0.26
B75H	B1/B2	0.74	0.55	0.57	0.99	0.43
B80H	B1/B2	0.80	0.57	0.46	1.00	0.54

[a] $\Phi_{1,4}$ = bulk volume fraction of 1,4-polybutadiene; F = fraction of polymer partitioned into 1,4-polybutadiene-rich regions; $\phi^{1,2}$ = 1,4-PB composition within 1,2-PB-rich regions; $\phi^{1,4}$ = 1,4-PB composition within 1,4-PB-rich regions.

Since the thermodynamic models used to describe these diblock copolymers assumed homogeneity on a length scale on the order of the radius of gyration, evidence of two glass transitions was used to infer the existence of concentration heterogeneities on a shorter length scale.[4] Similarly, we interpret the two glass transitions observed

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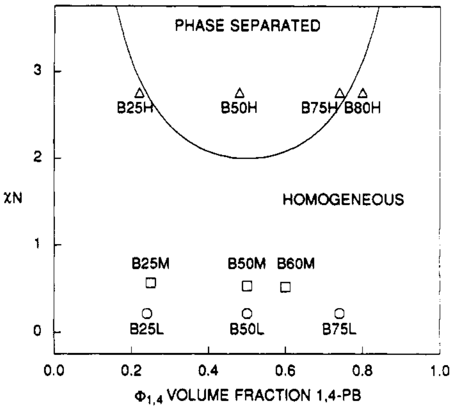

Figure 1. Phase diagram for the homopolymer blends using the interaction parameter determined for diblock copolymer BB1. The solid line indicates the spinodal calculated from the Flory–Huggins theory.

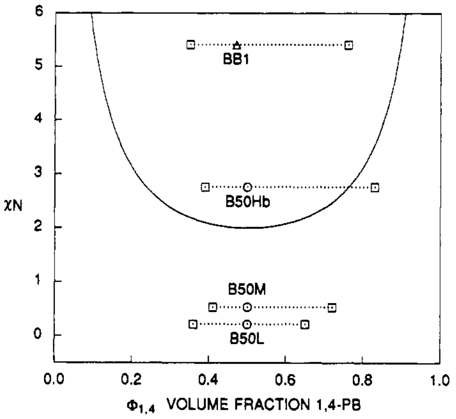

Figure 2. Comparison of concentration heterogeneities observed for diblock copolymer BB1 with those observed for blends with $\phi \sim 0.5$. The circles indicate the bulk composition, while the squares indicate the heterogeneity compositions determined dielectrically. The solid line indicates the spinodal calculated from the Flory–Huggins theory.

for the homopolymer blends as indications of concentration heterogeneities on a submolecular length scale, especially since it is well-known that the behavior of binary blends of homopolymers is often excellently modeled by mean-field theories which assume homogeneity on a molecular level. Using a statistical segment length of 5.0 Å for 1,2-polybutadiene monomers[7] and a degree of polymerization of 20 to calculate the radius of gyration for sample B6, the lowest molecular weight homopolymer used in this study, the length scale of the concentration heterogeneities in the homopolymer blends is thus estimated to be on the order of 25 Å or less.

Compositions of the heterogeneities in the homopolymer blends were estimated by fitting each of four transitions in the dielectric loss data at 1 kHz to a Gaussian in $1/T$, as discussed in detail in ref 4. The four transitions correspond to the α (glass) and β transitions of each population of chains. The results of this analysis are summarized for the blends in Table II and shown graphically for blends with $\phi \sim 0.5$ in Figure 2. Results for diblock copolymer BB1 are shown for comparison. In each case where two glass transitions are observed, most of the material has a composition close to that of the bulk. A smaller fraction of the blend is rich in the 1,4-polybutadiene component. This asymmetry resembles that observed for the block copolymers, where the fraction of material rich in 1,4-polybutadiene always deviated more from the bulk composition than the fraction that was rich in 1,2-polybutadiene.

The asymmetry in the composition diagram suggests that the volume fraction may not be the appropriate parameter to describe the blends on the length scales of the dielectric experiment. Matsuoka has proposed that the mole fraction of conformers be used to describe these submolecular phenomena, especially since we use the glass transition, an indication of local intermolecular interactions, as our experimental probe.[8] If the conformers are defined as the elementary units necessary for local motion of the polymer backbone (as in the conformer model of the glass transition[9]), the 1,4-polybutadiene monomer consists of three conformers while there are only two conformers in each 1,2-polybutadiene monomer. Using the conformer molar fraction to construct the composition diagram removes much, although not all, of the asymmetry. On the other hand, calculation of the configurational entropies of mixing assuming the blends are homogeneous on the molecular level but heterogeneous on the conformer level yields the result that the heterogeneities should be more asymmetric than observed here.

A final observation from the results in Table II is that composition diagrams such as Figure 2 (obtained at room temperature by varying N) are not equilibrium phase diagrams. The compositions of the concentration heterogeneities, $\phi^{1,2}$ and $\phi^{1,4}$, depend on the bulk composition $\Phi_{1,4}$, and do not define a phase envelope. For a true phase diagram, all blends with the same value of χN but different bulk compositions within the "two-phase" region would divide into two phases with the same values of $\phi^{1,2}$ and $\phi^{1,4}$ defined by the phase envelope. Only F, the amount of material partitioned into each phase, would vary with the bulk composition. In the results presented here, the heterogeneity compositions and the partitioning both are related to $\Phi_{1,4}$ for a given value χN.

In conclusion, we observe concentration heterogeneities in homopolymer blends that are expected to be homogeneous from their low values of χN. These results are similar to those reported previously in diblock copolymers.[4] We estimate that the length scale of the heterogeneities is on the order of 25 Å or less. Composition diagrams constructed from these results are asymmetric and suggest that the mole fraction of conformers may be a more appropriate parameter than volume fraction to describe these submolecular details. The heterogeneities described by these composition diagrams do not define a phase envelope and thus cannot be attributed to equilibrium phase behavior on a smaller length scale than that predicted by mean-field theories.

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Registry No. PB (homopolymer), 9003-17-2.