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Block Copolymers near the Microphase Separation Transition. 1. Preparation and Physical Characterization of a Model System

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ABSTRACT: A model set of 1,4-polybutadiene–1,2-polybutadiene diblock copolymers has been prepared and molecularly characterized. Physical characterization by differential scanning calorimetry (DSC) and qualitative identification of the flow behavior (liquid- vs. solid-like) over a period of several days have established the critical degree of polymerization for this system as $N_c = 1.20\ (\pm\ 0.14) \times 10^3$. Below the microphase separation transition the polymers exhibit a single broad glass transition, as measured by DSC, which has been attributed to local segment density fluctuations. This effect was found to be dependent on the degree of polymerization, as predicted from theory.

Introduction

The general phenomenon of polymer–polymer immiscibility is a natural consequence of the size of macromolecules, which results in a vanishingly small entropy of mixing relative to monomers. Homogeneous polymer–polymer systems are therefore quite rare, which severely hampers attempts to alloy polymers in the manner in which metals and ceramics are formulated. Nevertheless, it has been demonstrated that the blending of polymers can produce synergistic effects (e.g., polystyrene and poly(phenylene oxide)[1]) and considerable energy has been expended over the past several decades in an effort to elucidate the underlying physics which govern such systems.

Flory[2] provided one of the first representations for the free energy of mixing in homopolymer blends based on a liquid lattice model in which the energy of interaction of different chemical species per site is defined as

$$F_{\mathrm{int}} = kT\chi\Phi(1 - \Phi) \tag{1}$$

where k is the Boltzmann constant, T is the temperature, and Φ is the volume fraction of one component. χ is the dimensionless Flory interaction parameter, which persists today as the most common basis for describing the interaction energy between polymer segments (and solvents). In polymer blends governed by van der Waals interactions ($\chi \geq 0$), increasing χ above a critical value produces phase separation, while at very small (or negative) χ, entropy effects dominate, resulting in miscibility. In general, for $\chi \geq 0$, χ is assumed to be constant for a particular pair of polymers, and the product of χ and the degree of polymerization N is the parameter which determines miscibility for a given Φ. The critical point, defined as $\partial^3(F/kT)/\partial\Phi^3 = 0$, occurs at

$$\chi_c = (N_B^{1/2} + N_A^{1/2})^2/2N_AN_B \tag{2}$$

where N_A and N_B are the degrees of polymerization of each component. For the symmetrical case $N_A = N_B = N/2$, for which $(N\chi)_c = 4$.

Recently, Leibler[3] has derived a theory of microphase separation in block copolymers exhibiting an upper critical solution temperature (UCST). The criteria for stability and equilibrium are too cumbersome to be reproduced here and so only the results are shown in Figure 1. Such systems contain a single critical point at $\Phi = 0.5$ which is predicted to scale as

$$(N\chi)_c = 10.5 \tag{3}$$

where $N = N_A + N_B$.

The phase behavior of polymer blends is best studied by means of scattering experiments (e.g., light X-ray, or neutron scattering). The scattering power, $S(q)$, of a homogeneous blend of homopolymers increases and finally diverges at $q \rightarrow 0$ as the spinodal curve is approached from the homogeneous melt,[4] where q $(=4\pi\lambda^{-1} \sin (\theta/2))$ is the magnitude of the scattering wave vector. Such scattering results from the development of local segment density fluctuations. In practice, little data exist concerning such critical fluctuations in polymers since it is difficult to distinguish between the equilibrium and spinodal limits in a homopolymer blend and because such long times are required to attain equilibrium.

Block copolymers are considerably more attractive for studying polymer–polymer interactions in the homogeneous melt state and near the phase transition boundaries. The block nature of these materials limits the range of density fluctuations to molecular dimensions, thereby reducing the time required to attain equilibrium. In homopolymer blends the range of fluctuations is unbounded. Also, the elevated critical molecular weight provides a significant increase in N over which a given system should remain homogeneous. As illustrated in Figure 1, the equilibrium and stability boundaries are predicted to be almost commensurate. This provides an opportunity to measure equilibrium properties over almost the entire

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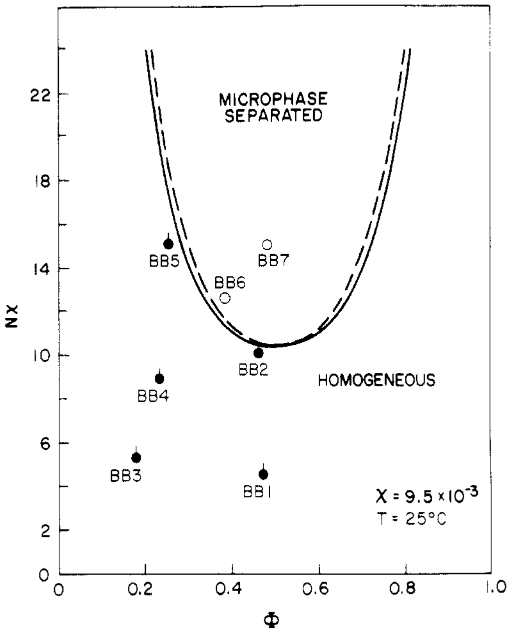

Figure 1. Microphase separation transition (—) and spinodal (- - -) curves for block copolymers as predicted by Leibler.[3] Heterogeneous (○) and homogeneous (●) data are plotted for $\chi = 9.5 \times 10^{-3}$. Points represented by (●) indicate samples which contain a perdeuterated block.

Table I
Molecular Characterization

sample	isotopes[a]	microstructure[b]	$N \times 10^{-2}$ [c]	Φ[d]	M_w/M_n [e]
BB1	d-h	1,4-1,2	4.7	0.47	1.05
BB2	h-h	1,4-1,2	10.6	0.46	1.03
BB3	d-h	1,4-1,2	5.8	0.18	1.04
BB4	d-h	1,4-1,2	9.4	0.23	1.04
BB5	d-h	1,4-1,2	15.9	0.25	1.5[f] (1.07)
BB6	h-h	1,4-1,2	13.3	0.38	1.05
BB7	h-h	1,4-1,2	15.5	0.48	1.05
B1	h	1,2	8.9	0	1.02
B2	d	1,4	41	1	1.12
B3	h	1,4	36[e]	0	1.10

[a] h corresponds to C_4H_6 and d corresponds to C_4D_6 segments. [b] 1,4 refers to 89% 1,4-polybutadiene (cis and trans) and 11% 1,2-polybutadiene, while 1,2 refers to >98% 1,2-polybutadiene as measured by ^{13}C NMR on B3 and B1, respectively. [c] Degree of polymerization as measured by membrane osmometry. [d] $\Phi = N_{1,4}/N$ as measured by FTIR (d-h isotopes) or ^{13}C NMR (h-h isotopes). [e] Measured by HPSEC. [f] The value in parentheses was determined without including the homopolymer fraction.

phase diagram without the ambiguities associated with a large metastable region as is found in homopolymer blends.[4]

Leibler[3] has predicted that the scattering function for a homogeneous diblock copolymer should display a maximum in $S(q)$ around $q \sim 2/R$ ($0.2 < \Phi < 0.8$), where R is the radius of gyration of an ideal chain of degree of polymerization N. This is similar to the correlation hole effect predicted by de Gennes,[4] although in this case the intensity has been directly related to χN. The peak in $S(q)$ for block copolymers diverges at the spinodal curve, analogous to the behavior of $S(0)$ in homopolymer blends. This raises the possibility of studying the detailed structure of the homogeneous melt by means of small-angle scattering (SAS), along with the corresponding macroscopic properties under equilibrium conditions. The latter include the effects of local segment density fluctuations on the glass transition and melt rheology.

Several authors have identified homogeneous block copolymer systems. Krause et al.[5] demonstrated by DSC that block copolymers of styrene and α-methylstyrene were single phase at a degree of polymerization as high as 5×10^3. Cohen and Ramos[6] showed by dynamic mechanical measurements that the critical degree of polymerization N_c for an isoprene–butadiene diblock copolymer was greater than 4×10^3. In a subsequent study, Cohen and Wilfong[7] demonstrated a similar phase behavior in a 1,4-polybutadiene–1,2-polybutadiene diblock copolymer system, although in this case N_c was estimated to be considerably lower ($<1.6 \times 10^3$).

The present study focuses on examining the structure of diblock copolymers near the microphase separation transition (MST). On the basis of the following criteria 1,4- and 1,2-polybutadiene are nearly ideal for such a study: N_c is expected to be $\sim 10^3$ which permits N to be accurately measured by membrane osmometry but is large enough to allow a comparison of $S(q)$ with the theory of Leibler.[3] Also, isotope effects on χN are not expected to be significant at this degree of polymerization.

Both polymers can be prepared by anionic polymerization and the monomer is available in the protio and deuterio form.[8] The latter requirement is necessary because $S(q)$ must be measured by SANS; monomers that provide X-ray contrast do not satisfy the first criterion.

The glass transition temperatures are well separated and below room temperature. This facilitates attainment of equilibrium and permits quantitative analysis of T_g.

In this initial report, we describe the synthesis, molecular characterization, and several physical properties of a model set of diblock copolymers exhibiting both microphase-separated and homogeneous phase behavior. The nature of the phase state has been identified by differential scanning calorimetry (DSC) and observation of the flow behavior above T_g. From these results, the interaction parameter χ has been determined accurately (±5%) according to the theoretical treatment of Leibler.[3]

The overall DSC behavior in the homogeneous melt as a function of Φ and N was found to be consistent with the predicted segment density fluctuations.[3] These observations also provided quantitative evidence as to the capability of this method in probing the physical state of polymer blends near the phase separation transition.

Experimental Section

Synthesis. All reactions were conducted under purified argon in glass vessels containing O-ring connectors and Teflon valves. Polymerizations were initiated with *n*-butyllithium in rigorously purified benzene in the presence of a threefold molar excess of anisole. Anisole selectively increases the rate of initiation without affecting the rate of polymerization or the product microstructure.[9]

Butadiene monomers were obtained from Matheson (C_4H_6, instrument purity) and Merck, Sharp and Dohme Ltd. (C_4D_6 98% deuterium labeled) and were purified by vacuum distillation from dibutylmagnesium. The first block of a diblock copolymer was prepared with either C_4H_6 or C_4D_6 monomer at 50 °C which results in predominantly 1,4 addition. Upon completion of the first block, the temperature was lowered to 6 ± 2 °C and 1,2-dipiperidinoethane (DIPIP) was added to the reactor at a twofold molar ratio relative to lithium. DIPIP is a polar modifier which has been shown to produce >99% 1,2 addition under the conditions employed.[10,11] Homopolymers of 1,2-polybutadiene (protio) and 1,4-polybutadiene (deuterio and protio) were also prepared under the same conditions as the corresponding blocks. 1,2-Polybutadiene polymerizations were terminated after 40–80% monomer conversion. All polymers were terminated with methanol, precipitated in methanol, dried under vacuum, and stored in an oxygen-free inert gas environment at room temperature.

Molecular Characterization. The number-average degree of polymerization N was measured in toluene at 30 °C on a Mechrolab recording membrane osmometer. These results are presented in Figure 2 and are listed in Table I. In each case N is in close agreement with the value calculated from the synthesis stoichiometry.

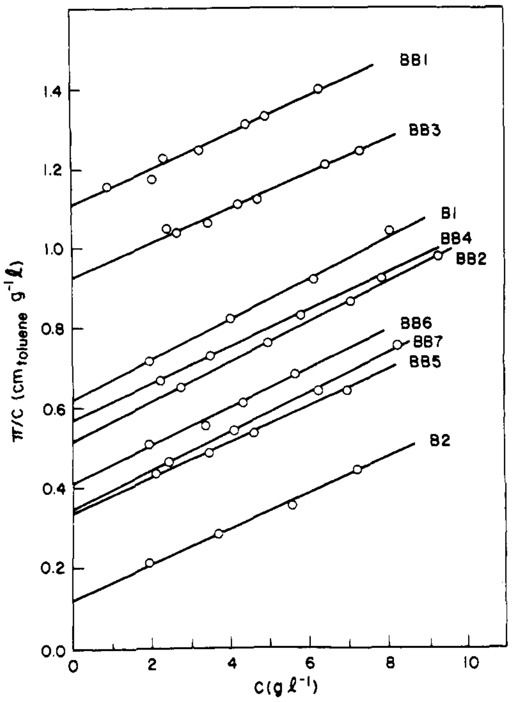

Figure 2. Membrane osmometry results for the samples listed in Table I.

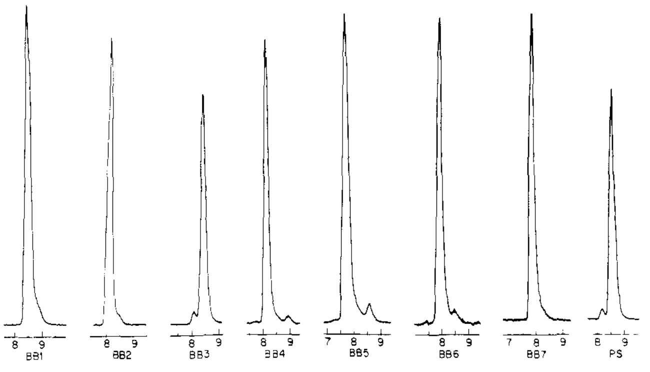

Figure 3. HPSEC traces for the diblock copolymers listed in Table I and a polystyrene standard (PS) for which $M_n = 5 \times 10^4$ and $M_w/M_n = 1.06$.

Polydispersity indices were obtained by high-pressure size exclusion chromatography (HPSEC) at 25 °C employing a set of Du Pont Zorbax PSM bimodal-S size exclusion columns with tetrahydrofuran as the mobile phase. The HPSEC instrument was calibrated with a set of nine monodisperse polystyrene standards (Pressure Chemical). All measurements fell within the linear portion of the calibration curve, which extended from 4 $\times 10^3$ to 1 $\times 10^6$ in molecular weight. Tung[12] has reported that the calibration curves of polystyrene and polybutadiene in THF are parellel, which provides for the direct determination of the polybutadiene polydisperisity index from the polystyrene calibration curve. Instrument peak broadening effects were found to be negligible based on the reported and measured polydispersities of the calibration standards. HPSEC traces for the seven diblock copolymers along with a polystyrene standard are presented in Figure 3 and the polydispersity indices are listed in Table I. In every case the homopolymer content is less than 5% (wt).

The microstructures of the 1,4-polybutadiene (89% 1,4 cis and trans, 11% 1,2) and the 1,2-polybutadiene (>98% 1,2) were determined for samples B3 and B1, respectively, by ^{13}C NMR. On the basis of these results, the 1,4-polybutadiene content, Φ, of samples BB2, BB6, and BB7 were obtained by ^{13}C NMR. Although the microstructure of the perdeuterated polybutadiene was not directly measured, there is no reason to expect deuterium substitution to influence the mechanism of polymerization. This is supported by the fact that sample B2 and B3 show no perceptible difference in glass transition temperature (see below).

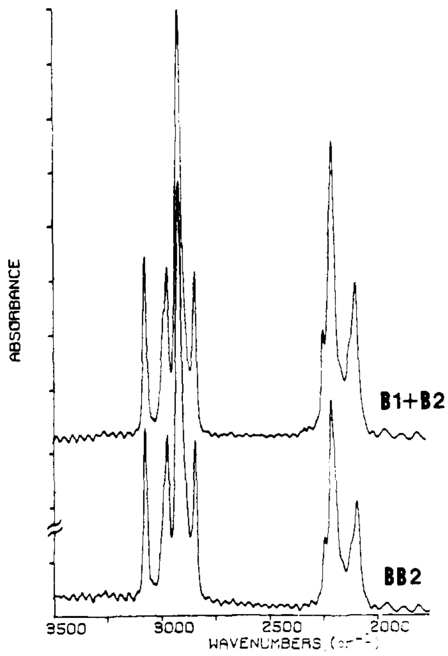

Figure 4. Infrared absorbance for a blend of protio-1,2-polybutadiene (B1) and perdeuterio-1,4-polybutadiene (B2) and for a corresponding diblock copolymer (BB2). Deuterium-labeled block copolymer compositions were determined by this method.

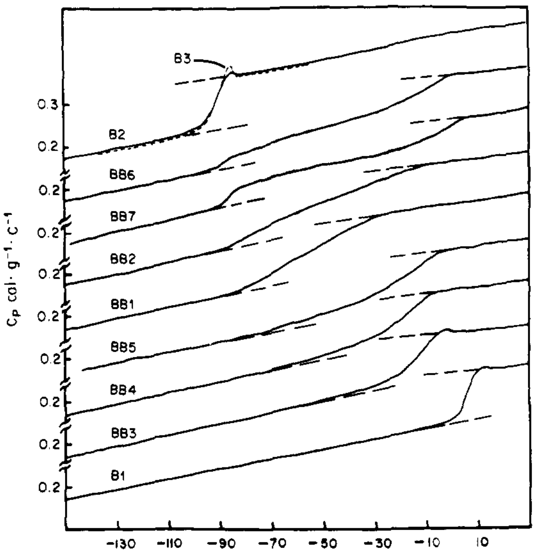

Figure 5. Specific heat measurements obtained at a scanning rate of 20 °C/min.

Φ was determined for the deterium-labeled block copolymers by infrared absorption on a Nicolet MX-1 FTIR spectrometer. Relative C–H and C–D stretching absorbances were obtained from a blend of samples B1 and B2 at a concentration of 5% (w/v) in CCl_4. Typical infrared results from a homopolymer blend and a diblock copolymer are illustrated in Figure 4. Measured diblock copolymer compositions are in excellent agreement with those expected from the synthesis stoichiometry and are given in Table I.

Differential Scanning Calorimetry. Polymer specimens (10–25 mg) were cooled rapidly (>200 °C/min) in a modified Perkin-Elmer Model 2 differential scanning calorimeter (DSC) and subsequently examined between −160 and +50 °C at a heating rate of 20 °C/min. Various repeat runs established a reproducibility of better than 2%. The results are presented in Figure 5.

Base lines were extrapolated to T_g from the linear portions of a DSC trace, before and after the overall thermal transitions. The change in specific heat, ΔC_p, associated with an overall thermal

Table II
DSC Results

sample	T_g,[a] °C	ΔT_g,[b] °C	ΔC_p, cal g^{-1} °C^{-1}
BB1	-56	60	0.113
BB2	-55	80	0.113
BB3	-16	57	0.115
BB4	-19	63	0.115
BB5	-21	74	0.117
BB6	-85, -8[c]	100	0.120
BB7	-86, -2[c]	103	0.116
B1	3	21	0.122
B2	-89	21	0.118
B3	-89	21	0.123

[a] T_g is the temperature at $\Delta C_p/2$. [b] Determined from the initial and final deviations from the linear regions of C_p vs. temperature. [c] Estimated from the two glass transitions apparent in the overall transition.

transition was determined at the temperature at which C_p was midway between the extrapolated base lines. In the case of samples exhibiting a single transition, this temperature is defined as T_g. For samples BB6 and BB7, a third base line was established between the two distinguishable thermal transitions from which the individual T_g values were estimated. ΔT_g was determined as the difference in temperature between the onset and termination of the overall thermal transition as established by the two linear portions of the DSC trace. T_g, ΔT_g, and ΔC_p are listed in Table II and specific heats are listed in Table III. A detailed description of the DSC experimental techniques employed can be found elsewhere.[13]

Results

Synthesis. Prepartion of 1,4-polybutadiene–1,2-polybutadiene diblock copolymers of specific N and Φ requires a knowledge of the kinetics for each reaction. Butadiene has been successfully reacted to completion at 50 °C in benzene based on a half-order dependence in anion concentration and a rate constant of 1.5×10^{-2} s^{-1} $mol^{-1/2}$.[14] Complete conversion of the deuterated monomer is essential during polymerization of the first block. The rate constant for the polymerization of butadiene in the presence of DIPIP has not been reported. Although the presently reported reactions were not conducted as a kinetic study, they have provided the information necessary to assign a rate expression at 6 °C. Anion concentration, [I], was estimated from N, the yield in grams and the reaction solution volume. Monomer conversion per unit time, $t^{-1}\ln([M_0]/[M])$, was determined from $1 - \Phi$, the overall yield and the amount of added monomer. These quantities are plotted in Figure 6 for each of the 1,2-polybutadiene polymerizations. The data are well represented by a rate expression that is first order in [I], in agreement with the findings of Worsfold et al.[11] At 6 °C, the rate constant is 2.3 min^{-1} mol^{-1} L, ±20%. Using this rate expression, we were able to conduct the reactions in the presence of excess monomer and terminate them at an intermediate conversion, thereby avoiding the unreasonably long reaction times associated with complete conversion.

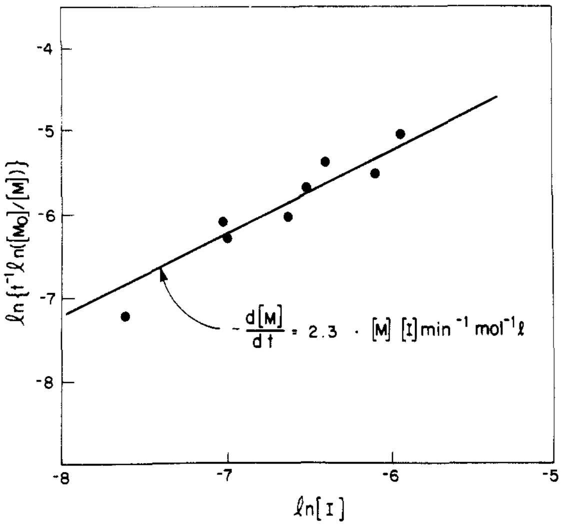

Figure 6. Kinetic data for the lithium-catalyzed polymerization of butadiene in benzene in the presence of a twofold molar excess of dipiperidinoethane at 6 (± 2) °C.

Properties. The DSC results presented in Figure 5 provide a qualitative indication of the phase state of the diblock copolymers. As documented in Table II, the glass transition of 1,4-polybutadiene is 92 °C lower than that of 1,2-polybutadiene. Perdeuteration has no apparent effect on the thermal behavior of 1,4-polybutadiene. Samples BB6 and BB7 each exhibit two glass transitions, which suggests that these samples lie above the microphase separation transition (MST) as shown in Figure 1. The remaining block copolymers are characterized by a single broad glass transition, intermediate in temperature to that of the corresponding homopolymers, indicative of a single-phase polymer blend. T_g for the homogeneous samples is plotted against Φ in Figure 7.

With the exception of samples BB6 and BB7 the block copolymers displayed the same liquid-like flow characteristics as the homopolymers, although the flow times between samples varied considerably. In contrast, samples

Table III
Specific Heats (cal g^{-1} °C^{-1})

T, °C	BB1	BB2	BB3	BB4	BB5	BB6	BB7	B1	B2	B3
-140	0.207		0.197	0.198		0.204		0.199	0.204	
-130	0.219	0.212	0.211	0.212	0.213	0.216	0.220	0.213	0.212	0.201
-120	0.232	0.225	0.226	0.226	0.224	0.224	0.232	0.225	0.224	0.214
-110	0.243	0.238	0.238	0.238	0.237	0.236	0.244	0.236	0.240	0.228
-100	0.255	0.251	0.252	0.252	0.248	0.252	0.258	0.249	0.259	0.250
-90	0.270	0.270	0.264	0.265	0.260	0.269	0.281	0.263	0.326	0.338
-80	0.290	0.296	0.276	0.280	0.273	0.303	0.326	0.275	0.393	0.388
-70	0.323	0.326	0.292	0.294	0.292	0.323	0.342	0.285	0.402	0.394
-60	0.357	0.351	0.305	0.310	0.307	0.342	0.359	0.295	0.411	0.398
-50	0.388	0.376	0.321	0.328	0.327	0.358	0.371	0.305	0.421	0.402
-40	0.422	0.398	0.336	0.349	0.346	0.375	0.382	0.315	0.433	
-30	0.451	0.417	0.355	0.373	0.373	0.393	0.391	0.325	0.444	
-20	0.463	0.441	0.388	0.415	0.409	0.415	0.408	0.336	0.459	
-10	0.472	0.459	0.458	0.467	0.455	0.447	0.429	0.349	0.471	
0	0.486	0.466	0.481	0.483	0.480	0.482	0.462	0.379	0.482	
10	0.489	0.477	0.484	0.490	0.489	0.490	0.484	0.496	0.495	
20	0.497	0.486	0.491	0.496	0.498	0.496	0.491	0.496	0.505	
30	0.507	0.494	0.495	0.500	0.507	0.504		0.502	0.516	

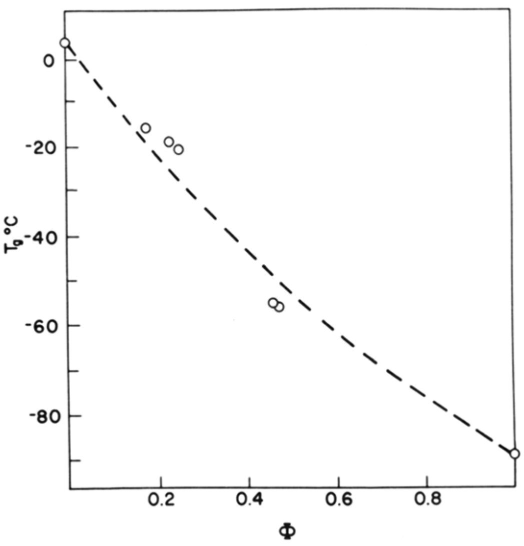

Figure 7. Glass transition temperature of the homogeneous diblock copolymers, defined as T at $\Delta C_p/2$, as compared with the Fox equation (dashed line).[26]

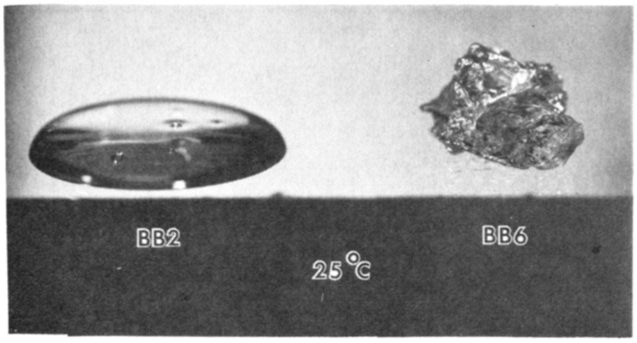

Figure 8. Comparison of the long-time flow characteristics of a rubbery diblock copolymer just below (BB2) and just above (BB6) the MST. This photograph was taken 24 h after the samples had been placed on a glass substrate, at which time they were nearly indistinguishable in form.

BB6 and BB7 underwent little flow and maintained a rough surface after several months. This rheological property is demonstrated for samples BB2 and BB6 in Figure 8 and is discussed below.

Discussion

According to Leibler,[3] the phase diagram of a block copolymer exhibiting UCST behavior can be described as shown in Figure 1. Above the MST, a mesophase structure exists. Most theoretical and experimental studies have focused on this region of the phase diagram. Below the MST, the system exhibits a disordered phase, characterized by segment density fluctuations. Both the amplitude of these fluctuations and the MST are predicted to scale with the product χN. We first discuss the MST.

The macroscopic properties of the seven diblock copolymers that have been examined fall into two general categories. BB6 and BB7 exhibit two distinct glass transitions by DSC and they do not flow like liquid homopolymers. These properties are consistent with microphase separation (see below). The remaining diblock copolymers display homopolymer-like viscous flow and a single glass transition. This behavior is consistent with a homogeneous liquid. On the basis of these observations, the critical degree of polymerization for this system lies between 1.06×10^3 and 1.33×10^3. According to Leibler's prediction, this places the following limits on the segment–segment interaction parameter for 1,2- and 1,4-polybutadiene:

$$8.9 \times 10^{-3} \leq \chi \leq 1.0 \times 10^{-2} \qquad (4)$$

These values are in reasonable agreement with the previous estimate[15] although considerably more precise. The data are plotted for $\chi = 9.5 \times 10^{-3}$ in Figure 1. Perdeuteration is not expected to significantly influence the phase behavior of these polymers. Boué et al.[16] demonstrated by SANS that blends of protio- and deuterio-polystyrene, $N_H = N_D = 6.3 \times 10^3$, were homogeneous over all Φ, which indicates $\chi < 3.2 \times 10^{-4}$. This is less than the experimental uncertainty in our estimate of χ.

An important but previously unreported observation concerning the MST is illustrated in Figure 8. Although this represents the simplest experiment we have conducted, it is clearly the most conclusive. Phase behavior in polymer blends is almost always determined by indirect, nonisothermal methods. Typically a sample is examined with a Rheovibron or, as in the present work, a DSC. Both methods require the sampe to be cooled below T_g. Near the spinodal curve, changes in temperature can produce a phase transition since χ is proportional to T^{-1}. This can be particular troublesome with the Rheovibron since the sample is cooled slowly (<1 °C/min[17]) relative to the expected spinodal decomposition times.[18] Furthermore, as presently demonstrated, the resulting spectra are difficult to interpret near the MST. Just below the phase transition, local fluctuations in composition produce a very broad glass transition, which can easily be misinterpreted as a combination of two individual glass transitions, particularly if the pure component T_g's are not well separated in temperature. Instead, samples BB2, BB6, and BB7 have been rheologically examined between 0 and 150 °C in a manner similar to that reported by Chung et al.[21] and Gouinlock and Porter.[22] These results, which are presented in detail in a separate report,[23] are summarized as follows. BB2 is rheologically similar to homopolybutadiene, while BB7 rheologically resembles microphase-separated block copolymer.[24] The behavior of BB6 resembles that of BB7 up to 108 ± 3 °C, at which point the elastic modulus and dynamic viscosity exhibit a dramatic discontinuous drop. Above 108 °C, BB6 rheologically behaves like BB2. Chung et al. and Gouinlock and Porter have reported a similar behavior in an SBS triblock copolymer, although in that case, the discontinuity occurred around 150 °C. This discontinuity in modulus upon raising the temperature results from the melting of a microdomain structure in a UCST system. While the complete description and presentation of these results are beyond the scope of this report, the impact they have on determining phase state can be very simply demonstrated as shown in Figure 8. The magnitude of the discontinuity in modulus is inversely proportional to frequency.[21,22] Flow under gravity, which represents the limiting low-frequency experiment, maximizes the effect. This simple, but important observation permits us to a unambiguously determine phase state, isothermally, and independent of the DSC measurements.

The overall DSC behavior of a polymer blend depends on the distribution of polymer segments within the sample. In block copolymers, this distribution continually changes in approaching and passing through the MST by changing either χ, N, or Φ. Differential scanning calorimetry is sensitive to such changes, as demonstrated in Figure 9, where we have held χ and Φ eassentially consant and varied N. These changes above and below the MST will be discussed separately with respect to current theories concerning block copolymer phase structure.

Helfand and Wasserman[25] have provided a detailed prediction of the domain structure of block copolymers lying above the MST. On the basis of their model, samples

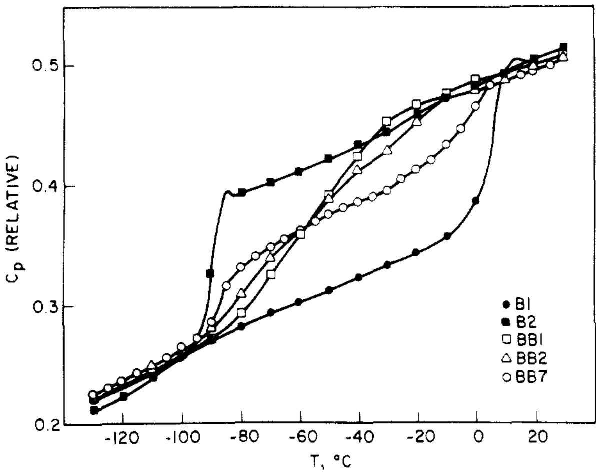

Figure 9. Changes in the DSC response of a diblock copolymer when passing through the MST at constant composition. In order to facilitate comparison of the shapes of these curves, the spectra have been shifted slightly vertically, relative to that of B2, so as to minimize the combined average deviation in C_p below−110 and above +10 °C.

BB6 and BB7 are predicted to contain a lamellar morphology with periodicities of 37 and 42 nm, respectively. The interfacial composition profile is given by

$$\rho_A(x) = \tfrac{1}{2}[1 - \tanh(2x/a_I)] \qquad (5)$$

$$a_I = (2/6^{1/2})b/\chi^{1/2}$$

where a_I is defined as the interfacial thickness, x is the distance from the center of the interface, and b is the Kuhn statistical segment length. The predicted magnitude of a_I has been independently verified.[8] Taking $b = 0.64$ nm and $\chi = 9.5 \times 10^{-3}$, a_I is calculated to be 5.4 nm. This large amount of interfacial mixing is reflected in the DSC traces of these samples. In each case the shape of the two glass transitions is skewed toward the center of the overall thermal transition, relative to the shape of the corresponding homopolymers. The estimated T_g values are also shifted in the same direction. These effects appear to be less dramatic in BB7 than in BB6 (Table II), which is expected, since BB7 lies further from the MST in phase space (Figure 1).

Below the MST, the diblock copolymers exhibit a single glass transition, which is compared with the prediction of the Fox equation[26] in Figure 7. Although the fit is not entirely satisfactory, the behavior of the block copolymers is consistent with that of a single-phase blend. Since assignment of T_g is somewhat arbitrary, a quantitative interpretation of this result is not warranted. The most striking aspect of these DSC traces is the breadth of the glass transition, ΔT_g. We contend that this reflects the structure present in the homogeneous melt as predicted by Leibler.[3]

The observed influence of N on ΔT_g is consistent with the predicted N dependence of the local segment density fluctuations; e.g., increasing N produces larger fluctuations about the average composition. Hence, samples BB1 and BB2 are characterized by almost identical T_g values but significantly different overall DSC traces. Sample BB1 clearly shows a single broad glass transition (Figure 9) spanning a 60 °C range. Doubling the molecular weight at constant composition (sample BB2) increases the breadth of the glass transition to an 80 °C range without modifying T_g. A similar behavior is observed with samples BB3, BB4, and BB5 (Figure 5 and Table II). SANS experiments on samples BB1 and BB3 have independently verified the existence of such composition fluctuations. These results are reported separately.[27]

We have demonstrated that the thermal characteristics of a *thermodynamically* homogeneous block copolymer can be considerably different from those of the homopolymer blend analogue. This finding is in conflict with a conclusion drawn by Gaur and Wunderlich[28] after studying a set of styrene–α-methylstyrene block copolymers by DSC. Our analysis indicates the difficulty of establishing phase state by differential scanning calorimetry alone, when operating near the microphase separation transition.

Conclusions

We have prepared a model set of 1,4-polybutadiene–1,2-polybutadiene diblock copolymers near the microphase separation transition (MST). The polymerization kinetics and critical degree of polymerization for this system have been identified. Location of the MST was established by differential scanning calorimetry (DSC) and simple observation of the block copolymer flow characteristics. Samples below the MST exhibited a molecular weight dependent DSC behavior which is consistent with the composition fluctuations which have been predicted for the homogeneous melt.

Future reports will address the issues of structure (by SANS) and rheology of block copolymers near the microphase separation transition.

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Registry No. Protio-1,2-polybutadiene (homopolymer), 9003-17-2; perdeuterio-1,4-polybutadiene (homopolymer), 29989-19-3; butadiene, 106-99-0.

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Effect of Autocatalytic Action of Perchloric Acid on Pseudocationic Polymerization of Styrene Initiated by the Acid

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ABSTRACT: Cationic polymerization of styrene initiated by perchloric acid shows some intriguing and unconventional features. These were attributed in the past to the formation of a hypothetical complex between perchlorate esters (the propagating species) and four molecules of styrene (the monomer). In this paper an alternative explanation is offered. An autocatalytic, perchloric acid induced decomposition of the esters is proposed and the appropriate mechanistic scheme is developed. The computer solution of the relevant differential equations shows all the interesting features claimed to be characteristic of this polymerization and provides a deeper insight into its behavior.

The kinetics of polymerization of styrene initiated in chlorinated hydrocarbons by anhydrous perchloric acid was described by Pepper and Reilly[1] and their results were confirmed by Gandini and Plesch.[2]

Both groups reported the following observations for a process proceeding at ~20 °C:

(1) Perchloric acid is consumed quantitatively and virtually instantaneously when added to a solution of styrene. In fact, its presence is undetectable during the main course of the ensuing polymerization.[3]

(2) The polymerization is first order in styrene up to ~90% conversion. The pseudo-first-order constant is proportional to the initial concentration of the added acid. The second-order rate constant is found to be ~10 M^{-1} s^{-1}. However, the consumption of styrene accelerates at ~90% conversion, and at that time the colorless and nonconducting solution suddenly discolorates and becomes conducting.

(3) After cessation of polymerization the reaction can be reinitiated by the addition of a second batch of styrene.

(4) Small amounts of water in the solvent have no influence on the course of polymerization even when its concentration exceeds the initial concentration of the acid by a factor of 3 or 4.

In his early papers[1] Pepper accounted for these observations by postulating an extremely rapid and quantitative proton transfer from the acid to the monomer, yielding carbenium ions or their ion pairs

$$HClO_4 + CH_2{=}CH(Ph) \rightarrow CH_3\overset{+}{C}H(Ph),ClO_4^-$$

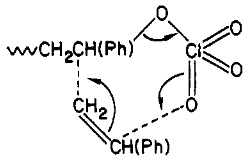
The subsequent cationic propagation was assumed to proceed without any termination, at least up to ~90% conversion, although it involves chain transfer as indicated by the low molecular weight of the product.

This mechanism was disputed by Plesch[2] since, as pointed out by him, the slowness of propagation, the inertness of the system to moisture, and the lack of conductance of the polymerizing solution are all incompatible with the supposedly ionic character of the reaction. Instead, he proposed initiation yielding a reactive perchlorate ester capable of propagating polymerization; i.e.

$$HClO_4 + CH_2{=}CH(Ph) \rightarrow CH_3CH(Ph)OClO_3$$

$$CH_3CH(Ph)OClO_3 + CH_2{=}CH(Ph) \rightarrow CH_3CH(Ph)CH_2CH(Ph)OClO_3, \text{ etc.}$$

To substantiate this mechanism, coined as a "pseudocationic polymerization", Plesch attempted a synthesis of styryl perchlorate by reacting $CH_3CH(Ph)Br$ with a solution of $AgClO_4$ in methylene chloride. However, the resulting product was unstable and decomposed. On the other hand, he reported that the same preparative method yielded an apparently stable ester when styrene was added to the solution of $AgClO_4$. The formed ester was claimed to induce polymerization of the added styrene, leading to a reaction similar in its behavior to the polymerization initiated by perchloric acid. This finding supports the pseudocationic mechanism involving the transition state of propagation:



Still two questions remained unanswered: Why is the ester unstable in the absence of styrene, and why do the polymeric esters decompose when the conversion is sufficiently high, e.g., at ~90% for $[\text{styrene}]_0$ ~0.3 M? To rationalize these phenomena, a complexation of the ester with styrene was postulated, i.e.

$$CH_3CH(Ph)OClO_3 + n(CH_2{=}CHPh) \rightleftarrows CH_3CH(Ph)OClO_3,(CH_2{=}CHPh)_n$$

presumably stabilizing the ester.

On the basis of some experimental data,[4] Plesch deduced a value of 4 for the stoichiometric coefficient *n*. Indeed, a large value of *n* is imperative if one wishes to explain the abrupt change in the behavior of polymerization as the concentration of styrene reaches some critical value. Above it the complexation equilibrium lies far to the right but, for large *n*, it shifts abruptly to the left as the styrene concentration falls below some critical value, causing then decomposition of the ester.

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