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Miscibility in Chlorinated Polybutadiene/Chlorinated Polyethylene Blends: Effect of Chain Microstructure

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ABSTRACT: Blends of fully chlorinated polybutadiene (CPB) and partially chlorinated polyethylenes (CPE) were studied. It was found that CPB forms miscible mixtures with CPEs having chlorine contents between 48 and 56% by weight. The blends display upper critical solution temperatures above 150 °C, depending on the chlorine content of the CPE, with reversible phase behavior. This phase behavior is in contrast to that observed in CPE/poly(vinyl chloride) (PVC) blends which are immiscible in the accessible equilibrium temperature range 110-180 °C. The difference in the behavior of these two systems is attributed to the different sequence distributions of comonomer units in CPB and PVC.

Introduction

Flory[1] and Huggins[2] developed a theory for miscibility in homopolymer blends by considering the chemical structures and molecular weights of the blend constituents, the compositions of the blends, and temperature. With the development of the expression for the free energy of mixing, Flory[1] provided the foundation for the thermodynamic theory of polymer mixtures. This expression quantifies the effects of combinatorial entropy and free energy associated with mean field interactions. A reduced free energy interaction parameter, χ_{blend}, is included in the expression which embodies not only the enthalpic contribution of the mixing of the polymeric entities but also noncombinatorial entropy effects. Subsequent developments have refined the theory with equation of state approaches[3,4] and by considering liquid lattice models.[5] These theories considered only mixtures of homopolymers.

The theory of miscibility in copolymer blends was initially developed by Scott[6] with more recent mean field developments by ten Brinke et al.,[7] Kambour et al.,[8] and Paul and Barlow.[9] Following ref 7 the constituents of a blend of random copolymers are represented in the form $[A_xB_{(1-x)}]_m$ and $[C_yD_{(1-y)}]_n$ and the net free energy interaction parameter for such a system is generalized as

$$\chi_{\text{blend}} = xy\chi_{AC} + x(1-y)\chi_{AD} + y(1-x)\chi_{BC} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (1)$$

where x is the mole fraction of repeat unit A in the first copolymer, y is the mole fraction of repeat unit C in the second copolymer, and χ_{ij} is the interaction parameter of repeat units i and j. In this mean field approximation for the interaction parameter, intramolecular interactions are taken into account as well as intermolecular interactions. A fundamental conclusion of this development is that strong repulsive interaction between comonomeric units in a chain favors miscibility of the two components.

In the special case of blends of two copolymers containing the same monomers and differing only in composition (i.e. A ≡ C, B ≡ D in eq 1; the "AB/AB system") the expression for the interaction parameter reduces to

$$\chi_{\text{blend}} = (x-y)^2\chi_{AB} \quad (2)$$

Thus in this approximation the blend interaction parameter depends on the composition differences of the two components and the compositional width of the miscibility window $|x-y|$ is then a function only of the single interaction parameter χ_{AB} and the degrees of polymerization of the respective components.[7]

Balazs et al.[10] have extended the theory of miscibility in copolymer blends to account for sequence distribution of the comonomers which is considered to play an important role in determining the relative strengths of inter- and intramolecular interactions. Each type of triad interaction which occurs in a copolymer system is assigned an interaction parameter and the overall interaction is determined by both the composition and sequence distributions of the constituent copolymers.

This theory has been applied to the analysis of phase behavior in AB/AB copolymer blends,[11] in which, again, the two components of the blend are composed of identical comonomeric units but may differ with regard to both overall composition and comonomer sequence distribution. In the general case, 16 triad interactions are possible. However, when degeneracies are considered, only nine interaction parameters need to be defined.

As an example of an AB/AB system, blends of chlorinated polyethylenes (CPE) were studied.[11] From the experimentally determined miscibility windows two unique triad interaction parameters were determined with an averaging of the remaining interactions. This permitted calculation of the overall interaction parameter. Close agreement was observed between experiment and calculated results. In addition, the parameters determined from CPE/CPE blends were used in the analysis of phase behavior in poly(vinyl chloride) (PVC)/CPE blends as a function of chlorine content of the latter component.[12] In this case PVC was treated as an alternating copolymer of CH_2 and CHCl units while CPE was regarded as a random copolymer of the same units. The theory correctly predicted immiscibility of these two components over a wide range of microstructures. The results conclusively demonstrate the importance of sequence distribution in copolymer blends.

The present study continues the investigation of copolymer blends and the effect of chain microstructure in two further AB/AB blend systems. The particular systems of interest are blends of chlorinated polybutadiene (CPB) ("head-to-head PVC") and chlorinated polyethylene (CPE) and of CPB with PVC. The composition of the constituents of these blends is represented as $[A_xB_{(1-x)}]_m/[C_yD_{(1-y)}]_n$ where A ≡ C ≡ CH_2 and B ≡ D ≡ CHCl. The polymers, while chemically similar, differ markedly in chain microstructure. Specifically, CPB can be considered to be an $(\text{-AA-BB-AA-BB-})_n$ alternating copolymer if the pendant group content arising from 1,2 addition in the parent polybutadiene can be neglected, while CPE is a

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Table I
Characterization of Blend Components

material	$10^{-4}\bar{M}_n$[a]	$10^{-4}\bar{M}_w$[a]	Cl (wt %)[f]	T_g (°C)[c]	n_{calcd}[g]
CPB	31.1	67.3	56.3[b]	70	
CPE 47.2[d]	...	...	47.2	<30	
CPE 48.0	3.98	17.3	48.0	~30	1.4×10^3
CPE 54.9	2.27	12.1	54.9	43	7.0×10^2
CPE 56.9	2.28	13.5	56.9	59	6.7×10^2
CPE 57.6	2.66	10.8	57.6	56	7.8×10^2
CPE 61.3	3.80	17.2	61.3	87	1.0×10^3
PVC	8.72	17.8	56.8[b]	87	
CPEF 42.2[e]	2.84	5.73	42.2	−3	1.1×10^3
CPEF 46.2	3.22	6.55	46.2	9	1.2×10^3
CPEF 47.9	3.20	6.58	47.9	17	1.1×10^3
CPEF 48.8	3.11	6.62	48.8	21	1.1×10^3
CPEF 50.7	2.99	6.35	50.7	26	1.0×10^3
CPEF 52.6	3.42	6.90	52.6	39	1.1×10^3
CPEF 56.1	3.42	6.21	56.1	52	1.0×10^3
CPEF 56.7	3.60	6.90	56.7	58	1.1×10^3
CPEF 62.0	4.11	7.77	62.0	85	1.1×10^3
CPEF 63.6	4.12	7.87	63.6	100	1.0×10^3

[a] Measured relative to polystyrene standards. [b] Theoretical chlorine content 56.8 wt %. [c] Measured as maximum in derivative curve. [d] Unfractionated polyethylene (CPE series). [e] Fractionated polyethylenes (CPEF series). [f] Chlorine contents have estimated accuracies of ±0.3%. [g] See text.

random copolymer of A and B units. PVC is simply an alternating AB copolymer. In the case of CPE we restrict ourselves to the range of chlorination in which the concentration of CCl_2 units is negligible.

Experimental Procedures

The chlorinated polyethylenes were synthesized by the controlled chlorination of fractionated and unfractionated samples of linear high density polyethylene. The fractionated polyethylene (Pressure Chemical Co.) had a relatively narrow molecular weight distribution ($M_n = 9.4 \times 10^3$, $M_w = 2.4 \times 10^4$). The unfractionated polyethylene was obtained from Chemplex ($M_n = 1.5 \times 10^4$, $M_w = 7.5 \times 10^5$). Chlorinated polyethylenes containing less than 56.5% Cl by weight were prepared according to the method of Walsh et al.[13] Polyethylene was dissolved in chlorobenzene (5% w/v) at 140 °C. Chlorine gas was bubbled through the solution, and the reaction was photoinitiated by using a tungsten lamp. The degree of chlorination was controlled by varying the reaction time. Polyethylenes chlorinated to a greater degree than 56.5 wt % were prepared according to the method of Saito et al.[14] In this technique polyethylene was dissolved in tetrachloroethane (1.0% w/v) at 110 °C. As with the previous reaction this one was photoinitiated with a tungsten lamp and again the degree of chlorination was controlled by varying the reaction time. In both cases the resulting chlorinated polyethylenes were precipitated into a tenfold excess of methanol and dried at reduced pressure and 60 °C for 1 week.

Fully chlorinated, 1,4-polybutadiene (see Table I) and the poly(vinyl chloride) were obtained from B. F. Goodrich Co. Both were purified by precipitation from THF solution into methanol followed by several methanol washes and dried at 50 °C under dynamic vacuum. The microstructure of the chlorinated polybutadiene sample was characterized by using ^{13}C NMR spectroscopy. Strong resonances attributable to $-CH_2-$ and $-CHCl-$ carbons in the polymer backbone were observed at 34 and 66 ppm, respectively (referenced to THF resonances at 25.5 and 67.0 ppm). Weak signals attributable to carbon nuclei of the pendant group arising upon 1,2 addition were observable at 70.0, 63.5, and 62.5 ppm. The ratio of integrated intensities indicated approximately 6% of 1,2 addition was present. Resonances assignable to sp^2 carbons were at or below the noise level.

The chemical composition of the blend components was determined by elemental analysis (Microanalysis Laboratory at the University of Massachusetts). Molecular weights were characterized in tetrahydrofuran solution by gel permeation chromatography. The results of these studies are listed in Table I. The average degrees of polymerization, n_{calcd}, have been calculated for the chlorinated polyethylenes from the measured chlorine content and number average molecular weight. The degrees of polymerization of the parent unfractionated and fractionated polyethylenes are 670 and 1100, respectively. The agreement between the degrees of polymerization of the unchlorinated polyethylenes and those calculated following chlorination is good, particularly in the case of the fractionated series, indicating that the degree of polymerization was not significantly affected by chlorination.

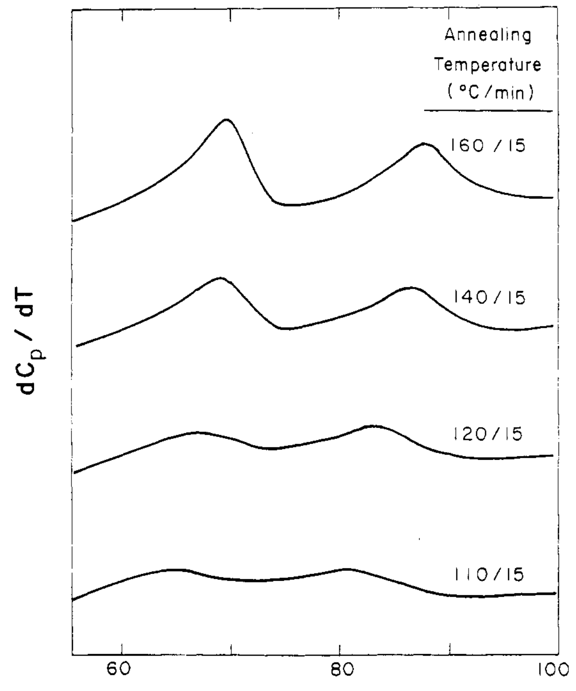

Figure 1. Derivative curves of DSC scans of a 50/50 wt % CPB/PVC blend. The annealing temperatures and times are indicated.

Blends were prepared by precipitation from a common solvent. Unless otherwise noted all blends contained 50% by weight of each component. The components were dissolved at room temperature in spectral grade THF (Fisher Scientific) and stirred for several hours. The polymer blend was then precipitated into a tenfold excess of reagent grade methanol (Fisher Scientific). After settling of the precipitate most of the clear solvent was decanted. The blend was washed with fresh methanol three times to ensure complete removal of THF and dried under reduced pressure at room temperature for several days.

Miscibility of the blends was determined by calorimetric observation of the glass transition. A Perkin-Elmer DSC-4 differential scanning calorimeter was employed for these measurements. Typically, the samples were annealed to obtain equilibrium at selected temperatures above the T_g of both components for 5–15 minutes in the DSC under N_2 flow and then quenched to a temperature below the lowest T_g. The glass transition temperature(s) of the blend was (were) measured by temperature scanning at a rate of 10 °C/min unless otherwise noted.

Results and Discussion

Miscibility is observed calorimetrically as a merging of the glass transition temperatures of the two blend constituents. In the case of a miscible blend a single glass transition is observed at a temperature intermediate between the T_g's of the pure components. Conversely, immiscibility is indicated by the simultaneous observation of the glass transitions of the two separate components.

First, we consider the results for the chlorinated polybutadiene/poly(vinyl chloride) blend, shown in Figure 1. The calorimetric behavior was observed after the same sample was subjected to various thermal histories. In Figure 1 the derivative of the DSC trace is plotted, a representation which has been found to reveal subtle changes in glass transition behavior.[15] In the temperature

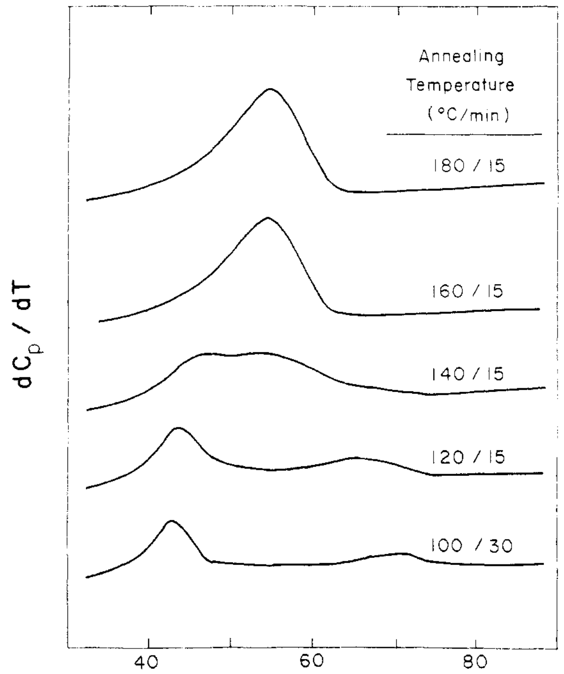

Figure 2. Derivative curves of DSC scans of a 50/50 wt % CPB/CPE 54.9 blend; see text. The annealing temperatures and times are indicated.

range examined two distinct glass transitions corresponding to those of the pure components were always seen; thus this blend is immiscible in the experimentally attainable range in which equilibrium can be obtained, i.e. between 110 and 160 °C. This result in itself is noteworthy since the components of this blend have identical chemical compositions and differ only in chain microstructure. We note, however, that similar behavior was previously seen in a blend of poly(vinyl chloride) with a chlorinated polyethylene of identical chlorine content (i.e. 56.8 wt %);[12] these polymers are also identical in chemical composition but are immiscible, for example, at 170 °C. [To observe equilibrium thermodynamic events the annealing temperature must be higher than the T_g's of both components (see Table I). On the other hand, the annealing temperature must be lower than the decomposition temperatures of the blend components (i.e. ~200 °C).]

The phase behavior of CPB/CPE blends as a function of the chlorine content of the latter constituent was then examined, again over the entire equilibrium temperature range. The results, for example, for the blend CPB/CPE 54.9 (see Table I for sample codes) stand in contrast to those of the CPB/PVC blend and are shown in Figure 2. After annealing at 100 °C for 30 min this blend displayed two glass transitions corresponding to those of the pure components. As the annealing temperature was increased the individual glass transitions became less distinct and after annealing at 160 °C for 15 minutes the system showed a single sharp glass transition at 54 °C. Subsequent annealing at 180 °C did not change the character of the single transition observed.

The particular chlorinated polyethylene (54.9% Cl by weight) used in this blend is again nearly identical in overall segmental composition to PVC (i.e containing 56.8 wt % Cl). The microstructure, of course, differs. The random chemical structure of the CPE results from the nature of the chlorination substitution reaction. NMR spectroscopic studies of solution chlorinated polyethylene[16] have shown that hindered-type substitution occurs at chlorine contents less than 60%. Therefore this and the other chlorinated polyethylenes used in this study are expected to consist preponderantly of randomly distributed CH_2 and CHCl units; for the CPEs used the small fraction of CCl_2 units can be neglected.

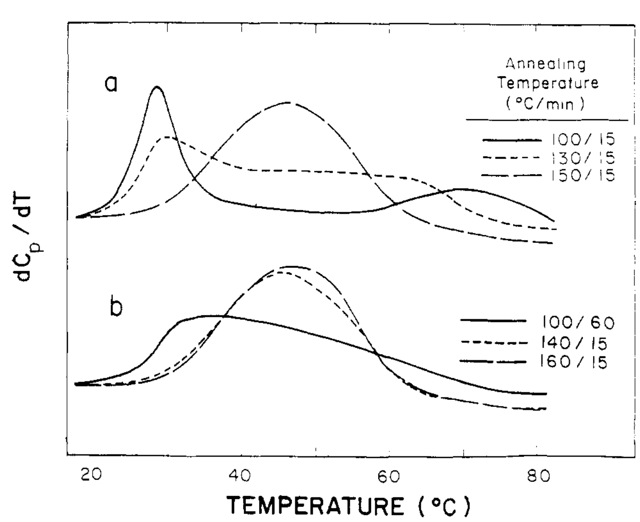

Figure 3. Derivative curves of DSC scans of the 50/50 wt % CPB/CPEF 47.9 blend showing reversibility of phase behavior. The annealing temperatures and times are as indicated. The heating rate was 20 °C/min: (a) homogenization of CPB and CPE phases; (b) same sample as in (a) demonstrating reversibility and rehomogenization.

To confirm that the observed merging of the glass transitions of the blended constituents corresponds to the miscibilization of the initially separated phases in these systems, two additional experiments were performed. First, the reversibility of the transition was tested by a cyclic annealing protocol. A typical result is shown in Figure 3. In Figure 3a the homogenization of separated phases in the blend CPB/CPEF 47.9 is observed. Thus after first annealing at 100 °C two separate transitions can be seen. These transitions were broadened and shifted to intermediate temperatures after further annealing at 130 °C. At 150 °C miscibility was observed; the blend showed a single glass transition. Figure 3b shows the reversibility of the phase behavior and rehomogenization in the same sample. Phase separation occurred after reannealing at a temperature of 100 °C for 1 h. When this sample was further annealed at elevated temperatures, homogenization proceeded rapidly. In the second type of experiment, a composite sample using the blend constituents CPB and CPE 54.9 was prepared in which the components were separated by an impermeable barrier. The glass transitions of this composite sample were then measured after several annealing regimes. Figure 4 shows the results of this experiment. Two separate glass transitions were observed for the sample before annealing. After annealing at 160 °C the sample showed sharp transitions at the temperatures of the pure component T_g's. If thermal degradation were occurring at these relatively low temperatures, then a change in glass transition behavior would be expected. Thus these results indicate that the merging of the glass transitions as shown in Figure 2 cannot be attributed to the thermal decomposition of the blend components or to a general broadening of the transitions upon annealing.

A further similarity exists between the CPB/CPE system studied here and blends of chlorinated polyethylenes[15] in that UCST phase behavior is observed. As noted with CPE blends[12] the free volume contribution to the interaction parameter may be expected to be particularly small in blends of structurally similar components, and the UCST behavior seen in CPB/CPE blends can be qualitatively rationalized on this basis.

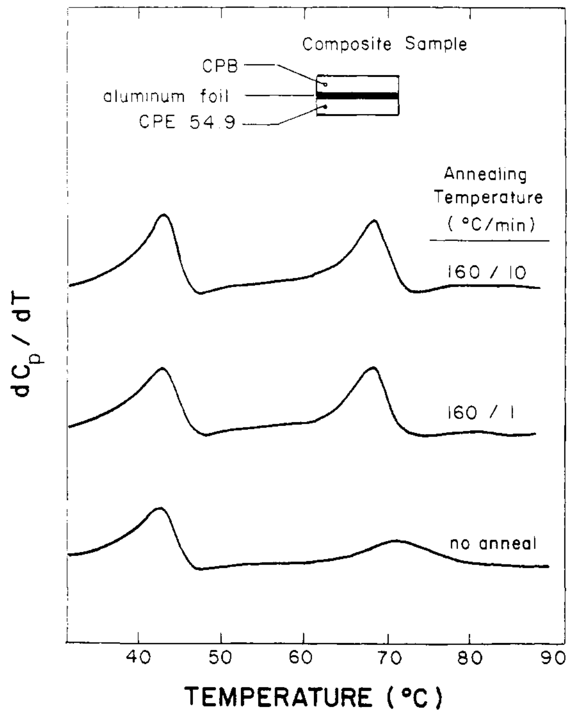

Figure 4. Derivative DSC scans of the composite CPB/CPE 54.9 blend. The blend constituents were separated by an impermeable barrier.

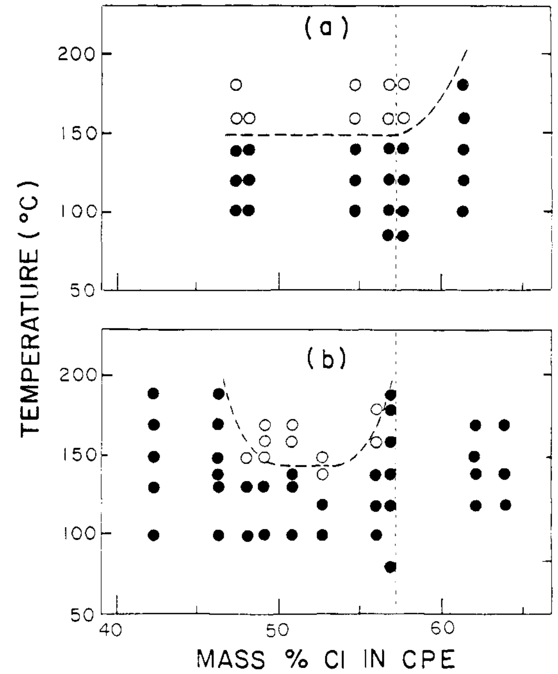

Figure 5. Miscibility windows for 50/50 wt % CPB/CPE blends containing (a) unfractionated CPE and (b) fractionated CPE. Miscibility, ○, or immiscibility, ●, is indicated after equilibrium annealing at the respective temperature. The composition of CPB is indicated by the vertical dotted lines.

The "miscibility windows" for blends of CPB with fractionated and unfractionated CPEs are shown in Figure 5. The results are almost the same for both constituents. A miscible regime is found at temperatures greater than 140 °C for CPEs containing 48% $\leq$ Cl $\leq$ 56% by weight. The phase behavior of this blend system thus showed little sensitivity to molecular weight distribution as is shown by the similar miscibility windows observed for fractionated and unfractionated CPEs.

At temperatures less than 140 °C all the blends examined were immiscible. This is particularly noteworthy for blends of CPE containing $\sim$56.8 wt % Cl, i.e. of the overall chlorine content as the CPB homopolymer. Equation 2 gives the nominal overall interaction parameter for an AB/AB blend when only compositional differences are considered. At this approximation blends of components having identical compositions would have no enthalpic contribution to the free energy of mixing and would be miscible solely on the basis of their entropy of mixing. However, as experimentally demonstrated in this study, factors in addition to chemical composition are involved. If the compositional difference alone dictated miscibility, then the CPB/CPE blends containing CPE of $\sim$56.8 wt % Cl would of course be miscible at all temperatures; in fact blends of CPB with both fractionated and unfractionated CPE's are immiscible below 140 °C.

When both components in an AB/AB blend are random copolymers, as in the case of the CPE/CPE system, miscibility is certainly observed for blends of nearly identical chlorine content.[12] In this case the blend components are identical or nearly so, not only in composition but also in the average sequence distribution of CH_2 and CHCl units. With CPB/CPE blends however the components differ with regard to sequence distribution. In light of the experimental results presented here, it is confirmed again that sequence distribution plays an important role in determining miscibility.

Another difference between the CPB/CPE and CPE/CPE systems is the symmetry of the miscibility windows. The treatment of the CPE/CPE system described by eq 2 predicts that the miscibility window should be symmetric with regard to copolymer composition. In fact the miscibility window of the CPB/CPE system (Figure 5) is shifted toward lower chlorine contents with respect to the reference line representing 50 mol % of A and B units.

A quantitative analysis of the CPB/CPE phase behavior was attempted by using the theory of Balazs et al.[10,11] In order to determine the segmental interaction parameters required to describe the system the full expansion of the Balazs formulation was used. As already stated, in this formulation there exist nine independent triad interaction parameters of the form $\chi_{hij;klm}$ where the subscripts represent A or B repeat units. The nine interaction parameters were sought by using statistical analysis of the data shown in ref 12 for the CPE/CPE blend system at 150 °C. However, while the data in this reference are extensive, the statistical analysis requires a more precise determination of the miscibility boundary to extract meaningful values of the nine parameters. As a result the parameters could not be obtained and the phase behavior of the CPE/CPB system could not be analyzed in these terms. An analysis should also, in principle, take into account the small 1,2 content of the CPB, but this would require a further set of intra- and intermolecular interaction parameters. It should be noted, therefore, the results presented apply to CPB with the given 1,2 content. It may be anticipated that the results would be sensitive to this parameter.

While a full theoretical description of phase behavior in CPB/CPE blends has not been achieved, some understanding can be gained from the values of the triad interaction parameters of CPE/CPE blends determined from the Balazs study.[11] These parameters show that the interactions of alternating CH_2 and CHCl segments are energetically favored over those of blocky or random segments. In light of this result it is reasonable to expect preferential interaction of PVC segments with themselves over those with the random or "blocky" segments of CPE and CPB. From this viewpoint immiscibility of CPB/PVC blends and of blends of PVC and CPE of identical chlorine content is less surprising. On the other hand, the statistical distribution of comonomer segments in CPE must lead to sufficient microstructural similarity to CPB such that some miscibility occurs. This is reasonable in CPEs of moderate to high chlorine contents where the number of -AA- and -BB- sequences is significant. The phase behavior of the blends examined apparently depends not on the overall mean field interactions but upon those associated with local comonomer sequence distributions.

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Distribution of Chain Ends inside the Polybutadiene Microspheres of SB Diblock Copolymers

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ABSTRACT: Two polystyrene-polybutadiene block copolymers were examined in small-angle neutron scattering (SANS) experiments designed to probe the location of the polybutadiene chain ends inside the polybutadiene microspheres of these specimens. One of the copolymers, SBm, was phase-matched; the B moiety was synthesized by using a suitable mixture of deuterio and normal butadiene monomer. The other copolymer, SBmBd, contained short perdeuteriated polybutadiene sequences at the end of the polybutadiene block of each of the molecules. Consideration of scattering intensities and the form of the scattering pattern exhibited by SBmBd indicated that the Bd chain ends are essentially uniformly distributed throughout the volume of the spheres. A model in which the Bd ends cluster at the core of the spheres failed to reproduce the essential features of the observed SANS pattern.

Introduction

Diblock copolymers of polystyrene (S) and polybutadiene (B) which display a bulk morphology of B spheres in S matrix have been examined at various levels of structural detail in our laboratory. Among the important features characterized in our previous work using small-angle neutron scattering (SANS) experiments were the BCC packing of the microspheres,[1] the relationship of sphere size to B molecular weight,[2,3] the nature of the interfacial zones between the B spheres and the S matrix,[2] and the effective radius of gyration of the B chain segments of the diblock copolymer.[4,5] Recently we reported on the distribution of S homopolymer added to the S matrix of the diblock.[6]

In this paper we address the following question: Where are the ends of the B chain segments located inside the microspheres? Two possible answers to this question are (a) the ends are essentially uniformly distributed throughout the B spheres and (b) the polybutadiene chain ends are preferentially clustered toward the center of each sphere. Figure 1 demonstrates that it should be relatively easy to discriminate between these two first-order hypotheses if an appropriate pair of diblock copolymers were available for SANS experiments. The necessary pair of copolymers is a phase-matched[7] diblock copolymer, SBm, and a triblock copolymer, SBmBd, in which the first two blocks S and Bm are identical with the phase-matched diblock, and the third, very short end block, Bd, is a perdeuteriated moiety. In the phase-matched diblock the polybutadiene block, Bm, is a random copolymer consisting of an isotopic mixture of protio- and perdeuteriobutadiene repeat units, the ratio of which is carefully selected[7,8] to exactly match the neutron scattering length density of polystyrene. This ideal diblock produces no structural scattering in a SANS experiment as suggested by Figure 1a. However, the triblock containing the short perdeuteriated end blocks will yield substantial amounts of structual scattering because the phase matching is no longer preserved. The detailed nature of the SANS scattering pattern observed for SBmBd will depend dramatically upon the spatial distribution of the Bd chain ends inside the microspheres; thus SANS experiments can be used to determine whether either part b or part c of Figure 1 is a reasonable representation of the chain end distribution in the SBmBd copolymer.

In what follows we describe the synthesis and molecular characterization of copolymers SBm and SBmBd and the examination of these copolymers using SANS experiments and transmission electron microscopy (TEM). Results of

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