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Miscibility in Blends of Branched Polymers

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ABSTRACT: The effect of branching on miscibility has been studied in model systems of chlorinated branched polyethylenes. The branched polymer molecule was represented as a copolymeric chain composed of end, linear interior, and branch-point segmental units, each of which could be either chlorinated or unchlorinated. An expression was derived for the overall interaction parameter for blends of the branched chlorinated polyethylenes based on counting intra- and interchain pair interactions between segmental units. Theoretically, when branching is unfavorable for mixing, the miscibility regime in a branched polymer/branched polymer blend (as represented in an isothermal copolymer–copolymer composition plot) is smaller than that of the corresponding linear polymer/linear polymer blend. When branched polymers are mixed with linear polymers, the symmetry of the miscibility regime in such a plot found with branched/branched or linear/linear blends disappears. The theoretical development was used in an analysis of the phase behavior of 50/50 wt % blends of amorphous CPE(B)/CPE(B), CPE(L)/CPE(SB), etc., where CPE(L), CPE(SB), and CPE(B) represent chlorinated linear, short-chain branched, and long-chain branched polyethylene, respectively. Miscibility of these blends was studied by using standard differential scanning calorimetry. The results support the theory qualitatively and show that the CPE(L) and CPE(SB) present similar miscibility behaviors because the short-chain branches only slightly disfavor mixing. However, CPE(B) generally has more limited miscibility; the long-chain branches have a rather profound effect on mixing.

Introduction

Miscibility in polymer blends can be strongly dependent on the chain microstructure. Composition and sequence distributions in a copolymer, stereoconfiguration (configurational sequences), branching, and cross-linking are all structural features affecting local environments, whereas the size (i.e., molecular weight) and shape of molecules (chain flexibility) have long-range effects. The effect of some of these parameters is already understood, at least in part. The effect of molecular size on miscibility is clearly described (for example) by Nishi and Kwei:[1] with increasing molecular weight, miscibility decreases. The combinatory entropy term in the Flory–Huggins theory accounts for this effect. The theory of random copolymer blends has provided a generalized explanation for the effect of chemical composition on miscibility;[2-4] phase behavior in these blends can be simply accounted for by the pair interactions among all the segments in the blends. The effects of chemical and configurational sequences have been addressed in several contributions, which base their treatments on an accounting of the interactions among triad sequences in polymers,[5-8] and in the probabilities of finding given triads in the blends. An understanding of the sequence distribution effect is now emerging. On the other hand, we have relatively little quantitative knowledge of the effects of branching or of chain flexibility on miscibility, although several relevant papers have recently appeared.[9-12]

In this paper we present the results of experimental studies of the miscibility of blends of chlorinated branched polyethylenes (CPE). We chose this group of compounds because of the existing data base for the miscibility of linear amorphous CPE(L)/CPE(L) blends.[6,8,13] Because solution chlorination of polyethylene is known to be a random substitution reaction of chlorine on the chain,[14] CPE(L) can be visualized as a random copolymer of CHCl and CH_2 segmental units. In principle, the structures of both linear low-density (short-chain branched, SB) and low-density (long-chain branched, B) polyethylene are also well-known.[15] If we assume that chlorine also distributes uniformly in the chain of a branched molecule, then CPE(SB) and CPE(B) can also be treated as random copolymers with the theoretical simplifications and reduction of independent parameters inherent in this assumption. Thus we can extend our work on amorphous CPE(L)/CPE(L) blends to blends of CPE(B)/CPE(B), CPE(L)/CPE(SB), and other binary permutations and thereby derive a general understanding of the effect of branching on miscibility.

Theoretical Section

Chlorinated branched polyethylene molecules are considered in terms of six segmental units: CH_3 (end), CH_2 (linear interior), CH (branch point), CH_2Cl (chlorinated end), CHCl (chlorinated interior), and CCl (chlorinated branch point). Table 1 shows these structures and the notation used in this paper to describe the generalized chain molecule. We have made two simplifying assumptions: (1) Each branch point generates one branch chain; thus, with a fraction δ of branch points, there is a fraction δ of end units and a fraction $(1 - 2\delta)$ of linear interior units. (2) The probabilities of chlorination of each of the three units are the same and are expressed by the molar fraction X, so the total fractional content of unchlorinated units is equal to $1 - X$. The treatment below can be modified, albeit at the expense of adding additional parameters, to remove (or partially remove) this assumption.

Counting the pair interactions among these segmental units yields the overall interaction parameter for the blend. As before, we have not directly considered the entropy change due to branching in the system, because this change is assumed to be negligible relative to the energy change due to branching. The same approach was used in a quantitative treatment of the phase behavior of solutions of branched polymer.[16] Further,

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Table 1. Segmental Units in Branched Chlorinated Polyethylenes

unit	molar fraction present[a]	*i*	*j*
CH_2Cl	δX	1	
CHCl	$(1-2\delta)X$	2	
CCl	δX	3	
CH_3	$\delta(1-X)$		4
CH_2	$(1-2\delta)(1-X)$		5
CH	$\delta(1-X)$		6

[a] δ is the molar fraction of branch points. X is the overall molar fraction of chlorinated segmental units.

our heat of mixing measurements also indicated that miscibility of CPE(L)/CPE(L) blends was enthalpy driven.[17]

Branched Polymer/Branched Polymer Blends. In chlorinated branched polymer/branched polymer (B/B) blends, there are, in principle, six types of segmental units, and there are thus 15 different pair interactions among the six units. We can at the onset reasonably assume that χ_{12}, χ_{13}, χ_{23}, χ_{45}, χ_{46}, and χ_{56}, where the interaction parameter subscripts are defined in Table 1, are very small in comparison to interactions between chlorinated (types 1–3) and unchlorinated (types 4–6; Table 1) moieties. It is understood that these interactions must nevertheless be finite to account for the immiscibility of the respective saturated polymers. By comparison, the remaining nine χ_{ij}'s are substantially larger and may well differ quantitatively from each other by amounts which are large compared with the absolute values of χ_{12}, χ_{23}, etc. Hence, to carry the following analysis further, we have set the six intragroup binary interactions at zero and allowed the remaining nine χ_{il}'s to assume finite and differing values. The overall interaction parameter for the blend can be written as

$$\chi_{\text{blend}}\phi_A\phi_C = \sum_{i,j}\chi_{ij}\phi_i\phi_j - \phi_A\sum_{i,j}\chi_{ij}\alpha_i\alpha_j = \phi_C\sum_{i,j}\chi_{ij}\gamma_i\gamma_j \quad (1)$$

where $i = 1, 2$, and 3 and $j = 4, 5$, and 6. The variables ϕ_A and ϕ_C are the volume fractions of the two copolymers A and C in the mixture. The variables ϕ_k, α_k, and γ_k ($k = 1-6$) are the volume fraction of unit k in the mixture, in polymer A, and in polymer C, respectively. We further assume that the volume fractions are the same as the molar fractions of the related units in the molecules. Thus α_k and γ_k are as indicated in Table 1, except that X (molar fraction of chlorinated units in polymer A) is replaced by Y (molar fraction of chlorinated units in polymer C) for γ_k. By mass conservation

$$\phi_k = \phi_A\alpha_k + \phi_C\gamma_k$$

Equation 1 can be rewritten as

$$\chi_{\text{blend}} = (X-Y)^2[\delta^2(\chi_{14}+\chi_{16}+\chi_{34}+\chi_{36}-4\chi_{25}) + \delta(1-2\delta)(\chi_{15}+\chi_{35}+\chi_{24}+\chi_{26}-4\chi_{25}) + \chi_{25}]$$

Since δ (the fraction of branch points; see above) is a small number, we can safely neglect the δ^2 terms. This assumption enables us to obtain a manageable expression for the blend interaction parameter:

$$\chi_{\text{blend}} = (X-Y)^2(\chi_{25} + \delta\Delta_1) \quad (2)$$

with

$$\Delta_1 = \chi_{15} + \chi_{35} + \chi_{24} + \chi_{26} - 4\chi_{25}$$

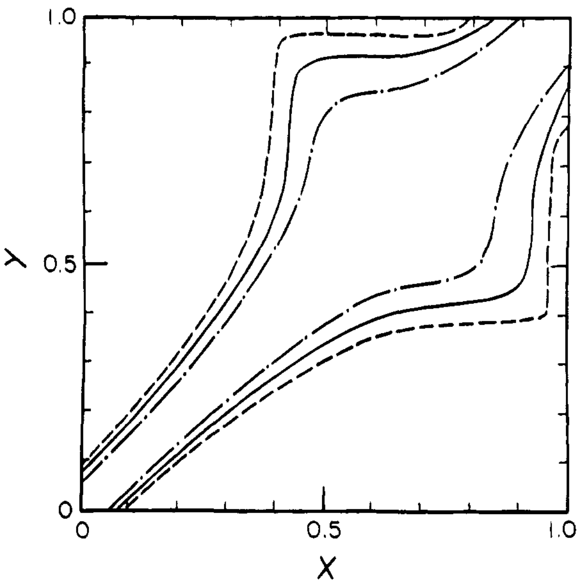

Figure 1. Miscibility boundaries of the branched/branched copolymer blends compared with that of the linear/linear copolymer blends (—); blends in which branching inhibits mixing (— • —); blends in which branching promotes mixing (- - -). X and Y are the respective mole fractions of chlorinated units in the linear and branched copolymers.

The variable Δ_1 indicates the energy change when four χ_{25} segment interactions are replaced by χ_{15}, χ_{35}, χ_{24}, and χ_{26} segment interactions. Segments 1, 3, 4, and 6 are the end units and branch points, and segments 2 and 5 are the linear interior segments; see Table 1.

Equation 2 shows that branching modifies the interaction parameter of linear polymer blends, because it introduces two new types of segments: the branch point and the end unit. If the term $\Delta_1 > 0$, then branching increases the overall interaction energy in the system, χ_{blend} is larger than the comparable term for linear blends, and miscibility decreases.

This can be seen by the location of the miscibility boundary, which, for convenience, is shown on a copolymer composition–composition plot for these blends and is defined by $\chi_{\text{blend}} = \chi_{\text{crit}}$. Blends for which $\chi_{\text{blend}} < \chi_{\text{crit}}$ lie in the one-phase region, and blends for which $\chi_{\text{blend}} > \chi_{\text{crit}}$ lie in the two-phase region. The critical value of the blend interaction parameter is derived from the usual combinatory entropy expression for the mixture:

$$\chi_{\text{crit}} = 0.5(r_A^{-0.5} + r_C^{-0.5})^2 \quad (3)$$

where r_A and r_C are degrees of polymerization for polymers A and C, respectively.

Figure 1 is a schematic representation of the situation. To generate Figure 1, we rewrite the blend overall interaction parameter as

$$\chi_{\text{blend}} = \chi_{\text{seq}} + (X-Y)^2\delta\Delta_1 \quad (4)$$

We must also take into account sequence distribution effects, which were discussed in a previous paper[8] (and which account for the observed "bulges" in the miscibility/immiscibility boundaries). In doing this, we have provided for sequences that contain the CH_2 and CHCl units (the major components of the polymers) in terms of the six subunits $CH_2CH_2CH_2$, $CHClCH_2CH_2$, $CHClCH_2CHCl$, CHClCHClCHCl, $CH_2CHClCHCl$, and $CH_2CHClCH_2$, in evaluating χ_{25}. This approach has been successfully applied in an earlier treatment of sequence distribution effects.[8] Thus in eq 4, $\chi_{25}(X - Y)^2$ has been effectively replaced by χ_{seq}, where the latter is defined as eq 12 in ref 8, in which the sequence distribution effect was incorporated. In Figure 1 we have plotted two arbitrarily selected illustrative cases: the miscibility region shrinks or expands as the term $(X - Y)^2\delta\Delta_1$ is equal to χ_{seq} (dot-dash lines) or to $-0.4\chi_{seq}$ (dashed lines), respectively. The solid curves are the miscibility boundaries of the base-line L/L blends. In all cases, x_{crit} has also been set at $\chi_{crit} = 0.002$.

When either (1) $\delta = 0$, where no branching is present, or (2) $\Delta_1 = 0$, in which case the branch point and the linear unit interact similarly with other units, eq 2 reduces to eq 5, the equation for blends of linear copolymers:

$$\chi_{blend} = (X - Y)^2\chi_{25} \qquad (5)$$

Linear Polymer/Branched Polymer Blends. In linear polymer/branched polymer (L/B) blends, the chlorinated linear polymer has only two units (units 2 and 5, Table 1); the second polymer is branched and has six units, as already defined. Equation 1 can be used to calculate the overall interaction parameter for such a blend; there is only one ϕ_A term, $-\phi_A\chi_{25}\alpha_2\alpha_5$, where $\alpha_2 = X$ and $\alpha_5 = 1 - X$. This expression then reduces to

$$\chi_{blend} = \chi_{25}(X - Y)^2 - \delta\Delta_1 Y(X - Y) + \delta\Delta_2(X - Y) \qquad (6)$$

with

$$\Delta_2 = \chi_{24} + \chi_{26} - 2\chi_{25}$$

The variable Δ_2 denotes the energy change when two χ_{25} segment interactions are replaced by χ_{24} and χ_{26} segment interactions. The replaced segment 5 and the new segments 4 and 6 are all unchlorinated segments. Note that the variable Δ_2 is a component of Δ_1, which reflects the total branching effect of unchlorinated units.

One extreme case is $\Delta_2 = 0$: the unchlorinated branch point and end unit do not change the overall interaction energy. Equation 6 then reduces to

$$\chi_{blend} = \chi_{25}(X - Y)^2 - \delta\Delta_1 Y(X - Y) \qquad (6')$$

The other extreme case is $\Delta_2 = \Delta_1$: the branching effect on the interaction energy change is completely due to the unchlorinated branch point and end units. Equation 6 reduces to

$$\chi_{blend} = \chi_{25}(X - Y)^2 + \delta\Delta_1(1 - Y)(X - Y) \qquad (6'')$$

For the two extreme cases in which either $\Delta_1 > 0$ (branching inhibits mixing in B/B blends) or $\Delta_1 < 0$ (branching promotes mixing in B/B blends), miscibility in L/B blends will show different behavior. At $X = Y$, $\chi_{blend} = 0$, so these blends should always be miscible, regardless of microstructure, according to this model.

Figure 2 illustrates the above situations. For calculating the curves in Figure 2, the two equations (6′) and (6″) were rewritten as

$$\chi_{blend} = \chi_{seq} - (X - Y)^2\delta\Delta_1\left(\frac{Y}{X - Y}\right)$$

and

$$\chi_{blend} = \chi_{seq} + (X - Y)^2\delta\Delta_1\left(\frac{1 - Y}{X - Y}\right)$$

in order to also incorporate the sequence distribution effect in the blends. The dot-dash curves are obtained for $(X - Y)^2\delta\Delta_1 = \chi_{seq}$ ($\Delta_1 > 0$); the dashed curves are obtained for $(X - Y)^2\delta\Delta_1 = -0.4\ \chi_{seq}$ ($\Delta_1 < 0$). When the linear polymer whose miscibility boundaries are shown by the two solid lines in Figure 1 is mixed with the branched polymer whose miscibility boundaries lie inside the linear polymer boundary in Figure 1, the boundaries of the resulting blends are shown in A (when $\Delta_2 = 0$) and B (when $\Delta_2 = \Delta_1$). When this linear polymer is mixed with the branched polymer whose miscibility boundaries lie outside the linear polymer boundary in Figure 1, the boundaries of the resulting blends are shown in C (when $\Delta_2 = 0$) and D (when $\Delta_2 = \Delta_1$). In all cases, the original symmetry of the miscibility regime in this representation necessarily found with B/B and L/L blends disappears. However, the blends are always miscible for $X = Y$, as already noted.

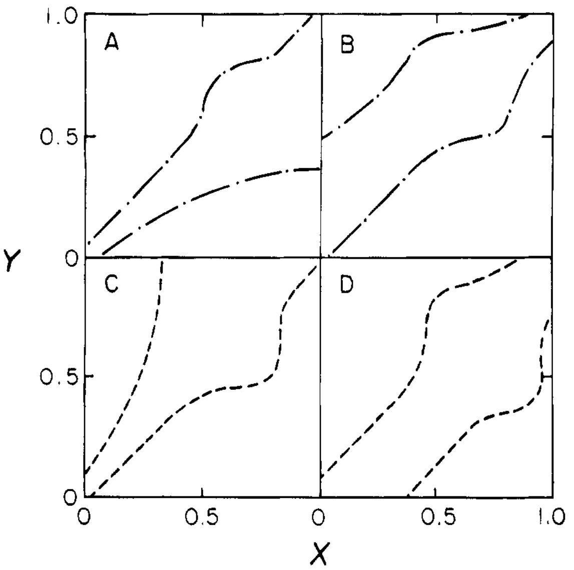

Figure 2. Miscibility boundaries of the linear/branched copolymer blends, when branching inhibits (– • –) or promotes mixing (- - -) in branched/branched copolymer blends. X and Y are the respective mole fractions of chlorinated units in the linear and branched polymers. X and Y scale from 0 to 1 in each diagram. Diagrams A and C: branching effect is due to the chlorinated branch point and end unit. Diagrams B and D: branching effect is due to the unchlorinated branching point and end units; see text.

Experimental Section

Three series of chlorinated polyethylenes (CPE) were prepared by solution chlorination. The chlorine content was determined by chemical analysis. Two base polymers, high-density polyethylene (linear, $d = 0.95$ g/mL, $T_m = 130$ °C) and low-density polyethylene (long-chain branched, $d = 0.92$ g/mL, $T_m = 115$ °C), were obtained from Aldrich. Linear low-density polyethylene (short-chain branched, $d = 0.92$ g/mL) was obtained from Dow and is a copolymer of ethylene and 1-octene. The microstructure of the polyethylenes was characterized by proton spectra (IBM AC200 FT-NMR spectrometer).[18] Samples (~1 wt %) were dissolved in a 50/50 (w/w) 1,3,5-trichlorobenzene/1,4-dichlorobenzene-d_4 mixture. All spectra were obtained at 100 °C. The $[CH_3]$/$1000[CH_2]$ ratios obtained were <1, 33, and 28 for high-density, low-density, and linear low-density polyethylene, respectively. One sample of each of the chlorinated PEs was characterized by GPC. The weight- and number-average molecular weights of these polymers were 332 000 and 48 000 for CPE(L) (54.4 wt % Cl), 249 000 and 40 000 for CPE(B) (50.5 wt % Cl), and 115 000 and 44 000 for CPE(SB) (56.3 wt % Cl), all relative to polystyrene.

The blends were prepared by dissolving the copolymers in a common solvent—tetrahydrofuran for the higher chlorine content polymers (>45 wt % Cl) or chlorobenzene for the lower chlorine content polymers (<45 wt % Cl)—at a concentration of 2 g/100 mL. The mixture was stirred overnight and then slowly evaporated. The blend ratio of two polymers was 50/50 by weight. The cast films were dried in a vacuum oven at 50 °C for 5–7 days.

The miscibility behavior of the amorphous blends at 70 °C was studied by observing the glass transition with a Perkin-Elmer DSC-4 instrument. The samples were annealed at 70 °C for at least 15 min in the DSC and then quenched to a temperature below that of the lower T_g. Thermal analyses of the annealed samples were carried out at a heating rate of 20 °C/min, with sample sizes ranging from 10 to 20 mg.

Results and Discussion

Chlorinated polyethylenes can be characterized in terms of their chlorine content (e.g., in wt %). At lower degrees of chlorination, the content of CCl_2 units in the macromolecule is negligible.[14] Such linear CPEs can be regarded simply as copolymers of CHCl and CH_2. For chlorinated linear polyethylenes, weight percentage (or weight fraction) of chlorine can be readily converted into mole fraction (X) of CHCl in these copolymers:

$$\frac{XM_2W_2}{XM_2 + (1 - X)M_5} = \text{Cl wt fraction}$$

where M_2 and M_5 are molar masses of CHCl and CH_2, respectively. W_2 is the weight fraction of chlorine in CHCl. Because the same mole fraction of chlorination (X) was assumed for the branch point and end unit, the above equation can also be used for chlorinated branched polyethylenes.

GPC results show that all the polymers have high molecular weight and broad molecular weight distribution. Thus the critical interaction parameters χ_{crit} and the spinodal curves of the blends investigated should be very close to each other, and we can neglect the effect of molecular weight and distribution on miscibility in this discussion.[1,19]

Figures 3–5 show miscibility results of respectively CPE(L)/CPE(L), CPE(SB)/CPE(SB), and CPE(B)/CPE(B) blends at 70 °C. Those blends having one glass transition in the thermogram were judged to be miscible. Figure 3, previously published,[8] is shown here for comparison.

It can be seen that in all three cases the two branches of the miscibility boundary are not parallel, as predicted for the simplest case of (A–B)/(A–B) systems by random copolymer blend theory.[3] The miscibility region expands somewhere relative to the axis $Y = X$ to yield either one or two convex regimes,[6,13] a phenomenon previously attributed to and accounted for by sequence distribution effects.[8]

When we compare the miscibility regimes of the CPE(L)/CPE(L) and CPE(B)/CPE(B) blends, we see that the CPE(L)/CPE(L) blends are relatively more miscible.

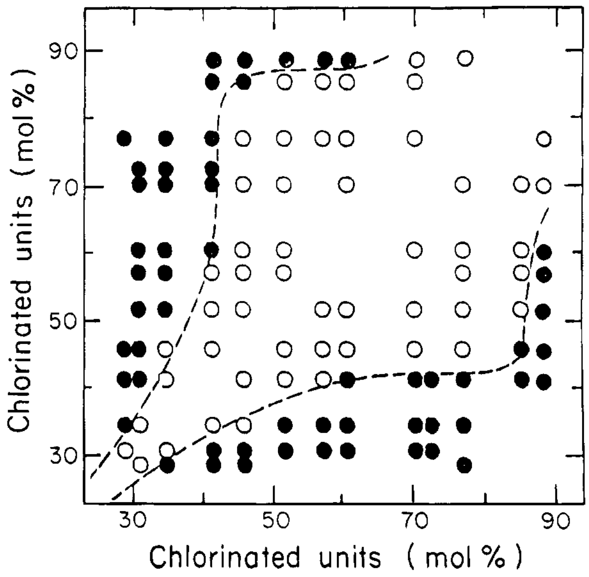

Figure 3. Isothermal phase behavior of CPE(L)/CPE(L) blends at 70 °C. The curves are the miscibility boundaries. The open and filled circles in this and in Figures 4–8 indicate one- and two-phase blends, respectively. (Reprinted from Chai, Z.; Sun, R.; Karasz, F. E. Aspects of Miscibility in Copolymer Blends. In *Mechanical Behavior of Materials—VI*; Jono, M., Inoue, T., Eds.; 1991; pp 263–268, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington 0X5 1GB, U.K.)

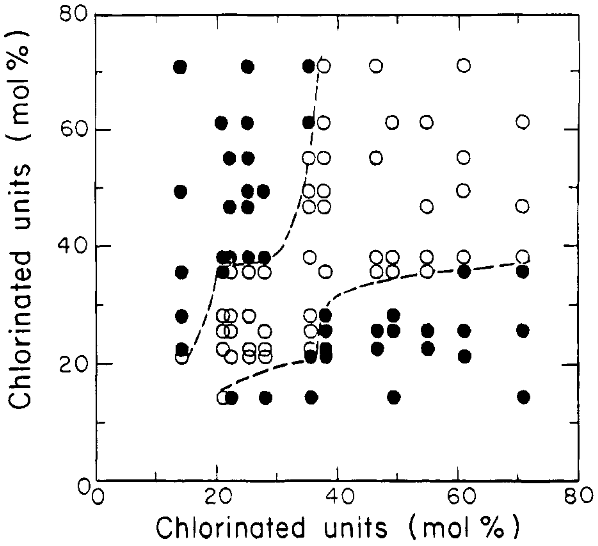

Figure 4. Isothermal phase behavior of CPE(SB)/CPE(SB) blends at 70 °C.

Branching appears to inhibit mixing in CPE/CPE blends. However, the blends containing short branches have a miscibility regime similar to that of the CPE(L)/CPE(L) blends. At mole fractions of chlorination >0.40, the miscibility regime of CPE(SB)/CPE(SB) blends is slightly broader than that of CPE(L)/(CPE(L) blends, but this difference is still within the error of experimental observations. When the mole fraction of chlorination is <0.40, the miscibility boundaries of CPE(SB)/CPE(SB) blends show a second expansion. An explanation is outside the scope of our present treatment of the sequence distribution effect. NMR results indicate that CPE(B) and CPE(SB) have similar degrees of branching. Our simple counting method over branch points, end units, etc., cannot account for their differences in miscibility. Koningsveld[16] has introduced the concept of "effective" branches to overcome this apparent

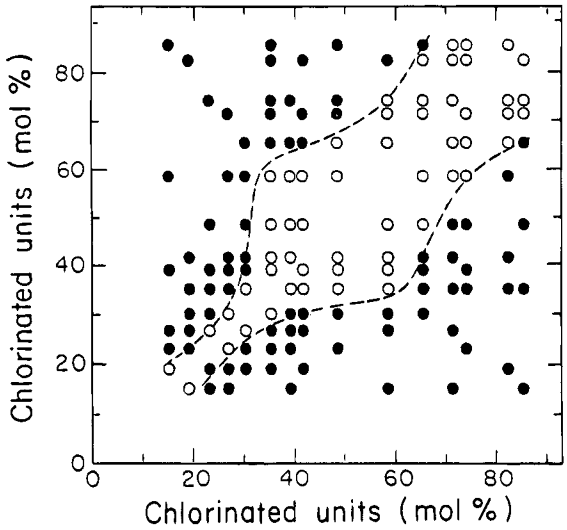

Figure 5. Isothermal phase behavior of CPE(B)/CPE(B) blends at 70 °C. (Reprinted from Chai, Z.; Sun, R.; Karasz, F. E. Aspects of Miscibility in Copolymer Blends. In *Mechanical Behavior of Materials—VI*; Jono, M., Inoue, T., Eds.; 1991; pp 263–268, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington 0X5 1GB, U.K.)

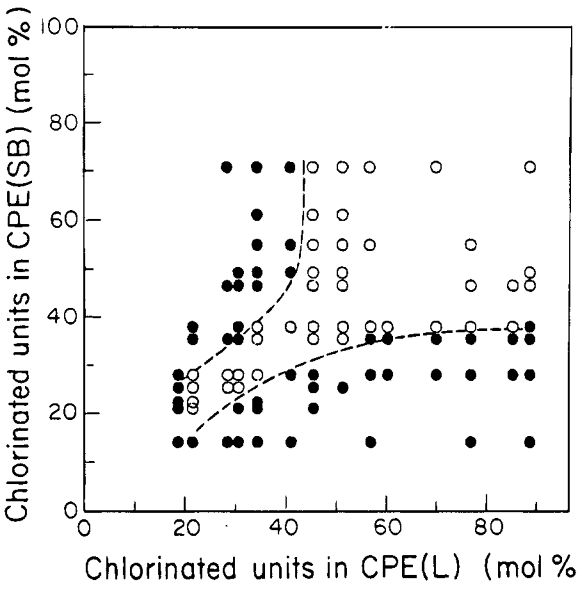

Figure 6. Isothermal phase behavior of CPE(L)/CPE(SB) blends at 70 °C.

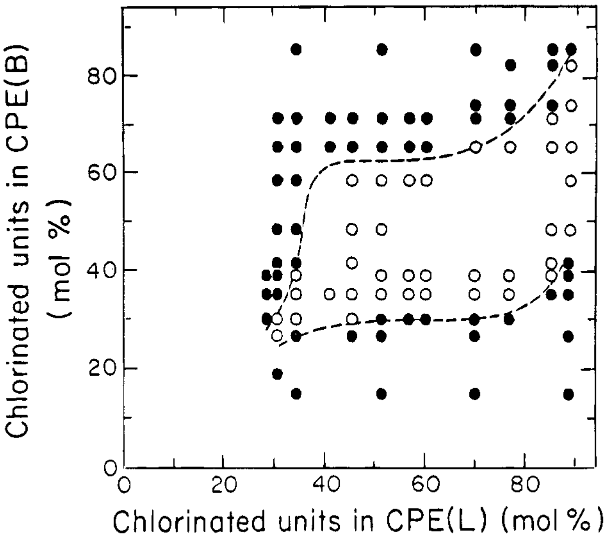

Figure 7. Isothermal phase behavior of CPE(L)/CPE(B) blends at 70 °C. (Reprinted from Chai, Z.; Sun, R.; Karasz, F. E. Aspects of Miscibility in Copolymer Blends. In *Mechanical Behavior of Materials—VI*; Jono, M., Inoue, T., Eds.; 1991; pp 263–268, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington 0X5 1GB, U.K.)

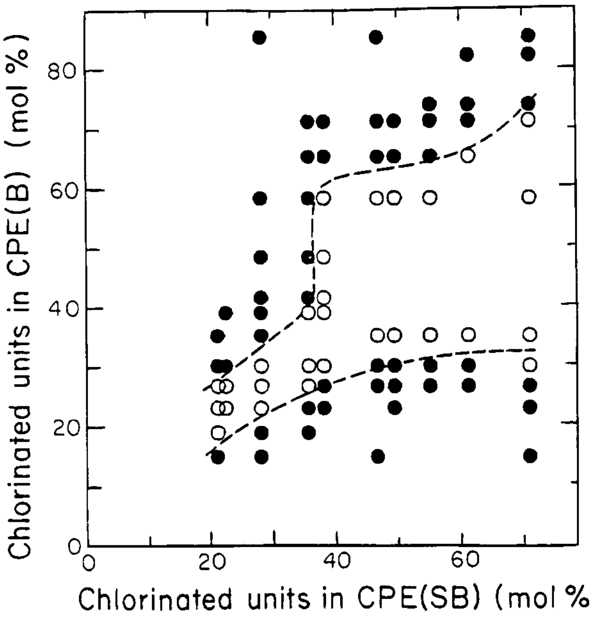

Figure 8. Isothermal phase behavior of CPE(SB)/CPE(B) blends at 70 °C.

discrepency. Thus, CPE(SB) should be regarded as containing fewer "effective" branches than CPE(B).

Figures 6–8 show the miscibility results for the "mixed" systems of CPE(L)/CPE(SB), CPE(L)/CPE(B), and CPE(SB)/CPE(B) blends, respectively. As predicted in the Theoretical Section, the miscibility regime of these blends is no longer symmetric around the $Y = X$ axis. The results for the CPE(L)/CPE(B) (Figure 7) system show that the miscibility boundary for $X < Y$ shifts toward the $Y = X$ axis, whereas the miscibility boundary for $X > Y$ moves toward the $Y = 0$ axis (X axis); we infer that these boundaries shift because CPE(L)/CPE(L) blends are relatively more miscible than CPE(B)/CPE(B) blends and the unfavorable branching effect is mainly due to the chlorinated branch point and end units. These results confirm our theoretical predictions; cf. Figure 2A. Note, however, that some blends lying almost on the $Y = X$ axis for $X > 0.7$ are immiscible, a result not predicted by the theory.

A close comparison of Figures 7 and 8 indicates that the two diagrams are nearly the same except for a few points at chlorination levels of from 20 to 30 mol %, where more miscible blends are found in the CPE(SB)/CPE(B) blends. One may speculate that these blends are miscible because CPE(SB)/CPE(SB) blends are themselves miscible at these chlorine contents. From Figures 3 and 4, we have already seen that CPE(L) and CPE(SB) have similar miscibility behaviors. Figures 7 and 8 further confirm this similarity, even when the two polymers are respectively mixed with a third polymer.

When the two polymers CPE(L) and CPE(SB) are mixed, the miscibility boundary is now asymmetric (Figure 6) at the same position as either that of the CPE(L)/CPE(L) or that of the CPE(SB)/CPE(SB) blends. Thus, when these two polymers are mixed, their minor structural differences are accentuated. We can see that the miscibility boundary shifts slightly toward the $Y =$

X axis when $X < Y$, relative to the position of the same boundary of the CPE(SB)/CPE(SB) blends (Figure 4). Also the other part of the curve shifts somewhat toward the X axis when $X > Y$, relative to that of the CPE(L)/CPE(L) blends (Figure 3). The resulting curve is again not symmetric about the $Y = X$ axis. This result shows that the short-chain branches in CPE also inhibit mixing, although this inhibition is small. We conclude that the order of miscibility (all other factors being equal) is

$$\mathrm{CPE(L)/CPE(L)} \geq \mathrm{CPE(SB)/CPE(SB)} > \mathrm{CPE(B)/CPE(B)}$$

Conclusions

In this treatment chlorinated branched polyethylene molecules are assumed to have a structure based on the following six segmental units: CH_3 (end), CH_2 (linear middle), CH (branch point), CH_2Cl (chlorinated end), CHCl (chlorinated linear middle), and CCl (chlorinated branch point). Counting the pair interactions among these units generates the overall interaction parameter of the blend, neglecting the entropy change due to branching in the mixture. Analysis shows that when the unfavorable interaction energy increases in the mixture as a result of branching, the miscibility region in composition–composition plots shrinks relative to that of L/L blends. When branched polymers are mixed with linear polymers, the miscibility boundaries shift relative to the equicompositional ($Y = X$) diagonal. In these cases the original symmetry is lost.

The experimental results support the theory qualitatively. When we compare the phase diagrams of CPE(L)/CPE(L), CPE(B)/CPE(B), and CPE(L)/CPE(B) blends, we see that the miscibility region of CPE(B)/CPE(B) blends is less than that of CPE(L)/CPE(L) blends. The miscibility boundaries of CPE(L)/CPE(B) blends are not symmetric; the two curves move toward the $Y = X$ and $Y = 0$ lines, respectively. This result suggests that the long-chain branches profoundly inhibit mixing and the unfavorable branching effect is mainly due to the chlorinated branch point and end units. The polymers CPE(L) and CPE(SB) have similar miscibility behavior, but their differences can nevertheless be observed in CPE(L)/CPE(SB) blends, in which the short-chain branches in CPE(SB) appear to inhibit mixing slightly.

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