Critical Miscibility Phenomenain Blends of Chlorinated Polyethylenes

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CRITICAL MISCIBILITY PHENOMENA IN BLENDS OF CHLORINATED POLYETHYLENES

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ABSTRACT

Critical miscibility phenomena in binary blends of chlorinated polyethylenes (CPEs) with a wide range of degree of chlorination (37 to 69 wt% Cl) were studied by measuring the glass transition behavior. At a given temperature the miscibility of the blends was principally dependent on the difference in chlorine content between the two component CPEs and also on the mean degree of chlorination. The miscibility of these systems at 150°C was maximal around an average mole fraction chlorination, $\bar{\beta}$, of 0.5. The systems displayed upper critical solution temperatures when $\bar{\beta}$ was below 0.5, while lower critical solution temperatures were observed when $\bar{\beta}$ was above 0.5. At a given $\bar{\beta}$, the consolute points converged as the difference in chlorine content of the blend constituents increased. It appears that this double consolute point temperature decreases with increasing average degree of chlorination. A more refined analysis, taking into account the possible presence of CCl_2 units and the microstructure of the CPEs, is also presented.

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INTRODUCTION

Although experimental and theoretical studies of the critical miscibility phenomena in polymers have been in progress for the last decade, an understanding of the miscibility of random copolymer blends in particular has been developed only recently [1–5]. To date, miscibility behavior in blends consisting of copolymer/homopolymer systems, copolymer/copolymer systems, and of copolymers containing the same monomer units but of differing compositions has been discussed.

The critical composition difference for the miscibility of copolymers containing the same monomer moieties but of different compositions was first predicted by Scott [1]. Molau [6] found that mixtures of styrene–acrylonitrile copolymers were miscible if the difference in acrylonitrile composition was below 3.5 to 4.5%. Kollinsky and Markert [7] reported that mixtures of methyl methacrylate–butyl acrylate copolymers were miscible if the difference in the methyl methacrylate content was below 10 to 20 mol% and that the miscibility decreased with increasing methyl methacrylate composition. Chai and Sun [8] determined miscibility in blends of chlorinated polyethylenes (CPEs) by assessing the transparency in films cast from chlorobenzene solution. They found that miscibility in blends of CPEs was dependent both on the degree of chlorination of the component polymers and on the difference in the chlorine contents of the constituent copolymers.

As a first approximation, chlorinated polyethylenes can be regarded as random copolymers consisting primarily of CH_2 and $CHCl$ units. At high chlorine contents a small fraction of CCl_2 units is also present. Starting from a given linear polyethylene, the $CH_2/CHCl$ ratio can be easily and systematically controlled. In addition, the microstructures of the CPEs are also relatively easily characterized. Thus, blends of CPEs represent an ideal model system for studying miscibility phenomena in copolymers.

It is well known that polymers in solution generally show upper critical solution temperatures (UCSTs), while mixtures of bulk polymers more often show lower critical solution temperatures (LCSTs). Some polymer solutions [9–12] show a UCST at a lower temperature and an LCST at a higher temperature. The UCST behavior of polymer solutions has been explained by the Flory–Huggins theory [13, 14] with varying degrees of refinement, but this theory is inadequate for predicting LCST behavior. According to theories more recently developed by Prigogine [15], Flory et al. [16], and Sanchez and Lacombe [17], LCST behavior is

related to free volume effects associated with a change in the volume of mixing. Patterson and Robard [18] pointed out that critical phenomena in polymer mixtures are primarily influenced by an interaction term in the equation of state.

MacMaster [19] and Patterson and Robard [18] noted that it would be difficult to find mixtures of polymers showing both a UCST and a LCST. Indeed, UCST behavior is uncommon in polymer blends. However, several mixtures of polymers showing UCSTs have recently been found: these include blends of chlorinated polyethylenes [20]; cis-1,4-polybutadiene and poly(styrene-co-butadiene) containing 45 wt% styrene [21]; protonated and perdeuterated 1,4-polybutadiene [22]; polystyrene and carboxylated poly(2,6-dimethyl-1,4-phenylene oxide) [23]; and chlorinated polybutadiene and chlorinated polyethylene [24].

The present paper describes the effects of the degree of chlorination on the UCST and LCST behavior of CPE–CPE systems for a wide range of degrees of chlorination.

EXPERIMENTAL

Chlorinated polyethylenes (CPEs) were prepared by two methods. Samples coded CPE I-1 to I-13 were prepared by solution photochlorination of a master batch of fractionated polyethylene following the procedure of Walsh et al. [25] as described previously [20]. More highly chlorinated polyethylenes (coded CPE II-1 to II-13, were prepared by using the procedure of Saito et al. [26]. In this procedure the fractionated linear high density polyethylene (Pressure Chemical Co., $\overline{M}_w = 23,700$, $\overline{M}_n = 9420$) was dissolved in 1,1,2,2-tetrachloroethane (1% solution) at 100°C. As in Ref. 20, chlorine was bubbled through the solution and the photoreaction was initiated with a tungsten lamp. CPEs with different chlorine contents were obtained by removing aliquots of this solution at appropriate times of reaction. The samples were precipitated with a tenfold excess of methanol and dried at 60°C for 1 week. In addition to the CPE I and II samples, CPEs were also prepared by solution photochlorination of unfractionated linear high density polyethylene (Chemplex 6230 HDPE, $\overline{M}_w = 75,200$, $\overline{M}_n = 15,200$).

The molecular weights of the CPEs were measured in tetrahydrofuran by GPC. Chlorine contents, expressed as weight percent, were determined by elemental analysis. These data and the codes used to identify the CPEs are listed in Table 1. The parenthetical quantities listed in

TABLE 1. Properties of Solution Chlorinated Polyethylenes

Sample code	Cl, wt%	Molecular weight[a]			$\overline{M}_w/\overline{M}_n$	T_g, °C[b]
		$\overline{M}_w \times 10^{-4}$		$\overline{M}_n \times 10^{-4}$		
I-1	36.8	5.28	—	2.44	2.16	−18.6
2	37.7	5.56	(5.53)[c]	2.79	1.99	−13.9
3	40.0	5.67	(5.72)	2.91	1.95	−9.0
4	42.2	5.73	(5.94)	2.84	2.01	−3.4
5	43.3	6.15	(6.05)	3.17	1.94	1.1
6	44.4	5.90	(6.16)	3.26	1.80	3.4
7	46.2	6.55	(6.34)	3.22	2.03	9.3
8	47.9	6.58	(6.57)	3.20	2.05	16.9
9	48.8	6.62	(6.68)	3.11	2.12	21.1
10	50.7	6.35	(6.93)	2.99	2.12	26.2
11	52.6	6.90	(7.18)	3.42	2.01	39.4
12	56.1	6.21	(7.73)	3.42	1.81	51.8
13	58.0	7.10	(8.04)	3.51	2.01	61.2
II-1	56.7	6.90	(7.81)	3.60	1.93	57.9
2	58.5	7.09	(8.12)	2.85	2.48	63.2
3	60.5	6.53	(8.51)	3.12	2.09	75.8
4	62.0	7.77	(8.59)	4.11	1.87	84.6
5	63.6	7.87	(9.19)	4.12	1.91	99.9
6	64.7	—	—	—	—	107.7
7	65.3	8.24	(9.59)	4.13	1.99	111.6
8	65.6	—	—	—	—	115.3
9	66.0	—	—	—	—	119.5
10	66.4	—	—	—	—	125.6
11	66.7	7.94	(9.80)	3.47	2.28	128.5
12	67.3	—	—	—	—	133.0
13	68.9	—	—	—	—	151.9

[a]Determined by GPC relative to polystyrene.
[b]Determined from maxima in DSC-obtained plots of dC_p/dT vs T.
[c]Calculated; see text.

Table 1 show the molecular weights calculated on the premise that the degrees of polymerization remain constant. The deviations are 10 to 20% above 50 wt% Cl contents and may be due to partial degradation of the polymers at higher degrees of chlorination.

In preparing a blend, selected CPEs were dissolved in THF (0.5% w/v); except as otherwise noted, the composition of the blends studied was 50/50 wt%. The mixtures of the CPEs were coprecipitated with a tenfold excess of cold methanol. The precipitated powders were washed several times with cold methanol and then dried at either 50 to 70°C for 4 to 7 days under reduced pressure. Films of mixtures of CPE I were obtained by compression molding at either 50 or 100°C for 15 min. The coprecipitated powders of the CPE I/CPE II and CPE II/CPE II mixtures were used in DSC measurements without molding.

The miscibility of the polymer blends was determined as described previously [20] by observing the glass transition temperatures using a Perkin-Elmer DSC-4 differential scanning calorimeter. Selected thermal histories were imposed by annealing the samples in the DSC. Samples were heated at 200°C/min to the desired temperature and annealed for 15 min unless otherwise indicated. The samples were then quenched to a temperature below that of the lowest component T_g. Thermal analyses of the annealed samples were carried out at a heating rate of 20°C/min. The T_g's were determined from the maxima in plots of dC_p/dT versus T (derivative DSC curves).

RESULTS

DSC Analyses

The presence of critical or phase boundary phenomena in polymer–polymer blends preferably needs to be confirmed by experimentally testing the reversibility of phase separation and rehomogenization. This is particularly the case for the type of system under consideration here where the "single observed T_g," which is the typical criterion for miscibility, might be the result of the overlapping of individual component T_g's too closely spaced to provide a definite conclusion regarding miscibility.

In an earlier communication [20] we presented derivative DSC plots that display such reversibility in detail. Thus, in the present report, only limited illustrative examples of the effect of time–temperature protocols are shown. Figure 1 shows an example of UCST behavior in which a
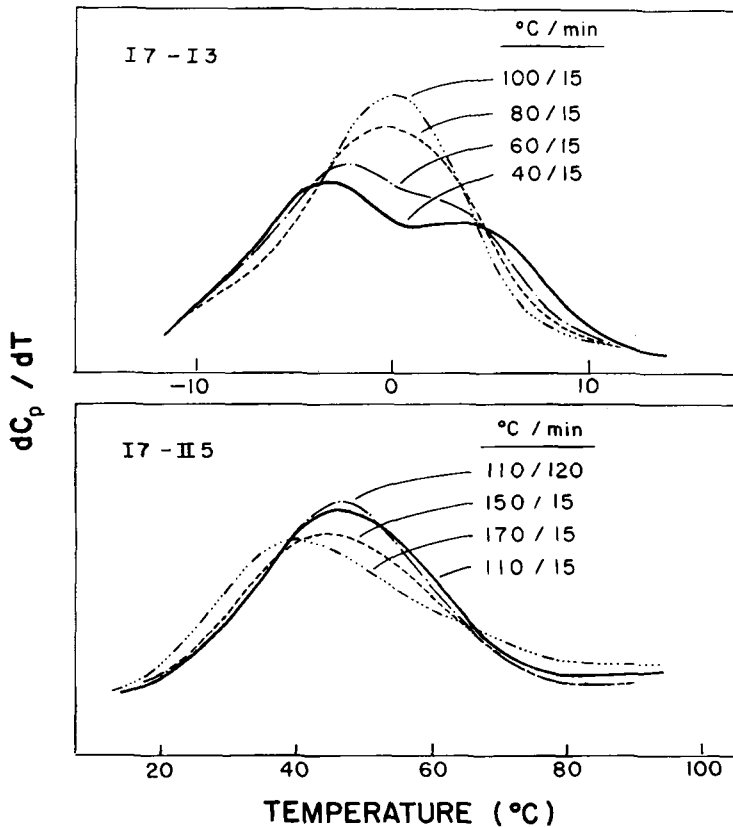
FIG. 1. DSC thermograms (dC_p/dT vs T) of 50/50 wt% blends of CPEs. I-7 (46.2 wt% Cl) and I-3 (40.0 wt% Cl), I-7 and II-5 (63.6 wt% Cl). Annealing conditions are indicated.

blend of I-7 and I-3 annealed at 40°C displays two well-separated T_g's. At higher annealing temperatures (60, 80, and 100°C) a single T_g is observed as the phase boundary is traversed. The mixture of CPE I-7 and I-3 annealed at 40°C shows two peaks at -3.2 and 3.7°C while the same sample annealed at 100°C shows one peak at 0°C. This peak temperature is reasonably close to the average of the T_g's of the two component CPEs (-9 and 9.3°C). These results suggest that a single phase can be obtained at a temperature above a critical point, i.e., UCST behavior.
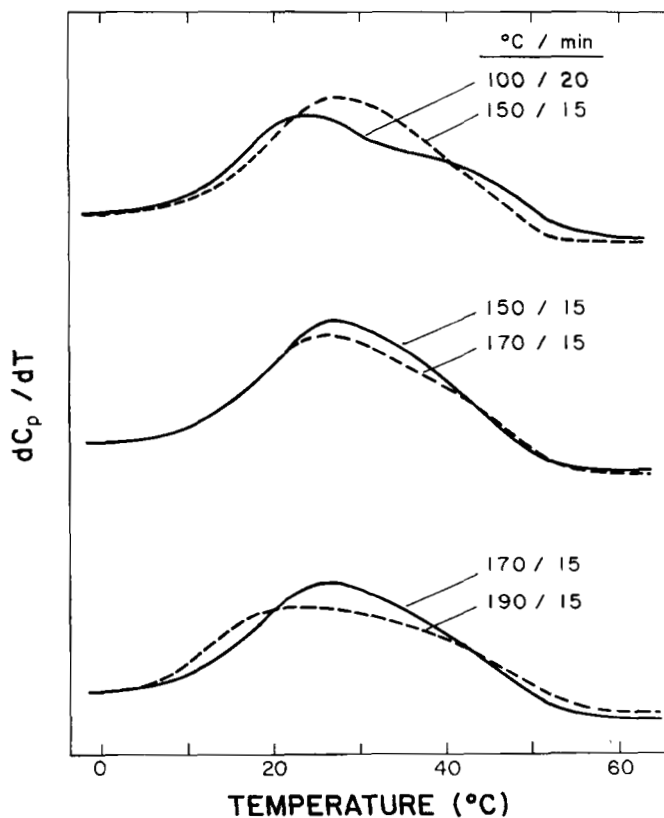
FIG. 2. dC/dT versus temperature for 50/50 wt% blends of the CPEs containing 45 and 57.2 wt% chlorine prepared from base polyethylene with M_w = 75,200, M_n = 15,200.

At higher Cl contents, the CPE I-7/II-5 blend annealed at 100°C shows a single peak at 47°C. The same sample was annealed at 170°C; as can be seen, the peak bifurcates. These results imply that phase separation occurs at a temperature above a critical point, i.e., LCST behavior.

Figure 2 shows dC_p/dT versus temperature curves of the mixtures of the CPEs containing 45.0 and 57.2 wt% Cl that were prepared from unfractionated PE. The sample annealed at 100°C displays two very
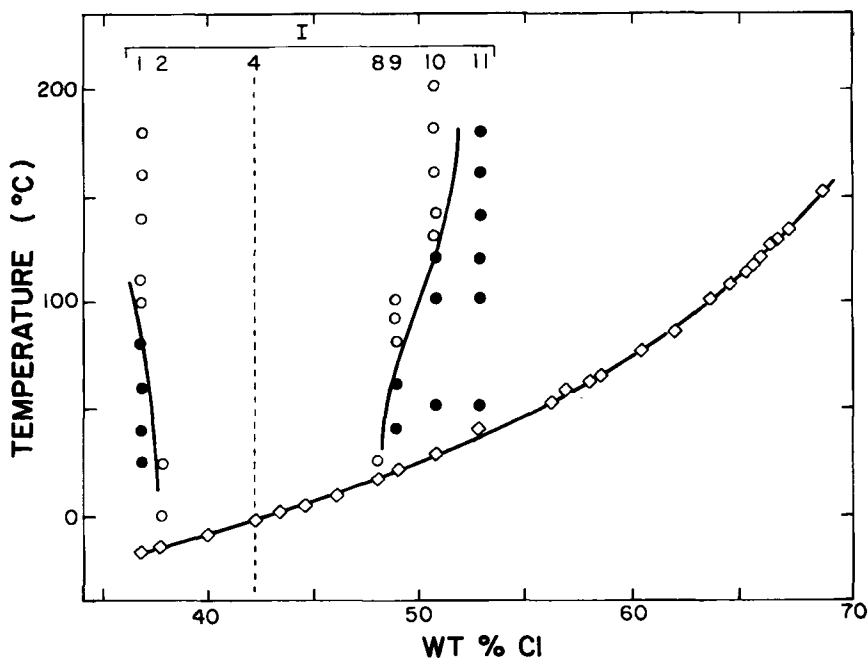
FIG. 3. Miscibility of 50/50 wt% blends of CPE as a function of temperature and chlorine wt%. The broken line indicates the common component CPE I-4 (42.2 wt% Cl). (○) Miscibility; (●) immiscibility; (◊) T_g's of pure CPEs.

broad peaks around 25 and 42°C, while the same sample annealed at 150°C appears to show one broad peak around 28°C. Two broad peaks are again observed by further annealing of the sample at 190°C. These results suggest that this mixture may show LCST behavior at lower temperature and UCST behavior at higher temperature.

Miscibility Diagrams

The miscibility diagrams, i.e., the phase behavior as a function of temperature and copolymer composition (expressed as chlorine weight percent), for mixtures of CPE I-4 with CPE I-1 through I-11 and CPE I-7 with CPE I-2 through II-7 are depicted in Figs. 3 and 4, respectively. The numbers in the diagrams indicate the sample codes of the second component CPE.
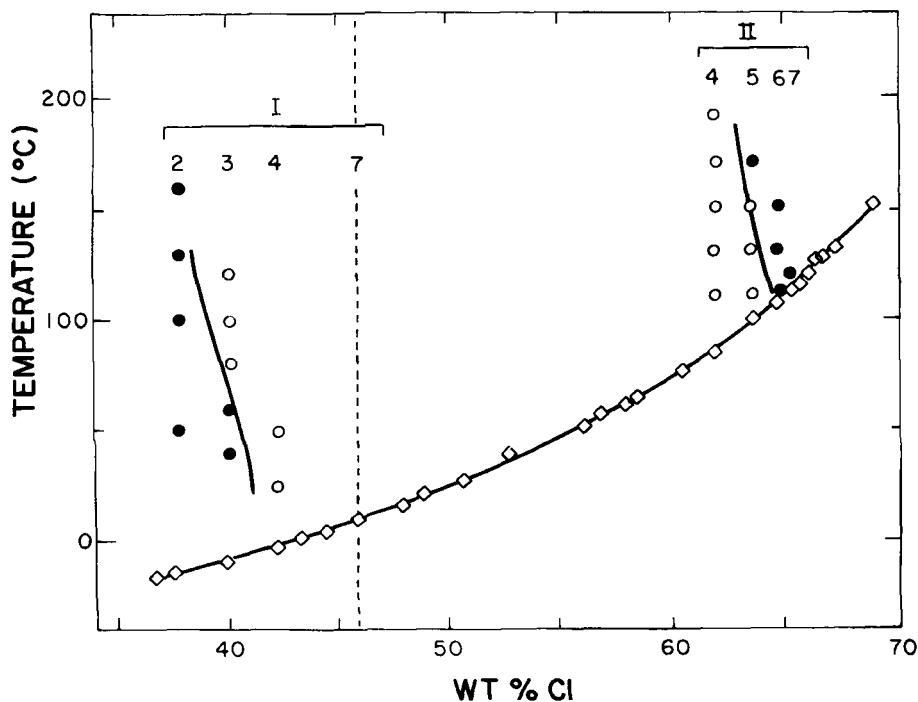
FIG. 4. Miscibility of 50/50 wt% blend of CPE as a function of temperature and chlorine wt%. The broken line indicates the common component CPE I-7 (46.2 wt% Cl). (○) Miscibility; (●) immiscibility; (◊) T_g's of pure CPEs.

Blends of CPE I-4 with CPE I-2 through I-8 are miscible in the temperature range from T_g to the degradation temperature of the polymers (around 200°C). On the other hand, the mixture of CPE I-4 and I-11 is immiscible in the whole temperature range. In the intermediate cases UCSTs are detected in the mixtures of CPE I-4 in which the second components are I-1, I-9, and I-10. LCSTs were not observed for any binary blend containing I-4. These results show that the LCSTs, if they exist, are above the degradation temperatures of CPEs in this system.

However, LCST behavior is observed with blends containing the more chlorinated CPE I-7 (Fig. 4). Thus, the mixture of CPE I-7 with the less chlorinated I-3 displays UCST behavior while the mixture of CPE I-7 with the highly chlorinated II-5 displays LCST behavior.
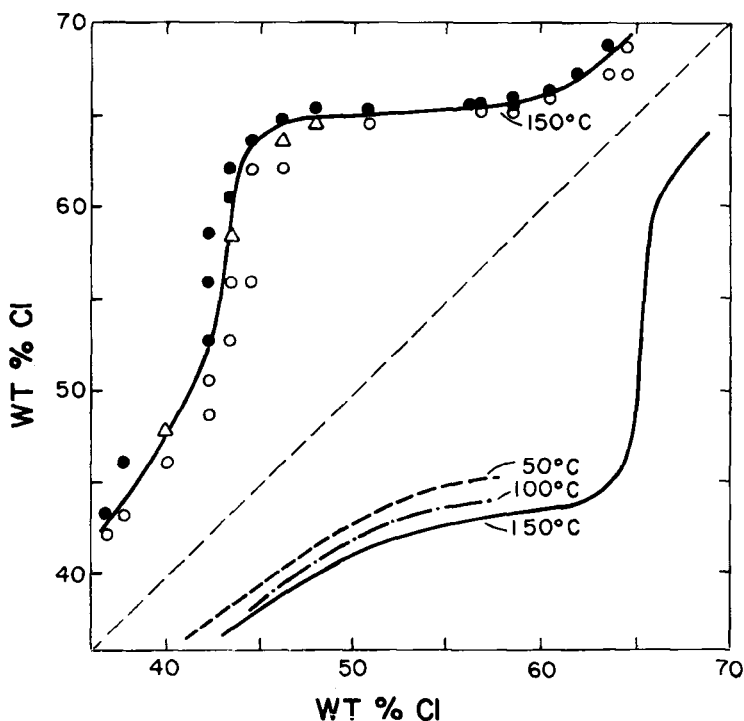
FIG. 5. Miscibility of 50/50 wt% blends of CPEs at 50, 100, and 150°C. (O) Miscibility; (●) immiscibility; (△) uncertain miscibility. The region between the curves represents miscibility.

As would be expected, the consolute temperatures associated with high temperature phase separation decrease with increasing difference in chlorine content, ΔCl, between the common component polymer and the second polymer, in contrast to the UCSTs, which increase with ΔCl. The consolute temperatures also depend on the molecular weights of the polymers: the UCST may be expected to increase and the LCST may decrease with increasing molecular weight. Thus, as can be seen in Fig. 2, the blend of CPEs with high molecular weights display both UCST and LCST behavior between the glass transition temperature and degradation temperature.

Isothermal Miscibility Diagram

The isothermal miscibility diagrams at 50, 100, and 150°C, i.e., miscibility as a function of chlorine weight percents for the entire range of CPE's, are shown in Fig. 5. Miscibility in these systems clearly depends upon the degree of chlorination. The blends in which one of the constituents contains less than 60 wt% Cl show UCST behavior; thus, the miscibility region is expanded with increasing temperature as shown in Fig. 5. On the other hand, the mixtures in which one of the constituents contains more than 60 wt% Cl show LCST behavior. This result implies that the double consult point shifts to a lower temperature range with increasing degree of chlorination.

Chai and Sun [8] also found that miscibility in blends of CPEs was dependent upon the degree of chlorination of the constituent polymers and on the difference in chlorine content between the two CPEs. In their study, miscibility was determined by observing the transparency of films cast from solvent; no temperature effects were studied.

DISCUSSION

Miscibility Diagram

As a first-order approximation, chlorinated polyethylenes can be regarded as copolymers consisting of CH_2 and $CHCl$ units at low degrees of chlorination. Thus, binary mixtures of CPEs containing the common monomer moieties, $A \equiv CH_2$ and $B \equiv CHCl$, i.e., $(A_xB_{1-x})_{n_1}$ and $(A_yB_{1-y})_{n_2}$, where x and y denote the copolymer compositions, will be miscible for a certain range of $|x - y|$, where $0 \leq |x - y| \leq |x - y|_{max}$, which is a function of the interaction of A and B and of the degrees of polymerization, n_1 and n_2. The quantity $|x - y|_{max}$ will also be a function of temperature. In common with many polymer systems, any given miscible mixture may be expected to show a high temperature phase separation regime with a concomitant lower critical solution temperature. In addition, the possibility of upper critical solution temperature behavior also exists. When these phenomena are displayed as a function of temperature versus the parameter $|x - y|$, the loci of the consolute points will be of the forms schematically shown in Figs. 6(a)
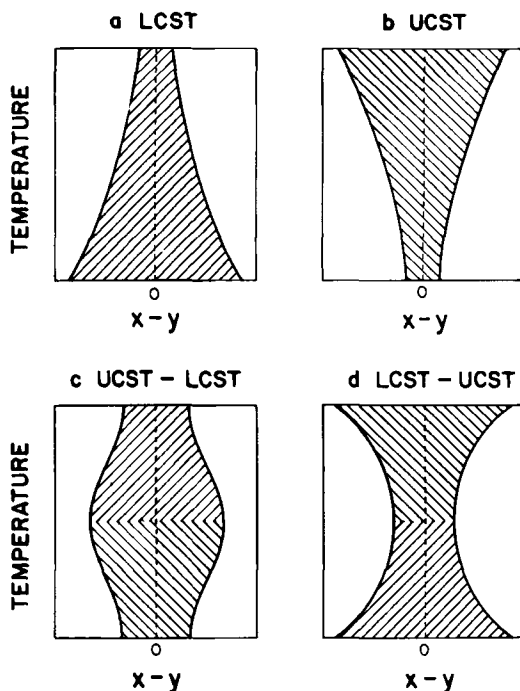
FIG. 6. Schematic illustration of the miscibility regions of copolymer mixtures $(A_xB_{1-x})_{n_1}$ and $(A_yB_{1-y})_{n_2}$. The region between the two curves represents miscibility. (a) Mixture displays LCSTs only, (b) mixture displays only UCSTs, (c) mixture displays a UCST at lower mixture and a LCST at higher temperature, (d) mixture displays a LCST at lower temperature and a UCST at higher temperature.

and 6(b), respectively. There is also the possibility that the consolute points merge; this behavior is shown in Figs. 6(c) and 6(d). The extrema in Fig. 6(c) correspond to the situation in which the LCST and UCST are just merged to form a double consolute point. In principle, for a system with a given $|x - y|$ less than that corresponding to the extrema, it would be possible to intersect both the boundary corresponding to a UCST and that corresponding to an LCST in the temperature plane. Whether this is in fact possible in a given system depends on the relative location of the accessible experimental "window" in the temperature plane which is bounded approximately by the glass

transition temperature and the degradation temperature of the respective blend.

For comparison of our experimental results with the schematic diagrams discussed above, it can be seen in Fig. 3 that the CPE I-4 system displays miscibility behavior corresponding to Fig. 6(b), i.e., the miscibility boundaries shown are the loci of a set of UCSTs for the respective value of $|x - y|$. As mentioned previously, the LCSTs of this system may be above the degradation temperature, and hence the miscibility diagram corresponding to Fig. 6(c) cannot be obtained experimentally.

According to the first-order mean field prediction, the maximum value of the difference in composition for miscibility at a given temperature T is given by [4]

$$|x - y|_{max} = (n_1^{-1/2} + n_2^{-1/2})/(2\chi_{AB}(T))^{1/2} \tag{1}$$

where $\chi_{AB}(T)$ is the first-order segmental interaction parameter (CH_2, $CHCl \equiv A, B$). If $\chi_{AB}(T)$ is independent of the copolymer composition, $|x - y|_{max}$ is a function only of temperature and the miscibility diagram of the "oil lamp" shape illustrated in Fig. 6(c) should be symmetric with respect to the broken vertical line at $|x - y| = 0$. In addition, the miscibility–immiscibility boundary in the isothermal miscibility diagram shown in Fig. 5 should be parallel to the diagonal.

The miscibility diagrams shown in Figs. 4 and 5 are both asymmetric with respect to the value $|x - y| = 0$ (broken line) representing the common component CPE of the mixtures. This result suggests that the interaction parameter $\chi_{AB}(T)$ must be a function of the degree of chlorination. The isothermal miscibility diagram depicted in Fig. 5 also clearly shows the dependence of $\chi_{AB}(T)$ on the degree of chlorination: $|x - y|_{max}$ also changes with the degree of this parameter.

The quantity $|x - y|_{max}$ given by Eq. (1) depends on the molecular weights of the constituent polymers. If n_1, $n_2 = \infty$ and χ_{AB} is greater than 0, $|x - y|_{max} = 0$. Thus $|x - y|_{max}$ decreases as the molecular weights of the constituent polymers increase. To illustrate the dependence of $|x - y|_{max}$ on molecular weight, Fig. 7 shows the isothermal miscibility diagram at 150°C by comparing mixtures of fractionated (FCPE) and unfractionated (UCPE) samples, where FCPEs are the samples (CPE I and II) prepared from fractionated polyethylene and UCPEs are the samples prepared from unfractionated PE with higher molecular weight. As expected, $|x - y|_{max}$ of the mixtures of the UCPEs is less than that of the FCPEs.
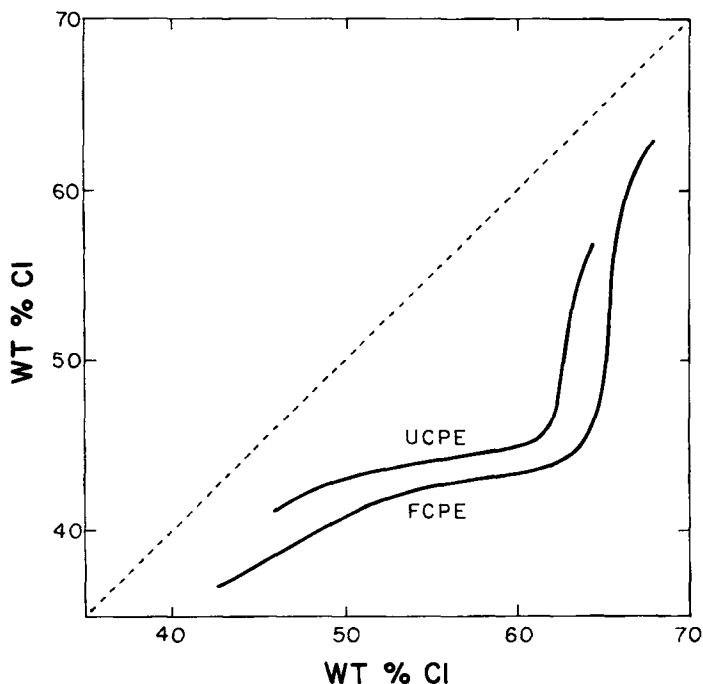
FIG. 7. Miscibility of 50/50 wt% blend of CPEs at 150°C. FCPE: CPEs prepared from base polyethylene with $M_w = 23,700$, $M_n = 9,420$ (CPE I and II). UCPE = CPEs prepared from base polyethylene with $M_w = 75,200$, $M_n = 15,200$.

Effect of Microstructure on Miscibility

Miscibility characterized by $|x - y|_{max}$ is related to the interaction parameter χ_{AB} reflecting chemical structures and microstructures of the constituent polymers. Thus the dependence of miscibility in mixtures of CPEs on the degree of chlorination can be associated with the micro-structures of CPE.

If we take into account the presence of CCl_2 units, CPEs can be regarded as copolymers consisting of three units, $A \equiv CH_2$, $B \equiv CHCl$, and $C \equiv CCl_2$, and miscibility in these systems is determined by the three interaction parameters χ_{AB}, χ_{AC}, and χ_{BC} (see Appendix). However,

CCl_2 units can be disregarded below 50 wt% Cl [27, 28]; hence the characteristic miscibility behavior in blends of CPEs shown in Fig. 5 may be caused by other microstructural factors such as the CHCl distribution along the polymer chain. In fact, Balazs et al. predicted an effect of sequence distribution on the miscibility of homopolymer/copolymer [29] and also copolymer/copolymer blends [30].

According to Balazs et al. [30], the interaction parameter of blends of copolymers (χ_{blend}) can be treated as the summation of two terms, χ_{comp} and χ_{dist}; χ_{comp} and χ_{dist} express the composition dependence of χ_{blend} and the comonomer sequence distribution dependence of χ_{blend}, respectively. χ_{dist} is expressed as a function of the interaction parameters $\chi_{AAA/BBB}$, $\chi_{BAB/ABA}$, and $\bar{\chi}_{AB}$; $\bar{\chi}_{AB}$ is an average value of 14 pairs of A-B interacting triplets except AAA/BBB and BAB/ABA. $\bar{\chi}_{AB}$ was set at zero and the value of $\chi_{AAA/BBB}$ obtained was 0.37 ± 0.03 and that of $\chi_{BAB/ABA}$ was -4.34 ± 0.40 (A $\equiv$ CH_2, B $\equiv$ CHCl) from a linear least-squares fit of the observed values of χ_{CH_2CHCl} obtained from the experimental results shown in Fig. 5 through Eqs. (2)-(4).

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

$$= (x - y)^2 \bar{\chi}_{AB} + \chi_{dist} \tag{3}$$

$$\chi_{AB}(\text{apparent}) = \bar{\chi}_{AB} + \chi_{dist}/(x - y)^2 \tag{4}$$

where

$$\chi_{dist} = \left[\frac{g_{AB}^2}{1-y} - \frac{f_{AB}^2}{1-x} - \frac{g_{AB}^2}{y} - \frac{f_{AB}^2}{x} \right] \Delta\chi^a$$

$$+ \left[\left(\frac{g_{BB}^2}{1-y} - \frac{f_{BB}^2}{1-x} \right) \left(\frac{f_{AA}^2}{x} - \frac{g_{AA}^2}{y} \right) \right] \Delta\chi^b \tag{5}$$

$$\Delta\chi^a \equiv \bar{\chi}_{AB} - \chi_{BAB/ABA} \tag{6}$$

$$\Delta\chi^b \equiv \chi_{AAA/BBB} - \bar{\chi}_{AB} \tag{7}$$

f_{AA}, f_{AB}, and f_{BB} are the joint probabilities of AA, AB, and BB pairs for

one component copolymer, and g_{AA}, g_{AB}, and g_{BB} are the joint probabilities of AA, AB, and BB pairs for the second component copolymer.

Balazs et al. obtained a good agreement between the predicted and observed values for $\bar{\chi}_{AB}$ for mixtures of CPEs. Their results suggest that the chlorine content dependence of miscibility in mixtures of CPEs, which is clearly shown in Fig. 5, is primarily associated with the sequence distribution of CHCl units in terms of triads.

APPENDIX

Interaction Parameter of Mixtures of Terpolymers

The interaction parameter, χ_{blend}, of binary mixtures of terpolymers, $(A_x B_{x'} C_{1-x-x'})_{n_1}$ and $(D_y E_{y'} F_{1-y-y'})_{n_2}$ can be derived by the first-order mean field theory in a manner similar to the treatment of ten Brinks et al. [4]. χ_{blend} is given by

$$
\begin{aligned}
\chi_{blend} &= xy\chi_{AD} + xy'\chi_{AE} + x(1 - y - y')\chi_{AF} + x'y\chi_{BD} \\
&+ x'y'\chi_{BE} + x'(1 - y - y')\chi_{BF} + (1 - x - x')y\chi_{CD} \\
&+ (1 - x - x')y'\chi_{CE} + (1 - x - x')(1 - y - y')\chi_{CF} \\
&- xx'\chi_{AB} - x(1 - x - x')\chi_{AC} - x'(1 - x - x')\chi_{BC} \\
&- yy'\chi_{DE} - y(1 - y - y')\chi_{DF} - y'(1 - y - y')\chi_{EF} \quad \text{(A1)}
\end{aligned}
$$

where x, x', y, and y' denote the copolymer compositions.

Several simple cases may be considered:

1. A copolymer ABC and homopolymer D. In this case:

$$
\begin{aligned}
\chi_{blend} &= x\chi_{AD} + x'\chi_{BD} + (1 - x - x')\chi_{CD} - xx'\chi_{AB} \\
&- x(1 - x - x')\chi_{AC} - x'(1 - x - x')\chi_{BC} \quad \text{(A2)}
\end{aligned}
$$

2. A copolymer ABC and homopolymer A. In this case:

$$
\begin{aligned}
\chi_{blend} &= x'(1 - x)\chi_{AB} + (1 - x - x')(1 - x)\chi_{AC} \\
&- x'(1 - x - x')\chi_{BC} \quad \text{(A3)}
\end{aligned}
$$

3. Two terpolymers that differ only in copolymer composition:

$$\chi_{blend} = -(x - y)(x' - y')\chi_{AB} + (x - y + x' - y')$$
$$\{(x - y)\chi_{AC} + (x' - y')\chi_{BC}\} \tag{A4}$$

The interaction parameter, χ_{blend}, is equal to the critical interaction parameter, χ_0, at the critical point for miscibility. Thus the miscibility/immiscibility boundary for Case 3 is determined by

$$-(x - y)(x' - y')\chi_{AB} + (x - y + x' - y')\{(x - y)\chi_{AC}$$
$$+ (x' - y')\chi_{BC}\} - \chi_0 = 0 \tag{A5}$$

where

$$\chi_0 = {}^{1/2}(n^{-1/2}_1 + n^{-1/2}_2)^2 \tag{A6}$$

Equation (A5) may be written

$$\chi_{AC}a^2 + (\chi_{AC} + \chi_{BC} - \chi_{AB})ab + \chi_{BC}b^2 - \chi_0 = 0 \tag{A7}$$

where $a = x - y$ and $b = x' - y'$.

The miscibility boundaries defined by Eq. (A7) can show three different forms according to the relative magnitudes of the x_{ij}.

(1) $(\chi_{AC} + \chi_{BC} - \chi_{AB})^2 - 4\chi_{AC}\chi_{BC} < 0$

In this case the region of miscibility is contained by an ellipse in a Cartesian coordinate system in which the copolymer composition differences form the ordinate and abscissa when the molecular weights of the component polymers are finite ($\chi_0 \neq 0$). When $\chi_0 = 0$, i.e., the constituent polymers have infinite molecular weights, there is no miscible region except at the terminal case $a = b = 0$. When $\chi_0 > 0$, χ_{BC} and χ_{AC} must be positive.

(2) $(\chi_{AC} + \chi_{BC} - \chi_{AB})^2 - 4\chi_{AC}\chi_{BC} = 0$

In this case the region of miscibility lies between two parallel straight lines defined by $b = -(\chi_{AC} + \chi_{BC} - \chi_{AB})a/2\chi_{BC} \pm (\chi_0/\chi_{BC})^{1/2}$. When $\chi_0 = 0$, the parallel critical boundaries are reduced to a single boundary for which $b = -(\chi_{AC} + \chi_{BC} - \chi_{AB})a/2\chi_{BC}$. When $\chi_0 > 0$, χ_{BC} and χ_{AC} must be positive or zero.
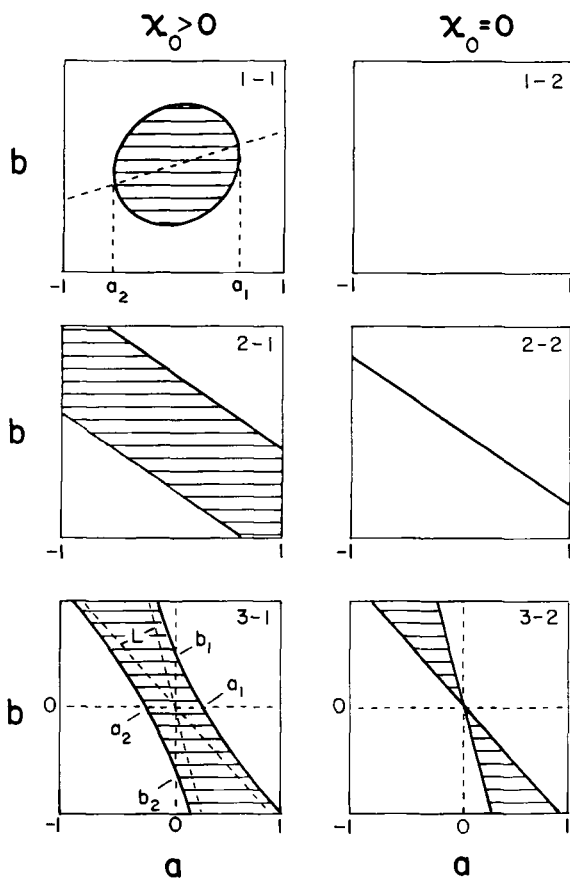
$\chi_0 > 0$　　　　　$\chi_0 = 0$

I-1

b

-1　a_2　　a_1　1

I-2

-1　　　　1

2-1

b

-1　　　1

2-2

-1　　　1

3-1

b　0

L　　b_1

a_1

a_2

b_2

-1　　0　　1

3-2

0

-1　　0　　1

a　　　　　　a

FIG. A1. Schematic illustration of miscibility of binary mixtures of terpolymers, $(A_xB_{x'}C_{1-x-x'})_{n_1}$ and $(A_yB_{y'}C_{1-y-y'})_{n_1}$. x, x', y, and y' denote the copolymer compositions, and a $= x - y'$, b $= x' - y$. The region between the curves represents miscibility.

1 − 1: $\chi_{AB} = 0.050$, $\chi_{AC} = 0.02$, $\chi_{BC} = 0.02$, $\chi_0 = 0.006$
1 − 2: $\chi_{AB} = 0.050$, $\chi_{AC} = 0.02$, $\chi_{BC} = 0.02$, $\chi_0 = 0$
2 − 1: $\chi_{AB} = 0.002$, $\chi_{AC} = 0.01$, $\chi_{BC} = 0.02$, $\chi_0 = 0.006$

The straight lines are given by $b = -(\chi_{AC} + \chi_{BC} - \chi_{AB})a/2\chi_{BC} \pm (\chi_0/\chi_{BC})^{1/2}$.
2-2: $\chi_{AB} = 0.002$, $\chi_{AC} = 0.01$, $\chi_{BC} = 0.02$, $\chi_0 = 0$
3-1: $\chi_{AB} = 0.01$, $\chi_{AC} = 0.100$, $\chi_{BC} = 0.02$, $\chi_0 = 0.006$

The straight lines L are given by $b = \{-f \pm (f^2 - g)^{1/2}\}a/2\chi_{BC}$, where $f = \chi_{AC} + \chi_{BC} - \chi_{AB}$, $g = 4\chi_{AC}\chi_{BC}$. $a_{1/2} = \pm(\chi_0/\chi_{AC})^{1/2}$, $b_{1/2} = \pm(\chi_0/\chi_{BC})^{1/2}$.

3-2: $\chi_{AB} = 0.01$, $\chi_{AC} = 0.100$, $\chi_{BC} = 0.02$, $\chi_0 = 0$

(3) $(\chi_{AC} + \chi_{BC} - \chi_{AB})^2 - 4\chi_{AC}\chi_{BC} > 0$

The region of miscibility is defined by the area between two symmetrically disposed hyperbolas when $\chi_0 > 0$; when $\chi_0 = 0$, the miscible region lies between two straight lines defined by $b = [-(\chi_{AC} + \chi_{BC} - \chi_{AB}) \pm \{(\chi_{AC} + \chi_{BC} - \chi_{AB})^2 - 4\chi_{AC}\chi_{BC}\}^{1/2}]a/2\chi_{BC}$.

These miscibility maps are schematically illustrated in Fig. A1.

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