Miscibility in (A–B)/(C–D) Copolymer Blends

Chai Zhikuan[†] **and Frank E. Karasz***

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received February 3, 1992; Revised Manuscript Received May 12, 1992

ABSTRACT: The phase behavior in 50/50 wt % blends of chlorinated poly(vinyl chloride) and poly(acrylonitrile-*co*-butadiene) [CPVC/(AN–BT)] and of chlorinated polyethylene and poly(acrylonitrile-*co*-butadiene) [CPE/(AN–BT)] was studied with differential scanning calorimetry. The boundaries of the miscibility regimes in isothermal copolymer–copolymer composition plots were elliptical and showed very little temperature dependence. Qualitatively the two systems showed similar miscibility behavior, although differences were observed when the chlorine contents of the CPVC and CPE components used were similar to that of poly(vinyl chloride) (PVC). These results for binary blends containing two random (or near-random) copolymers (i.e., an (A–B)/(C–D) system) were analyzed according to mean-field theory, from which the observed miscibility boundary shapes could be predicted and the values of the relevant segmental interaction parameters obtained. The analysis showed that miscibility in these systems results from repulsion between dissimilar segments in each copolymer.

Introduction

It has become clear that polymer miscibility can be attained (1) by introducing intermolecular-specific (favorable) interactions into the blended system or, less obviously, (2) by introducing intramolecular repulsive interactions into one or both of the constituent polymers. Mean-field (MF) theory for random copolymer blends provides a reasonable and consistent explanation for the second approach.[1-3] The basic MF theory employed here has three assumptions: (1) the free-volume effects need not be *explicitly* considered; (2) random mixing exists at or near the segmental level; and (3) the interactions among segments can be characterized by the individual segmental interaction parameters, which (in the simplest approximation) are not composition dependent. The theory is based on the standard Flory–Huggins expression for the free energy of mixing:

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \phi_1\phi_2\chi_{\text{blend}} \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, and r_1 and r_2 are their respective degrees of polymerization. The overall interaction parameter χ_{blend} is expressed as[4]

$$\chi_{\text{blend}} = \sum_{ij} C_{ij}\chi_{ij} \qquad (2)$$

where χ_{ij} ($i \neq j$) corresponds to each possible segmental interaction in a given system. The magnitudes of the coefficients C_{ij} are functions of the copolymer compositions, with $|C_{ij}| \leq 1$. Equation 2 indicates that miscibility may occur if the intramolecular mutual repulsion between dissimilar segments in a copolymer is sufficient to overcome the intermolecular repulsion between these segments and those of the second component of the mixture. This is because the coefficient C_{ij} in eq 2 is negative for *intra*molecular interactions, and positive χ_{ij}'s (repulsions, both inter- and intramacromolecular) may then cancel each other out to give an overall negative χ_{blend}.

The situation for the several different cases may be summarized as follows. If we consider binary blends that contain at least one random copolymer, we find that five binary combinations are possible (Table I). Blends of the first type, i.e., A/(A–B) systems, have a monomer (A) common to both the homopolymer and the copolymer; the blends of the second type, (A–B)/(A–B) systems, represent mixtures of the same copolymers with differing compositions. Both types of blends contain only two monomers and hence one segmental interaction parameter, χ_{AB}. Equation 2 then reduces to

$$\chi_{\text{blend}} = \chi_{AB}(1-x)^2 \qquad (3)$$

and

$$\chi_{\text{blend}} = \chi_{AB}(x-y)^2 \qquad (4)$$

for the two systems, respectively. Here x and y represent the mole fractions of A in the A–B copolymer species (see Table I). Relative to the miscibility in homopolymer (A/B) blends, the miscibility condition in these copolymer systems is relaxed by multiplying the interaction parameter with a composition factor, $(1-x)^2$ or $(x-y)^2$. Note that in these two types of blends (in contrast to those discussed below) miscibility *cannot* be achieved by intrasegmental repulsion. From a study of the miscibility behavior in these two groups, one can determine χ_{AB}.

Blends of the third type, A/(B–C) systems, contain three monomers and, therefore, three interaction parameters. Equation 2 reduces to

$$\chi_{\text{blend}} = x\chi_{AB} + (1-x)\chi_{AC} - x(1-x)\chi_{BC} \qquad (5)$$

Here x is the mole fraction of B in the B–C copolymer. Although in a given case all the χ_{ij}'s may be positive, i.e., the combinations of the corresponding homopolymers are immiscible, blends consisting of a homopolymer and a random copolymer may be miscible for a certain range of copolymer compositions because of segmental repulsion within the copolymer. This phenomenon has been termed a miscibility window.[2]

Blends of the fourth type, (A–B)/(C–B), again contain a common monomer. Three interaction parameters are also required to analyze these mixtures, and

$$\chi_{\text{blend}} = \chi_{AB}x^2 + (\chi_{AC} - \chi_{BC} - \chi_{AB})xy + \chi_{BC}y^2 \qquad (6)$$

(The composition variables x and y are defined in Table I.)

Blends of the fifth type, (A–B)/(C–D) systems—the most general case considered here—contain four monomers and

---

[†] Permanent address: Institute of Chemistry, Academia Sinica, Beijing, China.

0024-9297/92/2225-4716$03.00/0

Table I
Binary Blends of Random Copolymers

blends[a]	no. of segmental interaction param
$A_{r_1}/(A_xB_{1-x})_{r_2}$	1
$(A_xB_{1-x})_{r_1}/(A_yB_{1-y})_{r_2}$	1
$A_{r_1}/(B_xC_{1-x})_{r_2}$	3
$(A_xB_{1-x})_{r_1}/(C_yB_{1-y})_{r_2}$	3
$(A_xB_{1-x})_{r_1}/(C_yD_{1-y})_{r_2}$	6

[a] A, B, C, and D are monomeric units; r_1 and r_2 are degrees of polymerization of components 1 and 2; x and y are mole fractions.

require six interaction parameters; these will be discussed below.

Miscible blends of the type A/(B–C) have been extensively studied.[2,5–21] Systems of the types (A–B)/(C–B),[22–28] (A–B)/(A–B),[29–34] and (A–B)/(C–D)[35–41] have also been investigated.

We present here a further analysis of blends of the type (A–B)/(C–D) in the context of a study of the miscibility behavior in chlorinated poly(vinyl chloride)/acrylonitrile–butadiene copolymer [CPVC/(AN–BT)] and chlorinated polyethylene/acrylonitrile–butadiene copolymer [CPE/(AN–BT)] systems. Both partially chlorinated polymers can be regarded as random copolymers. Our study of CPVC/(AN–BT) blends has already been reported.[40] The present study included CPE blends, so that the effects of microstructural differences between CPVC and CPE in the two systems could be compared.

Theoretical Section

Miscibility Boundary. In the ten Brinke, Karasz, and MacKnight formulations,[2] the interaction parameter χ_{blend} between two random copolymers, $(A_xB_{1-x})_{r_1}$ and $(C_yD_{1-y})_{r_2}$ is written

$$\chi_{\text{blend}} = xy\chi_{\text{AC}} + (1-x)y\chi_{\text{BC}} + x(1-y)\chi_{\text{AD}} + (1-x)(1-y)\chi_{\text{BD}} - x(1-x)\chi_{\text{AB}} - y(1-y)\chi_{\text{CD}} \quad (7)$$

This equation reduces to eqs 3–6 for the respective special cases.

A function $g(x,y)$ is defined as

$$g(x,y) = \chi_{\text{blend}} - \chi_{\text{crit}} \quad (8)$$

where the combinatory term χ_{crit} is given (as usual) by

$$\chi_{\text{crit}} = \frac{1}{2}(r_1^{-1/2} + r_2^{-1/2})^2 \quad (9)$$

Miscibility or immiscibility in the equimolar blend is determined by the sign of $g(x,y)$; the region of miscibility is defined by the condition $g(x,y) < 0$ and the region of immiscibility by $g(x,y) > 0$. Thus the solution $g(x,y) = 0$ represents the miscibility–immiscibility boundary in the $0 \leq x, y \leq 1$ domain. Rearranging yields

$$\chi_{\text{AB}}x^2 + \chi_{\text{CD}}y^2 + (\chi_{\text{AC}} - \chi_{\text{BC}} - \chi_{\text{AD}} + \chi_{\text{BD}})xy + (\chi_{\text{AD}} - \chi_{\text{BD}} - \chi_{\text{AB}})x + (\chi_{\text{BC}} - \chi_{\text{BD}} - \chi_{\text{CD}})y + (\chi_{\text{BD}} - \chi_{\text{crit}}) = 0 \quad (10)$$

which has the generalized quadratic form

$$ax^2 + by^2 + cxy + dx + ey + f = 0 \quad (11)$$

The miscibility boundary is thus determined by the solution of a generalized quadratic equation whose variables are the compositions x and y of the two copolymers.

If χ_{ij}'s are regarded as independent of composition and concentration, several possible conic section miscibility boundaries are obtained from a consideration of eq 11 with the following conditions, as was shown by Ueda et al.[41]

condition: $c^2 - 4ab \equiv [(\chi_{\text{AC}} - \chi_{\text{BC}}) - (\chi_{\text{AD}} - \chi_{\text{BD}})]^2 - 4\chi_{\text{AB}}\chi_{\text{CD}}$	form of miscibility boundary
<0	ellipse
=0	parabola
>0	hyperbola

Schematic miscibility boundaries are shown in Figure 1, where the shaded and open areas represent the miscibility and immiscibility regimes, respectively. In principle, these domains could also be inverted. If $c \neq 0$, then the principal axes of the conic sections will be rotated relative to those shown in the schematic. The coefficients d and e (eq 11) determine the loci of the focal points of the curves. A parabolic boundary requires that $c^2 - 4ab = 0$ and is clearly rare. A number of other qualitative statements can be made. Examination of the condition for the miscibility boundary given above leads us to conclude that the first term on the left-hand side (c^2) represents the contribution of segmental dissimilarity in the two copolymers. The more dissimilar the two units in the copolymers are, the larger this term is, thus favoring a hyperbolic miscibility boundary. If both χ_{AB} and χ_{CD} have the same sign, then an elliptical boundary will be observed for large $\chi_{\text{AB}}\chi_{\text{CD}}$. If $\chi_{\text{AB}}\chi_{\text{CD}} = 0$ and at least one copolymer has two quite similar segments, then the miscibility boundary will again take the form of a hyperbola. If the term $\chi_{\text{AB}}\chi_{\text{CD}} < 0$, i.e., when one copolymer has repulsive intramolecular forces while the other has attractive intramolecular forces, a hyperbolic miscibility boundary will still be observed.

As already noted, the miscibility domain may lie either inside or outside the ellipse; its location is determined by the sign of $g(x,y)$. Typically, although all four possible pairs of homopolymers may be immiscible, one may find an elliptical boundary containing a regime in which the corresponding blends are miscible. A less probable situation may also obtain: even though the four pairs of homopolymers may be miscible, there may be blends of the corresponding copolymers whose phases are separated for certain compositions. Such systems could yield an ellipse containing an *immiscibility* region. The first case arises because of repulsion in the copolymers; the second is due to self-segregation in the copolymers (requiring very large negative intramolecular segmental interaction parameters). Essentially parallel arguments may be made for the parabolic and hyperbolic boundary cases.

Segmental Interaction Parameter. From eq 10 it is seen that six interaction parameters fully determine the miscibility boundary for (A–B)/(C–D) blends, but the converse situation is not true. Thus, when eq 11 is multiplied by the arbitrary parameter k ($-\infty < k < +\infty$), we obtain

$$\chi_{\text{AB}} = ka = k\chi_{\text{AB}}^\circ$$

$$\chi_{\text{CD}} = kb = k\chi_{\text{CD}}^\circ$$

$$\chi_{\text{BD}} = kf + \chi_{\text{crit}} = k\chi_{\text{BD}}^\circ + (1-k)\chi_{\text{crit}}$$

$$\chi_{\text{AD}} = k(a + d + f) + \chi_{\text{crit}} = k\chi_{\text{AD}}^\circ + (1-k)\chi_{\text{crit}}$$

$$\chi_{\text{BC}} = k(b + e + f) + \chi_{\text{crit}} = k\chi_{\text{BC}}^\circ + (1-k)\chi_{\text{crit}}$$

$$\chi_{\text{AC}} = k(a + b + c + d + e + f) + \chi_{\text{crit}} = k\chi_{\text{AC}}^\circ + (1-k)\chi_{\text{crit}} \quad (12)$$

where χ_{ij}° is the χ_{ij} for $k = 1$. Equation 12 shows that a given miscibility boundary cannot yield a unique solution

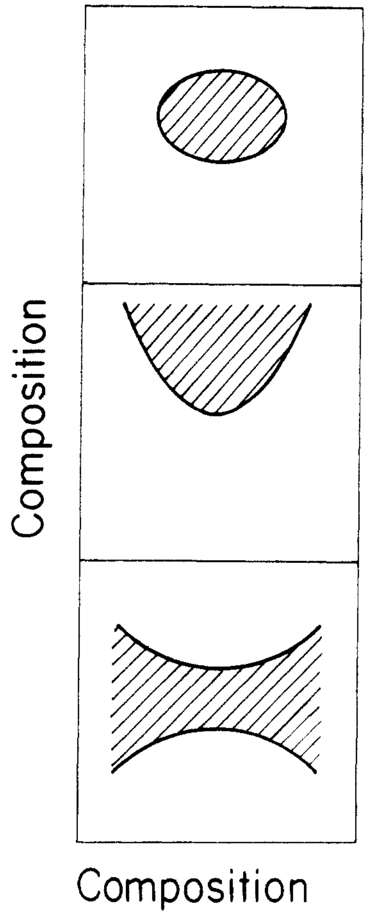

Figure 1. Schematic of theoretical miscibility boundaries for (A–B)/(C–D) blends. The shaded and open areas differentiate the miscibility and immiscibility regions; see text.

for all χ_{ij}; this is because only five of the six parameters, a, b, ..., f in eq 11 are independent.

We note, similarly, that for A/(B–C) blends, eq 5 can be rewritten as

$$ax^2 + bx + c = 0 \qquad (13)$$

It can be shown that only two of the three parameters in eq 13 are independent. A unique solution of χ_{ij} also cannot be obtained in this case from a simple determination of the miscibility boundaries. However, for (A–B)/(C–B) blends, eq 6 can be rewritten as

$$ax^2 + by^2 + cxy + d = 0 \qquad (14)$$

Three of the four parameters in eq 14 are independent. Because there are only three unknown χ_{ij} for blends of this type, a unique solution can be obtained from the miscibility boundary of (A–B)/(C–B) blends, as has been previously demonstrated.[22]

Experimental Section

Poly(vinyl chloride) (PVC; Geon 103-EP; M_w = 209 000, M_n = 136 000) was obtained from B. F. Goodrich. Linear high-density polyethylene (M_w = 23 700, M_n = 9420) was obtained from Pressure Chemical. CPVC and CPE fractions with specific chlorine contents were prepared by solution chlorinations of the PVC and polyethylene as described previously.[30,41] This reaction yielded copolymers of constant degrees of polymerization. The chlorine content was determined by elemental analysis (University of Massachusetts Microanalytical Laboratories). AN–BT copolymers and a polybutadiene homopolymer (M_w = 200 000) were obtained from Scientific Polymer Products and B. F. Goodrich, respectively.

The blends were prepared by dissolving AN–BT and PVC, CPVC, or CPE in a common solvent, tetrahydrofuran (2% w/v). The mixture was stirred overnight and then slowly evaporated. The ratio of the two polymers in the blends was 50/50 by weight. The cast films were dried in a vacuum oven at 50 °C for 5–7 days.

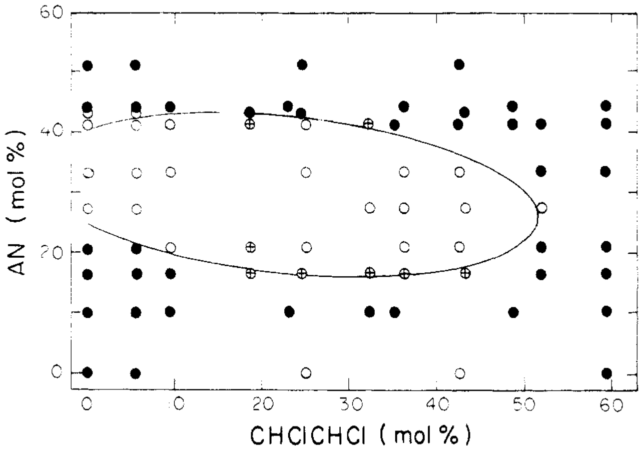

Figure 2. Isothermal phase diagram of 50/50 CPVC/(AN–BT) blends at 70 °C; (○) one phase; (●) two phases at 70 °C; (⊕) one phase at 70, 110, and 150 °C but two phases at 190 °C. Reprinted with permission from: Chai, Z.; Sun, R.; Karasz, F. E. *Mechanical Behaviour of Materials-VI* **1991**, *3*, 263.

The miscibility behavior of the blends was studied by observing the glass transitions using a Perkin-Elmer DSC-4 differential scanning calorimeter. The samples were annealed at elevated temperatures for 15 min in the DSC and were then quenched to a temperature below the lower component T_g. Thermal analyses of the annealed samples were carried out at a heating rate of 20 °C/min for sample sizes of 10–20 mg.

Results and Discussion

In the following discussion samples CPVC and CPE are identified by their chlorine content (wt %). At moderate levels of chlorination, the content of CCl_2 units in the molecule is assumed to be negligible in both polymers.[42,43] Thus, CPVC can be regarded as a random copolymer of CHClCHCl and CH_2CHCl units and can be represented as $[(CHClCHCl)_x(CH_2CHCl)_{1-x}]_{r_1}$; CPE can be represented as $[(CHCl)_x(CH_2)_{1-x}]_{r_1}$. The weight percentage chlorine content of the chlorinated polymer can be converted into mole fraction x of unit A in the copolymer by using the formula

$$\frac{xM_AW_B + (1-x)M_BW_B}{xM_A + (1-x)M_B} = \text{Cl wt \%} \qquad (15)$$

where M_A and M_B are the molecular weights of units A and B, and W_A and W_B are the weight fractions of chlorine in the units. CHClCHCl and CHCl represent unit A in the respective copolymers. AN–BT can be represented simply as $(AN_yBT_{1-y})_{r_2}$. Samples of this copolymer are identified by their mole fraction of AN. It is assumed that the mole fractions are equal to the corresponding volume fractions.

Figure 2 shows the miscibility behavior of CPVC/(AN–BT) blends at 70 °C, i.e., the temperature at which these samples were annealed in the DSC before measurement. Those samples exhibiting one glass transition in the thermogram were said to be miscible. The miscibility boundary is clearly seen to be an ellipse, and by conventional analysis, the equation for this ellipse was determined to be

$$0.0420x^2 + 0.1862y^2 + 0.0515xy - 0.0342x - 0.1205y + 0.0182 = 0 \qquad (16)$$

where eq 16 has been normalized to $k = 1$ by using a known value for one of the χ_{ij}'s (see below). Outside the ellipse, the blends are phase separated; inside the ellipse, the blends are in one phase. The samples were also annealed

Table II
Values of Segmental Interaction Parameters

interacting segments	χ_{ij} notation	 value
CPVC/(AN–BT) System		
$CHClCHCl/CH_2CHCl$	χ_{AB}	0.042[a]
CHClCHCl/AN	χ_{AC}	0.144
CHClCHCl/BT	χ_{AD}	0.027
CH_2CHCl/AN	χ_{BC}	0.085
CH_2CHCl/BT	χ_{BD}	0.019
AN/BT	χ_{CD}	0.186
CPE/(AN–BT) System		
$CHCl/CH_2$	χ_{AB}	0.092
CHCl/AN	χ_{AC}	0.113
CHCl/BT	χ_{AD}	0.030
CH_2/AN	χ_{BC}	0.123
CH_2/BT	χ_{BD}	0.040
AN/BT	χ_{CD}	0.186[b]

[a] From ref 22. [b] From the CPVC/(AN–BT) system.

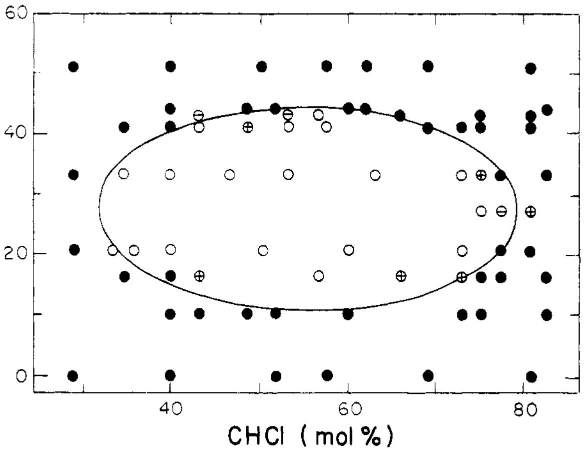

Figure 3. Isothermal phase diagram of 50/50 CPE/(AN–BT) blends at 70 °C: (○) one phase; (●) two phases at 70 °C; (⊖) one phase at 70 °C but two phases at 110 °C; (⊕) one phase at 70, 110, and 150 °C but two phases at 190 °C. Reprinted with permission from: Chai, Z.; Sun, R.; Karasz, F. E. *Mechanical Behaviour of Materials-VI* **1991**, *3*, 263.

at 110 and 150 °C; within experimental error, the miscibility boundary was unchanged at these annealing temperatures. However, when the samples were annealed at 190 °C, certain blends became phase separated (circled pluses in Figure 2). Thus this system exhibited LCST behavior.[40] No measurements were made above 190 °C because the chlorinated polymers were not sufficiently stable above that temperature.

As noted earlier, there are only five independent equations for the six unknown segmental interaction parameters that can be derived from an elliptical miscibility boundary. An additional equation is thus needed to obtain all the interaction parameters unequivocally. A previously obtained value[22] for the segmental interaction parameter $\chi_{(CHClCHCl/CH_2CHCl)} = 0.042$ was used. The parameter $\chi_{crit} = 0.001$ was calculated (eq 9) by using the known average degrees of polymerization. Using these two values, we obtained the other five interaction parameters, which are listed in Table II. The data are in good agreement with earlier results from this laboratory.[40]

Figure 3 shows the miscibility behavior of CPE/(AN–BT) blends at 70 °C. The miscibility boundary of this system was also elliptical, and the corresponding best fit equation is

$$0.0918x^2 + 0.1860y^2 - 0.1019x - 0.1030y + 0.0372 = 0 \quad (17)$$

(also normalized to $k = 1$). Again the blends outside the ellipse were phase separated, whereas the blends inside the ellipse were miscible. These blends also showed LCST behavior, a conclusion deduced from the fact that some miscible blends near the miscibility boundary became phase separated at higher annealing temperatures, as shown in Figure 3. For the reason mentioned above with respect to CPVC-containing blends, no measurements were performed above 190 °C for CPE-containing blends. Using eq 17 and the values $\chi_{(AN/BT)} = 0.186$ (obtained from analysis of the first system) and $\chi_{crit} = 0.003$ (calculated from the degrees of polymerization), we obtained the remaining five interaction parameters (Table II).

All the interaction parameters in the two systems were positive (Table II). Recall that the first four terms in eq 7 represent a tendency for demixing in the mixture and the last two terms characterize a mixing tendency. Thus, as seen previously, the blends were miscible for a certain range of copolymer compositions because of sufficiently repulsive forces between the different units in each copolymer, especially in AN–BT. Because $\chi_{(AN/BT)}$ is much larger than either $\chi_{(CHClCHCl/CH_2CHCl)}$ or $\chi_{(CHCl/CH_2)}$, χ_{blend} changes sharply with the AN–BT composition in the direction parallel to the y-axis of the copolymer–copolymer composition plot, which results in a narrower miscibility gap in this direction and, conversely, a broader miscibility gap in the direction parallel to the x-axis, as is clearly seen in Figures 2 and 3.

Each segmental interaction parameter must be assumed to be temperature dependent. However, χ_{blend} is a combination of the six χ_{ij}'s (eq 7), with some presumed cancellation of temperature-dependent terms, and thus in principle can yield a small overall temperature dependence. This can explain why the miscibility boundaries were unchanged over a relatively wide temperature range (70–150 °C).

The copolymers CPVC and CPE both contain only two basic units, CH_2 and CHCl. Therefore, samples of CPVC and CPE with a given chlorine content will differ only in their microstructures. The parent PVC contains an infinite sequence of alternating CH_2 and CHCl units; CPVC can be regarded as a derivation of the parent sequence containing randomly substituted CHCl units for CH_2 units. CPE, on the other hand, contains a completely random array of these two moieties. We assume here that the chemical modifications have been carried out to yield random structures. Thus any difference in the miscibility behavior when the two chlorinated polymers are mixed with a third polymer must be due to the sequence distribution. Differences are most likely to occur in those blends in which the chlorinated polymers have a chlorine content near that of PVC, because the two chains show the largest difference in microstructure at this chlorine content.

The two systems are compared in Figure 4 in terms of the chlorine content of the respective copolymers. (Note that the original ellipses are slightly distorted in this modified coordinate system.) The two miscibilities are quite similar at higher chlorine contents, but, around 57 wt % chlorine, some blends of CPE/(AN–BT) were miscible, whereas corresponding blends of CPVC/(AN–BT) were not. These immiscible blends were at the low AN weight percentage range, where the repulsion in AN–BT, as determined by the term $y(1 - y)\chi_{CD}$, eq 7, is not large enough to dominate the sign of χ_{blend}. We have also shown[41] that mixtures of CPVC and CPE with identical chlorine contents are largely immiscible; in this case their microstructural difference is the main factor in deter-

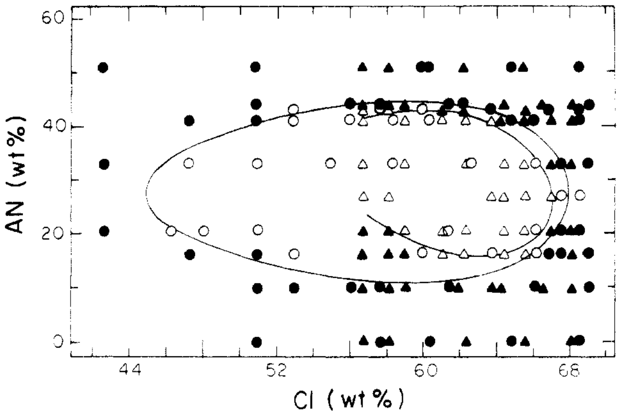

Figure 4. Comparison of miscibility behavior in CPVC/(AN-BT) (△, ▲) and CPE/(AN-BT) (○, ●) blends at 70 °C. The open and filled symbols indicate one and two phases, respectively.

mining miscibility. However, when either of these polymers is mixed with a third polymer of differing chemical structure, this difference becomes less important if there are sufficiently strong (dispersive or specific) interactions in the mixtures.

Conclusions

From an analysis of the mean-field theory of random copolymer blends, we find that the miscibility boundary of (A–B)/(C–D) blends takes one of three basic forms—ellipse, parabola, or hyperbola—in an isothermal copolymer composition–composition plot. The domain of miscibility may in principle lie on either side of the boundary. A unique solution for the segmental interaction parameters cannot be obtained from the measured miscibility boundary of either the A/(B–C) blend or the (A–B)/(C–D) blend. Such boundaries may, however, be used to obtain unequivocally the respective segmental interaction parameters for A/(A–B), (A–B)/(A–B), and (A–B)/(C–B) systems.

The CPVC/(AN–BT) and CPE/(AN–BT) systems display elliptically bounded miscibility domains as predicted. The interaction parameters obtained indicate that miscibility results from repulsion between the dissimilar units in each copolymer. The miscibility boundaries for these cases are nearly independent of temperature in the range of 70–150 °C. The two systems have generally similar miscibility properties, but some differences in the blends containing CPVC and CPE with chlorine contents similar to that of PVC are observed. The differences are due to the accentuated difference in microstructure between the two chlorinated polymers in this range.

Acknowledgment. We gratefully acknowledge support from B. F. Goodrich and the Air Force Office of Scientific Research through AFOSR Grant No. 91-001.

References and Notes

(1) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(2) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(3) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(4) Karasz, F. E.; MacKnight, W. J. *ACS Symp. Ser.* **1986**, *211*, 67.
(5) Hammer, C. F. *Macromolecules* **1971**, *4*, 69.
(6) Zakrzewski, G. A. *Polymer* **1973**, *14*, 347.
(7) Stein, D. J.; Jung, R. H.; Illers, K. H.; Hendus, H. *Angew. Makromol. Chem.* **1974**, *36*, 89.
(8) McMaster, L. P. *Adv. Chem. Ser.* **1975**, *143*, 43.
(9) Alexandrovich, P. R.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1977**, *18*, 1022.
(10) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1978**, *11*, 150.
(11) Chion, J. S.; Paul, D. R.; Barlow, J. W. *Polymer* **1982**, *23*, 1543.
(12) Goh, S. H.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1982**, *22*, 34.
(13) Vukovic, R.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1983**, *24*, 529.
(14) Vukovic, R.; Kuresevic, V.; Segudovic, N.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Polym. Sci.* **1983**, *28*, 1379.
(15) Chiu, S. C.; Smith, T. G. *J. Appl. Polym. Sci.* **1984**, *29*, 1797.
(16) Maeda, Y.; Karasz, F. E.; MacKnight, W. J.; Vukovic, R. *J. Polym. Sci., Part B* **1986**, *24*, 2345.
(17) Min, K. E.; Paul, D. R. *J. Appl. Polym. Sci.* **1989**, *37*, 1153.
(18) Kim, H. I.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1989**, *22*, 3498.
(19) Kim. J. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Part B* **1989**, *27*, 2211.
(20) Kressler, J.; Kammer, H.-W.; Morgenstern, U.; Litauszki, B.; Berger, W. *Makromol. Chem.* **1990**, *191*, 243.
(21) Cowie, J. M. G.; McEwen, I. J.; Nadvornik, L. *Macromolecules* **1990**, *23*, 5106.
(22) Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 2274.
(23) Cowie, J. M. G.; Lath, D. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 103.
(24) Kressler, J.; Kammer, H.-W.; Schmidt-Naake, G.; Herzog, K. *Polymer* **1988**, *29*, 686.
(25) Kim, J. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Part B* **1989**, *27*, 223.
(26) Shiomi, T.; Eguchi, T.; Ishimatsu, H.; Imai, K. *Macromolecules* **1990**, *23*, 4978.
(27) Brannock, G. R.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Part B* **1990**, *28*, 871.
(28) Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. *Polymer* **1990**, *31*, 905.
(29) Chai, Z.; Sun, R. *Polymer* **1983**, *24*, 1279.
(30) Ueda, H.; Karasz, F. E. *Macromolecules* **1985**, *18*, 2719.
(31) Braun, D.; Herth, J.; Hellmann, G. P. *Angew. Makromol. Chem.* **1989**, *171*, 53.
(32) Hellmann, G. P.; Kohl, P. R.; Herth, J.; Neumann, H. J.; Andradi, L. N.; Lowenhaupt, B. *Macromol. Chem., Macromol. Symp.* **1990**, *38*, 17.
(33) Kohl, P. R.; Seifert, A. M.; Hellmann, G. P. *J. Polym. Sci., Part B* **1990**, *28*, 1309.
(34) Salomons, W.; ten Brinke, G.; Karasz, F. E. *Polym. Commun.* **1991**, *32*, 185.
(35) Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 2644.
(36) Shiomi, T.; Suzaki, M.; Tohyana, M.; Imai, K. *Macromolecules* **1989**, *22*, 3578.
(37) Litauszki, B.; Schmidt-Naake, G.; Kressler, J.; Kammer, H.-W. *Polym. Commun.* **1989**, *30*, 359.
(38) Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. *Polymer* **1990**, *31*, 486.
(39) Cowie, J. M. G.; Elexpuru, E. M.; McEwen, I. J. *J. Polym. Sci, Part B* **1991**, *29*, 407.
(40) Huh, W.; Karasz, F. E. *Macromolecules* **1992**, *25*, 1057.
(41) Ueda, H.; Karasz, F. E. *Polym. J. (Jpn.)*, in press.
(42) Komoroski, R. A.; Parker, R. G.; Shockcor, J. P. *Macromolecules* **1985**, *18*, 1257.
(43) Chai, Z.; Shi, L.; Sheppard, R. N. *Polymer* **1984**, *25*, 369.

Registry No. AN/BT (copolymer), 9003-18-3.