

Miscibility in Blends of Copolymers: Sequence Distribution Effects

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ABSTRACT: Differential scanning calorimetry was used to study the phase behavior in binary blends of copolymers containing the same monomer units, but differing in composition. Examples are chlorinated poly(vinyl chloride) (CPVC), copolymers of methyl and ethyl methacrylate (MMA-EMA), and chlorinated polyethylene (CPE). We find that in the first two systems miscibility can be described in terms of simple mean-field theory for random copolymer blends. Thus the miscibility-immiscibility boundaries for these systems are represented in an isothermal copolymer-copolymer composition plot by two straight lines parallel to the diagonal. Specifically, it was not necessary to invoke sequence distribution effects to account for the observations. In contrast, the miscibility boundaries in the CPE system display deviations from the first-order mean-field theory; the miscibility-immiscibility boundaries display substantial convexities ("bulges") relative to the diagonal, a finding that has been interpreted previously—and in this contribution—in terms of a sequence distribution effect. A new equation based on a revised assumption for triad interaction parameters has been derived for χ_{blend} , the net copolymer-copolymer interaction parameter. The new equation gives an improved description of the observed miscibility. When $\chi_{\text{AAA;BBB}}$ (the triad parameter corresponding to homopolymer interactions in this approximation) is known, the remaining eight nonzero triad interaction parameters, including $\chi_{\text{ABA;BAB}}$, can be determined. In this analysis the large miscibility behavior difference between CPVC/CPVC and CPE/CPE blends can be attributed to the effect of microstructure. Triad interaction parameters $\chi_{ijk;lmn}$ as here defined represent segmental interactions between j and m segments, in each case flanked by the same or differing segments as indicated by the subscripts.

Introduction

The mean-field theory of random copolymer blends plays an important role in the thermodynamics of polymer miscibility.¹⁻³ The theory suggests a new approach to making a miscible polymer blend that takes advantage of the tendency of a copolymer to mix if the copolymer has two constituents that repel each other.

Both before and since the appearance of this treatment, there have been many studies of AB/C-type blends,⁴⁻²⁰ where AB represents a random copolymer of A and B moieties and C a homopolymer of C-mers. In fact, the discovery of the so-called miscibility window phenomenon in this group of blends promoted the development of the theory, which explains why, *inter alia*, even though the homopolymers A, B, and C are immiscible in any binary combination, C may be miscible with the AB random copolymer for certain compositions. Studies of each of the other classes of copolymer blends, such as A/AB, AB/AB,²¹⁻²⁶ AB/CB,²⁷⁻³³ and AB/CD³⁴⁻³⁸ blends, are so far less numerous.

In this contribution we discuss miscibility in one of the simplest cases, *i.e.*, in AB/AB blends. These are blends of two samples of the same copolymer that have different compositions. According to first-order random copolymer blend theory,² the interaction parameter of such a blend is

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

where χ_{AB} is the segment pair interaction parameter, and x and y are the molar fractions of A in the respective copolymers. In this approximation the isothermal miscibility-immiscibility boundaries are a pair of straight parallel lines symmetrically disposed with respect to the diagonal on a copolymer-copolymer composition plot,

defined by

$$\chi_{\text{crit}} = \chi_{\text{blend}} \quad (2)$$

The critical value of blend interaction is derived from the usual equation for the combinatorial entropy of the mixture:

$$\chi_{\text{crit}} = \frac{1}{2}(r_1^{-0.5} + r_2^{-0.5})^2 \quad (3)$$

where r_1 and r_2 are the number-average degrees of polymerization for components 1 and 2. Blends for which $\chi_{\text{blend}} < \chi_{\text{crit}}$ are in the one-phase region; blends for which $\chi_{\text{blend}} > \chi_{\text{crit}}$ are in the two-phase region. In previous work, we found, however, that the miscibility boundaries for CPE/CPE blends are not parallel straight lines. Instead, the miscible regime is enlarged by symmetrical bulges convex to the diagonal in the copolymer-copolymer composition plot.^{21,39}

Balazs et al. first explained this discrepancy in terms of a sequence distribution effect for both AB/C and AB/AB systems.^{39,40} They postulated that the interactions between two given monomer units are dependent on the nature of the respective intramacromolecular nearest neighbors. Therefore the theory was elaborated to include interactions between differing triads of monomer units in copolymers and finally predicted, for example, that, at a fixed composition, there is an optimal range of sequence distributions in which AB/C blends are miscible. This additional factor was also responsible for the nonparallel miscibility boundaries in an AB/AB system. In a further development, Cantow and Schulz proposed an alternative treatment for the sequence distribution effect of copolymer blends;⁴¹ they also used the triad interaction approach, but with different simplifying assumptions.

Balazs et al. assumed that in AB/C blends

$$\bar{\chi}_{\text{AC}} = \chi_{\text{BAB;C}} = \chi_{\text{AAB;C}} = \chi_{\text{BAA;C}} \neq \chi_{\text{AAA;C}} \quad (4a)$$

and defined

$$\bar{\chi}_{\text{BC}} = \chi_{\text{ABA;C}} = \chi_{\text{ABB;C}} = \chi_{\text{BBA;C}} \neq \chi_{\text{BBB;C}}$$

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$$\Delta\chi_A = \chi_{AAA;C} - \bar{\chi}_{AC} \quad (4b)$$

$$\Delta\chi_B = \chi_{BBB;C} - \bar{\chi}_{BC}$$

where BAB, AAB, and so on are triad sequences of monomer units in a copolymer, and $\chi_{\text{triad};C}$ is the interaction parameter of the particular triad with the monomer unit C of the C homopolymer. Cantow and Schulz made a different assumption:

$$\chi_{AAA;C} - \chi_{AAB;C} = \chi_{AAB;C} - \chi_{BAB;C} \quad (5)$$

$$\chi_{BBB;C} - \chi_{BBA;C} = \chi_{BBA;C} - \chi_{ABA;C}$$

and defined $\Delta\chi_A$ and $\Delta\chi_B$ as equal to these differences, respectively.

The first assumption (eqs 4) implies that all the triads with a given center segment will have the same interaction energy with C except for the homoblock triads AAA and BBB, whereas the second assumption (eqs 5) implies that the interaction energy changes as the number of respective monomer units changes, but the differences between interaction energies are equal. The Cantow-Schulz theory, however, has never been applied to experimental results.

In this contribution, we have studied three AB/AB systems—CPVC/CPVC, (MMA-EMA)/(MMA-EMA), and CPE/CPE—and have derived, on the basis of the Cantow-Schulz assumption, new equations for interactions between the components in AB/C and AB/AB blends. We also compare the analysis based on the new equations with that provided by the Balazs et al. theory.

Theoretical Section

AB/C Blends. We first consider the simplest case, namely, a copolymer-homopolymer blend system. For such an AB/C system, the net blend interaction parameter is given in the Balazs et al. treatment⁴⁰ by

$$\begin{aligned} \chi_{\text{blend}}\phi_{AB}\phi_C = & \chi_{BAB;C}\phi_A(f_{AB}/f_A)^2\phi_C + \\ & 2\chi_{BAA;C}\phi_A(f_{AA}f_{AB}/f_A^2)\phi_C + \chi_{AAA;C}\phi_A(f_{AA}/f_A)^2\phi_C + \\ & \chi_{ABA;C}\phi_B(f_{AB}/f_B)^2\phi_C + 2\chi_{ABB;C}\phi_B(f_{BB}f_{AB}/f_B^2)\phi_C + \\ & \chi_{BBB;C}\phi_B(f_{BB}/f_B)^2\phi_C + \bar{\chi}_{AB}^2\phi_A\phi_B - \bar{\chi}_{AB}\phi_{AB}/f_B \quad (6) \end{aligned}$$

In eq 6 the first six terms on the right-hand side represent the interactions of the triads in the copolymer with the homopolymer in the blend; the seventh term is the interaction of two monomeric segments of the copolymer in the mixture; the last term is the same interaction in the copolymer before mixing. Following Balazs' first paper,⁴⁰ all possible interactions between A- and B-centered triads are assumed to be equivalent, with an average interaction parameter $\bar{\chi}_{AB}$. The parameters ϕ_{AB} and ϕ_C are the volume fractions of the two polymers in the blends; ϕ_A and ϕ_B are the total segment volume fractions of A and B in the blend; f_A and f_B are the segmental volume fractions in the copolymer sequence; and f_{AA} , f_{BB} , and f_{AB} are the probabilities of finding AA, BB, and AB neighbor pairs in the copolymer. These variables are related through the following equations:

Table I
Triads in AB Copolymers

index no.	triad	index no.	triad
1	BAB	4	ABA
2	AAB, BAA	5	ABB, BBA
3	AAA	6	BBB

$$f_A = f_{AA} + f_{AB}$$

$$f_B = f_{BB} + f_{BA}$$

$$f_{AB} = f_{BA}$$

$$f_A + f_B = 1$$

$$\phi_A + \phi_B = \phi_{AB}$$

$$f_A\phi_{AB} = \phi_A$$

$$f_B\phi_{AB} = \phi_B$$

$$\phi_{AB} + \phi_C = 1 \quad (7)$$

Using eqs 5, the Cantow-Schulz assumption, we obtain the corresponding equation

$$\chi_{\text{blend}} = f_A\chi_{AAA;C} + f_B\chi_{BBB;C} - f_A f_B \bar{\chi}_{AB} - 4(\Delta\chi_A + \Delta\chi_B)\theta f_A f_B \quad (8)$$

where θ was introduced by Balazs et al. as

$$f_{AB} = 2\theta f_A f_B$$

The θ parameter describes the binary sequence distribution of the monomer units in a copolymer chain: for example, $\theta = 0, 0.5$, and 1 ($f_A = f_B = 0.5$ for the last case) describes block, random, and alternating copolymers, respectively.

The interaction parameter χ_{blend} is a linear function of θ ; and

$$\partial\chi_{\text{blend}}/\partial\theta = -4(\Delta\chi_A + \Delta\chi_B)f_A f_B \quad (9)$$

at a fixed composition of copolymer. Depending on the sign of $\Delta\chi_A + \Delta\chi_B$, either a more blocky or a more alternating structure will favor mixing in an AB/C system. From eqs 5, we observe, for instance, that $\Delta\chi_A + \Delta\chi_B < 0$ indicates $\chi_{AAA;C} + \chi_{BBB;C} < \chi_{AAB;C} + \chi_{BBA;C} < \chi_{BAB;C} + \chi_{ABA;C}$; i.e., the interactions between blocky triads and a C unit are smaller than that of the alternating triads with C units. The parameter χ_{blend} increases with θ in this case; therefore the more blocky sequence (ultimately $\theta = 0$) favors mixing. Because χ_{blend} is not quadratic in θ , it will not have an extremum, and one cannot predict either a miscibility or an immiscibility window as a function of sequence distribution at a fixed composition, in contrast to the result of Balazs et al. (Figure 2, ref 40).

AB/AB Blends. When two copolymers in a mixture differ only in composition, 6 triad sequences and therefore 15 triad interaction parameters $\chi_{a,b}$ are required to completely describe the system (Table I). If we let a and b correspond to the index numbers of the triad sequences listed in the table, then we see, however, that 6 of the 15 parameters can be set at zero, because the interacting pairs have identical center monomers: i.e., $\chi_{12} = \chi_{13} = \chi_{23} = \chi_{45} = \chi_{46} = \chi_{56} = 0$. Using assumptions parallel to those contained in eqs 5, we obtain the following six equations, five of which are independent. We can, in principle, solve for five interaction parameters; so, of the nine nonzero interaction parameters, only four remain unknown:

$$\begin{aligned}
\Delta_1 &= \chi_{36} - \chi_{26} = \chi_{26} - \chi_{16} \\
\Delta_2 &= \chi_{35} - \chi_{25} = \chi_{25} - \chi_{15} \\
\Delta_3 &= \chi_{34} - \chi_{24} = \chi_{24} - \chi_{14} \\
\Delta_4 &= \chi_{36} - \chi_{35} = \chi_{35} - \chi_{34} \\
\Delta_5 &= \chi_{26} - \chi_{25} = \chi_{25} - \chi_{24} \\
\Delta_6 &= \chi_{16} - \chi_{15} = \chi_{15} - \chi_{14}
\end{aligned} \quad (10)$$

It is easy to see that

$$\Delta_6 - \Delta_5 = \Delta_5 - \Delta_4 = \Delta_3 - \Delta_2 = \Delta_2 - \Delta_1$$

Following Balazs et al., we use $\phi_{AB'}$, ϕ_i' , g_i , and g_{ij} ($i, j = A, B$) to describe the second copolymer chain, where ϕ' and g have the same definitions as ϕ and f have for the first chain. The variables of this second set have the same relations as those in eqs 7, except that $\phi_{AB} + \phi_{AB'} = 1$ replaces $\phi_{AB} + \phi_C = 1$.

Counting the triad pair interactions in the same way as in eq 6, we obtain

$$\chi_{\text{blend}} = \chi_{25}(f_A - g_A)^2 + [\Delta_2(F_A - G_A) - \Delta_5(F_B - G_B)](f_A - g_A) + (\Delta_6 - \Delta_5)(F_A - G_A)(F_B - G_B) \quad (11)$$

where $F_A = f_{AA} - f_{AB}$, $F_B = f_{BB} - f_{AB}$, $G_A = g_{AA} - g_{AB}$, and $G_B = g_{BB} - g_{AB}$. When all $\Delta_i = 0$, the blend has no sequence distribution effect, and eq 11 reduces to eq 1.

If both copolymers in a blend have the same composition ($f_A = g_A$), eq 11 reduces to

$$\chi_{\text{blend}} = 4(\Delta_6 - \Delta_5)(f_{AB} - g_{AB})^2 \quad (11')$$

Miscibility is then determined only by the sign of $\Delta_6 - \Delta_5$. Using eq 10, we observe, for instance, that $\Delta_6 - \Delta_5 > 0$ implies

$$\chi_{16} + \chi_{34} > \chi_{14} + \chi_{36}$$

$$\chi_{15} + \chi_{24} > \chi_{14} + \chi_{25}$$

$$\chi_{26} + \chi_{35} > \chi_{25} + \chi_{36}$$

In this case, it is possible for a blend to be immiscible. The parameters χ_{14} , χ_{25} , and χ_{36} represent interactions between BAB and ABA, AAB and BBA, and AAA and BBB triads, respectively. The others are "cross" interactions between different types of triads.

If both copolymers have the same θ value (i.e., the same microstructure), from the condition $\partial\chi_{\text{blend}}/\partial\theta = 0$ at fixed f_A and g_A we obtain

$$\theta_C = \frac{(f_A - g_A)(\Delta_2 - \Delta_5)}{8(\Delta_6 - \Delta_5)(f_A f_B - g_A g_B)}$$

where χ_{blend} represents an extremum at θ_C (cf. Figure 2, ref 40). From the condition

$$\frac{\partial^2 \chi_{\text{blend}}}{\partial \theta^2} = 32(\Delta_6 - \Delta_5)(f_A f_B - g_A g_B)^2$$

we see that when $\Delta_6 > \Delta_5$ the χ_{blend} extremum is a minimum. The system thus may have a miscibility window for certain sequence distributions at fixed compositions of the two copolymers. In the opposite case, $\Delta_6 < \Delta_5$, either blocky or alternating copolymer blends would tend to be more miscible.

If both copolymers are exactly statistically random copolymers, then $\theta = 0.5$ and eq 11 becomes

$$\chi_{\text{blend}} = (f_A - g_A)^2[(\chi_{25} - \Delta_2 + 3\Delta_6) + (2\Delta_2 + 6\Delta_5 - 8\Delta_6)(f_A + g_A) + 4(\Delta_6 - \Delta_5)(f_A + g_A)^2] \quad (12)$$

As a special case, when $f_A = 1$, $g_A = 0$, or $f_A = 0$, $g_A = 1$ (i.e., for an A/B homopolymer blend), χ_{blend} (eq 12) reduces to χ_{36} [i.e., χ_{AB} (eq 1)], as it should.

Experimental Section

The polymers CPVC and CPE were prepared by solution chlorination, as previously described.²² The chlorine content was determined by chemical analysis. The starting polymers, PVC and high-density polyethylene, were obtained from Scientific Polymer Products and Aldrich, respectively. The number-average molecular weight of PVC was 57 300. The number-average molecular weight of a CPE sample (54.4 Cl wt %) was found by GPC to be 48 000 relative to polystyrene standards. The (MMA-EMA) copolymers were synthesized by Springborn Laboratories.

The blends were prepared by dissolving the copolymers in tetrahydrofuran (2% w/v). The mixture was stirred overnight and then slowly evaporated. The blend ratio of the 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 these blends was studied conventionally by observing the glass transition with a Perkin-Elmer DSC-4. The samples were annealed at elevated temperature for 15 min in the DSC and then quenched to a temperature below the lower of the T_g 's of the components. Thermal analyses of the annealed samples were carried out at a heating rate of 20 °C/min with sample sizes of 10–20 mg.

Results and Discussion

In the following discussion both CPE and CPVC are identified by their chlorine content in weight percentage. At low levels of chlorination, the content of CCl_2 units in the molecule is assumed to be negligible in both polymers.^{42,43} Thus CPE and CPVC can be regarded simply as a copolymer of CHCl and CH_2 or of CHClCHCl and CH_2CHCl , respectively. We can convert weight percentage (or weight fraction) chlorine content in the copolymer into mole fraction (X) of unit A in the copolymer with the formula

$$\frac{XM_A W_A + (1 - X)M_B W_B}{XM_A + (1 - X)M_B} = \text{Cl wt fraction}$$

where M_A and M_B are molecular weights of units A and B, and W_A and W_B are the respective weight fractions of chlorine in the units. CHCl and CHClCHCl are unit A in the respective copolymers. In the third system, (MMA-EMA) also is defined by the mole fraction of the first component. We further assume that these mole fractions are equal to the related volume fractions as required by the theory.

Figures 1 and 2 show the miscibility behavior of CPVC/CPVC and (MMA-EMA)/(MMA-EMA) blends at 150 and 70 °C, respectively. The samples were annealed at these respective temperatures in the DSC before measurement, and those blends having one glass transition in the thermogram were taken to be miscible. We found in both cases that the miscibility boundaries can be reasonably represented by a pair of straight parallel lines, a result that is in agreement with the first-order theoretical prediction. The number-average degrees of polymerization are estimated on the basis of the measured molecular weights, and thus (eq 3), $\chi_{\text{crit}} = 0.002$. This result yields (eqs 1 and 2) segment pair interaction parameters $\chi_{\text{CHClCHCl/CH}_2\text{CHCl}} = 0.050$ and $\chi_{\text{MMA/EMA}} = 0.013$. The

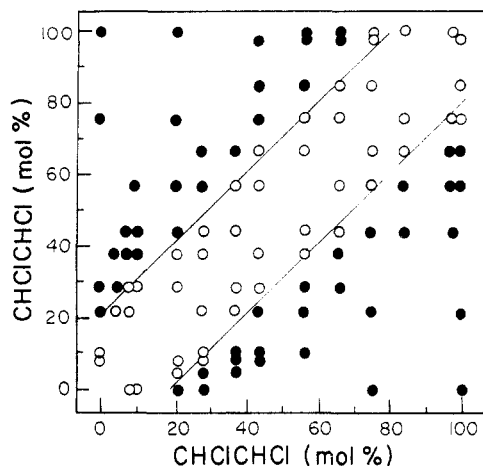


Figure 1. Isothermal phase diagram of CPVC/CPVC blends at 150 °C. The open and filled circles represent one and two phases, respectively. The parallel lines are the miscibility boundary with $\chi_{AB} = 0.050$; see text. Reprinted with permission from Chai, Sun, and Karasz: Jono, M., Inoue, T., Eds. *Mechanical Behavior of Materials-VI*; Pergamon Press PLC: London, 1991.

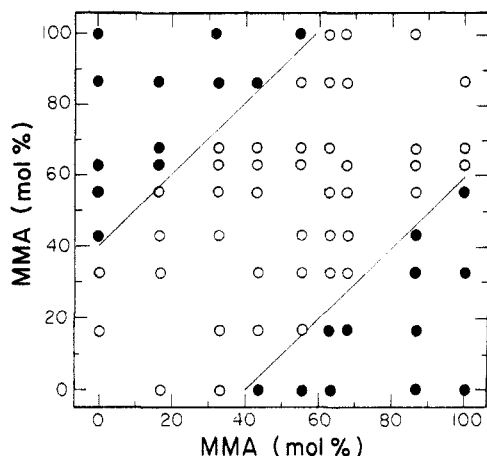


Figure 2. Isothermal phase diagram of (MMA-EMA)/(MMA-EMA) blends at 70 °C. The miscibility boundary is calculated with $\chi_{AB} = 0.013$. The open and filled circles represent one and two phases, respectively. Reprinted with permission from Chai, Sun, and Karasz: Jono, M., Inoue, T., Eds. *Mechanical Behavior of Materials-VI*; Pergamon Press PLC: London, 1991.

first value is close to the result of 0.042 of Shiomi,²⁷ which was obtained from a miscibility study of CPVC/(VC-VAc) blends (where VC is vinyl chloride and VAc is vinyl acetate). The latter system is of the AB/CB type, in which the two copolymers have one common monomer.

Figure 3 shows the miscibility boundaries for CPE/CPE blends at 70 °C. The result is qualitatively in accord with our previous reports,^{21,39} in which the miscibility regime features a large bulge, convex relative to the diagonal. The dashed parallel lines in Figure 3 represent the theoretical miscibility boundaries for cases in which only binary interactions are considered. These boundaries were calculated from eqs 1 and 2, the previously reported value $\chi_{CHCl/CH_2} = 0.092$,⁴⁴ and $\chi_{crit} = 0.002$. Clearly, first-order random copolymer blend theory cannot explain the experimental results, a discrepancy that we postulate is due to sequence distribution effects. Thus in the following analysis we apply the Balazs et al. theory and the newer theoretical treatment derived above to those observations.

A ¹³C NMR analysis indicated that the chlorine atoms distribute nearly randomly in the molecule of solution-chlorinated polyethylene,⁴² so CPE can be regarded as a random copolymer. Following the procedure of Balazs et al., we calculated the critical values of f_A and g_A from the

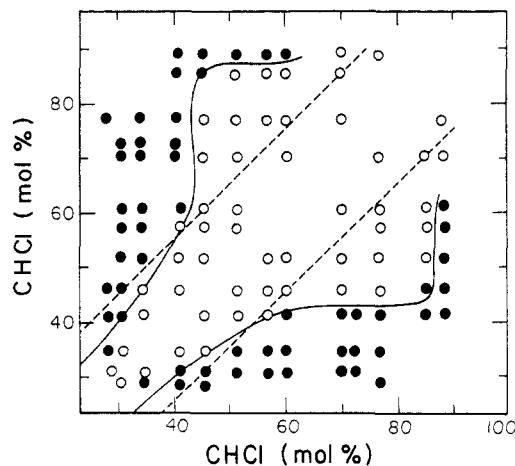


Figure 3. Isothermal phase diagram of CPE/CPE blends at 70 °C. The parallel dashed lines were calculated with $\chi_{AB} = 0.092$. The solid lines are the miscibility boundary calculated from eqs 2 and 12. The open and filled circles represent one and two phases, respectively.

miscibility boundary and calculated χ_{blend} from eqs 8, 9, and 17 in ref 39. The parameters χ_{AB} , $\chi_{ABA;BAB}$, and $\chi_{AAA;BBB}$ were obtained from least-squares fits of $\chi_{blend} = \chi_{crit}$ ($=0.002$) and were 0.27, 1.34, and -0.22 , respectively. Following ref 39, we have assumed that all triad interactions except $\chi_{AAA;BBB}$ and $\chi_{ABA;BAB}$ are equivalent and are assigned an average value χ_{AB} . Thus, we rewrote χ_{blend} as

$$\chi_{blend} = A_i \bar{\chi}_{AB} + B_i \chi_{ABA;BAB} + C_i \chi_{AAA;BBB} \quad (13)$$

where A_i , B_i , and C_i are functions of copolymer composition (f_A , g_A), and evaluated the three interaction parameters through

$$\frac{\partial \sum (\chi_{crit} - \chi_{blend})^2}{\partial \bar{\chi}_{AB}} = \frac{\partial \sum (\chi_{crit} - \chi_{blend})^2}{\partial \chi_{ABA;BAB}} = \frac{\partial \sum (\chi_{crit} - \chi_{blend})^2}{\partial \chi_{AAA;BBB}} = 0$$

From our eqs 1 and 12 and eqs 8, 9, and 17 in Balazs et al.,³⁹ we can see that the segment pair interaction parameter χ_{AB} in the mean-field theory of random copolymer blends is equal to $\chi_{AAA;BBB}$ in our model. The calculated $\chi_{AAA;BBB}$ is -0.22 for the CPE/CPE system; the corresponding experimental value of χ_{AB} is 0.092.⁴⁴ The difference between these two values is substantial. Further, the miscibility boundaries calculated with the three interaction parameters do not agree well with the experimental results, and the two homopolymers are predicted to be miscible, because $\chi_{AAA;BBB}$ is negative—an unlikely result. We also attempted a least-squares method to generate χ_{AB} and $\chi_{ABA;BAB}$ with a fixed $\chi_{AAA;BBB}$ ($=0.092$). The miscibility boundaries calculated in this way also are not in good agreement with the experimental results shown in Figure 3.

In applying our new equation (i.e., eqs 11 and 12), we obtained the following numerical values for the terms on the left-hand side of eqs 14 from a least-squares fit of $\chi_{blend} = \chi_{crit}$ ($=0.002$):

$$\chi_{25} - \Delta_2 + 3\Delta_6 = 0.69$$

$$2\Delta_2 + 6\Delta_5 - 8\Delta_6 = -1.03$$

$$4(\Delta_6 - \Delta_5) = 0.40 \quad (14)$$

Table II
Calculated Interaction Parameters in the CPE/CPE System

interaction param	value	interaction param	value
χ_{14}	-0.303	χ_{26}	0.151
χ_{15}	-0.047	χ_{34}	-0.020
χ_{16}	0.210	χ_{35}	0.036
χ_{24}	-0.162	χ_{36}	0.092 ^a
χ_{25}	-0.005		

^a From ref 44.

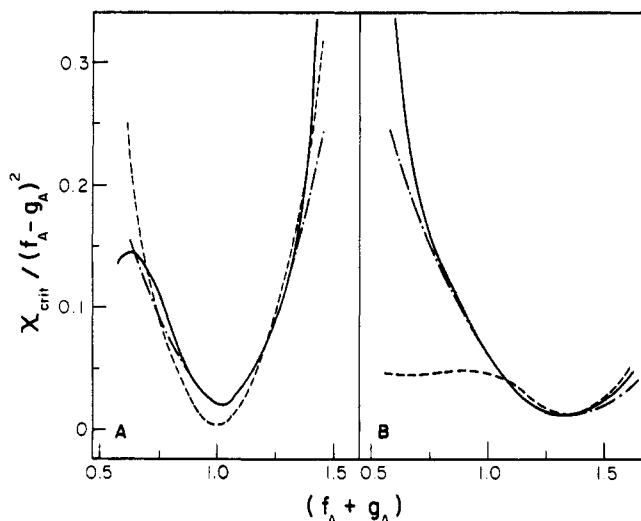


Figure 4. Plot of $\chi_{crit}/(f_A - g_A)^2$ as a function of $(f_A + g_A)$: (A) experimental data from Balazs et al.;³⁹ (B) experimental data of this study; (—) experimental boundaries; (---) best-fit boundaries calculated from the Balazs et al. equation; (-.-) best-fit boundaries calculated from eqs 2 and 12.

Because there are only three independent equations for four unknown triad interaction parameters, a unique solution cannot be obtained. (Note, however, that the Balazs et al. treatment, with fewer parameters, does provide a unique solution.) But, as mentioned earlier, χ_{36} ($\chi_{AAA;BBB}$) $\equiv \chi_{AB}$. When the experimental values $\chi_{AB} = 0.092$ is assigned as the value of χ_{36} , all the triad interaction parameters can be determined with eqs 14 and 10 (see Table II). Figure 3 also shows the miscibility boundaries calculated from eqs 2 and 12 with the three parameters given in eqs 14. In this case, agreement between theory and experiment is good.

Balazs et al. applied their theory to the miscibility boundary of a slightly different CPE/CPE system.³⁹ The new equations derived here also give a good description of the miscibility boundary of those experimental results. When we plot $\chi_{crit}/(f_A - g_A)^2$ against $(f_A + g_A)$ (Figure 4), we see that our new equation of χ_{blend} gives a better fit to both sets of experimental data for CPE/CPE blends, whereas the Balazs et al. theory fits only the earlier experimental data.

When we compare the miscibilities of the CPE/CPE and CPVC/CPVC systems, we see that CPE/CPE blends are more miscible. This increased miscibility is not due to a molecular weight effect, because both polymers have similar degrees of polymerization. In fact, almost all the CPE/CPE blends are in one phase when their chlorine content is 50–70 wt % (Figure 5). At the same range of chlorine content, however, only certain of the CPVC/CPVC blends are miscible. We also see that the miscibility regime of CPE/CPE blends is represented by the area dominated by the convex bulges relative to the diagonal in the copolymer–copolymer composition plot, whereas the miscible CPVC/CPVC blend domain is located within two straight dashed lines. (The latter are not parallel in the

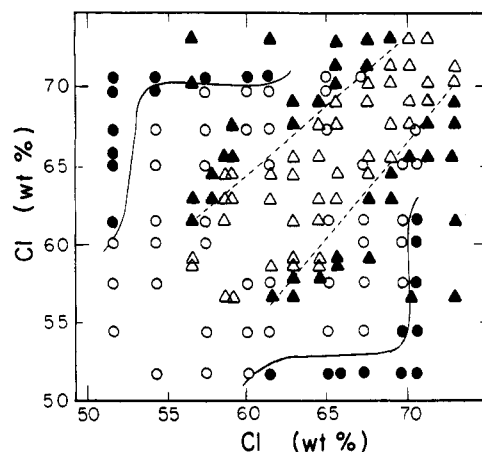


Figure 5. Comparison of miscibility behavior in blends of CPVC/CPVC (Δ , \blacktriangle) (dashed-line boundaries) and CPE/CPE (\circ , \bullet) (solid-line boundaries). The open and filled symbols represent one and two phases, respectively.

wt % Cl coordinate representation.) Both CPE and CPVC contain only two basic units: CH_2 and CHCl . When CPE and CPVC have the same chlorine content, they have the same mole fractions of CH_2 and CHCl units and the only difference lies in their microstructures. The parent PVC has head-to-tail sequences of CH_2 and CHCl units, and CPVC can be regarded as a sequence of alternating CH_2 and CHCl units with random substitutions of additional CHCl units for CH_2 . The polymer CPE is a random array of both units. Apparently, this subtle microstructural difference has a profound effect on miscibility.

We have recently reported that there is only a minor difference in the miscibility behavior of CPE/(AN-BT) and CPVC/(AN-BT) blends [(AN-BT) is the acrylonitrile–butadiene copolymer].⁴⁴ The implication is that when CPE and CPVC are mixed with a third polymer, their microstructural differences no longer affect miscibility, especially when there are strong interactions between the blend components. When CPE and CPVC are mixed together in CPE/CPVC blends, however, the microstructural effect is important, as shown directly by the finding that most mixtures of CPVC and CPE with identical chlorine contents are immiscible.⁴⁵ The present contribution provides another example of the large effect of microstructure on miscibility.

Conclusions

CPVC/CPVC and (MMA-EMA)/(MMA-EMA) blends manifest simple miscibility behavior in which the miscibility domain lies between two parallel straight lines and for which the calculated segment pair interaction parameter is in agreement with earlier literature.

In contrast, CPE/CPE blends show a strong sequence distribution effect, and the domain of miscibility falls within a large bulge along the diagonal of a copolymer–copolymer composition plot. An equation for χ_{blend} based on the Cantow–Schulz assumption of triad interactions gives a better description of miscibility than does the earlier Balazs et al. theory. With a known triad interaction parameter (for instance, $\chi_{AAA;BBB}$), all the interaction parameters can be assigned or calculated. A comparison of the miscibilities of the CPVC/CPVC and CPE/CPE systems clearly shows the strong effect of microstructure on miscibility.

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