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A Mean-Field Treatment of the Interactions in Blends of Poly(vinyl methyl ether) with Poly(styrene-*co*-nitrostyrene)

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ABSTRACT: A modification of the mean-field approach to polymer blends is described which allows the analysis of homopolymer–copolymer blends of the type A + C_yD_{1-y} in which the homopolymer is miscible with the copolymer between $y = 1$ (i.e., homopolymer C) and a single composition limit $y = y_1$, where $y_1 > 0$. The analysis utilizes the quadratic dependence of the blend interaction parameter (B_{blend}) on composition and equates the composition of the minimum value of B_{blend} to that of the maximum in the lower critical solution temperatures of the blends. Mixtures of poly(vinyl methyl ether) with poly(styrene-*co*-methyl methacrylate) and poly(styrene-*co*-*m*-nitrostyrene) are examined, and these yield a positive value for the styrene–vinyl ether interaction.

Introduction

The miscibility of copolymer blends, where there are no specific interactions leading to a negative heat of mixing, may be best explained by a "repulsion effect" of the comonomer units.[1,2] For a homopolymer A mixed with a copolymer C_yD_{1-y}, where y represents the volume fraction of C, the blend interaction parameter B_{blend} is given by the following function of composition

$$f(y) = yB_{AC} + (1-y)B_{AD} - y(1-y)B_{CD} = B_{\text{blend}} \quad (1)$$

Here B_{ij} is the interaction energy density in the sense introduced by Flory[3] and characterizes the heat of mixing contribution of an i–j segmental contact to the free energy of mixing through the van Laar type expression $\phi_A\phi_{CD}B_{\text{blend}}$, where ϕ_A and ϕ_{CD} are the volume fractions of homopolymer and copolymer, respectively. For infinite molecular weight polymers phase separation occurs when $f(y) = 0 = B_{\text{crit}}$.

Many systems have been examined where a homopolymer is miscible with a copolymer within a certain composition "window".[4-11] If y_1 and y_2, the miscibility limits of A in C_yD_{1-y}, are determined and if one of the B_{ij}'s in eq 1 is known, then the values of the remaining two interaction parameters may be readily evaluated from[8]

$$y_1y_2 = (B_{AD} - B_{\text{crit}})/B_{CD} \quad (2)$$

and

$$y_1 + y_2 = (B_{CD} + B_{AD} - B_{AC})/B_{CD} \quad (3)$$

Examples of blends where only one miscibility limit exists are also common.[12,13] In this case it is not directly possible to obtain similar solutions to eq 1. An analysis is, however, possible given additional experimentally accessible information. Equation 1 is a quadratic with a minimum in B_{blend} when

$$f'(y) = B_{AC} - B_{AD} - B_{CD} + 2yB_{CD} = 0 \quad (4)$$

Substituting for B_{AC} from eq 4 into eq 1 and setting $y = y_o$ to indicate the minimum gives

$$f(y)/B_{CD} = y^2 - 2y_oy + (B_{AD}/B_{CD}) \quad (5)$$

The first two terms on the right-hand side of 5 are a difference of squares, i.e., $y^2 - 2y_oy = (y - y_o)^2 - y_o^2$, so eq 5 can be equivalently expressed as

$$f(y) = (y - y_o)^2B_{CD} + (B_{AD} - y_o^2B_{CD}) \quad (5')$$

As in eq 1, $f(y) = B_{\text{crit}}$ at the phase boundaries, so

$$(y - y_o)^2 = (B_{CD}y_o^2 - B_{AD} + B_{\text{crit}})/B_{CD} \quad (6)$$

Thus the general solutions for the limits of miscibility (y_i, i = 1 and 2) for homopolymer A in copolymer C_yD_{1-y} are

$$y_i = y_o \pm [(B_{CD}y_o^2 - B_{AD} + B_{\text{crit}})/B_{CD}]^{0.5} \quad (7)$$

where, for polymers of finite molecular weight, B_{crit} is calculated from the polymer molar volumes (V_i) via

$$B_{\text{crit}} = (1/2)RT(V_A^{-0.5} + V_{CD}^{-0.5})^2 \quad (8)$$

Provided y_o and one of the B_{ij}'s are known, eqs 4 and 7 provide a means of determining the remaining two B_{ij}'s in blends with one miscibility limit. Equation 7 expresses the quadratic dependence of B_{blend} on the composition variable y, and Figure 1 shows this schematically for a homopolymer + copolymer blend exhibiting only one miscibility limit. Alternatively, since the y_i's are equidistant from y_o, a hypothetical value of the second miscibility limit may be obtained by extrapolation and eqs 2 and 3 used as before. We shall apply the method outlined above, first to data on blends of poly(vinyl methyl ether) (PVME) with poly(styrene-*co*-methyl methacrylate) (SMMA) reported by Chien, Pearce, and Kwei[13] and then to blends of PVME and poly(*m*-nitrostyrene-*co*-styrene) (mNSS).

Experimental Procedures

m-Nitrostyrene (mNS) was obtained from Aldrich and used as received. Statistical copolymers of mNS and styrene (S) were synthesized by conventional bulk polymerization at 333 K by using AIBN as a free-radical initiator. Conversions were kept to less than 10% and the compositions of the copolymers measured by elemental analysis. Molecular weights were determined by using gel permeation chromatography in terms of standard polystyrene (PS) equivalents, and details are given in Table I.

Both PVME and PS were obtained from Polysciences and were used as received; the molecular weight of the former was determined as 29 000 g/mol and that of the latter quoted by the supplier as 17 500 g/mol. Blends of PVME with mNSS (50/50 wt %) were prepared by coprecipitation from nitromethane solution into an excess of methanol and were dried for 24 h in vacuo at 303 K prior to use. The criterion of miscibility was the appearance of a single blend glass transition temperature (T_g) when examined by differential scanning calorimetry using a Perkin-Elmer DSC-2 scanning at 20 K/min.

The temperatures of phase separation of miscible blends were determined visually by using a Linkam PR600 programmable hot stage for toluene-cast thin films on glass slides.

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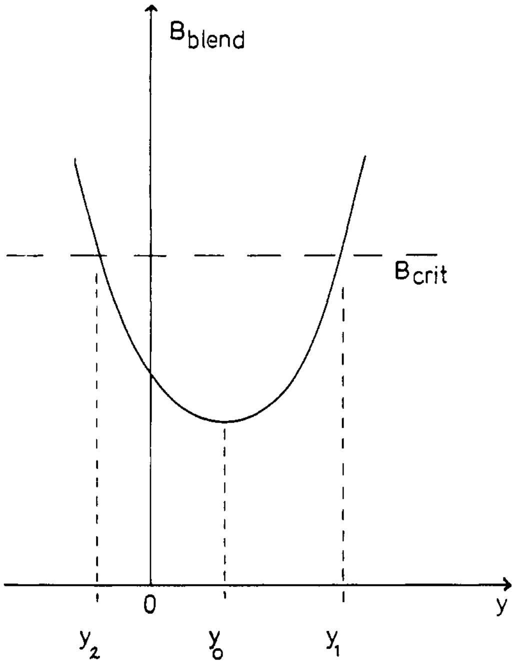

Figure 1. Schematic variation of B_{blend} on copolymer composition y for a homopolymer–copolymer blend. y_0 is the minimum in B_{blend} and y_1 the limit of miscibility. y_2 and y_1 are equidistant from y_0.

Table I
Details of the mNS–S Copolymers Used in Blending Studies

mol fraction of mNS in copolymer	T_g/K	$10^{-3}M_n$/g mol^{-1}
0.053	374	46
0.093	375	48
0.125	376	27
0.134	375	23
0.200	376	21
0.256	379	19
0.302	379	20
0.381	378	21
0.401	381	20
0.575	381	21
0.634	384	20
0.734	391	22
1	395	16

Discussion

Blends of polystyrene (PS) and PVME have been studied extensively.[14–21] The system is a marginally miscible one, exhibiting a lower critical solution temperature (LCST) at moderate temperatures. Chien, Pearce, and Kwei[14] have shown that PVME is also miscible with SMMA copolymers up to a composition limit (y_1) at room temperature of 0.60 mol fraction styrene. Blends of PVME and SMMA in this composition range also exhibit demixing behavior as they are heated; the value of the LCST is a function of copolymer composition and goes through a sharp maximum at 0.82 mol fraction styrene. The existence of a maximum in the miscibility window requires a minimum in B_{blend} corresponding to the condition of eq 4, which for the system PVME + S_yMMA_{1-y} lies at 0.82 mol fraction styrene (y_0).

In terms of volume fraction, $y_1 = 0.61_4$ and $y_0 = 0.83$. The SMMA volumes, evaluated from the molecular weight data provided[13] by using a group additivity scheme,[22] yield $B_{crit} = 0.152$ J cm^{-3}. The magnitude of the parameter $B_{SMMA} = 0.708$ J cm^{-3} was calculated from the work of Fukuda, Nagata, and Inagaki[23] by extrapolation to zero solvent content. The values of the system interaction parameters obtained from these data are listed in Table II.

Table II
Values of B_{ij} for the Blend System PVME + SMMA

ij	B_{ij}/J cm^{-3}	ij	B_{ij}/J cm^{-3}
SMMA	0.708	VMES	0.140
VMEMMA	0.609		

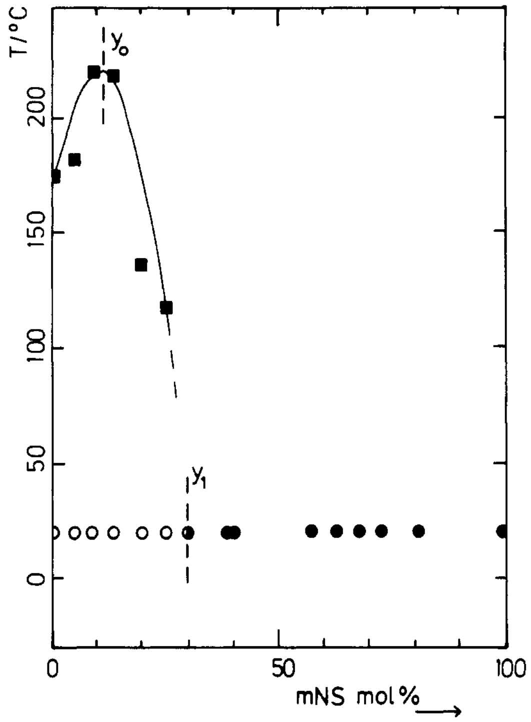

Figure 2. Results of blending studies of PVME with mNSS copolymers. ○ indicate a single-phase blend, and ● indicate a two-phase blend; ◐ show partial miscibility. ■ are the minima in the cloud-point curves for the miscible blends.

The experimental data for the blend system PVME + mNS_yS_{1-y} are shown in Figure 2, where it can be seen that miscible blends are obtained up to 0.30 mol fraction mNS (0.33 volume fraction, y_1). The cloud-point curves for the miscible blends are shown in Figure 3, and the LCST values (here identified as the minima in the cloud-point curves) are also shown in Figure 2. The minimum in B_{blend} is obtained as the maximum in the LCST data at 0.11 mol fraction mNS (0.12_5 volume fraction, y_0). From the polymer molar volumes a value of $B_{crit} = 0.234$ was evaluated for this system, and, along with B_{VMES} obtained as above, the interaction parameter set shown in Table III was obtained.

Both systems here show an enhanced solubility of PVME relative to PS. Min and Paul[12] have reported similar behavior for other styrenic copolymers blended with PVME, and they have rationalized the observed effect by considering the comonomer to give a material whose solubility parameter more closely matches that of PVME. The present analysis allows such behavior to be quantified through eq 1 directly in terms of B_{blend} as a consequence of the relatively strong SMMA and S–mNS "repulsion" interactions in this case.

Min and Paul[12] also suggest that B_{VMES} is negative on the basis of general blend behavior, and measurements of the Flory χ parameter[24] tend to support this contention. Strazielle and Ould-Kaddour[25] quote values of χ_{VMES} of −0.46 to −0.017 (dependent upon solvent) from light scattering; Kwei, Nishi, and Roberts,[15] using vapor sorption, obtained χ_{VMES} from −0.75 to −0.46, indicating both temperature and composition dependence; while exam-

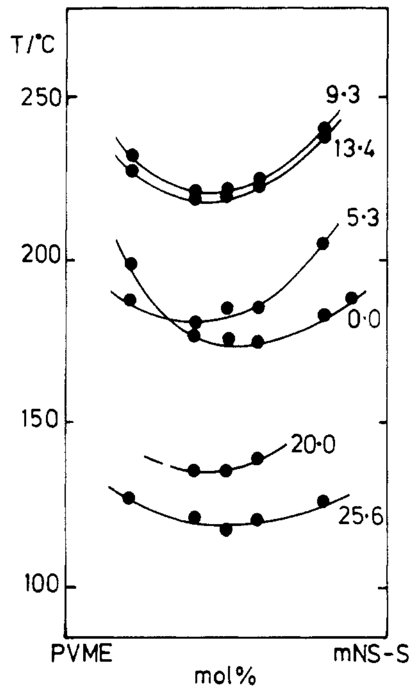

Figure 3. Cloud-point curves for the miscible blends of PVME with mNSS copolymers. The numbers alongside each curve indicate the mole percent of styrene in the mNSS copolymer blended with PVME.

Table III
Values of B_{ij} for the Blend System PVME + mNSS

ij	B_{ij}/J cm^{-3}	ij	B_{ij}/J cm^{-3}
VMES	0.140	VMEmNS	2.81
SmNS	3.56		

ination of the solvent-free blend by neutron scattering[19] gave a value of χ_{VMES} significantly closer to zero at -3×10^{-3}. Prolongo, Masegosa, and Horta[21] have recently commented on the variation in χ values obtained by different techniques for the PVME–PS system and have proposed a treatment based on equation of state theory, which accounts for the perturbing effect of solvent. Their data suggest a solvent-free positive value for B_{VMES} from 0.14 to 1.4 J cm^{-3}, depending on composition, which is much more comparable with the $B_{\mathrm{VMES}} = 0.140$ J cm^{-3} obtained here. However, it does seem to us that the matter requires some further comment.

Infrared analysis of PVME–PS blends strongly suggests that a degree of specific interaction exists[26] and that this may be the thermodynamic driving force for miscibility. From the estimation of solubility parameters,[22] B_{VMES}, or at least the dispersive component of B_{VMES}, is expected to be small but positive. The free-volume discrepancy between two polymers may also be approximated according to Patterson and Robard,[27] and this is always a positive contribution to B_{blend}. Specific interactions must therefore be significant for the PVME–PS pairing. This may also have some bearing on the variation of the χ_{VMES} values[15–25] given above, since the analytical expressions derived to express polymer–polymer interactions in solution apply strictly to mean-field situations and the effect of solvent on specific interactions is an unknown quantity. The mean-field approach embodied in the use of eq 1 explicitly ignores free volume, and any B_{ij}'s thus derived must subsume any contributions from free volume, if present, and also specific effects. In addition to being "portmanteau" parameters in this sense, an element of composition and temperature averaging must also be present.

We believe that B_{ij} values derived in this study and others (for example, ref 4 provides an extensive list) from consideration of phase boundaries are in a sense particular to the method used, and direct correlation of values with those from other sources (especially solvent-containing ternary systems) may not always be possible. This in no way limits their usefulness as evidenced in the considerable past successes of the mean-field treatment. Nevertheless, it is still a first approximation approach and it is to be hoped that, as data continue to accumulate, the relative importance of the effects discussed above will become clearer.

As a final observation we regard the value of B_{VMEmNS} as surprisingly unfavorable; it would appear that the inclusion of a single nitro group into the aromatic ring confers no "acceptor-like" properties (such as in multiply substituted nitro–aromatic charge-transfer interactions) that would induce favorable interactions with the ether oxygen of PVME.

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