is independent of n and the absolute value is larger at larger r_c/L. The former is in clear contrast to the molecule where the outer shell is constructed from the n pieces of "Gaussian subchains". In this molecule, as will be described in detail in a forthcoming paper,[10] $\langle S^2 \rangle_{app}/(R_G')^2$ depends strongly on n and it shows similar behavior as in Figure 12 only at $n \to \infty$.

Supplementary Material Available: Lists of the algorithms (FORTRAN programs) used for calculating $P_o(q)$ and $P_{io}(q)$; List 1 is for the former for $n = 32$, for example, and List 2 is for the latter (12 pages). Ordering information is given on any current masthead page. The $P_o(q)$ algorithms for other n values are available from the authors upon request.

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A Nearly Ideal Mixture of High Polymers

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ABSTRACT: Determination of the mixing free energy of blends of *cis*-1,4-polyisoprene (PIP) and atactic poly(vinylethylene) (PVE) was attempted by estimation of the critical molecular weights of the components. Phase separation could not be induced, however, at the highest available molecular weights, indicating a Flory-Huggins interaction parameter for this mixture that is less than 1.7×10^{-4}. This remarkably low magnitude, in the absence of specific interactions, results from the small change in van der Waals energy upon mixing in combination with a close similarity in the liquid structure of the components. The exchange enthalpy of the blend is significantly increased when the PVE has syndiotactic microstructure, resulting in immiscibility with PIP at moderate molecular weights. The glass transition of the PIP/PVE blend was observed to be unusually broad in the presence of a high concentration of PVE. This breadth is unrelated to phase segregation effects but likely reflects differences between components in the free volume necessary for segmental mobility.

Introduction

Ideal solutions result from the random mixing of molecules that have the same size and shape and in which the intermolecular forces between pairs of like segments of each type, as well as between unlike segments, are all equivalent. The mixing enthalpy associated with dispersive interactions (arising from correlation between charge fluctuations) favors phase segregation. For macromolecules, in which the combinatory mixing entropy is small, this usually restricts miscibility to only those mixtures in which the components chemically interact. This combinatory entropy is not negligible however and in blends of *cis*-1,4-polyisoprene and atactic poly(vinylethylene) has been shown to be sufficient to effect miscibility as a result of the small enthalpy change accompanying mixing.[1,2] The magnitude of the dispersion energy can be described by a series whose leading term corresponds to the well-known London equation[3]

$$E_{ij} = -\tfrac{3}{4} I_{ij} \alpha_i \alpha_j r^{-6} \qquad (1)$$

where α_i is the polarizability of the ith molecule or chain unit, separated by r from the jth unit, and I_{ij} is approximately equal to the ionization potential of the species. If no alterations of the local liquid structure accompany mixing, the Flory-Huggins interaction parameter, χ_{ij}, de-

scribing the enthalpy and noncombinatory entropy contributions to the free energy, can be directly related to the dispersion interaction energy according to[4]

$$\chi_{ij} = (E_{ij} - E_{ii}/2 - E_{jj}/2)/RT \qquad (2)$$

A negligible change of van der Waals energy upon mixing is primarily a consequence of similarity in the respective polarizabilities of the blend components. The ideal combinatory entropy change, per lattice (or chain unit) volume, is given for a two-component mixture by[4]

$$\Delta S = -R(\phi_i/N_i \ln \phi_i + \phi_j/N_j \ln \phi_j) \qquad (3)$$

where ϕ is volume fraction, R the gas constant, and N the degree of polymerization. By increasing N, this entropy can be diminished to an extent whereby the dispersive interaction energy is sufficient to effect phase separation. The critical point, or minimum on the spinodal curve, defines a value of the Flory-Huggins interaction parameter below which the system is miscible at all concentrations of the components. The composition at the critical point is deduced by equating the third derivative of the free energy with respect to concentration to zero and solving to obtain[5]

$$\phi_i^* = N_j^{1/2}/(N_i^{1/2} + N_j^{1/2}) \qquad (4)$$

with the corresponding critical value of the interaction parameter then given by

$$\chi^* = V_R/2[(V_i N_i)^{-1/2} + (V_j N_j)^{-1/2}]^2 \qquad (5)$$

[†] Geo-Centers, Inc., Fort Washington, MD.

where the arbitrary lattice value, V_R, is taken to be the geometric mean of the component segment molar volumes, V_i and V_j. Although deviations from Flory–Huggins theory are known when chemical reaction exists between the components of a blend, expectations are for better conformance of experiment to theory in regular solutions. However, recent results have suggested that even in mixtures of a polymer with its deuterated analogue, significant departures of the phase behavior from that given by eq 5 are observed.[6] Evidently in general the miscibility of polymer mixtures extends beyond the regime given by the Flory–Huggins model.

The occurrence of miscibility in a blend of high polymers in the absence of specific (chemical) interactions invites quantitative assessment of the mixing enthalpy. A direct approach to determination of the magnitude of the interaction in a blend is through small-angle X-ray- or neutron-scattering (SANS) measurements. The scattering intensity will have an angle dependence described by[5]

$$I(Q)^{-1} = [N_i\phi_i g_i(Q)]^{-1} + [N_i\phi_j g_j(Q)]^{-1} - 2\chi_{ij} \qquad (6)$$

where g is the Debye scattering function for an ideal chain, and Q the reduced scattering angle (momentum transfer). This approach has been applied to various polymer blends to obtain a measure of the interaction parameter. Such measurements can be made, of course, only if sufficient contrast exists between components in the blend to provide the required scattering intensities. For this reason, the usual practice is to substitute deuterium for the protons in one of the components and thereby rely on the large resulting difference in neutron–nuclear interaction to provide the necessary neutron-scattering contrast. Notwithstanding the popularity of this approach to characterizing blends, an excess free energy associated with isotopic substitution is well established.[6-9] Such effects are in some circumstances tolerably small or can be corrected for by measuring χ as a function of the concentration of labeled species. For PIP/PVE mixtures, however, in which χ must be very nearly zero,[1] an alternative method of determining χ is warranted.

In systems in which the only mechanism favoring mixing is the resulting increase in positional disorder, phase separation can be effected by increasing the molar mass of the components. By observation of the dependence on mixing entropy of the phase morphology of a PIP and PVE blend containing the critical concentration of the components, the magnitude of the interaction parameter for the system can be deduced from comparison with the critical value calculated from eq 5.

Experimental Section

Poly(vinylethylene) and its deuterated analogue (D-PVE) were synthesized in vacuo by using a modifier that yields primarily 1,2-addition.[10,11] Molecular weights were determined by gel permeation chromatography using a column suitably calibrated for the polybutadiene (PBD) microstructure. The other polydienes used were obtained from commercial sources. Their microstructure and macrostructure were provided by the manufacturers (the latter based on light scattering) and are listed, along with the those for all polymers used, in Table I.

Blends were prepared at the desired composition by dissolution in cyclohexane, precipitation into methanol, and vacuum drying for 24 h at 40 °C. Blend compositions and their designations are listed in Table II.

An interdiffusion sample was prepared by annealing plied films of PIP and D-PVE at 52 °C in vacuo for 162 h, at which time the specimen was quenched and maintained at 0 °C. Small-angle neutron scattering from it was subsequently measured at the National Bureau of Standards. An incident neutron wavelength of 6 Å and a sample-to-detector distance of 3.6 m in conjunction with a converging collimation system yielded measurements down

Table I
Microstructure and Macrostructure of Polydienes

| | butadiene, % | | | | |
	1,4-	1,2-	1,4-isoprene, %	N_w	N_w/N_n
PIP[a]			>95	23000	1.1
PIP[a]			>95	6700	1.1
PIP[a]			>95	4500	1.0
PIP[b]			93	90	1.1
PIP[b]			95	420	1.1
PBD[b]	92[e]	8		440	1.1
PBD[b]	91[e]	9		100	1.1
PVE[c]	3	97[e]		7700	1.2
D-PVE		95[f]		3200	1.3
PVE	3	97[e]		2600	1.2
S-PVE[d]	7	93[g]		2500	2.3

[a] Polymer Labs Ltd. [b] Scientific Polymer Products, Inc. [c] Firestone Tire and Rubber Co. [d] Japan Synthetic Rubber Co. [e] Atactic. [f] Deuteriated atactic. [g] Syndiotactic.

Table II
Blend Compositions

blend	component (N_w)	component (N_w)	ϕ_{PVE}
IA	PIP (23 000)	PVE (7700)	0.64
IB	PIP (90)	PVE (2600)	0.75
IC	PIP (4500)	PVE (2600)	0.32
IIA	PBD (100)	PVE (2600)	0.16
IIB	PBD (100)	PVE (2600)	0.75
IIC	PBD (440)	PVE (2600)	0.29
IIIA	PIP (6700)	D-PVE (3200)	0.75
IIIB	PIP (6700)	D-PVE (3200)	0.50
IIIC	PIP (6700)	D-PVE (3200)	0.25
IVA	PIP (420)	S-PVE (2500)	0.50

to 0.01 Å^{-1}. Background and detector sensitivity corrected data were converted to absolute intensity units by using a secondary silica standard.

A Perkin-Elmer DSC-2 with thermal analysis data station was employed for calorimetry measurements. Cooling rates from 5 to >200 °C/min with a constant heating rate of 20 °C/min were utilized, over the temperature range -125 to +30 °C. Sample weights were between 5 and 10 mg.

Dynamic mechanical measurements were made over the temperature range -100 to 50 °C at 11 Hz on a computer-controlled Rheovibron DDV-IIC.

Linear thermal expansivities were measured with a Perkin-Elmer TMA 7. Typically 0.2-cm-thick samples were used with a heating rate of 1 °C/min. The normal load exerted by the expansion probe, 95 Pa, was 0.01% of the rubbery plateau moduli of these materials.[2] By employment of only high molecular weight specimens for these measurements (N_w = 23000 and 7700 for PIP and PVE, respectively), error due to creep was minimized; nevertheless, the expansivities were only actually measured at temperatures up to 50 °C above the glass transition even for the highest molecular weight sample. The coefficient of thermal expansion

$$\bar{\alpha} = d \ln (V)/dT \qquad (7)$$

which for an isotropic material is 3 times the actually measured linear expansion coefficient, displays a theoretical dependence on temperature above T_g given by[12]

$$d\bar{\alpha}/dT = (7 + 4\bar{\alpha}T)\bar{\alpha}^2/3 \qquad (8)$$

This expression, while overestimating experimental values of the temperature dependence by about 25%, still predicts a negligible increase in $\bar{\alpha}$ over the range from T_g up through room temperature for both the PIP and the PVE.

Results

Phase Morphology and the Glass-to-Liquid Transition.
Blends of PVE and PIP have previously been reported to exhibit single glass transitions. Moreover the temperatures of the transitions were found to exhibit a composition dependence quantitatively in accord with theory for a random arrangement of the chain units.[1]
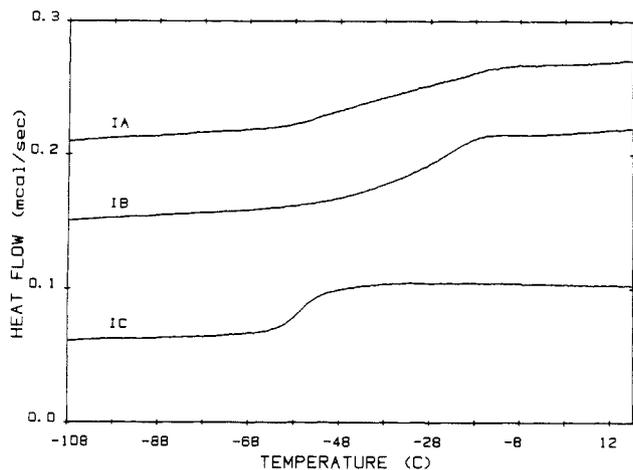
Figure 1. Calorimetry results for three miscible blends of PIP and PVE (sample designations in this and the ensuing figures are defined in Table II). The uppermost curve has the lowest critical interaction parameter value (1.7×10^{-4}). Broad glass transitions are observed in both it and the curve for blend IB, for which $\chi^* = 7.6 \times 10^{-3}$.

Displayed in Figure 1 are differential scanning calorimetry results (measured during heating) for three PVE/PIP blends of varying composition. Although only a single transition is observed for each mixture, it can be seen that in some cases the transition occurs over a broad temperature range. For example, while the temperature difference between the onset and midpoint of the heat capacity change at T_g was 2–3 °C for the pure components and typically 5–7 °C for blends, in certain blends this difference was over 20 °C. The breadths of these transitions are reproducibly observed irrespective of the rate at which the temperature is changed and remain essentially the same when T_g is approached from either direction. Miscible polymer mixtures invariably exhibit glass transitions that are broader than those of the corresponding pure components,[13-16] so that such breadth is not an unambiguous indication of phase segregation. Although thermodynamic miscibility can be inferred from the observation of a single glass transition, in the vicinity of the coexistence curve on the phase diagram supersaturation may be required for the nucleation and growth of concentration heterogeneities sufficient in size to exhibit distinct glass transitions. At the critical concentration, however (corresponding to ϕ_{PVE} = 0.64 for the highest component molecular weights employed herein), strong segregation effects are operative, and even in the case of very weak interactions the resulting concentration fluctuations are large.[17] Two of the glass transitions in Figure 1, however, transpire over an extremely broad temperature range (as much as 50 °C). It is noted that these correspond to compositions in which there exists a higher relative abundance of the higher glass transition component. The lowest critical χ (1.7×10^{-4} from eq 5), and therefore the least stability, is associated with the composition designated IA (see Table II). When the molar mass of both the PVE and the PIP are significantly reduced (sample IB with $\chi^* = 7.6 \times 10^{-3}$), the transition remains broad, suggesting that this breadth reflects not proximity to, or the onset of, a phase-separated state, but rather the higher concentration of the higher T_g constituent. Note that a *less* miscible sample (IC for which $\chi^* = 6.2 \times 10^{-4}$) has a relatively sharp glass transition, as a result of the altered relative concentration of the two components.

It is useful to obtain more unambiguous evidence of miscibility, particularly when the components are high in molecular weight. Accordingly the occurrence of any in-
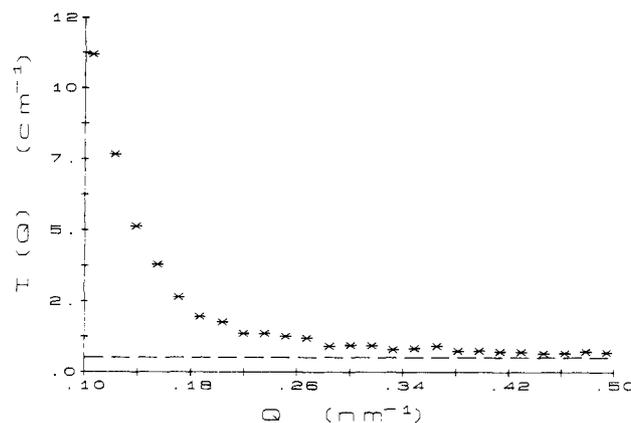

Figure 2. Small-angle neutron differential scattering cross section (asterisks) measured from a sample consisting of sheets of PIP (N_w = 23 000) and deuteriated PVE (N_w = 3200) that were in contact for 162 h at 52 °C. The scattering contrast significantly exceeds the incoherent background (- - -) determined from measurements on the individual polymers, evidencing their thermodynamic miscibility.

terdiffusion between the PIP (N_w = 23 000) and deuteriated PVE (N_w = 3200) was assessed from measurement of small-angle neutron scattering after specimens of each had been maintained in contact for 162 h at 52 °C. In Figure 2 is is observed that the magnitude of the resulting scattering contrast is significantly greater than the incoherent background intensity, the latter arising independently of any interdiffusion. The coherent SANS intensity indicates that interdiffusion has transpired, providing a direct indication of the thermodynamic miscibility of the PVE/PIP blend at these high molecular weights. It is thus made clear that the calorimetrically observed broad glass transitions are not related to the phase morphology. In principle the extent of interdiffusion can be extracted from the small-angle scattering data, and thereby a measure of the interaction parameter obtained.[18,19] The composition dependence of the structure factor for the blend (arising from the mismatch in molecular weights), as well as any composition dependence of χ itself, make such a determination difficult; nevertheless, SANS measurements directed along these lines are currently in progress.

An influence of blend composition on the abruptness of the heat capacity change at T_g is not unique to mixtures of PVE with PIP. Blends of PVE and 1,4-polybutadiene (PBD) are miscible when χ^* exceeds 4.4×10^{-3}.[20] Calorimetry measurements for three PVE/PBD mixtures are displayed in Figure 3. Sample IIA has a critical concentration of the components according to eq 4. The corresponding value for χ^* is calculated from eq 5 to be 7.4×10^{-3}, and accordingly phase homogeneity is existent as reflected in the single glass transition apparent in the DSC data. As the stability of the mixture is increased by altering the composition away from that associated with the critical point, the glass transition broadens when the concentration of the PVE is increased (sample IIB). At higher component molecular weights (sample IIC, for which $\chi^* = 2.4 \times 10^{-3}$), it can be seen that two distinct glass transitions are observed in Figure 3, reflecting the expected heterogeneous phase morphology. These results clearly demonstrate that a very gradual change from glass to liquid behavior with elevation of temperature cannot be taken as indication of reduced phase stability or the onset of segregation. The broadening of the transition is observed herein only in mixtures containing an abundance of PVE homopolymer. Equivalent mixtures, but in which the polybutadiene has about 15% 1,4 units randomly placed along the chain, do not exhibit such broad glass transi-
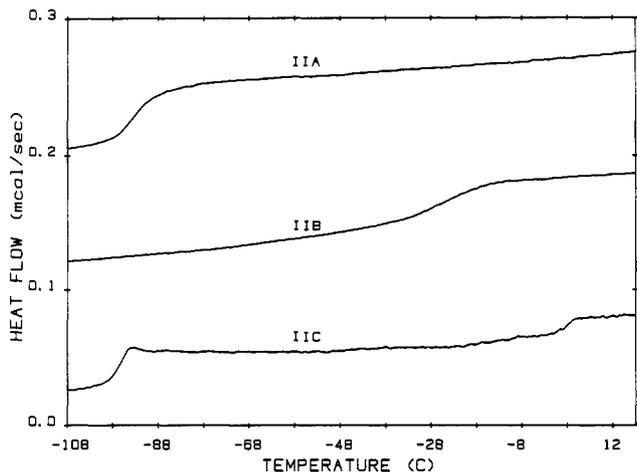
Figure 3. Calorimetry results for three blends of PVE with PBD, in which it can be seen that reducing χ^* from 6.4×10^{-3} (sample IIA) to 2.4×10^{-3} (sample IIC) effects phase separation. A broad T_g is observed only in the sample (IIB) with a high concentration of PVE, despite the fact that this is a more stable composition than IIA.
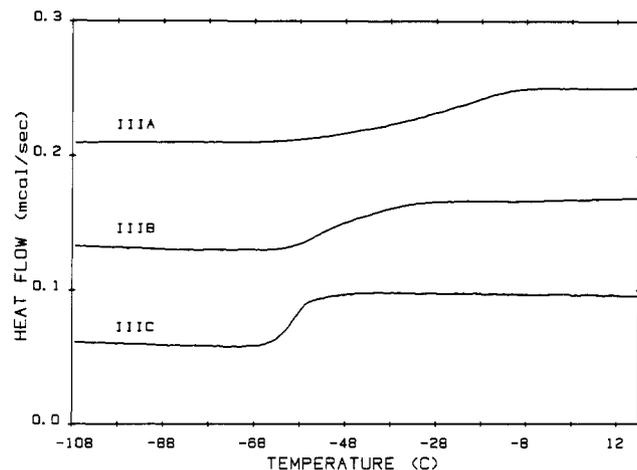

Figure 4. DSC measurements on three miscible blends of PIP with deuteriated PVE. The glass transition is increasingly broadened as the PVE concentration is increased.

Figure 5. Linear thermal expansion measured for two blends of PIP with deuteriated PVE (---), along with $\bar{\alpha}$, the calculated derivative (—). As is more clearly seen in the latter, the temperature range of the glass-to-liquid transition is significantly increased when the PVE has the higher relative abundance.

Figure 6. Ratio of the dynamic mechanical loss and storage moduli measured at 11 s^{-1} for the same compositions as in Figures 4 and 5. Anomalous broadening of the glass transition when the PVE is in high concentration is not observed.

tions.[1] Observation of this anomaly is dependent upon the presence of a relative abundance of PVE that is very high in 1,2 microstructure.

It has similarly been reported that miscible blends of poly(methyl methacrylate) with poly(styrene-co-acrylonitrile)[15] and of poly(2,6-dimethyl-1,4-phenylene oxide)[21] with either poly(p-chlorostyrene-co-o-chlorostyrene)[21] or polystyrene[14] exhibit broad T_g's when the more glassy component is present in high concentration. The origin of this effect, operative in only particular polymer blends, is not clear. From observation of a composition invariance of the distribution of relaxation times, it has been suggested that such anomalously broad transitions must result not from local concentration fluctuations but from an alteration of the structure of the glass.[14] The details of this structural change, or of the mechanism underlying it, remain to be specified. As stated, the anomalous breadth of the DSC transitions observed in the blends with a high PVE concentration is invariant to the thermal treatment imposed, demonstrating that the peculiar nature of the glassy state in these mixtures is not an artifact of nonequilibrium.

It can be seen in Figure 6 that whereas the discontinuities in the temperature dependence of both the enthalpy (Figure 4) and volume (Figure 5) display the anomalous broadening in certain blends, the corresponding mechan-
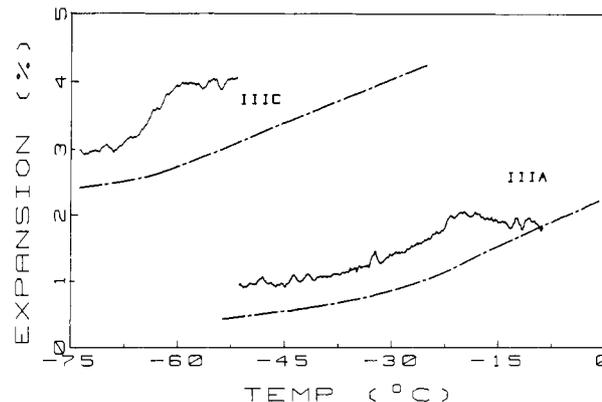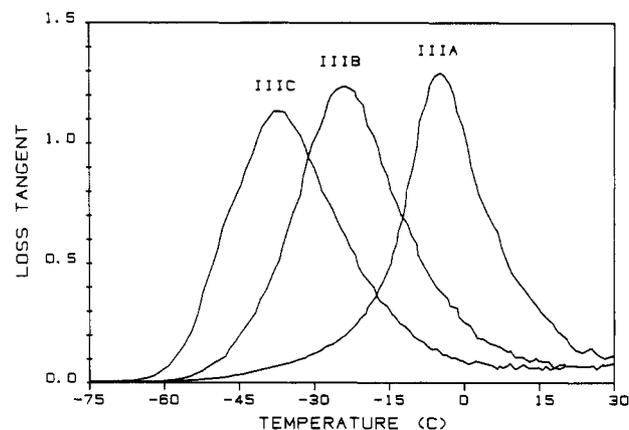
ical damping transitions exhibit only a slight broadening associated with the usual composition fluctuations in polymer mixtures. The least stable composition (designated IIIB) possesses the broadest damping peaks (both the loss tangent and the loss modulus), in accordance with its relative proximity to the critical point. This divergence in the transition breadths as determined by DSC and TMA from that seen in mechanical loss measurements is suggestive. The discontinuity in the expansivity at T_g arises from the sudden onset of configurational freedom due to the increased free volume. The heat capacity discontinuity likewise reflects the corresponding gain in configurational entropy. Although the mechanical response is obviously facilitated by free volume increases beyond that associated with the glassy state, in fact the rate at which the free volume fluctuates is of prime importance in providing for segmental mobility. Liquid or rubbery mechanical behavior is engendered only when free volume *converges* locally at a sufficient rate. The critical volume required for mechanical softening may correspond to a larger local accumulation of free volume than is reflected in the more direct thermodynamic probes employed in calorimetric and expansivity measurements. While the mixtures are homogeneous on the scale of any of the measurements, differences exist in the localized response to the respective techniques depending on the details of the free volume fluctuations in the vicinity of the transition temperature. Recent proton NMR experiments have revealed that despite compositional homogeneity that extends to the

subnanometer level, in the vicinity of the glass transition different chain subunits in these blends can simultaneously be exhibiting glassy and liquid-like motions.[22] Such results suggest divergence among the various segments in the free volume requirements for rubbery behavior.

Excess Free Energy of Mixtures. From application of eq 5 to the blend of components with the highest available molecular weights, an upper limit on χ equal to 1.7×10^{-4} is deduced. Actually the miscibility in polymer blends extends beyond the value of χ^* determined from eq 5, so this upper limit is probably underestimated.[6] Assuming validity of the Flory–Huggins model and given that χ must be nonnegative, (from ref 2 and eq 1 and 2), the interaction parameter for the PVE/PIP mixture would equal

$$\chi_{PIP,PVE} = 8.5 \times 10^{-5}$$

with a relative error of 100%, albeit small in absolute magnitude. This low value of χ reflects the remarkably small differences that exist in the strength of the force fields surrounding the various chain units in the PVE/PIP mixtures; consequently, the magnitude of the dispersion energy is virtually unaltered when a portion of like contacts are replaced by unlike contacts.

There will also be a contribution to the free energy of mixing from any differences in the liquid structure of the two components.[23,24] A difference in their degree of thermal expansion will result in a volume contraction upon mixing, which can influence both the mixing enthalpy and the mixing entropy. In fact, however, it has been reported that the specific volume of PIP/PVE blends varies between that of the pure components without indication of densification.[1] Although absence of a volume change upon mixing does not imply nonadditivity of the enthalpy and noncombinatory entropy, any such equation of state contributions to the free energy must be vanishingly small in order that miscibility be observed at these very high component molecular weights. The influence of the liquid-state properties on the volume change of mixing can be assessed from the respective magnitudes of the thermal expansion coefficients for the pure components. The equation of state parameters for the liquids are expressed as reduced quantities, where the reduction factors are the corresponding characteristic volume, v^* (the hard-core volume), and the characteristic temperature, T^*, and pressure, p^* (which are proportional to the intermolecular energy). The reduced equation of state parameters are given by[25]

$$\tilde{v}^{1/3} = 1 + \bar{\alpha}T/3(1 + \bar{\alpha}T) \tag{9}$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{10}$$

$$\tilde{p} = p/\gamma T \tilde{v}^2 \tag{11}$$

where γ is the thermal pressure coefficient. The contribution from differences in liquid structure of the components to the interaction parameter is given approximately by[24,26]

$$\chi_{vol} = v^* P^* / RT^* (\tilde{v}^{1/3}\tau^2/2(4/3 - \tilde{v}^{1/3})) \tag{12}$$

where τ, which characterizes the free volume differences, is equal to 1 minus the ratio of the respective T^* for the components. The measured thermal expansion coefficients for the PVE and the PIP had a difference that marginally exceeded the experimental error, indicating the similarity in their expansivities. The calculated equation of state parameters are listed in Table III. With a literature value for the thermal pressure coefficient of the PIP,[27] from eq 12 the contribution to the free energy of mixing due to the

Table III
Liquid-State Structural Parameters

	10^4 d ln V/dT^a	dp/dT^b	V^c	$\bar{v}$	$\tilde{T}$	p^{*d}
PIP	9.3	0.312	75.6	1.230	0.0651	138
PVE	9.2		60.4	1.228	0.0646	

[a] Per °C (isobaric). [b] cal/(mL °C) at constant volume. [c] mL/mol of monomer unit. [d] cal/mL.
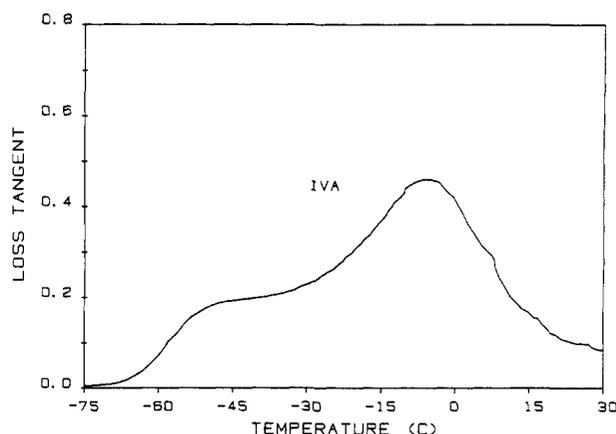

Figure 7. Measurement of the dynamic mechanical loss tangent at 11 s^{-1} for a blend of syndiotactic PVE with PIP, demonstrating heterogeneous phase morphology with χ^* is equal to 2.3×10^{-3}.

differences in the expansivity of the components is estimated to be

$$\chi_{vol} = 1 \times 10^{-4}$$

While this is at best only an order of magnitude approximation given the uncertainties in the $\bar{\alpha}$ employed, it does indicate that equation of state effects may be contributing significantly to the noncombinatory free energy of mixing. This is usual for polymers dissolved in a monomeric solvent, but presently the relative importance of the equation of state contribution reflects only the vanishingly small difference in contact energy density among the various chain units.

In Figure 7 are displayed mechanical damping measurements for a blend of syndiotactic PVE with PIP in which the critical interaction parameter has a value of 2.3×10^{-3}. This moderately high χ^* is sufficient to effect phase separation in this system as seen by the appearance of distinct glass transitions. This evidences the positive sign of the interaction parameter and also indicates that the enthalpy of mixing in PIP/PVE blends depends significantly on the tacticity of the PVE. In polymer mixtures wherein miscibility is arising from chemical reaction between the components, tacticity has been observed to influence the phase behavior.[28] The ability of the reacting moieties to assume the spatial arrangement most favorable for interaction is, not surprisingly, dependent on the stereochemical structure. The sequence distribution of the chain units may also influence the mixing enthalpy.[29] Similarly, stereochemical structure is seen to be import in the case of purely dispersive interactions between blend constituents. Bond polarizabilities can be characterized by a component parallel to the bond direction as well as a component transverse to this direction. In poly(vinylethylene) the polarizability transverse to the chain backbone is dependent on orientation with respect to the pendent vinyl group. The data in Figure 7 suggest that syndiotacticity of the PVE increases χ for the PIP blend to greater than 2.3×10^{-3}. Since an average polarizability cannot account for any dependency of the dispersion energy on the spatial orientation of the interacting induced

dipoles, it is obvious that group additivity approaches[30] to the calculation of solubility parameters are incapable of predicting such changes in interaction energy.

Summary

The observation of a change in phase morphology as a consequence of changes in the molar mass of the constituents is a direct and facile method for the determination of χ in blends for which χ is positive. The accuracy of such a determination is probably limited by the accuracy of the model employed to compute the dependence of excess free energy on the molecular weights and concentrations of the blend components. The morphology changes can be conveniently assessed from the observation of glass-to-liquid transition behavior; however, the breadth of these transitions determined from DSC measurements is not necessarily related to the phase structure.

The interaction parameter for atactic PVE in blends with PIP is circa 2×10^{-4}, which is remarkably low given the absence of specific chemical interactions. These mixtures most closely approximate ideal mixing behavior of any known pair of chemically distinct polymers. Even some mixtures of isotopes have been found to be more nonathermal than the PIP/PVE blends.[6,31,32] The differences in liquid structure of the PVE and PIP must be quite small for miscibility to be observed at the very high molecular weights employed herein. Crude estimates of such contributions to χ indicate that it does represent, however, an appreciable fraction of the free energy of mixing.

The interaction parameter in the PIP blends increases by an order of magnitude when the PVE is syndiotactic. It is clear that the relative magnitude of the van der Waals forces is not made obvious from inspection of the chemical structure of interacting chemical species. As indicated by the present results, the main-chain unsaturation common to both PIP and PBD does not preclude a weakening of their dispersion interaction, relative to that of the pure components, which greatly exceeds the reduction in van der Waals attraction accompanying formation of near-neighbor contacts between subunits of the PIP with those of PVE.

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