

# Rheology of a Miscible Polymer Blend

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## Synopsis

Difference spectra of blends of *cis*-1,4-polyisoprene and atactic poly(vinylethylene), obtained from the measured FTIR spectra of the pure components and the blends, indicate that mixing of these polymers is not accompanied by any specific chemical interactions. Miscibility in this system arises solely due to the small combinatorial entropy of mixing. The conformation and configuration of the polymer chains in the blends are, therefore, identical to those in the pure melts. As a consequence it was found that the entanglement density of the blends varied monotonically with composition. This variation, however, was not in accordance with predictions based simply on the mechanical interaction density. The principle rheological effect of miscible blending was a large change in the monomeric friction coefficient, which arises from the strong dependence of free volume on composition. The zero shear viscosity and the terminal relaxation time of the blends reflected this change in local chain mobility. Empirical relations, which have previously been proposed for the properties of miscible polymer mixtures, were found to be without merit in describing the obtained experimental results.

## INTRODUCTION

The growing number of miscible polymer blends has generated considerable research activity directed at both understanding the fundamental cause of the miscibility as well as attempting to exploit this feature to obtain improved material properties. Mixtures of atactic poly(vinylethylene) (PVE) and *cis*-1,4-polyisoprene (PIP) are miscible and of particular interest in view of the suggestion that the miscibility arises without specific chemical interactions between the components.<sup>1</sup> It is commonly believed that endothermic heats of mixing are only associated with the mixing of polymers of low molecular weight (less than a few thousand). Blends of PVE and PIP, therefore, represent a unique example of miscibility in high polymers resulting solely from the small combinatorial entropy accompanying mixing. This report describes efforts to probe the nature of the intermolecular forces in PVE/PIP mixtures and their influence on the rheological characteristics of the blends.

## EXPERIMENTAL

The PVE, obtained from the Firestone Tire and Rubber Co., was atactic 97% 1,2-polybutadiene with  $M_n = 344,000$  and  $M_w = 414,000$ . The 98% *cis*-1,4-polyisoprene was a fractionated portion of the Goodyear Tire and Rubber Co.'s Natsyn 2210. It was estimated to have an  $M_w = 360,000$  based on the measured zero shear viscosity (see below) and its published molecular weight dependence.<sup>2</sup> The fractionation procedure has previously been determined to yield narrow polydispersities ( $M_w/M_n < 2$ ).

Blends were prepared by dissolution in pentane at 2% concentration by weight. To samples subsequently employed for dynamic mechanical analysis,

1% of an antioxidant (a styrenated diphenylamine isolated from the Goodyear Tire and Rubber Company's Wingstay 29) was added. After solvent removal, the polymers were compression molded for 3 days at room temperature into discs 25 mm in diameter and 6 mm thick. FTIR specimens were prepared by casting a film on NaCl plates from similar solutions but without the stabilizer. After initial drying, the salt plates were dried in vacuum and then maintained in a desiccator.

Room temperature Fourier transform infrared spectra were obtained with a Perkin-Elmer Model 1800 spectrophotometer. Typically 200 scans were made at  $2\text{ cm}^{-1}$  resolution, although several bands were measured at  $0.5\text{ cm}^{-1}$  resolution as well. No significant differences were discerned at the higher resolution.

Dynamic mechanical measurements were carried out with a modified Rheometrics RMS 7200, in which the torsional motion was directed through a closed loop between the servomotor and a Trans-Tek Model 603-000 Angular Displacement Transducer using a Hewlett Packard 9825 controller. A Schlumberger 1254 Frequency Response Analyzer was employed to generate the sinusoidal waveform and analyze the resulting displacement and load signals. The samples were tested in a parallel plate geometry and were in all cases observed to exhibit linearity up to at least 30% shear strain. A maximum dynamic strain amplitude of 5% was typically employed at deformation rates from 0.01 to 20 cycles per second over a temperature range from about  $T_g$  to  $150^\circ\text{C}$ . During temperature changes the plate separation was adjusted by monitoring the normal force that developed in the sample due to thermal contraction or expansion. The temperature chamber was at all times purged with nitrogen. Data were repeatedly taken at the highest temperatures in order to assess the occurrence of thermal crosslinking or degradation. It should be noted that, due to an abundance of physical entanglements, the room temperature dynamic moduli (in the vicinity of the rubbery plateau region of the viscoelastic spectrum) are largely unaffected by low levels of crosslinking which nonetheless effect large alterations of the mechanical response in the terminal region corresponding to elevated temperatures. The results obtained at various temperatures were expressed as a single function of frequency by time-temperature superpositioning. The moduli were multiplied in the usual fashion by the ratio both of the reference temperature ( $T_R = 298^\circ\text{K}$ ) to that of the temperature of measurement and by the reference density (obtained from Ref. 1) to that of the density at the measurement temperature. These latter were calculated from the published thermal expansion coefficients,  $7.1 \times 10^{-4}$  and  $7.5 \times 10^{-4}$  per degree for PIP and PVE, respectively.<sup>3</sup> Shifting along the frequency scale was done empirically using either the storage or loss moduli, depending on which had more curvature in a particular region, such that the superpositioning procedure was less arbitrary.

## RESULTS

### FTIR Spectra

Any chemical interaction (e.g., hydrogen bonding, complex formation, charge transfer) occurring between unlike chains in a miscible blend, or the conforma-

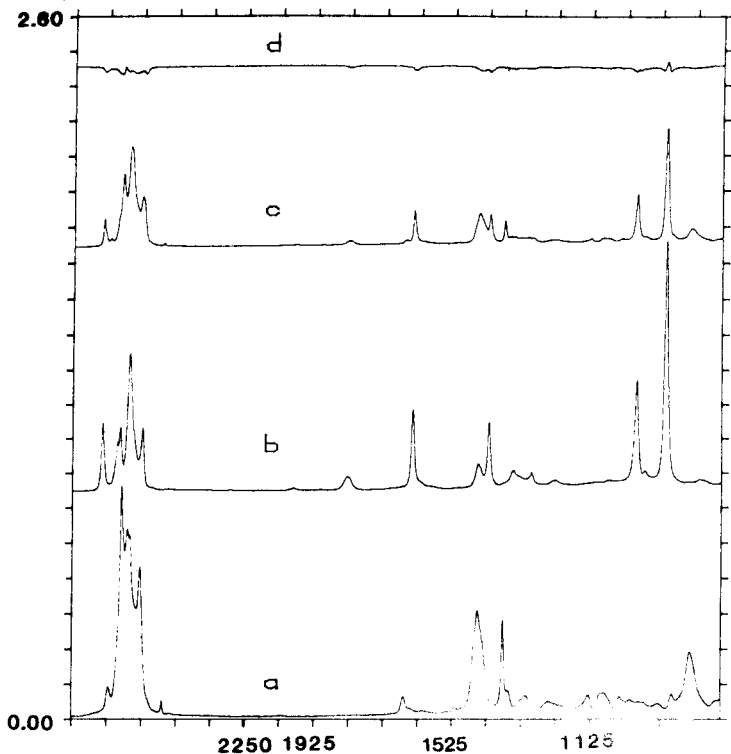


Fig. 1. The FTIR spectra of (a) PIP, (b) PVE, and (c) a 1:1 blend, along with (d) the calculated difference spectrum. The abscissa is expressed here, and in the ensuing Figures 2-7, in wave numbers and the ordinate scale is absorbance units.

tional changes induced by such interaction, can effect perturbation of the vibrational transitions accompanying infrared absorption or Raman scattering from the blend. Although the spectral changes are not necessarily expected to be large, in accordance with the magnitude of the intramolecular forces governing these transitions relative to the weak intermolecular potential, there exists substantial evidence for distortion of the infrared spectra of miscible polymer mixtures.<sup>4-9</sup> It has also been shown, moreover, that even interaction energies that make a negligible contribution to the free energy of mixing, in comparison to that from the combinatorial entropy, can nevertheless effect measurable "solvent" shifts in the IR spectrum.<sup>10</sup> If miscible blending of PIP and PVE transpires without specific interactions, the infrared spectra of the blends are expected, therefore, to correspond to the appropriate sum of the components' absorption spectra.

Displayed in Figure 1 are the respective FTIR spectra of pure PIP, pure PVE, a 1:1 blend of these polymers, and the calculated spectrum of the latter minus the sum of the former two. In using IR difference spectra to judge the occurrence of chemical interaction between dissimilar polymer molecules, the possibility exists for the appearance of artifacts in the calculated spectrum, particularly, for example, when a difference exists in the magnitude of the real part of the refractive index of the two polymer species. These optical effects can yield anomalous peaks and distorted absorption bands in the mixture

TABLE I

Frequency and Breadth of FTIR Bands Measured from the Pure Polymers and from Blends

Polymer	Assignment <sup>a</sup>	Neat		Blended <sup>d</sup>	
		Freq. <sup>b</sup>	FWHM <sup>c</sup>	Freq. <sup>b</sup>	FWHM <sup>c</sup>
PVE	CH <sub>2</sub> of CH <sub>2</sub> =CH out of plane def.	909	13	909	12
PVE	CH <sub>2</sub> of CH <sub>2</sub> =CH out of plane def.	994	14	994	14
PVE	C=C stretch	1641	10	1641	11
PVE	CH <sub>2</sub> =CH overtone	1827	26	1829	24
PVE	CH of CH <sub>2</sub> =CH stretch	3074	24	3074	24
PIP	CH of C(CH <sub>3</sub> )=CH out of plane def.	837	36	837	38
PIP	CH <sub>3</sub> symmetric def.	1376	8	1376	8

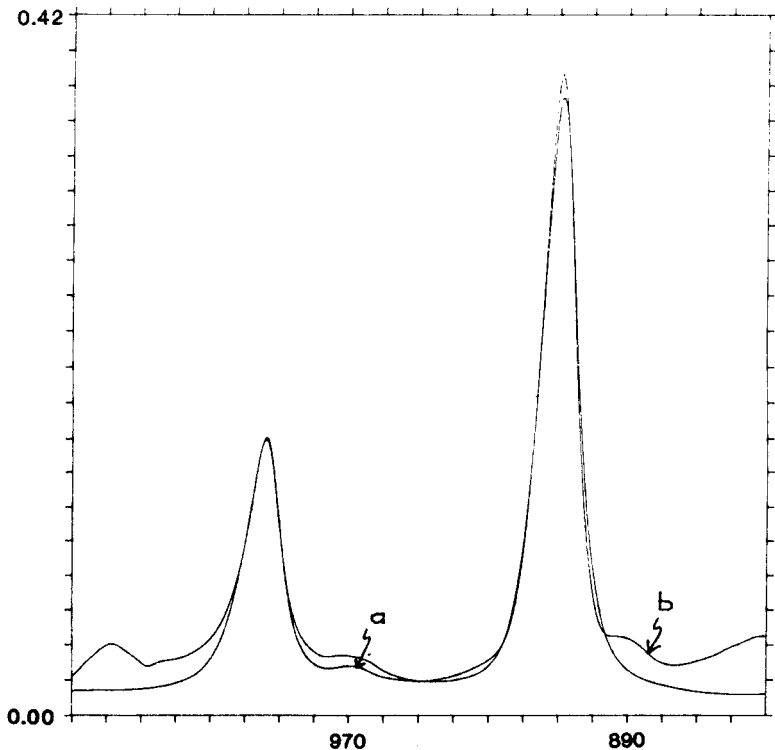
<sup>a</sup>References 33-35.<sup>b</sup>Frequency (in wave numbers) of maximum absorption.<sup>c</sup>Full width of band at half maximum intensity (in wave numbers).<sup>d</sup>Mixture with 5% concentration by weight of the indicated species.

Fig. 2. Two transitions in PVE involving out-of-plane deformation modes of the vinyl CH<sub>2</sub> (a) in the pure polymer and (b) after dilution 1:19 with PIP. The ordinate scale indicates the actual measured absorbance of the diluted species in this and in Figures 3-7.

which are unrelated to any chemical shifts.<sup>11</sup> The absence of significant structure in the difference spectrum in Figure 1 indicates that the blend FTIR spectrum is essentially the linear combination of the components' respective absorptions. This type of result has often been taken to demonstrate blend heterogeneity. For the PIP/PVE system, however, Figure 1 reinforces the concept that the miscibility is arising only from the combinatorial entropy of mixing<sup>1</sup>. The polarizabilities of the respective chain subunits are sufficiently similar such that the dispersive interaction energy is of insufficient magnitude to prevent segmental mixing of the polymer chains.

Since any spectral perturbations due to specific interactions might be weak, it is useful to attempt their amplification by measurement of the absorption spectrum of one component present in an excess of the second. Toward this end, difference spectra were obtained for blends containing 5% of one component in the other. Since the local monomer concentration due to a given polymer chain is small relative to the concentration of monomers from all chains (by roughly a factor proportional to the square root of the degree of polymerization<sup>12</sup>), a chain present in a 19-fold excess of the other component will be exposed to a predominance of unlike contacts. Any interaction-induced alterations of the vibrational spectrum should accordingly be magnified. Listed in Table I are five absorption bands of PVE that do not overlap intense bands in the PIP spectrum, along with two bands of PIP that are largely separated in frequency from strong PVE absorptions. These relatively isolated

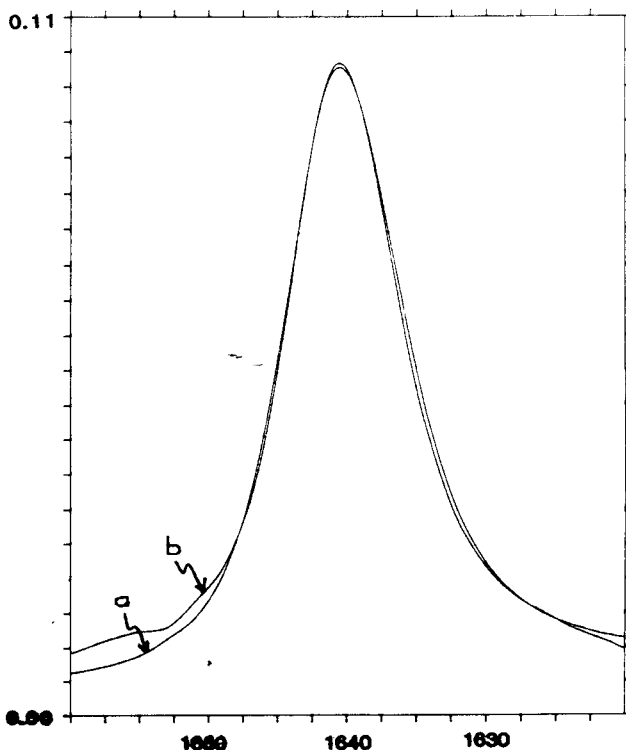


Fig. 3. Comparison of the C=C stretching vibration measured for PVE (a) neat and (b) at 5% concentration in PIP.

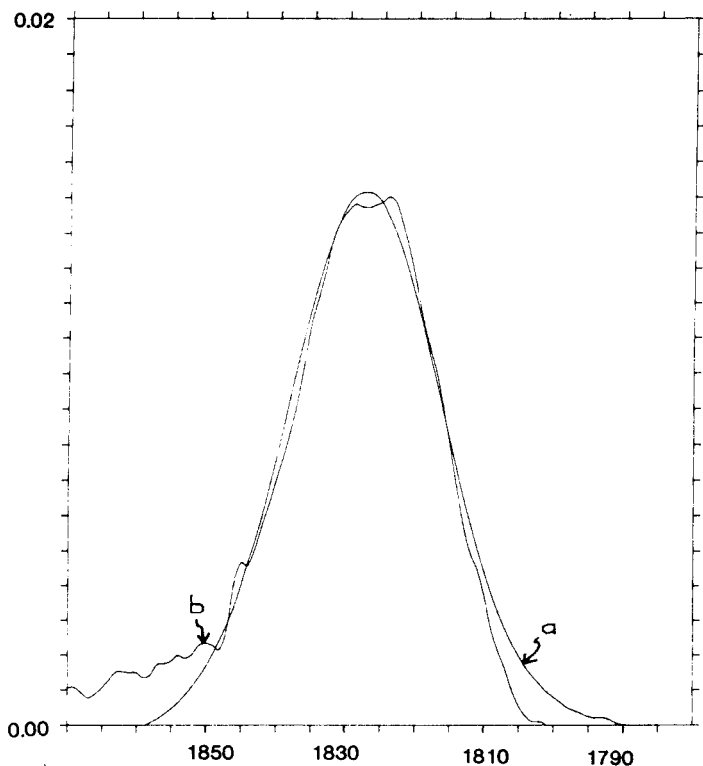


Fig. 4. Measured shape of the weakly absorbing  $\text{CH}_2=\text{CH}$  overtone band for (a) pure PVE and (b) a 1:19 blend with PIP.

transitions were employed to assess the extent of any changes in bandshape or position resulting from blending. The pendant vinyl group in the PVE is the most likely candidate for involvement in chemical interactions with the PIP, given its relative spatial accessibility and a slight polarity. Because of the distinct vibrational frequencies of the vinyl moiety, the isolated infrared absorptions of the PVE listed in Table I all correspond to motions involving this group. The difference spectra of these bands for a 19:1 dilution of the PVE in PIP are compared with the corresponding spectral regions measured for pure PVE in Figures 2-5. The shape, breadth and the frequency of the respective infrared bands are seen to be virtually unchanged after blending. No shoulders or new peaks are in evidence. Any dissimilarities apparent in these spectra are related to residual background intensity and the vagaries associated with the calculation of difference spectra. Difference spectra obtained from the PIP diluted 19-fold with PVE are similarly shown in Figures 6 and 7, which represent, respectively, transitions involving vibrational motions of the pendant methyl group and the main chain unsaturated carbons. No suggestion of any chemically induced perturbation of the FTIR spectrum can be observed. These results, summarized in Table I, are particularly persuasive in view of the errors inherent in obtaining difference spectra at high dilution, whereby the results represent small differences in the subtracted spectra, and any errors associated with the latter will accordingly be magnified.<sup>4,11</sup> These difference spectra provide a clear indication that the PIP/PVE system is a

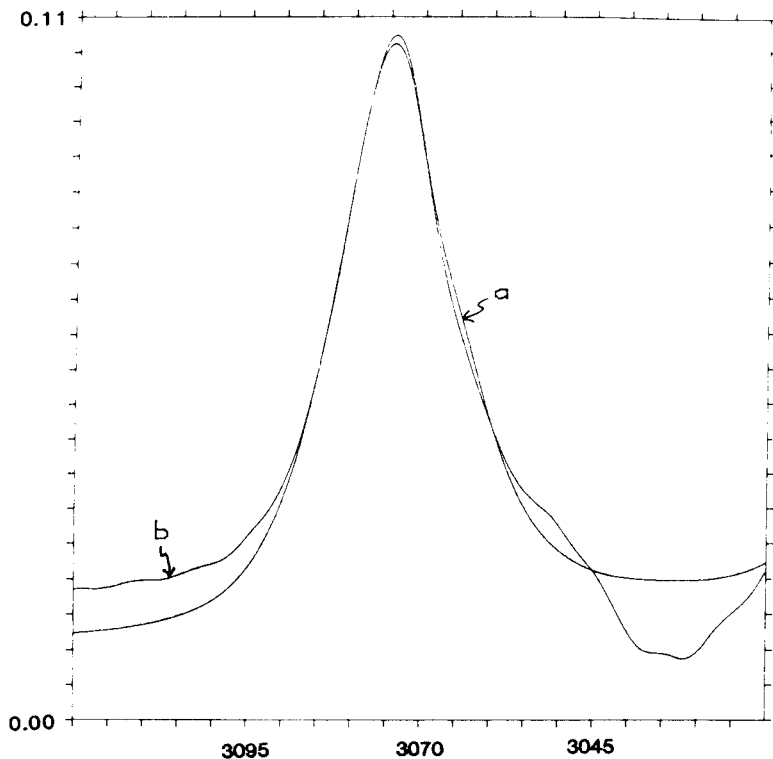


Fig. 5. Measured FTIR band arising from the stretching mode of the vinyl group CH in PVE (a) neat and (b) diluted to 5% concentration with PIP. This band is slightly to the high-frequency side of the group of very intense absorptions associated with the various aliphatic CH stretching modes in PVE and PIP (see Fig. 1).

unique example of a miscible high polymer blend in which the intermolecular forces between chemically distinct species are limited to van der Waals type interactions.<sup>1</sup>

### Dynamic Mechanical Spectra

The frequency dependence of the storage,  $G'$ , and loss,  $G''$ , dynamic shear moduli of PVE/PIP blends of varying composition are displayed in Figures 8 and 9, respectively. The most striking change in mechanical behavior with composition is the location of the viscoelastic spectrum on the frequency scale. The transition zone can be seen to transpire at increasingly higher frequency as the relative abundance of PIP in the blend is increased. This, of course, reflects primarily the composition dependence of the glass transition temperature. The PIP and PVE exhibit markedly different  $T_g$ 's, and it has been shown that the liquid to glass transitions in these blends occur at temperatures indicative of a random arrangement of the respective chain subunits.<sup>1</sup> This is a necessary consequence of a mixture in which only van der Waals interactions are existent. The frequency,  $\omega_g$ , at which the liquid to glass transition occurs at 25°C, as defined by the maximum in the ratio of the loss and storage moduli, is listed in Table II for all compositions. The time scale at which this

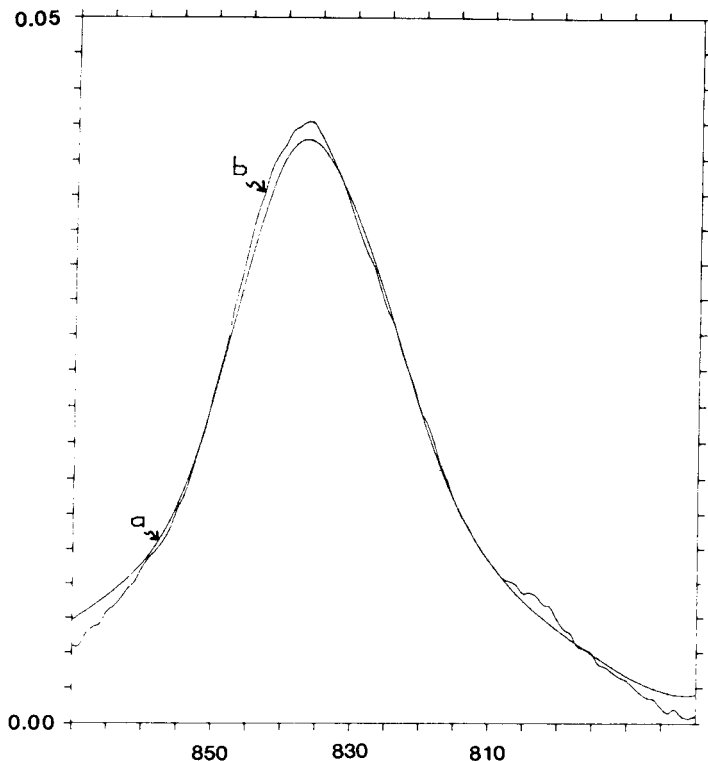


Fig. 6. PIP CH out-of-plane deformation mode in (a) the pure polymer and (b) diluted to 5% with PVE. The agreement between the two bands is remarkable in view of the low magnitude of the absorbance (transmission > 90%).

transition takes place is determined largely by the magnitude of the monomeric friction coefficient characterizing the local mobility of a chain subunit. The frictional drag exerted by neighboring chains depends both on the available free volume as well as the nature of the intermolecular potential. In the transition region of the spectrum where the moduli vary with the half-power of frequency,  $\omega$ , a value for the friction coefficient  $f_0$  can be obtained from<sup>13</sup>

$$f_0 = \frac{48C(m_0G')^2}{\omega kT(\rho lN)^2} \quad (1)$$

where for the blends average values can be used for the repeat unit molecular weight,  $m_0$ , and also (using literature values for the pure components<sup>14,15</sup>) for the Kuhn step length  $l$  and the characteristic ratio  $C$  of the blends, since the chain conformations are unchanged from the pure melt. In eq. (1),  $N$  represents Avogadro's number,  $k$  is the Boltzmann constant,  $\rho$  is the density, and  $T$  is the absolute temperature. As the blend composition is modified it can be seen in Table II that the monomeric friction coefficient smoothly varies between that of the pure components. As suggested by the invariance of the infrared spectra to blending, the intermolecular potential is unaltered by



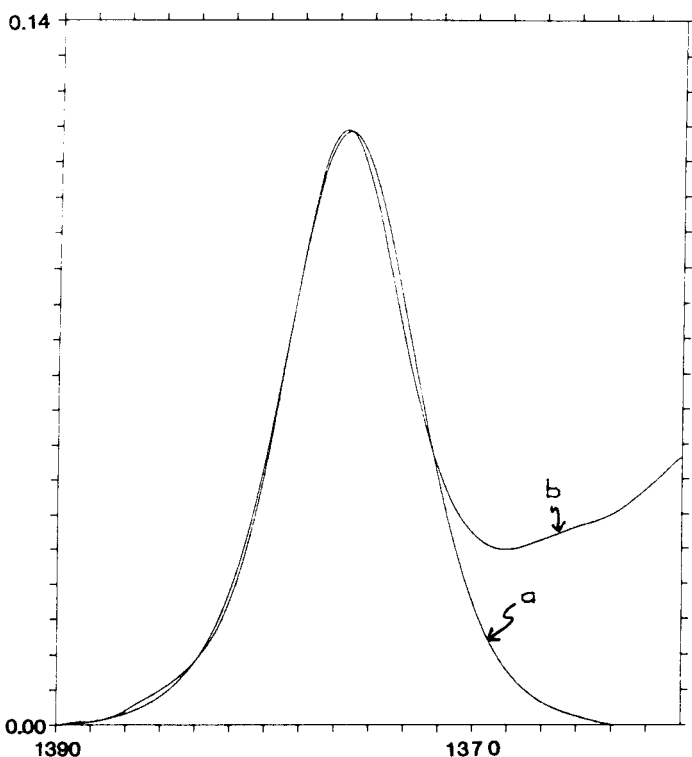


Fig. 7.  $\text{CH}_3$  symmetric deformation measured in (a) pure PIP and (b) a 1 : 19 blend with PVE. The extra background intensity on the low-frequency side of the blend spectrum is from some partially overlapping absorptions in the PVE.

changes in blend composition. In general the local viscosity reflects the nature of these intermolecular forces as well as free volume effects. In these mixtures the composition dependence of  $f_0$  is being governed by the latter. Miscible blending has in some instances been reported to be accompanied by a net volume contraction.<sup>16,17</sup> Density data provide no indication for this in PVE/PIP mixtures,<sup>1</sup> nor is it expected in the absence of specific interactions. The changes in free volume are arising from the composition dependence of the glass transition.

The processing characteristics of PVE/PIP blends will not, of course, necessarily parallel the magnitude of the monomeric friction coefficient. Displacement of a chain segment over a sufficiently large distance, on the order of the Kuhn step length, will perturb neighboring chains, and consequently such displacements engender chain reptation. The extent of entanglements and the time scale for configurational rearrangements of the chain will then influence to a large extent the rheological properties of the polymer fluid. The frequency of the maximum in the loss modulus observed in the low frequency region of Figure 9 defines a characteristic time  $\omega_T^{-1}$  associated with disengagement of a chain from the "tube" of entanglement constraints. Over the range of compositions this terminal relaxation time is observed to vary at room temperature from several seconds for pure PIP up to a few hours for the PVE (Table II).

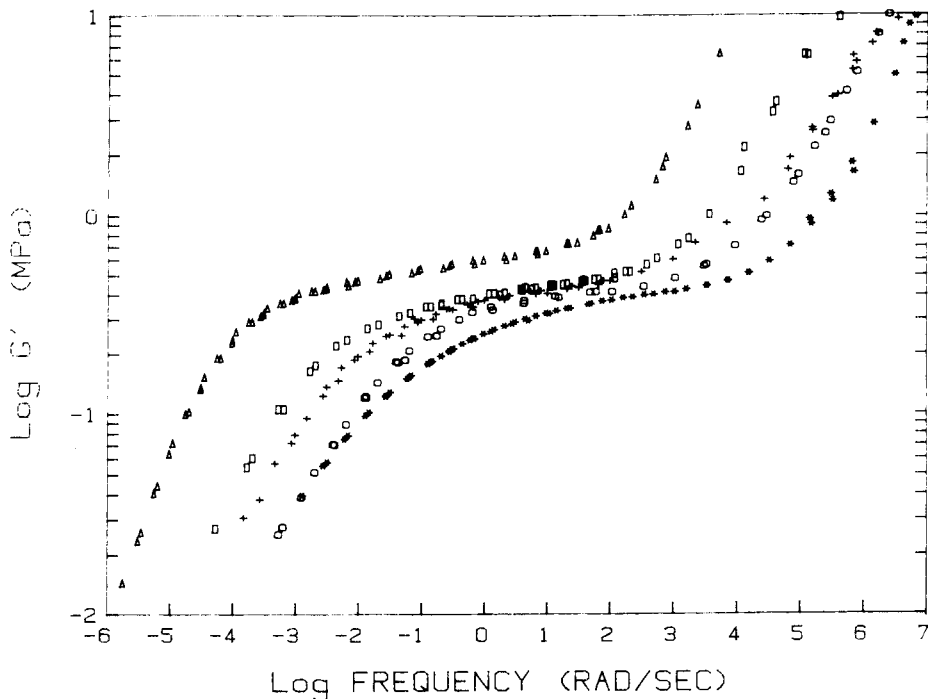


Fig. 8. Storage modulus measured in shear and expressed as a function of the WLF shifted frequency for PIP blended with 0% (\*), 20% (O), and 50% (+), 80% (□), and 100% (Δ) PVE. The moduli have been multiplied by the ratio of the product of the reference temperature (298 K) and the density at the reference temperature to the product of the temperature of measurement and the corresponding density.

It is useful to consider the extent to which this terminal relaxation time of the blends is being governed by the magnitude of the monomeric friction coefficient. According to reptation theory this relaxation time is given by<sup>13,18</sup>

$$\omega_{\Gamma}^{-1} = \frac{f_0 l^2 M^3}{C M_e m_0^2 \pi^2 k T} \quad (2)$$

where  $M_e$  is the average molecular weight of a chain segment between entanglement constraints. Although experimental evidence indicates that the influence of chain length on the relaxation time is stronger than the cubic dependence indicated by eq. (2), the linear proportionality between the friction coefficient and  $\omega_{\Gamma}^{-1}$  is valid provided the forces on the chain are weak (which is the case in the linear viscoelastic regime under consideration). The slight difference in molecular weight between the PIP and the PVE exerts some influence on the measured terminal relaxation times of the blends, since the blend  $M_w$  is the mass-weighted average of the components'  $M_w$ . This effect can be accounted for, of course, allowing assessment of the expected variation of  $\omega_{\Gamma}^{-1}$  due only to microstructural features of the components. This requires evaluation of  $M_e$ . The plateau in the storage modulus observed in Figure 8 results from the transitory network of entanglement couplings, and, according to classical rubber elasticity theory, this network modulus has a

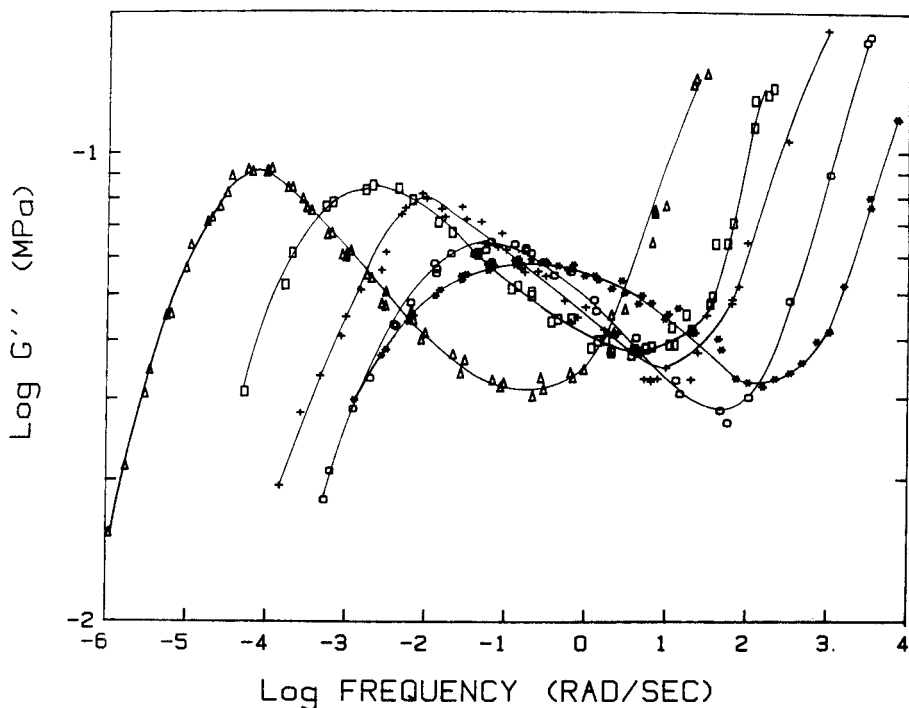


Fig. 9. Loss shear modulus results after time-temperature superpositioning for the PIP/PVE blends. The symbols are as defined in Figure 8. The high-frequency portion of the glass transition region has been omitted to allow expansion of the overlapping data on the terminal side of the plateau region.

TABLE II  
Viscoelastic Data for PIP/PVE Blends

Percent PIP	$w_g$ (rad/s)	$\log f_0$ (N-sec/M)	$w_T^{-1}$ (s)	$G_N^0$ (MPa)
100	$3.1 \times 10^6$	-8.81	7.4	0.28
80	$3.0 \times 10^5$	-8.22	15.9	0.31
50	$6.9 \times 10^4$	-7.74	119	0.39
20	$1.2 \times 10^4$	-7.16	493	0.41
0	$2.4 \times 10^3$	-5.76	12,200	0.44

magnitude equal to<sup>13,18</sup>

$$G_N^0 = \rho NkT/M_e \quad (3)$$

Since the modulus in the plateau region is not strictly independent of frequency, however, an alternative measure of this pseudoequilibrium modulus is required. Commonly it is evaluated from integration of  $G''$  in the terminal region<sup>3</sup>

$$G_N^0 = 2/\pi \int_{-\infty}^{+\infty} G''(w) d \ln w \quad (4)$$

Equation (4), however, requires extrapolation on the high frequency side to eliminate contributions from the overlapping transition region. A more precise measure of the modulus of the entanglement network is obtained from the magnitude of  $G''$  at  $\omega_T$ , which is predicted by a phenomenological theory<sup>19,20</sup> to equal

$$G_{\max} = 0.207G_N^0 \quad (5)$$

although empirical data on a variety of linear polymers have suggested that<sup>21</sup>

$$G_{\max} = 0.281G_N^0 \quad (6)$$

If it is assumed, given the similar macrostructure of the polymers employed, that the numerical factor in these relations, whatever its correct value, at least remains constant over the blend series, relative changes in the entanglement modulus can be obtained from either expression. From the data in Figure 9 values of  $G_N^0$  were calculated for the series of PIP/PVE blends using eq. (5). It is observed (Table II) that the entanglement density exhibits a monotonic variation over the entire composition range. Of course, since entanglements simply reflect the uncrossability of chain contours, nearly athermal mixing cannot be expected to significantly alter these topological features. In blends with specific interactions, moreover, interaction parameters of substantial magnitude (e.g., greater than  $10^{-2}$  in absolute magnitude) have been observed to have negligible effect on chain dimensions.<sup>22</sup> The large variation of the terminal relaxation time upon blending is therefore seen from eqs. (2) and (3) to be almost solely a reflection of local chain mobility, with only a very minor influence on  $\omega_T^{-1}$  arising from the change in entanglement density with blend composition.

These topological constraints have a concentration that has been shown to be related to the chain contour length per unit volume according to<sup>14</sup>

$$G_N^0 = KkT(\nu L)^a l^{2a-3} \quad (7)$$

where  $\nu$  is the concentration of chains of contour length  $L$ , and  $K$  and  $a$  are essentially species-independent constants. The variation in plateau modulus among different polymers can then be accounted for simply from differences in the density of chain crossings as expressed by the quantity

$$(\nu L^2)^a l^{-3} = (N^a b C / m_0)^a l^{2a-3} \quad (8)$$

where  $b$  is the number of main chain bonds per monomer unit. Taking the exponent  $a$  in eq. (7) to be equal to 2,  $G_N^0$  is predicted to be almost 2 times greater for PIP than for the PVE. The measured pseudoequilibrium modulus of PVE, however, exceeds that of the PIP by a factor of 1.6 (Table II). The unusually low entanglement density in *cis*-1,4-polyisoprene has been previously noted,<sup>14</sup> but the origin of this anomaly is unexplained. As PVE is added to the PIP, the concentration of entanglements increases due to greater overlapping of the chain contours. The predictions for the blend plateau moduli are depicted in Figure 10, which shows the composition dependence of

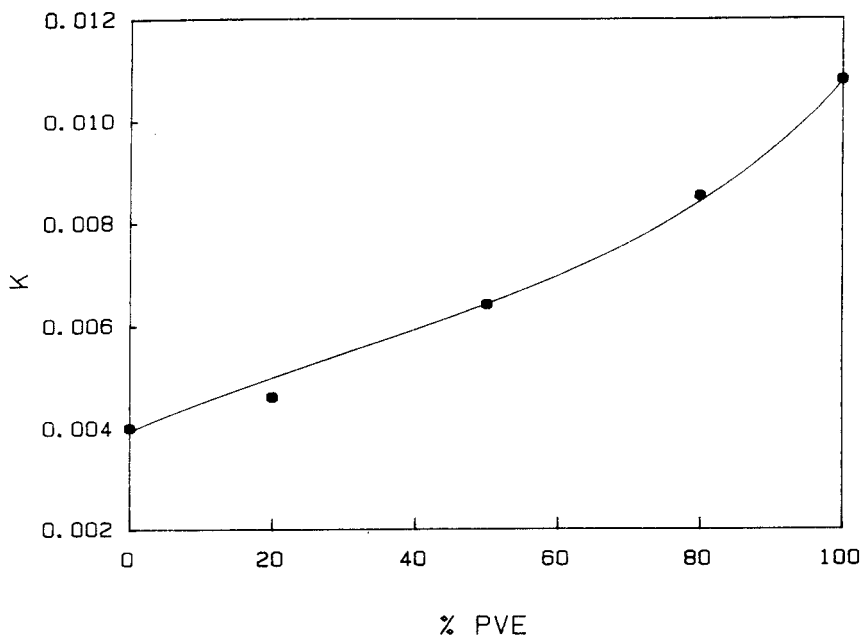


Fig. 10. The composition dependence of the parameter  $K$  [from eq. (7)] relating the pseudo-equilibrium modulus to geometric characteristics of the polymer chain. The value for PVE, 0.011, is in accordance with that obtained from data on a variety of linear flexible chain polymers,<sup>14</sup> whereas the PIP exhibits an unusually low entanglement density.

the parameter  $K$  determined using eq. (7) and the experimentally measured  $G_N^0$ . For the pure PVE  $K$  is in exact agreement with the reported value based on data from 15 different polymeric liquids.<sup>14</sup> The deviation in the predicted  $G_N^0$  from the experimental results can be seen in Figure 10 to increase with the concentration of the PIP. Although the source of such a species dependence in  $K$ , manifested in only a few polymers, is unclear, from the nonlinear dependence of  $K$  on PIP concentration apparent in Figure 10 it is tempting to ascribe this anomaly to intermolecular, rather than intramolecular, origin.

There have appeared other semiempirical correlations of  $G_N^0$  with various molecular features of flexible chain polymers.<sup>23-26</sup> These attempt to account for the major influences of polymer microstructure on chain entanglements. Neglect of details of the chain properties, as well as the errors associated with published experimental results, make these relations approximate at best, with individual polymer species exhibiting large scatter about a very general trend. A recent exhaustive compilation of data on both flexible and rigid chain molecules has suggested that the number of main chain atoms between entanglement couplings  $N_c$  exhibits a power-law dependence on the characteristic ratio of the polymer.<sup>27</sup> For flexible chains, moreover, the correlation indicates a value of 2 for the exponent. Using the  $G_N^0$  from Table II, however, the respective values of the quantity  $(N_c C^{-2})$  for the pure PIP and the PVE are found to differ by a factor of almost 5, with the polyisoprene observed to be less entangled (higher  $N_c$ ) than consideration of its characteristic ratio would suggest. Since it is clear that the particular molecular factors responsi-

ble for the entanglement concentrations in polymeric liquids are not fully understood, predictions of such in blends can at best be only approximate.

### Rheological Compatibility

The rheology of a polymer blend is expected to reflect in some fashion the constituents present. It therefore might be expected that the nature of the deformation and flow of the blend will provide an indication of the extent of miscibility of the components. In block copolymers the viscosity and modulus are found to markedly decrease in magnitude at the upper critical solution temperature due to dissolution of the ordered supramolecular structure associated with the phase-separated morphology;<sup>28,29</sup> however, there is no corresponding discontinuity in the mechanical properties of homopolymer blends in the vicinity of a critical solution temperature. The molecular quantities most significantly modified by the changes in blend composition are the monomeric friction coefficient and the terminal relaxation time; moreover, as discussed above, the composition dependence of  $w_T^{-1}$  is directly related to changes in the local friction constant. Since nearly athermal mixing will always be accompanied by negligible alterations in the configuration of the polymer chains, the results in Table II for the PIP/PVE blends are representative of very general expectations for the rheology of entropically driven miscible polymer mixtures.

The limiting viscosity in the terminal region of the viscoelastic spectrum was obtained for each blend from the relation<sup>13</sup>

$$\eta_0 = G_N^0/w_T \quad (9)$$

In all cases these viscosities were found to be somewhat less than the viscosities calculated from the ratio of the loss modulus and frequency at the slowest frequencies displayed in Figure 9. The viscosities calculated for the blend series from equation 9 are displayed in Figure 11. Numerous attempts have been made to predict the composition dependence of the viscosity of polymer blends, notwithstanding a noteworthy absence of success.<sup>30</sup> For miscible systems one empirical approach is to obtain predictions from simple mixing rules

$$\eta_{12}^n = \phi_1 \eta_1^n + \phi_2 \eta_2^n \quad (10)$$

based on series ( $n = 1$ ) and parallel ( $n = -1$ ) representations of blend properties in terms of the component properties, where  $\phi_i$  refers to the volume fraction of the  $i$ th species in the mixture. A popular variation is to take the exponent of eq. (10) to equal zero and employ the "logarithmic rule of mixtures"

$$\eta_{12} = \eta_1^{\phi_1} \eta_2^{\phi_2} \quad (11)$$

The viscosities calculated according to eq. (10) are displayed in Figure 11. It is seen that, although the experimental results can be roughly approximated by taking the exponent to be a fitting parameter, these "mixing rules" are

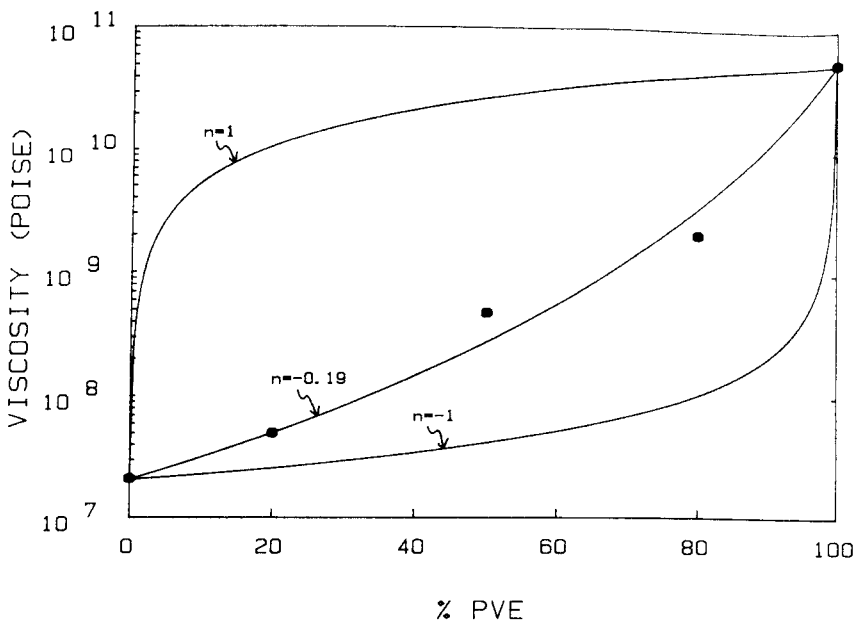


Fig. 11. Viscosity in the limit of zero shear rate measured for the PVE/PIP compositions using eq. (9). The curves represent the upper ( $n = 1$ ) and lower ( $n = -1$ ) bounds predicted by eq. (10), along with the calculated viscosity using a "best-fit" value of  $n = -0.19$ . Equation (11) would correspond to linear interpolation between the viscosities of the pure components.

without apparent merit for any detailed accounting of the properties of the mixtures.

Extension of a series model to second order might be expected to provide more accurate agreement with experimentally measured blend properties

$$\eta_{12} = \phi_1\eta_1 + \phi_2\eta_2 + x_{12}\phi_1\phi_2 \quad (12)$$

From application of an expression of this form to results on the glassy modulus of polymer blends, it has been suggested that a positive crossterm (i.e.,  $x_{12} > 0$ ) can be a criterion for polymer miscibility.<sup>31</sup> The zero shear viscosity of the PIP/PVE blends, as discussed above, is primarily determined by the magnitude of  $f_0$ , whose composition dependence is a result of the differences in free volume available at the reference temperature as the blend composition is varied. Using the result for the  $\phi_1 = \phi_2 = 0.5$  sample, the coefficient of the crossterm is calculated to be negative ( $x_{12} < 0$ ), ostensibly implying blend heterogeneity. In fact, however, eq. (12) is completely incapable of describing the viscosity results displayed in Figure 11, even to the limited extent of at least predicting blend viscosities that are greater than zero. Any success in applying empirical expressions such as eq. (12) to the description of blend properties is more related to the broader functionality provided by the extra "interaction" term than to a more accurate consideration of the relevant physics.

It has been stated that the Cole plot (i.e., the storage modulus as a function of the loss modulus) for a miscible blend is invariant to changes in the relative

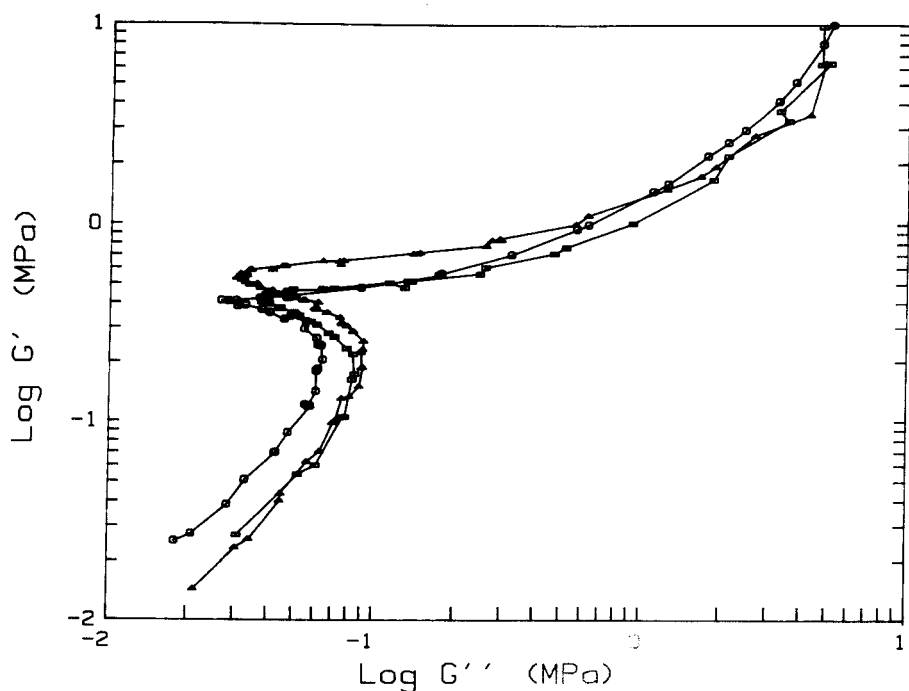


Fig. 12. Cole plot for PVE and two blends with PIP. The symbols are as defined for Figure 8.

abundance of the blend components, whereas for heterogeneous polymer mixtures such invariance is not observed.<sup>32</sup> Although if accurate it suggests that a blend's Cole plot can be used to assess miscibility, clearly no theoretical basis exists for the expectation that a composition independence of the relationship between  $G'$  and  $G''$  should accompany miscibility. The average molecular weight of a miscible blend will usually change as the relative amounts of the components change, and this will alter the shape of the Cole plot (for example, by modifying the depth of the minimum in the ratio of  $G''$  to  $G'$ ).<sup>20</sup> Also, since the monomeric friction coefficient varies with blend composition, the different  $f_0$  dependence of the storage and loss moduli in the terminal region<sup>13</sup> requires changes in the shape of the Cole plot with composition. Displayed in Figure 12 are the measured storage moduli for two of the PVE/PIP blends plotted against the corresponding loss moduli. It is evident that the Cole plots for each composition are unique, notwithstanding the miscibility. This particular means of looking at dynamic properties clearly has no general utility in the assessment of morphological homogeneity. At most it can be concluded that when the individual components of a blend have similar rheological properties, the rheology of the blend itself may be sufficiently insensitive to changes in composition such that the measured Cole plots appear equivalent within the experimental precision; however, it is not obvious that this statement must be restricted to blends that are miscible.

### SUMMARY

The blending of PIP and PVE gives rise to a polymer mixture homogeneous on the segmental level. The intermolecular forces in the blends are purely



van der Waals dispersive interactions as evidenced by the absence of perturbations of the FTIR spectra and in accordance with the essentially nonpolar nature of these hydrocarbon polymers. Miscibility arises owing to the nearly equivalent polarizabilities of the respective chain subunits, whereby the dispersion forces remain largely unchanged in magnitude upon blending. These mixtures represent an exception to the usual condition that miscibility in high polymers requires a negative Flory interaction parameter. Although dilution of one polymer with the other effects changes in local chain mobility, these are principally a consequence of the composition dependence of the free volume. Due to this invariance of the intermolecular potential, mixing is not accompanied by changes in the conformational state of the polymer chains, resulting in a density of topological constraints in the blends that varies monotonically between the entanglement concentrations found in the pure components. The rheology of these miscible mixtures is, from a practical point of view, simply a compromise of component properties without significant synergistic or novel features.

### References

1. C. M. Roland, *Macromolecules*, **20**, 2257 (1988).
2. D. S. Pearson, S. J. Mueller, L. J. Fetters, and N. Hadjichristidis, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 2287 (1983).
3. J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci. A2*, **6**, 967 (1968).
4. D. Garcia, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 107 (1984).
5. F. J. Lu, E. Benedetti, and S. L. Hsu, *Macromolecules*, **16**, 1525 (1983).
6. D. F. Varnell, J. P. Runt, and M. M. Coleman, *Macromolecules*, **14**, 1350 (1981).
7. M. M. Coleman and J. Zarian, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 837 (1979).
8. S. R. Fahrenholtz and T. K. Kwei, *Macromolecules*, **14**, 1076 (1981).
9. S. T. Wellinghoff, J. L. Koenig, and E. Baer, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 1913 (1977).
10. A. D. Buckingham and H. G. E. Hentschel, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 853 (1980).
11. D. L. Allara, *Appl. Spect.*, **33**, 358 (1979).
12. P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca 1979.
13. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., John Wiley & Sons, New York 1980.
14. W. W. Graessley and S. F. Edwards, *Polymer*, **22**, 1329 (1981).
15. X. Zhongde, N. Hadjichristidis, J. M. Carella, and L. J. Fetters, *Macromolecules*, **16**, 925 (1983).
16. H. B. Hopfenberg, V. T. Stannett, and G. M. Folk, *Polym. Eng. Sci.*, **15**, 261 (1975).
17. J. R. Fried, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **11**, 150 (1978).
18. M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford, 1986.
19. R. S. Marvin and J. Oser, *J. Res. Nat. Bur. Stand.*, **66B**, 171 (1962).
20. R. S. Marvin and J. Oser, *J. Res. Nat. Bur. Stand.*, **67B**, 87 (1963).
21. V. R. Raju, E. V. Menezes, G. Marin, and W. W. Graessley, *Macromolecules*, **14**, 1668 (1981).
22. M. Shibayama, H. Yang, and R. S. Stein, *Macromolecules*, **18**, 2179 (1985).
23. T. G. Fox and V. R. Allen, *J. Chem. Phys.*, **41**, 344 (1964).
24. D. W. van Krevelen, *Properties of Polymers*, 2nd ed., Elsevier, Amsterdam, 1976.
25. R. F. Boyer and R. L. Miller, *Rub. Chem. Tech.*, **51**, 718 (1978).
26. V. P. Privalko, *Macromolecules*, **13**, 370 (1980).
27. S. M. Aharoni, *Macromolecules*, **16**, 1722 (1983).

28. E. V. Gouinlock and R. S. Porter, *Polym. Eng. Sci.*, **17**, 535 (1977).
29. F. S. Bates, H. E. Bair, and M. A. Hartney, *Macromolecules*, **17**, 1987 (1984).
30. C. M. Roland, in *Handbook of Elastomers—New Developments and Technology*, (A. K. Bhowmick and H. L. Stephens, eds.), Marcel Dekker, New York, to be published.
31. L. W. Kleiner, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **19**, 519 (1979).
32. C. D. Han and H. K. Chuang, *J. Appl. Polym. Sci.*, **30**, 4431 (1985).
33. J. L. Binder, *J. Polym. Sci. A*, **1**, 37 (1963).
34. J. L. Binder, *J. Polym. Sci. A*, **1**, 47 (1963).
35. S. W. Cornell and J. L. Koenig, *Macromolecules*, **2**, 546 (1969).

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