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Entropically Driven Miscibility in a Blend of High Molecular Weight Polymers

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ABSTRACT: Molecular miscibility between *cis*-1,4-polyisoprene and atactic poly(vinylethylene), as evidenced by their spontaneous interdiffusion, is reported. It is suggested that miscibility arises in this blend of nonpolar hydrocarbons, not from specific interactions between moieties on the respective chains, but merely from the small combinatorial entropy accompanying mixing. This is made possible by fortuitous near equivalence of the dispersive energy densities of the respective chain subunits. The customary single glass transition is observed in the mixtures, at a temperature whose composition dependence is quantitatively in accord with theory for random arrangement of the statistical segments. No UCST was observed in this system, even for the least stable compositions, at temperature down to the onset of glassy behavior (ca. −45 °C). Crystallization of the polyisopropene is inhibited by the presence of the poly(vinylethylene); the latter, moreover, is apparently unable to disentangle from the crystallizing chains of the polyisopropene.

Introduction

The majority of polymer blends, notwithstanding any technological utility, are heterogeneous mixtures.[1] This is a consequence of the limited increase in positional disorder which accompanies their mixing, so that even a small positive mixing enthalpy will bring about phase separation. Specifically, for miscibility to occur over the entire composition range, the Flory interaction parameter, χ, for the polymer repeat units must be less than a critical value that is a measure of the combinatorial entropy[2,3]

$$\chi^* = \frac{1}{2N_1}\left\{1 + \left(\frac{N_1\nu_1}{N_2\nu_2}\right)^{1/2}\right\}^2 \qquad (1)$$

where ν represents the volume of the chain statistical segment and N is the number of statistical units per chain. In systems whose local interactions are dominated by van der Waals forces, χ will be positive; moreover, for the high molecular weights usually encountered (e.g., degrees of polymerization greater than 1000) it is observed that χ invariably is of sufficient magnitude to effect a multiphase blend structure.

When specific interactions are present (e.g., the ether complexes with phenyl groups in polystyrene–poly(vinyl methyl ether) blends[4] or hydrogen bonding in blends of novolac resins with certain carbonyl containing polymers[5]), a negative heat of mixing can result in miscibility. A net negative χ can also occur, in the absence of any specific interactions, when a copolymer is blended with a homopolymer whose subunits interact less unfavorably with the copolymer subunits than these copolymer segments interact among themselves.[6,7] Miscible systems exhibiting positive interaction parameters have been reported for 1,4-polybutadiene[8] and for polystyrene[9] when blended with their respective deuteriated analogues. The small difference in molar volume accompanying replacement of the protons with deuterium causes a reduction in volume upon mixing with consequent positive χ.[10] Its magnitude, however, is sufficiently low that such blends are most often found to be miscible.

In this paper a miscible blend is described whose components, atactic poly(vinylethylene) (PVE) and *cis*-1,4-polyisoprene (PIP), are essentially nonpolar aliphatic hydrocarbons in which the interactions are consequently of a dispersive nature. This blend system represents, therefore, a very unusual instance of miscibility between chemically distinct high molecular weight homopolymers despite a nonnegative interaction parameter. The miscibility arises solely due to the increase in positional disorder upon mixing. The influence of this blending on the crystallization of the PIP is also examined.

Experimental Section

The *cis*-1,4-polyisoprene, obtained from the Goodyear Tire and Rubber Co., had an isomeric purity of 97–98%. It was filtered prior to use yielding a GPC determined number-average molecular weight, M_n, equal to 245 000 and weight average, M_w, of 339 000. The poly(vinylethylene), obtained from the Firestone Tire and Rubber Co., was atactic 86% 1,2-polybutadiene based on the infrared spectrum, with $M_n = 308000$ and $M_w = 387000$. A 90% 1,4-polybutadiene (PBD), also from Firestone with $M_n = 108000$ and $M_w = 205000$, was synthesized by using the same catlayst as for the PVE but at higher temperature and without the modifier which yields 1,2 addition.[11]

Except where otherwise indicated, blend samples were prepared by mixing the PIP/PVE on an unheated two-roll mill. Stock temperatures were not allowed to exceed 60 °C. The samples were mixed for 10 min each and then annealed at room temperature for at least 1 month in all cases.

For adhesion testing, specimens were molded overnight at room temperature against aluminum foil. The foil was then removed and a pair of strips, 2.54 and 3.17 cm wide, respectively, were brought into contact by a windup procedure that avoids entrapped air. The strips were pressed together for 480 s with a 38.6-kPa load. The adhesion was subsequently measured at 5 cm/s in the 180° peel geometry at various time periods after removal of the compressive load. Details of the test method and factors influencing the obtained results are discussed elsewhere.[12]

Dynamic mechanical testing was performed with an automated Rheovibron on 2-cm-long strips with typically a 0.025 cm^2 cross-sectional area.

Density characterization was accomplished by the buoyancy method in methanol.

Differential scanning calorimetry was conducted by using a Perkin-Elmer DSC-2C with TADS data acquisition. Liquid nitrogen was the coolant. Sample weights of 5 to 12 mg were used. The glass transition temperatures were measured during both cooling and heating. No interesting differences existed between the two results and only the less noisy data obtained during heating are reported herein. Crystalline samples were prepared by placing preweighed, dried samples contained in DSC specimen holders into small desiccators which were then maintained at −9 °C for varying durations. Immediately prior to thermal measurements, these samples were placed in a small container of liquid nitrogen, transferred to the drybox enclosure, and loaded into the DSC. The head was held at −13 °C during this loading. The temperature was then reduced to −93 °C, followed by heating through the melting point of the PIP up to 60 °C. The temperature was subsequently brought back to −93 °C, followed by reheating through the glass transition. In all cases temperature changes were executed at 20 deg per min.

Results and Discussion

Miscibility. The retarded diffusion of macromolecules make problematical the attainment of a morphology that corresponds to thermodynamic equilibrium. Indeed, the structure developed during mixing of a heterogeneous blend reflects the competition between domain dispersion and coalescence, with the ultimate morphology being very path dependent.[13] Solution blending facilitates the attainment of equilibrium in so far as it enhances molecular mobility; however, miscibility between polymers in solution does not parallel their compatibility in the absence of solvent. At sufficient dilution any polymer pair will form a homogeneous solution in a common solvent. The nature of the final blend morphology can also depend on the details of the solvent removal process. In view of the fact that a nonequilibrium state is often obtained in mechanically or solution mixed materials, it is useful to rely on the spontaneous mixing of an initially separated pair of polymers to judge their miscibility. Thermodynamic compatibility is a necessary requirement for the interdiffusion. Of course, the slow rates of diffusion of macromolecules can limit the extent of this interdiffusion, so it is necessary to employ a probe of the morphology that is sensitive to the structure at the interface between the polymers since the bulk of the two layers may remain compositionally pure. The adhesion which develops at the interface reflects directly the spatial extent of interdiffusion, and when the experiment is carried out above the glass transition temperature of the components, the time scales for significant interdiffusion are readily accessible.[12]

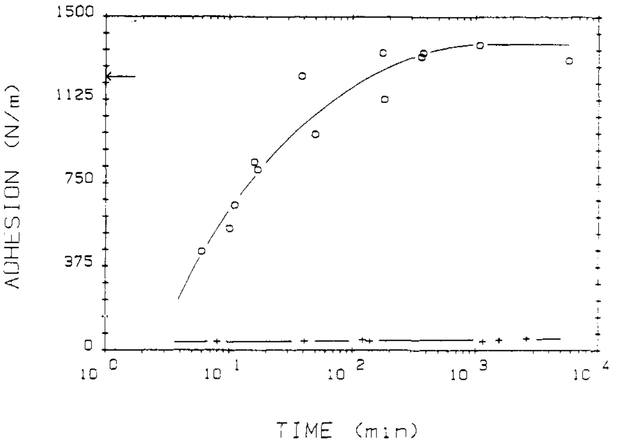

Figure 1. Peel adhesion measured as a function of contact time between PVE and PIP (○) and between PBD and PIP (+). For the former, the mode of failure changes from adhesive to cohesive as the bond strength approaches the plateau corresponding to the bulk cohesive strength. The peel adhesion of PIP to itself, indicated by the arrow, exhibited no time dependence due to the rapidity of the interdiffusion. In the case of autoadhesion of the PVE, testing after 17 min contact time resulted in destruction of the test specimens, indicating a lower limit of 1800 N/M for the cohesive strength.

Displayed in Figure 1 is the peel adhesion measured as a function of contact time for PIP plied against itself, PVE, and PBD. This adhesion parallels the extent of any interdiffusion of the polymer chains, eventually leveling off at a value limited by the cohesive strength of the materials. This corresponds to chain diffusion over distances roughly equal to the chain coil size. The self-diffusion coefficient, D, of the PIP is of the order 10^{-13} cm^2/s at room temperature.[14] With a radius of gyration, R_g, of about 100 Å, the adhesion should plateau at a level equal to the bulk strength over a time scale, τ, of roughly a few seconds

$$\tau \simeq R_g/2D \tag{2}$$

This is less than the time required to make the adhesion measurement; accordingly, the bonding of PIP to PIP is constant. The magnitude of the adhesion in this case is equal to the independently measured cohesive strength of the material, as can be inferred as well from the large deformation and bulk tearing that accompanies separation of the plied specimens. When the PIP is contacted against PBD, on the other hand, no interdiffusion is observed. The adhesion, as illustrated in Figure 1, remains low with a strictly adhesive mode of failure. Identical behavior is obtained for the adhesion of PVE to PBD. These are the usual results in experiments of this type, since the polymers are immiscible and consequently no driving force exists for interdiffusion.

More interesting behavior is observed when the PIP is brought into contact with PVE. The initially separated polymers spontaneously interdiffuse, which is possible only if they are thermodynamically miscible. The PVE/PIP blend is thus a remarkable example of miscibility between high molecular weight ($N > 10^3$) polymers in which, given their nonpolar, hydrocarbon character, no specific interactions are expected. Since only van der Waals forces, proportional to the respective component polarizabilities, are active in the blend, the replacement of a like contact with an unlike contact will reduce the overall dispersion energy density so that the enthalpy of mixing is expected to be positive. The combinatorial entropy of mixing is evidently sufficient to overcome this endothermic heat of mixing; that is, the condition expressed by eq 1 is fulfilled. The rate of interdiffusion between these polymer species can be described by a concentration-dependent coefficient that will vary as[15]

$$D = f(\phi)(\chi^* - \chi) \qquad (3)$$

where $f(\phi)$ relates the kinetics of the interdiffusion to the respective tracer diffusion coefficients, D^0 (i.e., D in the limit of the volume fraction, ϕ, going to zero)

$$f(\phi) = 2\phi(1 - \phi)[D_1^0 N_1 \phi + D_2^0 N_2 (1 - \phi)] \qquad (4)$$

This non-Fickian diffusion will transpire at a rate which reflects the degree of miscibility of the system. As χ approaches the critical value, χ^*, defined by eq 1, "thermodynamic slowing down" of the interdiffusion will occur.[16] Although the rate at which the peel adhesion increases in Figure 1 reflects the magnitude of the difference $(\chi^* - \chi)$, any composition dependence observed for χ, as well as the additional composition dependence of D expressed by eq 4, prohibits extraction of a value for χ simply from data of this type. Moreover, although it is tempting to conclude that the retardation of interdiffusion in the PVE/PIP system, relative to that observed for PIP or PVE self-adhesion, reflects this thermodynamic slowing down, the situation is in fact more complicated. The T_g of the blend is composition dependent, which imparts an additional composition dependence to D not accounted for in eq 3. It should also be pointed out that with certain elastomers, the buildup of self-adhesion has been found to transpire over a significantly longer time scale than the τ given by eq 2.[12]

It can be concluded that the occurrence of interdiffusion demonstrates that χ must be less than χ^*. This critical value can be evaluated from eq 1. In applying this it is noted that there is a dispersion of chain lengths in the materials employed. (Indeed, since the rate at which an entangled chain diffuses in the melt is proportional to the square of N, some segregation will occur over the course of the interdiffusion experiment. This will influence the rate at which the adhesion increases in Figure 1; however, the attainment of a bulk cohesive failure mode that is not localized at the interface attests to the completeness of the interdigitation process.) With the weight averages as an approximation,[17] the critical value obtained is $\chi^* = 0.0004$.

This value of the interaction parameter is expectedly low; only a small unfavorable heat of mixing would be sufficient to overcome the combinatorial entropy favoring mixing. What is unexpected is that the interaction parameter for a polymer pair of different chemical composition could be less than 0.0004 in the absence of specific interactions. Evidently any endothermic enthalpy change associated with mixing is of negligible magnitude. In principle one can deduce the absolute value (but not the sign) of the interaction parameter for a blend from the respective solubility parameters of the components. If only contributions from van der Waals forces are considered, the interaction parameter must be nonnegative and is given by[2]

$$\chi = \frac{\nu_1}{RT}(\delta_1 - \delta_2)^2 \qquad (5)$$

The critical value estimated above corresponds to a solubility parameter difference for these polymers of roughly 0.06 $(\mathrm{cal/m^3})^{1/2}$. Regrettably, however, the variance in the reported solubility parameters for PIP[18-20] spans a very broad range that does not allow comparison with that obtained from eq 5. The origin of the low value of χ for this system is attributable to the near equivalence of the cohesive energy density of the respective polymers. For dispersive interactions, such equivalence implies that negligible energy change accompanies replacement of a PIP segment in an environment of PIP molecules with that of a PVE chain segment. Only in the case of interactions that are strictly of the van der Waals type will equivalence of the cohesive energy densities imply a negligible χ and thus the potential for thermodynamic miscibility in high molecular weight polymers.

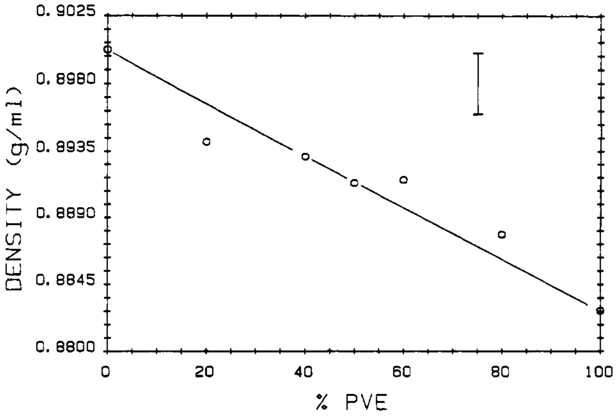

Figure 2. Density measured at room temperature for the series of PIP/PVE blends.

Since the free volumes of two polymers can differ, their miscible blending can effect a net contraction of the system, an effect favoring demixing. For the PIP/PVE mixtures it is simply observed that the room temperature density monotonically increases with PIP content (Figure 2). The T_g is composition dependent also (see below), so the net effect is the seemingly anomalous result that the density is observed to increase with increasing T minus T_g.

The domains in a heterogeneous blend can be directly observed in the electron microscope provided the electron density differences are of sufficient magnitude to provide contrast and extend over distances greater than the instrument resolution. After it was stained with OsO_4 the two-phase structure of blends of PIP/PBD and PVE/PBD was readily discernible in transmission electron micrographs. This indicates that sufficient differential reaction with the OsO_4 exists in these unsaturated polymers to obtain the necessary contrast. On the other hand, PVE/PIP blends prepared either by mechanical mixing or from solution revealed no structure in the TEM. Staining with either OsO_4 or RuO_4 did not alter the homogeneous appearance of the micrographs. This result is a necessary consequence of blend miscibility, although of itself it could not be taken as conclusive evidence of miscibility.

Glass Transition Behavior. The temperature at which a miscible blend changes from a glass to the liquid state is intermediate between the T_g's of the blend components. Due to the ready availability of means to make

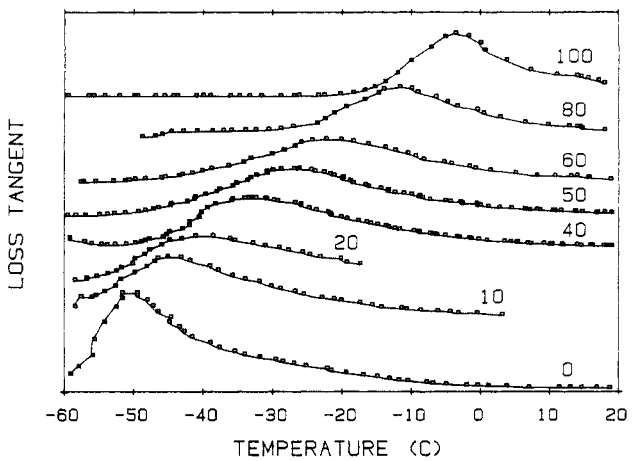

Figure 3. Temperature dependence of the dynamic loss tangent measured at 110 Hz for a series of PIP/PVE mixtures with the indicated volume percent of PVE.

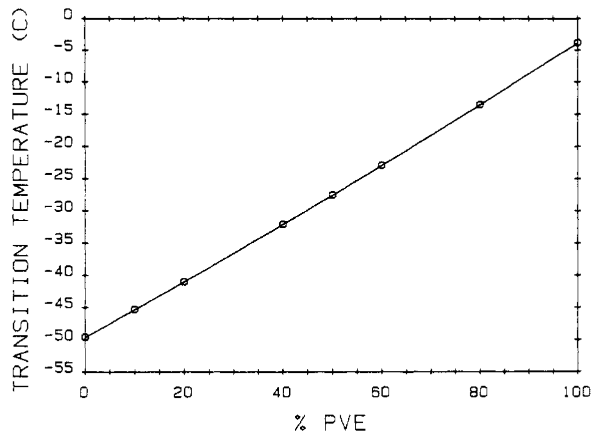

Figure 4. Comparison for the PIP/PVE blends of the measured temperature of the maximum in the loss tangent with the composition dependence calculated by using eq 6.

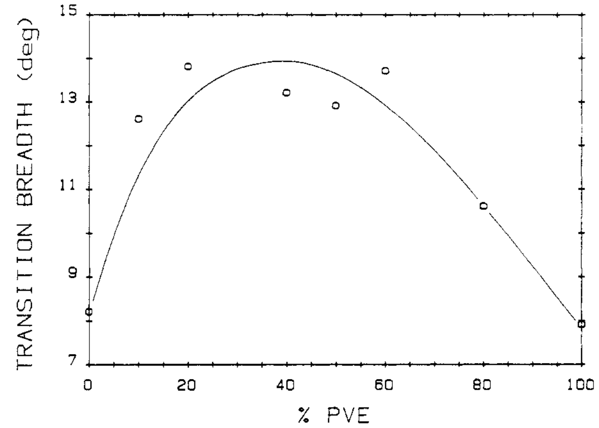

Figure 5. Breadth of the glass to liquid transition in blends of PIP and PVE as reflected by the temperature range over which the loss tangent decreased by 50% from its maximum value (i.e., the full width at the half-intensity points of the peak).

such measurements, the observation of a single glass transition temperature in a blend whose components possess distinct T_g's is the usual basis for assessing miscibility. Such an observation has in fact been reported for the PIP/PVE mixture.[21] Immiscible, two-phase blends can exhibit, however, a single intermediate glass transition when, for example, the domain size is small[22,23] or when a diffuse or interconnected interfacial region is present.[24] A single-blend glass transition can only be taken to indicate a certain level of homogeneity or intimate mixing, but does not demonstrate thermodynamic miscibility.

Displayed in Figure 3 is the temperature dependence of the dynamic mechanical loss tangent measured for a series of PIP/PVE compositions. The aspects of this data which may subtly reflect specific features of a miscible or almost miscible blend include the details of the T_g–composition relationship, as well as the breadth of the transitions. With the requirement that at the glass transition temperature the molar entropy of the glassy and liquid states be equal and the assumption that the heat capacities are independent of temperature, an expression for the glass transition temperature of a miscible blend can be obtained[25]

$$T_g = \exp\left(\frac{\rho_1\phi_1\Delta C_{p_1}\ln T_{g_1} + \rho_2\phi_2\Delta C_{p_2}\ln T_{g_2}}{\rho_1\phi_1\Delta C_{p_1} + \rho_2\phi_2\Delta C_{p_2}}\right) \tag{6}$$

where ρ represents the density of a given component. From the measured changes in heat capacity at the transition temperature, $\Delta C_p = 0.069$ and 0.072 cal g^{-1} deg^{-1} for the PIP and PVE, respectively, eq 6 is plotted in Figure 4, along with the experimental results of Figure 3. Notwithstanding the absence of any adjustable parameters, the agreement is quite satisfactory. This expression for the composition dependence of the glass transition temperature assumes random mixing. In blends in which specific interactions exist between the components, although a single blend T_g is observed, it is found to be less than that predicted by eq 6 due to local orientation effects promoted by the interaction.[26] The agreement illustrated in Figure 4 suggests random mixing of PIP/PVE, consistent with an absence of interactions (i.e., $\chi \geq 0$). Although mechanical damping is the most sensitive probe of the glass to liquid transition, there is no expectation that the maximum in the ratio of the viscous and elastic dynamic moduli occurs at a temperature corresponding to any thermodynamic definition of T_g such as equivalence of the glass and liquid entropies. This maximum occurs near the middle of the transition zone, however, and since, moreover, only the composition dependence of the maximum is of interest, concern regarding any lack of direct molecular interpretation of the temperature dependence of the loss tangent itself is obviated.

The temperature range over which this transition from glass to liquid transpires is displayed in Figure 5. It can be seen that the blends all exhibit a broader transition than do the pure components. Similarly the temperature difference between the onset of the abrupt change in heat capacity at T_g and the midpoint of the transition was found in the DSC measurements to increase from roughly 1 or 2 deg for the pure components to as much 4 deg for the blends. In immiscible blends this breadth is often attributed to phase interactions.[24,27] Clearly, the relaxation processes and configurational freedom available to polymer chain segments will be influenced by interfacial effects, particularly when the interfacial energy is low and thus the interfacial region extensive. In a truly miscible, one-phase blend, however, local fluctuations in composition arise, the extent of which is related to the magnitude of the interaction parameter.[28] Indeed, the small-angle scattering of neutrons or X-rays arising from these flutuations has an angle dependence which is governed by the spatial extent of the fluctuations and can therefore be used to measure χ.[3,8,29] These fluctuations in composition are specific to blends and therefore it is expected that a broader temperature range of the liquid to glass transition is observed for blends than for the corresponding pure polymers. Of course the magnitude of the loss tangent maximum is consequently reduced by this broadening.

It has been remarked that if the blend composition is present as a single phase the heat capacity change occurring through the transition should be a simple mass weighted average of the component ΔC_p's:[30]

$$\Delta C_{p_{12}} = \phi_1\rho_1\Delta C_{p_1} + \phi_2\rho_2\Delta C_{p_2} \tag{7}$$

For the PIP/PVE blends, in which, as noted above, the heat capacity change at T_g is essentially equal for PVE and PIP, the ΔC_p is not expected to change upon blending. Within the limited experimental precision of this measurement (about ±0.005 cal/(g deg)), it was found that ΔC_p was constant over the composition range. This suggests that all the material is participating in the transition; that is, the miscibility evidently extends over the range of molecular weights present in these samples.

When the interaction parameter is positive, an upper critical solution temperature (UCST) is expected.[31] This is principally due to reduction in the contribution of combinatorial entropy to the free energy of mixing as the temperature is lowered. Since a single glass transition is observed over the entire composition range, even at the low temperature of this transition for samples high in PIP content, the UCST is evidently too low to be observed for samples with these molecular weights. This is true even though a liquid state (and thus access to phase information) is maintained down to the lowest temperatures in the blends richer in one component. Such blend samples are the least stable (highest UCST) as a result of the composition dependence of χ that results from changes in local liquid structure upon mixing.[32] Observation of a UCST in PIP/PVE blends can be seen to require use of higher molecular weight polymers than those employed in this study.

Crystallization. The crystallization and melting behavior of a polymer can be altered by incorporation in a miscible blend. The lower free energy of the blend melt relative to that of the pure polymer effects a reduction in the equilibrium melting temperature of the crystals. By assuming that crystallization from the blend produces crystallites identical with those resulting from the crystallization of a pure component, the melting point depression has been related to the Flory interaction parameter[33]

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{-R\nu_1}{\Delta H_f^\circ \nu_2}(\chi\phi_2^2) \tag{8}$$

where T_m and T_m^0 are the respective equilibrium melting points in the blend and the pure material, and ΔH_f° is the perfect crystal heat of fusion. For the case of a positive χ, eq 8 has been incorrectly interpretted to imply that a melting point elevation will result from miscible blending.[33,34] The thermodynamic stability conferred upon the liquid by formation of a miscible blend reduces the relative stability of the crystalline state and thus must lower the equilibrium melting point irrespective of the sign of χ. The combinatorial entropy contribution to the free energy has been omitted in the derivation of eq 8.[33] When no enthalpy reduction accompanies mixing, however, as in the case of purely van der Waals forces between chain segments, a gain in positional disorder is a necessary requirement for miscibility. Although any alterations in the local liquid structure will also influence the entropy of the system, these equation of state effects can only reduce it.[35] The assumption of negligible combinatorial entropy is therefore equivalent to the assumption that χ is negative for miscibility; accordingly, eq 8 cannot be used to predict the melting point change accompanying endothermic mixing.

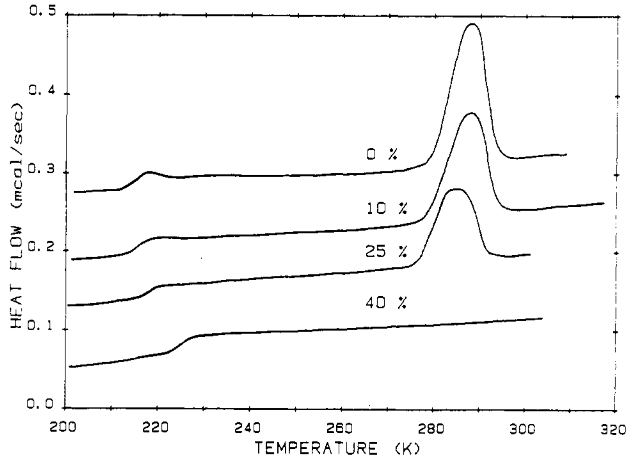

Figure 6. Representative DSC scans after crystallization for blends of PVE with the indicated volume fraction of PIP. The temperature at which heat capacity changed abruptly was in all samples shifted by about 2 deg in the ensuing scan following the melting.

Table I
Thermal Results Obtained for PIP/PVE Blends after 37 Days of Crystallization at -9 °C

% PVE	T_{melt}, °C	ΔH_f[a]	noncrystallinity[b]	% change in ΔC_p[c]
0	4.6 ± 0.5	4.5 ± 0.3	70 ± 1%	70 ± 3
10	4.8 ± 1.2	2.7 ± 0.9	82 ± 6%	79 ± 2
25	4.3 ± 2.3	2.6 ± 0.7	83 ± 1%	78 ± 5

[a] Calories per gram of PIP. [b] Based on ΔH_f. [c] ΔC_p for semicrystalline sample divided by ΔC_p measured after melting.

Retaining all contributions to the chemical potentials, the change in melting point upon blending can be written as[33]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-R\nu_1}{\Delta H_f^\circ \nu_2}\left[\frac{\ln \phi_1}{N_1} + \left(\frac{1}{N_1} - \frac{1}{N_2}\right)\phi_2 + \chi\phi_2^2\right] \tag{9}$$

For purely dispersive interactions between components, the largest change in melting temperature corresponds to ideal (athermal) mixing. For a PVE/PIP mixture in which the volume fraction of the crystallizing PIP is 0.75 and taking ΔH_f° = 15.3 cal/g,[36] the resulting pure entropically derived suppression of the melting point is calculated to be less than 0.01 deg. This is, of course, immeasurably small (justifying at least the usual neglect of combinatorial entropy in blends for which χ is negative).

A series of PIP/PVE blends were isothermally crystallized at -9 °C for varying duration up to 37 days with representative DSC scans displayed in Figure 6. The measured melting temperatures, averaged over several samples, are tabulated in Table I and are equivalent within the precision of the data. If this precision is taken to be 0.5, from eq 9 it can be calculated that $\chi > -0.09$, which is at least consistent with the supposition that $\chi \geq 0$. The melting points referred to in eq 9 are actually the equilibrium melting temperatures. In this work the slow crystallization of PIP was carried out at less than 13 deg below the measured melting point, so only a modest suppression of the melting point due to finite crystal size is expected.

The pure PIP attained a 30% extent of crystallinity based on the measured heat of fusion. It can be observed in Figure 7 that in blends the PIP appears to be significantly less crystalline, even after 37 days at -9 °C. Any difference in PIP crystallinity, however, between samples

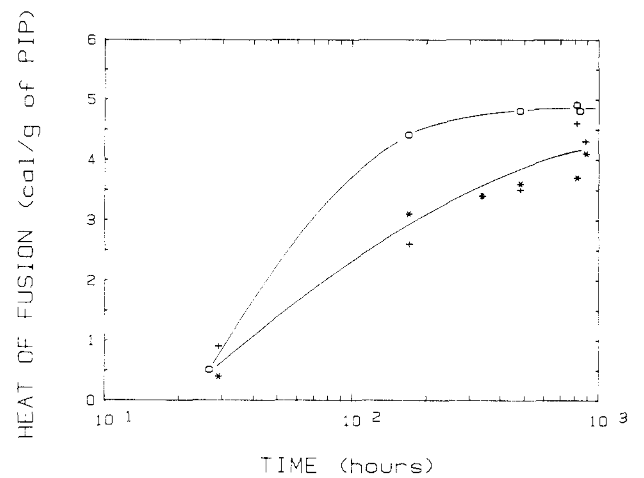

Figure 7. Enthalpy of fusion measured per gram of crystallizable component in blends with 100% (○), 90% (+), and 75% (☆) PIP after various time periods at −9 °C.

with 10% and 25% PVE was less than the precision in the measurement of ΔH_f. For samples with greater than 25% PVE, interestingly no melting endotherms could be detected, even though the instrumental sensitivity was more than sufficient if the reduction in crystallinity of the PIP was simply proportional to the concentration of PVE (Figure 6). It is generally expected that, while miscible blending can alter the rate of crystallization, the ultimate degree of crystallinity will be unchanged.[37] While not conclusive (since 37 days does not necessarily correspond to equilibrium), the results in Figure 7, showing the PIP crystallization leveling off at a reduced concentration in the blends, suggest that the PIP/PVE system may not conform to this expectation. Corroborating the measured reduction in ΔH_f in these blends is the finding (Table I) that the magnitude of the change in heat capacity at the glass transition paralleled the amorphous content of the samples. The increase in the change in heat capacity at T_g after melting is proportionally higher for the pure PIP, indicative of a higher extent of crystallinity.

In studies of spherulite growth rates, it has been observed that a spherulite radius will vary linearly with time if the composition of the melt remains constant during crystal growth (that is, the noncrystallizing component is incorporated into the interfibrillar or interlamellar regions).[38] If the rate of diffusion of the amorphous component away from the growth front is fast relative to the spherulitic growth rate, on the other hand, the amorphous phase will become progressively enriched in the noncrystallizing component. In a blend whose T_g is compositionally dependent, the T_g measured for the material in the semicrystalline state might reveal whether the amorphous regions in proximity to the crystals are identical in composition to the bulk amorphous phase.

In pure PIP the glass transition temperature was observed to decrease about 2 deg as a result of melting. This influence of crystallinity on T_g has been previously reported, with a slightly higher T_g of semicrystalline PIP attributed to reduced mobility of the amorphous chains adjacent to crystallites.[39] The T_g of the blends was also lowered 2 deg as a result of melting, with no indication of any T_g change due to alteration of the distribution of components in the melt. Since it is expected that there was ample time for equilibration of the blend samples after melting and prior to subsequent cooling below T_g, the inference is that in the blends the spherulite composition was identical with that of the melt; that is, during crystallization in the mixtures the PVE was trapped in the intercrystalline regions. From the values of the entanglement molecular weights ($M_e = 6400$ for PIP[40] and $M_e = 5300$ for PVE[41]), it is expected that a weight-average chain will have roughly 60 entanglement couplings, assuming that the chain configuration does not change upon blending, which is certainly true for small χ. Since, moreover, the temperature of crystallization was within a few degrees of the glass transition temperature of the pure PVE, it is not surprising to find that the PVE chains were unable to diffuse away from the growing crystallites. This would limit the concentration of PIP segments available at the crystal growth front and suppress not only the rate of crystallization but potentially the ultimate degree of crystallinity.

Summary

The blend of *cis*-1,4-polyisoprene and atactic 1,2-polybutadiene is unusual, not simply in view of its homogeneous nature but because its miscibility apparently arises without specific interactions commonly regarded as necessary for such miscibility when the molecular weights are high. The miscibility results from an interaction energy density that happens to be nearly equivalent for the unlike contacts and for like contacts in this system. A negligible enthalpy change accompanies blending so that the slight combinatorial entropy gain is sufficient for miscibility. This similarity in the van der Waals interaction densities is not obvious from mere inspection of the chemical structures. It can be observed that similarity in structure does not produce miscibility in PVE/PBD or PIP/PBD blends at high molecular weight.

The PVE/PIP blend is expected to exhibit an UCST. A single glass transition with a constant ΔC_p was observed over the entire composition range, however, indicating that higher molecular weights are required to observe this UCST. Currently, deuteriated PVE is being synthesized in order to provide neutron scattering contrast in blends with PIP. The angle dependence of the scattering will allow extraction of a measure of the Flory interaction parameter for these blends, which, in combination with infrared absorption measurements, can provide a definitive characterization of the intermolecular forces existent in this system. By extending the study to higher molecular weights, the phase diagram can also be examined.

The melting point of PIP was unaltered by blending, in accordance with a very low magnitude of χ. The crystallization of PIP appeared to be limited in extent by the presence of PVE, the chains of which are probably trapped within the growing spherulites. Efforts are currently under way to obtain a more detailed understanding of how the crystallization of PIP is influenced by miscible blending.

The mechanical properties of PIP/PVE are also under investigation. Synergistic properties have often been reported for miscible polymer mixtures. The PVE/PIP system is particularly interesting, moreover, due to the different cross-linking reactivities of main chain versus vinyl unsaturation. The latter is relatively unreactive for sulfur vulcanization, while its free radical cross-linking is accompanied by chain reaction and consequent high cross-link functionality. The mechanical behavior of the resulting networks and the PVE/PIP blends in general will be the subject of a subsequent paper.

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Solution-Cross-Linked Networks. 1. Swelling and Absorption Behavior of Natural Rubber Networks

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ABSTRACT: Swelling and absorption behavior of bulk and solution cross-linked natural rubber (*Hevea Brasiliensis*) networks was examined. The networks were prepared by irradiation of a 2–40-Mrd dose of γ-rays to solutions of a natural rubber sample at cross-linking concentrations C_x of 0.1–1 (bulk). Swelling and absorption tests were carried out at 308 K against pure benzene and benzene solutions of anionically prepared high *cis*-polyisoprene (*cis*-PI) of concentration ϕ. Equilibrium volume fractions of the solvent, v_1, the network, v_2, and the guest, v_3, were determined from the swelling ratio q ($=1/v_2$) and the absorption ratio $(v_2 + v_3)/v_2$ as functions of C_x and ϕ of the guest solution in which the network had been soaked. Results indicated that the solution-cross-linked networks swell/absorb more than the corresponding bulk-cross-linked networks having the same cross-link density. The classical Flory–Rehner theory has been modified by replacing the linear expansion coefficient α ($=q^{1/3}$) by α' defined as $\alpha C_x^{1/3}$ to explain the swelling/absorption behavior. The modified equation explains well the absorption/swelling behavior of the networks, although the agreement is only semiquantitative.

Introduction

As is well-known, the swelling behavior of a polymer network can be described by a balance between mixing and elastic free energies,[1,2] and usually, the entropy of mixing acts as the main driving force for swelling. If a network is placed in an undiluted linear polymer either of the same or different kind, it will barely swell because the entropy of mixing of the polymers is very small.[3,4] Therefore, an ordinary bulk-cross-linked network can absorb a bulk polymer only when the enthalpy of mixing between the network and the guest polymer is negative. Unfortunately, such polymer pairs are very rare.[5] For this reason, only a few studies have been made on the swelling of networks by polymers or polymer solutions. However, the systems consisting of guest polymers absorbed in networks are an interesting subject of studies on dynamic,[6] conformational,[7] and viscoelastic[8] properties of the entrapped guest polymers. The systems are somehow related to semiinterpenetrating polymer networks.[9]

Although the phantom network model has a defect, that the network should collapse to a point in the absence of external stresses, we take the model as a convenient starting point of analyzing the swelling behavior of a polymer network toward solvent and polymer solutions.[1,2,10] Other more sophisticated models incorporating the excluded volumes among the network segments[10-15] and/or

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