

Anomalies in the crystallization of *cis*-1,4-polyisoprene in blends with poly(vinylethylene)

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The crystallization of *cis*-1,4-polyisoprene (PIP) in miscible blends with atactic poly(vinylethylene) (PVE) was investigated. Normalized to the PIP content, the extent of crystallization and the crystallization rate were suppressed in the mixtures. A reduction in the degree of crystallinity is contrary to the behaviour usually exhibited by blends in the absence of crosslinking. More anomalous was the observation that the magnitude of the crystallization suppression in the uncrosslinked PIP was independent of PVE concentration over a range from 5 to 50% PVE. Furthermore, whereas α -lamellae predominate for pure PIP crystallization, blending with high-molecular-weight PVE caused preferential development of the β -lamellar form. This bias may be a reflection of the known ability of the β -lamellae to incorporate non-crystallizing entities more readily into the fold plane at the crystal surface. Changes in heat capacity at T_g measured before and after melting were consistent with the notion that PVE chains are trapped between the lamellae of the crystallizing PIP, with the extent of entrapment substantially greater for higher-molecular-weight PVE. The degree of crystallinity in the blends also varied with the molecular weight of the PVE, suggesting that suppression of the crystallization was a consequence of the entrapment of the PVE. In networks the suppression of crystallization significantly exceeded that observed in uncrosslinked blends and pure PIP networks. For free-radical crosslinking the presence of PVE increases the crosslink density of the PIP segments, contributing to the lower crystallinity in the crosslinked mixtures.

(Keywords: crystallization; blends; polyisoprene; poly(vinylethylene); differential scanning calorimetry; Fourier-transform infra-red spectroscopy)

INTRODUCTION

The crystallization and melting behaviour of miscible polymer blends has been studied by several investigators, with the work up to 1984 summarized in a review¹. The general observation is that, while the crystallization rate can either decrease or increase due to blending, the ultimate degree of crystallinity attained by the crystallizable component will be similar to that achieved in its pure state. Recently, results on many other semi-crystalline miscible blends have been reported²⁻¹³. Although there are blends for which suppression of the degree of crystallinity have been reported^{12,13}, these are not equilibrium results and thus may simply reflect retarded rates of crystallization.

Unoriented *cis*-1,4-polyisoprene crystallizes through lamellar growth into radial spherulites¹⁴⁻¹⁶. Crystallization induced by straining results in row nucleation of the lamellae, whose growth proceeds perpendicular to the strain direction^{15,16}. Two morphologically differing forms are known for *cis*-1,4-polyisoprene, the more stable α -lamella and the slower-forming β -lamella^{16,17}. Both lamellar types have the same crystal unit cell, but differ with respect to growth rates, lamellar thicknesses and morphologies. In a blend, the crystal phase should

comprise only PIP, with the non-crystallizing component restricted to the amorphous regions and possibly the interphase. This paper describes a study of the influence of composition on both the isotropic and the orientational crystallization of *cis*-1,4-polyisoprene (PIP) in blends with poly(vinylethylene) (PVE). The PVE is atactic and thus incapable of crystallizing. This blend is particularly interesting because it represents an unusual instance of miscibility in the absence of specific interactions^{18,19}.

EXPERIMENTAL

The *cis*-1,4-polyisoprene (PIP) was natural rubber (SMR-L grade of *Hevea brasiliensis*). The atactic PVE, obtained from the Firestone Tire and Rubber Co., was 96% 1,2-polybutadiene ($M_n = 134\,000$ and $M_w/M_n = 1.1$; PVE-h) or 93% 1,2-polybutadiene ($M_n = 23\,000$ and $M_w/M_n = 1.2$; PVE-l). Uncrosslinked blends were prepared by dissolution in cyclohexane and vacuum drying at 60°C. Compositions ranging from 0 to 50% by weight of the PVE were investigated.

Differential scanning calorimetry (d.s.c.) was employed for the isotropic crystallization experiments. Weighed samples (5 to 10 mg) were placed in d.s.c. specimen holders and maintained in a constant-temperature ($\pm 0.2^\circ\text{C}$) chamber for up to 90 days. The samples were

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quenched in liquid nitrogen for transfer to the calorimeter, with the loading done while the d.s.c. furnace was maintained at -30°C . For crystallinity measurements a Perkin-Elmer DSC-7 was used with data taken during heating from -30 to 40°C . To acquire glass transition data, a liquid-nitrogen-cooled Perkin-Elmer DSC-2 was utilized. After loading the samples, the temperature was lowered to -100°C , with data then taken during heating to 40°C . The samples, now amorphous, were cooled again to -100°C , followed by reheating through the glass transition temperature. All temperature changes were done at $20^{\circ}\text{C min}^{-1}$. The reported d.s.c. results herein represent averages of 7–12 measurements each.

Crosslinked blends were prepared by mixing the polymers and curative (1.5% by weight of dicumyl peroxide (DCP)) on an unheated two-roll mill. The rubbers were moulded under pressure at 80°C into films (thickness ≤ 0.1 mm) prior to curing at 140°C for 10 min. Some of the cured films of pure PIP were soaked in concentrated PVE/hexane solutions for several days, and the swollen films then dried in vacuum. The details of this procedure were adjusted to give 9–10% by weight of PVE absorbed in the crosslinked PIP.

For the room-temperature orientational crystallization measurements, films were manually stretched to various extensions with the elongation determined from fiducial marks. FTi.r. spectra were measured continuously beginning about 30 s after the stretching. Unpolarized spectra were obtained at 2 cm^{-1} resolution with a Perkin-Elmer 1800 spectrophotometer in double beam mode. The spectra were analysed by fitting Lorentzian curves to the absorption bands of interest. The absorptions at 1378 , 1362 and 1126 cm^{-1} all increase in intensity upon crystallization of the PIP. The most interesting behaviour is demonstrated by the C–H out-of-plane mode, which shifts from 836 to 844 cm^{-1} upon crystallization²⁰. The latter resonance can be considered specific for the crystalline phase, allowing determination of the degree of crystallinity from the integrated intensity of the 844 cm^{-1} band relative to that of the summed intensities of the 836 and 844 cm^{-1} absorptions. The crystalline band was deconvoluted from the overlapping 836 cm^{-1} band by subtraction of a spectrum from completely amorphous PIP. Representative FTi.r. results are displayed in Figure 1. Thickness variations occasioned by the stretching of the films were compensated for by using the absorption band at 1662 cm^{-1} (C=C stretching vibration) as an internal reference.

RESULTS

Crystallization

The results for crystallization of PIP at -25°C (the temperature of maximum crystallization rate for pure PIP²¹) are shown in Figures 2 and 3. The rate of crystallization decreases in proportion to the concentration of PVE-h in the blend. This is consistent with thermodynamic miscibility, since a phase-separated blend morphology would exert no influence on the crystallization kinetics (excepting interfacial effects). In miscible blends, increases or decreases in crystallization rate have been observed^{1,12,22–24}. Since the present blends exhibit no significant depression in the melting temperature of the PIP, the data in Figures 2 and 3

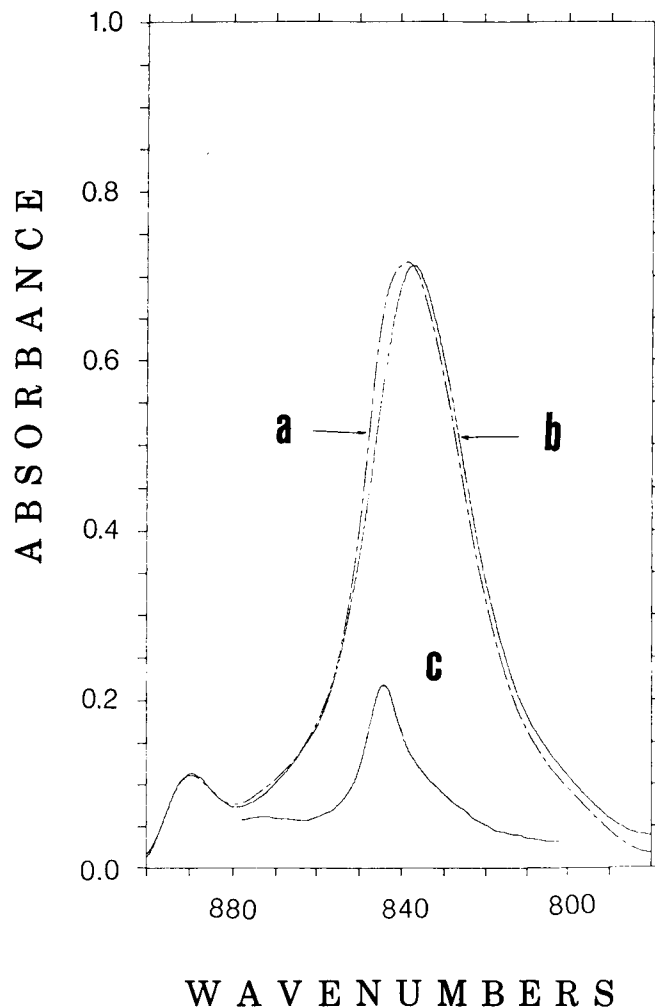


Figure 1 The infra-red absorption of PIP: (a) stretched to 600%; (b) in the unstretched, amorphous state; and (c) the difference of the two bands, corresponding to the crystalline phase

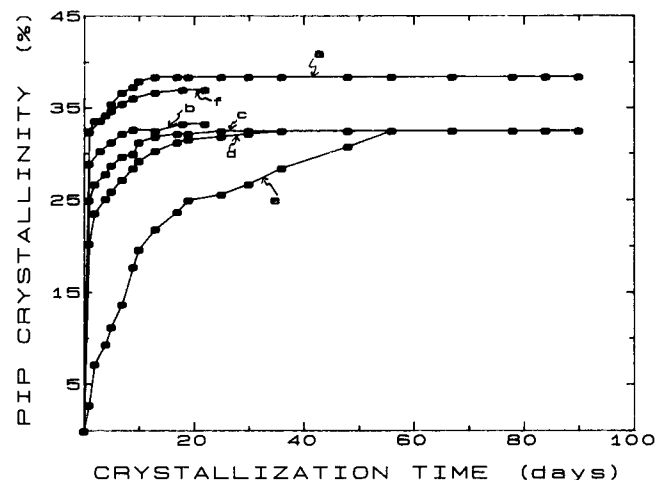


Figure 2 The level of crystallinity obtained after crystallization at -25°C for the indicated times: (a) pure PIP; (b) PIP blended with 5% by weight PVE-h; (c) PIP with 10% PVE-h; (d) PIP with 20% PVE-h; (e) PIP with an equal weight fraction of PVE-h; and (f) PIP mixed with 5% by weight of PVE-l. A perfect heat of fusion equal to 15.3 cal^{-1} (ref. 18) was assumed

correspond to crystallization at a constant degree of undercooling. Since the addition of PVE dilutes the crystallizable component of the blend and also increases its glass transition temperature, the observed retardation of PIP crystallization is expected.

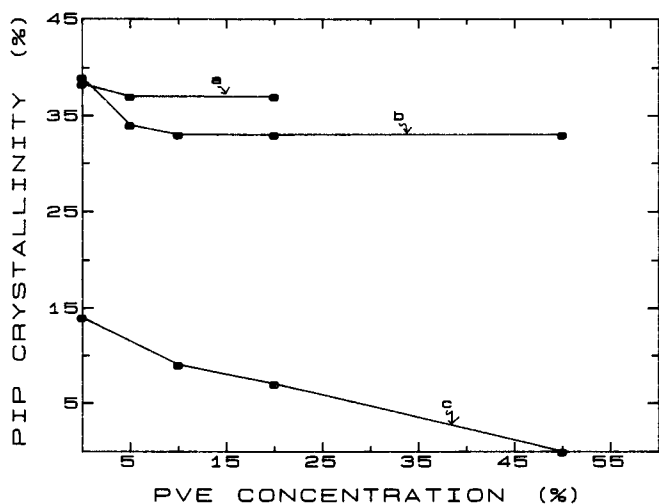


Figure 3 The dependence of the equilibrium degree of crystallinity on blend composition (assuming 15.3 cal g^{-1} as the perfect heat of fusion¹⁸) for PIP: (a) crystallized at -25°C in blends with PVE-l; (b) crystallized at -25°C in mixtures with PVE-h; and (c) co-cross-linked with PVE-h blends, then stretched to 600% at room temperature

Over the temperature range from -40 to 0°C the bulk crystallization rate of PIP is proportional to the lamellar growth rate¹⁵, indicating that nucleation is rapid (athermal). To the extent that the crystallization kinetics are governed by chain mobility, the effect of dilution on the kinetics can be isolated from this factor by carrying out the crystallization at constant $T - T_g$. The glass transition temperature of a 50% (by weight) PVE blend is 15°C higher than the T_g of pure PIP²⁵. When crystallization was carried out at -10°C , the time for an invariant (equilibrium) level of crystallinity to be attained in the 50% PVE mixture was reduced from 56 to 22 days. This is still a factor of 2 longer than the crystallization time of pure PIP at -25°C ; that is, dilution of the PIP *per se* has a measurable effect on the rate of crystallization, at least at the large undercoolings employed. At higher crystallization temperatures, the rate of crystallization would be governed more by the rate of nucleation of new layers at the crystal edge, with transport of material to the crystal edge being fast relative to this nucleation²⁶. Under these conditions, the influence of blending on the crystallization kinetics might be minimized; however, the slowness of such high-temperature crystallization in unoriented PIP makes experimental investigation difficult.

While the degree of crystallinity attained in the blends was equivalent at different crystallization temperatures, the ultimate extent of the crystallization (normalized by the PIP content) was always less than achieved by pure PIP (Figure 3). Interestingly the magnitude of this reduction was independent of composition. Blends of PIP with PVE-h in which the concentration of the latter ranged from 5 to 50% exhibited equivalent degrees of

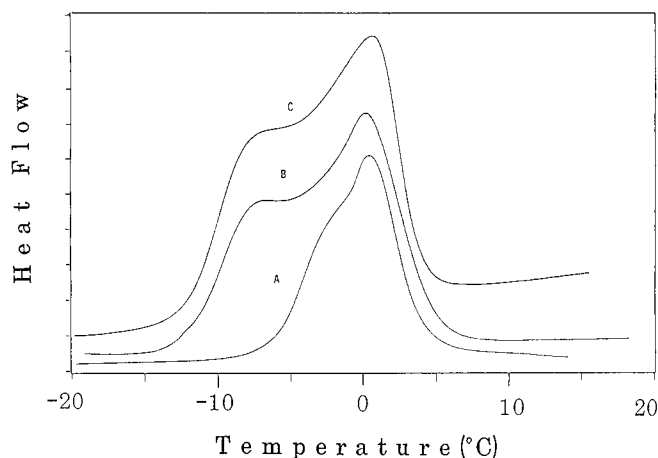


Figure 4 D.s.c. measurements of the melting endotherms in pure PIP that had been crystallized at -25°C for (A) 4 h, (b) 4 days and (C) 13 days

ultimate crystallinity (Figures 2 and 3). Similarly, the incorporation of PVE-l reduced the level of PIP crystallinity by an amount independent of the PVE-l concentration; however, the decrease was significantly less than for blends of PIP with PVE-h (Figures 2 and 3 and Table 1). An influence of blending on the degree of crystallinity is unusual; the invariance to composition of the magnitude of this suppression is very peculiar.

Crystal morphology

Crystallization of neat PIP produces two crystal morphologies, which have identical unit cells but differ in the orientation of the unit cell with respect to the direction of lamellar growth¹⁶. The early stages of crystallization are associated with formation of the thermodynamically more stable α -lamellae. The β -lamellae have a significantly higher end (fold) surface free energy and only develop subsequently. This behaviour is illustrated for pure PIP in the d.s.c. data of Figure 4. The endotherm at higher temperature, corresponding to the α -lamellae, predominates initially; however, continued crystallization gives rise to an increase in the magnitude of the lower-melting β form^{16,17}. The results for PIP blended with PVE-l (not shown) were very similar to these, with the relative intensity of the β -lamellae endotherm increasing with the degree of PIP crystallinity. These results demonstrate that the presence of the low-molecular-weight PVE has negligible influence on the crystallization behaviour of PIP.

The behaviour of the PIP blended with PVE-h is distinctly different (Figure 5). At the modest levels of crystallinity attained after brief crystallization times, only the lower melting transition is evident. The more stable α form develops at higher degrees of crystallinity. The relative concentrations of the two lamellar forms are also

Table 1 Results for PIP crystallized at -25°C

Blend composition	ΔH_f (J g^{-1})	Crystallinity (%)	ΔC_p ($\text{J g}^{-1} \text{K}^{-1}$)	$\delta(\Delta C_p)$	
				Equation (3)	Measured
100% PIP	24.6	39	0.306	1.64	1.69
20% PVE-h	20.8	33	0.365	1.47	1.96
20% PVE-l	23.7	38	0.352	1.58	1.70

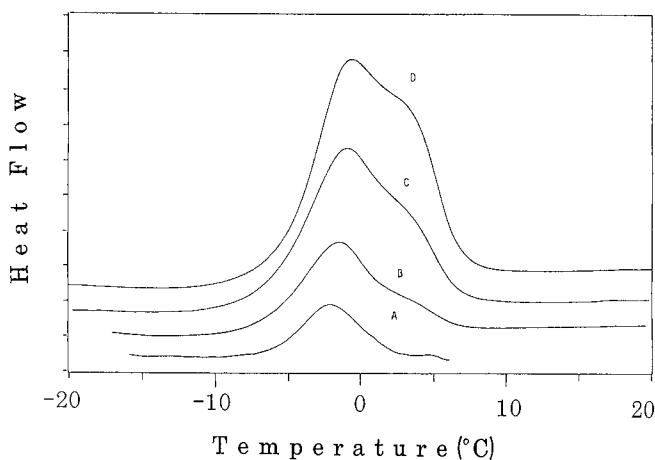


Figure 5 D.s.c. measurements of the melting endotherms in PIP in a 50% by weight blend with PVE-h after crystallization at -25°C for (A) 1 day, (B) 4 days, (C) 19 days and (d) 64 days

reversed from their concentrations in pure PIP or the PIP/PVE-I mixtures. In the presence of the PVE-h, the less stable β -lamellae were always found to be more abundant. The temperatures of the lower and higher melting transitions were, however, the same for pure PIP and for the blends.

There is another situation known to result in a higher concentration of the β -lamellae in PIP. In 1,4-polyisoprene containing more *trans* units (e.g. synthetic natural rubber), the growth rate of the β -lamellae relative to lamellar growth of the α form is increased by a factor of 2–3 over that in higher *cis* PIP^{13,16}. This effect has been attributed to differences in the fold surfaces, the end surface free energy of the β -lamellae being more than twice that of the α -lamellae¹⁶. This structural difference allows *trans* units or other non-crystallizing irregularities to be more readily incorporated into the back-folded chains at the crystal surface of the β -lamellae¹⁶.

It is proposed that the preferential formation of β -lamellae when PIP is blended with PVE-h reflects the greater capacity of this morphology to accommodate entrapped PVE chains. Note that, as PIP lamellar growth proceeds, the free volume of the local amorphous regions decreases. The glass transition temperature of pure PVE was measured to be -7 and -1°C for PVE-I and PVE-h respectively, so that PVE chains in a PVE-rich environment would have low mobility at the crystallization temperature of -25°C . In particular, diffusion of the PVE-h will slow. Crystallization may outpace segregation, leaving PVE-h entrapped between the lamellae. Although this is not a thermodynamically stable situation, the immobility of the PVE-h may preclude alteration of the morphology over the (months) timescale relevant herein. Diffusion of the PVE would be completely suppressed if any chain segments were literally occluded by or contained within the crystalline phase.

Conceivably some PVE may actually be incorporated into the crystals. This phenomenon is known for strain crystallization of PIP chains containing epoxidized co-units²⁷. The crystal unit cell expands to accommodate the epoxy units.

Glass transition

A partially crystalline material is expected to exhibit different glass transition behaviour than when it is completely amorphous. Although a few degrees

elevation in T_g has been previously observed in PIP due to crystallinity^{19,28}, herein the glass transition temperature was not found to differ significantly before and after melting. The magnitude of the heat capacity changes (ΔC_p) occurring through the transition, however, did vary measurably with the degree of crystallinity. This is an obvious consequence of the fact that only the amorphous phase undergoes the transition²⁹. If a blend is miscible the ΔC_p for the mixture is given by³⁰:

$$\Delta C_{p,\text{blend}} = w_{\text{PIP}} \Delta C_{p,\text{PIP}} + w_{\text{PVE}} \Delta C_{p,\text{PVE}} \quad (1)$$

where w_{PIP} and w_{PVE} are the weight fractions of the respective components, and $\Delta C_{p,\text{PIP}}$ and $\Delta C_{p,\text{PVE}}$ the corresponding heat capacity changes at T_g . This expression neglects any intrinsic temperature dependence of ΔC_p , in that the temperature of the transition *per se* will be strongly composition-dependent. Since only the PIP crystallizes, the heat capacity change at T_g in the semicrystalline state can be calculated as:

$$\Delta C_{p,\text{blend}} = (1 - \phi_{\text{xtal}}) w_{\text{PIP}} \Delta C_{p,\text{PIP}} + w_{\text{PVE}} \Delta C_{p,\text{PVE}} \quad (2)$$

where ϕ_{xtal} is the weight fraction of the PIP that is crystalline. This assumes an ideal crystalline phase; that is, there is negligible crystalline–amorphous interphase and no entrapped amorphous material. In fact, a measurable interphase is known to exist in many semicrystalline polymer blends^{13,31–33}, and, as mentioned above, in partially epoxidized natural rubber the unit cell expands to allow inclusion of the epoxy groups within the crystal phase²⁷. Tabulated in *Table 1* is the quantity $\delta(\Delta C_p)$:

$$\delta(\Delta C_p) = \frac{\Delta C_p(\phi_{\text{xtal}} = 0)}{\Delta C_p(\phi_{\text{xtal}})} \quad (3)$$

representing the ratio of the ΔC_p for the purely amorphous state to the ΔC_p when the PIP is partially crystalline. For pure PIP this increase in the heat capacity change at T_g due to melting is found experimentally to be about 3% higher than the prediction of equation (3). This small discrepancy can be attributed to the existence of interfacial material, which possesses a lower heat capacity than the liquid state, but is not included in the sharp melting endotherm used to quantify the degree of crystallinity.

For blends there is a larger discrepancy between the measured and calculated values of $\delta(\Delta C_p)$. While for PIP blended with 50% of PVE-I the increase is 8% higher than predicted, an equivalent blend of PIP and PVE-h exhibits a $\delta(\Delta C_p)$ 33% higher than the calculated $\delta(\Delta C_p)$. This result suggests that in the semicrystalline blend the PVE is not fully contributing to the heat capacity of the liquid state, consistent with the hypothesis that during crystallization some PVE becomes trapped within the lamellae. The constraints on the motion of entrapped PVE chains restricts their participation in the glass-to-liquid transition; hence, after melting, an increase is measured in ΔC_p beyond that attributable to the loss of PIP crystallinity.

The $\delta(\Delta C_p)$ data in *Table 1* imply that this entrapment is significantly more extensive in the case of the higher-molecular-weight PVE. The diffusion constant of a linear polymer scales with the square chain length³⁴, so that diffusion of PVE-h is roughly 30 times slower than that of PVE-I. Since the glass transition temperature of the PVE-h is also 6°C higher (*Table 2*), the competition between lamella growth and PVE-h segregation would

Table 2 Glass transition temperatures

Polymer	T_g (°C)
PIP	-67
PVE-l	-7
PVE-h	-1

more strongly favour the former than would be the case with the PVE-l. This probably underlies the preferential development of the β -lamellae. It may also be the origin of the greater suppression of crystallization in the blends of PIP with PVE-h, since crystal growth would terminate as the locally available PIP is depleted.

Orientalional crystallization

The crystallization of polymers is enhanced by orientation³⁵⁻³⁹, and this effect is particularly marked with PIP⁴⁰⁻⁴³. The accelerated rate is attributed to enhanced nucleation, since strain has no effect *per se* on lamellar growth rates in PIP¹⁵. Results on the strain-induced crystallization of crosslinked blends of PIP with PVE are given in *Figures 3 and 6* and *Table 3*. At room temperature, about 70% of the ultimate crystallinity is attained within 30 s, so that most of the kinetic information was unavailable in the present experiments. It was observed that the crystallization time for the blends varied inversely both with PIP content at a given strain and with elongation for a given composition.

Similarly, and unsurprisingly, the degree of crystallization induced by strain increases with the magnitude of the strain and decreases sharply with PVE content. Some of this suppression is an artifact of the dependence of the PIP crosslink density on composition. Although the amount of peroxide crosslinking agent was maintained constant, the crosslink density of the PIP increases with PVE content. This results from the nature of the free-radical reaction in these polymers⁴⁴. In PIP, a stable tertiary radical is formed, with termination usually occurring by combination to form tetrafunctional crosslinks. In PVE, on the other hand, the free radical formed at the vinyl carbons is unstable, and thus rapidly propagates with minimal termination. Hence PVE consumes a negligible amount of DCP in the blends; the peroxide concentration with respect to PIP increases with PVE concentration, effecting greater crosslinking of the PIP.

Although different vulcanizing methods can have different influences on the crystallization behaviour of PIP²¹, crosslinking always suppresses crystallization⁴⁵. For example, in polytetrahydrofuran networks the presence of a crosslink inhibits crystallization of eight chain units on each network strand adjoining the crosslink⁴⁶. The decrease in PIP crystallinity in the blends attributable only to the increase in PIP crosslink density was estimated from measurements made on pure PIP crosslinked to various degrees. It was found that the ultimate degree of crystallinity in neat PIP at 600% elongation decreased non-linearly with the extent of crosslinking. Using these data the suppression of the crystallization due only to crosslinking could be estimated for the blends. As seen in *Table 3*, the actual decrease in crystallinity exceeds that due only to crosslinking; that is, some suppression results from

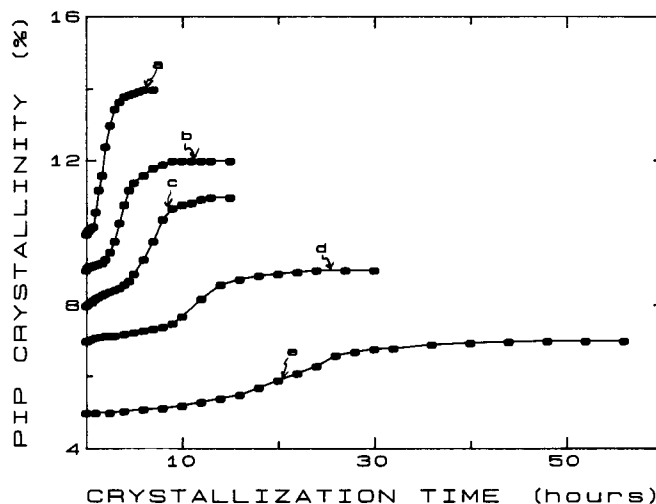


Figure 6 The level of crystallinity (using the FTi.r. bands displayed in *Figure 1*) attained in the blends upon room-temperature stretching to 600% for the indicated times. The PIP is: (a) pure; mixed respectively with 9% by weight of linear (b) PVE-l and (c) PVE-h; and blended prior to curing with (d) 10% by weight PVE-h and (e) 20% by weight PVE-h

Table 3 Crystallinity of crosslinked PIP at 600% elongation

PVE content (by weight)	0%	10%	20%	50%
Crystallization time ^a (h)	6	24	48	>168
Total crystallinity (%)	14	9	7	0
Calculated suppression due to crosslinking (%)	-	1	2	12
Deduced suppression due to blending (%)	-	4	5	2

^a To achieve equilibrium degree of crystallinity

diluting the crystallizable PIP chains with amorphous PVE. Dilution more strongly suppresses orientational crystallization of networks than the reduction observed herein for isotropic crystallization of uncrosslinked rubber. For example, while in the uncrosslinked mixtures, PIP with 50% PVE crystallizes to the same extent as PIP mixed with only 5% PVE, in the crosslinked blend of PIP with 50% PVE there was no crystallinity observed at any strain. This greater suppression of strain-induced crystallization is related both to the presence of the crosslinks as well as to the nature of the orientational crystallization process. In networks, diffusion of the PVE is prevented, and hence the segregation necessary for formation of a pure PIP crystalline phase is restricted. Moreover, the consequence of limited segregation is amplified in the case of strain-induced crystallization. Under orientation the fold length increases^{47,48}, corresponding to more intermolecular crystallization; that is, adjacent stems in the crystallite are more likely to originate from different chains. An isotropically crystallizing material, in which crystallites are formed to a greater extent by back-folding of the same chain, is less reliant on the local availability of other PIP molecules and hence on segregation from the non-crystallizing PVE.

Orientalional crystallization was also measured for blends obtained by soaking pure PIP networks in concentrated solutions of PVE. Although the overall composition of these blends was very close to those of the 90% PIP networks, the crystallinity attained in these materials at equivalent strains was higher than in

the co-crosslinked blends. Since PVE chains imbibed by the PIP are not connected to the network, their diffusion from the crystal growth front is facilitated, allowing the orientational crystallization of PIP to proceed faster and to a greater extent. Although not chemically bonded to the PIP network, the PVE chains did exhibit non-relaxing orientation. Such inducement of orientation by the presence of an oriented matrix has been observed previously for other mixtures of flexible-chain polymers⁴⁹⁻⁵². The description of this 'nematic interaction' in the PIP/PVE blends will be reported elsewhere⁵³.

SUMMARY

A plausible explanation for suppression of crystallization in the uncrosslinked rubber blends is entrapment of the PVE-h between the growing lamellae of the PIP. Further crystallization of the PIP is restricted upon encountering a PVE segment, since the PVE cannot be readily incorporated within the crystal unit cell. However, at least for the higher-molecular-weight, higher- T_g PVE-h, it cannot diffuse away from the lamella sufficiently fast. Hence the reduction in crystallinity is ascribed to entrapment of the PVE between the lamellae. The preferential growth of β -lamellae allows some accommodation of the PVE.

The greater mobility of PVE-l facilitates the segregation necessary for crystallization to proceed, and thus the degree of PIP crystallinity in mixtures with PVE-l is almost equal to that of pure PIP. The α -lamellar form is also preponderant in these mixtures, similar to the behaviour observed for pure PIP.

It can be argued that the invariance of the degree of crystallization to changes in the concentration of PVE may also be related to the entrapment. A small quantity of PVE, even a single chain present at the crystal front, constitutes a defect capable of terminating lamellar growth. Any additional PVE, if not residing in proximity to the crystal phase, would not obviously further alter the extent of crystallization. In principle, the lowering of the chemical potential of the amorphous phase by blending itself could reduce the level of crystallinity. Such an effect could only be observed in crystallization under near-equilibrium conditions, and would not be anticipated in blends of PIP and PVE, given their near-ideality^{18,19}.

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