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Melting behaviour and miscibility of poly(ϵ-caprolactone) + poly(4-hydroxystyrene) blends

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Differential scanning calorimetry has been used to study the melting behaviour, crystallinity and miscibility of poly(ϵ-caprolactone) (PCL) + poly(4-hydroxystyrene) (P4HS) blends. Three different heat treatments were selected. The development of PCL crystallinity was dependent on the blend composition. The increasing glass transition temperature (T_g) of blends, as they become richer in P4HS, was the cause of this dependence. The miscibility of the polymers was confirmed by detecting only a T_g in the blends, which could be closely described by the Fox rule. The thermograms exhibit double melting endotherms. The dependence of the melting temperature on the crystallization temperature shows that the lower endotherm corresponds to less stable crystals and the higher one to stable crystals. The lower endotherm was attributed to a secondary crystallization process. For the higher endotherm the thermodynamic melting temperatures of PCL in the pure state and in the blends were obtained using Hoffman-Weeks plots. The polymer-polymer interaction parameter was calculated from these data using the Nishi-Wang equation. The results are in good accordance with those obtained by inverse gas chromatography. Copyright © 1996 Elsevier Science Ltd.

(Keywords: blends; melting behaviour; miscibility)

INTRODUCTION

In previous papers[1-6] we have studied the miscibility of binary blends that contained the amorphous polymer, poly(4-hydroxystyrene) (P4HS). Most of the systems were amorphous polymer pairs, formed with a second polymer that had carbonyl or ether groups. The miscibility of these blends was achieved through hydrogen bond interaction between the hydroxyl group of P4HS and the carbonyl or ether group of the second polymer.

In the literature a significant number of studies of miscible blends involving crystallizable polymers are reported[7-18]. P4HS has been found to form miscible blends with some crystallizable polymers such as polyethers[14,18], polyamides[19,20] and polyesters[19,20], but to our knowledge only in its blends with poly(ethylene oxide)[18] or polyacetal[14] has the melting behaviour been discussed. In particular, with poly(ϵ-caprolactone) (PCL) a Fourier transform infra-red (*FT*i.r.) study[21] was performed and detected the interaction between hydroxyl and carbonyl groups. We selected this system PCL + P4HS, carrying out a first study on the miscibility in the molten state (170°C) by inverse gas chromatography (i.g.c.)[6]. We concluded that the components were miscible at that temperature in the whole composition range and we also reported the polymer-polymer interaction parameter, χ.

In the present work a calorimetric study is made of PCL + P4HS mixtures under various heating treatments. Specifically, the glass transition temperature and melting and crystallization behaviour of the mixtures are analysed. In addition, a thermodynamic study of the PCL melting temperature depression in the blends was done, from which the polymer-polymer interaction parameter was calculated and compared with those values obtained from i.g.c.

EXPERIMENTAL

Materials

The polymers used in this study, poly(4-hydroxystyrene) (P4HS) and poly(ϵ-caprolactone) (PCL), were provided by Polysciences (UK).

The average molecular weight of PCL, $M_n = 5 \times 10^4$ and $M_w/M_n = 1.6$, were obtained from gel permeation chromatography (g.p.c.). The average molecular weight of P4HS measured by vapour pressure osmometry was $M_n = 1.5 \times 10^3$ and g.p.c. experiments revealed $M_w/M_n = 2.0$.

Preparation of samples

Films of PCL, P4HS and blends of the two polymers with different compositions were prepared by mixing

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appropriate amounts of polymer solutions in tetrahydrofuran (THF) and casting onto a glass surface. THF was evaporated slowly at room temperature for 3 weeks and the resulting films were dried under vacuum at 30°C for 3 h to remove completely any residual solvent.

Heat treatments and differential scanning calorimetry measurements

A Perkin Elmer DSC-4 Differential Scanning Calorimeter was used for heat treating the samples and for the study of the glass transition temperature, melting and crystallization behaviour. Thermal analysis of the samples was performed at a heating rate of 10°C min^{-1} and always under nitrogen atmosphere. Subambient temperatures were reached using liquid N_2 to cool the DSC cell. The temperature scale was established using indium melting point as reference. In all cases, open aluminium pans were used with a sample weight ranging from 5 to 10 mg.

The following heat treatments were carried out.

(I) Solution-cast samples were heated at 10°C min^{-1} from −90°C to 150°C (first scan).

(II) The samples were conditioned at 150°C for 10 min to ensure complete melting of the PCL crystals before being cooled at 10°C min^{-1} to the crystallization temperature (T_c). Following the crystallization treatment at T_c, which lasted 45 min, the samples were fast-cooled to −90°C and were then heated at 10°C min^{-1} to 150°C to monitor their glass transition and melting behaviour (second scan).

(III) Finally, the samples were kept in the molten state (150°C) for 10 min and rapidly cooled in a nitrogen atmosphere at −140°C, trying to eliminate the crystallinity, and were then reheated at 10°C min^{-1} to 150°C to monitor their glass transition, crystallization and melting behaviour (third scan).

The glass transition temperatures (T_g) were taken at the midpoint of the heat capacity transition. In order to identify the multiple endotherms, the melting point of each endotherm was located in the maximum of their respective peaks. For the high endotherm the melting temperature (T_m) was also taken as the temperature at which the last detectable trace of crystallinity disappears. The thermodynamic calculations were carried out using these T_m values and those taken at the maximum.

RESULTS AND DISCUSSION

Crystallization and melting behaviour of PCL in the blends

It is well known that the melting behaviour of crystalline polymers depends on the conditions under which they have been crystallized. We have selected for the PCL + P4HS system several crystallization temperatures ranging between 20°C and 40°C and a fixed time of 45 min following heat treatment II.

Differential scanning calorimetry (d.s.c.) thermograms given in *Figure 1* show the behaviour of blends of various compositions (expressed in weight fraction of PCL), w_2, after isothermal crystallization at 30°C. It is apparent from the thermograms that PCL only has crystallized from blends having $w_2 \geq 0.7$. For $w_2 \leq 0.6$ no fusion endotherms were detected; there was only a glass transition which reveals the presence of a unique amorphous phase, which is confirmed by the transparency of the samples. The present system falls within the class of miscible crystalline amorphous polymer blends. In such a system it is typical for the crystallizable component to be partitioned between a pure crystalline and a mixed amorphous phase. This is the behaviour of PCL + P4HS blends with $w_2 \geq 0.7$, which display both the melting peak of PCL and the T_g of the corresponding amorphous phase. The thermograms exhibit double melting peaks. For reasons explained later, the maximum of the higher temperature endotherm is taken as the primary melting temperature, T_m. *Figure 2* summarizes the T_g and T_m of the samples crystallized at 30°C as a function of w_2.

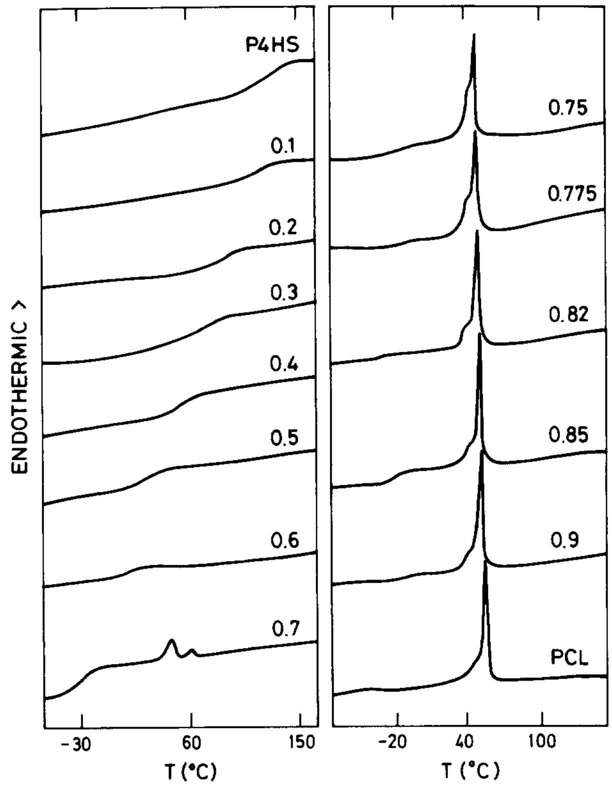

Figure 1 Thermograms of PCL + P4HS blends of several compositions, w_2, after isothermal crystallization at 30°C

The T_g *versus* w_2 curve appears to have an anomalous dependence for $w_2 > 0.7$ (half-filled circles in the figure). It may be noted that w_2 represents the overall blend composition. To calculate the composition of the amorphous phase we have considered the most simplistic model which assumes that the system is formed by two phases, a crystalline phase and a homogeneous amorphous phase. The amount of crystalline phase present was calculated through the heat of fusion of each sample, using the reported value of 32.4 cal g^{-1} for the heat of fusion of 100% crystalline PCL[22]. The representation of T_g *versus* w_2 of the amorphous phase displays a continuous variation with downward curvature as can be seen in *Figure 2* (open circles). For miscible systems with strong interactions between components, the upward curvature of T_g *versus* w_2 would be expected, reflecting the increase in stiffness due to the interactions[23,24]. But in this case, as in other similar

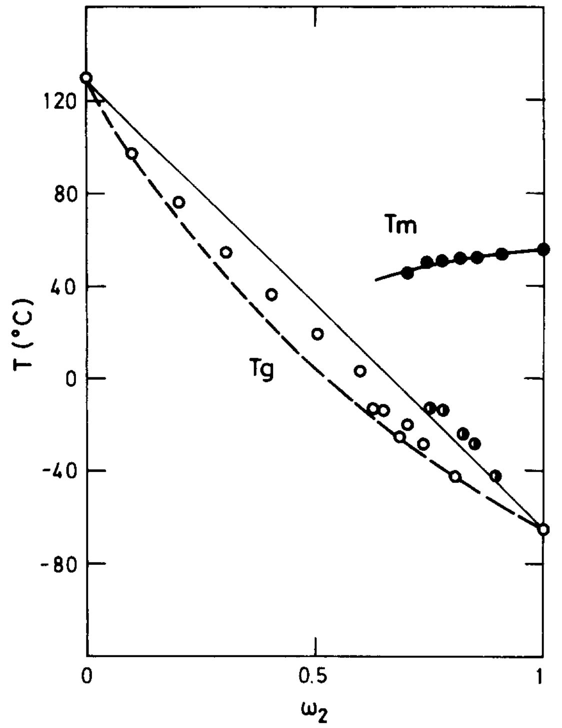

Figure 2 Dependence of melting temperature (●) and glass transition (◑), (○): see text for the meaning of the symbols of the samples crystallized at 30°C, on the weight fraction of PCL, w_2; - - - represents the ideal Fox rule

systems[3,4], the destruction of the self-association of P4HS by the other component produces the opposite effect. Both effects seems to compensate and the T_g *versus* w_2 behaviour could be closely described by the ideal rule of Fox[25]:

$$\frac{1}{T_g} = \frac{w_2}{T_{g_2}} + \frac{(1 - w_2)}{T_{g_3}} \quad (1)$$

Where T_{g_2}, T_{g_3} and T_g refer to the T_g of PCL, P4HS and the blend of composition w_2, respectively. This is illustrated in *Figure 2*.

In *Figure 2* a melting depression is also observed that is characteristic of miscible polymer–polymer melts in which thermodynamic equilibrium is achieved under the process. However, it has been suggested that morphological effects such as size and perfection of the crystalline regions could also be responsible for the lowering of the melting point, which will be discussed later.

The melting behaviour of PCL in blends of $w_2 \geq 0.7$ after being crystallized at different T_cs (10, 20, 25 and 35°C) has also been studied. The thermograms exhibited double melting peaks and there is clear evidence of the depression of the melting point of PCL crystals in the mixtures. The presence of P4HS in the blends not only modifies the melting behaviour of PCL but also perturbs the crystallization kinetics upon cooling from the molten state. *Figure 3* shows the measured heats of fusion per unit mass of total sample *versus* w_2 for the samples crystallized at 25°C. It is apparent that PCL crystallizes from the blends with $w_2 > 0.75$ to about the same extent as it does in the pure state. But for $w_2 < 0.75$ the crystallization kinetics of PCL is affected by the presence of P4HS, showing a significant reduction in the extent of crystallization that is inhibited for $w_2 \leq 0.6$. The degree of crystallinity was calculated from the heat of fusion per gram of PCL in the blend and using the reported value for the heat of fusion of 100% crystalline PCL[22]. The corresponding crystallinities for blends crystallized at different T_cs are summarized in *Table 1*. It may be noted that the crystallinity of unblended PCL is almost independent of the crystallization temperature and it is in good agreement with the values reported in the literature[8,22]. In the blends, the degree of crystallinity of PCL remains relatively constant for mixtures having a large amount of PCL ($w_2 > 0.8$). However, as the P4HS content is increased the degree of crystallinity decreases and becomes slightly dependent on T_c.

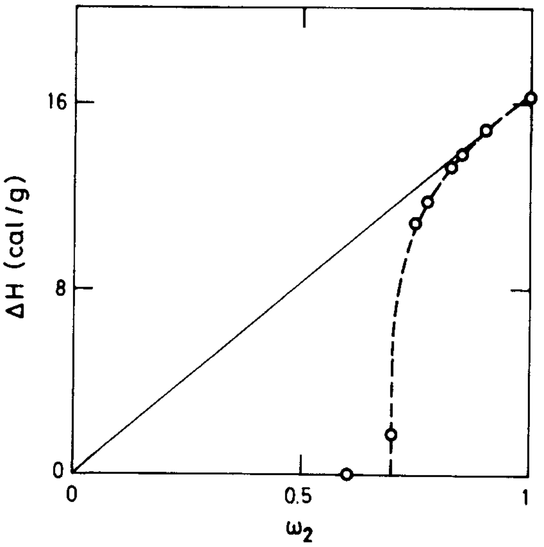

Figure 3 Heat of fusion per unit mass of the blend sample *versus* w_2, for samples crystallized at 25°C. The line represents the ideal behaviour in which P4HS does not interfere with PCL crystallization

It is well known that crystallization is a function of the T_g of the blend and also depends on the supercooling ($T_m - T_c$), which will vary upon blending if T_m changes. In the PCL + P4HS system the first condition (T_g of the blend) seems to be dominant in the crystallization process. These systems are formed by a crystallizable polymer of low T_g and a high T_g amorphous polymer. Thus as the amount of P4HS is increased, the T_g of the compatible amorphous phase rises (see *Figure 2*) and results in a stiffer matrix that delays the diffusion of the PCL segments in the blend, and if the T_g is close to the T_m the crystallization is inhibited. As can be noted in *Table 1*, there are no large changes in the degree of crystallinity at different T_cs for a given w_2, which means different supercooling, but for a given T_c, in all cases, the crystallinity decreased abruptly at $w_2 = 0.7$, as a consequence of the T_g of the matrix.

Table 1 Degree of crystallinity as a function of the crystallization temperature, T_c, for different blend compositions, w_2

	T_c (°C)					
w_2	15	20	25	30	35	40
0.7	11	6	6	2	–	–
0.75		45	45	44	42	–
0.775	–	47	47	48	44	–
0.825	–	–	50	50	48	47
0.85	–	–	50	50	49	47
0.9	–	–	51	51	50	48
1.0	–	–	50	49	50	49

On the other hand, for PCL ($T_m \approx 333$ K) and binary systems the maximum growth rate of the crystalline entities, and then the maximum crystallinity degree, could be expected in the range of T_c 265–300 K according to the general rule $T_{max}/T_m = 0.8$–0.9 for melt-crystallized polymers[26]. So the slight decrease of the crystallinity, for all compositions, with increase of T_c seems to indicate that for the selected crystallization temperatures, the thermodynamic driving force dominates over the diffusion.

Solution-cast samples (heat treatment I) show a similar melting behaviour but the degrees of crystallinity calculated were larger than those of melt-crystallized samples. The solvent-induced crystallization is attributed to the plasticizing action of the solvent, but in this case the larger crystallization times also have to be considered.

The thermograms obtained for samples under heat treatment III are represented in *Figure 4*. There is no indication of PCL crystals for mixtures with $w_2 \leq 0.7$, and they show a glass transition temperature intermediate between those of PCL and P4HS. On the other hand, the mixtures with $0.75 \leq w_2 \leq 0.85$ exhibit crystallization during the scan. This behaviour is an indication of the miscibility of both polymers in the molten state. The mixtures with $w_2 > 0.85$ were found to be fully crystallized during rapid cooling from the melt.

Figure 5 summarizes the variation of T_g, T_c and T_m with w_2 for the samples upon heat treatment III. There is again an anomalous dependence of T_g *versus* w_2 for blends with high PCL content. Calculation of the composition of the amorphous phase was done considering both the crystallization and melting heats. For samples with $w_2 = 0.75$ and $w_2 = 0.775$, as can be seen in the figure, both areas are similar and no correction was needed. After correcting the other three compositions richer in PCL, a Fox behaviour was obtained. Again, a depression in the melting temperature is observed and also the crystallization temperature falls progressively with the increase in w_3. In these experiments, in which the crystallization process does not occur at constant temperature, the depression in T_m could be determined not only by thermodynamic effects but also by the morphological contributions such as size and imperfection of crystals. On the other hand, the depression in T_c could be explained by the interplay between thermodynamics and kinetic factors that control the crystallization process.

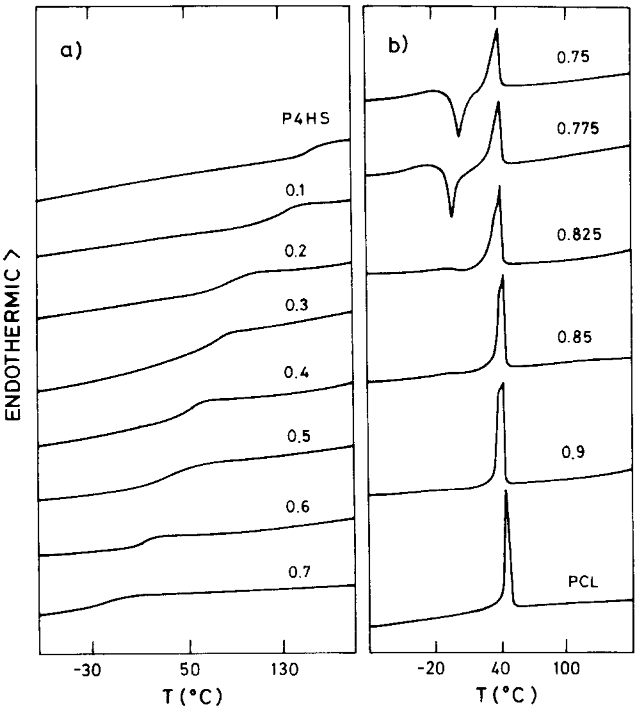

Figure 4 Thermograms of PCL + P4HS blends of several compositions, w_2, under the heat treatment III

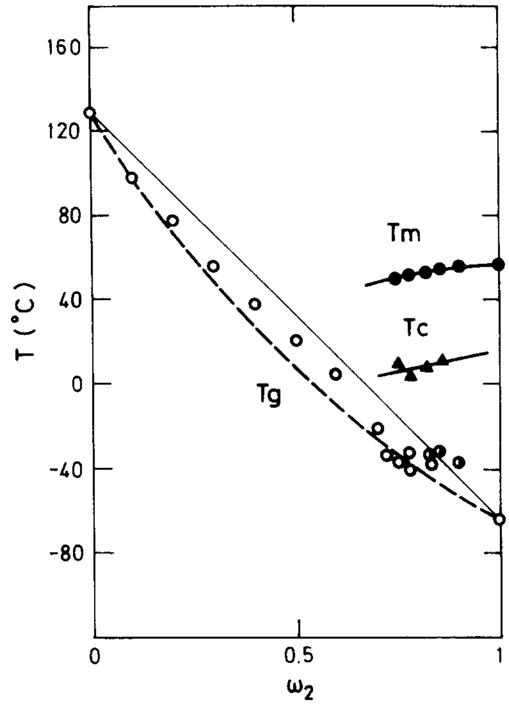

Figure 5 Dependence of the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_{m_2}) on the weight fraction of PCL, w_2, for samples under heat treatment III

Double melting behaviour: influence of the crystallization temperature

For unblended PCL the melting endotherm shows, as usual, a fairly narrow peak and a low temperature tail[22,27]. But for samples containing P4HS the endotherms are broader, presenting a double melting peak. This double melting behaviour is frequently found in miscible binary blends of semicrystalline and amorphous polymers[10,13,28,29].

In some systems this phenomenon has been explained by a mechanism based on melting, recrystallization and subsequent remelting during the d.s.c. scan[10]. The common check is to look for the increase in the ratio of the low to the high temperature endotherms as the heating rate increases. We have done some experiments with the blend of $w_2 = 0.8$ at different scan rates but no decisive conclusions could be made owing to the poor peak resolution obtained at high scan rates (20°C min^{-1}).

In other systems, particularly those containing PCL, the double melting was related to the original sample morphology[11–13]. This idea was basically supported by the dependence of the lower melting endotherm with the crystallization time. For the PCL/P4HS systems the two endotherms were present even at short crystallization times (5 min) and they can also be seen in samples that have been rapidly cooled from the melt (*Figure 4*); for the solvent-cast samples the long crystallization time seems to favour the structure that leads to the lower endotherm (see *Figure 4*). Moreover, the endothermic peak at lower temperature is relatively independent of the blend ratio. In order to clarify the origin of the double melting in this miscible blend we have studied the influence of the crystallization temperature on the fusion peaks.

Figure 6 shows the plots of the melting temperature corresponding to the higher temperature endotherm, T_m *versus* T_c for the different blends. As observed, a good linear correlation between T_m and T_c is obtained. The increase in T_m with T_c is a consequence of the more perfect crystals grown at lower supercooling. According to the Hoffman–Weeks approach[30] the equilibrium melting point, T_m^0, could be determined by extrapolation of T_m *versus* T_c to $T_m = T_c$. The isothermal crystallization is described by the equation:

$$T_m^0 - T_m = \phi(T_m^0 - T_c) \tag{2}$$

where ϕ is the stability parameter which depends on the crystal thickness.

A fit of the data shown in *Figure 6* yields the values for T_m^0 that are summarized in *Table 2*. A ϕ value of 0.18 is obtained independent of the blend composition, except for $w_2 = 0.7$ which yields a higher value of $\phi \approx 0.24$.

It should be noted that the values of ϕ are between 0 and 1; $\phi = 0$ implies $T_m = T_m^0$ with the most stable crystals, and $\phi = 1$ implies $T_m = T_c$ with inherently unstable crystals. Therefore the ϕ value obtained for PCL/P4HS at $w_2 > 0.7$ indicates that the crystals corresponding to the higher endotherm are fairly stable.

However, the behaviour of the lower-temperature endotherm is quite different, as illustrated in *Figure 7*. As we have already commented, this endotherm is not concentration dependent and consequently all the data fit a unique line, with a ϕ parameter of about 0.6 which is a clear indication of the low stability of the formed structure.

Figure 7 also displays the T_m *versus* T_c of the lower-temperature endotherm of unblended PCL (tail) which also gives a high value for the stability parameter ($\phi \approx 0.54$). It should be noted that both the lines, corresponding to PCL and the blends, extrapolate to the same T_m^0 value. This proves that the melting depression of the lower endotherm does not arise from thermodynamic effects and seems to be determined only by the decrease of the thickness of the crystalline lamellae of PCL, whereas the higher endotherm undergoes mainly a thermodynamic melting point depression.

Table 2 Equilibrium melting temperatures, T_m^0, and stability parameters, ϕ, for different blend compositions, w_2

w_2	T_m^0 (K)	ϕ
0.70	327.0	0.24
0.75	329.7	0.18
0.775	330.6	0.18
0.825	331.4	0.18
0.85	333.0	0.18
0.90	336.6	0.18
1.00	335.2	0.18

PCL melting temperature depression and the thermodynamic interaction parameter

The depression of the melting point of the crystalline component of a mixture where the amorphous phase is a miscible blend permits the study of the polymer–polymer interaction parameter. The data obtained in these studies are usually analysed in terms of the equation derived by Nishi and Wang[7] which is based on the Flory–Huggins equation to obtain the chemical potential of the crystallizable component in the amorphous phase:

$$\frac{1}{T_m^0} - \frac{1}{T_{m_2}^0} = \frac{-R}{\Delta H_{2u}} \frac{V_{2u}}{V_{3u}} \left[\frac{\ln \varphi_2}{x_2} + \left(\frac{1}{x_2} - \frac{1}{x_3} \right) (1 - \varphi_2) + \chi_{32}(1 - \varphi_2)^2 \right] \tag{3}$$

where V_{2u} and V_{3u} are the molar volumes of the repeating unit of the polymers, ΔH_{2u} is the heat of

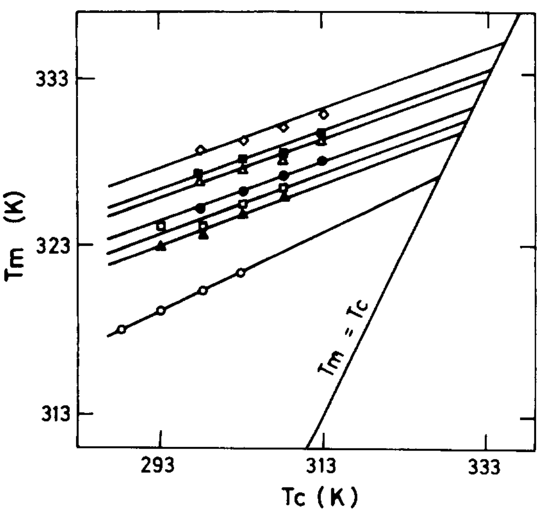

Figure 6 Melting temperature, T_m, of the higher endotherm *versus* the crystallization temperature, T_c, for blends of different composition, w_2: (□) 0.9; (△) 0.85; (●) 0.825; (□) 0.775; (△) 0.75; (○) 0.7; (◇) for PCL

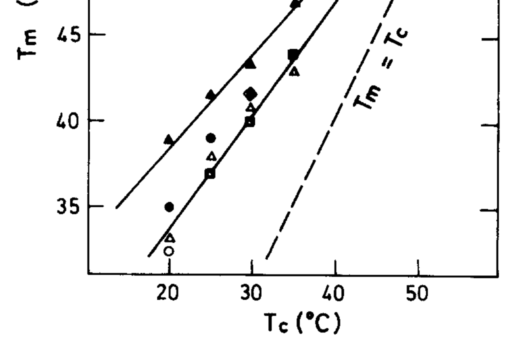

Figure 7 Melting temperature, T_m, of the lower endotherm *versus* the crystallization temperature, T_c, for blends of different composition, w_2: (○) 0.9; (□) 0.85; (△) 0.825; (◇) for 0.775; (●) 0.75; and (△) for PCL

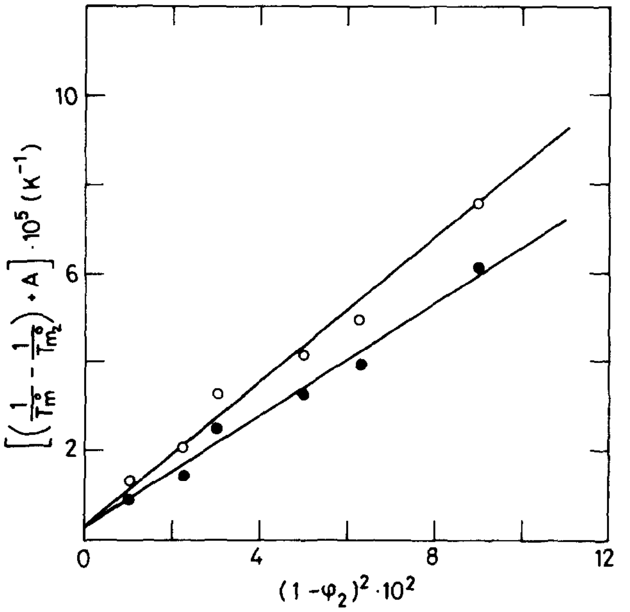

Figure 8 Plot of $[(1/T_m^0 - 1/T_{m_2}^0) + A]$ *versus* $(1 - \varphi_2)^2$ for the PCL + P4HS system: (○) without entropic contribution ($A = 0$); (●) with entropic contribution

fusion per mole of 100% crystalline PCL, x_2 and x_3 are the degrees of polymerization, φ_i is the volume fraction of the *i*th component, χ_{32} is the polymer–polymer interaction parameter, and T_m^0 and $T_{m_2}^0$ are the equilibrium melting temperatures in the blend and of pure PCL respectively. When x_2 and x_3 are both large, then the left-hand side of equation (3) is a linear function of $(1 - \varphi_2)^2$ that should go through the origin, and χ_{32} could be obtained from the slope. The resulting simplified equation given by Nishi and Wang[7] for high molecular weight polymer blends is:

$$\frac{1}{T_m^0} - \frac{1}{T_{m_2}^0} = \frac{-R}{\Delta H_{2u}} \frac{V_{2u}}{V_{3u}} \chi_{32}(1 - \varphi_2)^2 \tag{4}$$

In the PCL/P4HS system, it would be expected that there is some entropic contribution to the blend due to the low molecular weight of P4HS ($M_n = 1500$). For this reason in *Figure 8* both equations have been represented, given by $(1/T_m^0 - 1/T_{m_2}^0) + A$ *versus* $(1 - \varphi_2)^2$, where A involves the entropic contribution term. A least-squares fit results in a slope value of 7.79×10^{-4} K^{-1} when $A = 0$ (simplified equation) and 6.35×10^{-4} K^{-1} when $A \neq 0$. Besides using the data $\Delta H_{2u} = 3690$ cal mol^{-1}, $V_{2u} = 105$ cm^3 mol^{-1} and $V_{3u} = 100$ cm^3 mol^{-1}, the polymer–polymer interaction parameter has been finally determined as $\chi_{32}/V_3 = -1.3 \times 10^{-2}$ mol cm^{-3} without entropic contribution and $\chi_{32}/V_3 = -1.1 \times 10^{-2}$ cm^3 mol^{-1} taking into account this contribution. Comparison between the results indicates that not eliminating the entropic contribution favourable to the blend leads to χ_{32}/V_3 values that are 20% lower. It is important to point out that the same polymer–polymer interaction values were obtained when the melting temperature of each endotherm was taken as the temperature at which the last detectable trace of crystallinity disappeared.

These results are in good agreement with those that we obtained[6] for this system through a i.g.c. study at 190°C, $\chi_{32}/V_3 = -0.9 \times 10^{-2}$, -0.5×10^{-2} and -0.2×10^{-2} cm^{-3} mol^{-1} for $\varphi_2 = 0.76$, 0.51 and 0.26, respectively. As can be seen, there is a slight concentration dependence and the extrapolated value of χ_{32}/V_3 to $\varphi_2 = 1$ gives -1.2×10^{-2} cm^3 mol^{-1}, which is close to the value obtained from PCL melting point depression, although this should be considered as the polymer–polymer interaction parameter at the melting temperature of PCL (62°C). The negative value of χ_{32} confirms the miscibility of PCL with P4HS in the amorphous phase at high and low temperatures.

CONCLUSIONS

The crystallinity of PCL in blends above 0.82 wt% of PCL was not concentration dependent, but for blends richer in P4HS the crystallinity was dependent on the T_g of the amorphous phase. Essentially, the greater the P4HS concentration in the blends, the higher the T_g and the lower the crystallinity.

The blends behave as if formed by two phases, a crystalline and an amorphous phase. Only one T_g was detected for each composition, which was intermediate between the T_gs of PCL and P4HS, confirming the miscibility of the polymers. The variation of T_g with the amorphous phase composition was closely described by the Fox rule.

The thermograms exhibit double melting endotherms. Melting point depression was found for the higher endotherm. The thermodynamic melting points for PCL in the pure state and in the blends were obtained through the Hoffman–Weeks plots. The polymer–polymer interaction parameter was calculated using the Nishi-Wang equation. The negative value of χ_{32} confirms the miscibility of the system. The results are in accordance with those obtained previously by i.g.c. The lower melting endotherm was attributed to a secondary crystallization process in which less stable crystals are formed.

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