Crystallization and thermal behaviour of isotactic poly(1-butene) mixed with hydrogenated oligo(cyclopentadiene)

A. M. Bonfatti, M. Canetti, P. Sadocco and A. Seves
Stazione Sperimentale per la Cellulosa, Carta e Fibre Tessili Vegetali ed Artificiali, Piazza L. da Vinci 26, 20133 Milan, Italy

and E. Martuscelli*
Istituto di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, Via Toiano 6, 80072 Arco Felice, Naples, Italy
(Received 24 September 1991; revised 13 March 1992)

The crystallization and thermal behaviour of thin films of isotactic poly(1-butene)/hydrogenated oligo(cyclopentadiene) (PB-1/HOCP) mixtures are studied using differential scanning calorimetry and optical microscopy. The mixtures show a single glass transition temperature, whose value is dependent on composition. The overall crystallization rate, the spherulite growth rate and the equilibrium melting temperature of PB-1 decrease on the addition of HOCP. The melting point depression is analysed according to the Flory–Huggins theory and a negative interaction parameter is obtained. This leads to the hypothesis that PB-1 and HOCP are miscible in the melt even if some specific interactions and morphological effects are evident between the two components.

(Keywords: poly(1-butene); oligo(cyclopentadiene); spherulitic growth; crystallization kinetics; melting behaviour)

INTRODUCTION

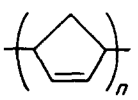
In a previous paper[1] we studied the influence of hydrogenated oligo(cyclopentadiene) (HOCP) on the kinetics of transformation of isotactic poly(1-butene) (PB-1) crystals from form II to form I. Pure PB-1 and its mixtures with HOCP crystallized from the melt in the crystalline form II. The presence of HOCP produced, in the crystallized mixture, an amorphous phase with reduced molecular mobility.

The variations of the kinetics of PB-1 crystal transformation were considered to be a consequence of the crystallization of PB-1 in the presence of an oligomer that is compatible in the melt state.

The present paper reports the results of an investigation into crystallization from the melt and the thermal behaviour of the crystalline form II of PB-1 mixed with HOCP. The spherulitic growth rate, the overall crystallization rate and the melting temperature of form II of PB-1 are depressed by the presence of HOCP. These results indicate that the two components are compatible in the melt state.

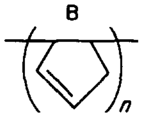
Oligo(cyclopentadiene) is obtained from 1,3-cyclopentadiene monomer, and can have the following two extreme structures[2]:

A



1,4 structure
(*cis* and *trans*)

B



1,2 structure
(*cis* and *trans*)

The commercial HOCP used here is a mixture of the *cis* and *trans* isomers of structures A and B which have been hydrogenated after oligomerization.

The compatibility between HOCP and another polyolefin has been demonstrated in a previous paper[3], where the crystallization and thermal behaviour of mixtures between isotactic polypropylene and HOCP were investigated.

EXPERIMENTAL

Binary mixtures of PB-1 (PB 8340, M_w 700000, from Shell) and HOCP (Escorez, M_w 630, from Esso Chemical), with contents of 5, 10, 20 and 30 wt% HOCP were prepared by mixing the components in a microextruder.

The morphology and the radial growth rates of PB-1 spherulites were studied on thin films by employing an optical polarizing microscope with an automatic hot-stage (Mettler model FP 82) controlled by Mettler FP 80 control processor.

The samples were sandwiched between microscope cover glasses and melted at 443 K for 10 min and then rapidly cooled to the crystallization temperature (T_c). During the isothermal crystallization process, the radius of the growing spherulites was measured as a function of time by taking photomicrographs at different intervals of time.

The overall kinetics of crystallization and the thermal properties of the PB-1 homopolymer and mixtures were analysed by differential scanning calorimetry (d.s.c.) using a Perkin-Elmer DSC-4 with Perkin-Elmer 3600 data station (TADS System). The samples (~5 mg) were

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* To whom correspondence should be addressed

0032-3861/93/050990–06

melted at 443 K for 10 min, then rapidly cooled to the desired T_c; the rate of heat evolution during the isothermal crystallization was recorded as a function of time. The baseline correction and elaborations of exothermal data were made by using the Perkin-Elmer TADS, DSC-4 kinetics software kit no. 0419-0332.

The weight fraction X_t of the material crystallized at time t was calculated by the relation:

$$X_t = \int_0^t \left(\frac{dH}{dt}\right) dt \Bigg/ \int_0^\infty \left(\frac{dH}{dt}\right) dt \qquad (1)$$

where the first integral is the heat generated at time t and the second is the total heat when the crystallization is complete.

After crystallization the samples were heated to the melting point at a scanning rate of 10 K min^{-1}. The observed melting temperature (T_m) and the apparent enthalpies of melting (ΔH^*), were obtained from the maximum and the area of the endothermic peaks, respectively.

The glass transition temperatures (T_g) were determined by heating the samples at a scanning rate of 40 K min^{-1}. The T_g values were taken at the midpoint of the transition and corrected for the error generated by the scanning rate. Before scans, the samples were melted and then immediately immersed in liquid nitrogen to obtain a completely amorphous material.

Gallium and indium standard samples were employed to determine the thermal lag due to the scanning rate and to calibrate the heat of transition.

RESULTS AND DISCUSSION

Glass transition temperature

The amorphous mixtures showed a single glass transition temperature T_g, with numerical value dependent on composition. The appearance of a single glass transition temperature should suggest that the mixture presents a single homogeneous amorphous phase, i.e. the two components are miscible in the amorphous phase. The dependence of T_g on the weight fraction of HOCP (referred to the overall amorphous content in the mixtures) is shown in *Table 1*. The glass transition temperatures determined for pure PB-1 and HOCP were 247 K and 340 K, respectively. As reported in *Table 1* the T_g values of the mixtures were also calculated by using the theoretical relation of Fox[4]:

$$\frac{1}{T_g} = \frac{W(\text{PB-1})}{T_g(\text{PB-1})} + \frac{W(\text{HOCP})}{T_g(\text{HOCP})} \qquad (2)$$

where W(PB-1), W(HOCP) and T_g(PB-1), T_g(HOCP) are respectively the weight fractions and the glass transition temperatures of the two components. As shown in *Table 1*, the experimental glass transition temperatures are always below the theoretical values. This behaviour could be an indication of specific interactions between the two components in the amorphous phase. Such interactions lead to mixtures with high molecular mobility[5].

Table 1 Experimental glass transition temperatures (T_g(ex)) and T_g calculated according to the Fox equation (T_g(theor)) for PB-1/HOCP mixtures

PB-1/HOCP (weight ratio)	T_g(ex) (K)	T_g(theor) (K)
100/0	247	–
95/5	249	250
90/10	253	254
80/20	254	261
70/30	255	269
0/100	340	–

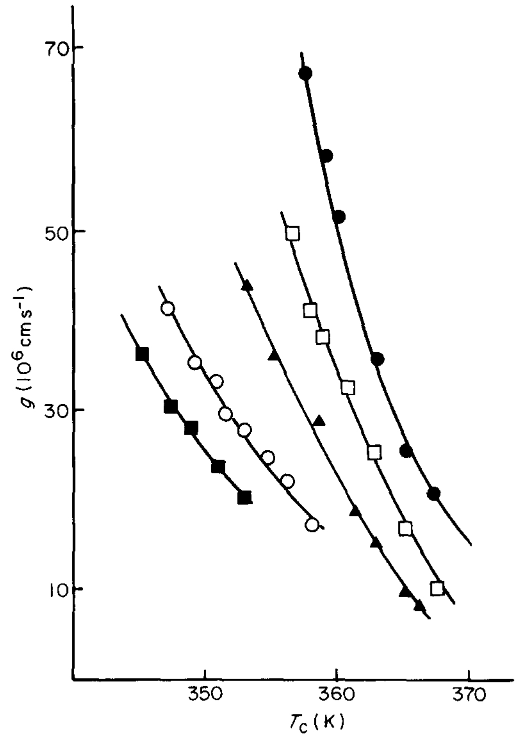

Figure 1 Spherulite radial growth rate (g) *versus* crystallization temperature (T_c) of pure PB-1 and PB-1/HOCP mixtures. PB-1/HOCP weight ratio: 100/0 (●), 95/5 (□), 90/10 (▲), 80/20 (○), 70/30 (■)

Morphology and spherulite growth rate

Thin films of pure PB-1 and PB-1/HOCP mixtures, when observed under the optical polarizing microscope during the isothermal crystallization process, show birefringent spherulitic structures. After complete crystallization the samples appear completely filled with impinged spherulites for all HOCP concentrations studied. The absence of HOCP domains from both the intraspherulitic regions and the interspherulitic contact zones, suggests that the HOCP is incorporated in the interlamellar or interfibrillar zones of PB-1 spherulites.

The spherulite radius, R, increases linearly with time for pure PB-1 and mixtures, for all T_c investigated. For all samples the isothermal radial growth rate, g, was calculated at different T_c as $g = dR/dt$.

As shown in *Figure 1*, for a given T_c, the addition of HOCP to PB-1 causes a depression of the g values, so allowing the control of the isothermicity of the PB-1 crystallization at lower T_c values.

Isothermal bulk crystallization kinetics

The isotherms of crystallization of PB-1 and mixtures, compared at the same T_c, demonstrate that the overall crystallization rate constant progressively decreases by increasing the amount of HOCP in the sample.

The isotherms of crystallization were obtained by plotting the crystalline weight fraction at time t (X_t)

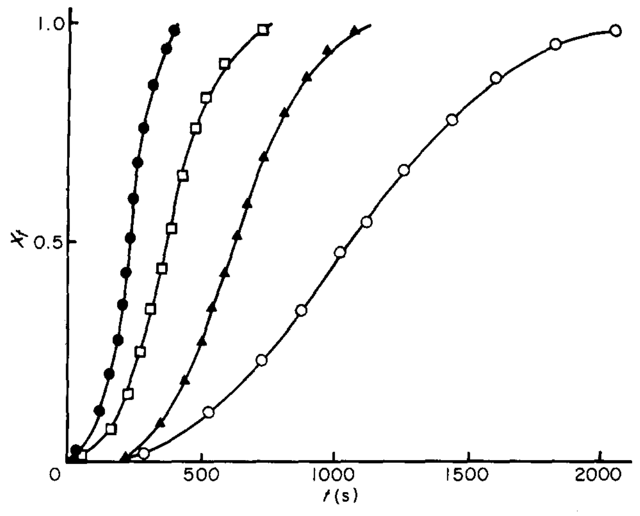

Figure 2 Isothermal curves of crystallization for pure PB-1 and PB-1/HOCP mixtures at $T_c = 357$ K. PB-1/HOCP weight ratio: 100/0 (●), 95/5 (□), 90/10 (▲), 80/20 (○); X_t = weight fraction of crystallinity developed at time t

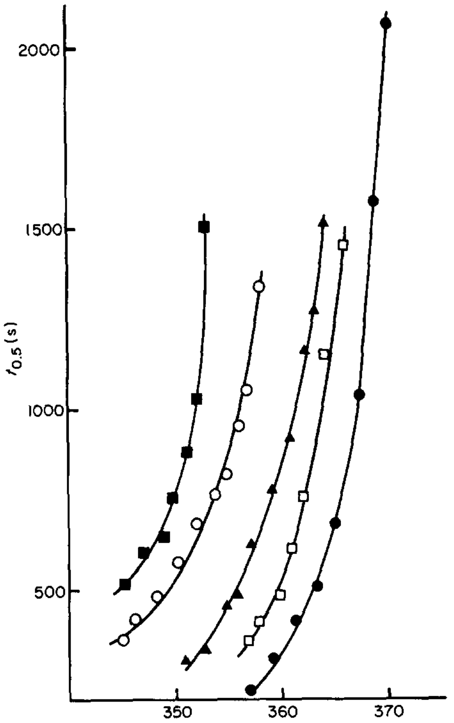

Figure 3 Half-time of crystallization ($t_{0.5}$) *versus* crystallization temperature (T_c) for different mixture compositions. PB-1/HOCP weight ratio: 100/0 (●), 95/5 (□), 90/10 (▲), 80/20 (○), 70/30 (■)

versus t. The plots for plain PB-1 and mixtures at $T_c = 357$ K are reported in *Figure 2*.

In *Figure 3* the half-time of crystallization, $t_{0.5}$ (defined as the time taken for half of the crystallinity to develop), is plotted against T_c for different mixture compositions. It can be observed that the addition of HOCP to PB-1 causes a reduction in the overall crystallization rate.

The overall kinetic rate constant K_n was calculated by using the Avrami equation[6]:

$$X_t = 1 - \exp(-K_n t^n) \qquad (3)$$

where n is a parameter depending on the type of nucleation and on the geometry of the growing crystals. The values of n and K_n were derived, for each T_c, from the slope and the intercept, respectively, of the straight lines obtained by plotting $\log_{10}[-\ln(1 - X_t)]$ *versus* $\log_{10} t$ (see *Figure 4*). The value of the Avrami exponent, n (about 3 for pure PB-1 and mixtures), indicates a three-dimensional growth of crystalline units, developed by heterogeneous nucleation.

Temperature dependence of g *and* K$_n$

The experimental g and K_n values were analysed according to the polymer-diluent theory[3,7–9]. According to this theory the equation describing the growth rate g of spherulites of a crystallizable polymer in a one-phase melt containing a second polymer acting as a diluent assumes the form:

$$\ln g - \ln \Phi_2 + \frac{U^*}{R(T_c - T_\infty)} - \frac{0.2T_m^\circ \ln \Phi_2}{\Delta T} = \alpha_1 = \ln g_0 - \frac{\Delta G_c}{T_c \Delta T f} \qquad (4)$$

where g_0 is the pre-exponential factor which includes all terms that are taken as effectively independent of temperature. The $U^*/R(T_c - T_\infty)$ term contains the energetic contribution to the growth rate of diffusional processes of the amorphous and crystallizable material: U^* is the sum of the activation energies for the chain motions in the melt of crystallizable and non-crystallizable molecules and T_∞ ($T_\infty = T_g - C$, where C is a constant) is the temperature below which such motions cease. T_m° is the equilibrium melting temperature and Φ_2 is the volume fraction of the crystallizable polymer. The term f is a correction factor ($f = 2T_c/T_m + T_c$); the term ΔG_c contains the free energy required to form a nucleus of critical size. The slope of the straight lines obtained, for each mixture, by plotting α_1 *versus* $T_m/(T_c \Delta T f)$, gives the $-\Delta G_c$ value (*Figure 5*).

Analogously the temperature dependence of the overall kinetic rate constant (K_n) can be expressed by the

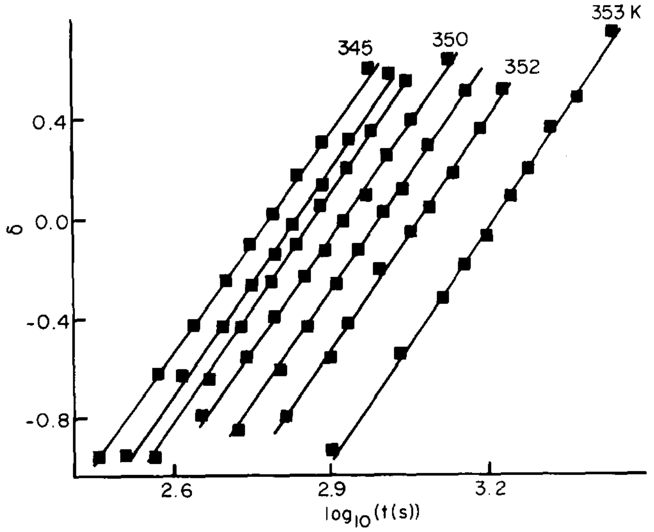

Figure 4 $\delta = \log_{10}[-\ln(1 - X_t)]$ *versus* $\log_{10} t$ according to the Avrami equation (equation (3)) of 70/30 PB-1/HOCP mixture. Crystallization temperatures T_c = 345–353 K, as indicated on curves

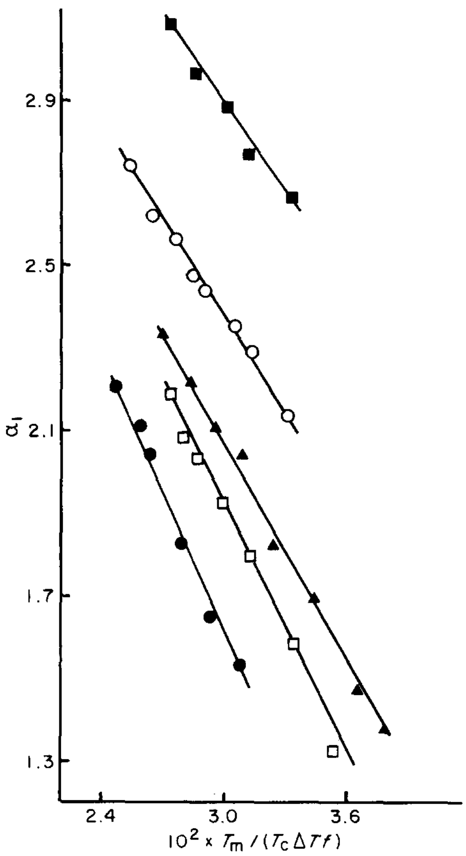

Figure 5 α_1 *versus* $T_m/(T_c \Delta Tf)$ according to equation (4) of pure PB-1 and PB-1/HOCP mixtures. PB-1/HOCP weight ratio: 100/0 (●), 95/5 (□), 90/10 (▲), 80/20 (○), 70/30 (■)

relation[10,11]:

$$\frac{1}{n}\ln K_n - \ln \Phi_2 + \frac{U^*}{R(T_c - T_\infty)} - \frac{0.2T_m^\circ \ln \Phi_2}{\Delta T} = \alpha_2 = \ln A_n - \frac{\Delta G_c}{T_c \Delta Tf} \qquad (5)$$

A_n is a constant equal to $\log g(4/3)N^{1/3}$, where N is the nucleation density. As heterogeneous nuclei form instantaneously as soon as the temperature reaches values below T_m, the nucleation process can be considered independent of crystallization temperature. The straight lines obtained by plotting α_2 *versus* $T_m/(T_c \Delta Tf)$ are reported in *Figure 6*, again the slope gives the $-\Delta G_c$ values.

As reported in ref. 3 the same values of $C = 30$ K and $U^* = 1500 \text{ cal mol}^{-1}$ ($= 6.28 \text{ kJ mol}^{-1}$) were used in both equations (4) and (5).

In our range of crystallization temperatures, according to Lauritzen[12], ΔG_c can be expressed as:

$$\Delta G_c = \frac{4b_0 \sigma \sigma_e T_m^\circ}{\Delta H k} \qquad (6)$$

where σ and σ_e are the lateral and folding surface free energy, respectively, T_m° is the equilibrium melting temperature, ΔH is the enthalpy of fusion per unit volume and k is the Boltzmann constant. The σ_e values, reported in *Table 2* as a function of the HOCP content in the mixtures, were calculated[13] with $b_0 = 7.49 \times 10^{-8}$ cm and $\sigma = 0.1 b_0 \Delta H$ and alternatively from the ΔG_c values obtained either by equation (4) or by equation (5). In *Table 2* it can be noted that the two series of σ_e values, so obtained, have a similar dependence on mixture composition (except for the 70/30 mixture in the series of σ_e values obtained from K_n). The σ_e values decrease by increasing the HOCP fraction in the mixture. Such depression may be accounted for by assuming that amorphous HOCP is likely to segregate in interlamellar regions inducing an increase in the surface entropy of folding. As a consequence, PB-1 lamellar crystals with a less regular fold surface are obtained when the PB-1/HOCP mixtures are isothermally crystallized from the melt in the examined range of T_c.

Melting behaviour

The observed melting temperature (T_m) linearly increases with the crystallization temperature for plain PB-1 and mixtures (*Figure 7*). The experimental data

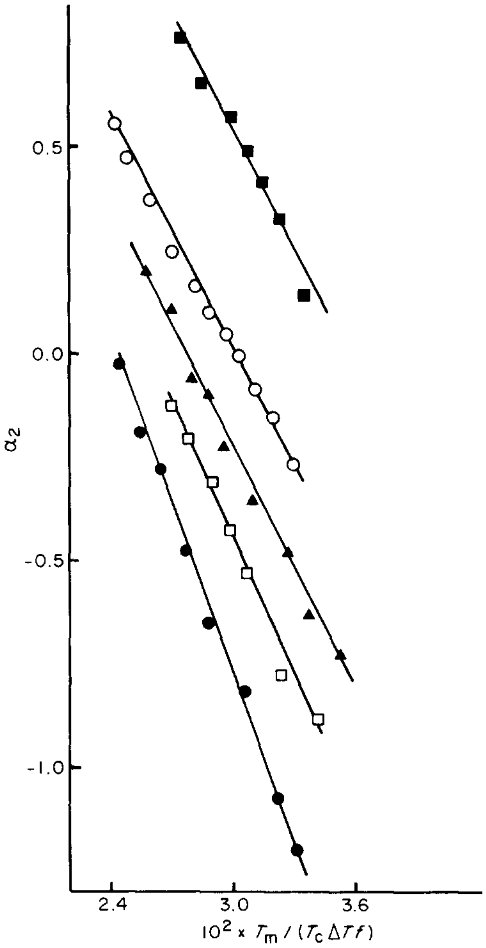

Figure 6 α_2 *versus* $T_m/(T_c \Delta Tf)$ according to equation (5) of pure PB-1 and PB-1/HOCP mixtures. PB-1/HOCP weight ratio: 100/0 (●), 95/5 (□), 90/10 (▲), 80/20 (○), 70/30 (■)

Table 2 Free energy of folding (σ_e) (erg cm^{-2}) calculated according to equation (6), from ΔG_c values obtained by equation (4) (σ_e from g) and equation (5) (σ_e from K_n)

PB-1/HOCP (weight ratio)	σ_e from g	σ_e from K_n
100/0	17	19
95/5	15	16
90/10	13	15
80/20	11	13
70/30	10	14

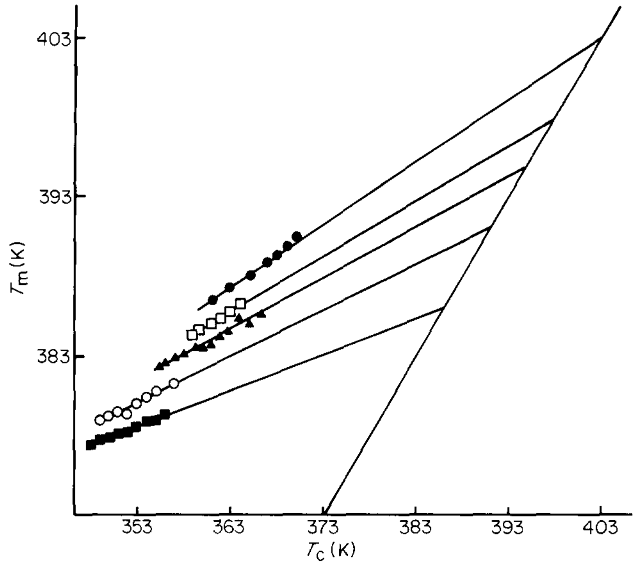

Figure 7 Observed melting temperature (T_m) of pure PB-1 and PB-1/HOCP mixtures as a function of crystallization temperature (T_c). PB-1/HOCP weight ratio: 100/0 (●), 95/5 (□), 90/10 (▲), 80/20 (○), 70/30 (■). Straight line curve without experimental points denotes $T_m = T_c$ curve

Table 3 Equilibrium melting temperature T_m° and $1/\gamma$ slopes from the Hoffman equation for pure PB-1 and PB-1/HOCP mixtures

PB-1/HOCP (weight ratio)	T_m° (K)[a]	$1/\gamma$
100/0	403	0.39
95/5	398	0.34
90/10	395	0.31
80/20	391	0.28
70/30	386	0.22

[a] The errors in the T_m° values were calculated as ±2 K

can be fitted by the equation of Hoffman[14]:

$$T_m = 1/\gamma T_c + (1 - 1/\gamma)T_m^\circ \qquad (7)$$

where $1/\gamma$ is the stability parameter which depends on the crystal thickness and T_m° is the equilibrium melting temperature. By increasing the fraction of HOCP a depression of the T_m value can be observed for every T_c explored. The extrapolated T_m° value is lower the higher the content of HOCP in the mixture. The T_m° accuracy was calculated from the standard deviations of the slope and intercept obtained from the linear relationship between T_c and T'_m (*Table 3*). In equation (7) $1/\gamma$ assumes values between 0 ($T'_m = T_m^\circ$ for all T_c) and 1 ($T'_m = T_c$). Therefore, the crystals are most stable at $1/\gamma = 0$ and inherently unstable at $1/\gamma = 1$ (ref. 15). The $1/\gamma$ values slightly decrease with increasing HOCP content, indicating an increase of the crystal stability (*Table 3*).

The melting point depression according to the Flory–Huggins theory is related to the polymer–polymer interaction parameter χ_{12} according to the relation[15,16]:

$$-\left[\frac{\Delta H V_1}{R V_2}\left(\frac{1}{T_{mb}^\circ} - \frac{1}{T_{mp}^\circ}\right) + \frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi_1\right] = \beta = \chi_{12}\phi_1^2 \qquad (8)$$

Subscripts 1 and 2 represent the non-crystallizable and the crystallizable polymer, respectively. ΔH is the perfect crystal heat of fusion of the crystallizable polymer, V is the molar volume of the polymer unit at the equilibrium melting temperature, R is the universal gas constant, T_{mp}° and T_{mb}° are the equilibrium melting temperatures of the pure crystallizable component and of the mixture, respectively, ϕ is the volume fraction of the components in the mixture and m is the degree of polymerization.

The following parameter values have been used in our calculations: $\Delta H = 1000\ \mathrm{cal\ mol^{-1}}$ ($4.19\ \mathrm{kJ\ mol^{-1}}$) (ref. 17); $V_1 = 69.87\ \mathrm{cm^3\ mol^{-1}}$ (ref. 17); $V_2 = 72.58\ \mathrm{cm^3\ mol^{-1}}$ (ref. 17); $m_1 = 9.3$ and $m_2 = 8911$. The T_m° values used are those reported in *Table 3*.

A plot of the left-hand side of equation (8) β *versus* ϕ_1^2 should give a straight line passing through the origin if the interaction parameter is assumed to be composition independent. The straight line calculated with the aforementioned parameters is plotted in *Figure 8*, it shows an intercept on the ordinate axis of about 1.3×10^{-2} and a slope of -0.196 which corresponds to the χ_{12} of the mixture.

The negative value of χ_{12} parameter in the PB-1/HOCP system should suggest that the two components can form a compatible mixture which is thermodynamically stable above the equilibrium melting temperature. The high value of the intercept can be due to composition dependence of χ_{12} and/or to contribution to T_m° of morphological and annealing effects[8] that are not taken into account in equation (8).

CONCLUSIONS

Our investigations have shown that the spherulitic growth rate, the overall crystallization rate and the melting temperature of PB-1 are depressed by the presence of HOCP. These results, together with the detection of a single glass transition, suggest that PB-1 and HOCP are miscible in the melt.

In agreement with the above considerations, the verified HOCP interferences[1] on the kinetics of PB-1 crystal transformation from form II to form I, indicate that in the crystallized mixtures the HOCP molecules

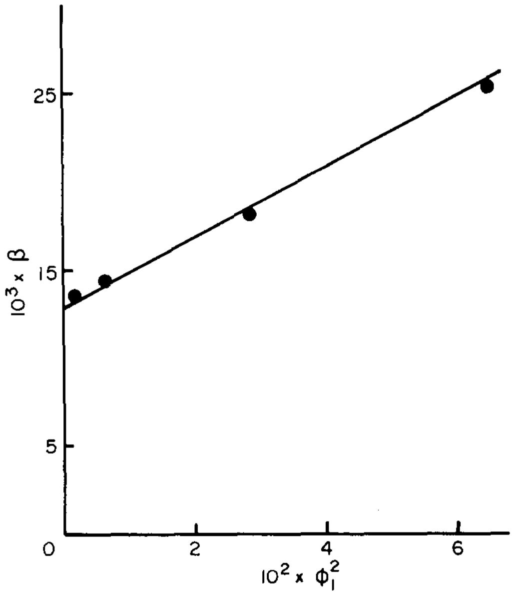

Figure 8 β *versus* ϕ_1^2 according to equation (8) of PB-1/HOCP mixtures

are rejected in interlamellar and/or interfibrillar regions of PB-1 spherulites where they form a homogeneous mixture with uncrystallized PB-1 molecules.

Nevertheless in spite of the above conclusions the results obtained in our work need further explanations.

The presence of T_g values lower than those predicted by the Fox equation, for the mixtures with high HOCP content, is an indication of specific interactions between the two components in the amorphous phase.

The existence of a contribution of morphological effects on the melting behaviour of PB-1 in the mixtures is evidenced by the variation of the stability parameter $1/\gamma$ with composition. The interaction parameter χ_{12} is also subjected to morphological effects (and/or annealing) as evidenced by the high value of the intercept at the origin of the straight line in *Figure 8*.

The results reported in this paper compared with those obtained by adding HOCP to another polyolefin (isotactic polypropylene), whose miscibility was demonstrated[3], show that the interaction of HOCP with PB-1 is stronger than that with polypropylene. In spite of this difference, the demonstrated possibility of employing HOCP as a second compatible component for polyolefin-based mixtures is of undoubted interest.

ACKNOWLEDGEMENT

This work was partly supported by 'P.F. Chimica Fine II Sottoprogetto Chimica e Tecnologia dei Polimeri' of CNR, Italy.

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