Study of the melting and crystallization behaviour of poly(ethylene oxide)–poly(vinyl alcohol) blends

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The melting and crystallization behaviour of blends of poly(ethylene oxide) and poly(vinyl alcohol) has been analysed. Hoffman–Weeks plots of the observed melting points *versus* crystallization temperatures are constructed. From these plots, melting-point depressions have been found. However, measurements of glass transition temperatures by dynamic mechanical thermal analysis have shown no changes for poly(ethylene oxide). Crystallization kinetics became slower as the poly(vinyl alcohol) content was increased.

(Keywords: melting; crystallization; blends; poly(ethylene oxide); poly(vinyl alcohol))

INTRODUCTION

The study of polymer compatibility has undergone an enormous expansion in recent decades. This interest is related to industrial applications and to the theoretical problems presented by analysis of large-molecule blends. Numerous studies of this kind can be seen in books about this subject[1,2]. However, no thermodynamic study to aid prediction of compatibility of polymers has yet been made, especially for bulk blends.

Usually, as Scott[3] proposed, using the Flory–Huggins model, the miscibility of large molecules is related more to a negative enthalpy of mixing than to the entropy of mixing, which is positive for this type of system. Consequently, the majority of these systems are immiscible, and the miscibility is related to specific interactions between the polymers via hydrogen bonds or polar forces.

For blends of amorphous polymers, thermal techniques have become accepted as a method of determining compatibility. The existence of two glass transition temperatures, T_g, indicates incompatibility, while one T_g corresponds to a compatible system. This one T_g appears between those of the pure polymers that form the blend. In the case of blends in which one of the components can crystallize, the miscibility of the system involves a decrease in the chemical potential of the blend components. This results in a decrease in equilibrium melting point of the crystalline polymer, which is a function of blend composition. The melting-point depression has also been considered as a miscibility criterion in many studies on polymer blends.

In this paper we study blends of poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVAL). The first is a highly crystalline polymer and it is only the amorphous phase that can be considered compatible. We have analysed the influence of PVAL on the melting and crystallization behaviour of PEO. PVAL contains hydroxyl groups, which could induce compatibility with PEO by means of hydrogen bonds or polar interactions with the ether groups of the PEO chains. The experimental results show variations in the melting and crystallization behaviour of PEO as a function of PVAL content in polymer blends. However, the presence of PVAL seems not to influence the glass transition temperature of PEO.

EXPERIMENTAL

The poly(ethylene oxide) (PEO) used in this work was a commercial product from Fluka. Its weight-average molecular weight determined by laser light scattering in methanol is $\bar{M}_w = 31\,000$ g mol^{-1}.

The poly(vinyl alcohol) (PVAL) sample was supplied kindly by Ercross S.A. (Bilbao, Spain). The $\bar{M}_w = 87\,000$ g mol^{-1} was determined by laser light scattering in dimethylacetamide. The degree of hydrolysis of the PVAL was 98%.

Blends of different compositions were prepared by dissolving both polymers in *N*,*N*-dimethylformamide. Polymer solutions were mixed in predetermined proportions in order to obtain the different compositions with a total polymer concentration of 2 g dl^{-1}. The mixture was stirred for 20 min and was then precipitated by an excess of diethyl ether. The precipitate was centrifuged and washed with diethyl ether. After this, it was dried under vacuum at room temperature for several days to eliminate all possible residues of solvent.

Differential thermal analysis (d.t.a.) was carried out using a Mettler TA-2000 differential calorimeter calibrated with indium. The melting temperatures of the different blends were measured using a heating rate of 5 K min^{-1}. After keeping the samples (about 5 mg) at 353 K for 15 min, these were quenched to the crystallization temperature. Crystallizations were realized isothermally.

Dynamic mechanical thermal analysis (d.m.t.a.) was carried out using a Polymer Laboratories model Mark II analyser. Samples were prepared at 373 K by pressing the polymer blends for 10 min. The blends were analysed in single cantilever mode with a heating rate of 3 K min^{-1} at a frequency of 1 Hz and an elongation of 64 μm peak-to-peak.

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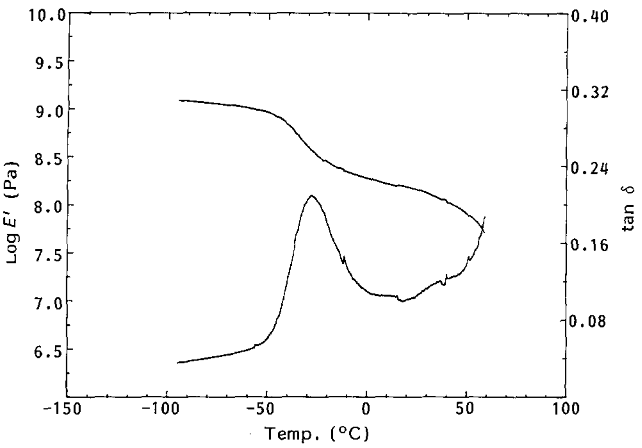

Figure 1 Variations of the storage modulus E' and loss tangent tan δ as functions of temperature for PEO

The blends used in d.m.t.a. were prepared by dissolving both polymers in water and blending the solutions in the desired proportions, the total polymer concentration being 2 g dl^{-1}. After vigorous stirring the blend solutions were freeze dried.

Laser light scattering measurements were carried out, at 298 K, with a modified FICA 42000 light scattering photometer, where both light source and optical block of the incident beam were substituted by a He–Ne laser (Spectra Physics model 157), which emits at 633 nm with a power of 3 mW. The cell compartment was thermostated to maintain the cell at 298.0±0.1 K. The light scattering cell was washed and rinsed with distilled water and acetone. Solutions were contained in cells fitted with glass stoppers to ensure that evaporation of methanol was minimized during measurements. All liquids and polymer solutions were clarified by centrifugation for 2 h at 14000 r.p.m. in a Heraus Labofuge 15000.

The light scattering photometer was calibrated with benzene using vertically polarized light and taking the Rayleigh ratio as $R_B = 12.55 \times 10^{-6}$ cm^{-1} (ref. 4); the constant K' was found to be equal to 0.735.

All measurements of laser light scattering were carried out using poly(ethylene oxide) concentrations ranging between 0.2 and 0.8 g dl^{-1}. The experimental data are processed by a Commodore Amiga 2000 computer employing a compiled BASIC program.

The necessary refractive index increments for light scattering measurements, dn/dc, were obtained with a Brice–Phoenix differential refractometer model BP-2000, using a He–Ne laser (Spectra Physics model 156) as a light source, which emits with a power of 1 mW, and employing a sealed-type differential cell with ground-glass stoppers to prevent loss of solvent. The calibration was made with aqueous solutions of highly purified KCl[5]. The temperature was kept constant at 298 K. The error in determining the refractive index increments was $\pm 10^{-5}$ units.

RESULTS AND DISCUSSION

The most general criterion for compatibility in a polymer blend is the existence of a single glass transition temperature T_g for the blend between the T_g values of the pure components. This behaviour implies the existence of intimate combination at the molecular level.

Using d.t.a. and d.m.t.a. we have found a T_g of 341 K for PVAL, and separately 243 K for PEO. As PEO and PVAL have very different glass transition temperatures, it is easy to study their blends. To determine the glass transition temperatures we have considered d.m.t.a. to be the most suitable technique, since PEO is crystalline and its glass transition is difficult to determine by d.t.a.

The melting temperature of PEO is about 335 K and in the d.m.t.a. curves PEO melting appears as a sharp decrease of log E. As in compatible blends the glass transition temperature shows a value between those of the pure polymers and depends on the blend composition, we have chosen blends with high PEO contents in order that the glass transition temperature is far enough from the PEO melting temperature and can be seen in the d.m.t.a. curves. *Figures 1* and *2* show some results obtained by d.m.t.a. for pure PEO and a blend with a PVAL content of 20%. These figures show the variation of the storage modulus E' and the loss tangent, tan δ, as a function of temperature. In both figures we can observe only one T_g corresponding to PEO. This suggests that there exists an amorphous phase constituted by pure PEO. Also between the glass transition temperature and the melting temperature of PEO there exist no damping peaks that can be attributed to parts of the material in which there is a mixture of components at the molecular level.

For all compositions, the crystalline samples exhibited melting endotherms similar to those of pure PEO. The degree of crystallinity is plotted as a function of weight fraction of PVAL in the blends in *Figure 3*. The values of the degree of crystallinity are ratios of the specific enthalpies of fusion of PEO in the blend and the perfect crystal heat of fusion of PEO (8.79 kJ mol^{-1}). As can be seen in *Figure 4*, several compositions show higher melting points than those of pure PEO. In order to know if this relatively rare occurrence was due to lamellar reorganization during thermal analysis, samples of PEO and PEO/PVAL (80/20) blend were melted at different heating rates; in all cases we have found the same experimental melting temperatures.

The apparent melting-point depression in a blend can be due not only to thermodynamic factors but to kinetic factors as well. These kinetic factors are related to variations in the crystal morphology as a function of blend composition. Therefore, to study the melting-point

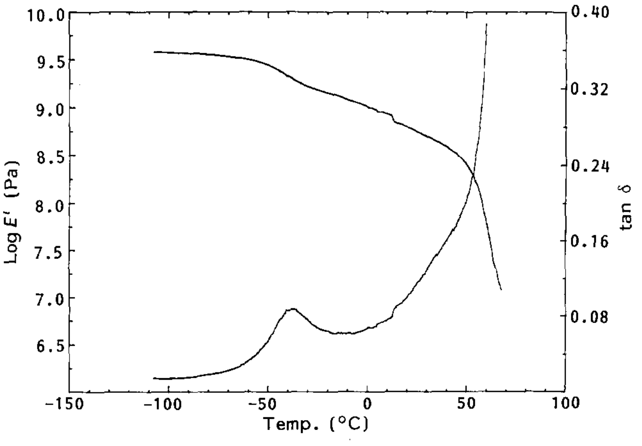

Figure 2 Variations of the storage modulus E' and loss tangent tan δ as functions of temperature for PEO/PVAL (80/20)

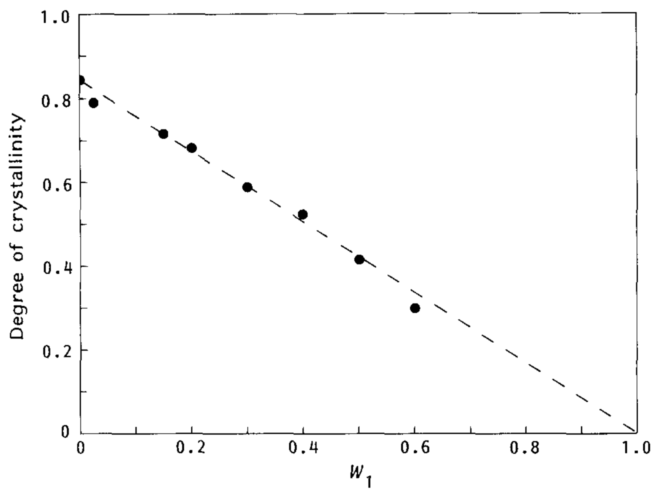

Figure 3 Degree of crystallinity for PEO/PVAL blends as a function of PVAL weight fraction W_1

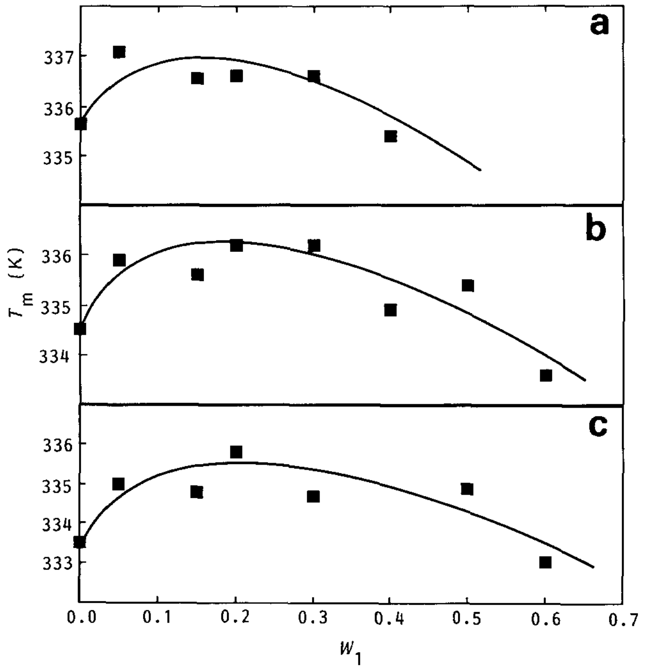

Figure 4 Variation of the experimental melting temperature T'_m with composition of PEO/PVAL blends for several crystallization temperatures (W_1 = PVAL fraction)

depression, equilibrium melting temperatures must be used in order to discard kinetic effects. These temperatures can be obtained using the Hoffman–Weeks equation[6]:

$$T'_m = T_m(1 - 1/\gamma) + T_c/\gamma \qquad (1)$$

where T'_m is the experimental melting temperature, T_m is the equilibrium melting temperature, T_c is the crystallization temperature and γ is a proportionality factor between the initial and final thicknesses of a chain-folded lamella.

By plotting the melting temperatures of samples crystallized at different temperatures against the crystallization temperatures, equation (1) allows the extrapolation to infinite lamellar thickness ($T'_m = T_c$). In this way it is possible to calculate the equilibrium melting temperatures of the crystallizable component in the blend.

In our system and for all studied compositions the melting temperatures vary linearly with the crystallization temperatures according to equation (1). This behaviour can be observed in *Figure 5* for different compositions of blends.

The obtained values of the equilibrium melting temperatures and the morphological factor γ for the different compositions are given in *Table 1*. As can be seen in *Figure 6*, there is a melting-point depression of PEO, which is attributed to the presence of PVAL. On the

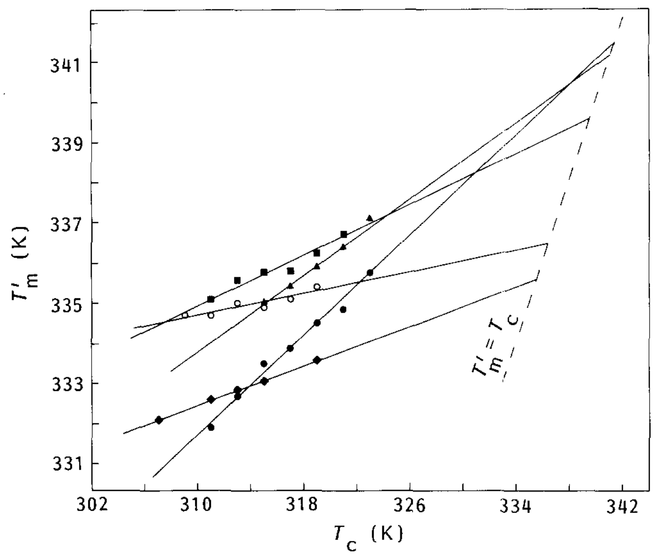

Figure 5 Hoffman–Weeks plots for PEO (●) and its PEO/PVAL blends: (▲) 95/5; (■) 80/20; (○) 50/50; (◆) 40/60

Table 1 Values of equilibrium melting temperatures T_m and morphological parameter γ calculated from Hoffman–Weeks plots and polymer–polymer interaction parameter χ_{12} for different PVAL weight fractions

W_1	T_m (K)	γ	χ_{12}
0	341.5	3.24	–
0.05	341.2	4.22	–
0.15	340.1	4.76	−0.33
0.20	339.6	6.25	−0.26
0.30	338.5	8.33	−0.17
0.40	337.4	7.25	−0.12
0.50	336.5	12.82	−0.07
0.60	335.6	8.00	−0.07

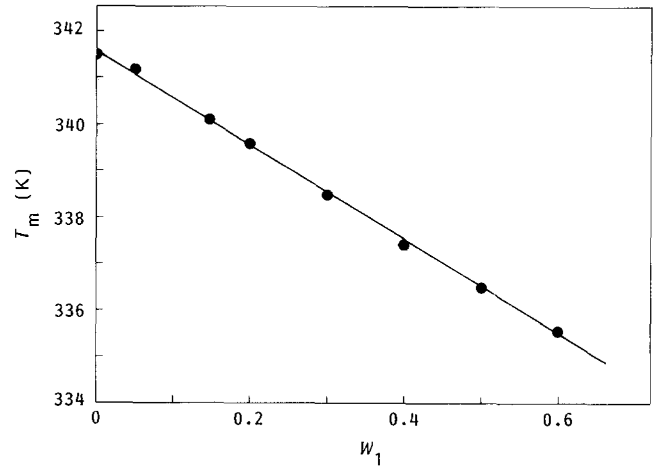

Figure 6 Equilibrium melting temperature T_m of PEO/PVAL blends as a function of PVAL weight fraction W_1

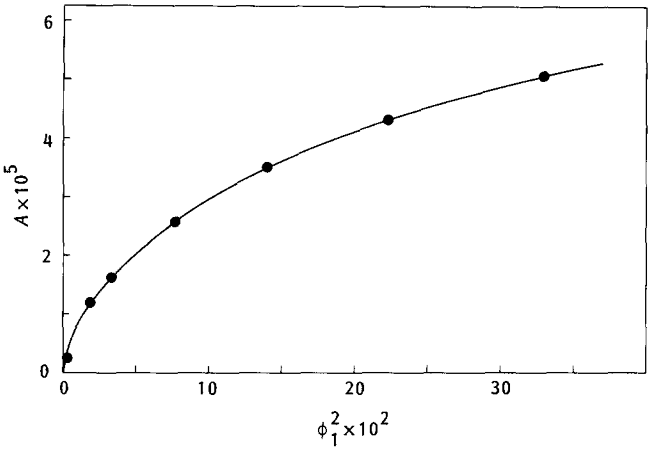

Figure 7 Plot of equation (2) for PEO/PVAL blends using equilibrium melting temperatures (the l.h.s. is written as A here)

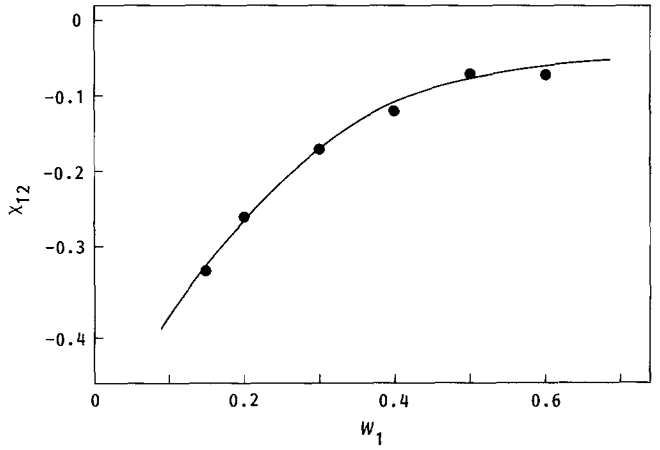

Figure 8 Polymer–polymer interaction parameter χ_{12} of PEO/PVAL blends as a function of PVAL weight fraction W_1

other hand, the presence of PVAL affects the morphological factor γ, which is not constant with composition in this case, and for some compositions has extremely large values.

In order to make a thermodynamic study of the melting-point depression in our system, we have used the following equation obtained by Nishi and Wang[7] for non-infinite molecular weight:

$$\frac{1}{T_m}-\frac{1}{T_m^\circ}+\frac{R\bar{V}_2}{\Delta H_f^\circ \bar{V}_1}\left[\frac{\ln\phi_2}{m_2}+\left(\frac{1}{m_2}-\frac{1}{m_1}\right)\phi_1\right]$$
$$=-\frac{R\bar{V}_2}{\Delta H_f^\circ \bar{V}_1}\chi_{12}\phi_1^2 \qquad (2)$$

Here the subscripts 1 and 2 represent the non-crystallizable and crystallizable polymers, respectively; T_m is the equilibrium melting point of the crystallizable component in the blend; T_m° is the equilibrium melting point of the pure crystallizable component; V is the molar volume of the polymer repeat unit ($V_1=35.0$ cm^3 mol^{-1} (ref. 8) and $V_2=38.9$ cm^3 mol^{-1} (ref. 8)); ϕ is the volume fraction of the component in the blend; m is the degree of polymerization ($m_1=1977$ and $m_2=705$); ΔH_f° is the perfect crystal heat of fusion of the crystallizable polymer (8.79 kJ mol^{-1} (ref. 9)); R is the universal gas constant; and χ_{12} is the polymer–polymer interaction parameter. The polymer densities were $\rho_1=1.26$ and $\rho_2=1.13$ g cm^{-3} (ref. 8).

A plot of the left-hand side of equation (2) (written as A in *Figure 7*) *versus* ϕ_1^2 would therefore be a straight line with zero intercept and slope proportional to χ_{12}. However, as shown in *Figure 7*, our data do not form a straight line, though the curve that is drawn through the experimental points seems to have an intercept very close to zero. This suggests that the polymer–polymer interaction parameter depends on blend composition (*Figure 8*). In all cases it is negative, but it becomes less negative as more PVAL is added, tending to a value close to -0.07. The values of χ_{12} have been calculated from the slope of the curve for each composition and are shown in *Table 1*.

The dependence of the interaction parameter on composition is well known in polymer–solvent systems and also it is not unusual in polymer blends. Morra and Stein[10] have found an analogous behaviour for poly(vinylidene fluoride)/poly(methyl methacrylate) blends using melting temperatures of γ crystal forms and high-crystallization-temperature data of α crystal forms.

The negative values of the interaction parameter obtained suggest that PEO/PVAL blends are probably compatible in the melt for the studied composition range, though χ tends to zero for compositions with high PVAL content. The melting-point depression obtained seems to be in apparent contradiction with the d.m.t.a. data, which suggest incompatible polymer blends. However, this behaviour could be explained if we consider that these blends are compatible in a limited range of crystallization temperature and composition, i.e. the system would have a lower critical solution temperature (*LCST*)[11].

On the other hand, a similar melting behaviour has been observed in pure homopolymers. So Gopalan and Mandelkern[12] have observed for linear polyethylene that the equilibrium melting temperatures and the γ factor depend on the crystallinity level. Also Beech and Booth[13] reported similar behaviour for PEO. These authors found that in any case the variation of T_m with T_c was linear. However, whereas for samples of 10% crystallinity and $T_c>57.7$°C they found an equilibrium melting temperature of 76°C and a γ factor of 1.9, for low crystallinity and $T_c<57.7$°C or for high crystallinity they found γ values of 3.8 and 7.4, respectively, and an equilibrium melting temperature of 69.1°C. The lower slopes of the T'_m *versus* T_c lines are due to the increasing importance of processes of crystallite perfecting, either by increase in the thickness of lamellar crystal or by decrease in the interfacial free energy. Thus, the melting-point depression for PEO/PVAL blends can be considered to be due to morphological effects and not to miscibility.

The crystallization kinetics have been analysed from the variation of the fraction of crystallized material, X_T, with time. Thus, for a time t, this factor was determined from the relation:

$$X_T=\int_0^t (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t\bigg/\int_0^\infty (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t \qquad (3)$$

Typical crystallization isotherms obtained by plotting X_T against time are shown in *Figure 9* for different blends at 323 K. As can be seen, on increasing the amount of PVAL in the blends, the overall crystallization rate becomes slower.

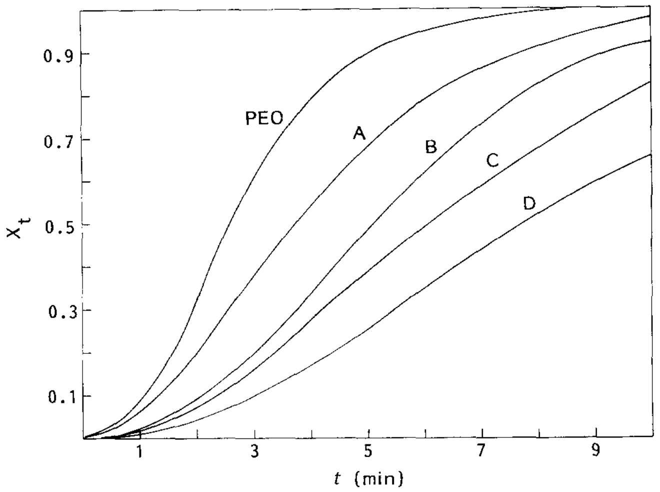

Figure 9 Influence of blend composition on the trend of the crystallization isotherms ($T_c = 323$ K) for PEO and PEO/PVAL blends: A, 90/10; B, 80/20; C, 70/30; D, 60/40

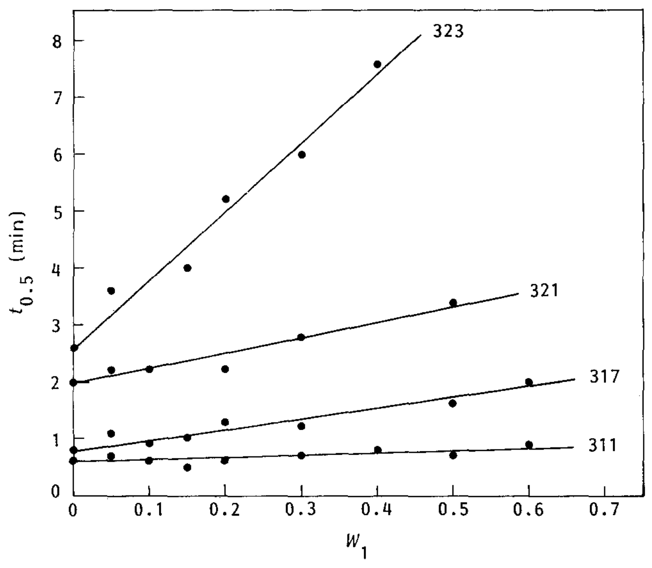

Figure 10 Half crystallization time $t_{0.5}$ *versus* PVAL weight fraction W_1 for different crystallization temperatures

The half crystallization time $t_{0.5}$, defined as the time taken for half of the crystallinity to develop, is plotted as a function of PVAL content for several crystallization temperatures in *Figure 10*. These curves show that the half crystallization time increases linearly with increase of the PVAL content for each crystallization temperature, showing the influence of PVAL on the crystallization of PEO.

The decrease of the crystallization rate as the PVAL content increases is a behaviour typical of compatible polymer systems. However, in the literature, for several binary polymer systems, a decrease in the crystallization rate for incompatible blends has been reported[14]. Martuscelli has suggested a decrease in the number of spherulites, caused by the heterogeneities constituting thermal nuclei in the matrix of the crystalline polymer being washed out by domains of amorphous polymer during the process of mixing. On the other hand, a decrease in the spherulite growth rate is possible, owing to the fact that during crystallization the domains of amorphous polymer can be rejected by the crystallizing front of the spherulite boundaries and/or they may be occluded and deformed.

The kinetics of isothermal crystallization were analysed by means of the Avrami equation[15]:

$$(1 - X_T) = \exp(-Kt^n) \tag{4}$$

where n is the Avrami exponent, a numerical value that can provide information on the type of nucleation and on the geometry of growing crystals; and K is the rate constant, which can also be calculated from the half crystallization time and the exponent n, since:

$$K = \ln 2/t_{1/2}^n \tag{5}$$

Table 2 Values of the half crystallization time $t_{0.5}$, the overall kinetic rate constant K and the Avrami exponent n at various crystallization temperatures T_c for PEO and PEO/PVAL blends

	T_c (K)	$t_{0.5}$ (min)	K (min^{-n})	n
PEO	323	2.6	0.10	2.0
	321	2.0	0.19	2.0
	319	1.4	0.35	2.1
	317	0.8	1.11	2.1
	315	0.7	1.38	2.0
	313	0.7	1.36	1.8
	311	0.6	1.83	1.9
PEO/PVAL (95/5)	323	3.8	0.06	1.8
	321	2.0	0.15	1.8
	319	1.1	0.60	1.5
	317	1.1	0.59	1.9
	315	0.9	0.81	2.0
	313	0.6	1.70	1.8
	311	0.6	1.68	2.1
PEO/PVAL (81/15)	323	3.9	0.05	1.9
	321	2.1	0.14	2.1
	319	1.3	0.39	1.9
	317	1.0	0.65	2.0
	315	0.8	1.05	2.2
	313	0.7	1.52	1.9
	311	0.5	2.34	1.9
PEO/PVAL (80/20)	323	5.2	0.02	2.1
	321	2.3	0.14	1.9
	319	1.7	0.22	2.1
	317	1.3	0.43	1.8
	315	1.0	0.75	2.0
	313	0.8	1.23	2.1
	311	0.7	1.59	2.0
PEO/PVAL (70/30)	323	6.0	0.03	1.8
	321	2.9	0.09	1.9
	319	2.0	0.16	2.1
	317	1.1	0.61	1.9
	315	0.9	0.92	1.8
	313	0.8	1.04	1.9
	311	0.7	1.46	2.2
PEO/PVAL (60/40)	323	7.7	0.02	1.8
	321	2.4	0.14	1.9
	319	1.8	0.21	2.2
	317	1.0	0.56	2.0
	315	1.0	0.70	2.4
	313	0.9	0.80	1.9
	311	0.8	1.12	2.3
	309	0.7	1.65	2.0
PEO/PVAL (50/50)	321	3.5	0.06	2.0
	319	1.9	0.18	2.1
	317	1.6	0.24	2.2
	315	1.3	0.41	2.1
	313	0.8	0.99	2.1
	311	0.7	1.41	2.1
	309	0.7	1.44	2.1

Plots of $\log[-\ln(1-X_T)]$ against $\log t$ are straight lines, which became curves at high values of $\log t$. This fact suggests that for all temperatures studied the crystallization kinetics of these blends follow the Avrami equation till a high degree of conversion. The Avrami exponent, the half crystallization time and the rate constant are shown for the different blends and crystallization temperatures in *Table 2*. As can be seen, in most cases the Avrami exponent is within $n = 2 \pm 0.2$ and does not depend on the PVAL content, as do the other kinetic parameters.

These values of the Avrami exponent do not correspond to the presence of spherulites, which are observed by microscopy. However, this phenomenon has been reported several times[16–19]. Most investigators suggest the cause to be an abnormally low number of crystallization nuclei on the non-specific character of the generating spherulites. Godonsky *et al.*[20] suggest that this phenomenon might be due to the fact that the Avrami parameters apply to the growth of crystallites rather than spherulites. The primary crystallization structures of PEO are lamellar crystallites formed by completely extended or multiply folded macromolecules. The enthalpy changes observed in the course of crystallization are due to the formation of the crystallite.

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