

# Crystallization and melting behaviour of poly(bisphenol A hydroxy ether)/poly(ethylene oxide) blends

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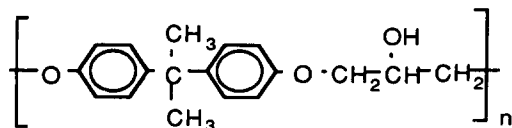
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The crystallization and melting behaviour of solution-cast films of poly(bisphenol A hydroxy ether)/poly(ethylene oxide) (PEO) blends were investigated as a function of composition by means of optical microscopy, differential scanning calorimetry and dilatometry. All blends show only one single value of glass transition temperature, intermediate between those of the pure polymers. The growth rate of PEO spherulites ( $G$ ) as well as the observed equilibrium melting temperature, for a given  $\Delta T$ , decrease as the phenoxy content increases. These results suggest that this blend is miscible for every composition investigated. Temperature and composition dependences of the radial growth rate  $G$  and the overall kinetic constant  $K$  have been employed to calculate the surface energy of folding  $\sigma_e$ . The interaction energy density  $B$  has been determined from the dependence of the equilibrium melting-point depression upon composition.

(Keywords: blends; poly(ethylene oxide); poly(bisphenol A hydroxy ether); crystallization; melting)

## INTRODUCTION

Blends of poly(bisphenol A hydroxy ether) (phenoxy, Ph):



are among the most studied polymer-polymer systems. Harris *et al.*<sup>1</sup> have studied numerous miscible and immiscible blends of this polymer with aromatic and aliphatic polyesters. Miscibility with poly(butylene terephthalate) and with polyethers and polyoxides has been reported by Robeson *et al.*<sup>2,3</sup>. Recently, we have reported a detailed study of the miscibility and phase separation in phenoxy/poly(vinyl methyl ether) blends<sup>4</sup>.

Poly(ethylene oxide) (PEO) blends with poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) have been studied<sup>5,6</sup> with emphasis on the PEO crystallization and melting behaviour in the presence of a second amorphous component. Robeson *et al.*<sup>3</sup> published the first results concerning blends of phenoxy and PEO. Glass transition temperatures, melting temperatures and heats of fusion at different compositions showed that phenoxy and PEO miscibilize each other. This observed miscibility was proposed to be the result of the potential capacity of phenoxy and PEO for hydrogen bonding. Because of its pendant hydroxyl, phenoxy can play the role of a proton donor against the proton-acceptor capacity of PEO.

In the present paper we report the results of a study concerning the influence of blend composition and crystallization conditions on:

- (1) the glass transition temperature;
- (2) the crystallization process of PEO from the melt blend (radial growth rate of spherulites, nucleation, overall kinetics of crystallization, Avrami index, . . .);
- (3) the overall morphology of the binary mixture; and
- (4) the melting behaviour of PEO (observed melting temperature, equilibrium melting temperature).

## EXPERIMENTAL

### Materials

Phenoxy was obtained from Quimidroga (Barcelona, Spain) and corresponds to the PKHH product of Union Carbide. Molecular-weight averages of the commercial sample, purified by solution-precipitation in dioxane-methanol, were measured by g.p.c. and adequate Mark-Houwink coefficients previously reported<sup>7</sup>. Poly(ethylene oxide) (PEO) was used as an unfractionated industrial sample (WSR-35, Union Carbide) but purified by repeated precipitation from a filtered benzene solution with excess *n*-heptane. It was characterized by viscometry in benzene at 25°C<sup>8</sup>. The molecular characteristics of the polymers are reported in Table 1.

### Preparation of the blends

The blends were prepared by means of solution casting, using dioxane as the solvent. The polymer concentration in the solution was about 10%. Dioxane evaporation was conducted at room temperature. The resulting films were dried in a vacuum oven at 60°C for 72 h until they

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**Table 1** Characteristics of polymers used

Polymer	Source and trade name	Molar mass		
		$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_v$
Phenoxy	Union Carbide (PKHH)	50 700	18 000	43 000
PEO	Union Carbide (WSR-35)	—	—	335 000

reached a constant weight and then stored *in vacuo* to avoid moisture adsorption.

#### Optical microscopy

The radial growth rates,  $G = dR/dt$  (where  $R$  is the radius of growing spherulites), were calculated by measuring the size of PEO spherulites as a function of time during the isothermal crystallization process, at a fixed crystallization temperature.

A Reichert polarizing optical microscope equipped with a Mettler calibrated hot stage (precision  $\pm 0.2^\circ\text{C}$ ) was used. The films were first melted at  $100^\circ\text{C}$  and kept at this temperature for 10 min; after that they were transferred to the Mettler hot stage at a fixed crystallization temperature where the blends crystallized isothermally.

Optical microscopy was also used in measuring the melting temperatures of the isothermally crystallized blends. Heating was conducted at a rate of  $0.1^\circ\text{C min}^{-1}$ , using a Mettler FP5 programming unit. Melting points were detected as the temperatures at which sample birefringence disappeared.

#### Dilatometric measurements

The overall rate of crystallization was analysed by means of dilatometry. Ordinary glass-mercury dilatometers with a capillary of 0.5 mm diameter and 0.2–0.3 g samples were used. Ordinary filling and measuring procedures were employed. Relative measurements were obtained.

The samples were heated to  $100^\circ\text{C}$  and kept at this temperature for 10 min. Then the dilatometers were rapidly transferred to the crystallization bath and the crystallization was followed by the height of the meniscus.

#### Calorimetric measurements

The melting behaviour of the blends was analysed by means of differential scanning calorimetry with a Perkin-Elmer DSC-2 apparatus. The samples (about 9 mg in weight), after previous melting at  $100^\circ\text{C}$  for 10 min, were rapidly cooled to the desired crystallization temperature ( $T_c$ ), then isothermally crystallized during the necessary time to reach only 10% crystallinity and finally heated at a rate of  $20^\circ\text{C min}^{-1}$ . The glass transition temperatures were obtained by heating the samples (about 10 mg), previously melted and quenched at  $-100^\circ\text{C}$ , from  $-100$  to  $150^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$  and by recording the heat evolved during the scanning process as a function of temperature.

## RESULTS AND DISCUSSION

#### Glass transition temperatures

The glass transition temperatures of PEO and phenoxy (Ph) were found, respectively, at  $-68$  and  $95^\circ\text{C}$ . All phenoxy/PEO blends exhibit a single value of  $T_g$  intermediate between the transitions of the pure components.

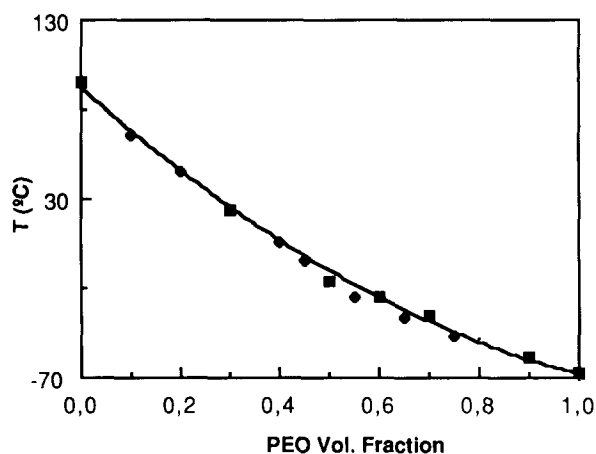
Consequently, it can be concluded that phenoxy/PEO blends are completely miscible in the solid state. In other words, there is extensive mixing of the segments of the two polymers. A selection of our data and those of Robeson *et al.*<sup>3</sup> in *Figure 1* show the agreement between the two series of values.

The  $T_g$ -composition data can be analysed by the Gordon-Taylor equation, which can be written as:

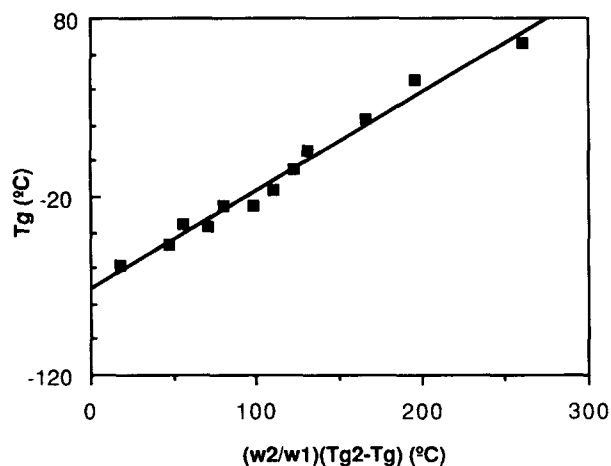
$$T_g = T_{g1} + k(\omega_2/\omega_1)(T_{g2} - T_g) \quad (1)$$

where  $T_g$  is the glass transition temperature of the blend and  $T_{g1}$  and  $T_{g2}$  those of components 1 and 2,  $\omega_i$  are the weight fractions and  $k$  is an adjusting parameter related to the degree of curvature of the  $T_g$ -composition diagram. A plot (*Figure 2*) of experimental values of  $T_g$  against  $(\omega_2/\omega_1)(T_{g2} - T_g)$  should be a straight line, the slope of which equals the adjusting parameter  $k$ . The  $k$  value found by this method was 0.549.

Belorgey and Prud'homme<sup>9,10</sup> have suggested that  $k$  can be taken as a semiquantitative measure of the strength of the interaction between the functional groups of the components of the blends. For instance, in blends of poly(caprolactone) with chlorinated poly(ethylene), poly(vinyl chloride) (PVC) and chlorinated PVC,  $k$  increases from 0.26 to 1.0. Some  $k$  values for phenoxy blends given in the literature are shown in *Table 2*. Lower values were obtained in the case of blends with weaker interactions (e.g. polystyrene/PVME,  $k = 0.21$  ref. 13).



**Figure 1**  $T_g$  vs. composition in PEO/phenoxy blends: (◆) ref. 3; (■) this work



**Figure 2** Determination of the Gordon-Taylor parameter  $k$ . Experimental data from *Figure 1*

**Table 2** Gordon-Taylor adjusting parameter  $k$  in phenoxy (Ph) blends

Blend <sup>a</sup>	$k$	Reference
PEO/Ph	0.548	This work
PVME/Ph	0.51	4
PBT/Ph	0.47	11
PVP/Ph	1.25	12

<sup>a</sup> PEO, poly(ethylene oxide); PVME, poly(vinyl methyl ether); PBT, poly(butylene terephthalate); PVP, poly(vinyl pyrrolidone)

### Morphology and spherulite growth rate

In the literature several studies are reported concerning the morphology<sup>14,15</sup> of melt-crystallized poly(ethylene oxide). They show that according to crystallization conditions it may crystallize from the melt with a spherulitic, hedritic or intermediate spherulite-hedrite morphology.

Thin films of PEO/Ph blends isothermally crystallized in the temperature range 18–61°C show, for all the compositions examined, spherulite morphology. Under the optical microscope, under crossed Nicols, the spherulites display a 'Maltese cross' birefringent pattern and have a regular shape with defined borders. With the increase in phenoxy content the texture of the spherulites becomes more irregular, but in no case were separated domains of uncrystallizable Ph component observed in the intra-spherulitic region. This behaviour is similar to that encountered by Martuscelli *et al.*<sup>5</sup> in PEO/PMMA blends.

The spherulite radius  $R$  increases linearly with time for all the temperatures and blend compositions and therefore the slope  $dR/dt$  remains unvariable. The dependence of the spherulite growth rate  $G = dR/dt$  on  $T_c$  is shown in Figure 3. The addition of Ph to PEO causes, at a given  $T_c$ , a depression in the  $G$  values. As shown in Figure 3 this depression effect greatly increases as the crystallization temperatures become lower. Similar behaviours have also been found in the case of poly-(caprolactone)/poly(vinyl chloride) blends<sup>16</sup>, poly(vinylidene fluoride)/PMMA blends<sup>17</sup>, PEO/PMMA blends<sup>5</sup> and PEO/PVAc blends<sup>6</sup>. The values of  $G$  of pure PEO and of its blends with Ph are compared in Table 3.

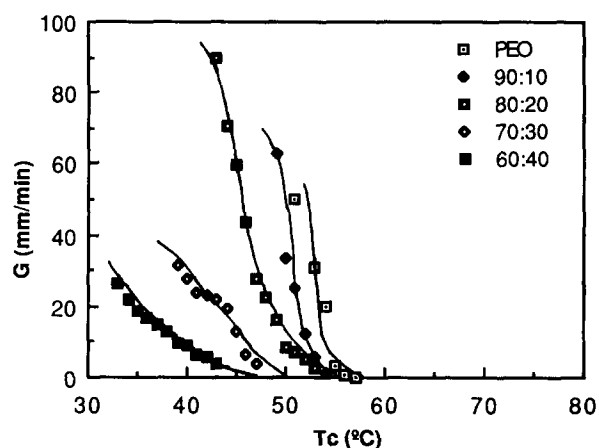
### Overall rates of crystallization

Typical crystallization isotherms obtained by plotting  $X_t$  (weight fraction of crystallinity at time  $t$ ) against time are shown in Figure 4 for two PEO/Ph blends. From these curves we can conclude that on increasing the amount of Ph in the blends the overall crystallization rate becomes progressively slower. The half-time of crystallization,  $\tau_{0.5}$ , defined as the time taken for half of the crystallinity to develop, is obtained from these curves and shown in Figure 5, at different  $T_c$  values.

The kinetics of the isothermal crystallization from the melt of all Ph/PEO blends have been analysed on the basis of the Avrami equation<sup>18</sup>:

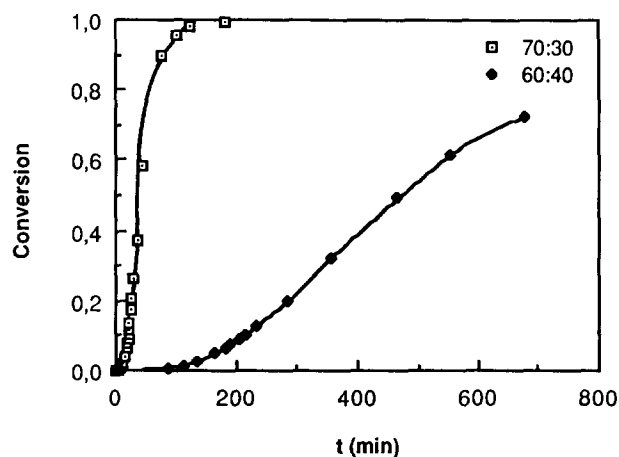
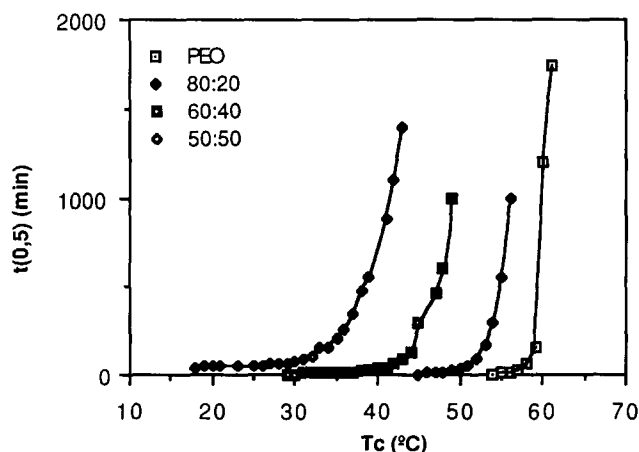
$$1 - X_t = \exp(-Kt^n) \quad (2)$$

where  $K$  is the overall kinetic rate constant and  $n$  is a parameter that depends on the type of nucleation and on the geometry of growing crystals. Plots of  $\log[-\ln(1 - X_t)]$  against  $\log t$  are always linear until a high degree of conversion is obtained (see Figure 6). The values of  $K$  and  $n$  have been derived from the intercept and the slope of these lines.


**Figure 3** Dependence of  $G$  on  $T_c$  for different PEO/phenoxy blends

**Table 3** Comparison between the  $G$  ( $\text{mm min}^{-1}$ ) of PEO and its blends with phenoxy

$T_c$ (°C)	PEO	90:10 PEO/Ph		80:20 PEO/Ph	
	$G$	$G$	$\Delta G$ (%)	$G$	$\Delta G$ (%)
328	3.23	1.04	68	—	—
326	30.66	7.64	75	2.41	92


**Figure 4** Crystallization isotherms of PEO/Ph blends at 47°C

**Figure 5** Half-time of crystallization for different PEO/phenoxy blends

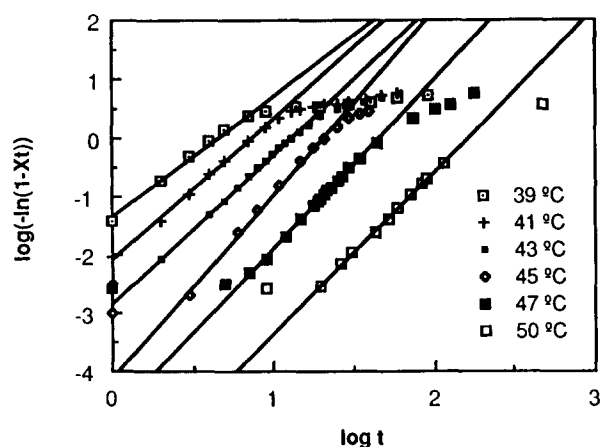


Figure 6 Avrami plots for a 70:30 PEO/phenoxy blend

Table 4 Values of the Avrami index for pure PEO and its blends with phenoxy

PEO/Ph blend	$T_c$ range (°C)	$n$
100:0	55–61	2.71 ( $\pm 0.18$ )
90:10	53–58	2.37 ( $\pm 0.17$ )
80:20	51–56	2.60 ( $\pm 0.14$ )
70:30	48–60	2.85 ( $\pm 0.22$ )
60:40	43–49	2.71 ( $\pm 0.27$ )
50:50	29–35	2.57 ( $\pm 0.12$ )

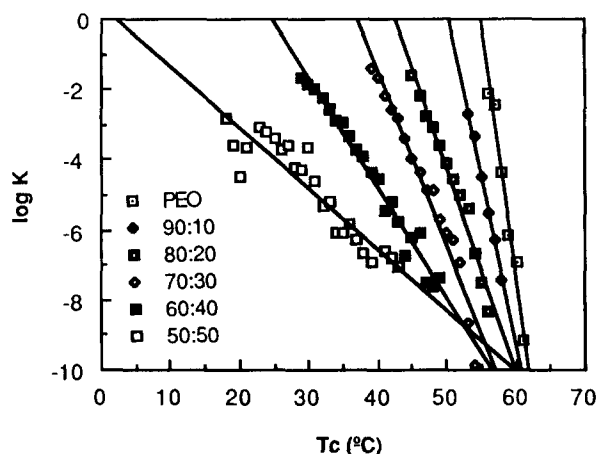


Figure 7 Temperature dependence of the kinetic constant  $K$

Table 4 shows the values of the Avrami index,  $n$ . Average values in a selected  $T_c$  range are given. The values of the Avrami constants of the blends are in the neighbourhood of that of the pure PEO and are almost independent of the composition. Figure 7 illustrates the  $T_c$  dependence of the kinetic constant  $K$  for pure PEO and its blends.

#### Melting behaviour

A better understanding of the kinetic aspects of crystallization in polymer blends can be had if thermodynamic interaction parameters, such as the Flory–Huggins parameter or the interaction energy density  $B$ , are evaluated. Among the available techniques for the determination of these parameters in a bulk system, the analysis of melting-point depression has been applied to

different blends constituted by a crystalline polymer and an amorphous one.

Different authors have analysed the melting-point depression using experimental or apparent melting points. In the present work equilibrium melting points have been determined using the well known Hoffman and Weeks analysis. Experimental temperatures  $T_m$  are expected to follow a linear relationship with the crystallization temperature<sup>19</sup>:

$$T_m^0 - T_m = \Phi(T_m^0 - T_c) \quad (3)$$

where  $T_m$  is the experimental melting temperature after an isothermal crystallization at  $T_c$  and  $T_m^0$  is the equilibrium melting temperature obtained by extrapolating the  $T_m$  vs.  $T_c$  relationship to  $T_m = T_c$ .  $\Phi$  is a stability parameter, which depends on the thickness of the crystal.

As in the case of PEO/PMMA blends<sup>5,20</sup> the observed melting points undergo an abrupt increase at low undercoolings. Crystal annealing during melting<sup>20</sup>, and possibly also during heating, and phase separation processes at  $T_c$ <sup>5</sup> have been proposed as a possible origin of such behaviour, making the experimental measurements difficult to obtain.

In a first approach to the thermodynamic parameters of this blend, the following criteria were followed in our melting experiments:

- samples were crystallized less than 10% in order to prevent impingements;
- not excessively low undercoolings were used; and
- experimental measurements of

$$\Delta T_m = (T_m^0)_{\text{pure polymer}} - (T_m^0)_{\text{blend}}$$

from d.s.c. (scanning rate  $20^\circ\text{C min}^{-1}$ ) and microscopy ( $1^\circ\text{C min}^{-1}$ ) were used in the calculation of  $B$ .

Table 5 summarizes the results of  $T_m^0$  and  $\Phi$  for the different blend compositions obtained by means of the two experimental techniques.

A quantitative analysis of the melting-point depression in binary polymer blends with components miscible in the melt has been presented by Nishi and Wang<sup>21</sup> and later by Imken *et al.*<sup>22</sup> based on an earlier treatment offered by Scott<sup>23</sup>. The results of this analysis lead to the conclusion that a plot of the melting-point depression  $\Delta T_m$  versus the square of the volume fraction of the non-crystallizable component should be linear with an intercept at the origin, if there are no entropic contributions to  $\Delta T_m$ . The following equation can in fact be derived:

$$\Delta T_m = -T_m^0(V_{2u}/\Delta H_{2u})B\phi_1^2 \quad (4)$$

where  $V_{2u}$  is the molar volume of the repeat units,  $\Delta H_{2u}$

Table 5 Analysis of melting behaviour after isothermal crystallization.  $T_m^0$  and  $\Phi$  are the equilibrium melting temperature and stability parameter of the crystals, respectively

PEO/Ph blend	$T_m^0$ (°C)		$\Phi$	
	D.s.c.	Microsc.	D.s.c.	Microsc.
100:0	76.6	71.4	0.51	0.51
90:10	75.0	69.6	0.49	0.37
80:20	74.6	68.1	0.38	0.32
70:30	71.0	66.5	0.31	0.22
60:40	70.0	63.6	0.40	0.28
50:50	66.2	–	0.25	–

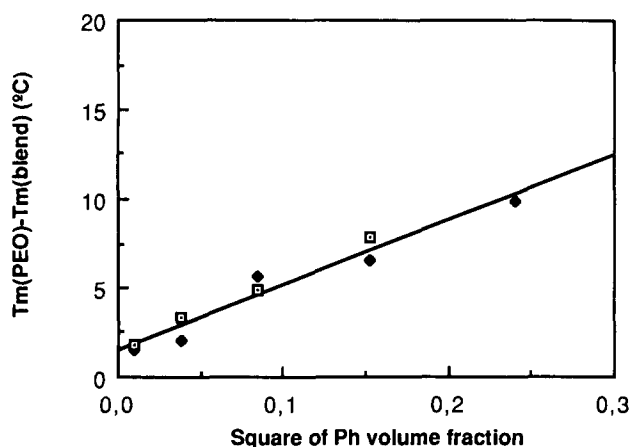


Figure 8 Equilibrium melting-point depression in PEO/phenoxy blends: (◆) D.s.c. data; (□) microscopy data

Table 6 Interaction energy density ( $B$ ) for different polymer/polymer systems

Blend <sup>a</sup>	$T$ (°C)	$B$ (cal cm <sup>-3</sup> )	Ref.
POE/h-PMMA	30	-1.10	26
POE/i-PMMA	30	-1.44	26
PBA/Phenoxy	61	-3.9	1
PEA/Phenoxy	49	-2.3	1
PCL/Phenoxy	56	-2.4	1
PES/Phenoxy	30	-5	27
POE/Phenoxy	74	-6	This work
PVC/Polyesters	-	-1.5 to -4	28
PMMA/PVF <sub>2</sub>	177	-2.8	29
PMMA/PVF <sub>2</sub>	160	-3.0	21

<sup>a</sup> POE, polyoxyethylene; PMMA, poly(methyl methacrylate); PBA, poly(butylacrylate); PEA, poly(ethyl acrylate); PCL, poly( $\epsilon$ -caprolactone); PES, poly(ether sulphone); PVC, poly(vinyl chloride); PVF<sub>2</sub>, poly(vinylidene fluoride)

is the enthalpy of fusion per mole of repeat unit and  $\phi_i$  is the volume fraction.  $B$  is the interaction energy density characteristic of the polymer pair in cal cm<sup>-3</sup>. Equation (4) can be written in terms of the well known interaction parameter  $\chi$  if  $B$  is substituted by:

$$B = RT_m \chi / V_{1u} \quad (5)$$

( $R$  is the gas constant) but, for our purposes, we prefer to use  $B$  since its basis is always clearly a unit of mixture volume, whereas  $\chi$  depends on the  $V_{1u}$  value. Especially in cases like this blend, where  $V_{1u}$  is very high, comparison between different  $\chi$  values can be obscure, as we will see at a later point.

As shown in Figure 8, irrespective of the absolute values of  $T_m^0$ , data from d.s.c. and microscopy follow a similar trend with the blend composition. For this reason, and in order to have a tentative value of  $B$ , data from the two techniques have been adjusted in a single plot, which gives the following relationship:

$$\Delta T_m = 1.55 + 36.51 \phi_1^2$$

Published density data<sup>4,24</sup> have been used to convert weight fractions into volume fractions and to calculate  $V_{1u}$  and  $V_{2u}$ . Also  $\Delta H_{2u} = 2.02$  kcal mol<sup>-1</sup> according to ref. 25. From the slope of Figure 8, a tentative value of  $B = -6.2$  cal cm<sup>-3</sup> has been obtained (at 74°C). As an example of the unrealistic significance of the absolute

values of the interaction parameter, mainly in cases with very different molar volumes, a  $B$  value of  $-6.2$  cal cm<sup>-3</sup> gives  $\chi_{12} = -1.9$  if the phenoxy unit is taken as a reference and  $\chi_{21} = -0.31$  if the PEO unit is the reference segment. Table 6 shows  $B$  data of other similar polymer/polymer systems.

#### Temperature dependence of $G$ and $K$

It has been shown<sup>5</sup> that a function of the overall growth rate can be written as:

$$f(G) = \ln G - \ln \phi_2 + \frac{C_1}{R(C_2 + T_c - T_g)} - 0.2 \ln \phi_2 \frac{T_m^0}{\Delta T} \\ = \ln G_0 - \frac{0.4b_0^2 \sigma_e}{k} \frac{T_m^0}{T_c \Delta T} \quad (6)$$

where  $G$  is the spherulite growth rate,  $G_0$  is a pre-exponential factor that at low values of  $\Delta T$  may be assumed constant,  $\phi_2$  is the volume fraction of the mixture,  $C_1$  is the activation energy for transport of crystallizable segments through the melt to the site of crystallization and is equal to 4120 cal mol<sup>-1</sup> and  $C_2 = 51.6$  K,  $T_c$  is the crystallization temperature,  $T_g$  the glass transition temperature,  $T_m^0$  the equilibrium melting point,  $\Delta T$  the undercooling,  $b_0$  the distance between two adjacent fold planes,  $\sigma_e$  the interfacial free energies for unit area perpendicular to the molecular chain axis,  $k$  is the Boltzmann constant and  $R$  the gas constant.

Analogously, for the overall crystallization rate it is possible to write:

$$f(K) = \frac{1}{n} \ln K - \ln \phi_2 - \frac{C_1}{R(C_2 + T_c - T_g)} - 0.2 \ln \phi_2 \frac{T_m^0}{\Delta T} \\ = \ln A_0 - \frac{0.4b_0^2 \sigma_e}{k} \frac{T_m^0}{T_c \Delta T} \quad (7)$$

By plotting the quantity  $f(G)$  or  $f(K)$  against  $T_m^0/T_c \Delta T$  straight lines are obtained for PEO and its blends. The pre-exponential factors ( $G_0$  and  $A_0$ ) calculated by extrapolation to the ordinate axis of linear plots of  $f(G)$  and  $f(K)$  versus  $T_m^0/T_c \Delta T$  respectively are shown in Figure 9 and the values of the free energy of folding  $\sigma_e$  have been calculated from the slopes by using<sup>30</sup>  $\Delta H = 2.1 \times 10^9$  erg cm<sup>-3</sup> and  $b_0 = 4.65 \times 10^{-8}$  cm.

The pre-exponential factors  $G_0$  and  $A_0$  depend on the blend composition, showing a parabolic curvature (see

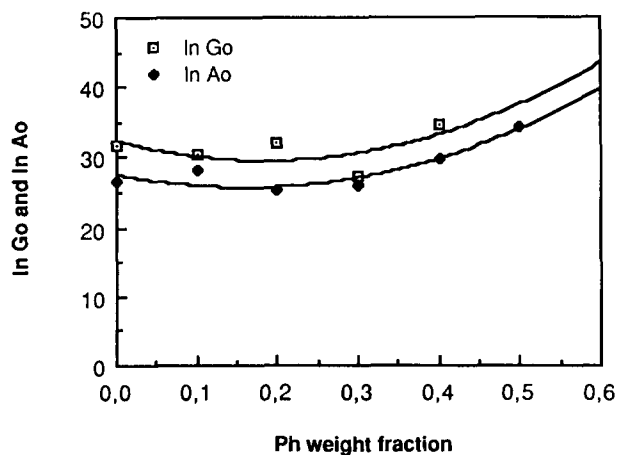


Figure 9 Pre-exponential factors  $G_0$  and  $A_0$  in different PEO/phenoxy blends

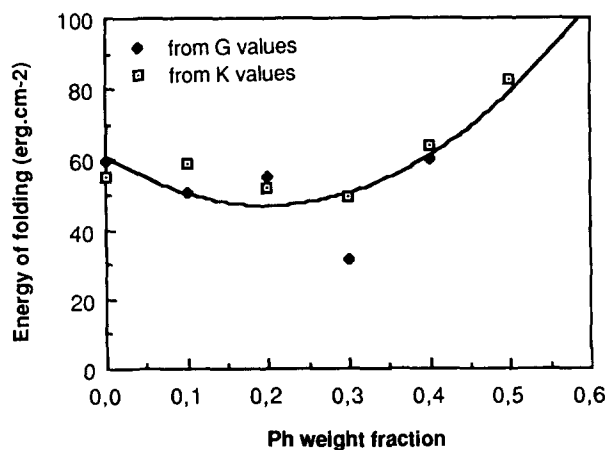


Figure 10 Variation of energy of folding with composition

Figure 9). Similar behaviour was observed by Martuscelli *et al.*<sup>5</sup> and in that case changes in viscosity of the melt and in  $T_g$  were assumed to be responsible for the composition dependence.

In Figure 10 the values of  $\sigma_e$  are plotted as a function of volume fraction of Ph in the blends. As shown,  $\sigma_e$  depends on the blend composition in both cases (values from K or G). Martuscelli *et al.*<sup>5</sup> have explained that, during crystallization, when Ph molecules are trapped in interlamellar regions, they may easily create entanglements with PEO molecules favouring the formation of larger loops on the surface of PEO lamellar crystals. Consequently the two terms of  $\sigma_e$ , i.e. entropic and enthalpic, increase. The observation of the  $\sigma_e$  dependence on the Ph content should be ascribed<sup>5</sup> to different variations of the entropic and enthalpic terms contributing to  $\sigma_e$ .

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#### REFERENCES

- Harris, J. E., Goh, S. E., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1982, **27**, 839
- Robeson, L. M. and Furtek, A. B. *J. Appl. Polym. Sci.* 1979, **23**, 645
- Robeson, L. M., Hale, W. F. and Merriam, C. N. *Macromolecules* 1981, **14**, 1644
- Uriarte, C., Eguiazábal, J. I., Llanos, M., Iribarren, J. I. and Iruin, J. J. *Macromolecules* 1987, **20**, 3038
- Martuscelli, E., Pracella, M. and Yue, W. P. *Polymer* 1984, **25**, 1097
- Martuscelli, E., Silvestre, C. and Gismondi, C. *Makromol. Chem.* 1985, **187**, 2161
- Iribarren, J. I., Iriarte, M., Uriarte, C. and Iruin, J. J. *J. Appl. Polym. Sci.* (in press)
- Allen, G., Booth, C., Hurst, S. J., Jones, M. N. and Price, C. *Polymer* 1967, **8**, 391
- Belorgey, G. and Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 191
- Belorgey, G., Aubin, M. and Prud'homme, R. E. *Polymer* 1982, **23**, 1051
- Eguiazábal, J. I., Cortázar, M., Iruin, J. J. and Guzmán, G. M. *J. Appl. Polym. Sci.* 1986, **32**, 5945
- Eguiazábal, J. I., Iruin, J. J., Cortázar, M. and Guzmán, G. M. *Makromol. Chem.* 1984, **185**, 1761
- Eguiazábal, J. I. and Iruin, J. J. unpublished results
- Allen, R. C. and Mandelkern, L. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1465
- Galeski, A. and Kryszevski, M. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 471
- Ong, C. J. and Price, F. P. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 45
- Wang, T. T. and Nishi, T. *Macromolecules* 1977, **10**, 421
- Mandelkern, L. 'Crystallization in Polymers', McGraw-Hill, New York, 1964
- Gopalan, M. and Mandelkern, L. *J. Phys. Chem.* 1967, **71**, 3833
- Alfonso, G. C. and Rusell, T. P. in 'Integration of Fundamental Polymer Science and Technology' (Eds. L. A. Kleintjens and P. J. Lemstra), Elsevier Applied Science, London, 1986
- Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909
- Imken, R. L., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1976, **16**, 593
- Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279
- Jain, R. K. and Simha, R. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1929
- Cortázar, M. M., Calahorra, M. E. and Guzmán, G. M. *Eur. Polym. J.* 1982, **18**, 165
- Marco, C., Fernández Dotu, C. and Fatou, J. G. *Anal. Quím.* 1987, **83**, 337
- Singh, V. B. and Walsh, D. J. *J. Macromol. Sci.-Phys. (B)* 1986, **25**, 65
- Woo, E. M., Barlow, J. W. and Paul, D. R. *Polymer* 1985, **26**, 763
- Morra, B. S. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 2243
- Lauritzen, J. I. Jr and Hoffman, J. D. *J. Appl. Phys.* 1973, **44**, 4340