

# Non-isothermal crystallization of poly(hydroxy ether of bisphenol-A)/poly( $\epsilon$ -caprolactone), PH/PCL blends

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*(Received 13 October 1994; revised 22 August 1995)*

The non-isothermal crystallization from the melt of the poly(hydroxy ether of bisphenol-A)/poly( $\epsilon$ -caprolactone) (PH/PCL) miscible blend was studied. Cooling rates between 0.31 and 20°C min<sup>-1</sup> were used. At a given cooling rate, the presence of PH reduces the overall PCL crystallization rate. For a given composition, the crystallization process begins at higher temperatures when slower scanning rates are used. The experimental data analysis shows agreement with both Ozawa and Avrami treatments, and agrees quite well with the theoretical results obtained using the Ziabicki method. Non-isothermal crystallization results of PH/PCL blends are compared with those reported in a previous paper studying the isothermal crystallization for the same system. Copyright © 1996 Elsevier Science Ltd.

(Keywords: PH/PCL blends; non-isothermal crystallization)

## INTRODUCTION

The final properties of semicrystalline polymers depend to a great extent on the crystallinity degree, which in turn is affected by the crystallization conditions. Therefore, the investigation of the kinetics of crystallization has a considerable practical significance. Moreover, kinetic crystallization treatments can be used to elucidate the mechanism of nucleation and growth in polymeric crystals, which is without doubt of great theoretical interest.

Isothermal crystallization measurements are usually used to study the crystallization behaviour of materials since their theoretical analysis is relatively easy. The treatment of dynamic crystallization data, in which the samples are observed at a constant cooling rate, is theoretically more complicated<sup>1</sup> although very important, since this type of crystallization approaches more closely the industrial conditions of polymer processing such as extrusion, moulding, melt-spinning of synthetic fibres among others, and is therefore of great practical importance<sup>2,3</sup>.

Numerous studies have been reported concerning the different effects observed during the isothermal crystallization of polymers. The number of publications dealing directly with a quantitative evaluation of the kinetic parameters for non-isothermal crystallization is comparatively low, although in recent years the interest in this subject has increased considerably. However, to our knowledge, very few papers have dealt with dynamic

crystallization kinetics of polymer blends, despite the fact that nowadays most plastic materials comprise a mixture of several polymers. Of the existing studies, some deal with binary blends of polyethylene with isotactic polypropylene<sup>4</sup> (iPP) and with polyethylene of different densities<sup>5,6</sup>. Also, Martuscelli *et al.* have reported the crystallization during cooling of binary blends of poly(ethylene oxide) (PEO) with poly(methyl methacrylate)<sup>7</sup> (PMMA) and with poly(vinyl acetate)<sup>8</sup> (PVAc). Recently, Hong *et al.*<sup>9</sup> have investigated the effect of a thermotropic liquid crystalline polymer on the dynamic crystallization of poly(phenylene sulfide) (PPS), and finally, Herrero and Acosta<sup>10</sup> have investigated not only the non-isothermal kinetics of binary blends of PEO with polyphosphazene (PPz) and poly(epichlorohydrin) (PECH), but also those corresponding to the ternary system PEO/PPz/PECH.

The crystallization behaviour in blends is influenced not only by the thermal treatment, as in the case of homopolymers, but also by the degree of compatibility between their components, as well as by their relative amounts. Focusing our attention on the blend to be studied, in the literature it has been found that blends of poly(hydroxy ether of bisphenol-A)/poly( $\epsilon$ -caprolactone) (PH/PCL) exhibit a single glass transition temperature<sup>11–13</sup>, and the polymer–polymer interaction parameters calculated through melting point depression<sup>12,14,15</sup> and inverse gas chromatography measurements<sup>16</sup> are in all cases negative. These observations indicate the miscibility between the amorphous polymer PH and the crystalline PCL at all temperatures and compositions studied. In a

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previous paper<sup>12</sup>, the crystallization of PCL and its mixtures with PH was studied through isothermal methods. Here, we present the non-isothermal crystallization behaviour of PH/PCL blends and the influence of composition and cooling rate on the kinetic parameters of PCL. Using these results as a starting point, the non-isothermal crystallization process is analysed by means of several kinetic equations proposed in the literature. The results are compared with those obtained by conventional isothermal methods.

## EXPERIMENTAL

The samples used throughout were prepared with purified PCL (purchased from Polysciences) with  $T_g = 213$  K and  $M_w = 17600$  and PH (supplied by Union Carbide) with  $T_g = 368$  K and  $M_w = 50700$ . The preparation method has been reported in a previous paper describing the isothermal crystallization of PH/PCL blends<sup>12</sup>.

The non-isothermal crystallization studies were carried out using a Perkin-Elmer DSC-2C differential scanning calorimeter. Temperatures obtained in d.s.c. experiments must be corrected due to the thermal lag originated either in the samples or in the instrument itself<sup>17-19</sup>. In our case, the former was minimized by using small masses of sample material (<10 mg). Furthermore, in order to enhance the thermal contact between the sample and the heat source, the samples, in the form of films, were previously melted to adopt the shape of the aluminium sample pan. The later corrections involve a calibration of the temperature scale, usually by reference to the melting point of a very pure substance. In our case, we used pure indium ( $T_m = 156.78^\circ\text{C}$ ) and *n*-dodecane of chromatographic quality ( $T_m = -9.3^\circ\text{C}$ ) as standards. Several scans were realised with these compounds at the cooling rates employed in our study. Finally, the temperatures obtained from non-isothermal crystallization were corrected for each scanning rate used because it is well known that the temperature indicated by the instrument and the actual one change on changing the scanning rate employed.

The samples were heated to 400 K and after 10 min at that temperature they were cooled using different and controlled cooling rates between  $0.31^\circ\text{C min}^{-1}$  and  $20^\circ\text{C min}^{-1}$ . The exothermic crystallization peak was then recorded as a function of time (or temperature), and the relative degree of crystallinity as a function of time (or temperature) was obtained from the integration of this exotherm, considering the origin of the time scale to be the point where the d.s.c. trace begins to deviate from the baseline. Operations were carried out in nitrogen.

## CRYSTALLIZATION ANALYSIS

To study the kinetic parameters of non-isothermal crystallization processes, several methods have been applied.

The Avrami equation describing the isothermal crystallization has been extended by Ozawa<sup>20</sup> to the non-isothermal crystallization process. Assuming that non-isothermal crystallization is the result of infinite

isothermal processes, the following equation has been derived:

$$\log\{-\ln[1 - X(t)]\} = \log K(T) - n \log \beta \quad (1)$$

where  $X(t)$  is the fraction of material crystallized at temperature  $T$ ,  $\beta$  is the cooling rate,  $K(T)$  is the cooling function and  $n$  is the Avrami exponent. Studying the process at different cooling rates and plotting  $\log\{-\ln[1 - X(t)]\}$  against  $\log \beta$  at a given temperature, if the Ozawa method is valid, a straight line should be obtained, and  $K(T)$  and  $n$  are determined from the intercept and slope, respectively.

Another approach used in the literature to describe the non-isothermal crystallization process consists of applying directly the Avrami analysis to the data obtained from the non-isothermal crystallization thermograms<sup>10,21</sup>.

$$X(t) = 1 - \exp(-K_n t^n) \quad (2)$$

Using equation (2) in double-logarithmic form, and plotting  $\log\{-\ln[1 - X(t)]\}$  against  $\log t$  for each cooling rate, one straight line is obtained, from which values of the two adjustable parameters,  $K_n$  and  $n$ , can be found. It must be taken into account that in non-isothermal crystallization, the values of  $n$  and  $K_n$  do not have the same physical significance<sup>21</sup> as in the isothermal crystallization due to the fact that under non-isothermal conditions the temperature changes constantly. This affects the rates of both nuclei formation and spherulite growth since they are temperature dependent. In this case,  $n$  and  $K_n$  are two adjustable parameters to be fitted to the data. Although the physical meaning of  $n$  and  $K_n$  cannot be related in a simple way to the isothermal case, the use of equation (2) provides further insight into the kinetics of non-isothermal crystallization.

A third method, so-called 'proportional expansion', was developed by Ziabicki<sup>3,22,23</sup> who obtained several kinetic equations describing the non-isothermal processes by extending the general phase transformation<sup>24-26</sup> KAE theory. This theory leads to the following well known equation:

$$X(t) = 1 - \exp[-E(t)] \quad (3)$$

If the overlapping of crystals is neglected,  $E(t)$  is the total volume of growing grains which have been nucleated at some instant in time,  $s < t$ . The analysis of the crystallization kinetics is reduced to a calculation of  $E(t)$  in equation (3). After following the treatment proposed by Ziabicki, equation (4) has been derived for  $E(t)$ :

$$E(t) = \ln 2 \left[ \int_0^t \left( \frac{ds}{t_{0.5}[\xi(s)]} \right) \right]^m \left\{ 1 + a_1 \left[ \int_0^t \left( \frac{ds}{t_{0.5}[\xi(s)]} \right) \right] + a_2 \left[ \int_0^t \left( \frac{ds}{t_{0.5}[\xi(s)]} \right) \right]^2 + a_3 \dots \right\} \quad (4)$$

where  $\xi(s)$  is the history of external conditions, which in our case is the thermal history  $T(s)$ ,  $s$  is the current time,  $a_1, a_2, \dots$  are the coefficients of the series which are time dependent and depend not only on the half-period  $t_{0.5}$ .

but also on the  $\xi$ -dependent nucleation rate and  $m$ :

$$m = n + 1 \text{ for homogeneous nucleation}$$

$$m = n \text{ for predetermined nucleation}$$

$n$  being the number of growing directions.

Ziabicki considers<sup>22</sup> that, under quasi-static conditions, the first term of the series (proportional approximation, PA) combined with empirical constitutive relations for  $t_{0.5}$ , offers a good approximation to interpret the crystallization processes when the samples are subjected to a function of some time-dependent parameter, such as the temperature. Thus, knowing the dependence of temperature with time, the Ziabicki treatment has been checked by employing the following equation:

$$E(t) = \ln 2 \left[ \int_0^t \left( \frac{ds}{t_{0.5}[T(s)]} \right)^m \right] \quad (5)$$

After calculating the  $E(t)$  values using equation (5), those of the relative degree of crystallinity can be obtained by substituting the  $E(t)$  values in equation (3). The  $X(t)$  values obtained in this way can be compared finally with the experimental ones.

## RESULTS AND DISCUSSION

From the typical thermograms obtained from the non-isothermal crystallization measurements, the time required by the sample to crystallize,  $\Delta t$ , i.e. the width of the time interval during which phase transition takes place, the temperature at which the maximum of the peak occurs,  $T_p$ , as well as the relative crystallinity as a function of time,  $X(t)$ , can be determined.

Changes of the crystallization peak temperatures of pure and blended PCL as a function of the PH content at different cooling rates are shown in Figure 1. At a fixed PH level, the crystallization peak temperature decreases with increased cooling rate. For a given cooling rate,  $T_p$  decreases as the amount of PH in the blend increases. This was the expected behaviour, taking into account that when the percentage of PH in the blend increases, three main factors contribute to reduce the overall rate of crystallization: the dilution of the crystalline polymer chains at the crystal growth front, the mobility reduction of these chains due to the higher  $T_g$  of the blend, and the drop in the thermodynamic driving force caused by the melting point depression of pure PCL. As can be seen in Figure 1, these factors are more significant when the amount of PH in the blend increases. It takes longer to reach the maximum heat flow, and therefore the peak maximum appears at lower temperatures.

$\Delta t$  is reported in Figure 2 for different PH/PCL blend compositions at different cooling rates. From this plot, it can be seen that for a given composition  $\Delta t$  increases at slower cooling rates. For the same cooling rate, up to about 20% of PH content in the mixture,  $\Delta t$  is almost constant with composition, while for blends with a higher PH content  $\Delta t$  increases when the PH content in the blend increases. The explanation for this behaviour could be the same as that given previously. The higher the amount of PH in the blend, the more significant are the effects of the three factors cited, reducing the crystallization rate and consequently increasing  $\Delta t$ . In

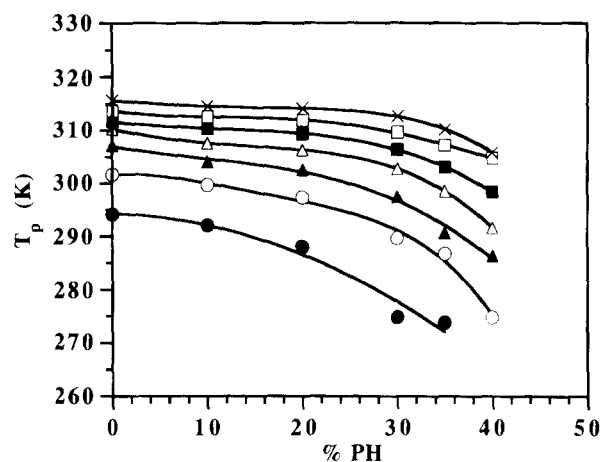


Figure 1 Variation of the peak temperature as a function of PH/PCL blend composition at different cooling rates: (●) 20°C min<sup>-1</sup>; (○) 10°C min<sup>-1</sup>; (▲) 5°C min<sup>-1</sup>; (△) 2.5°C min<sup>-1</sup>; (■) 1.25°C min<sup>-1</sup>; (□) 0.62°C min<sup>-1</sup>; (×) 0.31°C min<sup>-1</sup>

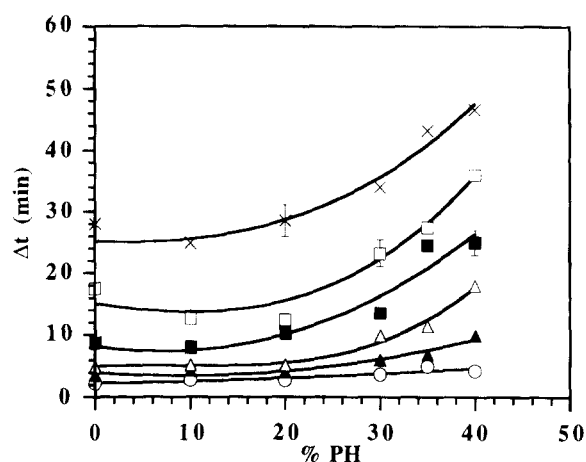
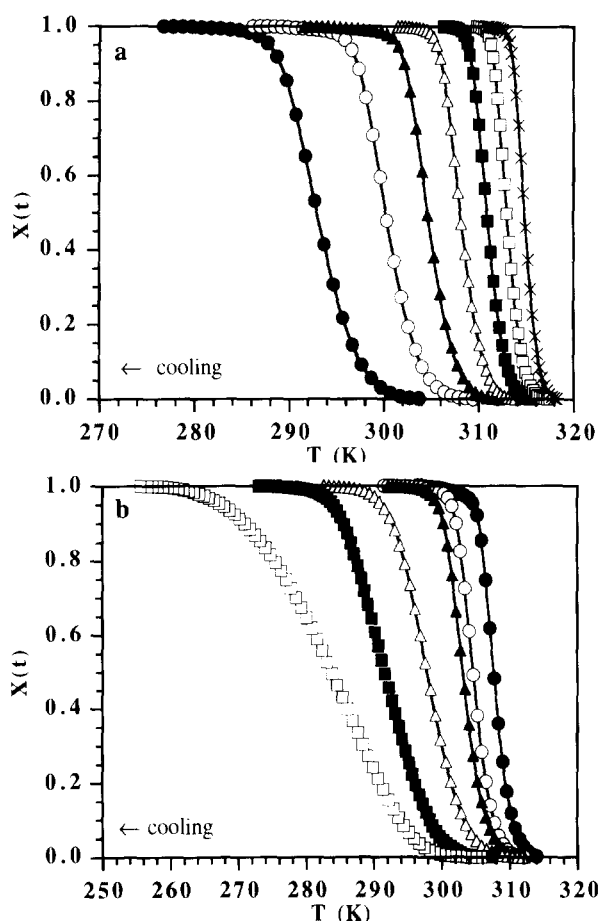


Figure 2 Variation of the time required by the sample to crystallize as a function of PH/PCL blend composition at different cooling rates: (○) 10°C min<sup>-1</sup>; (▲) 5°C min<sup>-1</sup>; (△) 2.5°C min<sup>-1</sup>; (■) 1.25°C min<sup>-1</sup>; (□) 0.62°C min<sup>-1</sup>; (×) 0.31°C min<sup>-1</sup>

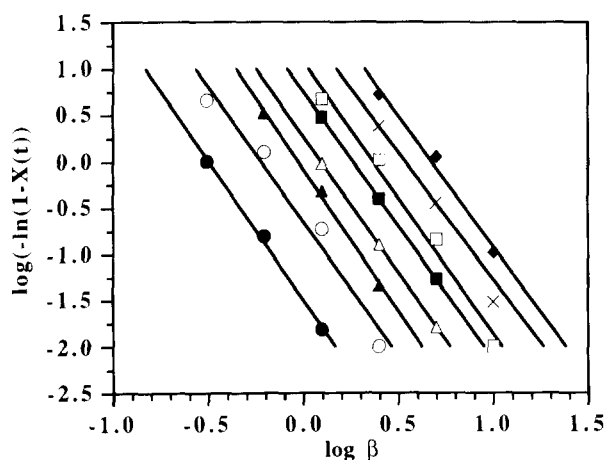
Figure 2, the error bars of some points are shown in order to visualize the precision in the determination of  $\Delta t$ .

Figure 3a shows the relative degree of crystallinity,  $X(t)$ , as a function of temperature for the PH/PCL 10/90 blend at different cooling rates. This figure was obtained by the integration of the exothermic peaks from the non-isothermal crystallization scans. From this plot, data of transformed material at a given temperature for each cooling rate can be taken, allowing application of Ozawa's treatment to yield the values of  $n$  and  $K(T)$ . As can be seen in this figure, for a given composition the crystallization process begins at higher temperatures for slower scanning rates. This could be because, there is enough time to activate nuclei at high temperatures, i.e. the nuclei are activated at lower temperatures as the cooling rate is increased. In Figure 3b, a similar plot of  $X(t)$  versus temperature for several compositions at the cooling rate of 5°C min<sup>-1</sup> shows that the rate of crystallization decreases as the amount of PH in the blend is increased.

In Figure 4, following Ozawa's treatment<sup>27-32</sup>, the plot of  $\log\{-\ln[1-X(t)]\}$  versus  $\log\beta$  for PH/PCL 20/80 blend at several temperatures is shown. For all



**Figure 3** (a) Extent of transformation as a function of temperature for the 10/90 PH/PCL blend crystallized non-isothermally at different cooling rates: (●) 20 C min<sup>-1</sup>; (○) 10 C min<sup>-1</sup>; (▲) 5 C min<sup>-1</sup>; (△) 2.5 C min<sup>-1</sup>; (■) 1.25 C min<sup>-1</sup>; (□) 0.62 C min<sup>-1</sup>; (×) 0.31 C min<sup>-1</sup>. (b) Extent of transformation as a function of temperature for various compositions of the PH/PCL blend crystallized non-isothermally at 5 C min<sup>-1</sup>: (●) 0/100; (○) 10/90; (▲) 20/80; (△) 30/70; (■) 36/65; (□) 40/60



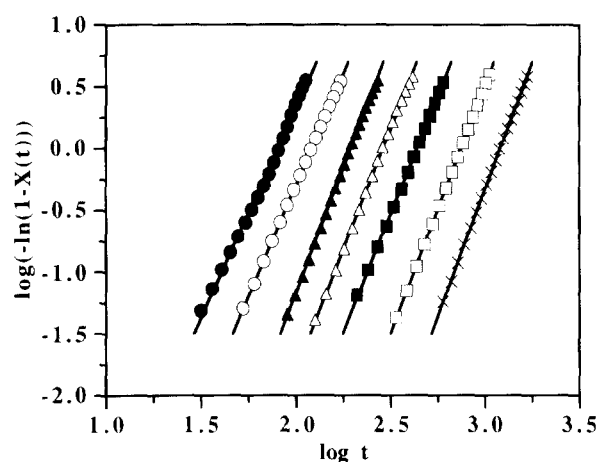
**Figure 4** Ozawa plot of  $\log\{-\ln[1-X(t)]\}$  versus  $\log \beta$  for the 20/80 PH/PCL blend at several temperatures: (◆) 302 K; (×) 304.4 K; (□) 306 K; (■) 307.6 K; (△) 309.2 K; (▲) 310.4 K; (○) 311.6 K; (●) 314 K

temperatures, and conversions between 0.02 and 0.98, straight lines were obtained, which reinforce the validity of applying Ozawa's method to PH/PCL blends. The Avrami exponents (Table 1) for pure PCL and several blends are in very good agreement with those found

**Table 1**  $n$  parameters for non-isothermal crystallization of PH/PCL blends obtained from the Ozawa theory

PH/PCL	$T_c$ range (K)	$n$	$\sigma^a$
0/100	316–309	2.9	0.2
10/90	315–301	3.0	0.2
20/80	314–299	3.0	0.2
30/70	312–288	2.6	0.2
35/65	305–279	2.5	0.4
40/60	304–290	2.2	0.2

<sup>a</sup> Standard error



**Figure 5** Avrami crystallization plots for the non-isothermal crystallization of the 30/70 PH/PCL blend at different cooling rates: (●) 20 C min<sup>-1</sup>; (○) 10 C min<sup>-1</sup>; (▲) 5 C min<sup>-1</sup>; (△) 2.5 C min<sup>-1</sup>; (■) 1.25 C min<sup>-1</sup>; (□) 0.62 C min<sup>-1</sup>; (×) 0.31 C min<sup>-1</sup>

isothermally<sup>12</sup>, the values being approximately 3, confirming again a three dimensional growth process and heterogeneous nucleation. However, the  $n$  values decrease when the quantity of PH in the blend is higher than 30%.

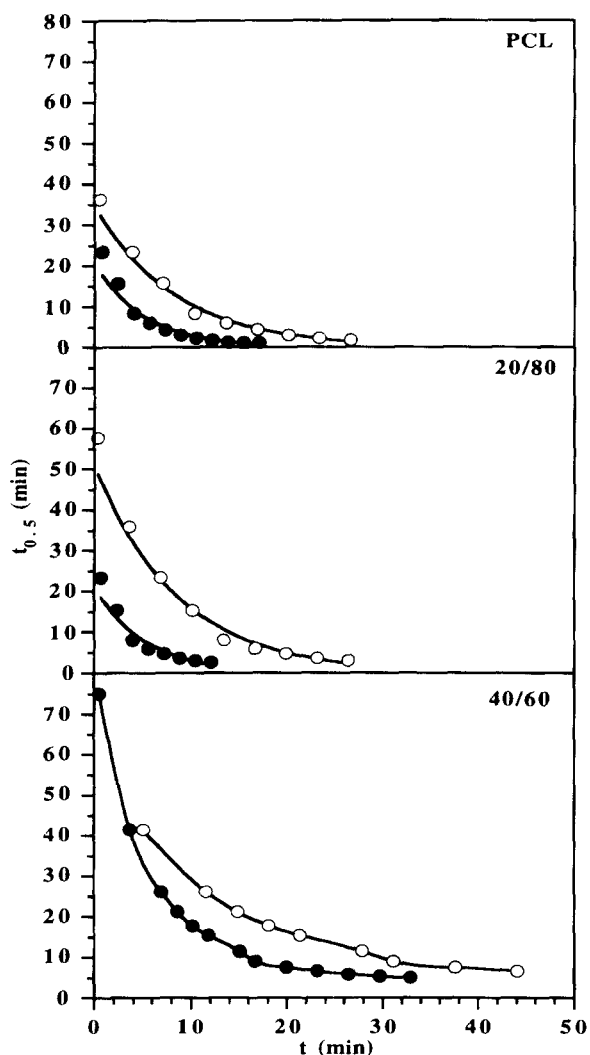
On the other hand, the sigmoidal shape obtained by plotting  $X(t)$  versus  $t$  suggests that a treatment for non-isothermal data based on the Avrami analysis [equation (2)] might be applicable. As was mentioned earlier, plotting  $\log\{-\ln(1-X)\}$  versus  $\log t$  (Figure 5), values of  $n$  and  $K_n$  for each cooling rate and composition can be calculated. The linearity maintained from the initial stages of crystallization until very high degrees of relative conversion indicates that Avrami's equation correctly describes the non-isothermal crystallization process, although  $K_n$  and  $n$  are only two adjustable parameters, as mentioned previously. A secondary crystallization, if it exists, has not been detected probably because it would be associated with a very small heat effect. Values of  $n$  listed in Table 2 are higher than those determined from isothermal crystallization. This behaviour can be explained, as supposed by Cebe<sup>21</sup> to changes in the linear growth rate during non-isothermal crystallization. Moreover, as he found, the standard error of the average experimental values of  $n$  for each composition in non-isothermal studies is higher than that from isothermal ones.

Finally, to apply the Ziabicki theory to non-isothermal data, a function of  $t_{0.5}$  with time has to be derived. To determine this function, apart from the knowledge of  $t_{0.5}$  derived from isothermal experiments, it is necessary to know the cooling rate employed and the times when the non-isothermal crystallization starts and ends.

**Table 2**  $n$  parameters obtained after applying the Avrami equation to the non-isothermal crystallization data of pure PCL and its blends with PH

PH/PCL	$n$	$\sigma^a$
0/100	4.0	0.2
10/90	4.0	0.2
20/80	3.9	0.3
30/70	3.8	0.2
35/65	3.8	0.4
40/60	3.1	0.5

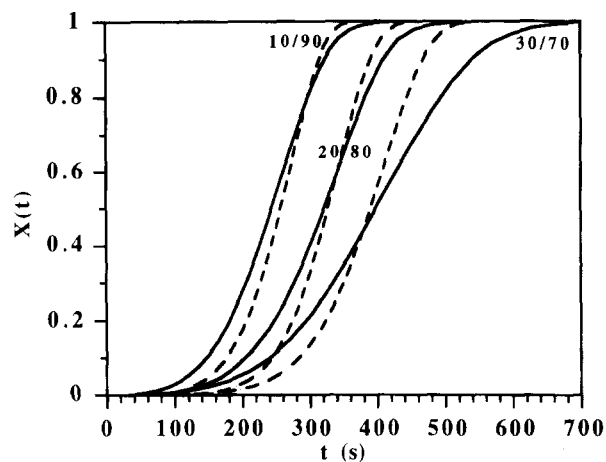
<sup>a</sup> Standard error



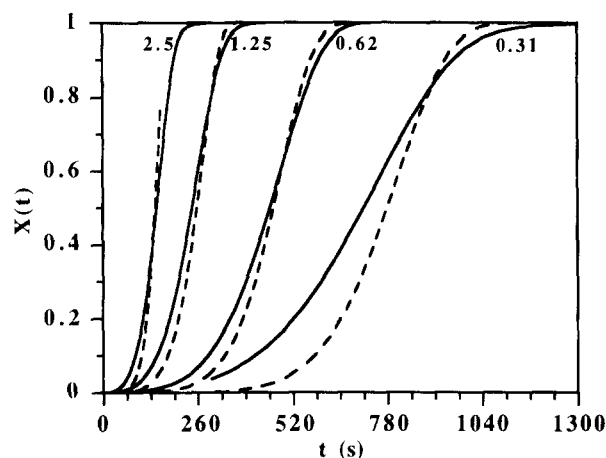
**Figure 6** Variation of  $t_{0.5}$  with crystallization time for the indicated PH/PCL blends at two different cooling rates: (●)  $0.62\text{ }^{\circ}\text{C min}^{-1}$ ; (○)  $0.31\text{ }^{\circ}\text{C min}^{-1}$

Subsequently, the values of  $E(t)$  can be easily calculated using equation (5), and the theoretical values of  $X(t)$  obtained after applying equation (3) can be compared with the experimental ones. The shortcoming of this theory is that it can be applied only in the range of temperatures and compositions where it is possible to follow the isothermal crystallization; i.e. in the absence of sufficient isothermal data, this theory cannot be applied unless the kinetic parameters needed can be extrapolated from the classical theory of crystallization.

The dependence of  $t_{0.5}$  on time for pure PCL and two of its crystalline blends with PH is shown in Figure 6, at



**Figure 7**  $X(t)$  as a function of time for the indicated PH/PCL blends at a cooling rate of  $1.25\text{ }^{\circ}\text{C min}^{-1}$ : (—) values calculated theoretically using Ziabicki's treatment; (---) experimental values



**Figure 8**  $X(t)$  as a function of time for the PH/PCL 10/90 blend at the indicated cooling rates: (—) values calculated theoretically using Ziabicki's treatment; (---) experimental values

cooling rates of  $0.31$  and  $0.62\text{ }^{\circ}\text{C min}^{-1}$  and, as can be seen, in all cases  $t_{0.5}$  decreases with time. In addition,  $t_{0.5}$  increases as the PH content in the sample is increased. This effect can be attributed again to the three factors reducing the overall rate of crystallization. The data were obtained from the isothermal crystallization of PH/PCL blends treated in a previous paper<sup>12</sup>. In our case, unlike the results reported by Martuscelli *et al.*<sup>7</sup>, the cooling rate influence is appreciable in both pure PCL and in its blends with PH.

The relative crystallinity,  $X(t)$ , obtained experimentally as a function of time for different blend compositions and at the cooling rate of  $1.25\text{ }^{\circ}\text{C min}^{-1}$ , is compared in Figure 7 with the  $X(t)$  obtained theoretically by using Ziabicki's theory. From this plot, it can be observed that, although in general this theory can be used to satisfactorily describe the non-isothermal crystallization of the PH/PCL system, the theoretical values of  $X(t)$  move away from the experimental values as the content of PH in the blend is increased. In this figure, the data corresponding to pure PCL have been omitted for clarity, since their experimental and theoretical plots overlapped those of the 10/90 blend. For a given composition, the agreement between theoretical and experimental curves can be observed in Figure 8. Rates

**Table 3** Values of the first coefficient  $a_1$ , for PH/PCL blends as a function of the crystallization time at two different cooling rates

$t$ (s)	$a_1$ (0.62 C min <sup>-1</sup> )					$a_1$ (0.31 C min <sup>-1</sup> )				
	PCL	10:90	20:80	30:70	40:60	PCL	10:90	20:80	30:70	40:60
200	21.6	10.5	62.8	79.8	89.0	126.5	504.4			
400	0.1	0.5	2.2	9.2	24.4	23.3	38	63.5		
600	-0.1	-0.1	0.0	1.7	7.3	2.9	4.9	13.8	159.6	
800				0.0	3.1	1.0	0.4	4.1	37.5	18.2
1000				-0.2	0.8	0.1	0.1	1.0	10.0	4.9
1200					-0.0	-0.2	-0.1	0.5	3.2	1.9
1400					-0.2		-0.2	-0.0	0.9	0.8
1600								-0.2	0.0	0.1
1800									-0.1	-0.1
2000									-0.3	-0.2

higher than 2.5 C min<sup>-1</sup> do not appear in Figure 8 since experimental data from isothermal crystallization required to obtain the theoretical  $X(t)$  curve over a significant range of conversion were not available.

Although the first term of equation (4) offers a simple way to treat the non-isothermal crystallization data, the validity of the PA can be checked by estimating the value of the first coefficient<sup>7,8,22</sup>  $a_1$  in equation (6), i.e. if  $a_1 \gg 0$ , the PA does not hold, and hence a clear discrepancy between theoretical and experimental  $X(t)$  values exists. To estimate  $a_1$ , the following relation can be used:

$$a_1 = \frac{E(\text{exp.})/E(\text{PA}) - 1}{\int_0^t \left( \frac{ds}{t_{0.5}[T(s)]} \right)} \quad (6)$$

where  $E(\text{exp.})$  is the value of  $E(t)$  obtained by using experimental values of  $X(t)$  and  $E(\text{PA})$  is the value of  $E(t)$  calculated using equation (5). The values of  $a_1$  obtained using the above equation are reported in Table 3 for pure PCL and several PH/PCL blends at two cooling rates. It is evident that for the same blend composition the values of  $a_1$  are very high at the beginning of the process and decrease during crystallization. Furthermore, comparing the  $a_1$  values at a given time, it can be seen that  $a_1$  increases as the content of PH in the blend is increased and when lower cooling rates are considered. The same conclusions about  $a_1$  were reported by Martuscelli *et al.* for PEO/PVAc blends<sup>8</sup>. However, there are few data in the literature from which to form definitive conclusions about the validity of applying equation (5) to non-isothermal processes in polymer blends. Further studies concerning the non-isothermal crystallization in blends would be necessary to draw adequate conclusions.

## CONCLUSIONS

Taking into account the theories considered, it can be concluded that the results shown here describe in a qualitative manner the non-isothermal behaviour of the PH/PCL blends. For a given composition, the crystallization process begins at higher temperatures when slow scanning rates are used. This observation could have interesting implications for blend processing.

The Avrami exponent in the analysis of the non-isothermal crystallization through Ozawa's treatment

agrees with that obtained in a previous paper after applying the Avrami equation to isothermal crystallization data, above all for rich PCL blends. The value of the Avrami index is  $\sim 3$ , suggesting a heterogeneous nucleation process followed by a three-dimensional growth.

There are several cases, such as the beginning of crystallization and high percentage of PH in the blend, for which the theoretical data obtained through Ziabicki's treatment move away from the experimental data.

In general, for all three theories applied to the non-isothermal data of the PH/PCL blend, the results are less satisfactory as the amount of PH in the blend increases. Finally, the non-isothermal crystallization of this system is not simple and needs further studies to describe it in a more scientific way.

## ACKNOWLEDGEMENT

We are pleased to acknowledge financial support of this work by the Diputación Foral de Gipuzkoa (Programa Marco de Apoyo a la PYME 1993).

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