Study of the non-isothermal crystallization of poly(ethylene oxide)/poly(methyl methacrylate) blends

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Crystallization during cooling of a poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA) blend has been studied using differential scanning calorimetry. Five different cooling rates V_r have been used (namely 10, 5, 2.5, 1.25 and 0.625°C min^{-1}). The presence of PMMA for a given V_r reduces the overall PEO crystallization rate. This effect can be ascribed to reduction of the mobility of the crystallizable chains due to the presence of the amorphous component. It was found that in quasi-static conditions at lower V_r, when nucleation and growth processes are determined by a thermal mechanism alone, the experimental data for the pure PEO and the PEO/PMMA 90/10 and 80/20 blends agree quite well with the theoretical results obtained using the zero-order approximation of Ziabicki's theory. At higher V_r, in the case of the blends, athermal nucleation cannot be neglected, and then the same approximation does not fit the experimental results. The experimental data analysed showed no agreement with Ozawa's theoretical predictions.

(Keywords: non-isothermal crystallization; poly(ethylene oxide); poly(methyl methacrylate); blends)

INTRODUCTION

The kinetics of crystallization in polymeric blends have been thoroughly studied, mainly with regard to isothermal processes; on the other hand, practical processes such as extrusion, moulding and film production usually proceed under dynamic, non-isothermal crystallization conditions. In order to reach the optimum conditions in an industrial process and to obtain products with better properties, it is necessary[1-4] to have quantitative evaluations of the non-isothermal crystallization process. Few attempts are reported in the literature on this subject and, to our knowledge, all the papers are concerned with the crystallization of homopolymers[1-13].

In this paper we report the results of a study on the influence of composition and cooling rate on the kinetic parameters related to non-isothermal crystallization from the melt state of poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA) blends. These blends have been studied extensively in our Institute[14-19]. It was found, among other things, that the spherulite growth rate, the overall kinetic rate constant and the equilibrium melting temperature of PEO crystallized isothermally from the melt state are depressed in proportion to the PMMA content. With these results as a starting point, we have begun the study of non-isothermal crystallization of PEO/PMMA blends, trying to investigate theoretically the kinetics of the processes of nucleation and growth, using Avrami's equation extended to non-isothermal conditions.

EXPERIMENTAL

Materials and preparation of blends

Poly(ethylene oxide) (PEO) (from Fluka) with number-average molecular weight $\bar{M}_n = 20\,000$ and poly(methyl methacrylate) (PMMA) (from BDH) with a weight-average molecular weight $\bar{M}_w = 116\,000$ were used.

Before blending, the PMMA was kept under vacuum at 140°C for 24 h in order to remove any residual solvent and traces of monomer[20].

Samples of the homopolymers and of the binary blends suitable for further investigation were prepared by solution casting from chloroform at room temperature. To ensure complete removal of the solvent, the films were kept under vacuum first at 70°C for 16 h and then at 120°C for 2 h. Finally the samples were cooled to room temperature under vacuum.

Calorimetric measurements

The overall kinetics of crystallization of the homopolymer and blends were analysed by differential scanning calorimetry (Mettler TA 3000).

The isothermal crystallization process was studied using the following procedure. The samples (about 10 mg) were heated to 20°C above the melting temperature of PEO and kept at this temperature for 10 min. The samples were cooled using different cooling rates (namely $V_r = 10$, 5, 2.5, 1.25 and 0.625°C min^{-1}), and the heat evolved dH/dt during overall isothermal crystallization was recorded as a function of time. The weight fraction

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$X(t)$ of the material crystallized at time t was calculated using the following equation:

$$X(t)=\frac{\int_{t_i}^{t}[Q(t)/\mathrm{d}t]\mathrm{d}t}{\int_{t_i}^{t_f}[Q(t)/\mathrm{d}t]\mathrm{d}t} \qquad (1)$$

where $\int_{t_i}^{t_f}[Q(t)/\mathrm{d}t]\,\mathrm{d}t$ is the total heat evolved during the entire crystallization process and $\int_{t_i}^{t}[Q(t)/\mathrm{d}t]\mathrm{d}t$ is the heat evolved up to time t.

THEORY

The Avrami[21] theory has been widely and successfully used for the interpretation of isothermal crystallization processes, and in fact it allows one to derive from experimental data information about the mechanisms of nucleation and growth of the crystals. In the general formulation of this theory, the degree of crystallinity at instant t amounts to

$$X(t)=1-\exp[-E(t)] \qquad (2)$$

where $E(t)$ is the total volume of the growing crystals:

$$E(t)=\int_0^t \dot{N}(s)\left(\prod_{i=1}^{n}\int G_i(z)\,\mathrm{d}z\right)\mathrm{d}s \qquad (3)$$

Here $\dot{N}(s)$ is the nucleation rate at some instant s, $\prod_{i=1}^{n}\int G_i(z)\,\mathrm{d}z$ is the volume at instant t of the crystals which have been nucleated at some instant $s<t$, and $G_i(z)$ is the growth rate in the ith direction at instant z. The situation becomes different when crystallization proceeds under variable external conditions, for two reasons:

(1) Nucleation and growth characteristics are known to be very sensitive to temperature, stress and molecular orientation.

(2) In a variable external field not only the rate of nucleation changes, but also the mechanism of nucleation can change.

Several attempts have been made to describe non-isothermal crystallization kinetics. Ziabicki[1,5-7] has derived, from the Avrami equation, kinetic equations describing the non-isothermal processes. His theory is based on the assumption that non-isothermal crystallization may be treated as a sequence of isothermal crystallization steps where the secondary crystallization is negligible. The equation he has derived represents the series expansion of the Avrami equation, obtained without any specific assumption. He showed that in quasi-static conditions, when the nucleation and growth rates are controlled by a thermal mechanism only, when their time dependence results only from the change of external conditions and when the dimensionality of Avrami's growth index n is a constant throughout the entire process, the non-isothermal kinetics can be formulated in terms of an observable half-time of isothermal crystallization $t_{1/2}$ and of the history of the external conditions[22,23]. The following equation is derived for $E(t)$:

$$E(t)=\ln 2\left(\int_0^t \mathrm{d}s/\mathrm{d}t_{1/2}\right)^n \times \left[1+a_1\int_0^t \mathrm{d}s/\mathrm{d}t_{1/2}+a_2\left(\int_0^t \mathrm{d}s/\mathrm{d}t_{1/2}\right)^2+a_3\ldots\right] \qquad (4)$$

where $a_1, a_2, \ldots, a_n$ are the coefficients of the series.

The first term of the series, combined with empirical constitutive relations for $t_{1/2}$, offers an extremely simple and tractable method of interpretation of crystallization processes with variation of external conditions. When $a_1=a_2=\ldots=a_n=0$ equation (4) becomes:

$$E(t)=\ln 2\left(\int_0^t (\mathrm{d}s/\mathrm{d}t_{1/2})\mathrm{d}t\right)^n \qquad (5)$$

and this can be used in the case that the ratio between nucleation rate $\dot{N}$ and growth rate G is constant with time (isokinetic approximation) and hence the athermal nucleation is negligible*.

Also Ozawa[4] extended Avrami's treatment to the case where the substance is crystallized in non-isothermal conditions. According to Ozawa's theory, the degree of conversion at temperature T amounts to

$$-\ln[1-X(t)]=K(t)/V_r^n \qquad (6)$$

$X(t)$ is the relative crystallinity at temperature T, as defined by equation (1), V_r is the cooling rate and n is Ozawa's exponent. From equation (6) it follows that

$$\log\{-\ln[1-X(t)]\}=\log K(t)-n\log V_r \qquad (7)$$

If we plot the left term of equation (7) against V_r at a given temperature and if the Ozawa theory is valid we should obtain a straight line. The kinetic parameters $K(t)$ and n can be derived from the slope and the intercept of this line. The exponent n is an integer and can assume values between 2 and 4 depending on the growth dimension, and $K(t)$ is the cooling function of the process.

RESULTS AND DISCUSSION

A typical thermogram of non-isothermal crystallization for pure PEO is reported in *Figure 1*. From this figure the induction time (t_i) and the time required by the sample to crystallize completely (t_f) can be obtained (see *Figure 1*).

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* In the melt, crystalline clusters (embryos) are present. When one of these embryos reaches the critical size, defined by the external conditions, a stable nucleus is formed. The nucleation rate can be considered to be the result of two different contributions: thermal nucleation and athermal nucleation. Thermal nucleation is due to fluctuation of the local density in the melt system, whereas athermal nucleation is due to variation of the thermodynamic boundary between embryos and nucleus (i.e. variation of the critical size of the nucleus) caused by the variation in the external conditions.

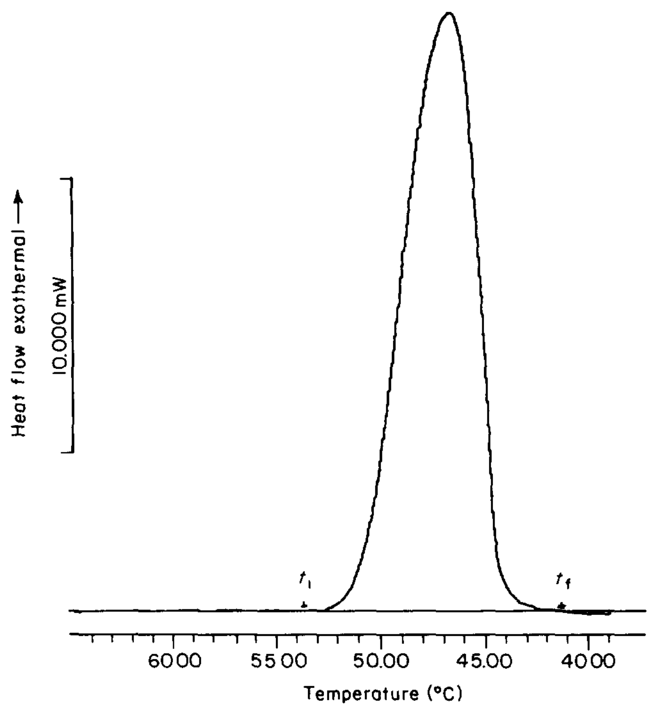

Figure 1 Typical thermogram of non-isothermal crystallization for pure PEO at $V_r = 2.5°C\,min^{-1}$

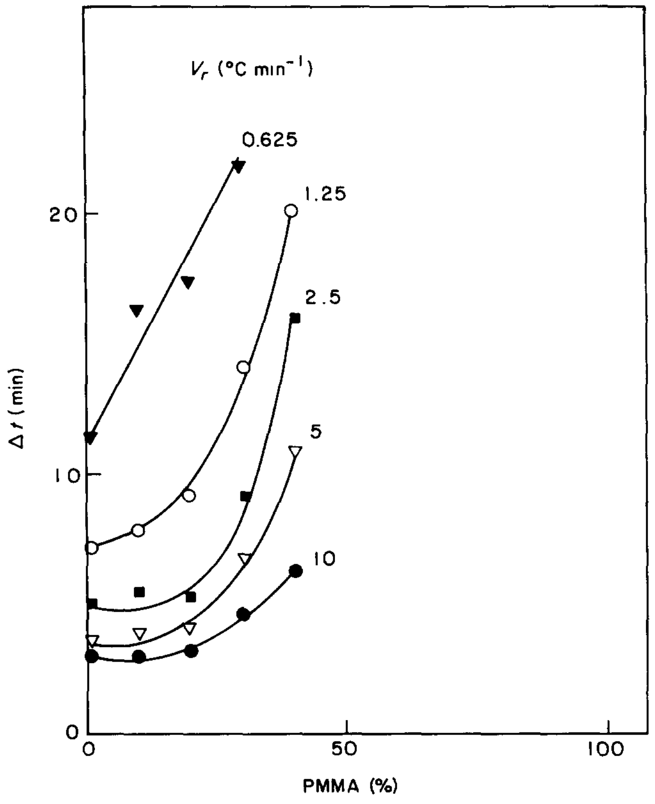

Figure 2 Time required by the samples in order to crystallize *versus* blend composition at different cooling rates

It is found that the kinetics of non-isothermal crystallization from the melt state of PEO/PMMA blends depend on the cooling rate and on the blend composition. In *Figure 2* the quantity $\Delta t = (t_f - t_i)$ as a function of composition, at different cooling rates, is reported. In particular Δt increases with increase of PMMA content in the blend and with decrease of the cooling rate. At a given V_r, the PMMA reduces the overall PEO crystallization rate, by analogy with the results found by Martuscelli and others[14,24] in the case of the same blends crystallized isothermally from the melt. Also in our experiments the magnitude of this depression increases with increase of PMMA in the blend and may be ascribed to the diluent effect of the non-crystallizable component. The PMMA acting as a diluent, in fact, causes a reduction of the mobility of the crystallizable chains. Such a reduction lowers the rate of diffusion of the chains to the growing crystals and hence the overall rate of crystallization.

The experimental data concerning the temperature dependence of the degree of conversion were analysed using both Ziabicki's and Ozawa's theories. In order to analyse the data using the Ziabicki theory, $t_{1/2}$ as a function of time has to be derived. This has been done using the $t_{1/2}$ obtained in isothermal conditions (see *Figure 3*), the time where the non-isothermal crystallization starts and ends (t_i and t_f) and the cooling rate. In this way it is possible to obtain the dependence of $t_{1/2}$ on time by solving the following system:

$$\begin{aligned} T &= T(t) \\ t_{1/2}(t) &= t_{1/2}(T(t)) \end{aligned} \tag{8}$$

In fact knowing the cooling rate and t_i and t_f, at any time there exists a corresponding temperature value and hence a corresponding value of $t_{1/2}(t)$ can be found by using the data of *Figure 3*. The dependence of $t_{1/2}$ on time for pure PEO and 90/10 and 80/20 PEO/PMMA blends at two different cooling rates (1.25 and 0.625°C min^{-1}) is shown in *Figure 4*. The $t_{1/2}(t)$ decreases with increase of the

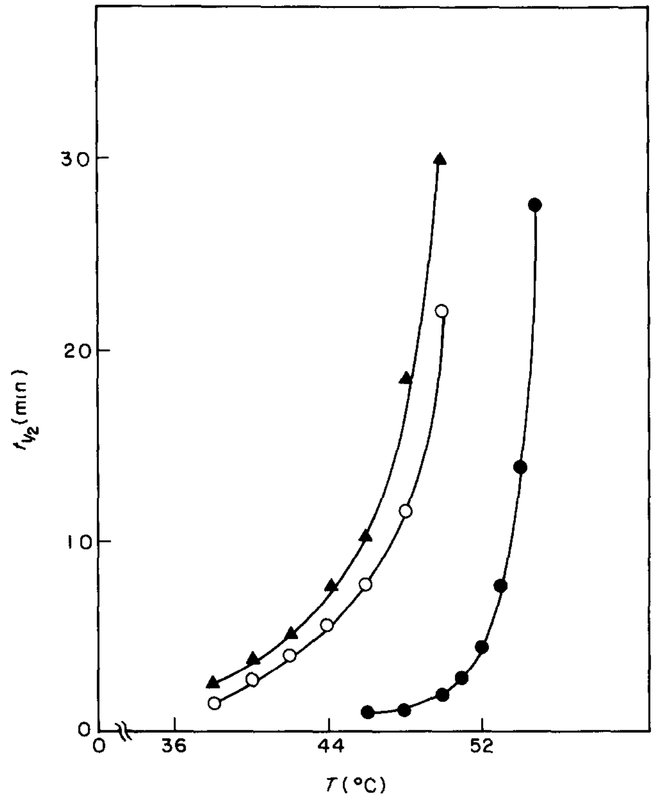

Figure 3 $t_{1/2}$ for pure PEO (●) and 90/10 (○) and 80/20 (▲) PEO/PMMA blends as a function of crystallization temperature obtained in isothermal processes

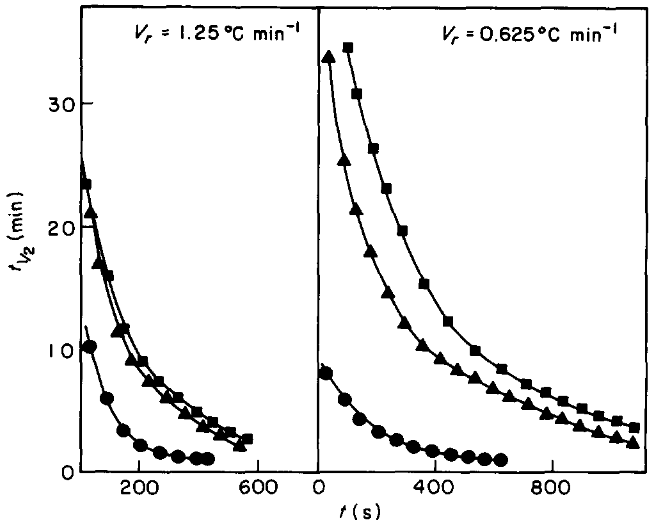

Figure 4 Variation of $t_{1/2}$ (t) with time of crystallization for pure PEO (●) and 90/10 (▲) and 80/20 (■) PEO/PMMA blends

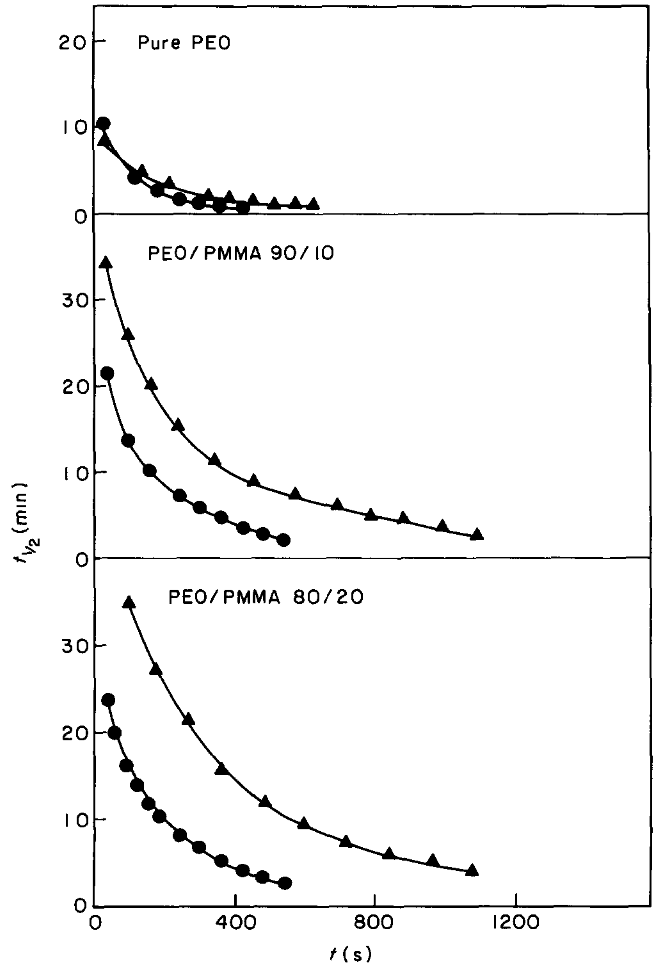

Figure 5 Dependence of $t_{1/2}(t)$ on cooling rate for different samples (●, $V_r = 1.25°C\,min^{-1}$; ▲, $V_r = 0.625°C\,min^{-1}$)

crystallization time. At a given time t, $t_{1/2}(t)$ increases with increase of the PMMA content in the blend.

The cooling rate does not seem to influence $t_{1/2}(t)$ values appreciably in the case of pure PEO, whereas it has a strong influence in the case of blends (see *Figure 5*).

In *Figures 6a* and *6b* the relative crystallinity $X(t)$ as a function of time for two cooling rates is reported. On the same figure the theoretical $X(t)$ obtained by using equations (2) and (5) are reported (full curves). The experimental results were compared with the theoretical ones only when the crystallization proceeded at lower cooling rates. In fact, at higher V_r, it is impossible to evaluate $t_{1/2}$ in isothermal conditions in the entire range of T where the non-isothermal process takes place.

From these figures it can be seen that the zero-order approximation of equation (4) can be used to describe non-isothermal crystallization only for the pure semicrystalline polymer at the two cooling rates investigated. In the case of blends the theoretical equation fits the experimental data satisfactorily only for crystallization processes that proceed at the lower cooling rate. Using the isokinetic approximation it is possible to obtain an estimate of the first coefficient a_1 for blends crystallized at higher V_r using the following relation:

$$a_1 = \frac{E(\text{expt})/E(\text{iso}) - 1}{\int_0^t \mathrm{d}s/\mathrm{d}t_{1/2}(t)} \tag{9}$$

where E(expt) and E(iso) are the values of $E(t)$ obtained by using experimental values of degree of crystallinity (equation (2)) and by using equation (5) respectively. The values of a_1 obtained using the above equation are reported in *Table 1*. Coefficient a_1 increases with increase of the PMMA content in the blend. For the same blend

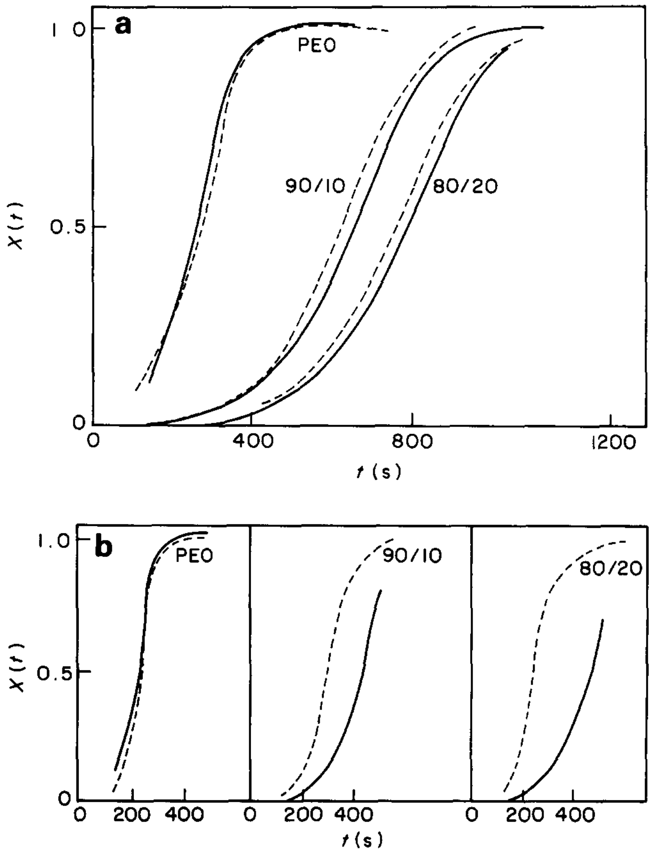

Figure 6 Relative crystallinity as a function of time for pure PEO, PEO/PMMA 90/10 and PEO/PMMA 80/20. The broken curves correspond to the experimental results; the full curves are obtained using the theoretical approach: (a) $V_r = 0.625°C\,min^{-1}$, (b) $V_r = 1.25°C\,min^{-1}$

Table 1 Values of the first coefficient a_1 for the 90/10 and 80/20 PEO/PMMA blends as a function of the crystallization time at $V_r = 1.25°C\,min^{-1}$

	a_1	
t (s)	PEO/PMMA 90/10	PEO/PMMA 80/20
180	11.96	93.17
210	–	67.52
240	7.86	38.65
270	7.95	25.45
300	6.22	17.63
330	5.12	–
360	3.42	6.45
390	1.23	–
420	–	2.21

composition a_1 values are very high at the beginning of the process (at high temperature) and decrease during crystallization. This may indicate that, at a higher cooling rate, compared to the end of the process when the isokinetic approximation can better represent the experimental results in a qualitative manner, the first stages of the crystallization of PEO/PMMA do not follow the above approximation at all. These results certainly suggest that in the case of blends athermal nucleation cannot be neglected when the external conditions vary more rapidly during the crystallization process. Therefore the PMMA seems to influence the entire nucleation process of PEO, as confirmed by morphological analysis of the samples (reported in previous papers)[19,25]. In that work it was found that, in the case of non-isothermal crystallization, the apparent nucleation density increases with the percentage of amorphous component as a consequence of a combination of different processes such as dilution of PMMA in the melt and growth rate and melting temperature depression.

In *Figures 7a* and *7b* $\log\{-\ln[1-X(t)]\}$ against $\log V_r$ is reported according to the Ozawa equation (equation (7)). The cooling crystallization of PEO and PEO/PMMA does not follow the Ozawa equation, probably because factors such as secondary crystallization and annealing phenomena cannot be neglected. The annealing phenomena during crystallization in the case of PEO have in fact been demonstrated to be very marked at high crystallization temperatures.

With the present theories, it is impossible to explain in detail the results obtained. Any explanation should take into account, as well as secondary crystallization and annealing phenomena, the relaxation time that represents the time required by the system to follow the variation of the external conditions. This time is dependent on temperature and on the chemical and physical nature of the system.

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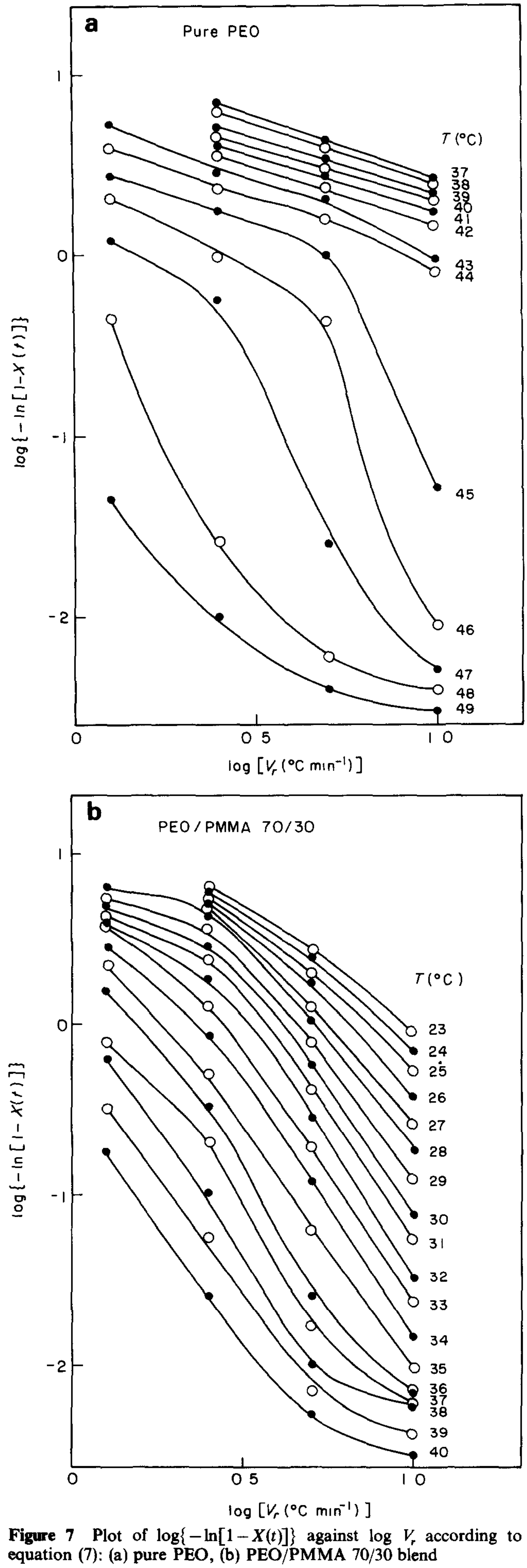

Figure 7 Plot of $\log\{-\ln[1-X(t)]\}$ against $\log V_r$ according to equation (7): (a) pure PEO, (b) PEO/PMMA 70/30 blend

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