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Non-isothermal crystallization kinetics of thermotropic polyesters with flexible spacers in the main chain

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The non-isothermal crystallization kinetics of two thermotropic polyesters with flexible spacers in the main chain were studied. The influence of the spacer type on the kinetics has been considered. The Ozawa theory for non-isothermal crystallization was used to analyse the differential scanning calorimetry data. The polyester with an oxyethylenic group as the flexible spacer followed the Ozawa equation and allowed the calculation of the Avrami exponent under non-isothermal conditions, but in the case of the polyester with methylenic groups as the flexible spacer the Ozawa theory is not valid. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Numerous studies have been reported of isothermal crystallization of high polymers[1,2]. The Avrami[3,4] equation has been proposed for these processes and isothermal crystallization was found to follow this kinetic equation. However, since isothermal crystallization conditions are rarely used in practice, it seemed desirable to study crystallization of polymers under non-isothermal conditions.

Ozawa[5] has extended the Avrami equation to the non-isothermal situation, assuming that the amorphous polymer is heated or cooled at a constant rate. The Ozawa equation has been tested for poly(ethylene terephthalate)[5–7], polyethylene[8], polypropylene[8], poly(p-phenylene sulphide)[9], and some thermotropic polymers[10]. In this work, non-isothermal crystallization of the two thermotropic liquid crystalline polyesters with different spacer groups in the main chain was studied by differential scanning calorimetry.

The chemical structure of thermotropic polyesters prepared by polycondensation in diphenyl ether and reported in previous papers[11,12] is shown in *Figure 1*.

The polyesters with oxyethylenic and methylenic groups as spacers exhibited a liquid-crystal behaviour and were capable of forming a nematic mesophase on melting. The relations between structure and property in thermotropic polyesters have been gradually clarified. The investigation of the crystallization behaviour of semi-flexible polyesters has recently gained significant interest. The application of non-isothermal analysis techniques to the study of nucleation and growth mechanisms of crystallization processes have had a strong theoretical and experimental interest in the last years. To evaluate the effect of the spacer type on the crystallization behaviour, the kinetics of crystallization of polyesters under non-isothermic conditions were studied.

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EXPERIMENTAL

The materials used were two thermotropic polyesters with flexible spacers in the main chain prepared in our research laboratory[11–13]. Polymerization reactions were carried out in diphenyl ether as described in a previous report[11]. Inherent viscosities determined in a phenol/1,1,2,2-tetrachloroethane mixture, with a volume ratio of 6/4, at 30°C and a concentration of 0.35 g dl^{-1} were 0.32 and 0.27 dl g^{-1} for Polymer 1 and Polymer 2, respectively.

The non-isothermal analyses were carried out using a Perkin Elmer DSC-7 apparatus under nitrogen atmosphere. In order to obtain reproducible crystallization conditions, about 6 mg of the materials were heated at 40°C min^{-1} beyond the melting point after being held in the molten state for 10 min. In order to prevent thermal lag originating in the samples, small masses of samples were used. Furthermore, in order to enhance the thermal contact between the sample and the heat source, the samples in the form of a powder were previously melted to adopt the shape of the aluminium sample pan. The calibration of the temperature scale was done by reference to the melting point of a very pure substance. Pure indium ($T_m = 156.78$°C) was used as standard. The different and controlled cooling rates subsequently used were 10, 12, 14, 16, 18 and 20°C min^{-1}.

RESULTS AND DISCUSSION

A well-known model for non-isothermal crystallization kinetics has been developed by Ozawa[5] as shown in:

$$\log\{-\ln[1 - X(T)]\} = Q - n \log R$$

where n is the Avrami exponent and Q is the value of the cooling crystallization function at certain temperatures under various cooling rates, R. The Avrami exponent has values between 1 and 4 depending on the nature of the nucleation and the growth processes. The relative crystallinity, $X(T)$, is the value of the exothermal heat from the
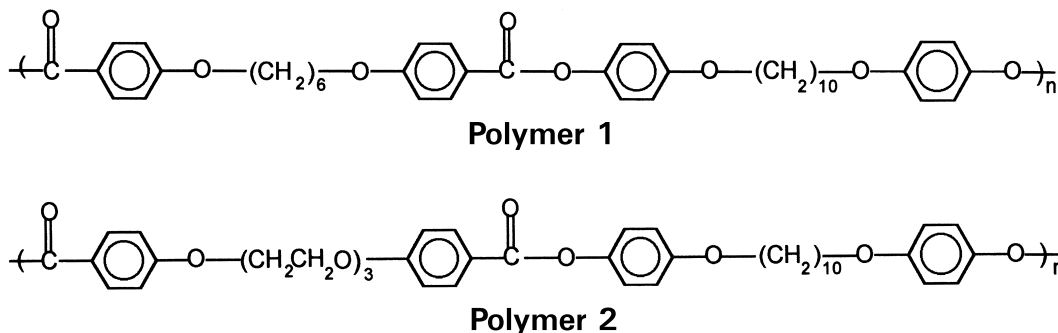
Polymer 1

Polymer 2

Figure 1 The chemical structure of the thermotropic liquid crystalline polyesters

initial crystallization temperature to the temperature T as divided by the total exothermal heat during crystallization.

The data treatment involves calculating $X(T)$ from the measurement of partial areas of the exotherms obtained upon cooling crystallization. The calculated amorphous fraction $[1 - X(T)]$ is plotted as a function of temperature for the different cooling rates, as shows in *Figure 2* for Polymer 1. Values of the amorphous fraction at a given temperature are taken from these plots at each cooling rate. Then the double logarithm of the amorphous fraction log $\{-\ln[1-X(T)]\}$ at constant temperature is plotted as a function of the cooling rate. If the Ozawa equation is valid, the curve corresponding to each temperature should be a straight line. The slope provides the fundamental parameter n or Avrami exponent and the intercept determines the value of the cooling crystallization function.

Figure 2 presents plots of the amorphous fraction as a function of temperature for Polymer 1 crystallized non-isothermally at various cooling rates. The effect of the different cooling rates is observed in these plots corresponding to Polymer 1. The higher the cooling rate, the lower the temperature range at which the crystallization occurs. Therefore, the transformation is controlled by nucleation. At slow cooling rates, there is sufficient time to activate nuclei at higher temperatures. On the contrary, at faster cooling rates, the activation of nuclei occurs at lower temperatures. Consequently, crystallization nucleates at higher temperatures when the polymer samples are cooled at slower scanning rates. *Figure 2* also shows the limits of cooling rates used in this study. The lower limit is $10°C \, min^{-1}$ and the upper one is $20°C \, min^{-1}$. Another important characteristic of *Figure 2* is the shape of the curves. All the curves of amorphous fraction *versus* temperature have approximately the same shape. This would indicate that the retardation effect of cooling rate on the crystallization is observed in these curves.

Figures 3 and 4 present plots representative of the Ozawa equation for Polymer 1 and Polymer 2, i.e. plots of $\log\{-\ln[1 - X(T)]\}$ as a function of $\log R$ at constant temperature.

Linearity at a given temperature shows the experimental data to be consistent with the Ozawa theory. The absence of curvature in Polymer 2 rules out the possibility of secondary crystallization[14–16].

It was found for Polymer 2 that the Avrami exponent varies with temperature. Values of n between 4.8 and 7.0 were obtained at 88–116°C. Such values of n, according to the theory of Avrami[3,4] and Morgan[17,18] correspond to sheaf-like aggregation without growing further into additional spherulites. This growth is a result of completion of the primary crystallization[16,19]. Probably, the high mobility
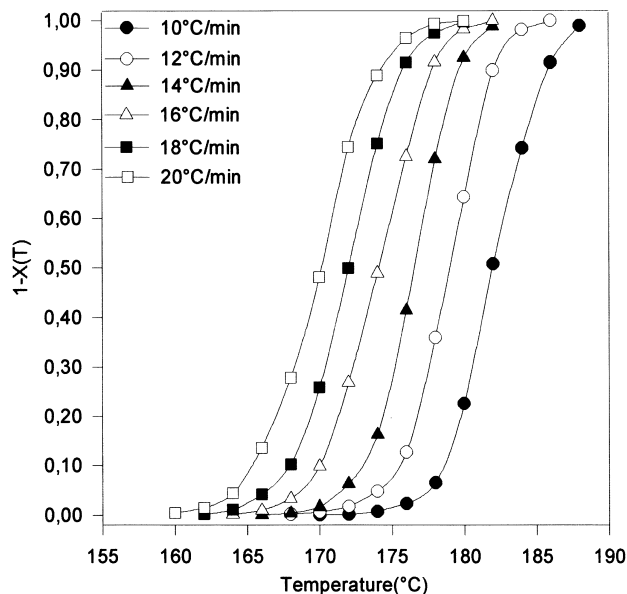

Figure 2 Plot of amorphous fraction as a function of temperature for Polymer 1 crystallized non-isothermally at various cooling rates
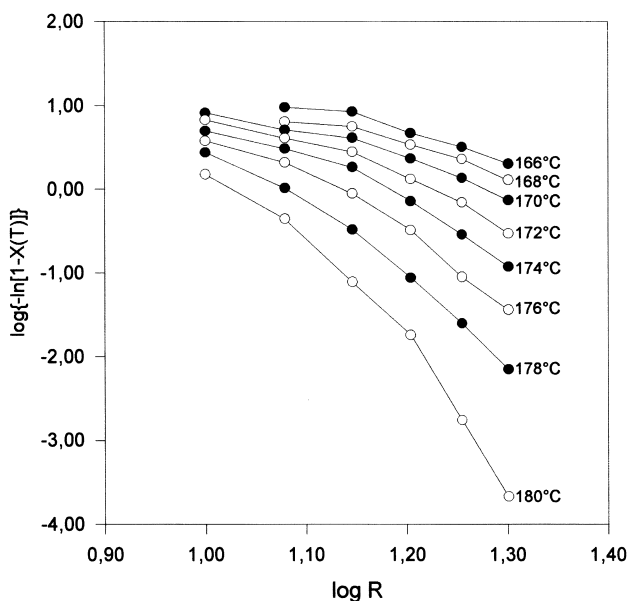

Figure 3 Plot of $\log\{-\ln[1 - X(T)]\}$ as a function of $\log R$ at various temperatures corresponding to Polymer 1
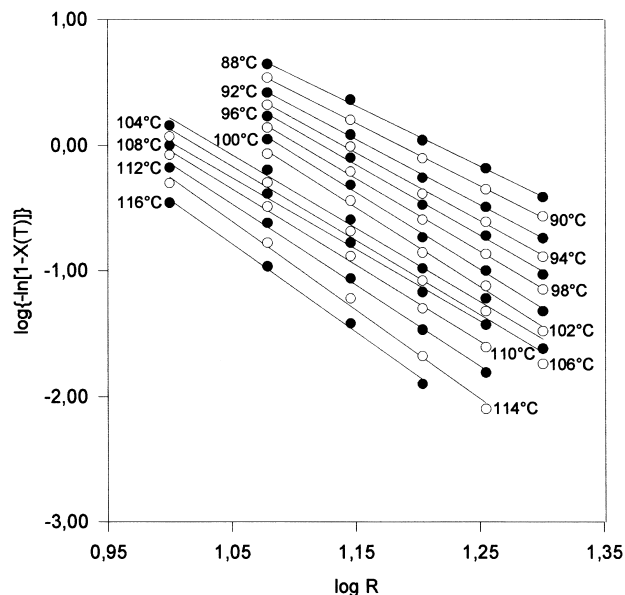
Figure 4 Plot of $\log\{-\ln[1 - X(T)]\}$ as a function of $\log R$ at various temperatures corresponding to Polymer 2

Table 1 Values of the Avrami exponent and crystallization function of Polymer 2

Temperature (°C)	Avrami exponent (n)	Q
88	4.8	19.1
90	5.0	15.1
92	5.2	12.7
94	5.5	10.5
96	5.7	9.6
98	5.9	8.0
100	6.2	7.2
102	6.3	6.0
104	5.9	3.3
106	5.9	2.7
108	5.7	2.1
110	6.1	1.8
112	6.5	1.5
114	7.0	1.3
116	7.0	0.8

of the macromolecules of Polymer 2 due to the presence of an oxyethylenic group under conditions of crystallization from the melt, may increase the facility for their penetration into clusters of super-critical dimensions. This causes an acceleration of nuclei formation and a considerable increase in their concentration in the melt occurs, and therefore the crystals formed cannot attain such perfect shapes as those of spherulites, owing to mutual interaction[13].

The values of the Avrami exponent determined by the Ozawa method are listed in *Table 1* as a function of temperature. Changes in the value of n from the low temperature process to the pre-melt process suggest a change in the crystallization mechanism during cooling. The change in the crystallization mechanism may be due to the nucleation rate and critical dimensions of the nuclei being highly sensitive to the supercooling conditions. The crystallization kinetics at higher temperatures exhibited higher values of n, probably corresponding to sheaf-like growth from sporadic nuclei. At lower temperatures the crystallization kinetics exhibited lower values of n which may be due to sheaf-like growth from instantaneous nucleation within the limits of calculation error.

The experimental values of $n > 4$ are surprising and difficult to account for at the moment, since such values

have only rarely been reported. Morgan[17,18], however, has theoretically accounted for values of $n > 4$ by considering a sheaf-like growth pattern with the sheafs consisting of non-branching fibrils.

The general curvature seen in *Figure 3* makes it impossible to determine the cooling crystallization function. The non-isothermal crystallization of Polymer 1 cannot be related to the temperature by the equation developed by Ozawa. *Figure 3* shows the non-linear dependence of log $\{-\ln[1 - X(T)]\}$ upon log R. Cooling crystallization of Polymer 1 does not follow the Ozawa equation, probably because of factors neglected in the Ozawa theory, such as secondary crystallization, dependence of lamellar thickness on crystallization temperature and variation of Avrami exponent with crystallization temperature. The lines show a distinct curvature similar to that observed in polyethylene[8], which may be attributed to the effect of secondary crystallization, an additional slow process, which is considered to involve improvement of the degree of crystalline order[8,14–16]. The changing slopes indicate that n is not constant with temperature during the primary crystallization process.

The cooling crystallization function, Q, was also determined for each temperature from the intercept of the plot of log$\{ - \ln[1 - X(T)]\}$ *versus* log R. The Avrami exponents and the Q values of Polymer 2 with various n values in the range of crystallization temperatures are presented in *Table 1*. The values of Q range from 0.8 to 19.1 for Polymer 2, showing a decreasing trend with increasing temperature. These values are in a similar range to those determined for PET by Ozawa[5]. This author showed that Q decreased with increasing temperature. Polypropylene also presented a similar trend[8]. The Q values are related to the overall rate of bulk crystallization increase with decrease in crystallization temperature[9].

CONCLUSION

The behaviour of non-isothermal crystallization was influenced by the spacer type as revealed by studies of d.s.c. The crystallization kinetics of a thermotropic polyester with a methylenic group as flexible spacer, Polymer 1, does not satisfy the Ozawa theory, while the Ozawa theory is satisfied for the thermotopic polyester with oxyethylenic group as flexible spacer, Polymer 2. Ozawa analysis allowed the study of the crystallization behaviour of Polymer 2 over a wider temperature range. This indicates that this technique can be useful for the investigation of the crystallization of other thermotropic polyesters.

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