

THE NON—ISOTHERMAL CRYSTALLIZATION KINETICS OF A LIQUID CRYSTALLINE RANDOM COPOLYESTER WITH DIFFERENT COMPOSITIONS

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ABSTRACT

The non-isothermal crystallization kinetics analysis of liquid crystalline random copolyester composed of p-oxybenzoate (B) and 2,6-oxynaphthoate (N) monomers was carried out by means of differential scanning calorimetry basing on Ziabicki and Jeziorny method. Although the composition of 58/42 B-N copolyester had poorer thermodynamic crystallizability comparing with those of 30/70 and 75/25, its kinetic crystallizability G_c was slightly larger. This fact was due to the poorer match of sequences of 58/42 B-N in domains of nematic melt, and therefore better mobility of chains during crystallization. The Avrami exponents of three composition species were all about 2.5, implying two dimensional growth in so-called non-periodic layer crystallites and a mixture of homogeneous and heterogeneous nucleation.

INTRODUCTION

The thermodynamic crystallizability of different compositions of the liquid crystalline random copolyester composed of p-oxybenzoate (B) and 2,6-oxynaphthoate (N) monomers is well known.^[1,2] According to non-periodic layer (NPL) crystallites argument^[3], 50/50 B-N has the lowest melting point and the smallest degree of crystallinity, therefore the poorest thermodynamic crystallizability, because of the lowest blockiness of molecules in crystallites and the smallest size of crystallites which have been predicted by statistic calculation.^[4] Nevertheless, the effects of composition on kinetics of crystallization behavior are still not clear. Avrami isothermal method using differential scanning calorimetry (DSC) has been widely applied in estimating crystal growth rate and Avrami exponent. Some studies has been reported on B-N copolyester.^[5] However, the non-isothermal crystallization kinetics analysis is of great importance for liquid crystalline polymers, because their thermal effects of crystallization in isothermal conditions

are slight and difficult to be determined. So non-isothermal experiments were carried out in this work to estimate the kinetic crystallizability and Avrami exponent of B-N copolyesters with different compositions.

EXPERIMENTAL

Materials

Three compositions of random copolyester B-N provided by Hoechst-Celanese Corporation were investigated. Their chemical structure is as follows, and the characteristics are listed in Table 1.

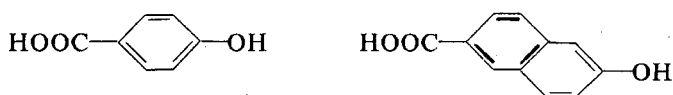


Table 1 Characteristics of B - N copolyesters

Sample designation	Composition (X/Y)	Degree of polymerization ^{a)}	$T_m^{b)}$ (°C)
30/70 B - N	30/70	150	302
58/42 B - N	58/42	150	247
75/25 B - N	75/25	150	287

a. Data provided by Hoechst-Celanese Corporation.

b. Data obtained by DSC on as-received materials (20°C/min).

Methods

A Perkin Elmer DSC-4 with thermal analysis data station was used for thermal treating and data gathering. The crystallization of the samples was performed at constant cooling rate after being held for 1 minute in the molten state of 20°C above their individual melting points under nitrogen. The crystallization exotherms were detected at given cooling rates; 10, 15, 20, 30, 40, 60, 80°C/min.

The approximate theory formulated by Ziabicki^[6] and Jeziorny^[7] was used to characterize the kinetics of non-isothermal crystallization. This theory is based on the assumption that crystallization follows first-order kinetics;

$$dX/dt = [1 - X]K(T)$$

Where X represents the normalized crystalline content and $K(T)$ is a rate constant dependent on temperature. A parameter known as kinetic crystal-

lizability G can be calculated by assuming the curve of rate constant versus temperature is represented by a Gaussian function.

$$G = \int_{T_g}^{T_m} K(T) dT = (\pi/\ln 2)^{\frac{1}{2}} K_{\max} D/2$$

Where $K_{\max}$ is the maximum value of the rate constant corresponding to the temperature $T_{\max}$; D is the half width of the crystallization curve. G characterizes the degree of transformation obtained over the entire crystallization range with unit cooling rate. After proper correction, considering the cooling rate of the polymer, the final form of this parameter will thus be as follows:

$$G_c = G/(dT/dt)$$

On the other hand, the Avrami exponent n can be estimated by Avrami equation after converting temperature to time according to the cooling rates. Here, n represents an average value of Avrami exponents within the determined temperature range.

RESULTS AND DISCUSSIONS

The results of parameters charactering the kinetics of non-isothermal B-N copolyester crystallization have been shown in Table 2. The Avrami exponents were achieved by the slope of Avrami plots as in Figure 1.

Table 2 Parameters charactering the non-isothermal crystallization kinetics of B-N copolyesters with different compositions

Cooling rate dT/dt (K/min)	Half-width D (K)			Kinetic crystallizability G_c			Avrami exponent n		
	30/70	58/42	75/25	30/70	58/42	75/25	30/70	58/42	75/25
10	9.7	3.2	7.6	— ^a	2.17	2.34	2.6	2.6	2.4
15	10.6	3.9	6.4	— ^a	2.27	2.07	2.3	3.0	2.6
20	8.5	4.3	7.2	— ^a	2.89	2.09	2.6	2.9	2.7
30	5.9	5.6	6.5	2.29	2.19	2.13	2.7	2.3	2.8
40	6.9	6.4	9.2	2.34	2.18	2.15	2.6	2.3	2.2
60	8.0	8.2	9.9	1.98	2.52	1.98	2.3	2.3	2.4
80	7.5	10.5	9.5	1.97	2.06	2.13	2.4	2.1	2.3
Average value				2.15	2.33	2.13	2.5	2.5	2.5

a. The data evidently deviated because of double peaks.

The consequences indicated that three composition species had considerably similar G_c values which were 2.1—2.3. According to Ziabicki^[6], the larger G_c is, the higher is the cooling rate necessary to quench a melt to the glassy state without crystallization in the course of cooling. G_c value of B-N copolyester had the same order as that of polyethylene terephthalate with $G_c=0.5-1.0$. Therefore B-N copolyester can be regarded as a material with poorer crystallizability, which can only crystallize on slow cooling. The average value of 58/42 B-N copolyester was slightly larger, implying that its kinetic crystallizability was somewhat better than those of the other two compositions.

In addition, the half-widths of peaks for 58/42 B-N copolyester exhibited in Table 2 were smaller than those of the other two species at most cooling rates, showing faster crystallization. This fact agreed with the results of G_c measurement. From Figure 1, most of the points lay on straight lines in Avrami plot. The curves of different cooling rates were almost parallel and their average slope gave the Avrami exponent $n=2.5$ for all three specimens. This may suggest that crystals develop in two dimensions with the coexistence of thermal nucleation and non-thermal nucleation, which was reasonable for NPL crystallites grown from nematic phase, although clearer elucidation needs further works.

In brief, 58/42 B-N copolyester which has a composition close to 50/50 gives more or less better kinetic crystallizability than 30/70 and 75/25 B-N copolyesters, although it has worse thermodynamic crystallizability. The reason is considered as follows. There is strong molecular order in the nematic melt.

The molecules register to obtain some sequence match in the domains. The match provided crystalline nuclei during cooling process, but

more critically the match hinders the mobility of molecules by physical

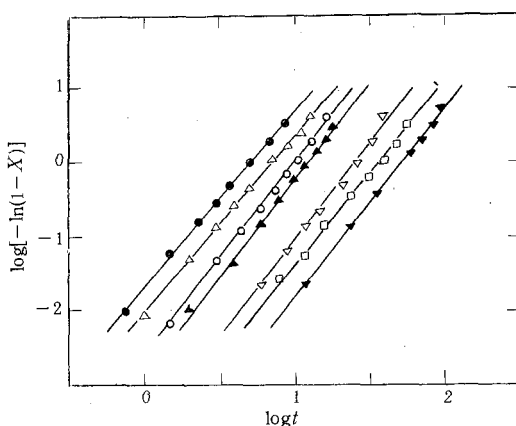


Fig. 1 Avrami plots of 30/70 B-N copolyester at different cooling rates;

($\blacktriangledown$) 10°C/min; ($\square$) 15°C/min; (∇) 20°C/min;
($\blacktriangle$) 30°C/min; ($\circ$) 40°C/min; ($\triangle$) 60°C/min;
($\bullet$) 80°C/min.

crosslink, hence the rate of crystal growth reduces. 58/42 B-N copolyester has shorter match length of non-periodic layer crystallites according to literature^[4]. It can be deduced that there is also shorter match in nematic melt for the same reason. 58/42 B-N copolyester consequently has lower chain mobility, which benefits the kinetic crystallizability.

Keywords:

Liquid crystalline; Copolyester; Non-isothermal Crystallization Kinetics; Avrami exponent

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