Crystallization kinetics of poly(1,3-dioxepane)

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The effect of molecular weight on the crystallization kinetics from the melt has been analysed for poly(1,3-dioxepane) fractions ranging in molecular weight from 5500 to 11 800. Kinetic data were obtained in the temperature interval from 6 to 17°C. The Avrami exponent is an integral number, 3, and is independent of temperature and molecular weight. The crystallinity of the different fractions is about 35% and it is independent of molecular weight, but the influence on the rate of crystallization is pronounced. The crystallization rate goes through a maximum and the location of this maximum depends on the undercooling. The crystallization temperature coefficient was analysed and the change of the interfacial free energy with molecular weight is from 3500 cal mol^{-1} to 2700 cal mol^{-1} in the analysed molecular weight range.

INTRODUCTION

Polyformals are the alternating copolymers of formaldehyde and ω-glycol with the general formula $-[OCH_2O(CH_2)_n]-_m$ and they show considerable differences in properties depending on the value of n. This first member of this series ($n=1$) is polyoxymethylene and the crystallization of this polymer has been widely analysed[1-3]. However, little attention has been paid to the crystallization kinetics from the melt of higher members of this series and only poly(1,3 dioxolane) has been analysed by Prud'homme *et al.*[4,5]. Poly(1,3 dioxepane) is the fourth member of the series of polyformals and the crystal and molecular structure of this polymer has been determined by X-ray diffraction and infrared spectroscopic methods[6]. Moreover, in the cationic ring-opening polymerization of 1,3 dioxepane, the bond scission of the ring, occurs exclusively at the same type of bond, giving rise to a regular head-to-tail polymer[6].

However, the crystallization from the melt and the influence of molecular weight and undercooling on the crystallization kinetics of poly(1,3-dioxepane) have not been analysed.

Crystallization of polyoxides have been extensively studied[7-9] in order to obtain a better understanding of the influence of the number of methylene groups in the repeat unit where polyethylene is a limitating case. Poly(1,3-dioxepane) corresponds to a perfectly alternating copolymer of polyoxymethylene and poly(tetramethylene oxide) and thus it is important to compare its properties with those of the homopolymers for a comprehensive analysis of the thermal properties and, more especially, the crystallization behaviour, of these copolymers. Here, we present the results of the crystallization of several fractions of poly(1,3-dioxepane), ranging in molecular weight from 550 to 11 800.

EXPERIMENTAL

Materials

1,3-dioxepane was prepared from 1,4 butanediol[10] and copolymerized by cationic ring-opening polymerization, using triethyl oxonium hexachloroantimoniate as catalyst at $-20°C$[11].

The polymer fractions used in this work were obtained by liquid–liquid separation method and the solvent–non solvent system was benzene–methanol. The fractionation temperature was 30°C and the fractions were purified by reprecipitation and freeze-drying.

Number-average molecular weights were determined in a Hitachi–Perkin Elmer 115 vapour pressure osmometer. The measurements were carried out at 37 C in chloroform. Five molecular weight fractions, ranging from 5500 to 11 800, were selected for crystallization.

Crystallization

The crystallization kinetics studied were carried out using dilatometric techniques previously described[12,13]. Dilatometers were built with a stem of 12–15 cm long and 0.5 mm diameter precision bore tubing. About 180–230 mg of polymer was used in the dilatometers filled with triply distilled mercury under vacuum, and, before crystallization, the melting influence on the kinetics was analysed following the method previously described[7]. When the melting temperature is 55°C higher for times between 10–20 min, the isotherms are completely reproducible. The observed dilatometer heights as a function of time were used to calculate the specific volume of the partly crystalline sample and to calculate the degree of crystallinity, assuming the additivity of the specific volumes of the amorphous and crystalline portions. The specific volume–temperature relationship for the completely amorphous polymer was determined in the melted state and is given by $\bar{v}_L = 0.940 + 3.1 \times 10^{-4} t$ where t is the temperature (°C). The relationship for the crystalline polymer is given by $\bar{v}_c = 0.813 + 2.4 \times 10^{-4} t$ taking 1.23 g ml^{-1} as the density of the crystalline polymer[6].

The fractions were crystallized, after melting at 55°C for 20 min, at temperatures in the range from 6 to 17°C, depending on molecular weight. Experimental data are given in *Table 1*.

X-ray diffraction

X-ray diffraction measurements were carried out by using a Phillips Geiger counter X-ray diffractometer. The

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Table 1 Crystallization parameters for poly(1,3 dioxepane) molecular weight fractions

$\bar{M}n$	Tc (°C)	$\tau_{0.1}$ (min)	$1-\lambda$ (%)
5500	7	60	33.1
	8	100	33.3
	9	180	33.2
	10	260	33.6
	11	360	32.8
	12	550	32.6
	13	1020	33.4
	14	1580	31.9
	15	2500	32.6
7000	7	20	33.4
	8	32	34.2
	9	52	33.5
	10	81	34.5
	11	122	33.6
	12	202	34.1
	13	405	34.3
	14	690	35.1
	15	1180	33.9
	16	2650	34.7
8300	7	11	23.7
	8	16	23.8
	9	22	22.8
	10	32	22.6
	11	42	22.4
	12	85	22.6
	13	125	22.9
	14	340	22.7
	15	505	22.9
	16	1150	22.3
9800	7	16	34.2
	8	20	34.4
	9	26	35.2
	10	35	34.6
	11	50	34.7
	12	78	34.4
	13	110	35.3
	14	205	34.7
	15	340	34.8
	16	650	34.7
11 800	6	36	37.4
	7	42	36.5
	8	60	36.8
	9	75	36.4
	10	130	35.9
	11	165	36.2
	12	300	35.7
	13	600	35.5
	14	1020	35.6
	15	2060	33.8

diagrams were recorded in the 2θ range between 4 and 35° with Nickel-filtered CuKα radiation. The samples were prepared by moulding the polymer at a temperature above the melting point and then isothermally crystallized. The diagrams were recorded after crystallization at 18°C to avoid melting.

RESULTS AND DISCUSSION

Quantitative kinetic data could be obtained in the molecular weight range from 5500 to 11 800 and in the temperature interval from 6 to 17°C. At higher temperatures the rates become too slow to be measured in a reasonable period and at lower temperatures the rates become so rapid as to preclude measurements by the dilatometric technique.

The crystallization kinetics have been analysed by using the Avrami equation[14] and the free-growth or Göler–Sachs approximation[15]. There is good adherence of the experimental data to these theoretical developments and the agreement with both formulations is approximately the same. The Avrami exponent, the slope of the double logarithmic plot of the extent of the transformation against time, is found to be independent of temperature and molecular weight in the range analysed. This exponent corresponds to 3 (*Figure 1*).

The Göler–Sachs equation is described in a double logarithmic plot of crystallinity against time. Again, a lineal relation is obtained in the first part of the total transformation with a slope of 3 (*Figure 2*).

After the deviations from linearity develop in both theories, the experimental results for a given molecular weight form a common straight line of small slope and this fact indicates that the degree of crystallinity over long periods is independent of the crystallization temperature. However, two facts are of considerable interest. Firstly, the crystallinity of the various molecular weight fractions after crystallization in the range from 6 to 17°C for a given time to ensure no further crystallization, is independent of molecular weight. Variations in crystallinity for molecular weight fractions are related with the influence of molecular weight on the crystallization and these variations are a common fact in the crystallization of many polymers

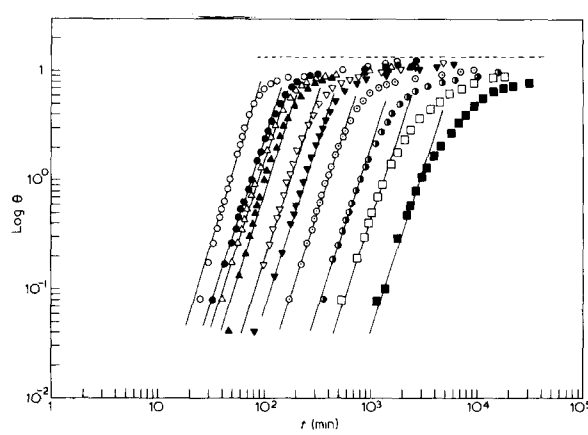

Figure 1 Double logarithmic plot of θ against time for fraction $\bar{M}_n$ = 11 800 at indicated temperatures: ○, Tc = 6°C; ●, 7°C; △, 8°C ▲, 9°C; ▽, 10°C; ▼, 11°C; ⊙, 12°C; ◑, 13°C; □, 14°C; ■, 15°C

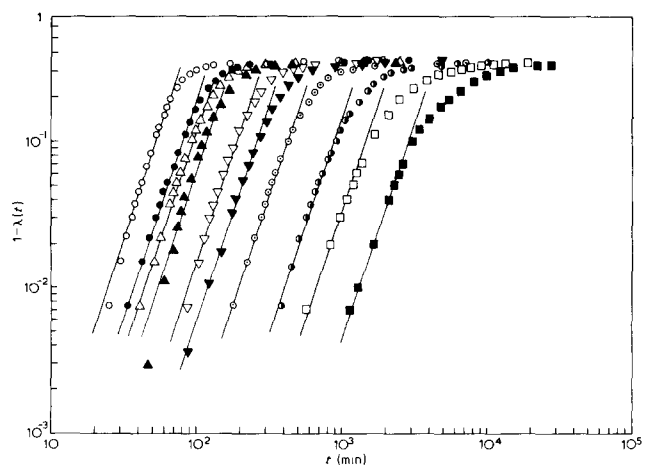

Figure 2 Double logarithmic plot of $1-\lambda$ against time for $\bar{M}$ = 11 800 at indicated temperatures: ○, Tc = 6°C; ●, 7°C; △, 8°C; ▲, 9°C; ▽, 10°C; ▼, 11°C; ⊙, 12°C; ◑, 13°C; □, 14°C; ■, 15°C

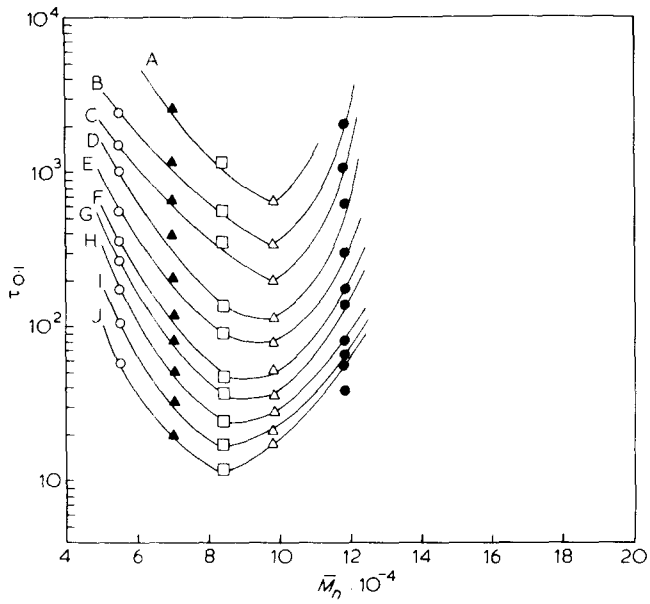

Figure 3 Double logarithmic plot of $\tau_{0,1}$ against molecular weight for indicated crystallization temperatures: *Tc*: A, 16°C; B, 15°C C, 14°C; D, 13°C; E, 12°C; F, 11°C; G, 10°C; H, 9°C; I, 8°C; J, 7°C

and have been described, specifically, in polyethylene[16] and in polyoxides[7-9]. Secondly, the degree of crystallinity reached is relatively low. The maximum crystallinity is about 35% dilatometrically measured at different crystallization temperatures. This value agrees with the values obtained from X-ray data.

On this point, it is important to comment the crystal structure of poly(1,3-dioxepane) which has been determined by X-ray diffraction and infrared spectroscopic methods[6]. The observed reflections were indexed with an orthorhombic unit cell ($a=8.50$ Å, $b=4.79$ Å and $c=13.50$ Å) with two molecular chains passing through a unit cell and two monomeric units are contained in the identity period which is far shorter than the value calculated by assuming the planar zig zag conformation. The identity period corresponds to two repeat units with the conformation.

$$g[g\ \ tg^-\ \ tg\ \ tg^-][g^-\ \ tg^-\ \ tg]g$$

The COCOC sequences have the *gauche–gauche* conformations and the strong preference for *gauche* states in the two central bonds in this sequence and the conformation in the crystalline state are in excellent agreement with the results obtained on rotational isomeric state calculations on this polymer[17].

Assuming a folded crystalline structure, the conformation in the fold surface imposes a certain strain and must correspond to an important interface diffuseness with relatively high interfacial energy.

Moreover, the experimental determination of the glass temperature is reliable in this polymer, as consequence of an important amorphous phase. The calorimetric determination of glass temperatures has shown that *Tg* changes with molecular weight and ranges from −110°C ($M=5500$) to −80°C ($M=11800$)[18]. Low crystallinity levels after isothermal crystallization have been found in other polymers where a large secondary crystallization process is present. A typical example is linear poly(tetramethylene oxide), which presents a low crystallinity fraction and an important secondary process[19-21]. It has been shown[19] that in crystallized poly(tetramethylene oxide) the average thickness of the amorphous layer is greater than the crystalline layers. The low crystallinity and the long secondary process have been considered to arise from high amorphous phase constraints and low translation rates through the crystallites. However, in the isothermal crystallization of poly(1,3-dioxepane), secondary crystallization is not important and the reason for the low crystallinity has not a clear explanation and needs further investigation on this point. The most reliable assumption at the moment is to attribute this fact to the amorphous phase constraints and high internal energy configurations in the fold.

However, the influence of molecular weight on the time scale of the crystallization is pronounced. In the lowest molecular weight range, the crystallization time decreases as the molecular weight increases and a minimum is reached for $M=8000$ at the lowest crystallization temperatures and at highest molecular weights the crystallization time increases again.

The position of the minimum depends on the crystallization temperature and it is shifted at higher molecular weights when the undercooling decreases. The minimum in time in *Figure 3* which corresponds to a maximum in the crystallization rate, has been found in other polymers[16,22,23] and corresponds to a general characteristic of the crystallization of polymers from the melt.

The crystallization rate can be expressed by the equation[24]

$$\ln(\tau_{0.1})^{-1} = \ln(\tau_{0.1})_0^{-1} - \frac{E_D}{RT} - \frac{\Delta F}{RT} \qquad (1)$$

where the free energy for forming a bidimensional stable nucleus is given by[25]:

$$\Delta F = 2\sigma_u \xi \qquad (2)$$

where ξ is the critical dimension of the nucleus and σ_u is the lateral interfacial free energy per structural unit.

In the limit of high molecular weight, ΔF is reduced to the known expression:

$$\Delta F = \frac{4\sigma_e \sigma_u T_m^o}{\Delta H_u \Delta T} \qquad (3)$$

where σ_e is the interfacial free energy per unit area in the basal plane and ΔH_u is the melting enthalpy.

Analysing the experimental data according to the conventional manner, $\log(\tau_{0.1})^{-1}$ vs. $T_m^o\ \Delta T$, all the fractions give straight lines and the slopes of these lines vary with molecular weight (*Figure 4*). Variations in the slopes represent a change in the values of σ_e or σ_u or both. If it is assumed that σ_u is constant ($\sigma_u = 10$ cal mol^{-1}), σ_e changes from 3500 cal mol^{-1} to 2700 cal mol^{-1} in the molecular weight range from 11 800 to 5500.

Analysis of the temperature coefficient according to equation (1) requires the specification of Tm^0 and ΔHu. Both parameters have been previously determined[22] and correspond to $\Delta Hu = 33.9$ cal gr^{-1} and $Tm^0 = 303$ K and ΔF can be calculated from equation (2) for each fraction.

The plot of $\ln(\tau_{0.1})^{-1}$ vs. $\Delta F/RT$ gives a unique straight line with slope 1, according to equation (1) (*Figure 5*).

These results show that the crystallization of poly-

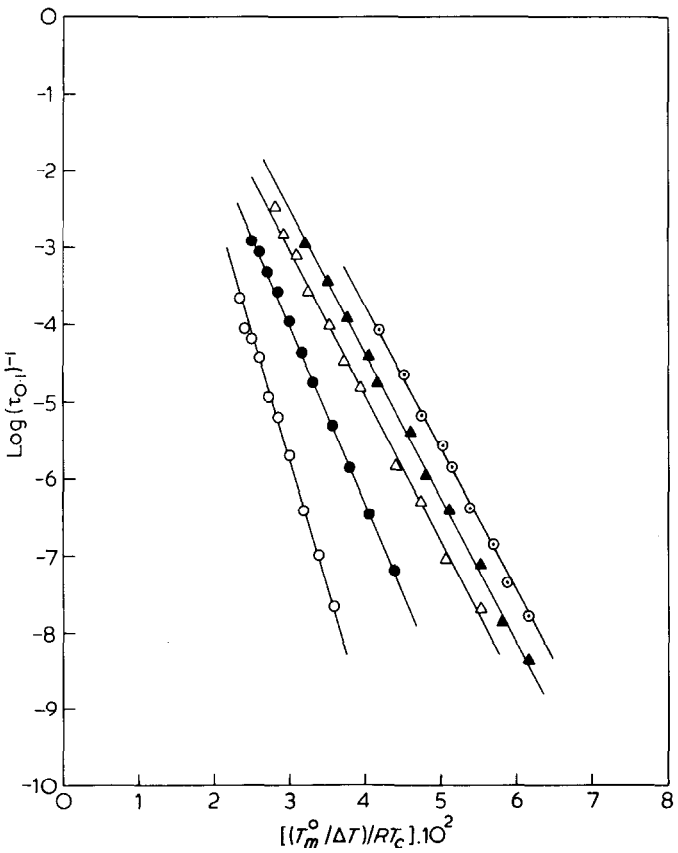

Figure 4 Plot of log $(\tau_{0,1})^{-1}$ against $(Tm/\Delta T)^2/RTc$ for indicated molecular weight fractions: ⊙, 5500; ▲, 7000; △, 8300; ●, 9800; ○, 11 800

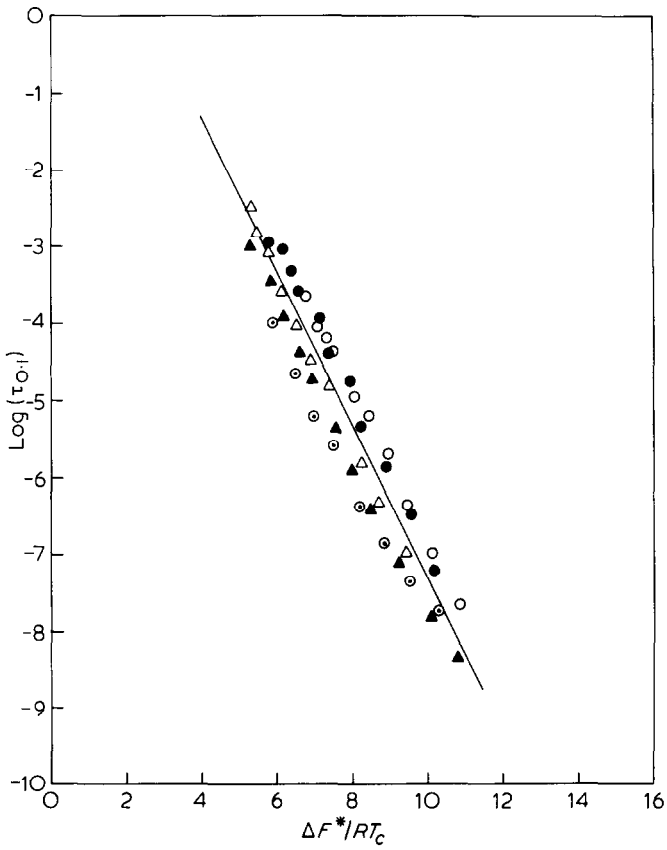

Figure 5 Plot of log $(\tau_{0,1})^{-1}$ against $\Delta F/RTc$ for indicated molecular weight fractions: ⊙, 5500; ▲, 7000; △, 8300; ●, 9800; ○, 11 800

dioxepane is governed by the nucleation and when the variation in the interfacial basal energy is stipulated, the transformation is described by the free energy for nucleation. This conclusion is general for the alternating copolymers where both units are cocrystallizable.

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