

# Crystallization of polyformals:

## 1. Crystallization kinetics of poly(1,3-dioxolane)

R. Alamo, J. G. Fatou and J. Guzmán

*Sección de Física y Fisicoquímica de Polímeros, Instituto de Plásticos y Caucho, C.S.I.C., Juan de la Cierva, 3; Madrid-6, Spain*

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Poly(1,3-dioxolane) fractions ranging in molecular weight from 8800 to 120 000 have been isothermally crystallized in the temperature range 25–41°C. From the dilatometric isotherms, the Avrami exponent is an integral number, 3, and is independent of temperature and molecular weight. The level of crystallinity is dependent on molecular weight and there is a change from ~55% for the highest molecular weight fraction to ~80% for the lowest molecular weight fraction. The overall crystallization rate temperature coefficient was studied using two dimensional nucleation theory and it was found that the interfacial free energies do not change with molecular weight. However, the usual plots are nonlinear in the whole range of crystallization temperatures. For the high crystallization temperatures the slope is about twice the low crystallization temperature slope, this change being related to a morphological transition.

**Keywords** Crystallization; polyformals; poly(1,3-dioxolane); kinetics; nucleation theory; morphological transition

### INTRODUCTION

The crystallization of polyformals with the general structure  $\{O-CH_2-O-(CH_2)_m\}_n$  has rarely been investigated and only scarce data are reported. However, structural studies of polyformals have been carried out by Sasaki *et al.*<sup>1</sup> and the formation of three crystal modifications has been reported for the case of poly(1,3-dioxolane) (PDOL). This molecular chain ( $m=2$ ) consists of regular head-to-tail sequences showing that the ring opening of 1,3-dioxolane occurs exclusively at the same type of CO bond in the cationic polymerization<sup>2</sup>.

Geil described the crystallization process and spherulitic growth in this polymer observing two phases by microscopy<sup>3</sup> and more recently, the crystallization kinetics and morphology of polydioxolane have been studied by Prud'homme *et al.*<sup>4-6</sup> but only low molecular weight samples were used. According to these authors, the passage from the low to the high crystallization temperature is associated with a change in the Avrami exponent. Also, a complicated process was revealed from the growth rates. At temperatures between 0° and 21°C, growth of two dimensional regular spherulites occurs and at temperatures higher than 21°C, the polymer presents two optical morphologies.

In order to explore the role played by molecular weight and molecular weight homogeneity both in the crystallization process and in the morphological nature of the crystalline state of PDOL, in this paper we report the crystallization kinetics by dilatometry of fractions of PDOL over a molecular weight range of  $8.8 \times 10^3$  to  $1.2 \times 10^5$ .

### EXPERIMENTAL

#### Materials

Poly(1,3-dioxolane) was prepared by solution polymerization of 1,3-dioxolane in methylene chloride at 0°C, using acetyl perchlorate as initiator<sup>7</sup>. The polymer was precipitated in hexane, filtered and dried in vacuum, and purified by dissolving it in benzene and further lyophilization.

The whole polymer was fractionated at 25°C in the system chloroform/hexane-methanol mixtures. Number average molecular weights were measured in a Hitachi-Perkin-Elmer vapour pressure osmometer for the low molecular weight range and in a Hewlett-Packard membrane osmometer for the higher molecular weight. The molecular weight of the fractions ranges from  $8.8 \times 10^3$  to  $1.2 \times 10^5$ .

#### Procedures

The crystallization kinetic studies were carried out using dilatometric techniques previously described in detail<sup>8,9</sup>. Before each crystallization measurement, the samples were allowed to melt at 70°–90°C for 60 min. The dilatometer was quickly transferred to another bath set at a predetermined crystallization temperature and controlled to  $\pm 0.01^\circ\text{C}$ . The level of the mercury column was recorded as a function of time and the specific volume of the partially crystalline sample was calculated. This was used to calculate the degree of crystallinity, assuming the additivity of specific volumes. The relationships between the specific volume of the amorphous and crystalline forms II and III and temperature  $T$  expressed in °C are

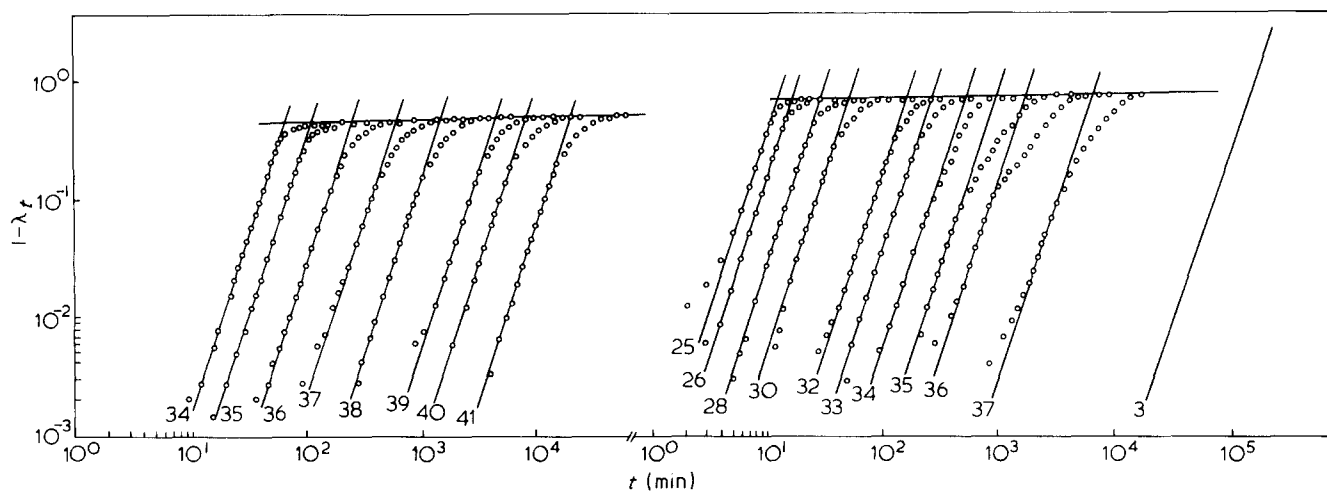


Figure 1 Double logarithmic plot of  $1 - \lambda_t$  against time at indicated temperatures. Left side:  $M_n = 120\,000$ ; right side:  $M_n = 8800$

given, respectively by<sup>6</sup>:

$$V_a = 0.7960 + 7.64 \times 10^{-4} T$$

$$V_{cII} = 0.6965 + 5.00 \times 10^{-4} T$$

$$V_{cIII} = 0.7350 + 6.50 \times 10^{-4} T$$

## RESULTS AND DISCUSSION

The crystallization process is continuous. The knees found by Archambault and Prud'homme<sup>6</sup> are not present in the crystallization of these fractions, independent of molecular weight and crystallization temperature, and quantitative kinetic data could be obtained in the temperature interval from 25° to 41°C. In order to analyse the data in more detail, it is convenient to obtain the isotherms as a function of the degree of transformation  $1 - \theta$  or as a function of the crystallinity  $1 - \lambda_t$ .

The degree of transformation increases when the molecular weight decreases and changes from 94% for  $M_n = 120\,000$  to 99% for  $M_n = 8800$ . Also, the degree of crystallinity increases when the molecular weight decreases.

If the Gölér-Sachs or free-growth approximation<sup>10</sup> is used, a linear relation must be obtained for the initial portion of the transformation in a double logarithmic plot of  $1 - \lambda_t$  against time. Typical experimental results are plotted in Figure 1. Despite the obvious simplicity of this analysis, there is a good adherence of the experimental data to the theory, and a linear relation is obtained for a significant portion of the transformation. For any given molecular weight fraction, the slopes of the linear portions are found to be independent of temperature. Moreover, these slopes have an integral value ( $n=3$ ) which is independent of molecular weight in the analysis range.

The Avrami equation<sup>11</sup> can be written in general form as

$$\ln(1 - \theta) = K t^n \quad (1)$$

and in this equation it is assumed that when two growing centres impinge upon each other, growth ceases. The agreement of the experimental data with the Avrami formulation is about the same as with the Gölér-Sachs approximation. Again, an integral value  $n=3$  is found,

independently of molecular weight and crystallization temperature.

These results are in disagreement with previous results by Prud'homme *et al.*<sup>4-6</sup> who found a change of  $n$  with crystallization temperature for low molecular weight unfractionated samples ( $M = 6700$ ). In their dilatometric results, Avrami exponents of  $n=2.8$  are found for crystallization conducted at 19.5° and 22°C,  $n=4.1$  at crystallization temperatures 25° and 28°C and a value of  $n=3.0$  at 35°C. Moreover, values of  $n=2$  in the range from 0° to 21°C were previously reported by these authors when the crystallization process is followed by calorimetry. These variations in the Avrami exponent suggested to these authors changes in nucleation modes.

However, when we analyse molecular weight fractions in the range of  $M_n = 120\,000$  to  $M_n = 8\,400$ , no changes in the Avrami exponent are found even for higher undercoolings than those obtained from the dilatometric data. Preliminary results obtained by calorimetry<sup>12</sup> show that for  $M_n = 8400$ , values of  $n=3$  are also obtained in the crystallization range from 10° to 20°C. The main conclusion is that when molecular weight fractions are used, no change in the Avrami exponent is found, independently of molecular weight and crystallization temperature.

An important observation that can be made from the experimental data is that the levelling-off value of the degree of crystallinity at very long times is independent of the crystallization temperature for each molecular weight. However, when the different molecular weights are compared, the level of crystallinity is dependent on molecular weight. These results are shown in Figure 2. There is a change from ~55% for the highest molecular weight fraction to ~80% for the lowest molecular weight fraction. This level of crystallinity is the highest reported for PDOL. The influence of molecular weight on the time scale of the crystallization process is pronounced for very low molecular weight fractions. Figure 3 shows the plot, on a double logarithmic scale, of the time required for 10% of the transformation to develop ( $\tau_{0.1}$ ) as a function of molecular weight, for different crystallization temperatures.

In the lower molecular weight range the crystallization times decrease as the molecular weight is increased. However, a minimum is not observed in the range

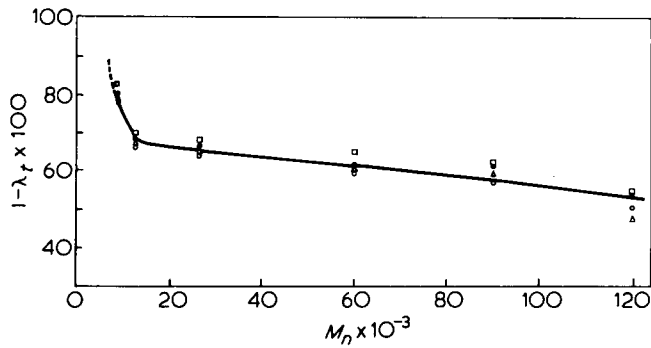


Figure 2 Crystallinity against molecular weight at different crystallization temperatures: ○, 34°C; △, 35°C; ●, 36°C; □, 37°C

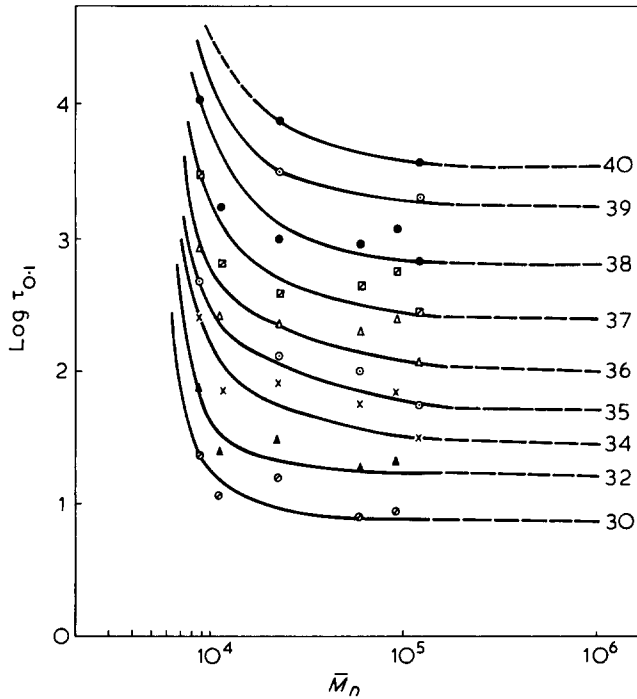


Figure 3 Plot of  $\log \tau_{0.1}$  against molecular weight for indicated crystallization temperatures

analysed, as is shown in other polymers<sup>13-15</sup>. The absence of this minimum is probably due to the relatively low molecular weight range which has been analysed. The increase in the left hand side of Figure 3 is related with the increase in the free energy of nucleation with decrease in molecular weight.

Temperature coefficient

The isothermal crystallization rate for the crystallization from the melt is described by the general equation<sup>16</sup>:

$$\ln(\tau_{0.1})^{-1} = \ln(\tau_{0.1})_0^{-1} - \frac{E_D}{RT} - \frac{\Delta F}{RT_c} \quad (2)$$

where  $T_c$  is the crystallization temperature.  $\Delta F$  is the free energy for forming a stable nucleus and  $E_D$  is the transport term.

For finite chains with  $x$  units, Mandelkern *et al.*<sup>17,18</sup> have shown that  $\Delta F$  is dependent on molecular weight and for the nucleation of the type described by Gibbs,  $\Delta F$  and the critical dimensions  $\xi^*$  and  $\rho^*$  are given by the expressions<sup>18</sup>:

$$\Delta F^* = 2\sigma_u \xi^*$$

$$\xi^* = \frac{2\sigma_e - RT \ln\left(\frac{x - \xi^* + 1}{x}\right)}{\Delta f_u - RT/x} \quad (3)$$

$$\rho^* = \frac{2\sigma_u}{\Delta f_u - RT/x - \frac{RT}{(x - \xi + 1)}}$$

where  $\sigma_e$  and  $\sigma_u$  are the interfacial free energy per unit area in the basal plane and the lateral interfacial free energy per structural unit, respectively, and  $\Delta f_u$  is the free energy of fusion per repeating unit for a chain of infinite molecular weight. In the limit of high molecular weights  $\Delta F$  is reduced to the known expression<sup>18</sup>:

$$\Delta F^* = \frac{4\sigma_e \sigma_u T_m^\circ}{\Delta H_u \Delta T} \quad (4)$$

where  $T_m^\circ$  is the equilibrium melting temperature,  $\Delta H_u$  the heat of melting and  $\Delta T = (T_m^\circ - T_c)$  the undercooling of the system. Both parameters,  $\Delta H_u$  and  $T_m^\circ$  have previously been determined<sup>19</sup> and correspond to  $\Delta H_u = 3700$  cal mol<sup>-1</sup> and  $T_m^\circ = 366$ K.

Analysing the data according to the conventional manner,  $\ln(\tau_{0.1})^{-1}$  is plotted against  $T_m^\circ/T_c \Delta T$  in Figure 4. The analysed fractions give straight lines with the same slopes, except for the lowest molecular weight fraction. These results are quite different from those found in other

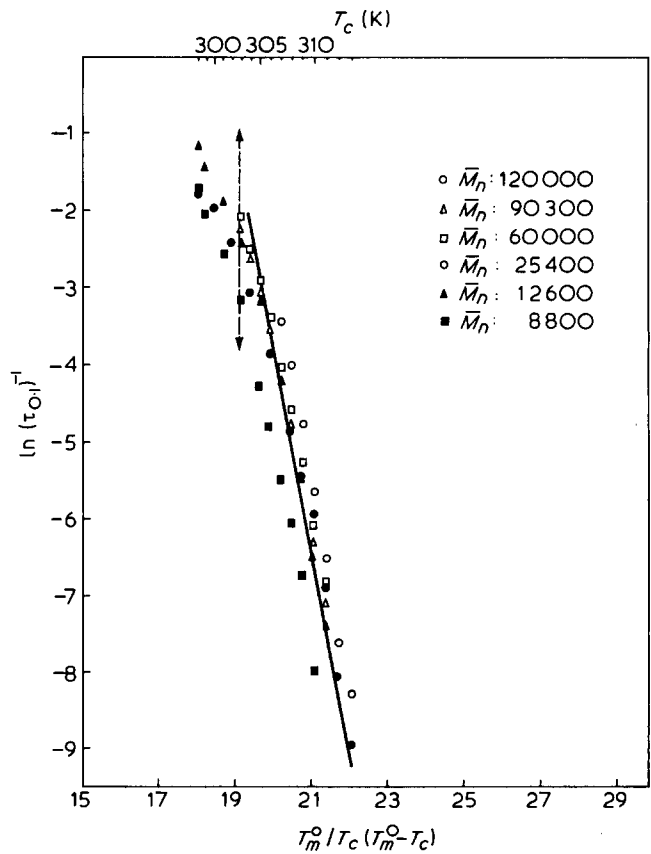


Figure 4 Plot of  $\log (\tau_{0.1})^{-1}$  against  $T_m^\circ/T_c \Delta T$  for indicated molecular weight fractions

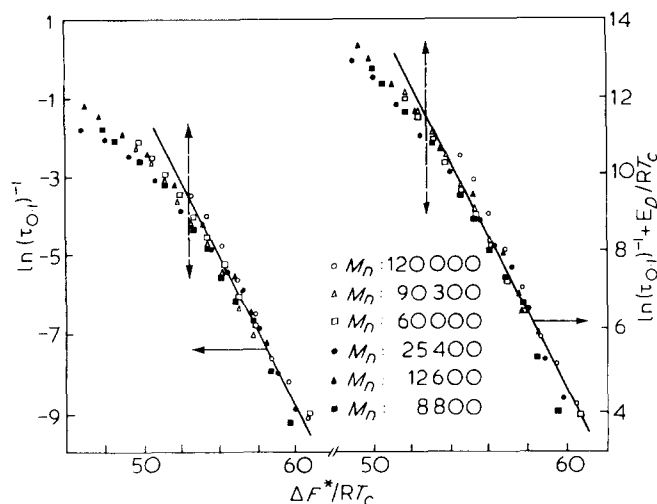


Figure 5 Plot of  $\log(\tau_{0.1})^{-1}$  (left side) and  $\log(\tau_{0.1})^{-1} + E_D/RT_c$  (right side) against  $\Delta F^*/RT_c$  for indicated molecular fractions

polymers where the slopes vary with the molecular weight; the lower the molecular weight, the lower the slopes are.

The lack of variation in the slopes represents a constant value of the product  $\sigma_e \sigma_u$  and the independence of the interfacial free energies on molecular weight in the range which has been studied. Assuming a value for  $\sigma_u = 370 \text{ cal mol}^{-1}$  (10% of the melting enthalpy),  $\sigma_e = 13350 \text{ cal mol}^{-1}$ . However, if either a higher value of  $\sigma_u$  or a lower value of  $T_m^\circ$  are taken,  $\sigma_e$  is lower, and for  $\sigma_u = 740 \text{ cal mol}^{-1}$ ,  $\sigma_e$  is  $6700 \text{ cal mol}^{-1}$ . These values for  $\sigma_e$  are higher than the values for polyethylene, poly(ethylene oxide) and poly(methylene oxide), corresponding to a very distorted basal interface.

Analysis of the temperature coefficient according to equation (3) for finite chains is shown for each fraction in the plot of  $\ln(\tau_{0.1})^{-1}$  vs.  $\Delta F^*/RT_c$  (Figure 5 left side). The most important fact of these figures is that the plots are nonlinear in the whole range of crystallization temperatures. It is possible to draw two straight lines through the experimental data which intersect at  $\sim 303\text{K}$ . A much smaller slope, about half of the slope for the high temperature range, is obtained from the straight line which represents the data for the lower crystallization temperatures.

However, this analysis has neglected the influence of the transport contribution, as embodied in the term  $E_D$ . This term has been used in certain analyses<sup>20-22</sup> taking arbitrary values or calculating  $E_D$  from the Williams-Landel-Ferry theory<sup>23-24</sup>. We examine the term which is given by:

$$E_D RT_c = \frac{2.303 C_1 C_2}{C_2 + T_c - T_g} \quad (5)$$

where  $C_1$  and  $C_2$  are constants equal to 17.4 and 51.6K and  $T_g$  is the glass transition temperature for each molecular weight fraction. This value changes from 206.8 to 210.5K, in the molecular weight range from 8800 to 120000, respectively<sup>19</sup>. Figure 5 (right side) shows the results for the plot  $\ln(\tau_{0.1})^{-1} + E_D/RT_c$  vs.  $\Delta F^*/RT_c$  and again, the same conclusions are obtained about the

existence of two different slopes. The complete set of data cannot be fitted by the correction introduced by the Williams-Landel-Ferry equation and this result is not surprising if it is realized that there is no direct proof of the validity of applying this equation to overall rate or growth rate of the crystallization.

Breaks in the temperature coefficient of the overall crystallization rate were reported by Ergoz *et al.*<sup>14</sup> in polyethylene fractions where the conventional plots  $\log(\tau_{0.05})^{-1}$  vs.  $T_m/T \Delta T$  were no longer linear, except for the higher molecular weights. The slopes in these plots for the high molecular weights and the high temperature lower molecular weights are the same, being almost twice those on the low temperature-low molecular weight slope. Hoffman *et al.*<sup>25</sup> have measured growth rates of the morphological forms that they observed in polyethylene and they found that the temperature coefficient of the axialites was twice that of the coarse-grained nonbanded spherulites. They explained the experimental results assuming two cases of crystal growth on a substrate, one in which the rate of lateral growth is much faster than the nucleation rate and the net growth rate perpendicular to the crystal faces,  $G$ , is proportional to the nucleation rate, and another one in which the growth rate will be dependent on nucleation rate and on the rate of lateral growth. For these two cases, the temperature coefficients of the growth rate are related by a factor of two. However, breaks in the growth rate have been found for other polymers with different morphologies and the ratio of the coefficients is not always two<sup>26,27</sup>.

Maxfield and Mandelkern<sup>28</sup> have studied the supermolecular structures of molecular weight fractions of linear polyethylene, covering the range from  $M_n = 2.53 \times 10^4$  to  $M_n = 8.0 \times 10^6$  and the different forms that were developed were established as a function of molecular weight and crystallization temperatures. In their work these authors have discussed the mechanistic explanation for the formation of the different morphological forms, comparing data of the temperature coefficient of overall crystallization rate and the growth rate.

According to Prud'homme *et al.*<sup>5,6</sup> in PDOL there is, around  $22^\circ\text{C}$ , a spherulite  $\rightarrow$  hedrite transition, similar to the one which is present in poly(oxymethylene)<sup>26,29,30</sup> where the formation of hedrites is favoured at high temperatures and regular spherulites are found at low temperatures of crystallization. From their data, there is no significant change in growth rate temperature dependence at the spherulite  $\rightarrow$  hedrite transition temperature, although the growth rate of the spherulite is different from that of the hedrite. In our present analysis, covering a wide range of molecular weights, it is possible to relate the different overall rate temperature coefficients with the transition. The two straight lines which have been drawn through the experimental data intersect at  $\sim 30^\circ\text{C}$ .

The first conclusion is that the change in the slopes is related with the morphological transition. However, the quantitative molecular understanding of the crystallization mechanism needs the determination of growth rates and the use of molecular weight fractions in a wide range, where under determined crystallization conditions, the supermolecular structure is strongly dependent on molecular weight and polydispersity. Caution must be exercised when interpreting results on unfractionated polymers or different fractions. In the

present work we concentrate our effort in the analysis of the influence of molecular weights on the kinetics of crystallization and on the overall rate temperature coefficient. Further work in progress includes the measurement of the growth rates and the analysis of the supermolecular structures. Both the temperature coefficients of overall rate and growth rate must be compared in order to understand the mechanism of formation of such superstructures.

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