Effect of molecular weight on the crystallization kinetics of poly(hexamethylene oxide)

C. Marco, J. G. Fatou and A. Bello
Sección de Física y Fisicoquímica, Instituto de Plásticos y Caucho, CSIC, Juan de la Cierva 3, Madrid-6, Spain

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Dilatometric crystallization isotherms have been analysed for poly(hexamethylene oxide) fractions ranging in molecular weight from 2200 to 33 500. Previously, the influence of the temperature and the time of melting in the reproducibility of the isotherms were studied. Deviations from the Avrami or Göler–Sachs free growth formulations are systematic with molecular weight and become more pronounced as the molecular weight increases. The Avrami exponent is an integral number, 4, and is independent of temperature and molecular weight. The crystallization rate goes through a maximum as a function of molecular weight and the location of this maximum depends on the undercooling. The crystallization temperature coefficient was studied using the three dimensional nucleation theory and it was found that the crystallization is described by a unique function of the free energy for nucleation when the change of the interfacial free energy with molecular weight is considered.

INTRODUCTION

The polyoxides, with the repeat unit – $(CH_2)_m$–O–, are semicrystalline polymers of simple and regular chemical structure, correlated with the limiting case of $m \to \infty$, polyethylene.

The crystallization kinetics of these polymers have been previously investigated for the lower members of this series, especially the influence of molecular weight on the crystallization for poly(ethylene oxide)[1–9]. However, little attention has been paid to the crystallization kinetics of higher polyethers, although the crystalline structures have been reported for the cases m = 6, 8, 10 and 12[10].

Here, we present the results of a dilatometric investigation of the crystallization of several fractions of poly(hexamethylene oxide), PHO, ranging in molecular weight from 2200 to 33 500 and the results are compared with the ones reported previously for poly(decamethylene oxide)[11] and polyethylene[12].

EXPERIMENTAL

Materials

Poly(hexamethylene oxide) was obtained by polycondensation of 1,6-hexanediol using sulphuric acid as catalyst[13]. The polymer fractions used in this work were obtained by the liquid–liquid phase separation method[14] and the solvent–non-solvent system was tetrahydrofuran–methanol.

The fractionation temperature was 40°C and the fractions were precipitated with reagent grade methanol, and the obtained samples were filtered, washed with methanol and dried in vacuum for 24 h at 40°C.

Viscosity and molecular weight measurements

The determination of the intrinsic viscosities and molecular weights of the fractions has been described previously[13]. In brief, the intrinsic viscosities were determined in an Ubbelhode type viscometer in the conventional manner by extrapolating the linear plot of (η_{sp}/c) against c to zero concentration. Number-average molecular weights were determined in a Hitachi–Perkin–Elmer 115 vapour pressure osmometer.

The relation $[\eta]/\bar{M}$ is given by:

$$[\eta] = 9.7 \times 10^{-4} M^{0.66}$$

for tetrahydrofuran at 30°C.

Crystallization kinetics

The crystallization kinetics studies were carried out using dilatometric techniques previously described[15,16]. About 120–240 mg of bubble-free polymer film was used in the dilatometers. These were built with a stem of 12–15 cm long and of 0.6 mm diameter precision bore tubing. The dilatomer bulb containing the sample was evacuated and filled with triply distilled mercury under vacuum.

Previous to crystallization, the melting influence on the kinetics was analysed. The dilatometer was placed in a silicone oil bath at the melting temperature for a given time and then it was quickly transferred to another silicone oil bath set at a predetermined crystallization temperature and controlled to better than 0.01°C. The time of transfer was taken as zero time and the level of the mercury column was recorded as a function of time. The observed heights were used to calculate the specific volume $\bar{v}$ of the partly crystalline sample and to calculate the degree of crystallinity $(1 - \lambda)$ assuming the additivity of the specific volumes of the amorphous and crystalline portions.

The specific volume--temperature relationship for the completely amorphous polymer was previously determined in the melted state, by introducing a sample of known density, 1.016 g/mol at 25°C. The relationship for the specific volume of the amorphous material was given by:

$$\bar{v}_e = 1.073 + 7.404 \times 10^{-4}(t - 25)$$

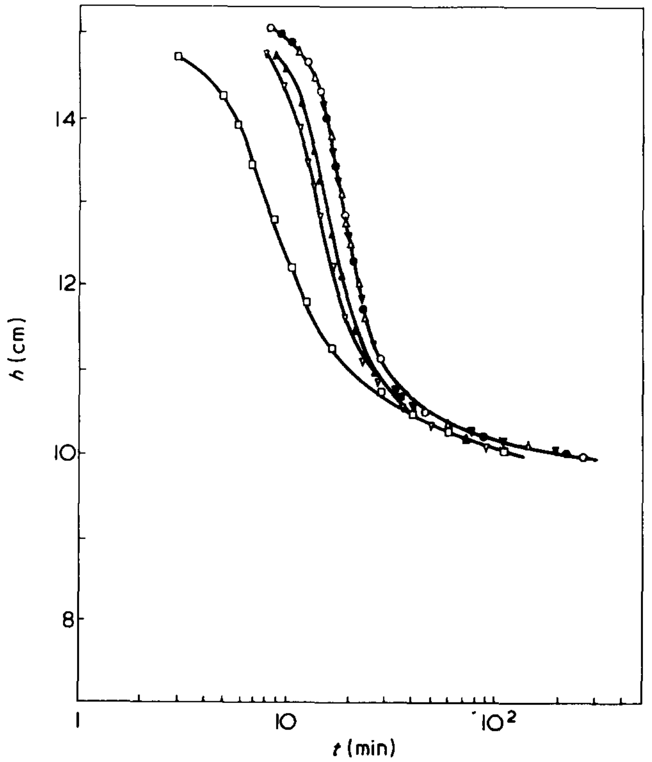

Figure 1 Crystallization isotherms at T_c = 53°C for fraction M = 35 500 after melting at predetermined temperatures: □, 80°C; ▽, 90°C; ▲, 100°C; ○, 116°C; ●, 130°C; ▼, 140°C; △, 150°C

where t is the temperature (°C).

The relationship for the specific volume of the completely crystalline polymer was given by:

$$\bar{v}_c = 0.934 + 3.0 \times 10^{-4} t$$

taking 0.934 as the specific volume of the crystalline polymer[10] and assuming the expansion coefficient to be the same as that in polyethylene[17]. The fractions were crystallized, after melting at 120°C for 20 min, at temperatures in the range from 49° to 58°C, depending on molecular weight.

RESULTS AND DISCUSSION

General results

Before crystallization it was important to assess whether there was any influence of melting conditions on the subsequent crystallization behaviour, and to examine this problem, the dilatometers were melted for periods of time which varied from 20 to 30 min at a series of predetermined temperatures in the range from 80° to 150°C. The results for the fraction M = 35 500 are indicated in *Figure 1* as a plot of the reading h against log (time). As is discerned from *Figure 1*, the crystallization isotherms are dependent on the treatment in the molten state. At the lowest temperatures, 80°, 90° and 100°C, the isotherms are dependent on melting conditions. When the melting temperature is 116°C or higher, the temperature of the melt and time held there have no influence on the ensuing crystallization isotherm. This observation is in agreement with previous studies on poly(ethylene oxide)[18], poly(decamethylene oxide)[12] and polyethylene[11]. The behaviour at lower temperatures, where the crystallization is faster the lower the melting temperature, corresponds to temperatures below the equilibrium melting temperature of the system, where persistent nuclei or impurities can act as nucleating agents.

Based on these results, the procedure of melting at 120°C for 20 min prior to crystallization has been adopted.

Quantitative kinetic data could be obtained in the molecular weight range from 2200 to 35 500 and in the temperature interval from 49° to 58°C. At lower temperatures, the rates become so rapid as to preclude measurements by the dilatometric technique, and at higher temperatures the rates become too slow to be measured in a reasonable period.

The Avrami equation[19] can be written in general form:

$$\ln(1 - \theta) = Kt^n \tag{1}$$

where θ is the extent of transformation and the Avrami exponent n is thus the slope of the double logarithmic plot of $(1 - \theta)$ against t. (*Figures 2* and *3*). The slopes of the linear portions are found to be independent of temperature and they have an integral value which is independent of molecular weight in the range analysed. The Avrami exponent corresponds to 4 and is the same as the value found for low molecular weight linear polyethylene[11] and poly(decamethylene oxide)[12]. The simplest interpretation of the exponent n = 4 is the occurrence of a homogeneous nucleation accompanied by three dimensional growth.

If the free growth analysis or the Göler–Sachs approxi-

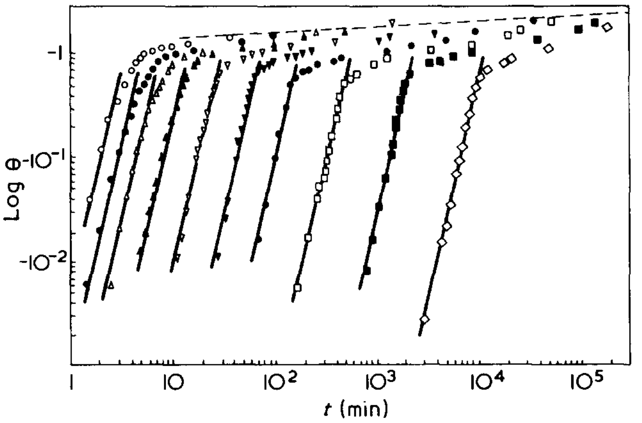

Figure 2 Double logarithmic plot of θ against time for fraction M = 8250 at indicated temperatures, T_c: ○, 49°C; ●, 50°C; △, 51°C; ▲, 52°C; ▽, 53°C; ▼, 54°C; ⊕, 55°C; □, 56°C; ■, 57°C; ◇, 58°C

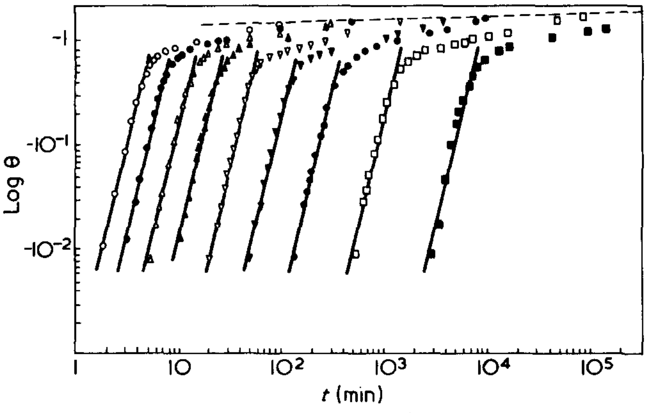

Figure 3 Double logarithmic plot of θ against time for fraction M = 35 500 at indicated temperatures, T_c: ○, 50°C; ●, 51°C; △, 52°C; ▲, 53°C; ▽, 54°C; ▼, 55°C; ⊕, 56°C; □, 57°C; ■, 58°C

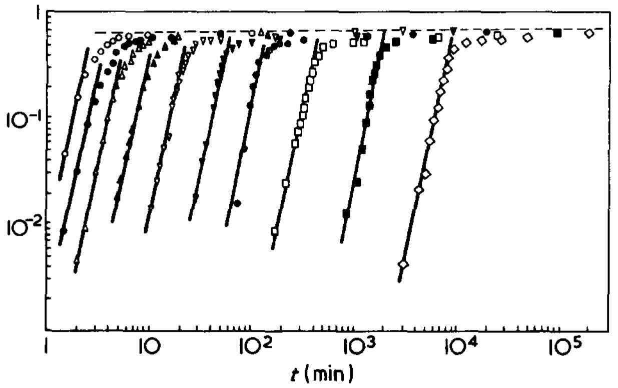

Figure 4 Double logarithmic plot of 1 − λ against time at indicated temperatures (T_c) for M = 8250; ○, 49°C; ●, 50°C; △, 51°C; ▲, 52°C; ▽, 53°C; ▼, 54°C; ⊕, 55°C; □, 56°C; ■, 57°C; ◇, 58°C

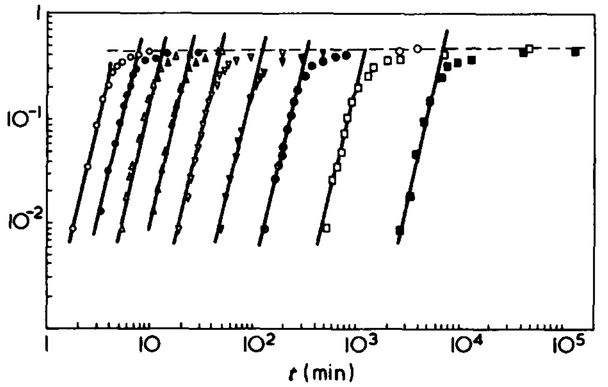

Figure 5 Double logarithmic plot of 1 − λ against time at indicated temperatures (T_c) for M = 35 500: ○, 50°C; ●, 51°C; △, 52°C; ▲, 53°C; ▽, 54°C; ▼, 55°C; ⊕, 56°C; □, 57°C; ■, 58°C

mation[20] is used, the same results are obtained. Typical experimental results are plotted in *Figures 4* and *5* according to the suggestion of the following equation:

$$1-\lambda(t) \simeq (K_3 t)^4/4 \tag{2}$$

There is a rather good adherence of the experimental data to these theoretical developments and the agreement with the Avrami and Göler–Sachs formulations is about the same. A linear relation is obtained in the first part of the total transformation and as the molecular weight increases, the discrepancy between the theory and experiment occurs at progressively lower levels of crystallinity.

After the deviations from linearity develop, the experimental results for a given molecular weight form a common straight line of very small slope. This fact indicates that the degree of crystallinity at very long times is independent of the crystallization temperature. Similar results have been found in polyethylene[11] and poly(decamethylene oxide)[12].

The crystallinity of the various molecular weight fractions, after crystallization in the range 49° to 58°C for a given time to ensure no further crystallization at the crystallization temperature, is plotted in *Figure 6*.

The maximum crystallinity is reached for M = 3250 and the crystallinity decreases monotonically with increasing molecular weight to a value of 45–46% for M = 35 500. These variations appear to be quite intimately connected with the influence of molecular weight on the crystallization. This influence can be seen in more detail in *Figure 7* where isotherms for the different molecular weights have been superimposed on one another.

On the other hand, the influence of molecular weight on the time scale of the crystallization process is very pronounced. In *Figure 8*, on a double logarithmic scale, the time required for 10% of the absolute amount of crystallinity to develop is plotted as a function of molecular weight. In the lower molecular weight range, the crystallization time decreases as the molecular weight is increased. This fact is observed at all accessible T_c and a smooth minimum in the time is reached which corresponds to a maximum rate. This

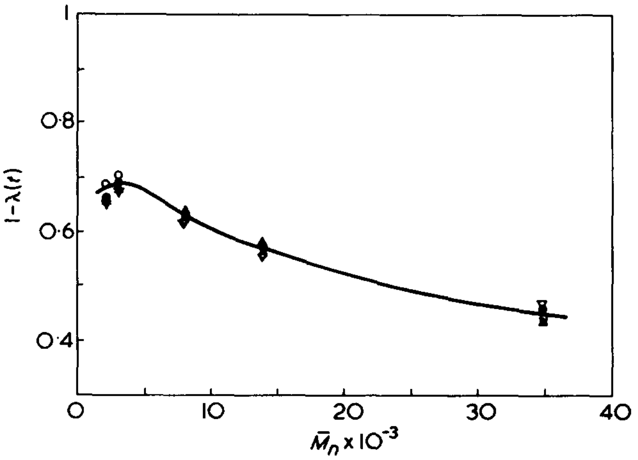

Figure 6 Crystallinity against molecular weight at different crystallization temperatures: ○, T_c = 56°C; ●, T_c = 55°C; △, T_c = 54°C; ▲, T_c = 53°C

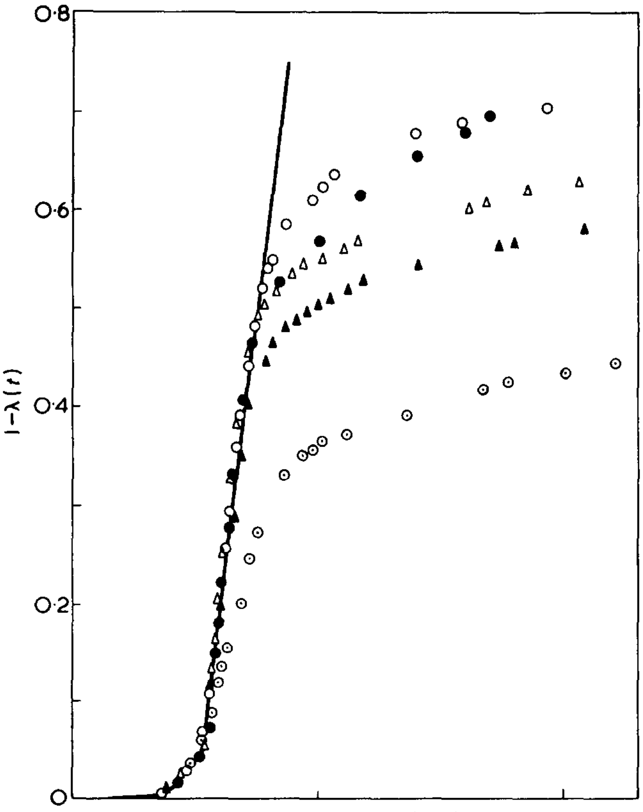

Figure 7 Superimposed isotherms (crystallinity against time) T_c = 55°C for indicated molecular weights: ●, 2260; ○, 3250; △, 8250; ▲, 13 940; ⊙, 35 500, ———, is the theoretical equation with n = 4

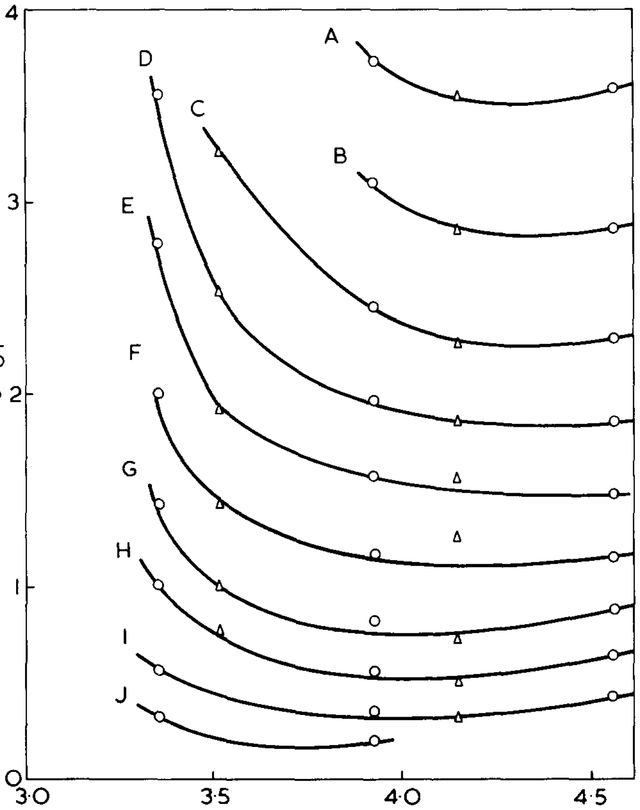

Figure 8 Double logarithmic plot of $\tau_{0.1}$ against molecular weight for indicated crystallization temperatures, T_c: A, 58°C; B, 57°C; C, 56°C; D, 55°C; E, 54°C; F, 53°C; G, 52°C; H, 51°C; I, 50°C; J, 49°C

maximum is descernible in the temperature range from 50° to 53°C and appears dependent on the crystallization temperature. At the highest molecular weights the rate is slightly dependent on molecular weight.

The observation of a maximum in the crystallization rate with molecular weight has been clearly shown in molecular weight fractions of polyethylene[11,21,22]. However the slight dependence, for molecular weights which exceed that for the maximum in the case of poly(hexamethylene oxide) must be due to the limited range of molecular weights which has been analysed.

The nucleation theories developed for finite chains by Mandelkern *et al.*[23,24] show that the free energy for nucleus formation is dependent on molecular weight in the region of the left hand side in *Figure 8* at molecular weights below 10 000 and this fact takes into account the decreased rates of crystallization. However, on the right side of *Figure 8* the changes in rates cannot be assigned to the free energy of nucleation and rate changes with molecular weight have been attributed to the transport term or rate of growth[11,21].

Temperature coefficient

The crystallization rate can be expressed by the equation[25]:

$$\ln(\tau_{0.1})^{-1} = \ln(\tau_{0.1})_0{}^{-1} - \frac{E_D}{RT} - \frac{\Delta F^*}{RT_c} \tag{3}$$

where T_c is the crystallization temperature, ΔF^* the free energy for forming a stable nucleus and E_D is the transport term.

For the case of a cylindrical nucleus, it has been shown that:

$$\Delta F^* = \pi^{1/2}\xi^*\rho^{*1/2}\sigma_u^2 \tag{4}$$

where ξ^* and ρ^* are the critical dimensions of the nucleus and σ_u is the lateral interfacial free energy per structural unit.

The critical dimensions for a finite chain, x, are given by the expressions[23]:

$$\xi/2\left(\Delta f_u - \frac{RT}{x} + \frac{RT}{x - \xi + 1}\right) = 2\sigma_e - RT_c \ln\left(\frac{x - \xi + 1}{x}\right) \tag{5}$$

and

$$\rho^{*1/2} = 2\pi^{1/2}\sigma_u/[\Delta f_u - (RT_c/x) - RT_c/(x - \xi + 1)] \tag{6}$$

where σ_e is the interfacial free energy per unit area in the basal plane and Δf_u, the free melting energy, is given by:

$$\Delta f_u = \Delta H_u(T_m{}^0 - T_{\hat{c}})/T_m{}^0$$

In the limit of high molecular weights, equation (4) is reduced to the known expression[25]:

$$\Delta F = 8\pi\sigma_e^2\,\sigma_u \frac{(T_m{}^0)^2}{\Delta H_{\hat{u}}{}^2(T_m{}^0 - T_c)^2} \tag{7}$$

Analysing the experimental data according to the conventional manner, $\log(\tau_{0.1})^{-1}$ is plotted against $T_{\hat{m}}{}^2/\Delta T^2$ in *Figure 9*. All the analysed fractions give straight lines and the slopes of these lines vary with molecular weight; the lower the molecular weight, the lower the slopes are. Similar results have been described in different polymers. Variations in the slopes in *Figure 9* represent a change in the values of σ_e or σ_u or both.

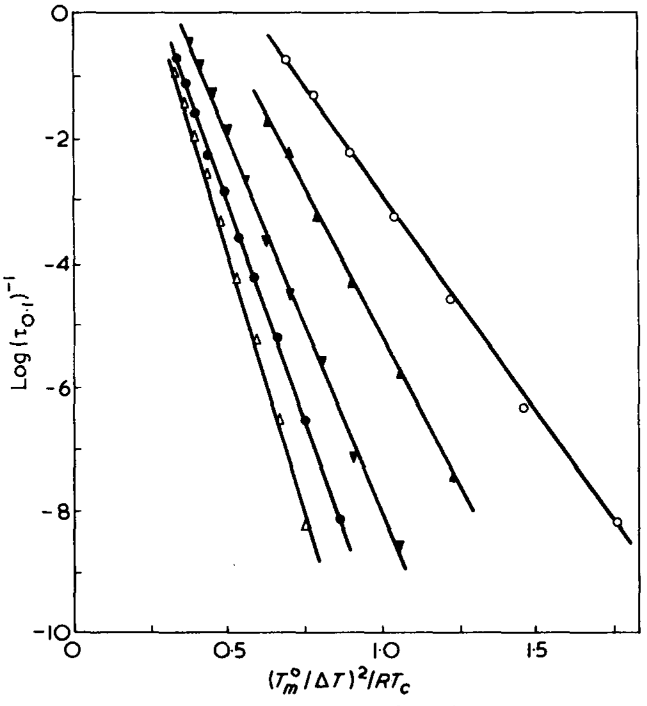

Figure 9 Plot of log $(1/\tau_{0.1})$ against $(T_m{}^0/\Delta T)^2$ $(1/RT_c)$ for indicated molecular weight fractions: ○, 2260; ▲, 3250; ▼, 8250; ●, 13 940; △, 35 500

Table 1 Basal interfacial free energies (σ_e cal/mol) for PHO molecular weight fractions

Molecular weight	T_m^0 (K)^a	$\sigma_e \sigma_u^2 \times 10^{-5}$	σ_e
2260	338	1.80	1800
3250	341	2.40	2400
8250	345	3.70	3700
13 940	345.5	3.80	3800
35 500	346.5	4.30	4300

^{a} Equilibrium melting temperatures[32]

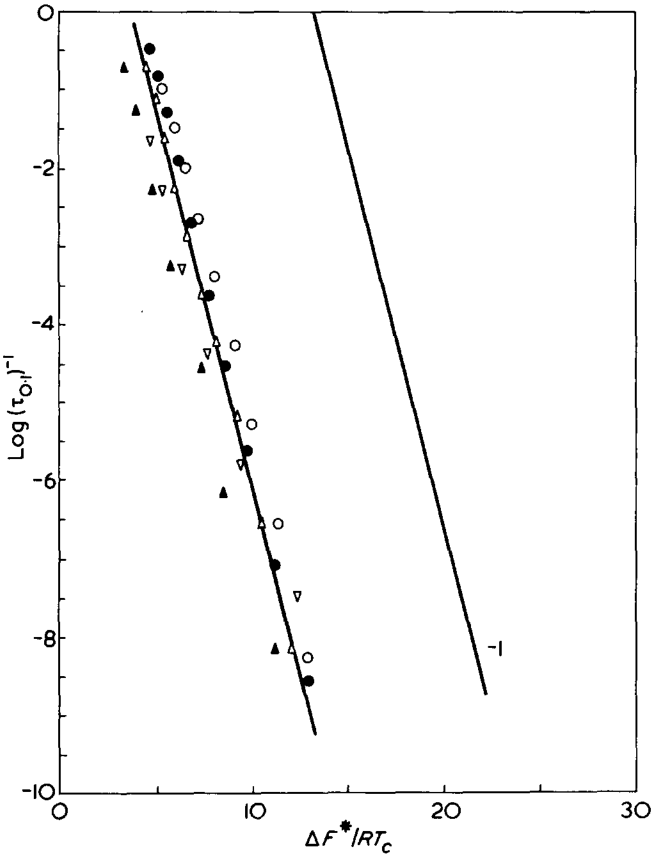

Figure 10 Plot of log $(1/\tau_{0.1})$ against $\Delta F^*/RT_c$ for indicated molecular weight fractions: ▲, 2260; ▽, 3250; ●, 8250; △, 13 940; ○, 35 500

If it is assumed that σ_u is constant, σ_u = 10 cal/mol, a value of σ_e is established for each molecular weight.

These values are indicated in *Table 1* and change from 4300 cal/mol to 1800 cal/mol in the molecular weight range from 2200 to 35 500. The value 4300 cal/mol for M = 35 500 compares quite well with the value of 4600 cal/mol for high molecular weight polyethylene, a value obtained from different kinds of experimental data[26–28].

The variation in σ_e with molecular weight has been shown in the analysis of polyethylene[22,29–31]. It has been assumed that the change of σ_e corresponds to the region of molecular weights in which there is a change in morphology in the crystallite. Fatou and Tinas[12] have demonstrated that this change is similar in the poly(decamethylene oxide). Only in the case of poly(ethylene oxide)[5] the dramatic decrease of σ_e with decreasing molecular weights has not been shown.

Analysis of the temperature coefficient according to equation (3) require exclusively the specification of $T_m{}^0$ and ΔH_u, without the need of establishing more or less arbitrary melting temperatures. For the case of poly(hexamethylene oxide), both parameters have been previously determined[32] and correspond to ΔH_u = 5700 cal/mol and T_m^0 = 346.5K, and ΔF^*, according to equation (4) can be calculated for each fraction and each crystallization temperature with the corresponding σ_e values. The plot of $\ln(\tau_{0,1})^{-1}$ vs. $\Delta F^*/RT_c$ as can be seen in *Figure 10* gives a unique straight line with slope 1 according to equation (3).

These results show that the crystallization process of poly(hexamethylene oxide) is governed by the nucleation of the system. In the analysis of the temperature coefficient of the crystallization which has been carried out, it has been assumed that the temperature coefficient is the same for both initiation and growth and this is a fairly common assumption. When the variation in the interfacial basal energy with molecular weight is stipulated, the phase transformation is described by the free energy for nucleation and this fact is general in the crystallization of polymers and independent of the mode which is stipulated for growing.

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