Crystallization of polyformals: 2. Influence of molecular weight and temperature on the morphology and growth rate in 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

(*Received* 10 *April* 1981; *revised* 27 *July* 1981)

The morphology and growth rates of crystallized molecular weight fractions of poly(1,3-dioxolane) covering the range M_n = 8800 to 120000 have been studied by polarized light microscopy. Two different supermolecular structures, dependent on molecular weight and crystallization temperature have been found. Spherulites are formed after rapid crystallization and a more disordered morphology is formed at the lowest undercoolings but there is a temperature region where both forms are observed. The disordered form appears first and a consecutive spherulitic growth takes place. The crystallization kinetics were analysed over the temperature range 10°C to 36°C. At crystallization temperatures lower than 15°–18°C, the growth rate is linear and only spherulites are found. In the temperature range from 18°C to 36°C a well defined break is observed in the growth rate but the spherulitic growth rate is always higher than that of the irregular form. The growth rate temperature coefficient was studied and the usual plots are not linear in the whole range of crystallization temperatures. For the high crystallization temperature region, the slope is about twice as great as the low crystallization temperature slope. This is the region where regular spherulites are formed. The comparison between dilatometric and growth rate data has shown that the overall rate and growth rate temperature coefficients are the same.

Keywords Crystallization; polyformals; poly(1,3-dioxolane); growth rate; morphology; spherulites

INTRODUCTION

In a previous paper[1], the crystallization kinetics of molecular weight fractions of poly(1,3-dioxolane) (PDOL) covering the range from $M_n = 8\,800$ to $M_n = 120\,000$ were studied by dilatometry. The main conclusions obtained are that when molecular weight fractions are used, no change in the Avrami exponent is found (the Avrami exponent is an integral value ($n = 3$) independent of molecular weight and crystallization temperature in the range from 10° to 40°C and that the overall rate temperature coefficient presents a break and two straight lines through the experimental data can be drawn which intersect at ~303K.

A much smaller slope is obtained from the line which represents the data for the lower crystallization temperatures, and the ratio of these slopes is two, leading to the conclusion[1] that the changes in slopes are related to a morphological transition.

The previous published results on the crystallization kinetics and morphology of PDOL are from Prud'homme *et al.*[2–4], who have shown, using only low molecular weight samples, that this polymer shows two phases when observed optically and when crystallization is conducted at low degrees of supercooling. In both optical phases, the inner phase is composed of disordered lamellae and corresponds to ovoids or hedrites and the outer phase is typically spherulitic. Moreover, for the low molecular weight fraction analysed ($M_n = 9400$) there is no break in the growth rate temperature coefficient, even though these authors found different Avrami exponents depending on the crystallization temperature.

Since there is a large effect of molecular weight and crystallization temperature[1] in this polymer, it is important to investigate the levels of crystallinity and the molecular structure of the lamellae crystallites and the organization of them into different levels of morphology, together with the measure of the growth rates of such supermolecular structures.

For these reasons, the main purpose of this paper is to study, extensively, the morphological properties of PDOL fractions and to analyse the crystallization kinetics by microscopy over a wide molecular weight range.

EXPERIMENTAL

Poly(1,3-dioxolane) was prepared by cationic polymerization, according to a previously described method[1]. The whole polymer was fractionated at 25°C in chloroform/hexane–ethanol mixtures. The number average molecular weights of the selected fractions were 8.8×10^3; 1.2×10^4; 2.5×10^4 and 1.2×10^5.

Microscopy studies were carried out using a Reichert polarizing microscope, Zetopan-pol, equipped with a 35

0032–3861/82/030379–06$03.00

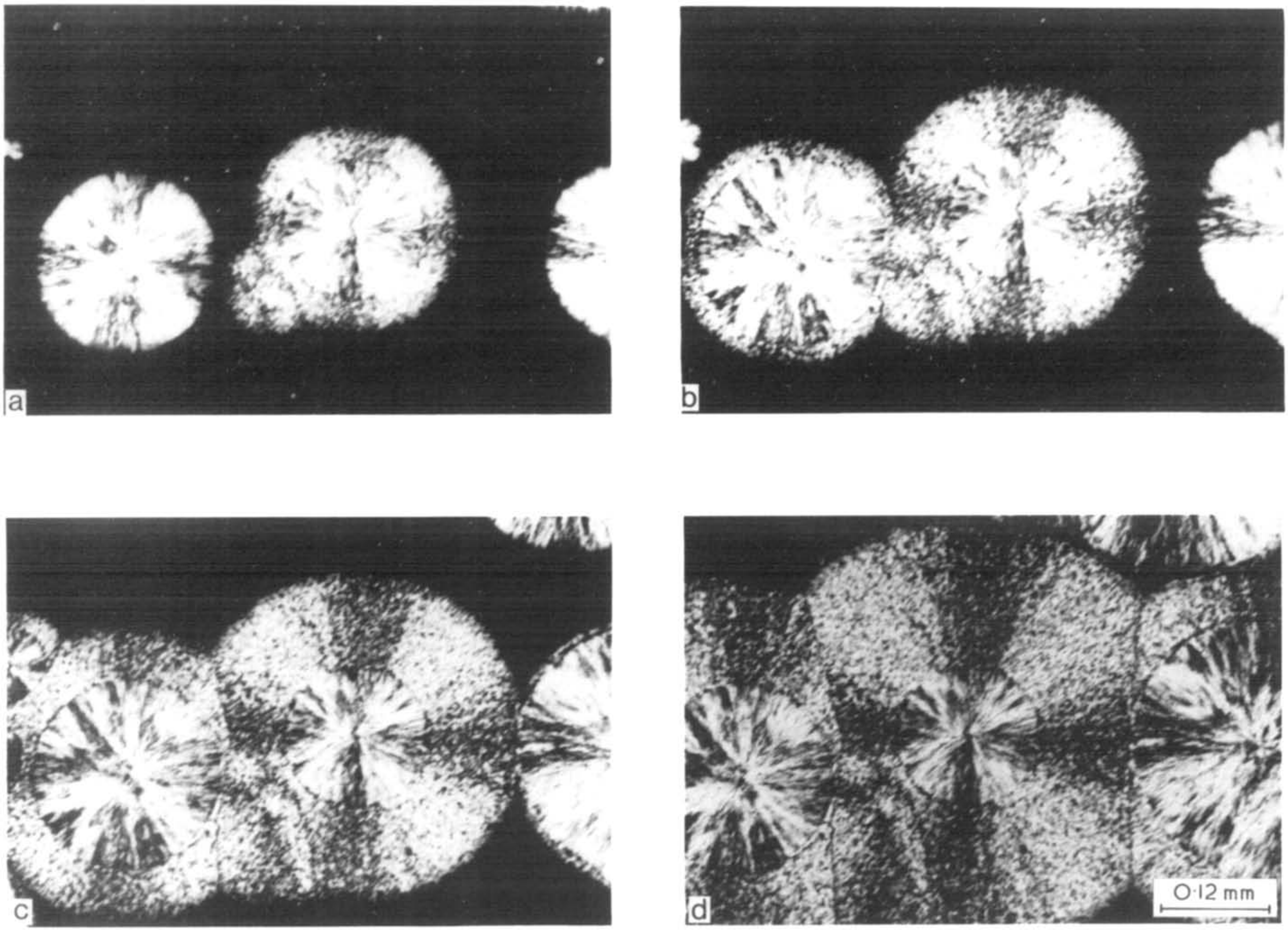

Figure 1 Polarized light photomicrographs of PDOL molecular weight fraction, M_n = 120 000, crystallized at 32°C. (a) At 44 min; (b) at 49 min; (c) at 56 min and (d) at 68 min

mm camera. The samples were maintained at the desired temperatures using a Mettler hot stage. Two types of experiments were carried out. First, the fractions were quenched from the melt in liquid nitrogen, or at temperatures of −40°C and 0°C. In another set of experiments the fractions were crystallized isothermally in the temperature range 10°C to 40°C, depending on molecular weight. Growth rate measurements were obtained by direct reading with a micrometer eyepiece or from the obtained photographs.

The SALS studies were carried out with an instrument similar to that described by Stein[5] and the patterns were obtained at room temperature, after crystallizing or quenching the samples at different temperatures.

RESULTS AND DISCUSSION

Morphology

The crystallization of PDOL was followed by microscopy in a temperature range from 10°C to 40°C. In the high temperature range ($18 < T_c < 40$) the growth follows a determined path leading to two optically different structures, as was reported by Geil[6] and later by Prud'homme *et al.*[2-4] Initially, disordered structures grow radially and when these structures develop, the boundary between them and the melt is sharp and nicely circular. However, the usual Maltese cross is not so perfect as in regular spherulites and there is considerable local birefringence. In some cases a dendritic nature is apparent, similar to the one in poly(ethylene oxide)[7]. When this form (Phase I, according to Prud'homme *et al.*[2-4]) reaches a critical size or when this form impinges upon a regular spherulite (Phase II), only typical spherulitic structures are formed.

A typical example is shown in *Figure 1* for the crystallization of the fraction $M_n = 120\,000$ at 32°C at four different crystallization times, and similar behaviour is found for crystallization temperatures between 18°C and 40°C. For lower molecular weight fractions $M_n = 8\,800$ to $M_n = 12\,000$ the range of crystallization temperatures where both forms coexist is between 15°C and 36°C. The number of nuclei which are formed decreases when crystallization temperature increases, and the formation of the typical spherulites occurs at longer times. *Figure 2* shows a schematic diagram of the dependence of the formed supermolecular structures on molecular weight and crystallization temperature. Well-developed spherulites with the characteristic Maltese cross extinction patterns are formed under relatively rapid crystallization conditions (Region A), and the sizes of the spherulites are about 0.7 mm radius, depending on T_c.

At temperatures higher than 40°C (for $M_n = 120\,000$) and 36°C (for $M_n = 8\,800$) (Region C), only irregular structures are formed. In region B, both structures coexist, and the upper and lower limits are molecular weight dependent at the indicated isothermal crystallization temperatures.

Moreover, the SALS patterns have the characteristic

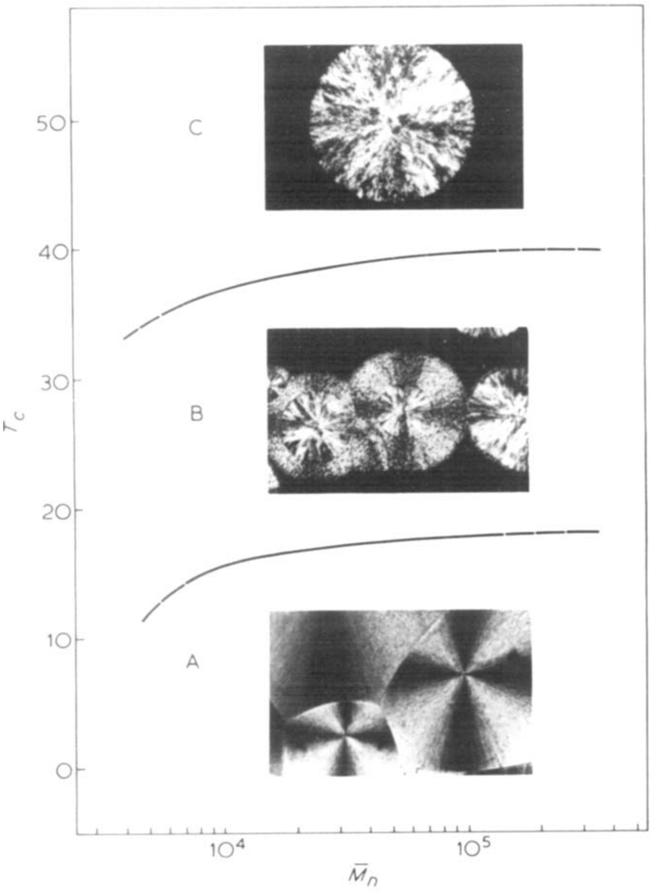

Figure 2 Schematic of the observed morphologies in PDOL fractions as a function of molecular weight and crystallization temperatures. Region A: Phase II; Region B: Phases I + II; Region C: Phase I

four-leaf clover appearance, similar to the one which has been observed in a variety of polymer systems, when the polymer is crystallized at very high undercoolings (*Figure 3*). However, the pattern becomes circularly symmetric with a quite different scattering structure when the polymer is crystallized at low undercoolings (*Figure 3b*).

Morphologically, the two forms differ by a larger extension of monocrystalline lamellae as is the case in hedrites. According to Prud'homme *et al.*[3] both structures I and II correspond to modified III and II crystals[8]. Modification II is orthorhombic and the unit cell dimensions are $a = 9.05$ Å, $b = 7.79$ Å and $c = 9.85$ Å with a crystalline density of 1.41 g cm^{-3}; modification III is hexagonal with unit cell dimensions of $a = b = 8.07$ Å, $c = 29.5$ Å and $\gamma = 120°$ with a crystalline density of 1.333 g cm^{-3}.

The crystal dimensions of both these modifications are very close and, for this reason the major differences between the two optical forms may be due exclusively to differences in superstructure.

Prud'homme *et al.*[4] have suggested a hedrite→oval→spherulite transition around 22°C. The appearance of high birefringence suggests the hedrite→oval transition, with the same order of crystallinity, and the subsequent growth leads to spherulites.

Formation of hedrites at high temperatures of crystallization or low undercoolings have been found in other related polyformals. Polyoxymethylene (POM) has been extensively analysed and different supermolecular structures have been found. Geil's early reports[9-10] indicated the presence of hedrites by slow crystallization together with structures with an oval shape. More recently, it has been shown[11,12] that when POM was isothermally crystallized from the melt, the crystallization occurred in the spherulitic form below 158°C while above this temperature hedrites, ovoids and spiral ovoids were obtained.

Although the spherulitic morphology was considered the universal mode of homopolymer crystallization, other morphological forms or supermolecular structures have been noted for different polymers. The spherulite–axialite transition in polyethylene has been analysed by Hoffman *et al.*[13] and, utilizing molecular weight fractions of linear polyethylene, four different morphological forms have been identified[14,15]. More recently, Maxfield and Mandelkern[16] have investigated the different forms that can be developed as a function of molecular weight and crystallization temperature.

However, it has been shown that different

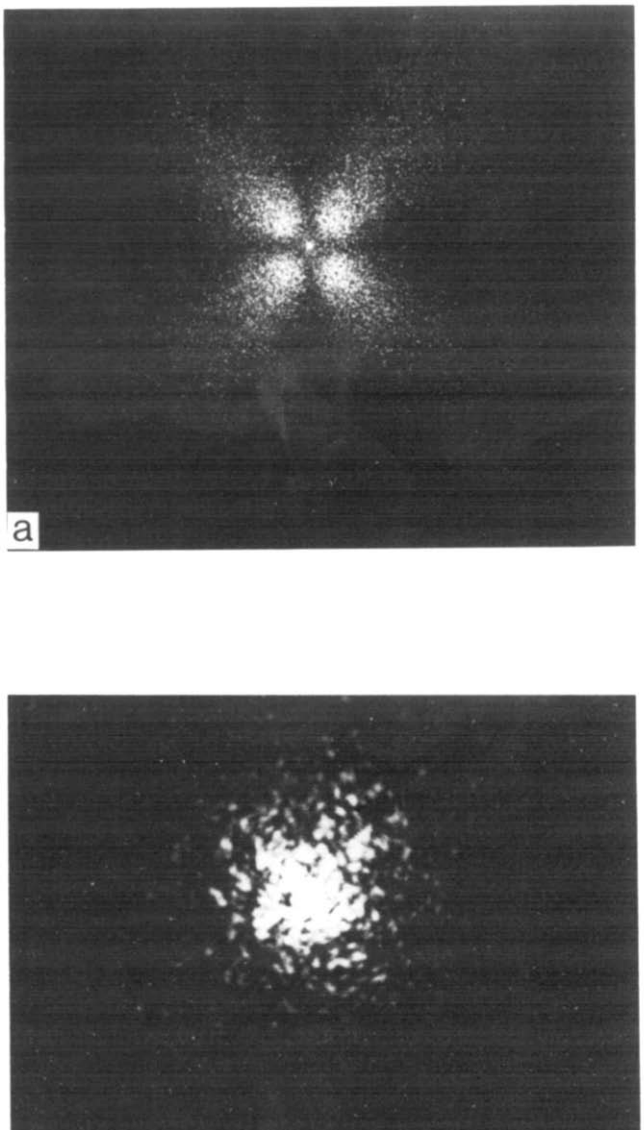

Figure 3 Hv small angle light scattering patterns for PDOL molecular weight fraction, M_n = 120 000; (a) rapidly quenched at −70°C; (b) crystallized at 30°C, for 96 h

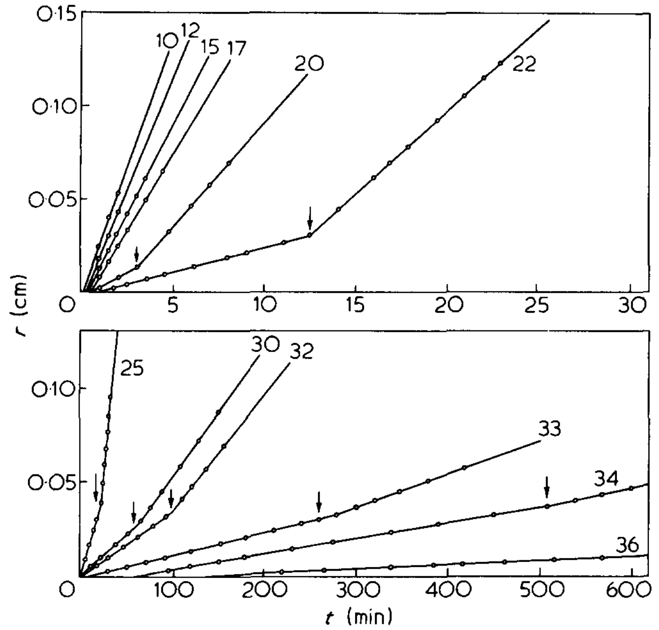

Figure 4 **Growth rates of PDOL molecular weight fraction (M_n = 1,20 000) at the indicated temperatures (in °C)**

morphologies can have the same degree of crystallinity and the differences are reflected in other thermodynamic quantities, such as the enthalpy of fusion. It is interesting to analyse the influence of this transition in the overall or growth crystallization rate, and this important point will be considered in the next section.

Growth rates

Quantitative rate data were obtained at different temperatures in the range from 10°C to 36°C, depending on molecular weight, and two apparently different behaviours have been found.

In general, at crystallization temperatures lower than 15°–18°C (the temperatures indicated in *Figure 2* for region A) the growth rate is linear and only spherulites are found over the complete time interval.

However, for crystallization temperatures in region B (T_c lower than 36°–40°C), a well defined break is observed in the growth rate curves (*Figure 4*), and the growth rate of structure II is always higher than that of structure I, although it has been reported[4] that the growth rate of II is, in all cases, slower than that of I. However, for the lowest molecular weight fraction ($M_n = 8800$) at high temperatures ($T_c \geqslant 30°C$), the plots of radius vs. time are only linear in the first part of the curve and the growth rate for structure I decreases with time. This is due to the impingement of the different growing species (very large in these cases) and structure II appears only for long enough times.

In the region where the two growth rates $G_{\rm I}$ and $G_{\rm II}$ can be measured, the ratio between $G_{\rm I}$ and $G_{\rm II}$ decreases when the crystallization temperature increases, after reaching a maximum at about 20°–22°C and in region C ($T_c \geqslant 40°C$) only straight lines are obtained when the rates are experimentally measurable, corresponding to the growth rates of structure I only.

The crystallization experiments by dilatometry[1] are in the temperature region where both optical structures I and II coexist, and the crystallization process is a continuous one and no knees or discontinuities are observed[4]. It can be concluded that the changes in superstructure are not correlated with a change in the isotherm shape or with a change in the degree of crystallinity.

However, the linear growth rate of spherulites is a nucleation-controlled process and can be expressed as[17]

$$\ln G = \ln G_0 - \frac{E_D}{RT} - \frac{\Delta F}{RT_c} \tag{1}$$

where G_0 is a constant, E_D is the activation energy for transport across the crystal–liquid interface, R is the gas constant, T_c the crystallization temperature and ΔF is the free energy required to form a nucleus of critical size. For the case of a two-dimensional growth nucleation process which involves the unimolecular deposition of chain units on an existing crystalline face, the critical conditions are[18]:

$$\begin{gathered} \Delta F^* = 2\sigma_u \xi^* \\ \xi^* = \frac{2\sigma_e - RT_c \ln[(x - \xi^* + 1)/x]}{\Delta f_u - RT_c/x} \end{gathered} \tag{2}$$

where σ_e and σ_u are the interfacial free energies per sequence as it emerges from the basal plane of the nuclei and the lateral interfacial energy, respectively, x is the repeating units per molecule and ξ^* is the number of units along the chain direction in the nucleus. Δf_u is the free energy of fusion per unit at T_c and it is given by $\Delta f_u = \Delta H_u (T_m^\circ - T_c)/T_m^\circ$.

At the limit of high molecular weights, ΔF is reduced to the known expression:

$$\Delta F = \frac{4\sigma_e \sigma_u T_m{}^\circ}{\Delta H_u \Delta T} \tag{3}$$

The equilibrium melting temperature, T_m°, and the heat of melting, ΔH_u, have been determined previously[19] and correspond to $T_m^\circ = 366$K and $\Delta H_u = 3700$ cal mol^{-1}. A previous analysis of the data, according to the conventional plot ln G against $T_m{}^\circ / T_c \Delta T$ is shown in *Figure 5*. In this Figure, the growth rates of Phase I and Phase II have been plotted in regions $G_{\rm I}$ and $G_{\rm II}$, respectively, when only one structure is formed. Between regions $G_{\rm I}$ and $G_{\rm II}$, the rates for the two consecutive growing structures are plotted.

However, there is a tendency at the lower crystallization temperatures to form straight lines with a slope which is approximately 0.4 of the slope in the high temperature region. It is possible to draw two straight lines through the experimental data which intersect at ~ 303K. All the fractions give, at the higher crystallization temperatures, straight lines with the same slopes. In this region, 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 from molecular weight.

By taking $\sigma_u = 370$ cal mol^{-1}, $\sigma_e = 13.350$ cal mol^{-1}, but if either a higher value of σ_u or a lower value of $T_m{}^\circ$ are taken, σ_e is lower. For $\sigma_u = 740$ cal mol^{-1}, σ_e is 6700 cal mol^{-1}. These values are identical with the values obtained from the analysis of the dilatometric data and are considerably higher than those reported by Prud'homme *et al.*[4].

An important conclusion at this point is that the overall rate of crystallization and the growth rate have the same

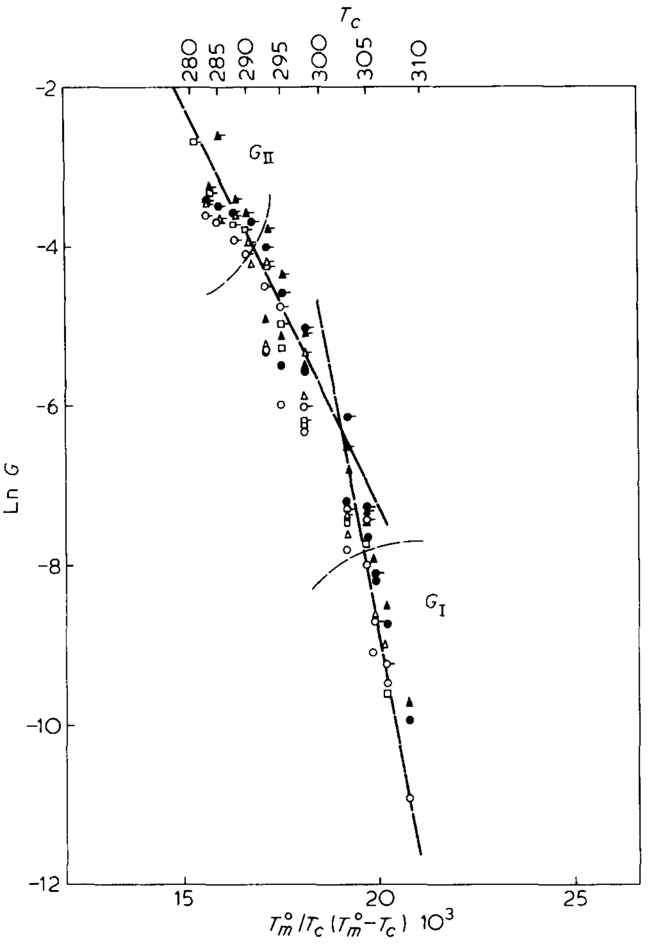

Figure 5 Plot of ln G against $T_m/T_c\ \Delta T$ for indicated molecular weight fraction: (○), 120 000; (△), 60 000; (●), 25 400; (▲), 12 000; (□), 8800. Points marked with a line correspond to growth rates of Phase II

temperature coefficient. This has been a fairly common assumption which has been used in the analysis of crystallization kinetics[20,21]. The comparison between our previous results on the overall rates of crystallization[1] and the growing rates analysed in this paper is experimental confirmation of this assumption.

With the obtained value for σ_e it is possible to calculate ΔF from equation (2) for finite chains, if the transport term E_D is introduced in this analysis, by calculation from the Williams–Landel–Ferry equation[22]. The ratio of the slopes is approximated to 0.5 (*Figure 6*).

It is important to comment on the breaks in the crystallization temperature coefficient. In a previous paper[1], the overall crystallization rates, obtained by dilatometry, present a break at about 30°C and the first conclusion was that the change in the slopes was related to the morphological transition.

Previously, breaks in the temperature coefficient of the overall crystallization rate were reported by Ergoz *et al.*[23] in polyethylene fractions. The slopes for the high molecular weights and the high temperature lower molecular weights are the same and they are almost twice as great as the low temperature low molecular weight slopes. Moreover, Hoffman *et al.*[24] measured growth rates of polyethylene and they observed that the temperature coefficient of the axialites was twice that of the coarse grained nonbanded spherulites. These results were explained in the Lauritzen[25] and Sanchez and Di Marzio[26] theories considering two limiting cases for the rate of growth normal to the substrate, one (Regime I) in which the growth step is allowed to sweep completely across the face of the crystal and a pause occurs before the next layer is nucleated. The rate of lateral growth is much faster than the nucleation rate and the net growth rate perpendicular to the crystal faces is proportional to the nucleation rate. A second case (Regime II) is where the new growth steps are allowed to nucleate before the previous layer has filled the substrate, and the growth rate will be dependent on nucleation rate and on the rate of lateral growth.

For these two cases, in terms of nucleation theory, the temperature coefficients of the growth rates differ by a factor of two. Maxfield and Mandelkern[16] have analysed the supermolecular structures of polyethylene fractions as a function of molecular weight and crystallization temperatures and they discussed the mechanistic explanations for the formation of different superstructures.

The ratio of the growth coefficients for the high to low temperature forms is not always two. In the case of polyoxymethylene, Pelzbauer and Galeski[11], for the growth model represented by two-dimensional surface nucleation, found values of $\sigma_e = 183$ and $95.5\ \mathrm{erg\ cm^{-2}}$ for the temperature regions of growth of spherulites and hedrites, respectively, and this means that the ratio of the temperature coefficient of the hedrites to spherulites is only one-half. For branched polyethylene[22], spherulites are observed at temperatures above and below the break, and the ratio of temperature coefficients is 0.25.

However, for PDOL, previous results from Prud'homme *et al.*[4] do not indicate any significant change in growth rate temperature dependence at the transition temperature. However the break obtained previously by dilatometry[1] and the present results show that this change is pronounced. In regime II, according to Hoffmann *et al.*[24], the multiple nucleation of a layer leads to

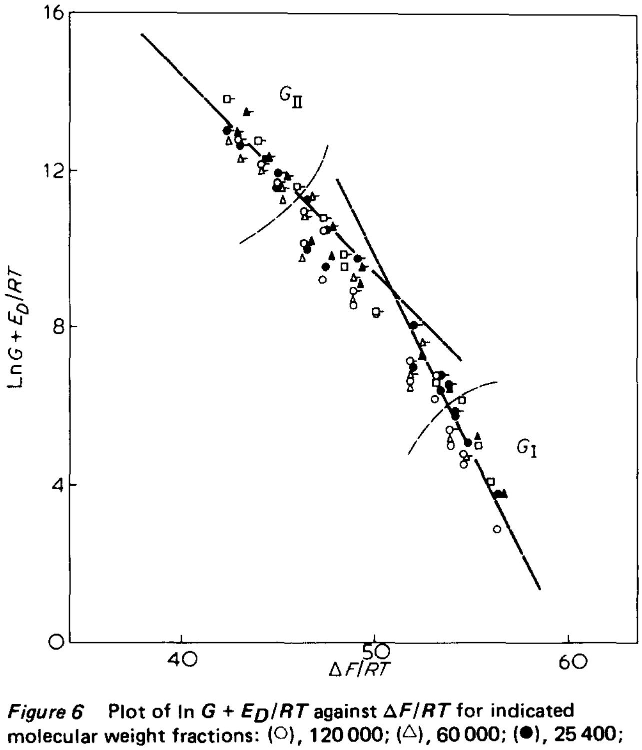

Figure 6 Plot of ln $G + E_D/RT$ against $\Delta F/RT$ for indicated molecular weight fractions: (○), 120 000; (△), 60 000; (●), 25 400; (▲), 12 000; (□), 8800. Points marked with a line correspond to growth rates of Phase II

spherulites, if these structures are formed as a consequence of the noncrystallographic branching of lamellae and in regime I a different structure can be expected. This theoretical approach, although it presents some limitations, and, especially as the influence of molecular weight is not considered, may be a reasonable explanation in the light of present available theoretical developments.

In summary, the crystallization of PDOL takes place with different supermolecular structures which are dependent on crystallization temperature and molecular weight. However, there is no change in the Avrami exponent, and although these exponents cannot be given a unique interpretation, a two-dimensional growth is considered in both cases. Moreover, the comparison between dilatometric and growth rate data has shown that the overall rate and growth rate temperature coefficients are the same, but a different coefficient (approximately half) is found in both cases at the lowest crystallization temperatures, where spherulites are predominantly formed. A rather wide morphological transition at $T_c \doteqdot 303$K is found from the break in the rate temperature coefficient.

REFERENCES

1 Alamo, R., Fatou, J. G. and Guzmán, J. *Polymer* 1982, **23**, 374

2 Neron, M., Tadif, A. and Prud'homme, R. E. *Eur. Polym. J.* 1976, **12**, 605

3 Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1619

4 Archambault, P. and Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 35

5 Stein, R. S. 'New methods of polymer characterization', B.Ke. 1964, J. Wiley–Interscience, New York

6 Geil, P. H. 'Polymer Single Crystals' R. E. Krieger, Hemtington, N.Y., 1973

7 Price, F. P. and Kilb, R. W. *J. Polym. Sci.* 1962, **57**, 395

8 Sasaki, S., Takahashi, Y. and Tadokoro, H. *J. Polym. Sci., Polym. Phys. Edn.* 1972, **10**, 2363

9 Geil, P. H. 'Growth and perfection of crystals' (Eds. R. H. Doremus, B. W. Roberts and O. Turnbull), 1958, Wiley, New York

10 Geil, P. H. *J. Polym. Sci.* 1960, **47**, 65

11 Pelzbauer, Z. and Galeski, A. *J. Polym. Sci. C* 1972, **38**, 23

12 Galeski, A. and Kryszewski, M. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 471

13 Hoffman, J. D., Frolen, L. J., Ross, G. S. and Lauritzen, J. I. *J. Res. Nat. Bur. Stand.* 1975, **A-79**, 671

14 Go, S., Prud'homme, R., Stein, R. S. and Mandelkern, L. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 1185

15 Mandelkern, L., Go, S., Peiffer, D. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1189

16 Maxfield, J. and Mandelkern, L. *Macromolecules* 1977, **10**, 1141

17 Mandelkern, L. 'Crystallization of Polymers', 1964, McGraw-Hill, New York

18 Mandelkern, L., Fatou, J. G. and Howard, C. *J. Phys. Chem.* 1965, **69**, 956

19 Alamo, R., Fatou, J. G. and Guzmán, J. (unpublished results)

20 Marco, C., Fatou, J. G. and Bello, A. *Polymer* 1977, **18**, 1100

21 Marco, C., Fatou, J. G., Bello, A. and Blanco, A. *Polymer* 1979, **20**, 1250

22 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701

23 Ergoz, E., Fatou, J. G. and Mandelkern, L. *Macromolecules* 1972, **5**, 147

24 Hoffman, J. D., Frolen, J. L., Ross, G. S. and Lauritzen, J. I. *J. Res. Nat. Bur. Stand., A*, 1975, **79**, 671

25 Lauritzen, J. I. *J. Appl. Phys.* 1973, **44**, 4353

26 Sanchez, I. C. and Di Marzio, E. A. *J. Res. Nat. Bur. Stand., A*, 1972, **76**, 213

27 Pakula, T. and Kryszewski, M. *Eur. Polym. J.* 1976, **12**, 47