Crystallization regimes in poly(3,3-dimethylthietane) fractions

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Overall crystallization rates of poly(3,3-dimethylthietane) fractions ranging in molecular weight from 6.5×10^3 to 1.04×10^5 have been analysed over the temperature range from -30 to 7°C. Kinetic analysis of the temperature coefficient shows that this polymer presents all three regimes of crystallization. The ratios of the temperature coefficients for Regime I to Regime II and of Regime III to Regime II are close to the theoretical value of 2. The transitions occur at an undercooling of 15–16°C for Regime I–Regime II and $\Delta T = 23$–26°C for Regime II–Regime III.

(Keywords: polysulphides; poly(3,3-dimethylthietane); crystallization kinetics; regimes)

INTRODUCTION

The crystallization kinetics and the temperature coefficient for this process have been extensively studied. An impressive body of experimental overall crystallization kinetics data from the melt and rates of growth for a variety of polymers have been accumulated. It has been also shown that the overall rate and the growth rate, in those cases in which both data are known, present the same temperature coefficient[1,2]. Most polymers follow a single straight line behaviour when analysing this coefficient. However, a very important observation is related to the existence of breaks or transitions in the temperature coefficient when either overall[3] or growth rate data[4] are examined.

The net growth rate has been analysed as a function of the relative values of the nucleation rate and of the lateral growth rate. Two extreme cases were considered for the growth on a substrate for low molecular weight substances by Hillig[5]. These cases have been adapted to polymers and named Regime I and Regime II[4,6–8]. In Regime I, the growth step is allowed to sweep across the face of the crystal and a pause occurs before the next layer is nucleated. The nucleation rate is thus slower than the rate of lateral growth. For Regime II new growth steps are allowed to nucleate before the previous layer has filled the substrate. Thus, the nucleation rate is higher than the lateral growth rate and multiple nucleation occurs, and the rate is thus dependent on both nucleation and growth. Since the temperature coefficient of the growth rate will be dominated primarily by the nucleation rate, it has been shown that the temperature coefficients for these two cases differ by a factor of two. However, this analysis is very formal and does not require the specification of the nucleus and no assumptions are needed with respect to the nature of the interfacial region. Experimental confirmation of the transition of one regime to another was reported for polyethylene, from microscopic growth data[4], and from overall rate data[3]. Thus, the observation of a break or a transition in the temperature coefficient does not depend on the experimental method that is used. Only another few polymers show these two regimes, poly(1,3-dioxolane)[1], poly(L-lactic acid)[9], i-polypropylene[10] and poly(ethylene oxide)[11–13].

More recently, the development of a break or transition at high undercoolings was observed in *cis*-1,4-polyisoprene[14] and formulated theoretically[15]. In this formulation, when the undercooling increases, several nuclei are formed on a single layer and the crystallization takes place on both sides of the nuclei, in the niches that remain among them. When the niches attain a length comparable to the width *a* of each element, it has been named Regime III. Regime I and Regime III have exactly the same temperature dependence for the growth rate. Examples of transition from Regime II to Regime III correspond to i-polypropylene[16,17], poly(oxymethylene)[15,18], *cis*-1,4-polyisoprene[19], poly(3-hydroxybutirate)[20] and poly(*p*-phenylene sulphide)[21]. However, there is no published experimental evidence for the existence of the three regimes in the same polymer, probably due to the limited domains of crystallization temperatures which have been used in most of the analysed polymers. For polyethylene, Regime III has been inferred with the use of two low temperature growth estimates[15,22]. The first case in which the three regimes has been observed corresponds to the analysis, based on growth rates, of *cis*-1,4-polyisoprene[23].

In this work, we report the results obtained on the overall crystallization rate of poly(3,3-dimethylthietane) (PDMT) fractions ranging in molecular weight from 6.5×10^5 to 1.04×10^5 over the temperature range from -30 to 7°C. The melting temperature and the heat of fusion were previously determined for this polymer[24]. Although the crystal structure of PDMT is still unknown, the wide angle X-ray patterns show a crystalline repeat distance of about 4.85 Å. We were also interested in analysing the factors that determine the temperature of

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the transitions among the three regimes, and providing experimental confirmation for them. Moreover, we report on the suitability of this analysis for the overall crystallization rates which yield comparable information to the analysis of growth rates of spherulites or other supermolecular structures.

EXPERIMENTAL

Poly(3,3-dimethylthietane) was prepared by anionic polymerization in tetrahydrofuran solutions of dimethyl thietane at low temperature (−78°C). The monomer was prepared by the method described by Searles *et al.*[25] and purified by the usual means[26]. The initiators were butyl lithium, to obtain the low molecular weight samples ($M_n = 6.5 \times 10^3$ and 2.3×10^4), and sodium naphthalene for the highest molecular weight sample ($M_n = 1.04 \times 10^5$). The whole polymer was dissolved in benzene and precipitated with methanol. The procedure was repeated several times and the precipitated product was isolated by filtration and dried in vacuum at 50°C for 24 h.

The ^{1}H n.m.r. spectrum was determined at 100 MHz in deuterated chloroform with tetramethylsilane as internal reference. The spectrum showed two absorptions, a single peak at 1.05 ppm and another at 2.65 ppm, due to the methyl and the methylene groups, respectively. The intensity ratio was 6:4, which corresponded to the structural unit. The off resonance ^{13}C n.m.r. spectrum showed three absorptions, a single peak at 1.57 ppm, a triplet at 1.98 ppm, and a quadruplet at 1.15 ppm, due to the tetrasubstituted carbon, the methylene groups and the methyl groups, respectively.

Number-average molecular weights were measured in Mechrolab 502, a Hewlett–Packard membrane osmometer, for the higher molecular weight samples, and a Knauer vapour pressure osmometer for the lower molecular weight sample (in tetrahydrofuran solutions at 25°C).

The polymerization at −78°C shows the main characteristics of living polymerization without transfer and termination reactions, and samples have a low polydispersity as shown by gel permeation chromatography (g.p.c.) analysis. For the fractions $M_n = 6.5 \times 10^3$ and 1.04×10^5, the ratio M_w/M_n is 1.3 and for the fraction $M_n = 2.3 \times 10^4$, this ratio is 1.1.

Crystallization kinetic studies were carried out using dilatometric techniques previously described[27]. The samples were previously melted at 40°C for 15 min and then were transferred to a bath at the desired crystallization temperature (controlled to less than 0.01°C). Dilatometric measurements were carried out in the range −30 to 7°C. The dilatometer heights were used to calculate the specific volume, and the degree of transformation and the degree of crystallinity, assuming additivity of the specific volumes of the amorphous and crystalline parts, were calculated from the specific volume. The relationship for the specific volume of the amorphous material was determined in the melted state and is given by

$$\bar{v}_a = 0.935 + 5.070 \times 10^{-4}\, T$$

where T is the temperature (°C).

The specific volume of the crystalline polymer was calculated from the relationship between the actual crystallinity, calculated from calorimetric measurements, and the specific volume of the polymer at different temperatures. This relation is given by

$$\bar{v}_c = 0.850 + 3.594 \times 10^{-4}\, T$$

RESULTS AND DISCUSSION

The influence of crystallization temperature on the time scale of the crystallization process in PDMT is very pronounced. *Figure 1a* shows the plot, on a logarithmic scale, of the time required for 50% of the transformation to develop as a function of the temperature. In order to compare the rates at the same undercooling, *Figure 1b* shows the results of $(\tau_{0.5})^{-1}$ vs. ΔT. This last parameter has been obtained when the equilibrium melting temperature for each fraction has been considered. The values of the melting temperatures depend on molecular weight and on the crystallization conditions, and the equilibrium melting temperatures can be obtained by extrapolation of the experimental relationship between the observed melting temperature (T_m) and the crystallization temperature (T_c) to the line representing the relationship $T_m = T_c$, as has been suggested previously[28,29]. The extrapolated equilibrium temperatures change from 281 to 291 K[30], and these are the values that have been used in the following analysis (*Table 1*).

When the overall rates are compared on the same undercooling, the rates decrease with increasing molecular weight. All the fractions show a maximum in the rate. Although the fractions exhibit a tendency towards the known bell-shaped curve, the two highest molecular weight fractions exhibit two discontinuities at $\Delta T = 26$–28 and 15–16°C, respectively. The lowest molecular weight fraction, $M_n = 6.5 \times 10^3$, shows only one discontinuity at $\Delta T = 14$–16°C.

An important observation is that these curves resemble those reported on growth rates[4,23] which were related to changes in regimes. That is, the curves exhibit breaks corresponding to Regime I–Regime II and Regime II–Regime III transitions, when overall rates are considered. This means that both type of data, microscopic and dilatometric, yield the same conclusions.

On the other hand, the overall crystallization rate is described, when the nucleation process involves the unimolecular deposition of chain units on an already existing crystalline face, by the general equation[31,32]:

Table 1 Slopes of the crystallization regimes

M_n	T_m° (K)	Regime I (× 10^4)	Regime II (× 10^4)	Regime III (× 10^4)	Ratio of I/II	Ratio of II/III
6.5×10^3	281.0	4.0	2.2	4.5	1.8	2.0
2.3×10^4	290.5	4.3	2.4	5.3	1.8	2.2
1.04×10^5	291.0	4.6	2.6	5.5	1.8	2.1

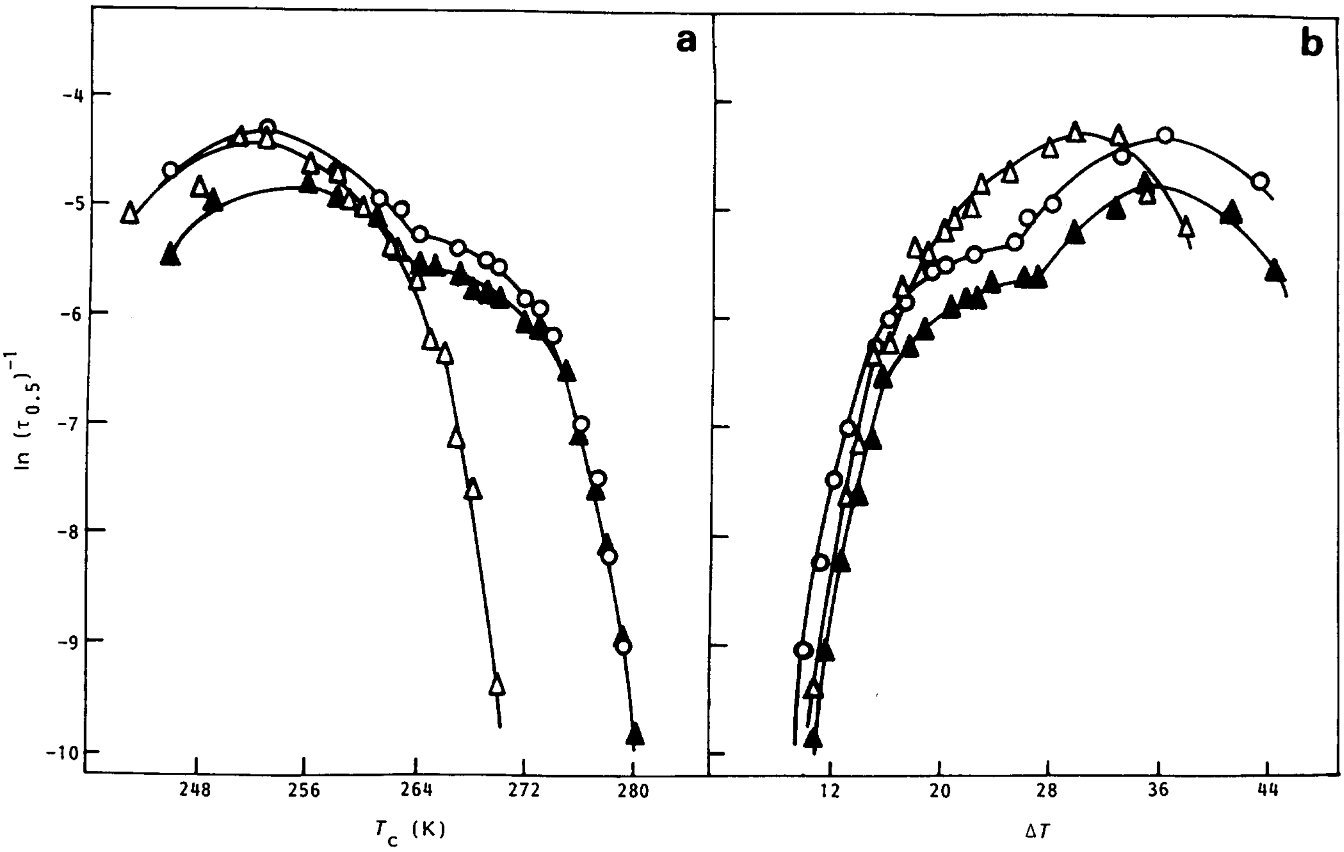

Figure 1 Plots of $\ln(\tau_{0.5})^{-1}$ against T_c (a) and ΔT (b) for PDMT at various molecular weights: △, $M_n = 6.5 \times 10^3$; ○, $M_n = 2.3 \times 10^4$; ▲, $M_n = 1.04 \times 10^5$

$$\ln(\tau_i)^{-1} = \ln(\tau_i)_0^{-1} - E_D/(RT_c) - K_2 T_m^\circ/(T_c \Delta T) \quad (1)$$

where T_m° is the equilibrium melting temperature, τ_i is the time required to obtain $i\%$ of the transformation, $(\tau_i)_0$ is a pre-exponential factor, E_D is the activation energy for transport across the crystal–liquid interface, K_2 is a constant and $\Delta T = T_m^\circ - T_c$. Equation (1) has the same form as the growth rate equation[31].

According to equation (1), a plot of $\ln(\tau_{0.5})^{-1}$ or $\ln(\tau_{0.5})^{-1} + E_D/(RT_c)$ against the appropriate temperature variables should give a straight line for a given value of K_2. The results obtained for PDMT in the simplest plot, $\ln(\tau_{0.5})^{-1}$ against $T_m^\circ/(T_c \Delta T)$, are shown in *Figure 2*.

A striking fact from *Figure 2* is that for the higher molecular weights, 1.04×10^5 and 2.3×10^4, it is possible to draw three straight lines through the experimental data that correspond to regime transitions. The lowest molecular weight fraction shows only two straight lines. The first conclusion from this behaviour is the importance of the molecular weight on the existence of the crystallization regimes.

Moreover, each segment of the straight lines would yield a slope and intercept, and the supercooling at which the change of the slopes takes place can be determined. The break for the Regime I–Regime II transition corresponds to $\Delta T = 15$–16°C, and for the Regime II–Regime III transition it corresponds to $\Delta T = 23$–26°C, in those cases where the change of slopes is observed. These values agree quite well with the undercoolings at which the discontinuities in the rate curve were detected (*Figure 1b*).

The existence of breaks in the temperature coefficient has been described when either overall[3] or growth rate data[4] were examined in polyethylene. Moreover, in previous kinetics studies with poly(1,3-dioxolane)[1,33] the results obtained from measurements of growth rate of the supermolecular structure and the overall crystallization rate give identical values for the break temperature and two straight lines can be drawn in both cases. The main conclusion was that both the overall rate and the growth rate present the same temperature coefficient. A different coefficient, approximately half, was found in both cases at the lowest crystallization temperatures and it was recognized as corresponding to a regime transition.

More recently, the results obtained for different polymers by the two usual methods, dilatometry and microscopy, have been analysed[14]. The temperature for the Regime I–Regime II transition is identical when both overall and growth rate data are considered.

It is important to note that it is not mandatory to use growth rates to obtain conclusions on changes of the temperature coefficient. Linear growth rates and overall crystallization rates are of equal importance, and both data yield the same information about breaks in the temperature coefficient, and the temperature of demarcation for these breaks is the same, irrespective of the kinetic method used. It is not necessary to analyse crystallization kinetics by direct visualization of spherulites or other superstructures, which are usually only formed in a restricted molecular weight range[34].

Another important observation is that the value of the undercooling where the breaks take place with a change in the slope is not a universal parameter and it depends upon the polymer structure. Thus, in PDMT, the delimitation between Regimes I and II occurs at $\Delta T_{\text{I–II}} = 15$–16°C and between Regimes II and III at $\Delta T_{\text{II–III}}$

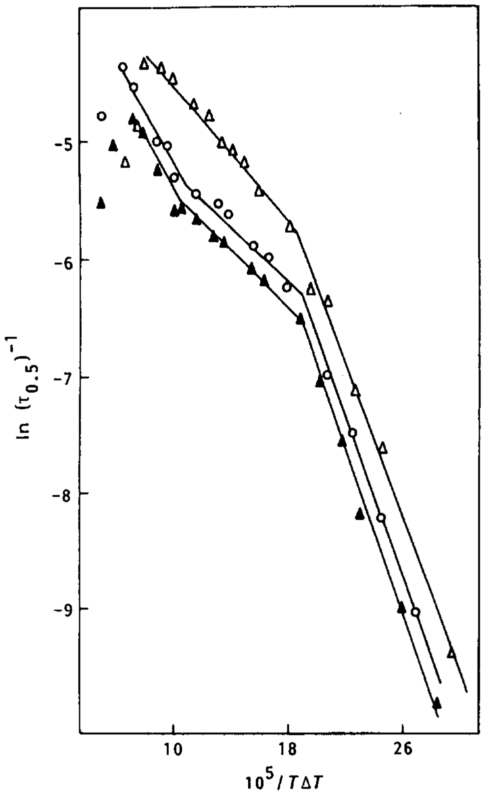

Figure 2 Plot of $\ln(\tau_{0.5})^{-1}$ against $1/(T_c\Delta T)$ for PDMT at various molecular weights: △, $M_n = 6.5 \times 10^3$; ○, $M_n = 2.3 \times 10^4$; ▲, $M_n = 1.04 \times 10^5$

= 23–26°C. Although these values are not too different when compared with those found for polyethylene, this fact can be considered fortuitous because there are various systems where the breaks have been observed at different undercoolings. *Table 2* shows these values. It is important to note the following remarks. For the case of polyethylene, the break temperature for the Regime II–Regime III change has been postulated with the use of two low temperature growth estimates[15,22]; for polyoxymethylene the only transition reported is Regime II–Regime III, and the transition Regime I–Regime II has been calculated; poly(1,3-dioxolane), poly(ethylene oxide) and poly(L-lactic acid) present only the Regime I–Regime II transition and poly(*p*-phenylene sulphide) only a Regime II–Regime III transition. Therefore, *cis*-1,4-polyisoprene and our data on PDMT are the only cases where the three regions have been delimited.

Molecular weight may influence the delimitation of the regimes. One point is the temperature or undercooling at which the break occurs. Analysis of data for polyethylene and poly(ethylene oxide) has shown that the undercooling at which the breaks take place is practically independent of molecular weight, and only with the lower molecular weight is there an increase in the undercooling[13]. The invariance of the undercooling at the break with molecular weight has been found also in PDMT. Only for the two lowest molecular weight fractions is the undercooling at the break 1 or 2°C higher than that for the higher molecular weight fractions. However, this invariance is not shown in other materials, where it has been reported that the transition from Regime II to Regime III presents an elevation in the transition temperature of 13°C when molecular weight changes by a factor less than two[23].

The previous analysis has neglected the influence of the transport contribution, as embodied in the term E_D in equation (1). This term has been used in kinetics by taking arbitrary values, by calculating E_D from the Williams–Landel–Ferry (WLF) theory or by taking other approximations. These approximations have been widely analysed[35]. The transport term can also be expressed in the form derived from the free volume theory according to the Vogel equation[36], and thus the transport term is given by

$$E_D/(RT_c) = B/(T_c - T_\infty) = B/(T_c - T_g + C_2) \qquad (2)$$

where B and C_2 are constants, T_g is the glass transition temperature and T_∞ is the temperature at which the viscosity is infinite. The transport values common to many polymers are given by $T_\infty = T_g - 30$ K, with a value of B about 750 cal mol^{-1} (ref. 8), and these have been the values that we have used for analysing the PDMT data, where T_g changes from 119 to 225 K for the molecular weight range analysed. The linearization of the lower temperature data, in the maximum rate region, has been obtained with a good correlation coefficient.

Figure 3 shows the relation in $(\tau_{0.5})^{-1} + B/(T_c - T_\infty)$ vs. $T_m^\circ/(T_c\Delta T)$ for the three fractions. It is evident that the introduction of the transport term shows the existence of a smooth transition from Regime I to Regime II and from Regime II to Regime III even for the lowest molecular weight fraction. These transitions were not apparent for this case in *Figure 2*. Moreover, the linearization of the points at the highest undercoolings, in the region of the maximum for the crystallization rates, is apparent. However, the breaks or transitions for the two highest molecular weight fractions take place at the same undercoolings which were obtained from *Figure 1*.

The corresponding slopes obtained by fitting the experimental points are given in *Table 1*. One of the conclusions from *Table 1* is that the ratio of the slopes from Regime I to Regime II is close to two, as expected from theory. Moreover, the ratio of the slopes from Regime II to Regime III is near 0.5, as is also expected. However, the absolute values, in both cases, seem to increase with molecular weight. As is known[31], the slope is related to the product of the basal and the surface interfacial energies.

In summary, we have found that PDMT presents two breaks in the temperature coefficient when the overall crystallization rate is analysed, and these are related to the three regimes of crystallization. The ratios of the slopes of Regime I to Regime II and of Regime III to Regime II are close to the theoretical values of 2. Finally,

Table 2 Values of ΔT for the delimitation of regimes

Polymer	I–II	II–III	Ref.
Polyethylene	16	23 (pred.)	15, 22
Polyoxymethylene	23 (calc.)	40	15, 18
Cis 1,4 polyisoprene	54	66	19, 23
Poly(L-lactic acid)	4	–	9
i-Polypropylene	56	48	10, 16, 17
Poly(ethylene oxide)	24	–	11–13
Polydioxolane	33	–	1
Poly(*p*-phenylene sulphide)	–	107	21
Poly(3,3-dimethyl thietane)	15–16	23–26	This study

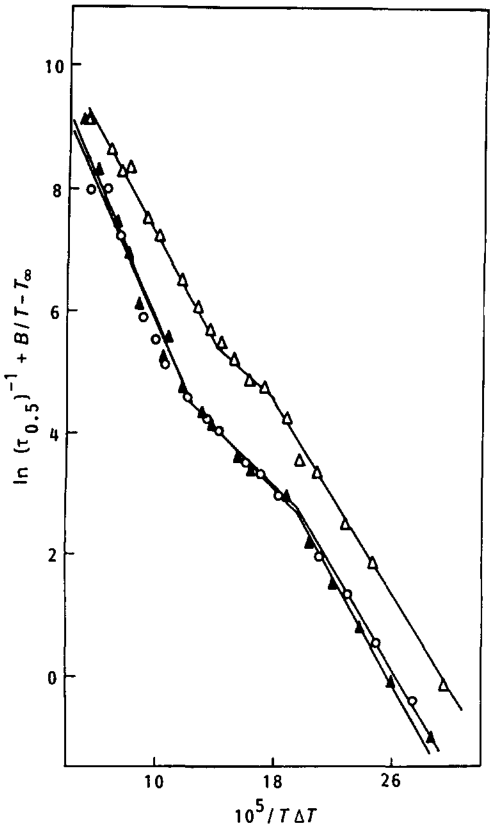

Figure 3 Plot of $\ln(\tau_{0.5})^{-1}+B/(T_c-T_\infty)$ against $1/(T_c\Delta T)$ for PDMT in Regimes I, II and III, for $B=750$ cal mol^{-1} and $T_\infty=T_g-30$ K, at various molecular weights: △, $M_n=6.5\times10^3$; ○, $M_n=2.3\times10^4$; ▲, $M_n=1.04\times10^5$

it must be pointed out that the analysis of the overall crystallization rate yields the same information as studies on growth rates of other polymers.

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