

Crystallization kinetics of poly(L-lactic acid)

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The morphology and crystal growth of poly(L-lactic acid), PLLA have been studied from the melt as a function of undercooling and molecular weight using hot stage microscopy. Attention has been given to the application of growth rate equation on the growth rate data of PLLA and thus various nucleation parameters have been calculated. The criteria of Regime I and Regime II types of crystallization has been applied for the evaluation of substrate lengths.

Keywords Kinetics; morphology; crystallization; nucleation parameters; poly(L-lactic acid); growth rate

INTRODUCTION

The effect of molecular weight on crystallization rate of polymers has been the subject of many papers¹⁻⁶. Not much work has been done in the past on the crystallization of lactide polymers. According to the recent formulation of kinetic theories⁷⁻⁹ the expression for the growth rate of a linear polymer crystal with chain folds is given by:

$$G = G_0 \exp\left[\frac{-u^*}{R(T_c - T_\infty)}\right] \exp\left[\frac{-Kg}{T_c \Delta T f}\right] \quad (i)$$

where Kg is the nucleation constant, T_c , the crystallization temperature; ΔT , the undercooling $T_m^\circ - T_c$; f , the factor $\frac{2T_c}{T_m^\circ + T_c}$ that accounts for the change of heat of fusion, Δh_f as the temperature is decreased below T_m° ; u^* , the activation energy for transport of segments to the site of crystallization; R , the gas constant, T_∞ , the hypothetical temperature where all the motion associated with viscous flow ceases and G_0 , the front factor. It has been shown⁹ that the above equation can be used to fit data on a number of polymers such as nylon-6, poly(tetramethyl *p*-silphenylene) siloxane, and isotactic polystyrene crystallized from the melt over a wide range of temperature with considerable accuracy.

Two types of crystallization behaviour namely regime I and regime II were observed in polymers. Growth rate, G is a function of i , surface nucleation rate, the rate at which the nucleus is formed and g , the velocity with which the surface nucleus spreads on the crystal surface. When the nucleation rate, i , is very small compared to g , then a single nucleus completes one layer of thickness, b and length L before another nucleus is formed, resulting in regime I type of crystallization. However, when the nucleation rate, i , is high and it spreads slowly at the velocity, g , then multinucleation occurs before the completion of one layer¹⁰; this type of crystallization is

called regime II. Accordingly the nucleation parameter Kg can have two different values:

$$Kg_I = \frac{4b\sigma_e T_m^\circ}{\Delta h_f k} \quad \text{regime I} \quad (ii)$$

$$Kg_{II} = \frac{2b\sigma_e T_m^\circ}{\Delta h_f k} \quad \text{regime II} \quad (iii)$$

where b is the layer thickness; σ_e , lateral surface energy σ_e , fold surface free energy; Δh_f , heat of fusion per unit volume and k , the Boltzmann constant.

A number of polymers (e.g.) poly(chlorotrifluoroethylene) conform to regime I at high temperatures while others (e.g.) isotactic polystyrene crystallize entirely in regime II⁸. Polyethylene in the intermediate molecular weight region ($M_w = 3 \times 10^4$ to 6.3×10^4) undergoes a sharp transition at 127°C from regime I to regime II¹¹. Below 127°C spherulites were formed and they grow according to regime II kinetics. Above 127°C axialities form which conform to regime I kinetics.

The main objective of our investigation was to determine the nucleation constants for the growth of poly(L-lactic acid), PLLA crystals from the melt as a function of undercooling and molecular weight. Attention has been given to the application of growth rate equation on the growth rate data of PLLA obtained in this study and to the application of criteria of regime I and regime II for the evaluation of substrate lengths.

EXPERIMENTAL

Sample preparation

Samples of different molecular weight were obtained by ring opening polymerization¹² of (L) dilactide (supplied by Boehringer and Sons, Ingelheim, Germany) using a catalytic stannous octoate at concentrations in the range

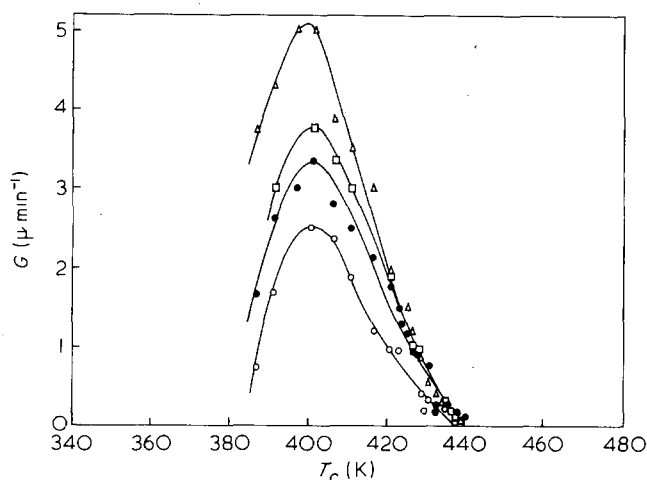


Figure 1 Radius growth rate, G as a function of crystallization temperature, T_c for different molecular weight samples of PLLA; \circ —A ($M_v = 6.9 \times 10^5$); \bullet —B ($M_v = 3.5 \times 10^5$); \square —C (2.6×10^5); \triangle —D ($M_v = 1.5 \times 10^5$)

of 5×10^{-5} – 1×10^{-4} mole/mole in evacuated glass vessels at 130°C for about 48 h. The dilactide was purified by recrystallization from ethylacetate before use. The polymer formed was freed from the unreacted dilactide by dissolving in methylene chloride (distilled over CaCl_2) followed by the precipitation in methanol. The polymer samples were dried in vacuum at 55°C and then stored over phosphorous pentoxide to avoid the absorption of water that may cause degradation when the sample was used at higher temperatures. Viscosity average molecular weight (M_v) was determined in chloroform at 25°C with an Ubbelohde viscometer using the relation¹²:

$$[\eta] = 5.45 \times 10^{-4} M_v^{0.73}$$

Instruments employed

Differential scanning calorimeter (Perkin Elmer DSC II) was employed to measure the glass transition (T_g) and melting temperatures (T_m). Thermograms were obtained at different scan speeds after crystallization at the required T_c for the equilibrium melting point (T_m^0). Calibration of d.s.c. apparatus was carried out by taking standard samples such as naphthalene, oxalic acid and indium. All the d.s.c. measurements were made by taking ~ 5 mg of the sample.

Bulk crystallization growth experiments were conducted on thin films of the polymer between microscope glass slides placed on a Mettler hot stage (FP52) and Zeiss optical microscope. The samples were heated 10° – 15° above the melting point, maintained at that temperature for 10 min and then cooled down rapidly to the required isothermal crystallization temperature.

Radius growth rates, G ($G = \frac{dx}{dt}$, where t is the time and x ,

the radius of a spherulite or one half of the largest dimension of an axialite) were measured by means of an ocular micrometer. Sufficient care was taken to see that all the measurements were made at the centre of the sample to avoid the degradation of the sample. All the measurements were duplicated and for each experiment fresh and new samples were used. Photomicrographs of the crystals were taken at certain crystallization temperatures where morphological changes were observed.

RESULTS AND DISCUSSION

Measurements of radius growth rates, G of PLLA samples using hot stage microscope showed the growth rate to be linear at all crystallization temperatures. The examination in the polarizing microscope indicated the presence of negatively birefringent spherulites showing a larger value of refractive index along the chain direction. The growth rate results for samples of different molecular weight over a wide range of temperature are shown in Figure 1. Below 114°C it was not possible to measure the growth rate because of high nucleation density. Self seeding technique was employed to induce nucleation at very high temperatures for measuring G . Figure 1 shows that G increases first reaching a maximum and then falls as the crystallization temperature was increased. Further it is also clear that the growth rate increases with decrease of molecular weight as observed in many polymers^{4,6,13,14}.

At very high undercoolings well defined spherulites were observed (Figure 2a). As the undercooling was reduced the spherulites were of irregular shape and coarse grained structure (Figure 2b). In the low molecular weight sample D, as the undercooling was reduced further and further, morphological change from spherulites to axialites were observed at 163°C (Figure 2c). It is quite interesting to find that in PLLA samples (E) of still lower

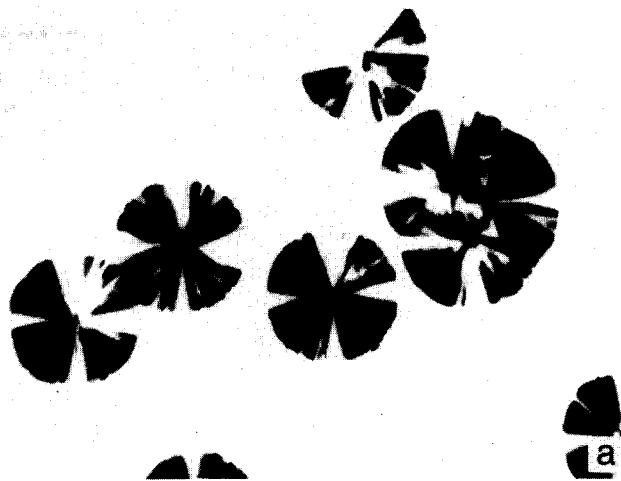


Figure 2a Spherulites grown at 124°C

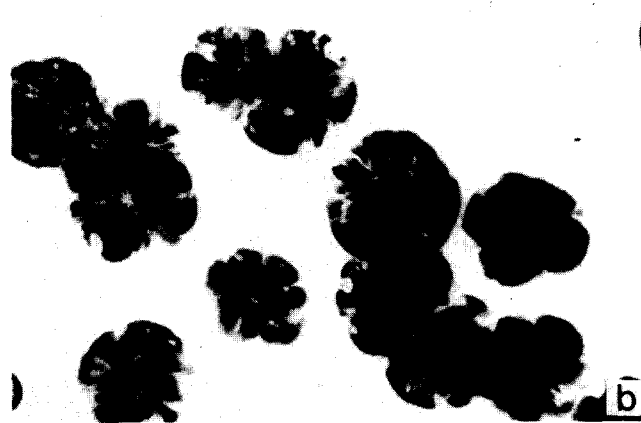


Figure 2b Coarse grained spherulites grown at 156°C

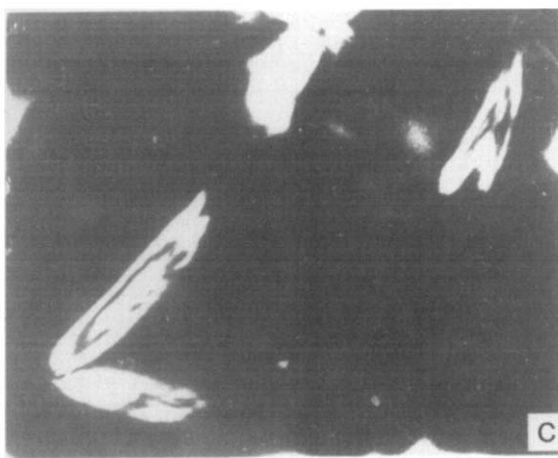
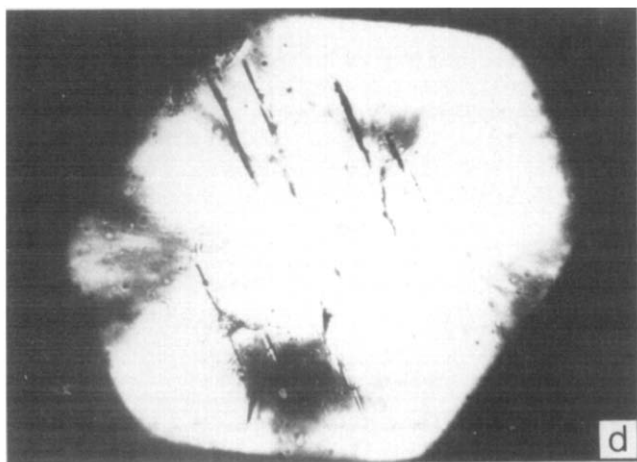


Figure 2c Axialites grown at 163°C


 Figure 2d Single crystals of PLLA ($M_v = 68\,000$) grown at 164°C from the melt

molecular weight ($M_v = 68\,000$) when crystallized from the melt at 164°C, hexagonal shaped single crystals²⁰ were formed (Figure 2d).

Hoffman and Weeks have shown¹⁵ the relation between melting temperature and crystallization temperature to be $T_m = T_m^0 \left(1 - \frac{1}{2\beta}\right) + \frac{T_c}{2\beta}$ where β is a constant depending on edge free surface energy. When secondary effects such as recrystallization and chain mobility effects are not involved, the value of β can be in the range of 0.75–2.

Figure 3 shows the relationship between crystallization and melting peak temperatures determined using d.s.c. measurements at 3 different scan speeds 4°, 5° and 8° min⁻¹. The extrapolation of T_m versus T_c to the line $T_m = T_c$ was carried out according to the above equation to get T_m^0 which was found to be 480K. From the slope of the lines one could obtain the value of β at different scan speeds.

Heating rate	β
8° min ⁻¹	1.4
5° min ⁻¹	1.3
4° min ⁻¹	1.2

The β values obtained are not far from the theoretical considerations. Further experiments on d.s.c. gave the

values of glass transition temperature T_g for PLLA samples, A, B, C and D and they are presented in the Table 2.

Growth rate data were analysed using the growth rate expression (i). It has been shown that the assumed values of $u^* = 1500$ cal mol⁻¹ and $T_x = T_g - 30$ K gave the best fit of the growth rate data for a number of polymers. The plot of $\log_{10} G + \frac{1500}{2.303 R(T_c - T_g + 30)}$ against $\frac{1}{T_c \Delta T f}$ will give the Kg in the slope and the intercept being $\log G_0$ (Figure 4). Tables 1 and 2 give the values of various parameters involved in the growth rate equation. The samples A, B and C behaved in a similar manner and they crystallized in the form of spherulites at all the measured temperatures shown in Figure 4. However, the sample D shows a sharp break (T_b) in the growth rate plot at 163°C as is evident from the 2 values of the nucleation constants (Table 2). It is

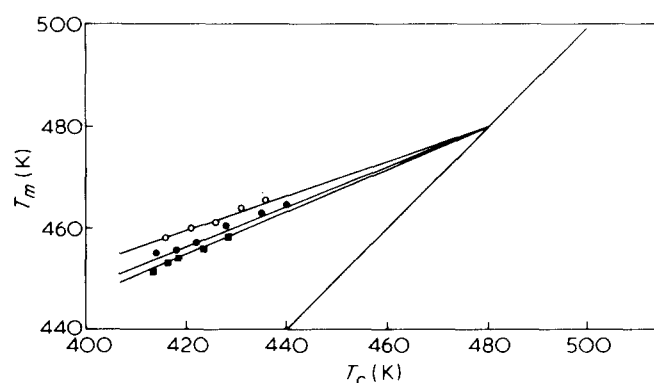


Figure 3 Melting point T_m , of PLLA as a function of crystallization temperature, T_c at different scan speed $\circ - 8^\circ \text{ min}^{-1}$; $\bullet - 5^\circ \text{ min}^{-1}$; $\blacksquare - 4^\circ \text{ min}^{-1}$. Extrapolation of the data to $T_m = T_c$ gives T_m^0 to be 480K

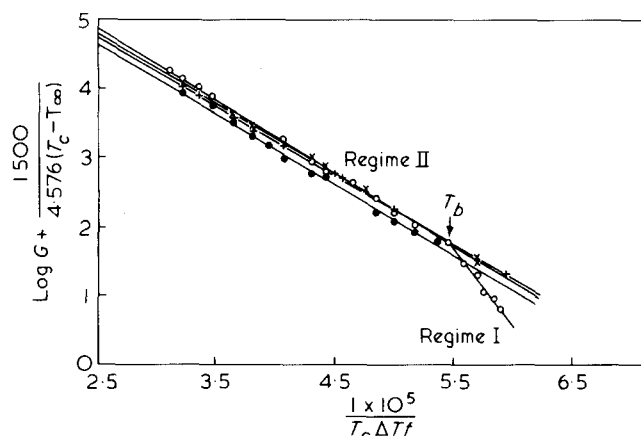


Figure 4 $\text{Log } G + 1500/4.576(T_c - T_\infty)$ as a function of $1/T_c \Delta T f$ for different samples of PLLA. $\bullet - A$; $+ - B$; $\times - C$; $\circ - D$

Table 1 Input data

Quantity	Value	Remarks
Heat of fusion, Δh_f	$111.083 \times 10^6 \text{ J m}^{-3}$	Ref. 19
Molecular width, a	$5.97 \times 10^{-10} \text{ m}$	
Layer thickness, b	$5.17 \times 10^{-10} \text{ m}$	Ref. 18
Fold surface energy, σ_e	$60.89 \times 10^{-3} \text{ J m}^{-2}$	
Lateral surface energy, σ	$12.03 \times 10^{-3} \text{ J m}^{-2}$	Calculated from $\sigma \sigma_e$

Table 2 Values of Kg , $\log G_0$ and $\sigma\sigma_e$ for PLLA

Sample no.	$M_V \times 10^{-5}$	T_g (K)	$\log G_0$	$G_0 (\mu\text{m min}^{-1})$	$Kg \times 10^{-5}$	$\sigma\sigma_e \times 10^6$ ($\text{J}^2 \text{m}^{-4}$)	Remarks
A	6.9	333	7.19	1.56×10^7	2.34	722	Regime II
B	3.5	331	7.21	1.63×10^7	2.29	706	Regime II
C	2.6	330	7.38	2.40×10^7	2.37	732	Regime II
D	1.5	328	7.53	3.38×10^7	2.44	753	Regime II
			13.33	2.13×10^{13}	4.87	752	Regime I

Av. 733

Table 3 Values of substrate lengths

Sample no.	$\frac{1}{T_c \Delta T f} \times 10^5$	Substrate length, L (μm)	Z Parameter	Remarks
A	5.00	4.0	1.0	Regime II
B	5.00	3.5	1.0	Regime II
C	5.00	5.0	1.0	Regime II
D	4.75	4.0	1.0	Regime II
	5.00	3.1	0.01	Regime I

also quite obvious that the ratio of the two Kg values is 2 as observed in the case of polyethylene by Hoffman *et al.*¹¹

It has been shown by Lauritzen¹⁶ and Frank¹⁷ that the value of Kg obtained in the above plot could be analysed for regime I and regime II by the application of Z test. The dimensionless quantity Z is given by:

$$Z \approx 10^3 \left(\frac{L}{2a} \right)^2 \exp \left[\frac{-X}{T_c \Delta T f} \right] \quad (\text{iv})$$

where L is the substrate length, a the molecular width and X is Kg for regime I with $Z < 0.01$; X is $2Kg$ for regime II with $Z > 1$.

When Z test of Lauritzen was employed, it was found that the samples A, B and C gave L values that are consistent with regime II while the sample D showed a transition at 163°C from regime I to regime II (Table 3). Above 163°C , regime I behaviour corresponding to axialite formation and below 163°C regime II corresponding to spherulitic morphology were observed (Table 3).

The growth rate plot (Figure 4) gives $\log G_0$ as the intercept and it decreases with the increase of molecular weight. The Kg data were further analysed for the calculation of surface free energies $\sigma\sigma_e$ using the equations (ii) and (iii) and the values of $\sigma\sigma_e$ are presented together

with G_0 in Table 2. From the average kinetic value of $\sigma\sigma_e$ ($733 \times 10^{-6} \text{J}^2 \text{m}^{-4}$), one could obtain an estimate for the lateral surface energy, σ to be $12.03 \times 10^{-3} \text{J m}^{-2}$.

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