Journal of Thermal Analysis, Vol. 47 (1996) 931-939

ISOTHERMAL MELT CRYSTALLIZATION KINETICS OF POLY(L-LACTIC ACID)

E. Urbanovici[*], *H. A. Schneider*[**], *D. Brizzolara and H. J. Cantow*

Freiburger Materialforschungszentrum FMF and Institut für Makromolekulare Chemie of the University, Stefan-Meier-Str. 21, D-79104 Freiburg, Germany

Abstract

A DSC study was carried out of the isothermal melt crystallization kinetics of poly(L-lactic acid), PLLA, at 110, 115, 120, 125 and 130°C. The experimental data were evaluated within the framework of the well-known Avrami kinetic model and an extended model involving an additional third kinetic parameter [8]. In order to perform the necessary numerical calculations, a number of functions built into the Mathematica® software system were used. The results showed that the isothermal melt crystallization kinetics of PLLA can be described adequately by both these kinetic models. It should also be stressed that the kinetic model of Urbanovici and Segal offers a better description of the experimental melt crystallization data of PLLA than the classical Avrami model.

Keywords: DSC, isothermal melt crystallization, kinetic parameters, Mathematica®, new kinetic model, poly(L-lactic acid)

Introduction

During recent decades, extensive attention has been paid to the study of poly(L-lactic acid), PLLA, because of its high mechanical strength, its resorption in the human body and its non-toxicity after biodegradation. Due to its properties, PLLA is considered to be a useful implant material in medical applications.

Although a knowledge of the crystallization kinetics of polymeric materials is important from the aspects of both fundamental research and practical application, only few studies have been carried out on the crystallization behaviour and especially the crystallization kinetics of PLLA. A detailed study of the crystallization of lactide stereo copolymers was carried out by Fischer *et al.* [1] in order to obtain information on the crystallization behaviour of these copolymers with different contents of noncrystallizable DL-lactide units. The crystallization

---

[*] Permanent address: Thermosis Ltd, P.O.Box 187, Sântu Gheorghe 4000, Romania.

[**] Author to whom all correspondence should be addressed.

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

behaviour of PLLA has also been investigated by Kalb and Pennings [2], who showed that PLLA is a semi-crystalline polymer that may crystallize both from the melt and from solution. Kishore *et al.* [3] studied the isothermal melting of PLLA spherulites in order to understand the melting mechanism. The dependence on undercooling and molecular weight of the morphology and crystal growth from the melt of PLLA was investigated by Vasanthakumari and Pennings [4]. Recently, Tsuji and Ikada [5] presented a study concerning the effects of annealing on the thermal properties, morphology and mechanical properties of PLLA films. Last but not least, mention must be made of the dynamic mechanical and calorimetric investigation onto the effects of thermal treatment on compression-molded PLLA of different molecular weights by Migliaresi *et al.* [6]. The results indicated that initially fully amorphous PLLA matrices attained very high degrees of crystallinity (up to 90%) following different annealing processes.

The present study deals with a DSC investigation of the isothermal melt crystallization kinetics of PLLA at five temperatures between 110 and 130°C. The experimental data were evaluated by using the well-known Avrami kinetic model [7] and a new model that involves three kinetic parameters [8].

Experimental

The high molecular weight PLLA (M_n=333.000 g mol^{-1}; M_w=737.000 g mol^{-1}) used in the present study was purchased from Boehringer Ingelheim (RS210), Germany. In order to avoid the absorption of water that may cause degradation at higher temperatures, the polymer was stored over phosphorus pentoxide (P_2O_5) in a desiccator.

The isothermal melt crystallization investigations were performed on samples of 10±0.1 mg of PLLA by using a Perkin-Elmer DSC 7. Additionally, DSC measurements were carried out with the aim of obtaining the most important thermal characteristics of the PLLA studied. The glass transition temperature (T_g) and the melting peak temperature (T_m), which are dependent on the measuring conditions (e.g. heating rate, sample mass, etc.), were found to be 63 and 185°C, respectively, for a 10 K min^{-1} heating rate. These values are in good agreement with the data presented in the literature [2–5]. The melting enthalpy (ΔH_f) was evaluated from the area under the melting peak by using samples crystallized at various temperatures; the resulting average value of 58 J g^{-1} is in satisfactory agreement with the literature data [2, 3].

The experiments on the isothermal melt crystallization of PLLA were carried out as follows: the samples were first melted and maintained for 20 min at 200°C. Subsequently, they were rapidly cooled down (approx. 80 K min^{-1}) to the constant test temperature. Five temperatures between 110 and 130°C were taken into consideration. At temperatures above 130°C, the crystallization process is slow and incomplete, while at temperatures below 110°C the crystallization is fast and it is difficult to extrapolate with appropriate accuracy the initial part of the isothermal DSC curve, the definition of t=0 thereby becoming uncertain [9].

Results and discussion

The DSC study of the isothermal melt crystallization of PLLA was performed at 110, 115, 120, 125 and 130°C. A typical isothermal crystallization thermogram for 110°C is shown in Fig. 1. The full line represents the original DSC curve, while the dotted line illustrates the approach to the initial part of the isothermal crystallization curve obtained by extrapolation.

The evolution with time of the crystallinity can be estimated by using the degree of crystallization, α, expressed by the ratio

$$\alpha = \Delta H_t/\Delta H_\infty \tag{1}$$

where

$$\Delta H_t = \int_0^t (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t \tag{2}$$

and

$$\Delta H_\infty = \int_0^\infty (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t \tag{3}$$

dQ/dt being the respective heat flow. ΔH_t is the partial area between the DSC curve and the time axis at time t, while ΔH_∞ is the total area and corresponds in

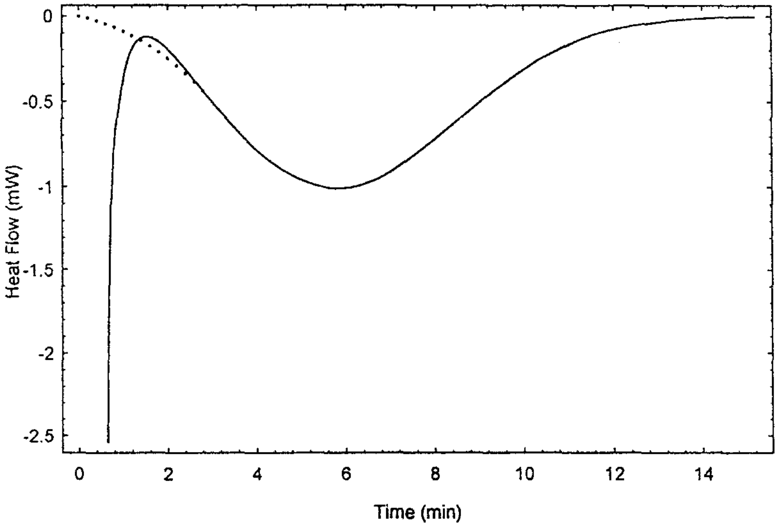

Fig. 1 Isothermal DSC curve obtained during melt crystallization at 110°C; the full line (—) depicts the original DSC curve, and the dotted line (....) the extrapolation to the initial part of the isothermal crystallization curve

fact to the overall heat of crystallization. It is very important to emphasize that the degree of crystallization, α, is not similar to the degree of crystallinity, which is the fractional extent of crystallinity of the polymer sample. In contrast, the degree of crystallization corresponds to the crystalline volume fraction developed at time t [10]. The numerical integration was performed by using the 'NIntegrate' function of the Mathematica® software system [11–13]. Figure 2 presents the experimentally obtained α *vs.* t data for the isothermal crystallization of PLLA at the temperature used in this study.

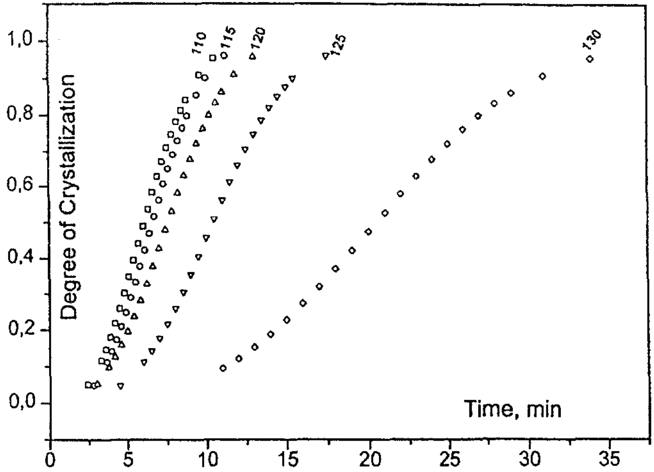

Fig. 2 Experimental data on the isothermal melt crystallization of PLLA at the temperatures used in this study

The kinetic study of the experimental data was performed by using the well-known Avrami approach [7–10, 14–16, 20] and also a new kinetic model involving an additional, third kinetic parameter [8]. According to the Avrami model, the time dependence of α can be described by the following kinetic equation:

$$-\ln(1-\alpha)=(kt)^n \tag{4}$$

or

$$\alpha=1-\exp[-(kt)^n] \tag{5}$$

where k is the temperature-dependent rate constant and n is the Avrami exponent. At this point, it should be mentioned that many papers consider the composite rate constant, i.e. $K=k^n$, instead of k [9, 10, 14–16]. However, we prefer to use k because its dimension is time^{-1} and it does not depend on the value of n, whereas the dimension of K is time^{-n}, and it depends on the value of the Avrami exponent. In a further paper, we intend to discuss in detail the use of k in-

Avrami exponent. In a further paper, we intend to discuss in detail the use of k instead of K. The new kinetic equation is in fact a generalization of the Avrami model [8]. In this case, the relationship between α and t can be expressed as follows:

$$[(1-\alpha)^{1-r}-1]/(r-1)=(kt)^{n} \qquad (6)$$

or

$$\alpha=1-[1+(r-1)(kt)^{n}]^{1/(1-r)} \qquad (7)$$

where k and n have the same meanings as in Eq. (4) and r is a parameter that satisfies the condition $r>0$. It should also be mentioned that, at limit for $r\rightarrow 1$, Eq. (6) becomes identical with the kinetic equation corresponding to the Avrami model [8].

Since both models describe sigmoid shaped α *vs.* t curves, it is important to determine α_{max}, i.e. the value of the degree of crystallization corresponding to the maximum value of the crystallization rate, by using the condition

$$(d^2\alpha/dt^2)_{max}=0 \qquad (8)$$

which leads after the performance of the detailed calculations [8] to

$$\alpha_{max}=1-\exp[(1-n)/n] \qquad (r=1);\ \text{Avrami model} \qquad (9)$$

$$\alpha_{max}=1-[(n+r-1)/(nr)]^{1/(r-1)} \qquad (r\neq 1);\ \text{new model} \qquad (10)$$

The kinetic parameters were evaluated by fitting the experimental data to the respective kinetic models. As relationships (5) and (7) describe nonlinear functions, the 'NonlinearFit' function of Mathematica® was used [17, 18]. The goodness of the fit can be assessed by

$$S=1/N\sum_{i=1}^{N}(\alpha_{calc,i}-\alpha_{exp,i})^2 \qquad (11)$$

where $\sum_{i}^{N}(\alpha_{calc,i}-\alpha_{exp,i})^2$ is the residual sum of squares, N is the number of experimental data points, α_{exp} is the experimental value of the degree of crystallization and α_{calc} is the value obtained by the fitting procedure. The smaller S, the better the fit. The number of experimental data points was in every case $N=30$. Table 1 shows the values of the kinetic parameters (k and n) and of S corresponding to the Avrami model, while the values of the kinetic parameters

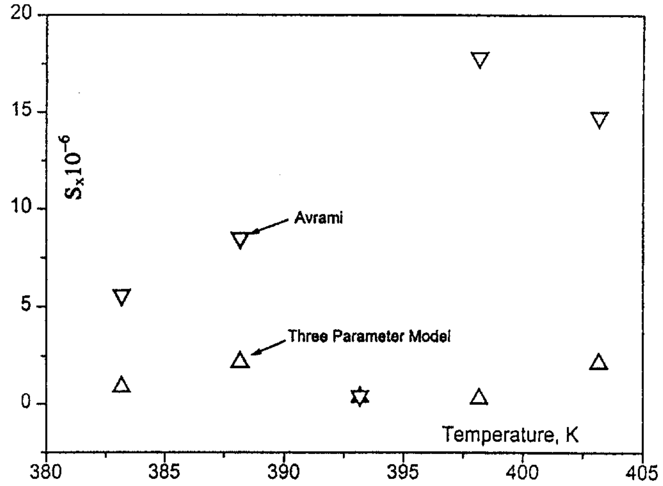

Fig. 3 Comparison between the values of S relating to the Avrami model and the new kinetic model

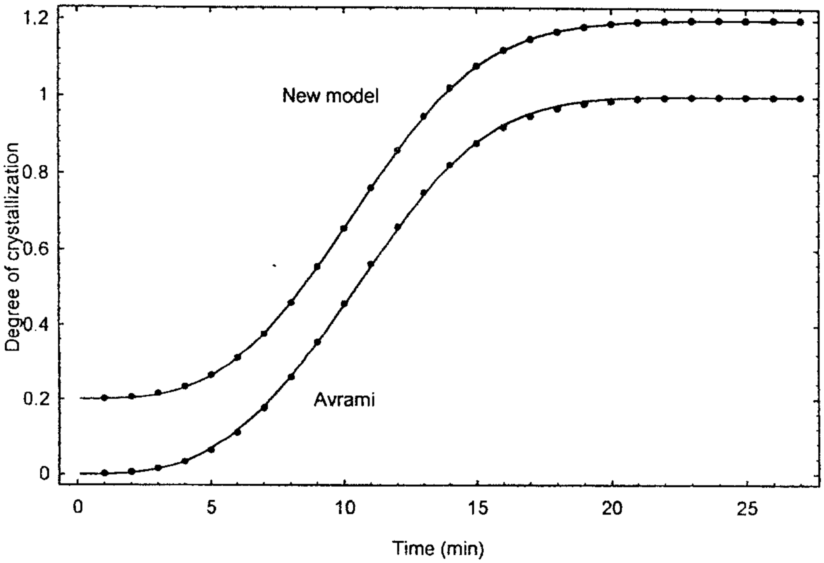

Fig. 4 Experimental data points (....) for 125°C and the calculated α *vs.* t curves (—) relating to the Avrami model and the new kinetic model (Eq. (7)); the coordinate of α for the new model is shifted by +0.2

The evaluated kinetic parameters can be inserted into Eqs (5) and (7) in order to generate theoretical α *vs.* t curves. Figure 4 presents the experimental α *vs.* t data points for T=125°C and the calculated α *vs.* t curves (full line) corresponding to the Avrami model and the new three-parameter model, respectively.

Table 1 The values of the kinetic parameters and S corresponding to the Avrami model

T/°C	n	k/s^{-1}	S
110	2.7611	2.3972×10^{-3}	5.5729×10^{-6}
115	2.9577	2.2235×10^{-3}	8.4981×10^{-6}
120	2.8074	1.9344×10^{-3}	4.1443×10^{-7}
125	3.1083	1.4171×10^{-3}	1.7818×10^{-5}
130	3.0764	7.1962×10^{-4}	1.4745×10^{-5}

Table 2 The values of the kinetic parameters and S corresponding to the new model described by Eq. (7)

T/°C	r	n	k/s^{-1}	S
110	1.0636	2.8394	2.4301×10^{-3}	8.8108×10^{-7}
115	1.0742	3.0546	2.2566×10^{-3}	2.1794×10^{-6}
120	0.9938	2.7996	1.9318×10^{-3}	3.6693×10^{-7}
125	1.1197	3.2773	1.4492×10^{-3}	2.8581×10^{-7}
130	1.0998	3.2162	7.3348×10^{-4}	2.1468×10^{-6}

Table 3 The experimental(exp) and calculated(calc) values of the degree of crystallization corresponding to the maximum crystallization rate

T/°C	t_{max}/min	α_{max}/exp	α_{max}/calc Eq. (9)	α_{max}/calc Eq. (10)
110	5.87	0.4681	0.4716	0.4624
115	6.43	0.4732	0.4841	0.4733
120	7.41	0.4803	0.4747	0.4756
125	10.25	0.4823	0.4925	0.4753
130	20.01	0.4740	0.4908	0.4764

The theoretical α_{max} values corresponding to the maximum crystallization rate were calculated for both kinetic models by using Eqs (9) and (10), respectively. They are compared with the experimentally obtained values in Table 3.

The data presented in Tables 1–3 permit the following conclusions.

1) From a consideration of the values of S, it can be concluded that both the Avrami model and the new kinetic model satisfactorily describe the isothermal melt crystallization of PLLA. However, as expected, the accuracy is better for the latter model, which involves three fitting parameters instead of the two of the Avrami model. The α_{max} values calculated by using relationships (9) and (10) are in good agreement with the experimental data. It is worth mentioning that, except for T=110°C, the values of α_{max} determined by using relationship

(10) agree better with the experimental α_{max} than those calculated by using relationship (9).

2) For both models, the values of the Avrami exponent (n) are centred for all five temperature around a value of 3. According to the literature, $n=3$ corresponds to homogeneous nucleation and two-dimensional linear growth of the nuclei during crystallization [14].

3) Except for the value at $T=120°C$, the values of parameter r of the new model are centred around an average of 1.09.

4) For each temperature, the value of the rate constant (k) corresponding to the Avrami model are very close to the values of the rate constant obtained with the new model.

5) The value of the rate constant (k) decreases with increasing temperature. Such a dependence is in contrast with the Arrhenius approach, which assumes an increase in the rate constant with increasing temperature [19]. The literature includes some attempts to explain such a variation of the rate constant of the crystallization of polymers [14–16, 20–22], but a widely accepted theory has not yet been developed. Figure 5 shows the values of ln$k$ as a function of temperature for both kinetic models. A detailed discussion of the temperature dependence of the rate constants of crystallization will be presented in a later paper.

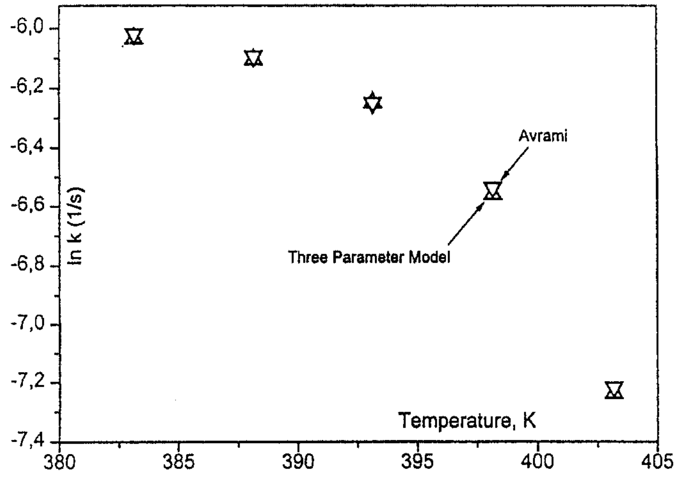

Fig. 5 Variation of ln$k$ with temperature for both kinetic models

Conclusions

A DSC study of the isothermal melt crystallization kinetics of PLLA is presented. The kinetic analysis of the experimental data obtained was performed by using the Avrami model and a new kinetic model involving three kinetic parameters. It was shown that the isothermal melt crystallization kinetics of PLLA can be described satisfactorily by using these kinetic models and that the new kinetic model offers a better description of the experimental data than the classical Avrami kinetic model. The values of the Avrami exponent, n, were found to be about 3 for both kinetic models, suggesting homogeneous nucleation and two-dimensional linear growth of the PLLA nuclei.

* * *

The financial support of the Deutsche Forschungsgemeinschaft, SFB(60), is gratefully acknowledged. One of the authors (E.U.) is indebted to the Alexander von Humboldt Foundation (Germany) for the financial support provided for his scientific activity. The assistance of Carola Sturm and Juan Arroyo in performing the DSC measurements is also gratefully acknowledged.

References

1 E. W. Fischer, H. J. Sterzel and G. Wegner, Kolloid-Z. Polymere, 251 (1973) 980.
2 B. Kalb and A. J. Pennings, Polymer, 21 (1980) 607.
3 K. Kishore, R. Vasanthakumari and A. J. Pennings, J. Polym. Sci., Polym. Phys. Edn., 22 (1984) 537.
4 R. Vasanthakumari and A. J. Pennings, Polymer, 24 (1983) 175.
5 H. Tsuji and Y. Ikada, Polymer, 36 (1995) 2709.
6 C. Migliaresi, D. Cohn, A. de Lollis and L. Fambri, J. Appl. Polym. Sci., 43 (1991) 83.
7 M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
8 E. Urbanovici and E. Segal, Thermochim. Acta, 171 (1990) 87.
9 M. J. Richardson, in C. Booth and C. Price (Eds.), Comprehensive Polymer Science, Volume 1, Polymer Characterization, Pergamon Press, Oxford 1989, p. 891.
10 G. Allegra, P. Corradini, H.-G. Elias, P. H. Geil, H. D. Keith and B. Wunderlich, Pure Appl. Chem., 61 (1989) 769.
11 Mathematica® Version 2.2, Wolfram Research, Inc., Champaign, Illinois, 1994.
12 S. Wolfram, Mathematica® – A System for Doing Mathematics by Computer, Addison-Wesley, Reading, Massachusetts, 1991, pp. 672–707.
13 T. B. Bahder, Mathematica® for Scientists and Engineers, Addison-Wesley, Reading Massachusetts 1995, pp. 381–389.
14 L. Mandelkern, Crystallization of Polymers, McGraw-Hill, New York 1964, pp. 215–290.
15 J. A. Ferrara, J. C. Seferis and C. H. Sheppard, J. Thermal Anal., 42 (1994) 467.
16 J. M. Kenny, A. Maffezzoli and L. Nicolais, Thermochim. Acta, 227 (1993) 83.
17 W. T. Shaw and J. Tigg, Applied Mathematical® Getting Started, Getting It Done, Addison-Wesley, Reading, Massachusetts 1994, pp. 116 - 118.
18 P. Boyland et al., Guide to Standard Mathematica® Packages – Version 2.2, Wolfram Research, Inc., 1993, pp. 396–399.
19 M. E. Brown, D. Dollimore and A. K. Galwey, Comprehensive Chemical Kinetics, Vol. 22, (Eds. C. H. Bamford and C. F. H. Tipper), Reactions in the Solid State, Elsevier, Amsterdam 1980, p. 87.
20 B. Wunderlich, Macromolecular Physics, Academic Press, New York 1976.
21 G. Adam and J. H. Gibbs, J. Chem. Phys., 43 (1965) 139.
22 J. A. Martins, J. J. C. Cruz-Pinto and M. J. Oliveira, J. Thermal Anal., 40 (1993) 629.