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Determination of spherulite growth rates of poly(L-lactic acid) using combined isothermal and non-isothermal procedures

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Dedicated to Prof. Bernhard Wunderlich on the occasion of his 70th birthday

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Abstract

A combination of isothermal and non-isothermal methods was used to measure spherulite growth rates (*G*) of poly(L-lactic acid) (PLLA). *G* was determined during cooling at a constant rate by monitoring the growth of a spherulite radius as a function of temperature. Coupling with a self-nucleation procedure permitted to highly enlarge the temperature range where *G* data can be obtained within a single experiment. Very good agreement existed between data gained with the proposed procedure and those obtained with the traditional isothermal method. Further enlargement of the temperature range was provided by using tailored temperature programs. After the first growing crystals had appeared, the samples were quenched in liquid nitrogen to stop crystal growth, then a conventional isothermal measurement was performed. Again the thermal treatment imposed on the sample did not affect the measured value of *G*. The use of combined isothermal and non-isothermal methods coupled with self-nucleation permitted to obtain *G* data of PLLA in a very wide temperature range. Spherulite growth rates of PLLA were analyzed with the Hoffman and Lauritzen theory, which allowed to detect a regime II–III transition at 120°C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Spherulite growth rate; Isothermal and non-isothermal crystallization; Poly(L-lactic acid)

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1. Introduction

Measurements of spherulite growth rates (*G*) are generally conducted in isothermal conditions, by monitoring the growth of a spherulite radius (*r*) as a function of time (*t*) [1]. With only a few exceptions, like in the presence of high levels of segregation of non-crystallizable species [2–6], at a fixed temperature the plot of *r* vs. *t* is linear and its slope gives the value of *G* at the selected temperature (*T*) for the measurement

$$G = \frac{\mathrm{d}r}{\mathrm{d}t}. \tag{1}$$

These isothermal measurements are usually very long and time consuming, as a single experiment is necessary to obtain *G* at each temperature. Recently a new non-isothermal procedure that allows to measure *G* data in a rather wide temperature range with a single experiment has been suggested [7,8]. When solidification is performed at a constant cooling rate, *G* can be estimated by taking the first derivative of the *r* vs. *T* plot at each experimental point

$$G = \frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\mathrm{d}r}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{2}$$

where d*r*/d*T* is measured point by point from the plot, and d*T*/d*t* is the cooling rate used.

This procedure has been further developed by Di Lorenzo et al. [9]: by using various cooling rates it is possible to enormously enlarge the temperature range where crystallization data can be obtained. Data measured at different cooling rates are well comparable and in agreement with those determined with traditional isothermal methods, as demonstrated for the measurement of spherulite growth rates of isotactic polypropylene, both plain and in blends with poly(α-pinene). Moreover, combining self-nucleation and non-isothermal temperature programs, the temperature range where growth rate data are measurable can be further expanded.

In this article the non-isothermal method coupled with self-nucleation, suggested in Ref. [9], has been applied to measure the spherulite growth rates of poly(L-lactic acid) (PLLA), a biodegradable and biocompatible polyester widely used in the biomedical field [10,11]. It will be

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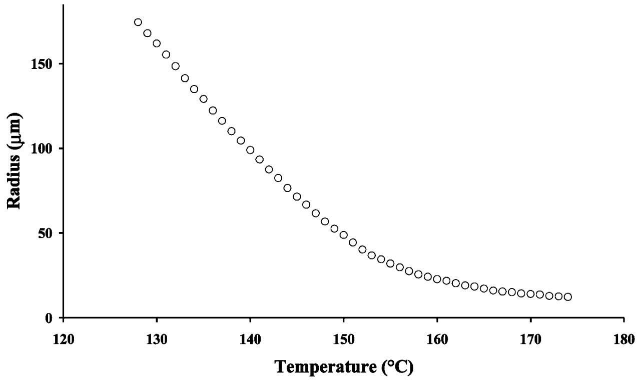

Fig. 1. Variation of the spherulite radius with temperature during cooling.

shown that with this procedure it is possible to determine *G* of PLLA in a very wide temperature range with a single measurement, with enormous savings of time compared to the traditional isothermal methods. Unfortunately, this non-isothermal plus self-nucleation method does not permit to enlarge the temperature range where spherulite growth rates of PLLA can be measured. Spherulite growth rate data of PLLA, determined with the traditional isothermal methods, have been reported in the literature only at temperatures above 114°C [12]. Below this limit, a very high nucleation density acts as an obstacle for the measurements. In order to obtain *G* at low temperatures, a different method, that combines self-nucleation and isothermal measurements, is proposed in this article. It will be shown that coupling tailored isothermal and non-isothermal procedures it is possible to highly expand the temperature range where spherulite growth rates of poly(L-lactic acid) can be measured.

2. Experimental part

2.1. Material

A poly(L-lactic acid) of molecular mass $M_w = 101,000$ Da, produced by Boehringer Ingelheim (Germany) and received in form of small chips, was used with neither further purification nor thermal treatment.

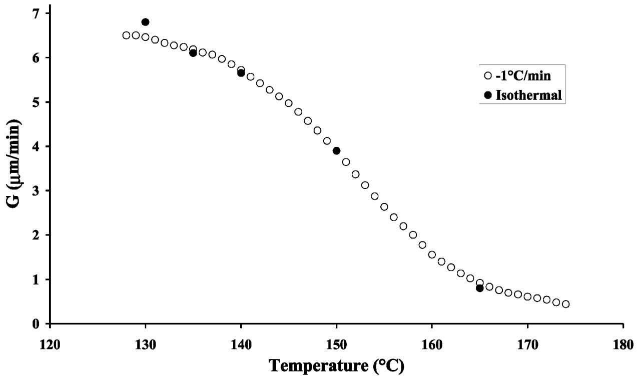

Fig. 2. Spherulite growth rates of PLLA measured during cooling at 1°C/min and in isothermal conditions.

2.2. Optical microscopy

Spherulite growth rates of PLLA were determined by optical microscopy, using a Zeiss polarizing microscope equipped with a Linkam TMHS 600 hot stage. A small piece of PLLA, weighing about 0.3 mg, was squeezed between two microscope slides, then inserted in the hot stage. The thickness of the squeezed sample was less than 10 μm. The radius of the growing crystals was monitored during solidification by taking photomicrographs at appropriate intervals of time, using a JVC TK-1085E Video Camera. Spherulite radii were measured with the software Image-Pro Plus 3.0. The combined usage of optical microscopy, video camera and image analysis software gave a resolution power of 0.3 μm, which allowed to detect differences in spherulite radii of 0.15 μm by measuring their diameter. During all measurements and thermal treatments dry nitrogen gas was purged throughout the hot stage.

Each PLLA sample was heated from 30 to 200°C at the rate of 20°C/min, kept at this temperature for 2 min to allow complete melting, then subjected to different thermal treatments, in dependence on the procedure used:

- Determination of *G* data during cooling was performed by using a self-nucleation procedure. A PLLA sample was cooled from the melt at 1°C/min until it reached 145°C, where the first spherulite was visible under the optical microscope, then the sample was heated up to 175°C at 4°C/min, kept at this temperature for 2 min, and finally cooled at 1°C/min. The radius of the growing spherulite was monitored as a function of the decreasing temperature during the final cooling at 1°C/min.
- Conventional isothermal crystallization measurements were performed by cooling the sample from the melt at 30°C/min to the desired crystallization temperature (T_c). During isothermal solidification, the increase of spherulite radius was recorded as a function of time.
- Determination of *G* data during heating was made by cooling the PLLA sample from the melt at 1°C/min to a temperature of 145°C, then the sample was rapidly removed from the hot stage and quenched in liquid nitrogen to arrest spherulite growth; the sample was then reinserted in the hot stage at room temperature, heated to the desired temperature at a rate of 30°C/min, held for 2 min, and finally heated at 1°C/min; the growth of a spherulite was followed during heating as a function of temperature.
- Further isothermal measurements at low temperatures were made after the sample was cooled from the melt at 1°C/min to 145°C and quenched in liquid nitrogen; after quenching, the sample was reinserted in the hot stage at room temperature, heated at 30°C/min to the desired T_c and kept at T_c for a time sufficient to complete

crystallization; the radius of a growing spherulite was monitored as a function of time.

3. Results and discussion

Spherulite growth rates of PLLA were measured during cooling at a constant rate using a self-nucleation procedure, as described in Section 2. The plot representing the variation of the spherulite radius as a function of temperature is shown in Fig. 1. From these data, *G* values were calculated by taking the first derivative of the *r* vs. *T* plot, according to Eq. (2), and the results are reported in Fig. 2. In order to calculate the first derivative, the following formula was used:

$$\text{Derivative} = \frac{1}{2}\left(\frac{y_{i+1} - y_i}{x_{i+1} - x_i} + \frac{y_i - y_{i-1}}{x_i - x_{i-1}}\right) \tag{3}$$

then the data were smoothed using adjacent-averaging. Fig. 2 also reports *G* values measured in isothermal conditions at a few selected temperatures (namely 130, 135, 140, 150 and 165°C) to prove that the non-isothermal method combined with self-nucleation allows a very reliable determination of spherulite growth rates. Spherulite growth rates can also be measured on cooling the PLLA sample directly from the melt at a constant rate. Performing a simple cooling from the melt at 1°C/min, data can be recorded only at temperatures not higher than 145°C. The self-nucleation procedure is needed to enlarge the temperature range where *G* can be measured in a single experiment, as it permits to obtain data at temperatures as high as 174°C. Fig. 2 also shows that *G* values can be obtained in a very large temperature range by performing one single measurement that lasts less than 2 h. To obtain data in a similar temperature interval with the conventional isothermal method would require several days of measurements.

The very good agreement of spherulite growth rates obtained with the isothermal and non-isothermal methods proves that neither the various thermal treatments at which the samples were subjected, nor the use of a non-constant temperature during the measurements affect experimental determination of *G*. Generally, measurement of crystallization rates in non-isothermal conditions must be performed with care to ensure that the temperature of the sample is properly monitored, as thermal gradients within the sample and between the cooling furnace and the sample can occur. Moreover, solidification is an exothermic process and the heat developed during the phase transition may cause some local heating and create additional thermal gradients within the sample. At very high cooling rates the heat evolved during crystallization can even cause a plateau in the sample temperature during a large portion of the solidification process [13,14]. As a consequence of all these thermal lags, transitions can occur at temperatures that do not correspond to those detected by the instrumentation. The thicker the sample, and higher the cooling rate, the more critical is this problem [15,16].

Few studies relating the influence of sample thickness and cooling rate on the occurrence of thermal gradients during non-isothermal crystallization have been reported in the literature. Monasse and Haudin estimated that, for 300 μm thick polypropylene samples and scanning rates not exceeding 80°C/min, using a Perkin–Elmer DSC 2B furnace, the thermal gradient between the furnace and the sample is negligible, whereas the difference between top and bottom of the sample is 1°C [17]. The samples used in the present study are very flat and thinner than 10 μm, which reduces the risks of having thermal gradients in the direction normal to the sample surface. In addition, a low cooling rate was used (1°C/min). In such a situation, negligible gradients within the sample and between the furnace and the sample are expected even during solidification, as the heat liberated during crystallization is very low, due to the low sample mass. Hence it is quite safe to assume that the effective temperature of the sample corresponds to that registered by the hot stage furnace.

The heat evolved during crystallization depends on the amount of sample that is involved in the transition. A high number of spherulites growing simultaneously correspond to a large amount of heat evolved. An ideal situation to perform crystallization under constant cooling rate would involve the monitoring of crystallite growth in a specimen where only one spherulite develops. This goal was achieved using the self-seeding procedure, at least at high temperatures. In fact, at the beginning of cooling from 176°C, until about 145–150°C, only one growing spherulite was present in the sample. On further cooling a few more spherulites started to develop and grow, but they were still low in number, and the heat evolved during the phase transition was not high enough to counterbalance the cooling power of the hot stage. The simultaneous growth of a few more spherulites did not disturb the measurement, as demonstrated by the very good agreement of *G* data obtained on cooling with those determined in isothermal conditions, as shown in Fig. 2.

Spherulite growth rates of PLLA samples of various molecular mass were also measured by Vasanthakumari and Pennings using the traditional isothermal method [12]. Data were gained at temperatures ranging from 114 to 168°C. This temperature range is of the same magnitude of that reported in Fig. 2, the difference lies in the time required for the measurements using the two methods. Isothermal *G* measurement of PLLA after cooling from the melt is possible only at temperatures higher than 114°C, due to the large nucleation density [12]. Also the non-isothermal method coupled with self-nucleation does not permit to measure *G* at low temperatures, due to the occurrence of multiple nucleation, hence other procedures need to be used to gain data at low *T*.

Quenching melt PLLA in liquid nitrogen allows to obtain a completely amorphous sample, preventing crystallization.

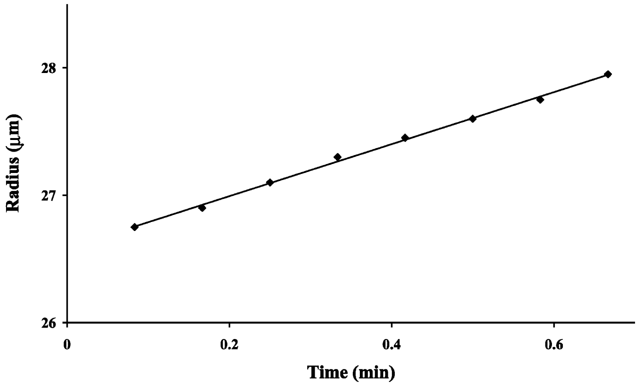

Fig. 3. Variation of the spherulite radius with time during isothermal crystallization at 95°C.

Also quenching a partially crystallized PLLA, containing only one or a few growing crystallites, permits to stop further crystal growth. This feature was exploited to measure *G* data at temperatures below the limit mentioned above, using self-nucleation and quenching the sample after the first growing nucleus was visible by the optical microscope. The following thermal treatment was used. The melt sample was cooled at 1°C/min until the first spherulite appeared, then was rapidly removed from the hot stage and quenched in liquid nitrogen to stop further growth. The sample was reinserted in the hot stage at 84°C, kept at this temperature for 2 min, then heated at 1°C/min. The radius of the growing spherulite was recorded during the final heating as a function of temperature, which allowed to obtain *G* data from 85 to 92°C. The temperature range where *G* of PLLA can be measured with this method is not very large, as at a certain temperature a high number of small spherulites start to grow, rapidly filling the space. The temperature at which nucleation rate becomes so high to obstacle the measurements depends on the scanning rate used, being higher for higher heating rates [18], but the choice of a different heating rate could raise the temperature range where *G* can be measured of only a few degrees.

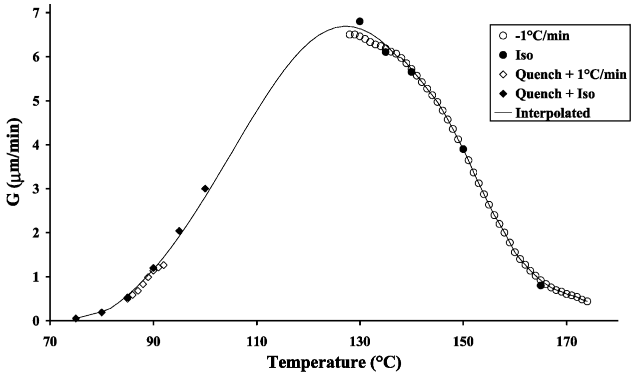

Fig. 4. Spherulite growth rates of PLLA measured with various methods: (○) cooling at 1°C/min after self-nucleation; (●) isothermal crystallization after cooling from the melt; (◇) heating at 1°C/min after self-nucleation and quenching; (◆) isothermal crystallization after self-nucleation and quenching. The solid line interpolates the experimental data.

Table 1
Spherulite growth rates (in μm/min) of poly(L-lactic acid) measured on cooling at 1°C/min after self-nucleation, isothermally after cooling from the melt, and isothermally after self-nucleation followed by quenching

Temperature (°C)	− 1°C/min	Iso	Iso after quench[a]
140	5.71	5.65	5.84
150	3.90	3.90	3.71
165	0.92	0.80	0.83

[a] Measurements at these selected temperatures after self-nucleation followed by quenching were performed by reinserting the PLLA sample in the hot stage at the indicated temperatures. Heating from room temperature to 140, 150 or 165°C would have resulted in highly densely nucleated sample, hindering the measurement.

A different method must be used to determine *G* in the low temperature side of the *G* vs. *T* plot. The method proposed is as follows. PLLA was cooled from the melt at 1°C/min until the first spherulite appeared, quickly removed from the hot stage and put into a liquid nitrogen bath (as before), then reinserted in the hot stage at room temperature and heated at 30°C/min until the desired crystallization temperature was reached, so that a conventional isothermal measurement could be performed. At the highest temperatures chosen, solidification is completed in a rather short time, due to sudden appearance of a high number of growing spherulites that cause rapid impingement. The use of a video camera that needs a very low exposure time allows to take photomicrographs at short intervals of time, as shown in Fig. 3. The trend of the spherulite radius vs. time is linear for all the temperatures chosen, which consents to easily determine *G*. Results are shown in Fig. 4 together with the data obtained with the other methods, reported for comparison. It is worth to note that the thermal treatment at which the samples were subjected (self-nucleation plus quenching) does not affect the determination of correct *G* values, as shown in Table 1 that reports spherulite growth rates of PLLA estimated at three selected temperatures with the three methods proposed (traditional isotherm, cooling after self-nucleation, and self-nucleation with quenching followed by an isotherm). For all the temperatures the three values are within acceptable experimental errors, which supports the reliability of the procedures used. The solid line of Fig. 4 was obtained by connecting the measured *G* values and interpolating the experimental data in the temperature range where data were not acquired. Hence, combining isothermal and non-isothermal methods it is possible to gain spherulite growth rates in a very wide temperature range, highly expanding the interval obtainable with traditional methods. In this way it has become possible to determine the whole crystallization curve of poly(L-lactic acid). The overall trend is a bell-shaped curve, as predicted by the theory [1]. Spherulite growth rates of PLLA are low at high temperatures, then gradually increase with the increase of the undercooling to reach a maximum at about

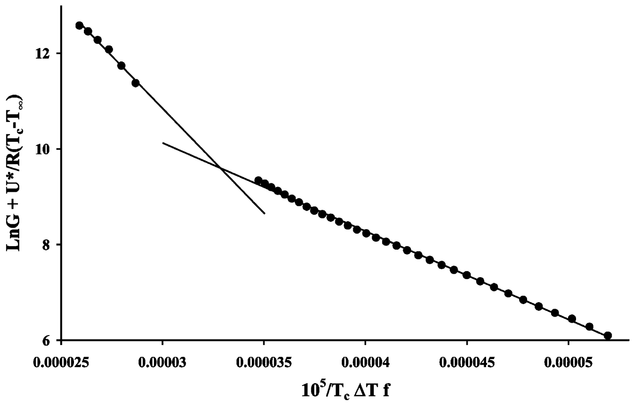

Fig. 5. Kinetic analysis of growth rate data of PLLA. $U^* = 1500$ cal/min and $T_\infty = T_g - 30$°C were used.

127–128°C, in agreement with the value reported in Ref. [12].

Experimental data of spherulite growth rate of PLLA were analyzed using the Hoffman and Lauritzen equation [19,20]

$$\ln G + \frac{U^*}{R\ (T_c - T_\infty)} = \ln G_0 - \frac{K_g}{T_c \Delta T f}, \tag{4}$$

where G_0 is a pre-exponential term; R the universal gas constant; U^* the energy required for the transport of macromolecules in the melt; T_c the crystallization temperature; T_∞ the temperature where all the motions associated with the viscous flow stop, and is defined as $T_\infty = T_g - C$, where C is a constant that can assume different values; ΔT the undercooling ($\Delta T = T_m^0 - T_c$, where T_m^0 is the equilibrium melting temperature); f is a corrective factor that takes into account the variation of the equilibrium melting enthalpy with temperature, defined as $f = 2T_c/(T_c + T_m^0)$; K_g is a term connected with the energy needed for the formation of nuclei of critical size, and is defined as

$$K_g = \frac{n b_0 \sigma \sigma_e T_m^0}{\Delta H_m^0 k}, \tag{5}$$

where n is a variable that depends on crystallization regime and is equal to 4 for regimes I (high temperatures) and III (low temperatures) and values 2 in regime II (intermediate temperatures), b_0 the thickness of the stem added on the substrate, σ the lateral surface free energy, σ_e the free energy of folding, ΔH_m^0 the enthalpy of fusion, and k is the Boltzman constant [20]. For the calculations literature values of $T_m^0 = 270$°C [12] and $T_g = 62.5$°C [21] were used. To fit experimental data, $U^* = 1500$ cal/mol and $C = 30$°C were utilized, as done in previous studies on PLLA [12,21].

The plot of $\ln G + U^*/R(T_c - T_\infty)$ as a function of $1/(T_c \Delta T f)$ is presented in Fig. 5. The growth rate data fall on two straight lines, supporting distinct regime transition. The observed break in the plots was taken as an indication of regime II-III transition, since the slope ratio is 2.37 [$K_g(\text{II}) = 1.85 \times 10^5\ \text{K}^2$, $K_g(\text{III}) = 4.38 \times 10^5\ \text{K}^2$], rather close to the value 2 predicted by the theory. The transition occurs at 120°C, a temperature slightly higher than that reported in Ref. [21] (115°C). The higher value of the transition temperature may be ascribed to a different molecular mass of the PLLA used (a higher molecular mass induces regime transitions to occur at higher temperatures [22]), or to the different method used for the calculation. In fact, in Ref. [21] Hoffman and Lauritzen equation was applied using half-times of crystallization ($\tau_{(1/2)}$), under the assumption that the crystal growth rates are inversely proportional to $\tau_{(1/2)}$, whereas in this work experimental values of the spherulite growth rates were used.

The K_g values were employed to calculate the free energy of folding according to Eq. (5). In order to determine the lateral surface free energy, the following empirical relation [23] was used

$$\sigma = \alpha(\Delta h_f)(a_0 b_0)^{(1/2)}, \tag{6}$$

where a_0 is the width of the stem added on the substrate, and $\alpha = 0.25$, as appropriate to high melting polyesters [24]. Using the literature values of $\Delta H_m^0 = 1.11 \times 10^8$ J/m^3 [25], $a_0 = 5.97$ Å [26], and $b_0 = 5.17$ Å [26], a value of $\sigma_e = 40.5$ erg/cm^2 was obtained, close to the data reported in the literature [26,27].

4. Conclusions

A combination of properly designed isothermal and non-isothermal procedures allows to measure spherulite growth rates of poly(L-lactic acid) in a very wide temperature range. Determination of G on cooling at a constant rate, combined with the self-nucleation technique, permits to overcome the problems due to the length of the experiments, easily allowing a fast determination of spherulite growth rates even at very high temperatures. At low temperatures G data can be obtained using self-nucleation followed by quenching, overcoming the problems due to the high nucleation rate and density that occur when crystallization rates are measured after cooling from the melt.

Combining the various methods proposed, spherulite growth rates of poly(L-lactic acid) were measured in a large temperature range. Analysis of experimental G data with the Hoffman–Lauritzen theory allowed to detect a regime II–III transition at 120°C. For the first time the occurrence of this transition has been demonstrated using directly measured G values.

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References

[1] Wunderlich B. Macromolecular physics, Crystal nucleation, growth, annealing, vol. 2. New York: Academic Press, 1976.

[2] Keith HD, Padden FJ. J Appl Phys 1963;34:2409.

[3] Keith HD, Padden FJ. J Appl Phys 1964;35:1270.

[4] Abo el Maaty MI, Bassett DC, Olley RH, Jääskeläinen P. Macromolecules 1988;31:7800.

[5] Di Lorenzo ML, Raimo M. Progr Polym Sci. Submitted for publication.

[6] Zheng S, Jungnickel BJ. J Polym Sci, Part B: Polym Phys 2000;38:1250.

[7] Chung CT, Chen M. Polym Prepr 1992;33:420.

[8] Chen M, Chung CT. J Polym Sci, Part B: Polym Phys 1998;36:2393.

[9] Di Lorenzo ML, Cimmino S, Silvestre C. Macromolecules 2000;33:3828.

[10] Vert M, Li SM, Splenlehauer G, Guerun P. J Mater Sci, Mater Med 1992;3:432.

[11] Grijmpa DW, Nijenhuis AJ, Van Wilk PGT, Pennings AJ. Polym Bull 1992;29:571.

[12] Vasanthakumari R, Pennings AJ. Polymer 1983;24:175.

[13] Ding Z, Spruiell JE. J Polym Sci, Part B: Polym Phys 1996;34:2783.

[14] Ding Z, Spruiell JE. J Polym Sci, Part B: Polym Phys 1997;35:1077.

[15] Wunderlich B. Thermal analysis. New York: Academic Press, 1990.

[16] Androsch R, Wunderlich B. Thermochim Acta 2000;364:181.

[17] Monasse B, Haudin JM. Colloid Polym Sci 1986;264:117.

[18] Di Lorenzo ML, Silvestre C. Prog Polym Sci 1999;24:917.

[19] Hoffman JD, Davis GT, Lauritzen JI. In: Hannay NB, editor. Treatise on solid state chemistry. New York: Plenum Press, 1976.

[20] Hoffman JD. Polymer 1983;24:3.

[21] Iannace S, Nicolais L. J Appl Polym Sci 1997;64:911.

[22] Silvestre C, Di Lorenzo ML, Di Pace E. Crystallization of polyolefins. In: Vasile C, editor. Handbook of polyolefins: second edition, revised and expanded. New York: Marcel Dekker, 2000. p. 223–48.

[23] Lauritzen JI, Hoffman JD. J Appl Phys 1973;44:4340.

[24] Hoffman JD. Polymer 1985;26:803.

[25] Fisher EW, Stergel HJ, Wegner G. Kolloid ZuZ, Polym 1973;251:980.

[26] Kalb B, Pennings AJ. Polymer 1980;21:607.

[27] Hoffman JD, Miller RL, Marand H, Roitman DB. Macromolecules 1992;25:2221.