Measurement of spherulite growth rates using tailored temperature programs

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Abstract

A method recently proposed for measuring spherulite growth rates (G) using temperature programs, tailored for each polymer, is reviewed. This method, compared to the conventional isothermal procedure, permits to expand the temperature range where spherulite growth rates can be measured. Examples of application of this method are reported, in particular, the spherulite growth rates of isotactic polypropylene (iPP) and poly(L-lactic acid) (PLLA) are analyzed. For iPP, growth rates were obtained from 112 to 148 °C using different cooling rates and a self-nucleation procedure. For PLLA, measurements in both isothermal and non-isothermal conditions allowed to overcome the difficulties due to the very high nucleation density that prevent determination of growth rates at low crystallization temperatures. For this polymer the entire curve of G vs. T was obtained.
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1. Introduction

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

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

The temperature range over which crystallization rate can be measured in isothermal conditions depends on crystal size, which, in turn, is determined by nu-

cleation and growth rates. If nucleation is slow and growth fast, few large spherulites result. When both nucleation and growth are very fast, solidification can start during cooling from the melt, and crystallization rates can be measured isothermally only at high temperatures, close to the melting point. In such cases, spherulite growth rates can be determined using alternative methods, like the one proposed by Chen and Chung [7,8]; crystallization is monitored during cooling at a constant rate, and G is 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 $\mathrm{d}r/\mathrm{d}T$ is measured point by point from the plot, and $\mathrm{d}T/\mathrm{d}t$ the cooling rate used. This method permits, with a single experiment, to gain data in

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a rather wide temperature range. To obtain data in a similar temperature range with traditional isothermal procedure, several separate measurements are required as for each point of the G vs. T plot a single experimental determination is needed. The temperature range covered by a single non-isothermal measurement can be further enlarged using various cooling rates and self-nucleation procedures [9,10]. Moreover, the non-isothermal method can be coupled with isothermal measurements in order to obtain data in an even wider temperature range [10].

This contribution presents data of spherulite growth rate obtained with combined isothermal and non-isothermal methods. It will be shown that using temperature programs tailored for each polymer, G data can be easily obtained in a temperature range much larger than that available with conventional isothermal methods.

2. Experimental part

2.1. Materials

The following materials were used:

- isotactic polypropylene (iPP) with $M_w = 300,000$ Da, produced by Shell;
- poly(L-lactic acid) (PLLA) with $M_w = 101,000$ Da, produced by Boehringer Ingelheim.

2.2. Optical microscopy

Spherulite growth rates were measured by optical microscopy, using a Zeiss polarizing microscope, equipped with a Linkam TMHS 600 hot stage. A small amount of each polymer, 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.

Before measuring the spherulite growth rates, each sample was melted at 200 °C (10 min for iPP and 2 min for PLLA) to erase any prior thermal history. Dry nitrogen gas was purged throughout the hot stage during all measurements and thermal treatments.

3. Results and discussion

In Fig. 1 the radius of an iPP spherulite grown on cooling from the melt at 1 °C/min is reported as a function of temperature. The use of Eq. (2) for the data of Fig. 1 permits to obtain G values for iPP in a range of 10 °C with a single measurement, as illustrated in Fig. 2. This temperature range was expanded using different cooling rates and a self-nucleation procedure. The non-isothermal plus self-nucleation procedure is
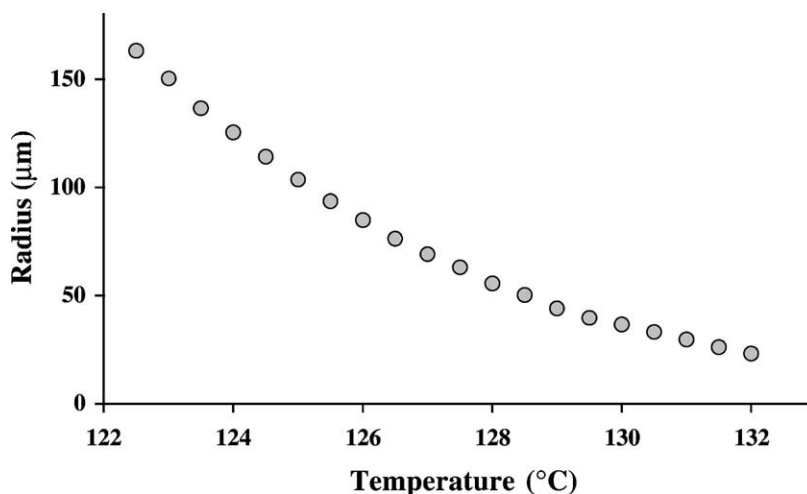

Fig. 1. Variation of the radius of an iPP spherulite with temperature during cooling from the melt at 1 °C/min.
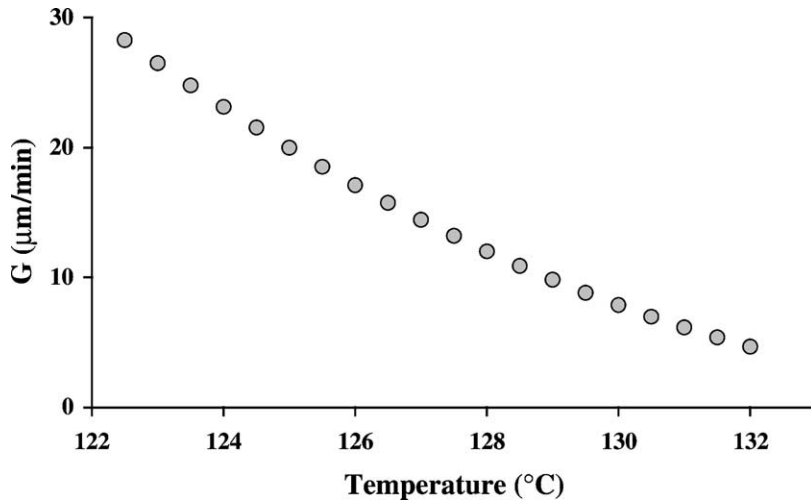
Fig. 2. Spherulite growth rates of iPP measured during cooling at 1 °C/min.

as follows: the iPP sample was cooled from the melt at 1 °C/min until the first spherulite became visible, then the temperature was raised to below the melting point and a second cooling at 1 °C/min was performed. The radius of the growing spherulite was monitored during the second cooling as a function of temperature. In Fig. 3 spherulite growth rates of iPP, determined with various cooling rates and self-nucleation, are presented. Data measured at different cooling rates are well connected to each other and in good agree-

ment with those obtained with the traditional isothermal method, reported for comparison. The very good agreement of spherulite growth rates obtained with isothermal and non-isothermal methods proves that neither the self-nucleation treatment nor the use of a non-constant temperature during measurements affects the experimental determination of G.

Fig. 3 also shows that the self-nucleation procedure allows to enlarge the G vs. T plot towards higher temperatures. Without self-nucleation, spherulite growth
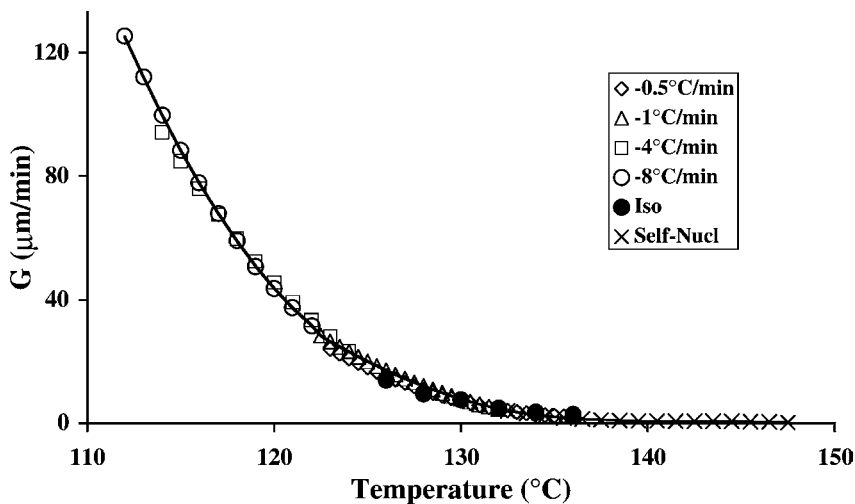

Fig. 3. Spherulite growth rates of iPP measured during cooling at various rates and in isothermal conditions.

rates of the iPP sample used can be measured only below 132 °C, using a cooling rate of 1 °C/min. To obtain G values at higher temperatures, a lower cooling rate could be used, as at lower rates there is more time to activate nuclei and crystallization can start at higher T [11]. However, only a limited raise in the onset temperature for crystallization can be obtained with the latter method: when the iPP sample is cooled at 0.5 °C/min, crystallization starts at 136 °C, a temperature only slightly higher than that available with a cooling rate of 1 °C/min ($T = 132$ °C). Using the self-nucleation procedure, instead, G data of iPP were gained at temperatures as high as 148 °C.

Conversely, higher cooling rates permit to obtain G values at lower temperatures. For the iPP sample used in this study, G was measured in isothermal conditions at temperatures from 126 to 136 °C, as reported in Fig. 3. Below 126 °C, the high nucleation and growth rates prevent the obtainment of truly isothermal data. With the non-isothermal method, instead, data can be measured at rather lower temperatures. Unfortunately, the use of high cooling rates increases the risks of thermal lags and temperature gradients within the samples. Few studies relating the influence of sample thickness and cooling rate to the occurrence of thermal gradients during non-isothermal crystallization have been reported in the literature. Monasse and Haudin [12] estimated that, for a 300 μm thick polypropylene sample and a scanning rate of 80 °C/min, using a Perkin-Elmer DSC 2B furnace, the thermal gradient between the furnace and the sample is negligible, whereas the temperature difference between top and bottom of the sample is 1 °C. 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 large parts 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 is the sample, and the higher is the cooling rate, the more critical this problem is [15]. For these reasons, in order to obtain reliable values of crystallization rates, scanning rate as well as sample mass and thickness should be limited. The samples used in the present study were very flat and thinner than 10 μm, and the cooling rates

used were not higher than 8 °C/min. In such a situation, thermal gradients within the sample and between the furnace and the sample should be negligible even during solidification, as the heat liberated during crystallization is very low, due to the low sample mass (∼0.3 mg). Hence it is quite safe to assume that the effective temperature of the sample corresponds to the one registered by the hot stage furnace.

Unfortunately, even using high cooling rates, for some polymers G can be measured only at high temperatures. For the iPP used in this study, G data were determined only above 112 °C using a cooling rate of 8 °C/min. At lower temperatures and/or higher cooling rates, crystallization rate becomes too high to be measured with the proposed non-isothermal methods, due to simultaneous fast growth of a large number of spherulites. For iPP, whose nucleation is mainly heterogeneous above 80–85 °C [16,17], the number of growing spherulites can be highly reduced by removing all traces of impurities that can act as heterogeneous nuclei. Homogeneous nucleation, instead, generally prevents measurements of G at low temperatures. This is the case of PLLA, for which growth rate data are available in the literature only at temperatures above 114 °C, due to the very high nucleation density below this limit [18].

Measurements of G of PLLA have been conducted with the non-isothermal method described above, using a cooling rate of 1 °C/min and the self-nucleation procedure. This allowed to determine G at temperatures ranging from 128 to 174 °C, a range similar to that reported in Ref. [18]. The differences between these two methods lie in the time required for the measurements. In fact our data were obtained with a single experiment that lasted less than 2 h, whereas for the data of Ref. [18] several separate isothermal measurements were needed to determine spherulite growth rates of PLLA. Unfortunately also the non-isothermal method coupled with self-nucleation does not permit to measure G of PLLA at low temperatures, due to the occurrence of multiple nucleation, hence other procedures need to be used to get data at lower T.

Quenching melt PLLA in liquid nitrogen allows to obtain a completely amorphous sample, preventing crystallization. Also the quenching of a partially crystallized PLLA, containing only one or a few growing crystallites, stops further crystal growth. This characteristic was exploited to measure G at temperatures

below the limit mentioned above. The following thermal treatment was used: the PLLA sample was cooled from the melt at 1 °C/min until the first spherulite appeared. Then it was rapidly removed from the hot stage and quenched in liquid nitrogen to stop further growth. Afterwards it was reinserted in the hot stage at 84 °C, kept at this temperature for 2 min, and finally 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. It is worth to underline that measurement of crystal growth rates during heating must be performed with care, as with the increase of temperature, crystal annealing and secondary crystallization can overlap with primary crystallization. In the present case, spherulite growth rates of PLLA were determined during heating at rather low temperatures, where annealing and secondary crystallization should be limited. Temperature range where G of PLLA can be measured with self-nucleation and quenching followed by heating is not very large, since 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 [11]. Unfortunately the choice of a different heating rate raises the temperature range where G can be measured of only a few degrees.

In order to determine G of PLLA in the low temperature side of the G vs. T plot, a different method was used. The PLLA sample 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 it was 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 digital methods can permit to take photomicrographs at very short intervals of time before crystallite impingement, as shown in Fig. 4, which allows to measure spherulite growth rates even in case of very fast crystallization kinetics. 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. 5, together with the data obtained with the other methods, reported for comparison.

The thermal treatments at which the samples were subjected (self-nucleation plus quenching) do not affect the determination of G values, as illustrated in Table 1, that reports spherulite growth rates of PLLA measured at a few selected temperatures with the three methods proposed (traditional isotherm, cooling after
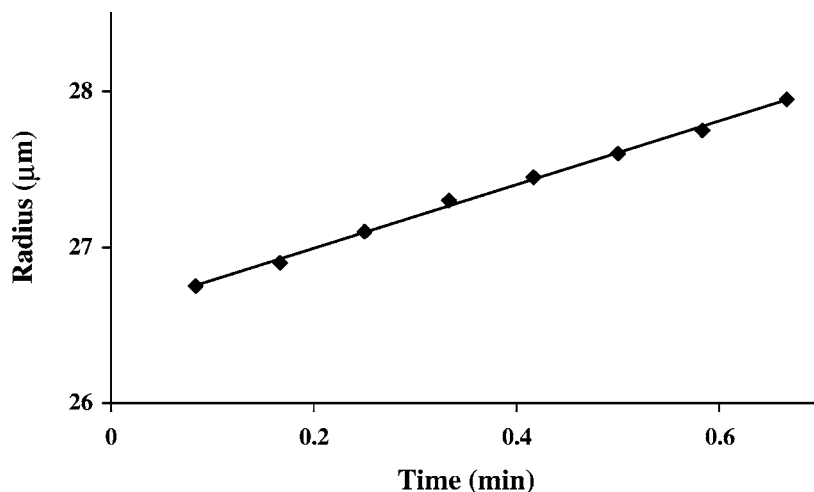

Fig. 4. Variation of the radius of a PLLA spherulite with time during isothermal crystallization at 95 °C.
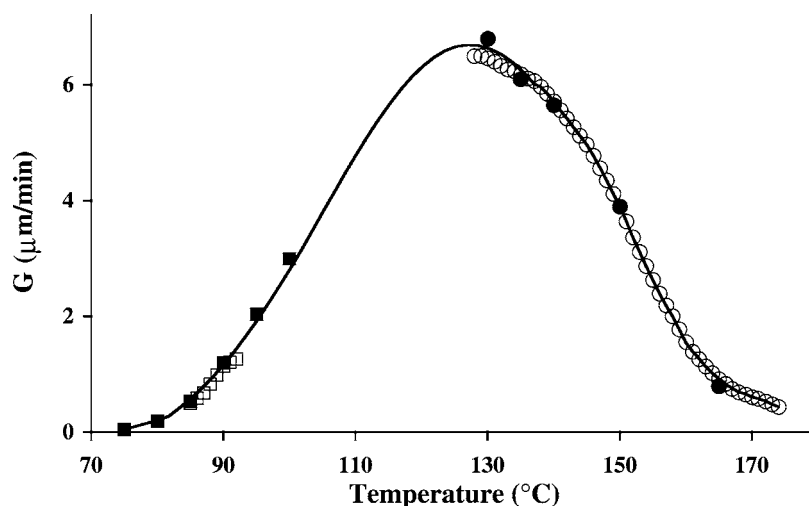
Fig. 5. Spherulite growth rates of PLLA measured with various methods: (○) cooling at 1 °C/min after self-nucleation; (●) isothermal crystallization after cooling from the melt; (□) heating at 1 °C/min after self-nucleation and quenching; (■) isothermal crystallization after self-nucleation and quenching. The solid line interpolates the experimental data.

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. 5 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 determine 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 PLLA. The overall trend is a bell-shaped curve, as predicted by the theory [1].

4. Conclusions

Spherulite growth rates of polymers can be measured in a wide temperature range using a combination of properly designed isothermal and non-isothermal procedures. Determination of *G* on cooling at a constant rate, combined with the self-nucleation technique, permits to reduce the length of experiments, easily allowing a fast determination of spherulite growth rates even at very high temperatures, with large savings of time compared to traditional isothermal methods. At low temperatures *G* data can be measured in isothermal conditions, after self-nucleation followed by quenching and re-heating, overcoming the problems due to the high nucleation rate and density that occur when crystallization rates are measured at large undercoolings.

Table 1

Spherulite growth rates (in μm/min) of PLLA 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)	Cooling	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.

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