

# Crystallization kinetics of two aliphatic polyketones

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## Abstract

This is to describe the kinetics of crystallization from the quiescent melt of two aliphatic polyketones (Shell Carilon) and to document a new device called 'Thin Slice Experiment II' that allows to determine the number of nuclei and the growth speed of spherulites of fast crystallizing polymers in the entire temperature range from the glass point to the melting point. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polyketone; Shell Carilon; Spherulitic growth rate

## 1. Introduction

In recent years the crystallization kinetics of isotactic polypropylene (i-PP) has been investigated extensively at Linz University. This happened in the course of a series of more general investigations on the fundamentals of structure development during the processing of crystallizable polymers [1–3]. Recently also other interesting crystallizable polymers became available to the research group at Linz. Two of these polymers are members of the aliphatic polyketones family supplied by Shell under the Carilon trademark (PK220 and PK230). These polymers are terpolymers of carbon monoxide with ethylene and propylene (PK220, 50:44:6; PK230, 50:47:3). The amount of propylene substituted for ethylene in the perfectly alternating olefin–CO terpolymer was controlled to optimize the melting temperature of the original copolymer from 257 to 220°C (PK220) or 230°C (PK230), in consideration of the degradation tendency at high temperatures [4]. It appears that the key mechanical properties of the final products are not substantially influenced to any extent by the low content of propylene in the reactants. The present contribution is devoted to these terpolymers.

It appears that progress in the understanding of crystallization kinetics can only be achieved in successive steps. First, the parameters for quiescent melts must be found. In those cases only the (external) cooling conditions are of importance. In complementary studies also the influences of 'weak' [1,5] and 'strong' [6] flow can be evaluated.

In previous fundamental papers of our group, a number of

arguments have been given in favor of a quite simple use of kinetic parameters which, nevertheless, enable a realistic mathematical description of structure development during the processing of crystallizable polymers. For a quiescent melt, two parameters are sufficient, viz. the number of primary nuclei per unit volume and the growth speed of spherulites, both as unique functions of crystallization temperature. Fortunately the physics of nucleation lends itself to our purposes! In principle, there are three sources for primary nuclei. The most trivial one consists of particles of foreign matter which form heterogeneous nuclei. But the number of these nuclei will certainly not be time and temperature dependent. The second source lies in the sporadic or thermal nucleation. In fact, from a historic point of view, this is the most popular source.

However, it has been shown that this nucleation is restricted to a range of temperatures just below the thermodynamic melting point. This is known as the range of metastable states [7]. For most polymers it extends to no more than some 40–50°C below the equilibrium melting point, which is not too much in view of the enormous undercoolings, which are characteristic for polymer processing. Theoretically, this range of metastable states can be estimated from the ratio of two thermodynamic quantities, viz. the latent heat of fusion and the specific heat of the melt [7]. In addition, it can be shown experimentally that the kinetics of the sporadic formation of primary nuclei is rather sluggish with polymer melts [8]. So, these two facts together make a considerable influence of the sporadic nucleation on the structure formation under processing conditions very improbable. In fact, in polymer processing, cooling speeds are high and crystallization takes place at temperatures far

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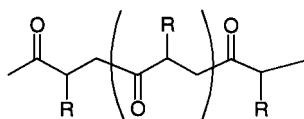


Fig. 1. Chemical structure of aliphatic polyketones (R=H and CH<sub>3</sub>).

below the melting point. The temperature passes through the range of metastable states at such a speed that there is practically no time for the development of sporadic nuclei. From the point of view of the mathematical description of structure formation, this fact brings about a great relief.

As a consequence, the third source of nucleation gains importance. It consists in the great stock of athermal nuclei. Our conclusion must be that, besides the heterogeneous nuclei, which have been used to accelerate crystallization in a range of temperatures closer to the melting point, the said athermal nuclei must be responsible for the structure formation in an extended range of processing temperatures. In the course of our investigations on *i*-PP, it could be shown that the number of these nuclei increases by about six decades, when the crystallization temperature is lowered from 130 to 85°C [9]. For an adequate judgment of the importance of this fact, one has to keep in mind that the melting point of *i*-PP is 212°C [10] whereas in injection molding, the temperature of the mold is usually kept at about 60°C. In the said papers it could be made plausible that the number of athermal nuclei per unit of volume is indeed a unique function of temperature.

An interesting side effect of one of these papers is the perception that, in contrast to the situation in quiescent melts, flow induced crystallization can also be very active in the temperature range of metastable states. Apparently this is because of the enormous acceleration of the kinetics as caused by any type of flow [1,3,5,11–14]. As will be worked out elsewhere, this fact does not necessarily form a disadvantage. In pertinent calculations, there will probably be no serious interference between the nucleation close to the mold wall, as caused by shear induction, and in the interior of the mold, where flow rates are unimportant.

For the moment, the goals of the investigation should be clear. In Part I the growth speed of spherulites as a function of temperature will be presented. In Part II the number of athermal nuclei per unit of volume as a function of crystallization temperature will be disclosed. The pertinent

techniques were partly developed in previous papers [1,8]; partly they are described first in this paper.

The extended early work by Magill and co-workers can only be mentioned here. It is restricted to rather slowly crystallizing polymers. Only one of the latest publications of this group is mentioned here [15], because of its containing many references of earlier work.

## 2. Polyketones

Semicrystalline polyketones represent a new class of potential engineering thermo-plastics. Their property set is positioned in the area of polyamides and polyacetals. They are characterized by their stiffness, high melting temperature and resistance against water and moisture. In particular, one should also mention chemical resistance, stability at hydrolysis conditions, impact toughness, flame resistance without additives containing halides or red phosphor, and short cycle times in injection molding. Aliphatic polyketones are proposed to be used in motor industries as well as in household utensils [4].

Attempts to synthesize aliphatic polyketones succeeded in 1951. Carbon monoxide and ethylene have been copolymerized [16]. The high melting temperature of 257°C has limited the application of this copolymer since it degrades too fast at processing temperature (approximately 25°C above the melting temperature).

For that reason no efforts were spared in finding aliphatic polyketones with melting temperatures significantly lower than 260°C (in combination with other novel technical solutions to the thermal stabilization problem). Copolymerization of carbon monoxide with olefines like propene, pentene and hexene could be accomplished. The mechanical properties of those materials, however, are unsatisfactory.

Finally, terpolymers of carbon monoxide, ethylene, and propylene (Fig. 1) were found to combine the lower melting temperature of the just mentioned copolymers [4] with the good mechanical properties of the original carbon monoxide/ethylene copolymer. Proper percentage of propylene was found to be 6% (PK220) or 3% (PK230). Shell Chemicals Company holds the patent on this synthesis [14]. Shell Chemicals' development products PK220 and PK230 were used as terpolymers for the present work. The data given in Table 1 have been available at the beginning of the work.

## 3. Experiments

### 3.1. Spherulitic growth

#### 3.1.1. Sample preparation

In two types of vacuum presses of 6 and 20 mm diameters, the original granules were melted for 10 min at 260°C in vacuum and subsequently pressed at 10 MPa and cooled to room temperature. The required samples were cut from such prepared cylinders.

Table 1  
Physical properties of the aliphatic polyketones

Property	PK220	PK230	Source
Propylene content (%)	6	3	[4]
Melting temperature (°C)	220	230	[4]
MFI 240/2.16	6.0 g/10 min	–	[4]
Specific gravity (kg/m)	1240	–	[17]
Glass transition temperature (°C)	15	–	[4]
Heat of fusion (J/g)	227	–	[18]

Table 2

Critical cooling rates as calculated for the two polyketones investigated (based on results that will be presented in the next section)

Polymer	$G_{\max}$ (m/s)	$k_G$ ( $K^{-1}$ )	$N_{\max}$ ( $m^3$ )	$q_{\text{crit}}$ (K/s) (via Eq. (3.6))
Carilon PK220	$9.7 \times 10^{-6}$	0.0364	$4 \times 10^{14}$	260
Carilon PK230	$5.4 \times 10^{-5}$	0.0446	$1 \times 10^{14}$	744

### 3.1.2. Hot stage microscope

In the higher range of temperatures, where the growth of spherulites is slow enough (from 1 nm/s to 1  $\mu\text{m/s}$ ), a hot stage microscope was used. Thin slices (5  $\mu\text{m}$ ), as cut on a microtome [19], were first melted for 2 min at 260°C and then cooled to the chosen temperature of crystallization  $T_C$  at a nominal cooling rate of  $-100$  K/min. Digital photos, as taken in proper time intervals with the polarizing light microscope, were evaluated in order to obtain the spherulite radii as functions of crystallization time according to the equation

$$r(t) = r_0 + G(T_C)(t - t_0), \quad (3.1)$$

where  $r$  is the spherulite radius,  $G$  the growth speed,  $T_C$  the crystallization temperature,  $t$  the time and  $r_0 = r(t_0)$ , the radius of spherulites (subsequently called ‘offset radius’) which started growing already during the period of cooling, at the time  $t_0$  when the sample reaches  $T_C$ .

### 3.1.3. Thin Slice Experiment I

This experiment could be used for the measurement of growth speeds up to 10  $\mu\text{m/s}$  in a temperature range down from the melting point to the temperature  $T_{\max}$ , where the maximum growth speed occurs. In this temperature range Thin Slice Experiment I permits quenches of the sample much faster than quenches with a hot stage microscope.

Sandwiches of thin polymer slices between cover glasses are melted on a metal block for 2 min at 260°C and then transferred to an oil bath at crystallization temperature  $T_C$ . The sample is kept in this oil bath for the crystallization time  $t_C$ . After that it is quenched in a bath of cold water to stop crystallization.

The morphologies, as found in samples prepared in such a way, are evaluated microscopically in terms of the diameter of the largest identified spherulite ( $r$ ) as a function of the chosen crystallization time  $t_C$ . The spherulitic growth rate could be determined from the measured data using the equation

$$r = G(T_C)t_C, \quad (3.2)$$

which is a special case of Eq. (3.1) with  $t_C = t - t_0$  and offset radius  $r_0 = 0$ .

The principle of Thin Slice Experiment I is described by Ratajski and Janeschitz-Kriegl [8].

### 3.1.4. Thin Slice Experiment II

For an observation of growth speeds of polyketones at temperatures lower than temperature  $T_{\max}$  of the maximum growth speed  $G_{\max}$  (around 140°C for polyketones), a new

experimental device had to be developed. It should possibly enable a quench of the sample to the crystallization temperature fast enough for the avoidance of any previous crystallization during the quench.

The value of such a cooling rate can be estimated. First, the minimum cooling rate is calculated for a transition to the glassy state. Therefore, the growth rate  $G$  is approximated by a function which is quadratic in the exponent. This function will be shown to fit the observed data properly:

$$G(T) = G_{\max} e^{-(k_G(T-T_{\max}))^2}. \quad (3.3)$$

Using the number of nuclei  $N_{\max}$  at the temperature of maximum growth rate  $T_{\max}$ , the number of nuclei  $N(T)$  as a function of temperature can be approximated reasonably well by a function, which is linear in the exponent:

$$N(T) = N_{\max} e^{-k_N(T-T_{\max})}. \quad (3.4)$$

If one considers a cooling process with constant cooling rate  $q$ , the temperature  $T$  at time  $t$  can be given by:

$$T(t) = T_{\max} - qt. \quad (3.5)$$

With these assumptions, Eder [20] obtained the following result for the minimum (critical) cooling rate (Table 2), if a final degree of crystallinity of 1% is admitted:

$$q_{\text{crit}} = 13.24 \frac{G_{\max} \sqrt[3]{N_{\max}}}{k_G}. \quad (3.6)$$

One of the goals of the present research was to find the relevant parameters.

The preliminary conclusion is that a surprisingly high cooling rate of approximately 750 K/s is required to quench the product PK230 without exceeding a degree of crystallinity of 1% during the quench.

For achieving a cooling rate as high as possible, we automated Thin Slice Experiment I and called it ‘Thin Slice Experiment II’. In a closed cell, the sandwiched sample (cover glass + thin polymer slice of 5  $\mu\text{m}$  + cover glass) is melted in a gas atmosphere. The cell is then flushed with a fluid at crystallization temperature  $T_C$  for a certain crystallization time  $t_C$ . Fig. 2(a) shows the apparatus during this crystallization step. After that, the first fluid is replaced by a second fluid of low temperature  $T_Q$  (e.g. ice-water at 0°C), which flushes the cell again. This final quench stops crystal growth.

With a thermocouple located as close as possible to the sample, a temperature–time profile is recorded, as shown in Fig. 2(b).

In analogy to Thin Slice Experiment I, the morphologies

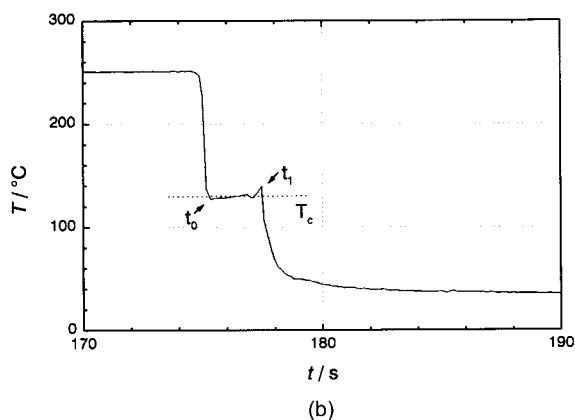
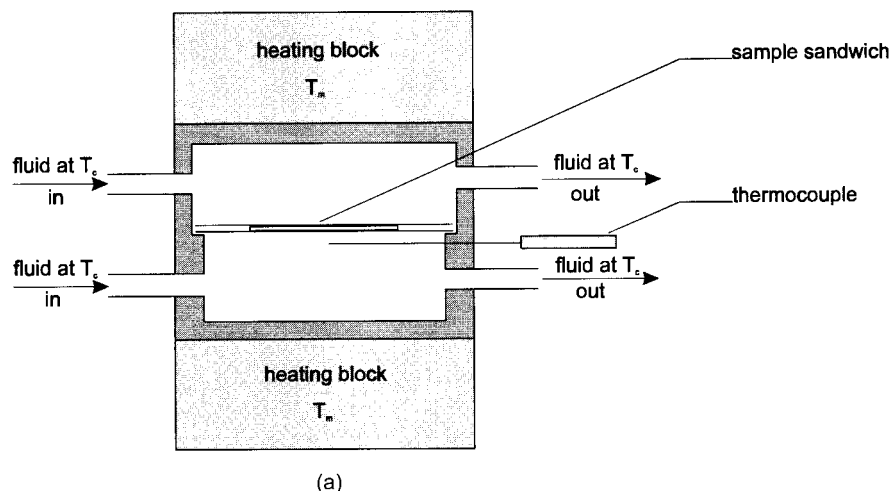


Fig. 2. Thin Slice Experiment II: (a) schematic drawing of the measurement device; (b) temperature–time profile ( $T_C = 130^\circ\text{C}$ ,  $t_C = 2$  s).

of the samples are evaluated microscopically in terms of the diameter of the largest identified spherulite ( $r$ ). In every series of experiments, one varies the crystallization time  $t_C$  while keeping the crystallization temperature  $T_C$  constant in order to measure the spherulite radius against crystallization time. Such an evaluation (for  $T = 170^\circ\text{C}$ ) is shown in Fig. 3(a).

At target temperatures below  $130^\circ\text{C}$ , spherulites apparently had started growing already during the quench. So, when the crystallization temperature is reached in the sample, there have already been formed spherulites with an offset radius  $r_0$ . Thus the growth rate can be evaluated from:

$$r = r_0 + G(T_C)t_C. \quad (3.7)$$

For illustration, Fig. 3(b) is introduced. This figure contains data obtained at  $T = 98^\circ\text{C}$ . The ‘initial’ radius was found to be zero for crystallization temperatures above the temperature of the maximum of  $G(T)$ , and of

the order of  $20 \mu\text{m}$  for temperatures below the temperature of the maximum.

Fig. 4 shows a typical morphology. This is a sample that crystallized at a temperature well below the temperature of the maximum of growth speed. Clearly isolated spherulites can be seen. Observed spherulite radii increase with increasing time of crystallization.

### 3.1.5. Light scattering experiment

For the purpose, an apparatus was used as developed earlier at Linz University. It was first successfully applied for measurements of the crystallization kinetics of polypropylene (i-PP) and polyethylene (HDPE) [8].

In this device, the sample is held in a vertical glass cylinder which is closed on both sides by metal plugs. Initially, the whole device is heated to a temperature well above the melting point of the sample. Between the upper plug and the sample a thin aluminum foil is placed. This foil prevents the adhesion of the sample to the upper plug and, at the same

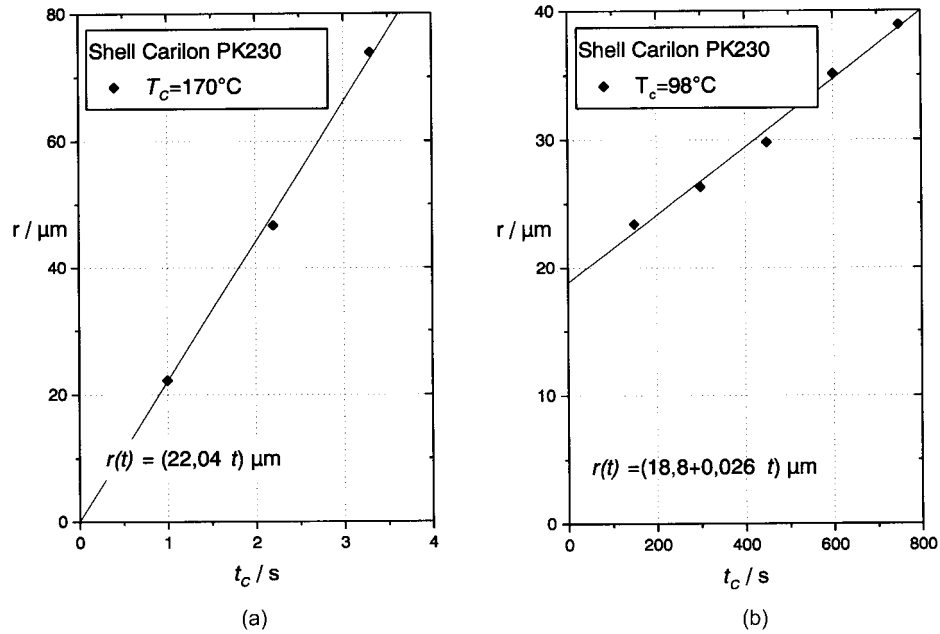


Fig. 3. Thin Slice Experiment II — spherulite radii versus crystallization time: (a)  $170^\circ\text{C}$  (no initial radius  $r_0$ ); (b)  $98^\circ\text{C}$  (the initial radius after cooling is  $18.8 \mu\text{m}$ ).

time, reflects a light beam. At a certain moment, the upper plug, which is kept at the initial temperature, is quickly replaced by another metal plug which is kept at the desired crystallization temperature by a thermostat liquid circulated through its internals. Because of the large differences in the products of heat conductivity, density and heat capacity of metals and polymers, the surface temperature at the aluminum surface is adjusted almost immediately to a temperature very close to the temperature of the replacing plug. In the lower plug two windows are located. Through one of

them a laser light beam enters under an oblique angle so that the light, which passes the translucent melt and is reflected from the aluminum foil, cannot return directly through the second window to a photo diode. It now turns out that the surface of the melt, which touches the aluminum foil, is very suddenly covered after some time by a thin fleece of crystallizing material. The moment when this occurs can also be determined with an ordinary stopwatch by visual observation. Apparently some stray light from the aluminum foil, which reaches the photo diode, is suddenly absorbed by the

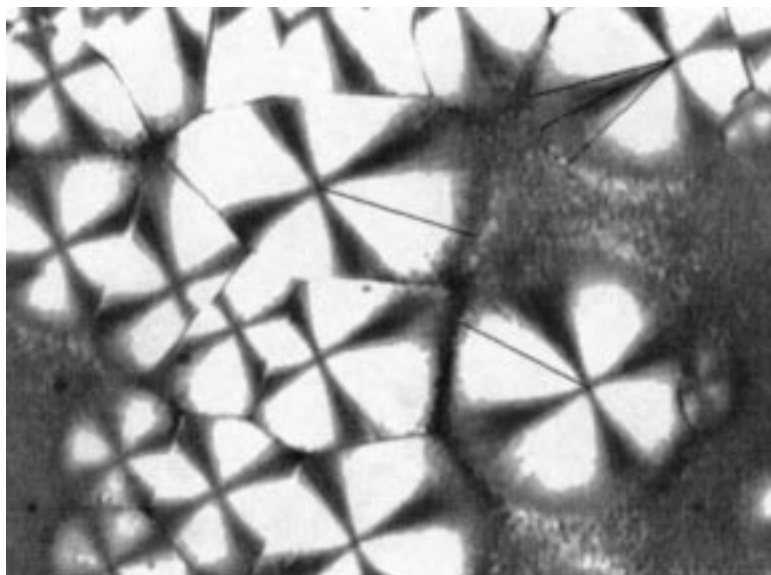


Fig. 4. Morphology of a sample, crystallized for 450 s at  $98^\circ\text{C}$ . The spherulite radius indicated by the black lines is  $r = 29.8 \mu\text{m}$ .

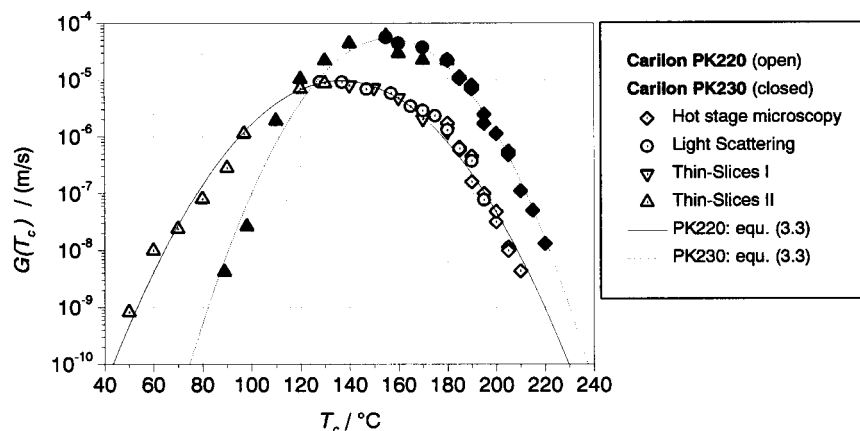


Fig. 5. Spherulitic growth rate  $G$  versus crystallization temperature  $T_C$  for both samples.

said fleece. The time span between the moment of the replacement of the upper plug and the disappearance of the stray light is called the ‘crystallization time’  $t_{LS}$ .

The following equation was used to determine the growth rate  $G$ :

$$G(T_C) = C/t_{LS}. \quad (3.8)$$

The optical constant  $C$  is found by calibration at a chosen high temperature, where  $G$  could be determined by independent measurements (e.g. in a hot stage microscope or by Thin Slice Experiment I or II, respectively).

By the way,  $t_{LS}$  appears to be no ‘induction time’ but the time needed until crystallization, which immediately starts at tiny nuclei, becomes optically detectable: at short times scattering intensity is proportional to the sixth power of time. As a consequence, one does not see anything for a rather long time. Later, the upward bent in scattering is apparently sharpened by multiple scattering. Confer Fig. 3(a) of this paper and many figures of previous publications [1,8] where, with respect to the spherulite radius, no induction time can be observed on the time-scale of interest.

### 3.2. Counting of nuclei

#### 3.2.1. Counter current method [9]

An apparatus was used, as developed earlier at Linz University. With this device one can cool a cylindrical sample (4 mm in diameter, 20 mm in length) at rates of up to  $-50$  K/s. Nevertheless, its temperature is made to swing quickly into the desired crystallization temperature by the application of a counter current. First, the sample is rinsed from one end with a fast moving fluid of a temperature far below the target crystallization temperature, in order to achieve a high initial cooling rate. A thermocouple is placed along the center-line of the sample. With this thermocouple the temperature–time profile, as obtained in the core, is recorded. As soon as the target temperature is passed, a counter current of a fluid of the desired target temperature

is applied. After a small undershoot, this temperature is reached.

Cross-sections of the completely solidified sample are prepared afterwards. In the core of these cross-sections the number of spherulites per area  $N_A$  is counted under a microscope. The  $3/2$ th power of this number is considered as the number of nuclei per unit volume  $N_V$ . The latter number is then plotted as a function of the crystallization temperature,

$$N_V = \sqrt{N_A^3}. \quad (3.9)$$

#### 3.2.2. Thin slice method

Thin samples (thickness  $D = 5 \mu\text{m}$ ) are crystallized isothermally with Thin Slice Experiment II. They are evaluated microscopically in terms of the number of spherulites ( $N$ ) counted per volume ( $V$ ) of the translucent sample. The sample volume is the product of sample thickness  $D$  and the area  $A$  visible in the microscope ( $V = AD$ ). The number of spherulites per unit volume ( $N_V$ ) is calculated according to:

$$N_V = \frac{N}{V}. \quad (3.10)$$

The main concern in these measurements is the accuracy of the determination of the sample thickness  $D$ . However, as will be seen from Fig. 6, an error in the sample thickness of 20–30% (as estimated by Stadlmann [21]) does not change the general picture.

The thin slice method yields very similar results to those achieved by the independent counter current method.

## 4. Results

This section is to present the growth speed of spherulites and the number of athermal nuclei per unit of volume as functions of crystallization temperature.

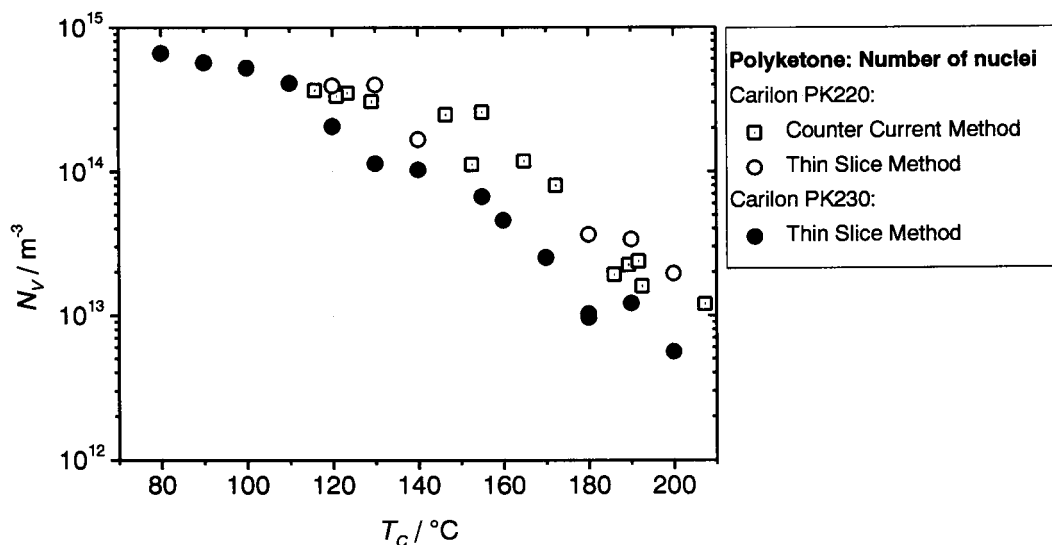


Fig. 6. Number of athermal nuclei  $N_V$  versus crystallization temperature  $T_c$ .

#### 4.1. Spherulitic growth

Results, as obtained with the four different techniques described, are compared in the total temperature range from 50 to 220°C. In particular, one has: (a) hot stage microscopy (180–220°C); (b) Thin Slice Experiment I (140–180°C); (c) Thin Slice Experiment II (50–180°C); and (d) Light Scattering experiment (130–180°C). The results are shown in Fig. 5.

Over a temperature range of 160°C, the speed of crystal growth varies by 4–5 decades between 1 nm/s and 0.1 mm/s. The experimental results are nicely fit by the simple empirical function, as given in Eq. (3.3), with a maximum growth speed  $G_{\max}$  as it occurs at  $T_{\max}$ , and a parameter  $k_G$  which reflects the temperature sensitivity of the growth speed. For the two materials the following fitting parameters are found (Table 3):

The terpolymer PK230 with a propylene content of 3% has a maximum growth speed ( $G_{\max}$ ) five times higher than PK220 with a propylene content of 6%. The temperature where the maximum occurs ( $T_{\max}$ ) is 136.5°C for the polyketone with 6% propylene (PK220). For the terpolymer with 3% propylene (PK230) it is 20°C higher.

Compared with other crystallizable polymers, both aliphatic polyketones show very fast crystallization. Take, for example, the maximum growth speed of polybutene ( $G_{\max} \approx 10^{-6}$  m/s) [22], or the one of polypropylene ( $G_{\max} \approx 10^{-5}$  m/s) [1,8]. The growth speed of polyketone-spherulites compares with that of polyethylene ( $G_{\max} \approx$

$10^{-4}$  m/s) [8]. The overall crystallization speeds, however, are also determined by the number of nuclei!

#### 4.2. Number of nuclei

The samples, of which the number of nuclei per unit volume were counted, were prepared in two different shapes: (a) cylinders (4 mm in diameter, 20 mm in length) and (b) thin slices (5  $\mu\text{m}$  in height). Both kinds of samples were cooled to crystallization temperature very fast and kept there until the material was crystallized completely.

From the number of spherulites per sample volume, as counted under the polarizing-light microscope, the number of spherulites per unit volume was calculated according to Eqs. 3.9 and 3.10. The results are shown in Fig. 6:

Over a temperature range of 120°C, the number of nuclei increases for PK230 by 2 decades, from  $6 \times 10^{12} \text{ m}^{-3}$  at 200°C to  $6 \times 10^{14} \text{ m}^{-3}$  at 80°C. The number of nuclei for the other polyketone are larger. They differ almost by a factor 4.

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Table 3

Fitting parameters for the growth speed of spherulites

Polyketone (propylene content)	$G_{\max}$ (m/s)	$T_{\max}$ (°C)	$k_G$ (°C $^{-1}$ )
Carilon PK220 (6%)	$9.7 \times 10^{-6}$	136.5	0.0364
Carilon PK230 (3%)	$5.4 \times 10^{-5}$	156.1	0.0446

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