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ORIGINAL CONTRIBUTION

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Crystallization of isotactic polypropylene in a temperature gradient

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Abstract The crystallization of isotactic polypropylene films was investigated in constant and in time-dependent temperature gradients. The temperature gradient influences a spherulitic pattern as well as an internal structure of spherulites. The gradient can accelerate conversion of the melt into spherulites although it has no effect on spherulitic nucleation. The acceleration of the local conversion results from a contribution of spherulites nucleated in colder parts of a sample. The observed effects intensify with the increase of the temperature gradient and they are also enhanced by a higher crystallization temperature.

Key words Polypropylene · Spherulites · Crystallization in a temperature gradient

Introduction

The crystallization and morphology of isotactic polypropylene (iPP) were intensively studied in previous years. Investigations of iPP have contributed to the understanding of the crystallization, the melting process, the spherulitic patterns as well as the internal structure of spherulites [1, 2, 3].

Recently a new technique – atomic force microscopy (AFM) – was developed, with the possibility of surface morphology studies of semicrystalline polymers. Work in which AFM was used concentrated on many aspects in selected polymers, for example, roughness of the growing front, a rate of lamellar growth, a lamellar thickness. Among other crystallizing polymers iPP was also studied by the AFM technique [4, 5, 6].

The investigations of iPP crystallization and structure concerned predominantly both isothermal and non-isothermal crystallization processes but for processes occurring in the absence of a temperature gradient. Although industrial processes of polymer solidification often involve crystallization in a temperature gradient, knowledge of spherulite crystallization under such conditions is scarce.

Nearly 20 years ago investigations of spherulite growth and the morphology formed during zone solidification were conducted for iPP [7, 8] and for other polymers [9, 10, 11, 12]. The zone solidification technique was based on the passage of a sample at a constant rate through a steep temperature gradient [7], sufficient for melting a polymer. The crystallizing interface established moved slowly through the length of the sample. In Ref. [7] the temperature gradient was up to 30 K/mm. The melt zone moved slowly (3 μm/min), so the temperature at the crystallization front was constant, independent of its position in the sample. Although the attention of authors was focused on the β crystalline form, the anisotropy of spherulite growth, the quasi-parabolic shapes of interspherulitic boundaries and the change in the orientation of lamellae towards the direction of motion of the crystallizing front were observed in iPP. The final polymer structure was composed of highly elongated spherulites with parallel lamellar fibrils. Also Fujiwara [13] and Crissman [14] solidified directionally polypropylene samples from a melt and studied the resulting microstructure by X-ray diffraction and mechanical relaxation, however without a detailed examination of spherulitic morphology.

Schulze and Naujeck [15, 16] derived expressions describing the shapes of spherulites and the directions of growth in a linear field of growth rate and in a linear temperature field. They confirmed the results by a comparison with shapes and lamellar growth directions of iPP spherulites crystallized in a unidirectional, constant temperature gradient in the range 8–11 K/mm.

The computer simulation of the spherulitic growth in a temperature gradient was described in Refs. [17, 18, 19, 20].

The experimental data concern mainly the crystallization during zone solidification. The zone solidification differs from the crystallization in a constant temperature gradient, where the temperature changes within a material, and it is also different from the crystallization in time-dependent temperature gradient. In the temperature gradient the nucleation and growth of spherulites vary within a sample, as they are temperature-dependent. The temperature and/or temperature gradient at the crystallizing fronts change as the spherulites enlarge. It could be expected that such conditions are closer to those inside a polymer solidified during industrial processing.

In the present work the crystallization of iPP films was studied in constant and also in time-dependent unidirectional temperature gradients by means of light microscopy. Additionally, the morphology of iPP spherulites crystallized in the temperature gradient was investigated by an AFM technique.

Experimental

The crystallization of iPP in the temperature gradient was carried out on a hot stage constructed for this purpose (Fig. 1). The stage consists of two copper blocks of surface area 35 × 15 mm and of height 7 mm, equipped with heaters and resistance platinum thermometers connected to two programmable temperature controllers (Cole Parmer 535 process controllers). The temperature of each copper block can be programmed separately.

The blocks are positioned parallel inside an aluminium cell with glass windows, allowing microscopic observations in transmitted light. The distance between the blocks can be adjusted by a screw. The gaseous nitrogen flow through the cell protects the samples from degradation. The accuracy of the temperature control of the blocks is 0.1 K. The stage is mounted in a polarizing microscope. Microscopic images are captured by a Panasonic BL 202 camera and recorded by a Panasonic video recorder or by a personal computer equipped with a frame grabber card (MV 1000, Mutech).

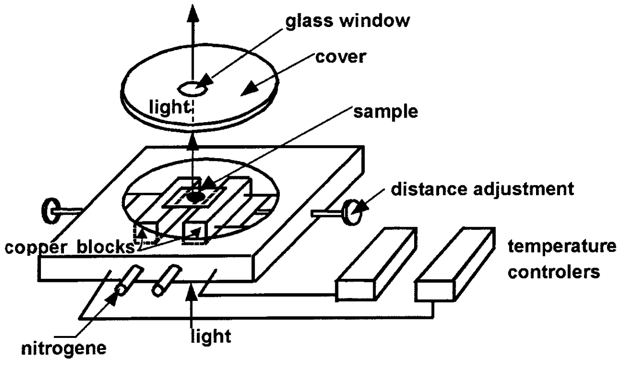

Fig. 1 Scheme of the hot stage for crystallization in a temperature gradient

The iPP used in this study was a product of Polysciences, USA, $M_w = 220{,}000$, $M_n = 17{,}000$. The films of thickness 10–12 μm, obtained by compression molding, placed between two cover glasses of size 7 × 7 mm, were positioned on the top of the copper blocks, bridging them. In order to improve the thermal contacts between the lower glass and the blocks a thin layer of the paste of heat conductivity 2.3 W/mK produced by Omega, USA, was applied. The iPP films were heated to 220 °C, melt annealed for 5 min and cooled at a rate of 25 K/min to a final constant temperature, which was different for each block, to obtain a steady unidirectional temperature gradient. The temperatures of the blocks and the distances between the blocks are listed in Table 1. The entire crystallization process was observed in a light polarizing microscope.

First, the temperature distributions in crystallizing iPP films, placed on the top of blocks having different temperatures, were determined with the help of the temperature dependence of a spherulite growth rate measured previously for the same polymer in isothermal conditions, on a Linkam hot stage by Nowacki et al. [21].

During gradient crystallization the growth rate of iPP spherulites, *G*, was measured for short distances in the direction perpendicular to the longest edges of the blocks. Then, *G* was used to evaluate the temperature distribution for each temperature difference and the distance between the blocks. We were aware of the possibility of the decrease in *G* in the iPP used by us owing to fractionation. The decrease in *G* owing to fractionation was observed during the isothermal crystallization of that polymer at a temperature of 128 °C and higher [21]. It depended, however, on the spherulite radius. Therefore, in the present study spherulites with small radii were chosen for the measurements to limit the error of the temperature estimation to ±0.25 K.

The isotherms were found to be lines parallel to the edges of the copper block. The exemplary temperature distribution, plotted in Fig. 2, shows that the temperature gradient is constant except for the areas adjacent to the blocks. The linearity of the temperature distribution in certain temperature ranges was preserved in all the crystallization experiments in the steady gradient. The values of the temperature gradient during the crystallization experiments were 20 K/mm in the range 127–139 °C and 35 and 37 K/mm in the range 123–143 °C (Table 1). It should be noted that the same constant temperature gradient was found in the samples labelled 170/100 and 180/95. The increase in the difference between the temperatures of the blocks resulted primarily in changes in the nonlinear temperature distribution in the vicinity of the blocks. Only a slight elevation of the constant temperature gradient was

Table 1 The conditions of crystallization of isotactic polypropylene (*iPP*) films in a constant temperature gradient. *L* represents the left block and *R* represents the right block

Symbol	Crystallization temperatures (°C)	Distance between blocks (μm)	Temperature gradient (K/mm)
170/100	L = 170 R = 100	1,050	35
180/95	L = 180 R = 95	1,050	35
180/95n	L = 180 R = 95	700	37
150/120	L = 150 R = 120	700	20
Isothermal	both: range 123–133	1,050	0

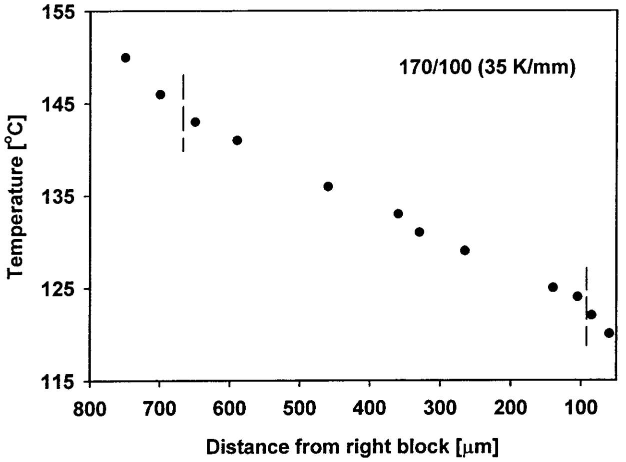

Fig. 2 Distribution of the temperature during crystallization of the isotactic polypropylene (*iPP*) film labeled 170/100

achieved by diminishing the distance between the blocks while using the same microscope glasses.

For comparison of the results obtained for the gradient crystallization the isothermal crystallization of iPP films was also conducted. In this case both blocks were cooled at a rate of 25 K/min to the same temperature in the range 123–138 °C.

An additional check of the temperature distribution in the iPP films during crystallization was performed by studies of a melting behaviour after the crystallization. The melting of samples crystallized isothermally and in the temperature gradients was investigated by polarized light microscopy during heating at a rate of 20 K/min. The melting temperatures of different parts of the iPP films which solidified in the temperature gradients correspond to melting temperatures of films crystallized isothermally at respective temperatures, which confirms the temperature distribution, determined by the measurements of the spherulite growth rate, *G*.

The entire crystallization process and the morphology of the spherulites were studied by polarized light microscopy. The local conversion of the melt into spherulites was studied during crystallization in the constant temperature gradient at selected isotherms. The degree of conversion, defined as the sum of the solidified sections at the isotherm considered to the total length of the isotherm, was measured as a function of the time elapsed from the moment the temperatures of the blocks stabilized. The nucleation density was determined for narrow zones at selected temperatures, ±0.5 K, in samples 170/100 and 180/95 by counting the spherulite centres and recalculating the numbers per volume unit of the polymer obtained. Several samples crystallized at the same conditions were taken into account. The time dependence of the degree of conversion and the nucleation density were also measured in the isothermally crystallized samples for comparison.

The samples crystallized with a free upper surface were also prepared and examined with an atomic force microscope (constructed at the University of Lodz, Poland) in contact mode. Melting, cooling and crystallization conditions were the same as in the case of the 170/100 sample. The samples crystallized isothermally with the free upper surface were also prepared and examined with the atomic force microscope for comparison. To prevent degradation, the crystallization was carried out under the flow of gaseous nitrogen.

In addition, the crystallization of iPP during the cooling of blocks at different rates was studied. The details of the temperature change programmes are given in Table 2. The iPP samples were melt-annealed at 210 °C for 1–2 min prior to cooling. The temperature and the time of melt-annealing were decreased in this case, compared with the procedure for the samples crystallized in the constant temperature gradient, because of rather slow cooling, resulting in a prolonged exposition to high temperature. In one case (sample 6) the cooling of the blocks was initially faster and then slower.

Table 2 The cooling conditions of iPP films crystallized in time-dependent temperature gradients. All samples were melt annealed at 210 °C for 2 min prior to cooling

Sample symbol	Cooling rate of left block (°C/min)	Cooling rate of right block (°C/min)	Distance between blocks (*μ*m)
1	2.5	5	1,050
2	8	12	700
3	10	12	700
4	4.5	6.5	700
5	2	3	700
6	12 to 160, then 0.6	20 to 130, then 4	700

Results

Crystallization in a constant temperature gradient

The temperature dependence of the nucleation density, *I*, in the iPP samples crystallized isothermally and in the temperature gradient in the temperature range 124–139 °C is shown in Fig. 3. The numbers of spherulite centres per cubic millimetre of the polymer determined experimentally follow the dependence $I = \exp[111.265-$

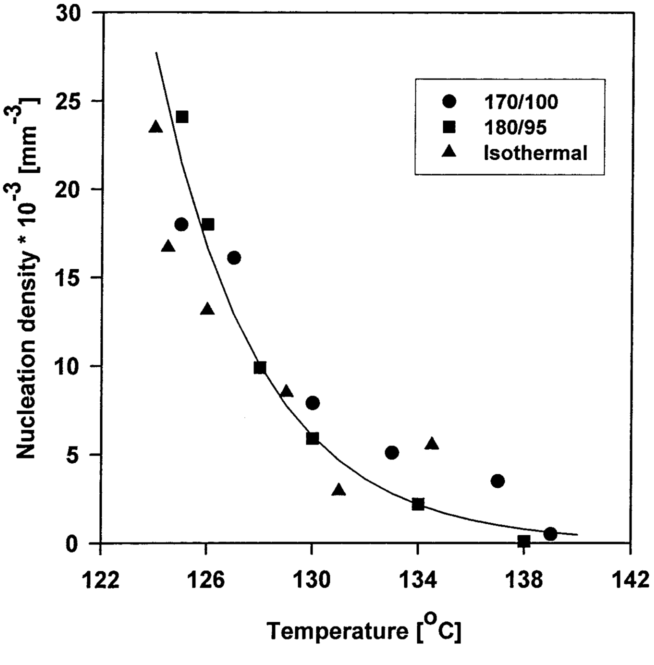

Fig. 3 Nucleation density in iPP crystallized isothermally and in a temperature gradient

0.2544(T + 273.15)], where T denotes the crystallization temperature in degrees Celsius. The comparison of the nucleation density values obtained for the samples crystallized isothermally and in the temperature gradient shows no significant influence of the gradient on the nucleation of the spherulites. It should be mentioned that the nucleation of the spherulites occurred in relatively short time intervals compared to the time needed for full conversion of the melt into spherulites. Therefore the results were not affected by the further acceleration of the conversion rate in the gradient-crystallized samples.

Various stages of iPP crystallization in the temperature gradients of 20 and 35 K/mm are shown in the micrographs in Figs. 4 and 5. During the gradient crystallization the spherulitic nucleation and growth strongly depend on the position, i.e. on the local temperature. The crystallization starts in the colder part of a sample and after a short time this area is completely filled with the spherulites, while the high-temperature part is still uncrystallized owing to the weak nucleation and slow growth of spherulites. Hence, the spherulites nucleated in the colder part of film can grow in the direction of increasing temperature. Shortly after the onset of crystallization they form a joint crystallizing front which occludes the spherulites nucleated ahead of it. With increasing time of crystallization the front becomes nearly flat, parallel to the direction of the isotherms. Owing to the weak nucleation in the hotter part of the film, especially in the gradient of 37 K/mm at a temperature above 130 °C, the crystallization occurs via the growth of the front formed by the spherulites nucleated in the colder part of the sample.

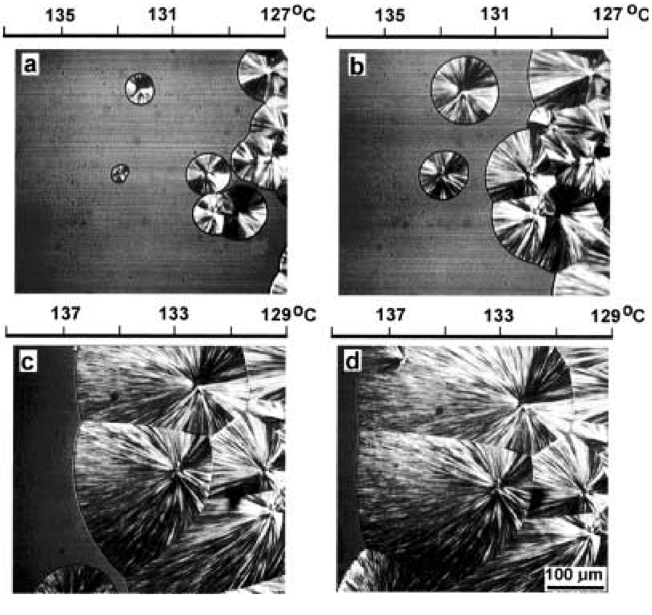

Fig. 4 Polarized light micrographs of subsequent stages of crystallization of the iPP film labeled 150/120 in a temperature gradient of 20 K/mm

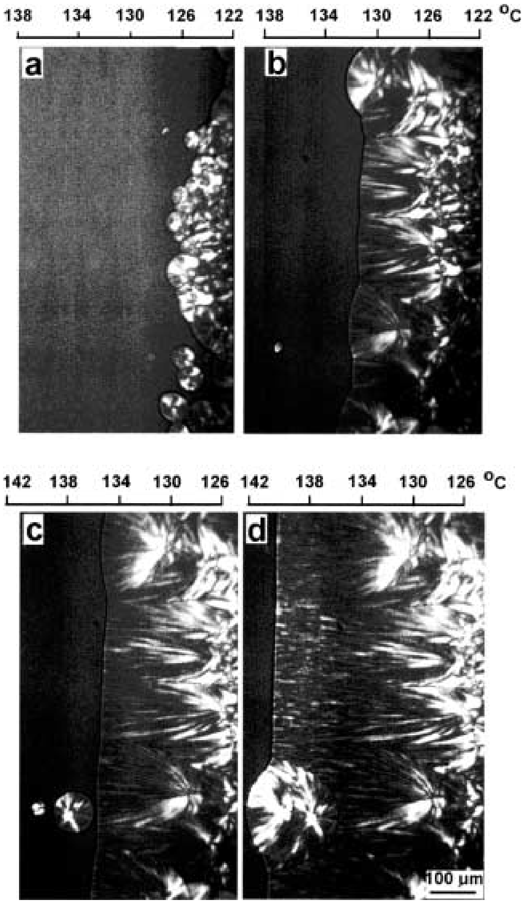

Fig. 5 Polarized light micrographs of subsequent stages of crystallization of the iPP film labeled 170/100 in a temperature gradient of 35 K/mm

The growing spherulites assume anisotropic shapes since their growth rate is slower at higher temperature. The anisotropy of the shape of unimpinged spherulites increases with the time elapsed from their nucleation and it is more pronounced in the gradient of 35–37 K/mm than in the gradient of 20 K/mm. The shape anisotropy is also enhanced by the higher crystallization temperature in the same gradient.

The directions of lamellae propagation and the crystallizing front are always perpendicular to each other during the spherulite growth. The growth directions of the lamellae tend towards the high-temperature side of the sample. Only the lamellae growing perpendicularly to the isotherms do not change the direction of growth. Within the flat crystallization front evolving during the gradient crystallization, the lamellae grow nearly parallel towards the higher-temperature side. Light micrographs and AFM images are shown of thesample crystallized in the temperature gradient of 35 K/mm in Fig. 6a and b.

The fragment of the sample seen in the AFM image and marked by the white rectangle in Fig. 6a was crystallized at approximately 130 °C.

Both the AFM and the light micrographs confirm the change in the directions of the growth of the lamellae in the samples crystallized in the temperature gradient. For comparison, Fig. 6c and d show corresponding light and AFM micrographs of a sample crystallized isothermally at 130 °C, where the lamellae curvature is not observed. The curvature of the lamellae directions is more pronounced in the gradient of 35–37 K/mm than in the gradient of 20 K/mm if parts of iPP films crystallized at the same temperatures are compared. As follows from Figs. 4, 5 and 6a and b the effect is also enhanced by the higher crystallization temperature.

Since the spherulites nucleated in colder parts of the sample continue to grow towards the higher-temperature side of the samples, they affect there the conversion of the melt into spherulites. The measurements of the degree of conversion by means of light microscopy conform to these observations. The time of full conversion of the melt into spherulites, measured from the moment of the equilibration of the temperatures of the blocks , is plotted against the crystallization temperature in Fig. 7a. The gradient of 20 K/mm has a little effect on the conversion, while the gradient of 35–37 K/mm speeds up the crystallization at a temperature above 130 °C. Exemplary time dependencies of the degree of conversion of the melt into spherulites are shown in Fig. 7b and c for the isothermal crystallization and the crystallization in the gradient of 35–37 K/mm. Similarly, as in Fig. 7a, the conversion acceleration caused by the temperature gradient increasing with the crystallization temperature is visible.

The sizes of the spherulites vary markedly across samples crystallized in temperature gradients owing to the temperature dependence of nucleation. The temperature gradient also causes the change in the shape of the interspherulitic boundaries, depending on the values of the gradient, the temperature and the positions of the centres of neighbouring spherulites. While the spherulites nucleated at the same time in a uniform temperature field form straight-line boundaries, in a temperature gradient the boundaries usually curve towards the higher temperature. The straight-line boundaries are formed only if neighbouring spherulites are nucleated at the same isotherm. The curvature of the boundaries is more pronounced in the higher-temperature gradient and it is

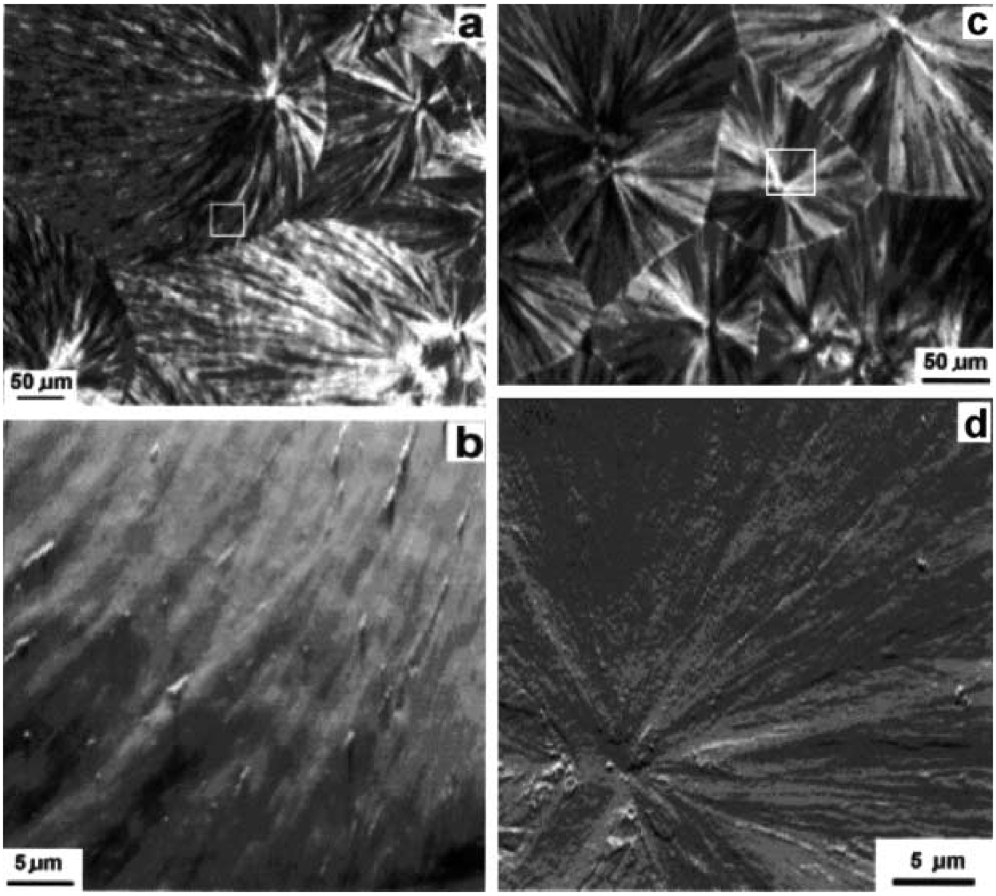

Fig. 6 Micrographs of iPP films: **a** polarized light micrograph of film crystallized with a free upper surface in a temperature gradient of 35 K/mm; **b** atomic force microscope (*AFM*) micrograph of the area marked with a *white box* in **a**, crystallized at 130 °C; **c** polarized light micrograph of an iPP film crystallized isothermally at 130 °C with a free upper surface; **d** AFM micrograph of the area marked with a *white box* in **c**

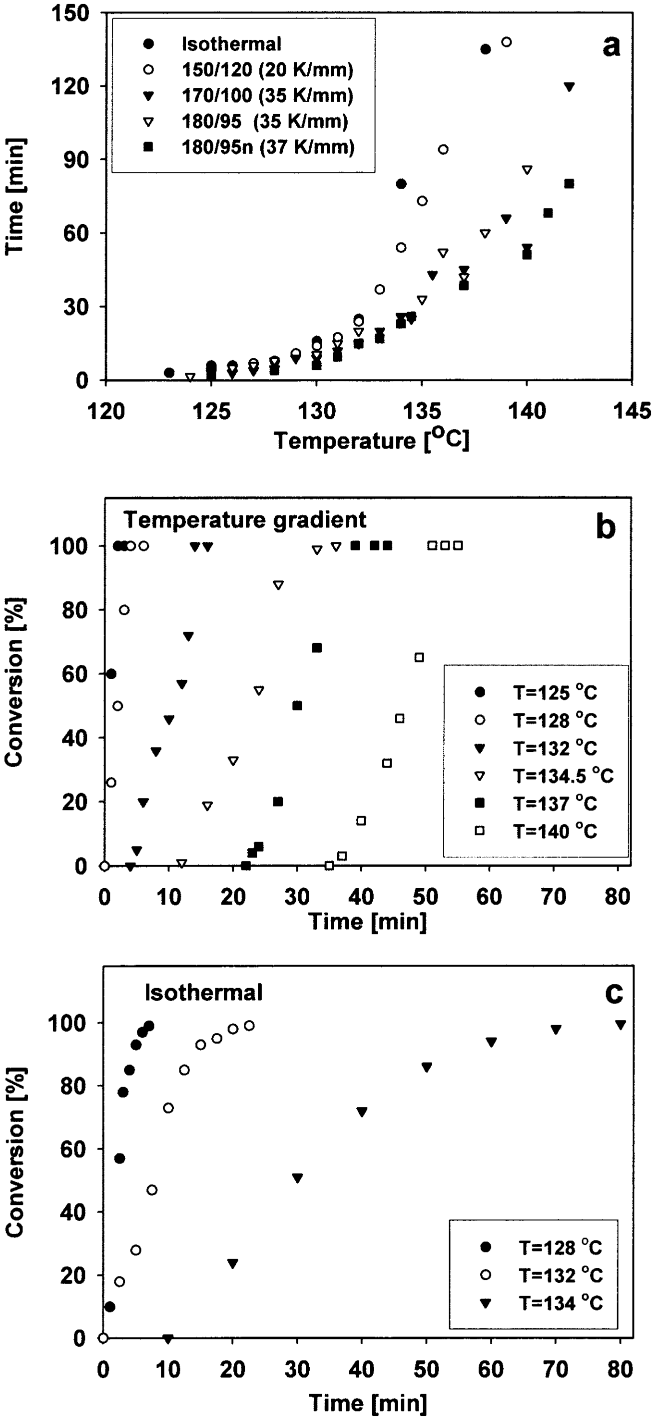

Fig. 7 **a** Full conversion time at various isotherms in iPP films crystallized in a constant temperature gradient and in iPP films crystallized isothermally; **b** time dependence of the degree of conversion at various isotherms in iPP films crystallized in a constant temperature gradient of 37 K/mm and at isotherm 134.5 °C in an iPP film crystallized in a constant temperature gradient of 35 K/mm; **c** time dependence of the degree of conversion in iPP films crystallized isothermally

also enhanced by the higher temperature of crystallization. It results in the elongated spherulites visible in Figs. 4, 5 and 6a and b.

A predominant crystalline phase in the samples studied is α. β-phase spherulites are nucleated only occasionally although they overtake α-phase spherulites owing to faster growth (Fig. 8). The boundaries between α-phase and β-phase spherulites are more curved compared with the boundaries between two α-phase spherulites with centres similarly situated.

In the past the formation of occluded pockets of melt between spherulites was investigated in iPP films [21, 22, 23], since the crystallization there is accompanied by a buildup of negative pressure and cavitation owing to volume deficiency. In iPP films crystallized in the constant temperature gradient the numerous pockets of the melt occluded by the spherulites were seen in the lowest temperature parts of the samples, similarly as in the samples crystallized isothermally. However, as the temperature increases with the distance from the colder block, such places become less frequent because of more and more unidirectional crystallization.

Crystallization in time-dependent temperature gradients

Independently of the applied procedure (Table 2) the crystallization proceeds in a similar way. During cooling, the intense nucleation process begins near the colder block when the temperature there reaches 125 °C. The spherulites grow fast in nearly circular shapes. After some time the nucleation also starts in the remaining part of the film, which prevents the formation of the uniform crystallizing front. Pockets of melt are frequently

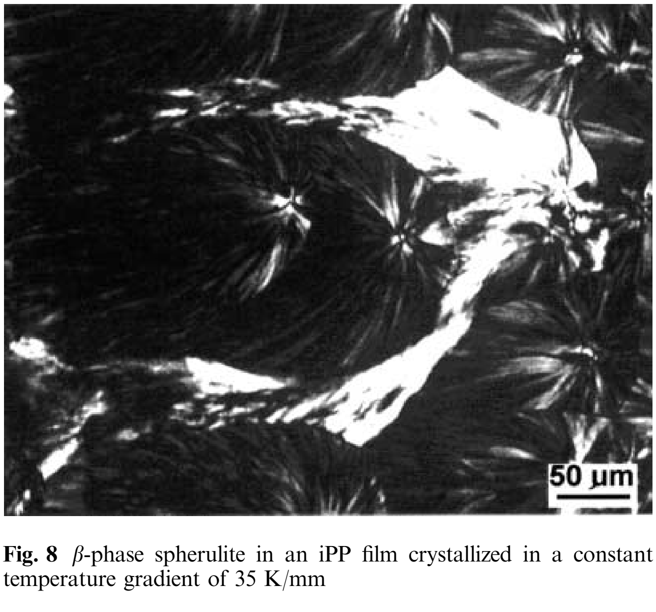

Fig. 8 β-phase spherulite in an iPP film crystallized in a constant temperature gradient of 35 K/mm

Fig. 9 Micrograph of an iPP film crystallized in a time-dependent temperature gradient obtained by cooling the left and right blocks at different rates: 2 and 3 K/min, respectively

occluded between spherulites. The crystallization proceeds fast, promoted by the decrease in the temperature inside the sample. The evident changes of structure are visible only in the sample shown in Fig. 9, crystallized on the support glass bridging the blocks cooled at different rates of 2 and 3 K/min. The crystallization in this case was slower and occurred at a higher temperature range than in other cooled samples.

Conclusions

The influence of a temperature gradient on the crystallization and the final morphology of iPP samples was observed. The crystallization kinetics and the spherulitic structure as well as the internal structure of spherulites are affected by the temperature gradient. The temperature gradient of 35–37 K/mm speeds up significantly the crystallization in iPP films above 130 °C although no enhancement of the spherulite nucleation is found. The conversion of the melt into spherulites occurs in the gradient crystallization also via the growth of spherulites growing from colder parts of a sample. The contribution of these spherulites to the conversion increases with temperature.

Since the spherulite growth rate is temperature-dependent, the spherulites assume anisotropic shapes. The growth directions of the lamellae bend towards the hotter side of the sample, while being perpendicular to the crystallizing front. These effects were also observed in the past [7, 16] and as follows from our study they are enhanced not only by the higher temperature gradient but also by the higher temperature of crystallization.

The changes in the shapes of the interspherulitic boundaries owing to the temperature gradient are also more pronounced at higher temperature as well as in the higher temperature gradient. All these features result from the anisotropy of the spherulite growth. Since, as it was pointed out in Ref. [20], the relative change of in the iPP spherulite growth rate owing to the temperature increment rises with the crystallization temperature at low and medium undercooling, the growth anisotropy and all its consequences are affected not only by the temperature gradient but also by the crystallization temperature. The additional reason is the weak spherulite nucleation at elevated temperature allowing the slower crystallization and enabling the spherulites from the colder side to become large and extend towards the high-temperature side of the sample.

The weak influence of the time-dependent temperature gradient on the morphology of the samples crystallized during cooling indicates again the role of the crystallization temperature in the observed phenomena. For samples crystallized below 125 °C the alterations in their structure owing to the temperature gradient were less visible.

The results obtained point out that in industrial processes of polymer solidification the temperature gradients are important for crystallization in thick-walled products where the temperature near the surfaces decreases faster than in the inner parts.

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