Crystallization of isotactic polypropylene in a temperature gradient

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).

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 \( \mu \)m, 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.

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

![Fig. 1 Scheme of the hot stage for crystallization in a temperature gradient](image-url)