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Spherulite growth of polybutene-1 in a thermal gradient

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Summary

Polybutene-1 can form oriented spherulites when crystallized in a thermal gradient because the nucleation is suppressed in the high temperature region and the spherulite growth is obstructed except towards the high temperature. The difference of the growth rate in different radial directions leads to the change of the lamellar growth direction from radial direction into unidirectional towards the higher temperature. A new method for measuring the isothermal spherulite growth rate is developed by using the thermal gradient.

INTRODUCTION

The thermal gradient has been applied in the field of polymers by a number of authors(1-7). Oriented spherulites can be obtained when polymers are crystallized in the thermal gradient because the nucleation is minimized at the higher temperature and the spherulites can grow only in one direction, from the lower temperature to the higher temperature. The development of the spherulites can be followed by the observation in the polarizing microscope. In this report, a polarizing microscope is employed to follow the spherulite growth of the polybutene-1 crystallizing in the thermal gradient. It is demonstrated that a single measurement of the spherulite growth in the temperature gradient is sufficient to calculate many crystallization isotherms.

EXPERIMENTAL

A thermal gradient instrument in which the heater was about 180°C and the cooler was about 20°C and the distance between the heater and the cooler was about 1 mm was employed (Fig.1). Azobenzol (T_m=68°C), benzil (T_m=95°C), acetanilid (T_m=114.5°C), phenacetin (T_m=134.5°C) and benzanilid (T_m=163°C) were used to measure the temperature distribution in the thermal gradient. Fig.2 gives the temperature distribution curve in the thermal gradient.

The isotactic polybutene-1 from Chemische Werke Marl (M_w=8x10^5) was used in this study. Polybutene-1 was prepared as films 0.1-0.5 mm thick and sandwiched between two glass slides. The specimen was first placed in the heater of the thermal gradient in order to melt and 20 minutes later, quickly moved into the thermal gradient. After the specimen was quenched to the room temperature at the low temperature side of the thermal gradient the spherulite development was observed.

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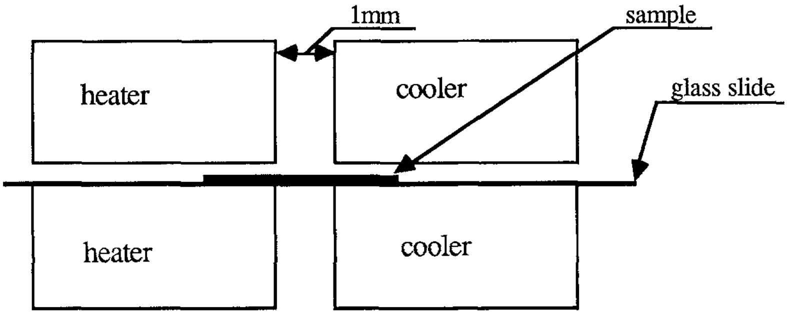

Fig.1 Scheme of the thermal gradient device.

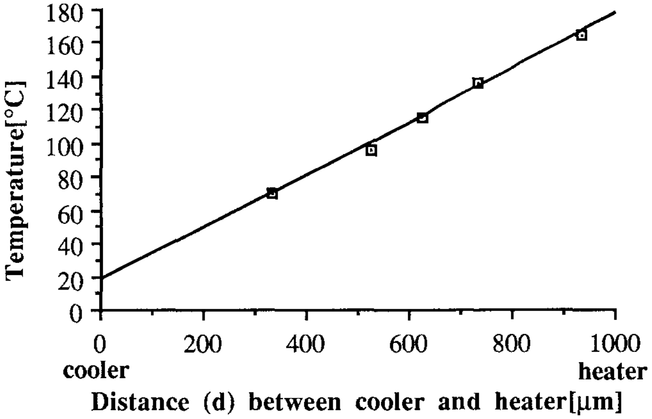

Fig.2 The distribution of temperature in the thermal gradient.

RESULTS AND DISCUSSION

·Polybutene-1 can easily orient in the thermal gradient. The photographs in Fig.3 show the process of the orientation of polybutene-1. When the specimen has been moved from the heater into the thermal gradient, both the nucleation and the crystal growth occure in the lower temperature region. No preferred orientation can be seen in the sample at this time. The crystals grow in the radial direction although the spherulites are not symmetrical. Two minutes later, however, the crystals grow gradually only into one direction, towards the higher temperature.The crystallization front gradually becomes a straight line, i.e. it is located at a line of a certain temperature. The oriented spherulites are obtained if the crystal continues to develop.

Oriented spherulites form when the nucleation is suppressed ahead of the crystallization front. From Fig.3 it can be seen that in the early period of the crystallization in the thermal gradient , nuclei are formed in the lower temperature region and the lamellar crystals grow in

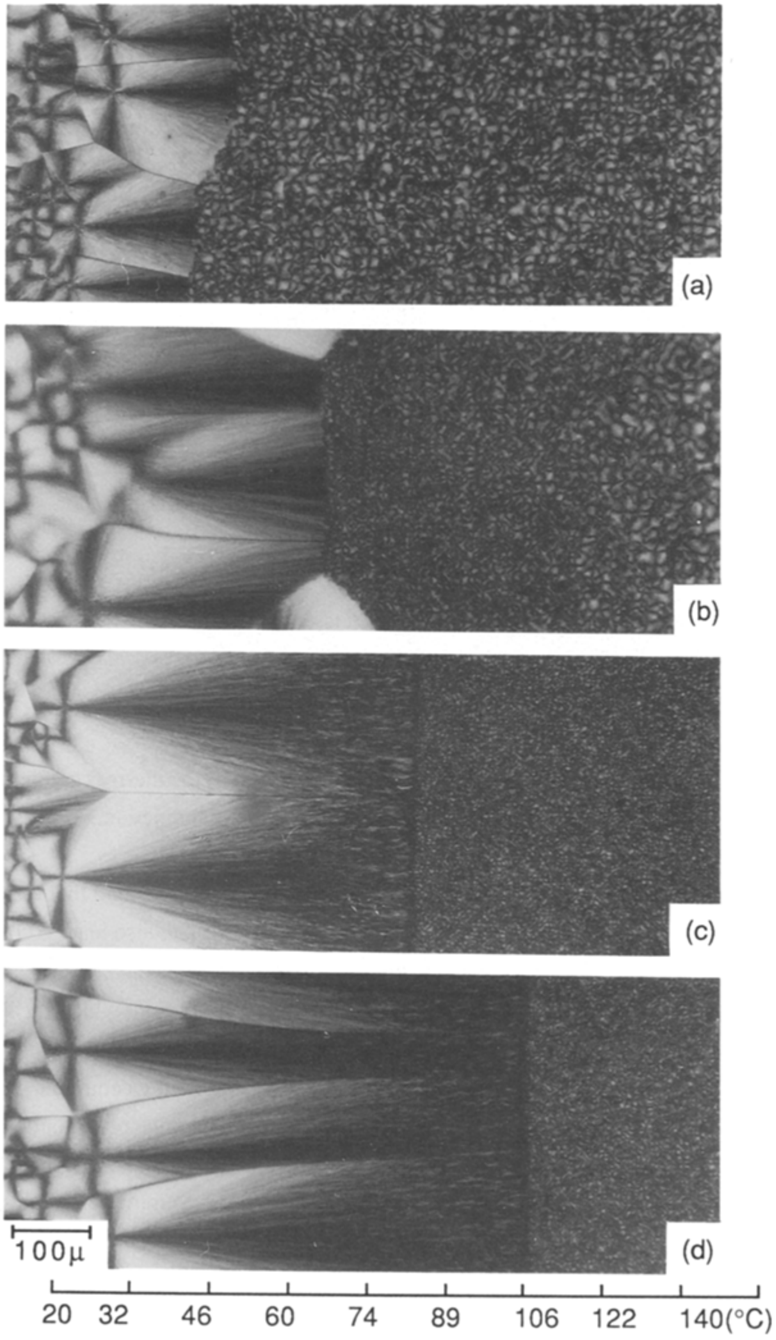

Fig.3 Micrographs of polybutene-1 crystallized in the thermal gradient for /a) 2 min, (b) 4 min, (c) 16 min and (d) 40 min and subsequently quenching to room temperature.

radial directions. In the higher temperature region, however, the nucleartion is suppressed. After the spherulites are large enough and contact each other, they can not grow in all radial directions but only perpendicular to the melt front. Therefore, the spherulites grow only into the higher temperature region caused by steric hinderance in the direction perpendicular to the thermal gradient.

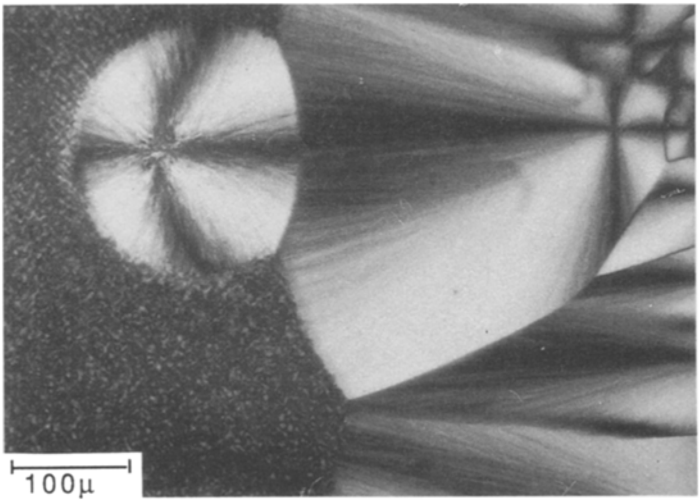

Fig.4 Micrographs of polybutene-1 crystallized in the thermal gradient for 4 min and subsequently quenching to room temperature.

If only a single spherulite grows in the thermal gradient, it can be found that the difference of the growth rate of lamellar crystals in different radial directions can also lead to changing the lamellar growth direction. In Fig.4, a spherulite is formed in front of the crystallization front. Its Maltese extinction cross bends towards the lower temperature region, which means that the lamellae parallel to the polarization direction of the polarizer move towards the lower temperature region. The nucleus of that spherulite is not at the spherulite centre but closer to the higher temperature region. This phenomenon results from the difference of the lamellar growth rate as function of temperature. The lamellar growth rate at this location is larger towards the lower temperature region than towards the higher(see also Fig.6). Summarizing the spherulitic growth in a temperature gradient, two effects influence the orientation of the lamellae within the spherulite:

(i) Steric hinderance of the growth of the lamellae in all direction but the direction perpendicular to the melt front [towards the thermal gradient(Fig.3)].

(ii) Different growth rates of the lamellae as depending on temperature.

For the case of the steric hinderance the Maltese extinction cross of the spherulite is rectangular but the shapes of the spherulites are extended into the higher temperature region. The thermal influenced orientation by different growth rates may extend the spherulite into the lower temperature region as in our case (Fig.4) or into the higher temperature region, depending on the location of the nucleus. If the nucleus is located above the crystallization maximum, the lamellae grow preferentially into the lower temperature region and *vice versa*. Both the effects, steric hinderance and thermal orientation, can be distinguished by the shape of the Maltese cross. For the thermal case, the Maltese cross extinction pattern is directed towards the lower temperature region(Fig.4) when the nucleus is located above the crystallization maximum temperature or towards the higher temperature region when it is located at the lower temperature side. Both the effects lead to an orientation of the lamellae into the direction of the thermal gradient but have entire different origins.

The crystallization curve with time in the thermal gradient(Fig.5) can be acquired from Fig.3. The crystallization front moves fast at the beginning of the crystallization but gradually slows down. Finally, the spherulite growth approaches zero when the crystallization time is long enough. This is because the crystallization is carried out in a thermal gradient and the crystallization temperature is different at different locations. In the initial stage, the crystallization takes place in the lower temperature region where the nuclei can easily be formed. After that, the crystallization front moves towards the higher temperature region at which the nucleation is suppressed but the lamellae continue to grow. The crystallization temperature increases with the crystallization time and the spherulites growth becomes gradually slower.

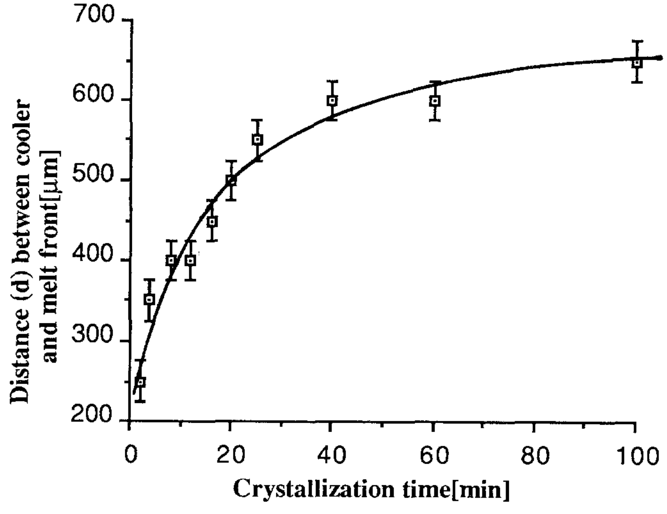

Fig.5 Spherulite growth curve of polybutene-1 vs. time in the thermal gradient.

The slope of the spherulite growth curve in Fig.5 is the spherulite growth rate. Using Fig.5 and Fig.2, a spherulite growth rate curve versus crystallization temperature can be obtained (Fig.6).[The slope of Fig.5 at a certain distance, d, is the growth rate of the lamellae at this location and with the help of Fig.2 a fixed temperature T can be correlated to this location. Hence, the crystallization curve "growth rate versus temperature" can be calculated from a single measurement in the temperature.] The spherulite growth rate decreases with the increasing crystallization temperature and is zero above 112°C. The crystallization maximum is below 60°C. The crystal structure of polybutene-1 crystallized in the thermal gradient is tetragonal(8)·The melting temperature is about 117°C, measured by DTA. In isothermal crystallization, there are both the nucleation and the crystal growth which influence the crystallization. If the crystallization temperature is too high, no crystallization occurs because the degree of undercooling is not high enough for the formation of nuclei. In the thermal gradient, however, the spherulites are nucleated in the lower temperature region and continue to grow into the higher temperatures region. Fig.5 actually presents the process of the spherulite-growth and not nucleation. Consequently, the curve in Fig.6 reflects the variation of the spherulite growth rate with the crystallization temperature only in the crystal growth period and excludes the nucleation. The crystallization curves obtained according to our method therefore represent only the high temperature side of the crystallization isotherms.

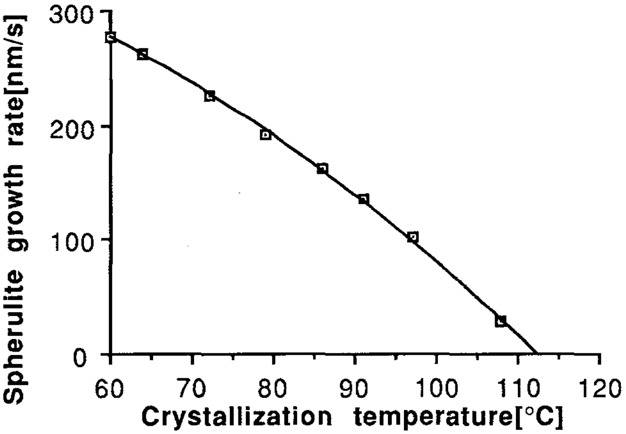

Fig.6 The spherulite growth rate of polybutene-1 at different temperature in the thermal gradient.

Considering only the crystal growth rate, the crystallization rates from Fig.6 may differ from those reported ealier. Table 1 gives the spherulite growth rates of polybutene-1 from Fig.6 and data from Powers(9) and Icenogle(10) measured isothermally. The results of the high temperature region are in reasonable accordance. At the lower temperature (below 95°C), the spherulite growth rates from Fig.6 are smaller than those of Powers and Icenogle, which is to be expected from the consideration mentioned above.

Table 1 Spherulite growth rate of polybutene-1

Tc(°C)		80	85	90	95	100	105
G (nm/s)	a	675	449	224	111	32.6	—
	b	—	—	338	—	60.4	19.6
	c	193	167	140	111	83	50

a: From *J, Polym. Sci., Polym. Phys. Ed.* **23**, 1369(1985)
b: From *J. Res. Natl. Bur. Stand.* **A69**, 335(1965)
c: From Fig.6.

The crystallization temperature can be controlled by moving the specimen through the thermal gradient at an appropriate zone velocity. When the specimen is moving through the thermal gradient with an appropriate speed, an isothermal crystallization process occurs. Additionally, moving the sample through the thermal gradient with a low speed, crystallization occurs at high temperatures where nucleation is excluded and the entire sample can be oriented(11-13).

CONCLUSION

The crystallization of polybutene-1 in a thermal gradient can orient the lamellae within the spherulites so that a preferred orientation of the lamellae parallel to the thermal gradient occurs. The orientation of the lamellae results from two entire different reasons:

- Steric hinderance in the growth directions but to the high temperature region.
- Anisotropic growth rates parallel and perpendicular to the thermal gradient.

From a single plot of the spherulite dimension parallel to the temperature gradient versus crystallization time and from the temperature distribution in the thermal gradient, crystallization isotherms can be evaluated for all temperatures, where the growth rates compared the nucleation rates are the crystallization rate controlling processes.

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