

# Transcrystalline Growth of Thermoplastics and LCPs During Isothermal Crystallization

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## SYNOPSIS

Two technical methods were developed for transcrystalline growth in order to create perfect transcrystalline growth for both thermoplastics and liquid crystalline polymers. A principle was suggested for oriented crystallization that the nucleation is created with high density along a one-dimensional or on a two-dimensional unit, while the nucleation in the matrix is suppressed. The steric hindrance was a key factor to create the transcrystalline growth in isothermal crystallization. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

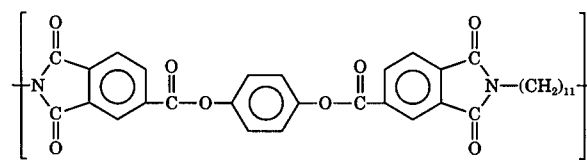
Many thermoplastics are semicrystalline polymers and are widely used in various fields. The formation of polymer spherulites and their morphology and structure have been studied fairly extensively.<sup>1,2</sup> Many high-performance semicrystalline thermoplastic composites have already been commercially used. Glass fiber,<sup>3,4</sup> carbon fiber,<sup>5,6</sup> and other types of fibers<sup>7</sup> have been added in thermoplastics in order to improve their physical and mechanical properties.

The fibers added in polymers influence the nucleation when they are crystallized. When nucleation occurs with sufficiently high density at the surface of substrates, the resulting radial growth produces a type of columnar or transcrystalline growth in contact with the surface.<sup>8</sup> The presence of transcrystalline regions may improve mechanical properties of some fiber-reinforced polymer composites.<sup>9,10</sup> Transcrystalline growth is mostly accompanied by the growth of normal spherulites when using the methods reported in the literature. How to produce transcrystalline growth with a minimum of normal spherulites is one of the technical problems to process the fiber-reinforced polymer composites. In this report, we describe the transcrystalline growth of oriented spherulites using the spe-

cial technique and the factors influencing the transcrystalline growth, and the formation of oriented spherulites in the isothermal crystallization are discussed.

## EXPERIMENTAL

A liquid crystalline poly(ester imide) used in the study was prepared and supplied by Prof. Kricheldorf and its molecular formula was as follows:<sup>11</sup>



The melting temperature of liquid crystalline poly(ester imide) is about 216°C and the transition temperature from anisotropic melt to isotropic one is about 230°C. The polypropylene was supplied by Hoechst AG, and its melting index is about 0.1–0.2. The isotactic polybutene-1 used in this study was from Chemische Werke Marl ( $M_w = 8 \times 10^5$ ). The carbon fiber (C6N) treated with acetone before use was supplied by BASF-AG.

Two technical methods were developed in this study. In the first, the polymers were prepared as films 0.1–0.5 mm thick and placed on the hot stage of which the temperature was about 25–80°C higher

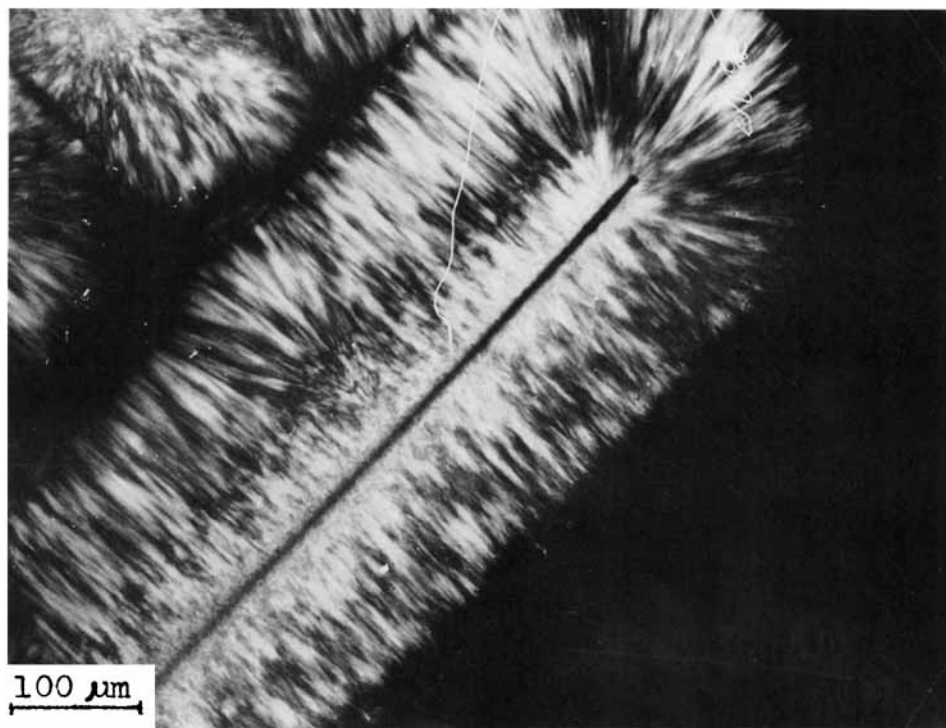
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than their melting temperature ( $T_m$ ) and 5–10 min later, the specimen was cooled at  $5^\circ\text{C}/\text{min}$  to crystallization temperature ( $T_c$ ). The fiber was subsequently put into the supercooled polymer melt at  $T_c$ , and the spherulite growth was observed with a polarizing microscope (POLYVAR, Reichert). In the second method, the same polymer film was prepared but with embedded fibers and placed on the hot stage of which the temperature is about  $25\text{--}80^\circ\text{C}$  higher than  $T_m$ ; 5–10 min later, the specimen was cooled to  $T_c$  and then the fiber was slightly drawn and the crystallization was observed by using the polarizing microscope. Additionally, linear irregularities in the thin melt film were produced by a scratching in the supporting glass slide and by scratching the hot melt film of the polymer.

## RESULTS AND DISCUSSION

The common technical method to produce transcrystalline growth is heating the specimen until the polymer is melted and, subsequently, cooling it to the crystallization temperature. In this process, both the polymer matrix and the fibers are heated and cooled, and normal spherulites are also formed in

the crystallization process beside the transcrystalline growth. The growth of the transcrystalline region is often obstructed by normal spherulites, and it is difficult to obtain a relatively large transcrystalline region. In order to get the transcrystalline growth without spherulites, elevated crystallization temperature is required to suppress the nucleation in the matrix. But high nucleation density on the fiber surface may be difficult to achieve, if the temperature of the fibers is the same as that of the polymer matrix. Therefore, a new method is developed. First, the pure polymer film is melted and subsequently cooled to  $T_c$ , at which the nucleation is mostly suppressed. The cold fibers are put into the polymer melt at this temperature. Because the fibers are cold, the nuclei are formed with high density on the fiber surface and grow in the low supercooling melt when the fibers are placed into the matrix. Figure 1 shows a polarized micrograph of the transcrystalline phase around the carbon fiber embedded into a polypropylene matrix. The nucleation density on the fiber surface is very high but low in the matrix. The spherulites on the fiber surface cannot grow laterally but only in the direction perpendicular to the fiber surface, and the "oriented" spherulites are formed. With this method, the transcrystalline re-



**Figure 1** Isothermal crystallization of polypropylene at  $130^\circ\text{C}$  with carbon fibers.

gion around the fiber can cover a large volume fraction (Fig. 2) because only a few nuclei appear in the matrix at this high crystallization temperature. The results suggest a principle for oriented crystallization. High nucleation density must be created along a one-dimensional (e.g., a very thin fiber) or on a two-dimensional (e.g., the surface of a platelet) unit, while the nucleation in the matrix is suppressed.

Two examples may demonstrate this principle:

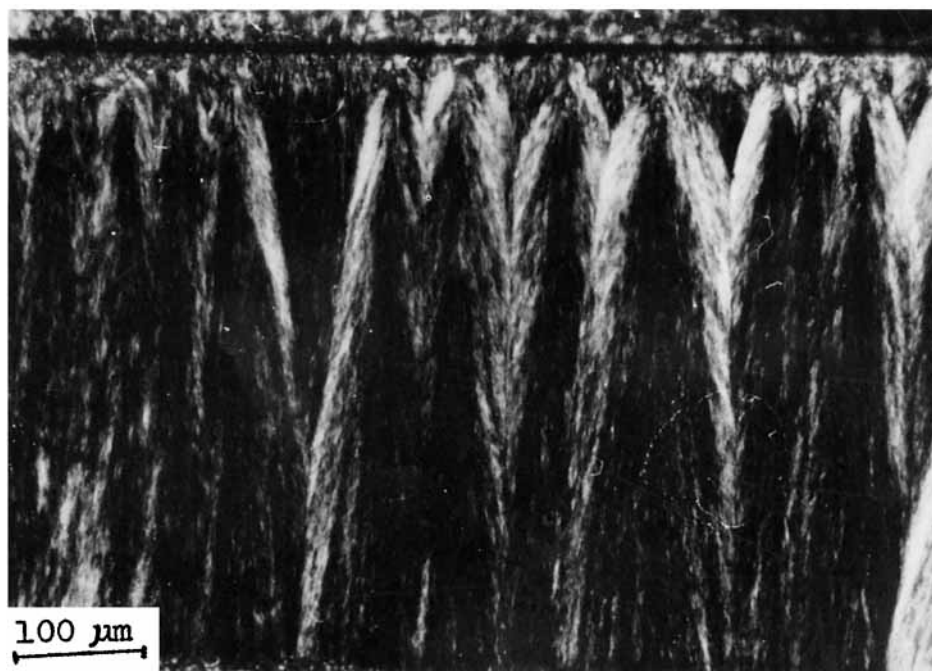
1. The polymer melt film is scratched with a razor at  $T_c$ . Strain-induced nucleation occurs around the scratch. Figure 3 shows the formation of the transcrystalline growth of polybutene-1 around such a scratch during isothermal crystallization at  $90^\circ\text{C}$ . The homogeneous nucleation in the matrix far from the scratch is suppressed due to the high crystallization temperature. Thomason and Van Rooyen<sup>12</sup> have reported a similar experiment: Polypropylene can form transcrystalline phase after the fibers are pulled out of the melt at an elevated  $T_c$ . It is obvious that the stress or strain is one of the factors to influence the nucleation. Furthermore, the nucleation area is relatively large, and the density of the nuclei is very high around the scratch because scratching leads to the deformation and the orientation of polymer chains near the scratch.

2. If the glass slide that supports the polymer

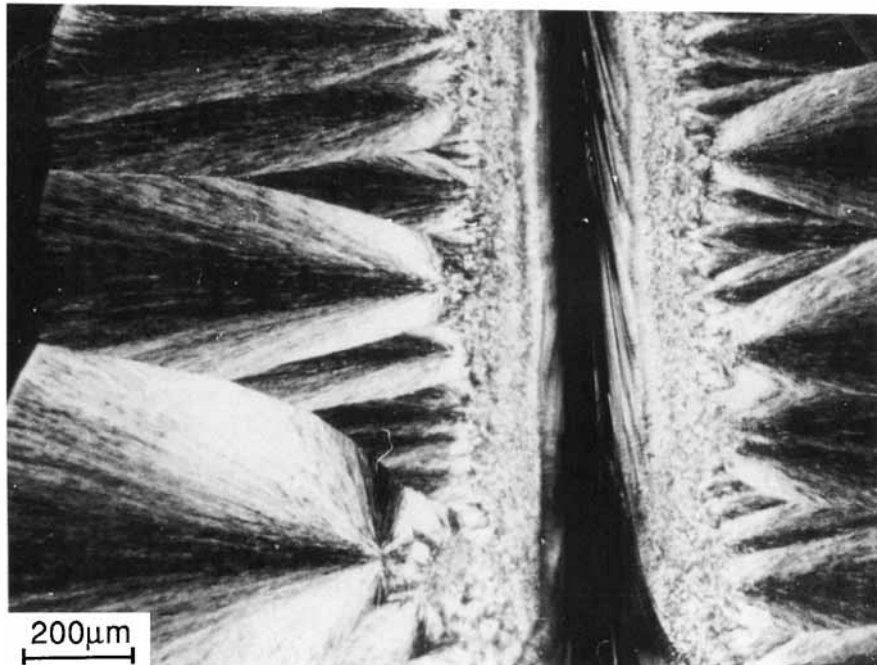
film has a crack, nuclei are formed with very high density along it. In this case, the crack causes the heterogeneous nucleation and the spherulites along the crack can grow in one direction, normal to the crack. Therefore, a perfectly oriented area is created around the crack (Fig. 4). The results reveal that the transcrystalline growth is not solely restricted to the interface areas but a more general phenomenon.

According to the principle mentioned above, therefore, another technical method is also developed for transcrystalline growth. First, the fibers are embedded in the polymer matrix and then the specimen is heated to above  $T_m$  and subsequently cooled to the  $T_c$ , at which the nucleation is suppressed. The fibers in the polymer matrix are slightly drawn and the nucleation caused by stress or strain occurs along the fibers. Figure 5 shows the formation of the transcrystalline growth of polypropylene around the carbon fibers which, are drawn slightly during isothermal crystallization at  $141^\circ\text{C}$ . It is clear that the transcrystalline growth is perfect around the fibers.

To our knowledge, the transcrystalline growth or the formation of oriented spherulites in liquid crystalline polymers (LCPs) have not been reported until now. It may be because the domains in the liquid crystalline phase cause nucleation when LCPs



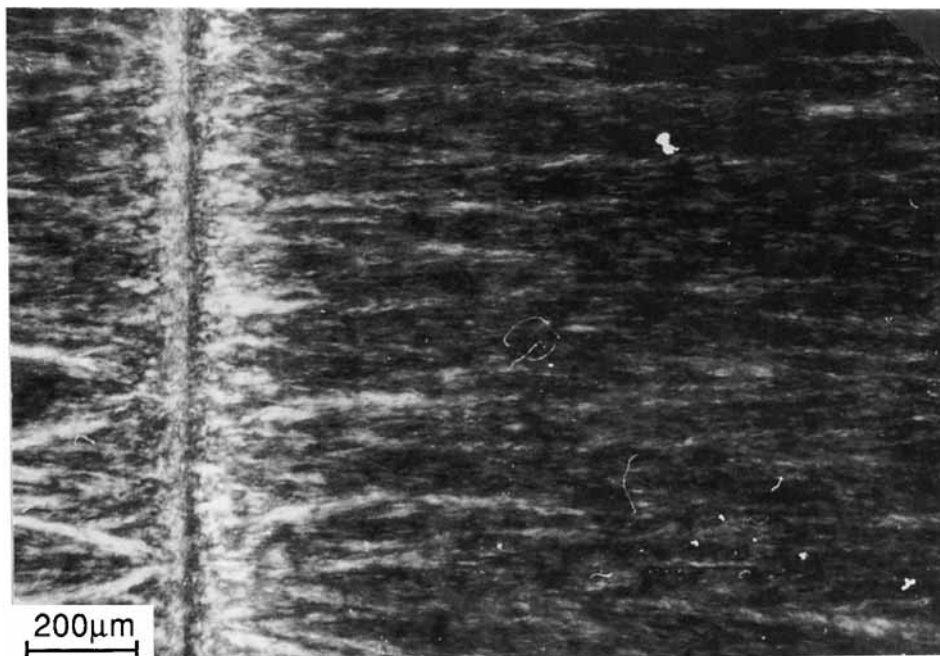
**Figure 2** Isothermal crystallization of polybutene-1 at  $90^\circ\text{C}$  with a carbon fiber.



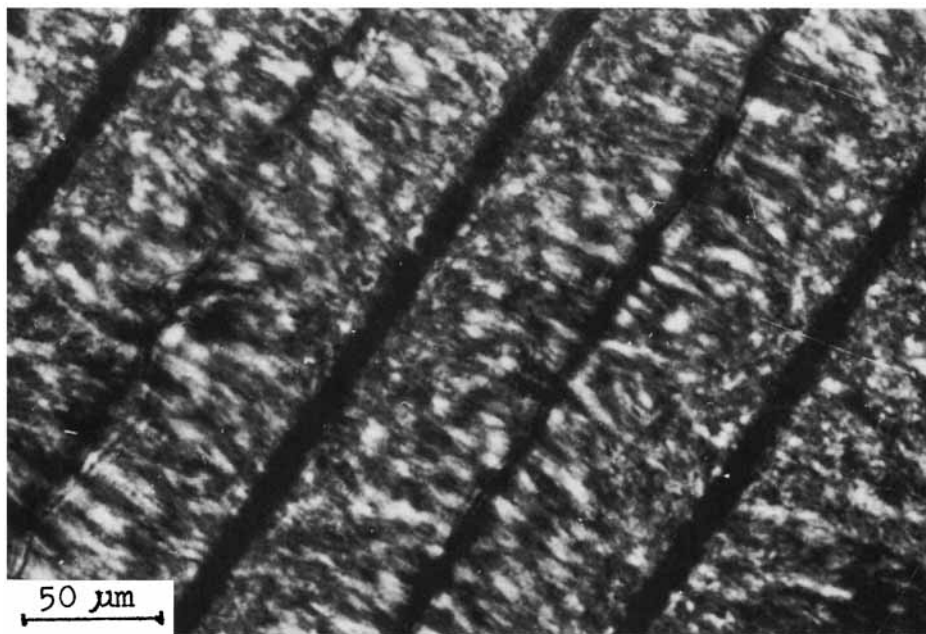
**Figure 3** Isothermal crystallization of polybutene-1 at 90°C around the scratch cracked with a small knife.

are crystallized. It is difficult to suppress the nucleation in the matrix for creating high-density nuclei along a one-dimensional unit. Therefore, the temperature of the formation of transcrystalline growth

for LCPs must be sufficiently high by using the method mentioned above. Liquid crystalline poly(ester imide) is a semicrystalline polymer and the crystallinity is about 37% after the liquid crys-



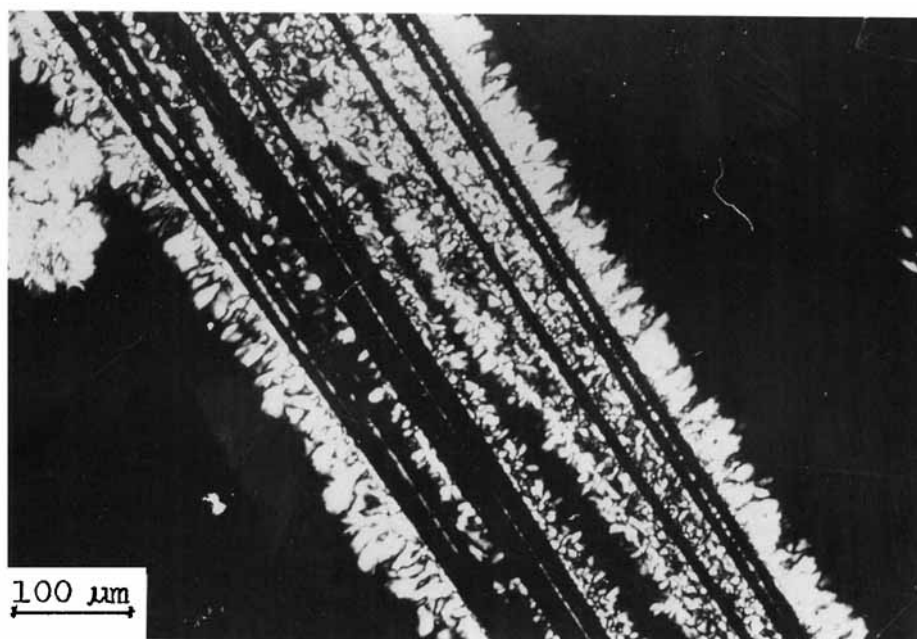
**Figure 4** Isothermal crystallization of polybutene-1 at 90°C around the crack in the glass slide.



**Figure 5** Isothermal crystallization of polypropylene at 141°C with carbon fibers that are drawn slightly.

talline poly(ester imide) is crystallized at about 210°C for 60 min and then cooled to room temperature. It is easy to crystallize when liquid crystalline poly(ester imide) is cooled from isotropic or anisotropic melt and the crystallinity of poly(ester imide)

is about 18%, even if it is quenched from anisotropic melt into liquid nitrogen. High-density nuclei is created along the carbon fiber by drawing the fiber and the transcrystalline growth of the liquid crystalline poly(ester imide) occurs around the fibers (Fig. 6).



**Figure 6** Transcrystalline growth of liquid crystalline poly(ester imide) with carbon fibers slightly drawn at 214°C.

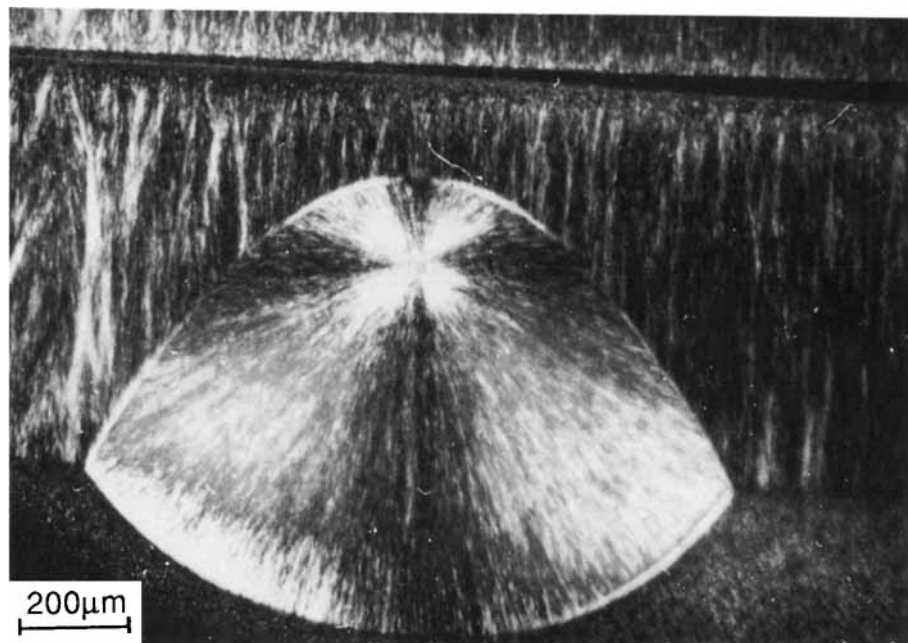


Figure 7 Micrograph of polybutene-1 crystallized isothermally at 90°C.

Like in thermoplastics, therefore, LCPs can also form the transcrySTALLINE growth or the oriented spherulites under the appropriate conditions.

When thermoplastics are crystallized in the thermal gradient, oriented spherulites are also formed, and two factors can influence the orientation of the lamellar crystals.<sup>13</sup> One is the steric hindrance of the growth of the lamellae in all directions but the direction perpendicular to the melt front (toward the temperature gradient), and the other is the different growth rate of the lamellae depending on temperature. In the isothermal crystallization, however, the growth rate of lamellae in all direction is the same and therefore, the effect on the orientation is only due to the steric hindrance. In Figure 7, a spherulite is formed in the front of the transcrySTALLINE phase. Its Maltese extinction cross is symmetrical, which means that the lamellar crystals grow always in radial direction. The morphology of the spherulite, however, looks like a fan due to the restricting growth of the lamellae in the directions except one of the transcrySTALLINE growth, which confirms that steric hindrance leads to the formation of the transcrySTALLINE growth in isothermal crystallization.

## CONCLUSIONS

Two technical methods, placing the cold fibers into the polymer matrix and drawing the fibers embedded

in the polymer matrix at the crystallization temperature, are developed to create the perfect transcrySTALLINE growth. By using the method suggested above, the liquid crystalline poly(ester imide) can form transcrySTALLINE phase around the carbon fibers. The formation of nuclei with high density along the fibers or on a two-dimensional unit and the suppression of the nucleation in the matrix are necessary for the formation of the transcrySTALLINE growth. In comparison with the formation of oriented spherulites of polymers in the thermal gradient, it is clear that the steric hindrance is a key factor to create the transcrySTALLINE growth in isothermal crystallization.

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