결정화 온도가 Isotactic Polypropylene용액으로부터 형성된 구정구조에 미치는 영향

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Effect of Crystallization Temperature on Spherulitic Morphology Formed from Isotactic Polypropylene Solution

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요 약: 적당히 농축된 *i*-PP 용액의 등온 결정화로부터 얻어지는 구정구조를 광학현미경을 통하여 관찰하였다. 용매는 dialkyl phthalate를 사용하였으며 액-액상분리가 발생하지 않는 온도조건에서 결정화시켰다. 낮은 온도에서 결정화시키면 빠르게 성장하는 구정이 서로 마주치면서 연속된 구조를 발생시킨다. 높은 온도에서 결정화시키면 구정은 완전히 성장할 때까지 서로 마주치지 않으며 어느 정도 자란 후 나뭇가지 모양의 구조를 형성한다. 결정화 온도를 약간씩 낮춤으로써 이와 같은 나뭇가지 모양의 구조는 보다 일찍 발생하고, 결정 성장시 구정구조로부터 나뭇가지 구조로의 변천은 완만하여진다. 이와 같은 구조의 형성은 Keith-Padden 이론에 근거한 주어진 온도조건에서 고분자 농도가 고분자의 결정화 및 용매의 확산에 미치는 효과를 고려함으로써 해석될 수 있다.

ABSTRACT: The spherulitic morphology by crystallization from moderately concentrated isotactic polypropylene (*i*-PP) solutions in dialkyl phthalate was investigated through optical microscopy under isothermal conditions at which the possibility of liquid demixing was excluded. When crystallized at a low temperature, a continuous structure was obtained by impingement of spherulites. Crystallization at a high temperature produced the spherulites followed by dendritic growth on their surface without impingement. In this case at a lower crystallization temperature the dendritic growth started to appear at an earlier time scale during crystallization and the structure transition from spherulitic to dendritic growth became more gradual. This morphology can be explained by the effects of polymer concentration on crystallization of a polymer and diffusion of solvent at a given temperature based on the Keith and Padden theory.

Keywords: crystallization, polymer solution, spherulite, dendrite, isotactic polypropylene.

INTRODUCTION

Highly crystallizable flexible linear polymers in bulk and in solutions may be commonly crystallizable in the form of spherulites composed of chain folded lamellae which grow outward radially.[1] A spherulite can be a three dimensional object since the lamellae branch suf-

ficiently often on growth. Understanding of the spherulite formation in crystallizable polymer solution would be important to control the morphology and to identify an origin of various structures observed in the thermally induced phase separation (TIPS) process.[2,3]

A phenomenological theory to account for spherulitic crystallization of polymer was first developed by Keith and Padden[4-6] in 1963 and was later reconfirmed by Goldenfeld.[7] According to the Keith and Padden (K-P) theory,[4,5] noncrystallizable components are rejected preferentially by growing crystals and a parameter of major significance is the quantity

$$\delta = \frac{D}{G} \tag{1}$$

where D is the diffusion constant for impurity (noncrystallizable component) in the melt and G represents the radial growth rate of a spherulite. The quantity δ, whose dimension is that of length, determines the lateral dimensions of the lamellae, and that noncrystallographic branching is observed when δ becomes small enough to be commensurate with the dimensions of the disordered regions on their surface. Thus δ is a measure of the internal structure of the spherulite or its coarseness. The present paper is concerned with the spherulitic morphology obtained from a moderately concentrated isotactic polypropylene (i-PP) solution under isothermal conditions. When the melting point depression and the change in mobility with dilution are appropriately taken into account, the structure formation may be explained in terms of the K-P theory. At a lower crystallization temperature, smaller δ is expected due to smaller D (slow diffusion of solvent) and higher G (rapid crystallization of polymer). Upon crystallization at a high temperature where the spherulite does not impinge each other for given concentration of i-

PP solution, δ would change with depletion of polymer since both diffusion of solvent and crystallization of polymer are influenced by the polymer concentration.

EXPERIMENTAL

Materials. Two fractions of highly crystalline i-PP, designated i-PP1 (M_w 1.2×10^5 and M_w/M_n 2.5) and i-PP2 (M_w 3.1×10^5 and M_w/M_n 3.4) were supplied from Himont R & D Center. The solvents were 1,2-didecyl phthalate and 1,2-dioctyl phthalate obtained from Pfaltz & Bauer and Exxon, respectively, which were chosen due to nonvolatility and strong solvent power in experimental conditions.[8] The solvents were used as received without further purification.

Sample Preparation. Dried thin films of i-PP with a thickness of $20 \sim 40$ μm were prepared according to the following procedure: the polymer powder was dissolved in hot decalin containing 2,6-di-tert-butyl-4-methyl phenol (0.5 wt% on polymer) under nitrogen to form about 0.5 wt% solution; the temperature was close to boiling point of decalin; the solution was held under reflux for 30 min after dissolution; the hot solution was quenched by pouring into an aluminum tray in an ice-water bath; the bulk of the solvent was allowed to evaporate in a current of air under ambient conditions, and a transparent film was obtained; the residual solvent was removed by extraction with methanol; the films were dried in vacuum.

Mixtures of i-PP and solvent were weighed carefully to obtain 5.0 wt% i-PP1 in didecyl phthalate and 2.5 wt% i-PP2 in dioctyl phthalate in concavity microslides and a cover glass was placed over the sample. The prepared concentrations are considered to be well above the critical concentration C^* at which the overlap of the polymer coils starts.[9]

Table 1. Polymer and Solvent Used, Polymer Concentration Prepared, and the Critical Concentration C^* above which the Polymer Coils are Overlapped

polymer	solvent	polymer concentration prepared	C^* calculated from Eq. (2)
i-PP1 (M_w 1.2×10⁵)	didecyl phthalate	5.0 wt%	0.9 wt%
i-PP2 (M_w 3.1×10⁵)	dioctyl phthalate	2.5 wt%	0.6 wt%

$$C^* \simeq \frac{3}{4\pi} \cdot \frac{M}{N_A R_g^3} \tag{2}$$

where M is the molecular weight of polymer, R_g the radius of gyration of the polymer coils, and N_A Avogadro's number. The values of C^* estimated from Eq. (2) using the proper molecular parameters[10] are listed in Table 1.

Morphology Observation. The spherulitic structures due to crystallization were observed by a Leitz polarizing microscope (Laborlux 12 pols) with a Mettler hotstage (FP82) and controller (FP80) under nitrogen purge. The sample was slowly heated to 175 ℃ which is much above melting temperature of the *i*-PP solutions. The heating was continued for 5~10 min to ensure the homogeneous state. The solution was cooled at a rate of 10 ℃/min to a temperature for crystallization and maintained the isothermal condition. The crystallization temperature was in the range of 100 ℃ to 132 ℃, at which the possibility of liquid demixing was excluded based on the experimental phase diagram.[8]

RESULTS AND DISCUSSION

The spherulitic structure observed for 5.0 wt% *i*-PP1 solution in didecyl phthalate at 100 ℃ is shown in Fig. 1. At this temperature the spherulitic formation was complete in a minute by impingement. Although a slight increase in
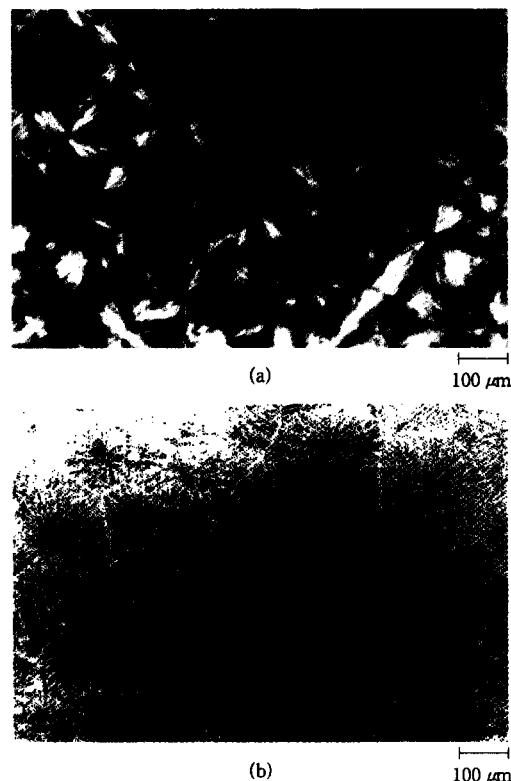

(a)   100 μm

(b)   100 μm

Figure 1. (a) Polarized light micrograph and (b) transmitted light micrograph of 5.0 wt% *i*-PP1 solution in didecyl phthalate crystallized at 100 ℃. Both pictures were taken on the same field of the specimen.

crystallinity was observed by the increased light intensity in crossed polars with duration of time, there was no change in structure. It is understood that the *i*-PP1 solution at 100 ℃ is quite viscous so that the growth rate of fibrous crystal is fast in comparison with the rate at which the solvent can diffuse away. As a result, the solvent molecules rejected by crystallization are entrapped between the growing fibers and there are no appreciable concentration gradients outside the confines of the spherulites until they approach closely one another.[4,5]

When the *i*-PP1 solution was crystallized at 125 ℃, the ultimate morphology did not show the impingement of spherulites and interesting-
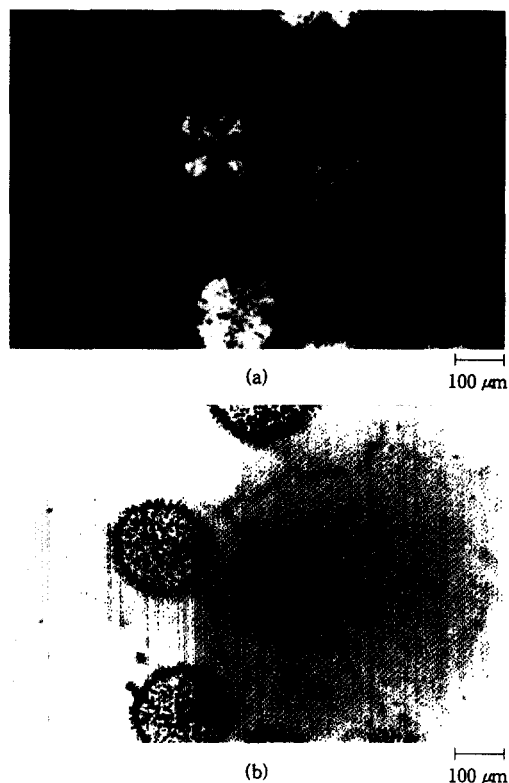
Figure 2. (a) Polarized light micrograph and (b) transmitted light micrograph of 5.0 wt% i-PP1 solution in didecyl phthalate crystallized at 125 ℃. Both pictures were taken on the same field of the specimen.

Figure 3. (a) Polarized light micrograph and (b) transmitted light micrograph of 2.5 wt% i-PP2 solution in dioctyl phthalate crystallized at 132 ℃. Both pictures were taken on the same field of the specimen.

ly a dendritic structure appeared on the periphery of spherulite, as is shown in Fig. 2. A similar morphology was observed for 2.5 wt% i-PP2 solution in dioctyl phthalate crystallized at 132 ℃ (Fig. 3). The optical microscopy revealed that the spherulites with well-defined shape existed at an early stage of crystallization in both cases and a dendritic growth started to appear in about 300 min for the i-PP1 solution and in about 360 min for the i-PP2 solution. Compared to crystallization at 100 ℃, the crystal growth rate was very slow and smaller number of nuclei were available at these elevated temperatures. As crystals grew at the site of nuclei, the nucleus-free region was depleted of the polymer
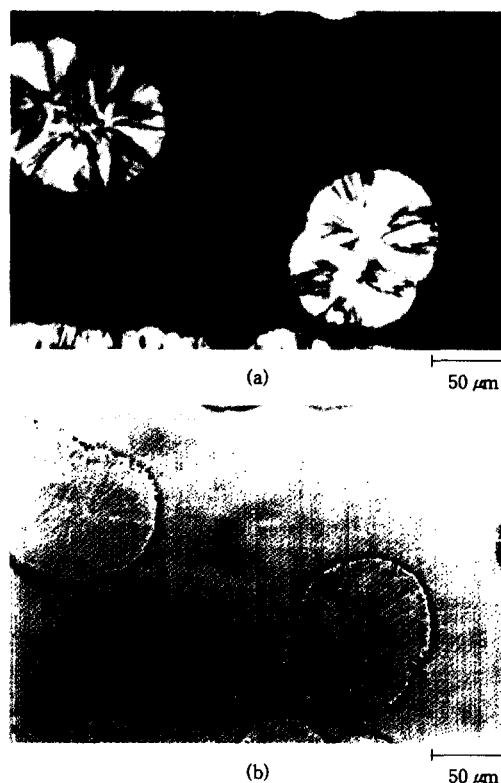
and eventually remained out of the polymer. Considering that a spherulite is the consequence of noncrystallographic branching on the growth of lamellae, the dendrite formation on the edge of a spherulite is not a new phenomenon. Since a compact spherulite can be obtained only when the branching frequency relative to the crystal growth rate is high enough, it is interpreted that the branching frequency should be reduced considerably at a certain stage when crystallized at a high temperature.

According to the K-P theory,[5] the quantity δ governs the over-all morphology of spherulite. With a greater value of δ, the diameters of crystalline fibers between which impurities become

concentrated during crystallization increase and a coarser texture is obtained. This suggests that the frequency of noncrystallographic branching relative to the crystal growth rate decreases with a larger δ. It is expectable that the i-PP1 solution at 125 ℃ has a greater δ value than at 100 ℃ due to more rapid diffusion of the solvent and slower growth rate of the crystal. Consequently the branching frequency should be reduced at 125 ℃, but it may be still high enough to produce a compact spherulite at an early stage of crystallization as is observed in Fig. 2. In order to explain the peculiar morphology formed at this temperature one has to take into account the effect of polymer concentration since the polymer concentration at the growth front of a spherulite becomes dilute by depletion of the polymer with the progress of crystallization.

Sanchez and DiMarzio treated theoretically the concentration dependence of the growth rate of chain folded crystals in the dilute range.[11] Concentration dependence is explained in terms of nucleation on the substrate by cilia from the previous layer; a given chain can be partly attached to the crystal while parts of it remain in solution. It was found that the growth rate was proportional to the concentration raised to a power less than unity for given molecular weight of polymer[11-13] and the exponent tended to increase as the crystallization temperature increased.[11,12] Shah and Lahti reported that in i-PP crystallization from solutions the crystallization rate decreases as the polymer concentration decreases and remains constant at a certain concentration.[14] The results suggest that the reduced supercooling due to melting point depression at a given temperature decreases the crystallization rate in semi-dilute or concentrated solutions, and the effective concentration in the swollen coils rather than the nominal concentra-

tion plays an important role in polymer crystallization from dilute solutions. With decreasing polymer concentration the diffusion constant of solvent at given temperature increases due to reduced viscosity and significantly rises around the critical concentration C^* below which overlapping of the domains of the polymer molecules in solution is released.[15]

The effects of concentration on polymer crystallization from solutions described above may clearly interpret the morphology observed from the i-PP1 solution crystallized at 125 ℃. At an early stage of crystallization the i-PP1 concentration as prepared is high enough to form the compact spherulites by frequent branching of growing crystals due to slow diffusion of the solvent relative to rapid growth rate of crystal. In this case the polymer concentration at the growth front may be maintained more or less constant by polymer molecules supplied from the nucleus-free region. As the crystallization progresses, the polymer concentration in solution becomes low and the branching frequency is significantly reduced due to rapid diffusion of the solvent relative to slow growth rate of crystals, resulting in the dendrite formation on the surface of spherulites. Although a more elaborate study is needed to determine the concentration at which the compact spherulite formation is obtained, it may be related to the critical concentration C^* above which the polymer coils are overlapped. A similar morphology was reported in polyethylene crystallization from dilute solutions.[16]

The spherulitic structures of 5.0 wt% i-PP1 solutions crystallized at 120 ℃ and at 115 ℃ are shown in Fig. 4 and in Fig. 5, respectively. In order to exhibit the evolution of dendrite formation, the intermediate (a and b) and the final (c and d) morphologies in the same fields of the specimens are illustrated. The shape of spheru-
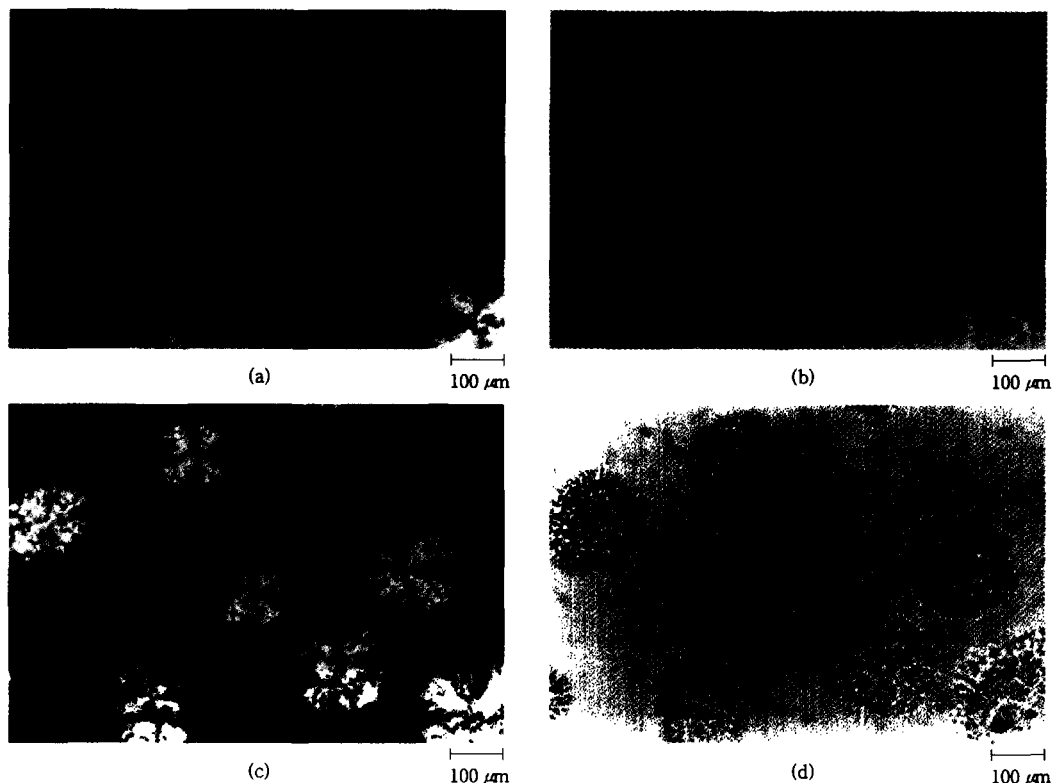
Figure 4. (a) and (c) Polarized light micrographs, and (b) and (d) transmitted light micrographs of 5.0 wt% i-PP1 solution in didecyl phthalate crystallized at 120 ℃ for 60 min (a and b), and for 400 min (c and d). All pictures were taken on the same field of the specimen.

lites started to deteriorate in about 36 min at 120 ℃ and in about 5 min at 115 ℃. Note that Fig. 4 (a) and (b) are the structures observed in 60 min at 120 ℃ and Fig. 5 (a) and (b) are in 12 min at 115 ℃. Thus as the crystallization temperature is decreased, the deterioration of spherulites into dendritic growth on their surface is observed in a shorter time scale; in 300 min at 125 ℃, in 36 min at 120 ℃, and in 5 min at 115 ℃. These results again demonstrate the effects of the polymer concentration at the growth front of crystals on the morphology. Since a lower crystallization temperature increases drastically the crystal growth rate and decreases the solvent diffusion rate,[17] a large value of δ at which the branching frequency of

growing crystals is not enough to form a compact spherulite would be achieved at the earlier time.

The morphologies of 2.5 wt% i-PP2 solution in dioctyl phthalate crystallized at 125 ℃ and of the same solution crystallized at a 115 ℃, which are given in Fig. 6, show also the spherulites followed by dendritic growth. The dendritic structure on the surface of the spherulite started to appear in about 90 min on crystallization at 125 ℃ and in a few minutes at 115 ℃. Thus when crystallized at a lower temperature, the deterioration of spherulites into dendritic growth is observed in an earlier time scale, as is the case of the i-PP1 solution.

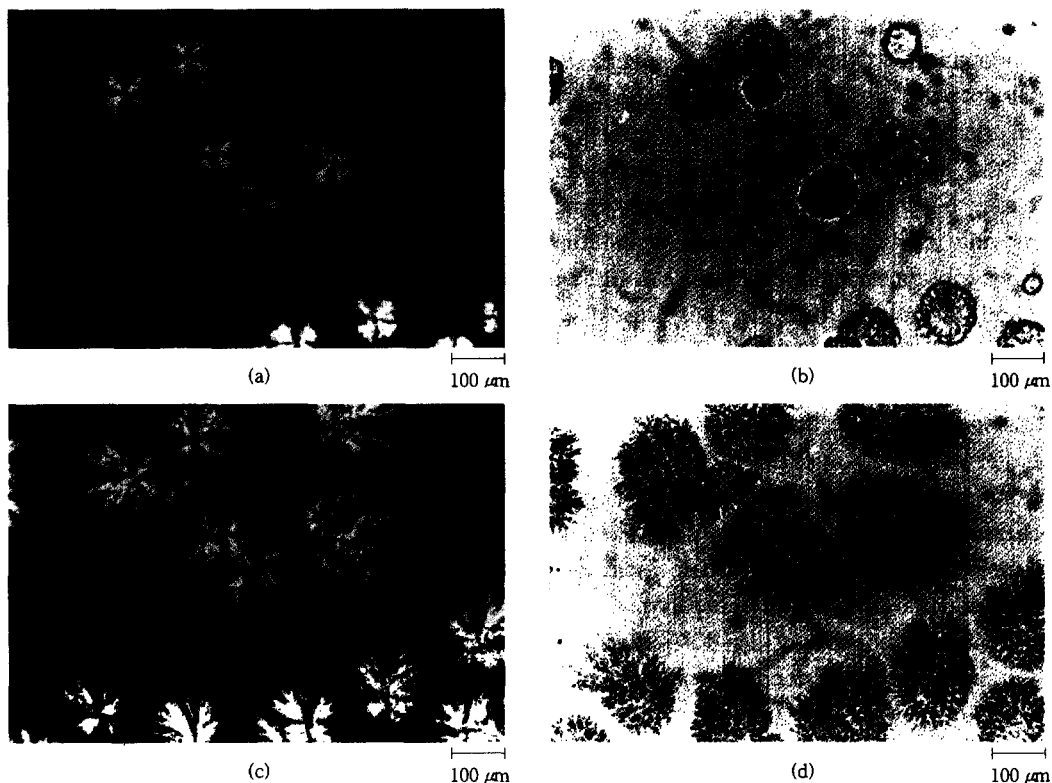It is observed for both i-PP1 solution (Fig. 2,

Figure 5. (a) and (c) Polarized light micrographs, and (b) and (d) transmitted light micrographs of 5.0 wt% *i*-PP1 solution in didecyl phthalate crystallized at 115 ℃ for 12 min (a and b), and for 120 min (c and d). All pictures were taken on the same field of the specimen.
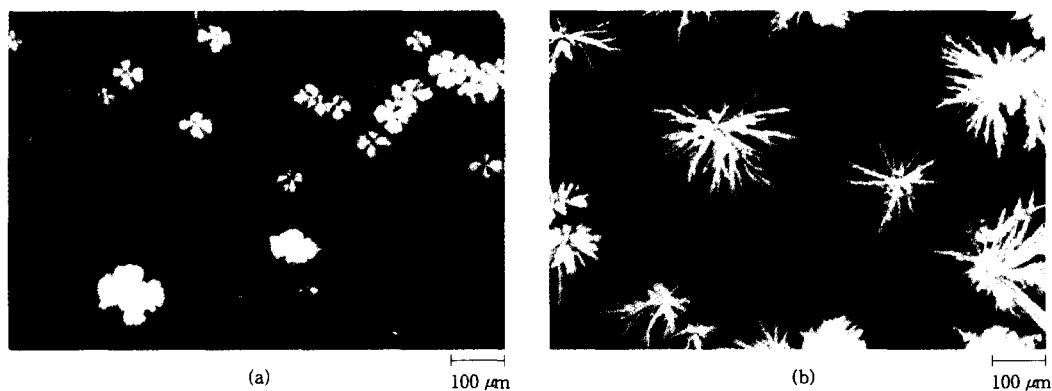

Figure 6. Polarized light micrographs of 2.5 wt% *i*-PP2 solution in dioctyl phthalate crystallized at 125 ℃ (a) and crystallized at 115 ℃ (b).

Fig. 4, and Fig. 5) and *i*-PP2 solution (Fig. 3 and Fig. 6) that the structure transition from spherulitic to dendritic growth became more gradual on crystallization at lower temperature.

This phenomenon may be partly attributed to less pronounced concentration dependence of crystal growth rate at lower temperature.[11,12] When crystallization occurs at a low temperatures, the local concentration at the growth front may be enriched by the solvent rejected by growing crystals due to a small δ and the dendrites can appear more easily as seen in Fig. 5 (c) and (d) and Fig. 6 (b). In these cases the dendritic growth is dominated in the surface of spherulites far away from others especially at a late stage of crystallization since the polymer molecules can be supplied readily. On the other hand when crystallization occurs at high temperatures as in Fig. 2 and in Fig. 3, the solvent molecules rejected can diffuse away instantly due to a large δ and the polymer concentration may not be localized resulting in the uniform growth of dendrites on the edge of spherulites.

CONCLUSIONS

The spherulitic morphology by crystallization from moderately concentrated i-PP solutions in dialkyl phthalate was investigated through optical microscopy under isothermal conditions. When crystallized at a low temperature, a continuous structure was obtained by impingement of spherulites. Crystallization at a high temperature produced the spherulites followed by dendritic growth on their surface without impingement. In this case with a lower crystallization temperature the dendritic growth started to appear at an earlier time scale during crystallization and the structure transition from spherulitic to dendritic growth became more gradual. This peculiar morphology can be qualitatively explained by the effects of polymer concentration at the growth front on the crystallization of polymer and the diffusion of solvent based on the Keith and Padden theory. At an early stage of crystallization the i-PP concentration as prepared is high enough to form the compact spherulites by frequent branching of growing crystals due to a small δ value. As the crystallization progresses, the polymer concentration in solution becomes dilute and the branching frequency of crystals is significantly reduced due to increased δ resulting in the dendrite formation.

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