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Conformational Change and Orientation Fluctuations of Isotactic Polystyrene Prior to Crystallization

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ABSTRACT: In order to clarify the preparation process of crystal nucleation of polymers, we have studied the conformational changes and orientation fluctuations of isotactic polystyrene (iPS) in the induction period of crystallization using time-resolved Fourier transform infrared (FT-IR) spectroscopy and depolarized light scattering (DPLS) techniques, respectively. Their measurements were carried out for the so-called cold crystallization, when it was crystallized somewhat above the glass transition temperature $T_g = 100°C$ from the glassy states. It is found from the time-resolved FT-IR measurements that the polymer chains begin to assume alternate conformations of *trans* (T) and *gauche* (G) in the induction period, which are characteristic to the 3/1 helix in the crystalline state. On the other hand, the time-resolved DPLS observations reveal that orientation fluctuations begin to grow in the induction period after a temperature jump to the crystallization temperature, which means that some rod-like segments of polymer chains actually start to orient parallel to one another prior to crystallization. These results are discussed in terms of the Doi's theory on the isotropic-to-nematic transition of liquid crystals where we assumed that the 3/1 helical segments are stiff and have a persistence length being almost equal to the length of the heilx axis. Thus, the growth of the helices involves the increase in persistence length and hence in excluded volume, to cause the parallel ordering of the helix parts as stiff segments.

KEY WORDS Cold Crystallization / Isotactic Polystyrene / Induction Period / Conformational Change / Parallel Orientation /

Recently, the structure formation during the induction period prior to crystal nucleation has received much attention.[1-8] We investigated the crystallization processes of poly(ethylene terephthalate) (PET) when it was annealed just above the glass transition temperature (T_g) using small-angle X-ray scattering (SAXS),[4,5] small-angle neutron scattering (SANS)[6,7] and depolarized light scattering (DPLS)[6,8] techniques. Surprisingly, we have discovered that a new SAXS peak following the kinetics of spinodal decomposition (SD) appears from the very early stage of the induction period prior to crystallization.[4,5] Such SD can be understood based on the kinetic theory for the isotropic-to-nematic transition of liquid crystals presented by Doi *et al.*[9-12]; the parallel orientation of stiff polymer segments induces a SD type microphase separation with a characteristic wavelength being larger than the value corresponding to the SAXS peak.[4,5] In fact, the parallel orientation was experimentally observed by DPLS measurements.[6,8] According to this theory, parallel ordering of rod-like polymers is induced only when their length exceeds a critical value. The SANS measurements with deuterium labeling[6,7] revealed that the persistence length of PET chains, *i.e.* the length of stiff segments, actually increases in the induction period to exceed the critical value.

In the preceding paper,[13] we investigated the crystallization processes of syndiotactic polystyrene with an extended chain conformation in the crystalline state by annealing at 120°C, *i.e.*, 20°C above T_g by means of time-resolved FT-IR and DPLS techniques. The FT-IR measurements have revealed that the rod-like segments in polymer chains extend as *gauche* conformations transfer to *trans* ones during the induction period before crystallization. It was expected from the Doi's theory[9-12] that this chain extension causes orientation fluctuations of the stiff segments when their length exceeds a critical value. Such orientation ordering in the induction period was actually confirmed by DPLS measurements.

It is interesting to investigate how the chain conformation changes during the induction period in the case of polymers assuming helical structure in the crystalline state. In this study, we have employed isotactic polystyrene (iPS) with 3/1 helix as an example of helical polymers and investigated the structural changes during the induction period when the polymer was crystallized from the glassy state. The conformational changes were detected by a time-resolved FT-IR spectroscopic method. In this case, it is absolutely necessary that the IR bands concerned should be well characterized. Fortunately, as for isotactic polystyrene, they have been well characterized in terms of tetrad sequences of *trans* and *gauche* by Kobayashi *et al.*[14,15] The parallel orientation of stiff segments during the induction period has also been measured for iPS by DPLS, and on the basis of these observed results, we discuss the structural formation processes during the induction period of crystallization, focusing on the relation between the 3/1 helix formation and the parallel ordering of 3/1 helix segments.

EXPERIMENTAL

The sample used for this study was isotactic polystyrene (iPS) with a weight-average molecular weight, $M_w = 4.0 \times 10^5$ and a polydispersity, $M_w/M_n = 2$. The glass transition temperature, T_g, was determined by DSC measurements to be 100°C. Amorphous thin films about

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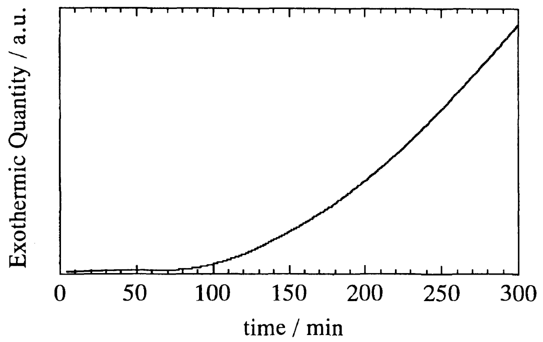

Figure 1. Annealing time dependence of crystallization isotherm for iPS glass. Annealing temperature was 135°C.

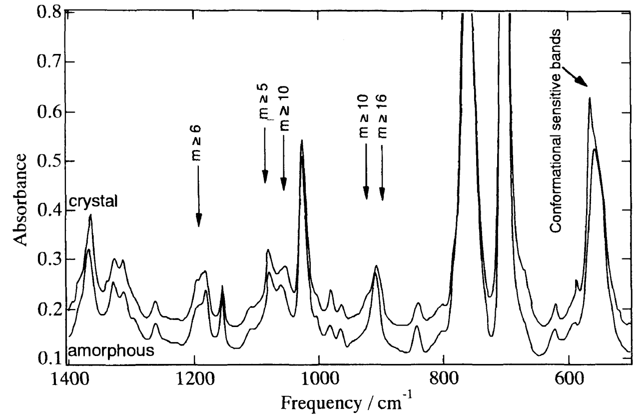

Figure 2. FT-IR spectra of crystalline (upper) and amorphous (lower) iPS in the region 500—1400 cm^{-1}. *m* indicates the minimum number of monomer units including in the 3/1 helix parts of the polymer chain.

50 μm thick were obtained by quenching the iPS melt into ice-water after being hot-pressed at 290°C for 5 min.

The time-resolved FT-IR measurements were performed on the melt-quenched sample under an isothermal condition at 135°C, *i.e.*, 35°C above T_g in a home-made temperature controlled cell. The IR absorption was recorded using a Nicolet Impact 410 system at 3.0 min intervals.

The time-resolved DPLS measurements were also carried out under the same annealing conditions at 135°C. The samples were irradiated by a plane-polarized He-Ne laser beam ($\lambda = 632.8$ nm) on a hot-stage and the scattered light intensity under depolarized conditions was recorded by a photodiode array system at 0.5 min intervals.

RESULTS AND DISCUSSION

Induction Period

Figure 1 shows the crystallization isotherm $\phi(t)$ of iPS measured by differential scanning calorimetry (DSC) using Perkin Elmer DSC 7 as a function of annealing time at 135°C. During the first 70 min, neither exotherm nor endotherm is observed, indicating that it is in the so-called induction period. We also confirmed from wide-angle X-ray diffraction measurements that no crystalline Bragg peaks except for amorphous halos are observed during the induction period; the measurements were carried out on several sample films quenched after annealing for given times before crystallization.

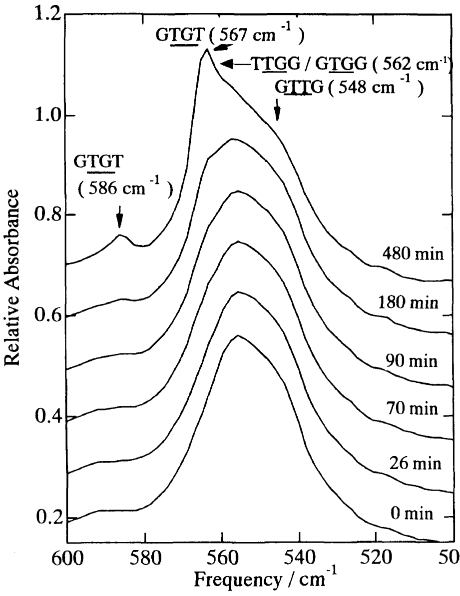

Figure 3. Annealing time dependence of IR spectra of iPS in the region 500—600 cm^{-1}. The bands at 548, 562, 567, and 586 cm^{-1} are assigned to GTTG, TTGG/GGTG, GTGT, and GTGT, respectively.

Detection of Conformational Change by FT-IR

Figure 2 shows the FT-IR spectra of iPS film samples melt-quenched and crystallized at 135°C for 400 min where the resulting crystal modification was the α form.[16] Characteristic differences between the spectra of the amorphous and crystalline iPS films are seen on the bands at around 550 cm^{-1} which are sensitive to the chain conformation with tetrad sequences of *trans* (T) and *gauche* (G)[15] and on the bands between 900 and 1300 cm^{-1} which are sensitive to the length of 3/1 helix conformation.[14]

Nakaoki and Kobayashi[15] have assigned the absorption bands of polystyrenes at around 550 cm^{-1} to out-of-plane modes of the phenyl group, whose frequencies depend on the local skeletal conformation in the neighborhood of the phenyl group. These bands are observed in both amorphous and crystalline spectra of iPS as seen in Figure 2 relating to the skeletal conformations with tetrad sequences as will be shown below.

In order to follow the conformational change in the induction period, we have carried out time-resolved FT-IR measurements after a temperature jump to 135°C. Figure 3 shows the time evolution of the enlarged spectra in the frequency range 500 to 600 cm^{-1} when the sample was annealed at 135°C. Here each curve is shifted along the axis of relative absorbance to make it easy to see. Four bands at 548, 562, 567, and 586 cm^{-1} are distinguished and indicated with arrows in Figure 3: the 548 cm^{-1} band has been assigned to GTTG conformation, the 562 cm^{-1} band to TTGG and GGTG, and the 567 and 586 cm^{-1} bands to GTGT, respectively. Here T and G are *trans* and *gauche* conformations, respectively, and the two middle-underlined letters indicate the conformations around the C–C bonds on the both sides of the carbon atom bonded to a phenyl group. For the quantitative analysis, we decomposed the spectra in the region 500—600 cm^{-1} into these four components by assuming a Lorentzian shape for each band as shown in

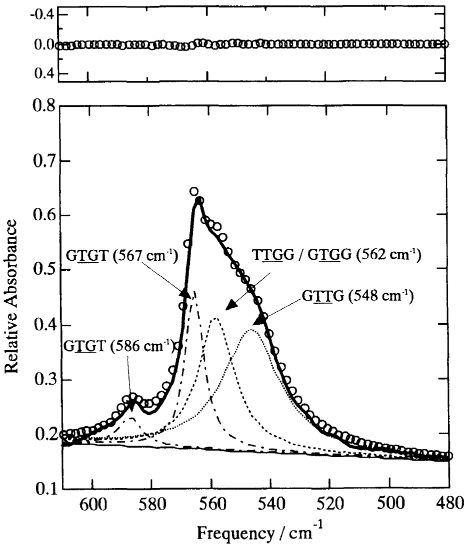

Figure 4. Separation of bands in the region 500—600 cm^{-1} of FT-IR spectrum of iPS. An example for the sample annealed at 135°C for 480 min.

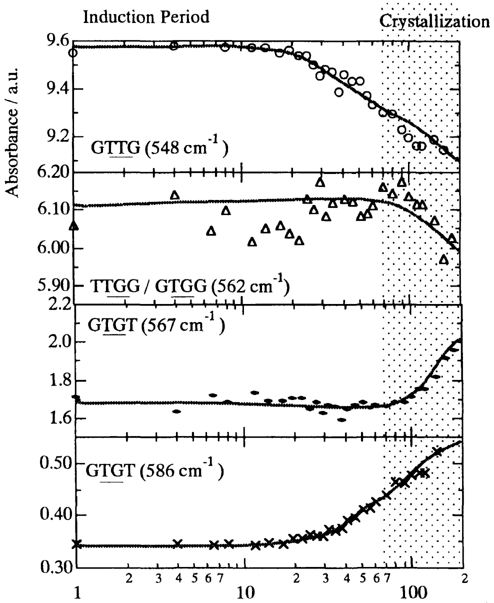

Figure 5. Annealing time dependence of the intensities of 548 (GTTG), 562 (TTGG/GGTG), 567 (GTGT), and 586 (GTGT) cm^{-1}. The intensity is normalized to the value immediately after temperature jump to 135°C.

Figure 4 for an example. The time evolution of intensities of these bands is plotted in Figure 5. If the polymer chain extends during the induction period, it is expected that GTGT bands increase in intensity because the conformation in the iPS crystal is the 3/1 helix of $(TG)_3$. This expectation can qualitatively be confirmed in Figure 5; the peaks of GTGT (567 and 586 cm^{-1}) increase in intensity with annealing time while those of GTTG (548 cm^{-1}) and TTGG/GGTG (562 cm^{-1}) decrease. The change of the 586 cm^{-1} band may imply that the formation of 3/1 helix starts to occur and proceeds even during the induction period of crystallization. In the crystallization stage after the induction period, the bands of GTGT conformations continue to increase in intensity.

On the other hand, several bands in the region 900—1200 cm^{-1} of Figure 2 are assigned to 3/1 helix bands by Kobayashi *et al.*[14] Their frequencies depend largely on the sequence length of the helix part, *i.e.*, the number m of monomer units in the helix part. The band at 899 cm^{-1} is assigned to the 3/1 helical segments including 16 or more monomer units ($m \geq 16$), the both bands at 920 and 1050 cm^{-1} are assigned to the helical ones with 10 or more units ($m \geq 10$), and the bands at 1081 and 1186 cm^{-1} to those with 5 or more ($m \geq 5$) and 6 or more ($m \geq 6$) units, respectively.

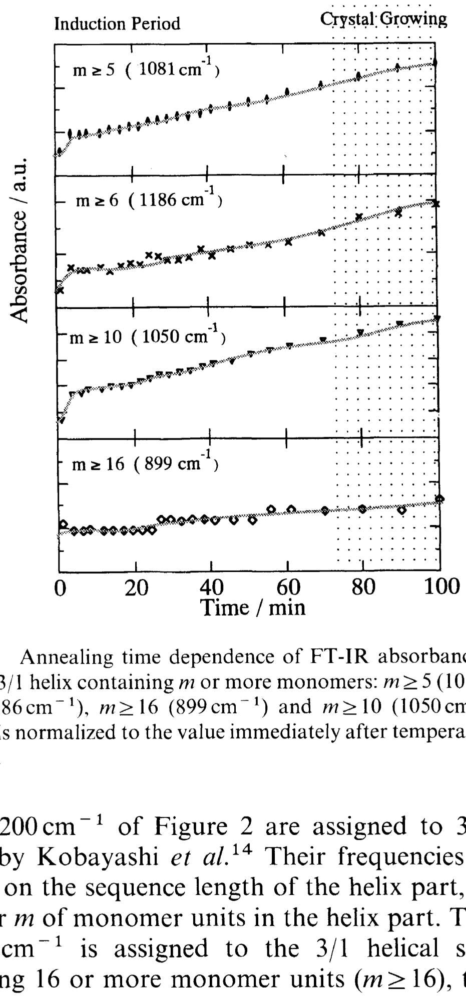

Figure 6. Annealing time dependence of FT-IR absorbance for the bands of 3/1 helix containing m or more monomers: $m \geq 5$ (1081 cm^{-1}), $m \geq 6$ (1186 cm^{-1}), $m \geq 16$ (899 cm^{-1}) and $m \geq 10$ (1050 cm^{-1}). The intensity is normalized to the value immediately after temperature jump to 135°C.

In order to see the growth of the 3/1 helix bands during the induction period of crystallization, annealing time dependence of the intensities of the 3/1 helix bands are shown in Figure 6. The absorbance of the 3/1 helix bands for $m \geq 5$, 6 and 10 gradually increases in intensity after a slight abrupt increase in the induction period while that for $m \geq 16$ increases considerably late, indicating that naturally it takes more time for the longer helix ($m \geq 16$) to be formed than the shorter ones ($m \leq 10$). In any case, the present FT-IR results show that in the induction period the 3/1 helix conformation increases and the polymer chains are extended with annealing time. It is also noted that the 3/1 helix bands continue to increase in intensity even after the beginning of crystallization.

The abrupt increase in absorbance between 0 and 3.0 min for $m \geq 5$, 6 and 10 as described above may mean the slight increase of the helical sequence length in the very early stage of the induction period. A similar initial extension of polymer chains was directly observed for PET by measuring persistence length using the SANS technique with a deuterium labeling method.[6,7] Though the persistence length of iPS has not directly been measured yet, the increase in absorbance of 3/1 helix bands may correspond to the increase of persistence length. The gradual increase between 3.0 and 70 min may indicate the gradual extension of polymer chains.

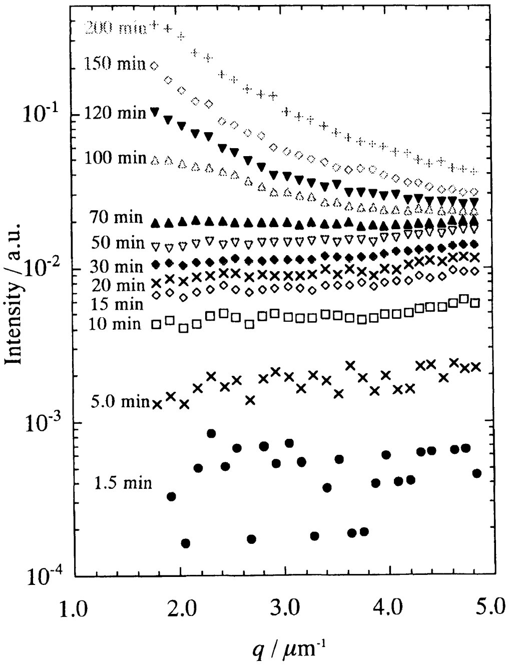

Figure 7. Depolarized light scattering profiles $I_{VH}(q)$ of iPS films annealed at 135°C as a function of annealing time.

Anyway, the present results of time-resolved FT-IR measurements suggest that the growth of chain conformations of 3/1 helix actually causes the chain extension during the indication period of crystallization.

Orientation Fluctuations from DPLS Measurements

As described in the Introduction, it is expected that the orientation fluctuations of stiff segments occur in the induction period when stiff segments extend over a critical value. In order to confirm whether or not such orientation fluctuations actually evolve with time during the induction period, DPLS measurements were performed under the same annealing conditions as for the FT-IR investigation. Figure 7 shows the semi-logarithmic expression of time evolution of the DPLS intensity at 135°C as a function of the length of scattering vector, q. There is no doubt that the depolarized intensity increases with the annealing time even in the induction period, suggesting that parallel ordering of polymer chain segments proceeds before crystallization. According to Stein *et al.*,[17] the Rayleigh factor $R_+(q)$ for depolarized light scattering from solids having randomly correlated orientation fluctuations can be expressed by

$$R_+(q)=\left(\frac{\omega}{c}\right)^4\frac{\langle\delta^2\rangle}{15}\int_0^\infty g(r)\,\frac{\sin(qr)}{qr}\,(4\pi r)\mathrm{d}r \qquad (1)$$

where ω is the angular frequency of incident radiation, c is the velocity of light, $\langle\delta^2\rangle$ is the mean-square anisotropy and $g(r)$ is the function of orientation defined as $g(r)=(3\langle\cos^2\phi_{i,j}\rangle_r-1)/2$, where $\phi_{i,j}$ is the angle between the optical axes of the ith and jth elements. The invariant due to the orientation fluctuations I_{VH} is given by

$$I_{VH}=\int_0^\infty R_+(q)q^2\mathrm{d}q=\frac{2\pi^2}{15}\left(\frac{\omega}{c}\right)^4\langle\delta^2\rangle \qquad (2)$$

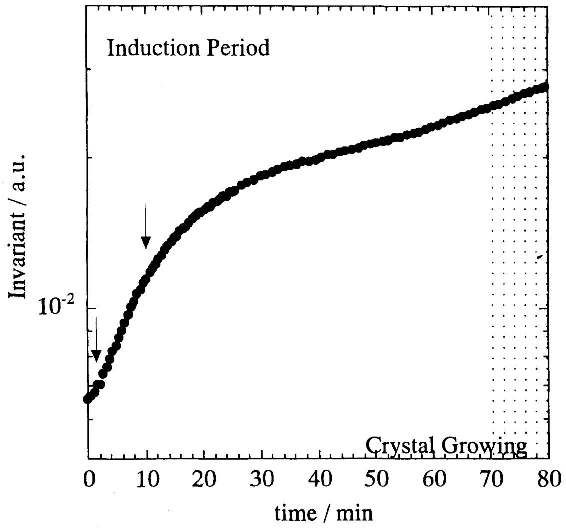

Figure 8. Annealing time dependence of the invariant for the depolarized light scattering intensity of iPS films in the induction period of crystallization.

These eq 1 and 2 give us a basis for interpretations of the results on the depolarized light scattering measurements.

As seen in Figure 7, during the induction period of crystallization the scattering profiles are almost independent of scattering vector, q, and the total intensity increases with annealing time. This result indicates that the sizes of oriented domains or their aggregates are much smaller than the scales corresponding to the measured q-range. But in the crystal growing period, the scattering profile becomes q-dependent; the intensity increases with decreasing q. This means that after the crystal growth the sizes of oriented domains or their aggregates have become comparable with the scale of q-range examined, which is probably because of the formation of spherulites. Similar results were observed in the crystallization processes of PET[6,8] and sPS.[13]

Figure 8 shows the time dependence of the invariant for the orientation fluctuations I_{VH} (eq 2), calculated within the present q-range. In the very early stage until about 3.0 min, the growth rate of the invariant is slow compared with that after 3.0 min. In this time region, we observed the abrupt increase of IR bands originated from the 3/1 helix conformation (see Figure 6). After this small increase, the invariant shows an exponential growth in the period between 3.0 and 10 min. Such exponential growth is one of the characteristic features of spinodal decomposition (SD) in the kinetics of isotropic–nematic transitions of liquid crystals as shown by Doi *et al.*,[9–12] and was actually observed in the induction period of PET[6,8] and sPS[13] crystallization. Then we can conclude that the orientation fluctuations are caused by the parallel ordering of the 3/1 helix segments in the induction period, following the kinetic process of isotropic–nematic transition. However, the initial delay until 3.0 min was not observed in the cases of PET and sPS, both of which assume extended conformations. Hence the time of the first 3.0 min after the temperature jump may be required for the helical segments to exceed a critical length. In the time range after 10 min the invariant shows a tendency of leveling-off while it begins to increase more steeply when the crystallization starts after 70 min. It is natural to consider that the steeper increase is caused by the growth of spherulites.

Doi *et al.* have theoretically investigated dynamics of liquid crystalline phase formation in a solution of stiff polymers using a kinetics of two order parameters of concentration and orientation. This theory predicts that the transition from isotropic to nematic state occurs when the system is brought into a thermodynamically unstable region. This unstable state is caused by the increase of excluded volume due to the polymer chain extension. The critical concentration at which the isotropic phase becomes unstable is given by[9]

$$\nu^* = \frac{4.19}{bL^2} \tag{3}$$

where b and L are the diameter and the length of the rod-like polymer and the term bL^2 is in the order of the excluded volume of this polymer. When the mean number ν of the rod-like polymers per unit volume is smaller than ν^*, the system is stable and the orientation fluctuations cannot grow with time, but when $\nu > \nu^*$, the system becomes unstable and the orientation fluctuations start to grow. This theory also predicts that the dynamics of isotropic–nematic transition is very similar to that of the spinodal-decomposition type phase separation. As shown above, we observed an exponential growth of orientation fluctuations between 3.0 and 10 min in the induction period (see Figure 8), which is one of the characteristic features of spinodal-decomposition type microphase separation. In what follows, we will examine whether the iPS system is under the unstable condition ($\nu > \nu^*$) when the orientation fluctuations begin to occur.

Although this theory was originally formulated for the polymer solutions of stiff polymers, we found that it is applicable to a flexible sPS in the bulk system[13] by assuming the hypothetical freely jointed chain model proposed by Flory[18] where the chain consists of connected stiff segments of a length being equal to its persistence length. Therefore, we again apply the theory to iPS that is also a flexible polymer. We have evaluated the criterion for the isotropic–nematic transition as follows. The concentration ν of rod-like segments in the glass can be evaluated from the persistence length L of the polymer and the density ρ, using eq 4

$$\nu = \frac{\rho N_A}{\left(\frac{L}{l_0}\right) M_0} \tag{4}$$

where l_0 and M_0 are the length and molecular weight of the monomer, respectively, and N_A is the Avogadro number. To describe the chain conformation of iPS the helical wormlike (HW) touched-bead model was employed.[19,20] For the glassy state of iPS, the persistence length L is given as 1.32 nm, and the density measured by flotation method was 1.04 g cm^{-3}. Further, b and l_0 can be taken as 1.40 nm and 0.222 nm, respectively. With these values, ν and ν^* are calculated to be 1.01 and 1.72 segments nm^{-3}, respectively. In this condition ($\nu < \nu^*$), the system is stable and the orientation fluctuations do not grow. In order to get into the unstable region, polymer chains must extend to reduce the critical concentration of eq 3. After annealing, the conformational changes begin to occur and the persistence length may increase because of the growth of 3/1 helix conformation. We assume that the persistence length is close to the average length of 3/1 helix parts. Then the length, L, must increase with annealing time during the induction period, leading to the decrease of ν^* (see eq 3). When the average length of the rod-like segments exceeds 2.24 nm, which gives a condition of $\nu = \nu^*$, the iPS system gets into the unstable region. From conformational point of view, 2.24 nm corresponds to ten monomers ($m = 10$) having five alternate *trans* and *gauche* conformations. This result seems to be reasonable because as seen from Figure 6, the bands for $m \leq 10$ start to increase in intensity from the very beginning but the intensity of the $m \geq 16$ band grows considerably late after about 25 min while the orientation occurs from the beginning (see Figure 8). The extension from 6 monomers to 10 monomers of the stiff segments requires a considerable time, which would cause the delay of 3 min in the increase of the DPLS invariant.

CONCLUSIONS

In order to elucidate the structure formation mechanism prior to crystal nucleation, we performed time-resolved FT-IR and depolarized light scattering measurements on iPS during the induction period of crystallization from the glassy state. In the time-resolved FT-IR measurements, the increase of alternating *trans* and *gauche* conformations is observed immediately after the temperature jump to 135°C as well as the increase of 3/1 helix bands. Further, the time-resolved DPLS measurements revealed that the orientation fluctuations begin to increase in the induction period, indicating that parallel ordering of polymer chains actually proceeds in the induction period. However, the orientation fluctuations of the main chain begin to arise at 3.0 min after temperature jump. These results suggest that in the case of helical the critical length of stiff segments considerably large, resulting in the delay of the parallel ordering of polymer chains. This is contrast to the cases of PET and sPS. The critical length for iPS was tentatively determined from the Doi's theory on isotropic–nematic transition of liquid crystalline polymers.

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