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Conformational Change and Orientation Fluctuations Prior to Crystallization of Crystalline Polystyrenes

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Aiming to clarify the cause of a spinodal decomposition (SD) type microphase separation occurring during the induction period of polymer crystallization, we have made quantitative investigations about the conformational changes using FT-IR spectroscopy as well as the orientation fluctuations of the polymer rigid segments using depolarized light scattering (DPLS). It is confirmed for syndiotactic and isotactic polystyrenes (sPS and iPS) that during the induction period, the polymer chains first transform partially from the amorphous to the crystalline conformation, involving in the increase of length of the rigid segments, which makes the system unstable to induce the orientation fluctuations of the SD type. Thus, the intensity of orientation fluctuations evolved exponentially with annealing time.

Keywords: Polymer Crystallization / Polystyrenes / Induction Period / Spinodal Decomposition / Conformational Change / Orientation Fluctuations

In the previous papers [1,2], we have reviewed the crystallization processes of poly(ethylene terephthalate) (PET) when it was crystallized directly from the melt, called 'melt crystallization' as well as from the glass, called 'glass crystallization'. It was discovered that a new peak in small-angle X-ray scattering (SAXS) appears from the very early stage of the induction period before nucleation. The detailed analysis of this new peak revealed a surprising result that a spinodal decomposition (SD) type microphase separation occurs during the induction period of crystallization. Such SD can be understood based on the kinetic theory for the isotropic-to-nematic transition of polymer liquid crystals by Doi et al.[3]; it is caused by parallel ordering of polymer rigid segments. This prediction was actually confirmed by depolarized light scattering (DPLS). However, the origin of such orientation fluctuations is unclear. We suppose that the polymer stiff segments corresponds to crystalline segments and their extension causes the increase of their excluded volumes to make the system unstable

and trigger the SD. In this study we therefore verify this hypothesis. For this purpose, the time-resolved Fourier transform infrared (FT-IR) spectroscopy and DPLS measurements during the induction period have been performed on syndiotactic polystyrene (sPS) and isotactic polystyrene (iPS) when they are crystallized by jumping the temperature to 120 °C for sPS, and to 135 °C for iPS from the glass [4,5].

Experimental

The samples used for this study were iPS and sPS with number-average molecular weights $M_n = 4.0 \times 10^5$ and 2.9×10^5 , respectively. The polydispersity, M_w / M_n , for the both samples is 2.0. The glass transition temperatures were determined by DSC measurements to be 100 °C for both iPS and sPS. Amorphous thin films of iPS and sPS were obtained by quenching their melts into ice-water after hot-pressed *i.e.* at 290 °C and 330 °C, respectively, for 5 min.

The time-resolved FT-IR measurements were per-

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Scope of research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with the intention of solving fundamentally important problems in polymer science. The main projects are: the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; formation process and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.



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formed on the melt-quenched sample under an isothermal condition in a home-made temperature-control cell. The IR absorption spectra were recorded at 3.0 min intervals. The time-resolved DPLS measurements were also carried out under the same condition of the FT-IR measurements. 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

FT-IR It is absolutely necessary that the concerned IR bands of the sample polymers should be well characterized. Fortunately, crystalline polystyrenes, both isotactic and syndiotactic, have been done in terms of sequences of *trans* and *gauche* by Kobayashi et al. [6] Here, we aimed at bands of sPS and iPS related to crystalline conformations and measured the time dependence of their absorbance. In case of sPS, the increase in absorbance of successive *trans* conformations (TT) was observed immediately after the jump to a crystallization temperature from the glass, indicating that sPS chains begin to assume the crystalline extended conformations and that the stiff segments of sPS may be lengthened even in the very early stage of the induction period of crystallization. On the other hand, the crystalline conformation of iPS is a 3/1 helix consisting of alternate *trans* and *gauche* (TG) conformations. In this case the time-resolved FT-IR measurements showed increase in absorbance of TG conformation bands after a similar temperature jump. Furthermore, as seen from Figure 1, the bands concerned with the length of 3/1 helix also increase during the induction period of 70 min, which is indicated with a solid line in the figure. This supports that iPS chains start to assume the crystalline conformation of 3/1 helix before crystallization. From these results, we calculated critical lengths that trigger parallel ordering of polymer stiff segments using the Doi's theory. In case of the amorphous state, the persistence length is 1.88 nm for

sPS or 1.32 nm for iPS [7]. In case of sPS, we calculated the critical length to be 2.51 nm, corresponding to 10 TT monomers. The parallel ordering begins when the stiff segments expand only by 0.7 nm, i.e. 2.5 monomers. The critical length is calculated to be 2.24 nm for iPS, corresponding to 3/1 helix consisting of 11 monomers. Figure 1 shows that the absorbance of 3/1 helix not longer than 10 monomers increases with time during the induction period while the band of helix shorter than 16 monomers hardly grows. This means that the critical value of the stiff segments is between 10 and 16 monomers because at the critical value a further extension may be suppressed due to the unstable state of the system, agreeing with the prediction of 11 monomers.

DPLS The total intensity of DPLS increased with annealing time during the induction period and the scattering profiles were almost independent of scattering vector, q , for both the polystyrenes. These facts indicate that the sizes of the oriented domains or their aggregates are much smaller than the laser wavelength or the sizes corresponding to the measured q -range between 2.0 and 5.0 μm^{-1} . In the crystal growing period, however, the scattering profile becomes q -dependent; the intensity increases with decreasing q , which means that the sizes of the oriented domains or their aggregates become comparable with those of the examined q -range by crystal growth probably because of formation of spherulites of iPS and sPS.

We calculated the integrated intensity for the orientation fluctuations, I_{vh} , of iPS and sPS within the present q -range. In the first stage until 3 min, the growth rate of the integrated intensity was very slow, while the crystalline conformation (3/1 helix) suddenly grows at the very initial stage as seen from in Figure 1. For sPS the first stage of the induction period is much shorter than that for iPS at any annealing temperatures. This suggests that conformational change, that is, extension of polymer segments emerges first of all. In conclusion we have proved the hypothesis that the microphase separation is triggered by extension of polymer segments. After the first stage, we can observe the exponential growth of the integrated intensity of DPLS for each polystyrene, which is one of characteristic features of SD. Hence it has as well been confirmed in the case of crystallization of PS's as in PET that the SD-like phase separation actually emerges during the induction period.

References

- [1] Imai M, Kaji K and Kanaya T, *ICR Annual Report*, **1**, 26 (1994).
- [2] Kaji K, Matsunaga S, Matsuba G, Kanaya T, Nishida K and Imai M, *ICR Annual Report*, **5**, 26 (1998).
- [3] Doi M and Edwards S F, *The Theory of Polymer Dynamics*, Oxford, Chapter 9 and 10 (1986).
- [4] Matsuba G, Kaji K, Nishida K, Kanaya T and Imai M, *Macromolecules*, **32**, 8932 (1999).
- [5] Matsuba G, Kaji K, Nishida K, Kanaya T and Imai M, *Polymer J.*, **31**, 722 (1999).
- [6] Kobayashi M, Akita K and Tadokoro H, *Makromol. Chem.*, **118**, 324 (1968).
- [7] Yamakawa H, *Ann. Rev. Phys. Chem.*, **35**, 23 (1984).

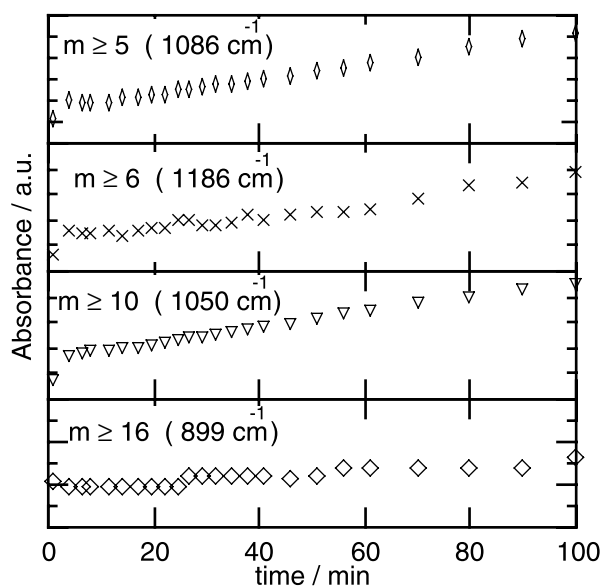


Figure 1. Time dependence of the absorbance of 3/1 helix bands of iPS annealed at 135 °C. Induction period 70 min.