Cluster Information of Melt Crystallized Isotactic Polystyrene by FTIR

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Abstract: **In situ Fourier transform infrared spectroscopy (FTIR) measurements were carried out to study the conformational changes during crystallization from molten isotactic polystyrene (iPS). The sample is melted and subsequently crystallized at a temperature, formed a well ordered spherulites with helix structure after an initial induction period. The later stage of the induction period, small ordered structure of helical moieties regarded as a sort of 3_1 helix with partially regular packing was identified. An increase of the melt temperature destroyed the longer helices in the crystal but the shorter helices can survive and form a cluster in the melt, initiated a primary nucleation site. The nucleation density was found to be a function of the survival shorter 3_1 helix.**

Keywords: **FTIR study / nucleation density / melt crystallization / isotactic polystyrene.**

I. INTRODUCTION

When a molten polymer is crystallized, the formation of a new three-dimensional solid phase takes an induction time. The induction time is the period needed to form a critical nucleus and is often employed as the primary nucleation. After nucleation the crystal starts to grow in all possible dimensions and form spherulites. The crystal nuclei are difficult to observe directly by standard methods because of their very small size. Therefore, small spherulites are assumed to have started on an active individual site and they are observed after an induction time, whereas the aggregation of polymer molecules is reversible up to the critical nucleus size. Beyond this time, an embryo with a size greater than the critical size becomes stable and the number of nuclei increases with time. The number of nuclei strongly depends on the previous melt temperature, whereas the melt temperature is below (partial melting) or above (complete melting) the end of DSC melting point. Even above the melting point, if the melt temperature or its holding time is insufficient, remnants of the previous structure (residual crystal) can survive and act as predetermined nucleation sites upon subsequent cooling. Such a phenomenon is referred to as self-nucleation or memory effect [1]. If a polymer is melted for sufficiently high temperature and time, all memory of the previous crystalline structure might be removed. Such temperature is usually higher than the equilibrium melt temperature. The crystal fragments of insufficient melting construct a molecular cluster or embryo in the melt and can make an effect on conformation during crystallization process.

Fourier transform infrared spectroscopy is one of the most suitable tools for the detection of the conformational changes and has been widely used for the characterization of various phases. Isotactic polystyrene has slow crystallization rate and longer induction time following crystallization conditions, makes it suitable to study the crystallization process by real time FTIR spectroscopy and the band assignment is well defined [2, 3]. The conformational changes during induction time of crystallization are very small; however, the small changes in spectrum are also a better resolved under the in situ measurement. Several reports have appeared in the literature based on the melt and crystallization process of iPS [4-6]. Jianming et al investigated the isothermal crystallization process of iPS from melt and glassy state by IR. They clearly

discussed the band assignment, where the amorphous and crystalline sensitive bands are quite different for the cold- and melt-crystallization processes [7].

Previously, we reported that the crystallization process from melt and glassy state are different and depends on the previous melt temperatures. In this paper, detailed studies of the cluster information as well as helix conformation as a function of melt temperatures are discussed by FTIR. A relationship between the survival helix conformation and the nucleation density has been drawn.

II. EXPERIMENTAL

Samples of iPS (M_w=17,800, M_n=10,600, M_w/ M_n=1.68, Tacticity: 96%) was supplied by Idemitsu Kosan Co., Ltd. The sample was melted between two cover glasses using a metallic spacer to form a given film thickness on a hot stage. In a typical experiment, DSC melting peak showed at about 224°C and the end of the melting curve (tail of the peak) at 228°C for iPS crystallized at 200°C for 8 hrs. The equilibrium melt temperature reported at 242°C (T_m^o) [3]. Therefore, several typical melt temperatures were selected from 225 to 250°C. Subsequently, the molten sample was cooled to a given crystallization temperature with a cooling rate of 30°C/min. Nucleation density was measured on a Linkam LK-600 temperature-controlled apparatus under an Olympus BH-2 optical microscope (OM) equipped with a Pixel 600ES-CU CCD camera. For FTIR measurements, the iPS film was prepared on silicon substrates. The sample was set into a same temperature controlled apparatus of hot stage, which was placed in the sample compartment of a Jasco FTIR 7000 Fourier transform IR system equipped with a DTGS detector. FTIR spectra of the specimens were collected at a 4 cm^{-1} resolution with a 2 min interval during the crystallization process. The temperature dependence FTIR spectra were taken with 2°C interval. The spectra were obtained by co-adding of 32 scans.

III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of iPS, isothermally crystallized at 160°C, melt from 230°C as a function of crystallization time as indicated in figure. The band assignments are used for the structure analysis as describe in references [2, 3]. The absorption band at 981 cm^{-1} is related with the degree of crystallinity (X_c), and the band at 1026 cm^{-1}, is the characteristic band for benzene ring act as an internal standard band [8]. The absorption bands at 1052 and 1083 cm^{-1} are related with 3_1 helix band. According to Kobayashi and co-workers, [3, 9] the intensity of 3_1 helix bands depend on the sequence length of the helix unit. A minimum sequence length is necessary for the 3_1 helix band to appear in the spectrum.
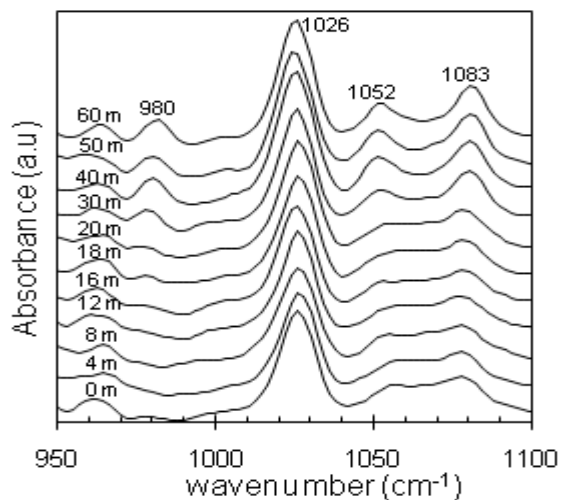

Fig. 1: Temporal changes of the FTIR spectrum as a function of crystallization times as indicated in figure, during crystallization at 160°C, after melt at 230°C.
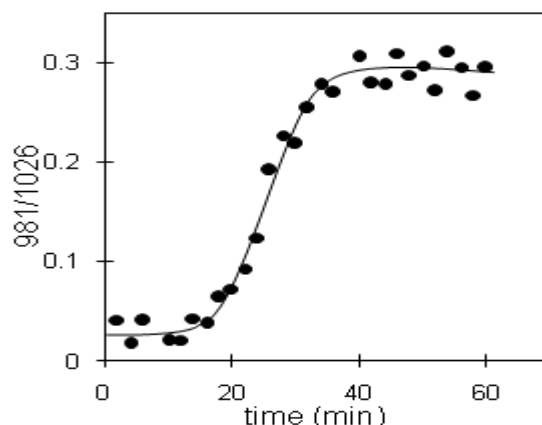

Fig. 2: Crystallization time dependent normalized FTIR spectra at 981 cm^{-1} for iPS crystallized at 160°C after melt from 230°C. The inset image shows time dependent number of nuclei (counted by OM) with same crystallization conditions as FTIR.

There are several characteristic absorption bands for 3_1-helix conformations in the polymer chain. For example, 3_1 helices composed of 5 monomeric units (5-helix) is related at 1083 cm^{-1} and 10 monomeric units (10-helix) at 1052 cm^{-1}. The splitting of the 1052 and 1083 cm^{-1} bands is mainly related to the regularity of the skeletal chain. It can be seen from figure 1 that the intensity at 981, 1052, 1083 cm^{-1} are increases with crystallization time. From the starting of the crystallization process the helix bands at 1052 and 1083 cm^{-1} are clearly distinguishable but the crystallization band at 981 cm^{-1} is less evident. The absorption band at 1026 cm^{-1} does not changes at all. To clarify in details figure 2 shows the crystallization time dependent normalized intensity at 981 cm^{-1}. Each absorption band was normalized by the peak height of the characteristic absorption band at 1026 cm^{-1}. The spectrum was taken during crystallization with two minutes interval. Figure shows that the crystallization time dependent intensity starts with the induction time, increases sporadically, subsequently crystallinity increase with the steady state and then reached to the constant value. It was found that after a certain period of crystallization time (induction period) the intensity starts to increases and, the intensity remains constant (crystallization complete). For example, an induction time of 12 min and completion time around 40 min can be read for crystallization at 160°C after melt from 230°C. There are several reports indicating the time dependence crystallinity, measured by IR. For example, Kimura et al. have found the induction time of overall crystallization about 50 min [10]. A similar result has been found for the induction time of iPS (about 60 min), crystallized at 130 °C from the glassy state [7], are much longer than the present study. The crystallized region associated with the total amount of nuclei at the saturated state is about 10% in the whole specimen. Such small crystallinity in the early stage of the nucleation will be difficult to detect by usual methods such as dilatometry, DSC, X-ray, and others. However, the number of nuclei is much easier to observe using OM by assuming that the spherulites have started on an active individual site and they are observed after a certain induction time whereas the aggregation of polymer molecules is reversible up to the critical nucleus size. Beyond that time, an embryo with a size greater than the critical size becomes stable and the number of nuclei increases linearly with time. The inset image of figure 2 shows time dependent nucleation density where the nucleation displays first an induction time, with sporadic appearance of spherulites. Subsequently the spherulites number increases steadily, before reach to saturation. The nucleation density seems to reach saturation within 180 seconds. The main increase in FTIR intensity beyond 180 seconds is related to the crystallization governed by the crystal growth rate. In fact, while the helix bands at 1052 and 1083 cm^{-1} are clearly distinguishable, the crystallinity band at 981 cm^{-1} is less evident during the induction time of the overall crystallization. Since the primary nucleation is finished before the large increase in helix bands in the overall crystallization, so a shorter induction time is much evidence. The induction time depends strongly on the amount of crystallized moiety, which is a function of primary nucleation rate and linear crystal growth rate. In other words, the induction time in overall crystallization is different from the induction time in primary nucleation.
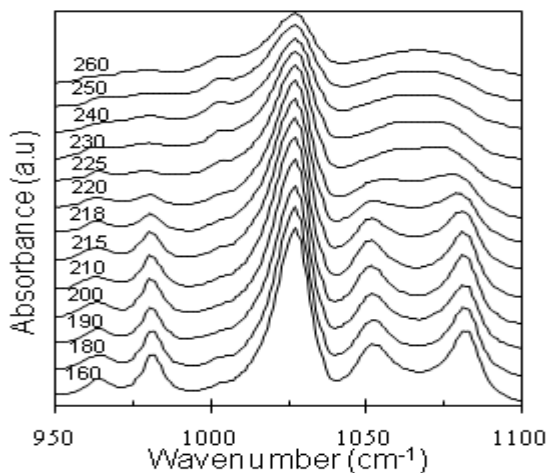

Fig. 3: Temperature dependence FTIR spectra for iPS at the indicated temperatures during the heating process. Prior to heating, the sample was crystallized at 160 °C for 8 h.
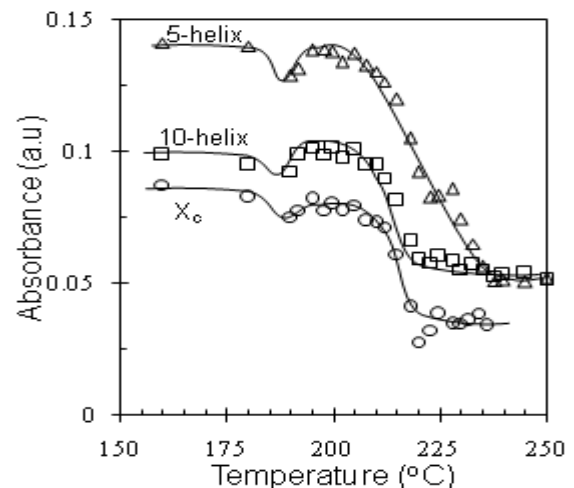
Fig. 4: Change in peak intensities at 981 cm^{-1} (X_c), 1052 cm^{-1} (10-helix), and 1083 cm^{-1} (5-helix) as a function temperature during the heating process.

Figure 3 shows the temperature dependence FTIR spectra at the indicated temperatures during the heating of the sample. Prior to heating, the sample was crystallized at 160°C for 8 h. It can be seen before 190°C, no significant changes in spectra were observed. Above 190°C, small changes were observed due to recrystallization process during heating scan. During the melting, the intensity of crystallization band at 981 cm^{-1} and the helix bands at 1052 and 1083 cm^{-1} decreases but the absorption band at 1026 cm^{-1} does not changes. Figure 4 shows the temperature dependence of the normalized bands for 5-helix, 10-helix, and X_c. In each of the characteristic bands, a small peak is observed at about 190°C, and the band intensity decreases above 204°C. The characteristic bands for the 10-helix and the degree of crystallinity are constant at about 228°C. However, the characteristic band of the 5-helix decreases in intensity as temperature increases, becoming constant at about 240°C. For details, figure 5 shows the DSC thermogram for the sample crystallized with same condition at 160°C as FTIR studies. An exothermic peak is observed at about 194°C, and this peak is caused by recrystallization of the sample during heating process. Two melting endotherms are observed in the temperature range of 204-228°C. The lower melting point increased linearly with the crystallization temperature, and its slope (the Hoffman-Weeks plot [11]) was almost 0.5, yielding an equilibrium melting temperature of 242°C, whereas the higher melting point was nearly independent of the crystallization temperature. The higher melting peak can be explained by melting of lamellae rearrangement (thickening) during the DSC heating process [12]. Comparing the results of figures 4 and 5, the peak at 190°C can be attributed to recrystallization during heating process. The decreasing intensity above 204°C can be associated with the melting of both the original and rearranged lamellae. Tails at 228°C in the FTIR intensities at 1052 and 981 cm^{-1} coincide with the end of the DSC melting curve. The plot of 10-helix against X_c showed a good linear relationship. On the other hand, the band at 1083 cm^{-1} for 5-helix becomes constant at about 240°C, which is higher than the end of the DSC melting curve. This indicates, the 3_1 helix composed of 5 monomeric units still remains even above the melting point and can give rise to cluster formation in the melt.
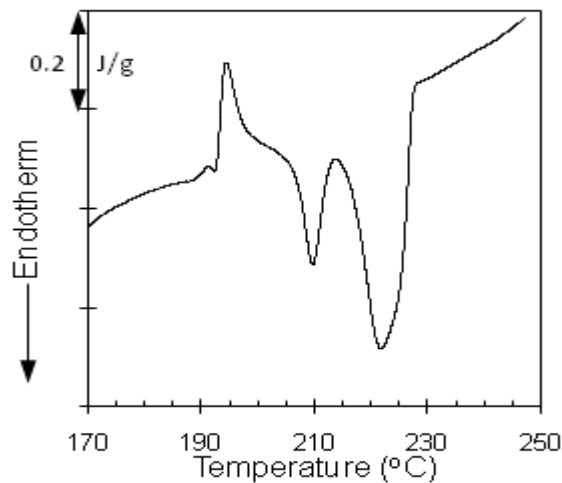

Fig. 5: DSC melting endotherm of iPS crystallized at 160 °C for 8 h from the melt at 250 °C.

The temperature dependence of the 3_1 helix was analyzed theoretically by Kobayashi et al. [2]. The total fraction of helices $F(m)$ composed with m monomeric units can be represented on the basis of the following simple statistical mechanical model given by equation 1.

$$F(m) = p^{m-1}\big[m - (m-1)p\big] -----(1)$$

Where

$$p = 1/\big[1 + \exp\{-(\Delta H - T\Delta S)/RT\}\big] -----(2)$$

Here, ΔH and ΔS are the enthalpy and the entropy differences per mole of monomeric units, respectively, between the random and the helical states. According to their method, the amount of the 3_1 helix composed of 5 monomeric units is plotted as a function of temperature as shown in figure 6 (data are normalized to 160°C). The solid curve is estimated by the best fitting

procedure based on eq. 2, yielding ΔH = 18 kcal/mol and ΔS = 34 emu/mol. These two estimated energies are larger than those reported by Kobayashi et al. Their reported values for these two energies are ΔH = 3.1 kcal/mol and ΔS = 9.9 emu/mol based on the 10-helix measured in solution from -100°C to room temperature. The difference between the present results and those by Kobayashi et al. could result from the different states of the samples, i.e., the solution state at low temperatures versus the molten state at high temperatures. However, the activation energy for the molten state can be compared with the activation energy for the destruction of a predetermined nuclei (21.3 kcal/mol) of isotactic poly(propylene) [6]. A pseudocrystalline order can exist in the melt for a long time. It is evident that a stable helix conformation exists even in a solution state [9], in the molten state [10], or in a glassy state [13]. When a crystalline part of iPS is melted, the longer helices in the crystal can be destroyed, but the shorter helices are able to survive and form a cluster in the melt. Such a cluster can initiate a primary nucleation site in the melt during subsequent cooling, and its size is strongly dependent on the melt temperature.
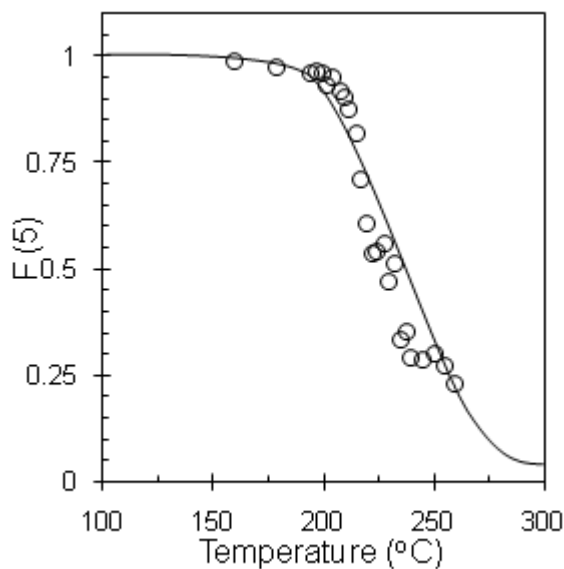

Fig. 6: Temperature dependence of the peak intensity at 1083 cm^{-1} (5-helix) normalized to the intensity at 160 °C. Solid line represents curve fitting based on eq. 2.
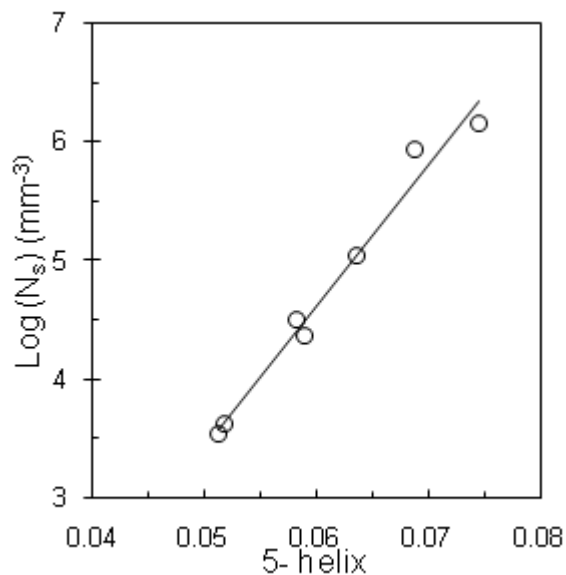

Fig. 7: Relationship between the saturated nucleation density (N_s) and the amount of 3_1 helix composed of 5 monomer units.

The temperature dependence of the absorption intensity of 5-helix seems to be proportional to the saturated nucleation density (N_s). Therefore, log of N_s is plotted against the 5-helix, yielding a good linear relationship as shown in figure 7. This relationship indicates that the saturated nucleation density is a function of the amount of 5-helix remaining in the melt. The structure of the 5-helix might be described as irregular helices without regular packing. However, the helices are distributed randomly in length and distance among their segments. The nearest-neighbor segments to the cluster will give rise to primary nucleation sites in the melt.

IV. Conclusions

In situ FTIR measurements were carried out on iPS to study the conformational changes during the crystallization from melt, especially in the course of the later stage of the induction period where the enhancement of the helix regularity and the packing of the helix moiety occur. These observations suggested that the ordered structure in the later stage of the induction period could be regarded as a sort of 3_1 helix with a little regular packing. Melt temperature dependence helix data indicates an increase of the melt temperature destroyed the longer helices in the crystal but the shorter helices can survive and form a cluster in the melt that can initiated as a primary nucleation site. The nucleation density was found as a linear function of the amount of 3_1 helix composed with 5 monomeric units.

Acknowledgment

References

[1]. E. Ergoz, J.G. Fatou, L. Mandelkern, "Molecular Weight Dependence of the Crystallization Kinetics of Linear Polyethylene. I. Experimental Results", Macromolecules, vol. 5, no. 2, pp. 147-157, 1972.

[2]. M. Kobayashi, K. Tsumura, H. Tadokoro, "Infrared spectra of polymer solutions. I. Conformational stability of isotactic polymer chains in solution", Journal of Polymer Science Part A-2: Polymer Physics, vol. 6, no. 8, pp. 1493-1508, 1968.

[3]. M. Kobayashi, T. Nakaoki, N. Ishihara, "Molecular conformation in glasses and gels of syndiotactic and isotactic polystyrenes", Macromolecules, vol. 23, no. 1, pp. 78-83, 1990.

[4]. P. Supaphol, J.E. Spruiell, "Crystalline memory effects in isothermal crystallization of syndiotactic polypropylene", J. Appl. Polym. Sci., vol. 75, no. 3, pp. 337-346, 2000.

[5]. J.H. Reinshagen, R.W. Dunlap, "The effect of melt history, pressure, and crystallization temperature on spherulite size in bulk isotactic polypropylene", Journal of Applied Polymer Science, vol. 17, no. 12, pp. 3619-3625, 1973.

[6]. G.C. Alfonso, A. Ziabicki, "Memory effects in isothermal crystallization II. Isotactic polypropylene", Colloid & Polymer Science, vol. 273, no. 4, pp. 317-323, 1995.

[7]. J. Zhang, Y. Duan, H. Sato, D. Shen, S. Yan, I. Noda, Y. Ozaki, "Initial Crystallization Mechanism of Isotactic Polystyrene from Different States", The Journal of Physical Chemistry B, vol. 109, no. 12, pp. 5586-5591, 2005.

[8]. H. Xu, B.S. Ince, P. Cebe, "Development of the crystallinity and rigid amorphous fraction in cold-crystallized isotactic polystyrene", Journal of Polymer Science Part B: Polymer Physics, vol. 41, no. 23, pp. 3026-3036, 2003.

[9]. M. Kobayashi, K. Akita, H. Tadokoro, "Infrared spectra and regular sequence lengths in isotactic polymer chains", Die Makromolekulare Chemie, vol. 118, no. 1, pp. 324-342, 1968.

[10]. T. Kimura, H. Ezure, S. Tanaka, E. Ito, "In situ FTIR spectroscopic study on crystallization process of isotactic polystyrene", Journal of Polymer Science Part B: Polymer Physics, vol. 36, no. 7, pp. 1227-1233, 1998.

[11]. J.D.W. Hoffman, J. J. , J. Res. Natl. Bur. Stand. , vol. A66, pp. 13, 1962.

[12]. T. Liu, "Melting behavior of isotactic polystyrene revealed by differential scanning calorimetry and transmission electron microscopy", European Polymer Journal, vol. 39, no. 7, pp. 1311-1317, 2003.

[13]. J. Zhang, Y. Duan, D. Shen, S. Yan, I. Noda, Y. Ozaki, "Structure Changes during the Induction Period of Cold Crystallization of Isotactic Polystyrene Investigated by Infrared and Two-Dimensional Infrared Correlation Spectroscopy", Macromolecules, vol. 37, no. 9, pp. 3292-3298, 2004.