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Surface Chain Orientation during Crystallization Induction Period of Poly(pentamethylene 2,6-naphthalate) Studied with Polarized FTIR-ATR

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ABSTRACT: Thermoinduced surface orientation behaviors were studied in situ by Fourier transform infrared spectroscopic (FTIR) measurements along with attenuated total reflection (ATR) and transmission methods during the cold crystallization of melt-quenched amorphous poly(pentamethylene 2,6-naphthalate) (PPN) film. The chain in the crystalline phase formed during the cold crystallization process was found to orient parallel with the film surface with a naphthalene ring perpendicular to the film plane. By observing the isothermal crystallization process via polarizing optical microscopy and wide-angle X-ray diffraction methods, it was revealed that PPN shows very slow crystallization kinetics, even when crystallized at the temperature associated with the fastest crystallization rate. Furthermore, the crystallization induction period was longer than 150 min, during which time a significant amount of crystalline phase was not to be formed. The chain orientation at the surface during the crystallization induction period was again measured via polarized FTIR-ATR spectroscopy. It was found that the preferential surface orientation occurs during the early stage of the induction period, and no further orientation was observed during the subsequent crystallization process. Rapid local ordering that occurred during the crystallization induction period, especially at the surface, appears to be followed by gradual packing of the locally ordered chain to form the crystalline phase.

Introduction

Many studies have been carried out to analyze the structural formation process of semicrystalline polymers during the crystallization period. Notably, the chain conformation change and local packing process during the induction period before the start of the major crystallization process have been the focus of a number of studies.[1−5] By monitoring structural changes during the melt spinning process of various semicrystalline polymers including polyethylene, Katayama et al. observed crystalline reflection, tilting of the *c*-axis, and sudden change of birefringence during the initial stage of the crystallization.[6] Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) have served as convenient tools to analyze the density fluctuation and formation of crystalline structures during the induction period of crystallization.[7,8−11] In a number of studies on the crystallization of unoriented poly(ethylene terephthalate) from the glassy state, Imai et al. observed the formation of a long-range ordered structure with a size of 20 nm during the induction period of crystallization. Long-range ordered structure was ascribed to spinodal decomposition, causing segregation of a rodlike conformation from more random chain conformation.[12] The existence of a transient stage prior to the onset of crystallization has also been reported in relation to the crystallization of PEN.[13]

Chain conformation change and orientation fluctuation during the crystallization induction period of semicrystalline polymers have mainly been studied with Fourier transform infrared (FTIR) spectroscopy.[14,15] From in-situ observations of the absorbance change of the conformation-sensitive peaks as well as the crystalline peak during isothermal crystallization of poly(bisphenol A-*co*-decane ether), Jiang et al. clearly demonstrated that the conformation change of the polymer chain preceded initiation of the crystallization process.[14] Using time-resolved FTIR and depolarized light scattering (DPLS) techniques, Matsuba et al. quantitatively investigated the conformation change of syndiotactic polystyrene during the induction period when crystallized from the glassy state.[15] The absorbance of trans conformation bands was found to increase not only during the induction period but also after crystallization, and this was ascribed to the extension of rodlike segments consisting of trans sequences. The increase of the excluded volume of the rodlike segments might make the system unstable, thus triggering the orientation fluctuation, i.e., local parallel ordering of chain segments, as directly confirmed from DPLS measurements.

Polarized Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy has been used in a number of our previous works to observe three-dimensional orientation change of various segments constituting the polymer chain, especially at the surface of the polymer film.[16−18] FTIR-ATR spectroscopy utilizes the total internal reflection of the propagating infrared radiation occurring at the interface between the optically denser medium (ATR crystal) and optically rarer medium (sample), when the angle of incidence exceeds the critical angle.[19] Upon reflection at the interface, the evanescent wave, the field strength of which decays exponentially inside the optically rare medium, might be absorbed selectively by the sample. One of the most important aspects of the FTIR-ATR method is that the electric field of the evanescent wave exists in all three spatial directions in the rarer medium. Therefore, orientation information not only within the film plane but also along the thickness direction can be obtained via this method.[16,17]

In this article, surface chain orientation of a poly(pentamethylene 2,6-naphthalate) (PPN) film during the induction period of crystallization is reported. Chain orientation at the

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surface is mainly studied using temperature-controlled, time-resolved FTIR-ATR spectroscopy during isothermal crystallization from the glassy state. The crystallization rate of PPN, an aromatic polyester derived from aliphatic diols and aromatic diacids, is very slow, making this material a suitable sample to study the surface orientation change during the induction period of crystallization.[20]

Experimental Section

Sample. The PPN sample studied in this work showed an intrinsic viscosity of 0.67 dL/g measured in a mixed solvent of 1,1,2,2-tetrachloroethane and phenol (1/1, w/w) at 25. In order to fabricate the melt-quenched amorphous film for the FTIR-ATR measurement, PPN chips were pressed at 160 °C ($T_m = 135$ °C) for 3 min with a melt-presser, followed by quenching in ice water. The thickness of the film was about 300 μm. For the FTIR transmission measurement, PPN solution (0.5 wt % in 1,1,1,3,3,3-hexafluoro-2-propanol) was cast on KBr or AgCl windows. The sample was initially dried at room temperature and further dried in a vacuum oven at 100 for about 10 h for complete evaporation of the solvent. The film on the AgCl disk was then heated again to 160 °C, followed by quenching in ice water to ensure an amorphous state. Film thickness for the FTIR transmission measurement was about 1 μm.

Measurement. FTIR-ATR spectra were obtained with an ATR setup developed initially by Sung and co-workers[21,22] that consists of a symmetrically double-edged parallelogram crystal and a rotatable sample holder. The ATR crystal was made of GaAs, and the incident angle at the interface between the ATR crystal and sample was set to 45°. All spectra (2 cm^{-1} resolution and 32 scans were averaged) were obtained using a Bruker IFS 66V/S FTIR spectroscope equipped with a DTGS detector. Polarization of infrared radiation was achieved by inserting a wire-grid polarizer (KRS-5, Harrick Corp.) between the ATR setup and detector. The structure change that occurred during the crystallization process was studied directly while the sample was being heated inside the temperature-controlled polarized FTIR-ATR setup.

Time-resolved polarizing optical microscopy (POM, Nikon, Optiphot2-pol) measurements were carried out during the isothermal crystallization process at a specific crystallization temperature (80−120 °C). The temperature of the sample was controlled with a hot stage (Mettler FP82HT), and the transmitted light intensity through the cross-polar could be recorded as a function of crystallization time. WAXD data were obtained using a 2D CCD detector at the 4C2 Beamline of the PAL (Pohang Accelerator Laboratory, Korea).[23] The wavelength of the incident X-ray was 1.54 Å. The crystallinity of PPN was calculated from the ratio of the crystalline peak area to the total peak area.

Results and Discussion

Figure 1 shows two polarized FTIR-ATR spectra of melt-quenched amorphous PPN film obtained at room temperature using two different polarizer directions (TM, TE mode). For TM mode spectra, the electric field direction of the incident infrared was set to be in the plane of incidence. For TE mode spectra, the electric field direction was set to be parallel with the interface between the ATR crystal and the polymer film.[17] As can be confirmed from the spectra in Figure 1, absorbance of the peaks in the TM spectrum is always higher than that in TE spectrum. In general, the absorbance of any infrared peak in the TM spectrum (A_{TM}) is twice that in the TE spectrum (A_{TE}), provided that the sample is in an isotropic state and the contact between the sample and ATR crystal is optically perfect.[19] The exact quantitative value of the absorbance ratio (A_{TM}/A_{TE}) can therefore be used to estimate the orientation of various chain segments at the surface.

In this work, a number of infrared peaks, the direction of the transition dipole moment and band assignment of which are listed in Table 1, are used to analyze the chain orientation during the crystallization process. In order to observe the chain orientation at the surface during crystallization and melting, the temperature of the melt-quenched amorphous PPN film was increased gradually with the temperature-controlled FTIR-ATR setup while the polarized ATR spectra were obtained. Using the collected ATR spectra, the absorbance ratio of three bands were calculated and are shown in Figure 2 as a function of temperature. At room temperature, the absorbance ratio of three bands is somewhere between 1.8 and 1.9, very close to the theoretical value of 2 for the isotropic state with an ideal optical contact between the ATR crystal and sample. Upon an initial increase of the temperature, the absorbance ratio shows a very slow increase up to about 80 °C, at which point the ratio shows a sudden deviation from the previous gradual, linear change. The absorbance ratio of the 1712 cm^{-1} band, of which the transition dipole moment is perpendicular to the main-chain direction, showed a positive deviation. However, the ratio of the 1602 and 1130 cm^{-1} bands, of which the transition dipole moment directions are parallel with the chain direction, displayed an opposite trend. This characteristic change of the absorbance ratio is a direct indication of the transition from an isotropic state to an anisotropic state at the film surface upon

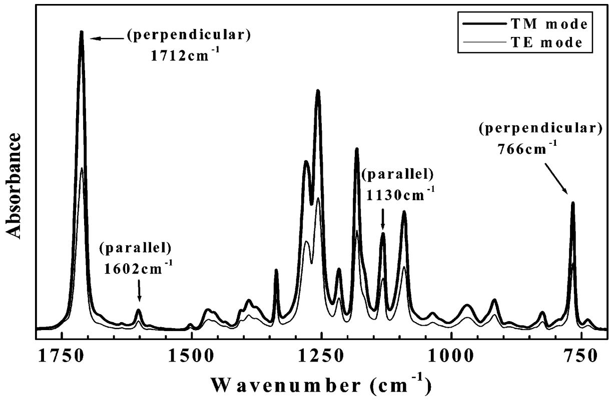

Figure 1. FTIR-ATR spectra (TM, TE mode) of melt-quenched amorphous PPN at room temperature obtained with two polarizer directions.

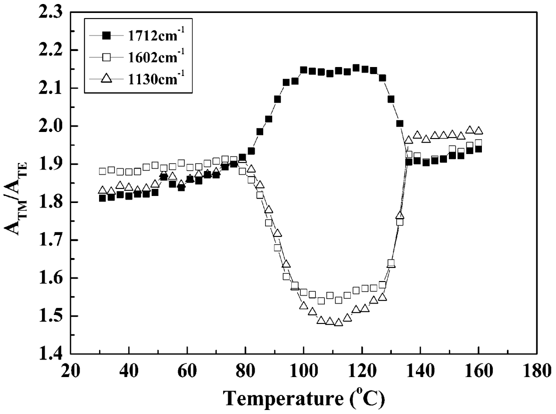

Figure 2. ATR absorbance ratio of selected bands of PPN film as a function of temperature.

Table 1. Transition Dipole Moment Direction and Vibrational Assignment of Selected Absorption Bands of PPN

wavenumber (cm^{-1})	transition dipole moment direction	assignment
1712	perpendicular	ester group C═O stretching
1602	parallel	ring C═C stretching
1130	parallel	ring C−H in-plane bending
766	perpendicular	ring C−H out-of-plane bending

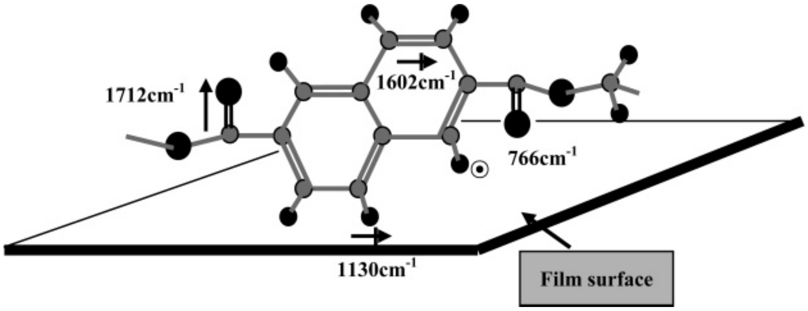

Figure 3. A schematic model showing the chain orientation at the surface upon the onset of cold crystallization of melt-quenched amorphous PPN film.

onset of cold crystallization. The absorbance change appears to persist until the temperature reaches ∼100 °C. Further increase of temperature to about 130 °C does not change the absorbance ratio significantly. Three absorbance values having very different values again merged to a similar value of about 1.9 when the sample was heated above the melting temperature of about 135 °C. The merging of three absorbance ratios is again due to the transition from anisotropic orientation to isotropic orientation upon melting, especially at the film surface.

The change of the absorbance ratio of three peaks upon the initiation of cold crystallization can be interpreted in terms of the preferential orientation of the polymer chains as well as of the aromatic rings in the chain, especially at the film surface, as shown schematically in Figure 3. The transition dipole moment directions of several vibration bands of the oriented chain are also included in the figure. It is noted that for the oriented chain in Figure 3 bands at 766 and 1712 cm^{-1} among four bands used extensively in this work have a transition dipole moment component perpendicular to the film surface. Increase of the 1712 cm^{-1} absorbance and decrease of the 1602 and 1130 cm^{-1} absorbance upon cold crystallization can be explained by the in-plane orientation of the chain with its ring perpendicular to the film surface. The infrared radiation passing through the GaAs ATR crystal used in this work shows a very low intensity at about 767.5 cm^{-1} wavenumber, and its intensity becomes negligible at the elevated temperature. The aromatic ring orientation at the surface could not be, therefore, deduced from the 776 cm^{-1} band in the case of ATR measurement using GaAs crystal. Since the aromatic ring was found to be coplanar with the carbonyl group in the crystal of PPN,[14] the aromatic ring orientation might be deduced from the 1712 cm^{-1} band orientation without any serious experimental uncertainty.

Preferential chain orientation in the cold crystallized film at the film surface has been reported in previous works for aromatic polyesters based on naphthalene rings.[24,18] Upon cold crystallization of poly(ethylene naphthalate) and poly(trimethylene naphthalate), the naphthalene rings in polymer chains in the crystalline phase were found to be flat in the film plane, especially at the surface. A precise explanation for the perpendicular orientation of the aromatic rings in the cold crystallized PPN is not yet available, and more studies have to be carried out to further clarify the factors determining the chain orientation at the film surface.

In order to estimate the temperature dependence of the crystallization rate, POM measurements have been made at various crystallization temperatures during the isothermal cold crystallization process. The temperature of the melt-quenched amorphous sample was raised quickly to a specific crystallization temperature using a microscope hot stage. The intensity of the light transmitting the cross-polar was then recorded as a function of time, and the results are shown in Figure 4. Also shown in Figure 4 is the relative crystallization rate ($1/T_{1/2}$) obtained from the time to reach the half of the maximum intensity ($T_{1/2}$). The maximum intensity could be reached after about 1200 min (20 h) crystallization time for three temperatures (90, 100, 110 °C) at which crystallization occurred at a relatively higher rate. Since the transmitted light intensity did not reach the saturated value even after 1400 min of crystallization time for the crystallization at two remaining temperatures (80, 120 °C), the $1/T_{1/2}$ value was estimated from the extrapolated intensity value. For all the crystallization temperatures considered in this work, an increase in the transmitted light intensity due to the onset of crystallization could not be detected during the initial 150 min of crystallization time. These results indicate that the PPN sample shows very slow crystallization kinetics, and thus it could serve as an ideal material to study the structural changes occurring during the crystallization induction period. Furthermore, PPN undergoes the fastest crystallization at temperatures near 100 °C.

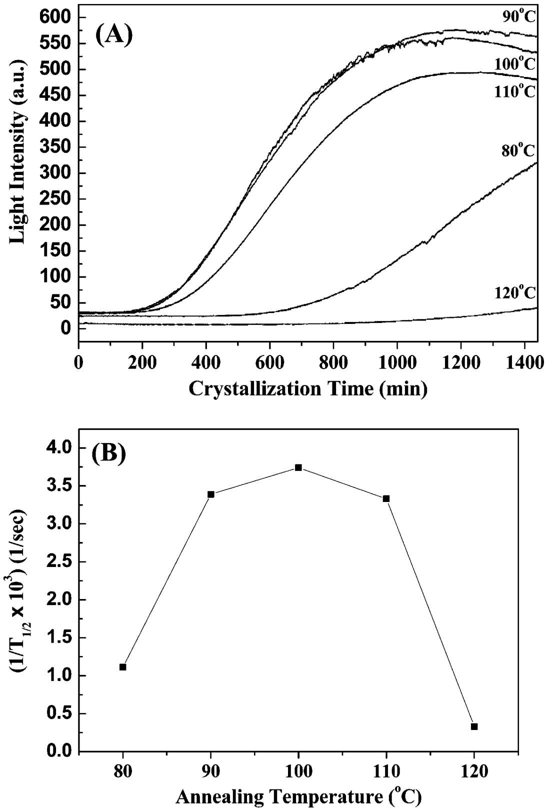

Figure 4. (A) Light intensity transmitting the cross-polar POM during the isothermal crystallization of PPN and (B) inverse of the time to reach the half of the maximum light intensity at various crytallization temperatures.

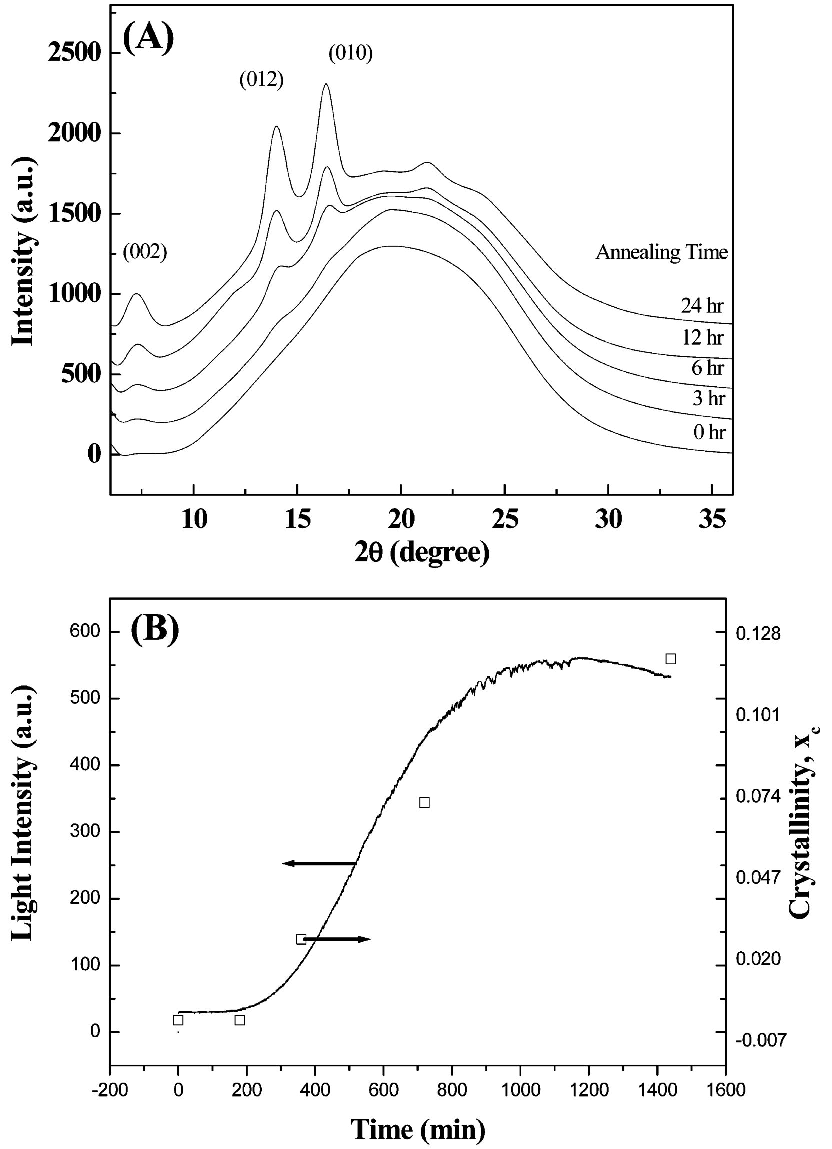

Figure 5. (A) WAXD profiles of PPN annealed at 100 °C for various times (0, 3, 6, 12, 24 h) and (B) crystallinity based on crystalline diffraction peak area. The transmitted light intensity through the cross-polar POM is also included for comparison.

The observation that PPN undergoes an extremely slow crystallization process has also been confirmed with WAXD measurements. WAXD profiles of various PPN samples isothermally crystallized at 100 °C for different periods of crystallization time were obtained and are shown in Figure 5A. In general, the crystalline diffraction peak area increases with increased annealing time. The crystallinity value estimated from the relative diffraction peak area of the crystalline phase with respect to the total peak area is shown in Figure 5B with the right ordinate. The transmitted light intensity data obtained with POM at 100 °C are also included for comparison. WAXD results show that the degree of crystallinity of the PPN sample annealed at 100 °C for 3 h is almost unnoticeable. In addition, it takes at least 1200 min to reach the equilibrium crystallinity, even at the temperature at which the crystallization process occurs at the fastest rate. On the basis of the results presented in Figures 4 and 5, it can be concluded that the crystallization process occurring during the induction period (initial 150 min, for example) is not significant, and the formation of most of the crystalline phase, which can be detected either with cross-polar POM or the WAXD method, occurs after at least 150 min of crystallization time.

Previous results indicate that the formation of crystalline phase by packing of localized extended chains takes a very long time for the sample studied in this work. However, this does not exclude the possibility of chain movement and localized orientation of the partially extended chains, especially during the crystallization induction period. It is not clear when the surface orientation due to the cold crystallization observed in Figure 2 is induced during the crystallization process. To further elucidate the exact timing for the chain orientation change during the cold crystallization process, the cold crystallization process was studied during the isothermal crystallization process. The melt-quenched amorphous PPN sample was quickly heated to a specific isothermal crystallization temperature (100 °C, for example), and the TM and TE spectra were collected successively by changing the polarizer direction. The absorbance ratio (A_{TM}/A_{TE}) of three infrared peaks were again calculated and are shown in Figure 6 as a function of crystallization time at 100 °C. Upon completion of 300 min isothermal crystallization, the temperature of the sample was then increased. The absorbance ratio (A_{TM}/A_{TE}) during the subsequent heating process is also included in Figure 6.

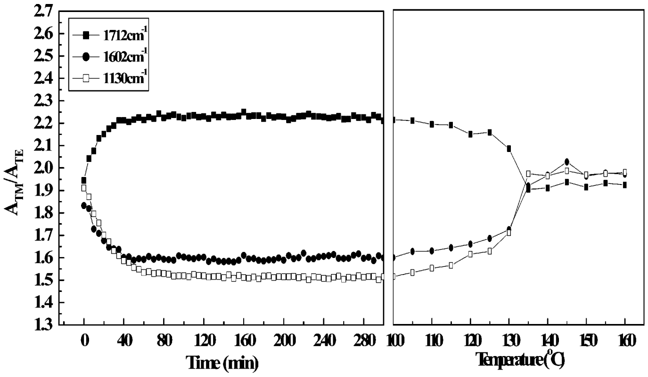

Figure 6. A_{TM}/A_{TE} absorbance ratio of selected bands (left side) during isothermal crystallization as a function of time and (right side) during the subsequent heating process as a function of temperature.

Upon heating the amorphous melt-quenched PPN film to 100 °C, the absorbance ratio (A_{TM}/A_{TE}) of all three peaks shows a value of ~1.9, which is again close to the theoretical value of 2 for an ideal isotropic contact sample. As the isothermal crystallization proceeded, the absorbance ratio of the 1712 cm^{-1} band showed a positive change while the ratios of the 1602 and 1130 cm^{-1} bands showed opposite trends. This increase and decrease of the absorbance ratios of the three bands corresponds closely with the results presented in Figure 2. As shown schematically in Figure 3, this change can also be explained in terms of the preferential orientation of the polymer chain at the film surface upon the start of the crystallization process. The anisotropic orientation of the crystallized PPN could be also confirmed upon subsequent heating of the isothermally crystallized sample. As shown in the right side of Figure 6, the absorbance ratios of the three peaks merge to a similar value of ~1.9 as the temperature of the sample approaches the melting temperature of PPN.

Interestingly, for all three peaks in Figure 6, the sudden change of the absorbance ratio appears to be completed within the first 100 min of crystallization, and no further change of that ratio could be observed during the continued crystallization process up to 300 min. Recalling the results in Figures 4 and 5, the degree of crystallinity developed during the initial 100 min was negligible. Most of the changes due to the development of the major crystalline phase observed with POM and WAXD measurements occurred after at least 200 min of crystallization, even at 100 °C where the fastest crystallization rate was observed. The sudden change of the absorbance ratio of the three bands at the start of isothermal crystallization, as shown in Figure 6, could therefore be related with the preferential chain orientation occurring at the surface during the crystallization induction period. During the early stage of the crystallization induction period, a certain fraction of the chains appears to quickly move to a preferred orientation, especially at the surface. The major crystallization process might proceed through gradual packing of locally oriented chains and does not induce any further orientation change at the film surface.

For the FTIR-ATR measurement, the sample surface has to be pressed against the ATR crystals in order to maintain good optical contact between them. Therefore, the chain orientation measured with the ATR setup at the polymer surface, which is in direct contact with the ATR crystal, might be different from the corresponding orientation at the surface exposed to air. In order to eliminate the effect of contact between the ATR crystal and sample on the surface orientation, FTIR transmission measurements were made again during the isothermal crystallization process. The temperature of the melt-quenched amorphous PPN film on the KBr disk was quickly raised to a specific crystallization temperature, and FTIR transmission spectra were collected as a function of isothermal crystallization time. The absorbance of three infrared bands is shown in Figure 7 as a function of annealing time. The absorbance values are shifted vertically for clarity. Even though the absolute magnitude of the absorbance changes less than 5%, it is clear that there is a sudden change in the absorbance value during the early stage of the crystallization induction period. This change could only be observed within the first 100 min of crystallization, and no further significant change could be measured during the subsequent crystallization process. This result is quite consistent with the ATR result shown in Figure 6. A certain fraction of the chains at the film surface that is in contact with either the ATR crystal or air changes its orientation from an isotropic state to an anisotropic state during the early stage of the crystallization induction period.

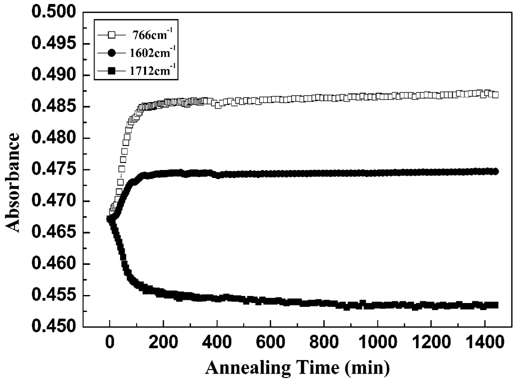

Figure 7. Absorbance of selected infrared bands of PPN from FTIR transmission spectra during isothermal cold crystallization of melt-quenched amorphous film cast on KBR window as a function of annealing time.

It is noted that for the transmission FTIR measurement the electric field component of the incident infrared radiation is in the film plane. Orientation of the transition dipole moment in the film plane, therefore, will show increased absorbance, whereas the moment along the thickness direction will be accompanied by decreased absorbance. The increase of absorbance of the 766 and 1602 cm^{-1} bands and the decrease of the 1712 cm^{-1} band during the early stage of the induction period can therefore be understood in terms of the anisotropic orientation of the chain at the surface, as shown in Figure 3. This FTIR transmission result also supports that some fraction of PPN chains align parallel to the sample surface with their naphthalene ring perpendicular to the film plane during the early stage of the induction period.

According to a theory by Doi et al.,[25] the isotropic-to-nematic transition, i.e., the parallel ordering of rod molecules, is triggered by extension of the rods when their length exceeds a critical value. The conformational changes of the polymer chains to a more rodlike conformation might take place before the start of the major crystallization process, as observed from a study on the isothermal crystallization behavior of poly(bisphenol A-*co*-decane ether).[14] Bands at 1470 and 1456 cm^{-1} wavenumber might be associated with CH_2 bending vibration of the trans and gauche conformers in the PPN chains.[26] The intensities of these bands, however, did not show any appreciable change during the crystallization process in this work.

Conclusions

In this study, we have shown that a preferential chain orientation might be induced at the film surface upon cold crystallization of a melt-quenched amorphous PPN sample. The main chain appears to be flat at the surface with its naphthalene ring perpendicular to the surface to form a preferential surface orientation. This type of perpendicular ring orientation at the surface has not been observed in previous studies on naphthalene-based polyesters having two or three methylene units, where the naphthalene rings were found to orient flat upon cold crystallization at the film surface.[18,24] More studies should be carried out in order to elucidate the exact reason determining the ring orientation at the surface upon cold crystallization of aromatic polyesters.

POM and WAXD results showed that PPN undergoes a very slow crystallization process, and there is a long crystallization induction period even when crystallized at the temperature associated with the fastest crystallization rate. Polarized FTIR-ATR studies during isothermal cold crystallization of PPN revealed that the preferential chain orientation at the film surface occurred during the early stage of the crystallization induction period. After the induction period, no significant orientation change at the surface was observed during the subsequent crystallization process during which most of the crystalline phase is formed. The surface orientation induced during the early stage of the induction period was confirmed again with FTIR transmission measurements, where one side of the film was exposed to air. During the cold crystallization of melt-quenched amorphous PPN, a local chain orientation appears to occur during the early stage of the crystallization induction period, especially at the film surface, and gradual packing of the ordered chains appears to proceed during the remaining crystallization process. No additional preferential surface orientation was observed during the formation of most of the crystalline phase of PPN.

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