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Conformational changes in the induction period of crystallization as measured by FT-IR

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Abstract

The isothermal crystallization behaviors of poly(bisphenol A-*co*-decane ether) (BA-C10) at different temperatures were studied in situ by means of Fourier transform infrared spectroscopic (FT-IR) measurements. Conformational changes during the induction period were investigated in details. The results suggest that conformational changes of polymer chains always take place before the start of changes in the characteristic FT-IR peaks of the crystalline phase.

Keywords: Induction time; Fourier transform infrared spectroscopy; Conformational change

1. Introduction

Many studies of semi-crystalline polymers have been focused on morphological and structural changes, such as primary nucleation and lamellar growth behaviors [1–4]. The structural formation during the induction period before the start of primary nucleation is of considerable interest to researchers. Recently, experimental results of semi-crystalline polymers obtained by simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) have revealed that the long-period peak emerges in the SAXS spectra before the crystalline peaks appear in the WAXS spectra. Katayama et al., first observed this phenomenon in the study of crystallization of an oriented polypropylene melt [5]. Later, other researchers observed the same phenomenon in other semi-crystalline polymers [3, 6–9]. Olmsted et al. [10], showed that such a phenomenon could occur even in the crystallization of quiescent melts. They postulated that the coupling between density and chain conformation could induce a liquid–liquid binodal within the equilibrium liquid-crystalline solid coexistence region. Moreover, the shearing of polymer melts can enhance the kinetic role of the hidden binodal. Matsuba et al. [11,12] found that during the crystallization of poly(ethylene naphthalene), a SAXS peak at 0.03 $\mathring{A}^{-1}$ had emerged and grew with time before the primary nucleation occurred. Using time-resolved Fourier transform infrared (FT-IR) spectroscopy and time-resolved depolarized light scattering (DPLS) measurements, they found that the absorbencies of the trans conformation bands and the orientation fluctuations increased exponentially with time in the induction period. Similar observations on other semi-crystalline polymers have also been reported by other researchers [13–20].

The crystallization rate of poly(bisphenol A-*co*-alkyl ether) (BA-Cn) is very slow, making this polymer an ideal subject of study by in situ atomic force microscopy (AFM) and FT-IR measurements [21–24]. The functional groups, such as the phenyl ring, the carboxyl group and the flexible alkyl segments of the BA-Cn polymers, give characteristic peaks in FT-IR spectra, making it easy to analyze the structural changes during crystallization. The crystallization behaviors of the BA-C10 have been studied by AFM and FT-IR measurements [24]. Our previous results suggest that the crystallization process involves both the intramolecular movements and intermolecular packing of the polymer chains. The coplanarity of a chain segment and the

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regularity of chain packing are reflected in the change in the intensity of characteristic FT-IR peaks.

In this study, the conformational changes during the induction period of crystallization were studied at different temperatures using FT-IR. The characteristic changes of the FT-IR peaks and their relationship with crystallization temperature were discussed in detail.

2. Experimental section

Poly(bisphenol A-*co*-decane ether) (BA-C10) was synthesized as described previously [21–24]. The glass transition temperature, melting point, weight-average molecular weight, and polydispersity index were measured to be approximately 10.5 °C, 95 °C, 29,500 g/mol, and 2.6, respectively.

The thermal behavior of BA-C10 was investigated using a differential scanning calorimeter (Perkin–Elmer DSC-4) under nitrogen purge. Temperature calibration was performed with an indium standard. The sample was first heated to 120 °C (about 35 °C above the melting point) under N_2 protection for 10 min to completely melt the polymer crystals. Then, it was quenched to a chosen isothermal crystallization temperature. The heat of crystallization as a function of time was also measured.

In situ FT-IR measurements were performed using a Bruker Equinox-55 FT-IR spectrometer equipped with a Specac variable temperature cell. To prevent moisture from condensing on the sample at low temperatures, the sample cell was kept under vacuum during measurement. In order to measure the instantaneous spectral changes, a liquid nitrogen-cooled MCT detector with a resolution of 4 cm^{-1} was used. A total of 32 scans were taken and the scanning was repeated every 180 s. The peak heights were measured using the OPUS software N method. A small amount of a 4 wt% BA-C10 chloroform solution was cast on a KBr plate. After the solvent evaporated, the plate was heated to 120 °C for 10 min to melt the polymer, which was then quenched to the required isothermal crystallization temperature.

3. Results and discussion

Fig. 1(a) shows the crystallization isotherm $\phi(t)$ at 65 °C as a function of annealing time t of a quenched BA-C10 sample. It can be seen that during the first 25 min, which is referred to as the induction time, neither exotherm nor endotherm is observed. The crystallization half time is about 87 min, suggesting that it takes quite a long time for the crystallization to complete. The crystallization half time at 55, 60, and 70 °C was also determined using DSC and the results are shown in Fig. 1(b). The maximum crystallization rate occurs at 65 °C.

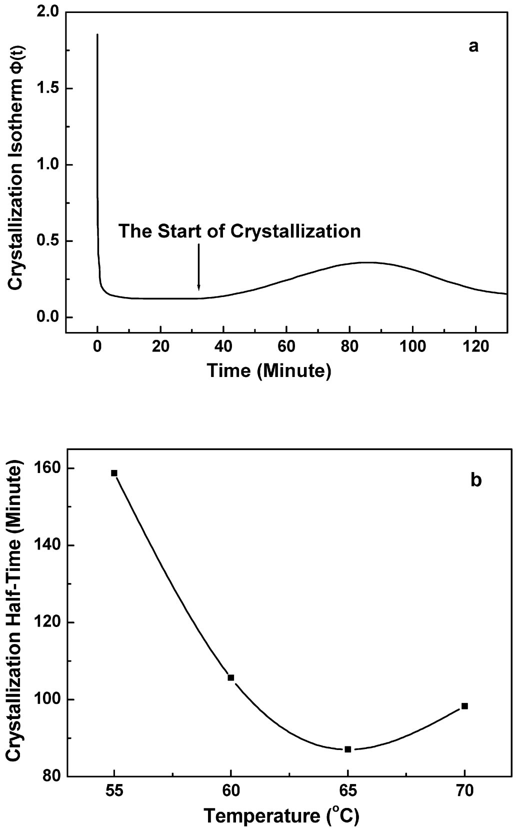

Fig. 1. (a) Crystallization isotherm at 65 °C for BA-C10 polymer after being quenched from the melt. (b) The crystallization half time as a function of crystallization temperature.

Fig. 2(a) and (b) show the in situ FT-IR spectra and the difference spectra, respectively, obtained during the isothermal crystallization at 35 °C of a BA-C10 sample, which was quenched from the melt. From our previous results [24], the bands in the region of 700–1100 cm^{-1} represent the distinctive conformational changes during crystallization. The peak at 763 cm^{-1} is newly generated during crystallization, as shown in Fig. 2(a). It is assigned to the CH_2 rocking vibration of the alkyl segments and the change of its intensity indicates the regular packing of the folded chain into crystal lattice due to the intermolecular interaction. Thus, this peak is called a characteristic crystalline peak. The characteristic peaks at 1020 and 1045 cm^{-1} are attributed to the C–O stretch vibration of the alkane groups. Their intensity increases evidently as crystallization progresses. It is suggested that polymer chains have to change their conformation in order to stack orderly in lamellar crystals. The C–O stretch vibrations are related to intramolecular conformational changes. The peak at 834 cm^{-1} is the diagnostic vibration of the 1,4-substitute benzene ring. The difference spectra at 834 cm^{-1} have sharp maximums and minimums, suggesting that the band shifts to a higher wave number during crystallization.

Fig. 3 shows the change in the intensity of the peaks at 763, 834, 1020 and 1045 cm^{-1} as a function of crystallization time. The intensity of each peak was normalized to its maximum value that was measured after the crystal-

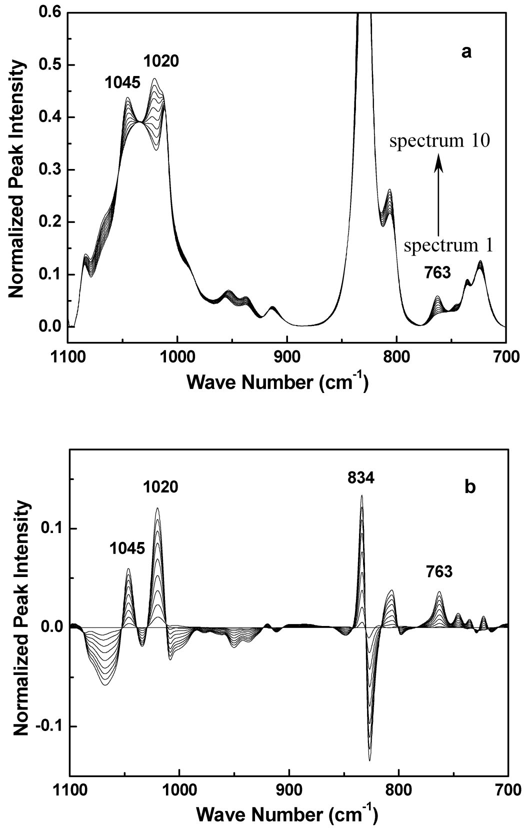

Fig. 2. (a) In situ FT-IR measurements for isothermal crystallization at 35 °C in the region of 700–1100 cm^{-1}. The spectrum from 1 to 10 was obtained at 0, 147, 219, 280, 322, 370, 418, 466, 532 and 898 min, respectively. (b) Difference spectra of (a) obtained by subtraction of the initial spectrum.

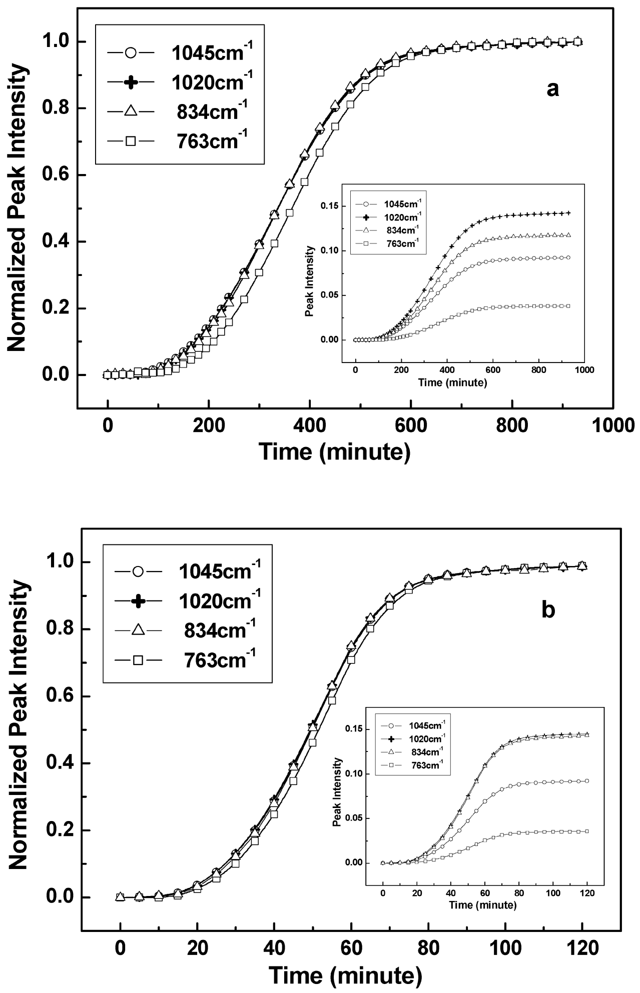

Fig. 3. The normalized peak intensity at 763, 834, 1020, and 1045 cm^{-1} as a function of crystallization time at (a) 35 °C and (b) 65 °C.

lization was completed. The peak at 2845 cm^{-1} was chosen as the internal reference to eliminate the influence of the film thickness. It can clearly be seen that the intensity of the characteristic peaks at 763, 834, 1020 and 1045 cm^{-1} increases significantly during the isothermal crystallization process. The same trend is observed at different temperatures, as shown in Fig. 3(a) and (b). During the induction period, no change in the intensity of these peaks is observed. However, once crystallization starts, the intensity of these peaks increases dramatically until the crystallization completes. It is of interest to note that the increase in the intensity of the peak at 763 cm^{-1} shows a time lag compared with that of the peaks at 834, 1020 and 1045 cm^{-1}. Here, we define this time lag as the retardation time of crystallization. The retardation time, $\Delta t = t_{763} - t_{1045}$, is the time lag between the emergence of the crystalline peak at 763 cm^{-1} and the conformational peak at 1045 cm^{-1}, as shown in Figs. 4(b) and 5(b). It has been suggested that during the crystallization of BA-C10 the intermolecular packing of the polymer chains leads to the increase in the intensity of the CH_2 rocking vibration of the alkane at 763 cm^{-1}. Moreover, the intramolecular conformational changes of a polymer chain contribute greatly to the intensity change of the correlative functional groups such as the C–O stretch vibration of the alkane groups at 1045 and 1020 cm^{-1} and the diagnostic vibration of the 1,4-substitute benzene ring at 834 cm^{-1}. Thus, the retardation time reveals that the intramolecular conformational changes occur some time before the start of intermolecular packing process.

The presence of the retardation time can be more clearly illustrated using the changes of the IR spectra in the induction period, as shown in Fig. 4. Fig. 4(a) shows the difference spectra obtained at 35 °C during the induction period and Fig. 4(b) shows the intensity variations of the peaks at 763, 1020, and 1045 cm^{-1} as a function of annealing time. The peak at 763 cm^{-1}, the characteristic crystalline peak, appears 100 ± 6 min after annealing. However, the peaks at 834, 1020 and 1045 cm^{-1}, the characteristic conformational peaks, appear 50 ± 6 min after annealing or even earlier, as shown in Fig. 4. These results confirm that the conformational changes occur about 50 min before the appearance of the crystalline peak. The functional groups of a polymer chain have to adjust their conformations first in order to enter the crystal lattice. This

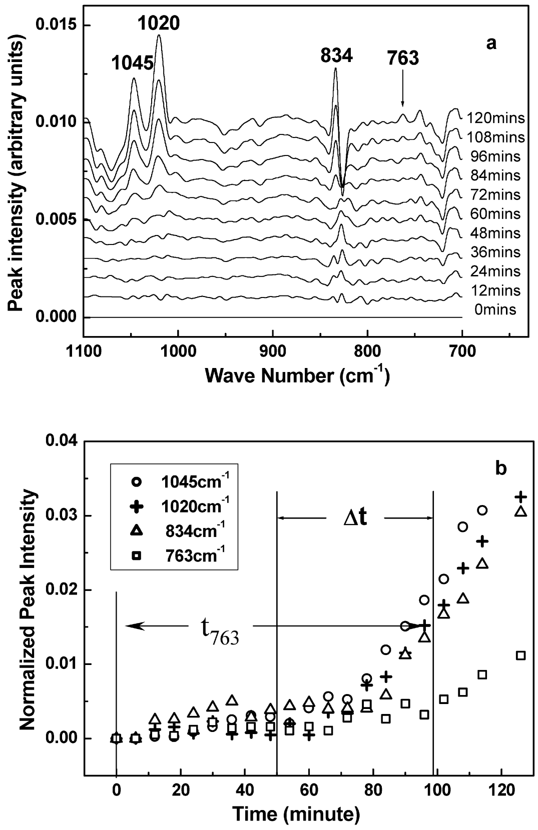

Fig. 4. (a) Difference spectra obtained at 35 °C. (b) The intensity of the peak in (a) as a function of time.

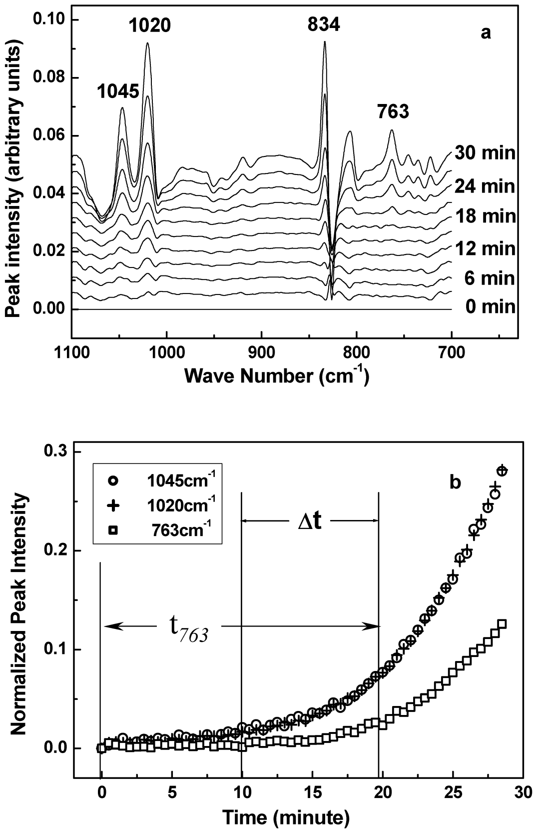

Fig. 5. (a) Difference spectra obtained at 65 °C. (b) The intensity of the peak in (a) as a function of time.

phenomenon has also been observed in polymers such as poly(ethylene terephathlate) [6], isotactic polystyrene [7], polypropylene [9], syndiotactic polystyrene [11], poly(ethylene naphthalene) [12,18], poly(aryl ether ketone ketone) [18], and *n*-alkane [20].

The variations in the characteristic IR peaks show a similar tendency at different isothermal crystallization temperatures. However, the retardation time of the 763 cm^{-1} peak at different temperatures varies significantly. Fig. 5 shows the retardation of the crystallization of BA-C10 when it was annealed at 65 °C. Fig. 5(a) is the difference spectra obtained during the induction period and Fig. 5(b) shows the intensity variations of the peaks at 763, 1020, and 1045 cm^{-1} as a function of annealing time. It can also be found clearly that the retardation time is approximately 10 min, which is much shorter than the retardation time at 35 °C, as shown in Fig. 4(b).

Fig. 6 shows plots of the induction and retardation time as a function of temperature. The induction time, t_{763}, is defined as the time when the crystallization peak at 763 cm^{-1} emerged. It can be seen that the intensity of the conformational peaks increases significantly during the retardation period while that of the crystallization peaks remains constant. After the induction time, crystallization takes place. From Fig. 6, the minimum induction time occurs at 65 °C, corresponding to the maximum crystallization rate of BA-C10. The retardation time is found to increase as crystallization temperature decreases.

The crystallization process can be divided into two steps: first the polymer chains need to adjust their conformations to a certain level, then the polymer chains with regular conformations fold into the crystal lattice. The mobility of polymer chains is very low at temperatures just above its glass transition temperature. Therefore, at low crystallization temperatures, the polymer chains need a much longer time to adjust their conformations before folding into

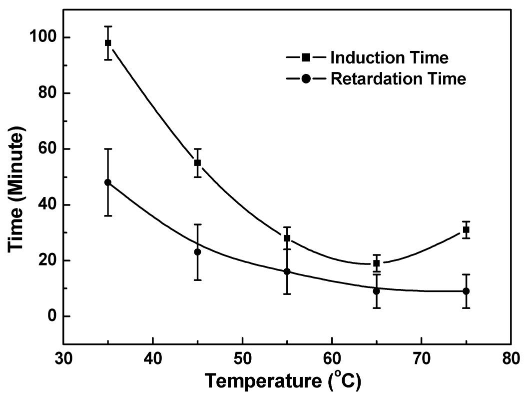

Fig. 6. Plots showing the average induction and retardation time as a function of crystallization temperature.

a lamellar crystal. Thus, the induction and retardation times are very long at low crystallization temperatures.

It is important to point out that FT-IR measures the peak intensity of the characteristic groups of a polymer. The change in the intensity of these characteristic groups can be measured as a function of annealing time, especially for polymers with a slow crystallization rate. Thus, the retardation and crystallization half time can be measured with reasonable accuracy. However, DSC measures the heat flow during the crystallization or melting of a polymer. For a polymer, such as BA-C10, which has a very slow crystallization rate, the measurement of the small heat flow can be very difficult. An accurate determination of the induction time is not possible. Thus, it is reasonable to see that the induction time and crystallization half time measured using DSC and FT-IR are not identical. Despite of the differences in the DSC and FT-IR results, our work shows that FT-IR complements DSC as a technique to study crystallization behaviors of polymers with a slow crystallization rate.

4. Conclusions

Time-resolved FT-IR measurements were performed to elucidate the conformational changes during the induction period of the crystallization of BA-C10 from the melt. The results show that the intramolecular conformational changes occur before the intermolecular packing process. The lower the crystallization temperature is, the longer is the retardation time.

Acknowledgements

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