***In Situ* Infrared Spectroscopic Study on Liquid Crystalline Phase Formation of a Random Copolyester Consisting of 60 mol% *p*-Hydroxybenzoic Acid/40 mol% Ethylene Terephthalate**

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(Received November 19, 1998)

ABSTRACT: Conformation change occurring during the formation of the liquid crystalline phase was investigated by using the *in situ* Fourier transform infrared spectroscopy. An isotropic glass of a random liquid crystalline copolyester consisting of 60 mol% *p*-hydroxybenzoic acid/40 mol% ethylene terephthalate was prepared with the cast from a solution and was heated from the room temperature up to 300°C. The onset of the transformation from the *gauche* conformers to the *trans* conformers of the ethylene glycol group was observed at *ca.* 60°C. The change in packing was indicated by the change in the intensity of the bands assignable to the aromatic rings around 150°C. Liquid crystalline phase formation observed with the optical method started to occur at *ca.* 200°C in association with the loss of the packing.

KEY WORDS Infrared Spectroscopy / Liquid Crystalline Polymer / Phase Transition / *p*-Hydroxybenzoic Acid and Ethylene Terephthalate Copolyester /

Study of the mechanism of liquid crystalline phase formation of liquid crystalline polymers (LCPs) from an isotropic phase would provide a basis of methods controlling liquid crystalline textures and related properties. The material used in this study, a random copolyester consisting of *p*-hydroxybenzoic acid and ethylene terephthalate, is a commercially available liquid crystalline polymer, and a number of studies have been reported on this material.^{1–11} However, few have been studied on the liquid crystalline phase formation from an isotropic phase at a molecular level probably because this copolyester as received does not exhibit an isotropic melt phase without concomitant thermal decomposition. This copolyester, however, does form an isotropic glass phase when cast from a solution,^{6,10} which enables the study of the phase transition from the isotropic glass phase to the liquid crystalline phase.

In this study, *in situ* Fourier transform infrared (FT-IR) spectroscopy is used to study the conformation change during the phase transition from the isotropic glass phase to the liquid crystalline phase. FT-IR is a powerful technique to study the conformation of polymers and has been applied to a number of polymers^{12–28} including poly(ethylene terephthalate),^{13–15,17–22} one of the constituent units of the copolymer used in this study. However, few reports are found on *in situ* FT-IR study on the phase transition behavior of this copolyester. Since the FT-IR technique provides the information of structure at molecular level, it is useful to study the pre-translational conformation change occurring prior to the liquid crystalline phase formation as well as prior to the crystalline phase formation.^{24,26–28} In this study, the mechanism of phase transition is discussed through the *in situ* FT-IR measurements in combination with the optical measurements.

EXPERIMENTAL

Sample Preparation

Sample used in this study was a Unitika random copolyester, Rodrum LC-3000, composed of 60 mol% *p*-hydroxybenzoic acid (HB) and 40 mol% ethylene terephthalate (ET) (hereafter referred to as PHB60/PET). As received pellets of PHB60/PET did not exhibit an isotropic phase by heating up to 300°C, but the pellets did exhibit an isotropic phase when cast from a solution. The pellets as received were dried at 90°C under vacuum for 12 h, dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol to obtain a 2 wt% solution. The solution was clear and used without filtration. Two or three droplets of the solution were dropped on a slide glass and on a KBr plate and dried in vacuum at room temperature for 2 days to obtain specimens for the optical and FT-IR measurements, respectively. The thickness of the films thus prepared was about 5 μ m. Poly(ethylene terephthalate) (PET) was hot-pressed at 280°C for 5 min, quenched in ice water to obtain an amorphous film. This film was then drawn by 480% at 60°C to obtain a stretched PET film. A crystalline sample of the PET was prepared by heating the amorphous film at 150°C for 2 h. Powder of PHB homopolymer (E-101), supplied by Sumitomo Chemical was dried and mixed with KBr powder to form a specimen for the infrared measurement.

Optical Measurements

Optical measurements were carried out on an Olympus BH-2 microscope equipped with polarizing system and a photomonitor. The specimen cast on the slide glass was covered with a cover glass and was set on a Mettler FP82HT hot-stage system, followed by the *in situ* optical measurements under crossed polars. The heating rate was 5°C min⁻¹. After the first run, the specimen was cooled to the room temperature by turning off the heater of the hot-stage. Then, the second run was carried out at the heating rate of 5°C min⁻¹.

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Figure 1. Infrared spectra of PET: (A) amorphous film, (B) film stretched by 480%, and (C) crystallized film. The bands around 1340 and 1370 cm^{-1} are assigned to *trans* and *gauche* conformers, respectively.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectra were obtained by using a Nicolet Magna-750 with the resolution of 2 cm^{-1} and 64 scans. The specimen cast on a KBr plate was covered with another KBr plate and was subjected to the *in situ* FT-IR measurements on the same hot-stage as used for the optical measurements. The heating rate was 5 $^{\circ}\text{C min}^{-1}$. The manner of the cooling and the second run was the same as for the optical measurements.

RESULTS AND DISCUSSION

FT-IR Band Assignments

For the sake of the later discussion, we first summarize the band assignments.^{18–20} In Figure 1, the spectra of the amorphous, stretched, and crystalline samples of PET are shown. Bands around 1340 cm^{-1} and 1370 cm^{-1} are assigned to the wagging vibration of *trans* and *gauche* conformers of the ethylene glycol group, respectively.¹⁹ Upon stretching or crystallization, the band at 1340 cm^{-1} increases in association with the decrease in the band at 1370 cm^{-1} . The band at 1340 cm^{-1} increases in intensity with increase in *trans* conformer by stretching or crystallization in association with the decrease in the band intensity at 1370 cm^{-1} assigned to the *gauche* conformer. The *trans* band in crystalline phase is located at a higher wavenumber than that in the amorphous phase and the stretched state. No bands assignable to the HB moiety appear in this region.

Figure 2 compares the infrared spectra of PHB, PHB60/PET, and PET. The band around 730 cm^{-1} is observed only in PET, and hence the band at 725 cm^{-1} in PHB60/PET is assigned to ET moiety. Since the band at 730 cm^{-1} for PET is assigned to the aromatic C–H out-of-plane bending vibration,¹⁸ we assign the corresponding band at 725 cm^{-1} in PHB60/PET to the same vibration mode attributed to the ET moiety. No assignment for the HB moiety is available in the literature, but the assignment for PET could support the following assignments: The band around 760 cm^{-1} in PHB60/PET is assigned to the HB moiety in comparison with the PHB spectrum and could be attributed to the aromatic C–H out-of-plane bending vibration mode of the aromatic ring of the HB moiety. The band at 1016 cm^{-1} is assigned to the aromatic C–H in-plane bending vibration of the ET and HB moieties.

Figure 2. Comparison of the infrared spectra of (A) PET, (B) PHB60/PET, and (C) PHB.

Figure 3. Infrared spectra of PHB60/PET measured upon heating of the isotropic cast film from 30 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$. The spectrum on the top is obtained after cooling to 30 $^{\circ}\text{C}$.

Conformation Change

Change in the spectrum of PHB60/PET around 1300 to 1400 cm^{-1} region during heating of an isotropic specimen from 30 to 300 $^{\circ}\text{C}$ is shown in Figure 3. The intensity of the band around 1340 cm^{-1} assigned to the *trans* conformer of the ethylene glycol group increases with temperature and reaches maximum near 150 $^{\circ}\text{C}$. This increase is associated with the decrease in the band intensity at 1370 cm^{-1} assignable to the *gauche* conformer. The band around 1340 cm^{-1} shifts to a lower wavenumber with increasing the temperature. A similar shift is also observed for other peaks when the temperature is changed. The spectrum for the sample cooled to 35 $^{\circ}\text{C}$ from 300 $^{\circ}\text{C}$ exhibits mostly the *trans* band. This observation suggests that the *trans* rich conformation attained upon heating is frozen on cooling. As a matter of fact, an optical measurement, which will be discussed later, indicates that a liquid crystalline phase taking place by heating is frozen upon cooling to produce a liquid crystalline glass.

According to the work by Lin and Koenig²⁰ on spectral change of PET on heating, the intensity change comprises a reversible contribution and an irreversible one. The former exhibits a linear decrease with increasing temperature, while the latter is associated with change in conformation. In Figure 4, the intensities of the bands assigned to the *trans* and *gauche* conformers for the ethylene glycol units observed around 1340 and 1370 cm^{-1} , respectively, are plotted against the temperature. The peak height is used for the measure of the intensity. Since these two peaks shift slightly depending on the temperature, the peak top is used to measure the intensity. The change in intensity starting around 60 $^{\circ}\text{C}$ is due to the change in conformation. This tem-

Figure 4. Change in intensity of the bands at 1340 cm^{-1} for *trans* conformer and at 1370 cm^{-1} for *gauche* conformer upon heating (5°C min^{-1}) of the isotropic cast film of PHB60/PET. After the first run (open circle), the heater was turned off and the specimen was allowed to be cooled slowly down to 35°C , followed by the second run (filled circle) at the heating rate of 5°C min^{-1} .

perature is close to the glass transition temperature T_g determined by DSC, ($57\text{--}67^\circ\text{C}$,¹ 61°C .^{2,8}) reported for the polymer of the same composition provided by Tennessee Eastman. With increasing temperature, the intensity of the *trans* conformer increases and reaches maximum around 150°C , in association with the decrease in the *gauche* conformer.

The decrease in the intensity of the *trans* conformer above 150°C does not mean the decrease of the *trans* conformer because little increase in the *gauche* conformer is observed. This decrease should be attributed to the change in the environment of the *trans* conformer, probably including the loss of the packing, and also attributed to the reversible decrease caused by the enhanced thermal fluctuation. Above 250°C , the intensity merges to the level for the second run. In the initial state of the second run, the intensity exhibits different value from the initial one, which indicates that the conformation change during the first run is irreversible.

In the second run, the decrease is linear in contrast to the first run. This decrease could be attributed to the reversible contribution, *i.e.*, the temperature effect, and hence indicates that little conformation change occurs during the second run. In the beginning of the second run, the *trans* conformer content is higher than that in the beginning of the first run and the *gauche* conformer content is low. This observation indicates that the *trans* conformer existing at 300°C remains on cooling without going back to the *gauche* conformer. In the temperature range between 100 and 230°C , the intensity of the first run exceeds that for the second run. This excess does not indicate that the *trans* content is higher in the first run than in the second run in this temperature range, but should indicate that the environment around the *trans* conformer is different between the first run and the second run.

Figure 5 shows the change in the intensity of the bands for the aromatic C–H out-of-plane bending mode for ET (725 cm^{-1}), the same mode for HB (760 cm^{-1}), and the aromatic C–H in-plane bending mode for ET and HB (around 1016 cm^{-1}) upon heating of the isotropic sample. The interpretation of the intensity change for these bands in the first run is not straightforward, in comparison to that of the *trans* and *gauche* conformers, because the intensity change is not ascribed directly to the increase

Figure 5. Change in intensity of the aromatic C–H vibration modes observed at 1020 cm^{-1} (HB and ET in-plane), 760 cm^{-1} (HB out-of-plane), and 725 cm^{-1} (ET out-of-plane). Open and filled circles represent the first run and the second run, respectively.

or decrease of a specific conformation. The intensity change is considered to be a reflection of the change in environment surrounding these ring structures as it was considered so in explaining the excess intensity for the *trans* conformers observed between 100 and 250°C . As a matter of fact, the in-plane mode (1016 cm^{-1}) behaves in a similar manner to the change of *trans* conformer shown in Figure 4, *i.e.*, the intensity for the first run exceeds that for the second run in the temperature range between 80 and 230°C . Also, the deviation from the second run is observed for the 760 and 726 cm^{-1} bands in a similar temperature range. The second run exhibits a linear decrease, which indicates that the reversible temperature effect is dominant.

We have observed the deviation (or excess) for the first run with respect to the second run both for the ethylene glycol groups and the aromatic rings in the temperature range approximately between 100 and 230°C , though the precise temperature range is slightly different depending on the individual bands. We have attributed this deviation to the difference in packing. This packing could be related to the crystallization: The temperature 100°C is about 40°C higher than T_g . The temperature 230°C is close to the melting point T_m ($247\text{--}257^\circ\text{C}$,¹ 212°C .⁸) determined by DSC or (235°C .⁶) by the wide angle X-ray measurement. This temperature range is referred to as 'quasi-liquid' in which cold crystallization can occur.⁸ As a matter of fact, it is reported⁶ that the wide angle X-ray diffraction due to HB sequence is observed around this temperature range. Though the X-ray diffraction does not exhibit clear crystalline patterns, the packing that we assume here could be partially related to the crystallization.

These facts could provide the following scenario to explain the deviation between the first and the second runs. At 160°C (close to T_g), the enhanced segmental motions are allowed to start and the *gauche* conformers transform to the *trans* conformers. Concomitantly, the crystallization of sequences rich in HB units starts to occur, which could contribute to the deviation (or excess)

Figure 6. Change in transmitting light intensity measured under crossed polars. Thermal history applied for the first and second runs are exactly same as for the infrared measurements.

of the band intensities through the change in packing. Around 150°C it is likely that the packing is maximized. With a further increase in temperature, the crystallized regions start to melt gradually, causing the change of the band intensities which end up with merging into the intensity level for the second run. Above 230°C (melting point), the melting occurs and the liquid crystalline phase is formed, where the crystalline packing is lost but the *trans* conformation remains. Upon cooling, the liquid crystalline phase is quenched to the liquid crystalline glass phase. In the second run, the crystallization of the sequences rich in HB units does not occur upon heating. In the first run, the packing for crystallization is facilitated by the transformation of the *gauche* conformers to the *trans* conformers, but in the second run, where the ethylene glycol groups are mostly in *trans* conformation, the packing for crystallization is realized only by the chain movement along the chain direction. This movement may occur but might take long time in comparison to the time scale of the current experiment (5°C min⁻¹). As a result, no crystallization is observed in the second run.

Polarizing Optical Microscopy

So far, we have discussed the conformation change viewed with the infrared spectroscopy. Now we discuss about the observation made with polarizing optical measurements. Figure 6 shows the change in the transmitting light intensity measured under the crossed polars during the heating at 5°C min⁻¹. In the first run, the increase in the transmitting light intensity, which is a reflection of the formation of the liquid crystalline phase, is not observed until *ca.* 200°C. This is in contrast to the observation for the FT-IR results where the conformation change starts to occur at as low a temperature as 60°C and the intensity reflecting the crystalline packing reaches maximum at 150°C. The spatial correlation of crystalline packing developing around 150°C is too short to be detected by microscopic observation.

The transmitting light intensity starts to increase around 200°C, which coincides with the onset temperature of the decrease in crystalline packing indicated by the change in FT-IR intensities. Above 200°C, the fluidity increases due to the enhancement of the chain mobility in association with the melting of the crystalline packing, enabling the formation of larger liquid crystalline

domains⁶ which can be detected by the optical measurement. In the second run, the level of the transmitting light intensity is same as that at the end of the first run at 300°C. Hence it is concluded that, on cooling, the liquid crystalline phase with larger domain size is frozen. This observation is in agreement with the infrared observations.

CONCLUSION

The formation of the liquid crystalline phase upon heating the isotropic glass is summarized as follows: (1) Upon heating, the conformation change starts at T_g (*ca.* 60°C) as observed with the increase in the *trans* conformers in the ethylene glycol groups. (2) This change is associated with the crystalline packing of HB rich regions. The packing seems to become maximum at *ca.* 150°C. At this stage, little change is observed in the optical measurement because the spatial correlation of this packing is shorter compared to the wavelength of the light. (3) Upon further heating, the melting of the crystalline packing starts to occur around 200°C, resulting in the onset of the liquid crystalline phase formation. The melting is completed around 250°C. Due to the enhanced fluidity, the size of the liquid crystalline domain increases, which is reflected by the increase of the transmitting light intensity measured under the crossed polars. (4) Upon cooling after the heating up to 300°C, the liquid crystalline phase is frozen to the liquid crystalline glass. High transmitting light intensity and *trans* contents are maintained. (5) In the second run, the liquid crystalline glass goes directly to the liquid crystalline phase without passing through the crystalline packing probably because of the kinetic reason.

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