Macromolecules **1992,** *25,* 1009–1010

Phase Transition of Thermotropic Liquid Crystalline Copolyester Film

Koichiro Yonetake,* Tsunehisa Sagiya, Kiyohito Koyama, and Toru Masuko

Faculty of Engineering, Yamagata University, Jonan-4, Yonezawa, Yamagata, 992 Japan

Received June 4, 1991
Revised Manuscript Received October 10, 1991

Introduction

The wholly aromatic copolyester prepared from 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) (HBA/HNA copolymer) exhibits a nematic liquid crystalline characteristic at elevated temperatures, as is known to transform into the extended chain conformations in the solid state from the nematic melt. The HBA/HNA copolymer (HBA/HNA = 75/25) shows a glass transition temperature at ca. 100 °C through thermal analysis[1] and dynamic viscoelastic methods.[2] An endothermic peak at 280 °C is observed in the DSC curve, which is assigned to crystal/nematic phase transition.[1,3,4]

Structural changes of this copolymer have been examined using melt-cast films,[5–7] injection-molded samples,[8] and melt-spun fibers.[9,10] Since such samples have complicatedly coagulated structures in the solid state, it seems difficult to investigate the structural change and phase transition of the HBA/HNA copolymer, because starting samples have partially crystalline and oriented structures.

In this study, HBA/HNA (73/27) copolymer films were prepared by a solution-casting method. Some films were considered to be amorphous. Phase transitions of the films during annealing processes were examined using DSC, polarized microscopy, and X-ray diffraction methods.

Experimental Section

HBA/HNA copolymer pellets (molar ratio: HBA/HNA = 73/27) were dissolved in a mixed solution of pentafluorophenol (PFP) and chloroform (weight ratio: PFP/chloroform = 3/7). The concentration of the solution was 0.3 wt %. The solution was filtered by glass filter to remove insoluble residue such as impurities and gel fractions. The films were prepared by a solution-casting method. The thickness of the films was ca. 20 μm. The solvents were extracted from the cast film with methylene chloride, and then the films were dried in a vacuum oven at 80 °C for 2 days to remove the methylene chloride. These cast films were annealed at various temperatures in a DSC 200 apparatus (Seiko Instruments & Electronics Ltd.) for 2 h under an N_2 purge.

Phase transition of the HBA/HNA copolymer films during a heating process was examined by use of a polarized optical microscope equipped with a hot stage (Linkam Co., TH-600RMS). A heating rate is programmed at 30 °C/min. The thermal properties of the films were investigated using the DSC 200 under an N_2 purge; heating and cooling rates were 30 and 20 °C/min, respectively. X-ray diffraction experiments were carried out by a RAD-rA diffractometer (Rigaku Denki Co., Ltd.) equipped with a heating device. Wide-angle X-ray diffraction (WAXD) traces were obtained by a step-scanning method using a scintillation counter system: the step width and fixed time were programmed for steps of 0.05° every 4 s. Changes in WAXD patterns during stepwise heating and cooling processes were recorded in the temperature range from 26 to 320 °C.

Results and Discussion

Characterization of a Solution-Casting Film. Some as-cast films prepared without residual stress are transparent and show dark in the fields of a polarized optical microscope. An X-ray diffuse halo was also obtained in a WAXD diagram of the film. Therefore, the films can be thought of as amorphous. Figure 1 shows changes in the DSC curves for the as-cast film. A glass transition is clearly observed at 110 °C in a first-heating DSC trace. Exothermic (A position) and endothermic (B position) peaks were also observed in this trace. In a polarized optical micrograph, light intensity increases rapidly in the temperature range of the exothermic peak. These findings suggest that molecular chains of the copolymer are rearranging their packing mode in the wide temperature range from 200 to 250 °C; the crystalline ordered state appears from the amorphous state at the temperature range.

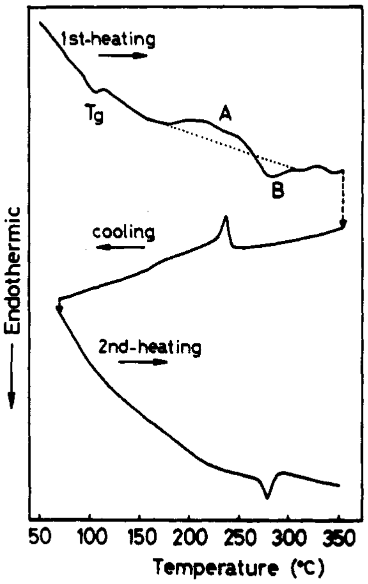

Figure 1. DSC thermograms of a HBA/HNA copolymer film.

On the other hand, the second-heating DSC trace shows only one endothermic peak at 280 °C; the base-line change of the glass transition and exothermic peak seems to disappear. The profile of the second-heating trace is almost the same as those of the samples obtained from the molten state such as melt-pressed films.[1,6] The endothermic peak at 280 °C is probably assigned to the crystal/nematic phase transition (T_{CN}).[1,3,4]

Fine Structural Changes of the Cast Film during Heating and Cooling Processes. The WAXD traces for the cast film during heating and cooling processes are shown in Figure 2. The WAXD pattern for the as-cast film is broad and diffuse. It becomes sharp gradually when heated up to 230 °C. Above 230 °C, however, the intensities of $2\theta_{max}$ decrease with increasing temperature. A nematic state is confirmed in the WAXD pattern at 300 °C. These X-ray results are consistent with those obtained by DSC analysis and polarized optical microscopy as already described, suggesting that crystalline-ordered structures are formed in the range below T_{CN}.

In a cooling process, the WAXD curves become comparatively sharp with decreasing temperature, and the reflection at $2\theta = 27°$ ($d = 0.33$ nm) appears below 230 °C. Some three-dimensionally ordered (3D) structure is formed in the film. The features in the WAXD pattern during the cooling process are similar to those of melt-cast samples.[6] The WAXD pattern obtained at 26 °C after cooling is different from that of the as-cast film. Thus, we consider that these results reflect the different fine structures between the as-cast and annealed films.

Figure 3 shows changes in *d* spacing of the film in both heating and cooling processes. This *d* spacing (0.45 nm)

0024-9297/92/2225-1009$03.00/0

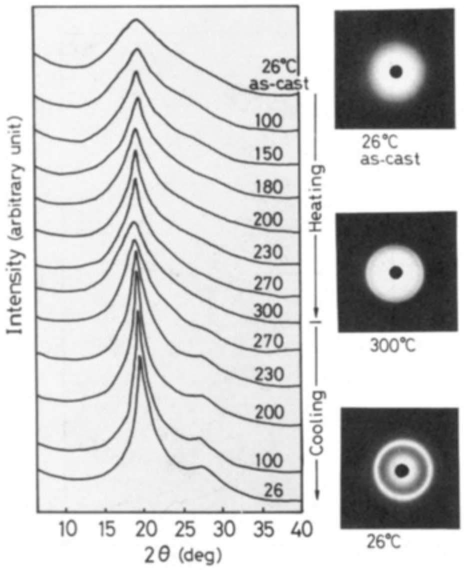

Figure 2. WAXD traces and patterns of a HBA/HNA copolymer film during heating and cooling processes.

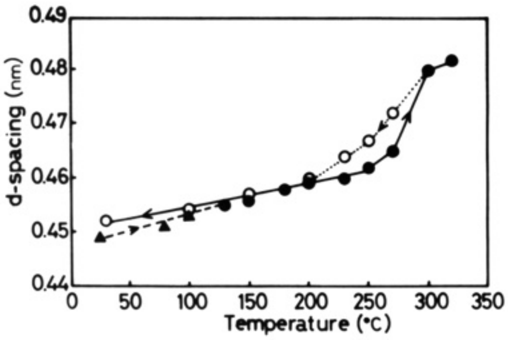

Figure 3. Change in *d* spacing of a HBA/HNA copolymer film during heating and cooling processes. Closed symbols denote *d* spacings on the heating process; open circles denote those of the cooling process. Closed triangles denote those of $2\theta_{max}$ of the amorphous scattering.

is assigned to a (110) reflection from the fiber diagram.[10] Closed and open symbols in Figure 3 indicate *d* spacings of the as-cast film during heating and cooling processes, respectively. The *d* values increase linearly with increasing temperature by thermal expansion. The *d* values below 100 °C, denoted by solid triangles are small, because they are associated with those of the intensity maxima for X-ray amorphous scattering. A state of crystalline order is thus constructed above 150 °C. The *d* values increase drastically above 270 °C, since the crystallites transform from 3D into 2D or more disordered structures.

In the cooling process, the *d* values are larger than those for the heating process in the temperature range from 200 to 300 °C. The irreversible change in *d* spacings probably comes from a supercooling effect. The *d* values for the cooling process coincided with those for the heating process when the sample was kept at desired temperatures long enough to reach an equilibrium state.

Thus, the formation of crystalline structure and crystal/nematic phase transition is also confirmed by the changes in *d* spacings.

Phase Transitions of Annealed Films. As-cast films were annealed at 100, 200, and 270 °C. These films are coded as C_{100}, C_{200}, and C_{270}. Figure 4 shows the DSC curves of these annealed films. The DSC profile of C_{100} is similar to that of the as-cast film shown in Figure 1, which exhibits a small peak at 110 °C. On the other hand, in the DSC curves of C_{200} and C_{270}, the T_g's are observed as a shoulder which is somewhat different from the peak of C_{100} annealed below T_g. The amorphous chains in C_{200} and C_{270} films are restricted by ordered structures formed by annealing above T_g.

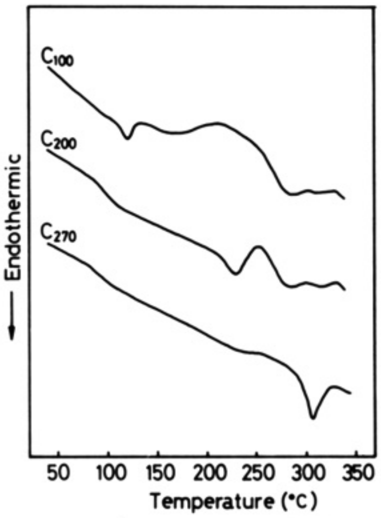

Figure 4. DSC thermograms of HBA/HNA copolymer films annealed at various temperatures. C_{100}, C_{200}, and C_{270} were annealed at 100, 200, and 270 °C, respectively.

In the DSC trace of the C_{200} film, a small endothermic peak is observed at 230 °C, which is attributable to the thermodynamically unstable structures formed by the annealing treatment. The DSC trace of C_{200} also exhibits an exothermic peak at 250 °C just below T_{CN}. The exothermic peak is probably associated with cold crystallization often appearing in a conventional polyester polymer.[11]

In the DSC curve of C_{270}, the base-line change of the glass transition disappears, and a larger endothermic peak of T_{CN} is observed at 307 °C. Thus, the volume fraction of nematic and more ordered structures increase in C_{270}, since the film is annealed at the temperature close to T_{CN}.

A schlieren texture characteristic of a nematic liquid crystal was observed in the HBA/HNA copolymer film annealed at 270 °C in the polarized microscope.

In conclusion, an amorphous HBA/HNA copolymer film was obtained by the solution-casting method, and the glass transition, cold crystallization, and nematic texture were clearly observed using the amorphous film.

References and Notes

(1) Cao, M.-Y.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 521.
(2) Blundell, D. J.; Buckingham, K. A. *Polymers* **1985**, *26*, 1623.
(3) Blundell, D. J. *Polymer* **1982**, *23*, 359.
(4) Butzbach, G.; Wendorff, J. H.; Zimmerman, H. J. *Polymer* **1986**, *27*, 1337.
(5) Windle, A. H.; Viney, C.; Mitchell, R.; Golombok, R.; Donald, A. M.; Mitchell, G. R. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 55.
(6) Yonetake, K.; Sasaki, K.; Koyama, K.; Masuko, K. *Rep. Progr. Polym. Phys. Jpn.* **1987**, *30*, 161.
(7) Bedford, S. E.; Windle, A. H. *Polymer* **1990**, *31*, 616.
(8) Kaito, A.; Kyotani, M.; Nakayama, K. *Macromolecules* **1990**, *23*, 1035.
(9) Lemmon, T. J.; Hanna, S.; Windle, A. H. *Polym. Commun.* **1989**, *30*, 2.
(10) Fa, X. C.; Takahashi, T. *Sen-i Gakkaishi* **1990**, *46*, 49.
(11) Kanetsuna, H.; Maeda, K. *Kogyo Kagaku Zasshi* **1966**, *69*, 1784.

Registry No. HBA/HNA (copolymer), 81843-52-9.