Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 453–458

THERMAL EXPANSION OF LIQUID CRYSTALLINE POLYESTERS HAVING PHENANTHRENE MOIETIES

Simultaneous DSC-XRD method

H. Yoshida[1], *Y. Houshito*[2], *K. Mashiko*[2], *K. Masaka*[2] *and S. Nakamura*[2]

[1]Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, Hachiouji, Tokyo 192-0397, Japan
[2]Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-Ku, Yokohama 221-8686, Japan

Abstract

Phase transition process of polyester from phenanthrene, poly(oxyheptamethyleneoxy-2,7-phenantrenedicarbonyl), a main chain type liquid crystalline polymer, was investigated by simultaneous DSC-XRD measurements using the synchrotron radiation facility (PF). Three exothermic DSC peaks were observed during cooling from the isotropic liquid state. These DSC peaks were assigned to the transition from the isotropic liquid to the smectic A, that from the smectic A to C, and that from the smectic C to the crystalline state, respectively, as determined by XRD profiles. The rate of transition from the smectic A to C was very slow compared with the liquid crystalline transition and the crystallization. From the DSC-XRD results, the thermal expansion along *c*-axis in the crystal and smectic phases are $4.1\cdot10^{-4}$ and $1.4\cdot10^{-3}$ nm K^{-1}, respectively.

Keywords: DSC-XRD, liquid crystalline polyester, smectic phase, thermal expansion

Introduction

Polyesters derived from 2,7-phenanthrene dicarbonic acid and alkylene diols (phenanthrene polyester; PPE) assume the smectic liquid crystal phase above their melting temperatures due to the intermolecular interaction between phenanthrene moieties [1, 2]. Phenanthrene moieties are connected by alkyl chain in the main chain of PPE and serve as mesogenic unit. The odd-even effect of alkyl carbon number was exerted in the phase transition temperature and the transition enthalpy of PPE. A complex thermal behavior was observed for PPEs with odd carbon number [1].

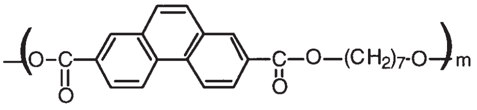
The simultaneous method of differential scanning calorimetry and X-ray diffraction (DSC-XRD) gives both thermodynamic and structural information of materials. The multiple phase transitions were assigned by the DSC-XRD method for poly(vinylidene fluoride) and isotactic poly(propylene) [3]. In this study, phase transition of PPE with seven-carbon number was investigated by the simultaneous DSC-XRD method from the viewpoint of thermal expansion of the crystal and liquid crystal phase.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Poly(oxyheptaleneoxyphenanthaloyl) (PPEn7) (Scheme 1) was prepared by polycondensation of 2,7-phenanthrene dicarbonicacid diethylester and heptaneglycol [4] and used throughout this study. The obtained PPEn7 was purified by the precipitation method. The dry PPEn7 was pressed into a disk with 0.5 mm thickness. The disk of PPEn7 with about 3 mg was sealed by aluminum foil and was clamped in the aluminum vessel for DSC-XRD measurement.



Scheme 1

Two types of DSC-XRD units were used through this study. For a wide angle measurement, the simultaneous DSC-XRD instrument [5] was set on a Mac Science MXP18 SRA X-ray diffractometer (DSC-WAXRD) operated at 40 kV and 300 mA. The wavelength of monochromatic X-ray was 0.1540 nm. The scintillation counter was scanned at 10° $\min^{-1}$ in the 2θ range from 4° to 8°, which corresponded to 1.1 nm $<S^{-1}=\lambda(2\sin\theta)^{-1}<$2.2 nm with the space resolution of 10^{-4} nm. For a small angle measurement, the DSC-XRD instrument was set on the small angle X-ray scattering optics (DSC-SRXRD) at BL-10C of Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of monochromatic X-ray for DSC-SRXRD was 0.1488 nm. The size of incident X-ray beam was 0.6 mm×0.6 mm. The scattering X-ray was detected by a one-dimensional position sensitive proportional photon counter (PSPC). The distance between sample and PSPC was 680 mm, which covered 1.25 nm$<S^{-1}=\lambda(2\sin\theta)^{-1}<$200 nm. The simultaneous DSC-XRD measurement was carried out at 5 K $\min^{-1}$, and XRD profiles were stored each 2.0 K (DSC-SRXRD) and 2.5 K (DSC-WAXRD), respectively.

Results and discussion

The thermal behavior of PPEn7 is shown in Fig. 1. The powder PPEn7 shows only melting at 165°C on heating (DSC curve 1). PPEn7 shows three exothermic peaks at 140, 120 and 100°C during cooling from the molten state (curve 4). However, the heating DSC curve shows one endothermic peak (curve 5). When sample was cooled from the molten state to 135°C (curve 2) and was heated immediately, two small endothermic peaks were observed at 160 and 165°C (curve 3). The transition enthalpy of the endothermic peak (1.16 kJ mol^{-1}, mol as the repeating unit) at 165°C on curve 3 was almost the same with that (1.02 kJ mol^{-1}) of the exothermic peak appeared in the higher temperature side on curve 2.

The structures of PPEn7 having different thermal history, prepared by quenching from 135 and 70°C during cooling, were investigated by a wide angle X-ray diffraction (WAXRD) at room temperature. WAXRD profile for PPEn7 having the same thermal history with DSC curve 2 in Fig. 1 shows a sharp diffraction peak at S=0.588 nm^{-1} and a broad peak at around S=2.2 nm^{-1}. However, WAXRD profile of PPEn7 quenched from 70°C shows diffraction peaks at S=0.62, 1.05, 1.60, 1.84, 2.26 nm^{-1}. These X-ray results indicate that the endothermic transitions at 135 and 100°C observed on cooling are the transition from the isotropic liquid state to the smectic phase and the crystallization, respectively.

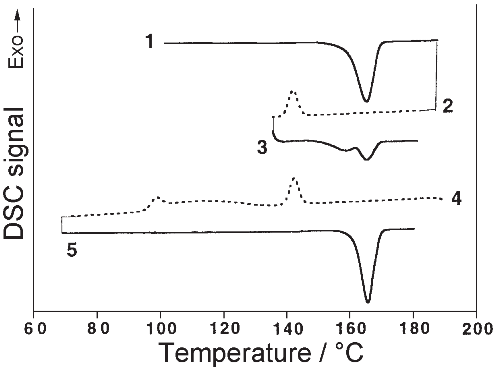


Fig. 1 1 – DSC curves of PPEn7 at 5 K min^{-1}; heating from room temperature; 2 – cooling from the molten state to 135°C; 3 – heating immediately after cooling to 135°C; 4 – cooling from the molten state to room temperature and 5 – heating immediately after cooling to room temperature

As the diffraction peak at S=0.588 nm^{-1} was observed in the meridian direction of the fiber of PPEn7 drawn at 130°C, this peak corresponded to (001) plane of the smectic phase. Temperature dependence of the (001) spacing ($d_{(001)}$) of PPEn7 was observed by DSC-WAXRD as shown in Fig. 2. On heating, the value of $d_{(001)}$ started to increase at 110°C and increased gradually at temperature above 150°C, at which the endothermic peak was observed. This diffraction peak vanished at the endothermic peak temperature, 165°C. On the other hand, the diffraction peak appeared at S=0.53 nm^{-1} at the temperature range below 145°C on cooling. The value of $d_{(001)}$ decreased linearly with decreasing temperature from 145 to 130°C, which corresponded to the higher exothermic peak (curve 4 in Fig. 1). The value of $d_{(001)}$ shifted from 1.85 to 1.80 nm in the temperature between 130 and 120°C, which corresponded to the broad exothermic peak on curve 4 in Fig. 1. The value of $d_{(001)}$ decreased again linearly with decreasing temperature from 120 to 100°C.

Thermal expansion coefficient of $d_{(001)}$ was evaluated from Fig. 2. The thermal expansion was obtained as follows;

Heating: $4.0\cdot10^{-4}$ nm K^{-1} (30–110°C), $8.0\cdot10^{-4}$ nm K^{-1} (115–150°C) and $2.5\cdot10^{-3}$ nm K^{-1} (150–165°C).

Cooling: $5.0\cdot10^{-4}$ nm K^{-1} (30–90°C), $3.0\cdot10^{-3}$ nm K^{-1} (100–120°C) and $3.0\cdot10^{-3}$ nm K^{-1} (120–140°C).

These results indicate that three phases existed during cooling and that at least two phases are in the liquid crystalline state. The thermal expansion coefficient of

$d_{(001)}$ in the crystalline state is almost the same on heating and cooling. Assuming the *trans* conformation of alkyl chain, the calculated length of repeating unit of PPEn7 is 1.9 nm, which shows a good agreement with the experimental data. From this result, it is expected that PPEn7 molecules are oriented perpendicular to the smectic layer at the temperature range between 120 and 140°C (smectic A). The change of $d_{(001)}$ value at temperature between 130 and 120°C was due to the transition from the smectic A to the smectic C, in which PPEn7 molecules were tilted in the smectic layer. Watanabe and Hayashi [6] reported the similar texture of smectic A and smectic C for the polyesters having mesogenic bibenzoate unit in the main chain.

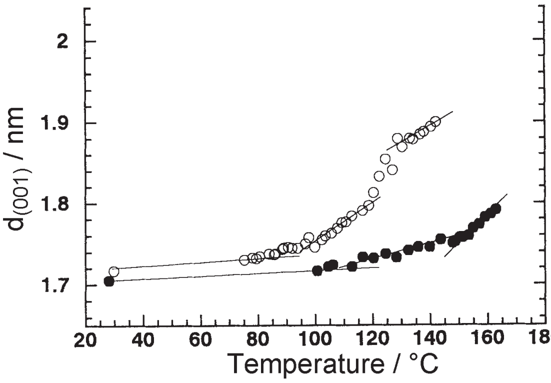


Fig. 2 Temperature dependence of $d_{(001)}$, (001) spacing of PPEn7 on heating (●) and cooling (o) at 5 K min^{-1}

The thermal expansion coefficient of $d_{(001)}$ in the liquid crystal states on cooling are almost the same with the value obtained in the melting on heating. As expected from Fig. 1, these results suggest that the melting endothermic peak contains the transition from the liquid crystal to the isotropic liquid state. The thermal expansion and the $d_{(001)}$ value results observed on heating suggest that the smectic C phase exists at temperature from 155 to 165°C.

DSC-SRXRD results of PPEn7 obtained by cooling from the molten state at 5 K min^{-1} were shown in Figs 3a (DSC) and 3b (XRD). As same as DSC curve 4 in Fig. 1, the cooling DSC curve showed three exothermic peaks at around 140, 120 and 100°C. Two XRD peaks at 0.53 nm^{-1} (d=1.92 nm) and 0.55 nm^{-1} (d=1.81 nm) are observed in this temperature range during cooling. The former peak ($d_{(001)}$ of smectic A) appeared at higher temperature and the latter peak ($d_{(001)}$ of smectic C) appeared at slightly lower temperature after the decrease of the former peak intensity. Intensity changes of both XRD peaks were plotted with DSC cooling curve in Fig. 4. The XRD peak of smectic A peak appeared at 145°C, and the peak intensity increased with DSC exothermic peak. Following the intensity of XRD peak of smectic A (d=1.92 nm) decreased at temperature region from 130 to 120°C, the XRD peak of smectic C (d=1.81 nm) appeared in the same temperature range. If molecular conformation in smectic C and A are same, the tilt angle of molecules in smectic C is expected to be 70° from the smectic layer surface. In the temperature range from 130 to 110°C, both smectic A and C phases were coexisted.

In Fig. 3b, the XRD peak at S=0.08 nm^{-1} was observed in the liquid crystal phase. This XRD peak was due to smectic layer structure. As the average thickness of smectic layer was 12 to 14 nm, at least seven repeating units existed in one smectic layer. Even in the isotropic liquid phase, the long range density fluctuation at around

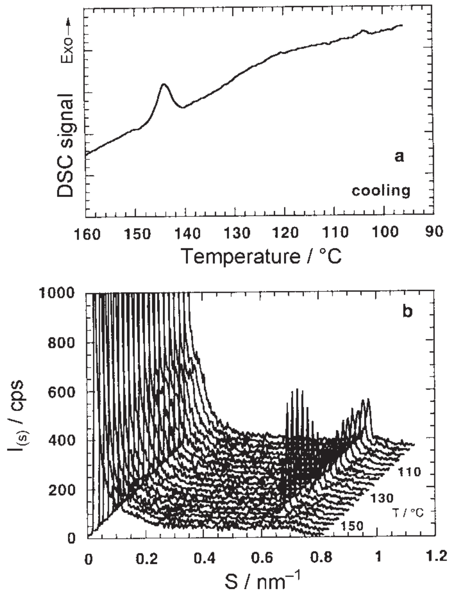


Fig. 3 The simultaneous a – DSC; b – XRD results of PPEn7 obtained by cooling from the isotropic liquid state at 5 K min^{-1}. XRD profiles changed from the isotropic liquid state (front) to the crystal state (back)

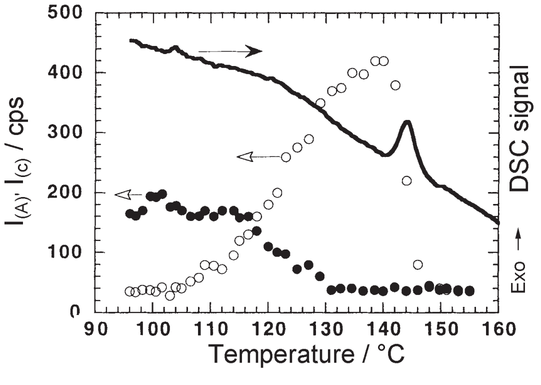


Fig. 4 Intensity changes of XRD peaks of smectic A, $I_{(A)}$ (open circle) and smectic C, $I_{(C)}$ (black circle) phases and DSC cooling curve

S=0.08 nm^{-1} was observed. This density fluctuation probably formed the smectic layer.

Conclusions

Thermal transition behavior of PPEn7 was investigated by the simultaneous DSC-XRD method. PPEn7 showed only one endothermic peak on heating, however, three exothermic peaks on cooling. Thermal expansion data evaluated by DSC-XRD measurement suggested that the smectic A and C phases were formed on cooling and that PPEn7 changed from the crystal state to the isotropic liquid phase via the smectic C phase on heating.

References

1 H. Yoshida, K. Masaka and S. Nakamura, Reports on Progress in Polymer Physics in Japan, 41 (1998) 211.
2 H. Yoshida, M. Honma, K. Masaka and S. Nakamura, Photon Factory Activity Report, 16 (1998) 117.
3 H. Yoshida, Thermochim. Acta, 267 (1995) 239.
4 S. Nakamura and K. Masaka, unpublished data.
5 H. Yoshida, R. Kinoshita and Y. Teramoto, Thermochim. Acta, 264 (1995) 173.
6 J. Watanabe and M. Hayashi, Macromolecules, 22 (1989) 4083.