

MELTING AND CRYSTALLIZATION BEHAVIOR OF AN AROMATIC POLY(AZOMETHINE ETHER) WITH NON-LINEARLY SHAPED MOLECULAR CONFORMATIONS*

HOU Jianan(侯建安) XU Mao(徐 懋)

(Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080)

LI Xiaofang(李小放) and ZHANG Qizhen(张其震)

(Department of Applied Chemistry, Shandong University, Jinan 250100)

ABSTRACT

The melting and crystallization behavior have been investigated for an aromatic poly (azomethine ether) with non-linearly shaped molecular conformations. This polymer was found to undergo multiple melting processes and its phase transition behavior was influenced sensitively by the thermal history of sample. A significant difference between the polymer chain aggregation abilities of samples cooled from the different states was observed. The possible molecular morphology and aggregation models for describing the structures of this polymer were proposed and discussed. The crystallization behavior of the samples cooled from the partially isotropic state and the influence of cooling rate on it have also been examined with DSC.

INTRODUCTION

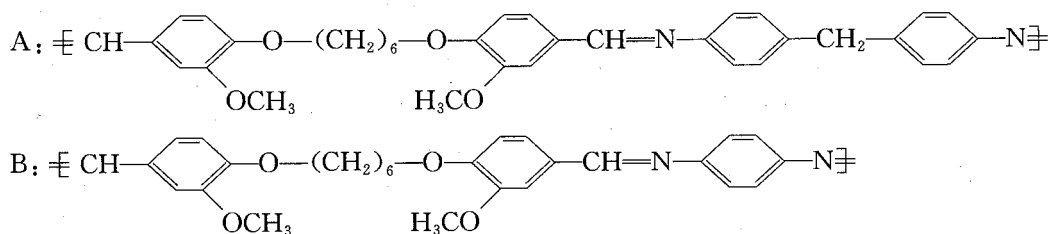
It is well known for main chain liquid crystalline polymers (LCPs) that the linearity of rod-like mesogens is in general required as one of the necessary conditions for organizing the mesomorphic structure. Although some main chain polymers are synthesized from monomeric units similar in structure to those of LCPs, they do not exhibit mesomorphic behavior after

* Project supported by the Youth Science Foundation of Academia Sinica and the National Natural Science Foundation of China.

Received November 8, 1993

melting, due to their spatially non-linear geometry in the chain conformation and the less molecular aggregation ability in melting state.

We have studied in detail the phase transition behavior and observed a unique microphase separation phenomenon for a series of thermotropic liquid crystalline random copolyethers which were composed of two similar aromatic azomethine ether units, A and B, with the chemical structures as follows^[1],



The B component was found to exhibit nematic mesomorphic behavior, but A showed no liquid crystallinity. The component content also influenced greatly on the phase transition and mesomorphic behavior of those copolymers.

For thermotropic LCPs, the molecular aggregation ability was found to influence sensitively on their phase transition behavior which may be also affected by the thermal history of samples. For example, some LCPs can only be transformed from the isotropic state to a mesophase but not to the original crystalline or semi-crystalline state in the cooling process^[2,3]. There were also reported the other cases, in which the LCPs were possible to crystallize in a cooling process from their mesomorphic state, but could not be crystallized if cooling from the isotropic liquid^[2,4].

It is also of great importance to expand our knowledge developed basically on the studies on LCPs to the investigation of the phase transition behavior for some non-liquid crystalline polymers with chemical compositions close to those of LCP systems, in connection with the molecular morphology and aggregation property. In this paper we will describe in detail the thermal behavior for one of the homopolymers shown above or the 100 mol% A specimen.

EXPERIMENTAL

The polymerization procedure is briefly described as follows. The

monomer 3,3'-dimethoxy-4,4'-diformyl- α,ω -diphenoxyhexane was prepared by a condensation reaction at room temperature for about 4 hours from 1,6-dibromohexane and vanillin in dimethylformamide and in the presence of anhydrous Na_2CO_3 . The obtained dialdehyde and 4,4'-diaminodiphenyl methane were then polycondensed under nitrogen atmosphere at about 110°C for 4 hours and with acetic acid as catalyst. The information of the polymer on molecular weight and its distribution, however, was difficult to be obtained, due to its very poor solubility in organic solvents.

Thermal transition behavior of the samples was analyzed with a Perkin Elmer DSC-4 differential scanning calorimeter. The instrument was linked on line to a computer that allows the output to be corrected for baseline curvature and to be calibrated in absolute units. The heating rates were 20°C/min and cooling rates were ranging from 20°C to 0.2°C/min, respectively. Optical microscopic observations were performed with an Olympus BHSP polarizing microscope equipped with a hot stage. Small angle light scattering (SALS) Hv pattern was photographically recorded using a LS-1 type apparatus with a 632.8nm wavelength He-Ne gas laser. X-ray diffraction measurements were carried out by using a Rigaku D/max-RB diffractometer (40kV, 120mA) with a graphite-monochromatized Cu-K α radiation ($\lambda=0.15418\text{nm}$).

RESULTS AND DISCUSSION

1. *Melting behavior*

In Fig. 1a is given the DSC thermogram of the as-synthesized polymer or the homopolymer A on heating. There appear totally three endothermic peaks at 174°C, 182°C and 192°C, respectively. In combination with the microscopic observations, it was found that the most parts of sample are melted and transformed into the isotropic state in the range of 175°C to 180°C, whereas the rest parts could still keep optically anisotropic below 192°C. Such a multiple melting behavior was considered to be originated from somewhat of widely distributed molecular weight and also probably due to certain different packing structures of polymer chains which may melt at different temperatures.

As mentioned in the introduction section, the thermal history of LCPs may influence significantly on the phase transition behavior and it seems also applicable to the present case. In Fig. 1 are several represented DSC curves

of the samples which have been cooled from the different states of this compound. Curves b and c are recorded for the samples cooled from 186°C (at this temperature the meltings related to the two DSC peaks around 174°C and 182°C are completed) with cooling rate of 20°C/min and 2°C/min, respectively.

During the cooling process the samples are crystallized for example around 145°C for the 20°C/min cooling case and higher crystallinity can be

reached if the rate was lowered. Thus obtained crystals melt and transform to the isotropic phase at about 170°C which is lower than the melting points (T_m) of the as-synthesized crystals. In Fig. 2 are compared the X-ray diffraction powder patterns of (a) the as-synthesized polymer and the samples cooled from 186°C but at different rate of (b) 2°C/min and (c) 0.5°C/min, respectively. It is suggested that the as-synthesized and cooled samples may be different in their crystal structures. The small endothermic peak at about 194°C in these DSC curves (Figs. 1b and 1c) was found to behave independently of the 170°C melting peak, and may be related to certain other transition process as discussed later.

If we cooled the sample from temperatures above the highest transition point at 192°C, then in this case, the isotropic liquid will not transform to a crystalline state, but changes only to an amorphous state under a glass transition temperature, regardless of changing the cooling rate. Except for a glass transition, the obtained sample shows no DSC peak in the reheating process (see curve d in Fig. 1). In other words, the sample has completely lost its recrystallization ability in the cooling process. In combination with the fact that the molecules are possible to crystallize in a cooling process from the partially isotropic state, then it is reasonable to suppose that there may exist a significant difference between the molecular structures in the partially and purely isotropic states. That is to say, the molecular

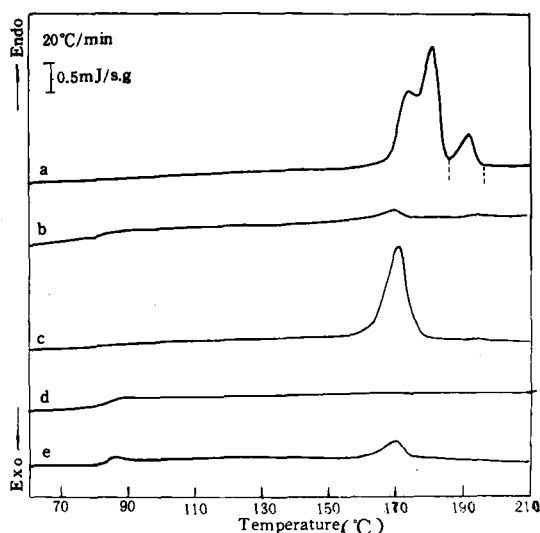


Fig. 1 DSC thermograms of the samples obtained by cooling the as-synthesized polymer from different states

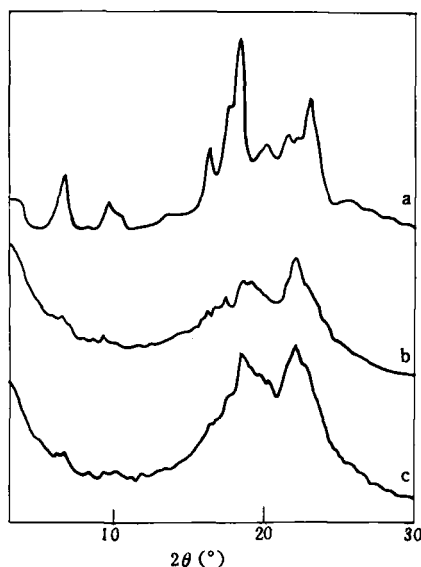


Fig. 2 X-ray diffraction patterns of (a) the as-synthesized polymer and (b), (c) the samples cooled from the partially isotropic state at rates of 2°C/min and 0.5°C/min, respectively

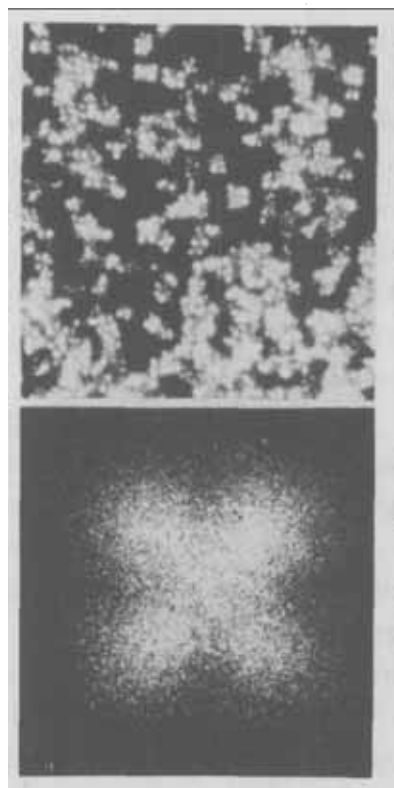


Fig. 3 Optical micrograph and SALS Hv pattern of the sample cooled from the purely isotropic state with applying a pressure to sample

conformations in the partially isotropic state may not be disordered very much yet, in comparison with those in the unmelting state. On the contrary, the conformations will be disturbed completely when raising the temperature beyond the highest transition point of about 192°C, and thus the disturbed molecular chains are not possibly returned to a morphology suitable for crystallization on cooling. The potential energy barrier between the different molecular structures in the crystalline phase and in the states from which the polymer chains are possible and impossible to crystallize may be somewhat higher, in comparison with conventional crystalline polymers.

Curve e in Fig. 1 shows a DSC thermogram in reheating process measured on a sample also cooled from the purely isotropic state. In this case we have applied a pressure during cooling process perpendicularly to two glass slides within which the sample was inserted. There grew up many

small size crystals after such a cooling, as shown in Fig. 3. The SALS Hv pattern is a typical four-leaf pattern of spherulites. These spherulites melt and transform to the isotropic phase almost within the same temperature region as in the cases of curves b and c in Fig. 1. The mechanism of the pressure-stimulated crystallization is not very clear at present, probably the pressure could lead the polymer chains to be oriented and crystallized more easily within a plane such as the plane parallel to the slides, by exceeding the potential energy barrier between the different chain conformations as well as the different aggregation states in the purely isotropic liquid and in the crystalline phase.

It has been surmised from the above discussions that the molecular morphology or chain conformation may affect strongly the polymer chain aggregation state as well as the thermal behavior of the samples. Because of its complicated chemical structure, the polymer chains may take various conformations especially in the melting state and they may be accumulated together with various aggregation styles. For main-chain LCPs, the linearity of rod-like mesogens is in general required as one of the necessary conditions for organizing the mesomorphic structure. However, the present nonliquid crystalline polymer is not spatially linear as can be seen in its fully extended structure illustrated schematically in Fig. 4. In this scheme only a planar

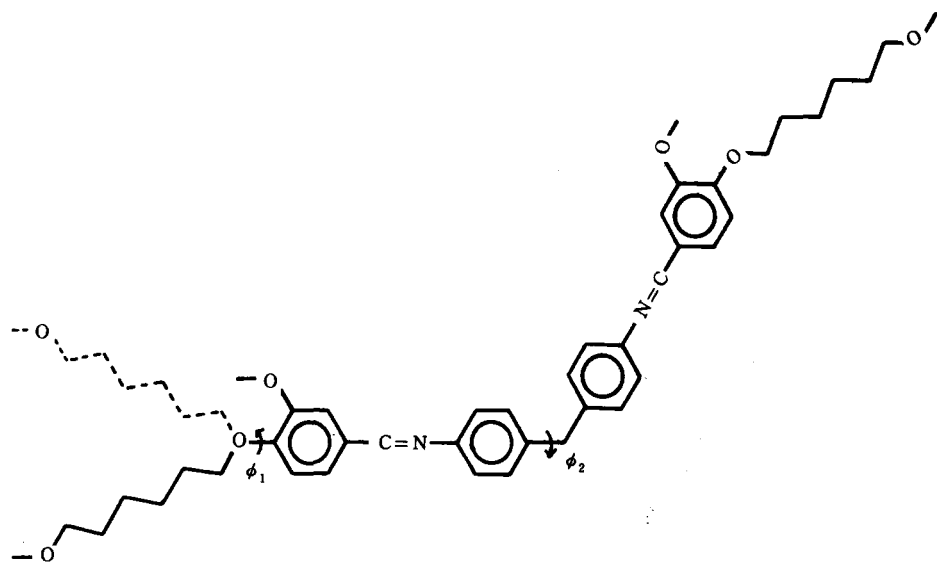


Fig. 4 Schematic illustration of a fully extended planar structure of polymer chain including a hard and two flexible segments

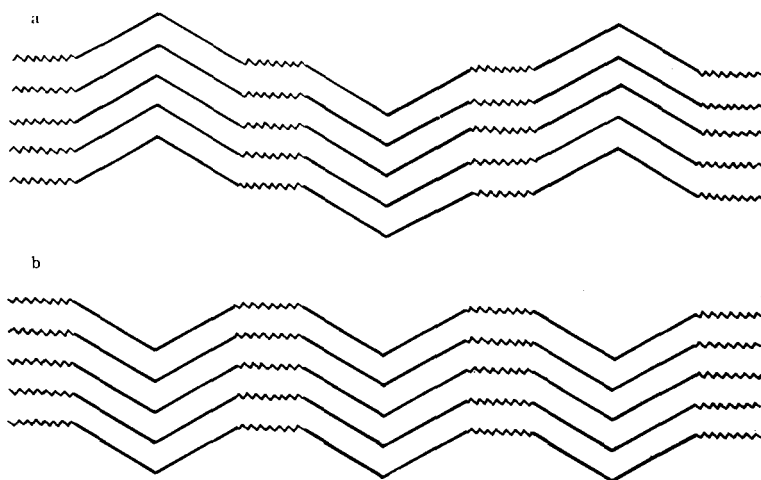


Fig. 5 Schematic illustration of possible polymer chain aggregation models. The solid lines and springs are used to represent the hard and flexible segments respectively

structure with the all-trans conformation in the flexible spacers is drawn for convenience, although the actual chain structure, especially the conformation in the spacers may be considerably irregular in the melting state. The non-linearity of the hard segments is due to the almost unchanged bond angle at the Ph-CH₂-Ph part. In such a situation, it is necessary to imagine how the polymer chains are aligned and aggregated in the crystalline and melting states. In the structure of Fig. 4 the two dihedral rotations around the Ph-O and Ph-CH₂ bonds expressed respectively by φ_1 and φ_2 are expected to be particularly important in altering the whole shape of the chain structure. It is obvious that under the geometry drawn by solid lines the two adjacent soft segments will be aligned nearly parallel to one another and along almost the same straight line. However if rotating largely the soft spacer around the Ph-O bond (φ_1 rotation) such as by an angle of 180°, then the nearly parallel or linear relationship between the soft segments will no longer be realized, resulting in quite bent or disordered geometry of polymer chains on the whole. We have considered two models, as illustrated schematically in Figs. 5a and 5b, for describing the possible chain structures and aggregation states in the crystalline state. The bent solid lines and springs are drawn to represent the hard segments and soft spacers, respectively. The soft spacers within and among polymer chains are all oriented parallel to each other and the corresponding bent hard segments between the different molecules are

also arranged in parallel with one another. In model a which was drawn by extending the chain structure of Fig. 4, the two neighboring hard segments along the polymer chains are supposed to be directed in an opposite sense or a sense of trans conformation with respect to the spacer between them. Although this model is drawn quite regularly, actually there may be introduced considerable disorders within the chain conformation and aggregation state particularly during the melting of crystals, and the hard segments are not necessarily all oriented just within the same plane as illustrated. If the conformations in the flexible spacers were destroyed and became sufficiently random, then the adjacent grouped hard segments along the chains are also possibly directed with the same sense as illustrated in model b.

In practice, the samples were found for the most part to melt and transform into the isotropic liquid around the two T_m points at 174°C and 182°C respectively, and only for a small part to remain optically anisotropic below the highest transition temperature of about 192°C. According to the fact that the crystallization is still possibly realized on cooling from the partially isotropic state (lower in temperature than 192°C), then we could consider that the polymer chain structure and aggregation state may not be disturbed very much yet at this melting stage. So as a plausible explanation, the phase transition around 192°C may be originated from a structural change between such a partially disturbed structure and the completely disordered liquid. At present, however, it is still difficult to ascertain this assumption, and we cannot exclude other possibilities that the small part of sample with optically anisotropic property is more or less related with the crystallinity or liquid-crystallinity. For convenience, hereafter we designate the temperature of this indefinite phase transition as T_x . Once heated the sample to the purely isotropic state over the T_x , then the nearly linear-like chain structures shown in Figs. 5a and 5b will be disordered completely and the sample will lose its recrystallization ability on cooling. Consequently, there may exist a relatively higher potential energy barrier in the chain conformation and aggregation state between the purely isotropic liquid and the crystalline phase, in comparison with the cases of conventional crystalline polymer. That is to say, the linear-like chain conformation and parallel packing manner are not easily obtained on cooling from a completely disordered structure. The pressure-stimulated recrystallization behavior on cooling from the purely isotropic liquid, however, may be originated from

certain easier modifications of chain conformation and aggregation style, by exceeding the potential energy barrier.

2. Crystallization behavior on cooling

We will describe in detail the crystallization behavior for the samples cooled from a partially isotropic state. In Fig. 6 are shown several DSC curves measured in the reheating process for thus obtained samples but with the different cooling rates. All of these samples were semi-crystalline at low temperatures. The melting point, T_m , the transition temperature, T_x , and also the corresponding enthalpy changes during these phase transitions,

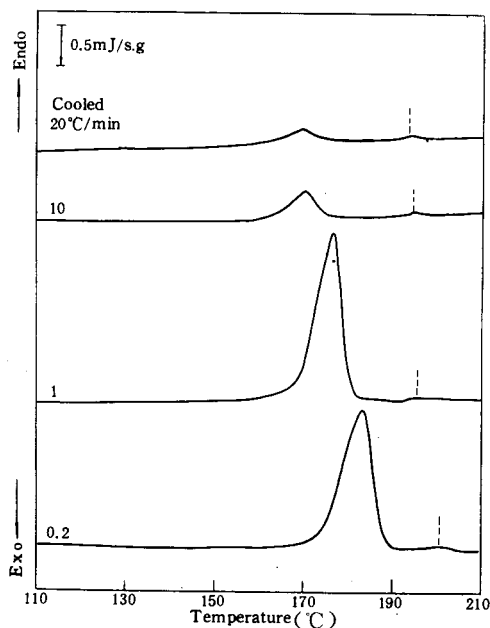


Fig. 6 DSC thermograms of the samples obtained by cooling the as-synthesized compound from its partially melting state but at different rates

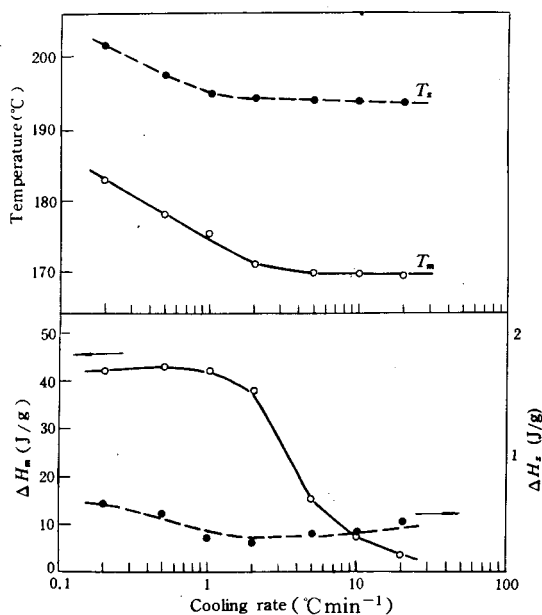


Fig. 7 Transition points, T_m and T_x , and enthalpy changes, ΔH_m and ΔH_x , plotted vs. the cooling rate

ΔH_m and ΔH_x , are plotted in Fig. 7 vs. the cooling rate. It can be seen that for the rapid coolings the obtained crystals have almost the same T_m of about 170°C and T_x of about 194°C, the former is lower and the latter is slightly higher than the corresponding temperatures of the as-synthesized compound (see Fig. 1). For slow cooling, however, not only the T_m but also T_x are increased significantly with decreasing cooling rate. It can also be observed a rapid increase in ΔH_m with decreasing cooling rate and such increase is

almost ceased when the rate is lower than $1^{\circ}\text{C}/\text{min}$. This indicates that the sample is easy to crystallize on cooling from the partially isotropic state and higher crystallinity can be reached if the cooling rate was lowered. From the fact that after getting a maximum of crystallinity the T_m is still increased in the slow cooling cases and the samples obtained by both the rapid and slow cooling may have the same crystal structure as supported by the X-ray diffraction data shown in Figs. 2b and 2c, then it could be considered that the increase in T_m may arise from more complete growth of crystals, such as a growth in crystalline domain size or thickening in lamellar structures.

As for the transition process occurring around T_x , the ΔH_x is much smaller than the ΔH_m and is almost unchanged by varying the cooling rate, but the T_x could still be increased remarkably as in the case of T_m . This increase may also be originated from more perfecting of the corresponding structure, leading to increase in its thermal stability. The T_x as well as T_m increasing behavior with lowering the cooling speed or crystallization rate is similar to some other polymer systems, in those cases the melting temperature was observed to be significantly raised by annealing the samples in their crystalline or melting state^[10-12].

Keywords:

Aromatic poly(azomethine ether); Nonlinearly shap conformation; Melting; Crystallization; Aggregation

REFERENCES

- [1] Hou, J. A.; Li, X. F.; Zhang, Q. Z., et al., *Ann. Rep. Polym. Phys. Lab., Academia Sinica*, **1992**, p. 76.
- [2] Hu, S.; Xu, M.; Li, J., et al., *J. Polym. Sci., Polym. Phys. Edn.* **1989**, 27, 1749.
- [3] Percec, V. and Lee, M., *Macromolecules*, **1991**, 24, 2780.
- [4] Wu, W.; Li, Z.; Zhou, Q., et al., *Ann. Rep. Polym. Phys. Lab., Academia Sinica*, **1992**, p. 72.
- [7] Ciferri, A.; Krigbaum, W. R. and Meyer, R. B., in "Polymer Liquid Crystals" Academic Press, New York, **1982**.
- [8] Blumstein, A., in "Polymer Liquid Crystals" Plenum Press, New York, **1985**.
- [9] Chung, T., *Polym. Eng. Sci.*, **1986**, 26, 901.
- [10] Wissbrun, K. F.; Kiss, G. and Cogswell, F. N., *Chem. Eng. Commun.*, **1987**, 53, 149.
- [11] Winter, H. H. and Lin, Y. G., *Polym. Prepn.*, **1989**, 30 (2), 524.
- [12] Lin, Y. G. and Winter, H. H., *Macromolecules*, **1991**, 24, 2877.