

THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS—SOLID STATE POLYMORPHISM

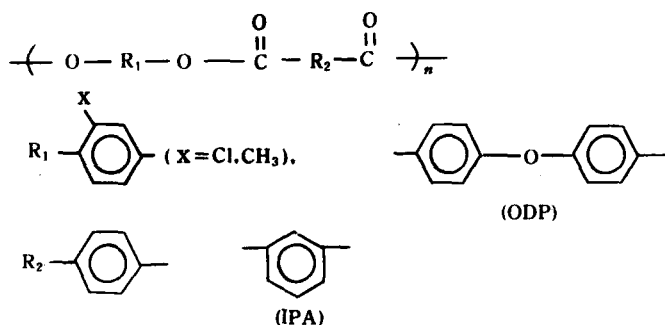
XIE ping (谢 萍), LU Daohui (陆道惠), BAO Jingsheng (宝净生)

(Institute of Chemistry, Academia Sinica, Beijing)

ABSTRACT

This paper offers some new evidence on the polymorphism of solid state of liquid crystalline aromatic copolyesters which were prepared in our laboratory. The effects of different treatment conditions (quenching and annealing) on solid structure have been examined mainly by DSC and X-ray diffraction. The discussion focuses on the supercooled mesophase and low temperature solid-solid transition, the shifting of double melting peaks of annealed samples and the changing of their ΔH data depending on the treatment temperature, time and thermal scanning rate.

In recent years there has been widespread interest in the polymer systems which display liquid crystalline behavior in the molten state. For the purpose of processing and application, in addition to mesophase and transitions in melt state, the solid structural feature is also a noticeable object for study. These polymers, like a number of low molecular weight liquid crystals, frequently show solid state polymorphism. This property is due to the existence of different metastable states which depend on the thermal and mechanical history of the samples. Previous reports confirmed the existence of supercooled mesophase and low temperature solid-solid transition for quenched liquid crystalline polymers^[1-3]. This paper offers some new evidences on the polymorphism of solid state of liquid crystalline aromatic copolyesters which were prepared in our laboratory^[4]. This series of LC polymers has the following structure:



EXPERIMENTAL

Preparation of samples

The synthesis of the copolymers was described in the previous paper^[4]. A small amount of the polymer was placed between two pieces of metal plate on an oven which had been preheated to the temperature of 40–50 °C above the melting point of the polymer, and pressed into film and then rapidly cooled down. Some of such films were annealed at constant temperature in heating tube or

DSC cell under nitrogen atmosphere.

The thermal properties were measured on Du Pont 1090 model Thermal Analyzer coupled to a DSC module under nitrogen atmosphere.

X-ray diffraction spectra was obtained by using 3014 model diffractometer (Japan Physical Electrical Machine Company) and powder method with $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Supercooled mesophase and solid-solid transition

Fast cooling the melt from its anisotropic phase leads to a glassy modification with supercooled mesophase. The most straightforward identification is the optical texture observed between crossed-polars (Fig. 1), which looks like that of nematic melt. Fig. 2 shows a group of DSC curves of quenched samples of LC copolyesters (chloro-series). Table 1 summarizes the corresponding data of T_g , T_{cc} (cold crystallization) and T_m obtained from DSC scans. They reveal that T_g 's of LC copolyesters are much higher than that of the general amorphous polymers and the intensity of melting peak is rather low, it is suggested to be due to the existence of a supercooled mesophase. The structured mesomorphic domains hinder the free rotation of segments and lead to higher T_g . Small melting peak may be attributed to the fact that there is no much structural difference between the melt and the solid.

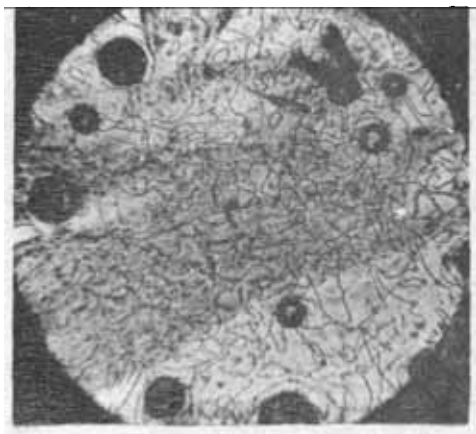


Fig. 1 Optical texture of supercooled mesophase

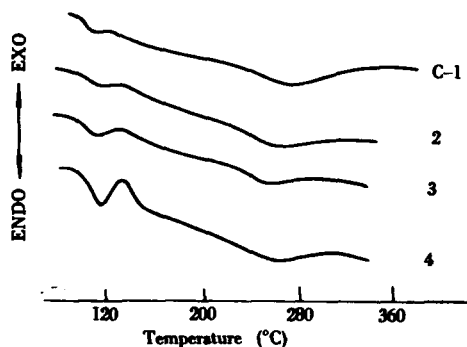


Fig. 2 DSC curves of quenched samples of LC copolyesters (chloro-series)

Cold crystallization

An exothermic peak is fairly well detectable above T_g . It is a solid-solid transition called cold crystallization. This transition may be attributed to local rearrangement of metastable supercooled mesophase towards a more highly ordered phase^[5,6]. Freeze-in liquid crystalline domains may be acted as the nuclei which induces the local ordering. The cold crystallization temperature increases with the increase of the content of kinking component, and this is easy to be understood. The molecular conformation of LC polymers with two kinds of kinking components may be simulated by elastic helical model which containing both torsional and bending energies.^[7,8] When increasing the content of the bending content IPA tightens the helix, the local ordering rearrangements should be carried out under higher temperatures.

Low temperature solid-solid transition

By heating the quenched samples from low temperature region, an endothermic peak occurs at

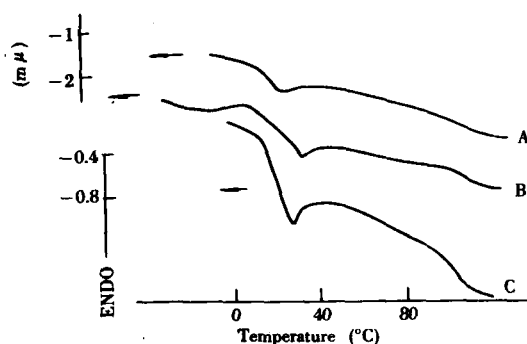
Table 1 T_g , T_{cc} and T_m of quenched samples of LC copolyesters

Number of samples	Content of kinking components (mole%)		T_g (°C)	T_{cc} (°C)	T_m (°C)
	ODP	IPA			
C-1	30	10	102.2	121.2	289.1
2	30	15	107.2	127.3	266.9
3	30	20	104.6	127.5	256.8
4	30	25	107.0	133.4	254.7
M-1	30	10	108.5	139.2	291.2
2	30	15	110.1	135.0	259.4
3	30	20	106.6	140.6	250.9
4	30	25	114.4	176.4	254.6

C- and M- refer to chloro- and methyl- series LC copolyesters respectively.

the low temperature region far below the T_g . Fig. 3 shows DSC curves of three samples quenched in different conditions. The position of the peak depends on the cooling rate. This low temperature solid-solid transition is also relative to the existence of the supercooled mesophase. By rapidly cooling the liquid crystalline melt, the structured mesophase domains would be frozen-in, and then it can be revealed in the form of residual enthalpy during thermal scanning. This situation is similar to that which was shown from physical-aged samples of some polymers, however with much larger enthalpy (ΔH 2J/g).

Frosini and others have also observed low temperature endothermic peaks at -225 and -235°K for LC copolyesters composed of rigid aromatic segments and flexible spacers,^[2] in accordance with our results. This indicates that the nature of this phenomenon does not depend on molecular composition, but only depends on the existence of the supercooled mesophase. Molecular composition only affects the energy level (position of peak) of this transition.

**Fig. 3** DSC curves of three samples quenched in different conditions (low temperature region)

(A) ice water; (B) air; (C) cold water

Annealing and double melting peaks

The quenched samples in form of film were annealed under nitrogen atmosphere and examined by DSC, the melting peak splitted into two. The lower temperature peak shifts to the higher temperature region with increasing annealing temperature and extending annealing time, while the area of the lower temperature peak increases and the area of the higher temperature peak reduces. As the samples was annealed at the temperature near melting point of original sample, the double peaks were nearly merged into a single one (see Fig. 4 and Table 2,3). This phenomenon has been observed for PET and many other polymers^[9-12]. According to the standpoint of Holdsworth^[10] and Yu^[9] the occurrence of double peaks is due to recrystallization during thermal scanning. As annealing at lower temperature, imperfect crystallites were formed. During the DSC thermal scanning partial melting and recrystallization of the imperfect crystallites led to the formation of more perfect crystallites. The lower temperature peak corresponds to the melting of imperfect crystallites and the higher peak corresponds to the melting of more perfect crystallites. It should be noticed that the higher temperature peak is broad and shallow. This suggests that the recrystallization is a process of numerous steps, and is finished only in a higher temperature region.

Table 2 Data of double melting peaks of LC copolyesters annealed at different temperatures (8 h)

Number of samples	C-1		C-2		M-2	
$T_m(^{\circ}\text{C})$ Annealing temp. ($^{\circ}\text{C}$)	T_1	T_2	T_1	T_2	T_1	T_2
no	289.1		266.9		259.4	
135	173.6	285.1	169.1	265.6	166.1	258.7
190	224.6	289.8	241.6		211.3	259.6
240	268.0		253.3		285.4	

Table 3 Data of double melting peaks of LC copolyesters (C-3) annealed at different times (200 $^{\circ}\text{C}$)

Annealing time (h)	$T_1 (^{\circ}\text{C})$	$T_2 (^{\circ}\text{C})$
1	219.7	258.6
2	221.2	258.4
5	225.1	257.8

The relative peak area (ΔH) is strongly dependent on the heating rate. Two samples were annealed in the following conditions: 130 $^{\circ}\text{C}$, 6.5 h and 180 $^{\circ}\text{C}$, 6.5 h were determined by DSC with different heating rates. (Fig. 6 & 7) ΔH increased with the increase of heating rate to a maximum and

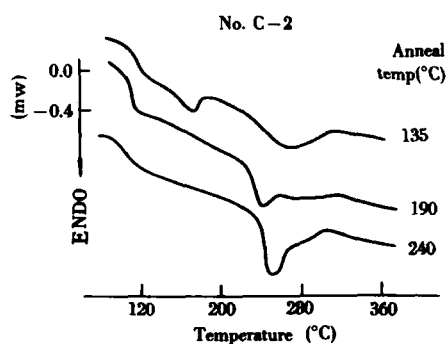


Fig. 4 DSC curves of the samples annealed in different temperatures (No. C-2, 8 h)

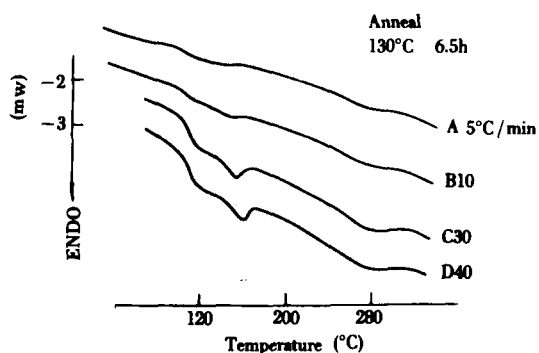


Fig. 5 DSC curves of annealed samples (130°C, 6.5 h) with different heating rates

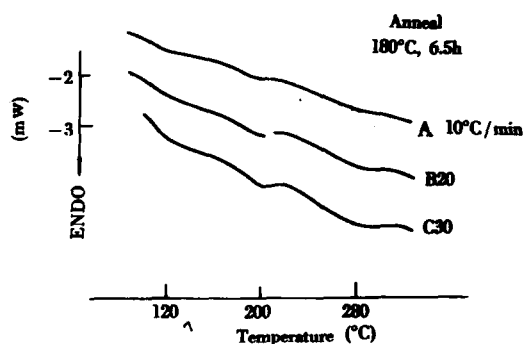


Fig. 6 DSC curves of annealed samples (180°C, 6.5 h) with different heating rates

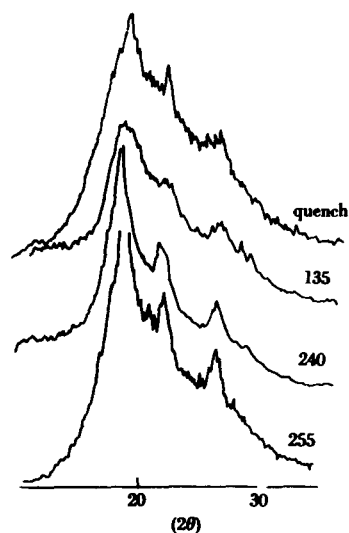


Fig. 7 X-ray diffraction curves of the samples annealed at different temperatures

then decreased with further increasing the heating rate (see Table 4). This is due to the fact that such recrystallization will occur only if its rate can catch up with the scanning rate. Slower heating rates allow more recrystallization, so that the melting enthalpy ΔH would be reduced due to the offset for the crystallization enthalpy. On the other hand, although the higher heating rates do not favor the recrystallization during scanning, yet ΔH may also decrease if the melting rates fall behind the DSC scanning rates. So over a maximum ΔH turns to decrease with further increase of the heating rate.

The experimental results demonstrates the existence of numerous metastable states in solid state of liquid crystalline polymers over a wide temperature range. This is relative to a long relaxation time. Polymorphism is the most obvious character of solid physics of thermotropic LC polymers. Some authors suggested^[11,12] that double melting peaks correspond to two fundamental different crystalline morphologies (the folded chain crystal and the extended micellar crystals). The occurrence of the double melting peaks of the rigid LC copolyesters indicates that this phenomenon may have origins other than the interconversion of the two fundamental different crystalline

Table 4 Effect of heating rate on double melting peaks

Annealing condition of samples	Heating rate (°C/min)	T_1 (°C)	ΔH_1 (J/g)	T_2 (°C)	ΔH_2 (J/g)
130 °C, 6.5 h	15	143	1.16	265.9	4.01
	10	148	1.85	267.2	4.45
	30	153.5	1.93	269.3	6.31
	40	158.5	2.00	270.7	6.49
	50	158.6	1.77	283.4	5.78
180 °C, 6.5 h	10	194.7	1.18	266.9	3.44
	20	201.3	1.81	278.6	4.23
	30	202.5	1.82	267.7	5.46

morphologies. X-ray diffraction curves (Fig. 7) show that the positions of several diffraction peaks of the samples with different thermal history are almost unchanged and the intensity of the diffraction increases with the increase of annealing temperature. This indicates that the parameters of the unit cell are almost unchanged, while the degree of the crystal perfectness increased with the increase of annealing temperature.

Keywords:

Supercooled mesophase, Cold crystalline, Low-temp. solid-solid transition, Double melting peaks.

Acknowledgement The authors thank Mr. Chen Shouxi for taking the photograph of optical texture.

REFERENCES

- [1] Frosini, V., and Marchetti, A., *Petris. S. de Polym. prepr.*, **1983**, 24(2), 302.
- [2] Frosini, V., and Marchetti, A., *Makromol. Chem., Rapid commun.*, **1982**, 3, 795—801.
- [3] Frosini, V.; De Petris, S.; Calli, G. and Chillini, E., "RECENT ADVANCES IN LIQUID CRYSTALLINE POLYMERS" Ed. by Lawrence, C.L., **1985**, 57—77.
- [4] Xie Ping, Lu Daohui, Bao Jingsheng, *Polym. Commun.*, **1985**(3), 250—257.
- [5] Crebowicz, J. and Wunderlich, B., *J. Polym. Sci. -Phys.* **1983**, 21, 141—150.
- [6] Balachandar, B.; Balakrishnan, T. and Kothandaraman, H., *Makromol. Chem.* **1983**, 184, 443—453.
- [7] Ten Bosch, A.; Maissa, P. and Sixou, P., *Polym. Prepr.* **1983**, 24(2), 246.
- [8] Fujii, M.; Nagasaka, K.; Shimada, J. and Yamakawa, H., *Macromolecules* **1983**, 16, 1613—1623.
- [9] 于同德、卜海山、胡家琨、张 炜、顾巧英, 高分子通讯 (*Polymer Communications*), **1981**(6), 461—467.
- [10] Holdsworth, P. J. and Jones, T. A., *Polymer*, **1971**, 12, 195.
- [11] Roberts, R. C., *Polymer*, **1969**, 10, 117.
- [12] Bell, J. P. and Murayama, T., *J. Polym. Sci., A-2*, **1969**, 7, 1059.