

MESOMORPHIC BEHAVIOR AND MULTIPLE MELTING TRANSITION OF AROMATIC POLYESTER FRACTIONS

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Abstract

Fractions of an aromatic polyester have been studied by DSC, polarizing microscopy, SALS and WAXS techniques. The intrinsic viscosity of the samples in tetrachloroethane is ranging from 0.197 to 0.591 dl/g. All the samples exhibit enantiotropic liquid crystal behavior, and the thermal stability of mesophase decrease with lowering the molecular weight of the fractions. The glass transition temperature keeps almost constant for all the samples, however its value for supercooled mesophase is about 20°C lower than that for amorphous phase. Multiple melting phenomenon was also found for samples crystallized from their mesophases and was similar to that observed for nonliquid crystal forming polymers.

INTRODUCTION

Thermotropic polymeric liquid crystals with mesogenic groups and flexible spacers along the backbone are currently the focus of extensive investigation. Besides the practical interest in searching for high strength, high modulus fibers which can be obtained by melt spinning, these studies will give insight into the structure and properties of a specific groups of polymers which may exist in mesophases in addition to the conventional crystalline and amorphous phases. Attention has been paid to studies on the stability of the mesophase and the morphology of unoriented and oriented states of liquid crystal forming polymers of different chemical structure^[1-13]. Although the molecular weight of these polymers should also be expected as an important factor affecting their morphology, molecular motion and properties as in the case of conventional polymers, there are only a few reports on the influence of molecular weight on liquid crystal behavior of polymers^[14-18]. In this paper the transitions of some fractions of an aromatic polyester have been studied.

EXPERIMENTAL

The polymer was synthesized by the solution polycondensation of monomers, 1, 10-bis (chloroformylbenzoyloxy) decane and 2-formyl-1,4-dihydroxybenzene^[14] and has the following structure:

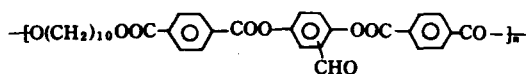


Table 1 The transition temperatures of the samples.

Sample	$[\eta](\text{dl/g})$	$T_g(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$	$T_{kn}(^{\circ}\text{C})$	$T_{nk}(^{\circ}\text{C})$	$T_{ni}(^{\circ}\text{C})$	$T_{in}(^{\circ}\text{C})$
1	0.197	59	33	160	91	173	163
2	0.254	57	38	162	97	178	172
3	0.301	61	36	164	93	182	175
4	0.355	59	40	167	96 (79)	189	184
5	0.474	56	38	166	98	188	186
6	0.591	57	40	162	71 (91)	186	178 (184)

Fractions were obtained by means of precipitation from solution in 1,1,2,2-tetrachloroethane by adding ethanol as the precipitant. A procedure was designed to recover the formyl groups in the fractions thus obtained, which may have been converted to acetals due to reaction with alcohol during fractionation^[14]. The intrinsic viscosity of the fractions in tetrachloroethane at 40°C is ranging from 0.197 to 0.591 dl/g and is given in Table 1.

Differential scanning calorimetry was carried out in a temperature range from -20°C to 220°C using a Perkin-Elmer DSC-4, purged with nitrogen. Indium was used as thermal standard for temperature and enthalpy calibration.

Small angle light scattering studies were performed on an apparatus type LS-1 with He-Ne gas laser ($\lambda = 6328 \text{ \AA}$). The scattering patterns were recorded photographically. A polarizing microscope was used for morphology observations.

The Ni-filtered $\text{CuK}\alpha$ radiation was used for WAXD measurements and the angular dependence of diffraction was recorded on a Rigaku Automatic X-ray Diffractometer type D/max IIIB operating in the reflection mode.

RESULTS AND DISCUSSION

The DSC thermograms of the fractions are given in Figure 1. The main endothermal peak at about 160°C, T_{kn} , is related to the melting of crystals, while a small endo-peak at still higher temperature, T_{ni} , isotropization transition. The data of T_{kn} and T_{ni} are listed in Table 1. These

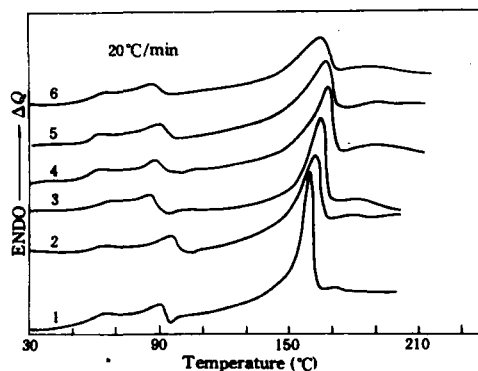


Fig. 1 DSC thermograms of sample 1-6. The heating rate is 20°C/min.

assignments were confirmed by polarizing microscopy observations. At temperatures between T_{kn} and T_{ni} typical texture of nematic mesophase was observed, and it disappeared at temperatures above T_{ni} (Figure 2). SALS studies of these samples have also shown strong mesophase scattering between T_{kn} and T_{ni} (Figure 3).

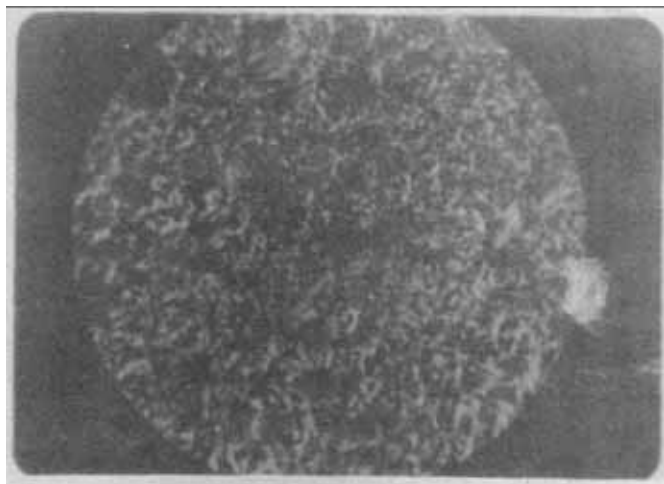


Fig. 2 Polarizing micrograph of sample 1 at temperatures between T_{kn} and T_{ni} .

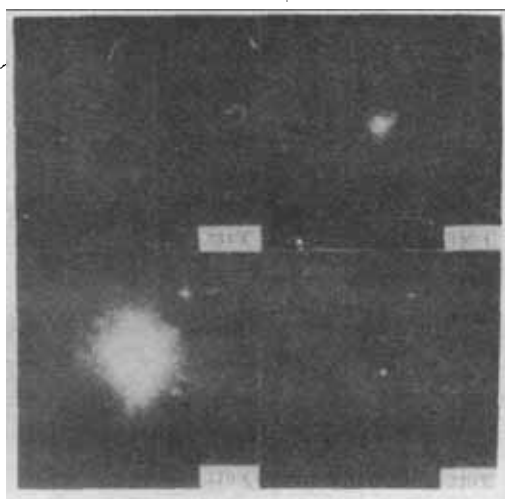


Fig. 3 Hv scattering patterns of sample 4 at different temperatures.

Figure 4 gives the DSC thermograms of these fractions in a cooling process from their isotropic melts. The peak temperatures for isotropic/nematic and nematic/crystalline transitions T_{in} and T_{nk} are listed in Table 1. The supercooling of T_{in} is moderate, usually less than ten degrees, while that for crystallization is as large as about 60 degrees. Some of the fractions show double peaks for T_{in} or T_{nk} transitions which may be resulted from some kind of polydispersity in molecular weight.

Our results indicate that all these fractions show enantiotropic mesophase behavior, although the width of liquid crystal range decreases with decreasing intrinsic viscosity of the fractions, when it is less than 0.3dl/g (Figure 5). However, the fraction 1 did not show a T_{ni} endopeak in heating

process of 10 °C/min as reported in a previous paper of the authors[14], and may seem to be monotropic. It means that the sensitivity in detecting small endopeaks can be improved, if higher heating rate is used. This is clearly shown in Figure 6 which gives the DSC thermograms of sample 5 with different heating rates.

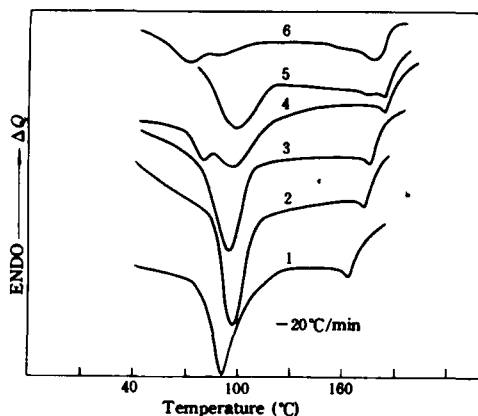


Fig. 4 DSC thermograms of samples 1—6 in the cooling process ($-20^{\circ}\text{C}/\text{min}$)

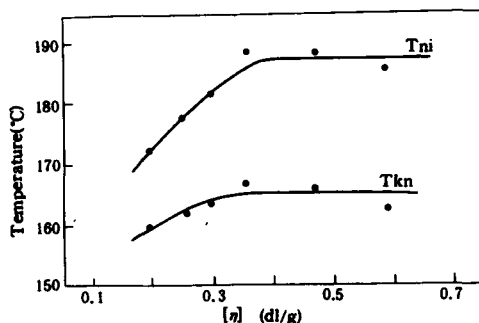


Fig. 5 Dependence of T_{kn} and T_{ni} on the intrinsic viscosity of the samples

The enthalpy change ΔH_{ni} for different samples is plotted in Figure 7. It increases rapidly at low intrinsic viscosities and keeps almost constant, when $[\eta]$ is larger than 0.4dl/g. If the mesomorphic state is considered to be homogeneous and the isotropization—close to an equilibrium transition^[6,10], the entropy change ΔS_{ni} can be calculated according to the equation

$$T_{ni} = \Delta H_{ni} / \Delta S_{ni},$$

and the results are also plotted in Figure 7. The molecular weight dependence of ΔS_{ni} is similar to that of ΔH_{ni} . It means that the monotropic mesophase behavior in the low molecular weight range, expressed as the rapid decrease of T_{ni} , is thermodynamically due to the faster decrease of ΔH_{ni} than ΔS_{ni} with decreasing molecular weight.

The glass transition temperature of samples obtained by precipitation from solutions is plotted against intrinsic viscosity in Figure 8. It keeps almost constant around 58°C in the used intrinsic viscosity range. The lack of molecular weight dependence is possibly due to the crystallization of the samples. The glass transition temperature T_g' for melt cast specimens is also given in Figure 8. T_g' is 20°C in average lower than T_g . As polarizing micrographs exhibit optical texture of mesophase for

all melt case specimens, T_g' should be the glass transition temperatures in the supercooled mesophase, or the transition of anisotropic glass. The liquid crystalline phase is usually supposed to be a more ordered or structured phase than the amorphous phase, and molecular motion is expected to be easier in the latter case. So it is rather surprised that T_g' is lower than T_g . Similar phenomenon has been observed for other liquid crystal forming aromatic polyesters^[19]. For a crystallizable polymer the degree of crystallinity and crystal morphology may significantly influence the molecular motion in the noncrystalline region. Blumstein et al. have shown that the molecules of polyesters with mesogenic groups and flexible spacers along the backbone are highly flexible in solutions as molecules of conventional flexible chain polymers^[20]. The conformation of molecules in the noncrystalline phase for the samples prepared by solution cast and melt cast could be quite different and, possibly, may also give influence on the molecular motion of the specimens. However the real cause of lower T_g' value is not clear yet. This phenomenon is of interest and needs further investigations.

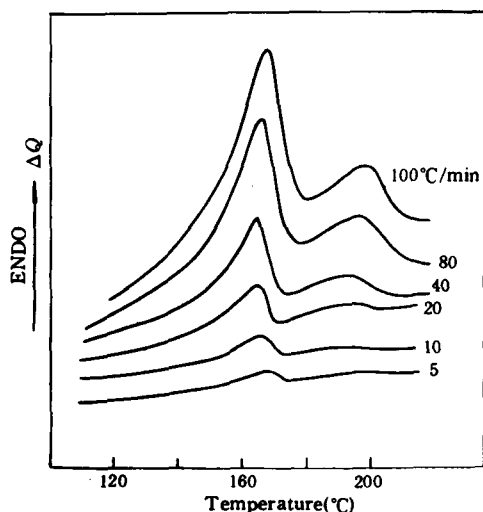


Fig. 6 DSC thermograms of sample 5 with different heating rates

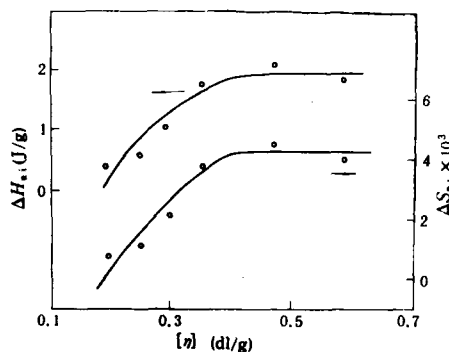


Fig. 7 Dependence of ΔH_{nl} and ΔS_{nl} on the intrinsic viscosity of the samples

For liquid crystal forming polymers, crystals may be formed from amorphous phase of mesophase in the case of solution cast and melt cast respectively. It is interesting to study the difference between these two situations. No difference was found for the melting points of specimens obtained by the two methods. However their enthalpy changes ΔH_{kn} have different values. Specimens obtained by melt cast give less ΔH_{kn} , especially for fractions of higher molecular weight. Annealing at different temperatures for 4 hrs did not increase the ΔH_{kn} value (Table 2). It may imply that the existence of mesomorphic order is, at least, not in favor of obtaining high crystallinity of the samples.

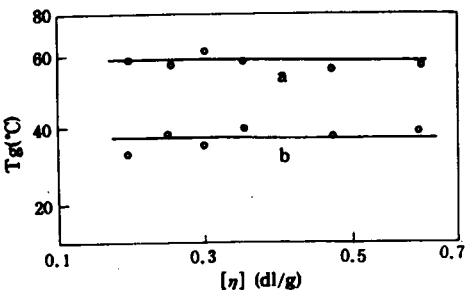


Fig. 8 Glass transition temperature of amorphous and supercooled liquid crystalline phases.
(a) solution cast specimens, (b) melt cast specimens

A small endopeak was observed between T_g and T_{kn} (Figure 1) for all the fractions. Similar phenomenon has been observed for other liquid crystal forming polymers^[1,3,5,8,11,19] and was supposed in some case to be the multiple melting behavior usually observed for polymers like polyethylene terephthalate^[21]. Our results show that the multiple melting phenomenon can also be

Table 2 The enthalpy change ΔH_{kn} of smaples

Sample	$\Delta H_{kn}(\text{J/g})$				
	Solution cast	Melt cast			
		DSC 2nd run	After annealing at		
			40°C	70°C	90°C
1	29.7	25.1	—	23.0	26.3
2	24.7	21.7	23.0	17.6	20.5
3	28.0	19.2	23.0	18.8	20.9
4	25.1	16.3	19.2	13.8	18.0
5	21.7	13.0	16.3	8.4	15.9
6	19.2	13.8	15.5	—	15.9

observed for samples crystallized from the mesophase. Figure 9 gives the DSC thermograms for specimens annealed at 75°C for 4 hrs after melt cast. There is a small endopeak at about 94°C for all the fractions. Results of samples 3 annealed at different temperature are shown in Figure 10. The low melting temperature shifts to higher temperatures with raising the annealing temperature and is 5

to 20°C higher than the latter. Exclusion was found for specimens annealed at 160°C, very close to the main melting temperature. An endopeak at 140°C was observed in this case, and it was supposed that the ordered structure related to this peak was not formed during annealing, but in the cooling process after annealing. X-ray diffraction patterns of samples 2 with different annealing treatments exhibit intensity peaks at the same diffraction angles (Figure 11). It means that the multiple melting behavior is related to crystallites of the same crystal form but of different degree of perfection.

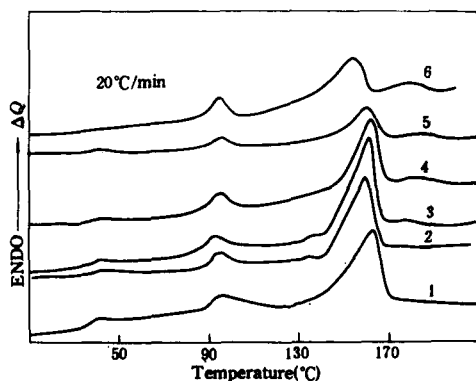


Fig. 9 DSC thermograms of melt cast samples 1–6 after annealing at 75°C for 4 hrs

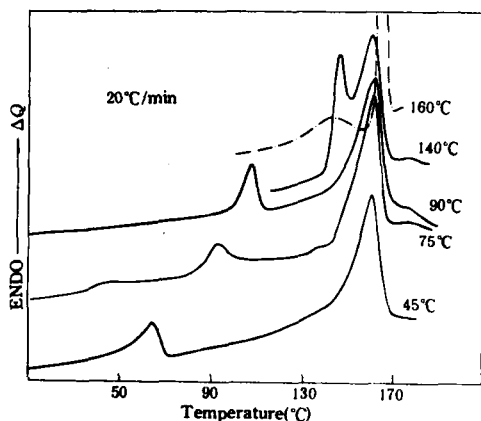


Fig. 10 DSC thermograms of melt cast samples 3 after annealing at different temperatures

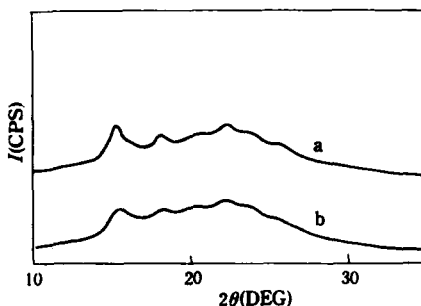


Fig. 11 X-ray diffraction patterns of samples 2. (a) solution cast specimen, (b) melt cast and annealed at 100°C

Keywords:

Aromatic polyester fractions; Thermotropic liquid crystal; DSC

Acknowledgement We are grateful to the National Natural Science Foundation of China for supporting this work under Grant.

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