

TRANSITIONS AND MORPHOLOGY OF MAIN-CHAIN LIQUID CRYSTALLINE POLYMERS WITH X-SHAPED MESOGENS*

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ABSTRACT

The transitions and morphology of a series of main-chain liquid crystalline polymer with X-shaped mesogens were studied by means of DSC, SALS and polarizing microscopy techniques. An even-odd effect was observed for samples with different size of the substituents on the mesogen ends. The isotropization process was similar to that of main-chain polymers with rod-like mesogens. No crystallization was detected for specimens cooling down from their isotropic melt state. However two of the samples may crystallize in cooling process directly from the liquid crystalline state.

INTRODUCTION

Studies on the mesomorphic behavior of thermotropic polymeric liquid crystals with mesogenic units and flexible spacers along the backbone have been reported from various laboratories. In most cases the mesogens were rod-like in shape. The influence of the structure of mesogens and spacers, including the rigidity, the aspect ratio of mesogens and the length of spacers, and also the molecular weight of the polymers on liquid crystalline behavior was investigated. Recently a number of new liquid crystalline polymers have been synthesized. In molecular chains of these polymers disc-like or two dimensional mesogens are introduced instead of the conventional rod-like

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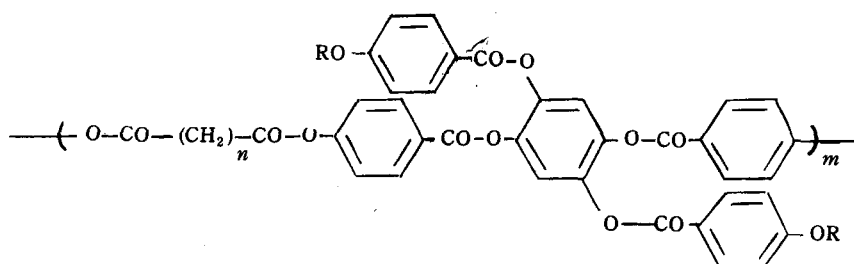
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ones. It is of great interest to study the mesomorphic behavior of these liquid crystalline polymers. In this work a series of main-chain aromatic polyesters having X-shaped mesogens was investigated in order to obtain more insight into the structure-property relationship of the liquid crystalline polymers.

EXPERIMENTAL

The main-chain liquid crystalline polymers used were synthesized by low temperature solution polycondensation of monomers 4, 4'-(alkylene dioxy) dibenzoyl dichloride and 2, 5-dihydroxyl-1, 4 phenylene di-p-alkyloxy-benzoate^[1] and have the following structure:



Polymers of different spacer lengths and alkyl substituents were prepared and were designated as $P(n', n)$, where n' is the number of carbons in the substituent R.

The thermograms of the samples were obtained by using a differential scanning calorimeter Perkin-Elmer DSC-4, purged with nitrogen. The heating and cooling rates were 20 °C/min, and indium was used as thermal standard for the temperature and enthalpy calibration.

Small angle light scattering studies were performed on an apparatus type LS-1 with He-Ne gas laser ($\lambda = 632.8\text{ nm}$). The scattering patterns were recorded photographically. The morphology of the specimens was studied by using an Olympus polarizing microscope type BHS-753P equipped with a hot stage.

RESULTS AND DISCUSSION

The original samples obtained by the precipitation after polycondensation in solution were usually crystalline. Fig. 1 shows the X-ray diffraction pattern of sample $P(4, 8)$ obtained by precipitation from the

solution. The DSC thermograms of a series of samples with different substituent sizes are given in Fig. 2.

They have the same spacer length $n=8$. Two or more endothermal peaks were detected for each sample. According to observations under polarizing microscope with a hot stage, it has been confirmed that the first endothermal peak counted from the high temperature side is related with the isotropization of liquid crystalline phase, while the second endothermal peak is the melting transition.

Typical threaded texture of nematic mesophase was observed in their mesophase temperature range. The other endothermal peaks observed at still lower temperatures may reflect the multiple melting transition phenomenon of the samples, which is well known for conventional polymers like polyethylene terephthalate^[2] and has also been studied for liquid crystalline aromatic polyesters^[3].

The melting temperature T_{kn} and clearing temperature T_{ni} of samples P(1,8)–P(5,8) and the corresponding enthalpy changes are listed in Table 1. The results for samples with the same substituent R, but different length of spacers are given in Table 2.

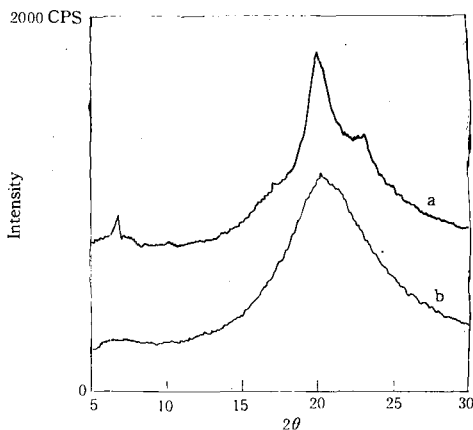


Fig. 1 WAXD pattern of sample P(4,8)
(a) as-precipitated, (b) cooled from isotropic state

Table 1 Data for samples with different substituent sizes

Sample	T_{kn} (°C)	ΔH_{kn} (cal/g)	T_{ni} (°C)	ΔH_{ni} (cal/g)	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
P(1,8)	—	—	208.0	1.11	5610	1.43
P(2,8)	175.8	1.41	222.5	1.18	13250	2.04
P(3,8)	126.1	1.79	195.4	0.88	16540	1.33
P(4,8)	166.0	3.05	195.6	1.22	3610	1.40
P(5,8)	128.6	1.92	169.9	0.94	4760	1.33

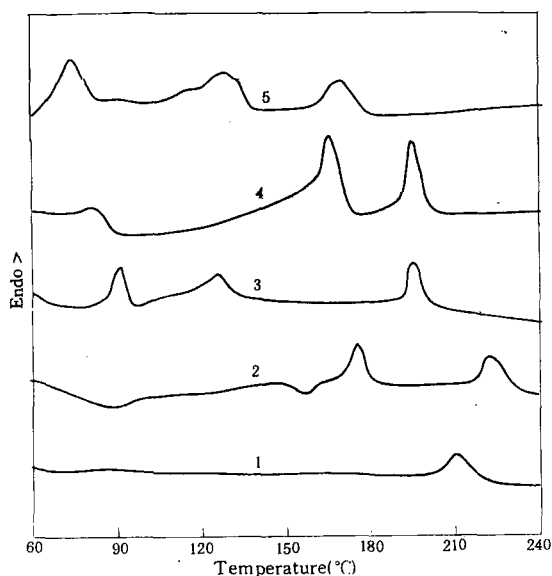


Fig. 2 DSC thermograms for samples (1) P(1,8), (2) P(2,8), (3) P(3,8), (4) P(4,8) and (5) P(5,8) in heating process

Table 2 Data for samples with different flexible spacer lengths

Sample	T_{kn} (°C)	ΔH_{kn} (cal/g)	T_m (°C)	ΔH_m (cal/g)	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
P(4,2)	138.5	0.46	192.6	0.76	3970	1.44
P(4,4)	149.0	1.96	220.0	1.06	6500	1.57
P(4,6)	166.8	1.25	202.4	1.14	5590	1.43
P(4,8)	166.0	3.05	195.6	1.22	3610	1.40

The influence of the flexible spacer length has been reported for main-chain liquid crystalline polymers with rod-like mesogens. Usually the transition temperature, both the melting temperature and the clearing temperature have a tendency to decrease with increasing the length of the spacer with an evident even-odd effect^[4-7]. No regular changes with spacer length were observed for these polymers with X-shaped mesogens in the backbone. However the even-odd effect can be seen for samples with different size of substituent as shown in Fig. 3.

The isotropization transition of samples with X-shaped mesogens was studied by polarizing microscope observations and SALS measurements. The variation of morphology for the sample P(5,8) in a heating process is given

in Fig. 4.

Specific two-phase textures were observed during the transition in a temperature range which was almost consistent with that covered by the T_{ni} endothermal peak in DSC measurements. At the beginning of the transition the new isotropic phase appears as small dark domains formed at places of high thread concentration due to intersection of two or more threads of thread coiling. These growing isotropic domains then contact and combine with each other. Finally a conversion occurs from an anisotropic continuous matrix to an isotropic matrix. At the end of this process the micrograph shows small bright domains embedded in a dark matrix. The size of them decreases with temperature and finally the specimen was completely isotropic.

Fig. 5 shows the SALS H_v patterns of sample P (5, 8) at different temperatures in a heating process. At the temperatures below the transition range circular symmetric H_v patterns were observed, which were typical for nematic mesophase. With increasing temperature in the transition range non-circular symmetric H_v patterns with scattering extended along the $+45^\circ$ azimuthal directions can be observed, especially at the end of the transition process. This scattering behavior can be explained as the result of the two-phase nature of the specimens in the phase transition temperature range^[8].

These transition phenomena are the same as have been observed for some main-chain polyesters with rod-like mesogens.^[8-10] It means that the introduction of X-shaped mesogens does not change the basic mesomorphic behavior of these main-chain thermotropic polymers.

Crystallization from mesophase is one of the basic problems in physics studies of liquid crystalline polymers. It is of great interest to learn whether the higher ordering in anisotropic melt than in isotropic melt will make it easy to crystallize. Fig. 6 shows the thermograms for samples P (1, 8)-P(5, 8) in a cooling process. Only a small exothermal peak related with the transition to liquid crystalline phase was observed for all the samples. The

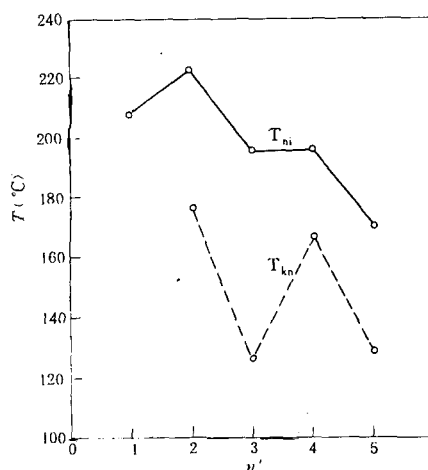


Fig. 3 Dependence of T_{kn} and T_{ni} on the size of the substituents

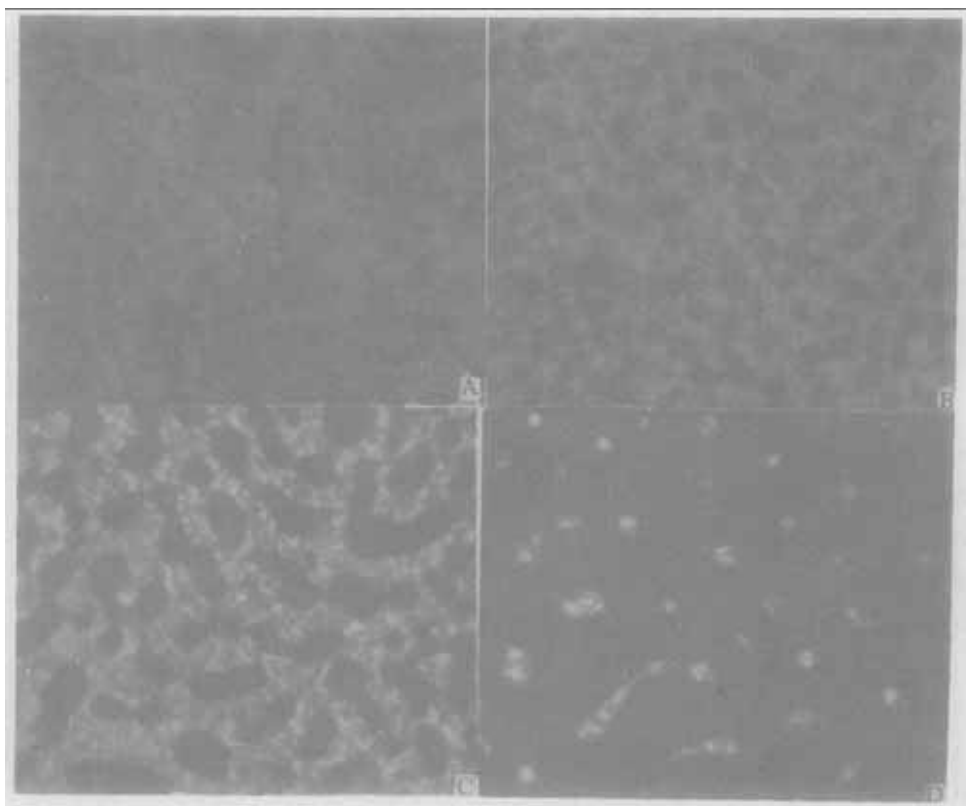


Fig. 4 Polarizing micrographs at different temperatures in a heating process for sample P(5,8) (a) 141°C, (b) 162°C, (c) 163°C, (d) 166°C

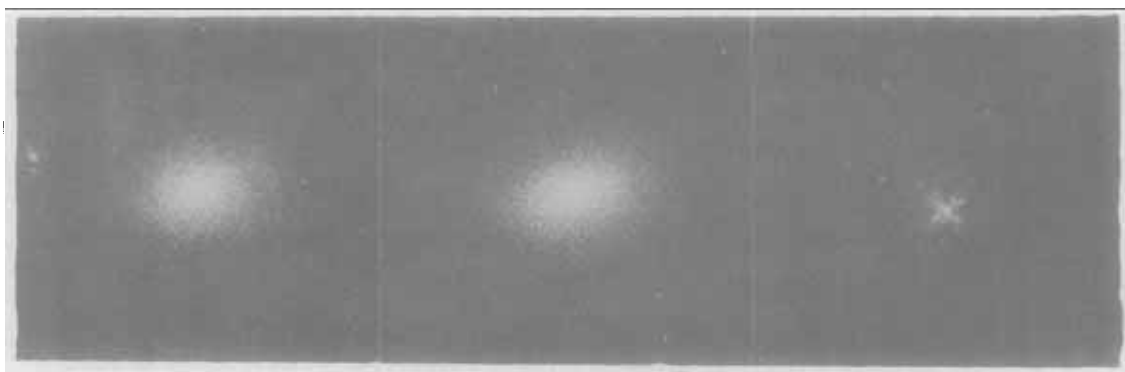


Fig. 5 H_v scattering patterns of sample P (5,8) at different temperatures in a heating process: (a) below T_{ni} transition temperature range, (b) on set of T_{ni} transition, (c) end of T_{ni} transition

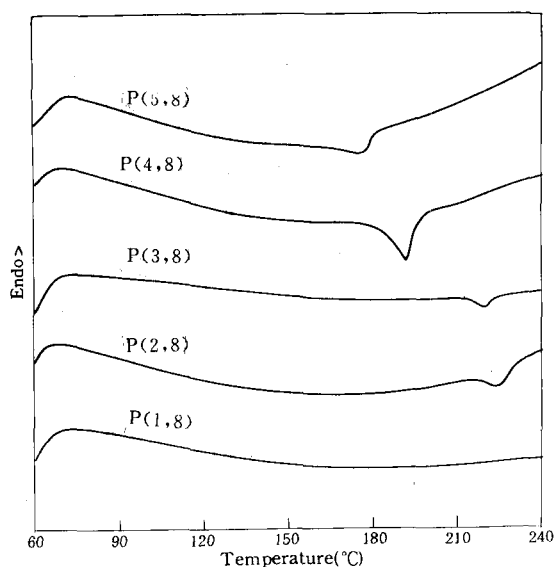


Fig. 6 DSC thermograms of samples P(1,8)-P(4,8) in a cooling process (20 °C/min) from their isotropic melt state

nature of this thermal effect was ascertained by direct microscopic observations in the cooling process and also the WAXD patterns of samples after cooling. X-ray diffraction data of sample P(4,8) is given in Fig. 1, a diffuse halo at about $2\theta = 20^\circ$ was obtained. The same results were observed for sample series P(4,2)-P(4,8). It indicates that these main-chain liquid crystalline polymers with X-shaped mesogen can only crystallize from solutions in a precipitation process but not from their mesomorphic state.

Fig. 7 gives the DSC thermograms for samples P(4,2)-P(4,8) in a cooling process directly from their mesomorphic state, which have never been heated to temperatures above T_{ni} . An exothermal peak indicating the crystalline transition was observed for samples P(4,6) and P(4,8). However

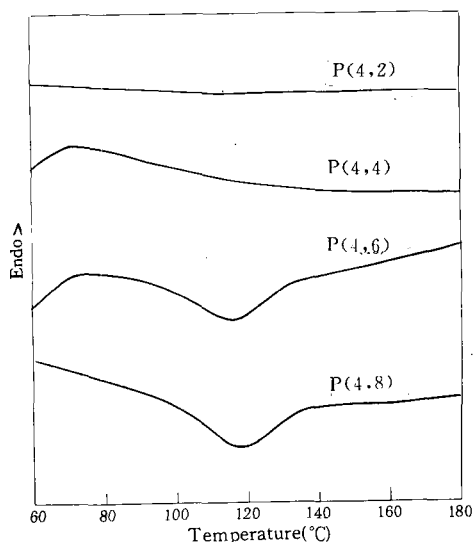


Fig. 7 DSC thermograms of samples P(4,2)-P(4,8) in a cooling process directly from liquid crystalline state

no crystallization occurs for other samples even in these conditions. The results of P(4,6) and P(4,8) imply that the mesomorphic state of these samples could be different depending on the thermal history of the samples.

Keywords:

Liquid crystalline polymer; X-shaped mesogen; Transition; Morphology

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