

SYNTHESES AND CHARACTERIZATION OF A NEW TYPE OF LIQUID CRYSTALLINE POLYESTERS*

BAI Ruke(白如科), WU Chengpei(吴承佩), ZOU Yingfeng(邹应芳),
SUN Wu(孙武) and PAN Caiyuan(潘才元)**

*(Department of Materials Science and Engineering, University of Science and
Technology of China, Hefei, Anhui, 230026)*

Toshiyuki Uryu

*(Institute of Industrial Science, Faculty of Engineering, University of
Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan)*

ABSTRACT

A new type of liquid crystalline polyesters with resorcin as one part of the mesogenic unit connected together by polymethylene, or phenylene group, and lateral groups consisting of a rigid azobenzene as another part of the mesogenic unit were synthesized by interfacial polymerization of diacyl chlorides in 1, 2-dichloroethane and 2,4-dihydroxy-4'-nitroazobenzene in aqueous alkaline solution. The polyester structures were confirmed by proton NMR and IR spectra. Their phase transition behavior and texture were studied by polarizing microscopy and DSC.

INTRODUCTION

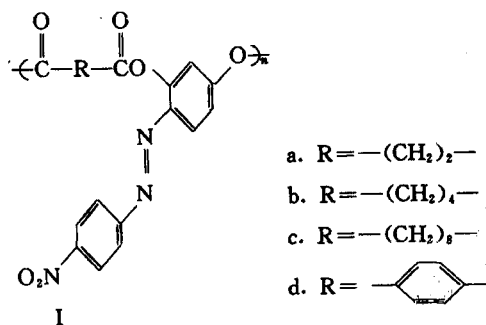
An extensive study on classical main chain and comb-like liquid crystalline polymers with rod-like mesogens results in a well understanding of structure-property relationship^[1]. Recent years, a new type of liquid crystalline polymers, in which the mesogens are attached directly or through flexible spacers to either semi-flexible backbones or rigid backbones has attracted great attention to polymer chemists for studying the influence of lateral groups on the thermal mesophase behavior and the phase structure of liquid crystalline main chain polymers^[2,3]. In general, the mesogenic side groups were attached to the polymer backbone through a flexible spacer in

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** To whom correspondence should be addressed

order to balance the competition between the backbone's random-coil conformation and the side group alignment. If the mesogenic unit as a part of main chain takes part in forming random-coil conformation, another part of the mesogenic unit acts as side chain to arrange anisotropically, the consequence on the mesophase properties should be of interest. Therefore, we designed and prepared a kind of polyester I a, b, c and d in which a part of mesogenic unit was on the backbone, another part acted as a side chain. Their phase transition and texture were investigated.



EXPERIMENTAL

Chemicals

Reagents used in this study were A. R. grade, and used without further purification. Diacyl chlorides were prepared according to the method described in the literature [4]. A white needle crystal of terephthalyl chloride was obtained by recrystallization from n-heptane. These compounds were confirmed by their proton NMR and IR spectra.

1. Preparation of 2,4-dihydroxy-4'-nitroazobenzene(II)

Concentrated hydrochloric acid (18 ml) was slowly added into a solution of p-nitroaniline(8g)in water(12 ml)and crushed ice (18g) with stirring and maintained at below 5°C. Into the reaction mixture, a solution of NaNO_2 (4.2g) in water (24ml) was added dropwise until the test paper of starch-KI became blue.

The obtained azo salt was slowly added into a solution of resorcin (6.38g) in 24 ml of water maintained at below 5°C with stirring. After addition was completed, reaction mixture was adjusted to pH7—9 by adding an aqueous solution of sodium hydroxide, then stirred for additional 2 hr. , and stood overnight. The crude product was collected by filtration and washed with hot distilled water three times. A red brown powder (yield,

70%) was obtained by recrystallization from methanol.

^1H NMR: δ (in $\text{DMSO}-d_6$), 5.87 (phenyl proton between two hydroxy groups, m, 1H); 6.30 (phenyl proton adjacent to hydroxy group, m, 1H); 7.30 (phenyl proton adjacent to azo group, m, 1H); 7.70 (phenyl protons adjacent to azo group, m, 2H); 8.27 (phenyl protons adjacent to nitro group, m, 2H)

IR spectrum: ν 1450cm^{-1} ($\text{N}=\text{N}$); 1315cm^{-1} (NO_2)

2. Condensation polymerization

All polyesters were obtained by interfacial polymerization. A typical polymerization procedure was as the following:

A solution of diacyl chlorides (8.04 mmol) in 1,2-dichloroethane was added into aqueous solution of II (7.72 mmol), tetraethylammonium bromide (0.4g) and sodium hydroxide (0.15g) in distilled water (12 ml) while vigorously stirring. After additional 2 hr, the precipitation occurred by pouring the reaction mixture into methanol. The precipitates were collected by filtration, washed with distilled water, then dried in a vacuum oven at 50°C . The purification of polymers was performed by extraction with methanol in a Soxhlet apparatus for 10 hr. in the case of Ia, Ib and Ic. And Id was purified by pouring its solution in THF into methanol, the precipitate collected by filtration was washed with methanol. All of the purified polymers were dried in the vacuum oven at 50°C .

3. Measurements

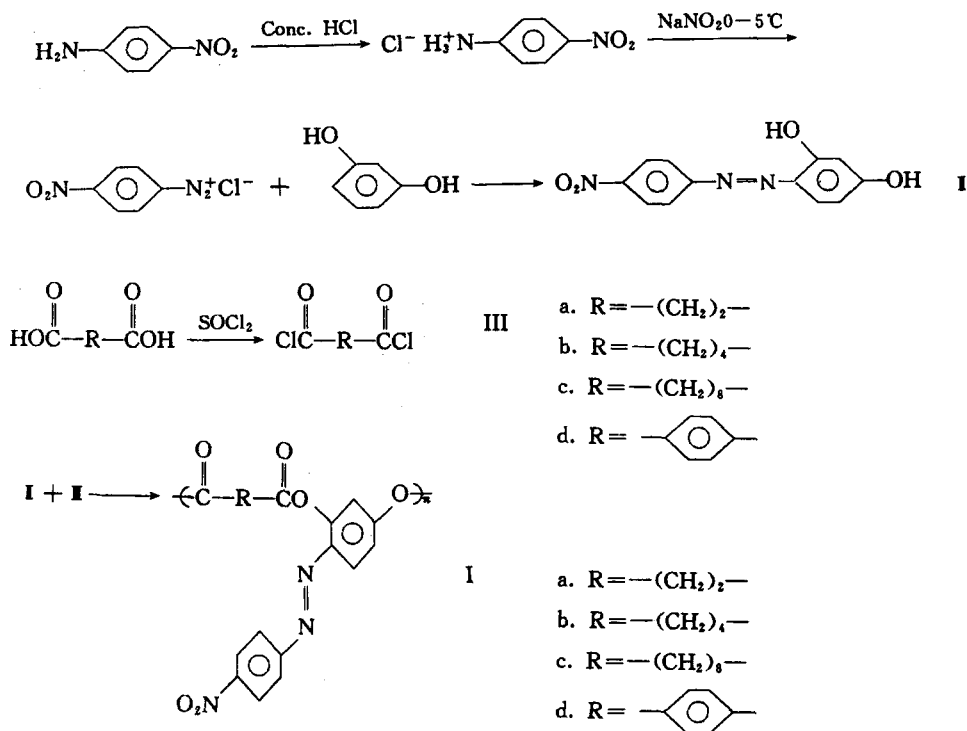
IR and ^1H NMR spectra of the monomers and polymers were measured on Shimadzu-440 IR Spectrometer and Varian EM-360 NMR Instrument respectively. The phase transition temperatures were measured using Perkin-Elmer 2C DSC Instrument operating at $10^\circ\text{C}/\text{min}$. The thermal data were determined from the second heating scans. The glass transition temperatures (T_g) were estimated from DSC. Optical observations were made by using a polarizing microscope (Olympus) equipped with a Mettler FP82 hot stage and FP-800 control unit. The molecular weights of the polymers were determined by GPC in THF on Waters Apparatus calibrated against polystyrene standard.

RESULTS AND DISCUSSION

1. Preparation of the polymers

The syntheses of this type of liquid crystal polymers are shown in

Scheme 1:

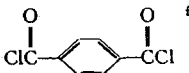


Scheme 1

In the first step, p-nitroaniline was converted to the azo salt which coupled with resorcin at ortho position to form compound II. Diacyl chlorides (IIIa-d) were prepared by treating the corresponding acids with thionyl chloride. Two methods of polymerization, interfacial and solution polymerizations were tried. The polymers with higher molecular weight were obtained only by using interfacial polymerization. Table 1 shows the conditions and results of polymerization. Table 1 shows the conditions and results of polymerization. The starting materials II and III are soluble in methanol. The obtained polyesters were purified by extraction with methanol. The proton NMR data of the polyesters (DMSO- d_6) are listed in Table 2. Comparison proton NMR data of the polymers with that of monomer II, it would be found that phenyl proton between two hydroxy groups and one of another two phenyl protons, which is adjacent to hydroxy group shifted towards lower field. This indicated the occurrence of esterification. The formation of polyesters was also verified by IR spectra of

the polymers in which were found absorption peaks at ν 1765 cm^{-1} in the case of Ia-Ic and 1743 cm^{-1} in the case of Id corresponding to carbonyl groups of ester, absorption peak at 1343 cm^{-1} indicative to nitro group and another peak at 1485 cm^{-1} corresponding to azo group (see Fig. 1). The molecular weight was measured by GPC. The low polymerization degree of the obtained polymers demonstrated that they were oligomers. It may be related to the non-equivalence of two starting monomers and polymerization conditions, such as stirring rate.

Table 1 The conditions and results of interfacial polymerization^{a)}

No.	Compound	Weight(g)	Weight of I ^c (g)	TEAB ^{d)} (g)	NaOH (g)	Yield (%)	$\bar{M}_w^e)$	$\bar{M}_n^e)$	$\bar{M}_w/\bar{M}_n^e)$
1		1.63	2.0	0.4	0.65	75			
2	$\text{ClOC}(\text{CH}_2)_2\text{COC1}$	1.25	2.0	0.4	0.65	80	2000	1100	1.92
3	$\text{ClOC}(\text{CH}_2)_4\text{COC1}$	1.47	2.0	0.4	0.65	78	1600	1200	1.36
4	$\text{ClOC}(\text{CH}_2)_8\text{COC1}$	1.92	2.0	0.4	0.65	70	4100	2600	1.64

a) Polymerization conditions; Temp. 25°C; Time; 2 hr.

b) In 12 ml of 1,2-dichloroethane

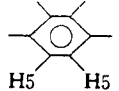
c) In 12 ml of distilled water

d) TEAB; Tetraethylammonium bromide

e) Measured by GPC in THF on Waters Apparatus calibrated against polystyrene standard

f) No solvent dissolving the obtained polymer was found

Table 2 ^1H NMR data of Ia-Id

Polyester		Chemical shift(ppm)					
No	R	H1	H2	H3	H4	H5	H6
	5 6						
Ia	—CH ₂ CH ₂ —	6.80	7.25	7.75	7.85-8.50	3.00-3.20	
	5 6 5	(1H)	(1H)	(1H)	(4H)	(4H)	
Ib	—CH ₂ (CH ₂) ₂ CH ₂ —	6.9	7.30	7.80	7.95-8.30	2.20-2.80	1.25-1.80
	5 6 5	(1H)	(1H)	(1H)	(4H)	(4H)	(4H)
Ic	—CH ₂ (CH ₂) ₆ CH ₂ —	6.85	7.25	7.25	7.95-8.40	2.20-2.80	1.10-1.75
	H5 H5	(1H)	(1H)	(1H)	(4H)	(4H)	(12H)
Id		6.85	7.25	7.80	7.90-8.40	8.25	
	H5 H5	(1H)	(1H)	(1H)	(4H)	(4H)	

2. Liquid crystalline behavior of the obtained polyesters

The liquid crystalline behaviors of the polyesters were investigated by

means of differential scanning calorimetry (DSC) and polarizing microscopy. The DSC scan rate was 10°C/min. The obtained DSC curves are

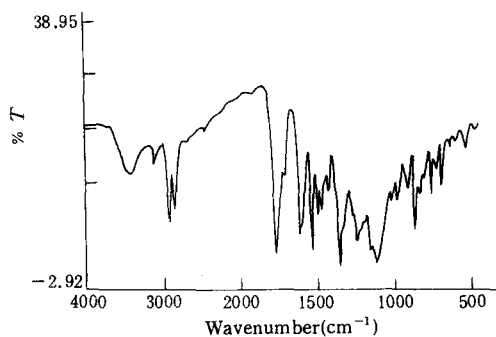


Fig. 1 IR spectrum of polymer Ic

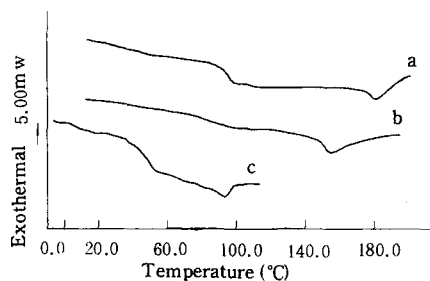


Fig. 2 DSC heating traces of polyesters a. IIa; b. IIb; c. IIC

shown in Fig. 2. The results are listed in Table 3. Generally, phase transition temperatures of liquid crystalline polymers increase as their molecular weight increases in the range of appropriate low molecular weight. It is found that the flexibility of main chain influences both the nature of the mesophase and their thermal transitions (see Table 3). The glass transition (T_g) and isotropization temperatures (T_i) decreased with the increasing number of methylene groups in the main chain. However, the length of alkylene group decreased the mesophase stability. T_g of polyaryl ester Id was not appeared up to 300 °C. Possibly, the hindrance of azo benzene ring which attached to the resorcin ring in the backbone restricted the rotation of main chain. The phenomenon that polyester turned slightly black at about 300 °C was possibly due to the decomposition of azo group before thermotropic liquid crystalline behavior appeared.

Table 3 The structure and phase transition temperature of liquid crystalline polyesters Ia-Id^{a)}

Samples No.	R	Phase transition temperature (°C) ^{b)}
Ia	$-(CH_2)_2-$	g 103n 181 i
Ib	$-(CH_2)_4-$	g 68n 135 i
Ic	$(CH_2)_8$	g 31n 74 i
Id		300°C dec. ^{c)}

a) Abbreviations: g, glass transition; n, nematic; i, isotropic melt

b) Measured by DSC at scanning rate of 10°C/min in the second heating

c) No melting phenomenon was observed up to 300°C

The optical observation of the texture by means of a polarizing

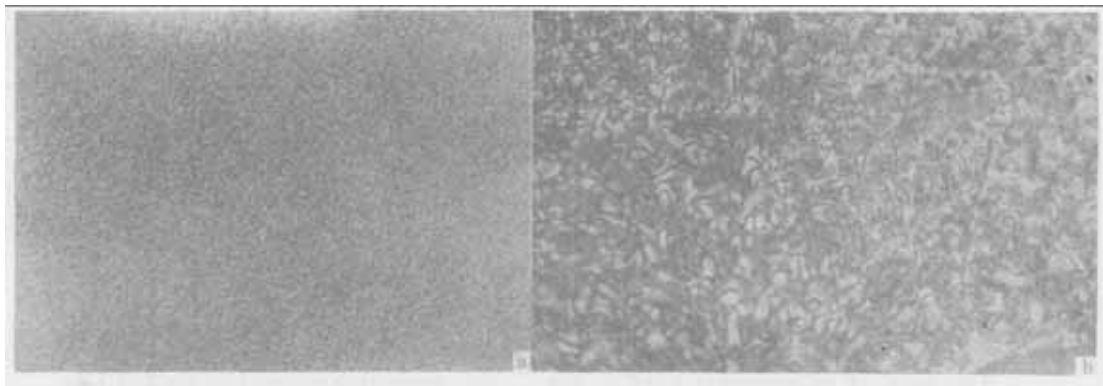


Fig. 3 Polarizing microphotograph of polyesters Ia and Ic on the first cooling run
a) Ic, at 54°C; b) Ia, at 160°C
Magnification: X 500

microscope indicated that the polymer Ic exhibited a nematic phase (see Fig. 3a) on heating and cooling runs between 30°C and 74°C. In fact, the LC texture was retained at room temperature. For polymer Ia and Ib, in addition to the glass transition, DSC trace showed one small endothermal peak at 180°C and 135°C respectively which demonstrated the occurrence of one phase transition. Optical microscopy observations indicated that they were nematic transition. For polymer Ia, on cooling from the isotropic liquid, droplets appeared at first, then further cooling to 160°C, a schlieren texture was observed (see Fig. 3b).

Keywords:

New liquid crystalline polyesters; Synthesis; Interfacial polymerization; Phase transition temperature; Texture of liquid crystalline polymers

REFERENCES

- [1] Percec, V. and Pugh, C., "Side Chain Liquid Crystal Polymers" Ed. McArdle, C. B., Chapman and Hall, **1989**, New York, 30.
- [2] Berg, S.; Krone, V. and Ringsdorf, H., *Makromol. Chem., Rapid Commun*, **1986**, 7, 381.
- [3] Rotz, U.; Lindau, J.; Diele, S., et al., *Mol. Cryst. Liq. Cryst.*, **1990**, 193, 229.
- [4] Wang, B. R., "Organic Synthetic Reactions" **1980**, Science Press, Beijing, 567.