

SYNTHESIS OF LIQUID CRYSTALLINE POLYACRYLATES WITH THIOESTER AS BRIDGE-BOND*

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ABSTRACT

A new series of acrylates with the same mesogens containing thioester as bridge-bond were synthesized, and the acrylates were characterized by H^1 NMR, IR and MS. The polymers were obtained by radical polymerization using AIBN as initiator. The monomers and polymers exhibit thermotropic-enantiotropic liquid crystalline behavior.

INTRODUCTION

Synthesis of new side-chain liquid crystalline polymers (SCLCP) is one of the active research fields of polymer science. The potential applications of SCLCP in electron-optical technology are promising in the development of these new polymers. These include applications in optical information storage^[1] and nonlinear optics^[2], as the materials will provide preferable characteristics, such as the ease of processibility and glassy behavior, over monomeric liquid crystals^[3].

It is known that the dielectric and optical properties of monomeric liquid crystals are mainly controlled by their chemical structure^[4]. For example, polar substituents have a large effect on the dielectric anisotropy, and thioester-containing liquid crystals possess positive dielectric anisotropy ($\Delta\epsilon$) and excellent physical properties^[5].

We have recently synthesized two series of sulfur-containing SCLCP^[6,7]. In these SCLCPs, methacrylate was used as the backbone and the spacer length and terminal group were varied. The results showed that they all exhibit liquid crystalline

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behaviors. In this work, a new series of sulfur-containing SCLCP was designed and synthesized. Acrylate was used to form the main chain in order to compare the influence of backbone on the properties of thioester-containing SCLCP, and the effect of the length of flexible spacer was also investigated.

EXPERIMENTAL

Chemicals and reagents

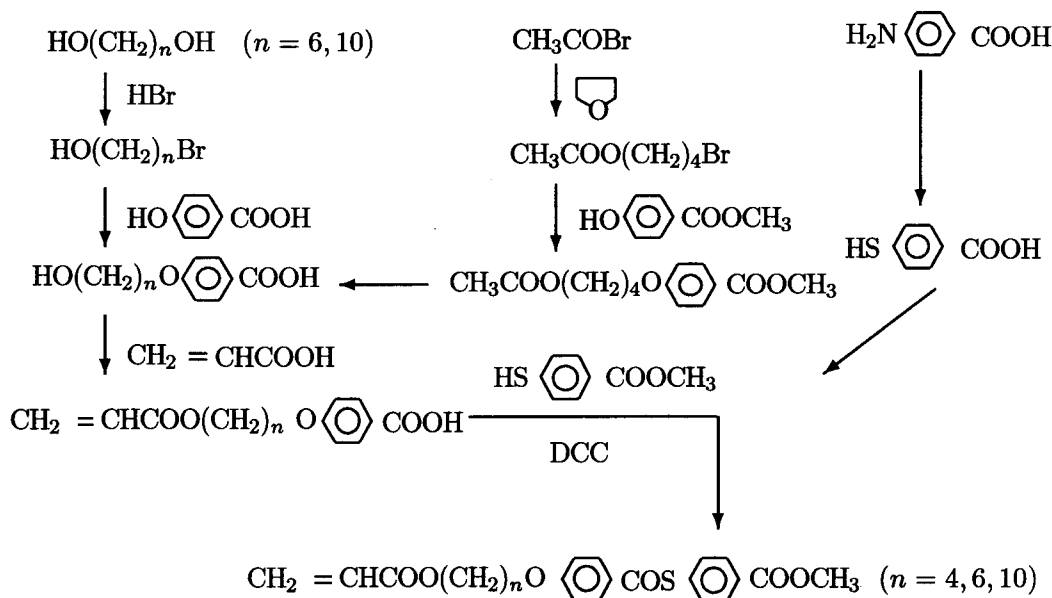
All the reagents and solvents used are commercially available and of C.P. grade.

Analytical methods

Infrared spectra were recorded on a Nicolet 50X FT-IR spectrophotometer. Proton NMR spectra were obtained in CDCl_3 with Me_4Si as an internal reference using a JEOL FX-90 MHz spectrometer. The melting point were measured by a X-6 melting-point tester. The molecular weights were determined by gel permeation chromatography (GPC) in CHCl_3 at 30°C using a WATERS apparatus equipped with Styragel columns in a flow rate of 2.0 ml/min. The textures of the samples were examined under crossed polarizers by a Leitz Orphoplan Microscope with a heating stage.

Reactions for synthesis

The reaction routes to synthesize the monomers are sketched as follows:



(1) Syntheses of intermediate compounds

Bromo-alkanol-1, 4-(ω -hydroxy-alkoxy) benzoic acid and 4-(ω -acryloyloxy-alkoxy) benzoic acid were synthesized using the methods described in ref. [8], [9] and [10], respectively. Table 1 lists the melting points of 4-(ω -acryloyloxy-alkoxy) benzoic acids obtained.

Table 1 Melting points and yields of 4-(ω -acryloyloxy-alkoxy) benzoic acids

Sample	C Number in alkoxy	m.p.(°C)	Yield (%)
M4	4	118—120	58.0
M6	6	88—90	63.0
M10	10	62—64	54.0

The *p*-mercaptobenzoic acid was synthesized as the method for *m*-mercaptobenzoic acid^{[11][6]} (m.p. 46—48°C).

(2) Monomer syntheses

Equal mole (25 mmol) of 4-(ω -acryloyloxy-alkoxy) benzoic acid, methyl 4-mercaptobenzoate, and N, N-dicyclohexanyl carbodiimide (DCC) were dissolved in 100ml dichloromethane. The mixture was stirred at ambient temperature for 12h. The insoluble by-product was removed by filtration, and the filtrate was washed with 5% Na₂CO₃ solution. The organic layer was filtered and concentrated to give crude product, which was then purified by liquid-solid column chromatography. The structures and nomenclature of the monomers are listed in Table 2. The transition temperatures of the monomers characterized by optical microscope are tabulated in Table 3.

Table 2 Structure and nomenclature of monomers

Sample	Structure	Nomenclature
AS4M	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_4\text{OC}_6\text{H}_4\text{COSC}_6\text{H}_4\text{COOCH}_3$	4-(ω -methoxycarbonyl) thiophenyl 4-(ω -acryloyloxy tetramethyleneoxy) benzoate
AS6M	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_6\text{OC}_6\text{H}_4\text{COSC}_6\text{H}_4\text{COOCH}_3$	4-(ω -methoxycarbonyl) thiophenyl 4-(ω -acryloyloxy hexamethyleneoxy) benzoate
AS10M	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_{10}\text{OC}_6\text{H}_4\text{COSC}_6\text{H}_4\text{COOCH}_3$	4-(ω -methoxycarbonyl) thiophenyl 4-(ω -acryloyloxy decamethyleneoxy) benzoate

Polymerization of the monomers

Two grams of monomer was dissolved in 20ml of distilled dry DMF with 1% mol of AIBN as initiator. The solution was degassed by passing nitrogen for 1h, and then polymerized at 60°C for 48h. The reaction mixture was poured into methanol

to obtain the polymer as a white mass and purified by dissolving and precipitating for three times with DMF and methanol. The obtained polymers were dried in the vacuum at 60°C for 48h.

Table 3 The transition temperature of monomers

Sample	Yield (%)	Phase transition temp. (°C)
AS4M	58	K 86.2 S 139.1 I
AS6M	55	K 80.2 S 131.6 I
AS10M	50	K 68.8 S 105.4 I

RESULTS AND DISCUSSION

The chemical structure of monomers

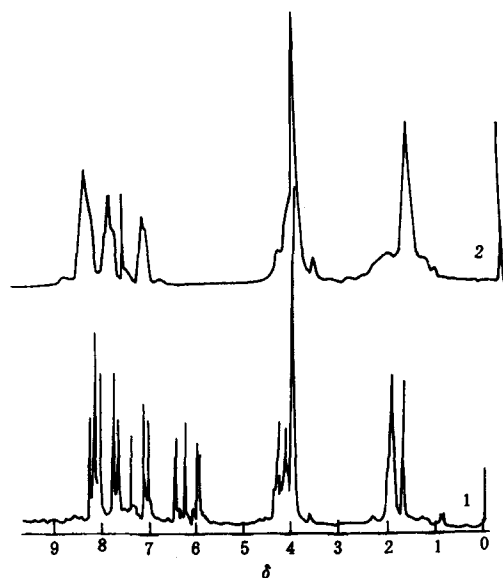


Fig. 1 ^1H -NMR spectra of AS4M and PAS4M

1. AS4M; 2. PAS4M

The chemical structure of three monomers were confirmed by H^1 NMR, IR and MS. Their spectra and corresponding data are shown and listed in Fig. 1—2 and Table 4—5.

The IR spectra of the monomers show that the absorption bands at 2863—2930 cm^{-1} , 1668—1718 cm^{-1} and 1637 cm^{-1} are assigned to the $-\text{CH}_2-$, the $-\text{C}=\text{O}$ and $-\text{CH}=\text{CH}-$ groups, respectively. The absorption band at 833 cm^{-1}

is associated with the benzene ring, and the band at 1675cm^{-1} is the characteristic absorption band of thiocarboxyl ester.

Table 4 ^1H -NMR spectral data for ASnM

Monomer	Chemical shift (δ , ppm) and assignment
AS4M	1.72~2.08 (s, 4H, Methylenic); 3.66~4.00 (m, 7H, methyleneoxy and methoxy); 5.84, 6.37 (w, 2H, $=\text{CH}_2$); 6.15 (w, 1H, $=\text{CH}-$); 6.82—8.20 (m, 8H, aromatic)
AS6M	1.40~2.00 (m, 8H, methylenic); 3.88—4.28 (s, m, 7H, methyleneoxy and methoxy); 5.88, 6.38 (w, 2H, $=\text{CH}_2$); 6.16 (w, 1H, $=\text{CH}-$); 6.84—8.20 (m, 8H, aromatic)
AS10M	1.20—1.86 (S, 16H, methylenic— $(\text{CH}_2)_8$ —); 3.80—4.20 (s, m, 7H, methyleneoxy—, CH_2O —, $-\text{OCH}_2$, methoxy—, $-\text{OCH}_3$); 5.85, 6.38 (w, 2H, methylene, $=\text{CH}_2$); 6.16 (w, 1H, methenyl $=\text{CH}-$); 6.84—8.20 (m, 8H aromatic)

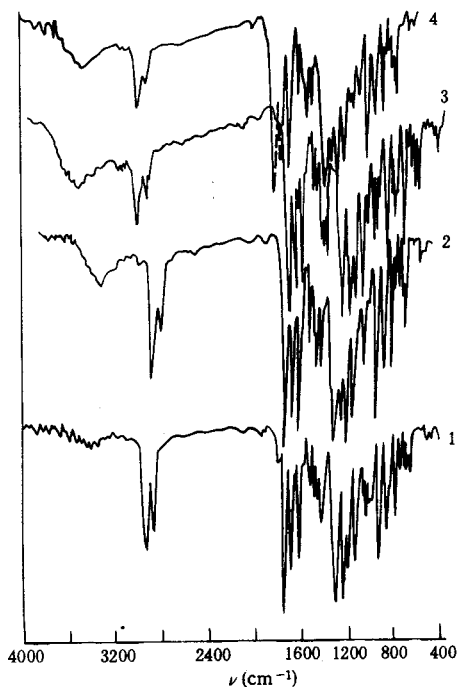


Fig. 2 IR spectra of ASnM and PASnM

1. AS10M; 2. AS6M; 3. AS4M; 4. PAS4M

The ^1H -NMR spectra of monomers all show that there are two four-spinning peaks in the region of 6.80—8.20ppm, indicating the presence of two disubstituted

benzene-rings in the monomers.

The electronic-ionize method was used when the MS spectra were recorded because the evaporation temperature of the monomers and *p*-nitrotoluene alcohol (used as a solvent) is quite high. The cleavage peaks of molecular-ion in the MS spectra are peaks of $M+1$, and are listed in Table 5.

Polymer characterization

The structures of the polyacrylates have been determined by ^1H NMR and FTIR. Fig. 1 and 2 are the representative spectra of the polyacrylate. The absorption band at 1640cm^{-1} is due to the $\text{C}=\text{C}$ groups, and the peaks at 5.88—6.38 ppm due to the vinyl protons of the acrylate disappear, confirming that the monomers have been polymerized. Some results of characterization on the polymers are given in Table 6. All the polymers exhibit liquid crystalline behavior.

Table 5 MS spectral data for ASnM

Monomer	Cleavage peak (m/e)
AS4M	415: $M+1$, 247: $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_4\text{OC}_6\text{H}_4\text{CO}^+$ 167: $^+\text{SC}_6\text{H}_4\text{COOCH}_3$; 55: $\text{CH}_2=\text{CHCO}^+$
AS6M	443: $M+1$, 275: $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_6\text{OC}_6\text{H}_4\text{CO}^+$ 167: $^+\text{SC}_6\text{H}_4\text{COOCH}_3$; 55: $\text{CH}_2=\text{CHCO}^+$
AS10M	499: $M+1$, 331: $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_{10}\text{OC}_6\text{H}_4\text{CO}^+$ 167: $^+\text{SC}_6\text{H}_4\text{COOCH}_3$; 55: $\text{CH}_2=\text{CHCO}^+$

Table 6 Some results of characterization on the polyacrylates

Sample	Yield (%)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	Transition temp. ($^{\circ}\text{C}$)
PAS4M	60	7,800	18,000	2.3	g 99.2 S _A 173.7 I
PAS6M	58	5,900	14,100	2.4	g 95.1 S _A 171.4 I
PAS10M	50	4,700	15,200	3.2	g 70.9 S _A 107.5 I

Keywords:

Thioester; Bridge-bond; Liquid crystalline polymers; Positive dielectric anisotropy

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