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Liquid Crystals

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Synthesis and thermal properties of side-chain liquid crystalline poly[1-({(4-methoxyazobenzene-4′-oxy)alkyl}thio)-2.3-epoxypropane]s

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A novel series of side-chain liquid crystalline copolymers, i.e. poly-[1-({(4-methoxyazobenzene-4′-oxy)alkyl}thio)-2.3-epoxypropane]s, were synthesised in which the number of methylene units in the alkyl group of the side chain varies from 3 to 6. The structures of compounds obtained were characterised by elemental analysis and ^{1}H NMR spectroscopy. Thermal properties were investigated using polarising optical microscopy, differential scanning calorimetry and X-ray diffraction analysis. The synthesised thiols and corresponding polyepichlorohydrin-based copolymers exhibited thermotropic liquid crystalline behaviour and nematic phases with schlieren textures. The thiols have lower transition temperatures than the corresponding copolymers. In addition, the degree of substitution of the copolymers synthesised increased with an increase in number of methylenes in the side chain. The phase transition temperatures increased and the mesomorphic temperature ranges widened with the increasing degree of substitution of the copolymers.

Keywords: liquid crystalline polymer; thiol; polyepichlorohydrin; thermal properties

1. Introduction

Side-chain liquid crystalline polymers (SCLCPs) containing a sulfur atom in the spacer and azobenzene derivatives as mesogenic units have attracted growing interest in recent years, for they combine ordinary liquid crystalline behaviour with some functional properties.

A SCLCP consists of three structural units: a polymer backbone, a spacer and a mesogenic group. The length and flexibility of the spacer play a significant role in determining the thermal stability, transition temperatures and the enthalpy change associated with the clearing transition of the copolymers and, to some extent, the relative tendencies of the mesogenic groups to self-assemble from the main chain (especially if rigid) to adopt a random coil configuration. The thioether unit can enhance the flexibility of the spacer and remove the crystallisation phenomenon of copolymers owing to the C–S bond. Larger ranges of mesophases have been obtained for such polymers in comparison with that for the similar SCLCPs containing ether in the spacer (*1, 2*). Furthermore, owing to the chelating feature of sulfur atoms, the copolymers have the ability for adsorption of metal ions, such as Au^{3+}, Ag^{+}, Cu^{2+}, etc, in aqueous solution, especially the selective adsorption towards certain metal ions after quenching (*3–5*). Liquid crystalline compounds containing sulfur can be adsorbed spontaneously by chemisorption onto metallic surfaces, such as Au, Pt, Ag, etc, to form monolayer-modified surfaces that provide a better understanding of the self-assembly in molecular systems (*6, 7*). However, examples of liquid-crystalline polymers containing thioether in the side-chain were not found to be reported in the literature, apart from the reports by Bonnans-Plais *et al.* (*8, 9*) of a series of polythirranes bearing alkyloxybiphenyl mesogens, prepared by means of anionic ring-opening polymerisation of thirrane using tetramethylammonium dithiobenzoate as initiator, and Gilles *et al.* (*2*) of the synthesis of a liquid crystalline polymer by the reaction of polysiloxane with an α-olefine containing cyanobiphenyls and thioether in the presence of hexachloroplatinic acid.

Azobenzene and its derivatives are widely used mesogenic groups and have been grafted onto many polymer backbones, such as poly(ethyleneimine) (*10*), polymethacrylates (*11, 12*), poly(4-hydroxystyene) (*13*), polysiloxane (*14*), etc., to form side-chain liquid crystalline polymers. In addition, due to a unique property, which is the possibility of changing the orientation of azobenzene through trans–cis–trans photoisomerisation cycles to photoinduce birefringence and linear dichroism in thin polymer films, azobenzene-containing copolymers are very promising for optical switching (*15*), digital and holographic storage applications (*16, 17*) and nonlinear optics device (*18*), etc.

Polyepichlorohydrin (PECH) is often used as the main-chain component of SCLCPs (*19, 20*). In this work, polyepichlorohydrin-based liquid crystalline polymers with a methoxyazobenzene mesogenic

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group and thioether unit in the spacer were synthesised in which the number of methylene units in the spacer varied from 3 to 6. The copolymers were obtained by means of nucleophilic substitution reaction of PECH with thiols. The study mainly focuses on the synthesis and thermal behaviour of the mercaptans and the copolymers and the effects of length of spacer and substitution degree on thermal properties.

2. Experimental

Materials

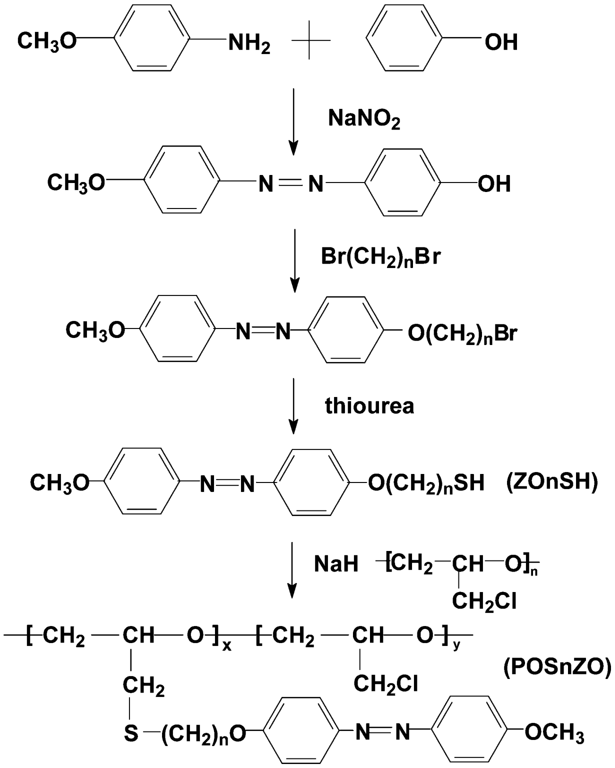
1,3-Dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane and 1,6-dibromohexane (C.P.) were purchased from Yixing East Fine Chemical Factory, China. A solution of tributylaluminium in toluene was provided by Wuhan Organic Synthesis Limit Co. Epichlorohydrin was distilled over anhydrous magnesium sulfate. Dibromoalkanes were distilled under reduced pressure. Toluene and 1,4-dioxane were refluxed with sodium and distilled. All other reagents were used without further purification.

Instruments

^{1}H NMR (300 MHz) spectra were recorded on a Varian Mercury VX-300 in $CDCl_3$ solutions, using tetramethylsilane (TMS) as internal standard. Thermal characterisations were performed by differential scanning calorimetry (DSC) on a TA DSC-Q10 instrument. Measurements were carried out with heating and cooling rates of 20°C min^{-1} under a dry nitrogen purge. The second heating and cooling runs were evaluated. The optical textures of the mesophases were studied by polarising optical microscopy (POM, Olympus BH-2, magnification 10×20) fitted with a Linkam THMSE 600 type heating stage at heating or cooling rates of 5°C min^{-1}. X-ray diffraction patterns were obtained using a D/MAX-IIIA diffractometer (Rigaku, Tokyo, Japan) with nickel-filtered Cu K_α radiation, at a scanning rate of 8° min^{-1}. The number-average molecular weight (M_n) of polyepichlorohydrin was determined using a gel permeation chromatographic (GPC) system equipped with a Waters 2690D separations module and Waters 2410 refractive index detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.3 ml min^{-1}. Waters millennium module software was used to calculate the molecular weight on the basis of a universal calibration curve generated by polystyrene standard with narrow molecular weight distribution.

Synthesis

The synthetic route used for preparation of the polymers is outlined in Scheme 1.



Scheme 1. Reaction scheme for the synthesis of mercaptans and copolymers.

Synthesis of monomers.

4-Hydroxyl-4′-methoxyazobenzene (**1**) was prepared according to the method described by Stewart and Imrie (*13*). Yield: 82%; m.p. 140–141°C. ^{1}H NMR ($CDCl_3$): δ 7.9, 6.9 (m, aromatic, 8H); 3.9 (s, OCH_3, 3H).

1-Bromo-ω-(4-methoxyazobenzene-4′-oxy)alkanes (**2**) were prepared using the procedures described by Imrie and co-workers (*11, 21*). A mixture of **1** (0.01 mol), α,ω-dibromoalkane (0.10 mol), potassium carbonate (0.10 mol) and acetone was refluxed while stirring for 24 h. The reaction mixture was filtered hot and the residue was washed thoroughly with acetone. The acetone was removed under reduced pressure. The petroleum ether (30–60°C) was added to the concentrated organic extracts. The resulting precipitate was filtered off and recrystallised twice from ethanol with hot filtration.

For 1-bromo-3-(4-methoxyazobenzene-4′-oxy) propane: yield 65%; m.p. 98–100°C. ^{1}H NMR ($CDCl_3$): δ 7.89–7.00 (m, aromatic, 8H), 4.18 (t, $O\underline{CH_2}$, 2H), 3.90 (s, $PhO\underline{CH_3}$, 3H), 3.62 (t, $\underline{CH_2}Br$, 2H), 2.4 (m, $CH_2\underline{CH_2}CH_2$, 2H).

For 1-bromo-4-(4-methoxyazobenzene-4′-oxy) butane: yield 50%; m.p. 112–114°C. ^{1}H NMR ($CDCl_3$): δ 7.89–7.00 (m, aromatic, 8H), 4.08 (t, $O\underline{CH_2}$, 2H), 3.90 (s, $PhO\underline{CH_3}$, 3H), 3.50 (t, $\underline{CH_2}Br$, 2H), 2.11–1.99 (m, CH_2 $(\underline{CH_2})_2CH_2$, 4H).

For 1-bromo-5-(4-methoxyazobenzene-4′-oxy) pentane: yield 75%; m.p. 94–96°C. ^{1}H NMR ($CDCl_3$): δ 7.88–6.99 (m, aromatic, 8H), 4.05 (t, $O\underline{CH_2}$, 2H), 3.89 (s, $PhO\underline{CH_3}$, 3H), 3.45 (t, $\underline{CH_2}Br$, 2H), 1.99–1.66 (m, CH_2 $(\underline{CH_2})_3CH_2$, 6H).

For 1-bromo-6-(4-methoxyazobenzene-4′-oxy) hexane: yield 40%; m.p. 106–108°C. ^{1}H NMR ($CDCl_3$): δ 7.88–7.00 (m, aromatic, 8H), 4.19 (t, $O\underline{CH_2}$, 2H), 3.90 (s, $PhO\underline{CH_3}$, 3H), 3.44(t, $\underline{CH_2}Br$, 2H), 1.54–1.91 (m, CH_2 $(\underline{CH_2})_4CH_2$, 8H).

To prepare (4-methoxyazobenzene-4′-oxy)alkylthiols (**3**, ZOnSH), **2** (10 mmol) and thiourea (0.1 g, 11 mmol) were dissolved in anhydrous ethanol at 80°C while stirring for 4 h. Then, an aqueous sodium hydroxide solution (1 g in 5 ml) was added. The reaction mixture continued to be stirred at 80°C under a nitrogen atmosphere for 4 h. The mixture was cooled to 50°C, and diluted H_2SO_4 ($2\,\mathrm{mol\,l^{-1}}$) was added dropwise until the solution became acidic (pH=2). Finally, the mixture was cooled in an ice bath and filtered off quickly at 0°C. The product was washed with ice water, recrystallised from ethanol and dried in vacuum. Structures were confirmed by elemental analysis and ^{1}H NMR spectroscopy. The letters in the ^{1}H NMR data listed in the following represent the H atoms shown in Figure 1(a).

For (4-methoxyazobenzene-4′-oxy)propylthiol (ZO3SH): yield 71%; m.p. 97–98°C. ^{1}H NMR ($CDCl_3$): δ 7.90 (m, b, 4H) 7.00 (m, c, 4H), 4.17 (t, d, 2H), 3.89 (s, a, 3H), 2.76 (t, e, 2H), 2.12 (t, p, 2H), 1.43 (t, k, 1H). Elemental analysis: calculated for $C_{16}H_{18}O_2N_2S$, C 63.58, H 5.96, N 9.26, S 10.58; found, C 63.62, H 5.90, N 9.21, S 10.32%.

For (4-methoxyazobenzene-4′-oxy)butylthiol (ZO4SH): yield 55%; m.p. 92–93°C. ^{1}H NMR ($CDCl_3$): δ 7.88 (m, b, 4H) 6.99 (m, c, 4H), 4.06 (t, d, 2H), 3.88 (s, a, 3H), 2.66 (t, e, 2H), 1.92 (t, p, 2H), 1.83 (t, q, 2H), 1.40 (t, k, 1H). Elemental analysis: calculated for $C_{17}H_{20}O_2N_2S$, C 64.56, H 6.33, N 8.85, S 10.11; found, C 64.60, H 6.35, N 8.95, S 9.96%.

For (4-methoxyazobenzene-4′-oxy)pentylthiol (ZO5SH): yield 70%; m.p. 79–80°C. ^{1}H NMR ($CDCl_3$): δ 7.89 (m, b, 4H) 6.99 (m, c, 4H), 4.03 (t, d, 2H), 3.88 (s, a, 3H), 2.56 (t, e, 2H), 1.82 (t, p, 2H), 1.67 (t, q, 2H), 1.59 (t, f, 2H), 1.37 (t, k, 1H). Elemental analysis: calculated for $C_{18}H_{22}O_2N_2S$, C 65.46, H 6.66, N 8.48, S 9.69; found, C 65.39, H 6.66, N 8.44, S 9.46%.

For (4-methoxyazobenzene-4′-oxy)hexylthiol (ZO6SH): yield 78%; m.p. 90–91°C. ^{1}H NMR ($CDCl_3$): δ 7.91 (m, b, 4H), 7.00 (m, c, 4H), 4.06 (t, d, 2H), 3.89 (s, a, 3H), 2.56 (t, e, 2H), 1.82 (t, p, 2H) 1.67 (t, q, 2H), 1.50 (t, f, 4H), 1.38 (t, k, 1H). Elemental analysis: calculated for $C_{19}H_{24}O_2N_2S$, C 66.28, H 6.97, N 8.13, S 9.23; found, C 66.33, H 7.03, N 8.09, S 8.98.

Synthesis of polymers.

For the polymerisation of epichlorohydrin to PECH, epichlorohydrin (20 g) was mixed with dry toluene (20 ml) and tributylaluminium in toluene (2 ml) was added. After being stirred at 100°C under a nitrogen stream for 5 h, the mixture was poured into methanol to precipitate the polymer. The resulting polymer was purified by precipitation from $CHCl_3$ solution into methanol and dried at 60°C in vacuum for 48 h. Yield: 65%. ^{1}H NMR ($CDCl_3$): δ 3.71–3.63(m), as shown in Figure 1(b). M_n=22 152, M_w/M_n=2.51.

Poly[1-({(4-methoxyazobenzene-4′-oxy)alkyl}thio)-2.3-epoxypropane]s (POSnZO) were synthesised using a method similar to that reported in the literature (*22, 23*). **3** (10 mmol) was dissolved in dry 1,4-dioxane under a nitrogen stream and sodium hydride (10 mmol) was added to form a slurry mixture. Then, PECH (0.63 g, 7 mmol) dissolved in dry 1,4-dioxane (20 ml) and tetrabutylamine bromoate (1 mmol) were added. After reaction at 100°C under a nitrogen atmosphere for 44 h while stirring, the mixture was centrifuged in order to remove sodium chloride and then poured into methanol. The crude polymer was purified by precipitation several times from chloroform into methanol until it was a single compound, which was confirmed by thin-layer chromatography. Finally, the resulting copolymer was dried in vacuum at 50°C for 48 h. Structures were confirmed by ^{1}H NMR spectroscopy. The letters in the ^{1}H NMR data listed in the following represent the H atoms shown in Figure 1(c).

For poly[1-({(4-methoxyazobenzene-4′-oxy)propyl}thio)-2.3-epoxypropane] (POS3ZO): yield 30%; substitution degree 58%. ^{1}H NMR ($CDCl_3$): δ (7.83 (s, b, 4H), 6.94 (s, c, 4H), 4.04 (s, d, 2H), 3.82 (s, a, 3H), 3.64 (s, h i m, 6.6H), 2.76 (s, g e, 4H), 2.03 (s, f, 2H).

For poly[1-({(4-methoxyazobenzene-4′-oxy)butyl}thio)-2.3-epoxypropane] (POS4ZO): yield 35%; substitution degree 65%. ^{1}H NMR ($CDCl_3$): δ 7.86 (s, b, 4H), 7.26 (s, c, 4H), 4.26 (s, d, 2H), 3.96 (s, a, 3H) 3.67 (d, h i m, 5.1H), 2.61 (s, g e, 4H), 1.86 (s, p, 2H), 1.76 (s, q, 2H).

For poly[1-({(4-methoxyazobenzene-4′-oxy)pentyl}thio)-2.3-epoxypropane] (POS5ZO): yield 38%; substitution degree 75%. ^{1}H NMR ($CDCl_3$): δ 7.82 (s, b, 4H), 6.93 (s, c, 4H), 3.92 (s, d, 2H), 3.81 (s, a, 3H),

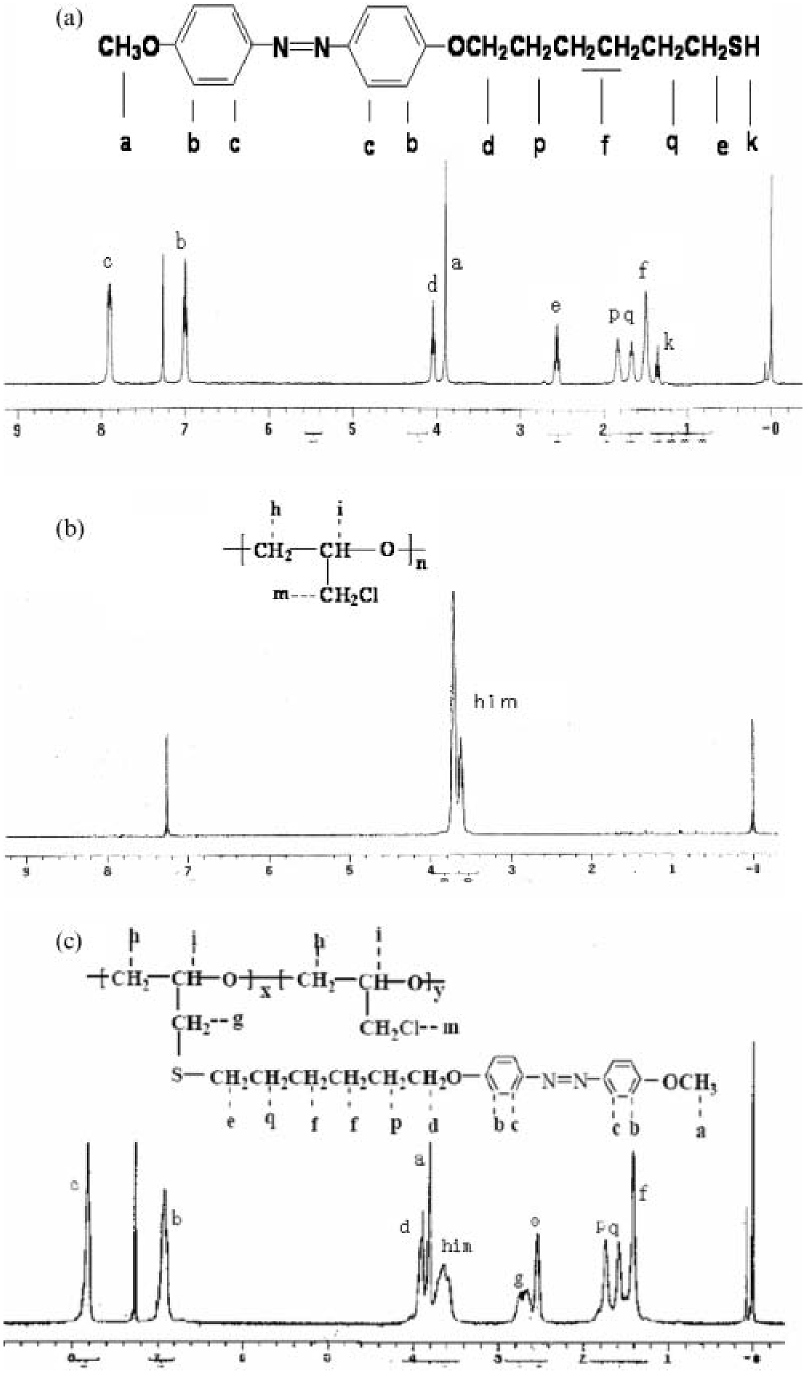


Figure 1. ^{1}H NMR spectra of (a) monomer ZO6SH, (b) PECH and (c) copolymer POS6ZO ($CDCl_3$, TMS).

3.65 (m, h i m, 5H), 2.74 (d, g, 2H), 2.55 (s, e, 2H), 1.75 (s, p, 2H), 1.62 (s, q, 2H), 1.52 (s, f, 2H).

For poly[1-({(4-methoxyazobenzene-4′-oxy)hexyl}thio)-2.3-epoxypropane] (POS6ZO): yield 60%; substitution degree 82%. ^{1}H NMR ($CDCl_3$): δ 7.88 (d, b, 4H), 7.00 (m, c, 4H), 4.03 (s, d, 2H), 3.89 (s, a, 3H), 3.65 (d, h i m, 4.1H), 2.70 (m, g, 2H), 2.54 (s, e, 2H), 1.83 (s, p, 2H), 1.74 (s, q, 2H), 1.49 (d, f, 4H).

3. Results and discussion

Synthesis and characterisation

Monomers (ZOnSH) and copolymers (POSnZO) were synthesised according to the route shown in Scheme 1. Since the thiols obtained were easily oxidised, the process was carried out under a nitrogen atmosphere and mercaptans were filtered quickly at low temperature (cooled in an ice bath). The substitution degree of

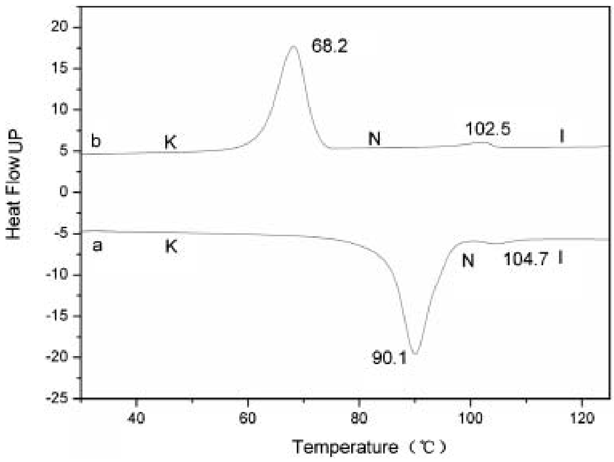


Figure 2. DSC thermogram of monomer ZO6SH at a rate of 20°C min^{-1} on (a) heating and (b) cooling.

mesogenic groups depends on the reaction time. For POS3ZO, an 8% increase of the substitution degree was obtained as the reaction time increased by 10 h. The substitution degree increased slightly when the reaction time was over 40 h. Therefore, the reaction time was 44 h for POSnZO. In addition, the substitution degree of mesogenic groups was observed to increase with the increasing number of methylene groups (*n*) of the spacer. This behaviour is in contrast with that of other similar copolymers (*19–24*), for which the substitution degree of the mesogenic groups decreased with increasing spacer length. The probable reason is that thiols and sodium thiolate were oxidised more easily as the molecule became smaller.

The chemical structures of the products mentioned previously were identified using elemental analysis and ^{1}H NMR. The ^{1}H NMR analysis of the starting PECH, ZOnSH and POSnZO products confirmed the attachment of the synthesised mesogenic compounds onto the PECH backbone through a thioether linkage, which is in agreement with reaction shown in Scheme 1.

The ^{1}H NMR spectra of monomer (ZO6SH), polymer (PECH) and copolymer (POS6ZO) are shown as representative examples in Figure 1. In the ^{1}H NMR spectrum of POS6ZO (Figure 1(c)), the signal ascribed to the proton resonance of –SH at δ=1.5 ppm disappeared and the new peaks that belong to the mesogenic group and the spacer were observed. The multiplets at δ=7.00 and δ=7.88 ppm were attributed to the resonances of aromatic protons. The resonance signals for aliphatic protons existing in –PhOCH$_3$ and –PhOCH$_2$– appeared at about δ=3.89 and δ=4.03 ppm, respectively. The peaks at δ=2.54 and δ=2.70 ppm were due to the –CH$_2$S– protons of the thioether linkage. These peaks indicate clearly that the monomer was successfully grafted to the polymer backbone. The spectroscopic data were in accordance with the proposed structures.

Thermal properties and optical textures

Thermal properties of the thiols and copolymers were examined by DSC measurements and POM observations.

Figure 2 showa a representative DSC trace of monomer ZO6SH. In the DSC heating scan, the trace displays a melting transition at about 90.1°C and a mesophase–isotropic phase transition at about 104.5°C. The cooling scan showed very similar phase behaviour, except that the crystallisation temperature was supercooled by 22°C. The phase transition temperatures and corresponding enthalpy changes of all synthesised monomers are listed in Table 1.

All the phase transitions reported in Table 1 were reversible during repeated heating and cooling cycles. When the spacer effect is considered, it can be seen that the melting temperatures decreased gradually as the spacer length increased and an odd–even effect was observed. All monomers revealed an enantiotropic nematic phase. A well-defined schlieren texture was observed for monomer ZO6SH by POM, as shown in Figure 3.

Figure 4 shows a representative DSC trace of POS6ZO, which reveals two endothermic peaks at about 111.8°C (ΔH=25.0 J g^{-1}) and 134.1°C (ΔH=1.9 J g^{-1}) in the second heating scan. During the second cooling scan, an isotropic–liquid crystalline phase transition at about 132.4°C (ΔH=1.6 J g^{-1}) and the crystallisation transition at about 98.6°C (ΔH=25.1 J g^{-1}) were observed. The POM image of POS6ZO shown in Figure 5 reveals a schlieren

Table 1. Thermodynamic data of monomers ZOnSH.

	Phase transition temperature /°C		Corresponding enthalpy change /J g^{-1}	
Sample	Heating	Cooling	Heating	Cooling
ZO3SH	Cr 95.9 N 108.8 I	Cr 65.3 N 106.2 I	Cr 44.6 N 1.5 I	Cr 42.2 N 1.4 I
ZO4SH	Cr 92.6 N 131.4 I	Cr 66.4 N 128.1 I	Cr 37.0 N 2.7 I	Cr 36.0 N 2.5 I
ZO5SH	Cr 80.0 N115.9 I	Cr 48.0 N 112.7 I	Cr 54.5 N 1.1 I	Cr 44.5 N 1.3 I
ZO6SH	Cr 90.1 N 104.5 I	Cr 68.2 N 102.5 I	Cr 83.1 N 1.8 I	Cr 81.1 N 1.7 I

Cr=crystalline, N=nematic, I=isotropic.

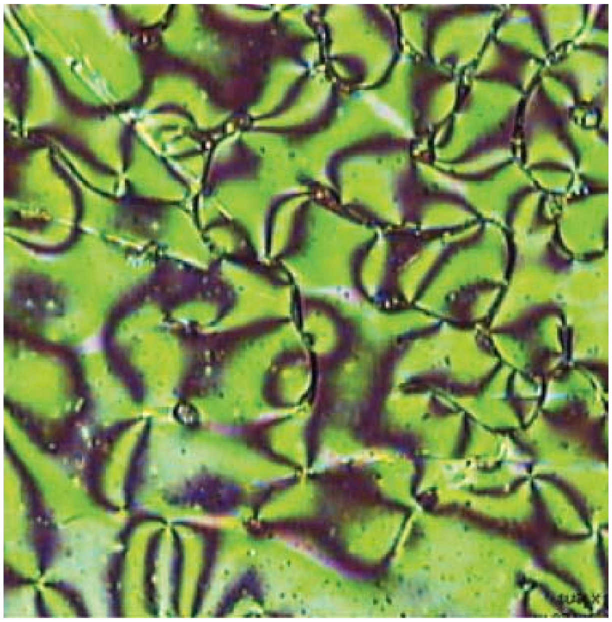


Figure 3. Polarising optical micrograph of monomer ZO6SH showing schlieren texture at 102°C upon cooling from the isotropic phase.

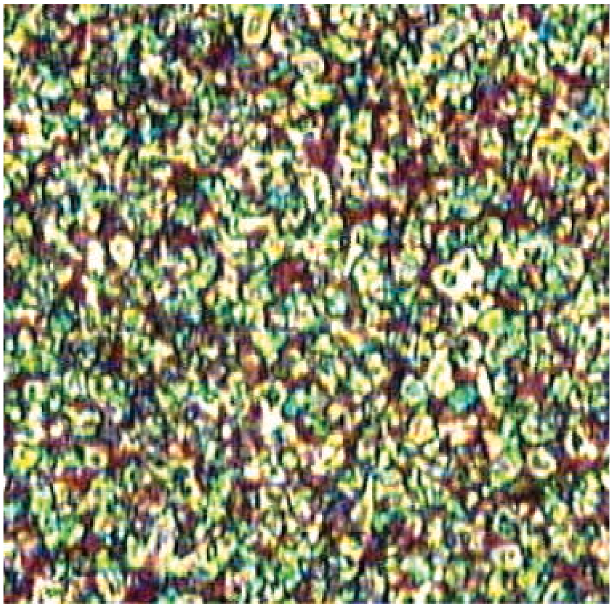


Figure 5. Polarising optical micrograph of copolymer POS6ZO showing schlieren texture at 134°C (on cooling from the isotropic phase).

texture at 130°C, indicating a nematic phase. The results from DSC measurements and POM observations were consistent.

The DSC traces in the second heating scan for the POSnZO copolymers are shown in Figure 6. The thermal data of the POSnZO copolymers, which were extracted from the second heating and cooling cycles, are listed in Table 2.

The DSC heating trace exhibited two endothermic peaks. All the copolymers revealed liquid crystalline–isotropic transitions due to their flexible backbones. However, POS3ZO failed to exhibit any exothermic peaks in the cooling scan. The reasons are as follows. First, the enthalpy changes for the isotropic–nematic phase transition were too small (about 0.21 and 0.23 J g^{-1}, respectively in heating scan) to be detected in the curves. Second, the process from melting state to solid state, as observed in our experiment, was very slow at room temperature and resulted in no peak ($T_{N\text{–}Cr}$). This phenomenon may be explained in the terms of lower substitution degree than that of the others, which was consistent with the other synthesised copolymers with different main chain and same side chain (to be reported in the future). According to

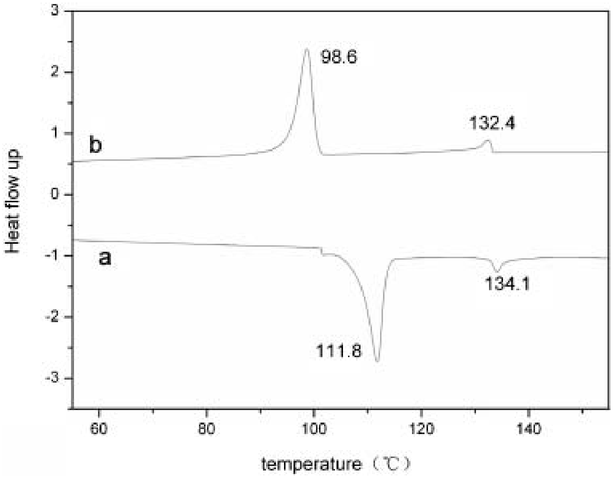


Figure 4. DSC thermogram of copolymer POS6ZO at a rate of 20°C min^{-1} on (a) heating and on (b) cooling.

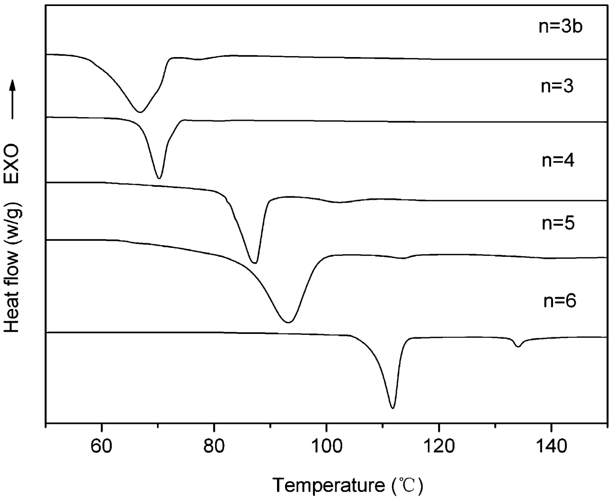


Figure 6. DSC thermograms of POSnZO copolymers at a rate of 20°C min^{-1} on second heating.

Table 2. The phase transition temperatures of copolymers POSnZO.

Copolymer	Substitution degree /%[a]	Phase transition temperature /°C			
		T_{m}[b]	T_{i}[c]	T_{N-Cr}[d]	T_{I-N}[e]
POS3ZO	50	66.9	77.6	—	75.5[f]
POS3ZO	58	70.2	81.2	—	80.2[f]
POS4ZO	65	87.4	102.0	49.1	98.6
POS5ZO	75	93.4	113.9	79.2	109.8
POS6ZO	82	111.8	134.1	98.6	132.4

[a]Determined from ^{1}H NMR measurements; [b]melting temperature; [c]isotropisation temperature; [d]transition from nematic to crystalline phase; [e]transition from isotropic to nematic phase; [f]determined by optical microscopy.

Table 2, the mesomorphic properties of POSnZO are affected by the substation degree and the length of spacer. It can be observed that the melting temperature (T_{m}) and the isotropisation temperature (T_{i}) increas as the degree of substitution and the length of spacer increase, but that T_{i} increased more than T_{m}. This suggests that a higher ratio of substitution and a longer flexible spacer leads to a wider mesomorphic temperature range (ΔT) and higher thermal stability.

When POSnZO was cooled from the isotropic phase, POS4ZO, POS5ZO and POS6ZO developed a well-defined schlieren texture, which was assigned as a nematic phase. POS3ZO gave a poor texture, but could still be identified as a mesophase.

X-ray diffraction

The existence of a liquid crystalline phase was further confirmed by X-ray measurements. The diffractograms of all POSnZO copolymers were similar to that of POS6ZO shown in Figure 7 as a representative example.

The diffraction pattern that was obtained with powder samples at ambient temperature without special treatment (Figure 7(a)) exhibited some sharp peak reflections in the wide-angle region (2θ≈19–25°) and even in the small-angle region, indicating the complex structure similar to quasi-crystal phase. The diffraction pattern that was obtained by heating the sample to the liquid-crystalline phase and then quenching in a liquid nitrogen bath (Figure 7(b)) revealed a diffuse broad halo in the wide-angle region. No peak was observed in the low-angle region. All the findings confirmed the presence of a nematic mesophase.

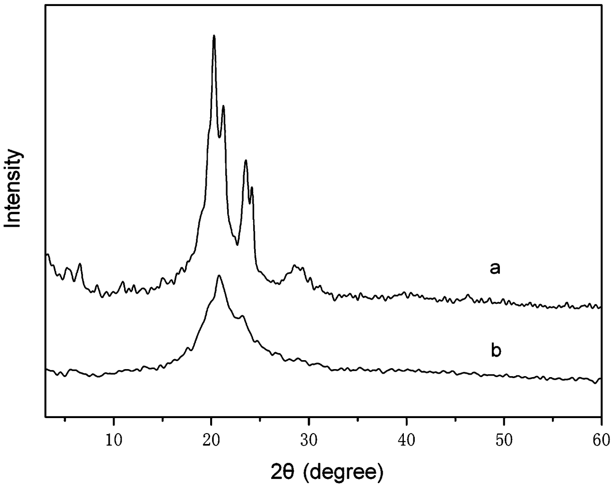


Figure 7. Wide-angle X-ray diffractograms of POS6ZO (a) before quenching and (b) after quenching.

4. Conclusion

A series of polyepichlorohydrin-based side-chain liquid crystalline copolymers containing a sulfur atom have been synthesised by the nucleophilic substitution reaction of mercaptans containing methoxylazobenzene with polyepichlorohydrin according to a previously developed synthetic approach. The structures of the synthesised compounds were confirmed by elemental analysis and ^{1}H NMR spectroscopy, which gave satisfactory data corresponding to the molecular structure expected. DSC measurements, POM investigations and WAXD studies indicated that the synthesised thiols and copolymers possessed liquid crystalline properties and displayed a nematic phase.

The substitution degree of all polymers synthesised increased with an increasing number of methylene units in the side-chain spacer. The flexible polyepichlorohydrin main chain and an excellent mesogenic group, i.e. methoxylazobenzene, contributed to the formation of nematic liquid crystals. When the number of methylene units in the side chain was 3 and the substitution degree was as low as 50%, the polymer still showed liquid crystalline behaviour.

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