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Synthesis and thermal behaviours of side-chain liquid-crystalline poly[N-(4-methoxyazobenzene-4′-oxyalkyl)ethyleneimine]

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A series of side-chain liquid-crystalline polymers, poly[N-(4-methoxyazobenzene- 4′-oxyalkyl)ethyleneimine](PEnZO), has been synthesised in which the number of methylene units in spacers varies from two to six. The structures of the synthesised monomers and polymers were confirmed by infrared (IR) and ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy. The thermal properties of these polymers have been investigated using differential scanning calorimetry (DSC), polarising optical macroscopic (POM) X-ray diffraction and thermogravimetric analysis (TGA). The test results indicated that the obtained polymers exhibited thermotropic liquid-crystalline mesomorphism of nematic type with schlieren textures. It was observed that the thermal behaviours of the polymers were strongly dependent on the degree of substitution and the length of spacers. Polymers containing less than 57% of mesogenic groups did not exhibit mesogenic phase and resembled amorphous polymer. A more pronounced odd–even effect in the melting points and their enthalpy changes was observed on increasing the spacer length in which the odd members displayed lower values, which were also slightly dependent on the substitution degree of polymers. The mesomorphic temperature ranges of odd members were wider than those of even members. The decomposition temperatures of copolymers were near 230°C.

Keywords: liquid-crystalline polymers; azobenzene; polyethyleneimine; thermal properties

1. Introduction

The side-chain liquid-crystalline polymers (SCLCP) containing azobenzene derivatives as mesogenic moiety and heteroatoms such as nitrogen, sulphur etc. have caused growing interest not only because of their great potential in a wide range of applications, such as information storage, holographic imaging (*1–3*) and non-linear optics (*4*) etc, owing to the *trans-cis-trans* photoisomerisation cycle of azobenzene moieties taking place during the UV and visible light irradiation, but also because they have the ability to adsorb some weight and noble metal ions for nitrogen lone-pair electrons possessing chelating feature and, therefore, can be used in the fields of separating and extracting these ions, such as Au^{3+}, Ag^+, Hg^{2+}, Pb^{2+}, Cu^{2+}, etc (*5–7*). Especially after quenching, these copolymers have a better order and selective adsorption for metal ions (*8*). Moreover, they could furnish a better understanding of self-assembly in molecular systems (*9–11*).

SCLCPs comprise three distinct units: a polymer backbone, a flexible spacer and a mesogenic unit. The thermal behaviours of SCLCPs depend on the structure and molecular weight of the main chain, the length of spacers, the constitution of mesogenic groups and their substitution degree. Polyethyleneimine (PEI) is a water-soluble polymer that can act as a backbone of SCLCPs. The SCLCPs using PEI as the main chain and 4′-cyanobiphenyl and 4′-methoxybiphenyl as mesogenic groups with different lengths of spacers, respectively, have been investigated (*8, 9*). Azobenzene derivates, which are a widely used mesogenic group, could be attached to many polymer backbones such as polyepichlorohydrin (*12, 13*), polymethacrylates (*14–16*), poly(4-hydroxystyene) (*17*), polysiloxanes (*18*), etc. to form corresponding copolymers which, even if with a lower substitution ratio, display mesomorphic properties. Ujiie (*19*) reported that a linear low molecule weight PEI (m = 5000) bearing mesogenic 4-methylazobenzene attached as a pendant group via six methylene spacers exhibited nematic phase. However, the copolymer showed a low glass transition temperature (10°C) and isotropisation temperature (87.2°C) owing to the lower molar mass of the PEI backbone. The corresponding ionic family had been synthesised and showed smectic phase. However, study of SCLCPs using PEI with a higher molecular weight as the main chain and 4′-methoxyazobenzene as a mesogenic group has not found dependence of thermal properties on the length of spacers and the substitution ratios.

In this paper, the attempt is made to synthesise the copolymers using PEI as the main chain and 4′-methoxyazobenzene as a mesogenic unit, in which the spacer length varies from two to six methylene units. The study focuses on the effect of the alkylene spacer

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length and the substitution ratio on thermal properties of resulting copolymers.

2. Experimental details

2.1 Materials

1,2-bibromoethane, 1,3-bibromopropane, 1,4-bibromobutane, 1,5-bibromopentane and 1,6-bibromohexan were purchased from Yixing East Fine Chemical Factory, China. PEI aqueous solution (50 wt%, $\overline{Mw}$ = 75,000) was purchased from BDH Laboratory Supplies, Poole, UK. Alkyl bromides and 1,4-dioxane were distilled under reduced pressure. Tetrahydrofuran (THF) was dried over an Na wire and distilled onto calcium hydride. All other reagents were used as commercially obtained.

2.2 Characterisation techniques

IR spectra were recorded using a Nicolet-60SXB FTIR spectrometer. ^{1}H NMR (300 MHz) spectra were recorded on a Varian Mercury VX-400 in $CDCl_3$ solutions, using tetramethylsilane (TMS) as an internal standard. Thermal characterisation was done via DSC on the TA DSC-Q10 instrument; the measurements were carried out with heating and cooling rates at 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 with Olympus BH-2 polarising optical microscopy (POM, magnification: 10×20) fitted with a Linkam THMSE 600 type heating stage. The X-ray diffraction patterns were obtained through a D/MAX-IIIA diffractometer (Rigaku, Tokyo, Japan) with nickel filtered Cu Kα radiation, at the scanning rate of 8° min^{-1}. TGA was conducted by using STA 449C (NETZSCH) instrument with a nitrogen atmosphere.

2.3 Synthesis

2.3.1 Synthesis of copolymers

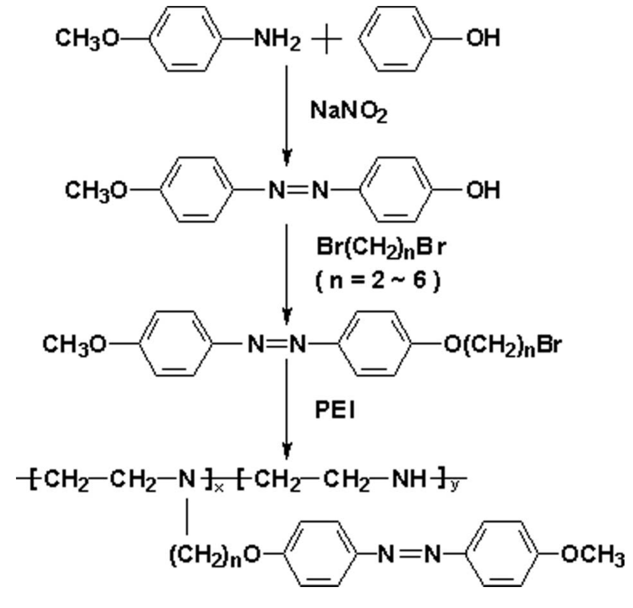
The synthetic route used for the preparation of copolymers, PEnZO, is outlined in Scheme 1.

2.3.2 Synthesis of monomers

2.3.2.1 4-Hydroxyl-4′-methoxy–azobenzene

4-Hydroxyl-4′-methoxy–azobenzene was prepared according to the method described by Stewart and Imrie (*16*). Yield: 37 g, 82%; mp: 140–141°C, IR (KBr, cm^{-1}): 3410(O-H), 2954 (C-H), 1230 (C-O, Ph-O-C); ^{1}H NMR ($CDCl_3$, δ ppm): 7.9–6.9 (m, aromatic, 8H), 3.9 (s, O$\underline{CH_3}$, 3H).

2.3.2.2 1-Bromo-ω-(4-methoxyazobenzene-4′-oxy) alkans (ZOn) Zon was prepared using the procedures reported in the literature (*12, 20*). In brief, a mixture of 1 (0.01 mol), α, ω-dibromoalkane (0.10 mol), potassium carbonate (0.10 mol) and dry acetone (100 ml) was refluxed with stirring for 24 h. The reaction mixture was filtered hot and the residue was washed thoroughly with acetone. The solvent 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 was recrystallised twice from ethanol with hot filtration.



Scheme 1. The reaction scheme for the synthesis of copolymers.

2.3.2.3 1-Bromo-2-(4-methoxyazobenzene-4′-oxy) ethane (ZO2) Yield: 65%; mp: 98–100°C; IR (KBr, cm^{-1}): 1249 (CH_2Br) 1498(–N=N–),^{1}H NMR ($CDCl_3$) δ (ppm): 7.89-7.00 (m, aromatic, 8H), 4.38 (t, $O\underline{CH_2}$, 2H), 3.86 (s, $PhO\underline{CH_3}$, 3H), 3.68 (t, $\underline{CH_2}Br$, 2H),

2.3.2.4 1-Bromo-3-(4-methoxyazobenzene-4′-oxy) propane (ZO3) Yield: 72%; mp: 98–100°C. IR (KBr, cm^{-1}): 1254 (CH_2Br), 1499 (–N=N–). ^{1}H NMR ($CDCl_3$) δ (ppm): 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).

2.3.2.5 1-Bromo-4-(4-methoxyazobenzene-4′-oxy) butyane (ZO4) Yield: 50%; mp: 112–114°C. IR (KBr, cm^{-1}): 1247 (CH_2Br), 1947 (–N=N–). ^{1}H NMR ($CDCl_3$) δ (ppm): 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).

2.3.2.6 1-Bromo-5-(4-methoxyazobenzene-4′-oxy) pentane (ZO5) Yield: 75%; mp: 94–96°C. IR (KBr, cm^{-1}): 1247 (CH_2Br), 1498 (–N=N–). ^{1}H NMR ($CDCl_3$) δ (ppm): 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).

2.3.2.7 1-Bromo-6-(4-methoxyazobenzene-4′-oxy) hexane (ZO6) Yield: 40%; mp: 106–108°C. IR (KBr, cm^{-1}): 1247 (CH_2Br), 1499 (–N=N–). ^{1}H NMR ($CDCl_3$) δ (ppm): 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).

2.3.2.8 Poly[N-(4-methoxyazobenzene-4′-oxyalky) ethyleneimine]s (PEnZO) PEnZO were synthesised by referring to similar methods (*7*, *19*) and using the improved method: 0.86 g (0.01 mol) of PEI (aqueous 50% solution), 1-bromo-ω-(4-methoxyazobenzene-4′-oxy)alkans and (0.01 mol) and 0.02 mol of sodium hydrogen carbonate were mixed in 20 ml of anhydrous ethanol. The reaction mixture was stirred at the reflux temperature under a dry nitrogen stream for 3 h. 20 ml of THF was added; after 6 h the solvent was removed in reduced pressure. Then, 30 ml of 1,4-dioxane was added and continued to be stirred at 90°C for 50 h. After the reaction, the mixture was filtered hot and the filtrate was concentrated and was poured into methanol. The obtained polymers were purified by repeated precipitation from chloroform into methanol until their being purified polymers was confirmed by thin layer chromatography. Finally the polymers were filtered off and dried under vacuum at 60°C for 48 h.

2.3.2.9 Poly[N-(4-methoxyazobenzene-4′-oxyethyl) ethyleneimine] (PE2ZO) Yield: 31%; substituting degree: 87%; IR (KBr, cm^{-1}): 3415(N-H); ^{1}H NMR ($CDCl_3$, δ ppm): 7.7–6.9 (m, aromatic, 8H), 4.0 (d, $OC\underline{H_2}$, $O\underline{CH_3}$ 5H), 2.5 (S, $N\underline{CH_2}$, 6.6H).

2.3.2.10 Poly[N-(4-methoxyazobenzene-4′-oxypropyl) ethyleneimine] (PE3ZO) Yield: 38%; substituting degree: 82%; IR (KBr, cm^{-1}): 3415(N-H); ^{1}H NMR ($CDCl_3$, δ ppm): 7.7–6.9 (m, aromatic, 8H), 3.8–3.9 (d, $O\underline{CH_2}$,$O\underline{CH_3}$, 5H), 2.5 (S, $N\underline{CH_2}$, 6.9H), 1.8 (s, $CH_2\underline{CH_2}CH_2$, 2H).

2.3.2.11 Poly[N-(4-methoxyazobenzene-4′-oxybutyl) ethyleneimine] (PE4ZO) Yield: 42%; substituting degree: IR (KBr, cm^{-1}): 3420 (N-H); 79%; ^{1}H NMR ($CDCl_3$, δ ppm): 7.7–6.9 (m, aromatic, 8H), 4.0 (d, $O\underline{CH_2}$,$OC\underline{H_3}$, 5H), 2.6-2.4 (S, $N\underline{CH_2}$, 7H), 1.8–1.5 (m, CH_2 $(\underline{CH_2})_2CH_2$, 4H).

2.3.2.12 Poly[N-(4-methoxyazobenzene-4′-oxypentyl) ethyleneimine] (PE5ZO) Yield: 59%; substituting degree: 76%; IR (KBr, cm^{-1}): 3418 (N-H); ^{1}H NMR ($CDCl_3$, δ ppm): 7.7-6.9 (m, aromatic, 8H), 4.0–3.9 (d, $O\underline{CH_2}$, $O\underline{CH_3}$, 5H), 2.6–2.5 (m, $N\underline{CH_2}$, 7.2H), 1.9–1.4 (m, CH_2 $(\underline{CH_2})_3CH_2$, 6H).

2.3.2.13 Poly[N-(4-methoxyazobenzene-4′-oxyhexyl) ethyleneimine] (PE6ZO) Yield: 62%; substituting degree: 70%; IR (KBr, cm^{-1}): 3421 (N-H); ^{1}H NMR ($CDCl_3$, δ ppm): 7.7–6.9 (m, aromatic, 8H), 3.9 (d, $O\underline{CH_2}$,$O\underline{CH_3}$, 5H), 2.8–2.4 (m, $N\underline{CH_2}$, 7.7H), 1.8–1.4 (m, CH_2 $(\underline{CH_2})_4CH_2$, 8H).

The substituting degree was calculated from ^{1}H NMR.

In synthesising, a series of PE3ZO with different substitution degrees were prepared by means of varying molar ratio of PEI to mesogenic group and other conditions shown in Table 1.

3. Results and discussion

3.1 Synthesis of copolymer PEnZOs

It was reported (*7*, *19*) that the alkylation of PEI with mesogenic alkyl bromides which was carried out in a mixed solution of THF and 1,4-dioxan or acetonitrile can achieve a high substitution degree. However, a

Table 1. The conditions and results of the preparation of PE3ZOs.

Sample	Solvent[a]	Molar ratio of PEI to mesogenic group	Temperature (°C)	Yield (%)	Substitution degree[b] (%)
PE3ZO46	A,B,C	1:0.5	70–90	85	46
PE3ZO57	A,B,C	1:0.65	70–90	83	57
PE3ZO63	A,B,C	1:0.75	70–90	79	66
PE3ZO71	A,B,C	1:0.85	70–90	70	71
PE3ZO79	A,B	1:1	70	65	79
PE3ZO85	A,B,C	1:1	70–90	73	85

[a] A: ethanol, B: tetrahydrofuran, C: 1,4-dioxane; [b] determined from ^{1}H NMR measurements.

large amount of solvent and long reaction time (96 h for 89% substitution degree) is required due to the low solubility of PEI in the solvent used. In addition, it was found that ethanol is a good solvent of PEI and mesogenic alkyle bromides can dissolve in hot ethanol as well. However, the resulting copolymer, which is insoluble in ethanol, was observed to precipitate in the reaction system. Therefore, further reaction may take place in a heterogeneous medium. This led to a low substitution degree for the final products (*7*).

In order to improve the conditions for the synthesis of PEnZOs, the choice of solvent was studied first in this work. After 3 h reaction of PEI with bromide in ethanol, THF, which can dissolve the resulting copolymer, was added into the system to ensure the following homogeneous reaction. The final copolymer with a substitution degree of 79% (PE3ZO79) was obtained in 56 h. Alternatively, the mixed solvent (ethanol and THF) was replaced with 1,4-dioxane after 6 h reaction as the above method was applied and the reaction temperature was elevated to 90°C. A higher substitution degree (85%) was achieved in another 50 h, probably due to the increased reaction temperature. In addition, only a slight increase in substitution degree was observed for a further longer reaction time. Nevertheless, a much shorter reaction time was required for the preparation of PEnZOs with a similar substitution degree via the method used in this work than via the methods reported before.

Using the improved method, a series of copolymers was synthesised with varied molar ratio of PEI chain unit to mesogenic group under identical reaction conditions. As shown in Table 1, the substitution degree of PEI increased with the increasing mesogenic group concentration. In addition, with the increasing spacer length (n = 2–6) the substitution degree decreased (see Table 2). This effect was in accordance with the reports on reaction of PEI with the cyanobiphenyl group (*7*) and chemical modification of polyepichlorohydrin (*21*).

3.2 *IR and ^{1}H NMR characterisation*

The chemical structures of the synthesised monomers and copolymers were characterised by IR spectroscopy and ^{1}H NMR to confirm the expected reaction routes and the resulting products.

Figure 1 shows the IR spectra of ZO3, PEI aqueous solution and PE3ZO as a representative example for PEnZOs. From the spectra, it can be found that the characteristic absorption bands at 1499 cm^{-1}, 3400 cm^{-1} and 1650 cm^{-1}, which are attributed to –N=N– in ZO3 and N-H in PEI, respectively (see Figure 1), have been observed in the IR spectrum of PE3ZO. This implied that the monomer ZO3 has been successfully grafted to the main chain of PEI.

The ^{1}H NMR spectra of mesogenic alkyl bromide and PE3ZO were measured as shown in Figure 2. It is evident that the shape of peaks in small molecule ZO3

Table 2. Thermal transition temperature and enthalpy change of PEnZOs.

		Phase transition temperature (°C) and enthalpy change (Jg^{-1})			
Sample	Substitution degree[a] (%)	T_m[b](ΔH)	T_i[c](ΔH)	$T_{n\text{–}k}$[d]	$T_{i\text{–}n}$[e](ΔH)
PE2ZO	87	83.9 (12.70)	123.7 (1.28)	–	119.0 (1.12)
PE3ZO	85	55.3 (8.20)	122.0 (0.83)	–	118.1 (0.94)
PE4ZO	79	93.6 (12.99)	135.4 (1.01)	–	132.0 (1.06)
PE5ZO	76	55.6 (7.83)	110.9 (1.10)	–	107.1 (1.09)
PE6ZO	70	89.3 (16.98)	122.4 (1.01)	–	120.9 (1.32)

[a] Determined from ^{1}H NMR measurements; [b] melting temperature; [c] isotropization temperature; [d] solidifying temperature; [e] transition from isotropic to nematic.

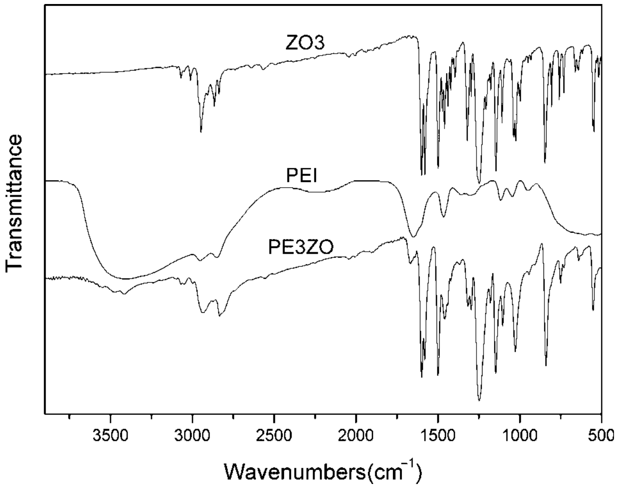


Figure 1. Infrared spectra of monomers ZO3, PEI and PE3ZO.

exhibited sharp multiplets (see Figure 1(a)), which became fewer or a broad singlet, shown in Figure 1(b), implying that the compound shown in Figure 1(b) was a polymer. In addition, the resonance peak at 3.6 ppm attributed to –CH$_2$Br in the monomer was replaced with a broad peak, which is attributed to –CH$_2$–N in the backbone. Furthermore, a small peak at 1.4 ppm was observed for the unreacted N–H in the main chain of PEI. The analysis above confirmed the attachment of the mesogenic groups onto the PEI backbone, which is in agreement with the reaction shown in Scheme 1. The ^{1}H NMR spectra of all PEnZOs (not shown) were similar to the model (Figure 1(b)).

3.3 Thermal properties

The thermal behaviour of the obtained copolymers (PEnZO, *n* = 2–6) has been studied by using DSC. The DSC traces of all selected samples displayed two endothermic peaks during heating, namely melting or glass transition and clearing transition, indicating that the copolymers exhibited thermotropic liquid-crystalline mesomophism. However, in cooling scanning curves, only a small exothermic peak, isotropic–nematic transition, has been observed and the phase transition from melting state to solid state was not found. This is probably due to the very slow process, i.e. the melting copolymers were unable to solidify in minutes even at a rate of 5°C min^{-1} to –20°C. Similar behaviour was detected for the compounds with a low substitution degree, while it was not found for the polymers with a high substitution degree (*13*). The probable reason is that the enthalpy changes associated with melting points are too small. As shown in Table 2, the maximum value of enthalpy change was 16.98 J g^{-1} for PE6ZO and the minimum was 7.83 J g^{-1} for PE5ZO, which is similar to that of low substitution

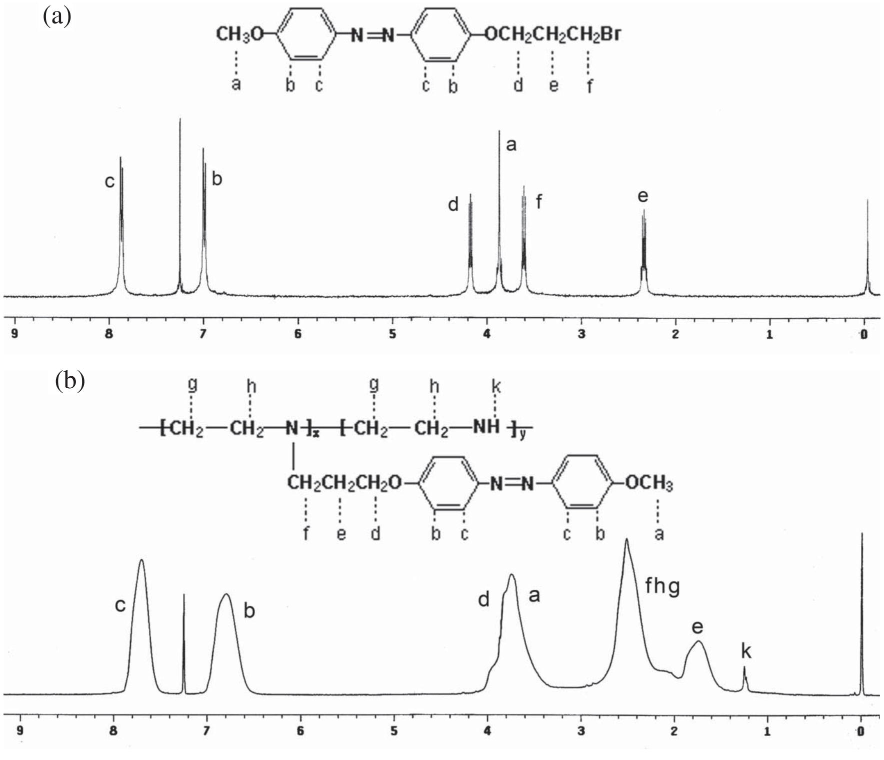


Figure 2. ^{1}H nuclear magnetic resonance spectrum of monomers ZO3 and PE3ZO.

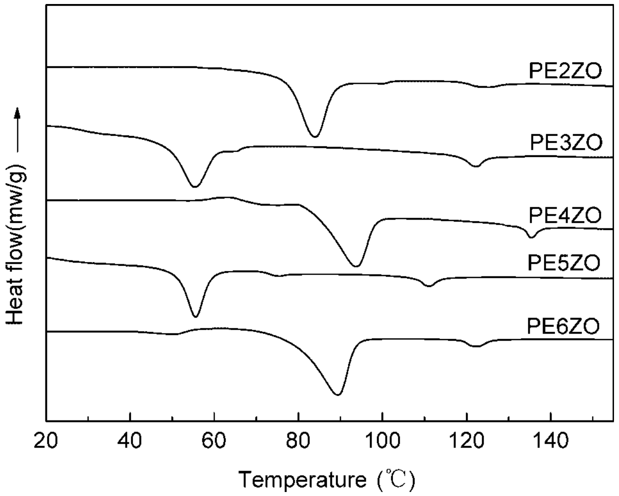


Figure 3. Differential scanning calorimetry thermogram of copolymer PEnZO at rate 20°C min^{-1} on second heating.

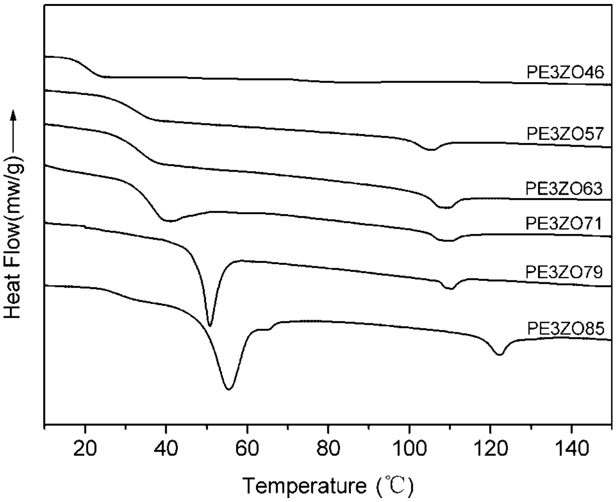


Figure 4. Differential scanning calorimetry thermogram of copolymer PE3ZOs at rate 20°C min^{-1} on second heating.

degree polyepichlorohydrin-based copolymers (*12*). The enthalpy changes associated with the transition between the liquid-crystalline phase and the isotropic phase were about 1 J g^{-1}, which indicated that all the polymers had an excellent mesogenic property. This is in accordance with the polarising optical observation (below).

The DSC curves of PEnZOs in a second heating are shown in Figure 3 and the data extracted from the second heating and cooling cycle are listed in Table 2. A significantly lower value in the phase transition temperature was obtained for PE3ZO and PE5ZO than for PE2ZO, PE4ZP and PE6ZO due to the odd–even effect of spacers. In addition, because the melting and clearing transition temperatures were influenced by the substitution degree of copolymers and the length of spacer, higher values were achieved for PE4ZO than for PE2ZO or PE6ZO.

To further investigate the effect of substitution degree on the thermal properties of Copolymers, a series of PE3ZOs with varied substitution degree was characterised by DSC. The DSC traces in the second heating scan are shown in Figure 4 and all the data extracted from the curves are listed in Table 3. Obviously, the thermal behaviour of copolymers was strongly dependent on the degree of substitution. Only one peak for glass transition was observed for PE3ZO46, resembling the typical amorphous polymer, while the clearing transition appeared in the DSC traces of all the copolymers with a substitution degree of more than 57%, indicating the existence of the liquid-crystalline phase. Moreover, the clearing transition temperature and enthalpy changes slightly increased with the increasing substitution degree (Table 3). On the other hand, PE3ZO57, PE3ZO63 and PE3ZO71 showed a broad peak (or a baseline shift) which is ascribed to a complex behaviour arising from several transitions and can be identified as a possible glass transition. However, the endothermic peaks of melting point appeared in the DSC traces of

Table 3. Thermal properties of PE3ZOs with different substitution degree.

		Phase transition temperature (°C) and enthalpy change (J g^{-1})			
Sample	Substitution degree (%)[a]	T^b	T_i^c	$T_{n-k}{}^d$	$T_{i-n}{}^e$
PE3ZO46	46	G23.5	–	–	–
PE3ZO57	57	G35.4	103.4 (0.71)	–	99.5 (0.86)
PE3ZO63	63	G37.4	104.8 (0.74)	–	100.4 (0.94)
PE3ZO71	71	G39.5	108.8 (0.82)	–	104.9 (1.18)
PE3ZO79	79	K50.7 (5.91)	110.0 (0.81)	–	107.7 (0.96)
PE3ZO85	85	K55.3 (8.20)	123.7 (0.83)	–	119.0 (0.94)

[a]Determined from ^1H NMR measurements; [b]G: glassy, K: crystalline; [c]isotropization temperature; [d]solidifying temperature; [e]transition from isotropic to nematic.

PE3ZO79 and PE3ZO85 at 50.7°C and 55.3°C, respectively. Furthermore, the glass transition temperatures (T_g) or melting point tended to increase as the substitution degree increased.

The glass transition temperature T_g reflects the mobility of chain segments and increases as the mobility of chain segments decreases. The T_g change means that ethyleneimine units can plasticise the copolymers. The polymer condensed state is considered in relation to the substitution degree of mesogenic groups. However, the mesomorphic temperature range did not appear any rule with the change of substitution degree. The reasons are expected to be further investigated.

3.4 *Liquid-crystalline phase structure*

The presence and type of liquid-crystalline phase can be detected by POMs in terms of texture of copolymers. In observation, the samples were heated to approximately 10°C above their clearing points and then cooled at 0.2°C min^{-1}. A schlieren texture was observed for all the selected PEnZOs when the isotropic phases were cooled to 120°C for PE2ZO, 130°C for PE3ZO, 122°C for PE4ZO, 100°C for PE5ZO and 129°C for PE6ZO (all samples are same with those in Table 2) and perfect patterns have been obtained, as partially shown in Figure 5, which is ascribed to nematic phase structure. Furthermore, it was found that the texture developing temperature was basically consistent with the respective second transition temperature measured by DSC (Figure 3). In addition, comparing the POM images of PE3ZOs with varied substitution degree, the poorer texture has been observed for the copolymer with lower substitution degree. The POM pattern of PE3ZO57 was like sands and a well-defined schlieren texture was obtained for PE3ZO85 (see Figure 5), whereas PE3ZO46 did not display any texture in the annealing process.

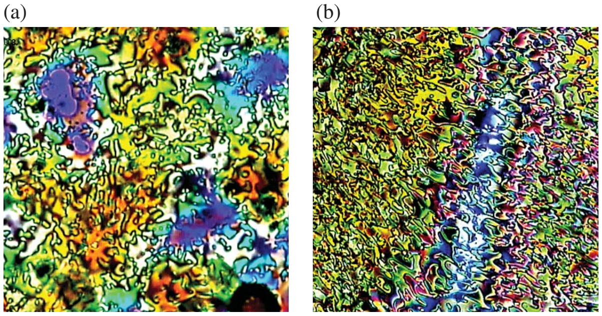


Figure 5. Polarizing optical micrograph of PE3ZO (a) and PE6ZO (b) schlieren texture taken at 118°C and 120°C, respectively.

X-ray diffraction measurement can further confirm the existence of a liquid-crystalline phase and identify the types of mesophase. The diffractograms of the mesophase for PEnZOs, which was obtained with copolymer powder samples at ambient temperature after being heated to liquid-crystalline phase and then quenched in a liquid nitrogen bath, presented a diffuse broad halo in the wide-angle region ($2\theta \approx 21°$) and no peaks in the small-angle region, which indicated that PEnZOs have no lamellar order in the direction of the molecular long axes and resemble amorphous polymers. The crystalline state diffractograms obtained with powder samples annealing from melting state at ambient temperature exhibited some sharp peak reflections in the wide-angle region ($2\theta \approx 19$–$25°$) and the small-angle region, which indicated the complex structure similar to the quasi-crystal phase. Figure 6 shows a PE4ZO diffraction pattern as a representative example. The other PEnZO patterns are similar to the model. All of the findings confirmed the presence of a nematic mesophase.

3.5 *Thermal stability*

The thermal degradation behaviour of a series of resulting copolymers PEnZO (n = 2–6) was investigated using TGA and the measurements were carried out under a nitrogen purge in the range of 50°C–500°C. The obtained TGA curves are shown in Figure 7, taking the samples PE3ZO and PE6ZO as representative examples. Obviously, a similar decomposition temperature for all the selected copolymers (approximately 230°C) could be observed, demonstrating that the thermal stability of PEnZO was weakly dependent on the length of spacers and the substitution degree for the cases studied.

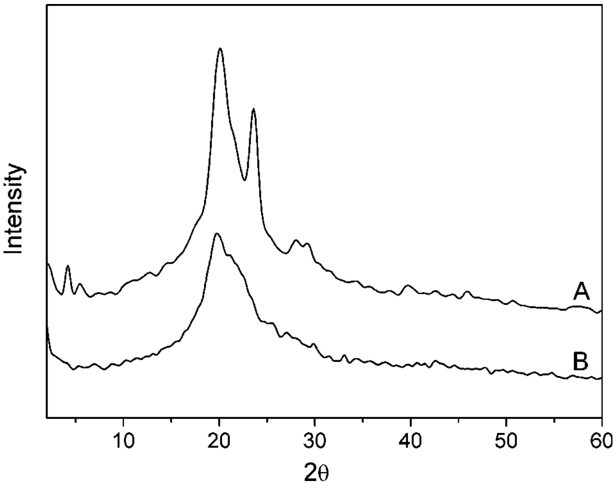


Figure 6. Wide-angle X-ray diffractograms of PE4ZO after annealing (A), after quenching in liquid nitrogen bath (B).

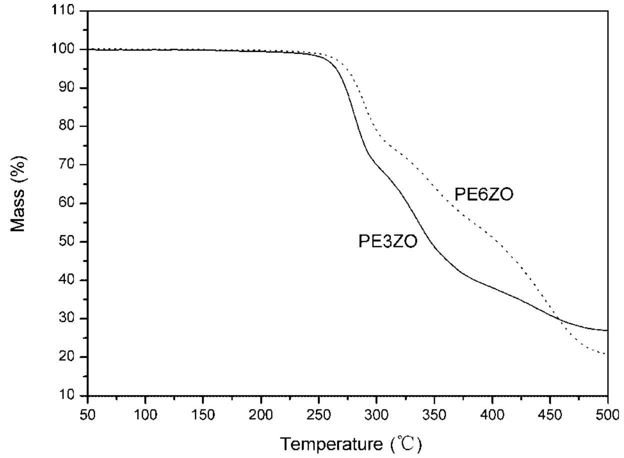


Figure 7. The thermogravimetric analysis curves of PE3ZO and PE6ZO under nitrogen.

3.6 The comparison of SCLCPs with different backbones

To establish the effect of backbone flexibility and structure of spacers on the transitional properties of SCLCPs, it is of interest to compare the glass transition temperatures or melting points and clearing temperatures, respectively, of the polyepichlorohydrin-based series (*12*), PEI-based series, poly(4-hydroxystyrene)-based series (*14*) and polymethacrylates-based series (*22*). Table 4 shows the transition temperatures for the polymers containing 4-methoxyazobenzene as the mesogenic unit, i.e. the Poly[N-(4-methoxyazobenzene-4′-oxyalkyl) ethyleneimine] (PEnZO), poly[4-[α-(4-meth-oxy-4′-oxyazobenzene)-ω-alkyl]oxystyrene (PSnZO), poly[1-({(4-methoxyazobenzene-4′-oxy) alkyl}thio) -2.3-epoxypropane]s (POSnZO) and poly[-(4′-methoxy-4-azophenyloxy)-methacrylates (PMAAZOn).

Among the four series, the change of glass transition temperatures or melting points and clearing points did not exhibit a common rule owing to the differences in their nature of main chains, the structure of spacers and the substitution degree of mesogenic groups. For the POSnZO series, the substitution degrees of the copolymers synthesised increased with the increasing number of methylene in the side chain. The phase transition temperature increased and the mesomorphic temperature range widened with the increasing substitution degree of the copolymers. For PSnZOs with a 100% substitution ratio, as for PEnZOs, a more significant odd–even effect in the melting points and clearing points was observed on increasing the spacer length in which the odd members displayed lower values. The PMAAZOns obtained by the free radical polymerisation of corresponding monomers displayed a pronounced odd–even effect in their clearing transition and no rules in the melting point or glass transition. In addition, POSnZO series and PEnZO series showed melting points and nematic phase in heating and the glass transition and smectic phase were observed for PSnZO series instead. PMAAZOns show nematic phase and glass transition (PMAAZO5 showed a melting point). Usually, it is thought that PEI is a backbone with relatively poorer flexibility than polyepichlorohydrin, poly(4-hydroxystyrene) and polymethacrylates. Flexible backbones tend to exhibit lower melting temperatures or glass transition temperatures than more rigid backbones. On the basis of backbone flexibility alone, it would be expected that the series based on the more rigid PEI backbone would yield SCLCPs possessing higher melting or glass transition temperatures than polyepichlorohydrin, poly(4-hydroxystyrene) and polymethacrylates. In fact, the expected trend has not been found. This should be mainly ascribed to the effect of spacers. The PEnZO series exhibits lower clearing temperatures than the other three series in general. This behaviour is in agreement with the view that increasing backbone flexibility enhances clearing temperature (*21*). Therefore, the properties of SCLCPs depend on the nature of the main chain, the structure and length of spacers and substitution degree of mesogenic groups besides the nature of mesogenic units.

4. Conclusions

This investigation demonstrated that PEI with a high molecular weight is flexible and has the ability to act as a suitable main chain component for side-chain liquid-crystalline polymers. It can react with 1-bromo-

Table 4. Phase transition temperature (°C) of SCLCPs with different backbones.

Polymers	PEnZO	POSnZO	PSnZO	PMAAZOn
$n = 2$	K83.9N123.7I			G112N161I
$n = 3$	K55.3N122I	K70N81I	G62	G71N116I
$n = 4$	K93.6N135.4I	K87N102I	G89S144I	G68N142I
$n = 5$	K55.6N110.9I	K93N114I	G72S110I	K102N128I
$n = 6$	K89.3N122.4I	K112N134I	G81S144I	G61K91N131I

G: glassy, K: crystalline, N: nematic, S: smectic, I: isotropic.

ω-(4-methoxyazobenzene-4′-oxy)alkans (n = 2, 3, 4, 5, 6) to yield poly[N-(4-methoxyazobenzene-4′-oxyalkyl)ethyleneimine]. Satisfactory spectroscopic data of IR and ^{1}H NMR corresponding to their expected molecular structures have been obtained. DSC traces, POM investigations and X-ray studies indicated that PEnZO (n = 2–6) samples exhibited liquid-crystalline phases of nematic type. It was proved that 4-methoxyazobenzene seems to be an excellent mesogenic group. The thermal properties and LC formation of the polymers were strongly affected by the degree of substitution in the side chain. The minimum substitution degree for liquid crystal formation seems to be 57%. The phase transition temperature, the clearing temperature and the stability of the mesomorphic phase increased as the substituting degree increased. A more pronounced odd–even effect was observed and the odd members displayed lower values in melting point and wider mesophase range than that of even ones. The decomposition temperatures of copolymers PEnZO were near 230°C.

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References

(1) Berg, R.H.; Hvilsted, S.; Ramanujant, P.S. **1996**, *Nature 383*, 505–508.
(2) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. **1992**, *Appl. Phys. Lett. 60*, 4–5.
(3) Rameshbabu, K.; Kannan, P. **2006**, *Polym. Int.*, *55*, 151–157.
(4) Xie, H.Q.; Liu, Z.H.; Liu, H.; Guo, J.S. **1998**, *Polymer 39*, 2393–2398.
(5) Zhang, C.C.; Li, X.; Pang, J.X. **2001**, *J. Appl. Polym. Sci. 82*, 1587–1592.
(6) Zhang, C.C.; Li, X.; Pang, J.X.; Wu, L.L. **2001**, *J. Wuhan Uni. Tec-Mater. Sci. Ed. 16*, 56–59.
(7) Xie, M.L.; Zhang, C.C. **2007**, *Liq. Cryst. 34*, 1275–1283.
(8) Zhang, C.C.; Xie, M.L. **2008**, *Polym. Prepr. 48*, 402–403.
(9) Kumar, S.; Kumar Pal, S. **2005**, *Liq. Cryst. 32*, 659–661.
(10) Ganesh,V.; Kumar Pal, S.; Kumarn, S.; Lakshminarayanan, V. **2006**, *J. Colloid. Inter. Sci. 296*, 195–203.
(11) Osuji, C.O.; Chao, Chi-Yang; Christopher, K.; Ober, Edwin L. Thomas **2006**, *Macromolecules 39*, 3114–3317.
(12) He, C.H.; Zhang, C.C.; Xie, M.L.; Zhang, S.Q. **2008**, *Liq. Cryst. 35*, 1321–1328.
(13) Hua, X.; Shanks, R.A.; Pavel, D. **2005**, *Euro. Polym. J. 41*, 984–991.
(14) Imrie, C.T.; Korasz, F.E.; Attard, G.S. **1992**, *Macromolecules 25*, 1278–1283.
(15) Cojocariu, C.; Rochon, P. **2004**, *J. Mater. Chem. 14*, 2909–2916.
(16) Stewart, D.; Imrie, C.T. **1996**, *Polymer 15*, 3419–3425.
(17) Zheng, Z.; Sun, Y.; Xu, J.; Chen, B.; Su, Z.Q.; Zhang, Q.J. **2007**, *Polym. Int. 56*, 699–706.
(18) Komitov, L.; Helgee, B.; Andersson, G.; Hjertberg, T. **2002**, *Macromol. Chem. Phys. 203*, 1724–1729.
(19) Ujiie, S.; Iimura, K. **1993**, *Polym. J. 25*, 347–354.
(20) Henderson, P.A.; Imrie, C.T. **2005**, *Macromolecules 38*, 3307–3311.
(21) Han, X.; Shanks, R.A.; Pavel, D. **2004**, *Macromol. Chem. Phys. 205*, 743–751.
(22) Zhang, H.C.; He, W.D.; Pan, C.Y. **1999**, *Acta Polym. Sin. 1*, 100–106.