Synthesis and Characterization of Side-Chain Liquid-Crystalline Polyacrylates Containing Azobenzene Moieties

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ABSTRACT: Syntheses of novel liquid-crystalline polymers containing azobenzene moieties were performed by a convenient route with an acrylate backbone. The azobenzenes were key intermediates of the monomers, and side-chain liquid-crystalline polymers were prepared, that is, poly[α-{4-[(4-acetylphenyl)azo]phenoxy}alkyloxy]acrylates, for which the spacer length was 3 or 11 methylene units. In addition, poly[3-{4-[(3,5-dimethylphenyl)azo]phenoxy}propyloxy]acrylate was prepared with a spacer length of 3 methylene units. The structures of the precursors, monomers, and polymers were characterized with Fourier transform infrared, ¹H-NMR, and ¹³C-NMR techniques. The polymers were obtained by conventional free-radical polymerization with 2,2′-azobis-isobutyronitrile as an initiator. The phase-transition temperatures of the polymers were studied with differential scanning calorimetry, and the phase structures were evaluated with a polarizing optical microscopy technique. The results showed that two of the monomers and their corresponding polymers exhibited nematic liquid-crystalline behavior, and one of the monomers and its corresponding polymer showed smectic liquid-crystalline behavior. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2653–2661, 2002

Key words: monomers; liquid-crystalline polymers (LCP); azo polymers; phase behavior

INTRODUCTION

Liquid-crystalline polymers have been attracting considerable interest in recent years because of their potential applications. In particular, side-chain liquid-crystalline polymers have potential technological applications, such as optical data storage, nonlinear optics, and ferroelectric devices.[1,2] Polymeric azobenzene liquid-crystal films have two advantages.[3] First, they have a much wider temperature range for the nematic phase, and so a wide temperature range is available for optical switching. Second, they have a glass-transition temperature, so they can function as image storage materials when they are operated at temperatures below the glass-transition temperature.

Polymer liquid crystals containing azobenzene moieties are potential materials for photonic applications such as digital and holographic storage.[4–8] Shibaev et al.[9] and Coles and Simon[10] reported laser-addressed polymer liquid-crystal storage displays in which heat-mode writing was exclusively employed. Photon-mode image storage in polymer liquid crystals was first demonstrated by Eich and coworkers[11,12] as holographic optical storage. Laser-beam-addressed recording has been achieved in side-chain polymer liquid crystals. They are mainly based on thermotropic effects, but photochemical reactions could play an important role in write-once storage materials.[13] An accepted mechanism was involved: photoselective trans–cis isomerization and consequent cis–trans back-isomerization. By the repetition of these trans–cis–trans isomerization cycles and the motion of their molecular long axis, the optic axis of azobenzene groups becomes aligned perpendicular to the electric field vector of polarized light.[14,15] To realize such potential applications, we prepared some novel liquid-crystalline polymers; mesogenic groups were used in the side-chain liquid-crystalline polymers, with a particular place held by *para*-acetylazobenzene as the mesogenic group.

MATERIALS AND METHOD

Materials

4-Aminoacetophenone, 3-bromopropanol, 11-bromoundecanol, and acryloyl chloride were commercially available (Fluka) and used as received. 2,2′-Azobisisobutyronitrile (AIBN; Merck, Darmstadt, Germany), sodium nitrite (BDH, Poole, England), 3,5-dimethyl aniline (Merck), urea (BDH), and phenol (Merck) were used as received. Dry tetrahydrofuran (THF) and triethylamine

(TEA) were obtained by distillation from calcium hydride before use. Other chemicals were used without further purification.

Synthesis of the monomers

4-(4-Acetylphenylazo)phenol (**L-1**)

4-Aminoacetophenone (10 g, 0.074 mol) was dissolved in 300 mL of acetone, and 27 mL of concentrated hydrochloric acid was added. The mixture was cooled and maintained within a temperature range of 0–2°C. Sodium nitrite (6.50 g, 0.0942 mol) in 20 mL of water was added dropwise to the cooled mixture and stirred for 1 h with a mechanical stirrer. Exactly 5 mL of a urea (1.21 g, 0.020 mol) aqueous solution was added for the decomposition of excess sodium nitrite for 10 min. Then, phenol (6.96 g, 0.074 mol) in 30 mL of acetone and 5 mL of water was added to the diazoted mixture and stirred for 2 h. The reaction was maintained at pH 6.8–7.0 with a sodium hydroxide solution. Thereafter, a saturated sodium acetate (ca. 15 g) solution was added for neutralization of the reaction mixture, and the precipitate was collected by filtration. The resulting product was recrystallized twice from methanol.

Yield: 12.11 g (68.1%). mp: 209°C. Fourier transform infrared (FTIR; KBr, cm^{-1}): 3323 (OH, ν), 1665 (C=O, ν), 1591 (N=N, ν), 1500, 1468 (aromatic $\nu_{C=C}$), 1398 (CH$_3$, δ), 1362 (OH, δ), 1245, 1140 (C—O, ν), 845 (aromatic δ_{C-H}). ^{1}H-NMR (CDCl$_3$, δ, ppm): 8.09 (2H, ArH—COCH$_3$), 8.07 (2H, ArH—N=N), 7.89 (2H, ArH—N=N), 6.97 (2H, ArH), 2.64 (3H, —OCH$_3$).

4-{[4-(3-Hydroxypropyloxy)phenyl]azo}acetophenone (**L-2**)

Compound **L-1** (3.00 g, 12.5 mmol) was dissolved in 40 mL of methanol and 15 mL of water containing 1.75 g of KOH (31 mmol) with a trace of KI was added. Then, 1.87 g of 3-bromopropanol (13.3 mmol) was added and refluxed for 12 h. The solvent was removed by reduced pressure, and dilute HCl was added to acidify the solution. The precipitate was collected by filtration, and the product was recrystallized from methanol.

Yield: 2.60 g (69.8%). mp: 200°C. FTIR (KBr, cm^{-1}): 3303 (OH, ν), 2942, 2854 (CH$_2$, ν), 1663 (C=O, ν), 1594 (N=N, ν), 1501, 1468 (aromatic $\nu_{C=C}$), 1360 (CH$_3$, δ), 1271, 1139 (C—O, ν), 845 (aromatic δ_{C-H}). ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.96 (2H, ArH—COCH$_3$), 7.92 (2H, ArH—N=N), 7.02 (2H, ArH—N=N), 6.97 (2H, ArH), 4.25 (2H, —OCH$_2$), 3.91 (2H, —CH$_2$O), 1.64 (2H, —CH$_2$), 2.67 (3H, —OCH$_3$).

4-{[4-(Acryloyl-3-oxypropyloxy)phenyl]azo}-acetophenone (**L-3**)

Compound **L-2** (2.00 g, 6.71 mmol) was dissolved in 50 mL of dry THF with TEA (1.91 g, 18.91 mmol), and the mixture was cooled to 0°C. Then, 1.17 g of acryloyl chloride (13 mmol) was added to the cooled mixture and refluxed for 6 h. The solvent was removed by reduced pressure, and the residue was dissolved in dichloromethane. The organic layer was washed with water, 10% NaHCO$_3$, and water. The resulting product was recrystallized from methanol.

Yield: 1.60 g (67.8%). mp: 148°C. FTIR (KBr, cm^{-1}): 3104 (acrylic =C—H, ν), 2940, 2855 (CH$_2$, ν), 1743 (ester C=O, ν), 1677 (C=O, ν), 1594 (N=N, ν), 1495, 1469 (aromatic $\nu_{C=C}$), 1359 (CH$_3$, δ), 1260, 1154 (C—O, ν), 850 (aromatic δ_{C-H}). ^{1}H-NMR (CDCl$_3$, δ, ppm): 8.09 (2H, ArH—COCH$_3$), 7.95 (2H, ArH—N=N), 7.32 (2H, ArH—N=N), 7.29 (2H, ArH), 6.03 (H, C=CH), 5.80 (H, CH=C), 6.28 (H, CH=C), 4.40 (2H, —OCH$_2$), 4.15 (2H, —CH$_2$O), 1.66 (2H, —CH$_2$), 2.64 (3H, —OCH$_3$).

4-{[4-(11-Hydroxyundecyloxy)phenyl]azo}-acetophenone (**L-4**)

Compound **L-1** (3.00 g, 12.5 mmol) and 1.75 g of KOH (31.2 mmol) with 0.30 g of KI were dissolved in 40 mL of methanol with 15 mL of water, and 3.38 g of 11-bromoundecanol (13.4 mmol) was added to the mixture. Compound **L-4** was prepared with the same method used for **L-2**.

Yield: 2.66 g (51.9%). mp: 171°C. FTIR (KBr, cm^{-1}): 3331 (OH, ν), 2927, 2857 (CH$_2$, ν), 1665 (C=O, ν), 1594 (N=N, ν), 1502, 1468 (aromatic $\nu_{C=C}$), 1366 (CH$_3$, δ), 1255, 1139 (C—O, ν), 844 (aromatic δ_{C-H}). ^{1}H-NMR (CDCl$_3$, δ, ppm): 8.05 (2H, ArH—COCH$_3$), 7.84 (2H, ArH—N=N), 7.01 (2H, ArH—N=N), 6.95 (2H, ArH), 4.03 (2H, —OCH$_2$), 3.62 (2H, —CH$_2$O), 3.35 (4H, —OCH$_2$CH$_2$), 3.32 (4H, —CH$_2$CH$_2$O), 1.54 (4H, —CH$_2$CH$_2$), 1.25 (6H, —CH$_2$CH$_2$CH$_2$) 2.64 (3H, —OCH$_3$).

4-{[4-(Acryloyl-11-oxyundecyloxy)phenyl]azo}-acetophenone (**L-5**)

Compound **L-4** (2.00 g, 4.87 mmol) was dissolved in 50 mL of dry THF and TEA (1.51 g, 14.95 mmol), and 0.90 g of acryloyl chloride (10 mmol) was added to the cooled mixture. Compound **L-5** was prepared with the same method used for **L-3**.

Yield: 1.68 g (74.3%). mp: 156°C. FTIR (KBr, cm^{-1}): 3104 (acrylic =C—H, ν), 2928, 2857 (CH$_2$, ν), 1744 (ester C=O, ν), 1677 (C=O, ν), 1594 (N=N, ν), 1495, 1413 (aromatic $\nu_{C=C}$), 1358 (CH$_3$, δ), 1298 (OH, δ), 1262, 1155 (C—O, ν), 849 (aromatic δ_{C-H}). ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.96 (2H, ArH—COCH$_3$), 7.91 (2H, ArH—N=N), 7.32 (2H, ArH—N=N), 7.28 (2H, ArH), 6.59 (H, C=CH), 6.01 (H, CH=C), 6.31 (H, CH=C), 4.12 (2H, —OCH$_2$), 4.01 (2H, —CH$_2$O), 3.33 (4H, —OCH$_2$CH$_2$), 3.30 (4H, —CH$_2$CH$_2$O), 1.56 (4H,

—CH$_2$CH$_2$), 1.24 (6H, —CH$_2$CH$_2$CH$_2$), 2.62 (3H, —OCH$_3$).

3,5-Dimethyl-(4-hydroxyphenylazo)benzene (L-6)

3,5-Dimethylaniline (10.00 g, 0.0650 mol) was dissolved in 250 mL of acetone with 22 mL of concentrated hydrochloric acid. Sodium nitrite (6.50 g, 0.0942 mol), 5 mL of a urea (2.00 g, 0.033 mol) solution, and 6.11 g of phenol (0.0656 mol) were added. Compound **L-6** was prepared with the same method used for **L-1**.

Yield: 8.56 g (57%). mp: 136°C. FTIR (KBr, cm^{-1}): 3430 (OH, ν), 2964, 2922 (CH$_3$, ν), 1599 (N=N, ν), 1506, 1430 (aromatic $\nu_{C=C}$), 1374 (CH$_3$, δ), 1383 (OH, δ), 1232, 1152 (C—O, ν), 852 (aromatic $\delta_{C—H}$). ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.84 (2H, ArH—N=N), 7.52 (2H, ArH—N=N), 7.07 (H, ArH), 6.92 (2H, ArH—OCH$_2$), 2.42 (3H, —CH$_3$), 2.40 (3H, —CH$_3$).

3,5-Dimethyl-{[4-(3-hydroxypropyloxy)phenyl]azo}-benzene (L-7)

Compound **L-6** (1.0 g, 4.4 mmol) was dissolved in 30 mL of methanol containing 0.58 g of KOH (10.3 mmol) with 0.10 g of KI, and 0.64 g of 3-bromopropanol (4.57 mmol) was added. Compound **L-7** was prepared with the same method used for **L-2**.

Yield: 0.80 g (63%). mp: 124°C. FTIR (KBr, cm^{-1}): 3462 (OH, ν), 2962, 2919 (CH$_3$, ν), 1738 (C=O, ν), 1594 (N=N, ν), 1495, 1405 (aromatic $\nu_{C=C}$), 1358 (CH$_3$, δ), 1291 (OH, δ), 1249, 1152 (C—O, ν), 853 (aromatic $\delta_{C—H}$). ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.82 (2H, ArH—N=N), 7.53 (2H, ArH—N=N), 7.10 (H, ArH), 6.92 (2H, ArH—OCH$_2$), 2.42 (3H, —CH$_3$), 2.39 (3H, —CH$_3$), 3.99 (2H, —OCH$_2$), 3.97 (2H, —CH$_2$O), 1.90 (2H, —CH$_2$).

3,5-Dimethyl-{[4-(acryloyl-3-oxypropyloxy)phenyl]-azo}benzene (L-8)

Compound **L-7** (0.50 g, 1.76 mmol) was dissolved in 20 mL of dry THF and TEA (0.50 g, 4.95 mmol) with 0.40 g of acryloyl chloride (4.44 mmol). Compound **L-8** was prepared with the same method used for **L-3**.

Yield: 0.45 g (67.43%). mp: 65°C. FTIR (KBr, cm^{-1}): 3122 (acrylic =C—H, ν), 2961, 2920 (CH$_3$, ν), 1737 (ester C=O, ν), 1664 (C=O, ν), 1602 (N=N, ν), 1547, 1417 (aromatic $\nu_{C=C}$), 1332 (CH$_3$, δ), 1227, 1152 (C—O, ν), 862 (aromatic $\delta_{C—H}$). ^{1}H-NMR (CDCl$_3$, δ, ppm): 8.18 (2H, ArH—N=N), 7.46 (2H, ArH—N=N), 7.40 (H, ArH), 7.10 (2H, ArH—OCH$_2$), 6.40 (H, C=CH), 6.34 (H, C=CH), 5.74 (H, CH=C), 2.42 (3H, —CH$_3$), 2.40 (3H, —CH$_3$), 3.20 (2H, —OCH$_2$), 3.01 (2H, —CH$_2$O), 1.90 (2H, —CH$_2$).

Polymerization

Polymer L-9

The monomer **L-3** (0.50 g, 1.42 mmol) and the initiator AIBN (5.7 mg, 0.035 mmol) were placed into a Schlenk-type flask with 10 mL of dry THF. The flask was sealed with a septum and degassed by N$_2$ for 20 min. Polymerization was performed in a water bath at 60°C for 24 h. The polymer was precipitated into methanol, and the product was washed several times with methanol for the removal of the monomer and then dried in vacuo.

Yield: 150 mg (30%). FTIR (KBr, cm^{-1}): 2931, 2852 (CH$_2$, ν), 1756 (ester C=O, ν), 1682 (C=O, ν), 1596 (N=N, ν), 1496, 1407 (aromatic $\nu_{C=C}$), 1361 (CH$_3$, δ), 1261, 1139 (C—O, ν), 847 (aromatic $\delta_{C—H}$).

Polymer L-10

The monomer **L-5** (0.50 g, 1.07 mmol) and AIBN (4.4 mg, 0.026 mmol) were placed into a Schlenk-type flask, and polymerization was performed with the same method used for **L-9**.

Yield: 161 mg (35%). FTIR (KBr, cm^{-1}): 2931, 2848 (CH$_2$, ν), 1756 (ester C=O, ν), 1682 (C=O, ν), 1598 (N=N, ν), 1498, 1407 (aromatic $\nu_{C=C}$), 1360 (CH$_3$, δ), 1264, 1140 (C—O, ν), 849 (aromatic $\delta_{C—H}$).

Polymer L-11

The monomer **L-8** (1.77 mmol) and AIBN (7.2 mg, 0.044 mmol) were placed into a Schlenk flask, and polymerization was performed with the same method used for **L-9**.

Yield: 122 mg (31%). FTIR (KBr, cm^{-1}): 2956, 2924 (CH$_2$, ν), 1739 (ester C=O, ν), 1601 (C=O, ν), 1598 (N=N, ν), 1535, 1407 (aromatic $\nu_{C=C}$), 1360 (CH$_3$, δ), 864 (aromatic $\delta_{C—H}$).

Characterization

FTIR spectra were recorded with a PerkinElmer (Spectrum BX II) spectrometer (Beaconsfield, England), and samples were tablets pressed with KBr. ^{1}H-NMR and ^{13}C-NMR spectra of the samples were recorded with a Bruker-DRX (300 MHz) spectrometer (Germany) with deuterated chloroform (CDCl$_3$) as a solvent. The thermotropic properties of the polymers were characterized with a PerkinElmer DSC-7 instrument. The rate of heating and cooling was 10°C min^{-1}, samples of 3–4 g were employed, and indium was used for calibration. The peak maximum was taken as the phase-transition temperature. Optical textures were observed with an Olympus BX50 polarizing optical microscope (Tokyo, Japan) equipped with a Linkam THMSE 600 heating stage (Waterfield, England) and a VTO 232 programmer (Waterfield, England). A Sony digital color video
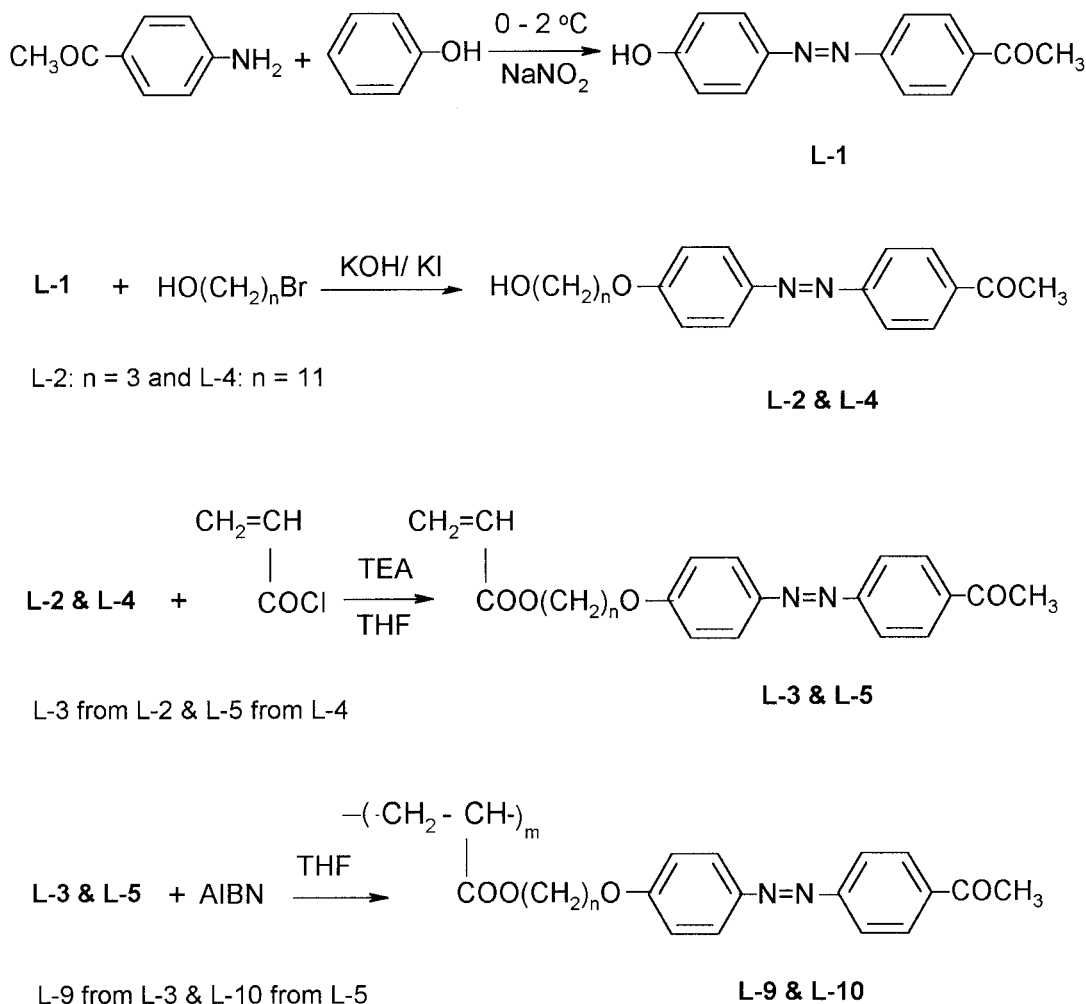
Scheme 1 Synthesis of polymers **L-9** and **L-10** from monomers **L-3** and **L-5**, respectively.

camera (Hyper HAD) and a Sony digital color printer (FVP-1E) were used for optical micrographs.

RESULTS AND DISCUSSION

Syntheses

Schemes 1 and 2 present an outline of the synthetic approach used to prepare the monomers and polymers containing azobenzene moieties. As shown in Scheme 1, the starting material was 4-aminoacetophenone, in which the amino group was diazoted with sodium nitrite in the presence of 3 equiv of hydrochloric acid. The diazonium salt was converted into **L-1** by coupling with phenol. The flexible spacer of the liquid-crystalline moiety was introduced by alkylation of the compound (**L-1**) with 3-brompropanol and 11-bromoundecanol and gave the corresponding compounds **L-2** and **L-4**, respectively, in the presence of potassium hydroxide as a base and a catalytic amount of potassium iodide. Esterification of the hydroxylated compounds **L-2** and **L-4** with acryloyl chloride in the

presence of dry TEA and THF yielded the polymerizable monomers **L-3** and **L-5**. Polyacrylates **L-9** and **L-10** were prepared from monomers **L-3** and **L-5** by free-radical polymerization with AIBN as an initiator with THF. Polymeric products **L-9** and **L-10** were precipitated in methanol, and the polymer yields were fairly low, ranging between 30 and 35%. Indeed, similar reaction yields were observed[16,17] in the polymerization of other acrylic monomers with azobenzene units.

In Scheme 2, the monomer and corresponding azo polymer were prepared by similar reactions, as described previously. The mesogenic part was prepared from the starting material 3,5-dimethyl aniline, in which the amino group was diazoted by sodium nitrite, and then the diazonium salt was coupled with phenol to produce the compound **L-6**. Alkylation of compound **L-6** with 3-brompropanol in the presence of potassium hydroxide as a base gave compound **L-7**. Compound **L-8** was prepared from **L-7** with acryloyl chloride by a similar method. Polymer **L-11** was pre-
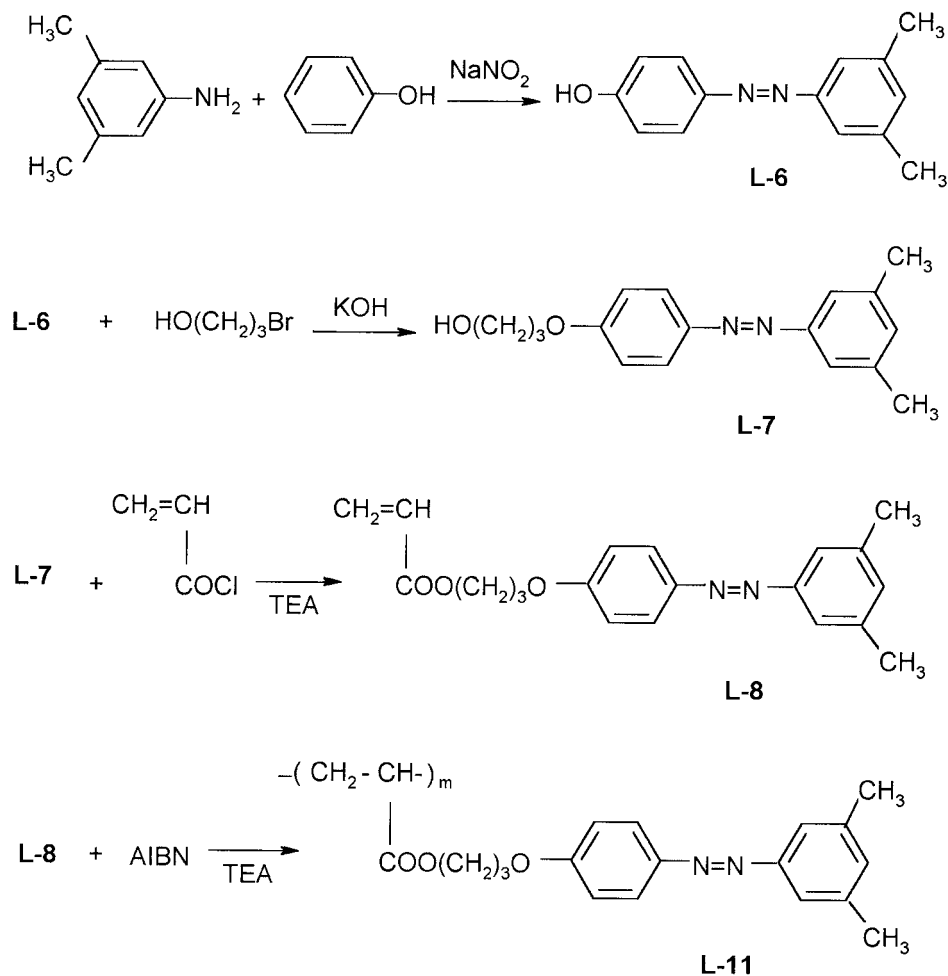
Scheme 2 Synthesis of polymer **L-11** from monomer **L-8**.

pared from **L-8** with AIBN, and the polymeric product was precipitated in methanol and washed several times with methanol to yield 120 mg (30%).

FTIR and NMR analyses

The IR spectra of monomers **L-3**, **L-5**, and **L-8** exhibited characteristic peak ν (=C—H) stretching at 3104, 3104, and 3122 cm^{-1}, respectively. However, no peaks were found in the corresponding polymers **L-9**, **L-10**, and **L-11**. This indicates that polymerization occurred in azobenzene moieties as side-chain polymers. ^{13}C-NMR spectra of monomers **L-3** and **L-5** are shown in Figure 1, and ^{1}H-NMR spectra of monomer **L-8** are also given in Figure 1.

Unambiguous information could be obtained from ^{13}C-NMR spectra of the monomer samples. The carbons of the aromatic, acrylate, and methylene spacers were assigned by the detailed NMR information already existing for 2-(6-{4-[(4-cynophenylazo)azo]-phenoxy}hexyl)-1,3-propenediol.[18] According to Hvilsted and et al.'s[18] suggestion, three additional peaks of monomer **L-3** in the aromatic region, at 131.3, 126.4,

and 124.8 ppm, are the meta (m), para (p), and ortho (o) carbons, respectively [Fig. 1(a)]. Similarly, three peaks of monomer **L-5** in the aromatic region, at 130.33, 128.6, and 125.1 ppm, are the meta, para, and ortho carbons, respectively, of a phenoxy moiety in azobenzene mesogenic groups [Fig. 1(b)].

The methylene carbons of flexible spacers of both monomers **L-3** and **L-5** are assigned at lower chemical shifts, from 25 to 67 ppm. The chemical shifts of acrylate carbons are higher than those of the aromatic region [Fig. 1(a,b)]. This rather detailed analysis of the displayed ^{13}C-NMR spectra of monomers **L-3** and **L-5**, and ^{1}H-NMR spectra of monomer **L-8** has been presented to extract the maximum possible structural information, and all visible resonances have, in fact, been assigned [Fig. 1(c)].

Phase behavior

Differential scanning calorimetry (DSC) was used to evaluate the phase transitions of the polymers. For each measurement, the sample was heated to 300°C, held there for 10 min for annealing, and gradually
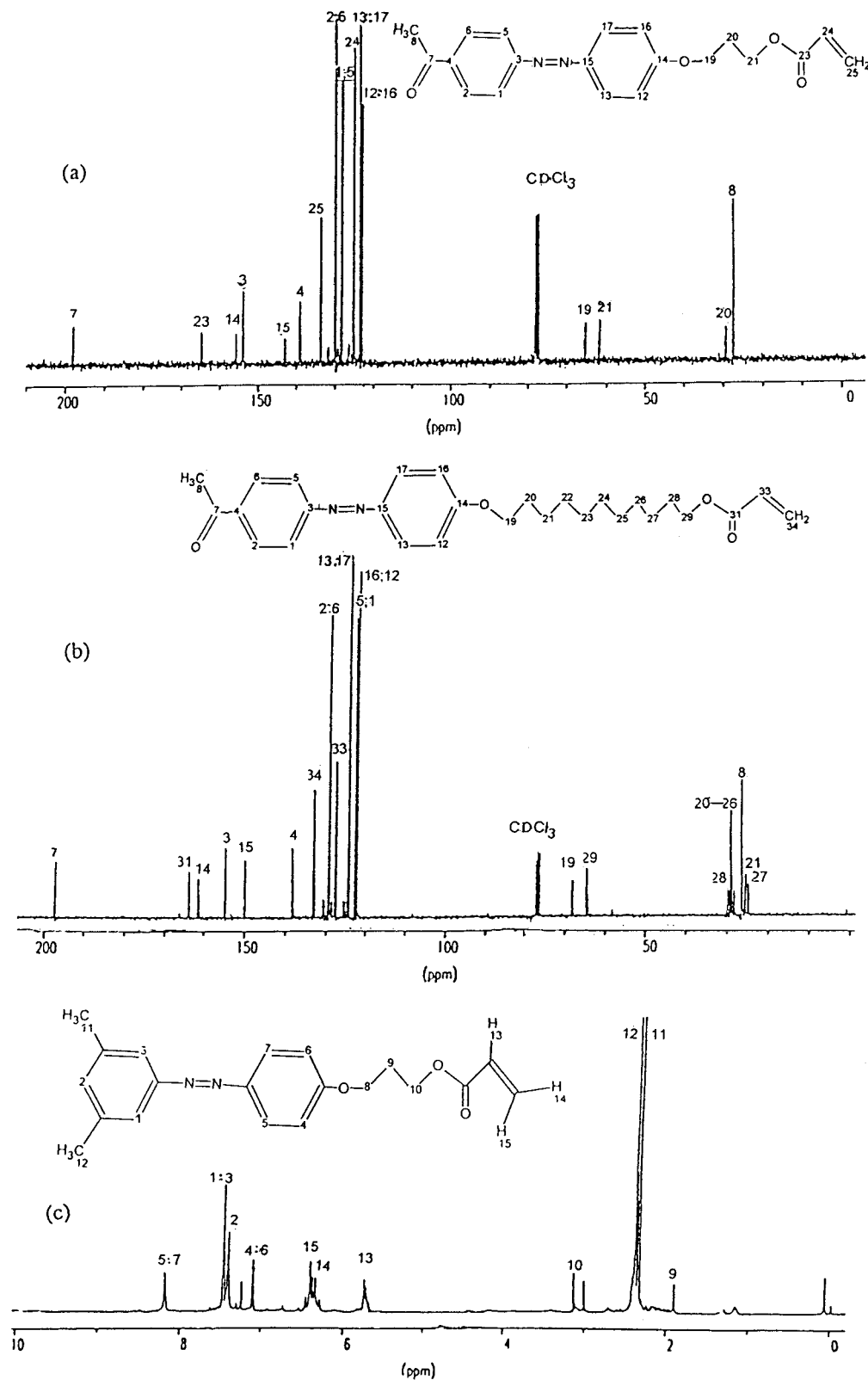
Figure 1 ^{13}C-NMR spectra of (a) monomer **L-3** and (b) monomer **L-5** and ^{1}H-NMR spectra of (c) monomer **L-8**.

cooled (10°C min^{-1}) to −20°C, at which temperature it was held for 10 min. Second heating and second cooling scans were taken from −20 to 300°C.

After cooling from an isotropic state, polymer **L-9** showed two exothermic peaks at 260 and 96°C corresponding to isotropic/liquid-crystalline and liquid-
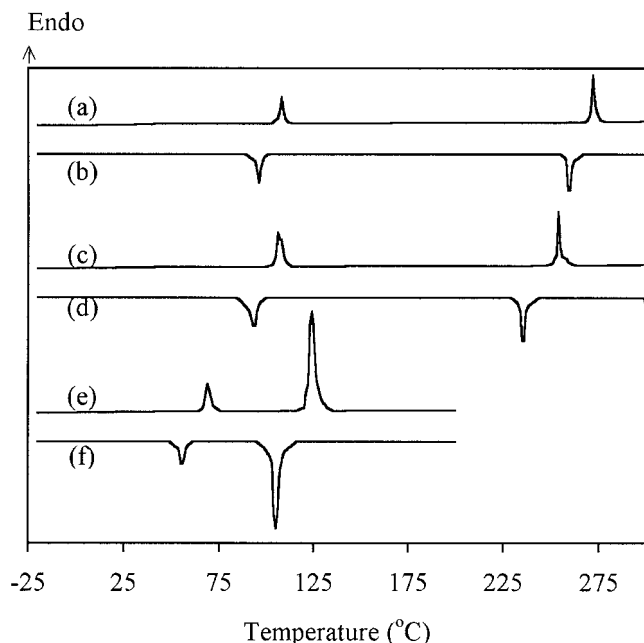
Figure 2 DSC thermograms of liquid-crystalline polymers for the second heating and second cooling at a rate of 10°C min^{-1}: (a) **L-9** on heating, (b) **L-9** on cooling, (c) **L-10** on heating, (d) **L-10** on cooling, (e) **L-11** on heating, and (f) **L-11** on cooling.

crystalline/crystalline transitions, respectively [Fig. 2(b)]. Polymer **L-9** also showed two endothermic peaks at 108 and 272°C under the heating cycle [Fig. 2(a)]. On cooling, polymer **L-10** showed phase transitions at 236 and 94°C corresponding to isotropic/liquid-crystalline and liquid-crystalline/crystalline transitions, respectively [Fig. 2(d)], and with heating, two endothermic peaks were observed at 107 and 254°C [Fig. 2(c)]. For cooling, the enthalpy changes for the isotropic/liquid-crystalline transitions were 2.51 and 2.62 (J g^{-1}), corresponding to polymers **L-9** and **L-10**, respectively. The small enthalpy changes of **L-9** and **L-10** indicated that both polymers exhibited a nematic phase. Polymer **L-11** showed two exothermic peaks on cooling at 105 and 56°C [Fig. 2(f)] and two endothermic peaks at 69 and 124°C under heating [Fig. 2(e)]. The large enthalpy change (11.52 J g^{-1}) of the isotropic/liquid-crystalline transition of **L-11** indicated that the polymer exhibited a smectic phase. No glass-transition temperature was detected in the given temperature range for all members of the polymers. DSC results for all polymer compounds are summarized in Table I.

The melting and nematic–isotropic transition temperatures for the monomers and polymers were dependent on the number n of CH$_2$'s in the alkyl segment. The isotropic point decreased with increasing spacer length. The mesophase properties of the polymers (**L-9**, **L-10**, and **L-11**) were markedly different

from those of the polymers, in which the azobenzene unit was replaced at the 4-position by a linear alkyloxy chain containing a variable number n of carbon atoms.[16] The lower homologues (n = 1–3) of the polymer series exhibited one nematic mesophase, whereas with further increasing n (n = 4 or 5), an additional smectic phase formed; the polymer became purely smectic for $n > 6$ according to Angeloni et al.[16]

The phase structures observed by polarizing optical microscopy during cooling from the isotropic point and in the liquid-crystalline phases are shown in Figure 3. The polarized optical micrographs of monomer **L-3** and its corresponding polymer **L-9** observed in their liquid-crystalline phases on cooling are shown in Figure 3(a,b), respectively. A typical schlieren texture for monomer **L-3** and polymer **L-9** was observed at 140 and 259°C, respectively, which are assigned nematic phases. The micrographs of monomer **L-5** and its corresponding polymer **L-10** in their liquid-crystalline phases exhibit typical nematic droplets on cooling from the isotropic state at 114 and 234°C, respectively. The photomicrographs of **L-5** and **L-10** are shown in Figure 3 (c,d), respectively. The monomer **L-8** and its corresponding polymer **L-11** also exhibited a schlieren texture at 56 and 104°C, respectively [Fig. 3(e,f)], which are assigned smectic phases.

Considering the results of DSC and polarizing optical microscopy analyses, we can conclude that two members of the monomer and polymer showed nematic liquid-crystalline behavior, and one monomer and polymer showed a tentative smectic phase. The polymers (**L-9** and **L-10**) possessed a greater propensity to give rise to a stable and persistent nematic mesophase, indicating that the replacement of an oxygen atom by a carbonyl group strongly enhanced the nematogenic character of the azobenzene group in the side-chain polymer.

In conclusion, the liquid-crystalline polymers containing azobenzene moieties in the side chain were prepared with an ordinary free-radical process. The mesophase behaviors of the polymers were investigated along with those of the analogous monomers, and the polymers (**L-9** and **L-10**) exhibited a nematic

TABLE I
Thermal Properties of Polymers L-9, L-10, and L-11

Polymer	Phase transition temperature (°C) and enthalpy change (J/g)	
	Second cooling	Second heating
L-9	I 260 [2.51] N 96 Cr	Cr 108 N 272 [3.01] I
L-10	I 236 [2.62] N 94 Cr	Cr 107 N 254 [3.51] I
L-11	I 105 [11.52] S 56 Cr	Cr 69 S 124 [12.60] I

The phase transition temperature was determined by DSC with a heating and cooling scan rate of 10°C/min. Cr = crystal; N = nematic; S = smectic; I = isotropic state.
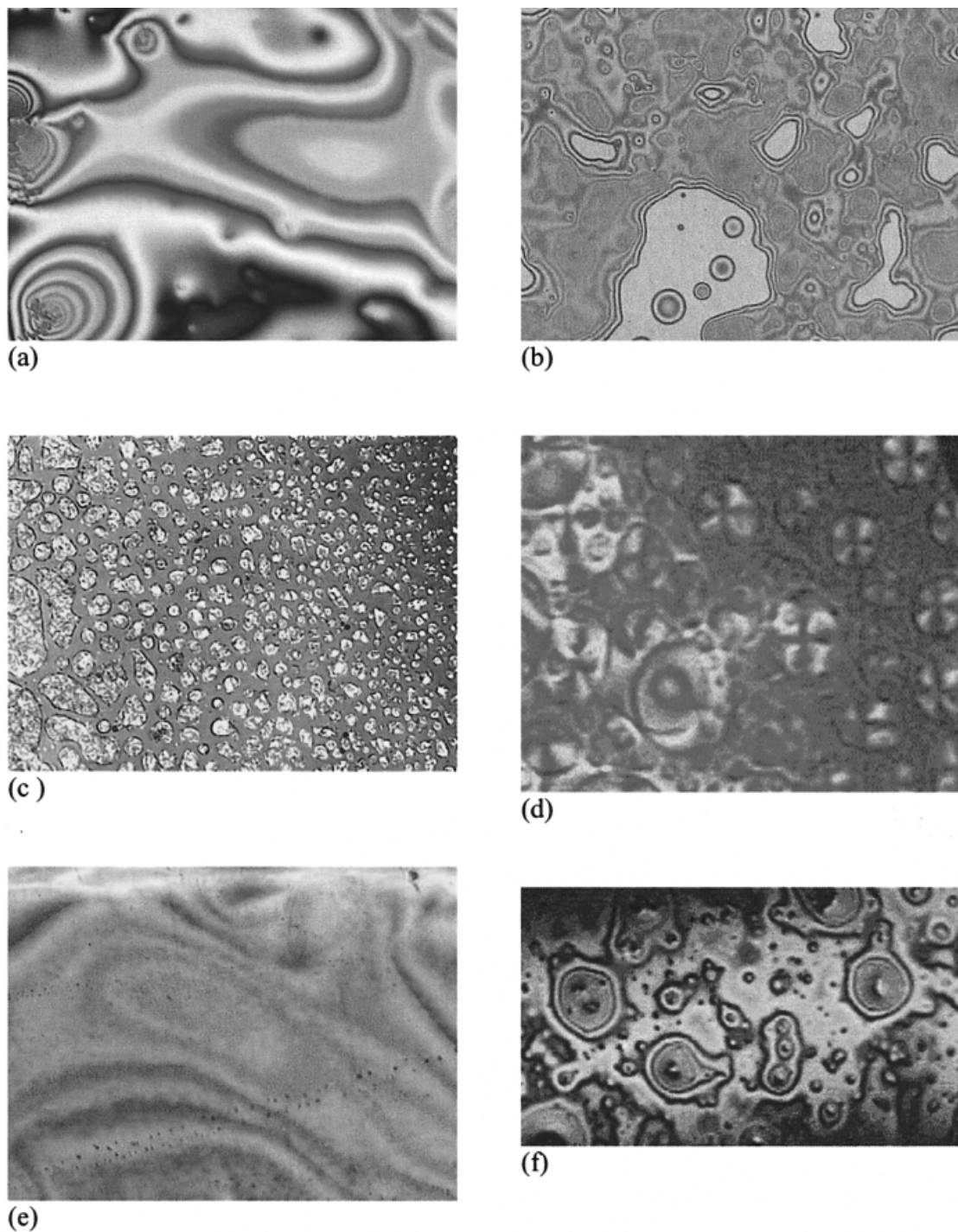Enthalpies are in square brackets.

Figure 3 Polarizing optical microscopy photographs of the monomers and corresponding polymers in their liquid-crystalline phases: (a) **L-3** at 140°C, (b) **L-9** at 259°C, (c) **L-5** at 114°C, (d) **L-10** at 234°C, (e) **L-8** at 56°C, and (f) **L-11** at 104°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

phase near the isotropic point. This study will be further extended to optical data storage materials.

References

1. Side Chain Liquid Crystal Polymers; McArdle, C. B., Ed.; Blackie: New York, 1989.
2. Kyu-Sik, K.; Takashi, K.; Toshiyuki, U. J Polym Sci Part A: Polym Chem 1999, 37, 3877.
3. Ikeda, T.; Shin, H.; Durga, K. B.; Seiji, K.; Shigeo, T. Macromolecules 1990, 23, 36.
4. Ikeda, T.; Tsutsumi, O. Science 1995, 208, 1873.
5. Eich, M.; Wendorf, J. H. J Opt Soc Am B 1990, 7, 1428.
6. Sasaki, A. Mol Cryst Liq Cryst 1986, 139, 103.

7. Ikeda, T.; Shin, H.; Durga, K. B.; Seiji, K.; Shigeo, T. Macromolecules 1990, 23, 42.

8. Kumar, S.; Manickam, M. Liq Cryst 1999, 26, 939.

9. Shibaev, V. P.; Kosttromin, S. G.; Plate, N. A.; Ivanov, S. A.; Vetrov, V. Y.; Yakovlev, I. A. Polym Commun 1983, 24, 364.

10. Coles, H. J.; Simon, R. Polymer 1985, 26, 1801.

11. Eich, M.; Wendorff, J. H.; Ringsdorf, H.; Schmidt, H. W. Makromol Chem 1985, 186, 2639.

12. Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. Makromol Chem Rapid Commun 1987, 8, 59.

13. Crivello, J. V.; Deptolla, M.; Ringsdorf, H. Liq Cryst 1988, 3, 235.

14. Tsutsumi, O.; Tahkeshi, S.; Ikeda, T.; Giancarlo, G. J Phys Chem B 1997, 101, 1332.

15. Ikeda, T.; Sasaki, T.; Ichimura, K. J Am Chem Soc 1994, 116, 625.

16. Angeloni, A. S.; Caretti, D.; Carlini, C.; Chielini, E.; Galli, G.; Altomare, A.; Solaro, R.; Laus, M. Liq Cryst 1989, 4, 513.

17. Galli, G.; Chielini, E.; Laus, M.; Angeloni, A. S.; Caretti, D.; Fanelli, E.; Poeti, G.; Gallot, B. Liq Cryst 1994, 16, 115.

18. Hvilsted, S.; Andruzzi, F.; Kulinna, C.; Siesler, H. W.; Ramanujam, P. S. Macromolecules 1995, 28, 2172.