Preparation and Characterization of Polyacrylate Containing Azobenzene Moieties in The Side Chain

M. R. Lutfor1, S. Silong1, M. J. Haron1, M. Z. Ab Rahman1, W. M. Z. Wan Yunus1, M. Ahmad1, Y. B. Che Man2 and C. P. Tan2

1Department of Chemistry
2 Department of Food Technology
Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

(Received 6 September 2000)

Abstract: Novel liquid crystal polymers have been prepared based on acrylate backbone. The liquid crystal polymers contain azobenzene moieties of poly[α-{4-[(3,5-dimethylphenyl)diazenyl]phenoxy}alkyloxy]acrylate in the side-chain without spacer or with spacer length of 3 methylene units. The characterization of precursor and monomer was carried out using FT-IR and NMR techniques. The ordinary free radical polymerization was used to obtain the side-chain liquid crystal polymers. The thermal behavior of the polymer was carried out using differential scanning calorimetry. The mesophase behavior of the polymers were investigated with those of the analogous monomers, the α-{4-[(3,5-dimethylphenyl)diazenyl]phenoxy}alkyloxy acrylate. It was observed that all polymers exhibited nematic phase near isotropic point.


Introduction

Before 1960, liquid crystals were virtually unknown. Today, they are all around us. They are used in the displays for calculators, lap-top computers, and pocket television set etc. Their greatest technological impact has been in displays, where liquid crystals are second only to the cathode ray tube in a multi-billion-dollar market. Their greatest potential is in tomorrow’s flat-panel television, optical computers, and integrated optical devices for communications. Polymer liquid crystals (PLCs) with azobenzene moieties in the side chain are promising materials for photonics. The azobenzene LCs change their molecular shape reversibly on photoirradiation [1-2]. The LC to I phase transition may be induced very quickly if the trans-cis photoisomerization of the azobenzene is brought about simultaneously by the use of a laser pulse. From the view-point of their application to optical devices, such fast response is quite favorable. This way of the photochemical phase transition of the polymer azobenzene LCs can be used as optical switching above Tg and as optical image storage materials below Tg [3-5].

We presented here the synthesis of polyacrylates bearing azobenzene mesogens. Essentially, the structures of the monomers are characterized, focusing on the phase behavior of liquid crystal polymers. The aim of this work is to study the effect of the structure of the azobenzene groups of the liquid crystalline behavior.

Materials and Method

3,5-Dimethyl aniline (Merck), 3-bromopropanol and acryloyl chloride was purchased from Fluka and was used as received. Dry tetrahydrofuran (THF) was freshly distilled over sodium and triethylamine (TEA) was distilled over calcium hydride.

Synthesis of monomers

4-{(4-hydroxyphenyl)diazenyl}3,5-dimethylphenylene (L-16): 3,5-dimethylaniline (0.0650 mol) was dissolved in 250 ml methanol with 22 ml of conc. HCl and the mixture was cooled at 0°C. Sodium nitrite (0.0942 mol) in 20 ml of water was added for 1 h. About 5 ml of urea (0.033 mol) solution was added to the diazoted mixture and it was stirred for 2 h. Sodium acetate (about 12 g) solution added for neutralized the reaction mixture and the precipitate was collected by filtration. The resulting product L-16 was recrystallized from methanol. Yield 8.56 g (57.94%) and m.p. 136 °C. IR ν/cm⁻¹ (KBr): 3430 (O-H str.), 2964.4 (C-H str.), 1599.6 (N=N str.). 1H NMR (CDCl₃): 7.84 (2H, ArH), 7.81 (2H, ArH), 7.47 (2H, ArH), 7.07 (2H, ArH), 6.75 (H, PhOH), 2.40 (3H, CH₃), 2.39 (3H, CH₃).
4-[(4-(3-hydroxypropoxy)phenyl)diazenyl]3,5-dimethylphenylene (L-23): The compound L-16 (0.0044 mol) was dissolved in 30 ml methanol, and 10.3 mmol KOH in 10 ml water with 0.10 g KI. Then 0.64 g of 3-Bromopropanol (4.57 mmol) was added and reflux for 12 h. Solvent was removed by reduced pressure and dilute HCl was added to acidified the solution. The precipitate was collected by filtration and the product was recrystallized from methanol. Yield 0.80 g (63%) and m.p. 124 °C. IR ν/cm⁻¹ (KBr): 3462.3 (O-H str.), 2919.2 (C-H str.), 1741.5 (C=O str.), 1594.6 (N=N str.).

3-[(4-(3,5-dimethylphenyl)diazenyl)phenoxy]propyl acrylate (L-24): The compound L-23 (1.76 mmol) was dissolved in 20 ml THF with TEA (4.95 mmol) and the mixture was cooled to 0°C. Then acryloyl chloride (4.44 mmol) was added to the cooled mixture and stirred for 6 h at 0°C. Solvent was removed and the residue was dissolved in dichloromethane. The organic layer was washed with water, 10% NaHCO₃ and water. The resulting product was recrystallized from ethanol. Yield 0.45 g (67.43%) and m.p. 65 °C. IR ν/cm⁻¹ (KBr): 3438.5 (O-H str.), 3122.7 (C=C str.), 2961.4 (C-H str.), 2920.4 (C-H str.), 1741.5 (C=O str.), 1602.3 (N=N str.). ¹H NMR (CDCl₃): 7.46 (2H, ArH), 7.40 (2H, ArH), 7.10 (2H, ArH), 8.18 (2H, ArH), 6.41 (H, -CH-), 6.34 (H, -OCH-), 5.74 (H, -CH-), 2.24-2.04 (4H, -CH₂CH₂-), 1.90 (2H, -CH₂-), 2.42 (3H, CH₃), 2.39 (3H, CH₃).

4-[(3,5-dimethylenyl)diazenyl]phenoxy)propyl acrylate (L-25, L-27): The compound L-16 (0.0044 mol) was dissolved in 30 ml THF and TEA (9.90 mmol) and the mixture was cooled to 0°C. Then acryloyl chloride (8.88 mmol) was added to the cool mixture and reflux for 6 h at 0°C. The compound L-27 was prepared as same method of L-25. Yield 0.80 g.
Polymers (L-25, L-27): The monomer L-24 (1.77 mmol) and the initiator AIBN (4 mg) was placed into a Schlenk flask with 10 ml THF. The flask was sealed by septum and degassed by N₂ for 20 min. Polymerization was performed in water bath at 60 °C for 24 h. The polymer was recovered into methanol and the product was washed several times with methanol to remove monomer and air-dried. Yield 120 mg (30%) and m.p. 220 °C. IR ν/cm⁻¹ (KBr): 3436.9 (O-H str.), 2961.8 (C-H str.), 2925 (C-H str.), 1602 (N=N str.).

Polymer (L-27): The monomer L-26 (1.64 mmol) and 3 mg AIBN was placed into a Schlenk type flask and polymerization was performed by free radical polymerization in solution with 2,2'-azobis-isobutyronitrile (AIBN) as an initiator at 60 °C using THF. Polymeric products were recovered in methanol and washed several times with methanol for removing the monomer. Polymerization yields were not high ranging between 30 and 35%. Indeed, similar reaction yields were observed [2-3] in the polymerization of other acrylic monomers containing the same azobenzene units.

Characterization

The IR spectra of the polymers indicated no characteristic absorption peak of the monomers. The monomer L-24 and L-26 exhibited the characteristic peak νC=C stretching at 3122 cm⁻¹ and 3028 cm⁻¹ respectively. On the other hand no peaks found in the respective polymers. This indicates polymerization occurred in the azobenzene moieties. ¹H NMR spectrum of the monomer L-24 is shown in Fig. 1, and the NMR data are given for proofs of the monomer.

Results and Discussion

Synthesis

The synthetic approach used to prepare the monomers and polymers are shown in scheme 1. The mesogenic part was prepared from the starting material of 3,5-dimethyl aniline in which amino group is diazotized by sodium nitrite in presence of 3 equivalent HCl at 0 °C and then diazonium salt was transformed into 4-[(4-hydroxyphenyl)diazenyl]3,5-dimethylphenylene (L-16) by coupling with phenol. 4-[(4-(3-hydroxypropoxy)phenyl)diazenyl]3,5-dimethylphenylene (L-23) was prepared by esterification with 3-bromopropanol and the phenolic compound (L-16) in presence of aqueous KOH and catalytic amount of KI. The final reaction between hydroxylated compounds (L-23) and acryloyl chloride was performed in presence of dry triethylamine using THT as solvent. Polyacrylates (L-25, L-27) were prepared by esterification with 3-bromopropanol and the phenolic compound (L-16) in presence of aqueous KOH and catalytic amount of KI. The final reaction between hydroxylated compounds (L-23) and acryloyl chloride was performed in presence of dry triethylamine using THT as solvent. Polyacrylates (L-25, L-27) were prepared by free radical polymerization in solution with 2,2’-azobis-isobutyronitrile (AIBN) as an initiator at 60 °C using THF. Polymeric products were recovered in methanol and washed several times with methanol for removing the polymer. Polymerization yields were not high ranging between 30 and 35%. Indeed, similar reaction yields were observed [2-3] in the polymerization of other acrylic monomers containing the same azobenzene units.

Characterization

The IR spectra of the polymers indicated no characteristic absorption peak of the monomers. The monomer L-24 and L-26 exhibited the characteristic peak νC=C stretching at 3122 cm⁻¹ and 3028 cm⁻¹ respectively. On the other hand no peaks found in the respective polymers. This indicates polymerization occurred in the azobenzene moieties. ¹H NMR spectrum of the monomer L-24 is shown in Fig. 1, and the NMR data are given for proofs of the monomer.
Phase behavior
DSC thermograms of the polymers L-25 and L-27 are shown in Fig. 2. In each measurement, the sample was heated to a temperature ~220 °C, then held 10 min for annealing and gradually cooled down to a temperature -20 °C and kept for 10 min. Second heating scans are taken at the temperature range from -20 to 250 °C. We observed for polymers L-25 and L-27, two endothermic events: one occurring at a temperature 12 °C due to glass transition (T_g) of the polymers and other correspond to nematic phase transition near isotropic point of the polymer liquid crystals (Fig. 2).

Fig. 2: DSC thermograms of polymers L-25 and L-27.

Conclusion
The liquid crystal polymers containing azobenzene moieties in side-chain is poly{α-[4-[(3,5-dimethylphenyl)diazenyl]phenoxy]alkyloxy}acrylate prepared using ordinary free radical process. The mesophase behavior of the polymers were investigated with those of the analogous monomers, the α-[4-[(3,5-dimethylphenyl)diazenyl]phenoxy]-alkyloxy acrylate. All polymers exhibited nematic phase near isotropic point. This study will further extended for investigation of optical imaging and switching behavior.

Acknowledgment
This research was supported from a IRPA grant (No. 09-04-02-0057), Ministry of Science and Technology, Malaysia, 1997.

References