Synthesis And Comparison Of Liquid Crystal Polymers And Monomers Containing Azobenzene Mesogens


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Abstract: The syntheses of novel liquid crystal polymers containing azobenzene moieties were carried out according to convenient route having a acrylate backbone. The azobenzenes are key intermediates of the monomers and the side-chain liquid crystal polymer is the poly[α-{4-(4-acetylphenyl)diazenyl]phenoxy}alkyloxy]acrylate in which spacer length is varied from 3 to 11 methylene units. The precursors and monomers were characterized by using FT-IR, NMR techniques. The polymers were obtained by conventional free radical polymerization using AIBN as an initiator. The thermal properties of the polymers were studied by using differential scanning calorimetry. The thermal behavior of the polymers are compared with those of the analogous monomers, the α-{4-(4-acetylphenyl)diazenyl]phenoxy}alkyloxy acrylate and it was found that all polymers exhibited nematic phase near isotropic point and no phase transition observed in the monomers.


Introduction

Liquid crystals (LC) have been most extensively used as display materials. Successful applications of the LC display for calculators, sentences display, word processors, and full-color TV display [1]. Polymer liquid crystals (PLC) for image storage materials has been reported by several groups [2-4]. Photoinduced alignment of PLCs containing azobenzene moieties has attracted much attention in the last decade, mechanism involves the photoselective trans-cis isomerization and cis-trans back isomerization. Repetition of trans-cis-trans isomerization cycles and motion of their molecular long axis, the optic axis of azobenzene groups becomes aligned perpendicular to the electric field vector of polarized light. Inert mesogens undergo alignment together with the azobenzene groups for cooperative motion [5].

In this communication, we report a novel liquid crystal polymer preparation and properties of the polyacrylates bearing photoresponsive azobenzene mesogen, as well as those of the relevant monomers and intermediates.

Materials And Method

4-Aminoacetophenone, 3-bromopropanol, 4-chlorobutanol, 11-bromoundecanol, acryloyl chloride were purchased from Fluka. Dry tetrahydrofuran (THF) was distilled over sodium and triethylamine (TEA) was distilled over calcium hydride (CaH2).

Synthesis of monomers

1-{4-[(4-hydroxyphenyl)diazenyl]phenyl}ethanone (L-15): 4-Aminoacetophenone (0.0740 mol) in 300 ml methanol with 27 ml of conc. HCl and mixture was cooled at 0°C. Sodium nitrite (0.0942 mol) in 20 ml of water was added and stirring for 1 h. About 5 ml of urea (0.020 mol) was added and phenol (0.0740 mol) in 30 ml acetone with 1.0 g NaOH was added to the diazotized mixture for 2 h. Sodium acetate (15 g) solution was added, neutralized the reaction mixture and the precipitate was collected by filtration. The crude product L-15 was recrystallized from methanol. Yield 12.11 g (68.10%) and m.p. 209°C.

1-(4-[(4-(3-hydroxypropoxy)phenyl]diazenyl]phenyl)ethanone (L-17): The L-15 (0.0125 mol) in 40 ml methanol and 1.75 g KOH in 15 ml water with a trace of KI. Then 3-bromopropanol (0.0133 mol) was added and reflux for 12 h. Solvent was removed by reduced pressure and dilute HCl was
added to acify the solution. The precipitate was collected by filtration and the product was recrystallized from methanol. Yield 2.60 g (69.79%) and m.p. 200 °C.

3-{4-[(4-acetylyphenyl)diazenyl]phenoxyl}propyl acrylate (L-18): The compound L-17 (6.71 mmol) in 50 ml THF with TEA (18.91 mmol) and the mixture was cooled to 0°C. Then acryloyl chloride (13 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 methanol. Yield 2.60 g (69.79%) and m.p. 130 °C. IR ν/cm⁻¹ (KBr): 3457 (O-H str.), 3104 (C=C str.), 3000.6 (C-H str.), 1743.4 (C=O, str.), 1677.7 (C=O, str.), 1594.2 (N=N str.). ¹H NMR (CDCl₃): 3.60 (4H, -CH₂CH₂-), 3.33-3.30 (6H, -CH₂CH₂ CH₂-), 2.61 (3H, CH₃).

Polymerization

Polymer (L-19): The monomer L-18 (1.4 mmol) and AIBN (4 mg) placed in a schlenk flask with 10 ml THF. The flask was sealed by septum and degassed by N₂ for 20 min and warmed in a water bath at 60°C for 24 h. The polymer was precipitated into methanol, re-precipitated in fresh methanol to purified from unreacted monomer and air-dried. Yield 150 mg (30%) and m.p. 189 °C. IR ν/cm⁻¹ (KBr): 3450 (O-H str.), 2931 (C-H str.), 1756 (C=O str.), 1682.3 (C=O str.), 1596.5 (N=N str.).

Polymer (L-22): The monomer L-21 was polymerized as same method of L-19. Yield 155 mg (31%) and m.p.180 °C. IR ν/cm⁻¹ (KBr): 3494.6 (O-H str.), 2931.5 (C-H str.), 2850 (C-H str.), 1756.4 (C=O str.), 1682.5 (C=O str.), 1598 (N=N str.).

Polymer (L-30): The monomer L-28 was polymerized as same method described in L-19. Yield 120 mg (30 %) and m.p. 185 °C. IR ν/cm⁻¹ (KBr): 3451.9 (O-H str.), 2937.5 (C-H str.), 1756.1 (C=O str.), 1681.6 (C=O str.), 1596.7 (N=N str.).

Results and Discussion

Syntheses

Scheme 1 is the outline of the synthetic approach used to prepare the monomers and the polymers. The starting material is 4-aminoacetophenone in which amino group is diazoted by sodium nitrite in presence of 3 equivalent HCl at 0 °C. The diazonium salt was converted into 1-{4-{[(4-hydroxy phenyl)diazenyl]phenyl}ethanone (L-15) by coupling with phenol. 1-{4-{[(4-3-Hydroxypropoxy)phenyl]diazenyl}phenyl}ethanone (L-17) and 1-{4-{[(4-hydroxyundecanoxy)phenyl]diazenyl}phenyl}ethanone (L-20 were prepared by esterification with 3-bromopropanol and 11-bromoundecanol, respectively, using the phenolic compound (L-15) in presence of aqueous KOH and catalytic amount of KI. Another esterification of 1-{4-{[(4-hydroxybutyloxy)phenyl]diazenyl}phenyl}ethanone (L-28) was carried out with 4-chlorobutanol of phenolic (L-15) in presence of anhydrous K₂CO₃. For the monomers, the reaction between the appropriate hydroxylated compound (L-17, L-20, L-28) and acryloyl chloride was performed in presence of dry triethylamine using THT. Polyacrylates (L-19, L-22 or L-30) were prepared by free radical
polymerization with 2,2’-azobis-isobutyronitrile (AIBN) as a initiator at 60 °C using THF as the solvent. Polymeric products were recovered in methanol and polymers yield were ranging between 30 and 35%. Indeed, similar reaction yields were observed [2-5] in the polymerization of other acrylic monomers containing the same azobenzene units.

Characterization
The IR spectra of monomers L-18, L-21 and L-29 exhibit the characteristic peak $\nu_{\text{C=C}}$ stretching at 3104 cm$^{-1}$, 3104 cm$^{-1}$ and 3110 cm$^{-1}$ respectively. On the other hand, the peaks are absent in the corresponding polymers. This indicates polymerization occurred in azobenzene moieties. $^{13}$C NMR spectrum of monomer L-18 and L-21 are shown in Fig.1.

Phase behavior
DSC thermograms are shown in Fig. 2 for the polymers L-19, L-22 and L-30. In each

\begin{center}
\begin{align*}
\text{L-15} & : 
\begin{array}{c}
\text{CH}_3\text{OC} \text{H}_2\text{NH}_2 + \text{HO-CH}_2\text{OH} \rightarrow \text{HO-CH}_2\text{N=CH}_2\text{OH} + \text{COCH}_3 \\
\text{L-17, L-20, L-28}
\end{array} \\
\text{L-17, L-20, L-28} + \text{HO(CH}_2)_n\text{O} \rightarrow \text{HO(CH}_2)_n\text{O-N=CH}_2\text{CH}_2\text{COCH}_3 \\
\text{L-18, L-21, L-29}
\end{align*}
\end{center}

\begin{center}
\begin{align*}
\text{L-15} + \text{HO(CH}_2)_n\text{O} \rightarrow \text{HO(CH}_2)_n\text{O-N=CH}_2\text{CH}_2\text{COCH}_3 \\
\text{L-18, L-21, L-29} + \text{AIBN} \rightarrow \text{L-19, L-22, L-30}
\end{align*}
\end{center}

Fig. 1: $^{13}$C NMR spectra of monomer L-18 and L-21.

Fig. 2: DSC thermograms of polymers L-19, L-22 and L-30. From top to bottom: L-19, L-30 and L-22
measurement, the sample was heated to a temperature ~ 300 °C, then held 10 min for annealing before gradually cooled down to temperature -20 °C and kept for 10 min. Second heating scans are taken from -20 °C to 300 °C. We observed two endothermic events: one occurring at -10 °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 for L-19, L-22 and L-30 at 272, 261 and 252 °C respectively (Fig. 2). The corresponding monomers exhibited only one endothermic transition near isotropic points.

**Conclusion**

New side-chain liquid crystal polymer containing azobenzenes moieties is prepared, the poly[α-{4-[(4-acetylphenyl)diazenyl]phenoxy}alkyloxy]acrylate. The thermal properties of the polymers and monomers were studied and it was found that all the polymers exhibited nematic phase near isotropic point and no phase transition observed in monomers. This study will be further extended to the characterization for image storage materials.

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**References**