*Macromolecules* **1993,** *26,* 7103–7105 **7103**

# Synthesis and Characterization of Main-Chain Liquid Crystalline Polymers Containing a *p*-Phenyleneazo Group

**Muthusamy Saminathan, Chennakkattu Krishna Sadasivan Pillai,* and Chorappan Pavithran**

*Council of Scientific and Industrial Research,*
*Polymer Section, Regional Research Laboratory,*
*Trivandrum 695 019, India*

*Received April 28, 1993*
*Revised Manuscript Received September 30, 1993*

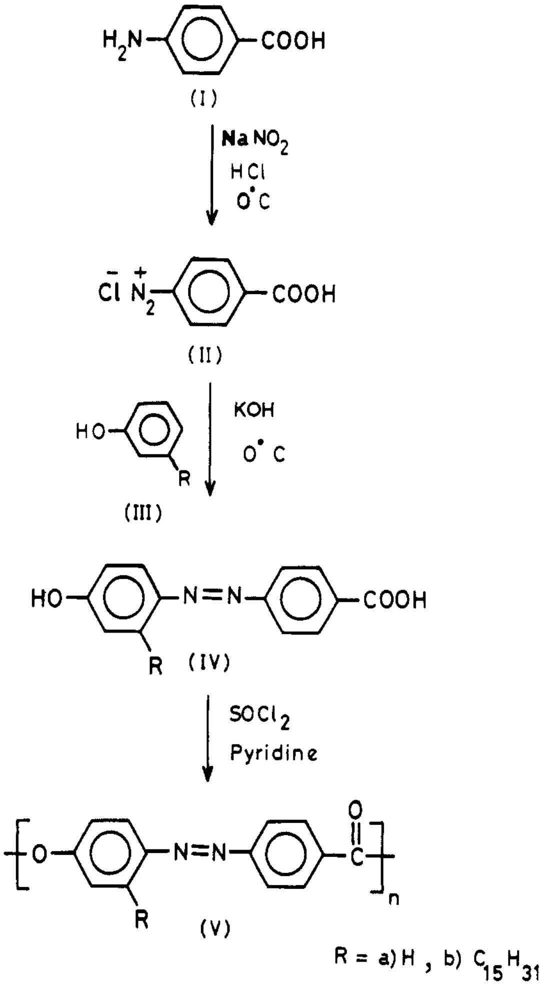
**Introduction.** Interest in *p*-phenyleneazo-group-containing liquid crystalline (LC) polymers has been expanding recently because of their nonlinear optical and related properties.[1–5] One of the limitations in their use is their lack of solubility in common organic solvents.[5,6] The use of flexible spacer/side-chain pendant groups to improve solubility in the case of LC copolyesters and copolyamides is well-known.[1,2,7–12] In this paper we report the synthesis of a *n*-pentadecyl-substituted *p*-phenyleneazo-group-containing LC polyester having a better solubility than the unsubstituted counterpart. The 2-*n*-pentadecylphenyl group is derived from a naturally existing material known as cardanol. In our earlier papers[12–17] we have shown that cardanol possesses special structural features that allow it to be transformed into high-performance polymers, the specialty properties mainly arising from the presence of a side chain. This prompted us to use 3-*n*-pentadecylphenol, the hydrogenated derivative of cardanol, for the present study.

**Experimental Section. 4-[(4-Hydroxy-2-pentadecylphenyl)azo]benzoic Acid (IVb).** *p*-Aminobenzoic acid (**I**; 13.71 g, 0.10 mol) was dissolved in dilute HCl (20 mL of concentrated HCl in 200 mL of water) and diazotized with a sodium nitrite (6.90 g, 0.10 mol in 20 mL of water) solution at 0 °C with stirring. The solution was diluted with chilled methanol (400 mL). 3-*n*-Pentadecylphenol (**IIIb**; 30.45 g, 0.10 mol) (obtained by hydrogenation of cardanol)[18] was dissolved in a chilled solution of potassium hydroxide (10.77 g, 0.19 mol) in methanol (100 mL) and added dropwise to the diazonium salt solution. The red dye formed was stirred for a further 2 h and poured into a dilute HCl solution with stirring. The red solid separated was filtered, washed thoroughly with water, and dried. The dye was then purified by column chromatography on silica gel (60–120 mesh) using chloroform as eluent. Solvents were removed and recrystallized from a methanol–water mixture: yield 36.61 g (81%); red orange; mp 151–152 °C; IR (KBr) 3320, 2920, 2860, 1700, 1605, 1580, 1425, 1300, 1230, 1110, 860, 820, 780 cm$^{-1}$; $^1$H NMR ($CD_3COCD_3$) δ 0.7–3.4 (m, 31 H), 5.4 (bs, 1 H), 6.7–8.5 (m, 7 H). Anal. Calcd for $C_{28}H_{40}N_2O_3$: C, 74.30; H, 8.91; N, 6.19. Found: C, 72.80; H, 9.40; N, 5.65.

**4-[(4-Hydroxyphenyl)azo]benzoic Acid (IVa).** The monomer was prepared following the same procedure for **IVb**. A total of 17.5 g (76%) of the product was obtained from *p*-aminobenzoic acid (**I**; 13.71 g, 0.10 mol), sodium nitrite (6.9 g, 0.10 mol), and phenol (**IIIa**; 9.41 g, 0.10 mol): orange; mp 274–275 °C; IR (KBr) 3470, 1670, 1590, 1550, 1505, 1470, 1430, 1410, 1280, 1240, 1140, 850 cm$^{-1}$; $^1$H NMR ($CD_3COCD_3$) δ 6.8–8.4 (m, 8 H). Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.17; N, 11.56. Found: C, 61.40; H, 4.56; N, 10.81.

**Polymerization.** Polymerizations were carried out in *o*-dichlorobenzene at 80 °C for 12 h using thionyl chloride and pyridine. The polymers were precipitated in methanol, washed with hot acetone thoroughly to remove unreacted monomer and soluble oligomers, and dried in vacuo for 12 h at 60 °C.

**Scheme I**



A typical procedure is as follows: **IVb** (1.0 g, 2.2 mmol) was refluxed with an excess of thionyl chloride (1 mL) for 1 h with stirring. The excess thionyl chloride was distilled off with a nitrogen flush. *o*-Dichlorobenzene was added to dissolve the acid chloride, and then 2 drops of pyridine was added. The polymerization was continued for 12 h at 80 °C, and the products precipitated.

**Poly[4-[(4-hydroxy-2-pentadecylphenyl)azo]benzoic acid] (Vb)**: yield 0.71 g (73.9%); IR (KBr) 2920, 2860, 1740, 1600, 1590, 1410, 1260, 1210, 1150, 1060, 1010, 860 cm$^{-1}$. Anal. Calcd for $C_{28}H_{38}N_2O_2$: C, 77.37; H, 8.81; N, 6.44. Found: C, 76.19; H, 8.85; N, 5.45.

**Poly[4-[(4-hydroxyphenyl)azo]benzoic acid] (Va)**: yield 0.76 g (82.1%); IR (KBr) 3060, 1735, 1600, 1580, 1500, 1410, 1320, 1260, 1200, 1140, 1060, 1010, 860, 770 cm$^{-1}$. Anal. Calcd for $C_{13}H_8N_2O_2$: C, 69.63; H, 3.59; N, 12.5. Found: C, 68.10; H, 3.43; N, 12.28.

**Results and Discussion.** The monomer synthesis (Scheme I) was carried out according to the modified procedure of Pansare et al.[19] The solid red dyes obtained were purified by column chromatography and recrystallized from a methanol–water mixture and used for polymerization. The purities of the monomers were confirmed by elemental and spectral analysis.

The polyesters were synthesized (Scheme I) by a conventional polycondensation method using thionyl chloride and pyridine. Excess thionyl chloride was used to make acid chlorides. The acid chlorides thus prepared were used without further purification. Polymer **Va**

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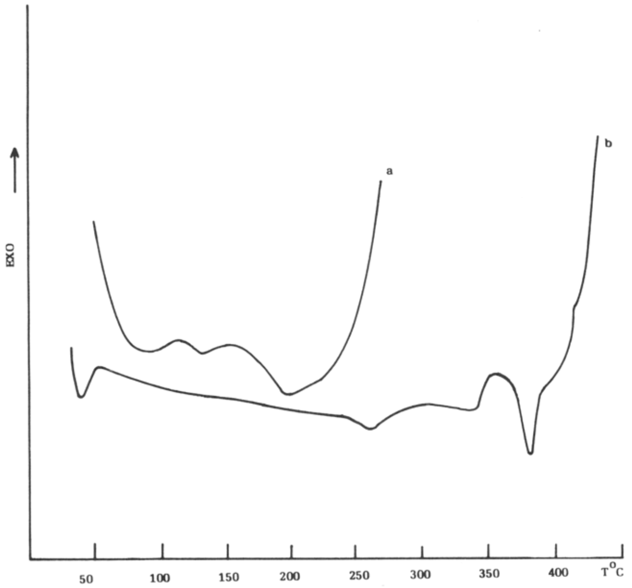

**Figure 1.** DSC thermograms of (a) **Vb** and (b) **Va**.

started precipitating soon after the addition of pyridine. Solubility studies showed that polymer **Vb**, having a hydrocarbon flexible pendant group in its structure, is, as expected, soluble in common organic solvents such as chloroform, tetrahydrofuran, dioxane, etc., whereas polymer **Va** is found to be soluble only in concentrated $H_2SO_4$ and methanesulfonic acid.

The formation of the polymer was inferred from elemental analysis and IR spectroscopy (see the Experimental Section). IR spectra were obtained from a Perkin-Elmer 882 infrared spectrometer. The IR spectra of polymers **Va** and **Vb** gave the characteristic ester carbonyl stretching vibration of 1735 and 1740 $cm^{-1}$, respectively. Simultaneously, the peaks at 3500–3300 $cm^{-1}$ of the hydroxyl groups and 1700–1670 $cm^{-1}$ of the carboxy groups of monomers **IVa** and **IVb** vanished or largely decreased on polyester formation. The C–H stretching vibrations of the aliphatic pendant group of polymer **Vb** were observed at 2920 and 2860 $cm^{-1}$.

Molecular weight determined by end-group analysis[21] gave a value of $M_n$ = 14 706 for **Vb**. A similar method could not be applied to **Va** due to its insolubility in common organic solvents. The thermal and phase behaviors of polymers **Va** and **Vb** were investigated by DSC and polarized light microscopy (PLM). The DSC thermograms were obtained from a Du Pont DSC V2.2 A 9900 system under nitrogen at a 20 °C/min heating rate (Figure 1), and the LC texture was observed under a Leitz-1350 hot stage coupled cross-polarized light microscope at a 20 °C/min heating rate (Figure 2). The DSC scan of polymer **Va** (Figure 1b) shows one low-temperature endotherm at 40 °C and three well-defined endotherms at 262, 337, and 382 °C. Kricheldorf et al.[20] describe the appearance of such a low-temperature endotherm as due to crystalline modification. When observed under PLM on a heating stage, polymer **Va** started melting at 265 °C and exhibited the typical threaded nematic texture which remained up to the isotropization temperature at 382 °C. At 338 °C a waterlike flow of the polymer was observed without any change in texture. This phenomenon could not be explained at this stage, and further investigation on the origin of this interesting thermal behavior is underway.

The effect of the pendant flexible substituent $-C_{15}H_{31}$ in polymer **Vb** is evident from the large decrease observed in the transition temperatures of polymer **Vb** as compared to those of polymer **Va**. The DSC scan of polymer **Vb** (Figure 1a) gave two transitions at 130 and 197 °C. When observed under PLM, the polymer melted and exhibited a schlieren texture of the nematic phase at 135 °C and isotropized at 262 °C which did not appear in the DSC scan. At 202 °C, a waterlike flow of the polymer without any texture change was observed as in the case of polymer **Va**. Thus the presence of the pendant flexible hydrocarbon substituent in polymer **Vb** lowers its transition temperature of crystal to mesophase by 130 °C and its isotropization temperature by 120 °C. Earlier it was shown that the presence of a side chain enhances the solubility of polymer **Vb** in common organic solvents.

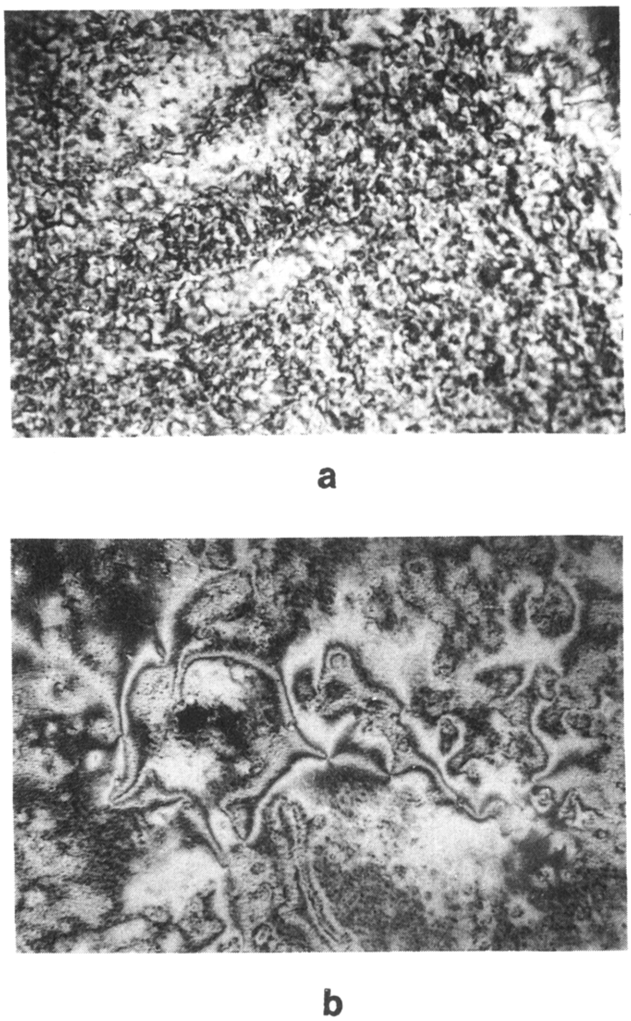

**Figure 2.** Polarized light micrographs (320×) of (a) **Va** at 320 °C and (b) **Vb** at 200 °C. Magnification has been reduced for publication.

In the case of polymer **Vb** partial decomposition was observed above 210 °C. On cooling from the isotropic melts of both polymers, there was no reappearance of the mesophase possibly due to decomposition (in the case of polymer **Vb**) or due to the monotropic nature of the polymers.

UV–visible spectra of **IVb** and **Vb** were taken on a Shimadzu UV-160A spectrophotometer from 200 to 1100 nm with chloroform as the solvent. Figure 3 shows the spectra of polymer **IVb** ($\lambda_{max}$ 369 nm, $\epsilon$ 9000 × $10^{-2}$ $m^2$ $mol^{-1}$; 262 nm, 11 000 × $10^{-2}$ $m^2$ $mol^{-1}$) and **Vb** ($\lambda_{max}$ 361 nm, $\epsilon$ 10 000 × $10^{-2}$ $m^2$ $mol^{-1}$; 246 nm, 5400 × $10^{-2}$ $m^2$ $mol^{-1}$). The $\epsilon$ of the polymer was calculated based on a unit mer weight. The shift in the wavelength and the decrease in the absorbance of monomer (262 nm) to polymer (246 nm) is obvious from the point that the hydrogen bonding in monomer is lost when polymerized.

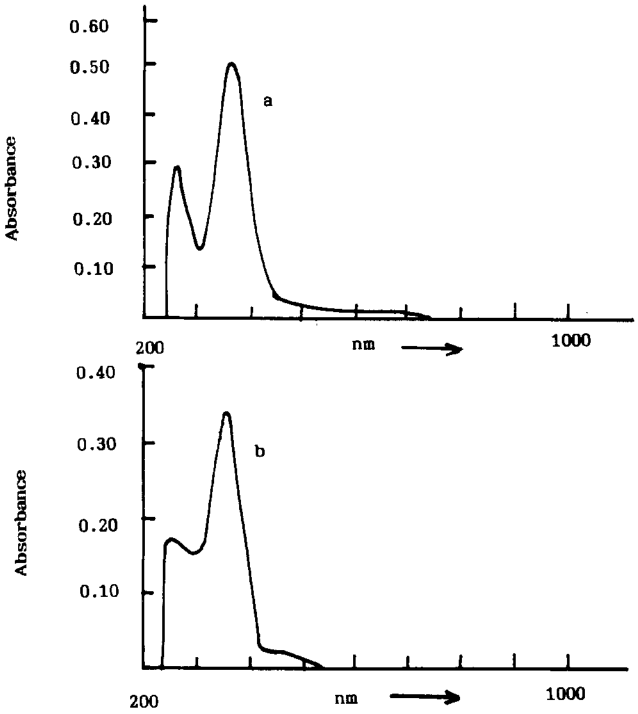

**Figure 3.** UV–visible spectra of (a) **IVb** and (b) **Vb**.

It is well-known that the wavelengths beyond 800 nm are of interest for telecommunication and nonlinear optical application.[5] For such application, the polymer should not exhibit any absorption in this region and azo-based polymers have been reported to show such properties. Figure 3 shows that the monomer **IVb** and polymer **Vb** have little or no absorption beyond 715 and 550 nm, respectively. So, these materials could find application in telecommunication and nonlinear optics. Studies on the further characterization of these polymers are under investigation.

**Acknowledgment.** Thanks are due to Dr. A. D. Damodaran, Director, Regional Research Laboratory, Trivandrum, India, for support and encouragement.

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