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Synthesis and characterization of azoxy based mesogenic diols

Khudbudin B Mulani[a], Nitin V Ganjave[b] &
Nayaku N Chavan*[a]

[a]Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune 411 008, India

[b]Department of Chemistry, Fergusson College, F.C. Road, Pune 411 004, India

E-mail: nn.chavan@ncl.res.in

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Azoxy based rigid mesogenic diols have been synthesized using two steps. Phenol/cresol is used as starting material. Synthesized diols are characterized by IR, ^{1}H and ^{13}C NMR, and mass spectroscopic methods. Thermal properties have been determined by thermo gravimetric analysis method and crystallinity patterns have been obtained by wide angle X-ray diffractogram. Substituted phenol (methyl) is used to study the effect of substitution on physical and thermal properties of rigid azoxy mesogenic diol. The detailed characterization of azoxy based rigid diols is reported in this communication, which is highly useful for fundamental and applied research, particularly in liquid crystals and liquid crystalline polymers. The experimental results reveal that phenol based rigid mesogenic diols have high thermal stability and degree of crystallinity than methyl substituted rigid mesogenic diols.

Keywords: Azoxy, mesogen, diol, degree of crystallinity, phenol, thermal stability

The liquid crystal phase is a state of matter, which is an intermediate state of the liquid and solid. Flow of liquid crystal is similar to liquid, but normal liquids are transparent and isotropic, where as liquid crystals are milky and turbid. This is because the fluctuation of the orientation of the long molecular axes of the liquid crystals causes strong stir opalescence[1].

Liquid crystal molecules are highly anisotropic, because these molecules are structured as rigid rods or ellipsoid molecules in which length is greater than their width. Mesogen is the fundamental unit of a liquid crystal which induces structural order in the crystals. Typically, a liquid crystalline molecule consists of rigid and flexible moieties. The rigid part aligns molecules in one direction, whereas the flexible parts induce fluidity in the liquid crystal. This rigid part is referred to as mesogen, and it plays an important role in the molecule. The optimum balance of these two parts is essential to form liquid-crystalline materials[2,3].

A large number of chemical compounds are known to exhibit one or several liquid crystalline phases. Despite significant differences in chemical composition, these molecules have some common features in chemical and physical properties. The molecular shape should be relatively thin or flat and the axial ratio should be at least 4.3 (Ref. 4).

The structure should not be branched or angular. An extended, structurally rigid shape seems to be the main criterion for liquid crystalline behavior. Thus, most of the liquid crystalline materials are based on benzene rings, because aromatic double bonds increase polarity and simultaneously rigidity[5]. Thermotropic liquid crystals are the types of liquid crystals which are formed on heating. These crystals are formed while heating a solid or cooling an isotropic liquid. Thus, they are temperature dependent.

The synthesis methodologies of rigid mesogens required for thermotropic liquid crystalline phases are reported by several authors. Leonard *et al.* reported the synthesis of azoxy based mesogenic diol using phenol and potassium nitrite as starting materials to produce *p*-nitroso phenol, which on further treatment with *p*-toluene sulphonyl chloride generates *p*-azoxy phenol[6]. Nelson *et al.* reported the synthesis of azoxy compounds containing alkyl, aryl, ester, acyl and amide groups[7]. Wood *et al.* prepared aryl azoxy compounds from the oxidation of hydroxylamine using pyridine chlorochromate as catalyst[8].

The objective of this research was to synthesise azoxy based mesogenic diols using phenol/cresol and potassium nitrite as starting materials to obtain thermotropic liquid crystalline polymers[9].

In this communication, the synthesis and detailed characterization of azoxy based mesogenic diols using phenol/cresol as starting material is reported. Although little information is available on the synthesis of these azoxy mesogenic diols, but detailed characterization has not been reported so far, which is useful for fundamental as well applied research, because these azoxy mesogenic diols have high potential for applications in a number of research areas.

Results and Discussion

Synthesis

Synthesis of azoxy based mesogenic diols is presented in **Scheme I** using two step synthesis

procedure. First step involved the synthesis of *p*-nitroso phenol/cresol using phenol/*m*-cresol and potassium nitrite as starting materials. In second step, *p*-nitroso phenol/cresol was treated with *p*-toluene sulfonyl chloride. These diols are named as 4,4′-dihydoxy azoxy benzene (R = H, **PAZ**) and 4, 4′-dihydoxy-2,2′-dimethyl azoxy benzene (R = CH_3, **2-M-PAZ**).

Thermal analysis

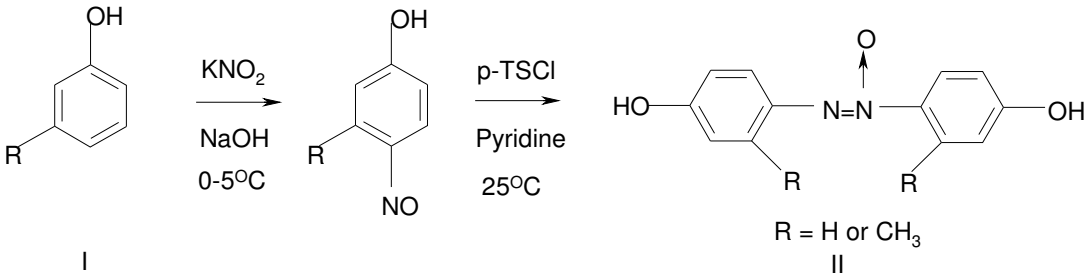
It has been observed that the introduction of methyl group on phenyl moiety of azoxy diol influences the physical and thermal properties of polymers, particularly it improves solubility in rigid polymers. By keeping this in mind, methyl substituted azoxy mesogenic diols were prepared.

Thermo gravimetric analysis (TGA) thermograms of azoxy mesogenic diols are depicted in **Figures 1** and **2** for **PAZ** and **2-M-PAZ** respectively. The **PAZ** was stable up to 250°C and strong peak of Tmax was observed at 264.8°C, indicating that maximum decomposition took place at that temperature.

Thermal stability of the **2-M-PAZ** was affected by the substitution of methyl groups on azoxy aromatic diol. In the case of **2-M-PAZ**, the thermal stability was up to 230°C and the strong peak of Tmax was observed at 237.4°C which reveals that maximum decomposition occurred at that temperature. The above observations illustrate that azoxy based mesogenic rigid diols are thermally stable and show almost single step degradation. The thermal stability of mesogenic diol **PAZ** is higher than **2-M-PAZ**. It indicates that substitution reduces thermal stability, because methyl substitution lowers tendency to crystallize, thus causing reduction in melting point, thermal stability and decomposition temperature[10].

X-ray Diffraction

Wide angle X-ray diffractogram of **PAZ** was performed at RT. It exhibits relatively sharp and



Scheme I — Synthesis of azoxy based mesogenic diols

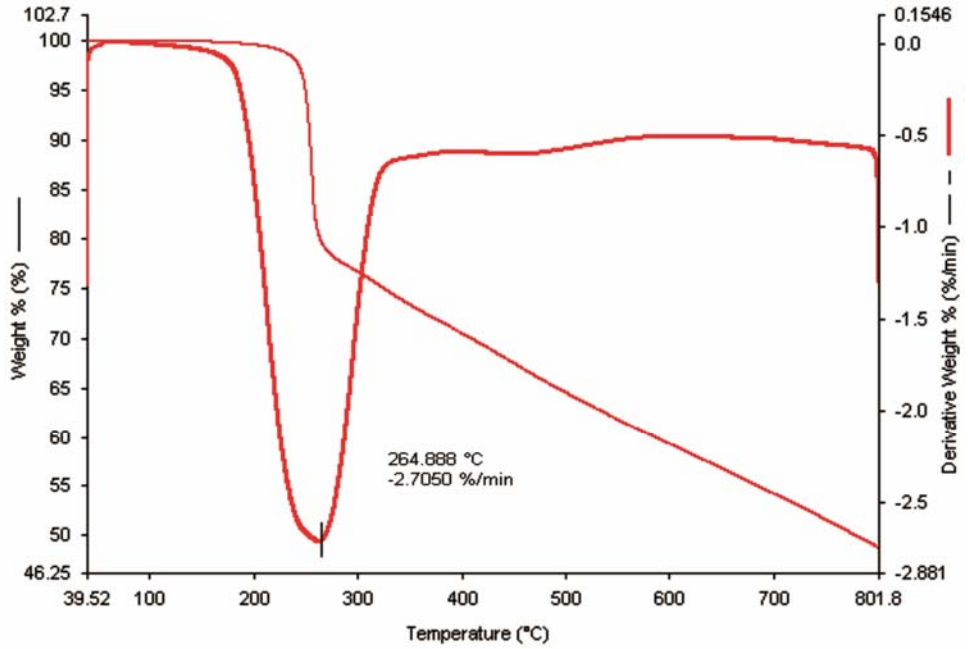


Figure 1 — TGA thermogram of azoxy based mesogenic diol **PAZ**

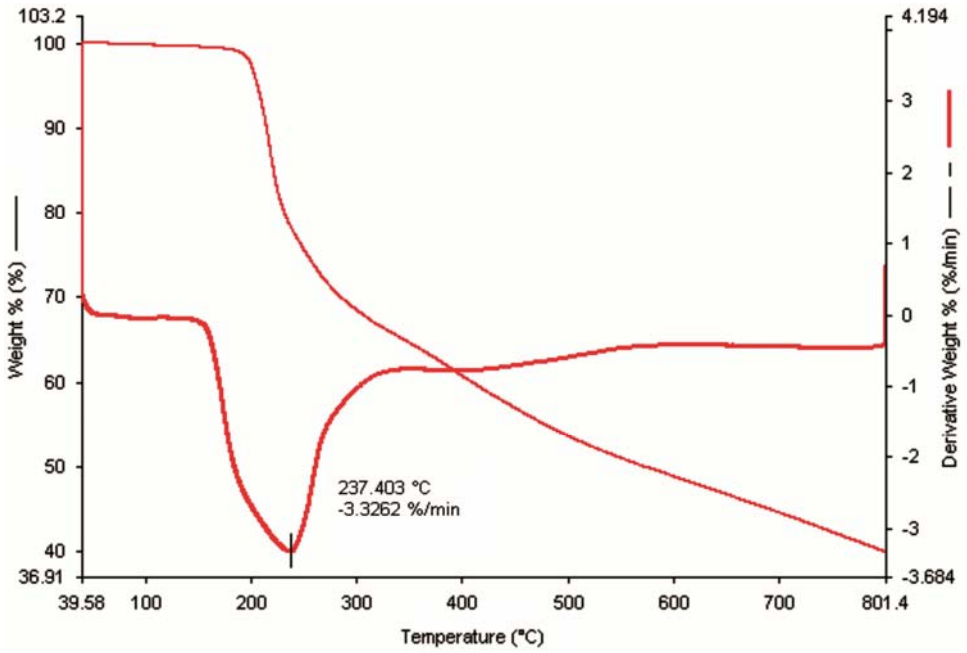


Figure 2 — TGA thermogram of azoxy based mesogenic diol **2-M-PAZ**

strong absorption peaks at 2θ of 10, 14 and 15, medium absorption peaks observed at 2θ of 5, 18, 26 and 28, and weak peaks observed at 2θ of 16, 18, 20, 22, 23, 24, 43, 44 and 45. Similarly, wide angle X-ray diffractogram of **2-M-PAZ** was conducted at RT. It exhibits relatively sharp and strong absorption peaks at 2θ of 15 and 16, whereas medium absorption peaks observed at 2θ of 18, 24, and 26 and 28 and weak peaks observed at 2θ of 10, 11, 24, and 29. X-ray diffractograms reveal that percentage crystallinity decreases with substitution due to the chain packing frustration, and leads to the tendency towards amorphous nature[11].

Experimental Section

Pyridine received from Loba Chemie (India), was purified by refluxing and distilling over potassium hydroxide. Phenol, *m*-cresol, potassium nitrite, sulfuric acid, *p*-toluene sulphonyl chloride and potassium hydroxide were procured from Merck and were used as received. Melting points are uncorrected and were determined with a capillary melting point apparatus. ^{1}H NMR was recorded on 300 MHz Brucker spectrometer using TMS as an internal standard. FTIR spectra were obtained with KBr pellets on Perkin-Elmer spectrometer. Elemental analysis was performed on Flash EA 1112 series, ThermoFischer Scientific. Thermogravimetric analysis was conducted on a Perkin-Elmer-7 applying a heating rate of 10°C/min in nitrogen atmosphere to determine thermal stability. Wide angle X-ray scattering (WAXS) curves were obtained by a Philips PW X-ray diffractometer equipped with 1830 generator and 1710 adjustment with Cu-Kα radiation and a scanning angle of 2-40°.

Preparation of azoxy based mesogenic diol

Azoxy based mesogenic diols were prepared from phenol/cresol as starting materials. The procedure of synthesis is given below[6].

p-Nitrosophenol

To a three necked 500 mL round bottom flask, a solution of 6 g (0.064 mol) of phenol, 2.7 g (0.068 mol) of sodium hydroxide, and 6.68 g (0.078 mol) of potassium nitrite in 150 mL of water was added and cooled to 0°C. To this solution, 15.0 g (0.142 mol) of sulphuric acid in 40 mL of water was added while stirring slowly at low temperature and was stirred for an additional 2 h. The brownish crystalline precipitate was filtered. The product was washed with 100 mL ice-water and then air dried. Yield: 70%; m.p. 124-126°C (decomp.); lit. m.p. 137°C (decomp.)[12].

4,4′-Dihydoxyazoxybenzene

To a 250 mL three necked round bottom flask, a mixture of 0.99 g (0.0073 mol) of *p*-nitroso phenol, 1.0 g (0.0057 mol) of *p*-toluene sulfonyl chloride and

7.0 mL of pyridine were added, stirred and allowed to stand at 25°C for 12 h. The reaction mixture was heated on steam bath for 20 min, cooled, and acidified with 25% sulfuric acid. The resulting black mixture was extracted with ether. The ether extract was treated with carbon black, and concentrated to near dryness. Recrystallization from 50% aq. ethanol gave yellow needles of 4,4′-dihydoxyazoxybenzene (**PAZ**). Yellow solid. Yield 40%; m.p. 231-33°C (decomp.), lit. m.p. 234-35°C (decomp.). IR (KBr): 3342 (OH), 1597 (CH=CH), 1474 (C-H), 1367 (N-O), 1237 (C-O), 837 cm^{-1} (*p*-substitution); ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.90-6.96 (d, 4H), and 8.08-8.19 (d, 4H); ^{13}C NMR (DMSO-d_6, 300 MHz): δ 115.46, 123.72, 127.82, 158.90, 160.54. Anal. Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.34; N, 12.18. Found: C, 62.41; H, 4.03; N, 11.95%.

A similar procedure was employed for the synthesis of 4,4′-dihydoxy-2,2′-dimethyl azoxybenzene (**2-M-PAZ**). Yellow solid; Yield: 42%; m.p. 158°C (decomp.)[13]. IR (KBr): 3375 (OH), 1583 (CH=CH), 1492 (C-H), 1342 (N-O), 1239 (C-O), 958, 727 (methyl substitution), 857 cm^{-1} (*p*-substitution); ^{1}H NMR (DMSO-d_6): δ 2.34-2.39 (s, CH_3), 6.74-6.78 (d, 4H), 7.56-7.61 (d, 2h), 8.48-8.53 (d, 2H) and 9.98-10.06 (s, 2-OH); ^{13}C NMR (DMSO-d_6, 300 MHz): δ 19.24, 112.17, 113.62, 118.05, 124.04, 125.86, 132.87, 138.44, 158.91. Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.18; H, 5.42; N, 10.84. Found: C, 64.29; H, 5.08; N, 10.13%.

Conclusion

Azoxy based mesogenic diols have been prepared from phenol/cresol and potassium nitrite as starting materials. Synthesized diols have been characterized by elemental analysis, IR and NMR spectroscopy, thermal analysis and X-ray diffraction spectroscopy. Introduction of methyl group on mesogenic diol moiety decreases thermal stability and percent crystallinity, which confirms the tendencies towards the amorphous nature.

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