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## Synthesis and Evaluation of a Carbazole Based Polymeric Azodye Containing Naphthalene Moiety

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During research on carbazole based copolycondensates<sup>1</sup> we observed that literature on carbazole based polymeric azodye systems, is meagre. Relevantly, polyazoarylenes have been explored in regard to their conductance behavior,<sup>2</sup> while, Biswas and Das reported<sup>3</sup> the synthesis of a polymeric azodye from carbazole and bisphenol-A and its thermal stability, dielectric and conductance characteristics. Interested to find out how the replacement of bisphenol-A by a condensed aromatic system such as naphthalene, with higher resonance stability and enhanced conjugation than benzene would influence the properties as above, we prepared and characterized a polymeric azodye from *N*-methylcarbazole-3,6-diamine and 1,8-dihydroxy naphthalene-3,6-disodium sulfonate. Our results highlighted in this article show that thermal stability, conductance, dielectric characteristics are considerably influenced by a change in the structure of the polymeric azodye.

### EXPERIMENTAL

#### *Materials*

Carbazole (BDH) was recrystallized from the alcohol solution. 1,8-Dihydroxy-naphthalene-3,6-disodium sulfonate (Fluka AG), di-

methyl sulfate (BDH) were used as supplied.

#### *Preparation of the Polymeric Azodye (CN-PAD) (I)*

A mixture of 0.43 g (2 mmol) of *N*-methylcarbazole-3,6-diamine,<sup>3</sup> 4.2 ml conc. HCl and 4.2 ml water was kept at 0°C for 3 h with frequent shaking. To this, was added dropwise a cold solution of 1.6 g sodium nitrite in 8 ml water for 30 min with vigorous stirring (at 0°C) and the resulting diazonium salt solution was kept at 0°C for 3 h with constant stirring. The cold solution was added slowly to a solution of 0.73 g (2 mmol) of 1,8-dihydroxy naphthalene-3,6-disodium sulfonate in 16 ml of cold 10% aqueous sodium hydroxide for 30 min in an ice-salt bath with vigorous stirring, and kept at 0°C for 3 h with constant stirring. A dark violet compound separated out which was poured into 200 ml ethanol with stirring, filtered, washed several times with dry ethanol and finally dried at room temperature, resulting in a dark violet polymeric azodye (yield 50%). N% 12.71 (calcd 12.65), S% 14.08 (calcd 14.00), characteristic. IR absorption (cm<sup>-1</sup>) (KBr) 2200, 1620 (—N=N—, strong bands), 1620 (C=C, aromatic stretching), 1200, 1100, 1030 (strong bands for —SO<sub>3</sub>H group), 3400 (phenolic —OH, stretching), 1380

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phenolic -OH, bending).

### Characterization

Nitrogen was estimated by Micro-Dumas method<sup>4</sup> and sulfur by a standard procedure. The reduced viscosity of the polymeric azodye was measured in DMSO at a concentration of 0.5 g dl<sup>-1</sup> at 25°C. IR spectra was recorded on a Perkin-Elmer 237B grating spectrophotometer. The magnetic susceptibility constant for CNPAD was determined by a Gouy balance. The thermal characteristics were studied with a Stanton Redcroft thermal analyzer at temperature upto 1100°C in static air (10°C min<sup>-1</sup>). The dielectric constant and dielectric loss were measured by an Impedance Bridge (HP, A 4192) at room temperature. CNPAD was used as pellets (diameter 1.06 cm, thickness 0.21 cm) with silver coating on the surface. Conductivity *versus* temperature measurements were made by a 1666 DC Resistance Bridge (General Radio) with silver coated sample in the pellet form (diameter 1.03 cm, thickness 0.21 cm).

## RESULTS AND DISCUSSION

The reduced viscosity of CNPAD in DMSO is 0.32 dl g<sup>-1</sup> which is of the same magnitude as the carbazole-bisphenol-A azodye (CBPAD).<sup>3</sup>

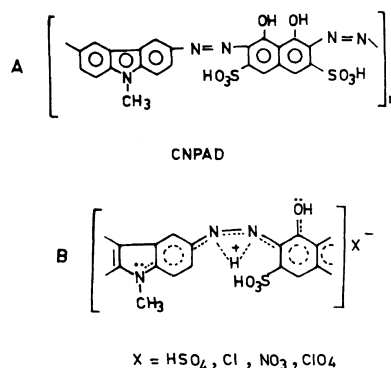
During magnetic measurements, CNPAD shows a weight difference of  $-0.17 \times 10^{-3}$  g which implies that it is repelled by a magnetic field, a behavior typical of diamagnetic substances. The magnetic susceptibility constant was calculated to be  $-0.35 \times 10^{-6}$  which compared with the value of  $-0.45 \times 10^{-6}$  for CBPAD.

Like CBPAD, CNPAD develops different colors with acids (Table I), due to an internal salt formation stabilized by electron delocalisation.<sup>5</sup> The deepening of the color may be attributed to resonance<sup>6</sup> among charged canonical structures (Figure 1B). CNPAD also develops a deep red color with concentrated aqueous NaOH due to the formation of the

**Table I.** Characteristic chemical properties of CNPAD

Solvent	Solubility	Color	Color on large dilution with water
Organic solvents	+, (DMSO)	Deep violet	—
Conc. HCl	+	Yellow	Pale yellow
Conc. H <sub>2</sub> SO <sub>4</sub>	+	Deep blue	Pale violet
Conc. HNO <sub>3</sub>	+	Orange-red	Pale yellow
HClO <sub>4</sub>	+	Blue	Pale violet
Aqueous NaOH	+	Violet	Pale violet
Ammonia solution	+	Red	Pale blue

(+ soluble).



**Figure 1.** A: Structure of CNPAD. Resonance structure of CNPAD in presence of acids.

sodium salt of CNPAD.

### Thermal Characteristics

Figure 2 shows that CNPAD is initially stable upto *ca.* 150°C whereafter it loses weight upto *ca.* 12.5% at 160°C. Further weight loss continues at a comparatively slower rate till 60% decomposition occurs at 700°C, followed by a limiting weight loss of *ca.* 80% from 1000°C onwards. The DTA curve displays an exothermic effect at 160°C (12.5%) due to the disappearance of the azochromophore group implying the degradation of the polymer through cleavage of -N=N- bond. The IR spectrum of the product obtained from CNPAD by heating it upto 160°C shows the disappearance of azo-group absorption band at 2200 and 1620 cm<sup>-1</sup>. The DTA

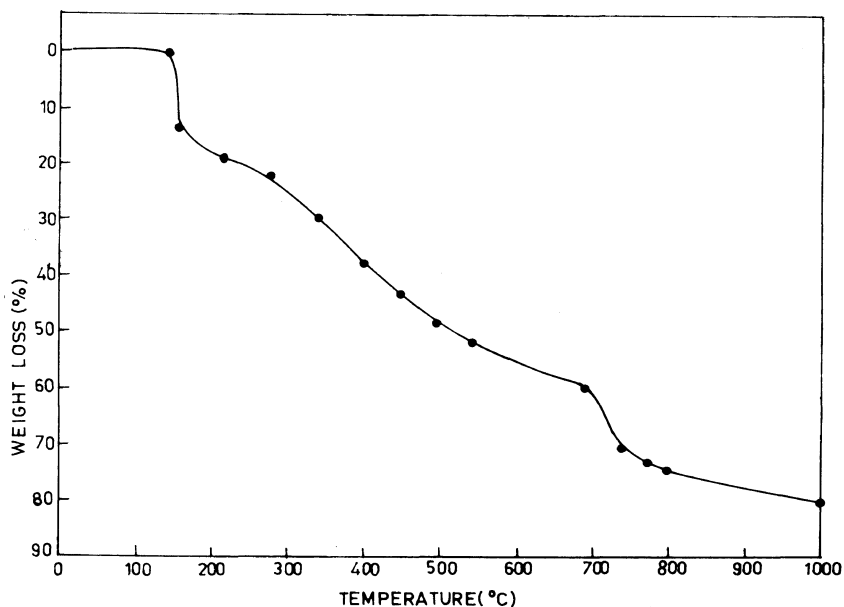


Figure 2. Thermogram of CNPAD.

Table II. Comparison of thermal characteristics of CNPAD and CBPAD

Temperature °C	Weight loss/%		DTA characteristics	
	CNPAD	CBPAD	CNPAD	CBPAD
160	12.5	11.4	Small exotherm	Small exotherm
40	38.0	33.0	Exotherm	Exotherm (peak at 370°)
510	50.0	65.0	Exotherm	—
755	73.0	91.4	Sharp exotherm	A broad exotherm from 370—720°
		(constant from 720°C)		

exothermic peaks at 400°C, 510°C, and a very strong peak at 755°C signify destructive oxidation processes occurring in the intermediate compounds.

Table II shows that in general, CNPAD exhibits somewhat higher stability than CBPAD, apparently due to the presence of a condensed aromatic moiety in the chain.

#### Dielectric Characteristics

Figure 3 suggests that CNPAD possesses a high dielectric constant at low frequency, 94 at  $10^4$  Hz which sharply falls to a limiting value of 14 at  $10^7$  Hz. Being a polar polymer with the

preponderance of electro-negative elements as N, S, and O, CNPAD undergoes asymmetric charge distribution giving rise to strong coupling in the electrical fields which are dependent on the applied frequency.<sup>7</sup> CNPAD shows a consistent increase in  $\tan \delta$  from 0.40 at  $10^4$  Hz to a peak 0.60 at  $10^{5.75}$  Hz and thereafter decreases sharply to 0.23 at frequency  $10^{7.2}$  Hz.  $\tan \delta_{\max}$  occurring at  $f = 10^{10.6}$  Hz coincides with a corresponding inflection in the dielectric constant-frequency curve. This behavior is a typical of polar polymers exhibiting a dipole segmental loss and a dipole group loss.<sup>8</sup> In CNPAD, intra/inter molecular hydrogen

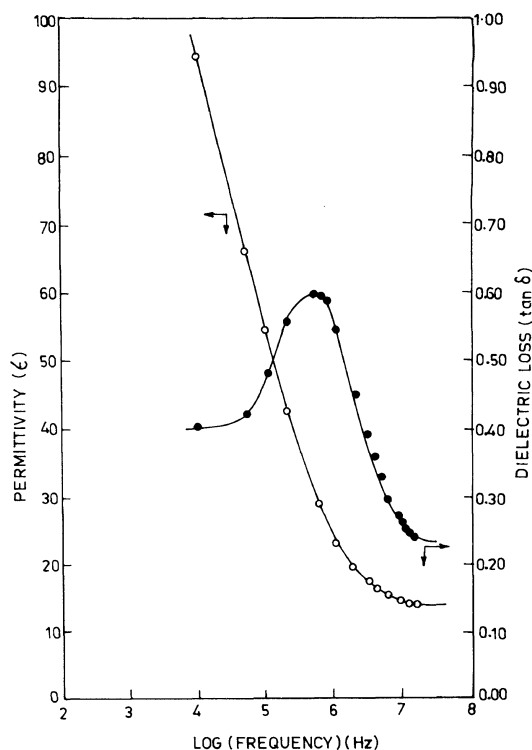


Figure 3. Dielectric behavior of CNPAD.

bonding facilitated by the presence of strong polar groups such as  $-\text{N}=\text{N}-$ ,  $-\text{SO}_3\text{H}$  and  $-\text{OH}$  and orientation polarization are believed<sup>7</sup> to be more significant at lower field frequency and is responsible for the major increase in  $\tan \delta$ . At higher electric field frequency, hydrogen bonding is expected to be weak and less stable and thereby the contribution by orientation polarization will decrease.

#### Conductivity Characteristics

In the temperature range  $23^\circ\text{C}$  to  $160^\circ\text{C}$ , the d.c. conductivity of CNPAD varies from  $10^{-8}$  to  $10^{-6}$   $\text{ohm}^{-1} \text{cm}^{-1}$ . The thermal activation energy (Figure 4) for conduction is calculated to be  $0.74 \text{ eV}$ . The  $\Delta E$  values (Table III) for a number of monomeric diazo derivatives of naphthalene bearing  $-\text{OH}$ ,  $-\text{SO}_3\text{H}$  moieties fall in the range  $2.50$ – $1.00 \text{ eV}^2$ . Sulfo groups usually enhance an intermolecular transport

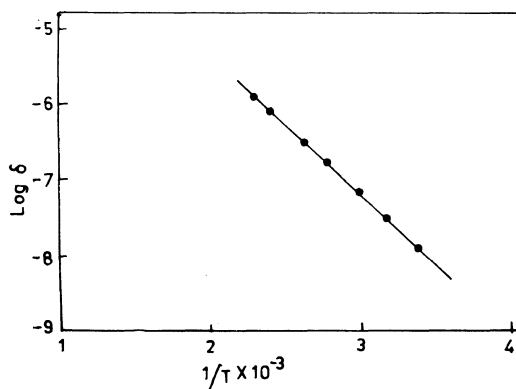


Figure 4.  $\log(\text{conductivity})/(1/T)$  plot for CNPAD.

Table III. Conductivity values of different polymers

Compounds	Conductivity	References
	$\text{ohm}^{-1} \text{cm}^{-1}$	
CNPAD	$10^{-8}$ – $10^{-6}$	This work
Azodye containing $-\text{N}=\text{N}-$ , $-\text{SO}_3\text{H}$ and $-\text{OH}$ group	$1.10^{-7}$ – $2.10^{-6}$	2
Polyazodiphenylene and polyazomethoxy phenylene	$10^{-12}$ – $10^{-15}$ (at $100^\circ\text{C}$ )	2
Polynaphthalenes	$10^{-10}$	2
Polyvinyl carbazole	$4.3 \times 10^{-16}$	1
Polycondensed product of diazo-aromatic diamine with quinones	$< 10^{-10}$	2

by forming intermolecular hydrogen bonds and causing higher conductivity and consequently low  $\Delta E$  values.<sup>2,4</sup> Moreover,  $\Delta E$  decreases with an increase in the size of the molecule.<sup>2</sup> In addition, delocalization of the  $\pi$  electrons over the entire structure with conjugated double bonds also helps to achieve a very high conductivity and consequently a low  $\Delta E$  values.<sup>2,9</sup> Thus in CNPAD, conjugation is strongly favored through the heterocyclic (carbazole) and the naphthalene moiety containing  $-\text{SO}_3\text{H}$  and  $-\text{OH}$  groups as well as the  $-\text{N}=\text{N}-$  group. As such, the high conductivity and low  $\Delta E$  values are reasonable.

## CONCLUSIONS

Carbazole based polymeric azodye bearing the naphthalene moiety exhibits higher overall thermal stability than the corresponding dye carrying bisphenol-A moiety. These dyes exhibit d.c. conductivity in the range  $10^{-8}$ — $10^{-6}$   $\text{ohm}^{-1}\text{cm}^{-1}$  which falls nearly in the semiconductor range. They behave as high loss polymers with dielectric constants falling sharply with frequency.

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## REFERENCES

1. M. Biswas and S. K. Das, *Polymer*, **23**, 1713 (1982).
2. H. Meier, "Organic Semiconductors," Vol. 2, Verlag Chemie, Weinheim, 1974, pp 209—238 (also p 148).
3. M. Biswas and S. K. Das, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3155 (1981).
4. A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans-Green, London, 1962.
5. A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans-Green, London, 1959.
6. I. L. Finar, "Organic Chemistry," Vol. I, Longmans-Green, London, 1973, p 885.
7. A. D. Jenkins, "Polymer Science," North-Holland, London, 1972, pp 1233—1237.
8. A. Tager, "Physical Chemistry of Polymers," Mir, Moscow, 1972, pp 273—286.
9. H. W. Gibbsor, "New Monomers and Polymers," Vol. 25, M. M. Culbertson and C. U. Pittman, Jr. ed, Plenum Series, New York and London, 1984, pp 381—398.