

Synthesis, characterization and chelating properties of poly[azo-(6-hydroxy-1,3-phenylene)]

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Abstract. Poly[azo(6-hydroxy-1,3-phenylene)] (PAHP) was prepared by alcoholic alkaline reduction of 2,4-dinitro phenol (DNP). The polymers prepared at various time intervals were characterized by elemental analyses, IR spectra and thermogravimetric analysis. The number average molecular weight (\bar{M}_n) was determined by non-aqueous titration. Viscometric study in DMF of all the three polymers were carried out and indicates polyelectrolyte behaviour. Viscometric study in DMF–water (85:15) (v/v) containing 1% KBr shows normal behaviour.

Polymeric metal chelates of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} and Cr^{2+} with PAHP polymer were prepared and characterized.

Keywords. 2,4-Dinitro phenol (DNP); poly[azo(6-hydroxy-1,3-phenylene)] (PAHP); poly-chelates of PAHP.

1. Introduction

Perusal of the literature reveals that till now no polymers have been prepared, based on alcoholic alkaline reduction of dinitro phenols; inspite of azo phenols being prepared by alcoholic alkaline reduction of nitro phenols (Willstatter and Benz 1906). However, the preparation of azo arylene polymers based on dinitro arylene has been reported (DeSouza and DeOliveria 1978). Hence it was thought to be of interest to study the polymers based on alcoholic alkaline reduction of 2,4-dinitro phenol (DNP). So the work described in the present communication is connected with the synthesis, characterization and chelation with metal ions of poly[azo(6-hydroxy-1,3-phenylene)] (PAHP).

2. Experimental

2.1 *Materials and methods*

All the chemicals used were of either analytical grade or laboratory grade.

2.1a *Preparation of poly[azo(6-hydroxy-1,3-phenylene)] polymers by self-polymerization of DNP:* Self-polymerization of DNP was carried out by the method

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reported for polymerization of dinitro arylenes (DeSouza and DeOliveria 1978). The polymerization was carried out for different time intervals. A typical method of polymerization is given here and the details of all the polymers are furnished in table 1.

To a solution of DNP (16.8 g, 0.1 mol) in triethylene glycol (150 ml), KOH (44.8 g, 0.8 mol) was added gradually and stirred well at room temperature up to complete dissolution of KOH. Then the reaction mixture, under mechanical stirring, was warmed to 80–85°C for 15 min. The temperature was then increased to 135–140°C and the reaction was continued for 5 h. The reaction was stopped by lowering the temperature to 100°C and neutralized by adding a mixture of ethanol–HCl (50:50) (v/v). The resulting neutralized mixture was then poured into ice water (500 ml) and the solid product was collected by filtration and dried in an oven. Finally, it was purified by dissolving in DMF and reprecipitating by addition of water. The yield of black powder was 84%.

2.1b Preparation of polychelates of PAHP polymers: As a typical procedure, the preparation of Cu^{2+} polychelate of PAHP is described. To a hot solution of copper acetate (5 mmol) in 50 ml DMF, a hot solution of PAHP (10 mmol) in 50 ml DMF was added dropwise. A saturated solution of sodium acetate was added to maintain the pH at ~ 4.0 . A dark chelate precipitated out, it was allowed to settle, and was separated by decantation. It was washed with DMF, hot water and ethanol respectively and then dried at 100°C.

Following the same procedure, the polychelates PAHP- Ni^{2+} , PAHP- Co^{2+} , PAHP- Zn^{2+} , PAHP- Mn^{2+} and PAHP- Cr^{2+} were prepared. The details and the results of analyses of these polychelates are presented in table 2.

3. Analyses of PAHP polymers and polymeric chelates

The elemental analyses of polymers and their polychelates were carried out on a C, H, N, O, S Elemental Analyser, Carlo Erba, Italy. The analyses of metal ions in the polymeric chelates were carried out by the decomposition of a known amount of chelate by mineral acids. The metal content was estimated by a method reported in literature (Vogel 1979).

The IR spectra of PAHP polymers and polychelates were scanned as KBr pellets on a Perkin-Elmer 983 Spectrophotometer.

The reflectance spectra of the polychelates were recorded on a Beckmann DU spectrometer with a reflectance attachment using MgO as the reference.

Conductometric titrations of PAHP polymers were carried out in pyridine against sodium methoxide (NaOMe) in pyridine as standard. The value of the number average molecular weight (\bar{M}_n) was calculated following a method of conductometric titration reported by Chatterjee (1970).

Viscometric measurements of polymer solutions in DMF and in DMF–water (85:15) (v/v) containing 1% KBr were carried out using an Ubbelohde suspended-level viscometer at $30 \pm 0.1^\circ\text{C}$.

Thermogravimetric analyses of polymers and polychelates were carried out on a Du Pont 950 thermogravimetric analyzer in air at a heating rate of $10^\circ\text{C}/\text{min}$.

Table 1. Characterization of PAHP polymers.

Polymer sample	Time for polymerization (h)	Elemental analysis ^a (found) (%)			Number average molecular weight (M_n)		Viscometric ^b data in DMF	$[\eta]$ (dl. g ⁻¹) in DMF H ₂ O (85:15) (v/v) + 1% KBr	Weight loss (%) at various temperature (°C)							
		C	H	N	By VPO	By conductometric titration			$A \times 10^4$ (dl. g ⁻¹)	$B \times 10^4$ (dl. ² g ²)	100	200	300	400	500	600
PAHP-1	5	58.8	4.0	22.9	1225	1250	5.0	0.8	0.55	10	15	23	32	41	58	78
PAHP-2	10	59.3	3.9	23.0	1700	1655	4.2	0.54	1.86	11	17	28	38	47	66	87
PAHP-3	15	59.4	4.0	22.9	2270	2235	1.7	0.32	2.32	10	16	24	34	44	69	82

^a Calculated for repeating unit C₅₉H₅₂, H 4.13 and N 23.14(%); ^b Application empirical relation (1).

Table 2. Characterization of polychelates of PAHP polymer.

Polymer chelate	Metal content (%)		Nitrogen content (%)		Weight loss at various temperatures (°C)						
	Calcd.	Found	Calcd.	Found	100	200	300	400	500	600	
PAHP-Cu ²⁺	21.0	20.9	18.7	18.5	15	23	28	40	53	70	
PAHP-Ni ²⁺	19.8	19.7	18.9	18.6	19	27	30	42	54	71	
PAHP-Co ²⁺	19.8	19.8	18.9	18.4	14	22	27	36	71	—	
PAHP-Zn ²⁺	21.5	21.4	18.5	18.4	8	14	19	28	44	71	
PAHP-Mn ²⁺	18.7	18.6	19.1	19.0	15	24	28	40	73	—	
PAHP-Cr ²⁺	17.9	17.9	19.3	19.2	23	32	40	51	66	74	

4. Results and discussion

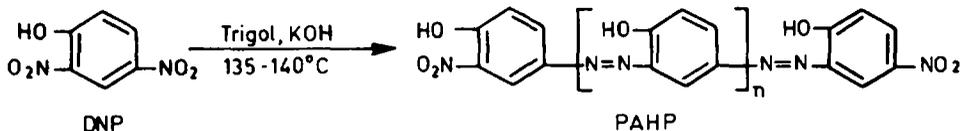
4.1 Characterization of the PAHP polymers

All the PAHP polymers prepared under the various conditions are dark powders. They are insoluble in common organic solvents but are soluble in DMF. They are easily soluble in aqueous alkali and can be regenerated by addition of dil. HCl. They do not melt upto 360°C. The C, H, N contents of all polymers (table 1) agree with calculated values.

The IR spectra of all polymers are similar in all aspects. The broad band extending from 2,700 to 3,500 cm^{-1} belongs to ν_{OH} groups. Bands around 1,575 to 1,632 cm^{-1} are observed and they are characteristic of the azo ($-\text{N}=\text{N}-$) groups. Bands appearing in the region 1,210 to 1,350 cm^{-1} are due to the $-\text{C}-\text{N}=\text{C}-$ moiety.

The presence of $-\text{NO}_2$ groups was detected by the absorption bands at 1,520 and 1,345 cm^{-1} . In all the spectra, bands due to aromatic rings have been observed, and are similar in their relative intensities and shapes. For better understanding, the IR spectra of all polymer samples were compared with the spectra (figure 1) of 4,4'-azo phenol, prepared by the method reported (Willstatter and Benz 1906). It was observed that the important IR spectral characteristic bands of the produced polymers are almost consistent with those of model 4,4'-azo phenol.

Hence on the basis of the structure of azo phenol as well as of polyazo arylene (DeSouza and DeOliveria 1978) and the reactive $-\text{NO}_2$ groups of the used monomer (i.e. DNP), the structure of the PAHP polymer is proposed as shown in scheme 1.



Scheme 1. Steps involved in the polymerization.

The values of \bar{M}_n (table 1) of the polymers, estimated by conductometric titrations and also by vapour-pressure osmometry agree well, within limits of experimental error. Results also show that prolonged time periods of self-polycondensation of DNP afford high molecular weight polymers.

The viscometric behaviour of solutions in DMF and DMF-water (85:15) (v/v) of all three polymer samples do not obey the relation proposed by Huggins, but show the polyelectrolyte behaviour (Eisenberg and King 1977; Flory 1953). Fuoss and Strauss (1948) proposed the empirical relation below for the reduced viscosity of a solution containing linear polyelectrolyte.

$$\eta_{sp}/C = A/(1 + BC^{\dagger}), \quad (1)$$

where A and B are constant characteristics of each sample. As the polymers produced are linear and behave as polyelectrolytes the above empirical relation (1) was employed for the viscosity data.

The plots according to (1) are linear and indicate that all the polymers are polyelectrolytes in DMF. The values of A and B listed in table 1 suggest that the polymers expanded in DMF in the following order:



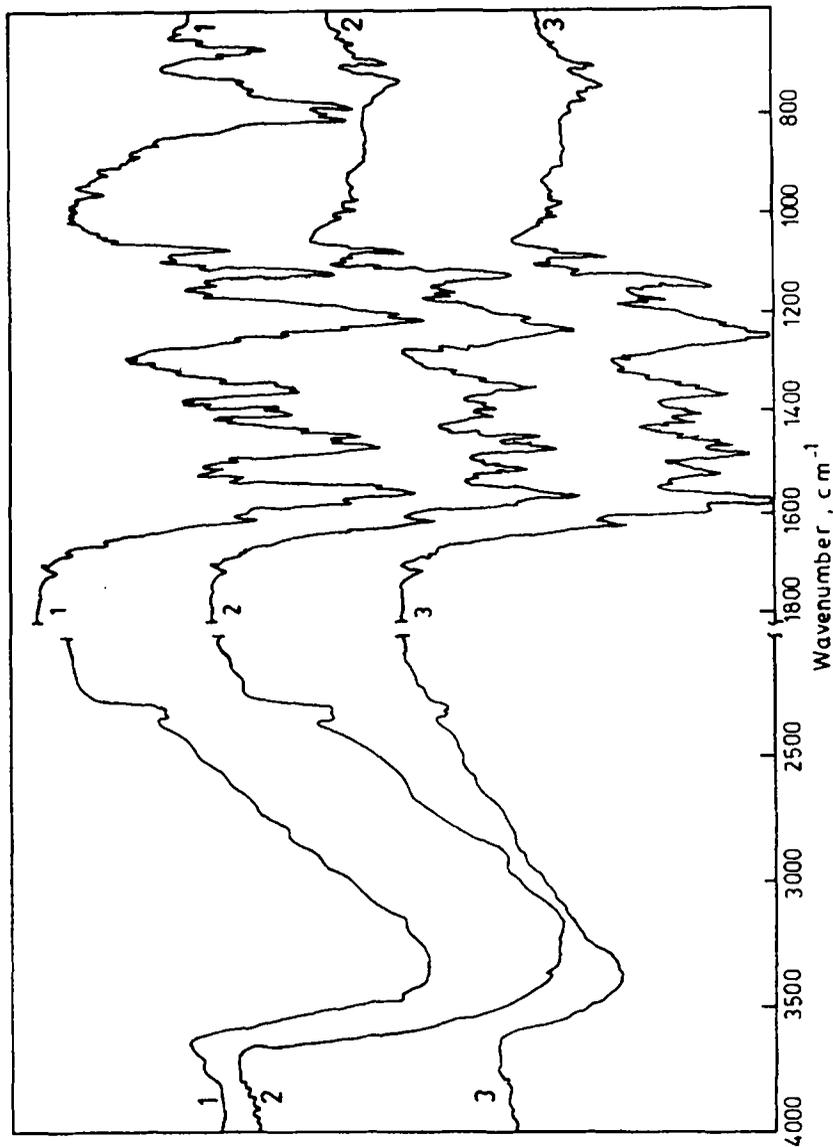


Figure 1. IR spectra of (1) 4,4'-azo phenol (2) PAHP polymer, and (3) PAHP-Cu²⁺ polychelate.

i.e. the higher molecular weight polymer is least expanded in DMF. This may be due to the lesser number of DMF solvent molecules surrounding the phenolate part of the polymer.

The viscosity of the solutions of polymers in DMF–water (85:15) (v/v) mixture containing 1.0% KBr shows normal behaviour. Thus such a mixture suppresses the polyelectrolyte behaviour. Hence, the measurements were also carried out in the mixture of DMF–water (85:15) (v/v) containing 1.0% KBr. Plots of the reduced viscosity versus the concentration were made for each set of data. The intrinsic viscosity $[\eta]$ was measured from the corresponding linear plots. The values of $[\eta]$ are presented in table 1.

Thermogravimetric analyses of all three polymer samples (table 1) reveal that they degrade in one step. They decompose in the region from 180° to 200°C and lose around 15% of their weight depending upon the nature of the polymer. Each polymer loses about 80% of its weight when heated to 700°C. The TGA results (table 1) of all three polymers show the following trend of thermal stability,



Comparison of the thermal stability of PAHP with those of polyazoarylene reveals that the polyazoarylenes are more thermally stable. The lower thermal stability of the polymers produced may be due to less close approach (i.e. presence of –OH groups in phenylene ring) of the polymer chains.

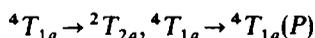
4.2 Characterization of the polychelates of PAHP

All the polychelates listed in table 2 are insoluble in common organic solvents. They are apparently unaffected when heated to 360°C.

The results of metal analyses are shown in table 2. The metal contents suggest that the metal–ligand [M:L] ratio is 1:2 for all the bivalent metal ions.

The IR spectra of the polychelates were similar in general shape and relative intensity of bands. Comparison of the IR spectra of polychelates with the ligand PAHP reveals that the broad absorptions in the region 2,700–3,500 cm^{-1} in the spectra of the ligand PAHP, due to ν_{OH} groups, are much less broad in the spectra of the polychelates. This indicates the decrease in internal H-bonding due to chelation, is in agreement with results of studies of chelation of azo phenols. The weak band at 1100 cm^{-1} is attributed to C–O–M stretching frequency (Irving and Williams 1956). The band observed at 1430 cm^{-1} in the IR spectrum of the ligand PAHP, attributed to the in-plane OH group (Charles *et al* 1958), is shifted towards higher frequencies for the polychelates indicating the formation of a metal–oxygen bond.

The diffuse electronic spectra of Cu^{2+} polychelates show broad bands around 15,383 and 22,727 cm^{-1} , the first band may be due to a ${}^2T_{2g} \rightarrow {}^2E_g$ transition and the second to charge transfer. The first band shows a structure suggesting a distorted octahedral structure for the Cu^{2+} polychelate (see figure 2). The higher value of μ_{eff} (2.01 BM) of the Cu^{2+} polychelates supports this view. The Ni^{2+} and Co^{2+} polychelates give two absorption bands respectively at 17,240 and 24,100 cm^{-1} and at 17,240 and 22,730 cm^{-1} which can be assigned respectively to



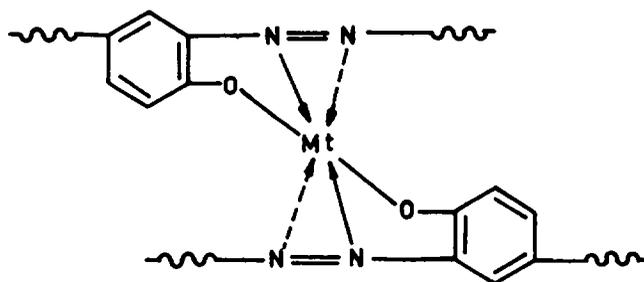


Figure 2. Polychelate of PAHP.

transitions. These absorption bands and the μ_{eff} values of 2.92 and 4.03 BM respectively for Ni^{2+} and Co^{2+} polychelates indicate octahedral configurations for Ni^{2+} and Co^{2+} polychelates. As the spectra of Zn^{2+} , Cr^{2+} and Mn^{2+} polychelates are not well-resolved, no attempt was made to analyse them. As expected the Zn^{2+} polychelate is found to be diamagnetic.

Examination of the thermograms (not shown) (table 2) of the polychelates reveals that, like the PAHP polymer, each polychelate degraded above $100^{\circ}C$ in one step. The rates of decomposition of the polychelates are greater than that of PAHP i.e. the polychelates are thermally less stable than PAHP. It seems that the metal ion accelerates the decomposition of the polychelates (Horowitz and Perros 1964). Among the polychelates produced the PAHP- Zn^{2+} polychelates are the most stable.

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