PAS-Formaldehyde Polymer as a Polymeric Ligand

S. D. Patel[a]; H. S. Patel[a]; S. R. Patel[a]

[a] Department of Chemistry, Sardar Patel University, India

PLEASE SCROLL DOWN FOR ARTICLE

PAS-Formaldehyde Polymer as a Polymeric Ligand

S. D. PATEL, H. S. PATEL, and S. R. PATEL

Department of Chemistry
Sardar Patel University
Vallabh Vidyanagar 388120, India

ABSTRACT

p-Aminosalicylic acid (PAS) was condensed with formaldehyde in the presence of aqueous oxalic acid and aqueous sodium hydroxide. The polymer sample (PAS-F,1) obtained with acid catalyst was characterized by IR spectral study, by its $\overline{M}_n$ determined by nonaqueous conductometric titration both against standard acid and alkali, by viscometric study in formic acid, and by DTA. The IR spectral and general characteristics of a polymer sample (PAS-F,2) prepared in the presence of aqueous alkali resemble those of a polymer sample (AP-F) prepared similarly from m-aminophenol and formaldehyde, indicating decarboxylation of PAS during the base-catalyzed polymerization of PAS with formaldehyde. Polymeric metal chelates of Fe(III), Cu(II), Zn(II), and Mn(II) ions with the PAS-F,1 polymer sample have been prepared and characterized by elemental analyses, IR spectral study, measurements of magnetic moments, and thermal analyses. Chelation ion-exchanging properties of the PAS-F,1 polymer sample have also been studied employing the batch equilibration method.

INTRODUCTION

Polymers prepared by condensation of salicylic acid and formaldehyde are known to be ion exchangers [1-4]. Perusal of the literature

1335

reveals that such polymers have not been prepared from p-amino-salicylic acid (PAS) and formaldehyde. However, there are reports on the preparation of other types of polymers from PAS. A polyamide is reported to have been prepared by self-polymerization of PAS [5]. A p-aminosalicylate of poly(vinyl alcohol) is reported in literature [6]. The preparation of two tercopolymers based on the condensation of formaldehyde with a mixture of two phenols (of which one is PAS and the other a phenol, either 4,4'-dihydroxydiphenylsulfone [7] or resorcinol [8]) has been reported.

The work described in the present communication is in connection with the synthesis and characterization of a PAS-formaldehyde polymer. PAS-F,1 polymer, prepared in the presence of aqueous oxalic acid, showed all the characteristics of a salicylic acid nucleus. However, the condensation of PAS with formaldehyde in the presence of aqueous alkali yields a polymer which is found to be different from polymer sample PAS-F,1 but similar to that prepared from m-aminophenol and formaldehyde in the presence of aqueous alkali. The metal chelates were prepared by using the sodium salt of the PAS-F,1 polymer sample. The metal:ligand ratio, IR spectral characteristics, and magnetic moment of the polymeric chelates have been studied. The thermal properties of polymeric chelates revealed by DTA have been compared with those of the corresponding parent polymer. The batch equilibration method, developed by Gregor et al. [9] and DeGeiso et al. [3], was adopted for the study of chelation ion-exchanging properties of the PAS-F,1 polymer sample. The effect of various electrolytes on the absorption of Cu(II) metal ions by PAS-F,1 polymer at a constant pH has been studied. The rates of the uptake of metal ions like Cu(II), Zn(II), and Mn(II) were determined under specified conditions. The distribution of these metal ions between the polymeric ligand and the liquid phase was studied at different pH values.

EXPERIMENTAL

Materials

PAS was regenerated from sodium-p-aminosalicylate (Na-PAS) obtained from Cadila laboratories, Ahmedabad, India. Formaldehyde (37%), m-aminophenol, acetic acid, perchloric acid (70%), and tetra-n-butylammonium hydroxide (0.1 M solution in methanol-toluene) were obtained from BDH Chemicals Ltd., Poole, England.

Formic acid (98%) was obtained from Reidel-De Haen AG, Seelze-Hannove, Germany.

Oxalic acid, sodium hydrogen carbonate, sodium hydroxide, hydrochloric acid, metal chlorides, and electrolytes (sodium chloride, nitrate, perchlorate, acetate) were of special chemical grade and were used without purification.

Preparation of Polymers

Condensation of PAS with Formaldehyde in the Presence of Aqueous Oxalic Acid

A mixture of PAS (15.3 g; 0.1 mol) in water (80 mL), aqueous formaldehyde (37%) (40 mL; 0.5 mol), and a 1% solution of oxalic acid in water (100 mL) was heated at 100°C with stirring for 5 h. The solid mass obtained in the form of granules was filtered, washed with boiling water, then with an ethanol:water (volume ratio 1:1) mixture and finally with dilute acetic acid and dried. It was freely soluble in an excess of aqueous hydrogen carbonate solution. The polymer did not melt up to 360°C. The sample was designated as PAS-F,1. Yield 15.0 g.

Analysis: Calculated for $(C_8H_7NO_3)_n$:N, 8.4%. Found: N, 7.8%.

Condensation of PAS with Formaldehyde in the Presence of Aqueous Sodium Hydroxide

To a well-stirred suspension of PAS (15.3 g; 0.1 mol) in water (80 mL), aqueous formaldehyde (37%) (40 mL; 0.5 mol) was added in 5 lots. To this suspension an aqueous solution of sodium hydroxide (5% w/v; 20 mL) was added with stirring. The reaction mixture was left aside for 2 h and then heated at 100°C for 2 h with continuous stirring. The dark-colored polymeric product was purified in the manner described above. It was insoluble in aqueous hydrogen carbonate solution and partially soluble in aqueous alkali. The polymer did not melt up to 360°C. This sample was designated as PAS-F,2. Yield 12.0 g.

Analysis: Calculated for $(C_7H_7NO)_n$: N, 11.6%. Found: N, 8.9%.

Combustion was carried out for a longer time in order to obtain better results for nitrogen estimation. A certain amount of material remained in the boat, and this was responsible for the lower value of estimated N. This also happened in the case of the polymer sample AP-F described below.

Condensation of m-Aminophenol (AP) with Formaldehyde in the Presence of Aqueous Sodium Hydroxide

To a well-stirred suspension of m-aminophenol (1.09 g; 0.01 mol) in water (80 mL), aqueous formaldehyde (37%) (4.0 mL; 0.05 mol) was added in 5 lots. To this suspension aqueous solution, sodium hydroxide (5% w/v; 20 mL) was added with stirring. The dark-colored polymeric product was purified in the manner described above. It was partially soluble in dilute aqueous alkali. This sample was designated as AP-F. Yield 1.0 g.

Analysis: Calculated for $(C_7H_7NO)_n$: N, 11.6%. Found: N, 8.8%.

Preparation of Polymeric Chelates

Sodium Salt of PAS-F,1 Polymer (NaPAS-F)

To a well-stirred suspension of PAS-F polymer (16.5 g; 0.1 mol) in 250 mL of water, 24 mL of 4 $\underline{M}$ aqueous sodium hydroxide was added dropwise. The resulting brownish red solution (pH = 8.5) was filtered through a sintered glass Grade 2 funnel and evaporated to dryness on a water bath to obtain a dark brown powder. This sodium salt was washed with ethanol. It was freely soluble in water. On acidification of the aqueous solution of the sodium salt, a solid was precipitated. It was collected, washed, and dried. Its IR spectrum was exactly similar to that of the PAS-F,1 polymer sample, indicating that there was no decarboxylation during the preparation of the sodium salt.

PAS-F-Cu(II) Chelate

The NaPAS-F sample (3.75 g; 0.02 mol) was dissolved in 25 mL of water and heated to about 60° on a water bath. To this a hot solution of $CuCl_2 \cdot 2H_2O$ (1.71 g; 0.01 mol) in 10 mL of water was added dropwise with constant stirring. After the addition of a metal ion solution was completed the brown suspension of the polymeric chelate was digested for about 1 h on a water bath and filtered. The solid was then washed with water and finally with ethanol and dried in air. The polymeric chelate weighed 4.0 g. Polymeric chelates, viz., PAS-F-Fe(III), PAS-F-Zn(II), and PAS-F-Mn(II), were prepared following this procedure. The results of the analyses of these polymeric chelates are presented in Table 1.

Apparatus and Methods of Characterization

Elemental analyses (N) of polymers and polymeric metal chelates were carried out on a Coleman Nitrogen analyzer. The metal ion content in the polymeric chelates was estimated by decomposition of a known weight of the chelate by mineral acid followed by dilution with distilled water and estimation of the metal ions in solution by methods given in literature [10].

The IR spectra were taken in KBr on a Perkin-Elmer No. 5102-1000 spectrophotometer.

The number-average molecular weight of the PAS-F,1 polymer sample was estimated by the conductometric titration method [11, 12]. Metrohm Herisau Konductoskop E 365, Switzerland, was used for the conductometric titrations. The polymer solution in the titration vessel (Conductance Cell EA 645, England) was stirred with a magnetic stirrer, and stirring was stopped during each measurement. The conductometric titration of the PAS-F,1 polymer solution in a 1:1 (v/v) mixture of formic acid and acetic acid was carried out against a

TABLE 1. Characterization of Polymeric Chelates

Polymeric chelate	Molecular weight of the repeating unit (g)	% metal content		% nitrogen		μ_{eff} (BM)
		Calculated	Found	Calculated	Found	
PAS-F-Cu(II)	389.57	16.32	15.92	7.12	6.52	1.82
PAS-F-Fe(III)	544.85	14.62	12.47	5.06	7.33	5.2
PAS-F-Zn(II)	391.38	16.42	16.71	7.15	6.82	Diamagnetic
PAS-F-Mn(II)	380.93	14.23	14.42	7.14	7.35	5.58

0.1 M solution of perchloric acid in acetic acid. For the titration, a solution of 50 mg of polymer sample in a 50 mL formic acid–acetic acid mixture was employed. The conductance of the solution was measured after the addition of each lot of the solution of perchloric acid. The steps in the plot of conductance vs mmol of titrant added per 100 g of polymer sample were quite distinct. The relevant details of measurement and calculations are presented in the literature [11, 12].

The conductometric titration of a solution of polymer sample PAS-F,1 in pyridine was carried out against a 0.01 M solution of tetra-n-butylammonium hydroxide (TBAH) in pyridine following the details described above. The polymer sample (10 mg) dissolved when suspended in the form of a fine powder in pyridine (50 mL) and stirred for about 1 h, leaving a small residue in the form of a swollen powder. The conductometric titration of such a solution-suspension of the polymer in pyridine could be carried out satisfactorily. After the addition of each lot of a standard reagent a period of about 2 to 3 min was allowed to lapse while the solution-suspension being titrated was stirred and before noting the conductance reading. The solution became clear toward the end of the titration.

The viscosity of solution in formic acid of polymer sample PAS-F,1 was measured at 35 ± 0.1°C with an Ubbelohde-type dilution viscometer (made of Pyrex glass). The solvent and solution were passed through a sintered glass crucible (G-4) to free them of any dust particles. The measurements were carried out in the concentration range from 0.384 to 1.0 g/dL. The intrinsic viscosity [η] was measured from a linear plot of η_{sp}/C vs concentration.

Magnetic susceptibility measurements of polymeric metal chelates were carried out at room temperature by the Gouy method. Hg[Co-(NCS)₄] was used for calibration [13]. The molecular susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants [13].

Differential thermal analysis (DTA) of the PAS-F,1 polymer sample and its polymeric chelates was carried out with a Linseis (Germany) DTA analyzer in air at a heating rate of 10°C/min.

Ion-Exchange Properties

An air-dried PAS-F,1 polymer sample, described earlier, was ground to pass 100-mesh and swollen under the conditions of study, and was used in all experiments described for batch equilibration in an ion-exchange study.

Study of the Effect of Various Electrolytes on the Metal Ion Uptake under Equilibrium Conditions at a Fixed pH

The PAS-F,1 polymer sample (1 g) was stirred in the solution of a given electrolyte (200 mL) of known concentration and the pH was

TABLE 2. Evaluation of the Influence of Different Electrolytes on the Uptake of Cu(II) Metal Ions: $[Cu(NO_3)_2]$ = 0.1 mol/L[a]

[Electrolyte] (mol/L)	Weight (in mg) of the metal ion taken up in the presence of			
	NaCl	NaNO₃	NaClO₄	NaOAc
0.01	0.32	0.64	0.64	0.96
0.05	1.59	0.96	2.86	2.22
0.1	1.59	1.27	3.49	2.54
0.5	0.64	1.59	4.45	4.45
1.0	-	1.91	4.76	5.49

[a]Volume of electrolyte solution, 200 mL; volume of metal ion solution, 10 mL; pH, 2.5; time, 24 h; temperature, 25°C.

adjusted to the required value (in the present case to 2.5) using either 0.1 M HCl or 0.1 M NaOH. The mixture was stirred for 24 h at 25°C. To this suspension 10 mL of a 0.1 M solution of Cu(II) metal ion was added and the pH was adjusted to 2.5. Stirring was continued at 25°C for 24 h. The filtrate and washings were collected, mixed, and diluted to 250 mL. The diluted solution (25 mL) was titrated against standard EDTA to estimate the metal ion [10]. A blank experiment was also carried out in exactly the same manner and for the same time without adding the polymer sample. The difference in the metal ion concentrations in the blank and in the actual experiment was used to calculate the amount of metal ion taken up by the polymer under the given conditions of the experiment.

Such experiments were carried out for Cu(II) ions using four electrolytes at five different concentrations while keeping pH of the solution constant, viz., 2.5. The results of this study are reported in Table 2.

Evaluation of the Rate of Metal Ion Uptake

Experiments of the type described above were carried out using 1 g of the PAS-F polymer sample and 10 mL of 0.1 M Cu(II), Zn(II), and Mn(II) metal ion solutions, respectively, in the presence of 1 M NaNO₃ (50 mL) at pH 3.0 and 25°C. The time interval of the experiment was varied from 0.5 h to a time beyond which there was no change in the amount of metal ion absorbed. The amount of metal ion taken up by the same amount of polymer is expressed as % attainment at the state of equilibrium using the formula given in Footnote b of Table 3 in which the results of this study are reported.

TABLE 3. Comparison of the Rates of Metal (M_t) Ion Uptake[a]

Time (h)	Percentage of the attainment of the state of equilibrium[b]		
	Cu(II)	Mn(II)	Zn(II)
0.5	30.77	6.19	84.14
1	38.57	18.76	87.42
2	53.84	25.02	96.74
3	76.63	37.5	97.12
4	–	–	–
5	84.76	74.99	–
7	92.43	81.19	–

[a]$[M_t(NO_3)_2]$ = 0.1 mol/L; volume = 10 mL. $[NaNO_3]$, mol/L; volume, 50 mL; pH, 3; temperature, 25°C.

[b]$\dfrac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal ion absorbed at equilibrium}}$

Evaluation of Distribution of Metal Ions at Different pH Values

The distribution of each of the metal ions Cu(II), Zn(II), and Mn(II), between the polymer phase and aqueous phase as the ratio

$$\frac{\text{mg of metal ions taken up by 1 g of polymer}}{\text{mg of metal ions present in 1 mL of solution}}$$

was estimated in the presence of a 1 M $NaNO_3$ solution at 25°C. The experiments were carried out as described earlier at different pH values ranging from 1 to 7. The results are presented in Table 4.

RESULTS AND DISCUSSION

The polymer sample (PAS-F, 1) prepared in the presence of an acid catalyst had a light brown color similar to that of PAS. This polymer sample was insoluble in common organic solvents and soluble to some extent in formic and acetic acids. It was soluble in excess aqueous hydrogen carbonate solution and in aqueous alkali. .It was insoluble in hydrochloric acid. Neutral solution of polymer sample reacted characteristically with Fe^{3+} ions (i.e., violet-blue colored precipitates).

TABLE 4. Distribution Ratios, D,[a] of Different Metal Ions as a Function of the pH

pH	Distribution ratio ($D \times 10^2$ mL/g) of the metal ions ($\pm 5\%$)		
	Cu(II)	Zn(II)	Mn(II)
1	0.51	0.991	0.35
2	0.65	1.16	0.91
3	0.89	1.31	0.93
4	1.90	1.54	1.05
5	4.97	2.55	1.76
6	8.76	4.71	3.74
7	9.34	6.11	3.97
8	98.50	8.57	4.43

$$^{a}D = \frac{\text{mg of metal ions taken up by 1 g of polymer}}{\text{mg of metal ions present in 1 mL of solution}}, \text{ mL/g.}$$

Polymer sample, 2 g; $[Mt(NO_3)_2]$ = 0.1 mol/L; volume, 10 mL. $[NaNO_3]$ = 1 mol/L; volume, 240 mL; temperature, 25°C; time, 24 h (equilibrium state).

The dark brown colored product PAS-F,2, formed using aqueous alkali as catalyst, was not soluble in aqueous hydrogen carbonate and its neutral solution in aqueous alkali did not give the characteristic color with Fe^{3+} ions. The dark brown colored polymer prepared from m-aminophenol and formaldehyde in the presence of aqueous alkali was also insoluble in aqueous hydrogen carbonate and was sparingly soluble in an excess of strong aqueous alkali solution.

The important features of the IR spectrum (Fig. 1) of the polymer sample PAS-F,1 are a broad band due to a chelated system [14] extending from 3550 to 2550 cm^{-1}, and with inflections around 2925 cm^{-1} and 2850 cm^{-1} attributed to asymmetric and symmetric stretching of CH of $-CH_2-$ bridges, Carbonyl band at 1660 cm^{-1} are due to COOH of the repeating unit [14]. A band at 870 cm^{-1} may be attributed to an isolated aromatic hydrogen atom. The band at 1050 cm^{-1} can be attributed to the $-CH_2OH$ end group. These features can be explained in terms of the structure proposed for the polymer sample PAS-F,1 on the basis of the structure of the monomer [14] and the reactivity of positions on the monomer molecule. The number-average molecular weight estimated by nonaqueous conductometric titration of PAS-F,1 against base and acid has been found to be nearly equal.
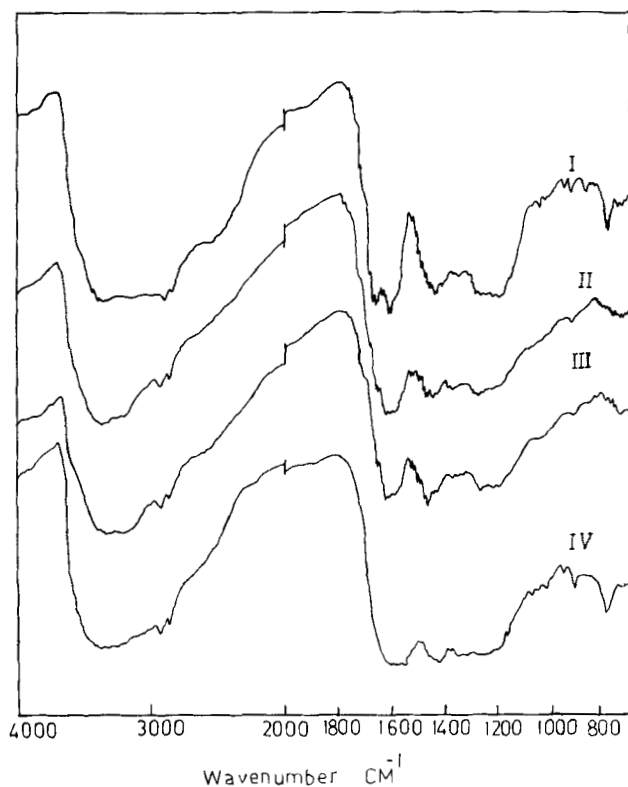
FIG. 1. IR spectra of polymers. I: PAS-F,1. II: PAS-F,2.
III: AP-F. IV: PAS-F,1-Fe(III) chelate.

The values of $\overline{M}_n$ were 775 obtained by base titrant and 800 obtained
by acid titrant. This suggests the equivalence of the number of moles
of NH_2 and COOH groups per mole of repeat units.

The IR spectrum (Fig. 1) of the polymer sample PAS-F,2 prepared
in the presence of aqueous alkali is characteristically different from
that of the polymer sample PAS-F,1 but is similar to that (Fig. 1)
of the polymer sample prepared from m-aminophenol and formalde-
hyde in the presence of aqueous alkali. This and other properties
reported earlier indicate that in the base-catalyzed condensation of
PAS with formaldehyde the monomer PAS undergoes decarboxylation.
PAS is reported to decarboxylate in hot aqueous solution on standing
[15].

The intrinsic viscosity $[\eta]$ of PAS-F,1 in formic acid at 35 ± 0.1°C
was found to be 0.104.

   The polymeric chelates were found to be insoluble in common organic solvents and were decomposed by mineral acids to give the original polymeric ligands. The polymeric chelates were apparently unaffected when heated to 300°C. The results of metal and nitrogen analyses are shown in Table 1. The results of the metal composition suggest that the metal:ligand (M:L) ratio is 1:2 for all divalent metal and 1:3 for trivalent metal ions. These results were also supported by the results of the nitrogen content of polymeric chelates.

   The IR spectra of all polymeric chelates resembled each other in their general shapes and relative intensity of bands. Comparison of the IR spectrum of a polymeric chelate with that of its parent polymer reveals that in the OH-stretching region the band in the spectrum of the chelate is much less broad than that of the parent polymeric ligand, as expected. A band around 1600 cm^{-1} was observed in the spectra of all the polymeric chelates. This was attributed to the carboxylate ion (COO⁻) of the repeating unit. Because of the very low intensity of the bands in the concerned region, it was not possible to observe the band due to the metal-carbon bond with any certainty. This region was rendered complex due to the presence of C–H out-of-plane bending vibrations in this region. The above properties can be explained on the basis of the expected structure of the polymeric chelate which is shown below.
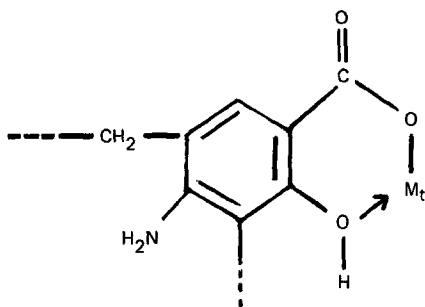
$$M_t = \frac{Cu(II)}{2} , \frac{Zn(II)}{2} , \frac{Mn(II)}{2} , \frac{Fe(III)}{3}$$

   It is reasonable to expect that the magnetic behavior of a polymeric chelate could be predicted on the basis of that of the simple chelate forming the repeating unit. Magnetic moments (μ_{eff}) of polymeric chelates were estimated from magnetic susceptibility data. These estimations are based on the assumption that there is no orbital contribution. The results are shown in Table 1.
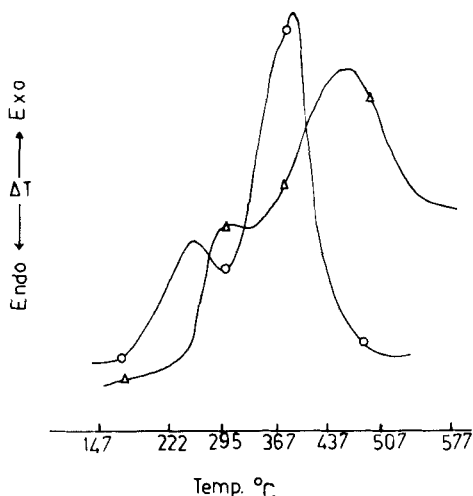
FIG. 2. DTA thermograms of PAS-F,1 polymer (△) and PAS-F,1-Cu(II) chelate (○).

Examination of these results reveals that the magnetic moments of polymeric chelates are in the expected range as reported for complexes of salicylic acid [16] and thiosalicylic acid [17]. The PAS-F-Zn(II) chelate is diamagnetic and others are paramagnetic. Paramagnetic complexes are expected from the octahedral species [18, 19]. However, on the basis of the magnetic moments, it is not possible to draw definite conclusions about the geometry of these complexes.

Thermograms of the PAS-F,1 polymer sample and its Cu(II) chelate are shown in Fig. 2. Examination of the thermograms of the PAS-F,1 polymer reveals that its decomposition commences around 220°C. Beyond this temperature the thermogram rises very rapidly and passes through a small inflection. The second stage of decomposition appears to commence around 360°C. The second part of thermogram has a maximum around 460°C. After this temperature the rate of decomposition decreases rapidly and the exotherm appears to terminate around 580°C. The thermal behavior of the present polymer appears to be similar to the reported behavior of the salicylic acid-formaldehyde polymer. The latter is reported to decompose in two stages [2], the first stage of decomposition, extending from 190 to 260°C, is reported to be due to a decarboxylation reactions [2].

The DTA thermogram of PAS-F,2 reveals that it decomposes in a single step, with decomposition commencing around 350°C and continuing to 700°C. It has been reported that a polymer sample prepared on condensing m-aminophenol with formaldehyde loses about 40% of its weight when the temperature reaches 800°C [20].

Examination of DTA thermograms of polymeric chelates reveals that, like the parent polymer, each polymeric chelate degrades at a temperature above 220°C in two stages. The first step of degradation is smaller than the second step. The maximum of the second step in the degradation of all four polymeric chelates falls around 400 ± 30°C. If the temperature corresponding to this maximum in the second step is considered to be a criterion for judging relative stability, then the polymeric chelates can be considered to be less stable than their parent polymeric ligand.

Ion Exchanging Properties of PAS-F,1 Polymer

Influence of Electrolytes on the Cu(II) Metal Ion Uptake

Examination of the data presented in Table 2 reveals that the amount of Cu(II) ions taken up by the polymer sample increases with an increasing concentration of electrolytes (e.g., sodium perchlorate, sodium nitrate, and sodium acetate). However, in the presence of sodium chloride the amount of Cu(II) ion absorbed by the polymer sample increased until the sodium chloride concentration increased to 0.1 M. With a further increase in the concentration of sodium chloride, the amount taken up by the polymer sample continued to decrease.

Rate of Metal Uptake

Table 3 shows the dependence of the rate of metal ion uptake on the nature of the metal. The study revealed that the rate of uptake of metal ions follows the order Zn(II) > Cu(II) > Mn(II).

Distribution Ratios of Metal Ions at Different pH Values

The results of the effect of pH on the amount of metal ions distributed between two phases are presented in Table 4. Examination of the data indicates that the amount of metal ions taken up by the polymeric material increases with an increase in the pH of the medium. The study was carried out only up to pH 8 to prevent hydrolysis of metal ions at a higher pH. In the case of the Cu(II) ion, the distribution ratio becomes 200 times with change in pH from 1 to 8. In the case of Zn(II) and Mn(II), the distribution ratio becomes nearly 10 times for such a change in the pH value.

REFERENCES

[1] L. G. Donaruma, U.S. Patent 3,052,515 (1962) to E. I. du Pont de Nemours and Co.; Chem. Abstr., 57, 13467a (1962).
[2] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, J. Org. Chem., 27, 1424 (1962).

[3] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, Anal. Chem.,
     34, 845 (1962).
[4] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, Ind. Eng.
     Chem., Process Des. Dev., 2, 43 (1963).
[5] H. Z. Lecher and B. G. Buell, U.S. Patent 2,831,573 (1958) to
     American Cyanamide Co.; Chem. Abstr., 53, 1731C (1959).
[6] S. N. Ushakov, L. B. Trukhmanova, E. V. Drozdova, and T. M.
     Murkelova, Dokl. Akad. Nauk SSSR, 141, 1117 (1961); Chem.
     Abstr., 56, 12795d (1952).
[7] German Patent 1,247,328 (1967) to Badische Aniline & Soda-
     Fabrik A.G.; Chem. Abstr., 67, 91317f (1967).
[8] M. M. Dyaltova, V. Ya. Temkina, E. S. Kolesnik, G. F. Yaro-
     shenko, and R. P. Lastovskii, Tr. Vses. Nauchna-Issled. Inst.
     Khim. Reakt., 25, 91 (1963); Chem. Abstr., 61, 777e (1964).
[9] H. P. Gregor, M. Tieter, L. Citavel, and E. I. Becker, Ind.
     Eng. Chem., 44, 2834 (1952).
[10] A. I. Vogel, A Text-Book of Quantitative Inorganic Analysis,
      2nd ed., Longmans, London, 1960.
[11] S. K. Chatterjee, J. Polym. Sci., Part A-1, 8, 1299 (1970).
[12] S. K. Chatterjee, Ibid., 9, 3225 (1971).
[13] A. Earnshaw, Introduction to Magnetochemistry, Academic,
      London, 1968.
[14] N. G. Gujrathi and C. I. Jose, Indian J. Chem., 9, 822 (1971).
[15] K. G. Rosdohl, Svensk Kem. Tid., 60, 12 (1948); Chem. Abstr.,
      42, 3744 (1948).
[16] Jiri, Kohout, Juraj, and Krutsmar-Smogrovic, Chem. Zvesti,
      22(7), 481 (1968); Chem. Abstr., 69, 101022p (1968).
[17] C. Nair and H. L. Nigam, Indian J. Chem., 12, 769 (1974).
[18] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry,
      Wiley-Interscience, New York, 1964.
[19] S. L. Davadov and N. A. Plate, Coord. Chem. Rev., 16(3), 195
      (1975).
[20] C. K. Sack, L. H. Jung, and J. J. Hguk, Deehan Hwahak.
      Hwoejee, 17, 60 (1973); Chem. Abstr., 78, 160665j (1973).