Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis, Characterization, and Applications of Poly(Salicylaldehyde-Acrylate-Divinylbenzene) Oxime as a Chelate Polymer to Ni(II), Co(II), and Cu(II) Ions

L. D. Prabhakar[a]; C. Umarani[a]
[a] Department of Chemistry, Annamalai University, Tamil Nadu, India

To cite this Article Prabhakar, L. D. and Umarani, C.(1995) 'Synthesis, Characterization, and Applications of Poly(Salicylaldehyde-Acrylate-Divinylbenzene) Oxime as a Chelate Polymer to Ni(II), Co(II), and Cu(II) Ions', Journal of Macromolecular Science, Part A, 32: 1, 129 — 142

To link to this Article: DOI: 10.1080/10601329508011069

URL: http://dx.doi.org/10.1080/10601329508011069

J.M.S.—PURE APPL. CHEM., A32(1), pp. 129–142 (1995)

SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS OF POLY(SALICYLALDEHYDE-ACRYLATE-DIVINYLBENZENE) OXIME AS A CHELATE POLYMER TO Ni(II), Co(II), AND Cu(II) IONS

L. D. PRABHAKAR* and C. UMARANI

Department of Chemistry
Annamalai University
Annamalainagar 608002, Tamil Nadu, India

ABSTRACT

A three-dimensional polymer backbone was prepared from salicylaldehyde-acrylate monomer using benzoyl peroxide as the catalyst at 80 ± 0.2°C by the suspension polymerization technique. Through a post-polymerization reaction, a chelating group, oxime, was attached to the aldehydic functional group. The oximated resin was treated with Ni(II), Co(II) and Cu(II) ions. The parent polymer, functionalized polymer, and its Ni(II), Co(II), and Cu(II) metal chelates were characterized by IR, ^{1}H-, ^{13}C-CP/MAS NMR, EPR, TG-DTA, magnetic studies, and optical and SEM microphotographs. The maximum capacity of the resins for the metal ions and the recyclability of the resins were established. The physical aspects of the beads are discussed through optical and SEM photographs.

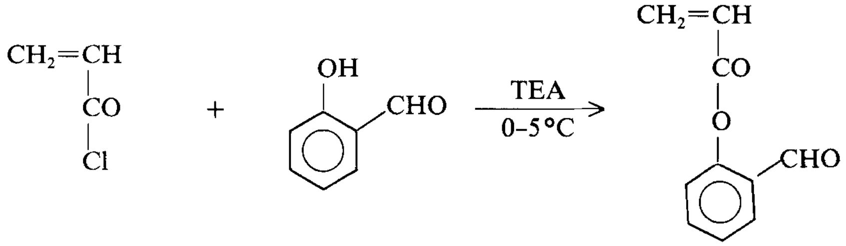
INTRODUCTION

The interaction between metal ions and polymerized ligands leads to the formation of polymeric compounds in which the metal ions are bound by ligand molecule [1, 2]. Anchoring reagents to insoluble supports is known as solid-phase synthesis. Based on the pioneering efforts of Merrifield [3] in polypeptide synthesis, developments include not only polypeptide synthesis on polymer supports, but also immobilized photosensitizers and immobilized transition metal complexes [4]. Synthesis of polymer-anchored transition metal chelates is a field of active research [5-10]. In continuation of our earlier research work [11, 12], we now report the preparation and properties of coordination polymers of Ni(II), Cu(II), and Co(II) with poly(salicylaldehyde-acrylate-divinylbenzene) oxime.

EXPERIMENTAL

Preparation of Monomer (addition of acryloyl chloride to salicylaldehyde)

To 0.2 mol salicylaldehyde in ethyl methyl ketone, 0.2 mol triethylamine was added and stirred at 0-5 °C. To this mixture, 0.2 mol acryloyl chloride in ether was added in a dropwise manner over 45 minutes. Stirring was continued for 2 hours. The precipitate that resulted was filtered, and the filtrate was washed with ether three times. The ethereal layer was evaporated to obtain salicylaldehyde acrylate monomer. The product was identified through NMR spectral [13] data. Mp: 5-6 °C.

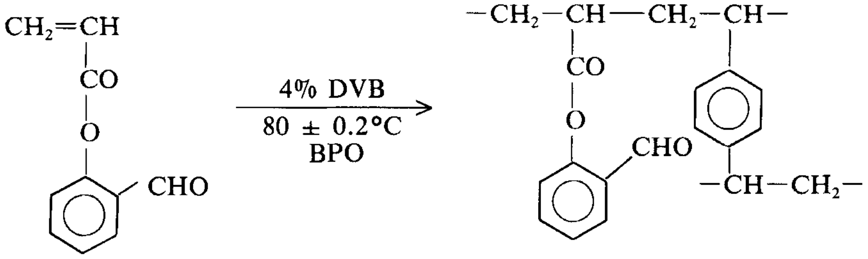


^{1}H NMR (δ, ppm): 9.8 (H), 7.3-7.9 (4H), 6.11-7.01 (3H).

^{13}C NMR (δ, ppm): 133.2 ($\underline{C}H_2$), 126.8 ($\underline{C}H$), 163.7 (^{3}C), 151.5 (^{4}C), 134.7 (^{5}C), 129.9 (^{6}C and ^{8}C), 127.9 (^{7}C), 136.5 (^{9}C), 196.0 (^{10}C).

Polymerization of Monomer

Bead polymerization was carried out at 80 ± 0.2 °C with polyvinyl alcohol as the stabilizer and benzoyl peroxide as the catalyst. A controlled stirring rate of 400 rpm was maintained for 12 hours. 4% Divinylbenzene was applied as the crosslinking agent. The beads that resulted were filtered and washed with petroleum ether, ethyl methyl ketone, acetone, and dichloromethane to remove unreacted monomer. The product was dried in a vacuum oven at 60 °C. Yield: 80%.



The product was identified through solid-state ^{13}C-CP/MAS NMR and IR spectra.

Functionalization of Polymers

Functionalization of poly(salicylaldehyde-acrylate) was achieved by incorporating an oxime moiety through a postpolymerization reaction.

Crosslinked polymer (5 g) and oxime (10 g) in dimethylformamide were placed in a 500-mL round-bottomed flask and refluxed for 12 hours.

The functionalization was maximized and became constant after 12 hours. The contents were filtered, and the functionalized beads were collected, washed with solvents, and dried in a vacuum oven at 60°C.

Preparation of Metal Complexes

Five grams of metal salts [Ni(II), Co(II), and Cu(II) in the form of nickel(II) chloride hexahydrate, cobalt(II) chloride hexahydrate, and copper(II) chloride dihydrate, respectively] in a dimethylformamide-water mixture were treated with 5 g of a functionalized polymer and refluxed for 10 hours in triply distilled water as the medium at a pH of 6.9 ± 0.1. The reaction mixture was filtered, and the resulting light green (nickel), pink (cobalt), and green (copper) metallated polymers were washed with hot water, DMF, and acetone, respectively, and dried in a vacuum oven at 60°C. See Fig. 1.

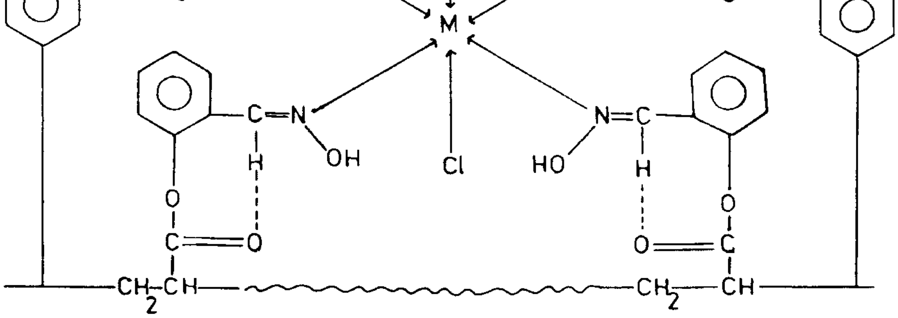


FIG. 1. Possible structure of salicylaldehyde-acrylate-divinylbenzene oxime polymer-metal complex. M = Cu^{2+}, Ni^{2+}, Co^{2+}.

RESULTS AND DISCUSSION

Elemental Analysis

Elemental analysis data are presented in Table 1. The data show that the conversion of functionalization is 31% and that of metallation is 29, 45, and 38%, respectively, for the Ni(II), Co(II), and Cu(II) complexes.

Solid State ^{13}C-CP/MAS NMR Spectroscopy

The ^{13}C-NMR spectra of the crosslinked polymer as recorded on a Bruker 300 MSL CP-MAS is shown in Fig. 2. The backbone methylene carbon appears as a very sharp signal at 44.88 ppm in solution-state NMR and it appears in solid-state NMR spectra at 40.156 ppm. The sharp signal at 126.8 ppm is due to ^{2}C in the monomer whereas in the crosslinked polymer it appears at 126.0 ppm. The aldehydic carbonyl of salicylaldehyde appears at 196.0 ppm as a sharp signal in the monomer whereas it appears in the crosslinked polymer at 186.3 ppm as a medium intensity peak. It is not present in the SAA-DVB oxime system. The phenyl ester carbonyl [14] gives a sharp signal at 163.7 ppm in the monomer and at 160.6 ppm in solid-state NMR. The ^{4}C, ^{5}C, ^{7}C, and (^{6}C and ^{8}C) of aromatic carbon signals appear at 151.5, 134.8, 127.9, and 129.9 ppm in the monomer. Due to residual broadening, a clear separation of the signals is not observed in the solid-state spectra. The ^{9}C aromatic carbon appears at 136.5 ppm in the monomer whereas it appears at 136.99 ppm in solid-state NMR.

IR Spectral Studies

The IR spectra show a 2932 cm^{-1} band because of aromatic —CH and backbone methylene stretching vibration. The ester carbonyl of SAA-DVB appears at 1755 cm^{-1} [15]. The strong absorption at 1602 cm^{-1} is attributed to the C=C skeletal vibration of the phenyl ring. The C—O—C stretching vibration is identified

TABLE 1. Elemental Analysis Data of Salicylaldehyde-Acrylate-Divinylbenzene Oxime Polymer and Its Metal Complexes

	C, %	H, %	N, %
SAA-DVB oxime	63.068	7.105	2.178 (7.000)[a]
SAA-DVB-Ni(II) complex	50.559	6.616	1.558)[a] (5.381)[a]
SAA-DVB-Co(II) complex	49.821	5.743	2.434)[a] (5.377)[a]
SAA-DVB-Cu(II) complex	52.556	6.236	2.014)[a] (5.279)[a]

[a]For 100% calculated value.

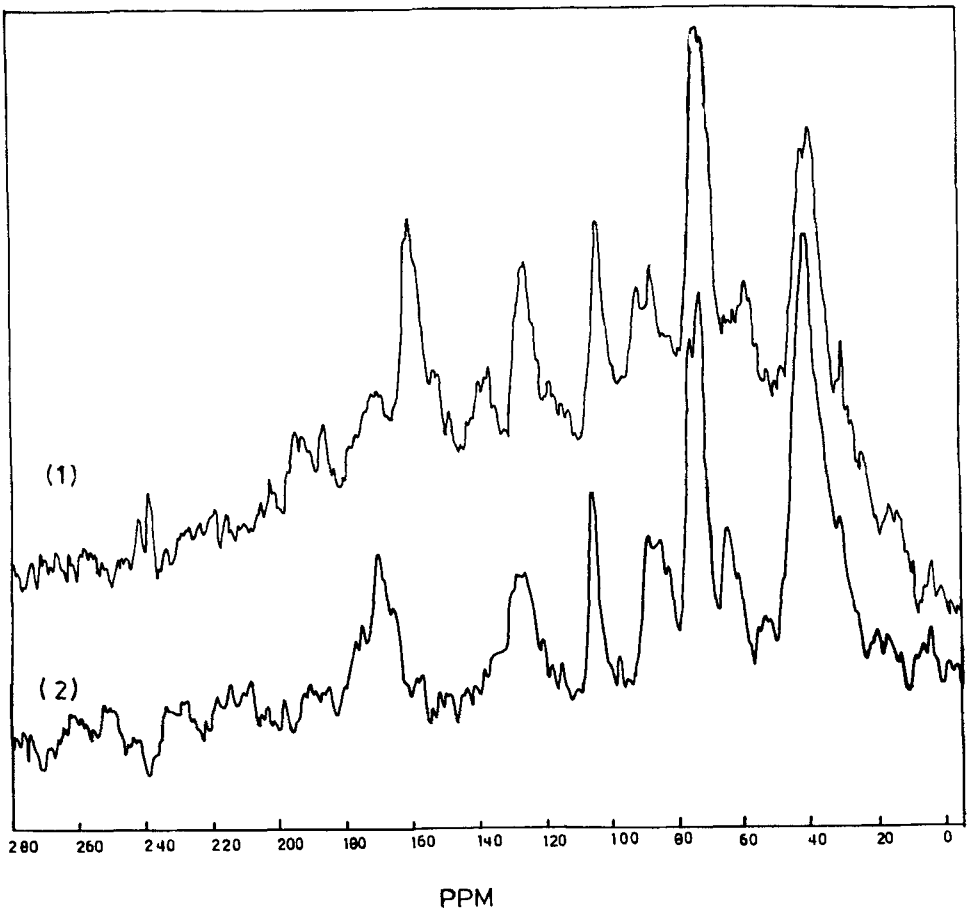


FIG. 2. Solid-state ^{13}C-CP/MAS NMR spectra of (1) salicylaldehyde-acrylate-divinylbenzene copolymer and (2) salicylaldehyde-acrylate-divinylbenzene oxime derivative.

in spectra around 1125 cm^{-1}. Absorption at 1701 cm^{-1} indicates the presence of an aldehydic ketone [16-18].

The oxime derivative shows a broad band around 3400 cm^{-1} which is attributed to the presence of the oxime hydroxyl group. The band at 1701 cm^{-1} (due to an aldehydic ketone) in the polymer is absent in the corresponding oxime derivative. Further, a number of small bands, probably combinations of ($C{=}N + C{=}C$), in the 1480 to 1560 cm^{-1} range are also observed in the oximated product but are absent in the parent polymer spectra, which supports the formation of the oxime.

In metal complexes, the $\nu(C{=}N)$ vibrations appear at 1545 and 1577 cm^{-1} for the Ni(II) and Co(II) complexes, respectively, which indicates functionalized polymer coordination to the metal ion through the nitrogen atom.

EPR Studies

The EPR parameters calculated by the Kneubuhl [19] method for the copper complex are found to be Cu:A = 137.5 G; $g_{\parallel}$ = 2.41; $g_{\perp}$ = 2.10.

The EPR spectrum of Cu(II) is presented in Fig. 3. The EPR spectrum of the cupric complex shows a strong signal characteristic of bivalent copper [20]. The signal of copper complexes of univalent copper is zero. It is shown in the literature that the lower part of the strong signal is a doublet for bivalent copper in a square planner belonging to *dsp*^{2} coordination. Our complex did not show any doublet in the lower part of the strong signal. Therefore, we assume an almost planar cupric [21] ion in the center with the nitrogen, carbonyl oxygen, and chloride groups on the *X* and *Y* axes according to the reaction conditions. Thus, the results of EPR measurements corroborated the conclusions from our analysis of the IR spectra.

The EPR signals corresponding to an Ni(II) and Co(II) complex are not observed at room temperature.

Magnetic Studies

The magnetic data reveal that the three complexes are paramagnetic. The values are given in Table 2.

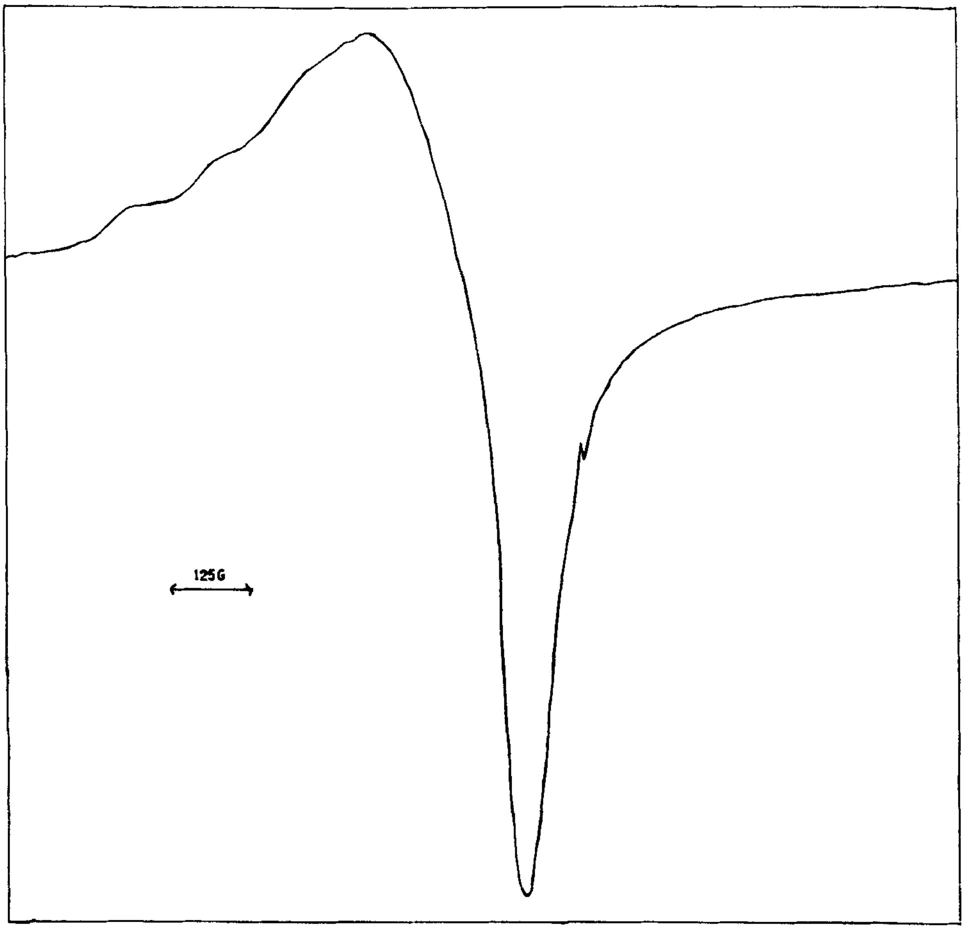


FIG. 3. EPR spectrum of Cu(II).

TABLE 2. Paramagnetic Moments (EMU) of Salicylaldehyde-Acrylate-Divinylbenzene Oxime and Its Metal Complexes

Field (kG)	Moment, EMU		
	Ni(II)	Co(II)	Cu(II)
2	0.062×10^{-2}	0.066×10^{-2}	0.025×10^{-2}
4	0.095×10^{-2}	0.123×10^{-2}	0.041×10^{-2}
6	0.133×10^{-2}	0.170×10^{-2}	0.056×10^{-2}
8	0.179×10^{-2}	0.230×10^{-2}	0.073×10^{-2}

Optical and Scanning Electromicroscopy

The spherical nature of the beads was observed by optical microscopy. These microphotographs are presented in Figs. 4–6. The SEM of the SAA-DVB copolymer is shown in Fig. 7. It can be seen from the microphotograph that the particles are spherical and relatively similar in size. This micrograph confirms the success of suspension polymerization.

Thermogravimetric Analysis

The thermolysis curves of the SAA-DVB copolymer and its oxime are shown in Figs. 8 and 9, respectively. The degradation of SAA-DVB copolymer occurred in two stages. The first stage degradation took place in the 493 to 686 K range, and the

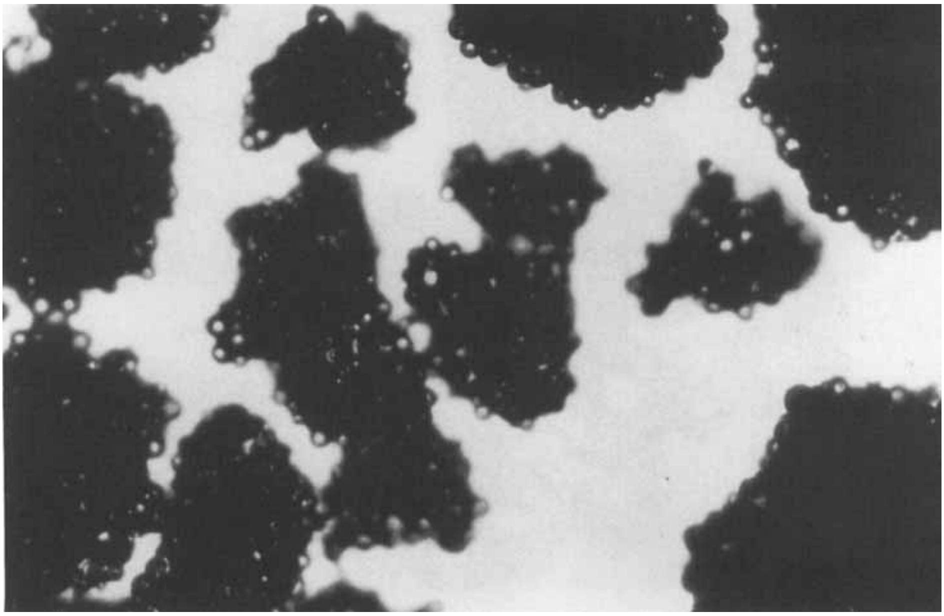


FIG. 4. Optical photograph of salicylaldehyde-acrylate-divinylbenzene copolymer.

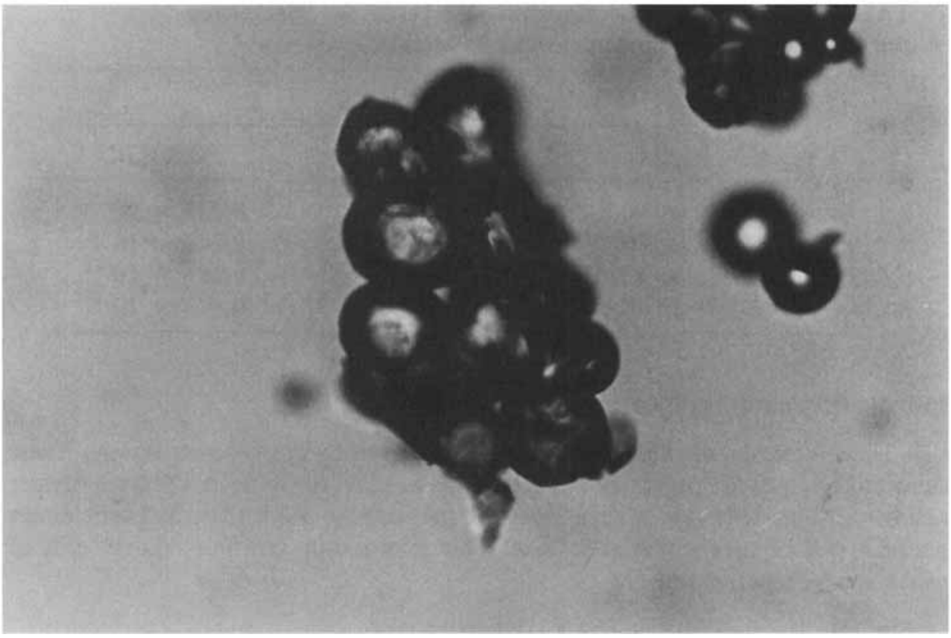


FIG. 5. Optical photograph of salicylaldehyde-acrylate-divinylbenzene oxime derivative.

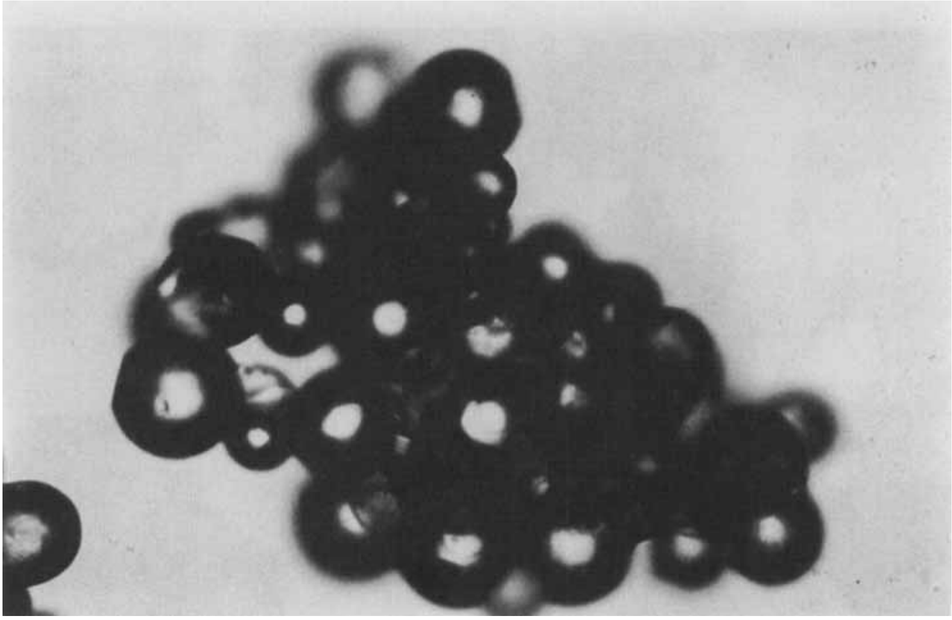


FIG. 6. Optical photograph of salicylaldehyde-acrylate-divinylbenzene oxime Ni(II) complex.

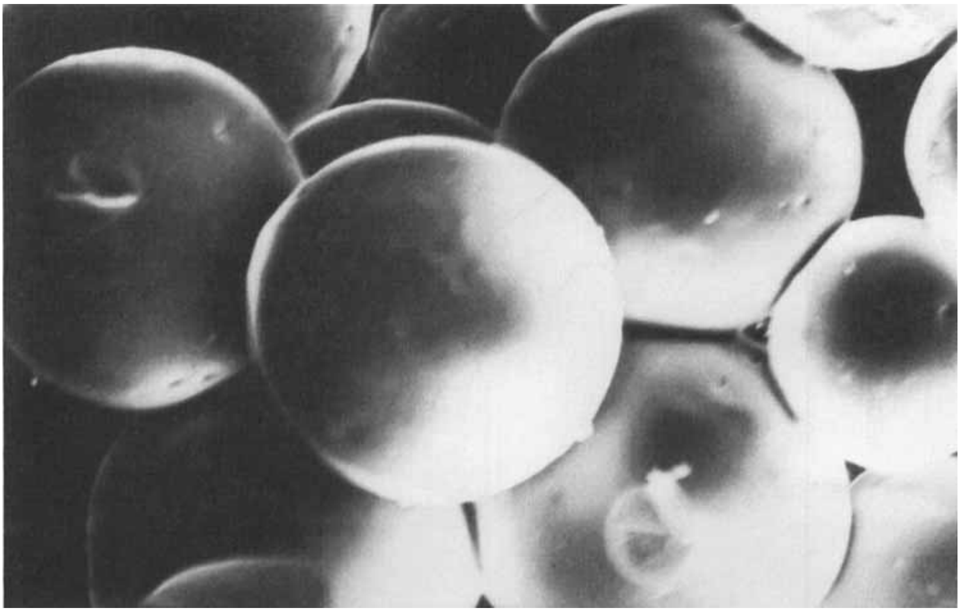


FIG. 7. SEM photograph of salicylaldehyde-acrylate-divinylbenzene copolymer.

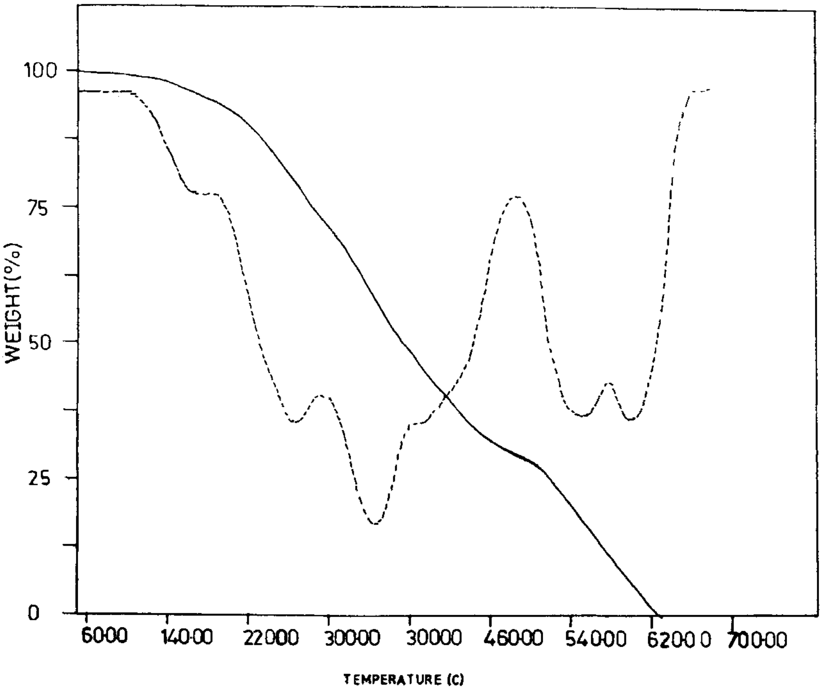


FIG. 8. Thermolysis curves of salicylaldehyde-acrylate-divinylbenzene copolymer.

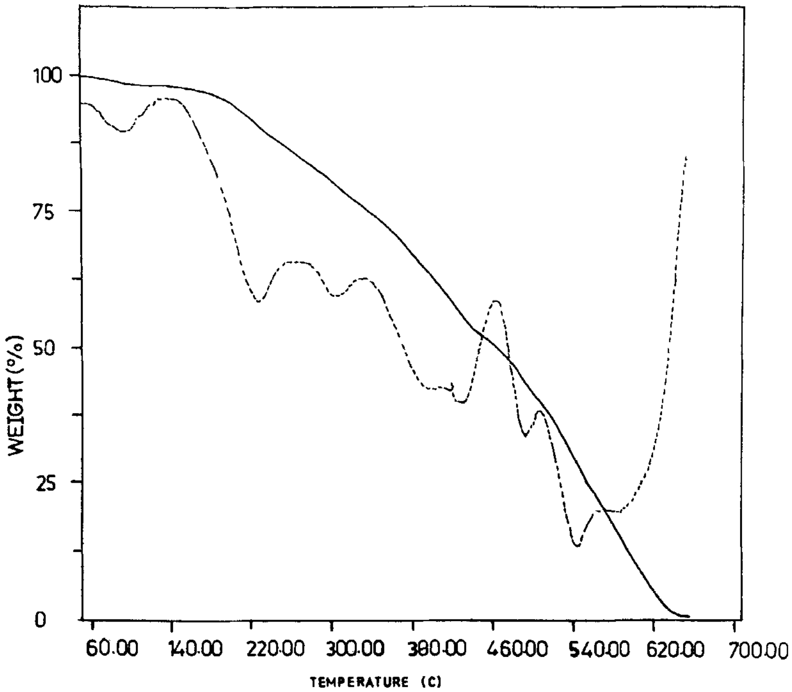


FIG. 9. Thermolysis curves of salicylaldehyde-acrylate-divinylbenzene oxime derivative.

weight loss found was 55%. The second stage decomposition was observed from 686 to 903 K; the weight loss involved in this stage was 44.6%.

The degradation of oxime also occurred in two stages. The first stage of decomposition commenced at 312 K, was completed at 372 K, and the weight loss in this stage was 5%. The second stage of degradation occurred in the 372 to 912 K range with a weight loss of 94.28%.

In order to determine the thermal stabilities of the copolymer and its functionalized resins, the energy of activation, entropy of activation, and enthalpy of activation involved in the degradations were calculated by the Coats and Redfern (CR) [22], Doyle (DY) [23], Horowitz and Metzger (HM) [24], and Freeman and Carroll (FC) [25] methods.

The kinetic parameters were calculated on the basis of the above methods by assuming the reaction order to be 1; the values are presented in Table 3. The ΔS values are negative in all the cases, indicating a more ordered structure of the activated complex than of the reactants. The reactions proceed slowly [26]. This is also confirmed by the low values of Z [27].

APPLICATIONS

Time Course of Metal Ion Complexation

The time course of resin-metal interaction is of considerable importance if the resin is to be used in a dynamic system such as a packed column or a flowing

TABLE 3. Thermal Decomposition Kinetic Parameters of SAA-DVB Copolymer and Its Functionalized Resins

Copolymer	Decomposition range, °K	Peak temperature T_s, °K	Method	E, $\mathrm{kJ \cdot mol^{-1}}$	S, $\mathrm{kJ^{-1} \cdot mol^{-1}}$	H, $\mathrm{kJ^{-1} \cdot mol^{-1}}$	Z, $\mathrm{s^{-1}}$	r
SAA-DVB	493–686	163	CR	19.23	−242.95	−148.93	0.26×10^1	.98221
			DY	28.80	−209.87	−128.65	1.39×10^2	.99729
			HM	28.57	−218.41	−133.88	4.98×10^1	.98643
			FC	19.29	−191.95	−117.66	1.20×10^3	.99991
	686–903	813	CR	39.26	−217.03	−176.45	7.79×10^1	.98977
			DY	53.14	−183.84	−149.46	4.22×10^3	.99297
			HM	55.95	−197.68	−160.71	7.99×10^2	.99999
			FC	33.98	−193.96	−157.69	1.25×10^3	.99998
Oxime derivative	312–372	365	CR	16.65	−248.65	−90.76	0.68×10^0	.99808
			DY	22.30	−223.23	−81.48	1.66×10^1	.99859
			HM	25.67	−182.68	−66.67	2.18×10^3	.99999
			FC	23.78	−161.22	− 58.84	2.88×10^4	.98775
	372–912	843	CR	19.99	−248.34	−209.35	$0.1o \times 10^1$	.98953
			DY	30.24	−213.61	−180.07	1.22×10^2	.98381
			HM	49.10	−210.23	−177.23	1.83×10^2	.99606
			FC	21.90	−199.25	−167.97	7.39×10^2	.99997

stream. If complexation is not sufficiently rapid for certain metal ions, then their concentration on a column is unlikely owing to the short contact time between the resin and the solution. In such cases, batch extraction with a large excess of resin should be conducted over an extended time period. The much slower exchange rates of many chelating resins have been reported [28, 29] to cause problems with their commercial use. The rate of complexation depends on the chemical nature of the metal ion and of the ligands as well as on the structure of the polymer matrix. Steric constraints in a dense macromolecular matrix lower the reactivity of ligand functions.

In order to optimize the time required for complexation toward Ni(II) and Co(II) ions, batch studies were carried out [30]. The time dependence on the complexation of the functionalized SAA-DVB copolymer resin toward Ni(II) and Co(II) ions is followed by a change in the concentrations of the metal salt solutions at regular intervals. The results are shown in Fig. 10.

The complexations of Ni(II) and Co(II) are completed in 1.5 and 1 hour, respectively, for oxime derivatives, as shown in Fig. 6.

Recyclability of Complexed SAA-DVB Functionalized Resin

The most important advantage of chelating resins is that they can be reused. Our resin can be brought back to its original form by desorbing the complexed Ni(II) and Co(II) by hydrochloric acid and neutralizing. Recycling of the neutralized resin by the addition of fresh Ni(II) and Co(II) solution results in the intake of almost the same amounts of Ni(II) and Co(II) ions as were initially present. The process was repeated four times, and the results are shown in Fig. 11. The retention of the initial capacity even after four operational cycles suggests that the resin can be used several times without any reduction in capacity. If the resin decomposes on acid treatment, it should again be subjected to functionalization.

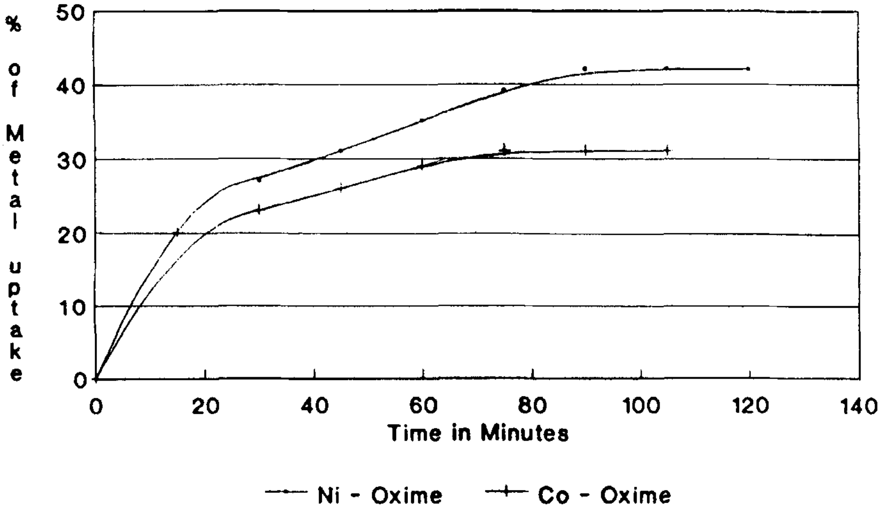


FIG. 10. Comparison of Ni(II) and Co(II) uptake by chemically modified cross-linked resins derived from salicylaldehyde-acrylate-divinylbenzene copolymer.

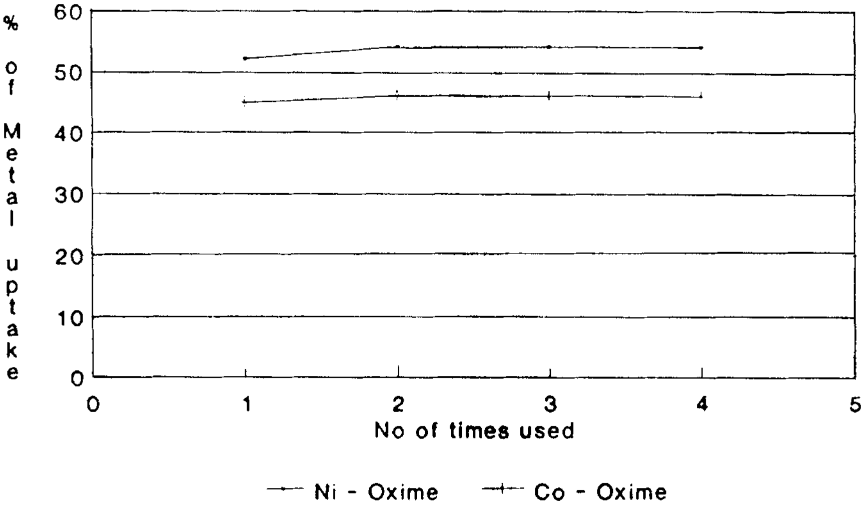


FIG. 11. Study of recyclability of the resins for uptake of Ni(II) and Co(II) metal ions.

SUMMARY

Transition metal ions [Ni(II), Co(II), and Cu(II)] were attached through coordinate bonds to a functionalized polymer backbone. Polymer synthesis was confirmed through ^1H and ^{13}C-CP/MAS NMR spectra. All the complexes are paramagnetic. Thermogravimetric analysis of the ΔS values are negative in all the cases, indicating a more ordered structure of the activated complex than of the reactants. The copper complex is square planar, and a possible structure has been assigned for the complex.

REFERENCES

[1] B. T. Block, *Inorg. Macromol. Rev.*, *1*, 115 (1970).
[2] J. C. Bailer Jr., in *Organometallic Polymers* (C. E. Carraher Jr., J. E. Sheats, and C. V. Pittman Jr., Eds.) Academic Press, New York, 1978, p. 313.
[3] R. B. Merrifield, *Science, 150*, 178 (1965).
[4] D. C. Neckers, *J. Chem. Educ., 52*, 695 (1975).
[5] E. V. Gouinlock, *J. Polym. Sci., Polym. Mater., 13*, 1975 (1961).
[6] M. Biswas and S. Moitra, *J. Polym. Mater., 7*, 89 (1990).
[7] G. Challa and W. Chen, *Eur. Polym. J., 26*, 1211 (1990).
[8] N. C. Morosoff, S. D. Clymer, and J. M. Skelly, *J. Appl. Polym. Sci., Polym. Symp., 46*, 315 (1990).
[9] E. L. Sonbatil and Z. Adel, *Transition Metal Chem., 16*, 45 (1991).
[10] E. M. Sul'man, L. M. Bronshtein, T. V. Ankudinova, E. Sh. Mirzoeva, S. V. Vinogradova, and P. M. Valetski, *Khim. Farm. Zh., 25*(2), 61 (1991).

[11] M. Uma, L. D. Prabhakar, C. B. Palanivelu, and V. Thanikachalam, *J. Macromol. Sci.—Pure Appl. Chem., A29*, 173 (1992).

[12] L. D. Prabhakar, M. Uma, and C. B. Palanivelu, *J. Polym. Mater., 9*, 185 (1992).

[13] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th ed., Wiley, New York, 1981.

[14] B. S. Rao, P. J. Madec, and E. Marechal, *J. Macromol. Sci.—Chem., A24*(7), 719 (1987).

[15] Y. R. Sharma and O. P. Vig, *Elementary Organic Spectroscopy*, Chand, New Delhi, 1980.

[16] I. Weiliao and B. E. Eichinger, *J. Polym. Sci., Polym. Chem. Ed., 28*(3), 559 (1990).

[17] M. L. Bender and J. Figueras, *J. Am. Chem. Soc., 75*, 6304 (1953).

[18] A. Torikai, A. Takeuchi, S. Nagaya, and K. Fueki, *Polym. Photochem., 7*, 279 (1986).

[19] F. K. Kneubuhl, *J. Chem. Phys., 33*, 1074 (1960).

[20] E. Kalotova, Z. Radova, K. Ulbert, J. Kalal, and F. Svec, *Eur. Polym. J., 13*, 299 (1977).

[21] W. E. Blumberg and J. Peisach, *J. Biol. Chem., 240*, 870 (1965).

[22] A. W. Coats and J. P. Redfern, *Nature, 68*, 201 (1964).

[23] C. D. Doyle, *J. Appl. Polym. Sci., 5*, 285 (1961).

[24] H. H. Horowitz and G. Metzger, *Anal. Chem., 35*, 1464 (1963).

[25] E. S. Freeman and B. Carroll, *J. Phys. Chem., 62*, 394 (1958).

[26] A. A. Frost and R. G. Pearson, *Kinetics and Mechanisms*, Wiley, New York, 1961.

[27] S. S. Swahney, S. D. Kapila, K. K. Pathak, and S. K. Chandel, *Thermochim. Acta, 59*, 389 (1982).

[28] R. Turse and V. Reiman, *J. Phys. Chem., 65*, 1821 (1961).

[29] M. Matsuzura and Y. Wadachi, *Bull. Chem. Soc. Jpn., 48*, 3456 (1975).

[30] H. Nishide, J. Deguchi, and E. Tsuchida, *J. Polym. Sci., Polym. Chem. Ed., 15*, 3023 (1977).

Received October 9, 1993
Revision received March 8, 1994