

Preparation of Poly(4-vinylpyrrolidone)-*g*-Poly(*N*-hydroxyacrylamide) and Study of Its Metal Binding Properties

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ABSTRACT: Crosslinked poly(*N*-vinylpyrrolidone), preirradiated in air with γ rays, was grafted with ethyl acrylate in dioxane and water. A detailed study of grafting was made under various reaction conditions. The graft copolymer was treated with potassium hydroxamate in ethanol. The resulting polymer contained pendant hydroxamic acid groups ($-\text{CO}-\text{NHOH}$) and was studied for the formation of complexes with Fe(III), Cu(II), and Ni(II). The effect of pH on the metal ion uptake by the polymer was also studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 475–483, 2000

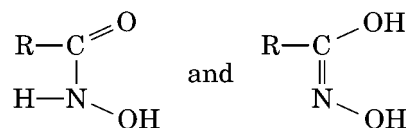
Key words: γ ray; initiated grafting; crosslinked poly(*N*-vinylpyrrolidone); metal complexes; hydroxamic acid pendants

INTRODUCTION

The strong and inert polymer, crosslinked poly(*N*-vinylpyrrolidone) (PVPy), is available in beaded form; it is prepared by the suspension polymerization of VPy with a crosslinking agent.^{1–5} Crosslinked PVPy swells well in aqueous and alcoholic media, facilitating the diffusion of substances soluble in these media in and out of the beads. This property makes PVPy an excellent support for use in organic and analytical chemistry. Unless exposed to exceptionally high doses of γ radiation at a high rate, PVPy does not undergo gross changes in structure. Indeed, γ radiation was used for the polymerization of VPy.⁶ Acrylonitrile was grafted on PVPy in benzene or carbon tetrachloride with γ rays at dose rates ranging from 5 to 40 rad/s.⁷ In 1996 we studied the graft-

ing of poly(4-vinylpyridine) onto PVPy and modified the graft copolymer for use in organic synthesis.⁸ Detailed studies of the grafting of poly(maleic anhydride-*co*-styrene) were also made and the resulting graft copolymer, which possesses succinic anhydride residues, was examined for the immobilization of proteins.⁹

The present article describes the γ -radiation induced grafting of poly(ethyl acrylate) on PVPy. A detailed study of changing the various reaction parameters and their effects on grafting was made and optimum conditions for grafting were determined. When treated with potassium hydroxamate, the grafted copolymer (resin I) forms a resin possessing pendant hydroxamic acid (resin II). In solution hydroxamic acid exists in the following two tautomeric forms:



The keto form predominates in an acid medium and the enol form in an alkaline medium.¹⁰ They

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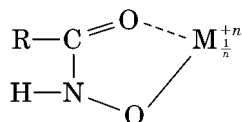
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Table I Effect of Reaction Media on Percentage of Grafting of Ethyl Acrylate on PVPy

Medium		Grafting (%)
Water (mL)	Dioxane (mL)	
0.00	3.00	0.00
0.75	2.25	36.25
1.50	1.50	150.99
2.25	0.75	76.85

PVPy, 100 mg; total dose, 46.0 kGy; ethyl acrylate, 1 mL.

are known to form complexes with a large number of metal ions. Most hydroxamic acid metal complexes have the following structure:



We examined the resin for the formation of complexes with Fe(III), Cu(II), and Ni(II) in buffers of different pHs. The results and their significance in several areas of chemistry are discussed in this article.

EXPERIMENTAL

PVPy in beaded form was received from Fluka Chemie AG, Buchs. Ethyl acrylate (Fluka) was freshly distilled before use. Samples of PVPy were irradiated in air from a 2100 Ci cobalt-60 γ radiation source installed in a Gamma Chamber 900 supplied by Barc (Bombay, India).

General Procedure

PVPy (100 mg) was irradiated in air in the Gamma Chamber 900 at a constant dose rate (0.50 kGy/h) for 24–120 h. A predetermined amount of ethyl acrylate was added to the irradiated PVPy in 1 : 1 water–dioxane (see Table I) and the reaction mixture was gently refluxed at 110°C. The homopolymer poly(ethyl acrylate) formed during the reaction was completely removed by thorough washing with warm acetone in a weighed sintered crucible. The crucible was dried at 50°C to a constant weight. The percent-

age of grafting was calculated from the increase in the initial weight of the PVPy and was expressed as follows:

$$\text{percent grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the weight of the original PVPy and W_2 is the weight of the grafted PVPy. The percentage of grafting was determined as a function of the total dose, the molar concentration of ethyl acrylate, the time of refluxing, and the composition of the reaction medium. Hydroperoxide groups generated as a result of irradiation were estimated as a function of the total dose. The swelling behavior of PVPy, irradiated PVPy, and PVPy irradiated and heated in water and a water–dioxane mixture (1 : 1) were studied for a qualitative check of any unintended crosslinking during the reactions performed on the PVPy.

Effect of Radiation Dose on Formation of Hydroperoxide Groups

The 100-mg samples of PVPy were irradiated in the Gamma Chamber 900 with total doses ranging from 19.0 to 72.0 kGy. Irradiated samples were taken in deaerated water, and KI (0.01M, 5.0 mL) and H₂SO₄ (0.1N, 1.0 mL) were added. The contents were thoroughly stirred and left in the dark for 2 h, and the liberated iodine was titrated with sodium thiosulfate (0.01N). The amount of hydroperoxide groups per gram of PVPy was calculated. The results are presented in Figure 1.

We observed that keeping the irradiated samples in air for 24 h did not alter their hydroperoxide contents.

Effect of Composition of Reaction Medium

Samples of PVPy (100 mg) irradiated for 92 h were refluxed with ethyl acrylate (1 mL) for 3 h in 3 mL of mixtures of water and dioxane of different compositions. The results are presented in Table I.

Effect of Total Dose on Grafting

The 100-mg samples of PVPy were irradiated to a total dose of 12–60 kGy. Irradiated samples were gently refluxed for 3 h at 110°C with 1 mL ethyl

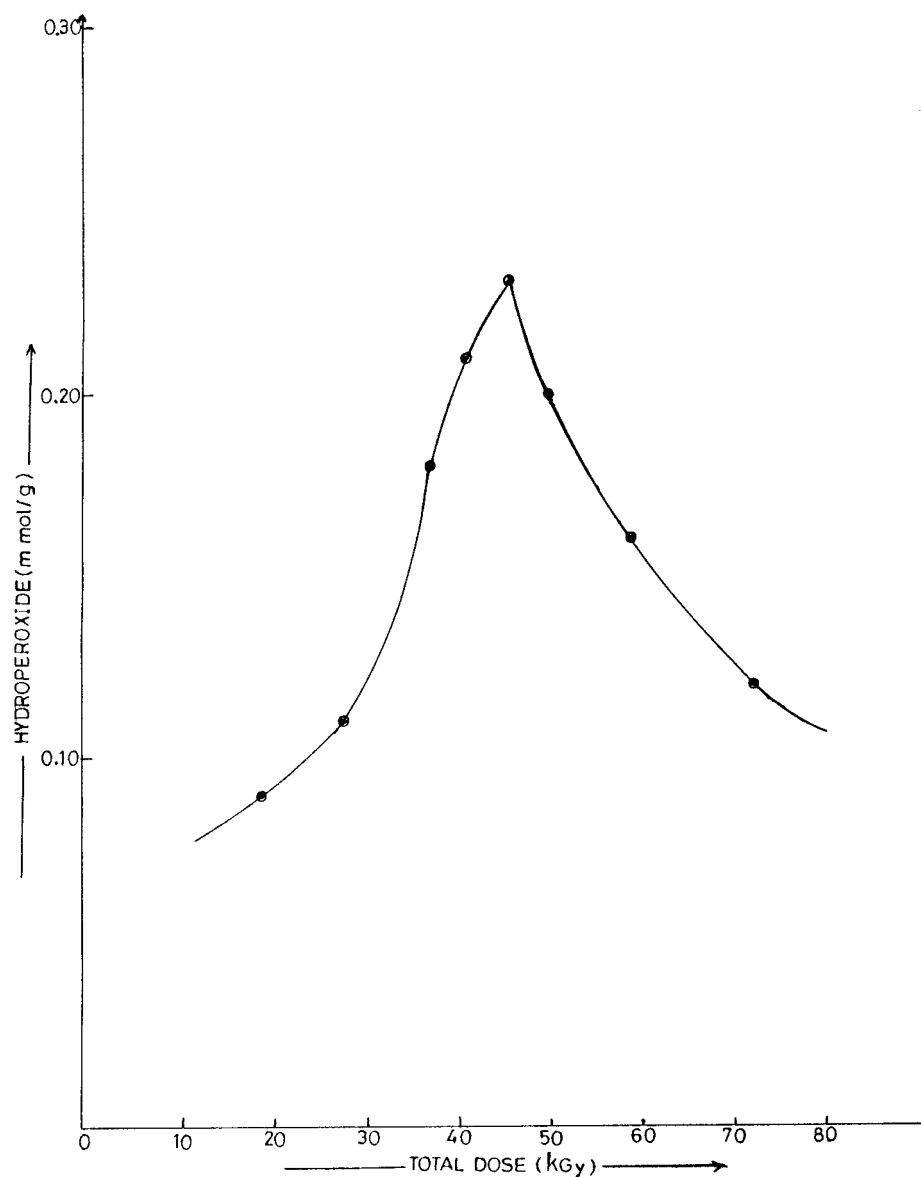


Figure 1 The effect of total dose on the hydroperoxidation of PVPy.

acrylate in a mixture of water (1.5 mL) and dioxane (1.5 mL). Figure 2 presents the results.

Effect of Time of Refluxing

Samples of PVPy (100 mg) irradiated for 92 h were refluxed with ethyl acrylate (1 mL) in 3 mL of aqueous dioxane (1 : 1) for different periods of time. Figure 3 presents the results.

Effect of Molar Concentration of Ethyl Acrylate

The 100-mg samples of PVPy were irradiated for 92 h and were refluxed for 3 h with different

amounts of ethyl acrylate in a mixture of water (1.5 mL) and dioxane (1.5 mL). After completely removing the homopolymer, the percentage of grafting was calculated in each case. The results are presented in Figure 4.

Effect of Various Modifications on Swelling Behavior of PVPy

Samples (100 mg) of PVPy, irradiated PVPy (140 h), and irradiated and heated (3 h in dioxane-water, 1 : 1) PVPy were placed in water and left for 14 h at room temperature. The bed volumes of the swollen polymer samples were determined for

1 g of polymer. The bed volumes of 1 g of polymer samples swollen in dioxane and a dioxane–water (1 : 1) mixture were also determined in a similar manner. The results are presented in Table II.

Preparation of Resin II

A solution of potassium hydroxamate was prepared by mixing together hot methanolic solutions of hydroxylamine hydrochloride (11.70 g in 60 mL) and potassium hydroxide (14.0 g in 35 mL) and cooling and removing the precipitated KCl.¹¹ Resin I (4 g) with 74.40% grafting was stirred gently overnight with the solution of potassium hydroxamate. The resin was then filtered and washed thoroughly with water and aqueous methanol (50%) to remove the salts and dried at 50°C.

Characterization of PVPy Derived Graft Copolymers

The IR spectra (KBr) showed the following absorptions: PVPy: 1650 cm^{-1} , pyrrolidone C=O

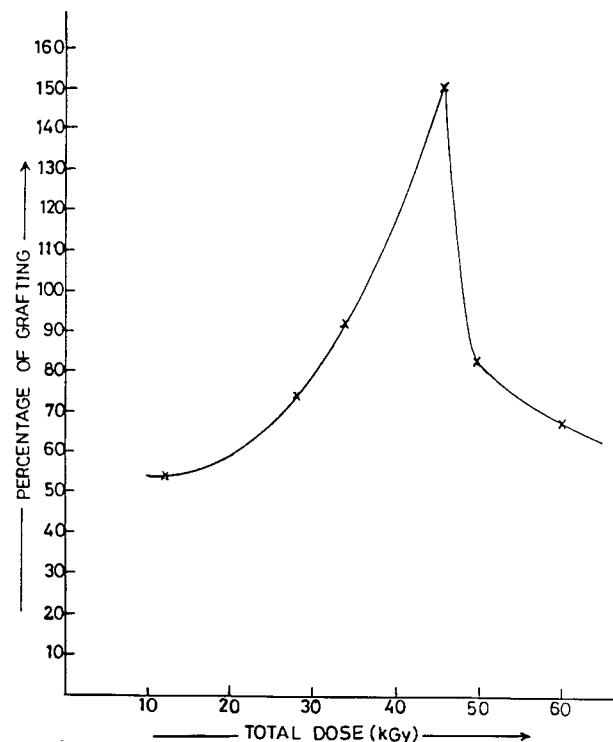


Figure 2 The effect of the total dose on grafting of ethyl acrylate on PVPy with 100 mg PVPy, 9.24 mmol ethyl acrylate, 1.5 mL H_2O , and 1.5 mL dioxane at 110°C for 3 h.

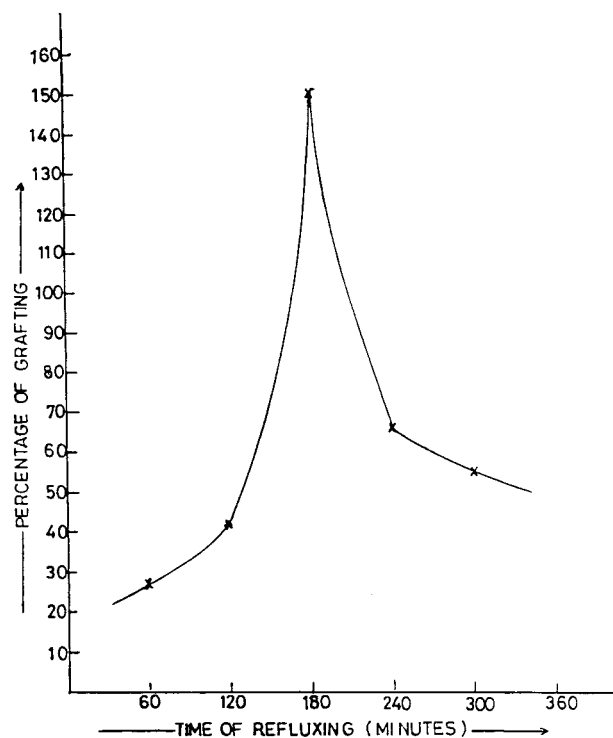


Figure 3 The effect of the time of reaction on the grafting of ethyl acrylate on PVPy with 100 mg PVPy, 9.24 mmol ethylacrylate, and 1.5 mL H_2O at 110°C and a total dose of 46 kGy.

(stretching); PVPy-g-poly(ethyl acrylate): 1740 cm^{-1} , ester C=O (stretching) and 1240 cm^{-1} , ester C—O (stretching); and PVPy-g-poly(*N*-hydroxyacrylamide): 3300 cm^{-1} , N—H (stretching). In addition, the immediate formation of Fe(III) chelate with the last polymer alone showed the presence of hydroxamic acid groups.

Metal Ion Binding by Resin II

Iron(III)

A solution of $\text{Fe}_2(\text{SO}_4)_3$ (0.01M) was made in sodium acetate buffer (0.2M, pH 3.6) and resin II (0.025g) was added to 5 mL of this solution.¹² The mixture was left for 20 h at room temperature with occasional shaking and the resin was filtered out. The filtrate (2.5 mL) was mixed with a solution of KCNS (2M, 0.3 mL), nitric acid (4N, 0.2 mL), and distilled water (60 mL). The absorbance of this solution was read at 480 nm, and the amount of Fe(III) present in the solution was calculated from a standard linear curve. The dif-

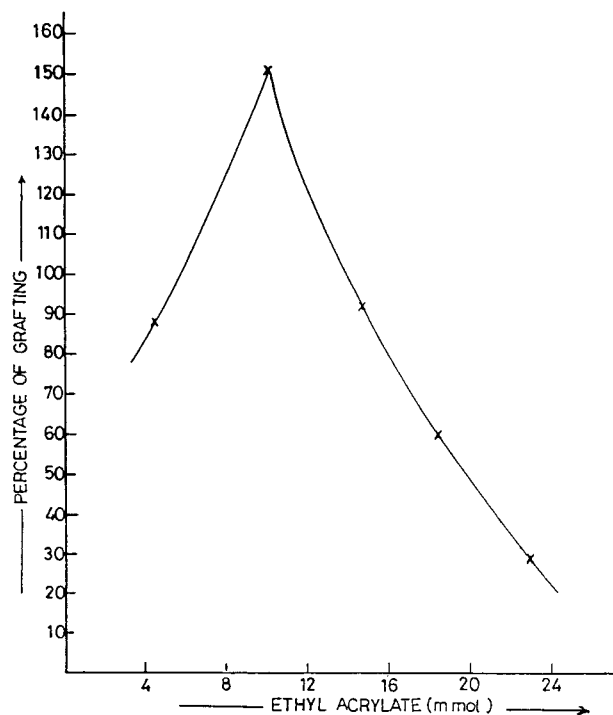


Figure 4 The effect of the molar concentration of ethyl acrylate on grafting on PVPy with 100 mg PVPy, 46 kGy a total dose of, 1.5 mL H₂O, and 1.5 mL dioxane at 110°C for 3 h.

ference between the amount of Fe(III) in the original solution and the amount left after treatment with the resin gave the amount of Fe(III) that complexed with the resin.

The experiment was repeated at pH 4.0, 4.6, 5.2, 5.6, and 6.5 in acetate buffer (0.2M). The results are presented in Table III.

Copper(II)

A solution of CuSO₄ (0.01M) was prepared in sodium acetate buffer (0.2M, pH 3.6). Resin II (0.025 g) was added to 5 mL of this solution that

was left for 20 h with occasional shaking. The resin was filtered off and a solution of NH₄OH (12.5%, 2.5 mL) was mixed with 2.5 mL of this filtrate. The amount of Cu(II) in this solution was determined from its absorbance at 600 nm. The experiment was repeated in acetate buffers (0.2M) of pH 4.0, 4.6, 5.2, 5.6, and 6.5. The amount of Cu(II) retained by the resin was calculated, and the results are presented in Table III.

Nickel(II)

Resin II (0.025 g) was added to 5 mL of a solution of NiSO₄ (0.01M) in sodium acetate buffer (0.2M, pH 3.6), and the mixture was left for 20 h at room temperature with occasional shaking. The resin was filtered out, and citric acid (5 g) was added to the suitably diluted filtrate in a separating funnel. The pH was adjusted to 7.5 with NH₄OH, and dimethylglyoxime solution (0.1% in 25% NH₄OH, 20 mL) was added. The mixture was vigorously shaken with chloroform (15 mL) and left for 5 min to settle. The amount of Ni(II) was determined from the absorbance of the chloroform layer at 366 nm corrected against a blank. The experiment was repeated in acetate buffers (0.2M) at pH 4.0, 4.6, 5.2, 5.6, and 6.5. The results of Ni(II) retained by the resin are presented in Table III.

Control experiments were run for the binding of Fe(III), Cu(II), and Ni(II) by PVPy and PVPy-g-poly(ethyl acrylate) (Resin I) in acetate buffers of their salts (0.01M) at pH 3.6 and 6.5. The results are presented in Table III.

RESULTS AND DISCUSSION

Assuming that the grafting of ethyl acrylate on PVPy (I) that was preirradiated in air takes place through the generally accepted mechanism,¹³ the

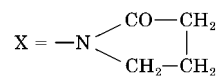
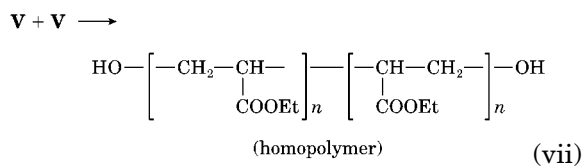
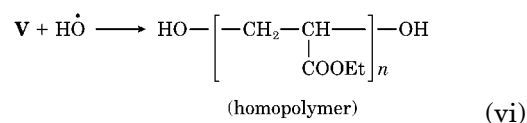
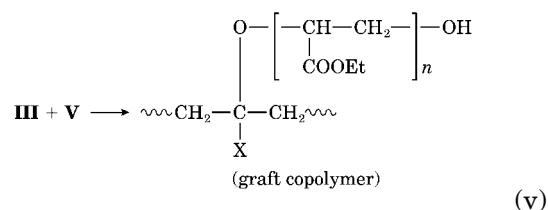
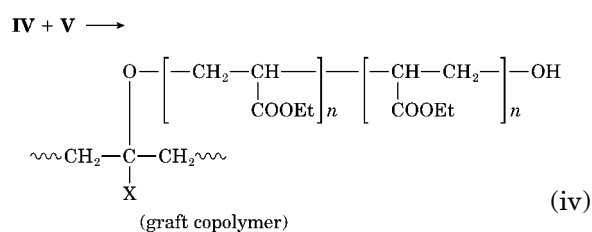
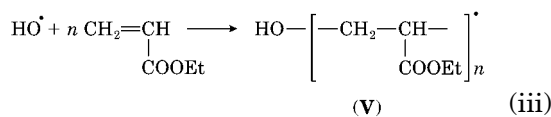
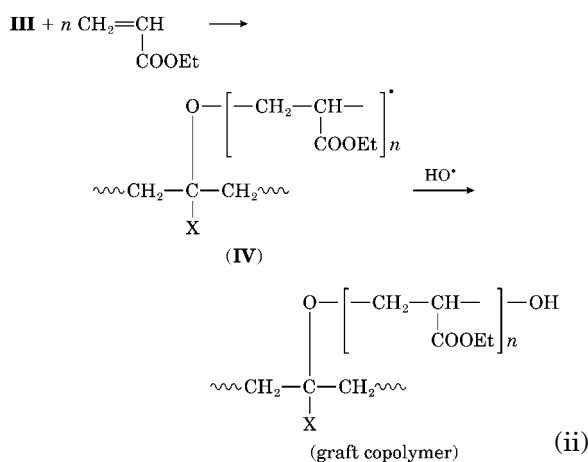
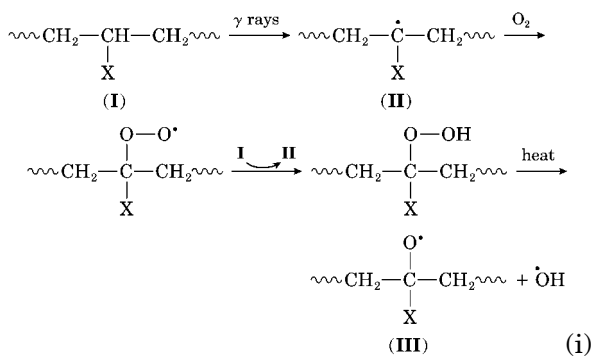
Table II Bed Volumes of Swollen Polymer Samples in Water, Dioxane, and Water-Dioxane

Polymer	Bed Volume of Swollen Polymer (1 g) in		
	Water (mL)	Dioxane (mL)	1 : 1 Dioxane-Water (mL)
PVPy	8.80	7.21	8.00
Irradiated PVPy	8.82	7.22	8.04
Irradiated and heated PVPy	8.84	7.21	8.02

Table III Retention of Metal Ions by Resins

Metal Ion	Polymer	Metal Ion Retained (mmol/g Polymer) at pH					
		3.6	4.0	4.6	5.2	5.6	6.5
Fe(III)	PVPy	0.00	—	—	—	—	0.00
	Resin I	0.00	—	—	—	—	0.00
	Resin II	1.87	1.80	1.74	1.66	1.49	1.37
Cu(II)	PVPy	0.00	—	—	—	—	0.00
	Resin I	0.00	—	—	—	—	0.00
	Resin II	1.13	1.24	1.38	1.50	1.56	1.66
Ni(II)	PVPy	0.00	—	—	—	—	0.00
	Resin I	0.00	—	—	—	—	0.00
	Resin II	0.22	0.31	0.37	0.58	0.60	0.77

following reactions are possible in the course of grafting:



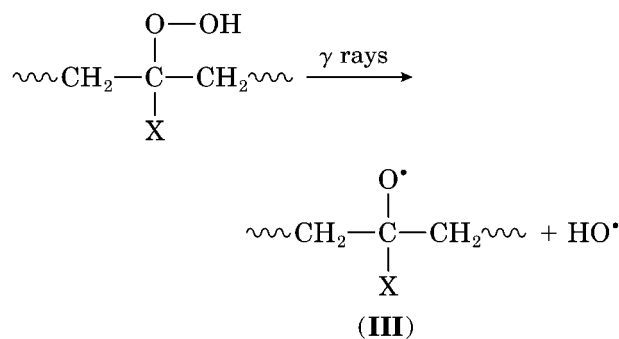
It is evident that the formation of graft copolymer from **III** (steps ii, iv, and v) is in competition with

the formation of homopolymer (steps vi and vii). Whenever a poly(ethyl acrylate) radical is unable to graft onto PVPy it will end up in the formation of the homopolymer molecules. The conditions that favor the latter are the low mobility of the large poly(ethyl acrylate) radicals and steric and topological restrictions on their intimate contact with the radical sites on PVPy.

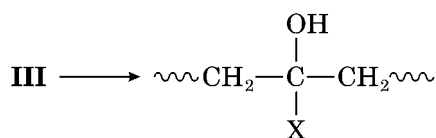
From the elongation behavior of polyethylene irradiated in air, Chapiro¹⁴ suggested as early as 1955 that, at low dose rates and high total doses, peroxidic crosslinks are formed in the polymer that break down on heating. Chapiro¹⁵ also suggested that, at room temperature, chain peroxidation leading to hydroperoxidation occurs in polymers like polypropene that contain labile hydrogen atoms.

The percentage of grafting of ethyl acrylate on PVPy follows the familiar pattern noted with earlier studies.^{8,9} With the increase in total dose, a maximum is observed at a dose of 46.0 kGy (Fig. 2).

The hydroperoxide contents of the polymer samples irradiated for different periods of time show a maximum of 0.23 mmol/g of polymer at a total dose of 46 kGy (Fig. 1). This approximately follows the trend of grafting with respect to total dose (Fig. 2) and hints at the correspondence between the hydroperoxide groups on the irradiated sample and the grafting yields of the monomer. It is possible that prolonged irradiation causes the scission of the peroxy bond of the hydroperoxide groups on the polymer.



The macrooxy radical **III** then forms inactive hydroxide,



or is annihilated by dimerization.

The possibility of dimerization of radicals like **III** is low in the case of PVPy because of the rigid crosslinked structure. A look at Table II shows that the swelling behavior of irradiated PVPy and irradiated and heated PVPy is not different from the original PVPy. This indicates the absence of any prominent structural modifications including crosslinking under these conditions. The low dose rate of irradiation also precludes gross changes.

In the γ -ray irradiation of a fluoropolymer, Tefzel, it was observed from FTIR studies that there was a continuous increase in the hydroperoxides and alcohols up to a total dose of 95.8 Mrad. Beyond this the decomposition of hydroperoxides began to dominate over its formation.¹⁶

When heated with ethyl acrylate, PVPy exposed to a high radiation dose should show reduced grafting because the hydroperoxy groups are diminished and replaced by inactive hydroxide groups and increased XH concentration promotes homopolymerization. One study showed that polymer-bound radicals initiated the polymerization of methyl methacrylate much more efficiently than free radicals in solution, and this is due to the fact that immobilization of free radicals hinders termination.¹⁷ Step (vi), and to some extent (vii), in our scheme above becomes a strongly competing reaction to (ii), (iv), and (v). This causes a decline in grafting and a consequent increase in the formation of the homopolymer.

The effect of increasing the molar concentration of ethyl acrylate on the percentage of grafting is presented in Figure 4. As the concentration of ethyl acrylate increases, grafting increases through steps (ii), (iii), (iv), and (v) because higher amounts of ethyl acrylate and poly(ethyl acrylate) radicals are available. Beyond the optimum concentration, the low mobility of homopolymer radicals in the highly viscous medium and their large size hinders their approach to the radical sites of the PVPy gel. In this situation the radicals preferably terminate through steps (vi) and (vii).

The effect of increasing the time of reaction on the percentage of grafting of ethyl acrylate is presented in Figure 3. Grafting occurs at a more or less uniform rate up to 3 h. After that there is a decrease in the percentage of grafting that could possibly be the result of depolymerization of the grafted chains brought about through "backbiting." Backbiting may be intrachain, interchain, or between a grafted chain and a homopolymer rad-

ical. All these processes should increase the formation of homopolymer at the cost of grafting.

Grafting of ethyl acrylate was studied in mixtures of water and dioxane of different compositions (Table I). PVPy swells in water and to a lesser extent in dioxane; but we found that pure dioxane, which dissolves the monomer as well, is not a suitable medium for grafting onto PVPy. A 1 : 1 mixture of dioxane and water proved to be the best medium. The same effect of medium was noticeable in the grafting of 4-vinylpyridine⁸ and a mixture of styrene and maleic anhydride⁹ and that was in spite of the fact that 4-vinylpyridine is soluble in water and styrene is insoluble.

In our experiments the samples after irradiation were immediately treated with ethyl acrylate for grafting. However, we observed that the concentration of hydroperoxy groups remained unchanged when leaving the irradiated polymer for 24 h. Gawish et al. reported that the graft yields on preirradiated polypropylene remained unaffected even after 5 days of storage of the irradiated samples.¹⁸

Esters are known to react with potassium hydroxamate under mild conditions and form acylhydroxamic acids, (*N*-hydroxyacylamides)¹¹:



This property was exploited in the preparation of polymer-bound acylhydroxamic acid (resin II):



(resin I)



(resin II)

Acylhydroxamic acids were introduced in polypropylene by grafting acrylonitrile first and then converting the —CN group into a —CO—NHOH group in several steps.¹⁹ The procedure described in this article is simple, fast, and better suited when the backbone polymer is hydrophilic.

Hydroxamic acids are excellent ligands for various metal ions. This property is utilized in the detection and determination of either the hydroxamates or metals. Beaded PVPy and PVPy-g-

poly(ethyl acrylate) swell in water, alcohol, or aqueous alcoholic media. Water compatibility is further enhanced when the pendant ester groups of the graft are converted into polar acylhydroxamic acid, making resin II highly suitable for working with metal salts. Swollen beads allow easy diffusion of metal ions in and out of the beads. A number of metal ions form strong complexes with the —CO—NHOH groups and are retained by the insoluble polymer.

Hydroxamates form complexes with many metal ions. Depending upon the valence state of the ion and the concentration of hydroxamate, more than one hydroxamate group will form a complex in solution. The situation with polymer-bound hydroxamate is different however. The accessibility of more than one hydroxamate group to a polyvalent cation is dependent upon several factors including free rotation of pendant —CO—NHOH groups, the rigidity imposed by the crosslinked backbone polymer, and the freedom or restrictions enjoyed by poly(*N*-hydroxyacrylamide) chains grafted onto PVPy relative to each other. Whatever the case, the metal ion is most likely to be retained by the resin.

The results of studies on the three representative metal ions Fe(III), Cu(II), and Ni(II) provide some interesting conclusions. In control experiments with PVPy and PVPy-g-poly(ethyl acrylate) (resin I) at pH 3.6 and 6.5, we found that none of these resins bind the metal ions at all. The retention of each ion by resin II, which possesses acylhydroxamic acid pendants, is different at a given pH, which may be a consequence of the differences in their stability constants. The retention of metal ions at different pHs is quantitatively different, which may be the result of the differences in the nature and/or stability of the complexes. It is also noticeable that the retention of Cu(II) and Ni(II) by resin II increases linearly and runs almost parallel to each other as the pH of the medium is raised (Fig. 5). On the contrary, the retention of Fe(III) decreases as the pH is raised. By choosing the right conditions, resin II may be employed for chromatographic separation of metal ions. The studies may be extended to more metal ions, and conditions for concentrating rare or expensive metals may be explored. The resin may also be an addition to the repertoire of agents useful in cleaning industrial effluents and drinking water. PVPy is one of the most nontoxic polymers known. The use of its derivatives in medicine for the detoxification of the stomach or

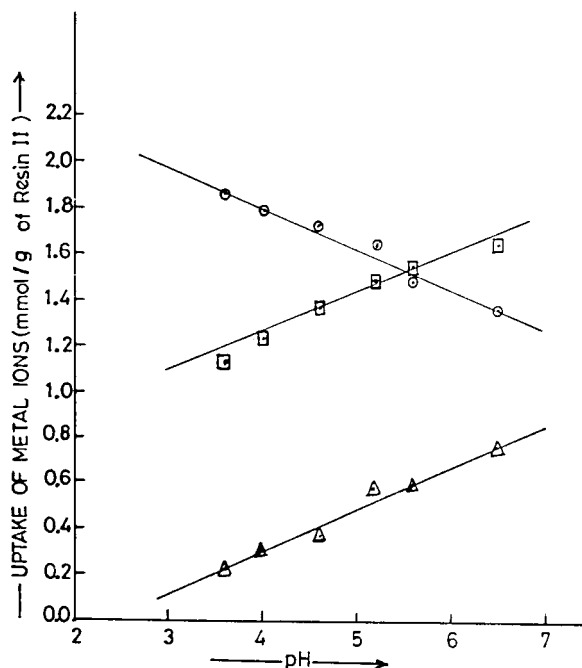


Figure 5 The uptake of metal ions by resin II: (○) Fe(III), (□) Cu(II), and (△) Ni(II).

gut in accidental metal poisoning seems to be a possible application open for further exploration.

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REFERENCES

- Merijan, A. U.S. Pat. 3,350,366, 1967.
- Field, N. D.; Williams, E. P. Ger. Pat. 1,929,501, 1970.
- (a) Dorst, P. W. PB Report; U.S. Department of Commerce, Office of Technical Services: Springfield, VA, 1945; p 4116; (b) U.S. Department of Commerce. Bibliographic Technical Report 1; U.S. Department of Commerce: Springfield, VA, 1945; p 327.
- (a) Rose, C. E.; White, R. D. U. PB Report; U.S. Department of Commerce, Office of Technical Services: Springfield, VA, 1945; p 1308; (b) U.S. Department of Commerce. Bibliographic Technical Report 1; U.S. Department of Commerce: Springfield, VA, 1945; p 223.
- Slifin, S. C. PB Report; U.S. Department of Commerce, Office of Technical Services: Springfield, VA, 1947; p 78256; (b) U.S. Department of Commerce. Bibliographic Technical Report 7; U.S. Department of Commerce: Springfield, VA, 1947; p 616.
- Sandler, S. R.; Karo, W. In *Polymer Synthesis*; Academic Press: New York, 1977; Vol. II, p 236.
- Henglein, A.; Schnabel, W. *Macromol Chem* 1957, 25, 119.
- Pande, C. S.; Gupta, N. *J Appl Polym Sci* 1996, 62, 1793.
- Pande, C. S.; Gupta, N. *J Int Acad Phys Sci* 1997, 1, 19.
- Hervey, A. E.; Manning, D. L. *J Am Chem Soc* 1950, 72, 4498.
- Blatt, A. H., Ed. *Organic Synthesis*; Wiley: New York, 1967; Vol. 2, p 67.
- Vogel, A. I. In *Textbook of Quantitative Chemical Analysis*; ELBS edition, 5th ed.; Addison Wesley Longman Ltd.: London, 1996; p 181, 690.
- Hori, Y.; Fukrumaga, Z.; Shimada, S.; Kashiwabara, H. *Polymer* 1979, 20, 181.
- Chapiro, A. *J Chem Phys* 1955, 52, 246.
- Chapiro, A. *J Polym Sci* 1960, 48, 109.
- Prasad, A. V.; Singh, R. P. *J Macromol Sci* 1996, A33, 91.
- Ajayghosh, A.; Francis, R.; Dias, S. *Eur Polym J* 1990, 29, 63.
- Gawish, S. M.; Kantouch, A.; El-Naggar, A. M.; Mosleh, S. *J Appl Polym Sci* 1992, 44, 1671.
- Kabay, N.; Katakai, A.; Sugo, T.; Egawa, H. *J Appl Polym Sci* 1993, 49, 599.