

# The Use of Polymers as Sequestering Agents for Toxic Metal Ions

A. N. EBOATU, S. T. DIETE-SPIFF, L. O. EZENWEKE, F. OMALU

Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, P.M.B., 5025 Awka, Anambra State, Nigeria

Received 13 March 2001; accepted 21 November 2001

**ABSTRACT:** Polymer–metal complexes were formed by nonsolvent precipitation technique for the metals Co, Pb, Ni, Cr, and Fe, and polystyrene (Pst), Poly(vinyl chloride) (PVC), and Nylon 66. By means of Fourier transform Infrared studies, it was established that chemical bonds actually do exist between the metal ions and the polymers (i.e., that the metal ions are not simply adsorbed on the surface of the polymers). It was observed also that the degrees of metal–polymer interaction vary from polymer, from metal ion to metal ion, and depend on the metal ion concentration. These observations are explained in terms of the atomic radii and charges on the transition metal ions. The number and type of interaction sites/ligands on the substrates are also considered relevant. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2781–2786, 2002

## INTRODUCTION

Polymers have the tendency of coordinating with metal ions; for example, in a previous work it was shown that poly(methyl methacrylate) (PMMA) in solution or in suspension complexes with  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cr}^{3+}$ . During the last few decades, there was a spate of interest in the phenomenon of polymer–metal ion interaction.<sup>1–3</sup> The applications of these polymer–metal complexes are many and include detoxification,<sup>1,2</sup> chemotherapy,<sup>4</sup> ion-exchange resins, sheet formation aids, catalysis, soil release, and antistatics in textiles,<sup>5,6</sup> to mention just a few. In the present article, we report on the sequestration of some toxic metal ions (viz.,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$ ) from their solutions, by polyvinyl chloride (PVC), polystyrene (PSt), and Nylon 66.

## EXPERIMENTAL

### Materials

Nitrates of Co, Pb, Ni, Cr, and Fe were obtained from BDH, Poole, U.K., while PSt, PVC, and Nylon 66 pellets were procured from Aldrich.

### Methods

#### *Making of Metal Ion Solutions*

For each metal ion, 200 ppm stock solution was prepared in deionized water.

#### *Making of Polymer Stock Solutions*

Exactly 20 g of PVC was taken in 5000 cm<sup>3</sup> chloroform in a volumetric flask. The flask, with contents, was shaken vigorously at room temperature until a clear solution was attained. In a similar manner, stock solutions of equal concentrations of Pst and Nylon 66 were prepared by using toluene and formic acid as solvents.

#### *Making of Polymer–Metal Complexes*

Exactly 10 cm<sup>3</sup> cobaltous nitrate stock solution was taken in each of the five conical flasks. To the first, no PSt solution was added; to the second, 5 cm<sup>3</sup> PSt was added with stirring; to the third, 15 cm<sup>3</sup>; to the fourth, 30 cm<sup>3</sup>, and 40 cm<sup>3</sup> was added to the fifth flask. Because deionized water used in making the nitrate solutions is also a nonsolvent for the polymers, almost instantaneous precipitation was observed on addition of the polymer solution to the metal solution. The resulting mixture was stirred vigorously for 30 min. The pre-

Correspondence to: A. N. Eboatu.

*Journal of Applied Polymer Science*, Vol. 85, 2781–2786 (2002)  
© 2002 Wiley Periodicals, Inc.

**Table I** Changes in Metal Ion Concentration on Polymer–Metal Complex Formation

Vol of Polymer Soln. Added to 10 cm <sup>3</sup>	Metal Ion Concentration (ppm)									
	Fe		Cr		Ni		Pb		Co	
	Theo.	Obs	Theo.	Obs	Theo.	Obs	Theo.	Obs	Theo.	Obs
PSt (cm <sup>3</sup> )										
0	160.0	160.0	160.0	160.0	160.0	160.0	160.0	160.0	160.0	160.0
5	106.6	48.6	10.6	44.3	106.6	72	106.6	58.6	106.6	68.1
15	64.0	15.2	64.0	11.5	64.0	27.7	64.0	40.5	64.0	38.1
30	40.0	1.8	40.0	2.1	40.0	3.6	40.0	6.5	40.0	11.2
40	32.0	1.1	32.0	0.0	32.0	5.1	32.0	2.8	32.0	5.6
PVC (cm <sup>3</sup> )										
0	160	160	160	160	160	160	160	160	160	160
5	106.6	81.2	106.6	72	106.6	88.6	106.6	70.3	106.6	70.5
15	64.0	12.6	64.0	20.2	64.0	31.6	64.0	23.7	64.0	48
30	40.0	5.6	40.0	3.7	40.0	10.1	40.0	8.8	40.0	16.9
40	32.0	5.0	32.0	1.8	32.0	8.8	32.0	4.4	32.0	3.8
Nylon 66 (cm <sup>3</sup> )										
0	160	160	160	160	160	160	160	160	160	160
5	106.6	10.6	106.6	8.1	106.6	11.2	106.6	12.2	106.6	22.2
15	64.0	3.1	64.0	1.2	64.0	5.2	64.0	6.6	64.0	9.8
30	40.0	1.0	40.0	2.0	40.0	1.7	40.0	4.0	40.0	0.9
40	32.0	0.5	32.0	0.0	32.0	1.0	32.0	0.9	32.0	1.0

Theo, theoretical; Obs, observed.

cipitate was filtered, rinsed with deionized water, dried in the oven at 105°C, and later stored in the desiccator until required. The control, (i.e., polymer solution) was also treated in a similar manner. The same procedure was followed in making the polymer–metal complexes of nickel, iron, chromium, and lead.

#### Atomic Absorption Spectroscopic Studies

The filtrates obtained after the formation of polymer–metal complexes, as outlined above, were analyzed to see if there is any change in the metal ion concentrations. An ATI/Unicam Solar 969 AAS Double Beam machine was employed, with appropriate lamps used.

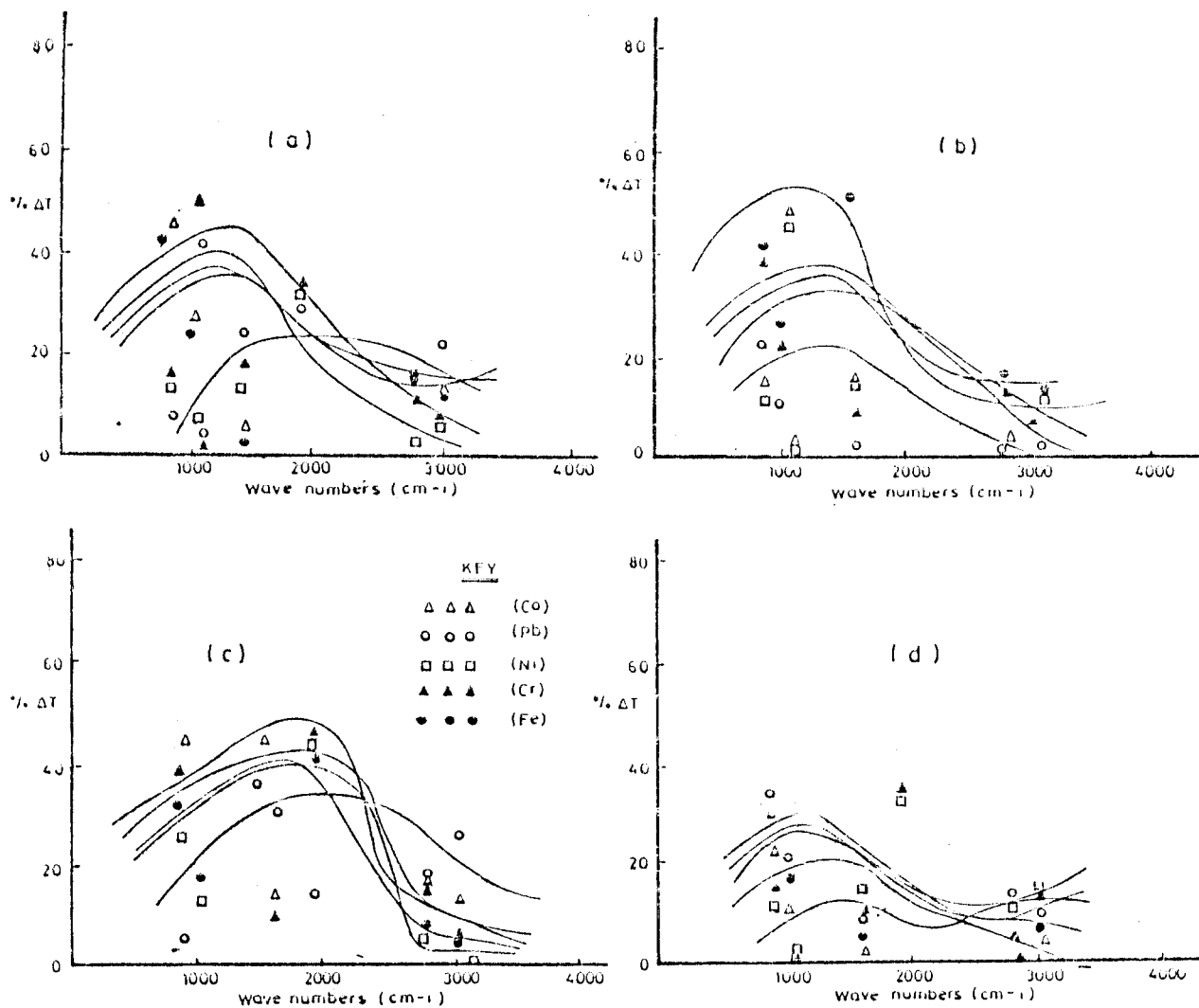
#### Infrared Studies

A Fourier transformed infrared (FTIR) machine, ATI Mattson Genesis Series FTIR, was employed. About 3 mg of polymer or polymer–metal complex powder was evenly sprinkled on the sodium chloride windows and then scanned from 4000 to 400 cm<sup>-1</sup>. By means of a computer, incorporated into

the system, absorption frequencies, transmittances, and peak correlations were obtained.

## RESULTS AND DISCUSSION

A cursory look at Table I shows that the addition of polymer solution to the metal ion solution and subsequent filtration of the complex formed leads to definite reductions in metal ion concentrations. It is also seen that the quantity of metal sequestered depends not only on the nature of the metal but also on the concentration of the polymer; as the polymer concentration increases, more of the metal ions are removed. Furthermore, it is observed that the abilities of the polymers in removing the metal ion also vary a great deal. Although a clear trend is not easy to establish, a more thorough examination of this result indicates that generally Nylon 66 tends to remove the metals more than either PSt or PVC. On the other hand, it appears chromium and iron are more readily removed than the rest of the metal ions. The above results unequivocally establish that the

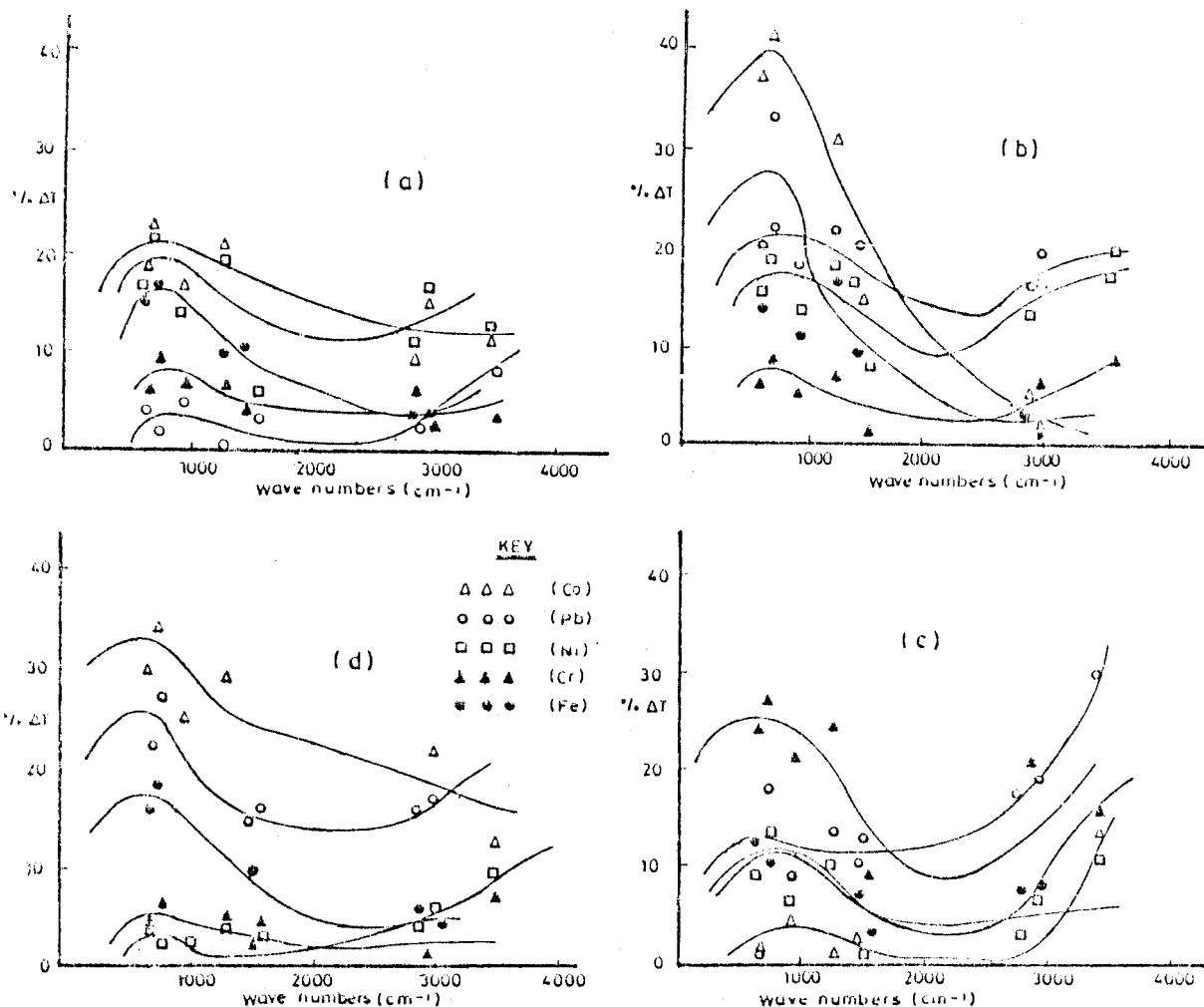


**Figure 1** Evidences of interaction between transition metal ions and Pst at (a) 66.66 ppm, (b) 120 ppm, (c) 150 ppm, (d) 160 ppm metal ion concentration.

three polymers remove these toxic heavy metals from their solutions. There are principally two mechanisms for this phenomenon: either that on precipitating from its solution on contact with the nonsolvent, the polymer coils flocculate the metal ions (i.e., ions are merely physically deposited on the polymer surfaces or occluded within the coils). If this were the case, ordinary rinsing with deionized water would clean off the metal. This was not observed in our preliminary studies.

Another mechanism may be that the polymers do form complexes with the metal ions, in which case some sites on the polymers act as ligands. In a previous work, it was shown<sup>6</sup> that PMMA in

solution forms complexes with these metals. In that report, IR spectroscopic analysis was used to show the formation of a coordination bond between the PMMA carbonyl group and the metal ion. This is a handy method of indicating complex formation<sup>7</sup> and is based on the fact that if there is interaction between an organic moiety and a metal, this is manifested by a shift in the transmittance of characteristic frequencies. Although there are other methods of doing this, the IR method was employed in this work. The results shown in Figures 1–3, as well as Figure 4, show consistent evidence that the introduction of metal ions to these polymers shift [%ΔT] the character-



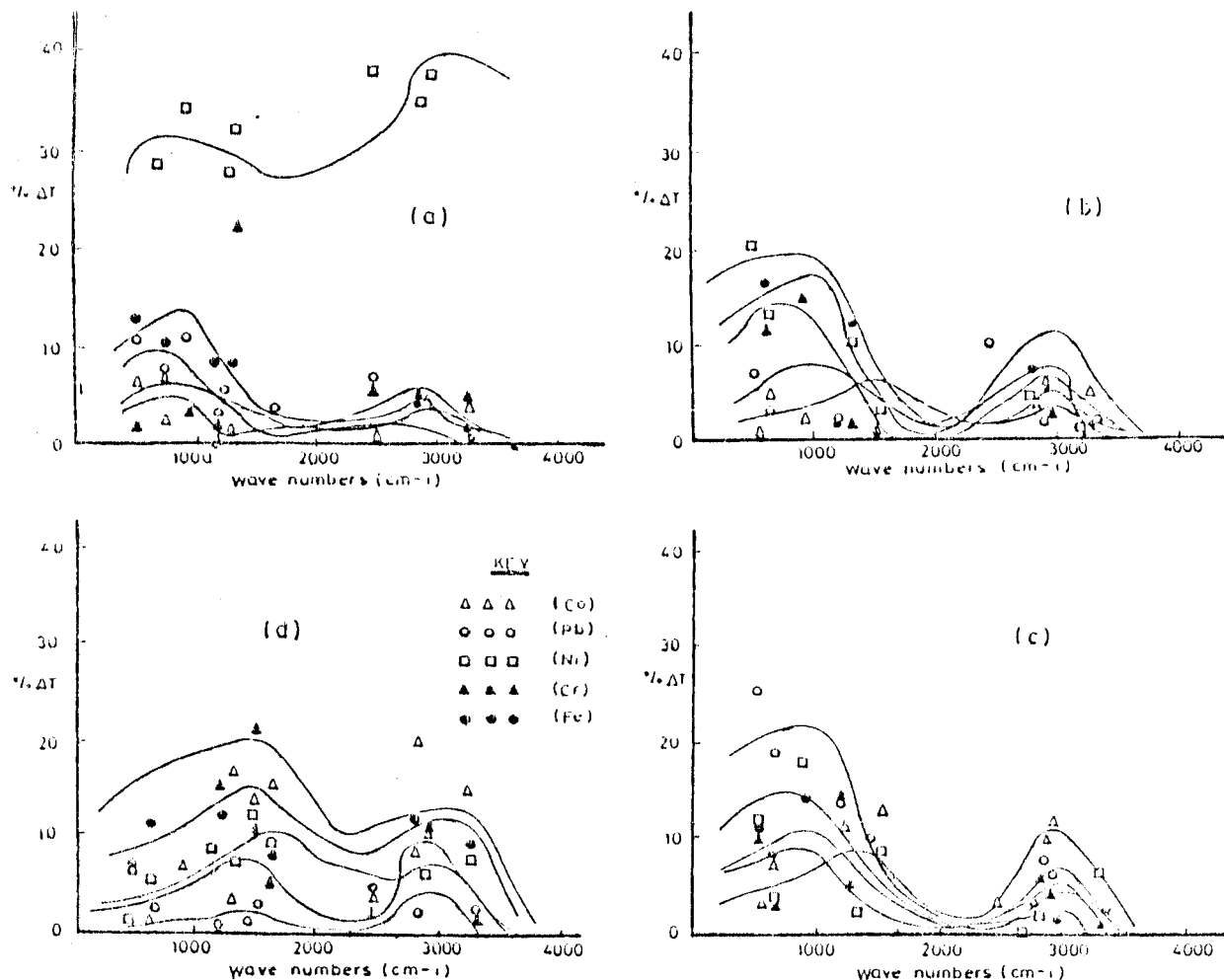
**Figure 2** Evidences of interaction between transition metal ions and PVC at (a) 66.66 ppm, (b) 120 ppm, (c) 150 ppm, (d) 160 ppm metal ion concentration.

istic transmittances of the functional groups, thereby indicating that the metal ions do interact chemically with these polymers to form complexes, not just cellularly adsorbed on the polymer surfaces. The peaks in the curves indicating frequencies of maximum shifts the functional groups responsible for these peaks were identified. It is also observed from these results that the extents of interactions vary from metal to metal and are different for the three polymers. In fact, it appears that generally for all metal ions the trend is PSt > PVC > Nylon.

However, it is not possible to establish a definite trend among the metal ions. Furthermore, for each polymer-metal system the degree of interaction depends on the polymer concentration.

A detailed study of these results further reveals that for the PSt-metal system (Fig. 1), the highest interaction occurs at  $1492\text{--}1900\text{ cm}^{-1}$ , corresponding to the aromatic C=C frequency. For PVC (Fig. 2), the interaction peaks at  $680\text{--}780\text{ cm}^{-1}$ , indicating complexation via the C-Cl moiety. The case of Nylon 66, as expected, is interesting in that there are two prominent peaks at  $1200$  and  $3200\text{ cm}^{-1}$ , respectively, corresponding to the amide C=O and amine C-N functions. Thus, Nylon 66 is at least a bidentate ligand with possible chelating characteristics.

The complexes formed can be envisaged as in the scheme. It is noteworthy that even though Nylon 66 removes metal ions more than either PSt or PVC (Table I), in Figure 1-3, it is clear that it has the



**Figure 3** Evidences of interaction between transition metal ions and Nylon 66 at (a) 66.66 ppm, (b) 120 ppm, (c) 150 ppm, (d) 160 ppm metal ion concentration.

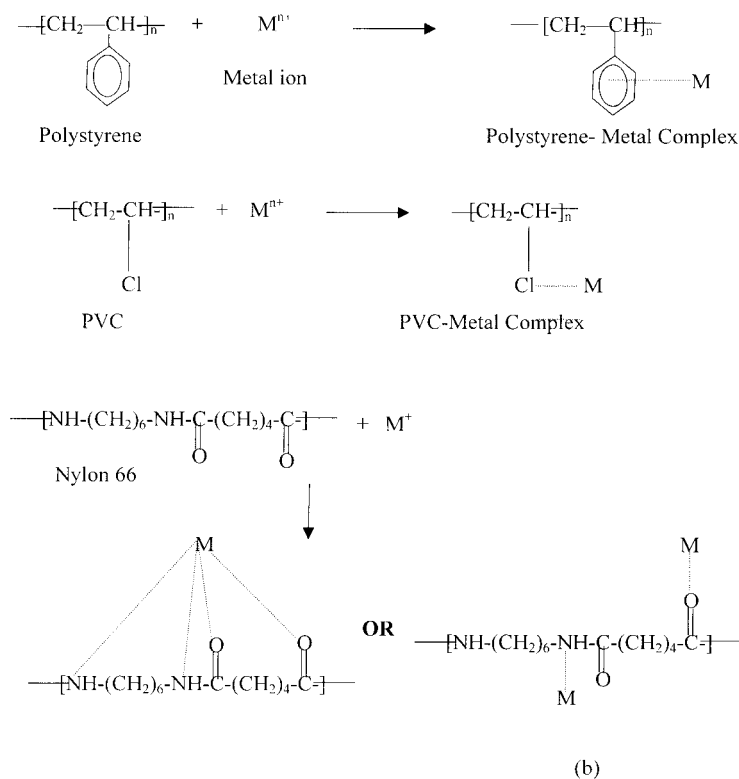
least degree of interaction. This is difficult to explain. Perhaps the second structure [Fig. 4(b)] is dominant, in which case at least two metal ions are attracted per nylon polymer segment.

Complex formation is a natural interaction phenomenon, which depends, among other things, upon the structures of the components. From our results, the points of interaction on the polymers were shown. These are of high electron density, which would interact with the positive charges on the metals by dipole–electrostatic means. This, however, does not completely exclude contributions by other modes such as dipole–dipole phenomenon. For the time being, our observations were explained on the former interaction mechanism, as it is felt to be dominant in these systems. Perhaps the simplest formula that

explains the metal–ligand interaction is that of Klotz,<sup>7</sup> which has the form:  $1/r = 1/n + 1/nkc_0$ , where  $r$  is the number of moles of bound ions per base mole of polymer, while  $n$ ,  $k$ , and  $c_0$  are the number of binding sites, the intrinsic binding constant, and the equilibrium concentration of the substrate, respectively. This equation shows that the quantity of metal ions removed depends on the concentration of the polymer as well as on the number of binding sites on it. Our result is not at variance with this postulate.

## CONCLUSIONS

The following conclusions are made from this investigation:



**Figure 4** Reaction scheme for complex formation between the heavy metals and Pst, PVC, Nylon 66.

- The three polymers are sequestering agents for the toxic heavy metal of  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Co}^{2+}$ .
- Definite chemical bonds are formed between sites on the polymers and the metal (i.e., the metals are not merely deposited on the surfaces of the polymers coils).
- The quantity of metal ions removed increases with polymer concentration as well as on the number of binding sites on the polymers.
- The degree of interaction does not necessarily indicate the quantity of metal ion removed.
- These polymer solutions can be used for decontamination of the environment.

## REFERENCES

1. Kolawole, E. G.; Matheison, S. M. *J Polym Sci, Polym Phys Ed.* 1977, 15, 2291.
2. Bekturov, E. A.; Kudaibergenov, S. E.; Kanap-yarova, G. S.; Kuramanbaera A. *Polym Chem* 1984, 25, 220.
3. Shojishima, H. *J Polym Sci, Lett Ed* 23 (1985) 245.
4. Gent, A. N.; Rodgers, W. R. *J Polym, Sci, Polym Chem Ed* 23 (1985) 829
5. Gary, D.; Jaycose, R.; Smid, J. *J Polym Sci* 20 (1982) 1629
6. Eboatu, A. N.; Alhaji, S. M. *J Therm Anal* 36 (1990) 2383–2391
7. Davidora, S. L.; Plate, N. A. *Coord Chem Rev* 16 (1975) 195