

# Construction of Template Polymeric Ligand with 8-Hydroxy Quinoline

A. RAY, S. N. GUPTA

Department of Polymer Science and Technology, Calcutta University, 92, Acharya Prafulla Chandra Road, Calcutta-700 009, India

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**ABSTRACT:** 8-Hydroxy quinoline was coupled with half diazotized *p*-phenylene diamine. Complexes of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$  were prepared with the resulting dye–ligand. The complexes were then covalently bound into a crosslinked polymer matrix based on styrene–acrylamide copolymer through the ligand moiety. After removal of the metal ions from the polymer matrix, the metal ion absorption capacities of the polymer bound ligands were measured. The procedure could induce some specificities with template effect. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1215–1219, 1998

**Key words:** 8-hydroxy quinoline; *p*-phenylene diamine; styrene–acrylamide; template

## INTRODUCTION

Various ligands capable of complexing with metal ions have been incorporated into polymeric matrices to prepare ion exchange resins. Polymeric ligands can show selectivity to some extent, depending on the nature of ligand moiety or polymeric matrix structure. Based on the idea of Wulff et al.<sup>1</sup> and Shea,<sup>2</sup> the so-called template or memory effect has been utilized for selective photochemical synthesis<sup>3–5</sup> or selective metal ion absorption<sup>6–8</sup> with varying degrees of efficiency.

8-Hydroxy quinoline, a well-known ligand for many metal ions has been incorporated earlier<sup>9–12</sup> into polymeric structure to prepare polymeric ion exchange resins. In the present work, we have synthesized rigid crosslinked polymeric matrices in which the metal chelate complex is bound covalently. The idea is to fix a metal chelate complex covalently through the ligand moiety into a rigid

crosslinked polymer so that when the metal ion is removed, it leaves the ligand bound and a cavity more supportive to the particular metal ion. This may provide selective absorption independent or less dependent on the equilibrium constant. The suitability of the technique has been studied by preparing four template polymers made with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  ions; and the selectivity of each has been measured. The template synthetic procedure is shown in Scheme I.

## EXPERIMENTAL

### Synthesis of Styrene–Acrylic Acid Copolymer

Freshly distilled styrene (20 mL) and acrylic acid (10 mL) in benzene (40 mL) was polymerized with benzoyl peroxide (0.1 g) in nitrogen atmosphere at 70°C for 4 h. The resulting polymer was precipitated in petroleum ether (40–60°C) and extracted with water; and the water insoluble polymer was purified by repeated precipitation from tetrahydrofuran solution, followed by drying in a vacuum oven at 60°C. The polymer was insoluble in benzene. The percentage of acrylic acid in

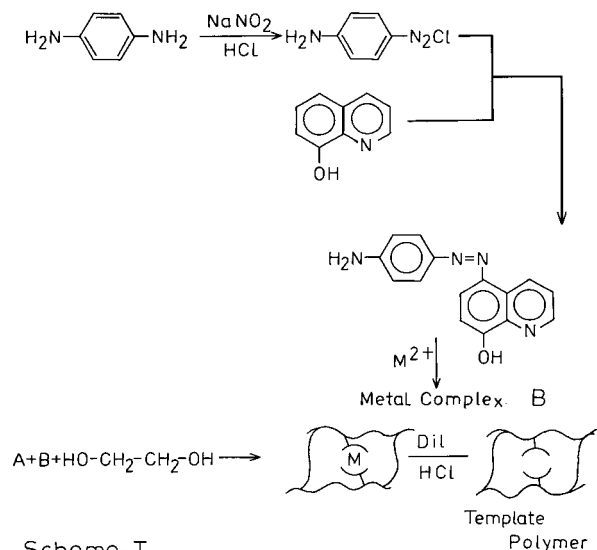
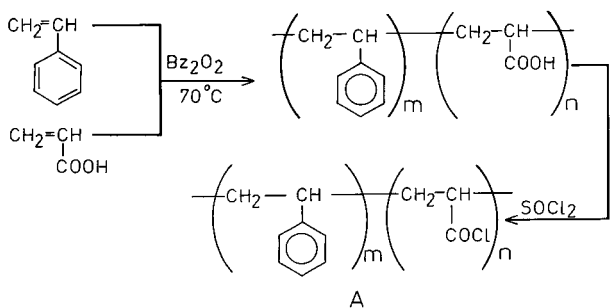
Correspondence to: S. N. Gupta.

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the copolymer was determined by infrared (IR) spectroscopy. With propionic acid as standard, the acrylic acid content in the copolymer was found to be 30 mol % (yield 19 g).

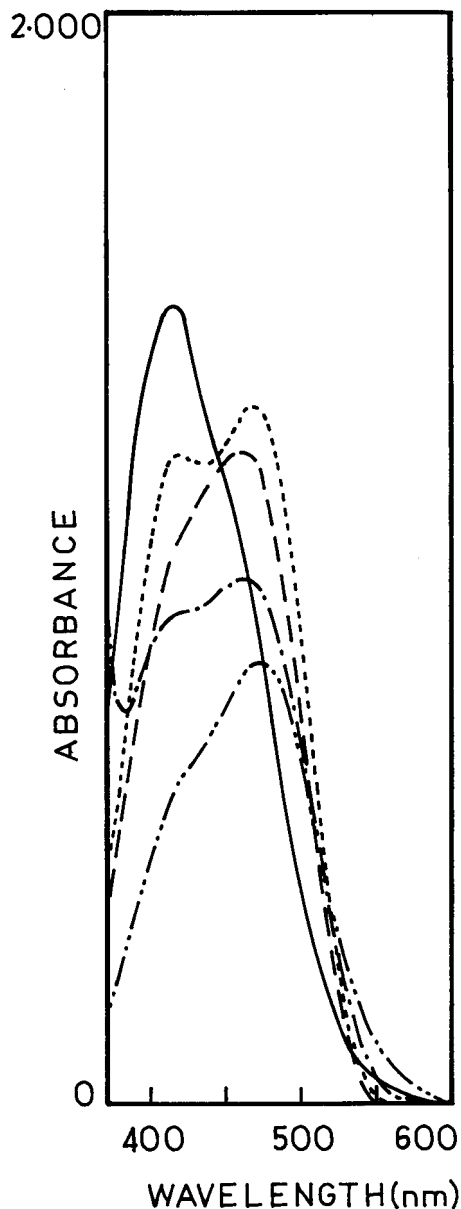
#### Preparation of Acid Chloride of the Copolymer

Styrene-acrylic acid copolymer (8 g) was refluxed with thionyl chloride (30 mL) for 3 h. Excess thionyl chloride was removed by distillation, and the polymer was purified by repeated precipitation with dry hexane from a solution in dry benzene.

#### Synthesis of Azodye by Coupling Half-Diazotized *p*-Phenylene Diamine with 8-Hydroxy Quinoline

*p*-Phenylene diamine (5.4 g, 0.05 mol) was dissolved in 50% (v) HCl and diazotized by addition of sodium nitrite (44.0 g, 0.058 mol) in 20 mL water at a temperature 0–5°C in an ice bath. A

solution of 8-hydroxy quinoline (7.25 g, 0.05 mol) in 10% NaOH was cooled and kept in an ice bath. To the vigorously stirred diazonium solution, 8-hydroxyquinoline solution was added slowly. The red crystals of the azo dye gradually separated out. After the addition was completed, the solution is kept in the ice bath for 30 min with occasional stirring. The product was filtered, washed, dried, and



**Figure 1** Absorption spectra of the ligand and its metal complexes in methanol: (—) azodye of 8-hydroxy quinoline; (— · — · — · —) Cu-complex; (· · · · ·) Ni-complex; (-----) Zn-complex; (- · - · - · - · -) Co-complex.

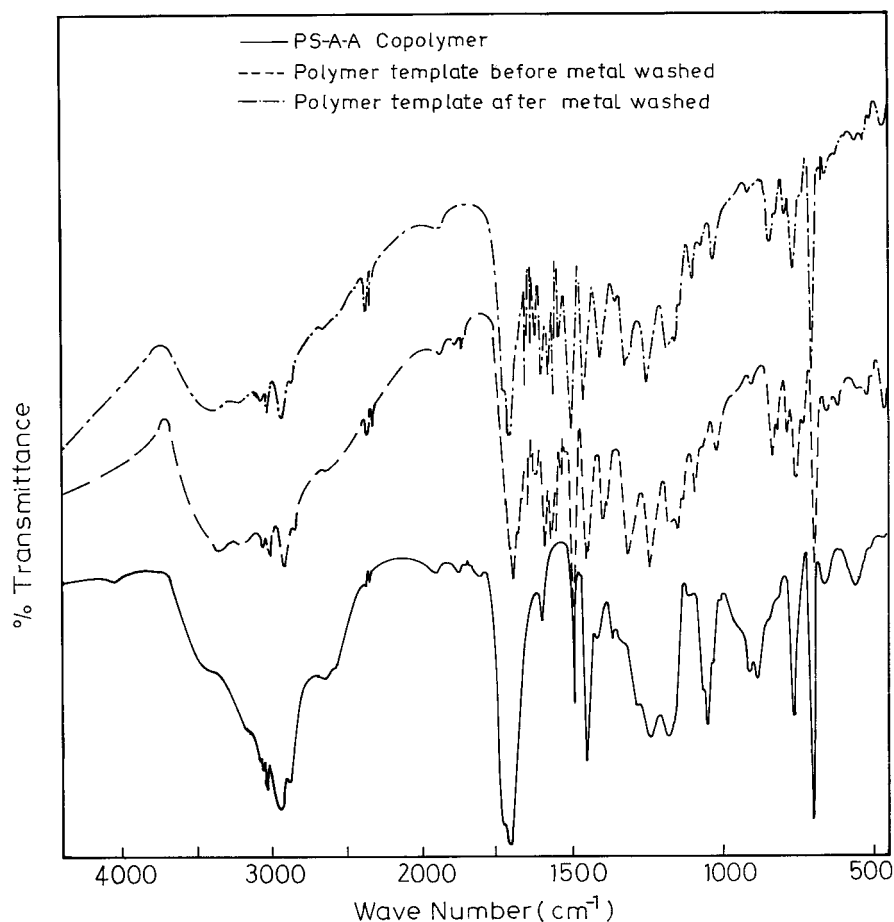


Figure 2 IR spectra of polymers.

extracted with methanol. The dye was crystallized from methanol (9.5 g yield).

(.008 mol) and  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  (0.004 mol) in each case.

#### Synthesis of Dye–Metal Complex

Four metal complexes were prepared separately in dry distilled dimethyl formamide with the dye

#### Synthesis of Template Polymer

Polymer-bound metal complexes were prepared by reacting the metal complexes with the styrene

Table I Ligand Availability of Various Polymers

Template Polymer Type	8-Hydroxy Quinoline Content (mmol/g)	Metal Absorption (mmol/g)	Mol % Ligand Available to Template Metal	Stability Constant Log K
Cu—Template	0.80	0.24 (Cu)	60	23.4
Ni—Template	0.97	0.23 (Ni)	47	21.3
Zn—Template	0.70	0.15 (Zn)	43	18.8
Co—Template	0.94	0.17 (Co)	36	17.2

**Table II Absorption Capacities of Various Metals**

Type of Template Polymer Matrix	Metal Absorption (mmol/g)			
	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Co <sup>2+</sup>
Cu—Template	0.24	0.15	0.13	0.09
Ni—Template	0.19	0.23	0.10	0.09
Zn—Template	0.16	0.14	0.17	0.11
Co—Template	0.13	0.11	0.10	0.15

acrolol chloride copolymer in dry distilled dimethyl formamide (DMF) in the presence of pyridine. The polymeric metal complexes were then crosslinked with ethylene glycol through the residual acid chloride groups. The precipitated out crosslinked polymer was separated and washed repeatedly with methanol and water until no color was observed in the washings. The metal ions were removed from the polymer by washing with N/10 HCl. The amount of ligand attached to the polymers was determined by nitrogen analysis.

#### Determination of Metal Absorption Capacities

A known amount of each expected template polymers free from metal ions was taken in excess dilute solution of the metal ion, stirred for 30 min, and filtered; and the metal content in the filtrate estimated by titration with ethylene diamine tetraacetic acid (EDTA). The polymer was then freed from the absorbed metal ion by N/10 HCl, washed with water, and dried; and

**Table III Ligand Reactivity with Various Metal Ions**

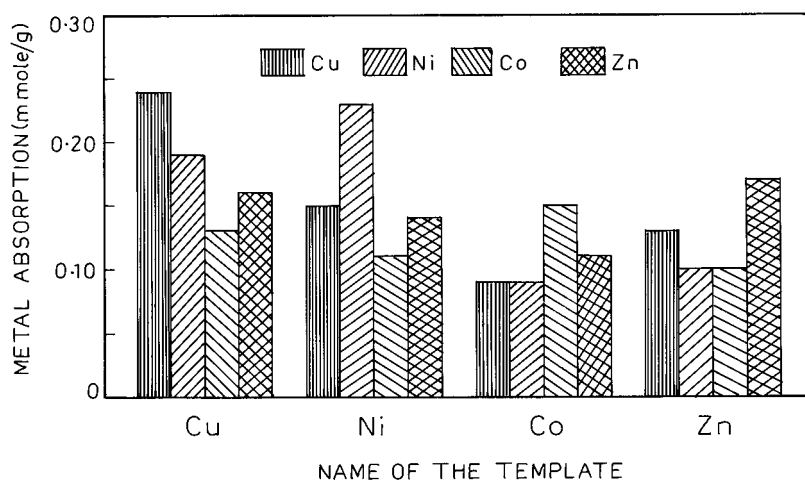
Template Polymer Type	Mol % Ligand Available to Metal Ion			
	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Co <sup>2+</sup>
Cu—Template	60	37	22	32
Ni—Template	39	47	18	21
Zn—Template	37	31	43	28
Co—Template	34	29	23	36

the metal absorption capacity of the same or different metal ions was measured again, as mentioned above.

## RESULTS AND DISCUSSION

The visible spectra of the dye and its metal complexes are shown in Figure 1. The distinct change in peak positions is caused by the formation of respective metal complexes. From the IR spectra shown in Figure 2, it can be observed that the carbonyl peak due to acid group in the copolymer at 1724 cm<sup>-1</sup> has been shifted to 1700 cm<sup>-1</sup> due to the formation of amide on reacting with the dye. The new absorptions at the 3300 cm<sup>-1</sup> region is due to the phenolic group of the attached 8-hydroxy quinoline.

8-Hydroxy quinoline content of the polymers and their metal ion absorption capacities are given in Table I. It is observed that the percentages for complexation vary from metal to metal

**Figure 3** Bar chart showing the template effect.

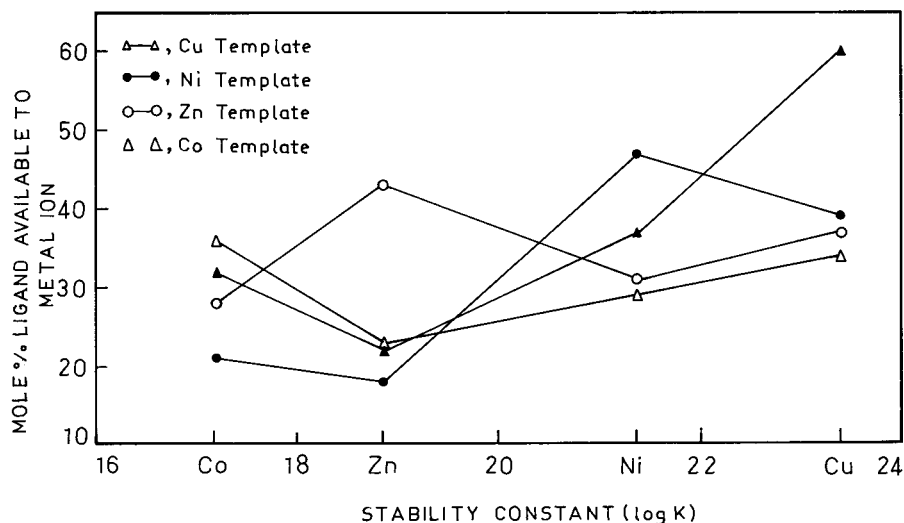


Figure 4 Selectivity curve showing the template effect.

and are obviously proportional to their stability constants. Moreover, about half of the attached ligand is structurally restrained from absorbing metal ion due to collapse of the molecules from solution to solid state on crosslinking. Considering the hydrophobic nature of the base polymer and the situation of ligand and metal ion in different phases, this may be expected.

The data given in Tables II and III show the extent of specificity achieved. It can be seen that the amount of metal ions absorbed by a polymeric ligand is maximum for the metal ion from which the template is formed, irrespective of the stability constant. Quantities of other metal ions absorbed are much lower, even when their stability constants are higher. Comparative pictures are shown in Figures 3 and 4.

The metal ions chosen have close ionic radii. It is, therefore, imperative that the specificity observed was not totally dependent on the hole size but also on the frozen geometry and/or conformation of the ligand in the solid polymeric matrix.<sup>7,13,14</sup>

It may be concluded that significant memory or template effect could be achieved by method presented, though it is not very high. It has also been observed that the metal absorbing capacity did not decrease on repeated use of the same polymer, nor did any ligand leach out in the experimental condition. By altering the crosslinking agent and the distance between the active sites of the ligand and main chain backbone, it may be possible to enhance the specificity, which is a matter of our further study.

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## REFERENCES

1. G. Wulff, A. Sarhan, and K. Zabrocki, *Tetrahedron Lett.*, **20**, 4329 (1979).
2. K. J. Shea, *J. Org. Chem.*, **43**, 4253 (1978).
3. J. Damen and D. C. Neekers, *J. Am. Chem. Soc.*, **102**, 3265 (1980).
4. J. Damen and D. C. Neekers, *J. Org. Chem.*, **45**, 1382 (1980).
5. J. Damen and D. C. Neekers, *Tetrahedron Lett.*, **21**, 1913 (1980).
6. H. Nishide and E. Tsuchida, *Makromol. Chem.*, **177**, 295 (1976).
7. H. Nishide, H. Degushi, and E. Tsuchida, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 3023 (1977).
8. S. N. Gupta and D. C. Neekers, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1609 (1982).
9. J. I. Kroschwitz, Ed., *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 2nd ed., Vol. 3, pp. 363–383.
10. T. Hamaya, K. Hiratani, and K. Ohashi, *Chem. Lett.*, **3**, 615 (1994).
11. X. Chen, I. Ren, H. Hissannori, and O. Kazuhisa, *Kousaburo Bunseki Kagaku*, **42**, 707 (1973).
12. A. Yoneda and T. Hakushi, *Nippon Kagaku Kaishu*, **6**, 580 (1994).
13. H. Nishide, N. Shimidzu, and E. Tsuchida, *J. Appl. Polym. Sci.*, **27**, 4161 (1982).
14. M. Yamada, M. Takagi, and K. Ueno, *J. Coord. Chem.*, **10**, 257 (1980).