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Chelation Properties of Poly(8-Hydroxyquinoline 5,7-diylmethylene) Crosslinked with Bisphenol-A Toward Lanthanum(III), Cerium(III), Neodimium(III), Samarium(III), and Gadolinium(III) Ions

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ABSTRACT

The chelation behavior of poly(8-hydroxyquinoline 5,7-diylmethylene) crosslinked with various amounts of bisphenol-A toward some trivalent lanthanide metal ions, such as La(III), Ce(III), Nd(III), Sm(III), and Gd(III), has been investigated by a static batch equilibration technique. The effects of crosslinking on the chelation characteristics of these resins were studied. The optimal capacity of metal-ion uptake was achieved by incorporating 5–10% of bisphenol-A into the polymer matrix. A scanning electron microscope was used to analyze the surface morphology of the polymers. The measured water-regain values have shown that the hydrophilicity of the crosslinked polymers increases as the degree of crosslinking is increased.

Key Words. Bisphenol-A; Chelate-forming polymers; Crosslinking; Lanthanide metal ions

INTRODUCTION

In recent years, chelate-forming polymers (1–15) have found widespread applications for the separation and monitoring of trace heavy metals from aqueous solutions. Considerable effort has been directed toward the improvement

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and optimization of the chelating properties of chelating ion-exchange resins (13–17). Vernon (18) has summarized the desirable properties of chelating polymers. They exhibit high capacity for the metal(s) of interest; high selectivity; fast kinetics of metal-ion uptake by the polymers, and high mechanical strength and durability. The optimization of these properties for a given polymer is a more difficult problem than has generally been admitted. Kabay and Egawa (13) reviewed attempts to optimize the properties of chelating polymers containing amidoxime groups used for the recovery of uranium from seawater. In general, improved rates of uranium uptake were achieved by the optimization of the porosity and the specific surface area in the polymer. Macroreticular chelating resins containing amidoxime groups with various degrees of crosslinking exhibited high adsorption capacity for uranium (19–21).

Although the condensation of phenol and formaldehyde is one of the most well-known reaction routes to produce chelating polymers (22), it continues to attract a great deal of interest (1–7). An interesting feature of these condensation reactions is the wide variation in the properties of the resulting polymers under differing reaction conditions. This explains why some phenolic chelants have been investigated repeatedly by several research groups under differing reaction conditions in an attempt to improve the hydrophilicity and chelation capacity of phenol-formaldehyde chelating polymers. A typical example is 8-hydroxyquinoline (commonly known as oxine) (23–30). This important chelating agent may serve as a model system to test the importance of various factors that influence the chelation properties of this class of chelating polymers.

The effect of crosslinking on the sorption behavior of poly(8-hydroxyquinoline 5,7-diylmethylenes) toward some trivalent lanthanide metal ions such as La(III), Ce(III), Nd(III), Sm(III), and Gd(III) ions is considered here. This is a continuation of recent work (1–3) on the chelation properties of chelate-forming phenol-formaldehyde resins toward some divalent and trivalent metal ions.

EXPERIMENTAL

Materials

Unless otherwise indicated, all materials were of analytical grade and were used without further purification. Bisphenol-A was obtained from Acros Organics (USA); 8-Hydroxyquinoline was obtained from Riedel deHaan (Germany); formaldehyde solution (37–41%) was purchased from BDH Chemicals Ltd. (England); the lanthanide salts, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained from Fluka Co. (Switzerland), and the salt $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ was obtained from Koch-Light Laboratories Ltd. (England).

TABLE 1
The Composition of the Reaction Mixture for Polymers I–V

Polymer	37–40% Formaldehyde mol (mL)	Oxine mol	Bisphenol-A mol	Bisphenol-A %
				Oxine mol%
I	0.40 mol (30 mL)	0.20	2.0×10^{-4}	0.1%
II	0.40 mol (30 mL)	0.20	6.0×10^{-4}	0.3%
III	0.40 mol (30 mL)	0.20	1.0×10^{-3}	0.5%
IV	0.40 mol (30 mL)	0.20	4.0×10^{-3}	2.0%
V	0.40 mol (30 mL)	0.20	2.0×10^{-2}	10.0%

Preparation of Crosslinked Polymers

The crosslinked polymers I, II, III, IV, and V were prepared by the following procedure. A mixture of 8-hydroxyquinoline and 37–41% aqueous formaldehyde and bisphenol-A (see Table 1) and 120 mL of an aqueous ethanol solution (50%) was adjusted to pH 9.0 with 1.00 M NaOH and placed in a 500-mL round-bottomed flask. The composition of the reaction mixture for polymers I, II, III, IV, and V are summarized in Table 1. The reaction mixture was then refluxed for 1 h. The orange-yellow solid polymers obtained were purified by reprecipitation from *N,N*-dimethylformamide (DMF) by excess methanol, dried at 90°C under vacuum, then crushed and sieved (35–60 mesh).

Measurements

Infrared spectra of polymers and their metal chelates were recorded, as KBr discs using a Nicolet Impact 400 FT-IR spectrophotometer from 400 to 4000 cm^{-1} . Complexometric titrations were performed with a Metrohm 655 Dosimate titrator. Scanning electron microscope (SEM) photographs were recorded with a DSM 950 electron microscope, which allows a wide range of magnification, up to $\times 1000$. Water regain parameter, α (in g g^{-1}), of the polymers was determined using the procedure of Sugii et al. (31).

Sorption of Metal Ions

The metal chelation characteristics of each metal ion were investigated by the batch equilibrium technique. Duplicate experiments involving 0.5 g of 35–60 mesh resin samples were equilibrated with 75 mL of sodium acetate–acetic acid buffer solution for 3 h. To this mixture, 25 mL of metal-ion solution containing a total of 50.0 mg of metal ion was added. After being shaken for a definite period at 25°C, the mixture was filtered and the amount

of metal ion remaining in the filtrate was determined by complexometric titration using standard EDTA solutions and xylenol-orange solution as an indicator. The rate of metal-ion uptake was studied under similar experimental conditions where the contact time was varied from 1 to 24 h at 25°C and pH 7.0. Similar experiments were performed in buffer solutions of pH values of 5.0 to 8.0 for a fixed contact time of 6 h.

RESULTS AND DISCUSSION

Characterization of the polymers and their chelates

The IR spectra of the polymers and their chelates are consistent with the structures assigned to them. A typical structure of these polymers is depicted in Fig. 1. The IR spectra exhibited broad bands in the 3000–3500 cm^{-1} region; these bands have been assigned to the hydroxy groups of 8-hydroxyquinoline intramolecularly hydrogen bonded to the nitrogen (30). These bands were also observed in the spectra of the polymeric chelates, since only a fraction of the ligand moieties on the polymer are involved in chelate formation. Weak absorption bands in the 3060–2950 cm^{-1} and 2930–2850 cm^{-1} regions have been attributed to the aromatic C–H stretching and to the C–H stretching of the methylene groups linking the aromatic rings, respectively.

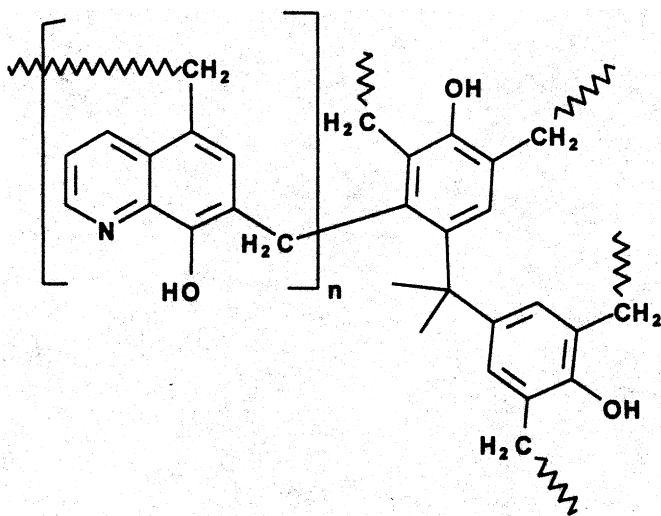


FIG. 1 A typical structure of poly(8-hydroxyquinoline, 5,7-diylmethylene) crosslinked with bisphenol-A.

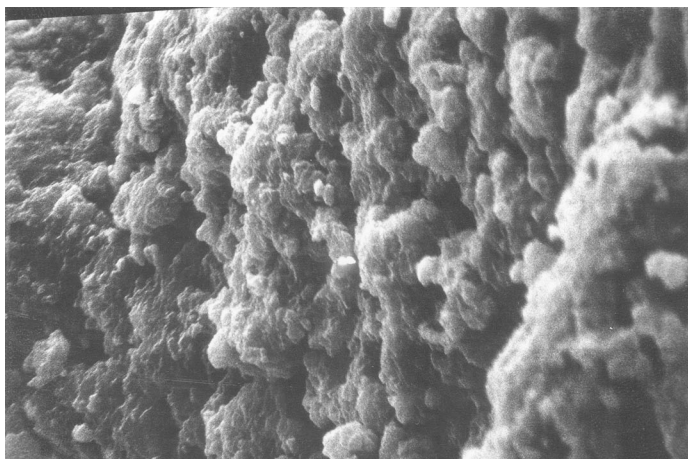


PLATE 1 Scanning electron microscope photograph for polymer I (0.1% crosslinked).

Chemical and physical properties of solid polymeric materials are governed by their surface characteristics (32, 33). In the present work, scanning electron microscopy was used to analyze the surface morphology of resins. Typical SEM plates 1, 2, and 3 show the surface structures of the purified and dried resins crosslinked with 0.1, 2.0, and 10.0% bisphenol-A, respectively; they reveal that porous resins with more voids on the surface are obtained when rel-

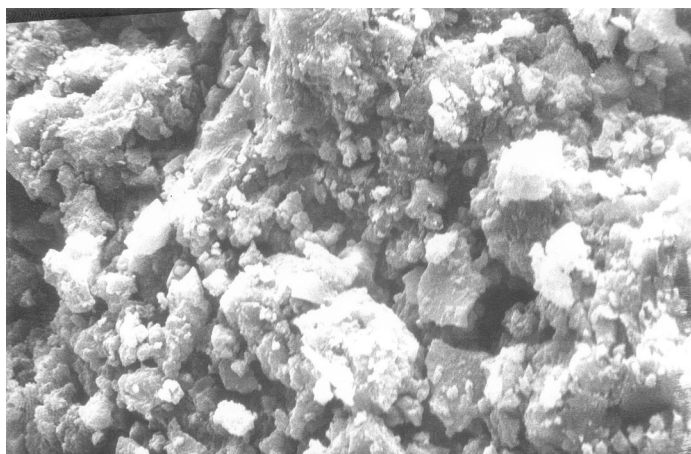


PLATE 2 Scanning electron microscope photograph for polymer IV (2.0% crosslinked).



PLATE 3 Scanning electron microscope photograph for polymer V (10% crosslinked).

atively larger quantities of the crosslinker, bisphenol-A, are incorporated into the resin. Thus, by optimizing the degree of crosslinking, the porosity of the resin may be controlled. However, excessive crosslinking ($>10\%$) may lead to slower rates of metal-ion uptake (18).

Water-regain parameter α provides an indirect measure of the hydrophilic character of the polymer (31). The experimental α values were: 1.07, 1.92, 1.95, 2.04, and 2.08 gg^{-1} for polymers I, II, III, IV, and V, respectively. These values clearly show that as the degree of crosslinking increases α also increases, indicating the presence of microporous hydrophilic sites. The availability of such hydrophilic micropores provides water-transport channels, which are of paramount importance for the effective sorption of metal ions from aqueous solutions.

Sorption of Lanthanide Metal Ions on the Polymer

The extent of interaction between the trivalent lanthanide ions and the polymers (I–V) was studied by a batch equilibration technique. In this technique, and prior to the sorption experiment, 0.5 g of dry 35–60 mesh samples of the resins were preconditioned by allowing the resin to equilibrate for 3 h with the acetate buffer solution of known pH. The sorption experiments were performed at 25.0°C under continuous stirring as a function of contact time (1–24 h). The results are presented in Fig. 2. These results indicate that the rate of metal-ion uptake increases in the first 1–3 h and reaches a steady state after 6

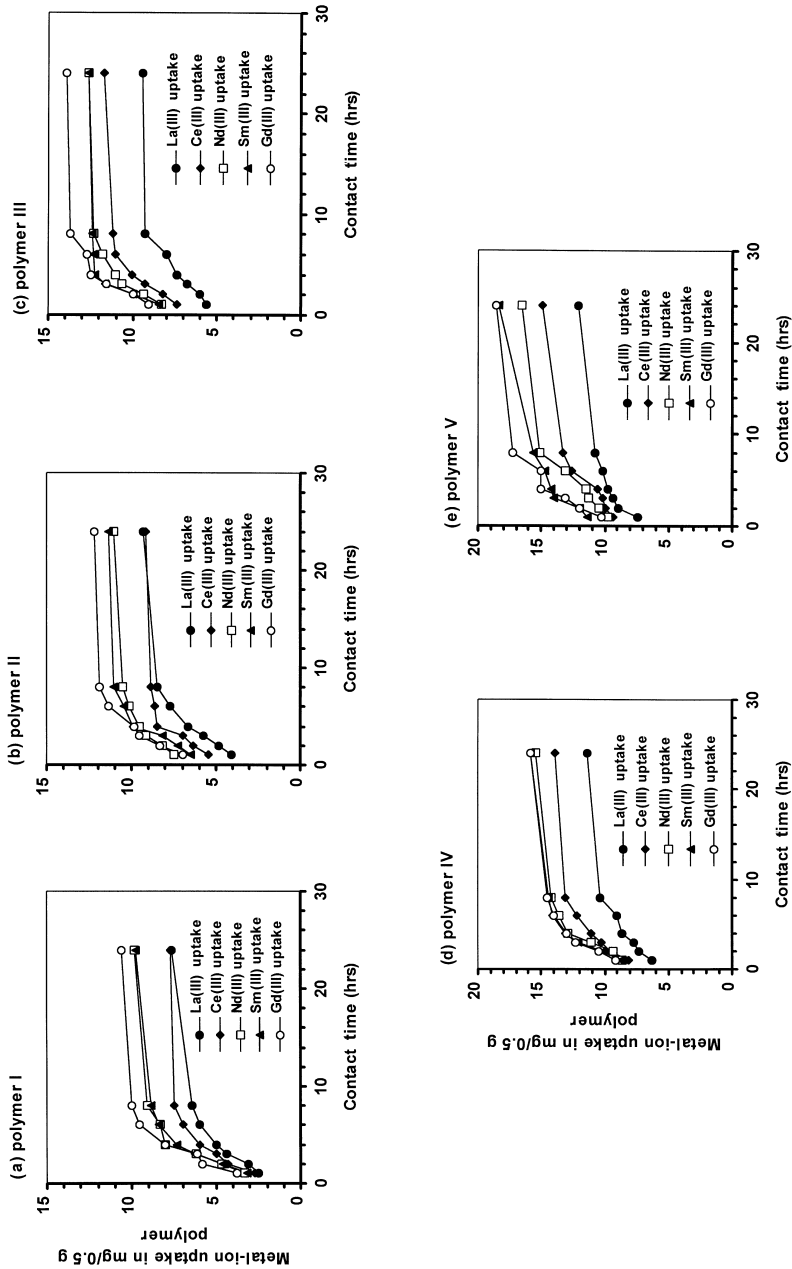


FIG. 2 The rate of metal-ion uptake by polymers I, II, III, IV, and V at 25°C and pH 7.0. Volume of solution = 100 mL. Initial metal-ion content in solution = 50.0 mg. Mass of polymer sample = 0.50 g.

h. Metal-ion uptake observed for these resins follows the order



Typical sorption behavior of polymers I–V towards Gd(III) ions, shown in Fig. 3, indicates that the sorption process of the polymers is highly affected by the relative amount of the crosslinker; polymer V (10.0% crosslinked) displayed the highest metal-ion uptake capacity. Apparently the presence of bisphenol-A provides larger voids and possible channels that may facilitate the movement of the metal ions. Although the most plausible sorption site is through the O and N of an 8-hydroxyquinoline moiety forming a six-membered chelate ring, the possibility also exists for binding through the phenoxy groups of bisphenol-A.

The pH-dependence of metal-ion uptake by polymers was investigated in the pH range 5–8 for a fixed contact time of 6 h. The results illustrated in

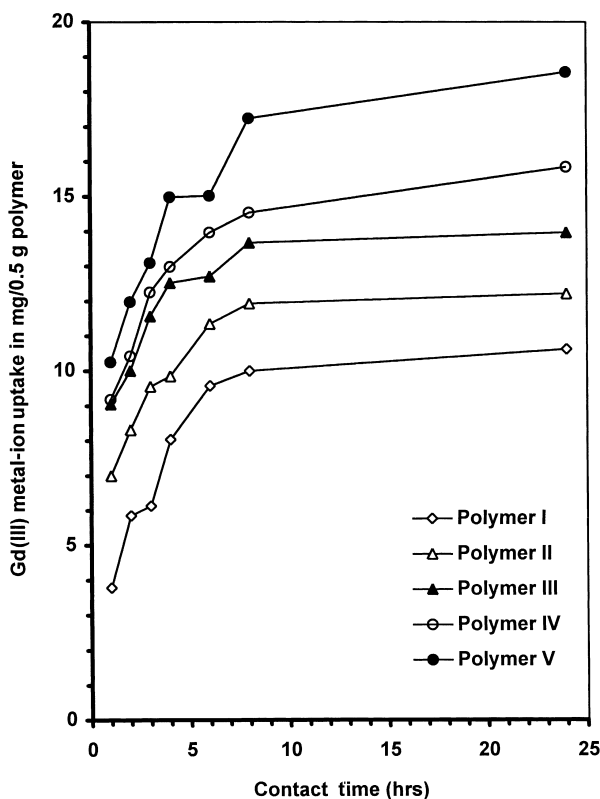


FIG. 3 The rate of Gd(III) metal-ion uptake by polymers I–V.

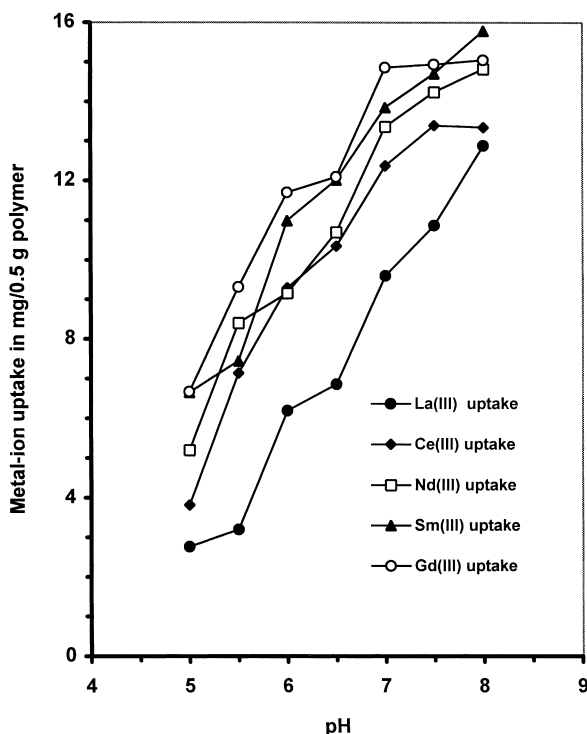
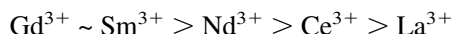


FIG. 4 The pH-binding capacity profiles for metal-ion uptake by polymer V.

Fig. 4 reveal that the binding affinity of the polymers toward metal ions increases with pH. Metal ion uptake observed for these resins at pH > 7.0 follows the order



This order is in satisfactory agreement with the stability constants of the monomeric 8-hydroxyquinoline complexes of La^{3+} , Nd^{3+} , and Sm^{3+} (34, 35). Furthermore, the observed trend of metal-ion uptake is inversely correlated with the ionic radii of the trivalent lanthanide ions; the relatively smaller Gd^{3+} ions are expected to pass readily through voids on the surface, leading to relatively higher metal-ion uptake.

CONCLUSION

The chelation characteristics of a chelate-forming polymer are determined by the nature of the active chelating group and by surface morphology and

porosity. The present study has demonstrated the use of bisphenol-A as a crosslinker to modify surface characteristics. A 10% crosslinked poly(8-hydroxyquinoline, 5,7-diylmethylene) gave the highest capacity resulting from the formation of large voids on the surface that may facilitate the movement of the metal ions. Thus, by judicious choice of the crosslinker and the degree of crosslinking, it is possible to enhance and optimize the capacity and selectivity of phenol-formaldehyde chelating polymers toward heavy metal ions. An extension of this work, to include other crosslinkers and multicomponent aqueous metal-ion mixtures, is planned.

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