

Chelation Properties of Poly(2-hydroxy-4-acryloyloxybenzophenone) Resins Toward Some Divalent Metal Ions

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ABSTRACT: The chelation behavior of poly(2-hydroxy-4-acryloyloxybenzophenone) [poly(2H4ABP) or polymer I] obtained through the free-radical polymerization of 2-hydroxy-4-acryloyloxybenzophenone monomer and for crosslinked polymers prepared from the monomer and known amounts of the crosslinker divinylbenzene (DVB) [4 mol % of DVB for polymer II, 8 mol % of DVB for polymer III, and 16 mol % of DVB for polymer IV] toward the divalent metal ions Cu^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} in aqueous solution was studied by a batch equilibration technique as a function of contact time and pH. The

effect of the crosslinker, DVB, was also studied. The metal-ion uptake of the polymers was determined with atomic absorption spectroscopy, and the highest uptake was achieved at pH 7.0 for polymers I, II, III, and IV. The selectivity and binding capacity of the resins toward the investigated divalent metal ions are discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3180–3184, 2008

Key words: crosslinking; FTIR; radical polymerization; resins; synthesis

INTRODUCTION

Metal chelating polymers¹ constitute an important class of versatile polymeric materials that have found widespread applications in environmental remediation and the monitoring and separation of trace heavy metal ions from aqueous solutions.

Chelating polymers are normally produced by the incorporation of active chelating groups into a polymeric matrix.² Such chelating groups may be covalently bound to a polymer matrix as pendent groups or incorporated into the repeating units of the polymer backbone by the polymerization of a suitable monomer containing the required chelating group. It has been demonstrated that the nature of intervening groups connecting the active chelating ligands in chelating polymers plays an important role in the chelation process.^{2,3}

In the interaction between a chelate-forming resin and metal ions, the electrostatic exchange is accomplished by a rapid chemical reaction, which in many cases, leads to strong metal ligand bonds. The intensity of the chelating interaction is governed by such properties of the metal ion as its oxidation state, electronic configuration, stereochemistry, and basicity and the polarization of the ligand on the resin.⁴ The nature of the metal species, the functional group, and/or donor atom capable of forming com-

plexes with metal ions are also of fundamental importance in metal extraction by polymers.

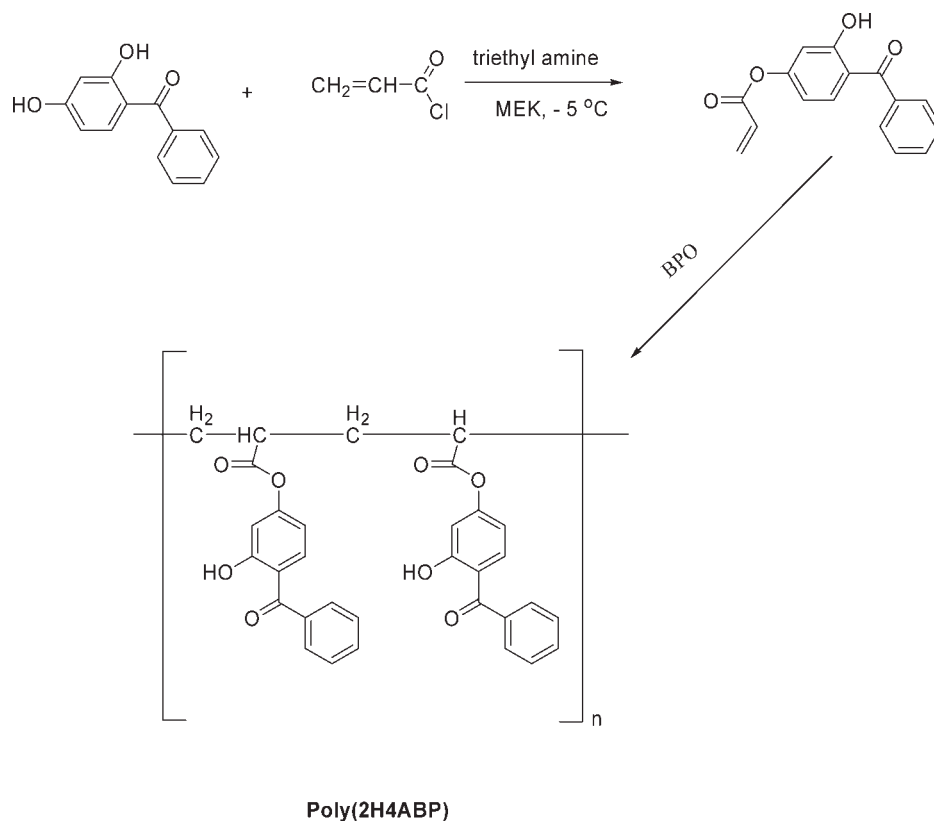
In connection with our recent work on the synthesis and sorption properties of chelate-forming polymers,^{5–14} in this article, we report the synthesis and chelation properties of poly(2-hydroxy-4-acryloyloxybenzophenone) [poly(2H4ABP) or polymer I] toward divalent transition-metal ions (Cu^{2+} , Zn^{2+} , Ni^{2+} , and Pb^{2+}) in aqueous solution under different experimental conditions of contact time and pH. The effect of crosslinking with various amounts of divinylbenzene (DVB) on the properties and sorption properties of the polymer is also discussed.

EXPERIMENTAL

Reagents

Unless otherwise indicated, all chemicals were obtained from commercial sources and were used as received. 2,4-Dihydroxybenzophenone, triethylamine, and acryloylchloride were obtained from Acros (Geel, Belgium). Benzoyl peroxide (BPO) and hydroquinone were obtained from Fluka (Buchs, Switzerland). DVB was obtained from Merck (Darmstadt, Germany), and acetic acid was obtained from GCC (Clwyd, England). The following metal-ion salts were also used without further purification: copper(II) acetate dehydrate (98%), $(\text{CH}_3\text{COO})_2\text{Cu} \cdot 2\text{H}_2\text{O}$ from Fluka, nickel(II) acetate tetrahydrate from BDH (Poole, England), zinc(II) acetate dihydrate from Riedel deHaen (Seelze, Germany), and lead(II)

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Scheme 1

acetate trihydrate from S. D. fine Chemicals, Ltd (Mumbai, India).

Instrumentation

Infrared spectra of the polymers and their monomer were recorded with a Nicolet Impact 400 Fourier transform infrared spectrophotometer (Madison, WI) from 400 to 4000 cm^{-1} . KBr discs were used for all of the solid samples by the mixture of 1.0 mg of the sample with about 100 mg of KBr. Atomic absorption data were obtained with a Varian atomic absorption spectrophotometer (Mulgrave, Victoria, Australia) model AA-250 plus. Samples were shaken and thermostated with a GFL-1083 shaker (Burgwedel, Germany). Elemental analyses were acquired with the aid of a Eurovector Euro EA3000 CHNS—O elemental analyzer (Milan, Italy). EIMS spectra were obtained with a Finnegan MAT TSQ-70 mass spectrometer at 70 eV (Bremen, Germany). A Metrohm pH meter model 525A (Herisau, Switzerland) was used for the pH measurements.

Preparation of the chelating polymers

Preparation of the 2-hydroxy-4-acryloyloxybenzophenone (2H4ABP) monomer

This monomer was synthesized according to a published procedure¹⁵ (Scheme 1), which involved the

mixing of 10.7 g of 2,4-dihydroxybenzophenone (0.05 mol), 5.1 g of triethylamine (0.05 mol), 0.5 g of hydroquinone, and 700 mL of methyl ethyl ketone (MEK) in a two-necked, 1-L flask equipped with a thermometer and funnel. After the solution was cooled to -5.0°C , 4.53 g of acryloyl chloride (0.05 mol) dissolved in 150 mL of MEK was added dropwise and with stirring at this temperature. The solution was allowed to attain ambient temperature, and stirring was continued for another 2 h. The formed salt was filtered, the filtrate was washed with distilled water and dried over anhydrous sodium sulfate, and the solvent was evaporated. The resulting crude solid of 2H4ABP was recrystallized from ethanol to afford yellow crystals: mp = $80\text{--}81^{\circ}\text{C}$, literature mp = $81\text{--}82^{\circ}\text{C}$,¹⁶ mass spectrum (70 eV) $m/z = 268$ (69) $[\text{M}^+]$, 213 (44) $[\text{M} - 55]^+$, 137 (21) $[\text{M} - 131]^+$, 105 (16) $[\text{M} - 163]^+$, and 55 (100) $[\text{M} - 213]^+$. The $^1\text{H-NMR}$ spectrum agreed with the assigned structure.

Preparation of poly(2H4ABP) (polymer I)

The titled polymer was prepared by the free-radical polymerization of 2H4ABP monomer with BPO as an initiator according to the procedure outlined by Kaliyappan et al.,¹⁵ as shown in Scheme 1. The procedure involved the dissolution of 0.94 g of 2H4ABP (3.5 mmol) and 0.5 g of BPO in 50 mL of MEK. The

mixture was deaerated with nitrogen for 30 min and was kept in a reaction tube at 70°C for 10 h. A large excess (200 mL) of methanol was added to the contents of the tube, and the precipitated polymer was collected by filtration and washed with methanol. After Soxhlet extraction with methanol for 24 h, the resulting solid polymer was dried *in vacuo* at 50°C for 24 h and sieved through a mesh size of 35–60 (250–500 μm). Satisfactory elemental analyses were obtained:

ANAL. Calcd for $[\text{C}_{16}\text{H}_{12}\text{O}_4]_n$: C, 71.64%; H, 4.48%. Found: C, 72.13%; H, 4.39%.

Preparation of crosslinked poly(2H4ABP) (polymers II–IV)

The same general procedure that was used for the synthesis and purification of polymer I was used for the preparation and purification of polymers II–IV by the addition of certain amounts of the crosslinker DVB to the reaction mixture. The following molar percentages of DVB with respect to monomer were used: 4 mol % resulted in a pale yellow solid for polymer II, 8 mol % resulted in an orange solid for polymer III, and 16 mol % resulted in a dark orange solid for polymer IV. The polymers had decomposition points greater than 220°C.

Sorption of metal ions on the polymers

The metal chelation characteristics of the resins for each metal ion were investigated by the batch equilibrium method; duplicate experiments involving 0.1000 g of dry 35–60 mesh resin samples were suspended in 25.0 mL of sodium acetate–acetic acid buffer (pH = 6.0) for 2 h of continuous shaking for equilibration. An amount of 25.0-mL solution containing 15.0 mg of metal ion was then added, and the mixtures were shaken at 25°C for a specific period of time (0.08–24 h). The samples were filtered out, and the amount of metal ion remaining in solution was determined by atomic absorption spectroscopy with standard solutions for calibration.

The extent of metal-ion uptake was studied under similar experimental conditions, where the contact time was varied from 0.08 to 24 h at 25°C after the solution was equilibrated with distilled water. Similar experiments were also carried out in buffered solutions, in which the pH was varied between 4.0 and 7.0 for a fixed contact time of 6 h.

RESULTS AND DISCUSSION

Characterization of the polymers

The IR spectra of the polymers were in agreement with the structures assigned to them. The broad

bands in the 3600–3615- cm^{-1} region in the spectra were attributed to the intramolecularly hydrogen bonded O–H stretching vibration;¹⁶ these bands were also observed in the metal chelates because only a fraction of the ligand moieties on the polymers were involved in chelate formation. The strong bands around 1760–1770 and 1618–1630 cm^{-1} were ascribed to the C=O of ester and ketonic groups, respectively.¹⁵ The absorption bands in the region 3050–3060 cm^{-1} were attributed to the aromatic C–H stretching vibrations, whereas those between 2870 and 2960 cm^{-1} were due to the aliphatic C–H stretching vibrations.

The water regain parameter (α) provides an indirect measurement of the hydrophilic character of resins.¹⁷ A high α may indicate the presence of microporous hydrophilic sites, which provide the water-transport channels required for the effective sorption of metal ions from aqueous solutions. Water regain (α) is calculated from the following relationship:

$$\alpha = \frac{\text{Mass of polymer bound water (g)}}{\text{Mass of dry polymer (g)}}$$

The experimental values were 3.98, 2.97, 2.67, and 2.05 g^{-1} for polymers I, II, III, and IV, respectively. From these values, it is obvious that polymer I had the highest water regain, and the value of α decreased with the increase in crosslinker percentage.

Sorption of the metal ions on the polymers

The sorption of various divalent metal ions on resins I, II, III, and IV as a function of contact time was investigated by a batch equilibration technique at a fixed pH of 6.0 and with a total ionic strength of 0.20M (with sodium perchlorate). Figure 1 shows a typical dependence of metal-ion uptake on contact time for polymer I. The results indicate fast rates of equilibration; about 50–60% of metal-ion uptake was

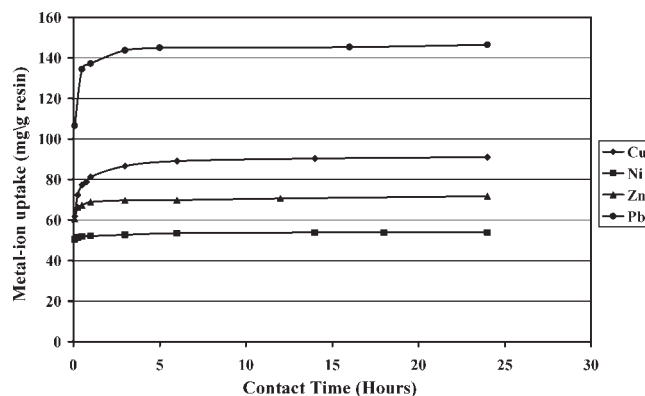


Figure 1 Rate of metal-ion uptake by polymer I as a function of contact time.

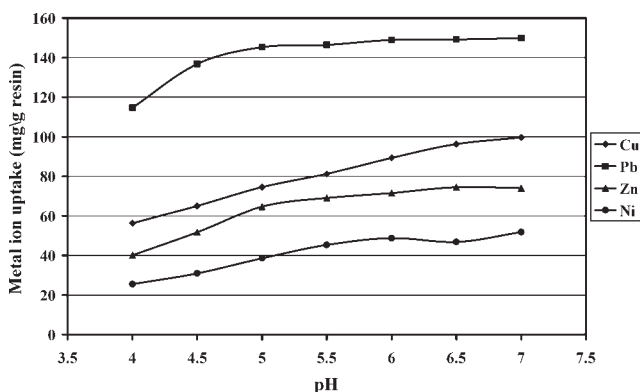


Figure 2 pH binding capacity profiles of metal-ion uptake by polymer I.

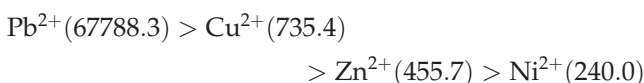
achieved after 1 h, and it reached a steady state after 5–6 h.

The chelation characteristics of polymers are more conveniently compared in terms of the equilibrium distribution coefficient (K_d)¹⁴ defined as

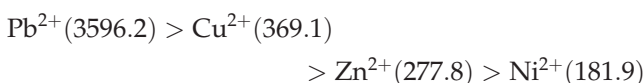
$$K_d = [M]_{\text{resin}}/[M]_{\text{solution}}$$

where $[M]_{\text{resin}}$ is the amount of metal ions taken by 1 g of resin (mg) and $[M]_{\text{solution}}$ is the concentration of metal ions remaining in solution (mg/mL). The calculated values of K_d at a contact time of 24 h were used to compare the metal-ion uptake capacity of the chelate-forming polymers toward various metal ions. The following trends were found on the basis of K_d values (enclosed within parentheses):

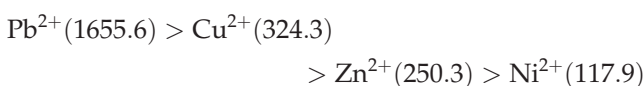
Polymer I:



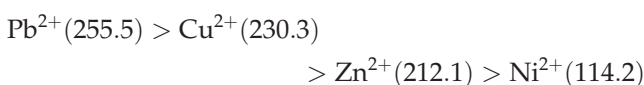
Polymer II:



Polymer III:



Polymer IV:



This trend was attributed to a combination of factors, including the metal–ligand stability constants,

metal-ionic radii, and stereochemical configuration of active chelating sites, among others.¹² Apparently, the formation constant of Pb^{2+} ion–polymer was higher than those of other metal ions; this behavior has also been observed by other researchers.¹⁵

The binding capacities of polymers I, II, III, and IV toward the various divalent metal ions was investigated in the pH range 4.0–7.0 under continuous shaking for a fixed contact time of 6 h at 30°C and at an ionic strength of 0.20M. At higher pH values, the hydrolysis of the metal ions investigated became significant and may have competed with polymer chelate formation. Typical pH binding capacity profiles for polymer I are illustrated in Figure 2. The results reveal that the metal-ion uptake increased with the pH of the medium. This behavior could be explained by the nature of the chelating agent; the hydroxyl group existed in equilibrium, which involved protonated and unprotonated forms in the investigated pH range. Therefore, at higher pH values, the divalent metal ions competed favorably toward donor sites compared with hydrogen ions, in accordance with our recent work.^{6,13} In addition, metal ions were coordinated with these polymers through the oxygen of the carbonyl group and the oxygen of the phenolic –OH group, as suggested by Kaliyappan et al.¹⁵

Effect of the crosslinker on the metal-ion uptake

The effect of crosslinker on the chelation properties of the polymers was investigated by the preparation of polymers containing various amounts of the crosslinker DVB. When we compared the metal-ion uptake capacities of the polymers, we observed that the extent of metal-ion uptake by these polymers toward the investigated divalent metal ions followed the order I > II > III > IV; these results are displayed in Figure 3. The results reveal that the chela-

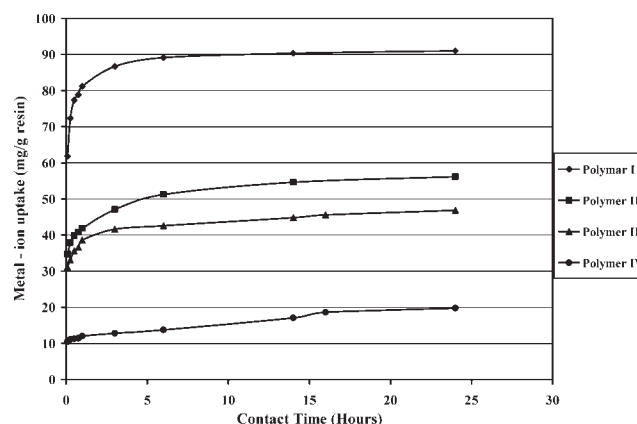


Figure 3 Rate of Cu(II) uptake as a function of contact time for I, II, III, and IV.

tion process was highly affected by the relative amount of crosslinker; polymer **I** (0% crosslinking) displayed the highest metal-ion uptake capacity, whereas polymer **IV** (16% crosslinking) displayed the lowest metal-ion uptake capacity. The decrease in the metal-ion uptake capacity with crosslinking may be explained by the presence of steric hindrance of the DVB crosslinker, which hindered complete coordination with metal ions. This behavior was observed earlier in our laboratory.^{6,13}

CONCLUSIONS

The chelation properties of poly(2H4ABP), obtained through the free-radical polymerization of 2H4ABP monomer, toward some divalent metal ions in aqueous solution were investigated with a batch equilibrium method. The chelation properties of the crosslinked polymers **II–IV**, produced by the addition of certain amounts of the crosslinker DVB during the polymerization process, were also studied under different experimental conditions of contact time and pH. The investigation revealed that polymer **I**, the uncrosslinked polymer, had the highest metal-ion uptake capacity, and the extent of metal-ion uptake followed the order: **I** > **II** > **III** > **IV**.

The effect of exposure time on the metal-ion uptake was also investigated. The results indicate that the rates of metal-ion uptake increased in the first 1–3 h and reached a steady state after about 5–6 h and that 50–60% of the metal ions were taken by the polymers in the 1st hour. The pH binding capacity profiles showed that the metal-ion uptake of the resins increased with increasing pH of the medium and reached a maximum at pH 7.0. The effect

of crosslinking on the sorption properties of the polymers was also studied; the results reveal that the uptake decreased as the amount of crosslinker (DVB) increased.

References

- Hodgkin, J. H. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1985; Vol. 3, p 363.
- Warshawsky, A. In *Critical Reports on Applied Chemistry*; Blackwell Scientific: London, 1987; p 166.
- Kantipuly, C.; Katragadda, S.; Chow, A.; Gesser, H. D. *Talanta* 1990, 37, 491.
- Schmuckler, G. In *Encyclopedia of Polymer Science and Technology*; Interscience: New York, 1976; Vol. 2, p 197.
- Ebraheem, K. A. K.; Mubarak, M. S.; Yassien, Z. J.; Khalili, F. *Solvent Extr Ion Exch* 1998, 16, 637.
- Ebraheem, K. A. K.; Mubarak, M. S.; Yassien, Z. J.; Khalili, F. *Sep Sci Technol* 2000, 35, 2115.
- Al-Gharabli, S. I.; Ebraheem, K. A. K.; Mubarak, M. S. *J. Saudi Chem Soc* 2001, 5, 399.
- Ismail, A. I.; Ebraheem, K. A. K.; Mubarak, M. S.; Khalili, F. I. *Solvent Extr Ion Exch* 2003, 21, 125.
- Ebraheem, K. A. K.; Mubarak, M. S.; Al-Gharabli, S. I. *J Macromol Sci Pure Appl Chem* 2002, 39, 217.
- Salem, N. M.; Ebraheem, K. A. K.; Mubarak, M. S. *React Funct Polym* 2004, 59, 63.
- Al-Rimawi, F.; Ahmad, A. A.; Khalili, F. I.; Mubarak, M. S. *Solvent Extr Ion Exch* 2004, 22, 721.
- Ahmad, A. A.; Al-Rimawi, F.; Khalili, F. I.; Mubarak, M. S. *J. Saudi Chem Soc* 2005, 9, 331.
- Alakhras, F. A.; Abu Dari, K.; Mubarak, M. S. *J Appl Polym Sci* 2005, 97, 691.
- Shafa-Amry, N. N.; Khalili, F. I.; Ebraheem, K. A. K.; Mubarak, M. S. *React Funct Polym* 2006, 66, 789.
- Kaliyappan, T.; Rajagopan, S.; Kannan, P. *J Appl Polym Sci* 2003, 90, 2083.
- Osawa, Z.; Matsui, K.; Ogiwara, Y. *J Macromol Sci Chem* 1967, 1, 581.
- Sugii, A.; Ogawa, N.; Hashizume, H. *Talanta* 1979, 26, 189.