

일반논문

페닐 스티릴 케톤 수지의 합성과 이들의 수용액상의 납(II)과 구리(II) 이온의 흡착에의 응용

Tashfeen Akhtar, Rizwan N. Paracha, Shahid Hameed[†], Nasim H. Rama, and Masud Riaz^{*}

Department of Chemistry, Quaid-I-Azam University, Islamabad-45320, Pakistan

^{*}Applied Chemistry Laboratories, PINSTECH, P. O. Nilore, Islamabad, Pakistan

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Syntheses of Phenyl Styryl Ketone Resins and Their Applications to the Uptake of Lead(II) and Copper(II) Ions in Aqueous Solutions

Tashfeen Akhtar, Rizwan N. Paracha, Shahid Hameed[†], Nasim H. Rama, and Masud Riaz^{*}

Department of Chemistry, Quaid-I-Azam University, Islamabad-45320, Pakistan

^{*}Applied Chemistry Laboratories, PINSTECH, P. O. Nilore, Islamabad, Pakistan

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Abstract : Phenyl styryl ketone ligands 1-5 containing different functional groups were synthesized and attached to the aminated poly(styrene-divinylbenzene) copolymer through diazotization. The coupling of the ligand with polymer was confirmed by FT-IR. The variation of the uptakes of Pb(II) or Cu(II) ions loaded in the prepared polymers (6-10) was examined at different pH values. An increase of metal uptake in the polymers was observed with the increase in pH value in aqueous solution.

Keywords : chelating resins; phenyl styryl ketones; metal ions; uptake.

Introduction

Chelating polymers have been widely used for the recovery of heavy metal ions from aqueous solutions and waste material. Among the heavy metals, lead is the most common contaminant, the major source being tetra-alkyl lead used in vehicle fuel. It is also a threat to the aquatic life.^{1,2}

There are different methods for the attachment of ligands to the polymer backbone for metal uptake purposes. Among these, chemical modification of the base polymer with different functional groups is the most widely used method. Polymer bound ligands like amines, amidoximes, oxazolines and Schiff's bases, have been used for the separation of Zn(II), Pb(II), Fe(II), Hg(II), Mn(II), etc from aqueous solutions at different pH values.^{1,3-5} Ligand bound polymers have also been applied to chromatographic separations.⁶⁻⁸ Keeping in mind the metal binding property of 2-hydroxyacetophenone and 2-hydroxybenzaldehyde derivatives,^{1,4} we synthesized phenyl styryl ketones. The styryl group is expected to increase the electron density on carbonyl oxygen. This may help in complexation of the ligand with metal ions when anchored to the polymer backbone. The electron

density on carbonyl oxygen of phenylstyryl ketone may also be varied by substituting the styryl group with different electron donating and electron withdrawing groups. This led us to the synthesis of ligands 2-5. The ligands were attached to the backbone of poly(styrene-divinylbenzene) (PS-DVB) copolymer through diazotization method. For this purpose, PS-DVB was subjected to nitration and reduction followed by diazo coupling with the ligand (1-5).⁸ The metal uptake studies were carried out for Pb(II) and Cu(II) ions at different pH values.

Experimental

Apparatus and Materials. Poly(styrene-divinylbenzene) copolymer (25% crosslinked) was used as the base polymer. 2-Hydroxyacetophenone was a product of Aldrich. Benzaldehyde, 4-chlorobenzaldehyde, 4-fluorobenzaldehyde, 4-nitrobenzaldehyde and 4-methoxybenzaldehyde were the products of Fluka Chemical Company. Sodium nitrite, Lead(II) acetate trihydrate and Copper(II) acetate monohydrate were obtained from Merck.

The metal uptake studies were carried out using batch method on a flame atomic absorption spectrophotometer (Shimadzu AA670, Japan). Mechanical shaking was carried

[†]To whom correspondence should be addressed.
E-mail: shameed@qau.edu.pk

out using Yamato BT-47 mechanical shaker. FT-IR spectra were recorded on FTX 3000 MX BioRad Excalibur Series IR spectrophotometer.

Synthesis of Phenyl Styryl Ketones (1-5).⁹ A solution of sodium hydroxide (80 mL, 10%) was added to 60 mL of absolute ethanol in a conical flask and cooled in an ice bath to 0 °C. Freshly distilled 2-hydroxyacetophenone (0.028 mol) was added and the mixture stirred for half an hour at this temperature. Benzaldehyde/4-substituted benzaldehyde (0.028 moles) was then added and the mixture stirred vigorously for 2-3 h. The reaction mixture was kept at 0 ~5 °C overnight. The thick oil obtained was diluted with chilled water and neutralized with 6 N hydrochloric acid. The product was obtained as a yellow precipitate. The precipitate was filtered and recrystallized from aqueous ethanol. The physical and IR data of these compounds is tabulated in Table 1.

Nitration of PS-DVB. Poly(styrene-divinylbenzene) copolymer (10 g, 25% crosslinked) was added to 100 mL of nitrating mixture at 0 °C. The reaction vessel was cooled in an ice bath, stirred for 30 min with a mechanical stirrer and the temperature increased gradually to 60~70 °C. The stirring was continued until the evolution of yellow fumes ceased. The reaction mixture was then poured into one liter of ice cooled water in small portions. The polymer was filtered and washed with 0.1 M sodium hydroxide solution followed by distilled water. The nitrated polymer was dried for 24 h in drying pestal under vacuum over phosphorous pentaoxide. The colour of the nitrated poly(styrene-divinylbenzene) copolymer was bright yellow. IR (KBr, cm⁻¹) : 3080, 2924, 1603, 1522, 1347, 698.

Reduction of Nitrated PS-DVB. A mixture of SnCl₂ · 2H₂O (130 g), hydrochloric acid (130 mL) and ethanol (150 mL) was taken in a 1 L three-neck round bottomed flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer. Nitrated PS-DVB copolymer (10 g) was added and

refluxed with stirring for 24 h. The bright brown product was filtered and washed with distilled water, 0.1 M sodium hydroxide and again with distilled water till the filtrate was neutral to litmus. It was dried for 24 h in a drying pestal under vacuum over phosphorous pentaoxide. IR (KBr, cm⁻¹): 3474, 3415, 2921, 1618.

Diazotization of Aminated PS-DVB. A mixture of 25 mL distilled water and 25 mL hydrochloric acid was cooled in an ice salt mixture to 0 °C. Aminated poly(styrene-divinylbenzene) copolymer (5.0 g) was added with constant stirring. A solution of 7.0 g of sodium nitrite in 20 mL distilled water was prepared separately and added drop wise over a period of 45 min while the reaction temperature was maintained below 0 °C. After addition of about 10 mL of sodium nitrite solution brown fumes of nitrous oxide were observed. The reaction mixture was stirred for an additional one hour at 0 °C. The polymer was immediately filtered and washed with ice cold water, containing few grams of sodium chloride till the washings were neutral to litmus. The diazotized poly(styrene-divinylbenzene) copolymer was subjected to diazo-coupling reaction.

Coupling with the Ligands. A solution of 3.6 g of sodium hydroxide in 25 mL of water was taken in a beaker and 0.022 mol of the ligand were added. The mixture was cooled to 0 °C, freshly prepared diazotized polymer was added and stirred for 10 min at 0 °C. Stirring was continued for 30 min as the temperature reached 10 °C. The polymer after filtration was washed with water, methanol and acetone one after the other and was dried at 80 °C for 18 h. The condensation of the ligands with polymer was confirmed by IR spectroscopy (Table 2).

Metal Uptake Studies.

Preparation of Samples : Lead(II) acetate and Copper(II) acetate were used as source of Pb(II) and Cu(II) ions, respectively. A 100 ppm solution of Pb(II) ions was prepared by dissolving 0.046 g of Pb(II) acetate, 3H₂O in 500 mL of

Table 1. Physical and IR Data of Phenyl Styryl Ketones (1-5)

| Compound | mp (°C) | Yield (%) | IR Absorptions (cm ⁻¹) | | | | |
|--|---------|-----------|------------------------------------|------|------|------|------------|
| | | | -O-H | =C-H | C=O | C=C | R |
| 1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (1) ¹⁰ | 78 | 80 | 3472 | 3058 | 1658 | 1515 | -- |
| 1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (2) ¹¹ | 110 | 79 | 3315 | 3049 | 1637 | 1495 | 1190 |
| 1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3) ¹¹ | 135 | 75 | 3375 | 3041 | 1651 | 1496 | 1526, 1345 |
| 3-(4-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (4) ¹⁰ | 142 | 73 | 3460 | 3034 | 1652 | 1578 | 715 |
| 3-(4-Fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (5) ¹⁰ | 130 | 70 | 3396 | 3048 | 1657 | 1573 | 1135 |

Table 2. IR Spectral Data of PS-DVB-Phenylstyrylketone Resins (6-10)

| Polymer | IR Absorptions (cm ⁻¹) | | | | | |
|---|------------------------------------|------|------|------|------|------------|
| | OH | CH | CO | C=C | N=N | C-R |
| PS-DVB-Phenylstyrylketone Resin (6) | 3256 | 3053 | 1640 | 1567 | 1470 | -- |
| PS-DVB-Phenylmethoxystyrylketone Resin (7) | 3293 | 3034 | 1637 | 1495 | 1482 | 1183 |
| PS-DVB-Phenylnitrostyrylketone Resin (8) | 3375 | 3041 | 1639 | 1543 | 1495 | 1516, 1348 |
| PS-DVB-Phenylchlorostyrylketone Resin (9) | 3490 | 3047 | 1635 | 1567 | 1470 | 704 |
| PS-DVB-Phenylflourolstyrylketone Resin (10) | 3460 | 3057 | 1650 | 1556 | 1491 | 1158 |

distilled water. Similarly, a 100 ppm solution of Cu(II) ions was prepared by dissolving 0.268 g of Cu(II) acetate.H₂O in 500 mL of distilled water.

Metal Ion Uptake Experiments : Metal ion uptake experiments using batch method were carried out by adding 0.30 g of the resin to 25 mL of metal ions solution. The contents of the flask were shaken with a Yamato BT-47 mechanical shaker (110 strokes per minute) at 25 °C for 24 h. The polymer was filtered and the metal uptake was studied on flame atomic absorption spectrophotometer. In order to get the accurate value of metal ions uptake blank references for each pH were also studied and the exact amount of metal ions determined by using the equation:

$$\text{Metal ions Conc.} = \text{Conc. in blank sample} - \text{Conc. in polymer sample}$$

Studies of the Effect of pH on Metal Uptake : The metal uptake experiments were performed at different values of pH using the above procedure. The pH was controlled using acetic acid/sodium acetate buffer.

Results and Discussion

Metal Uptake Studies. The solutions of Pb(II) and Cu(II) ions were prepared as described in the experimental section. The metal uptake of PS-DVB-phenylstyrylketone resin (6) was studied for these ions at three different values of pH (*i.e.* 3.4, 4.4, and 5.2). It was observed that the metal uptake for both the ions decreases with a decrease in pH. In case of Pb(II) ions the metal uptake was 96.34% at pH 5.2 which decreases to 31.85 % at pH 4.4 and 12.01% only at pH 3.4 (Table 3). It appears that the synthesized polymer has a better chelating property for Pb(II) ions as compared to Cu(II) ions as indicated by the metal uptake of the latter which at pH 5.2 is only 23.15%. However, the decreasing trend in metal uptake with decreasing pH was also observed in case of Cu(II) ions, the uptake being 15.48% and 0.6% at pH 4.4 and 3.4, respectively.

To study the effect of variation of electron density on metal complexation, polymers 7-10 having different electron densities on carbonyl oxygen were synthesized and their

Table 3. Metal Uptake of Pb(II) and Cu(II) Ions at Different pH Values

| Polymer | Pb(II) Ions [ppm(%)] | | | Cu(II) Ions [ppm(%)] | | |
|---------|----------------------|---------|---------|----------------------|---------|---------|
| | pH 3.4 | pH 4.4 | pH 5.2 | pH 3.4 | pH 4.4 | pH 5.2 |
| 6 | 6.15 | 16.41 | 46.93 | 0.21 | 6.36 | 7.96 |
| | (12.01) | (31.85) | (96.34) | (0.6) | (15.48) | (23.15) |
| 7 | 11.39 | 17.08 | 48.18 | 0.60 | 10.48 | 31.09 |
| | (22.32) | (33.15) | (98.91) | (1.73) | (25.52) | (90.43) |
| 8 | 26.05 | 25.21 | 45.74 | 0.26 | 10.25 | 21.44 |
| | (51.06) | (48.94) | (93.90) | (0.75) | (24.96) | (62.36) |
| 9 | 20.88 | 27.10 | 48.06 | 1.34 | 16.28 | 31.35 |
| | (40.93) | (52.61) | (98.66) | (3.88) | (39.65) | (91.18) |
| 10 | 14.55 | 19.89 | 48.05 | 0.71 | 11.28 | 31.68 |
| | (28.52) | (38.61) | (98.64) | (2.05) | (27.47) | (92.14) |

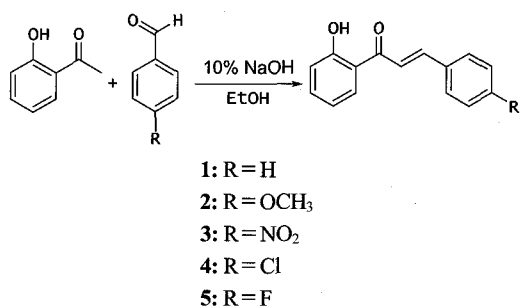
metal uptake studied. It was observed that by increasing the electron density on carbonyl oxygen of the ligand, the metal uptake for Pb(II) ions increased slightly. The values being 98.91, 98.66, and 98.64% at pH 5.2 for polymers 7, 9, and 10 having methoxy, chlorine, and fluorine substituents, respectively. The values for different substituents are comparable, for methoxy substituent being slightly higher. This is consistent with the higher electron donating ability of the oxygen atom as compared to halogens. It was also observed that substitution by a nitro group (lower electron density on carbonyl oxygen) in 8 resulted in a decrease in metal uptake (93.90%) as expected. In case of Cu(II) ions maximum uptake at pH 5.2 was observed for polymer 10 being 92.14% followed by 91.18% and 90.43% by polymers 9 and 7, respectively.

Although, to the best of our knowledge, the synthesis and uptake studies of the polymers with phenylstyryl ketone ligands anchored to the polymers have not been reported in the literature, there have been reports^{1,4} on the synthesis and uptake studies by the polymers bearing 2-hydroxyphenylcarbonyls as pendant groups. Furthermore, the uptake values for Pb(II) ions by our synthesized polymers are higher when compared to these earlier reports⁵ showing a maximum of 90% uptake of Pb(II) ions. The metal uptake values for Cu(II) ions by our polymers are only slightly inferior when compared to the earlier reported^{12,13}

best values of 95% for these metals.

Synthesis and Characterization of Ligands and Coupling to PS-DVB. The synthesis of ligands 1-5 was carried out by the reaction⁹ of *o*-hydroxyacetophenone and the corresponding benzaldehyde in presence of 10% NaOH solution in ethanol (Scheme 1).

In order to anchor the synthesized ligands to PS-DVB copolymer, the method of diazotization was adopted. For this purpose, PS-DVB copolymer was nitrated using nitrating mixture (75% HNO₃ and 25% H₂SO₄). In FT-IR spectrum, the assym-NO₂ stretching at 1522 cm⁻¹ and symm-NO₂ stretching at 1347 cm⁻¹ were evident for NO₂ substitution of PS-DVB copolymer. The nitrated PS-DVB copolymer was reduced using SnCl₂·2H₂O and HCl. The conversion of nitro group to amino was indicated in the FT-IR spectrum by the appearance of NH₂-stretching vibration at 3474 cm⁻¹ and 3415 cm⁻¹ and disappearance of symmetric and asymmetric NO₂ stretching vibrations. The primary N-H bending was observed as a very sharp peak at 1618 cm⁻¹. Aminated PS-DVB was first subjected to diazotization and then coupled with ligands 1-5 using standard literature

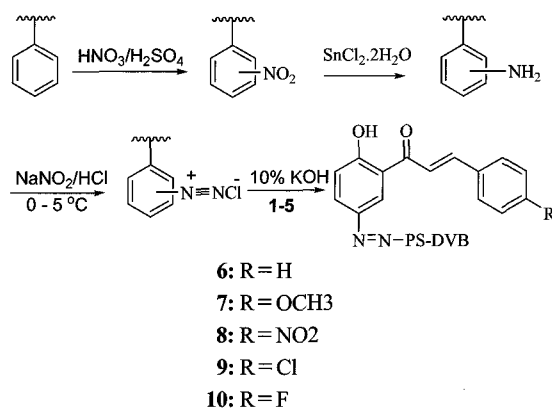


Scheme 1. Synthesis of ligands.

procedure¹⁴ (Scheme 2). The coupling of these ligands with the polymer was confirmed in the IR spectra by the appearance of -N=N- stretching vibrations in the region 1470~1495 cm⁻¹. A sharp peak in the region of 1637~1650 cm⁻¹ was attributed to the stretching vibrations of carbonyl group present in the ligands. A representative FT-IR spectrum of 8 is presented in the Figure 1.

Conclusions

Phenyl styryl ketones containing different substituents were successfully anchored onto the polymer backbone. The effect of pH on metal uptake of Pb(II) and Cu(II) ions in aqueous solutions was studied and an increasing trend for metal uptake with increase in pH was observed. The ligands with halogen atom and methoxy group in conjugation with the carbonyl showed somewhat better uptake for Pb(II)



Scheme 2. Fabrication of phenyl styryl ketone resins from PS-DVB copolymer.

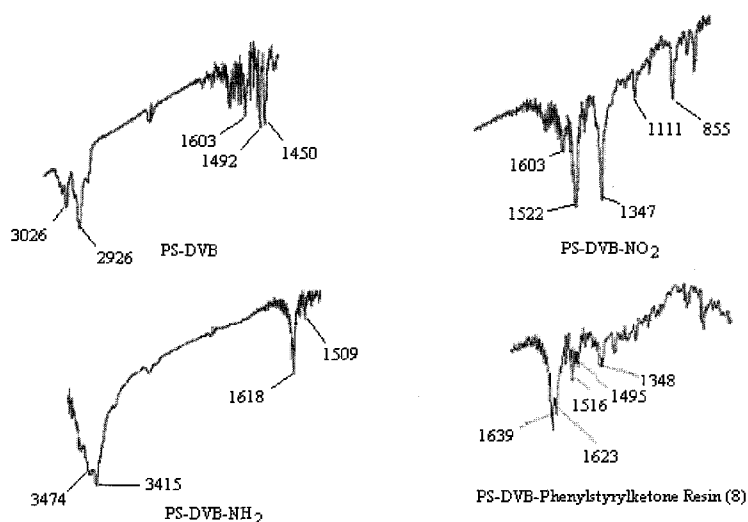


Figure 1. Comparison of FT-IR spectra of fabricated polymers.

and Cu(II) ions as compared to unsubstituted and nitro containing ligands. However, the metal uptake by polymers containing halogen atoms and methoxyl group in the ligand was comparable indicating that there is no prominent effect of increasing the electron density on carbonyl oxygen. It was observed that all the polymers exhibit better binding properties for Pb(II) ions as compared to Cu(II) ions.

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