

**Synthesis and characterization of polymeric
mono aza dibenzo 18-crown-6**

Abstract

The synthesis and characterization of immobilized mono aza dibenzo-18-crown-6 ether on XAD-4 resin, Merrifield resin, Polyacryloyl chloride and Polymethacryloyl chloride, by attaching with nitrogen of mono aza dibenzo 18-crown-6 ether is described. Mono aza dibenzo 18-crown-6 was synthesized by etherification reaction between catechol and bis (2-chloro ethyl) ether. This open crown ether was further reacted with N-tosyl ditosylate of diethanol amine. The synthesized mono aza dibenzo 18-crown-6 ether was chemically attached with functionally modified polymers viz. chloroformoyled XAD-4 resin, Merrifield resin (chloromethylated polystyrene resin), poly(acryloyl chloride) and poly(methacryloyl chloride). The synthesized polymeric aza crown ethers sorbent were characterized by FT-IR spectral technique.

INTRODUCTION

Polymer supported reagents capable of complexing targeted metal ions from aqueous solutions are important for environmental remediation and for use as sensors^{1,2}. There are many polymers used as solid support in column chromatographic materials as sorbent with macrocyclic compounds³. Many scientists have synthesized ion selective crown ether polymers³⁻⁶ but very little attention is paid to synthesis and characterization of aza crown polymer⁷⁻⁹.

Immobilizing aza crown ethers onto cross linked polymers can combine the aza crown's selectivity with the polymer's ease of recovery and recyclability. In case of crown ether there are three principal methods by which these macrocycles can be incorporated in to polymer matrices. The first mode is direct polymerization of the crown ether through a step-growth mechanism; the second mode is polymerization through a chain-growth mechanism and the third mode is post functionalization wherein crown ether is covalently bounded to pre-formed polymer backbone. The last method requires the crown to have a reactive functional group that can bond to the polymer. Various types of neutral polymers such as Amberlite XAD-4 resin¹⁰, polymeric fiber¹¹ and amborsorb¹² have been used as solid supports with ligand as well as with macrocycles. They have no selectivity for metal ions but good surface area and pore size suitable for functionalization and are routinely used for attaching various ligands. Chemical modification is always essential to enhance the selectivity and efficiency of separation of the polymeric adsorbents.

A new type of promising polymers are prepared by the combination of aza crown ether with different polymers that have the remarkable properties of complexation with cations especially alkali and alkaline^{13,14}, and also with some heavy metal ions like Cu(II), Ni(II), Pd(II),

Co(II)^{15,16}. Due to their unique ability to form stable complexes with various cations, the prepared polymers were used for preconcentration and separation of metal ions using solid phase extraction. The efficiency of the polymeric aza crown ethers for the selective separation of metal ions prompted us to prepare a few new macrocyclic polymeric adsorbents. Hence, in the present investigation mono aza dibenzo 18-crown-6 has been synthesized and coupled with various polymers. The XAD-4 [mono aza dibenzo 18-crown-6] (XAD-4[MADB18C6]) has been synthesized by chloroformoyled XAD-4 resin and mono aza dibenzo 18-crown-6 in presence of triethylamine, while Merrifield[mono aza dibenzo 18-crown-6] sorbent has been synthesized by reaction of Merrifield resin (chloromethylated polystyrene). Poly acrylo-[mono aza dibenzo 18-crown-6] (PA-MADB18C6) has been synthesized by coupling of poly(acryloyl chloride) and mono aza dibenzo 18-crown-6 (PM-MADB18C6) and the polymer polymethacrylo-[mono aza dibenzo 18-crown-6] has been synthesized by reaction of poly(methacryloyl chloride) and mono aza dibenzo 18-crown-6. The synthesized compounds were purified and characterized by FT-IR spectra.

Experimental

Chemical and Reagent

All the chemicals used were A.R. grade of BDH or Merck or Ranbaxy unless otherwise specified.

Apparatus

Melting points are taken in sealed capillary tube using Toshniwal (India) melting point apparatus and are uncorrected. Infrared spectra are obtained on FT-IR/Bruker Tensor 27 spectrometer. UV spectra are obtained on Hitachi 3210 spectrophotometer.

Synthesis of bis (2-chloro ethyl) ether

A mixture of 47 g (0.44 mol) diethylene glycol, 250 mL benzene and 77 mL (1.0 mol) pyridine was heated to 86 °C and refluxed. Then 116 gm (1.0 mol) thionyl chloride was added drop wise with stirring in a period of 3 h. The mixture was heated for another 16 h and was then acidified with 2 M hydrochloric acid. The upper benzene layer was distilled and the fraction between 170-180 °C was collected. The distillate was collected; bp 178 °C, yield 50 g (81 %). Reported²⁶, bp 178 °C, yield (84%)

Synthesis of bis [2-(o- hydroxyl phenoxy) ethyl] ether

A mixture of bis (2-chloroethyl ether) 143 g (1 g/mol), catechol 220 g (2 g/mol) and 80 g (2 g/mol) sodium hydroxide was added in 2000 mL of water under nitrogen atmosphere. The biphasic system was refluxed at 102°-103 °C for 24 h and then the mixture was acidified with concentrated hydrochloric acid. The unreacted bis (2-chloro ethyl ether) and 1000 mL water was removed by distillation, the mixture was separated into two layers. The organic layer was recovered and treated with 700 mL methanol and chilled ice water. On cooling precipitates of the

product were obtained which were purified by recrystallisation in methanol; mp 85 °C and yield 67 to 74 g(23 to 25.5 %) ²⁷.

Synthesis of N-tosyl diethanol amine

In a 500 mL of three necked round bottom flask equipped with condenser and mechanical stirrer, a mixture of diethanol amine 42 g (0.4 mol) and powdered potassium carbonate 55 g (0.4 mol) in 300 mL water was heated at 70 °C for 30 min and then tosyl chloride 100g (0.4 mol) was added in little portions at maintained temperature. The mixture was further refluxed for 1h at 100 °C and was poured over ice with agitation, which resulted the precipitation of the product. The product was crystallized from methanol. mp 99-100 °C, yield 100 gm (78 %), reported²⁸ mp 100 °C.

Synthesis of ditostylate of N-tosyl diethanol amine

N-tosyl diethanol amine 92.5 g (0.357 mol) was dissolved in 600 mL of pyridine. The solution was stirred with mechanical stirrer at -10 °C in ice-salt bath, and tosyl chloride 136.1 g (0.722 mol) was added at such a rate so that the temperature was maintained below -8 °C. The reaction mixture was stirred for 1 h, the product obtained was refrigerated overnight, and poured in to 500 mL of slury of ice and 6 N Hydrochloric acid. Dichloro ethyl ether was added, and the layers were separated. The organic layer was washed with 6 N hydrochloric acid (3×50 mL) and water (2 × 50 mL) and evaporated to dryness in vacuum. The product was obtained as golden oil and triturated with methanol which solidified after 30 min. Recrystallisation from methanol gave 150.2 g (74 %) of a white solid with mp 96-98 °C reported²⁹.

Synthesis of N-tosyl mono aza dibenzo 18-crown-6

Bis [2-(o-hydroxy phenoxy) ethyl] ether 29 g (0.1 mol) and 28 g potassium carbonate powder was added in 500 mL acetonitrile. Ditosylate of N-tosyl diethanol amine 19 g in 100 mL acetonitrile was added in 3 h at regular interval. The mixture was refluxed for 18 h. The solvent was distilled out in vacuum and product redissolved in hot ethanol, obtained product was triturated white powder obtained was again recrystallised in ethanol gave 20 g (63%) of a white solid with mp 208-209 °C. The results obtained for elemental analysis $C_{27}H_{31}NO_7S$ (MW 513), C, 63.12; H, 6.05; N, 2.71; S, 6.25 % is comparable to the calculated values of C, 63.14; H, 6.08; N, 2.73; S, 6.24%.

Detosylation of N-tosyl mono aza dibenzo 18-crown-6

In a 100 mL of round bottom flask take mixture of N-tosyl mono aza dibenzo 18-crown-6 (10 g, 19 mmol) and 10 mL 4 M sulfuric acid and was heated at 60 °C for 30 min. The mixture was neutralized with saturated sodium bicarbonate solution. Precipitated product was washed thoroughly with water and recrystallised with ethanol; gave 4.0 g (57%) of white solid mp 170-172 °C. The results obtained for elemental analysis of $C_{20}H_{25}NO_5$ (MW 359) C, 66.82; H, 7.00; N, 3.91 % is comparable to the calculated values of C, 66.83; H, 7.01; N 3.90%.

Synthesis of XAD-4 [mono aza dibenzo 18-crown-6] sorbent

Synthesis of acetyl XAD-4

In to a 250 mL three necked round bottom flask, acetylation of 15 g XAD-4 with 16.5 mL (0.232 mol) acetyl chloride was carried out by the Friedel-Crafts method using 17.2 g (0.129 mol) anhydrous $AlCl_3$ in 150 mL 1,2 dichloromethane. The reaction mixture was stirred for 2h at 35 °C quenched by pouring it in to a mixture of crushed ice, and was acidified with concentrated hydrochloric acid. After 8 h the resin was filtered and rinsed with methanol, water

and finally with methanol and dried in oven. The result obtained for elemental analysis C, 82.16; H, 6.89; O, 10.94% is comparable to the calculated values of C, 82.13; H, 6.85, O, 10.94%, yield 94.48 reported⁵.

Synthesis of carboxy XAD-4

About 10 g of acetylated XAD-4 resin was taken in to a 250 mL of round bottom flask and was refluxed with 12% of aqueous solution of sodium hypochlorite for 12 h. The reaction mix was further acidified with hydrochloric acid to give dark yellow coloured resin, which was filtered and thoroughly rinsed with water until free from chloride ions. It was further washed with methanol and dried overnight in oven. The results obtained for elemental analysis C, 72.96; H, 5.43, O 21.60. % was comparable to calculated values of C, 72.95, H 5.44, O, 21.58%, yield 86%.

Synthesis of chloroformoyl XAD-4

In a three necked flask 8 g carboxy XAD-4 was refluxed with 8 mL of (0.110 mol) thionyl chloride at 70-75 °C with intermittent stirring. The chloroformoyl XAD-4 was isolated and washed with diethylether and dried. The result obtained for elemental analysis C, 64.88; H, 4.23; Cl, 21.28; O, 9.60. Is comparable to the calculated value C, 64.87, H, 4.23; Cl, 21.28; O, 9.59 %. Yield 86%.

Synthesis of XAD-4 [mono aza dibenzo 18-crown-6]

In a 500 mL three necked round bottom flask was placed 200 mL of dry toluene and 2 mL of triethylamine and then 0.1 g (2.38 m mole) of mono aza dibenzo 18-crown-6 in a 50 mL of dry toluene was added slowly through a funnel along with 1.5 g (2 m mole) of chloroformoyl XAD-4 resin in 50 mL of dry toluene through another funnel. After the mixture

was stirred for 72 h at 80 °C, the residue was washed with water to remove triethylamine hydrochloride and the resin was collected by filtering. The final product was rapidly washed from benzene and dried in vacuum. The results obtained for elemental analysis C, 71.15; H, 6.38; N, 2.86; O, 19.61 % is comparable to the calculated value of C 71.14; H.6.38; N, 2.85; O, 19.60 %.

Synthesis of sorbent 2

Merrifield resin [mono aza dibenzo 18-crown-6]

In to a dry 500 mL of four neck round bottom flask, taken 200 mL of dry toluene and 2 mL of triethylamine and placed slowly 1.5 g (2.085 m mole) of mono aza dibenzo 18-crown-6 in a 50 mL of dry toluene through one funnel and 2.0 g (2.72 m mole) of Merrifield resin in 50 mL of dry toluene through another funnel. Then, the mixture in presence of N₂ gas was stirred for 72 h at 80 °C. After the completion of the reaction the residue was washed with water to remove triethylamine hydrochloride and evaporated to dryness in vacuum. It gives pale yellow resin bead. The result obtained for elemental analysis C, 73.24; H, 6.99; O, 17.68 % is comparable to the calculated value C, 73.22; H, 6.89; O, 17.68 %.

Synthesis of sorbent 3

Synthesis of poly(acryloyl chloride)

A mixture of 3 g of poly (acrylic acid) and 6 mL of thionyl chloride was refluxed for 20 h. The excess of thionyl chloride was removed under reduced pressure. The result obtained for elemental analysis C, 39.81; H, 3.34; Cl, 39.17; O, 17.68 % was comparable to the calculated value C,39.80; H, 3.34; Cl, 39.16; O, 17.66 %.

Synthesis of poly acrylo-mono aza dibenzo 18-crown-6 ether

In a 250 mL of tree necked round bottom flask equipped with mechanical stirrer, 2 g of mono aza dibenzo 18-crown-6 in a 100 mL of toluene and a suspension of 2.47 g of sodium bicarbonate in 20 mL of water were added. The mixture was stirred and 2 g of poly (acryloyl chloride) was added over 20 min. The stirring was continued for 12 h at 110 °C. The residue thus obtained was washed with water and dried over phosphorous pentoxide. The result obtained for elemental analysis C, 66.81; H, 6.58; O, 23.22 % was comparable to the calculated value 66.80; H, 6.57; O, 23.21 %, yield 74%.

Synthesis of sorbent 4

Synthesis of poly(methacryloyl chloride)

A 100 mL round bottom flask equipped with a stirrer, condenser and thermometer is charged with 30 mL of methacrylic acid and 10 mL of phosphorous trichloride. This agitated mixture was then kept at 60-70 °C for 15 min and finally at room temperature for 2 h. After cooling the mixture was separated in to two layers. The upper layer was removed and after the addition of 0.5 g of cuprous chloride the solution was distilled under vacuum at room temperature.

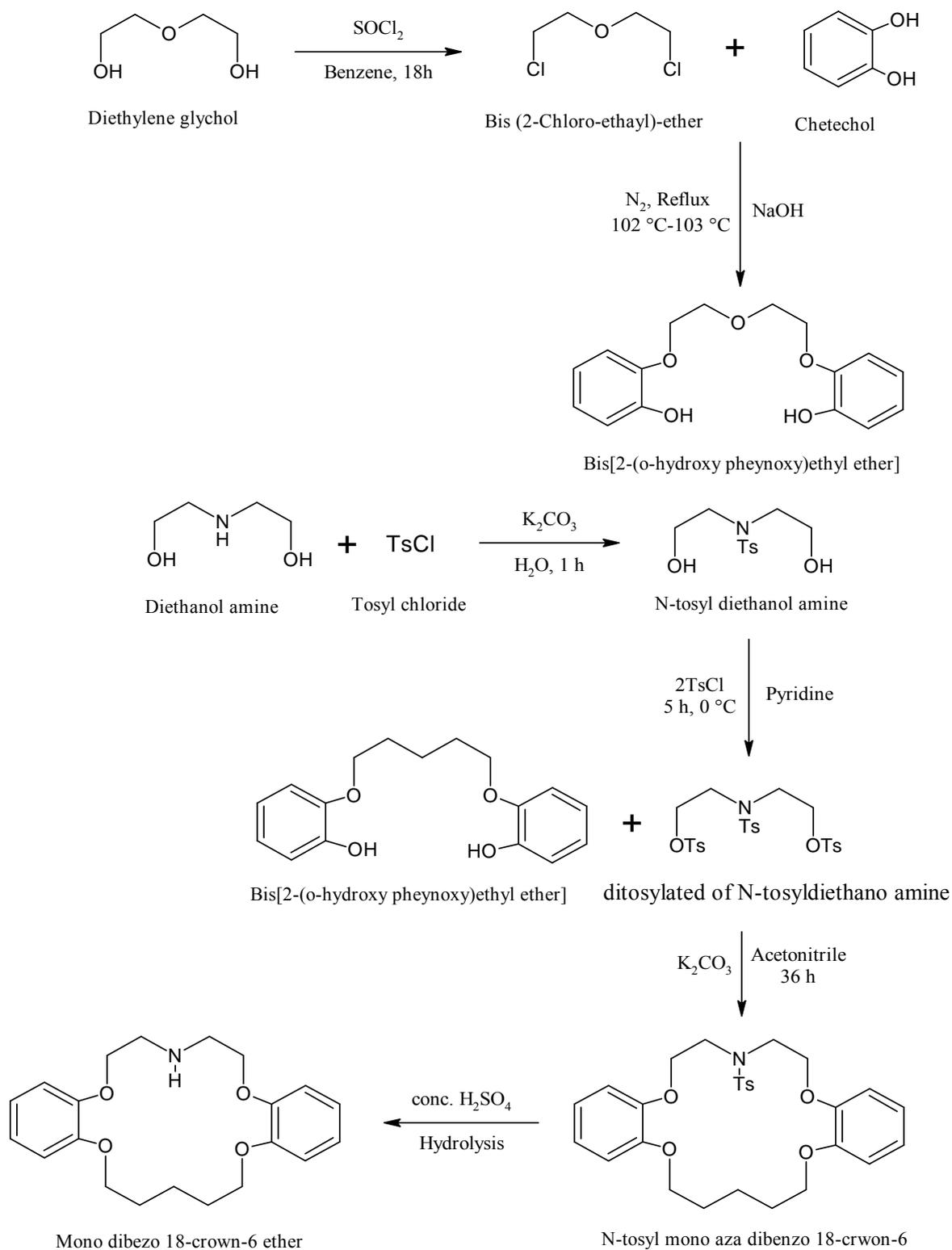
In a 100 mL of round bottom flask equipped with reflux condenser and mechanical stirrer were added 10 mL of methacryloyl chlorides, 27 mL of toluene and cyclohexane (1.9 v/v) mixture and 0.3 g of azobisisobutyronitrile. The contents were kept at 70 °C for 12 h. The excess solvent was decanted from the obtained solid polymer, the polymer was then completely removed under reduced pressure. The solid polymer poly (methacryloyl chloride) thus obtained was dried in oven. The results obtained for elemental analysis C, 45.96;

H, 4.82; Cl, 33.91; O, 15.31 % was comparable to the calculated value C, 45.95; H, 4.81; Cl, 33.89; O, 15.32 %.bp 95-96 °C, yield 70 % reported⁶.

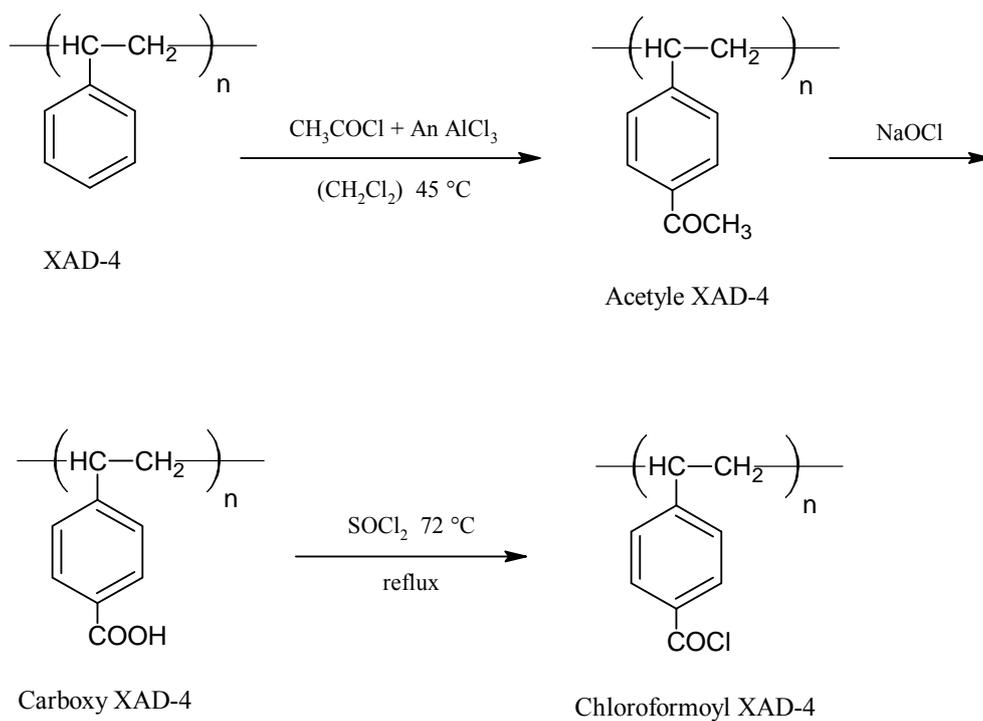
Synthesis of polymethacrylo-mono aza dibenzo 18-crown-6 sorbent

In a 250 mL three necked flask, equipped with mechanical stirrer was placed 3.54 g (4.92 m mol) of mono aza dibenzo 18-crown-6 ether in 50 mL of toluene, an aqueous suspension of 5.3 g sodium bicarbonate in 10 mL of water was added 3.0 g poly(methacryloyl chloride) in small portions at regular intervals. The mixture was stirred at 110 °C for 18 h. After completion of the reaction 200 mL of distilled water was added. Further the mixture was stirred for 10 min. The residue was filtered and washed with water and dried it 200 °C in oven. The result obtained for elemental analysis C, 67.43; H, 6.84; N, 3.28; O, 22.46 was comparable to the calculated value C, 67.42; H, 6.86; N, 3.27; O, 22.45, yield 67%.

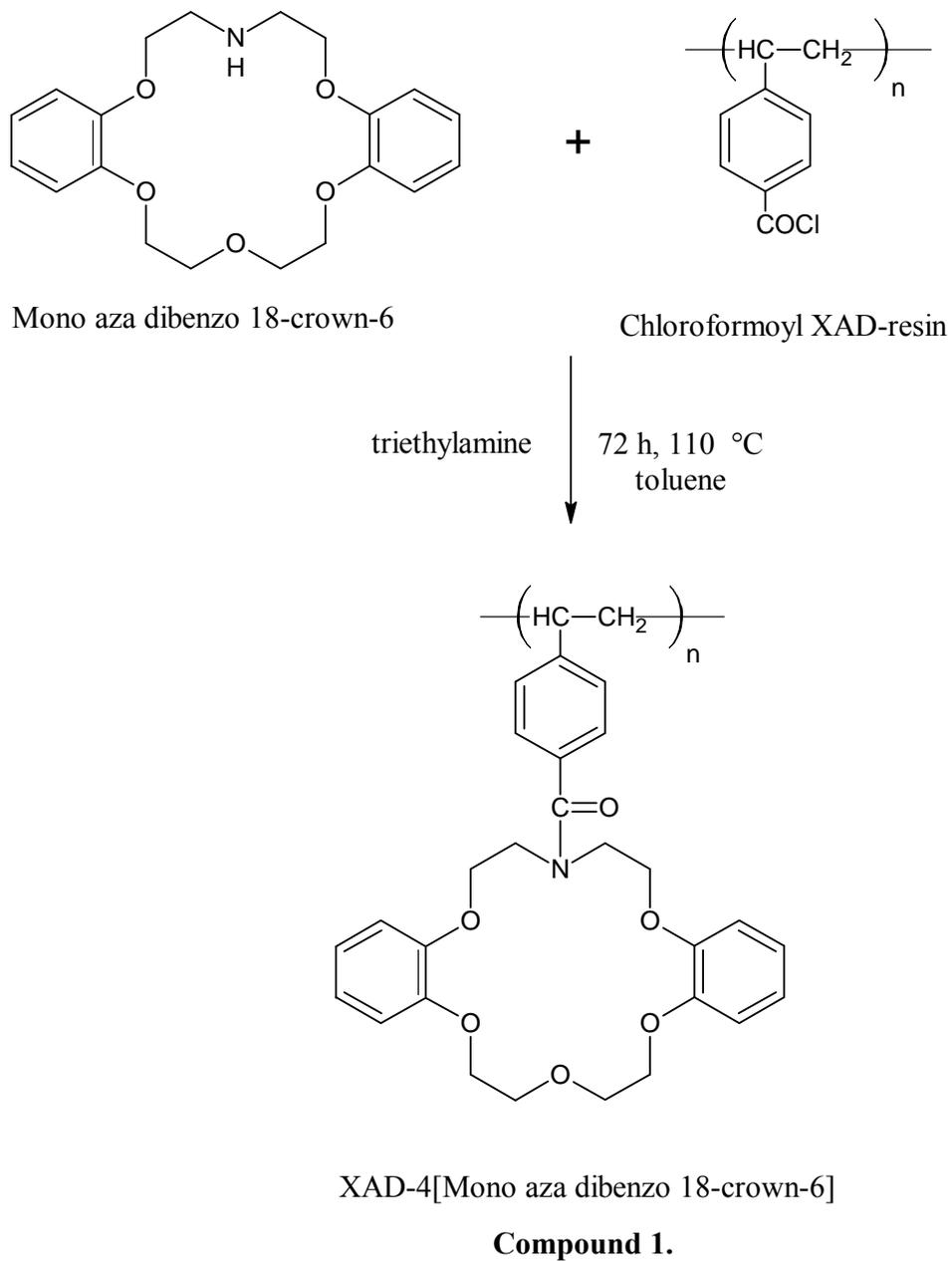
Scheme 1. Synthesis of mono aza dibenzo 18-crown-6 ether



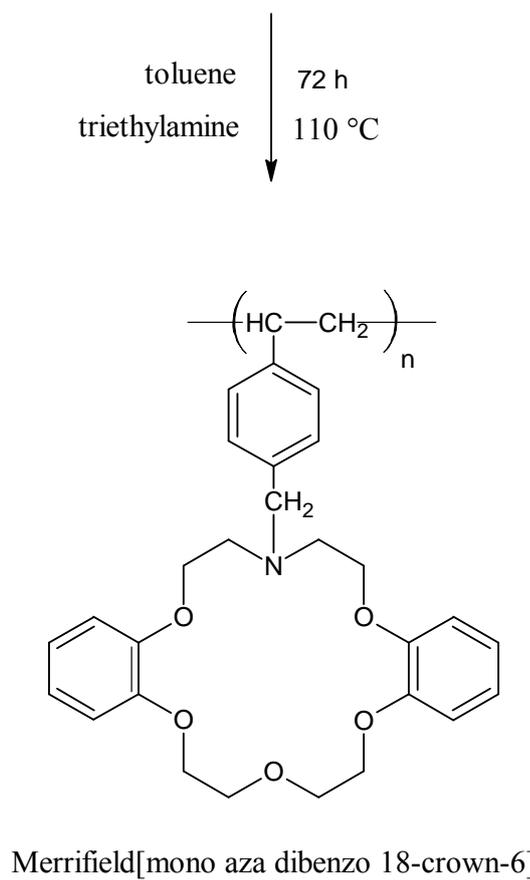
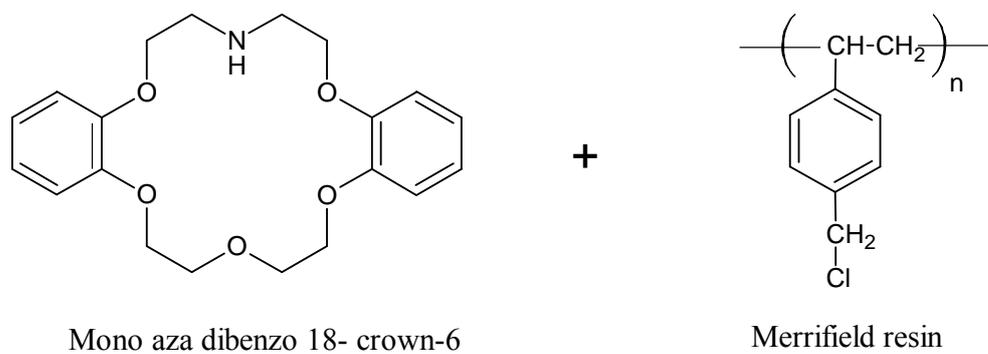
Scheme 2. Synthesis of Chloroformoyl XAD-4



Scheme 3. Synthesis of XAD-4[mono aza dibenzo 18-crown-6]

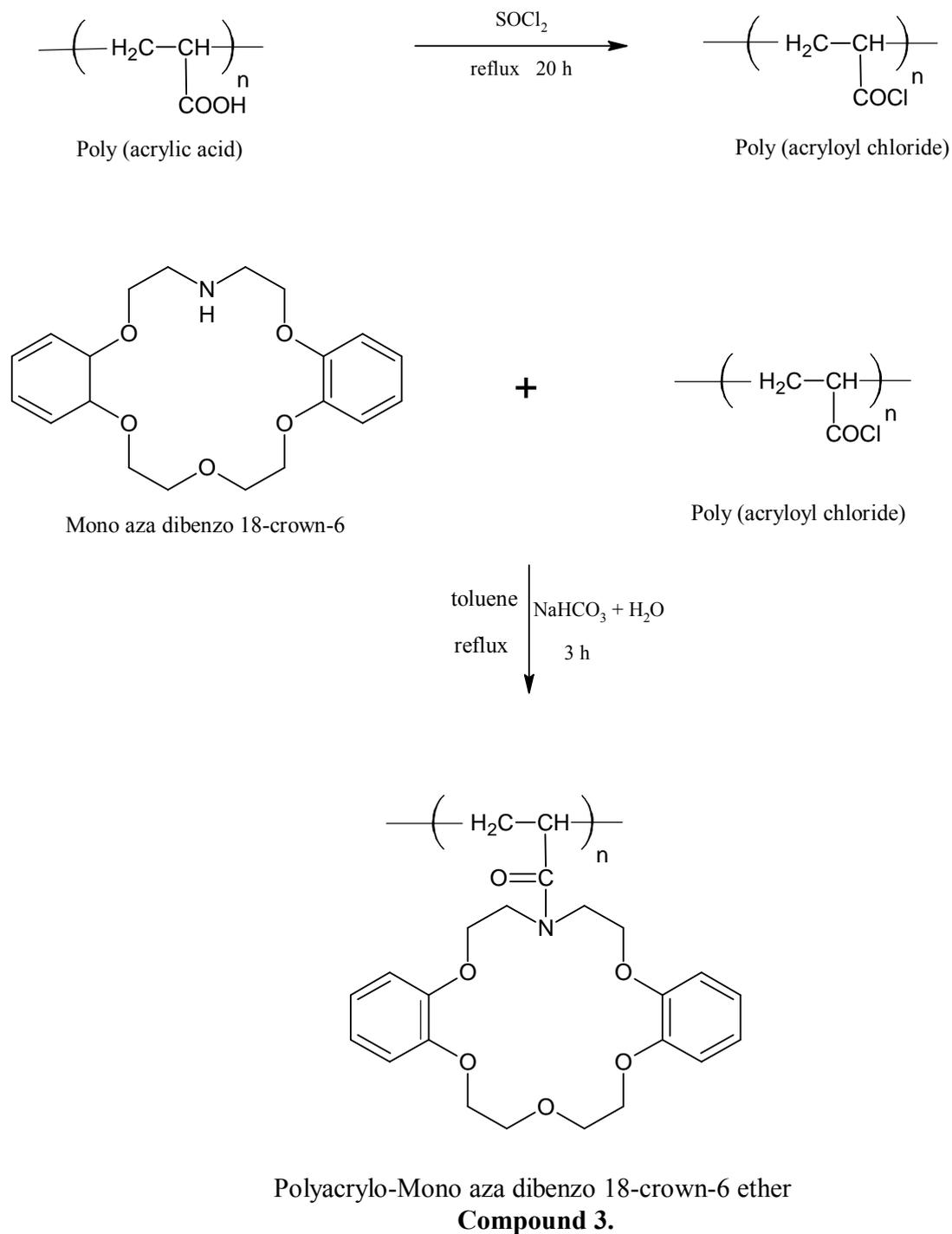


Scheme 4. Synthesis of Merrifield[mono aza dibenzo 18-crown-6]

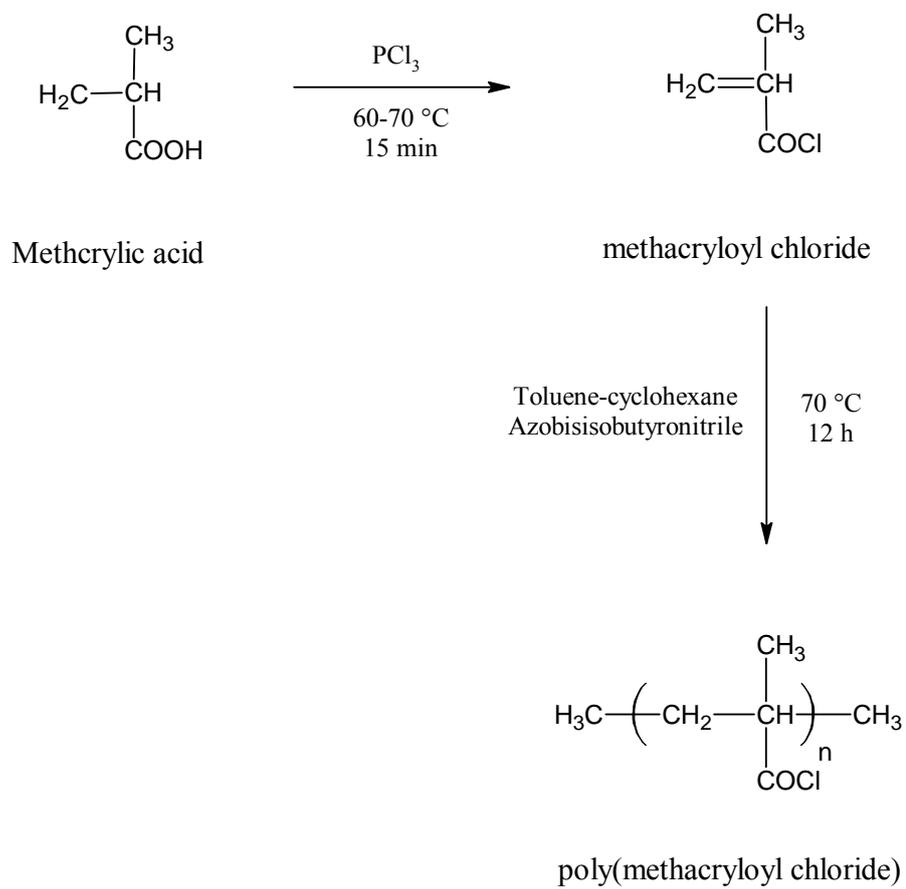


Compound 2.

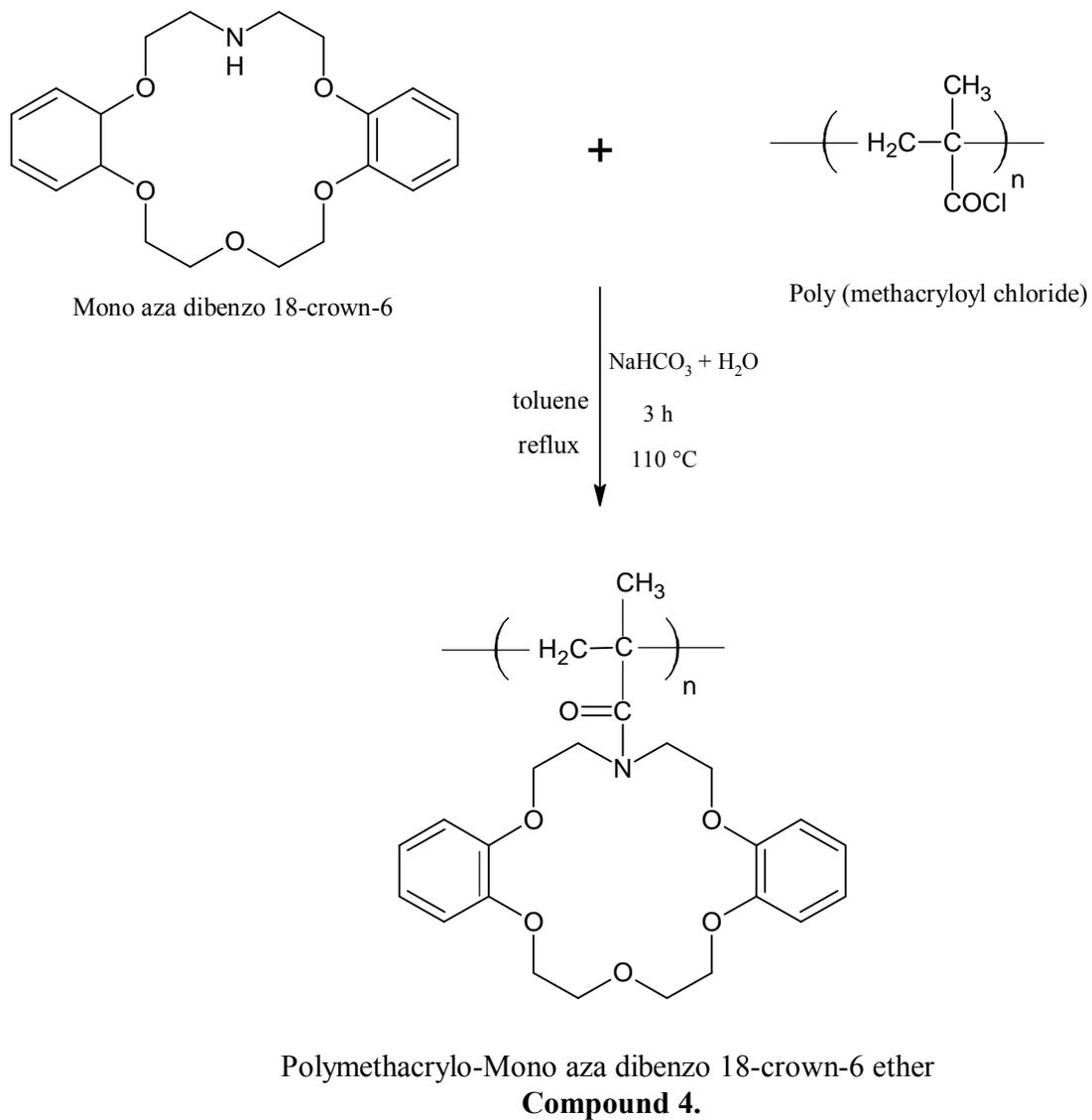
Scheme 5. Synthesis poly acrylo-mono aza dibenzo 18-crown-6



Scheme 6. Synthesis of Polymethacryloyl chloride



Scheme 7. Synthesis of Polymethacrylo-mono aza dibenzo 18-crown-6



RESULT AND DISCUSSION

Synthesis of mono aza dibenzo 18-crown-6 ether

The polymeric crown ethers were synthesized by attaching XAD-4 resin, Merrifield resin, poly(acryloyl chloride) and poly(methacryloyl chloride) to the mono aza dibenzo 18-crown-6 ether. The synthetic route is given in schemes 1-5.

The mono aza dibenzo 18-crown-6 was synthesised by detosylation of N-tosyl mono aza dibenzo 18-crown-6 which was synthesized by reacting the podant, bis [2- (o-hydroxy phenoxy)-ethyl] ether with detosylate of N-tosyl diethanol amine in the presence of potassium carbonate in acetonitrile medium. This modification in the synthesis of mono aza dibenzo 18-crown-6 resulted in better yield compared to the reported method⁷ in which N-alkyl bis(2-chloro-ethyl) amine is reacted with bis [2-(o-hydroxy phenoxy)]ether to prepare the aza crown, further, the detosylation of the modified is simpler than the reported method.

Properties

The synthesized compound N-tosyl mono aza dibenzo 18-crown-6 is a colourless crystalline with molecular weight 513 corresponding the molecular formula $C_{27}H_{31}NO_7S$ with a sharp mp 208°-209°C. Mono aza dibenzo 18-crown-6 is a colorless crystalline solid with molecular weight 359 corresponding the molecular formula $C_{20}H_{25}NO_5$ with a sharp mp 170°-172°C.

Acetylation of the resin

The acetylation of the resin is carried out by Friedel-Crafts reaction¹³ according to reaction method, the anhydrous $AlCl_3$ and dichlorethane was mixed and then XAD-4 resin was added. After that, acetyl chloride was added slowly to the mixture at 35°C temperature. The reaction mixture was continuously stirred for 2 h at 35°C, the reaction mixture turned from

yellow to brown after 30 min. The product was purified by washing with methanol and finally with water.

The color of substituted resin was pale yellow. This change is due to the bonding of a carbonyl group and phenyl ring of resin. The reaction should be carried out at controlled temperature to protect the resin getting crushed.

Oxidation of resin

The oxidation of acetylated resin was carried out in presence of sodium hypochlorite¹⁴. For the oxidation of acetylated XAD-4 sodium hypochlorite was used in place of Br₂ and KMnO₄ which made the reaction faster and easier.

Chloroformoylation of XAD-4 resin

The chloroformoylation of XAD-4 resin is carried out by thionyl chloride because isolation of XAD-4 is convenient and no risk factor like the one associated with phosphorus penta chloride. Other advantage of using thionyl chloride is that the recovered thionyl chloride can be used for next reaction. Chloroformoylation is carried out by treating the resin with thionyl chloride at 70°C for 2 h, after the completion of reaction the colour of yellow resin was turned in to brown. The resin was isolated by filtering the reaction mixture and was then washed with diethylether.

XAD-4 [mono aza dibenzo 18-crown-6]

The polymeric crown ether XAD-4 [mono aza dibenzo 18-crown-6] is synthesized by coupling chloroformoyled XAD-4 resin and mono aza dibenzo 18-crown-6. The reaction of chloroformoyl XAD-4 resin and mono aza dibenzo 18-crown-6 was carried out in presence of toluene and triethylamine and was refluxed for 72 h at 110°C. Isolation and purification is described in the synthesis. To get good yield of product it is required that both

reactants should be added slowly in the dry solvent, because the chloroformoyl XAD-4 resin is sensitive to moisture.

Merrifield [mono aza dibenzo 18-crown-6]

The Merrifield resin [mono aza dibenzo 18-crown-6] is synthesized by same reaction procedure which has been described in preparation of XAD-4 [mono aza dibenzo 18-crown-6]. The Merrifield resin (chloromethylated polystyrene) was immobilized to the mono aza dibenzo 18-crown-6 in presence of triethylamine and reaction medium was toluene. Isolation and purification of product is described in synthesis scheme.

IR spectra

The IR spectra of polymeric aza crown ether show peak at 1680 cm^{-1} in XAD-4 [mono aza dibenzo 18-crown-6 ether]. This peak is assigned to carbonyl C=O stretching due to Ar-CO-N in polymeric aza crown ether. The spectrum showed a peak at 2928 cm^{-1} due to aromatic C-H stretching and the peak at 1266 cm^{-1} is attributed to Ar-O-C stretching of the aza crown ether ring. The absence of any peak in the range of 3000 to 3500 cm^{-1} is assigned to the absence of secondary amine group N-H stretching of aza crown ether. Moreover the absence of C-Cl stretching in the molecule indicate that XAD-4[mono aza dibenzo 18-crown-6] is formed by condensation of acid chloride group of XAD-4 acid chloride and amine group of aza crown ether.

The spectrum of Merrifield (mono aza dibenzo 18-C-6) showed the absence of N-H stretching peak between range of 3000 - 3500 cm^{-1} and absence of C-Cl stretching peak indicate the conformation of the linkage between $-\text{CH}_2\text{-Cl}$ group of Merrifield resin and amine group $-\text{N-H}$ of aza crown ether by $\text{CH}_2\text{-N}$ bond. The peak observed at 690 cm^{-1} due to CH_2Cl

group of Merrifield resin disappears in Merrifield [mono aza dibenzo 18-crown-6]. This result indicates the binding of resin and aza crown ether with each other.

The spectra of compounds polyacryloyl(manoazadibenzo-18-crown-6) and polymethacryloyl(manoazadibenzo-18-crown-6) showed peaks at 1730 cm^{-1} and 1717 cm^{-1} corresponding to carbonyl C=O stretching respectively. Other prominent peaks such as 2939 cm^{-1} , 2938 cm^{-1} corresponding to Ar-CH stretching were also observed. In this case also absence of N-H stretching and C-Cl stretching indicates the presence of amide linkage in the molecule.

References

1. Sherrington, D. C.; Hodge, P. *Syntheses and separations using functional Polymers*. Chichester, U. K., Wiley, **1988**.
2. Alexandratos, S. D.; Crick D. W.; *Ind. Eng. Chem. Res.* **1996**, 35, 635.
3. Pethrick, R. A.; Wilson, M. J.; Affrossman, S.; Holmes, D.; Lee, W. M.; *Polymer* **2000**, 41, 7111-7121.
4. Havashita, T.; White, J. C.; Lee, H. J.; Bartsch, R. A. *Sep. Sci. Technol.* 28, **1993**, 2607-2620.
5. Favre-reguillon, A.; Dumort, N.; Dunjic, B.; Lemaire, *Tetrahedron* **1997**, 53, 1343-1360.
6. Zong, Z.; Dong, S.; Hu, Y.; Xu, Y.; Liu, W. Liu, *Eur. Polym.J.* **1998**, 761-766.
7. Van de water, L.G.A.; F. Hoonte ten; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. *Inorg. Chim. Acta* **2000**, 303, 77-85.
8. Kutchukov, P.; Ricard, A.; Quivoron, *Eur. Polym. J.* **1980**, 753-758.
9. Nakajima, M.; Fujiwara, Matsushita, T.; Shono, *Polyhedron* **1986**, 5, 1601-1605.
10. Mohite, B. S.; Burungale, S. H.; *J Radioanal. Nucl. Chim. Acta* **1999**, 86, 290.
11. Krakowiak, K. E.; Brandshaw, J. S.; Zamecka-Krakowiak, D.J. *Chem. Rev.* **1989**, 89, 292.
12. Bradshaw, J. S.; Krakowiak, K. E.; Izatt, R. M. *Heterocyclic Compounds*, Taylor, E. C., Ed., John wiley & Sons, New York, **1993**, 5.
13. Altava, B.; Burguete, M. I.; Fraias, J. C.; Garcia-Espana, E.; Luis, S. V.; J. F. Miravet. *Ind. Eng. Chem. Res.* **2000**, 39, 3589-3595.

14. Van de water, L. G. A.; Driessen, J.; Reedijk, D. C.; Sherrington, *Eur. J. Inorg. Chem.* **2002**, 221-229.
15. Van de water, L. G. A.; Ten Hoonte, W. L.; J. Reedijk,; D. C. Sherrington, *Inorg. Chim. Acta* 303, **2000**, 3589-3595.
16. Nakatsuji, Y.; Kawamura, N.; Okahara, M. *Synthesis*. **1981**,42
17. A. Sugii, J. P. **1986**, 76, 117118.
18. Bradshaw, J. S.; Izatt, R. M. *Acc. Chem. Res.* **1997**, 30, 338.
19. Tsukube H. *Talanta* **1993**, 40, 1313.
20. Pedersen C. J. *J. Am. Chem. Soc.* **1967**, 89, 7017.
21. Ijeri, V.S.; Srivastava, A. K. *Polyhedron* **2003**, 22,569.
22. Su, C. C.; Chang M. C.; Liu L. K.; *Anal Chim. Acta* **1999**, 50, 376.
23. Luca, C, Mohora, T, Lupu, S. *Rev. Chim (Bucharest)* **1999**, 50, 276.
24. Elshani, S.; Noriyuki R.; Wai, C. M.; Natale, N. R.; Bartsch, R. A. *J. Hetrocyclic Chem* **1998**, 35, 875.
25. Tong, A. J.; Song, Y. S.; Li, L. D.; Hayashita, T.; Teramae, N.; Park C. *Anal. Chim. Acta* **2000**, 57, 420.
26. Oh, K. C.; Kang, E. C., jeong, K. S.; Paeng, K, J.; *Bull. Korean. Chem. Soc.* **1999**, 20, 556.
27. Kim, D. W.; *Bull. Korean Chem. Soc.* **2001**, 22, 6.
28. Fakestorp, J.; Christiansen, J. A.; Pederson, J. G. A. *Acta chem. Scand.* **1953**, 7, 134.
29. U. S. Patent 3, 847,949.
30. Grat, E.; Lehn, J. M.; *Helv. Chem. Acta* **1981**, 64, 1051-1065.
31. Vaidhya, B.; Zak, J.; Basiaans, G. J.; Porter, M. D.; *Anal. Chem.* **1995**, 67, 4101-4111.