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# Immobilization of lithium-selective 14-crown-4 on crosslinked polymer supports

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## Abstract

The immobilization of octamethyl-14-crown-4 onto crosslinked polymer supports is reported and the selectivity for Li(I) from aqueous solutions quantified. The amount of Li(I) complexed by the crown ether is affected by the polarity of the polymer matrix: Complexation increases with increasing matrix hydrophilicity. Poly(glycidyl methacrylate) is the preferred support matrix for the crown ether.

*Keywords:* Polymer-supported reagent; Ion; Selective

## 1. Introduction

Crown ethers are ion-selective reagents that have been widely studied within separations science [1,2]. Stability constants have been determined with transition metal ions [3–5]. The crown ether structure has been modified in numerous ways to change the observed selectivity: Crown ethers with linear side chains have been studied for their lanthanide selectivity [6] while those with a dansyl moiety bound to 16-crown-5 may be used as sensors for sodium ions [7], bis(crown ether)s are selective for lead ions [8], tetrabenzo-24-crown-8 has a high affinity for cesium [9], and dibenzo-24-crown-8 is able to complex U(VI) [10].

Polymer-supported reagents capable of complexing targeted metal ions from aqueous solutions are important for environmental remediation and as sensors [11,12]. Ligands immobilized onto crosslinked polymers for the selective complexation of metal ions include bis(imidazol-2-yl)-methylaminomethane [13], 1-(2-aminoethyl)-piperazine [14], aminothiophosphonate [15], and ketophosphonates [16].

Immobilizing crown ethers onto crosslinked polymers can combine the crown ether's selectivity with the polymer's ease of recovery and recyclability. This immobilization can be accomplished by copolymerization or grafting of appropriately substituted monomers [17,18]. Acryloyl groups have been bonded to crown ethers with subsequent polymerization occurring through those groups [19,20]. Immobilization by grafting can be done if the crown ether has a functional group that can react with a group on the polymer. For example, nitrogen-containing crown ethers have been bonded to poly(glycidyl methacrylate) through a nucleophilic reaction [21]. Grafting may increase accessibility of the crown ether to substrates in solution [22].

Crown ethers with 12 to 16-membered rings containing four oxygen atoms have high selectivity for the lithium cation [23,24]. That these crown ethers are promising for lithium binding was known in the case of 14-crown-4 ethers in one of the earliest reports of metal ion binding by crown ethers [25]. Alkylation of the 14-crown-4 ring has been associated with enhanced selectivity relative to the unsubstituted ring [26–29], making possible uses in, e.g. membrane electrodes [30]. Structural [31] and theoretical [32] data lend some understanding of the substituent effects in terms of conformational strain. An alkylated example is 2,2,3,3,6,9,9,10,10-nonamethyl-14-crown-4, which features high selectivity over sodium (Li/Na selectivity factor of 75.8 in liquid–liquid extraction) and ease of synthesis [28].

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This report describes the immobilization of a derivative of this alkylated 14-crown-4 through a hydroxy group attached to the 6-methyl group.

## 2. Experimental

All chemicals were purchased from the Aldrich Chemical Co. unless otherwise noted.

### 2.1. Synthesis of 6-hydroxymethyl-2,2,3,3,9,9,10,10-octamethyl-14-crown-4 (Me14C4–OH)

Ten grams of 6-methylene-2,2,3,3,9,9,10,10-octamethyl-14-crown-4 (**1a**) [31] was dissolved in anhydrous tetrahydrofuran and cooled in an ice bath. Borane-methyl sulfide complex (4 mL) was added and the mixture stirred for 1 h. A solution of 25 mL 30% $H_2O_2$ and 25 mL 3.0 M NaOH was then added dropwise via an addition funnel and the mixture stirred for 1 h after the ice bath was removed. The product (**1b**) was extracted into 100 mL hexane, washed with saturated sodium bicarbonate, dried over magnesium sulfate, and isolated by evaporating the solvent (Fig. 1).

### 2.2. Synthesis of polymer supports

The polymers were synthesized by solution or suspension polymerization. The latter method produced microporous (gel) and macroporous (MR) beads crosslinked with 2, 5, and 8 wt% divinylbenzene (DVB) and a particle size of 150–250 μm.

Poly(vinylbenzyl chloride-*co*-acrylamide) was prepared with the monomers in an equimolar ratio by solution polymerization. A solution of 1.18 g azobisisobutyronitrile (AIBN), 4.27 g technical grade (55.4%) DVB, 72.7 g vinylbenzyl chloride (VBC) and 35.7 g acrylamide in 250 mL dioxane was heated at 60 °C for 17 h. The resulting copolymer was extracted in a Soxhlet extractor, dried and ground to 150–250 μm.

Suspension polymerization to produce macroporous poly(vinylbenzyl chloride) with 4-methyl-2-pentanol as the porogen has been reported [33]. Gel and MR poly(glycidyl methacrylate) beads were also prepared by suspension polymerization. Boric acid (4.75 g), 0.720 g pharmagel (Knox Gelatin Co.), and 8.93 g poly(diallyl dimethylammonium chloride) (PADMAC, Calgon Corp.) in 234 g water adjusted to pH 10.3 with 50% NaOH was combined with 1.50 g benzoyl peroxide, 5.42 g DVB and 143.0 g glycidyl methacrylate (GMA); the preparation of MR beads included the addition of enough isobutyl acetate as the porogen to give a 60 wt% solution within the organic phase [34]. Upon stirring, the resulting suspension was heated to 80 °C over a 2 h period and then held at that temperature for 10 h. To ensure complete polymerization, the reaction mixture producing the gel beads was refluxed for 2 h at 100 °C and the mixture producing the MR beads underwent a 6 h steam distillation to remove the isobutyl acetate. The beads were then washed with water, extracted with toluene, and dried.

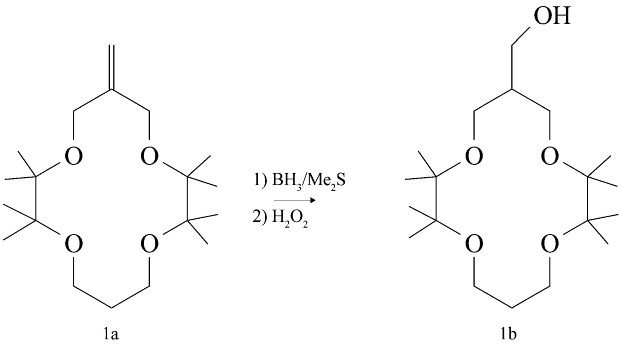

Fig. 1. Synthesis of hydroxy derivative (**1b**) from 6-methylene-2,2,3,3,4,4,9,9,10,10-octamethyl-14-crown-4 (**1a**).

### 2.3. Bulk and solution polymerizations with 6-methylene-2,2,3,3,9,9,10,10-octamethyl-14-crown-4

Monomers (Table 1) were weighed into a 20 mL borosilicate scintillation vial and swept with nitrogen for 1 min. The vial was then sealed and placed in an oil bath set at 70 °C for 17 h, after which time the copolymer was removed, crushed, extracted with toluene and dried.

### 2.4. Etherification reactions

#### 2.4.1. Poly(VBC)/Me14C4–OH

One gram of poly(VBC) beads crosslinked with 5% DVB was swollen with 20 mL anhydrous dioxane in a 100 mL roundbottom flask. In another flask to which was attached a Claisen adapter fitted with a nitrogen gas inlet and outlet, 5.90 g Me14C4–OH was contacted with 0.681 g NaH (60% oil dispersion) in 30 mL anhydrous dioxane. The Me14C4–OH solution was stirred for 1 h, added to the flask containing the beads, and refluxed for 72 h under nitrogen. The product (**2**) was washed three times each with ethanol, water, ethanol, and acetone, then dried (Fig. 2).

#### 2.4.2. Poly(VBC-co-acrylamide)/Me14C4–OH

The preparation of poly(VBC-*co*-acrylamide)/Me14C4–OH (**3**) from the copolymer of poly(VBC) and acrylamide followed the procedure above. The mole ratio of Me14C4–OH:NaH:$CH_2Cl$ (on the beads) was 2.5:2.5:1 (Fig. 3).

#### 2.4.3. Poly(GMA) gel/Me14C4–OH

The crown ether was immobilized onto poly(GMA) gel beads in the manner described above to give product **4**. Modifications to the procedure were such that polymer **5** was produced when the Me14C4–OH solution was heated at 60 °C for 1 h while polymer **6** was produced when the crown ether solution was heated at 60 °C for 17 h (Fig. 4).

Table 1
Bulk and solution copolymerizations with 6-methylene-2,2,3,3,9,9,10,10-octamethyl-14-crown-4 (Me14C4=CH$_2$)

| Resin | Monomer (mmol) | | | | | Initiator | Cl elemental analysis | | |
|---|---|---|---|---|---|---|---|---|---|
| | Me14C42= CH$_2$ | Vinylbenzyl chloride (VBC) | Acrylonitrile (AN) | Ethyl acrylate (EA) | Divinylbenzene (DVB) | Benzoyl peroxide BPO (%) | Exptl | Calc w/ incorp'n | Calc w/out incorp'n |
| A | 1.8 | 7.2 | | | 2.5 | 1 | 4.61 | 3.48 | 4.88 |
| B | 1.8 | 7.2 | | | 1.1 | 1 | 6.28 | 3.91 | 5.73 |
| C | 1.8 | 2.0 | | | 2.5 | 1 | 3.46 | 1.64 | 3.26 |
| D | 1.8 | 7.2 | | | 2.5 | 0.1 | 4.94 | 3.49 | 4.92 |
| E | 1.8 | 7.2 | | | 2.5 | 0.5 | 4.86 | 3.49 | 4.90 |
| F | 1.8 | 7.2 | | | 2.5 | 1 | 4.61 | 3.48 | 4.88 |
| G | 1.8 | 7.2 | | | 2.5 | 8 | 4.84 | 3.22 | 4.38 |
| H | 1.0 | 10.0 | 10.0 | | 2.5 | 1 | 4.37 | 3.62 | 4.11 |
| I | 1.0 | 10.0 | 10.0 | | 2.5 | 5 | 4.77 | 3.46 | 3.91 |
| J | 1.8 | 1.5 | | 8.9 | 2.5 | 0.25 | 1.30 | 0.75 | 1.00 |
| K | 1.8 | 1.5 | | 8.9 | 2.5 | 0.50 | 1.28 | 0.68 | 0.95 |
| L | 1.8 | 1.5 | | 8.9 | 2.5 | 1.0 | 1.41 | 0.76 | 1.05 |
| M | 1.8 | 1.5 | | 8.9 | 2.5 | 4.0 | 1.53 | 0.74 | 1.02 |
| N[a] | 1.8 | 7.2 | | | 2.5 | 1 | 5.20 | 3.48 | 4.88 |
| O[b] | 1.8 | 7.2 | | | 2.5 | 1 | 4.81 | 3.48 | 4.88 |
| P[c] | 1.8 | 7.2 | | | 2.5 | 1 | 5.08 | 3.48 | 4.88 |

[a] Two milliliters toluene.

[b] Three milliliters toluene.

[c] Six milliliters toluene.

### 2.4.4. *Poly(GMA) MR/Me14C4–OH*

Polymers **7** and **8** were produced as above except for a change in Me14C4–OH:NaH:CH$_2$Cl reactant mole ratios 3:3:1 for the former and 5.3:5.3:1 for the latter; additionally, the reflux time for **8** was increased to 7 days.

### 2.4.5. *Metal ion contact studies*

The polymers (0.10 g) were shaken with 5 mL of a given concentration of lithium nitrate solution in nanopure water for 24 h. After the beads were filtered from the solution, the concentration of metal remaining uncomplexed was measured by atomic emission on a Perkin–Elmer 3100 atomic absorption spectrometer. Results are reported as distribution coefficients, percent metal complexed, and, from more concentrated solutions, as millimoles Li$^+$ per gram polymer.

## 3. Results and discussion

Initial bulk and solution copolymerization reactions attempted to incorporate the vinylidene octamethyl-14-crown-4 (**1a**, Me14C4=CH$_2$) directly into the backbone of the polymer chain with a variety of monomers (Table 1). The first set of polymerizations used only Me14C4=CH$_2$, VBC, divinylbenzene (DVB) and benzoyl peroxide (BPO). VBC was chosen as co-monomer not only because it would permit a subsequent functionalization reaction but also because the degree of Me14C4=CH$_2$ incorporation could be evaluated by comparing the experimental chlorine capacities with theoretical values calculated on the basis of complete or no incorporation. FTIR spectra were difficult to analyze: No peak could be unambiguously assigned to the crown ether due to the peak positions of the polymer support.

At a constant amount of Me14C4=CH$_2$, polymers were formed at different levels of crosslinking (A, B), VBC (C), and BPO (D–G). No Me14C4=CH$_2$ incorporation is evident, given the similarity in experimental chlorine capacities with the theoretical values calculated for the absence of Me14C4=CH$_2$ incorporation.

In earlier research, the sterically hindered tetraethyl

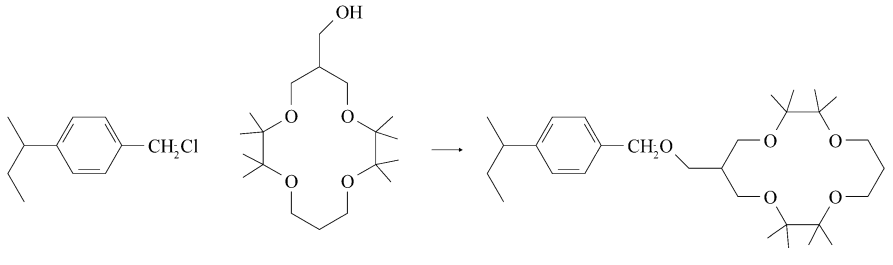

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Fig. 2. Immobilization of hydroxy crown onto poly(vinylbenzyl chloride) to give immobilized crown (**2**).

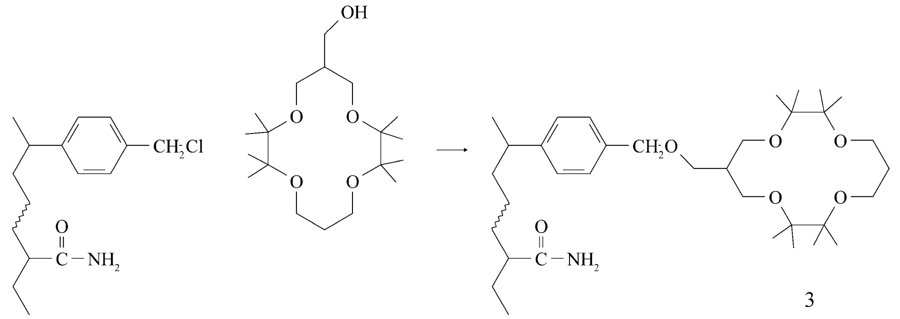

Fig. 3. Immobilization of hydroxy crown onto poly(vinylbenzyl chloride-*co*-acrylamide) to give immobilized crown (**3**).

vinylidene-1,1-diphosphonate was incorporated into a polymer matrix by adding a readily polymerizable monomer, acrylonitrile (AN) [35]. Bulk polymerizations were thus done with Me14C4=CH$_2$, VBC, AN and DVB (H, I). The chlorine capacities reveal no incorporation of crown ether. Replacing AN with ethyl acrylate (EA) in the next set of polymerizations (J–M) again gives no evidence of incorporation.

The final set of polymerization reactions examined the effect of solvent. Me14C4=CH$_2$, VBC, DVB and BPO were dissolved in toluene (N–P). The chlorine capacities are similar to those from runs A and F and show no incorporation. It is thus concluded that it may not be possible to incorporate Me14C4=CH$_2$ directly into the backbone of a polymer matrix through the vinylidene group, perhaps due to its steric bulk and the possibility of allylic chain transfer.

Post-functionalization of polymer beads can be an effective strategy for immobilizing bulky ligands [36]. Thus, the hydroxymethyl-octamethyl-14-crown-4 (**1b**, Me14C4–OH) was first reacted with macroporous polyVBC to determine whether immobilization could occur via an etherification reaction. Chlorine elemental analysis indicates that reaction occurs, given a decrease in value from 5.85 to 3.51 mmol Cl/g. This calculates to a 20% degree of functionalization. The resin (**2**) was then contacted with $10^{-4}$ N Li$^+$, but no sorption of the ion from solution was observed. Since this may be a result of the resin's hydrophobicity, a variable known to play an important role in the complexation of metal ions by polymer-supported reagents [35], VBC was polymerized with acrylamide to give a polymer with chlorine and nitrogen elemental analyses of 2.32 and 3.82 mmol/g, respectively. The polymer-supported crown ether (**3**), formed after reaction with Me14C4–OH/NaH, complexed 40% of the Li$^+$ from a $10^{-4}$ N solution, pointing to the importance of resin polarity to ionic accessibility.

A further increase in resin polarity was achieved by using poly(glycidyl methacrylate) [poly(GMA)] as the support. Immobilization was done on poly(GMA) gel (resin **4**) and macroporous beads. Contact with $10^{-4}$ N Li$^+$ solution gave quantitative complexation of the lithium ions by both resins. The hydrophilicity of the polymer support is thus a controlling variable for the extent of Li$^+$ complexation by the immobilized crown ether (poly(GMA) itself, when contacted with the $10^{-4}$ N Li$^+$ solution, sorbed no lithium whatsoever).

The lithium saturation capacities of the poly(GMA) /14C4 resins from 0.10 N LiNO$_3$ solution were used to approximate the degree of functionalization (Table 2). In the initial reaction of the poly(GMA) gel with Me14C4–OH, deprotonation of the hydroxyl group by NaH was carried out at room temperature for 1 h before contact with the beads and reflux (A 1 h contact time for hydroxyl group deprotonation by NaH has been reported [37]). The resulting resin, **4**, complexed Li$^+$ quantitatively from $10^{-4}$ N solution, but the amount sorbed from 0.10 N solution was below the limit of detection, indicating a low degree of functionalization. Nonetheless, the 14C4 immobilized on the polymer is selective for Li$^+$ relative to Na$^+$. Resin **4** sorbed 99.6% of the Li$^+$ from a solution of $10^{-4}$ N LiNO$_3$/ $10^{-1}$ N NaNO$_3$ (distribution coefficient, $D_{\mathrm{Li}^+} = 12,500$).

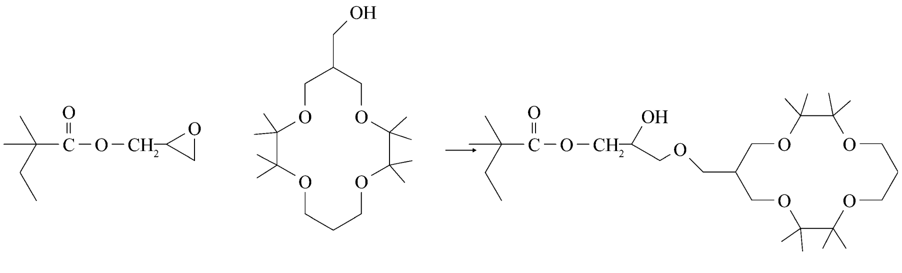

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Fig. 4. Immobilization of hydroxy crown onto poly(glycidyl methacrylate) to give immobilized crown (**4**).

Table 2
Lithium ion capacity of poly(GMA)/14C4

| Resin | Deprotonation of Me14C4–OH | Reflux time (h) | $LiNO_3$ conc (N) | %$Li^+$ complexed | mmol/$g_{resin}$ |
|---|---|---|---|---|---|
| **4** | 1 h, 25 °C | 72 | $10^{-4}$ | 100 | – |
| | | | $10^{-1}$ | <1 | 0.0 |
| **5** | 1 h, 60 °C | 72 | $10^{-4}$ | 100 | – |
| | | | $10^{-1}$ | 1.74 | 0.085 |
| **6** | 17 h, 60 °C | 72 | $10^{-4}$ | 100 | – |
| | | | $10^{-1}$ | 8.25 | 0.41 |
| **7** | 1 h, 25 °C | 72 | $10^{-4}$ | 100 | – |
| | | | $10^{-1}$ | 8.60 | 0.44 |

In studying whether deprotonation of Me14C4–OH is complete at room temperature, the NaH reaction temperature was increased to 60 °C to give resin **5**. That resin complexed 100% of the lithium from the $10^{-4}$ N solution and 1.74% from the 0.10 N solution (0.085 mmol $Li^+/g_{resin}$). Increasing the deprotonation time to 17 h gave resin **6** which complexed 100% $Li^+$ from the $10^{-4}$ N solution and 8.25% from the 0.10 N solution (0.41 mmol $Li^+/g_{resin}$). The degree of functionalization is thus affected by the conditions under which the –OH group is deprotonated.

The influence of the deprotonation reaction temperature and time on the degree of functionalization by the crown ether is coupled to the macroporosity of the polymer support. Resins **4**, **5**, and **6** were microporous. When deprotonation of the Me14C4–OH was carried out at room temperature for 1 h and the solution contacted with a macroporous poly(GMA) support, the resulting resin, **7**, complexed 100% of the $Li^+$ from the $10^{-4}$ N solution and 8.60% $Li^+$ from the 0.10 N solution (0.44 mmol $Li^+/g_{resin}$). The level of functionalization is thus identical to the gel resin prepared from the Me14C4–OH solution deprotonated at 60 °C. It is possible that the higher temperature produces a greater amount of the Me14C4–$O^-Na^+$ and that this greater concentration gradient is needed to penetrate the microporous structure of the gel resin. The level of functionalization has probably been maximized since increasing the reflux time from 72 h to 7 days results in no significant increase in the amount of $Li^+$ complexed. FTIR spectra of poly(GMA)/14C4 resins show the representative peaks in the poly(GMA) spectrum for epoxy ring vibrations and C–H stretch (including peaks at 850, 910, 1340, and 1480 $cm^{-1}$), though clearly less intense than in the poly(GMA) spectrum. Again, no peak could be unambiguously associated with the 14C4 portion of the molecule.

## 4. Conclusions

Immobilization of the 14C4 moiety onto crosslinked polymer beads is possible through an etherification reaction involving a pendant –OH group. The amount of lithium ion that can be complexed by the immobilized 14C4 is affected by the hydrophilicity of the polymer matrix. Poly(GMA) performs best of three copolymers studied due to its hydrophilicity and reactivity toward Me14C4–$O^-Na^+$. Two additional variables important to determining the level of 14C4 functionalization on poly(GMA) are the deprotonation conditions and matrix porosity. Immobilized 14C4 retains a high affinity for the lithium cation and is highly selective in competition with sodium ions.

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