Pergamon

Tetrahedron, Vol. 53, No. 4, pp. 1343-1360, 1997
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0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)01072-1

Polymeric and Immobilized Crown Compounds, Material for Ion Separation

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Abstract: We describe the synthesis of ionoselective polymers bearing different pendant crown ethers. The synthesis was applied to various macrocycles. We discuss the influence of macrocyclic cavity size and rigidity of the polymers on the extraction behavior. Accessibility of active sites can be achievied with immobilized functionalized polyurethanes chemically bound to an inorganic solid support, with no change of ionoselective properties. © 1997, Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Despite recent improvements in both sensitivity and selectivity of analytical methods, separation and preconcentration remain essential steps in many chemical analyses. Tailor-making metal-specific ligands by attaching them to polymeric carriers is an excellent way of meeting the increasing demand for materials suitable for the separation of metal ions from complex sources. The variety of monomers and polymerization methods provides an inexhaustible number of chelating materials[1] with the selectivity required to capture extremely low levels of ions.

The complexation behaviour of alkali and alkaline earth elements can best be described in terms of "host-guest complexation" which requires complementary size matching of ionic radii and ligand cavities. Several unique properties of crown ethers make them ideal candidates for such use. Macrocycles have been used to perform cation separations by liquid/liquid extraction[2], and as carriers in liquid membrane systems.[3] In recent years, highly selective extraction chromatographic materials have been developed in which macrocycles are covalently attached[4] or sorbed[5] onto solid supports. Such materials allow the repeated use of macrocycles since the material can be regenerated after each use. Thus, the initial high cost of synthesis is amortized over the time. In addition, loss of the macrocycle to the environment and the use of diluent are minimized.

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A series of crown ether functionalized polymers based on a poly(methacrylate-*co*-ethylene glycol dimethacrylate)[6] or poly(styrene-*co*-divinylbenzene)[7] have been described. Introduction of ionic exchange sites in the macromolecular matrix raised the hydrophily of the polymeric ligands and enhanced the kinetics of cation binding.[7,8] The reaction of glycidylated polymers with functionalized ligands [8] and crown ethers[9] afforded polymers with very favourable uptake kinetics.

We wish to present here an original and general synthesis of ionoselective hydrophilic polymers based on crown ethers.

RESULTS AND DISCUSSION

Poly(ethylene glycol) (PEG) is soluble in both water and (to various degrees) in many organic solvents.[10] PEGs possess a variety of properties pertinent to hydrometallurgy.[11] Binding crown ethers on such polymers could contribute to the higher efficiency of extraction because of the hydrophilicity of PEG. Solid materials with reasonable mechanical properties and porosity can be obtained by cross-linking.

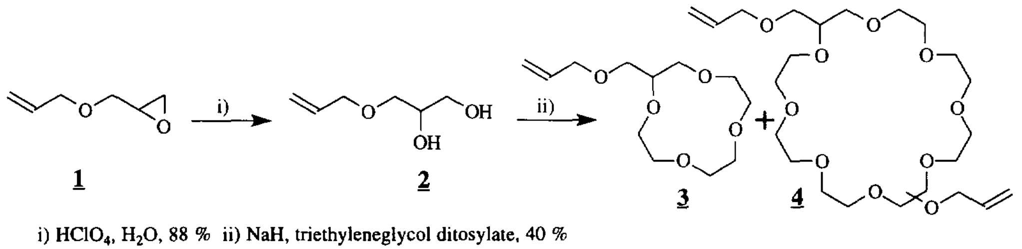
Another approach was to immobilize functionalized crown ether on a polyurethane elastomer. These polyurethanes were prepared by the catalysed polyaddition of diisocyanate with functionalized crown ethers. Their mechanical properties can also be varied by changing the degree of cross-linking.

In both types of polymers, hydrophilicity and mobility of crown ethers are very important factors. To improve accessibility of crown ethers, polymers should be flexible, with low temperatures of glass transition. The high mobility of the polyether chain could contribute to the higher efficiency of the extraction.

First, crown ethers were incorporated on polyethers by polymerisation of functionalized macrocycles.

Synthesis of glycidylated monomers and polyethers

The first monomer synthesized was functionalized 12-crown-4. The monomer was synthesized from allyl glycidyl ether **1** (AGE) according to the procedure described[12] for the synthesis of functionalized 15-crown-5. Treatment of the diol with triethyleneglycol ditosylate (1.0 eq.) and NaH (2.4 eq.) in THF afforded the (allyloxy)methyl-12-crown-4 **3** contaminated by 24-crown-8 derivatives **4** (Scheme 1).

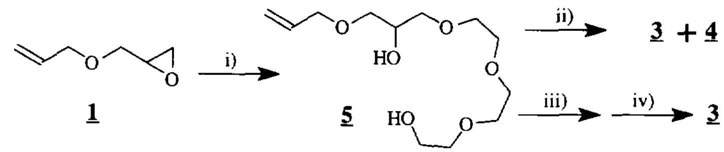


i) $HClO_4$, H_2O, 88 % ii) NaH, triethyleneglycol ditosylate, 40 %

Scheme 1. (Allyloxy)methyl 12-Crown-4 and 24-Crown-8 from Allyl Glycidyl Ether

The simultaneous formation of 24-crown-8 during the synthesis of 12-crown-4 has already been observed [13] and induced difficult separation using liquid chromatography. To prevent the formation of 24-crown-8 derivatives, an intramolecular cyclisation[14] was used.

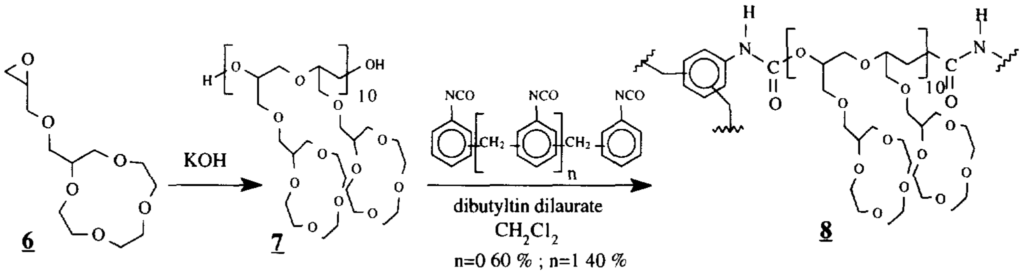
In our reaction conditions, the nucleophilic attack of triethyleneglycol on AGE led to the production of only one isomer 5, contrary to results previously described.[14] One step cyclisation of 5 allowed the formation of the (allyloxy)methyl-12-crown-4 3 and the dimer 4 (Scheme 2). This could be avoided by separation of the mono tosyl derivative.



i) triethyleneglycol, KOH, 74 % ii) NaH, pTosCl, THF
iii) NaOH, H_2O, pTosCl, 91 % iv) NaH, THF, 56 %

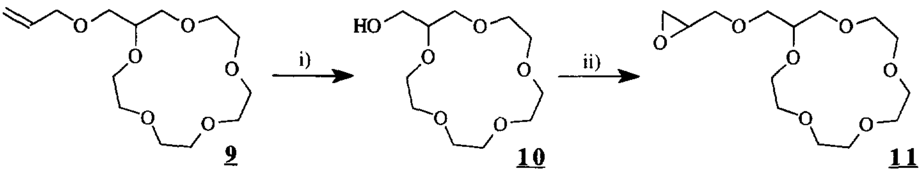
Scheme 2. Synthesis of (Allyloxy)methyl-12-Crown-4 3

Then, treatment of the 12-crown-4 ether 3 with mCPBA afforded the monomer 6. Both anionic and cationic polymerisations were attempted, but only anionic polymerisation gave 7 with quantitative conversion.[15] The number-average molecular weight ($\overline{Mn}$) of 7 was 4500 g/mol which corresponds to about 20 crown ethers units in the polymer chain. Polymer 7 was a viscous brown liquid, soluble in organic solvents and partially soluble in water. Terminal OH groups were used in cross-linking reactions. The cross-linking of 7 was carried out in bulk at room temperature using a mixture of di- and tri- phenylmethane diisocyanate as a cross-linking agent. We obtained the polyurethane elastomer 8 (Scheme 3).



Scheme 3. Synthesis of Polyurethane Elastomer 8

Synthesis of polymers with more than 12 atoms in the macrocycle was then attempted. The (allyloxy)methyl-15-crown-5 9 was synthesized according to the procedure described[12] (Scheme 1) with tetraethyleneglycol ditosylate. No dimers were detected. However, epoxidation of 9 was unsuccessful under various conditions.[16] Similar poor reactivity of allyloxy group had been observed in the presence of 15-crown-5.[17] The method ultimately developed into the preparation of 11 was shown in Scheme 4.

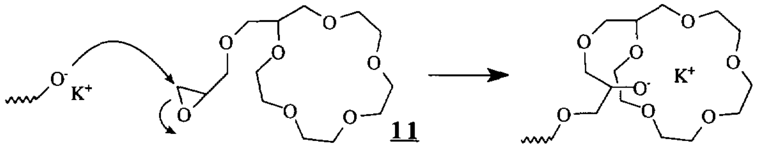


i) $HClO_4$, H_2O/EtOH, Pd/C, 92 % ; ii) NaH, THF, epichlorohydrin, 86 %

Scheme 4. Synthesis of 2-(2,3-Epoxypropyloxy)methyl-15-Crown-5 11

Olefinic crown 9 was converted to hydroxymethyl-crown-ether 10 by a one-pot process using palladium-on-carbon under acidic conditions.[14] The (benzyloxy)methyl group was also studied as a protective group.[18] However, the yield of the synthesis of (benzyloxy)methyl-crown and conversion to hydroxymethyl were lower. The reaction of 10 with epichlorohydrin, in the presence of sodium hydride in THF, gave the corresponding glycidyl ether 11.

Compound 11 shows poor reactivity in the conditions of anionic polymerisation, despite the variety of conditions tested (use of CsOH instead of KOH, increasing temperature). The inhibition of the polymerisation could be explained by the formation of a hindered ion-pair (Scheme 5).



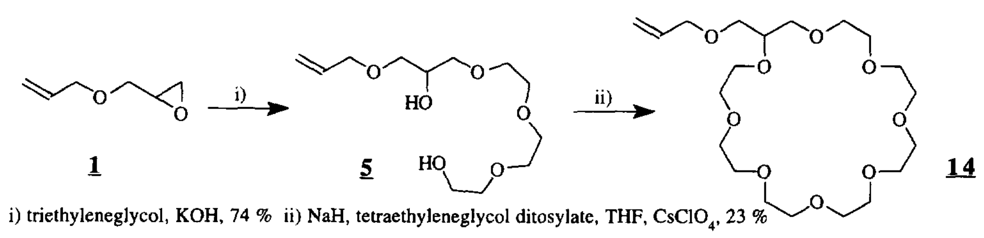
Scheme 5. Proposed Mechanism for the Inhibition of the Anionic Polymerisation with 11

This hypothesis was confirmed by studying the anionic polymerisation of AGE in the presence of different solvents. In particular, inhibition was observed when 15-crown-5 was used as solvent (1 eq. per AGE). Immobilisation of macrocycles larger than 12-crown-4 ether on PEGs cannot be achievied by polymerisation of functionalized glycidyl ether because the presence of equimolar amount of macrocycle inhibited the chain growth.

Synthesis of diol-functionalized crown ethers and polyurethanes

Another approach was to immobilize functionalized crown ethers on a polyurethane elastomer.[19] Polyurethanes can be prepared by catalysed polyaddition of diisocyanate with diol-functionalized crown ethers. The diol derivatives were synthesized by dihydroxylation of allyl group. Thus, the synthesis of (allyloxy)methyl-crown with 12 to 24 atoms in the macrocycle were studied.

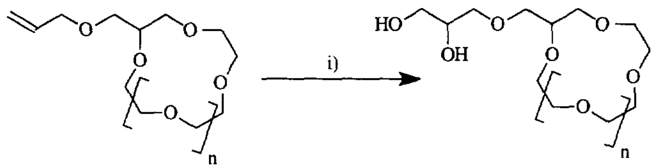
(Allyloxy)methyl-18-crown-6 12 and 21-crown-7 13 were synthesized by cyclisation of the diol with the corresponding ditosylate. For (allyloxy)methyl-24-crown-8 we used the diol 5 obtained by nucleophilic attack of triethyleneglycol on AGE 1. Treatment of 5 with tetraethyleneglycol ditosylate and NaH in THF afforded (allyloxy)methyl-24-crown-8 14 in 23 % yield (Scheme 6). So, functionalized 24-crown-8 was obtained in two steps, from AGE 1, with improved yield compared to the method previously reported.[20]



i) triethyleneglycol, KOH, 74 % ii) NaH, tetraethyleneglycol ditosylate, THF, $CsClO_4$, 23 %

Scheme 6. Synthesis of (Allyloxy)methyl-24-Crown-8 **14**

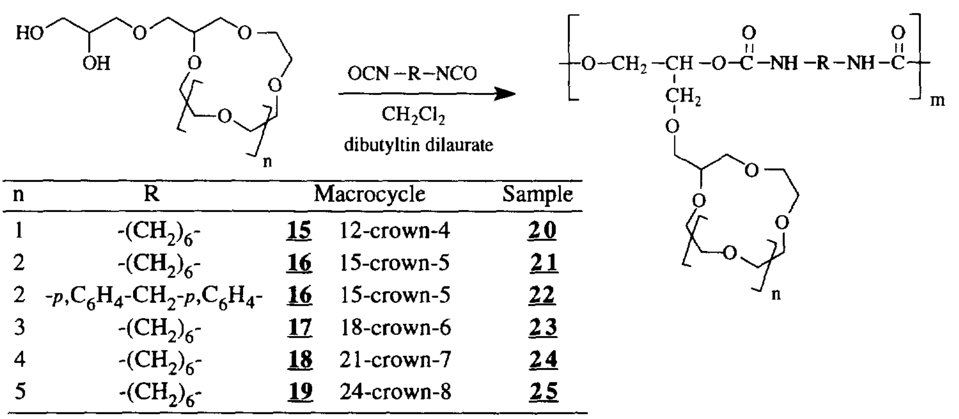
The dihydroxylation step (Scheme 7) was carried out using catalytic amounts of osmium tetraoxide.[21] Yields varied depending on the hydrophilic character of the products.



i) OsO_4 cat., 4-Methylmorpholine N-oxide, H_2O/Acetone
n = 1, **15** (39%) ; n = 2, **16** (45%) ; n = 3, **17** (63%) ; n = 4, **18** (61%) ; n = 5, **19** (66%)

Scheme 7. 2-(2,3-Dihydroxypropyloxy)methyl-Crown Ether from (Allyloxy)methyl-Crown Ether

Polymers were prepared by catalysed[22] polyaddition with diisocyanate (Scheme 8). By using pure diisocyanate, one can change the degree of cross-linking by varying the excess of diisocyanate in the reaction mixture. In order to determine the influence of the rigidity of the matrix on the accessibility of active sites, we synthesized two polyurethanes derived from the same macrocycle (15-crown-5).[19] In the case of **21**, we used flexible hexamethylene diisocyanate, while **22** was obtained by using rigid diphenylmethane diisocyanate. For this evaluation the cross-linking of polymers was achieved by using a 20% excess of isocyanate groups. The procedure described above is the most direct way of preparing immobilized pendant crown compounds on polymers.



n	R		Macrocycle	Sample
1	$-(CH_2)_6-$	**15**	12-crown-4	**20**
2	$-(CH_2)_6-$	**16**	15-crown-5	**21**
2	$-p,C_6H_4-CH_2-p,C_6H_4-$	**16**	15-crown-5	**22**
3	$-(CH_2)_6-$	**17**	18-crown-6	**23**
4	$-(CH_2)_6-$	**18**	21-crown-7	**24**
5	$-(CH_2)_6-$	**19**	24-crown-8	**25**

Scheme 8. Polyaddition of Diisocyanates with Diol-Functionalized Crown Ethers

Evaluation of ionoselective properties

The different polyurethanes were immersed in liquid nitrogen and then crushed. The cation binding properties of polymers were determined via a competitive extraction of five alkali-metal cations. Evaluation of new materials with a multicomponent solution was meant to determine if the use of polymeric immobilized crown ethers justified further investigation. Methods previously described for the evaluation of ionoselective properties with multicomponent solutions determine the efficiency of sorption using a stripping method.[23-25] The stripping is performed with an aqueous HCl solution. In those cases, for the correct evaluation of ionoselective properties the stripping step should be completed. Nevertheless, it has been shown that the efficiency of the back-extraction step was dependent on the type of alkali-metal cations and anions involved.[23] Furthermore, the results could be altered by uncomplexed alkali-metal salts from the resin bed. In those cases, extraction efficiencies were the result of a two steps process (sorbtion / stripping).

For our evaluation, we used a solution of five alkali-metal nitrates. The distibution coefficient (D) is defined as the ratio of concentrations of the cations on the polymer and in the solution after 8 hours of contact. The distribution coefficient (D), calculated from the concentration of each cation in solution before and after extraction, is given by Eq. 1:

$$D=\left(\frac{C_O}{C_f}-1\right)\times\frac{V}{M} \qquad (1)$$

Where : C_0 = concentration in solution before extraction, C_f = concentration in solution after extraction, V = volume of the solution (L), M = weight of the sample (kg).

The concentrations of the salts and the ratio between the volume of solution and mass of polymer were manipulated in order to improve extraction and precision, thus margins of error were minimized. The results of the solid/liquid extractions carried out are listed in Table 1.

Table 1. Distribution Coefficients for Polymers

Sample	Macrocycle	D (L/kg)				
		Li^+	Na^+	K^+	Rb^+	Cs^+
8	12-crown-4	0 *	**3.8** *	0.3 *	0.1 *	0 *
20	12-crown-4	0	**0.8**	0	0	0
21	15-crown-5	0	0.3	**1.4**	0.5	0.2
22	15-crown-5	0	0	**0.1**	0	0
23	18-crown-6	0.4	0.5	**5.0**	1.7	0
24	21-crown-7	0	0	1.0	**2.4**	**2.1**
25	24-crown-8	0	0	0.2	0.4	**0.6**

Conditions: $[Li^+]=[Na^+]=[K^+]=[Rb^+]=[Cs^+]=0.25$ M, $[HNO_3]=1.4$ N, V=2 mL, M= 1 mmol macrocycle

* *Conditions: $[Li^+]=[Na^+]=[K^+]=[Rb^+]=[Cs^+]=0.25$ M, V=2 mL, M= 0.45 mmol macrocycle*

Margin of error: ± 0.2 L/kg

The polymers containing crown ether units with different cavities bound metals according to the "size-fit" concept (samples **23** to **25**), with exceptions. In the presence of different alkali-metal cations, extraction of lithium by polymers **8** and **20** was not detected, one could expect from macrocycle size. This could be explained by the higher degree of hydration of lithium [26] and by the fact that, unlike the other alkali cations, lithium forms a more stable six-membered chelate ring rather than the five-membered one.[27]

Polymer **8** strips sodium off with sodium/lithium and sodium/potassium selectivity greater than **18** and **7** respectively. This high loading capacity and selectivity for sodium can be explained by the formation of 2:1 complexes by cooperative action of two adjacent 12-crown-4 ether moieties.[28] Conversely, the very small capacity of **20** is due to the difficulty in forming 2:1 complex, as in the case of **8**.

Polymer **21**, bearing 15-crown-5 ether bound potassium more than sodium. This is probably due to the presence of extracyclic oxygen.[29] As illustrated by samples **21** and **22**, greater capacity is reached by increasing active site accessibility and mobility. Polymer **21**, with the flexible chain, has a loading capacity ten times greater than **22**. It also displays an increased selectivity towards potassium. Polymer **24** bearing 21-crown-7 possesses good binding properties for cesium. When the size of the cavity increases, e.g. polymer **25** bearing 24-crown-8, the capacity and the selectivity drop.

The glass transition (Tg) of each sample was determined by Differential Scanning Calorimetry (D.S.C.). Tg's of the different polymers are given in Table 2.

Table 2. Glass Transition Temperatures For Polymers

Polymer	Crown ether	Diisocyanate	Tg (°C)
20	12-crown-4	OCN-$(CH_2)_6$-NCO	+ 18 °C
21	15-crown-5	OCN-$(CH_2)_6$-NCO	- 10 °C
22	15-crown-5	OCN-*p*,C_6H_5-CH_2-*p*,C_6H_5-NCO	> + 50 °C
23	18-crown-6	OCN-$(CH_2)_6$-NCO	- 19 °C
24	21-crown-7	OCN-$(CH_2)_6$-NCO	- 23 °C
25	24-crown-8	OCN-$(CH_2)_6$-NCO	≤ - 30 °C

In the case of samples derived from hexamethylene diisocyanate, Tg decreases when the size of the crown ether increases. This is explained by the increase of the molecular weight between two cross-linking points.

Accessibility of active sites and kinetics of cation binding in resin polymers are linked to the solvatation of the macromolecular matrix. As data on Tg for polymers **20** to **25** refers to the solid state no direct comparison could be made regarding the capacity of the different polymers which were determined in aqueous media. Nevertheless, for a given polymer with the same functional groups, the presence locally of more mobile polymer chains would enhance accessibility. From Table 3, one can conclude that the mobility and the accessibility of active sites in polymer **22** were lower than polymer **21**. This is in accordance with the results of the extraction (Table 2).

Back-extraction (stripping) of the extracted metal salts from the polymers was accomplished by shaking with deionized water. No deterioration in the performance of the polymers (as evidenced by a decrease in loading capacity and selectivity) was observed after several cycles of consecutive loading and stripping.

Influence of conditions on distribution coefficient

Polymer 24 bearing 21-crown-7 possesses good binding properties for rubidium and caesium with a high selectivity towards sodium. In order to confirm this selectivity, polymer 24 was tested in different conditions. The change of the concentrations of the alkali-metal cations gave different distribution coefficients (Table 3).

Table 3. Effect of the Conditions on Distribution Coefficients for Polymer 24

Entry	Ratio cations / crown ether	Volume (mL)	Concentration (mol/L)	D (L/kg) Li^+	Na^+	K^+	Rb^+	Cs^+
1	2,5 / 1	1	0.25	0	0	1.0	2.4	2.1
2	2,5 / 1	5	0.05	0	0	2.3	7.0	5.3
3	1,25 / 1	5	0.025	0	0	3.4	11.2	9.3

Conditions: $[Li^+]=[Na^+]=[K^+]=[Rb^+]=[Cs^+]$, $[HNO_3]=1.4$ N, M = 0.5 mmol macrocycle, polymer 24

Margin of error: ± 0.2 L/kg

With the same ratio of cations/crown ether, but with different concentrations of cations (Entries 1 and 2), the distribution coefficients increased when lower concentrations of cations were used. This is explained by the definition of the distribution coefficient which is the ratio of the concentration of the cation in polymer and in solution after extraction. To verify that diffusion did not alter the distribution coefficient, we kept constant the ratio volume of solution/mass of the polymer but the concentration again decreased (Entry 3). In these conditions, an increase in the distribution coefficient was observed.

The distribution coefficient could vary due to changes in the conditions, but the equilibrium constant K_{ex} should stay the same if all sites have the same complexing properties. For caesium, the equilibrium constant is defined by Eq. 2, the overline denotes the species existing in the organic (polymeric) phase.

$$Cs^+ + NO_3^- + \overline{CE} \overset{K_{ex}}{\rightleftharpoons} \overline{[CE \cdot Cs^+ \cdot NO_3^-]} \qquad (2)$$

Equilibrium constant K_{ex} for the extraction of caesium could be calculated according to Eq. 3 in which all terms are known :

$$K_{ex} = \frac{\overline{[CE \cdot Cs^+ \cdot NO_3^-]}}{[Cs^+] \times [NO_3^-] \times \overline{[CE]}} \qquad (3)$$

The unextracted caesium concentration $[Cs^+]$ is determined by atomic emission and $\overline{[CE]}$ is the concentration of free ligand calculated according to a 1:1 extraction with all the alkali-cations. The extracted caesium concentration $\overline{[\mathrm{CE}\cdot \mathrm{Cs}^+\cdot \mathrm{NO}_3^-]}$ can be calculated using Eq. 4, where the subscript i refers to initial conditions:

$$\overline{[\mathrm{CE}\cdot \mathrm{Cs}^+\cdot \mathrm{NO}_3^-]}=[\mathrm{Cs}^+]_i-[\mathrm{Cs}^+] \quad (4)$$

From different experiments (Table 3, entries 1-3) we can calculate the loading capacity of polymer 24 in different conditions and the percentage of occupied sites. Thus, the equilibrium constant for caesium can be calculated from Eq. 3 (Table 4).

Table 4. Effect of Conditions on Loading Capacity and Extraction Constant for Polymer 24

Entry	Loading capacity (mmol/g)	Occupied sites (%)	Kex Cs ($mol^{-2}.L^2$)
1	0.9	55	2.0
2	0.5	28	3.1
3	0.4	22	4.9

The loading capacity of polymer 24 is 0.9 meq./g (Entry 1) which means that 55 % of its sites are occupied. This was considered to be an interesting result because the polyurethane based crown ether 24 is used in the shape of massive pellet. The hydrophilic character of the polyurethane enhanced the accessibility of the active site. The loading capacity decreased with the concentration of cations. In those cases, the equilibrium constant for caesium varies from 2.0 to 4.9 $mol^{-2}.l^2$. This indicates sites with various efficiency. Nevertheless, the selectivity Cs^+/Rb^+ keeps relatively constant ($Cs^+/Rb^+=0.8\pm0.1$) (Table 3) which means that the size of the cavity of crown ethers is the only factor which governs the selectivity of this kind of polymer. Different polymers were tested using lower concentrations of ions. The results of the solid/liquid extraction are listed in Table 5.

Table 5 : Distribution Coefficients for Polymers

Polymer	Macrocycle	D (L/kg)				
		Li^+	Na^+	K^+	Rb^+	Cs^+
21	15-crown-5	0	1.5	**3.9**	0.2	0
22	15-crown-5	0	0.6	**2.0**	0.3	0
24	21-crown-7	0	0	3.4	**11.2**	**9.3**
25	24-crown-8	1	2	4.2	**7.8**	**7.0**

Conditions: $[Li^+]=[Na^+]=[K^+]=[Rb^+]=[Cs^+]=0.025$ M, $[HNO_3]=1.4$ N, V=5 mL, M= 0.5 mmol macrocycle

Margin of error: ± 0.2 L/kg

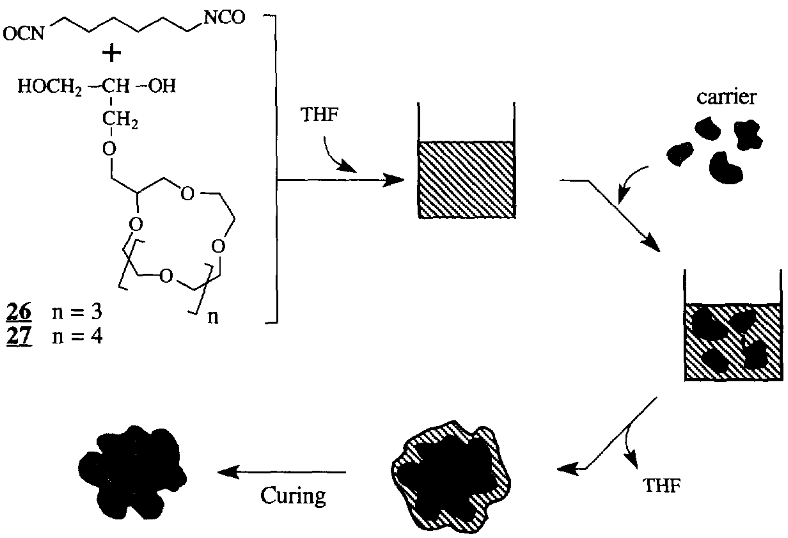
Under these conditions the polymers showed higher distribution coefficients but the order of selectivity was the same. The influences of the mobility of crown ethers on ionoselective properties were confirmed (samples 21 and 22). Polymer 24 showed under these conditions very high selectivity for caesium ($Cs^+/Na^+ \geq 46$). In a competitive extraction system, polymer based 24-crown-8 25 showed lower capacity and selectivity for caesium.

The decrease of equilibrium constant for caesium, when the percentage of sites increases, (Table 5) can be explained by the fact that inner macrocycles were hardly accessible. To overcome this disadvantage, we prepared a new type of immobilized polymeric crown ethers.

Preparation of polyurethane-coated silica-gel

Polyurethanes based crown ethers are elastomers. Improvements in physical properties and a much higher utilisation efficiency of the crown compound can be achieved with immobilized crown compounds bound chemically to the surface of a solid support. However, many steps are needed to synthesize silica-gel supported crown compounds[30] or polymeric crown ethers.[31]

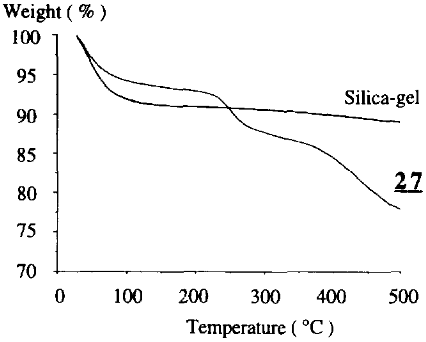
In an attempt to overcome this disadvantages, monomers were reacted on the surface of a solid carrier to form a thin coating film of crown based resin.[32] Such materials have crown ethers in the main chain and this limits their mobility and accessibility. Our approach allows simple preparation of supported flexible polymers with mobile crown ethers in pendant chains. Functionalized crown ether was reacted with hexamethylene diisocyanate on the surface of a solid carrier (silica gel) to form thin coating film of crown ether. The immobilization method is illustrated in Scheme 9.



Scheme 9. Preparation of Polyurethane-Coated Silica-Gel

The adhesion of the crown based resin is stable in protic and aprotic solvents. Furthermore, during the polyaddition and curing process, excess isocyanate which is present could react with the silanol groups on the surface of silica-gel. Such linkage could also contribute to improve the adhesion, even if such linkage is a hydrolytically labile one.

Two kinds of polyurethanes bearing 18-crown-6 and 21-crown-7 were immobilized. The amount of polymer present on the silica-gel was confirmed by thermogravimetric measurements (TG) (Scheme 10). Comparison between crude silica and polymer supported silica gave the weight of coating film which corresponds to the quantity introduced, i.e. 0.2 mmol/g.



Scheme 10. TG Curves for Silica-Gel and Polyurethane-Coated Silica-Gel 27

Evaluation of polyurethanes-coated silica-gel 26 and 27

Cation-complexing abilities for alkali-metal cations of samples 26 and 27 supported on silica gel are given in Table 6. The results of the extraction show that the polymers supported on silica-gel kept their selectivity. Those silica gel supported polymers can be reused without significant loss of capacity and selectivity.

Table 6. Distribution Coefficients for Polymers

Sample	Macrocycle	D (L/kg)				
		Li^+	Na^+	K^+	Rb^+	Cs^+
26 / SiO_2	18-crown-6	0	0	**4.2**	1.8	1.5
27 / SiO_2	21-crown-7	0	0	2.8	**5.5**	**5.1**

Conditions: $[Li^+]=[Na^+]=[K^+]=[Rb^+]=[Cs^+]=0.0025$ M, V=5 mL, M= 250 mg
Margin of error: ± 0.2 L/kg

The results of this study demonstrate that polyurethane, obtained by catalysed polyaddition of diisocyanate with diol-functionalized crown ethers, provides hydrophilic polymers for the selective extraction of ions. The ionoselective properties of these materials are based on the recognition of ions by highly selective synthetic organic ligands covalently attached to hydrophilic polymers. In addition those polymers could be immobilized on silica gel. Those potential chromatographic materials are more easily prepared than poly(crown ether) modified silica[31] and could provide higher selectivity compared to crown ether modified one.[4,33]

These features provide a separation system with the selectivity required to capture extremely low levels of ions. These new materials could be useful in analytical purposes in several ways: concentrating analytes, removing unwanted matrix ions to purify solutions and allowing concentration even in solutions of moderate acidity.

EXPERIMENTAL SECTION

General Information

^{1}H NMR spectra were recorded at 200 MHz with a Bruker AC 200 spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 50 MHz with a Bruker AC 200 spectrometer with the solvent carbon signal as standard. FTIR spectra were recorded on a 1720-X Perkin Elmer spectrometer. Microanalyses, high and low resolution mass spectra were performed at the "CNRS, Service Central d'Analyse, Vernaison, France". Differential scanning calorimetry was performed on a Perkin-Elmer DSC-4. Thermogravimetric measurements were made on a TGA V5.1A 2000 Dupont Instruments. Samples (10mg) were heated at 10°C min^{-1} in a dynamic helium atmosphere. The molecular weight of soluble polymers was determined by GPC in THF on a Waters 410 apparatus equipped with a linear ultrastiragel column. Columns were calibrated using narrow-dispersity polystyrene standards.

All chemicals were reagent grade and used without futher purification. Ethylene glycol ditosylate was prepared as described in ref. 34. All the syntheses were performed under a dry argon atmosphere. Concentrations of solutions were determined by atomic emission spectroscopy (Perkin Elmer type 1100M: air-acetylene flame).

3-Allyloxy-1,2-propanediol $\underline{2}$ was prepared from allyl glycidyl ether $\underline{1}$ as described in ref. 14 and was purified by distillation, (88%), b.p.: 99-103°C/3 10^{-6} bar (76-83°C/0,04 torr ref.9), ^{1}H NMR (CD_2Cl_2): 2.0-2.4 (m, 2H, CH_2OH); 3.5-3.6 (m, 1H, CHOH); 3.6-4.0 (m, 4H, $=C-CH_2$, $O-CH_2$); 4.1 (b, 2H, OH); 5.0 (m, 2H, $=CH_2$); 5.8 (m, 1H, CH=), ^{13}C NMR (CD_2Cl_2): 63.97 (CH_2OH); 71.07 (CHOH); 71.18 (CH_2O); 71.53 (CH_2O); 117.43 ($=CH_2$); 134.67 (CH=)

General synthesis of (allyloxy)methyl-crown derivatives

NaH, 95% (3.64g, 144mmol) was suspended in THF (200 mL, vigorous stirring). Alkaline perchlorate (60mmol) was then added. The mixture was heated to reflux. Compound $\underline{2}$ (7.93g, 60mmol) dissolved in THF (100 mL) was added dropwise over 1 hour, then ethyleneglycol ditosylate (60mmol) dissolved in THF (100 mL) was added dropwise over 2 hours. The mixture was stirred vigorously at reflux for 24 hours, allowed to cool, and then water was added with caution. THF was stripped away on a rotary evaporator and the residue taken up in H_2O. The aqueous mixture was extracted with CH_2Cl_2. The combined organic phases were dried and filtered. The crude product mixture was chromatographed over alumina with 0-20% (v/v) cyclohexane/ethyl acetate as eluent.

Mixture of (allyloxy)methyl-12-crown-4 3 and di-(allyloxy)methyl-24-crown-8 4 were prepared from 2, lithium perchlorate (6.38g, 60mmol) and triethylene glycol ditosylate (27.51g, 60mmol). Colorless oil, 5.91 g.
3 GC/MS (E.I. 70eV) m/z (%): 87 (100); 175 (50, M-C_4H_7O); 205 (4.5, M-C_3H_5); 247 (4.5, M+1)
4 GC/MS (E.I. 70eV) m/z (%): 87 (100); 421 (2, M-C_4H_7O); 451 (3, M-C_3H_5); 493 (0.6, M+1)

(Allyloxy)methyl-15-crown-5 9 was prepared from 2, sodium perchlorate (7.35g, 60mmol) and tetraethylene glycol ditosylate (30.16g, 60mmol). Colorless oil, 10.10 g (58%).
MS (E.I. 70eV) m/z (%) : 87 (100); 219 (52, M-C_4H_7O); 249 (5.1, M-C_3H_5); 291 (4.3, M+1), FTIR (NaCl): 2933: $\nu_{as}CH_2$; 2861: ν_sCH_2 ; 1642: $\nu C{=}C$; 1124 : $\nu_{as}CH_2OCH_2$; 981, 920: $\delta_{=C\text{-}H}$, ^1H NMR(CD_2Cl_2): 3.4-3.8 (m, 21H, CH_2O); 3.9-4.0 (m, 2H, CH_2-C=); 5.1-5.3 (m, 1H, CH_2= trans); 5.3-5.4 (m, 1H, CH_2= cis); 5.8-6.0 (m, 1H, CH=), ^{13}C NMR (CD_2Cl_2): 70.35; 70.62; 70.69; 70.71; 70.74; 70.83; 70.93; 71.01; 71.20; 71.64; 72.45 (CH_2O); 78.93 (CH0); 116.53 (CH_2=); 135.40 (CH=)

(Allyloxy)methyl-18-crown-6 12 was prepared from 2, potassium perchlorate (8.31g, 60mmol) and pentaethylene glycol ditosylate (32.80g, 60mmol). Colorless oil, 11.44 g (57%).
MS (E.I. 70eV) m/z (%) : 87 (100); 263 (48, M-C_4H_7O); 293 (3, M-C_3H_5); 335 (1.4, M+1), FTIR (NaCl): 2943: $\nu_{as}CH_2$; 2854: ν_sCH_2 ; 1644: $\nu C{=}C$;1116:$\nu_{as}CH_2OCH_2$; 996, 904: $\delta_{=C\text{-}H}$, ^1H NMR (CD_2Cl_2): 3,4-3,8 (m, 25H, CH_2O); 3.9-4.1 (m, 2H, CH_2-C=); 5.1-5.3 (m, 1H, CH_2= trans); 5.3-5.4 (m, 1H, CH_2= cis); 5.8-6.0 (m, 1H, CH=), ^{13}C NMR (CD_2Cl_2): 69.87; 70.54; 70.74; 70.80; 70.87 (several carbon atoms); 71.03; 71.07; 71.72; 72.46; (CH_2O); 78.54 (CH0); 116.57 (CH_2=); 135.41 (CH=)

(Allyloxy)methyl-21-crown-7 13 was prepared from 2, caesium perchlorate (13.94g, 60mmol) and hexaethylene glycol ditosylate (35.44g, 60mmol). Colorless oil, 11.44 g (44%).
MS (E.I. 70eV) m/z (%) : 87 (100); 307 (41, M-C_4H_7O); 337 (5, M-C_3H_5); 379 (1.2, M+1), FTIR (NaCl): 2928: $\nu_{as}CH_2$; 2851: ν_sCH_2 ; 1640: $\nu C{=}C$; 1117 : $\nu_{as}CH_2OCH_2$; 989, 914: $\delta_{=C\text{-}H}$, ^1H NMR (CD_2Cl_2): 3.4-3.8 (m, 29H, CH_2O); 3.9-4.0 (m, 2H, CH_2-C=); 5.1-5.2 (m, 1H, CH_2= trans); 5.3-5.4 (m, 1H, CH_2= cis); 5.8-6.0 (m, 1H, CH=), ^{13}C NMR (CD_2Cl_2): 71.67; 72.21; 72.37; 72.52; 72.61 (several carbon atoms); 72.65; 72.86; 72.96; 73.59; 74.05 (CH_2O); 80.32 (CH0); 118.15 (CH_2=); 137.01 (CH=)

1-((Allyloxy)methyl)-3,6,9-oxa-undecane-1,11 diol 5 was prepared from allyl glycidyl ether 1 as described in ref. 11 and was purified by distillation to give 5. Colorless oil, 19.56 g (74%), b.p.: 120-125°C/1 10^{-6} bar (138-151°C/0,01 torr ref.11), FTIR (NaCl): 3356: $\nu O\text{-}H$; 2937: $\nu_{as}CH_2$; 2859: ν_sCH_2 ; 1642: $\nu C{=}C$; 1117 : $\nu_{as}CH_2OCH_2$; 989, 914: $\delta_{=C\text{-}H}$, ^1H NMR (CD_2Cl_2): 3.4-3.7 (m, 17H, CH_2O); 3.7-3.9 (sb, 2H, OH); 3.9-4.1 (m, 2H, CH_2-C=); 5.1-5.4 (m, 2H, CH_2=); 5.8-6.0 (m, 1H, CH=), ^{13}C NMR (CD_2Cl_2): 61.79 (CH_2OH); 69.76 (CHOH); 70.41; 70.78; 70.89; 71.04; 71.67; 72.52; 73.14; 73.52 (CH_2O); 116.76 (CH_2=); 135.34 (CH=)

(Allyloxy)methyl-12-crown-4 3. A mixture of sodium hydroxide (1.32g, 33mmol) dissolved in water (50 mL) and 5 (7.93g, 30mmol) in THF (25 mL) was placed in a jacketed flask and cooled to 0°C with mechanical stirring. To this mixture was added dropwise p-toluensulfonyl chloride (5.71g, 30mmol) in THF (100 mL) over 2 hours with continuous stirring and cooling off the mixture. The solution was stirred for an additional 2 hours and then extracted with dichloromethane. The combined organic extracts were washed twice with water and once with satured aqueous sodium chloride solution, and then dried over anhydrous $MgSO_4$. The solvent was stripped away on a rotary evaporator. Yellow oil, 11.42 g (91%).
NaH (0.7g, 30mmol) was suspended in THF (150 mL, vigorous stirring). Lithium perchlorate (6.38g, 60mmol) was then added. The mixture was heated to reflux. Monotosylated derivative (8.37g, 20mmol) was dissolved in THF (150 mL). This solution was added dropwise over 1 hour. The mixture was stirred vigorously for 12 hours at reflux. The workup procedure was carried out as described for 9. Colorless oil, 4.13g (56%). FTIR (NaCl):2939:$\nu_{as}CH_2$; 2861:ν_sCH_2; 1126:$\nu_{as}CH_2OCH_2$; 985,910: δ=C-H, ^{1}H NMR (CD_2Cl_2): 3.4-3.9 (m, 17H, CH_2O); 3.9-4.1 (m, 2H, CH_2-C=); 5.1-5.3 (m, 1H, CH_2= trans); 5.3-5.4 (m, 1H, CH_2= cis); 5.8-6.0 (m, 1H, CH=), ^{13}C NMR (CD_2Cl_2): 70.70; 70.93; 71.04; 71.21; 71.31; 71.43; 71.50; 72.28; 72.84 (CH_2O); 79.15 (CHO); 116.95 (CH_2=); 135.63 (CH=), MS (E.I. 70eV) m/z (%): 87(100); 175(50, M-C_4H_7O); 205 (4.5, M-C_3H_5); 247 (4.5, M+1)

(Allyloxy)methyl-24-crown-8 14. NaH (1.8g, 72mmol) was suspended in THF (200 mL, vigorous stirring). Caesium perchlorate (7g, 30mmol) was then added. The mixture was heated to reflux. 5 (7.93g, 30mmol) was dissolved in THF (100mL). This solution was added dropwise over 1 hour, then tetraethyleneglycol ditosylate (15g, 30mmol) dissolved in THF (200 mL) was added dropwise over 2 hours. The mixture was stirred vigorously for 24 hours at reflux. The workup procedure was carried out as described for 9. Colorless oil, 2.9 g (23%). MS found 422.2511 ($C_{20}H_{38}O_9$ requires 422.2515), FTIR (NaCl): 2933: $\nu_{as}CH_2$; 2868: ν_sCH_2 ; 1644: νC=C ; 1122 : $\nu_{as}CH_2OCH_2$; 985, 910: δ=C-H, ^{1}H NMR (CD_2Cl_2): 3.4-3.8 (m, 33H, CH_2O); 3.9-4.1 (m, 2H, CH_2-C=); 5.1-5.4 (m, 2H, CH_2=); 5.8-6.0 (m, 1H, CH=), ^{13}C NMR (CD_2Cl_2): 70.78; 71.34; 71.47; 71.64; 71.71; 71.91 (several carbon atoms); 72.00; 72.68; 73.17 (CH_2O); 79.48 (CHO); 117.26 (CH_2=); 136.12 (CH=)

General preparation of the diol functionalized crown ether

Olefin (5mmol) was dissolved in acetone/water (1/2, v/v, 3 mL). To this was added N-methylmorpholine N-oxide (0.75g, 6.4mmol) followed by 150 µL of OsO_4 (2.5% pds in t-butanol). The mixture was stirred overnight at ambient temperature and NaS_2O_3 (500mg) was added. Acetone (15 mL) was added to the reaction mixture, and the mixture was filtered throught Celite. The Celite cake was washed with additional acetone, and the washings were combined with filtrate and reduced in vacuo. The residue was acidified with 2N HCl and extracted with chloroform. The chloroform extract was washed with water and dried over anhydrous $MgSO_4$. The crude product was decolorized using a short alumina column with acetone/cyclohexane (1/1, v/v) as eluent.

(2,3-Dihydroxypropyloxy)methyl-12-crown-4 **15** was prepared from (allyloxy)methyl-12-crown-4 **3** (1.23g, 5mmol), colorless oil, 0.54 g (39%), MS (E.I. 70 eV) m/z (%): 87 (100); 175 (41, M-$C_4O_3H_9$); 262 (9, M-H_2O); 281 (4, M+1), FTIR (NaCl), cm^{-1}: 3324 ν_{OH} ; 2963 $\nu_{as}CH_2$; 2875 ν_sCH_2; 1457; 1118 : $\nu_{as}CH_2OCH_2$; 946, ^1H NMR (CD_2Cl_2): 2.6-2.8(b, 2H, OH), 3.2-3.8(m, 22H), ^{13}C NMR (CD_2Cl_2):64.77 (CH_2OH); 70.31; 70.70; 70.93; 71.09; 71.36; 71.49; 71.72; 72.26; 72.47 (CH_2O); 74.03 (CHOH); 79.37 (CH)

(2,3-Dihydroxypropyloxy)methyl-15-crown-5 **16** was prepared from (allyloxy)methyl-15-crown-5 **9** (1.45g, 5mmol), colorless oil, 0.73 g (45%), MS (I.E. 70 eV) m/z (%): 87 (100); 219 (19, M-$C_4O_3H_9$); 306 (5, M-H_2O); 325 (3, M+1), FTIR (NaCl), cm^{-1}: 3326 ν_{OH} ; 2919 $\nu_{as}CH_2$; 2869 ν_sCH_2; 1456; 1133 : $\nu_{as}CH_2OCH_2$; 915, ^1H NMR (CD_2Cl_2): 2.8-3.0(b, 2H, OH), 3.5-3.8(m, 26H), ^{13}C NMR (CD_2Cl_2): 65.86 (CH_2OH); 71.61; 72.03; 72.11; 72.22; 72.35; 72.50; 72.58; 72.74; 72.80; 72.91; 73.55 (CH_2O); 78.08 (CHOH); 80.19 (CH)

(2,3-Dihydroxypropyloxy)methyl-18-crown-6 **17** was prepared from (allyloxy)methyl-18-crown-6 **12** (1.67g, 5mmol), colorless oil, 1.16 g (63%), MS (I.E. 70 eV) m/z (%): 87 (100); 267 (14, M-$C_4O_3H_9$); 350 (3, M-H_2O); 369 (1, M+1), FTIR (NaCl), cm^{-1}: 3336 ν_{OH} ; 2937 $\nu_{as}CH_2$; 2868 ν_sCH_2 ; 1455; 1118 : $\nu_{as}CH_2OCH_2$; 944, ^1H NMR (CD_2Cl_2): 2.8-2.9(b, 2H, OH), 3.5-3.8(m, 30H), ^{13}C NMR (CD_2Cl_2): 64.14 (CH_2OH); 69.73; 70.26; 70.54; 70.69 (several carbon atoms); 70.80; 71.12; 71.51; 71.92; 72.42 (CH_2O); 74.25 (CHOH); 79.84 (CH)

(2,3-Dihydroxypropyloxy)methyl-21-crown-7 **18** was prepared from (allyloxy)methyl-21-crown-7 **13** (1.89g, 5mmol), colorless oil, 1.25 g (61%), MS (I.E. 70 eV) m/z (%): 87 (100); 307 (5, M-$C_4O_3H_9$); 394 (3, M-H_2O); 413 (1, M+1), FTIR(NaCl), cm^{-1}: 3336 ν_{OH} ; 2926 $\nu_{as}CH_2$; 2870 ν_sCH_2 ; 1456; 1114 : $\nu_{as}CH_2OCH_2$; 948, ^1H NMR (CD_2Cl_2): 3.3-3.4 (s, 2H, OH); 3.4-3.9 (m, 34H), ^{13}C NMR (CD_2Cl_2): 65.77 (CH_2OH); ; 71.43; 71.45; 72.19; 72.42; 72.53 (several carbon atoms); 72.59; 72.65; 72.84; 73.17; 73.21; 74.68 (CH_2O); 74.90 (CHOH); 80.06 (CH)

(2,3-Dihydroxypropyloxy)methyl-24-crown-8 **19** was prepared from (allyloxy)methyl-24-crown-8 **14** (2.11g, 5mmol), colorless oil, 1.50 g (66%), MS (I.E. 70 eV) m/z (%): 87 (100); 351 (4, M-$C_4O_3H_9$); 438 (6, M-H_2O); 457 (0.2, M+1), FTIR(NaCl), cm^{-1}: 3326 ν_{OH} ; 2935 $\nu_{as}CH_2$; 2871 ν_sCH_2; 1455; 1131 : $\nu_{as}CH_2OCH_2$; 946, ^1H NMR (CD_2Cl_2): 2.6-2.9 (s, 2H, OH); 3.3-3.9 (m, 38H), ^{13}C NMR (CD_2Cl_2): 64.63 (CH_2OH); 70.44; 70.92; 71.16; 71.31; 71.41 (several carbon atoms); 71.46 (CH_2O); 73.85 (CHOH); 79.07 (CH)

(2,3-Epoxypropyloxy)methyl-12-crown-4 **6** . Compound **3** (9.78g, 39.7mmol) was dissolved in dichloromethane (50 mL). The flask was cooled to 0°C and a solution of m-chloroperoxybenzoic acid (50% pds) (13.68g, 39.7mmol) in dichloromethane (200 mL) was added dropwise with stirring. After 4 hours stirring at room temperature, the flask was cooled again to 0°C and another portion of m-CPBA (13.68g, 39.7 mmol) was added. The mixture was stirred for 4 hours at room temperature and then washed successively with diluted $Na_2S_2O_3$, satured $NaHCO_3$ and water. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to yield **6**. Colorless oil, 10.10g (97%), ^1H NMR (CD_2Cl_2): 2.6 (m, 2H, CH_2O); 3.1 (m, 1H, CHO); 3.5-3.8 (m, 19H, CH_2O), ^{13}C NMR (CD_2Cl_2): 44.1 (CH_2O); 50.8 (CHO); 69.7; 70.0; 70.7; 70.9; 71.2; 71.5; 72.0 (CH_2O); 78.3 (CHO)

Hydroxymethyl-15-crown-5 10 was prepared from 9 as described in ref. 11. The crude mixture was purified with a short alumina column with i-propanol/cyclohexane (1/1, v/v) as eluent. Colorless oil, 5.45 g (92%), FTIR (NaCl), cm^{-1}: 3250 νOH ; 2930 $\nu_{as}CH_2$; 2870 ν_sCH_2; 1135 : $\nu_{as}CH_2OCH_2$; 985, 910: δ=C-H, ^1H NMR (CD_2Cl_2): 3,2 (s, 1H, OH), 3,4-3,7 (m, 21H, CH_2O, CH_2OH, CHO), ^{13}C NMR (CD_2Cl_2): 62,88 (CH_2OH); 69,75; 70,06; 70,43; 70,52; 70,66; 70,82; 70,99; 71,39; 71,46 (CH_2O); 80,07 (CHO)

(2,3-Epoxypropyloxy)methyl-15-crown-5 11. NaH (0.3g, 12mmol) was suspended in THF (50 mL, vigorous stirring). 10 was dissolved in THF (50 mL). This solution was added dropwise over 1 hour, and stirred at room temperature for 2 hours. Then, epichlorohydrine (0.92g, 10mmol) dissolved in THF (50 mL) was added dropwise over 1 hour. The mixture was stirred vigorously for 24 hours at room temperature and then water was added with caution. The solution was neutralized with diluted hydrochloric acid (0.1N). 11 was extracted with $CHCl_3$. The combined organic phases were dried and concentrated. Colorless oil, 2.63g (86%), ^1H NMR (CD_2Cl_2): 2.6-2.7 (m, 2H, CH_2O); 3.0-3.1 (m, 1H, CHO); 3.5-3.7 (m, 23H, CH_2O), ^{13}C NMR (CD_2Cl_2): 44.86 (CH_2O); 51.61 (CHO); 70.95; 71.17; 71.24; 71.33; 71.40; 71.53; 71.78; 72.03; 72.53; 72.60; 73.16; 73.21 (CH_2O); 79.51 (CH)

Anionic polymerisation of 6. KOH (40mg, 0.7mmol) was dried at 200°C for 4 hours under vacuum. After cooling, the monomer 6 (1.9g, 7.2mmol) was introduced and the slurry was stirred for 7 days under argon at room temperature. The polymer was washed with diluted acid and dried at 60°C in vacuo. The yield was quantitative. $\overline{Mn}$=4500g/mol, ^1H NMR ($CDCl_3$): 3.5-3.8 (m) ^{13}C NMR ($CDCl_3$): 69.8-72.8 (m, several carbon atoms), FTIR (NaCl), cm^{-1}: 2916, 2864, 1366, 1098, 910, 852

Cross-linking of polymer 7. Diol 7 (1.5g, 5.7mmol) was dissolved in 1,2-dichloroethane (3 mL). One drop of dibutyltin dilaurate was added and then diphenylmethane diisocyanate (Merck N°820797, mixture of isomers) (1.5g, 6mmol) was added dropwise with stirring. After 48 hours stirring at room temperature, the mixture was heated to 50°C for 12 hours. Yield was quantitative. The polyurethane obtained was then crushed.

General procedure of cross-linking of diols functionnalised crown ether

Diol (3mmol) was dissolved in 1,2-dichloroethane (3 mL). One drop of dibutyltin dilaurate was added and then diisocyanate (3.6mmol) was added dropwise with stirring. After 72 hours stirring at room temperature (48 hours with diphenylmethane diisocyanate), the mixture was heated to 50°C for 12 hours. Yields were quantitative. The obtained polyurethanes were immersed in liquid nitrogen and then crushed.

Characteristics of the polymers: the results of elemental analysis were not all reliable. This could be explain because of partial polycondensation.

Polyurethane 20, Tg=18°C, Anal. calcd. for **15** + 1.2 **OCN-$(CH_2)_6$-NCO**: C, 53.8; H, 8.0; N, 7.0; O, 31.2.Found: C, 53.22; H, 8.06; N, 6.90; O, 31.58.

Polyurethane 21, Tg=-10°C, Anal. calcd. for **16** + 1.2 **OCN-$(CH_2)_6$-NCO**: C, 53.7; H, 8.2; N, 6.4; O, 31.8. Found: C, 52.16; H, 8.47; N, 6.27; O, 32.99.

Polyurethane 22, Tg>+50°C, Anal. calcd. for **16** + 1.2 **OCN-C_6H_4-CH_2-C_6H_4-NCO**: C, 61.5; H, 6.4; N, 5.4; O, 26.7 Found: C, 60.98; H, 6.57; N, 5.38; O, 27.05.

Polyurethane 23, Tg=-19°C, Anal. calcd. for **17** + 1.2 **OCN-$(CH_2)_6$-NCO**: C, 53.9; H, 8.2; N, 5.9; O, 32.0 Found: C, 50.68; H, 8.86; N, 5.84; O, 34.61.

Polyurethane 24, Tg=-23°C, Anal. calcd. for **18** + 1.2 **OCN-$(CH_2)_6$-NCO**: C, 54.0; H, 8.3; N, 5.5; O, 32.3 Found: C, 53.16; H, 8.48; N, 5.38; O, 32.93.

Polyurethane 25, Tg< -30°C, Anal. calcd. for **19** + 1.2 **OCN-$(CH_2)_6$-NCO**: C, 54.0; H, 8.3; N, 5.1; O, 32.6 Found: C, 53.02; H, 9.06; N, 5.35; O, 32.49.

General procedure for the immobilisation on silica-gel

Silica-gel (5g) was suspended in THF (50mL, vigorous stirring). Diol derivatives (1mmol) in THF (5mL), 1,6-diisocyanatohexane (200mg, 1.2mmol) in THF (5mL) and a drop of dibutyltin dilaurate were then rapidly added. The mixture was stirred vigorously for 1 hour at 40°C on a rotary evaporator. The solvent was then evaporated at atmospheric pressure and the resulting silica was heated at 90°C for 12 hours on air. Then the materials were washed thoroughly with chloroform/ethanol (1/1, v/v).

Extraction Experiments.

Solutions were prepared by dissolving the required quantity of alkalin nitrate in distilled water. pH was adjusted using nitric acid. A known amount of polyurethane was shaken for 8 hours (equilibrium was reached) with the solution of salts. After filtration, the concentration in the solution was determined by atomic emission spectroscopy.

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Acknowledgment

The authors are grateful to J. Rawlings-El Kassmi and S. Thomson for helpful discussions.

(*Received in Belgium* 15 *May* 1996; *accepted* 18 *November* 1996)