

PREPARATION AND APPLICATION OF POLYMERS WITH CYCLIC POLYETHER ANCHOR GROUPS

E. Blasius and K.P. Janzen

Universität des Saarlandes, Anorganische Analytik und Radiochemie,
Im Stadtwald 11, 6600 Saarbrücken, FRG

Abstract: Polymers with cyclic polyethers as anchoring groups can be prepared by various methods. They have a wide range of applications. Particularly the analytical applications in ion chromatography and the preparative application for catalysis of organic reactions must be mentioned.

1. INTRODUCTION

Crown compounds and cryptands are cyclic polyethers. Monomeric cyclic polyethers can be bound to polymeric matrices by different methods. Here the application of such cross-linked polymers as selective sorbents in analytical and preparative chemistry (1-11) is reported. Figure 1 shows the two most important representatives of the classes of cyclic polyethers.

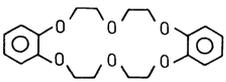
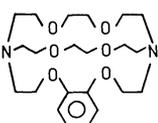
Type of compound	Example	Nomenclature
Monocyclic polyethers or crown ethers	 Dibenzo-18-Crown-6	2 Benzene rings, 18 membered ring, 6 of them are O-atoms
Bicyclic polyethers or cryptands	 Monobenzo-Cryptand [2.2.2]	2 N-Atoms, 3 bridges each with 2 O-atoms. B is the symbol for an additional benzene ring in a bridge

Fig. 1: Examples for Crown Ethers and Cryptands

The complexes which the polyethers form with salts are held together by interactions between the cations and the C-O dipoles of the polyethers, that means, the polyethers are neutral ligands. Variable ring sizes as well as the type, the number and the positions of the donor atoms in the ether ring permit the selective adaption to a certain cation. Together with the cation an anion is taken up because of the electroneutrality. Complexation of organic molecules is also known. Cyclic polyethers find a wide range of application in analytical and preparative chemistry because of the variability of the ring systems by which a gradual complexation of inorganic salts and organic compounds is possible. Particularly the use of the polymers in ion chromatography, phase transfer catalysis and synthesis of living polymers must be mentioned. Figure 2 shows a survey of the applications.

<u>Monomeric Cyclic Polyethers</u>	<u>Cross-linked Polymeric Cyclic Polyethers</u>
Analytical Chemistry	
Separation Methods:	Separation Methods:
Masking	Column Chromatography(Low-pressure and High-pressure Liquid Chromatography, Ion Chromatography)
Extraction	Thin-layer Chromatography
Extraction Chromatography	Thin-layer Electrophoresis
Determination Methods:	Determination Methods:
Photometry	Ion-sensitive Electrodes
Potentiometry	
Conductometry	
Polarography	
Voltammetry	
Ion-sensitive Electrodes	
Preparative Chemistry	
Phase Transfer Catalysis	Salt Conversion
Synthesis of Living Polymers	Phase Transfer Catalysis
	Synthesis of Living Polymers

Fig. 2: Applications of Cyclic Polyethers

2. RESULTS

The investigations include the preparation, characterisation and application of the new polymers with cyclic polyethers as anchoring groups.

2.1. Preparation of the polymers

Numerous exchangers which are able to bind definite inorganic salts or organic compounds are obtained by condensation, substitution or copolymerization reactions with cyclic polyethers of different structure and ring size. They have a wide range of applications. The different syntheses of the polymers with cyclic polyethers as anchoring groups are listed in Figure 3.

Procedure of synthesis	Matrix	Starting materials for polymers	
		Anchor group	Structural framework, Cross-linking reagents
Condensation	Methylene bridges	Dibenzo crownether Dibenzo cryptands	Formaldehyde
	Methylene bridges, Additional cross-linking reagent	Monobenzo crownether Monobenzo cryptands	Formaldehyde, Toluene (Xylene, Phenol, Resorcinol)
	Methylene bridges, Polystyrene	Monobenzo crownether Dibenzo crownether Phenyl crownether	
Polymerisation	Polystyrene	Monovinylmonobenzo crownether	Divinylidibenzo crownether Divinylbenzene
Substitution	Polystyrene, Amino bridges	Aminomonobenzo crownether Monocyclic cryptands	Chlormethylated polystyrene
	Polystyrene, Ether bridges	Hydroxymethylmonobenzo crownether Non-cyclic ethers	
	Silica gel, methoxy bridges Methoxy bridges	Hydroxymethylmonobenzo crownether	Silica gel
	Silica gel, Alkane bridges	ω -bromoalkanemonobenzo crownether	

Fig. 3: Procedure of Synthesis

Dibenzo crown compounds are condensed with formaldehyde in formic acid and thereby cross-linked by methylene groups. With monobenzo crown compounds and monobenzo cryptands, additional cross-linking agents, such as toluene, xylene, phenol or resorcinol are used.

It is also possible to bind monobenzo and dibenzo crown compounds at a polystyrene surface via methylene bridges by condensation reactions with formaldehyde, or to coat solid beads (polystyrene or silica gel) with these compounds as polymeric films.

Polymerization reactions of monovinylbenzo crown compounds with divinyl dibenzo crown compounds or divinylbenzene as cross-linking agents lead to polystyrene-like matrices.

Substitution reactions can be performed with chloromethylated polystyrene as well as with silica gel. Monobenzo crown compounds substituted by amino, hydroxymethyl or ω -bromoalkyl groups are linked to the matrix by -C-NH-C-, -C-O-C-, -C-C-C- or -Si-NH-C-, -Si-O-C and -Si-C-C- bonds.

The monomeric polyethers shown in Figures 4-6 are introduced into polymeric matrices by such synthesis reactions.

Figure 4 shows polymers containing only O as heteroatom.

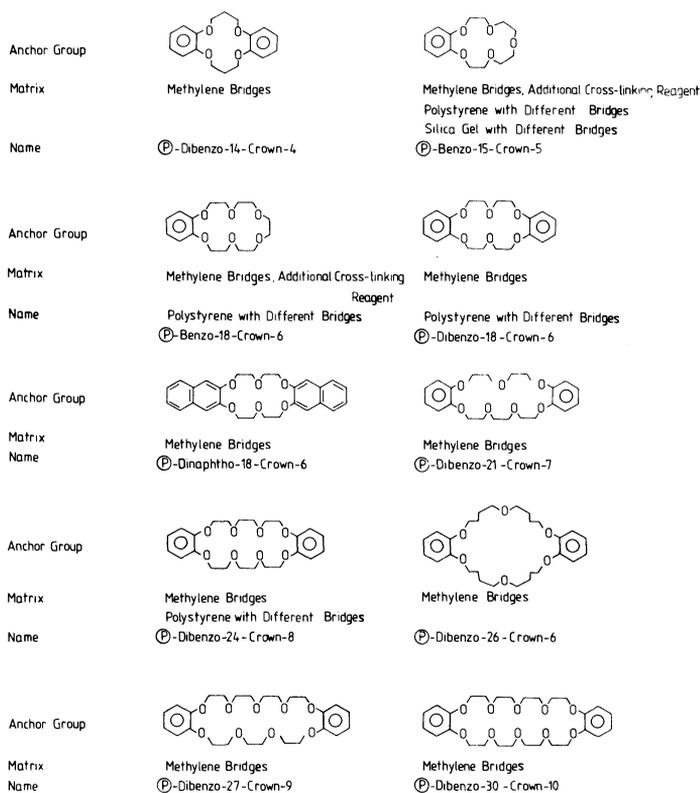


Fig. 4: Crown Ethers with O as Heteroatom

Benzo-15-crown-5, benzo-18-crown-6 and dibenzo-18-crown-6 can be introduced into polymeric matrices by all synthesis reactions described. Among all polymers prepared by condensation, that with dibenzo-18-crown-6 as anchoring group is best studied.

Polymers containing crown ethers with O and N or O and S as heteroatoms are shown in Figure 5.

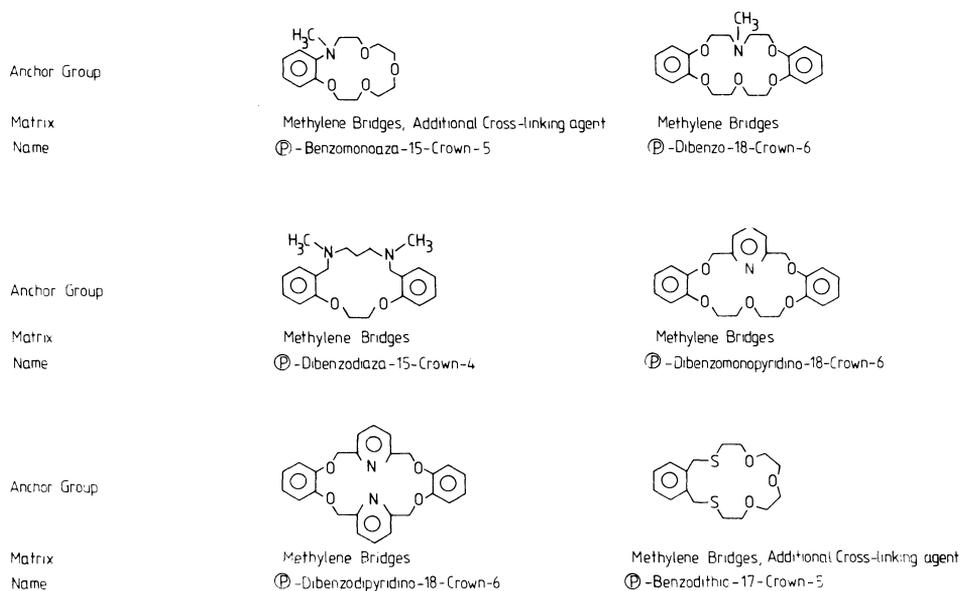


Fig. 5: Crown Ethers with O and N or S as Heteroatoms

The relative stabilities of complexes of these anchoring groups with alkali salts and the selectivity series are very similar to those of benzo-15-crown-5 and dibenzo-18-crown-6.

Figure 6 exhibits polymeric crown ethers containing cryptands or analogous urea compounds with O and N as heteroatoms.

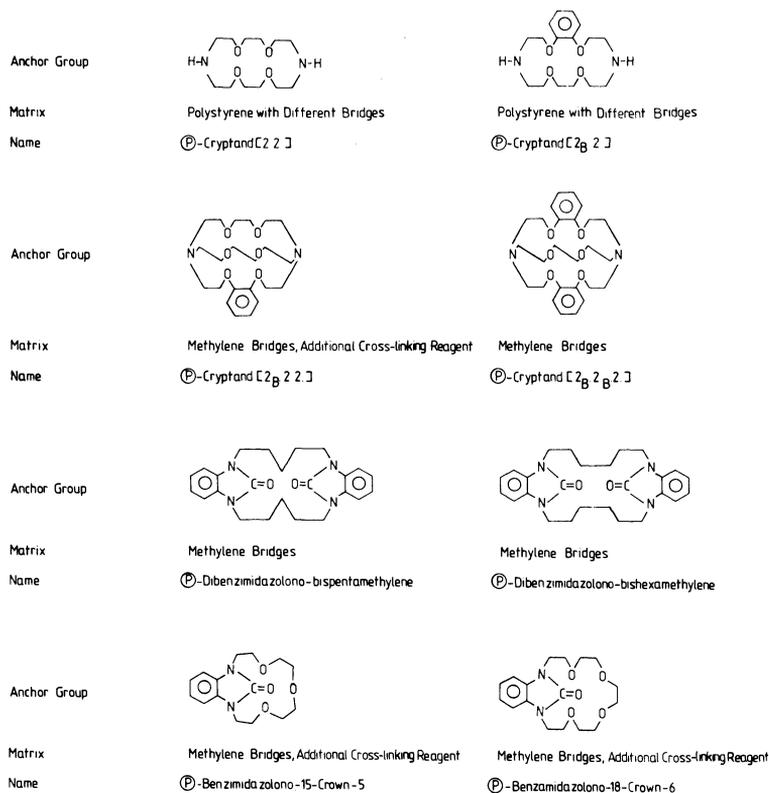


Fig. 6: Crown Ethers, Cryptates or Urea Analogues with O and N as Heteroatoms

Except for K[2.2.] and K[2_B.2.], here the anchoring groups are aminopolyethers.

2.2. Properties of the polymers

The most notable properties of the polymers with cyclic polyethers as anchoring groups, compared to those of commercially available exchangers, are listed in Figure 7.

High resistance to chemicals, temperature and radiolysis

Neutral ligands as anchoring groups

Simultaneous uptake of cations and anions to maintain electroneutrality

Degradation or stripping of the solvent shell of the cation and anion

Binding of the ions is facilitated in solvents which are less polar than water, e.g. methanol

Stability of the polyether complexes depends on cation, anion, solvent, size of polyether ring and on the number, type and position of the heteroatoms (O, N, S)

Activation of anions

Salt uptake: only O as heteroatom: independent of pH
O and N as heteroatoms: pH-dependent at pH < 3

Elution by pure solvents: no pollution of the eluate

Fig. 7: Notable Properties in Comparison with Commercial Exchanger

Furthermore, the following factor is important:

Maximum capacities and stabilities of the polyether complexes show parallels. Thus, the acid and base theory of Pearson is valid. In methanol the maximum capacities are about 1-2 mmol/g whereas in water they are about half of it.

With the anions the salt uptake generally increases in the order of their polarizability. In some cases hydroxide ions occupy an exceptional position.

The thermal stability of the polymers decreases with rising ring size from about 250°C down to 180°C. Condensation resins are thermally more resistant than copolymerization resins. In comparison with the -C-C- bonds in copolymers, the linkage of the anchoring group to the styrene matrix by -C-NH-C- or -C-O-C- bonds causes a decrease in the thermal stability.

Condensation resins are resistant to organic solvents. Likewise, oxidants such as dilute KMnO₄ or H₂O₂ solutions do not change the capacity.

Cyclic polyethers bound to silica gel by ether bridges are readily hydrolyzed. They may not be used with acidic or alkaline samples. The silica gel matrix dissolves with pH > 8. In comparison with that, silica gels coated with polymeric cyclic polyethers can be used in the whole pH range.

With all exchangers containing nitrogen in the anchoring group, a complete protonation of the nitrogen atoms occurs at pH < 2. Then, complex formation with salts does not take place any longer. Due to the quaternary amino groups formed, an anion exchanger results.

Condensation resins are more resistant to radiolysis than polymerization resins. For example, no change in the capacity of an exchanger containing dibenzo-24-crown-8 as the anchoring group and prepared by condensation is observed after irradiation of 10⁹ rad. This stability is probably due to the presence of hydroxymethyl groups acting as radical scavengers.

2.3. Analytical applications of the polymers

By introducing cyclic polyethers of variable ring size specific polymers able to bind definite inorganic or organic compounds are obtained.

Possible applications are:

- separations of cations
- separations of anions
- separations of non-salt-like organic compounds
- water determinations

Choosing a special polymer suited for a certain problem is facilitated by the fact that the selectivity series show parallels to the capacity series.

Furthermore, a simple rule helps in finding the suited polymer. The polymers prefer that cation for which the following relation is best fulfilled:

$$\frac{\text{diameter of the cation (according to Goldschmidt)}}{\text{diameter of the polyether ring}} = 0.80$$

With all polymers, anions are separated in the order of their polarizability.

Mention must be made of the use of special stationary phases with cyclic polyether as anchoring groups in ion chromatography. Cyclic polyethers bound to silica gel or polystyrene as well as silica gels and polystyrene coated with cross-linked polymeric cyclic polyethers are suited for the fast separation of cations and anions by means of high-pressure liquid chromatography. In contrast to the ion chromatographs commercially available which have ion exchangers sulfonated or aminated at the surface, as stationary phases, the new supporting materials are suited for fast separations within the whole range of pH. The eluents are pure solvents, such as methanol or water. A suppressor column is not necessary. Therefore, conductivity detectors can be applied without any problems. Numerous organic compounds can be likewise separated. There is no longer need of time-wasting regeneration of the stationary phases.

In the following, examples for the application of the polymers shown in Figure 8 will be given.

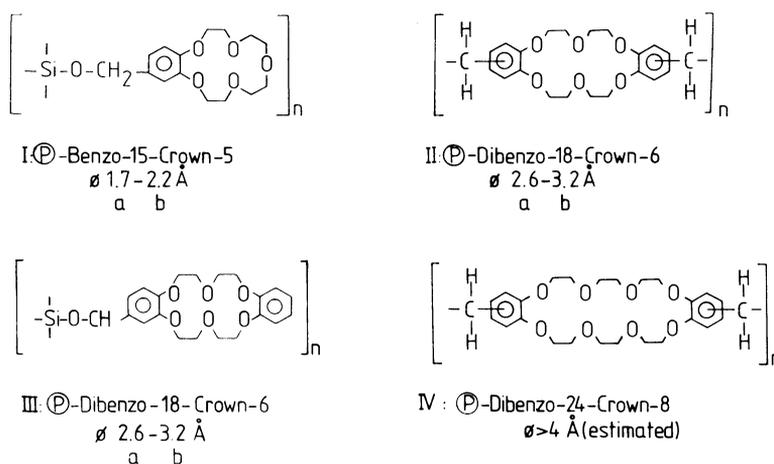


Fig. 8: Ring Diameter in Accordance with the Atomic Models of

- a) Corey-Pauling-Koltun
- b) Fisher-Hirschfelder-Taylor

2.3.1. P -Benzo-15-crown-5 Matrix: Silica gel

The reaction of 4-hydroxymethylbenzo-15-crown-5 with chlorinated silica gel ads to a stationary phase suited for high-pressure liquid chromatography. Because the Si-O-C bond is readily hydrolyzed, only water-free solvents can be used as eluents. Therefore the high sensitivity of the conductivity detectors cannot be utilized completely.

For a fast separation of alkali chlorides silica gel beads modified by benzo-15-crown-5 are used, the size of the beads being 10 μm . With a pressure of 24 MPa the separation will take 18 min (Figure 9).

2.3.2. P -Dibenzo-18-crown-6 Matrix: Silica gel or Methylene Bridges

Polymers with dibenzo-18-crown-6 as anchoring groups can be easily prepared. Among all polymers they have the widest field of application.

The best stationary phase for ion chromatography are beads of 10 μm coated with the condensation resin P -DB-18-C-6. The separation of bases is also possible (Figure 10).

The separation of anions is of particular importance, as these can be analyzed only incompletely, or even not at all, by other apparative analytical methods such as emission spectral analysis, atomic absorption analysis or X-ray fluorescence analysis.

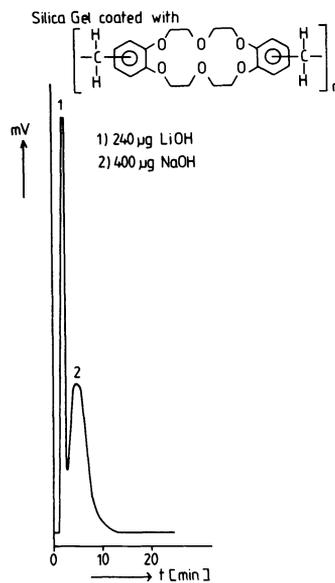
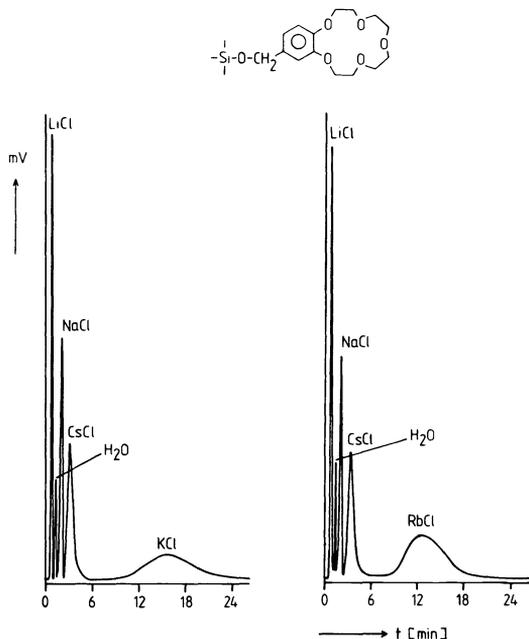


Fig. 9: Separation of Alkali Halides by Elution with Methanol
 left: 0.020 LiCl, 0.080 mg NaCl, 0.330 mg KCl and 0.276 mg CsCl
 right: 0.020 LiCl, 0.080 mg NaCl, 0.423 mg RbCl and 0.276 mg CsCl
 Flow Rate: 5.0 ml/min
 Pressure: 24 MPa

Fig.10: Separation of LiOH and NaOH by Elution with Methanol
 Flow Rate: 1.6 ml/min
 Pressure: 5 MPa

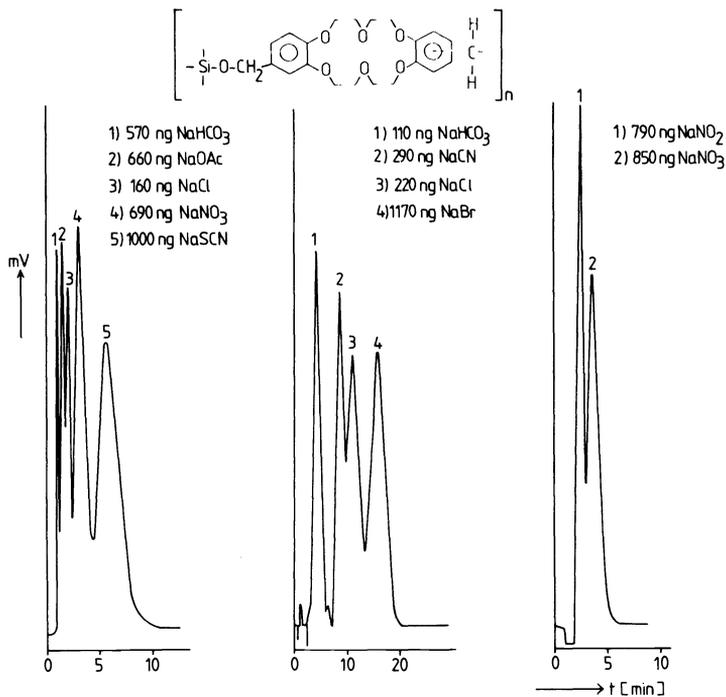


Fig. 11: Separation of Sodium Salts by Elution with Methanol
 Flow Rate: 1.7 ml/min
 Pressure: 24 MPa

Here, irregularly shaped silica gel particles modified by 4-hydroxymethyl-dibenzo-18-crown-6, are used, the size of the particles being 10 μm . The separation column is not yet optimized with regard to the stationary phase, density of packing, eluent and elution rate. With a column length of 30 cm only 160 theoretical plates have been achieved. Nevertheless, chromatograms can be evaluated quantitatively (Figure 11).

Also CN^- can be determined, whereas by the ion chromatographs commercially available CN^- ions are transformed in the suppressor column to HCN which cannot be measured by a conductivity detector.

Fast separations of anions can also be performed successfully by means of condensation resins. The separation of $\text{NaCl}/\text{Na}_2\text{SO}_4$ is shown as example (Figure 12).

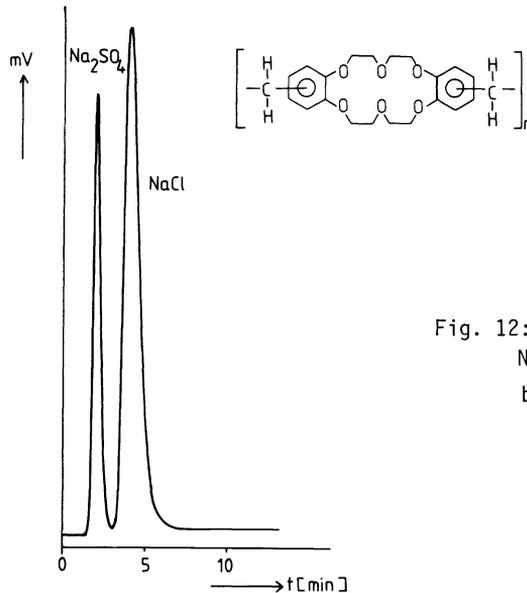


Fig. 12: Separation of 0.43 mg Na_2SO_4 and 0.58 mg NaCl by Elution with Water

The separation takes 8 min and is possible even with traces of Na_2SO_4 up to a molar ratio of 1:10.000. The prerequisite is a column carefully packed with very small particles (5 μm). With a column length of 30 cm and a good permeability, up to 1.200 theoretical plates can be achieved.

Anions with the same cation will be separated in the order of polarizability. With rising polarizability the eluent volumes needed increase (Figure 13).

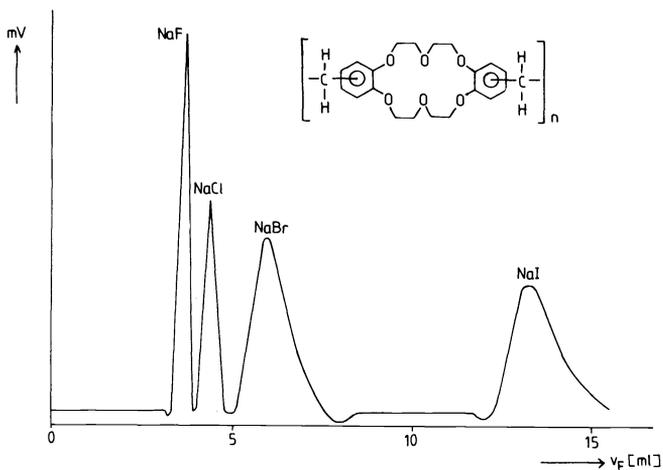


Fig. 13: Separation of Sodium Halides by Elution with Water
0.42 mg NaF , 0.35 mg NaCl , 0.62 mg NaBr and 2.25 mg NaI

An example for the quantitative application of elution chromatography on exchangers with cyclic polyethers as anchoring groups is the determination of water in methanol as solvent. The methanol itself (Merck p.a) contains 0.01% H_2O at most. However, this does not interfere with the measurement, as a differential refractometer is used as detector.

Additional traces of water in methanol or other organic solvents lead to a water band in the elution diagram. Thus, constitutional or adsorbed water in salts or organic compounds can be determined in concentrations down to 1 ppm.

Figure 14 shows the elution curves of some salts with various content of water.

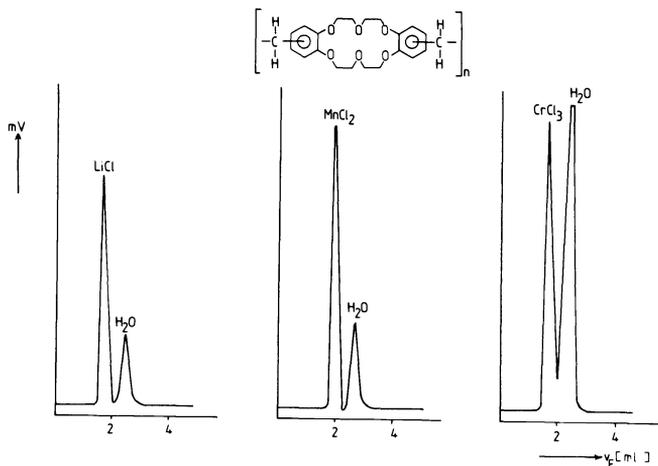


Fig. 14: Water Determination by Elution with Methanol
 left: 0.02 mg $\text{LiCl} \cdot x\text{H}_2\text{O}$ middle: 0.09 mg $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ right: 0.35 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

With salts which are bound more strongly than water, the water band comes before the salt band.

2.3.3. P -Dibenzo-24-crown-8
 Matrix: Methylene bridges

The selectivity for a certain cation is determined by the size of the polyether ring. Thus, P -dibenzo-18-crown-6 prefers K(I) salts, P -dibenzo-21-crown-7 prefers Rb(I) salts and P -dibenzo-24-crown-8 prefers Cs(I) salts. The high selectivity of P -dibenzo-24-crown-8 for Cs(I) is illustrated by Figure 15.

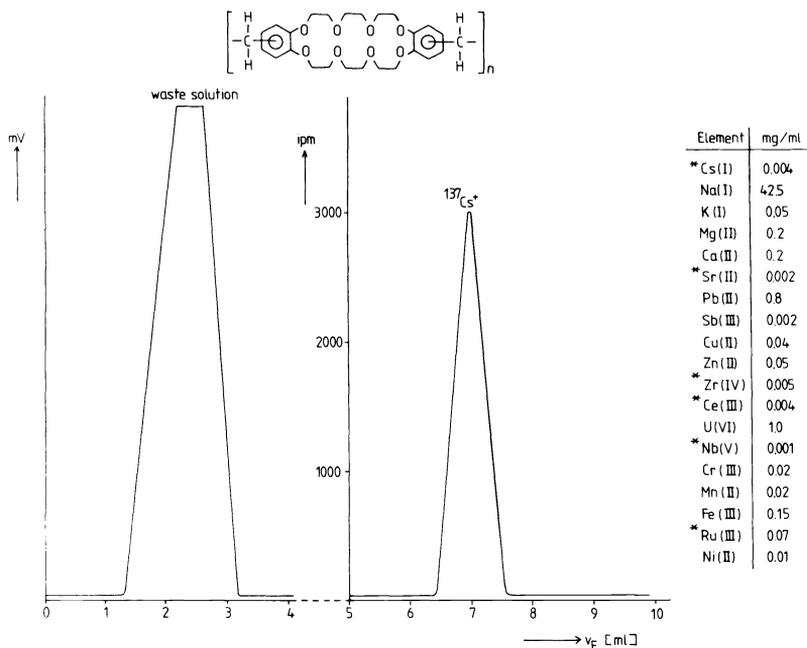


Fig. 15: Separation of 0.0004 mg Cs^+ (labelled by $5 \mu\text{g Ci } ^{137}\text{Cs}$) from Simulated Nitric (1 mol/l) Middle-active Waste Solution by Elution with Water

2.3.4. Separations of Non-Saltlike Organic Compounds

On all polymers, separations of organic compounds can be carried out on account of matrix effects. Additional interactions with the anchoring groups are possible.

Organic compounds which show these interactions are e.g. thiourea and urea as well as aromatic and heterocyclic compounds. In general, compounds containing sulphur are strongly bound, so that the separation of benzene from water or thiophene is possible. With increasing number of nitrogen atoms in the heterocycles, the forces of the binding to the polymer grow. The eluent volumes required for these heterocycles increase in the order O, S, N.

2.4. Preparative Chemistry

The preparative application of the exchangers includes salt conversions (interchange between the anions or cations of two salts), purification of organic compounds and anion activation in organic reactions.

2.4.1. Salt Conversions

An example for a salt conversion is the reaction of LiSCN with RbCl to give LiCl and RbSCN (Figure 16).

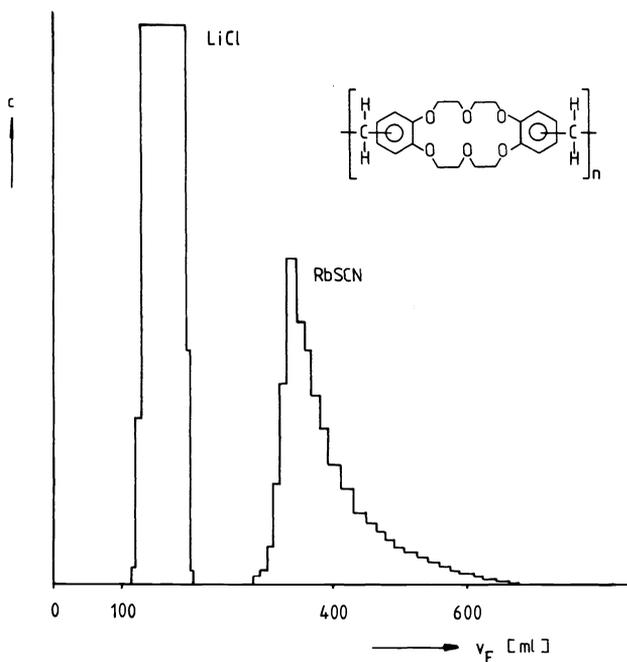


Fig. 16: $\text{LiSCN} + \text{RbCl} \longrightarrow \text{LiCl} + \text{RbSCN}$
Salt Conversion of 0.520 g LiSCN and 0.975 g RbCl by Elution with Water

By the column process a yield of 100% is possible. This yield is not reached by the batch method, but here only little equipment is necessary. After the batch process, the chromatographically and spectroscopically pure salts can be washed from the polymer in a Soxhlet apparatus.

In this way, thiocyanates and iodides of alkali and alkaline earth elements difficult to prepare can be obtained in water solutions in the g scale.

2.4.2. Anion Activation

The complexation of inorganic salts by cyclic polyethers leads to ligand-separated ion pairs. The anions exhibit increased reactivity. This can be used in many fields of preparative organic chemistry.

2.4.2.1. Phase transfer catalyses

A difficulty often encountered in preparative organic chemistry is that water-soluble salts react only poorly with organic compounds slightly soluble in water. By means of phase transfer catalysis such reactions are accelerated or even rendered possible. For this purpose

cross-linked polymers with cyclic polyethers are particularly well suited. In contrast to monomers or soluble polymers they do not contaminate the reaction system and they can be recovered for re-using. The concentration of anchoring groups guarantees high yields in short times under mild reaction conditions. The reaction process in the gas phase saves solvents and offers some interesting aspects for industrial applications.

A comparison of the prepared polymers with each other and with some other polymers described in literature shows, that D -dibenzo-18-crown-6 is best suited for phase transfer catalysis with regard to yield, reaction time, thermal stability and easy and inexpensive preparation.

The catalytic effect decreases in the order:

Polymers with crown ethers or cryptands > podands \geq tetraalkyl phosphonium groups \geq tetraalkyl ammonium groups.

D -Dibenzo -18-crown-6 catalyzes substitution, dichlorocarbene and polymerization reactions which do not take place, or only with low yields, without catalysts. The application of D -dibenzo-18-crown-6 is possible in liquid as well as in gaseous systems.

a) Substitution Reactions in the Liquid Phase

With regard to the preparation of alkyl and aryl halides, the catalytic efficiency follows the order of the capacities of D -dibenzo-18-crown-6 for the corresponding potassium salts: $\text{KSCN} > \text{KI} > \text{KCH}_3\text{COO} > \text{KCN} > \text{KNO}_2 > \text{KCl} > \text{KF}$

Halides, nitriles, thiocyanates, nitro compounds, ethers, thioethers and ketones have been prepared (Figure 17).

Reactants	Product	Solvent	Reaction Time [h]	Temperature [°C]	Yield		
					with D -DB-18-C-6 [%]	without D -DB-18-C-6 [%]	
$\text{C}_6\text{H}_5\text{-CH}_2\text{-Br}$	KCl	Chloride	Toluene / H_2O	1	110	94	6
$\text{C}_6\text{H}_5\text{-CH}_2\text{-Cl}$	KBr	Bromide	Toluene / H_2O	3	110	83	1
$\text{C}_6\text{H}_5\text{-CH}_2\text{-Br}$	KI	Iodide	Toluene / H_2O	0.5	110	94	18
$\text{CH}_3\text{-(CH}_2\text{)}_7\text{-Br}$	KCN	Nitrile	Toluene / H_2O	2	110	83	0
$\text{CH}_3\text{-(CH}_2\text{)}_7\text{-Br}$	KCH_3COO	Ester	Toluene / H_2O	18	110	93	0
$\text{CH}_3\text{-(CH}_2\text{)}_7\text{-Br}$	KSCN	Thiocyanic Acid Esters	Toluene / H_2O	3	110	95	0
$\text{CH}_3\text{-(CH}_2\text{)}_7\text{-Br}$	KNO_2	Nitro Compounds	Toluene / H_2O	6	110	60	0
$\text{CH}_3\text{-(CH}_2\text{)}_3\text{-Br}$	KOC_6H_5	Ether	Toluene	1	110	93	5
$\text{CH}_3\text{-(CH}_2\text{)}_3\text{-Br}$	KSC_6H_5	Thioether	Toluene	1	110	57	10
$\text{C}_6\text{H}_5\text{-CH}_2\text{-CO-CH}_3$	KOH	Ketone	Toluene / H_2O	2	110	70	15

Fig. 17: Substitution Reactions in Liquid Phases
 $\text{R-CH}_2\text{-Y+KX} \rightleftharpoons \text{R-CH}_2\text{-X+KY}$

b) Substitution of Halogens in the Gas Phase

In contrast to the phase transfer catalysts hitherto used for the gas phase, D -dibenzo-18-crown-6 is very inert and exhibits the large surface needed. The excellent thermal stability permits reaction temperatures up to 250°C.

By the reaction of 1-chlorobutane with KI, 1-iodobutane is obtained in a high yield within a short time (Figure 18).

Reactants	Product	Reaction Time [h]	Temperature [°C]	Yield		
				with P-DB-18-C-6 [%]	without P-DB-18-C-6 [%]	
Discontinuous Process						
$\text{CH}_3\text{-(CH}_2\text{)}_3\text{-Cl}$	KI	Iodide	0.5	135	56	0
Continuous Process						
$\text{CH}_3\text{-(CH}_2\text{)}_3\text{-Cl}$	KI	Iodide	0.5	135	51	0
			1.0	135	62	0
			1.5	135	76	0

Fig. 18: Halide Substitution in the Gas Phase
 $\text{CH}_3\text{-(CH}_2\text{)}_3\text{-Cl} + \text{KI} \rightleftharpoons \text{CH}_3\text{-(CH}_2\text{)}_3\text{-I} + \text{KCl}$

c) Dichlorocarbene Reactions in Liquid Phases

Concerning the preparation of dichlorocyclopropanes in the presence of P -dibenzo-18-crown-6, an excess of KOH, with regard to CHCl_3 , effects higher yields. The yields decrease with the reactants α -methylstyrene > cyclohexane > styrene.

Without P -dibenzo-18-crown-6 only little amounts of dichlorocyclopropanes are obtained (Figure 19).

Reactants	Product	Solvent	Reaction Time [h]	Temperature [°C]	Yield	
					with P-DB-18-C-6 [%]	without P-DB-18-C-6 [%]
CHCl_3 KOH $\text{C}_6\text{H}_5\text{-C}(\text{CH}_3)=\text{CH}_2$	1-Phenyl-1-methyl-2,2-dichlorocyclopropane	1 ml CHCl_3 / 1 ml 50% KOH	24	50	19	0.3
		1 ml CHCl_3 / 2 ml 50% KOH	10	50	40	0.3
CHCl_3 KOH $\text{C}_6\text{H}_5\text{-CH}=\text{CH}_2$	1,1-Dichloro-2-phenylcyclopropane	1 ml CHCl_3 / 1 ml 50% KOH	24	50	14	0.4
		1 ml CHCl_3 / 2 ml 50% KOH	10	50	15	0.4
CHCl_3 KOH 	7,7-Dichloronorcaradiene	1 ml CHCl_3 / 1 ml 50% KOH	24	50	6	0.4
		1 ml CHCl_3 / 2 ml 50% KOH	16	50	33	0.4

Fig. 19: Dichlorocarbene Reactions in Liquid Phases
 $\text{CHCl}_3 + \text{KOH} \rightleftharpoons \text{CCl}_2 + \text{KCl} + \text{H}_2\text{O}$

2.4.2.2. Preparation of Living Polymers

The preparation of living polymers by anionic polymerization is restricted to the polymerization of diene compounds and ring-opening reactions.

By using monomeric crown ethers and cryptands the anion concentration is raised in aprotic and polar solvents. The propagation rate of the chain may rise to values up to 100 times higher than before.

The reaction conditions are mild. A disadvantage is the possibility of a disturbance of the polymer chain by the introduction of crown ethers or cryptands.

The preparation of living polymers by using polymers with cyclic polyethers as anchoring groups is characterized by narrow molar mass distribution, possibility of chain length

regulation, mild reaction conditions and highly pure, linear products. It is possible to solve special problems by controlling the sequence of segments and introducing functional groups at the chain ends.

Ⓟ-dibenzo-18-crown-6 is well suited for starting anionic ring-opening polymerizations. Examples for the preparation of living polymers in a high vacuum system are poly(ethylene oxide), poly(propylene sulfide), poly(β -propiolactone), poly(2-pyrrolidone), poly(ϵ -caprolactone) and poly(methyl methacrylate) (Figure 20).

Reactants [mg]	Amount of Exchanger [mg]	Charge of Initiator Salt [mg]	Reaction Temperature [°C]	Reaction Time	Yield [%]	Molar Mass	
						Theoretical	Osmometrical
$\text{Oxirane} + \text{K}^+ \left[\text{C}_{18}\text{H}_{12}\text{N}_2 \right]^- \longrightarrow \left[\text{C}_2\text{H}_4\text{-CH}_2\text{-O} \right]_n + \text{K}^+ \left[\text{C}_{18}\text{H}_{12}\text{N}_2 \right]^-$							
Ethylene Oxide	1170 1677	88 512	20 4.8	25 25	14 d 27 d	46 53	- 38 000 35 000
$\text{Propylene Sulfide} + \text{K}^+ \left[\text{C}_{18}\text{H}_{12}\text{N}_2 \right]^- \longrightarrow \left[\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{S} \right]_n + \text{K}^+ \left[\text{C}_{18}\text{H}_{12}\text{N}_2 \right]^-$							
Propylene Sulfide	929 1460	93.0 17.8	2.2 2.1	25 25	30 min 30 min	65 89	268 000 126 000 209 000 208 000
$\beta\text{-Propiolactone} + \text{K}^+ \text{CH}_3\text{COO}^- \longrightarrow \left[\text{C}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{O} \right]_n + \text{K}^+ \text{CH}_3\text{COO}^-$							
β -Propio- lactone	2636 3210	425.2 362.0	11.7 7.4	25 25	24 h 24 h	90.5 90.7	1000 3900 2100 4200
$\text{2-Pyrrolidone} + \text{K}^+ \left[\text{C}_{18}\text{H}_{12}\text{N}_2 \right]^- \longrightarrow \left[\text{C}-\text{C}(\text{H})-\text{C}(=\text{O})-\text{N} \right]_n + \text{K}^+ \left[\text{C}_{18}\text{H}_{12}\text{N}_2 \right]^-$							
2-Pyrrolidone	2173 5581	82.4 43.6	Traces	30 40	4h 4h	61 82	- - - -
$\epsilon\text{-Caprolactone} + \text{K}^+ \left[\text{C}(\text{CH}_3)_2\text{-C}(\text{O})-\text{O} \right]^- \longrightarrow \left[\text{C}-\text{C}(\text{CH}_3)_2-\text{C}(\text{O})-\text{O} \right]_n + \text{K}^+ \left[\text{C}(\text{CH}_3)_2\text{-C}(\text{O})-\text{O} \right]^-$							
ϵ -Caprolactone	1520 4510	1601 166	178 17	-20 -50	2 h 2 h	10 20	- - - -
$\text{Methyl Methacrylate} + \text{K}^+ \left[\text{C}(\text{CH}_3)_2\text{-C}(\text{O})-\text{O} \right]^- \longrightarrow \left[\text{CH}_2-\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3) \right]_n + \text{K}^+ \left[\text{C}(\text{CH}_3)_2\text{-C}(\text{O})-\text{O} \right]^-$							
Methyl Methacrylate	1350 1550	133 251	2.5 2.8	0 0	24h 24h	70 75	- - - -

Fig. 20: Anionic Polymerization Reactions in the Presence of Ⓟ-DB-18-C-6

After the reaction has been finished, Ⓟ-dibenzo-18-crown-6 is separated from the prepared linear polymer by filtration and can be used again as initiator. The theoretical masses correspond to the masses experimentally measured.

The polymerization of ethylene oxide or propylene oxide is possible by using the polymer charged with potassium carbazolate in tetrahydrofuran at low temperatures. The molar masses osmometrically determined for the two polymers correspond to the theoretical values. That means that the polymerization is catalyzed by the anion. The molar mass can be varied by the amount of polymer used as catalyst. The industrial polymerization by basic catalyst is performed at temperatures of 100 to 200°C. 20% of the ethylene oxide applied form undesirable by-products.

The polymerization of β -propiolactone to give a polyester is an example for the anionic ring-opening polymerization. Here the polymer charged with KCH_3COO_2 is used, with tetrahydrofuran as solvent.

In order to polymerize 2-pyrrolidone to give a polyamide, 2-pyrrolidone is heated above its melting point (24°C) in a high vacuum apparatus. Then the fluid is allowed to pass a thin coating of potassium to form a small amount of potassium pyrrolidonate. In contact with Ⓟ-dibenzo-18-crown-6, this starts the ring-opening polymerization. According to the methods hitherto used, potassium pyrrolidonate had to be prepared outside the system.

Anionic ring-opening of six-membered heterocycles is not possible. But the seven-membered ring of ϵ -caprolactone forms very reactive carbanions, which react with the growing chain

to give shorter oligomers. The yield of long linear polymers therefore is very low.

Methylmethacrylate can be polymerized by using P-dibenzo-18-crown-6 charged with potassium tertiary butylate. With the monomeric cryptand K[2.2.2.] elementary sodium is needed.

3. CONCLUSIONS

The application possibilities of polymers with cyclic polyethers as anchoring groups are numerous. Particular mention must be made of the analytical application in ion chromatography and the preparative application in the catalysis of organic reactions. The best results are obtained using polymers containing dibenzo-18-crown-6 as anchoring group.

Investigations on the application of the polymers in ion chromatography have just started. A disadvantage of the silica gels modified by cyclic polyethers is their low resistance to hydrolysis. Binding cyclic polyethers to polystyrene or coating silica gels or polystyrene lead to polymers stable within the whole pH range. The same stationary phase is able to separate cations, anions or organic compounds within all ranges of pH.

The application of the condensation resin P-dibenzo-18-crown-6 in phase transfer catalysis can be extended to other reaction types such as saponifications, oxidations, reductions, extrusions and isomerization reactions. For the preparations of living polymers, the expensive vacuum technique may be replaced by reactions under inert atmosphere or by using solvents azeotropically distilled. Further aims are, among other things, the preparations of peptides and polysiloxanes.

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