Synthesis and ion binding properties of polyesters and polyamides with diazacrown-ethers

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The synthesis of polymers containing a [22] diaza-crown-ether in the backbone is described. These compounds are obtained by polycondensation of *N, N'*-diethylene amine and *N, N'*-diethylene alcohol derivatives of the cyclic diamine [23] with various acid dichlorides, leading to polyesters and polyamides. The cation binding properties of these polymers are studied by water–chloroform extraction using picrate salts, and compared with the properties of the analogous monomeric molecules. The binding properties are strongly dependent on the polymeric structure and comparison with the analogue molecules clearly demonstrates that the observed decrease in complex stability is due mainly to the presence near the rings of ester or amide groups. An intramolecular structure is proposed, based on interactions between the nitrogen bridges and the ester or amide groups which lead to the formation of a five-membered ring.

INTRODUCTION

In a previous paper[1] the ion binding properties of epoxy polymers containing diaza-crown-ethers in the backbone were studied and compared with the properties of analogous corresponding molecules. We have shown that the stability constants for the polymeric complexes in chloroform are comparable with those of the monomeric analogues previously studied[2], independent of the ratio of complexation.

This paper describes the synthesis and study of polyesters and polyamides containing the same type of crown-ether. Our interest lies in the influence of the chemical structure of these polymers on their binding properties and the exploration of the possibility of preparing selective membranes or materials. We find that the binding properties are greatly influenced by the nature of the chemical groups near the rings.

EXPERIMENTAL

All the solvents used were purified and distilled by classical methods. The cyclic diamine [22] (1, 7, 10, 16-tetraoxa-4, 13-diazacyclooctadecane) (Kryptofix^{R}22-Merck) was purified by recrystallization from heptane. All the starting reagents were received from Fluka and used without further purification except where stated.

Synthesis of NN' *substituted diamines [22]*

NN'-*(dihydroxyethylene) diamine [22] or [22] EtOH (I)* One method of synthesis of this compound has been described previously [7], A simpler method was used in this work. To 2.5 g (9.5 mmol) of diamine [22] dissolved in 50 ml of water, 3.5 ml (23.75 mmol) of triethylamine and 2.98 g (23.75 mmol) of 2-bromoethanol was added. The mixture was stirred for 24 h at room temperature. After evaporation 50 ml of 0.5 N HCl was added to the solid and the aqueous solution was extracted with 3 x 50 ml $CHCl_3$. The aqueous layer was adjusted at pH 12 with a 20% aqueous solution of tetraethyl-ammonium hydroxide and extracted with 7 x 100 ml $CHCl_3$. After concentration, the extract was filtered on 50 g basic alumina with a mixture of toluene–chloroform (50–50). The oily residue was obtained by evaporation of the solvents and dried overnight in vacuo to yield 3.05 g (90%), m.p. <0°C.

N.m.r. ($CDCl_3$), δ 3.13 (t,$-CH_2-$N), 3.97 (m,$-CH_2-$0,–OH) *Analysis.* Calculated for $C_{16}H_{34}N_2O_6$: C, 54.84; H, 9.78; N, 7.99; O, 27 39. Found: C, 54.36; H, 9.86; N, 7.32; O, 27.90

NN'-*(diacetoxyethylene) diamine [22] or [22] EtOCOCH$_3$ (II)* To 1 g (2.9 mmol) of I dissolved in 100 ml of toluene was added under a nitrogen atmosphere 1 ml (7.1 mmol) of NEt_3 and 0.5 ml (7.1 mmol) acetyl chloride; the mixture was stirred for 16 h at room temperature. After filtration and evaporation of toluene, the residue was passed over a column of 100 g neutral alumina and eluted with II ether with 1% ethanol. After evaporation of solvents and recrystallization from ether, 1.01 g (yield 81%) of product was obtained.

N.m.r. ($CDCl_3$), δ 1.96 (s, CH_3-), 2.77 (t,$-CH_2-$N), 3.57 (t,$-CH_2-O-$), 4.06 (t,$-CH_2-O-CO-$)

Analysis. Calculated for $C_{20}H_{38}N_2O_8$: C, 55.28; H, 8.81; N, 6.45; O, 29.46. Found: C, 55.16; H, 8.92; N, 6.38; O, 29.59

p-*Toluene sulphonyl aminoacetic acid (III).* To 26 g (0.35 mol) of aminoacetic acid (glycine) dissolved in 250 ml of water, 15 g (0.35 mol) of NaOH was slowly added. The

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mixture was stirred for 1 h at room temperature. 4.5 g (0.39 mol) of p-toluene sulphonyl chloride was added and the reaction was allowed to proceed for 20 h at 40°C. During this time the pH was controlled and adjusted to pH>10 with NaOH. The mixture was warmed to 80°C and 10 g NaOH carefully added. After 2 h, 30% aqueous HCl was added to obtain pH 1. On cooling, the crystallized product was filtered washed with cold water, and 70 g (88% yield) was obtained after recrystallization from water and drying in vacuo m.p. 148°C.

N.m.r. (CF_3COOH), δ 2.3 (s, CH_3–), 3.2 (s, N–H), 4.7 (s, CH_2), 7.05–7.2–7.45–7.6 (q, φ).

Analysis. Calculated for $C_9H_{11}NO_4S$: C, 47.15; H, 4.83; N, 6.11; O, 27.91 S, 13.98. Found: C, 46.83; H, 4.79; N, 5.82; O, 27.84; S, 13.84.

p-Toluene sulphonyl aminoacetyl chloride (IV): To 20 g (0.087 mol) of III in suspension in 100 ml of toluene and 3 drops of pyridine was added under anhydrous conditions, 20 ml (0.23 mol) of oxalyl chloride. The mixture was stirred for 24 h until a clear solution was obtained. After filtration under a nitrogen atmosphere, heptane was added until a cloudy solution was obtained. After standing overnight at −10°C, the crystals obtained were recrystallized in toluene–heptane, dried *in vacuo* yielding 18 g (85%) of pure compound, m.p. 96°C, with decomposition.

N.m.r. ($CDCl_3$), δ s 2.3 (s, CH_3–), 3.2 (s, NH), 4.7 (s, CH_2), 7.1–7.2–7.5–7.6 (*q*, φ)

Analysis. Calculated for $C_9H_{10}ClNO_3S$: Cl, 14.31. Found: Cl, 14.32.

NN'-(di-p-toluenesulphonyl aminoacetamide) [22] (V). To 5.5 g (0.02 mol) of diamine [22] in 150 ml of toluene was added 6.1 ml (0.044 mol) of triethylamine. To the stirred mixture under a nitrogen atmosphere, was added dropwise 10.9 g (0.044 mol) of IV dissolved in 200 ml of toluene; the product was stirred for 1 h after complete addition. Evaporation gave a residue which was dissolved in 200 ml of aqueous LiOH (pH 12), then acidified with 50 ml 6N HCl. Filtration of the solid, followed by drying *in vacuo* and recrystallization from nitromethane, gave 12.5g (yield 90%), m.p. 237°C with decomposition. N.m.r. ($CDCl_3$), δ 2.3 (s, CH_3–), 3.4 (m, CH_2–CH_2–N, CH_2–O) 3.6 (m, N–CH_2–CO), 7.1–7.2–7.5–7.6 (q, φ)

Analysis. Calculated for $C_{30}H_{44}N_4O_{10}S_2$: C, 52.62; H, 6.48; N, 8.18; 0, 23.36; S, 9.36 Found: C, 52.53; H, 6.42; N, 8.08; o, 23.44; S, 9.24.

NN'-(di-p-toluenesulphonyl aminoethylene) diamine [22] (VI). To 10 g (0.015 mol) of V dissolved in 200 ml THF was carefully added 5.52 g (0.15 mol) of $LiAlH_4$ with stirring and under an N_2 atmosphere. The mixture was refluxed for 17 h, cooled to room temperature and excess $LiAlH_4$ destroyed with water–THF (10–90). 4 g SO_4Na_2 and 40 ml of CH_3OH were added. After filtration and evaporation, the oily residue was filtered on a column of 30 g basic alumina and eluted with toluene–$CHCl_3$ (50–50) giving 9.15 g (yield 95%) of pure compound after evaporation, recrystallization from toluene and drying *in vacuo*, m.p. 102°C. N.m.r. ($CDCl_3$), δ 2.3 (s, CH_3), 2.5 (t, N–$(CH_2)_3$), 2.8 (m, CH_2–NHTs), 3.5 (t, CH_2–O), 7.1–7.2– 7.5–7.6 (q, φ)

Analysis. Calculated for $C_{30}H_{48}N_4O_8S_2$: C, 54.86; H, 7.37; N, 8.53; 0, 19.49; S, 9.75. Found: C, 54.95; H, 7.27; N, 8.62; 0, 19.48 S, 9.95.

NN'-(diaminoethylene) diamine [22] or [22] EtNH$_2$ (VII). 500 ml NH_3 was condensed in 8 g (0.012 mol) of VI dissolved in 25 ml of THF plus 3 ml of CH_3OH, maintained at −40°C. 1 g (0.012 mol) of Li was added slowly to the mixture. Stirring was continued for 30 min after the complete addition and 2 g of NH_4Cl was added to destroy the excess Li. The residue obtained after evaporation of NH_3 was dissolved in 250 ml 6 N HCl and the aqueous layer extracted with $CHCl_3$ (5 x 250 ml). The extracts were dried over $MgSO_4$ and after evaporation, the residue was dissolved in 200 ml water and adjusted to pH 12 with 20% aqueous tetraethylammonium hydroxide. The solution was extracted with $CHCl_3$. After drying over $MgSO_4$, the $CHCl_3$ was evaporated and the residue eluted with toluene through a column of 10 g basic alumina.

The toluene was evaporated and the solid recrystallized from a mixture of toluene–pentane, yielding 3.5 g (80%), m.p. 127°C.

N.m.r. ($CDCl_3$), δ 2.6 (m, CH_2–N), 3.5 (t, CH_2–O).

Analysis. Calculated for $C_{16}H_{36}N_4O_4$: C, 55.15; H, 10.41; N, 16.08; 0, 18.36. Found: C, 54.83; H, 10.59; N, 15.99; 0, 18.58.

NN'-(diacetamido-ethylene) diamine [22] or [22] EtNHCOCH$_3$ (VIII). This compound was prepared from VII according to the procedure described above for II. It was obtained by elution with a mixture of toluene–$CHCl_3$ (50–50) through a column of basic alumina. After evaporation of the solvents and drying *in vacuo*, an oily compound was obtained in 80% yield. N.m.r. ($CDCl_3$), δ 2 (s, CH_3CO), 2.7 (t, $(CH_2)_3$–N), 3.3 (t, CH_2NCO), 3.5 (t, CH_2–O). Analysis. Calculated for $C_{20}H_{40}N_4O_6$: C, 55.33; H, 9.32; N, 12.95; O, 22.19. Found: C, 56.94; H, 8.72; N, 11.95; O, 22.47.

Synthesis of polymers

Poly[NN'-(diethylene) diamine [22]-terephthalate] or *P[22]EtOH–terephthalic. Solution procedure.* To 2 g of [22] EtOH (5.7 mmol) dissolved in toluene with 1.16 g (11.5 mmol) of NEt_3, was added slowly 1.16 g of terephthaloyl chloride (5.7mmol) recrystallized from dry hexane with stirring under a nitrogen atmosphere. The mixture was stirred for 3 h at 60°C. After filtration, the polymer was precipitated twice into heptane, filtered, washed and dried in vacuo to give a yield of 60%. Analysis. Calculated: C, 59.98; H, 7.55; 0, 26.63; N, 5.83. Found: C, 59.88; H, 7.37; O, 27.19; N, 5.55.

Interfacial procedure. To a solution of 0.5 g (1.43 mmol) of [22] EtOH and 0.26 g (2.9 mmol) of NMe_4 OH in 5 ml water was added a solution of 0.29 g (1.43 mmol) terephthaloyl chloride in 5 ml of $CHCl_3$, all at once with vigorous stirring at 20°C. Stirring was continued for ½ h and the polymer was obtained from the organic layer and purified as above–yield 50%. For polymerization in the presence of cation, exactly the same procedure was used with 2.9 mmol of salt dissolved in the aqueous phase.

Poly[NN'-(diethylene) diamine [22] adipate] or P [22] EtOH–adipic and poly [NN'-(diethylene)diamine [22] sebacate] or P[22] EtOH–sebacic. These polymers were prepared according to the solution procedure described for P[22] EtOH–terephthalic. Acid chlorides were distilled before used. Analysis. Calculated for P[22] EtOH–adipic: C, 57.37; H, 8.75; O, 27.79; N, 6.08. Found: C, 57.02; H, 8.67; O, 28.48; N, 5.81.

Analysis. Calculated for P[22] EtOH–sebacic: C, 60.44; H, 9.36; O, 24.77; N, 5.42. Fpund: C, 60.14; H, 9.50; O, 25.02; N, 5.32.

Poly[NN'-(diethylene)diamine[22] triglycolate] or P[22] EtOH–triglycolic. Triglycoloyl chloride was prepared according to the method of Dietrich *et al.*[3]. To a solution of 1.5 g of [22] EtOH (4.3 mmol) and 0.89 g (8.8 mmol) NEt_3 in

Table 1 Polycondensations with diaza-crown-ethers and derivatives

Ligand	Acid dichloride	Polymerization conditions	Yield (%)	M_n
[22]	Terephthaloyl	$CHCl_3$, 60°C, 48h	96	3500
	Sebacoyl	$CHCl_3$, 50°C, 48h	95	3200
	(reduction)	$LiAlH_4$, THF	16	1800
[22] EtOH	Adipoyl	Toluene reflux, 2h	65	3500
	Sebacoyl	$CHCl_3$, reflux, 60h		2700
	Terephthaloyl	Toluene 60°C, 3h	60	3800
	Terephthaloyl	Interfacial 0.5h	50	3000
	Trigylcoloyl*	Benzene 25°C, 24h	75	
[22] $EtNH_2$	Terephthaloyl	Toluene 60°C, 3h	60	
	Sebacoyl*	Interf. 0.5h	56	2200

* Water soluble

50 ml benzene was added 0.95 g (4.3 mmol) of triglycoloyl chloride with stirring and under N_2 atmosphere. After 24 h at room temperature the solution was filtered, evaporated and the polymer dissolved in a minimum amount of CH_3OH, precipitated twice into ether, and dried in vacuo to give a yield of 75%. The product was soluble in water and $CHCl_3$.

Poly[NN'-(diethylene)diamine [22] sebacamide] or P[22] $EtNH_2$–sebacic. Interfacial procedure. To a solution of 1.2 g (0.1 ml) of [22] $EtNN_2$ and 0.16 g (0.2 mol) of LiOH in 35 ml of water was added a solution of 0.82 g sebacoyl chloride in 12 ml $CHCl_3$ all at once, with vigorous stirring at 20°C for 0.5 h. After evaporation of the solvents the polymer was obtained as already described in a yield of 56%. For polymerization in the presence of salt exactly the same procedure was used with 0.2 mol of salt dissolved in the aqueous phase.

Poly[NN'-(diethylene) diamine [22]-terephthalamide] or *P[22] $EtNH_2$–terephthalic.* This polymer was prepared according to the solution procedure described for P[22] EtOH–terephthalic. Yield, 60%.

Poly[diamine [22]-sebacamide] or P[22]–sebacic. To 3.84 g of diamine [22] (14.6 mmol) and 2.96 g (29.3 mmol) of NEt_3 in 10ml $CHCl_3$ was added 3.5 g (14.6 mmol) sebacoyl chloride in 5 ml $CHCl_3$ slowly and with stirring under an N_2 atmosphere. The mixture was stirred for 48 h at 50°C. The polymer was obtained in 95% yield by two precipitations in petroleum ether.

Poly[Decane diamine [22]] or P[22] decane. To 4.8 g (11.2 mmol) of P [22]–sebacic was added 8 g of $LiAlH_4$ in 300 ml of THF with stirring under an N_2 atmosphere. After 48 h, the mixture was hydrolysed to destroy excess $LiAlH_4$, adjusted to pH 3 with HCl and filtered. The polymer was precipitated by adjusting the solution to pH 12 and purified by dialysis at pH 3. 0.7 g (yield 16%) was obtained after precipitation at pH 12 with NMe_4OH, washing and drying. I.r. showed no absorption at 1720 cm^{-1}.

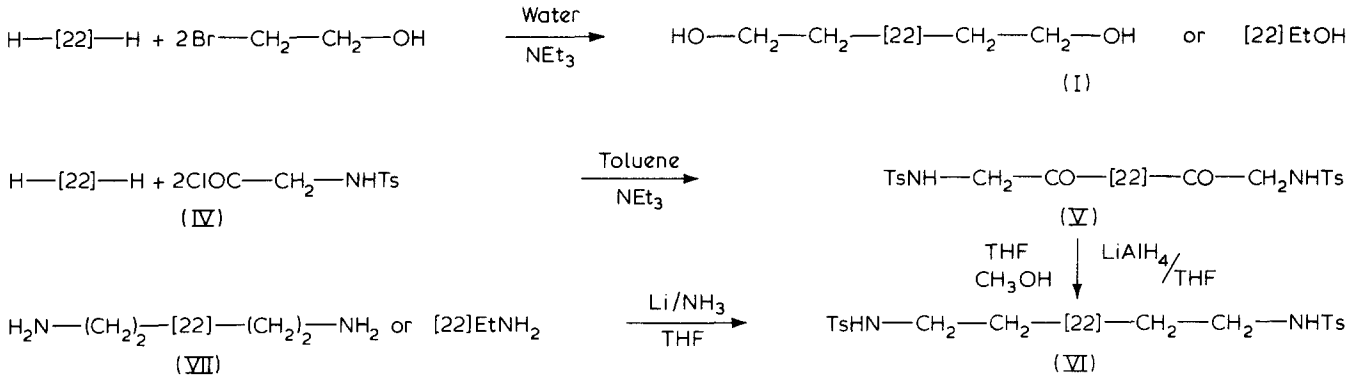
Measurements

The molecular weights of the polymers were determined by g.p.c. in THF. The experimental procedure used for the water–chloroform extractions and for the determination of the stability constants by pH analysis in water are similar to those recently reported.

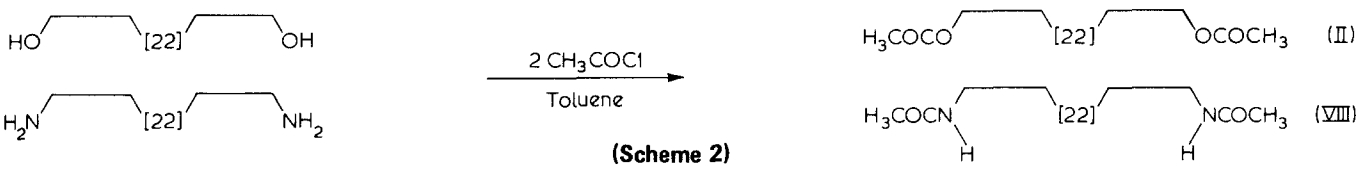
RESULTS

Synthesis

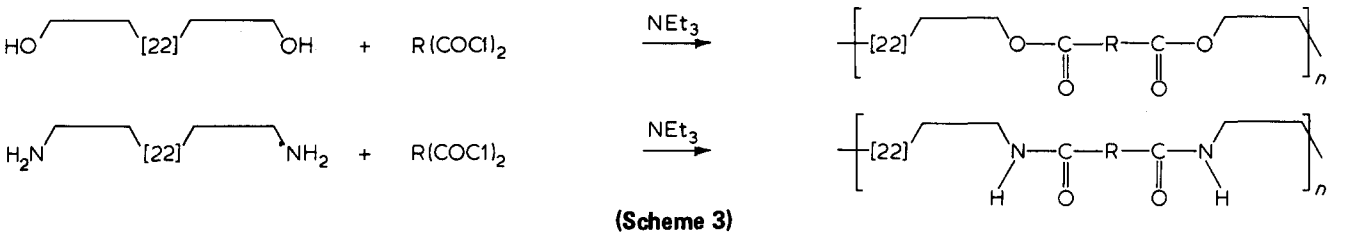
Diaza-crown-ether derivatives. To prepare polyesters and polyamides with diaza-crown-ether linkages along the backbone, dialcohol and diamine derivatives of the diamine [22] were synthesized according to the reactions in Scheme 1. So that the complexing properties of polymers could be compared with those of analogous monomeric molecules, diacetyl derivatives (Scheme 1) were also prepared.



(Scheme 1)



(Scheme 2)



(Scheme 3)

Table 2 Interfacial polycondensations (water–$CHCl_3$). Effect on the molecular weight of salt dissolved in the aqueous phase (one complexable cation per ligand)

Polymer	Salt	M_w
P[22] $EtNH_2$–sebacic	LiOH	3200
	NaOH	3800
	NaOH + NaSCN	4100
P[22] EtOH–terephthalic	NMe_4OH	3100
	NMe_4OH + PiK	6900

Polymers. Polyesters and polyamides (Scheme 3) were prepared by condensation of dialcohol or diamine derivatives with acid dichlorides.

In most cases, a solution process was used, leading to a number-average molecular weight between 4000 and 2000. *Table 1* summarizes the results obtained with experimental conditions and molecular weights. The polymer P[22] decane was obtained by reduction of P[22] sebacic with $LiAlH_4$. Under our experimental conditions a significant molecular weight degradation was observed and no attempt was made to determine better conditions. In some cases interfacial polymerization was used and experiments were carried out to study the influence of the presence of a complexable salt in the aqueous phase. *Table 2* summarizes the results obtained with a polyamide and a polyester. The presence of a complexable cation in the aqueous phase together with the crown-ether, increases the molecular weight of the resulting polymer. In the same way, an increase of the lipophilicity of the anion leads to higher polymers. These observations can be interpreted as the results of accelerated phase transfer. We have shown[2] that the partition coefficient of the ligands between aqueous and organic phases ($CHCl_3$) is strongly increased in favour of the organic phase when complexes are formed. The configuration adopted by the ligand in the complexes increases its lipophilicity and thus increases the rate of diffusion of the monomers in the organic phase: as a consequence, dichloride deactivation reactions are prevented. This mechanism can be interpreted as a autocatalytic effect.

Ion binding properties

Ion binding properties of the polymers and analogous molecules were determined in chloroform, using a liquid–liquid extraction process. The experimental procedurce is similar to that recently reported[1,2]. An aqueous solution of picrate salt MA is shaken repeatedly with a chloroform solution of the ligand L. To avoid protonation of the ligand, the aqueous phase is adjusted to pH 10 with NMe_4OH. At equilibrium we have, in the chloroform phase:

$$MA + L \underset{}{\overset{K_c}{\rightleftharpoons}} LMA \qquad (1)$$

where LMA is a complexed ligand. It is assumed that a 1:1 complex is formed and that the ionic species present in the organic phase are in the form of ion pairs[4]. K_c is calculated from the expression:

$$K_c = \frac{[MA]_T - [MA]}{[MA]\,[[L]_0 - [MA]_T + [MA]]}$$

where $[L]_0$ and $[MA]_T$ are respectively the total concentration of ligand and salt in the chloroform phase, and [MA] is the concentration of the uncomplexed salt. Salt concentration in chloroform is determined by u.v. spectroscopy and/or atomic absorption. In the case of a water-soluble ligand the partition coefficient between aqueous and chloroform phases is previously determined by n.m.r. The solubility of the salts in chloroform is determined by a preliminary extraction process. Since a large excess of salt in aqueous phase is used, [MA] is equal to the solubility of the salt in chloroform in the absence of ligand.

The interpretation of experimental data at equilibrium (1) assumes that 1:1 complexes of cation with ligand are obtained whatever the concentration. This is easily verified for analogous monomeric molecules by n.m.r. spectroscopy. The shift of the characteristic bands observed in the presence of a known quantity of salt, is plotted as a function of the stoichiometry. A maximum shift is obtained for the ratio 1:1. For polymeric ligands, the stoichiometry was determined by liquid–solid extraction experiments. The polymer dissolved in chloroform is placed in contact with a gradually increasing quantity of solid picrate salt; after some weeks, the content of dissolved picrate is determined. A 1:1 stoichiometry has been observed in all cases. *Table 3* gives stability constants for different polymeric ligands with picrate salts in chloroform. The polymeric structure greatly influences the binding properties. Polyamide structure leads to poor binding properties. Better properties are obtained with the polyesters and the stability constants depend on the nature of the comonomeric unit; the stability decreases from adipic to sebacic and terephthalic sequences. The triglycolic polyester appears to be a special case. Binding properties are better than those for other polyesters and, more interestingly, the complexation is not selective–the same values are obtained

Table 3 Stability constants in chloroform of polymeric complexes with picrate salts (10^{-3} M). The ligand concentration is 10^{-4} M

	$K_c \times 10^{-5}\ M^{-1}$			
polymers	Na^+	K^+	Cs^+	Rb^+
P[22]–sebacic	<0.01	<0.01		
P[22]–decane	29	60		
P[22] $EtNH_2$–terephthalic	<0.01	<0.01	<0.01	
P[22] $EtNH_2$–sebacic	<0.01	≤0.01		
P[22] EtOH–adipic	1	4		0.3
P[22] EtOH–sebacic*	0.8	2.1	0.6	0.3
P[22] EtOH–terephthalic	<0.01	0.5	<0.01	0.02
P[22] EtOH–triglycolic	6	5.7	6	

* K_c = 0.4 (Ca^{2+}), 1.8 (Sr^{2+}), 3.0 (Ba^{2+})

with Na^+, K^+ or Cs^+. Optimum properties are obtained with [22] decane polymer for which the stability constants are comparable with those of the monomeric analogue [22] CH_3.

Three factors may be considered to explain such differences: the nature of the polymer; the chemical nature of the comonomer; and the nature of the chemical groups present near the rings. Examination of results obtained under the same conditions with some analogous monomeric molecules (*Table 4*) clearly demonstrates the major influence of the chemical groups near the rings. Taking the ligand [22] CH_3 as reference, it is observed that an ester group decreases the stability by a factor of 40 and an amide group by a factor greater than 3000. Another important factor when examining the stability of the complexes, is the solvent. Intramolecular interactions are strongly dependent on the polar or non-polar nature of the solvent. Experiments have been carried out in water to determine if the observed strong decrease in the stability of amide and ester complexes is due to the non-polar nature of the chloroform. The stability constants in this solvent were determined by pH titration using the method previously described[2]. Results are presented in *Table 5* for five alkali and alkaline-earth cations. The same phenomenon is observed: the presence of ester or amide groups near the ring decreases the stability by factors of 50 or 25, respectively.

DISCUSSION

The binding properties of a polymer containing macrocyclic ligands can be analysed in terms of structural interactions of three types, excluding ionic and solvent interactions.

Substituent effect

Since the nature and electronic properties of the binding sites are the major factors affecting the stability of cyclic complexes, it may be expected that any substituent may interact with the binding sites and affect the complex stability[5]. For diaza-crown-ethers, interactions with electron deficient species may lead to electron delocalization on the nitrogen and thus a decrease in their basicity binding properties.

Table 4 Stability constant in chloroform of diaza-crown-ether derivatives (10^{-4} M) with potassium picrate (10^{-3} M)

$K_c \times 10^{-5}\ M^{-1}$ with K^+ Picrate	
[22] CH_3	26
[22] EtOH	30
[22] $EtNH_2$	6
[22] $EtOCOCH_3$	0.7
[22] $EtNHCOCH_3$	<0.01

Pod effect.

The presence near the ring of attached chemical groups which can give additional binding sites may contribute to the

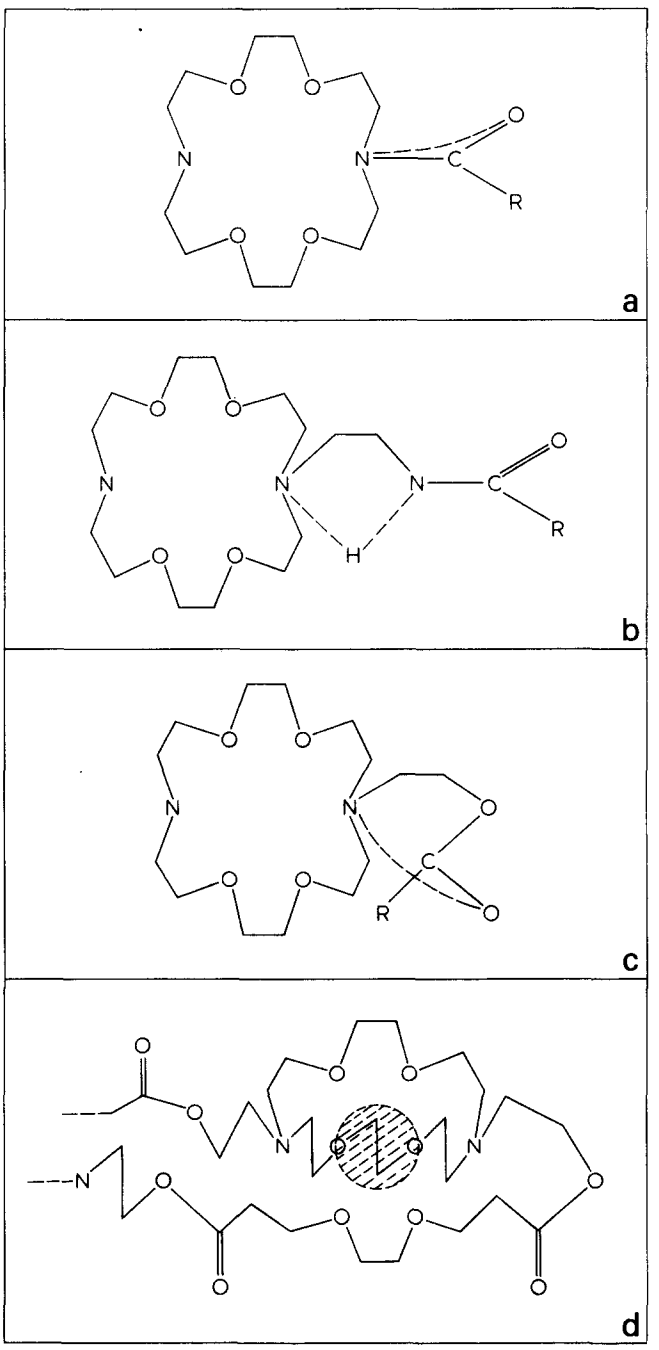


Table 5 Protonation and stability constants in water of diaza-crown ether derivatives at 20°C in presence of 0.1M NMe_4Br

Cation		pK_1	pK_2	pK/M^{-1}				
				Na^+	K^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ligand	[22] CH_3	9.6	7.6	1.1	1.0	2.4	4.2	3.8
	[22] EtOH	8.4	6.9	1	1	3.7	4.3	5.3
	[22] $EtNH_2$*	10.8	8.8	1	1	2.5	2.9	3.2
	[22] $EtOCOCH_3$	7.3	5.7					2.1
	[22] $EtNHCOCH_3$	7.8	5.1					2.4

* $pK_3 = 5.0$; $pK_4 = 3.0$

stability of the complexes[6]. With polymeric cyclic ligands such additional binding sites can appear as a result of the polymerization[1].

Polymeric effect:

The polymeric nature of the ligand favours intramolecular interactions between the rings or between a ring and another part of the chain. Furthermore, one major difference between a conventional ligand and a polymeric ligand is the possibility in the latter case of having variable complexation on the same molecule. This can influence not only the configuration of the polymers but also the conformation of the complexes and their stability constants.

All our results show that the binding properties of the polyesters and polyamides studied are strongly dependent on their structure. If we exclude the case of the triglycolic polyester, which will be discussed later, the same kind of dependence is also observed with the analogue molecules. It can be concluded that the interactions leading to such changes in binding properties are mainly due to a substituent effect. The poor properties of the [22] sebacic polyamide are easily understood by considering the direct interaction between the nitrogens and the carbonyl groups (*Figure 1a*). In the other cases, due to the presence of two methylene groups between the nitrogens and the amide or ester groups, such direct interactions are not possible. A more probable explanation is the possibility of interactions resulting from the formation of five-member ring structures as shown in *Figures 1b* and *1c*. These rings are energetically favourable and are well-known with amide groups. In the case of ester functions, no hydrogen bonding is involved and we can expect (and observe) a less stable structure leading to a moderate decrease of the complex stability.

In terms of interactions, the results obtained with the triglycolic polyester is interesting, particularly the fact that no selectivity is observed. This can be understood if we consider a pod polymeric effect: the glycolic bridges participate in complex formation (*Figure 1d*) and make possible the accommodation of cations of any size, leading to a poorly selective structure.

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1 Gramain, Ph. and Frere, Y. *Macromolecules* 1979,
2 Gramain, Ph. and Frere, Y. *Nouveau J. de Chimie* 1979, **3**, 53
3 Dietrich, B., Lehn, J. M., Sauvage, J. P. et Blanzat, J. *Tetrahedron* 1973, **29**, 1629
4 Wong, K. H., Yagi, K. and Smid, J. *J. Membrane Biol.* 1974, **18** 379
5 Ungaro, R., El Haj, B. and Smid, J. *J. Am. Chem. Soc.* 1976, **98**, 5198
6 Simon, J. *Thèse* University of Strasbourg (1976)