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Polymeric Pseudocrown Ethers. 1. Synthesis and Complexation with Transition Metal Anions

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Abstract: Polymeric pseudocrown ethers (PPCE) are prepared by the reaction between chloromethylated styrene–divinylbenzene copolymers and polyoxyalkylene under Williamson ether-synthesis conditions. Synthetic aspects, the polymer selection, and reaction conditions are discussed. Effective PPCE synthesis is obtained with flexible polymers, and high cyclization yields are obtained, even when 3 molar excess of the diol is used. A detailed study of the coordination of transition metals, including Au^{3+}, Fe^{3+}, and Zn^{2+}, as chlorides, bromides, or iodides in HX and/or NaX solutions show that PPCE coordinate MX_4^- or MX_4^{2-} complexes (M = Au, Fe, Zn; X = Cl, Br, I) without competition from large excess of hydrogen or X^- ions. The coordination patterns of the various PPCE show that coordination is most effective when the anions fit well in the PPCE cavity (whose dimensions were estimated from Corey–Pauling–Koltun models). The coordination of MX_4^- or MX_4^{2-} anions (ionic diameter 9–11 Å) is most effective with PPCE-14 (incorporating 14 oxygens, cavity diameter 10.5–13 Å) and falls off to zero with PPCE-4 (incorporating four oxygens).

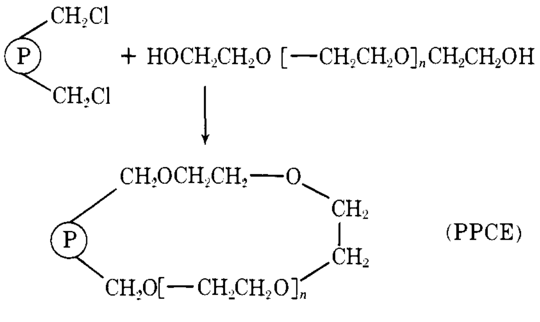
I. Introduction

The synthetic work of Pedersen on macrocyclic ethers[1] has attracted the attention of many workers in various research areas. Major efforts have been directed toward the design and synthesis of ligands,[2] the correlation between ligand structure and transport phenomena in biosystems,[3] and the preparation of synthetic membranes.[4] The thermodynamics of cation–ligand interaction has been thoroughly studied,[5] and the feedback to organic chemistry in host-guest chemistry[6] and phase transfer catalysis[7] has been very significant.

Soluble polymers incorporating pendant crown-ether groups were synthesized by Smid and co-workers from 4′-vinylbenzo-15-crown-5 and 4′-vinylbenzo-18-crown-6 monomers,[8] and were found to be very similar to the monomers[9] in their cation complexation properties. In addition, owing to their good water solubility,[10] they bind organic solutes as picrate ions, methyl orange, phenolphthalein, as well as other organic neutral and anionic solutes.[10,11] Poly(vinylbenzo-18-crown-6) dissolved in water catalyzes the decarboxylation of 6-nitrobenzisoxazole 3-carboxylate by a factor of 2300.[12]

Fritz's report,[13] that a polymer incorporating pendant ester groups (Amberlite XAD-7) strongly binds gold as $AuCl_4^-$, followed with our studies on the coordination of thiocyanate complexes of platinum group metals,[14] suggested that metal ion coordination is accomplished by a cooperative effect of many ester groups and that the close proximity of the polymer backbone is not deleterious. This led us to assume that the synthesis of macrocyclic ethers incorporating a part of the macromolecular network would result in polymers of high coordinating power.

This work describes the synthesis of a range of such polymers described as "polymeric pseudocrown ethers" (PPCE),[32] prepared by the general scheme of eq 1.


(1)

(PPCE)

Anion complexation is an intriguing problem of similar importance to cation complexation. Graf and Lehn[15,16] have described anion inclusion by specially designed cryptates and Schmidtchen[17] has recently synthesized macrocyclic quaternary ammonium compounds.

This paper is concerned mainly with the synthesis of polymeric pseudocrown ethers and their coordination with anionic halide complexes of the transition metals. The complexation of acids[18] and $HFeCl_4$ complexation in phosphoric acid media[19] are presented in forthcoming papers in this series.

II. Selection of Polymeric Precursors

The network structure of the polymer has an important role in the synthesis of polymeric pseudocrown ethers, as it has in the synthesis of other ion coordinating polymers.[21] Let us consider the various possibilities as described in Scheme I.

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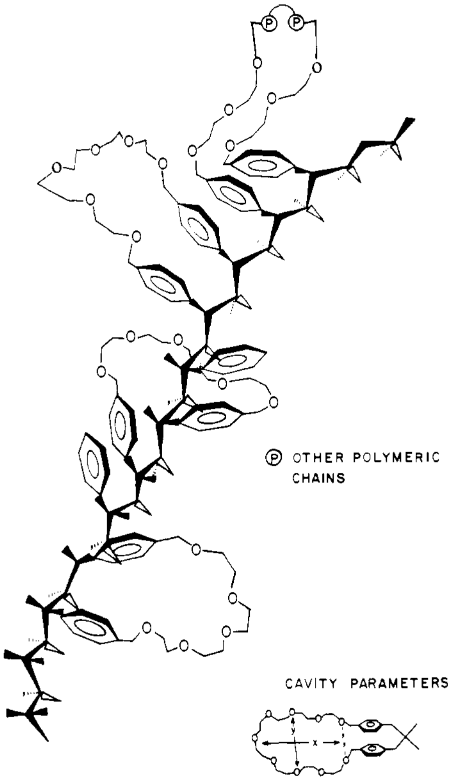
Table I. Comparison between Various Polymeric Matrices[a]

polymer no.	matrix[b]	polyether	chlorine replaced[c] %	polyether groups[d] introduced, %	calcd functional group, mmol/g: total oxygen	calcd functional group, mmol/g: polyether	sp vol,[e] mL/g
10	XE-305	decaglycol	100	99.2	7.43	0.67	2.78
11	XAD-1	decaglycol	74.4	83.8	6.83	0.62	2.05
12	XAD-4	decaglycol	56.7	40.9	3.54	0.32	2.16

[a] Conditions: 10 g of polymer, 30 mmol of glycol, 60 mmol of NaH, 100 mL of dioxane, 24 h at 100 °C. [b] XE-305, 1.86 mmol/g Cl; XAD-1, 2.67 mmol/g Cl; XAD-4, 3.07 mmol/g Cl. Surface areas (m^2/g): 48 for XE-305, 180 for XAD-1, 700 for XAD-4. Average pore diameter (Å): 1400 (XE-305), 200 (XAD-1), and 50 (XAD-4). [c] As defined in footnote *a*, Table III. [d] As defined in footnote *c*, Table III. [e] Specific volumes (mL/g): (XE-305)-CH_2Cl, 3.41 (dry), 6.65 (dioxane); (XAD-4)-CH_2Cl, 2.12 (dry), 2.55 (dioxane); (XAD-1)-CH_2Cl, 2.19 (dry), 2.95 (dioxane).

Scheme I. Formation of Polymeric Pseudocrown Ethers



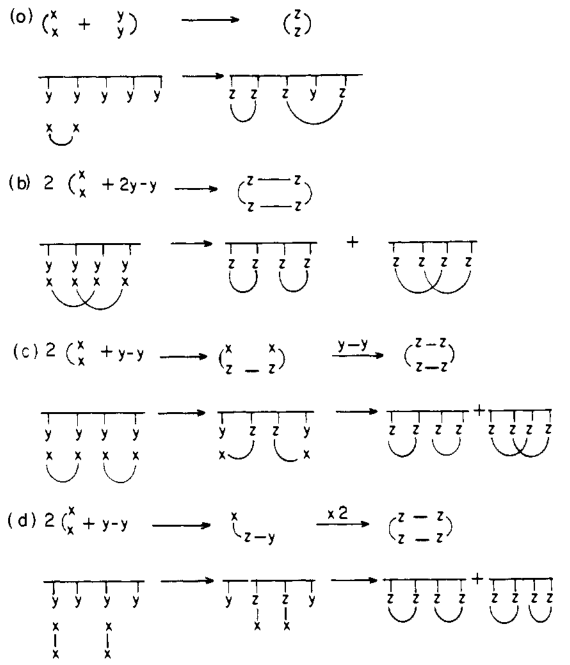
The reaction between linear chloromethylpolystyrene (Y = CH_2Cl) and diols (X = OH) in homogeneous solution (case A) resembles very closely the ordinary symthesis of crown ethers (Z = -O-) which usually leads to a mixture of cyclic crown ethers and linear polyethers.

The synthesis with cross-linked polymers is more complicated. Rigid polymers (case C) are better juxtapositioned for cyclization reactions, but they will have a low accessibility to large polyglycols, and they will resist any conformational modifications required by the incoming polyglycols. Slightly cross-linked polymers with intermediate flexibility will be a good compromise because they offer the following advantages: (a) good accessibility (good swelling and diffusion) to large polyether molecules; (b) good conformation adaptability; (c) minimal further cross-linking.

Our previous experience with Amberlite XE-305, a 4% divinylbenzene-styrene copolymer,[20,21] has suggested that this polymer might be a suitable precursor for this study.

The reaction between decaethylene glycol and various chloromethylpolystyrene matrices, which vary in the concentration of cross-linking agent (divinylbenzene), in the pore structures, and in the swelling properties, is described in Table 1. The percent polyether formation (proportional to the percent chlorine replaced) falls in the order of increasing degree of cross-linking from 99.2% polyether formation for [XE-305]-CH_2Cl to 83.8% for XAD-1 to 56.7% for XAD-4. This comparison makes [XE-305]-CH_2Cl the optimal polymeric material for this study.

Scheme II. Methods in Crown Ether Synthesis, and the Polymeric Analogues



III. Results

1. Reaction Conditions. Chloromethylated XE-305[20] containing 17-22% Cl (67.3-91.8 mmol % of chloromethyl-substituted aromatic rings) swollen in a good solvating solvent, dioxane (swelling ratio 1.95:1), was reacted with the disodium salt of the polyether. Initially, superdry distilled dioxane was used. Later it was found that distilled dioxane, dried over anhydrous Na_2SO_4 or $MgSO_4$, was adequate.

Two different sodium hydride addition methods were tried: (a) formation of the disodium salt, then reaction with the chloromethylated polymer; (b) simultaneous disodium salt formation and reaction with the chloromethylated polystyrene. Owing to excessive froth formation, the first method of preliminary formation of the disodium salt is time consuming and the second method was usually preferred.

In crown-ether synthesis (see Scheme II) the molar ratio diol:halide decides both the nature and the yield of the product; it was therefore interesting to see the influence of such variations on the synthesis of polymeric pseudocrown ethers.

The ratio of diol:halide was varied between 0.64 and 2.2, that

Table II. Component Variations in the Synthesis of Polymeric Pseudocrown-14[a]

	[XE-305]-$\mathrm{CH_2Cl}$		molar ratio			product		chlorine	
no.	starting wt, g	– Cl	polyether/ (XF-305)-$\mathrm{CH_2Cl}$	NaH/ polyether	disodium salt/ (XE-305)-$\mathrm{CH_2Cl}$	wt, g	% Cl	replaced, %	conversion figures[b]
1	100	20.4	0.64	0.92	0.59	206	1.03	89.6	2.07
2	75	21.4	0.68	2.95	2.0	150	0.56	94.7	2.00
3	10	21.84	1.60	1.25	2.0	19.89	0.70	94.1	1.99
4	10	17.53	2.0	0.625	1.25	20.0	0.13	98.7	1.95
5	100	17.40	2.0	1.25	2.5	204.1	0.43	95.0	2.01
6	44	18.00	2.2	0.59	1.3	87.7	0.20	97.8	1.94

[a] Polyoxyethylene[13] (av mol wt 600) at 100 °C for 36 h, 10 mL of dioxane per g of polymer, 50% NaH in oil. [b] mmol of polyoxyalkylene[13] introduced for each g of starting polymer; average error ±0.05.

Table III. Synthesis of Various Polymeric Pseudocrown Ethers. Reaction Conditions[a]

				no. of	XE-305-$\mathrm{CH_2Cl}$		molar ratio	
no.	polymer	mol wt	source	oxygens n	W_s, g	a (% Cl)	polyether [XE-305]-$\mathrm{CH_2Cl}$	NaH polyether
1	ethylene glycol	62		2	10	18.16	1.95	1.25
2	diethylene glycol	106		3	10	18.16	3.34	0.73
3	triethylene glycol	150		4	10	18.16	1.95	1.25
4	pentaethylene glycol	238	PEG-200	6	10	21.84	1.63	1.25
4a	pentaethylene glycol	238	synth	6	10	21.84	0.5	2
5	heptaethylene glycol	326	PEG-300	8	10	21.84	1.63	1.25
5a	heptaethylene glycol	326	synth	8	10	21.84	0.5	2
6	decaethylene glycol	458	PEG-400	11	10	21.84	1.63	1.25
6a	decaethylene glycol	458	synth	11	10	21.84	0.5	2
7	dodecaethylene glycol	546	synth	13	10	21.84	0.5	2
8	tridecanethylene glycol	590	PEG-600	14	10	17.40	2.0	1.25
9	heptapropylene glycol	438	PPG-425	8	10	21.84	1.63	1.25
10	decaethylene glycol	468	synth	11	10	6.6	1.0	2

[a] Conditions: 100 mmol of polyether, 6 g of 50% NaH in oil, 100 mL of dioxane, 24 h at 100 °C.

Table IV. Synthesis of Various Polymeric Pseudocrown Ethers. Products

		product		chlorine replaced[a]		groups introduced			calcd functional groups concn, mmol/g			
						OH,[b]	polyether					sp
polymer no.	no. of oxygens n	W_p, g	b (% Cl)	mmol	%	mmol	mmol[c]	%[d]	total oxygen[e]	OH	pseudocrown	vol. mL/g[g]
1	2	9.84	17.06	3.86	7.56	0	0			0.04		
2	3	11.36	0.18	50.57	98.82	2.73	29.15	104.4	7.70	0.24	2.57	
3	4	12.16	0.05	50.98	99.67	1.52	26.4	95.9	8.68	0.125	2.17	
4	6	15.02	0.11	61.04	99.22	1.95	35.9	97.44	12.29	0.41	2.39	
4a	6	14.76	4.04	44.73	72.7		25.59	114	10.40		1.73	
5	8	16.33	0.13	60.92	99.03	1.96	28.31	87.70	12.85	0.11	1.73	
5a	8	16.59	2.17	51.38	83.51		25.04	97.47	12.07		1.51	2.94
6	11	18.12	0.28	60.09	97.68	0	25.63	85.30	13.60	0	1.41	
6a	11	19.87	1.30	54.24	88.17		25.20	92.92	13.05		1.26	3.22
7	13	18.98	3.47	42.97	69.84		18.90	88.0	12.94		0.99	2.70
8	14	20.40	0.43	46.54	94.96	0	20.11	86.40	14.02	0	0.99	
9	8	18.63	0.75	57.5	93.60	0	25.25	87.80	11.36	0.09	1.35	
9a	6	12.34	0		100				5.88		0.98	2.90
9b	8	11.56	0		100				6.10		0.76	2.82
10	11	13.66	0		100				7.43		0.67	2.78

[a] Calculated from mmol chlorine replaced = $M^{\mathrm{R}}_{\mathrm{ch}} = (aW_s - bW_p)/3.55$. % chlorine replaced = $(M^{R}_{ch}/aW_s) \times 35.5$. [b] $M_{\mathrm{OH}} = W_p \times$ no. of OH groups. % OH introduced = $(M_{\mathrm{OH}}/M^{\mathrm{R}}_{\mathrm{ch}}) \times 100$. [c] Calculated from mmol polyether introduced = $M_{\mathrm{PE}} = ([(W_p - W_s) + (aW_s - bW_p) \times 10^{-2}]/(\text{av mol wt of polyether})) \times 10^3$. [d] Percent pseudocrown formed = $\% P_{\mathrm{C}} = ((M_{\mathrm{PE}} - M_{\mathrm{OH}})/M^{\mathrm{R}}_{\mathrm{ch}}) \times 2 \times 100$. [e] Calculated from $M_{\mathrm{PE}} \times$ av no. of oxygens/W_p. [f] Calculated from M_{PE}/W_p. [g] The specific volume of XE-305-$\mathrm{CH_2Cl}$ = 2.93 mL/g (dry), 6.45 (dioxane).

of sodium hydride:diol between 0.59 and 2.95, and that of the disodium salt of the diol:halide was varied between 0.50 and 2.5. All the variations did not cause any significant change in the yield of polyether, which varied between 1.94 and 2.07 mmol of polyethylene glycol introduced per g of starting polymer. Polymers of examples 4–6 (Table II) with 17.4–18.0% chlorine showed similar conversion figures to polymers with higher chlorine content (examples 1–3). This suggests strongly that a certain fraction of chlorine sites are inaccessible to large polyethers.

The second conclusion is that an equimolar amount of the disodium salt is sufficient to push the formation of the polymeric ether to completion.

2. Synthesis of Various Polymeric Pseudocrown Ethers. The synthesis of various polymeric pseudocrown ethers by the reaction with various polyoxyalkylene compounds is described in Tables III and IV. The polymer samples were dried very carefully under high vacuum over P_2O_5 to constant weight. Azeotropic distillation with toluene showed such samples to be practically dry (less than 0.01 mL of H_2O released per 10

Figure 1. Chloromethylated XE-305, internal structure ×7220.

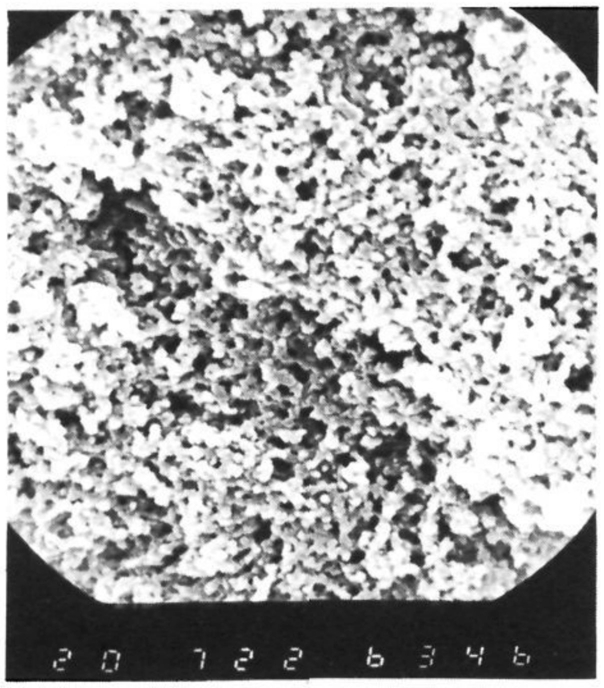


Figure 2. Polymer no. 8, PPCE ⟨14⟩, internal structure ×7220.

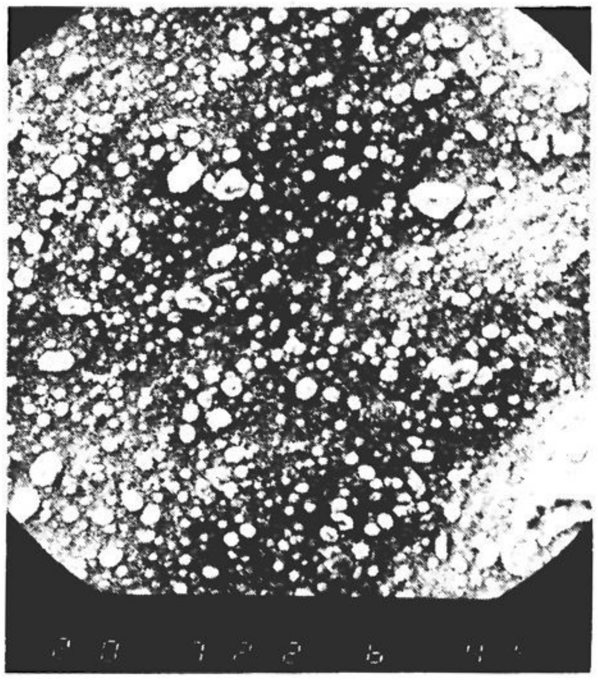


Figure 3. Polymer no. 8, PPCE ⟨14⟩, surface ×7220.

g of polymer). Weight additions for the 10-g samples were large enough for accurate weighing and the largest source of error in the method is in the chlorine analysis (±3%). Elemental analysis data (see Experimental Section) shows good agreement with predicted empirical formulas for the polymeric pseudocrown ethers. However, since the empirical formula does not consider the 4% divinylbenzene present as cross-linking agent, or corrects for averages of oxyethylene units or residual chlorine content, the % Pc formula presented later served to calculate the percent formation and PPCE concentrations on the polymers.

$$\%\ \mathrm{Pc} = \frac{M_{\mathrm{PE}} - M_{\mathrm{OH}}}{M^{\mathrm{R}}_{\mathrm{ch}}} \times 2$$

where M_{PE} = mmol polyether introduced, $M^{\mathrm{R}}_{\mathrm{ch}}$ = mmol chlorine replaced, and M_{OH} = mmol hydroxyl group introduced, and where

$$M^{\mathrm{R}}_{\mathrm{ch}} = \frac{aw_{\mathrm{s}} - bw_{\mathrm{p}}}{3.55}$$

$$M_{\mathrm{PE}} = \frac{(W_{\mathrm{p}} - W_{\mathrm{s}}) + (aW_{\mathrm{s}} - bW_{\mathrm{p}})10^2}{\text{av mol wt of polyether}} \times 10^3$$

a is the chlorine percent of the starting polymer and W_{s} is its weight. b is the chlorine percent of the product and W_{p} is its weight. M_{OH} was determined by reaction with 3,5-dinitrobenzoyl chloride (see Experimental Section). The % Pc formula presented above is based on the assumption that M_{OH} represented hydroxyl groups of pendant polyether groups.

From diethylene glycol to the highest polyglycol (13 oxyethylene units, average mol wt 600) the reactivity is very high, with chlorine conversion yields between 93.6 and 99.2%. The polymeric pseudocrown ethers contain 7.7–14 mmol oxygens per g, and 1–2.6 mmol crown ethers per g. The free hydroxyl groups range between 0 and 0.4 mmol/g. The low M_{OH} figures indicate that the formation of linear polyethers with pendant hydroxyl groups is very low.

3. Scanning Electron Microscope Examination. In order to determine the microscopic structure of the various polymeric pseudocrown ethers, scanning electron microscope (SEM) photographs of the surface of the beads and the internal structure of fractured beads were taken, using X7220 magnifications. Figure 1 describes the inner structure of chloromethylpolystyrene (XE-305 type), the starting polymer in the synthesis of the polymeric pseudocrown ethers. Like other macroretricular polymers and ion-exchange resins, this polymer possess the microsphere-agglomerate structure.[22] Examining SEM pictures of various polymeric pseudocrown ethers, it is possible to notice the development of an organized sieve-type structure.

Polymeric pseudocrown ⟨14⟩ has a very rough surface (Figure 2) with protruding globular points. The internal morphology is highly organized (Figure 3) with pore diameters of 1400–3000 Å. The increase in pore diameter (the average pore diameter of XE-305 is 1400 Å[23]) is expected during the process of the incorporation of large macrocyclic ethers. On the other hand, interchain cross-linking should be accompanied by matrix contraction and decrease in pore diameter and contribute very little to an organized morphology. The structure of the network explains also the very high mechanical stability of the polymers and their excellent ion diffusion characteristics as expressed by the high ion exchange kinetics.[19]

4. Structure of the Polymeric Ethers. Scheme II presents the synthetic methods applied in the synthesis of crown ethers as summarized by Lehn,[2] and, in parallel, their analogues in polymeric pseudocrown ether synthesis. The two-component condensation (path (a)) in the presence of templating cations[1,15,33] is the most convenient route to macrocyclic crown ethers. But the variation of the experimental conditions, including ratio between components, reagent addition order, and reagent concentration (or rather dilution), will lead to various macrocycles via routes (b)–(d) in solution.

In the synthesis of polymers, the nature of the polymer plays an important role in directing the course of the reaction and

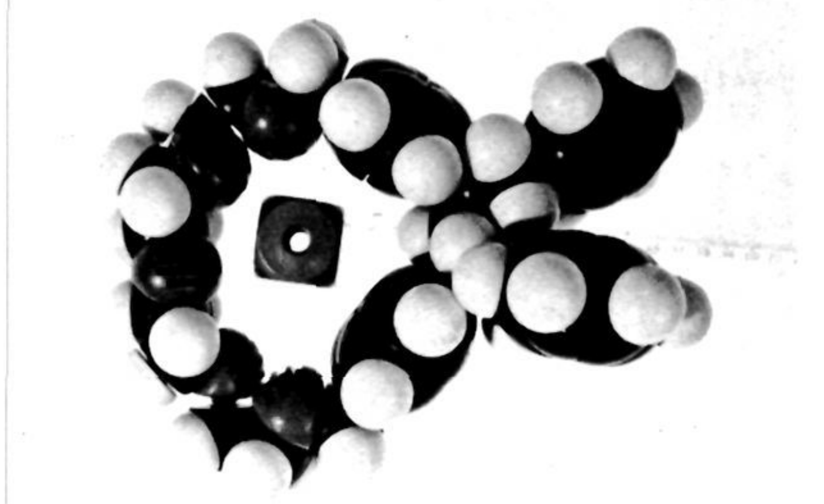


Figure 4. CPK model of PPCE-5, cation complex.

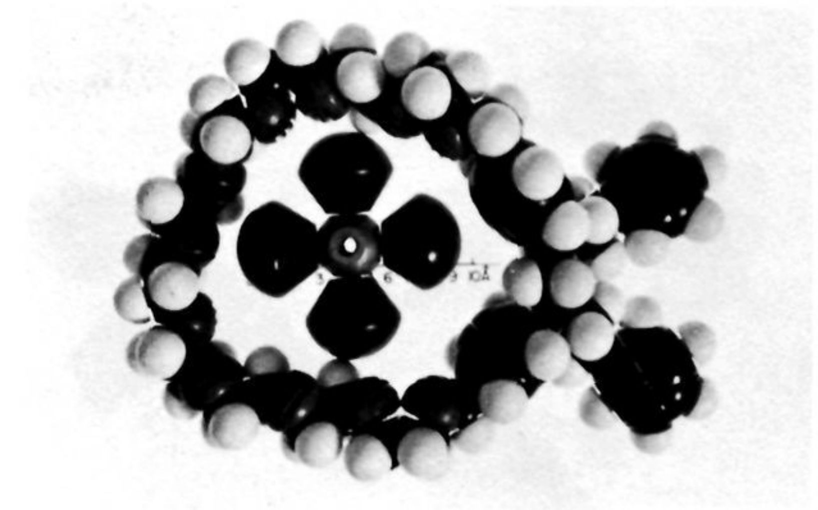


Figure 5. CPK model of PPCE-11, MCl$_4^-$ complex

overweighs other factors. The largest volume expansion for [XE-305]-CH$_2$Cl in dioxane (120% v/v compared to 35% for [XAD-1]-CH$_2$Cl and 20% for [XAD-4]-CH$_2$Cl) ensures maximum chain separation and the lowest risk of interchain cross-linking for this polymer. The specific volume of the polymers does not change much during the conversion from the polybenzyl chloride stage to the polyether stage (2.93 mL/g for [XE-305]-CH$_2$Cl and 2.8–3.2 mL/g for polymeric ethers).

Usually, increases in cross-linking of polymeric matrices are accompanied by volume contraction [e.g., specific volumes of the polybenzyl chloride, XE-305 (4% DVB) 3.41 mL/g and XAD-4 (~40% DVB) 2.12 mL/g]. It is reasonably assumed, therefore, that the polyether formation is predominantly free from interchain cross-linking.

The structure of the polymeric ethers depends therefore strongly on the structure of the chloromethylpolystyrene precursor. It is known that the chloromethylation of polystyrene is a shell progressive reaction,[34] and the distribution of chlorine sites is a function of the experimental conditions. We have found[14] that exhaustive chloromethylation in chlorodimethyl ether (without solvent) produces a homogeneous chlorine profile throughout the bead cross section, as shown by quantitative electron microprobe analysis of isothiouronium–polystyrene resins derived from [XE-305]-CH$_2$Cl.[35]

In the synthesis of polymeric pseudocrown ethers, the reaction conditions chosen (high expansion during swelling, templating with sodium ions, equimolar ratio of diol to polymer) were designed to minimize the risk of interchain cross-linking and lead predominantly to pseudocrown ether structure. In analogy to the synthesis of macrocyclic crown ethers in solution, the formation of other macrocycles via paths (b)–(d) is possible. Against this stand the arguments (1) that the vicinal dianion intermediate postulated in paths (c) and (d) will, owing to charge repulsion of the anions, cyclize to pseudocrown structures by reaction with the neighboring chlorine groups rather than interthread to yield catenane-like structures, and (2) the restricted mobility of the polymeric chains makes reactions like path (b)–(d) involving three- or four-component condensations very tenuous.

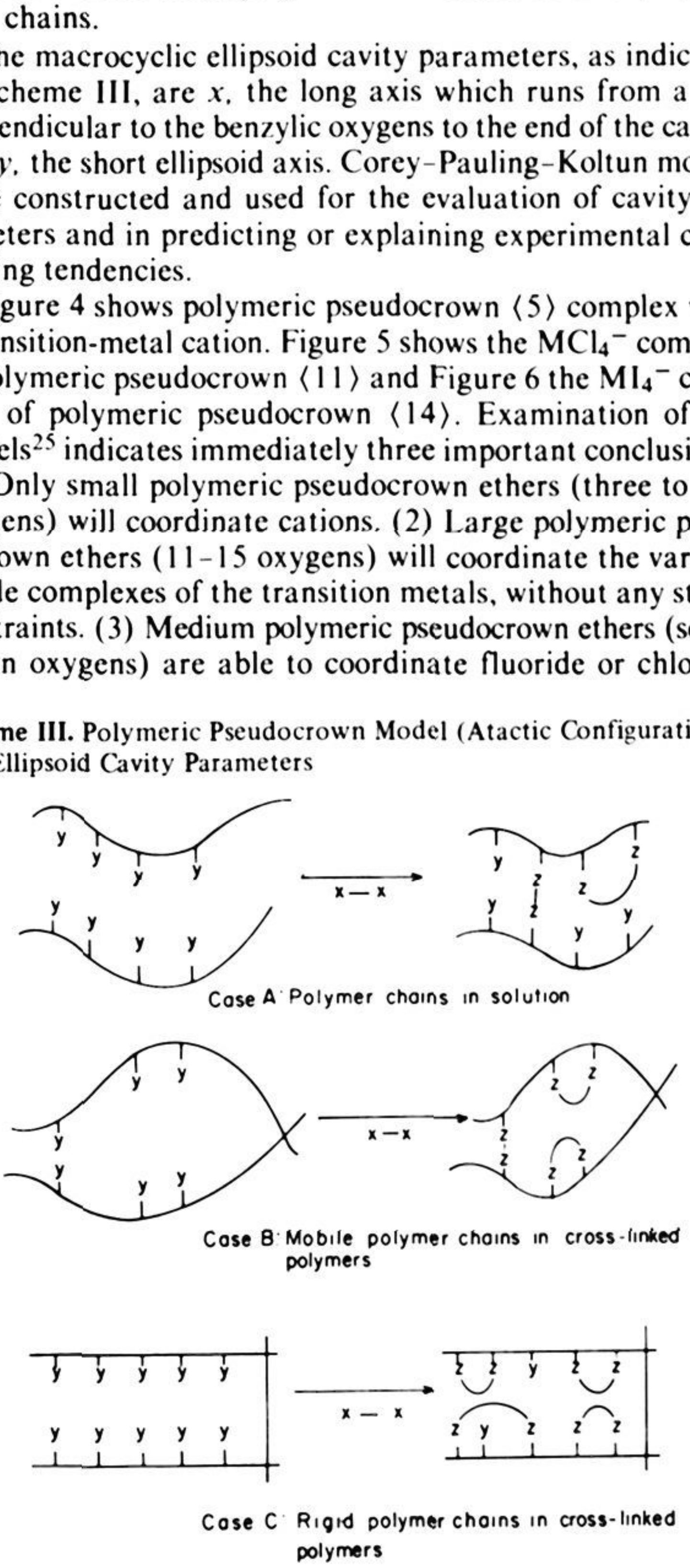
The formation of polyethers via paths (b)–(d) is therefore *theoretically possible. But cyclic pseudocrown structures, or* linear oligoether segments forming interchain cross-linking units, are the predominant structures expected. The metal ion coordination data should be examined in view of fitting one of those two realistic models.

5. Polymeric Pseudocrown Ether Model and Dimensions. Examination of atactic, isotactic, and syndiotactic configurations of polystyrene chains suggests that only the formation of small pseudocrown ethers (with three or four oxygens) may be critically dependent on polymer configuration, whereas the formation of larger polyethers is free from such constraints. The polymeric pseudocrown ether model presented in Scheme III is relevant to atactic polystyrene, obtained during radically initiated polymerization. The macrocycles are randomly distributed, on both sides of the backbone, with intermittent nonsubstituted benzene rings in the middle and occasional macrocycles attached on both sides of the backbone chain, or occasional cross-chain polyether units bound to other polymer [Ⓟ] chains.

The macrocyclic ellipsoid cavity parameters, as indicated in Scheme III, are *x*, the long axis which runs from a line perpendicular to the benzylic oxygens to the end of the cavity, and *y*, the short ellipsoid axis. Corey–Pauling–Koltun models were constructed and used for the evaluation of cavity parameters and in predicting or explaining experimental complexing tendencies.

Figure 4 shows polymeric pseudocrown ⟨5⟩ complex with a transition-metal cation. Figure 5 shows the MCl$_4^-$ complex of polymeric pseudocrown ⟨11⟩ and Figure 6 the MI$_4^-$ complex of polymeric pseudocrown ⟨14⟩. Examination of the models[25] indicates immediately three important conclusions: (1) Only small polymeric pseudocrown ethers (three to five oxygens) will coordinate cations. (2) Large polymeric pseudocrown ethers (11–15 oxygens) will coordinate the various halide complexes of the transition metals, without any steric constraints. (3) Medium polymeric pseudocrown ethers (seven to ten oxygens) are able to coordinate fluoride or chloride

Scheme III. Polymeric Pseudocrown Model (Atactic Configuration) and Ellipsoid Cavity Parameters



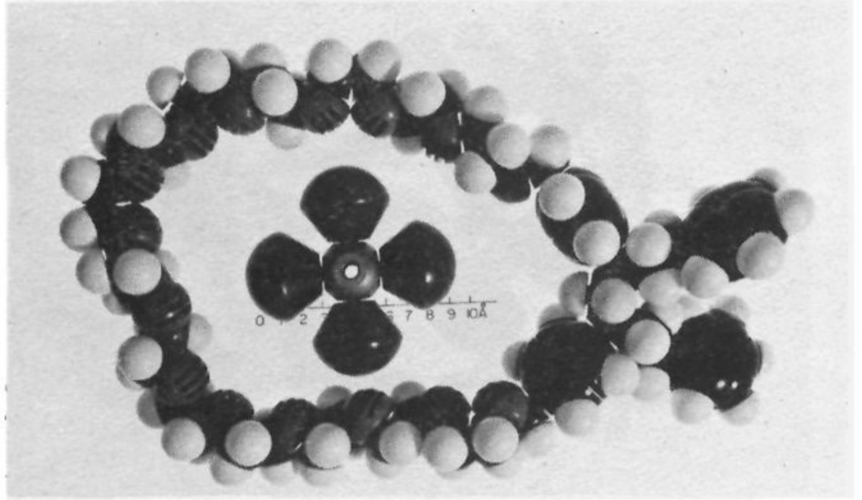


Figure 6. CPK model of PPCE-14, MI_4^- complex.

Table V. Estimated Crown Cavity Parameters[a] for Polymeric Pseudocrown Ethers

polymer no.[b]	av no. of oxygens (n)	X, Å	Y, Å
2	3	1.5	3
3	4	2.5	5
4	5	3.5	5.5
	6	5.5	6
5	7	6	6.5
	8	8.5	7
	9	8	9
6	10	9.5	9.5
	11	11.0	10.5
	13	12.5	10.5
7	14	13	10.5
	15	14	12

[a] Estimated from Corey-Pauling-Koltum models. [b] See Table II.

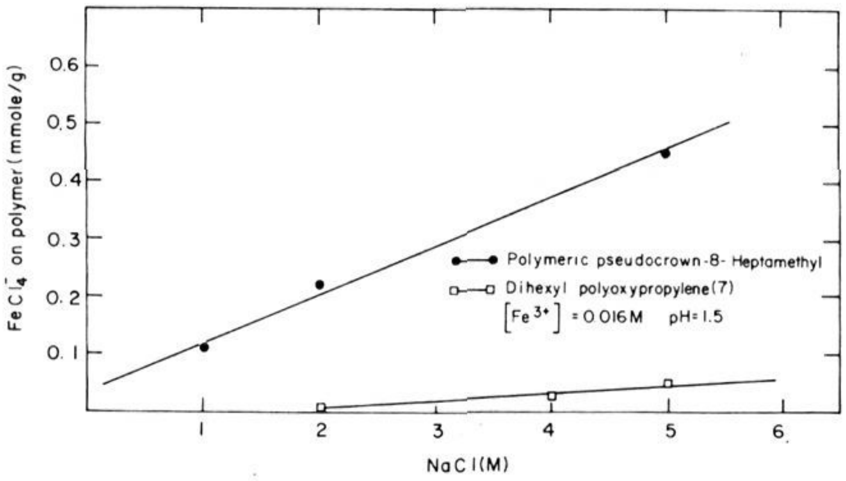


Figure 7. Coordination of MCl_4-type complexes by polymeric pseudocrown-14.

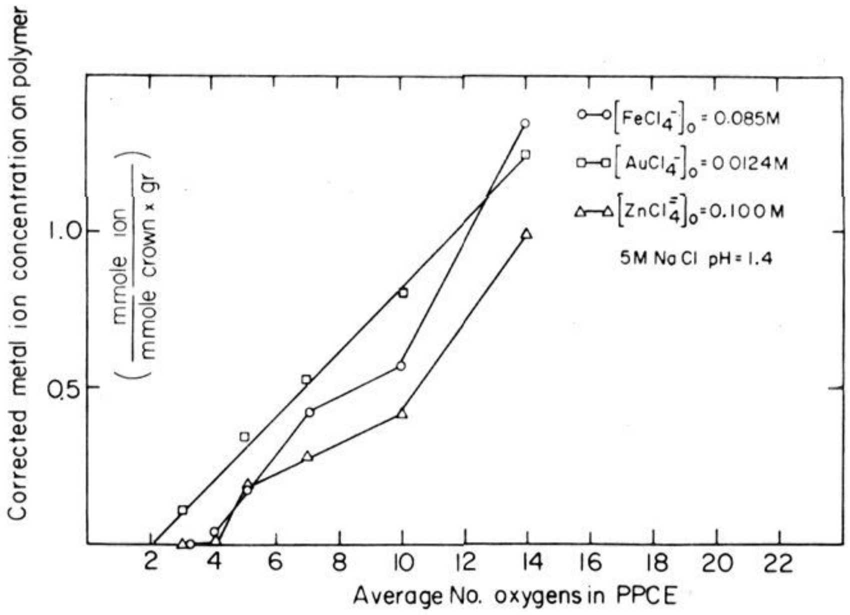


Figure 8. $ZnCl_4^{2-}$ coordination by polymeric pseudocrown-14, in the acid range 10^{-3}–3 M HCl.

complexes, but the larger bromides or iodides may not fit well in the crown cavity.

In order to relate data on ionic dimensions of various cations or anions to cavity dimensions of the various polymeric pseudocrown ethers, cavity parameters were calculated from the CPK models and are presented in Table V.

IV. Coordination of Anionic Halogen Complexes of Transition Metals by Polymeric Pseudocrown-14

Hard metal cations (a type) form very weak halide complexes with stability order $F^- \gg Cl^- > Br^- > I^-$, whereas soft metal ions (b type) form strong halide complexes in the order $F^- \ll Cl^- < Br^- < I^-$. The stability of the transition-metal anionic complex is very much dependent on the d electron configurations, and varies therefore from one metalic ion to the other and with halide concentration.[26] It is therefore clear that anion coordination should be studied under their optimum formation conditions. For that reason anion complexation by polymeric pseudocrown ⟨14⟩ was determined first in aqueous solutions of varying halide concentrations.

Figure 7 shows formation of MCl_4 complexes in various concentrations of HCl (the same formation curves are measured in NaCl solutions). $AuCl_4^-$ and $HgCl_4^{2-}$ exist in very dilute chloride ion concentrations and form the strongest type of complexes. $FeCl_4^-$, $ZnCl_4^{2-}$, and $CuCl_4^{2-}$ are formed only at $[Cl^-] > 1$ M and the coordination of these ions is effective only in such solutions. Figure 8 describes the $ZnCl_4^{2-}$ extraction dependency on H^+ and Cl^- concentrations. In HCl solutions the extraction is directly related to $[Cl^-]$, but in 5 M NaCl the extraction is independent of hydrogen ion concentration, which was varied between 10^{-5} and 10^{-1} M. The same tendencies were observed for gold(III) and iron(III), which were studied in the acid concentration range between 10^{-2} and 10^0 M.

The stoichiometry of the coordination of the metal complex anions by polymeric pseudocrown ⟨14⟩ was determined by equilibrating polymer samples with iron(III), gold(III), and zinc(II) chlorides in 5 M NaCl at pH 1.4 to the point where the solution concentration did not decrease. The maximum polymer capacities range between 0.90 mmol/g for Zn(II) and 1.42 mmol/g for Fe(III). Since the theoretical PPCE ⟨14⟩ capacity for a 1:1 type complex is 0.99 mmol/g, the figures reported here indicate the formation of 1:1 and 1:2 PPCE ⟨14⟩ to metal complexes. The formation of 1:2 and even 2:3 complexes between cations and large macrocyclic ethers has been reported by Pedersen and Frensdorff.[24]

V. Coordination of Anionic Halide Complexes of the Transition Metals by Other Polymeric Pseudocrown Ethers

The synthesis of a wide range of polymeric pseudocrown ethers with the numbers of ligating oxygens varying from 3 to 14, as described in Table IV, offers the possibility of studying the relationship between the coordination ability of the polymers and the corresponding compatibility of the pseudocrown cavity to the anion size. Ionic diameters of several transition-metal halide anions, particularly the chloro, bromo, and iodo complexes of Zn^{2+} and Au^{3+}, were calculated from known atomic distances of the complexes in crystalline compounds,[27] and are presented in Table VI. Examining the ionic diameter of the halide complex anions (9.5–11.2 Å) and comparing with the crown cavity parameters estimated from CPK models (see Table V) it is possible to conclude that polymeric pseudocrown ethers with nine or ten oxygens will accommodate comfortably the aforementioned anions.

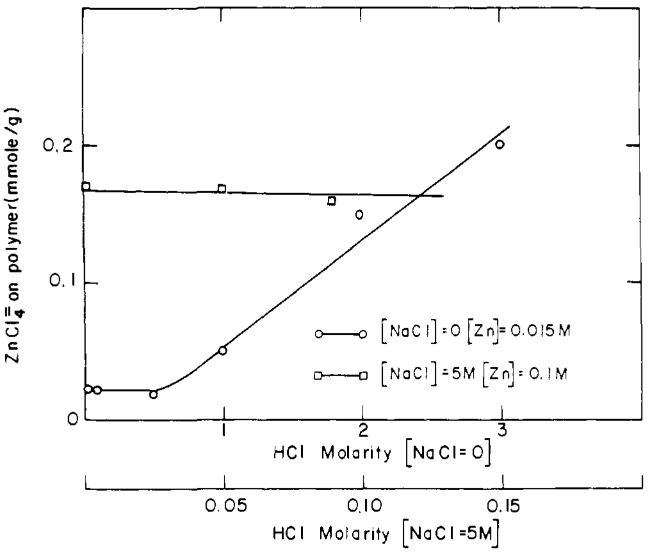


Figure 9. Complexation efficiency of chloride complexes as function of cavity parameters.

Table VI. Calculated Ionic Diameters of Several Halide Complexes of Transition Metals[a]

metal complex	crystalline M-halogen distance, Å	calcd ionic diameter, Å[b]
$ZnCl_4^{2-}$	2.26	9.62
$ZnBr_4^{2-}$	2.39	10.16
ZnI_4^{2-}	2.42[c]	10.64
$AuCl_4^-$	2.30	9.92
$AuBr_4^-$	2.57	10.74
AuI_4^-	2.60[c]	11.22
$FeCl_6^{4-}$	2.30	9.50
$CdCl_6^{4-}$	2.64	
$CoCl_4^{2-}$	2.34	

[a] The distances taken from ref 27. [b] Atomic diamters (Å): Zn^{2+}, 1.48; Au^{3+}, 1.70; Fe^{3+}, 1.28; Cl^-, 1.81; Br^-, 1.95; I^-, 2.16. [c] M-I distances available from MI_2 salt.

It is known that cation complexation occurs with crowns of less than optimum cavity diameter; it can be expected therefore that PPCE with less than nine oxygens will complex anions.

The efficiency of anion complexation by various polymeric ethers in relationship to cavity parameters was established under standard conditions, namely, 5 M NaX solution (X = Cl, Br, I) at pH 1.4. Polymer samples were equilibrated with large excess of the 0.01–0.1 M metal salt solutions for 24 h at 25 °C, so that the residual uncoordinated metal concentration was 80% of the original concentration or higher.

Figure 9 shows the corrected metal ion concentration on the polymer, expressed as mmol of metal ion coordinated for each mmol of pseudocrown group on the polymer per g polymer. Evidently, PPCE ⟨14⟩ is best host for all three anions, $AuCl_4^-$, $FeCl_4^-$, and $ZnCl_4^{2-}$. As predicted earlier, PPCE with nine or ten oxygens show efficient ion coordination (50% of highest value). PPCE with four oxygens or less do not coordinate anions. The coordination of other halide complexes under the same conditions is shown in Table VII (for polymers prepared from glycols synthesized in this work) and in Figure 10 (for polymers prepared from glycols obtained from commercial polyethylene glycol mixtures). The coordination patterns presented in Table VII and Figure 10 are very similar and suggest that glycols obtained from commercial polyethylene glycol mixtures can be used in the preparation of polymeric pseudocrown ethers. In examining the coordination patterns for all MX_4 type complexes studied, the order of anion coordination by polymeric pseudocrown ethers is

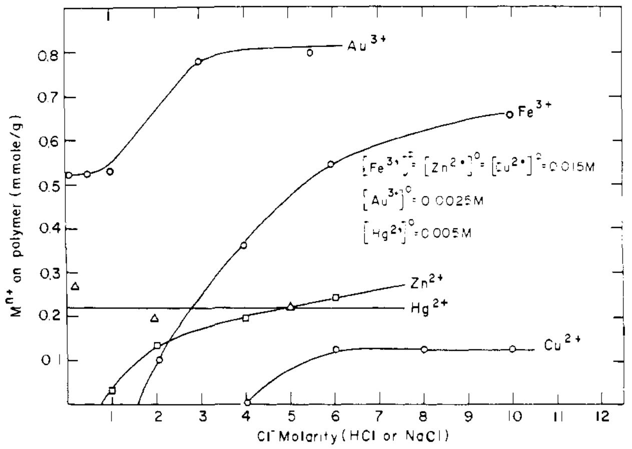


Figure 10. Complexation efficiency of halide complexes as function of cavity parameters.

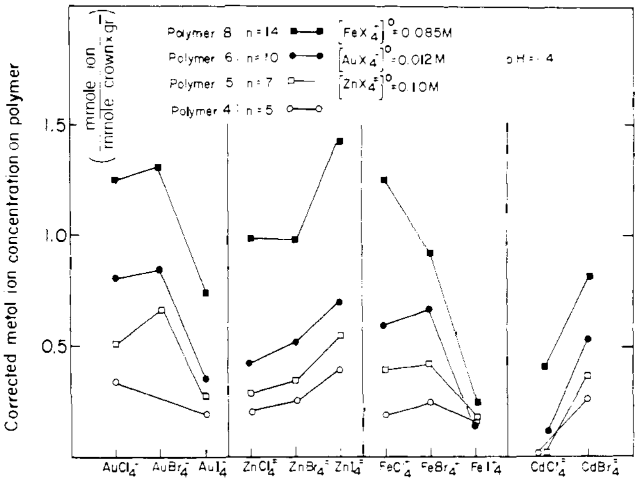


Figure 11. Comparison between polymeric pseudocrown-8-heptamethyl and noncyclic analogue.

PPCE ⟨14⟩ > PPCE-10 > PPCE-7 > PPCE-5

Metals which form strong monovalent halide complexes, e.g., Au^{3+} and Fe^{3+}, show complexation orders of MBr_4^- > MCl_4^- > MI_4^-. Since the stability constants order is MI_4^- > MBr_4^- > MCl_4^-, this indicates that the bromo complex has the best fit into the pseudocrown cavity. The iodo complex, although most stable in solution, does not fit the cavity and is coordinated very weakly. Metals which form weak, divalent halide complexes, e.g., Zn^{2+} and Cd^{2+}, show complexation orders of MI_4^{2-} > MBr_4^{2-} > MCl_4^{2-}, which reflects the order of the corresponding ion activities in solution under identical concentrations.

VI. Comparison between Polymeric Pseudocrown Ethers and Noncyclic Analogues, Including Linear Polymeric Ethers

It is well established that cyclic ethers form very stable complexes with cations. However, it is now recognized that linear polyethers existing in cyclic conformations form stable complexes. Many such complexes were prepared by Vogtle and co-workers.[28] Warshawsky et al.[29] have used noncyclic terminally blocked polyethers to extract $HFeCl_4$ from HCl-H_3PO_4 mixtures. Figure 11 compares the coordination behavior of polymeric pseudocrown ether no. 9 (Table IV) for $FeCl_4^-$ in varying NaCl concentrations and pH 1.5 with di-

Table VII. Corrected Ion Concentrations[a] for Various Polymeric Pseudocrown Ethers

polymer[b] no.	polyether	no. of oxygens (n)	cor metal ion concn, mmol ion/mmol ether × g								
			$AuCl_4^-$ [c]	$AuBr_4^-$	$ZnCl_4^{2-}$ [c]	$ZnBr_4^{2-}$	ZnI_4^{2-}	$FeCl_4^-$	$FeBr_4^-$	FeI_4^-	
4a	pentaglycol	6	0.44	0.42	0.046	0.13	0.10	0.73	0.22	0.12	0.001
5a	heptaglycol	8	0.58	0.62	0.126	0.21	0.08	0.96	0.40	0.33	0.001
6a	decaglycol	11	0.87	0.84	0.26	0.32	0.34	1.32	0.62	0.39	0.001
10	decaglycol	11	0.80			0.07			0.70		
7	dodecaglycol	13	1.16	1.0	0.56	0.30	0.74	1.0	0.30	0.50	0

[a] Determined by successive 1-h equilibrations of the polymers in 0.1 M solution of the metal halide in 5 M sodium halide at pH 1.5 until saturation. [b] See Table III. [c] For polymers 10, 11, and 12, similar results were obtained in 0.1 M metal halide in in 5 M HCl.

Table VIII. Anion Complexation by Linear Polymeric Decaglycols[a]

polymer[b] no.	matrix	mmol decaglycol/ g polymer	cor metal ion concn mmol ion/mmol ether × g	
			$ZnCl_4^{2-}$	$FeCl_4^{2-}$
6a	XE-305	1.26	0.32	0.62
10	XE-305	0.67	0.070	
11	XAD-1	0.62	0.060	0.240
12	XAD-4	0.32	0.076	0.160

[a] 0.05 M metal halide in 5 N HCl. [b] See Table IV.

hexylpolyoxypropylene (no. 7). The curves show that dihexylpolyoxypropylene (no. 7) shows poor coordination power in comparison to polymer no. 9.

A comparison with noncyclic polymeric ethers is provided by polymers no. 11 and 12 (Table I). Those polymers which contain a significant concentration of noncyclic structures are indeed much less effective (see Table VII) as metal coordinating structures, as compared to the polymeric pseudocrown analogues.

The data on noncyclic analogues as presented in Figure 11 and Table VIII points out that the polymeric pseudocrown ethers presented in this work may contain a small but significant proportion of noncyclic structures. The coordination stoichiometry as established in Figure 10 agrees well with a predominant cyclic pseudocrown-metal anion relationship. A quantitative analysis of the ratio between cyclic and noncyclic structures inside insoluble polymers is extremely difficult at this stage.

VII. Coordination Mechanism and Comparison with Amines

The driving force for the coordination process of an ion pair is derived from (1) coordination of the cation or (2) coordination of the anion. In the case of ligands with electron-donating atoms, such as oxygen or nitrogen, coordination of the cation is the first step in the coordination process. For example, in the ion-pair extraction by amines, the following equilibria exist:[30]

protonation: $R_1R_2NH + HCl \overset{K_N}{\rightleftharpoons} R_1R_2NH \cdot HCl \ldots$

anion exchange:

$R_1R_2NH \cdot HCl + MX_4^- \overset{K_N^{ex}}{\rightleftharpoons} R_1R_2NH \cdot HMX_4 + Cl^- \ldots$

The optimum range of the ion-pair coordination is determined by the ratio K_N/K_N^{ex}, in other words, by the two competing reactions: protonation, which is driven forward by excess H^+, and ion-pair dissociation, which is driven by excess Cl^-. As a result the extraction curves for amine in a phase-transfer reaction show a maxima between 2 and 6 M HX (X = Cl, Br, I) concentration and then fall off sharply. In the ion-pair extraction by dialkyl ethers, the following analogous equilibria exist:[31]

protonation: $R_1OR_2 + HCl \overset{K_E}{\rightleftharpoons} [R_1\text{-}\underset{H}{\overset{+}{O}}\text{-}R_2]Cl^-$

anion exchange:

$[R_1\text{-}\underset{H}{\overset{+}{O}}\text{-}R_2]Cl^- + MX_4^- \overset{K_E^{ex}}{\rightleftharpoons} [R_1\text{-}\underset{H}{\overset{+}{O}}\text{-}R_2]MX_4^- + Cl^-$

However, as ethers are much weaker bases, protonation occurs when $[H^+]$ rises over 4 M. As a result ion pair extraction by simple ethers starts at 4 M HX and reaches a maximum at 6–8 M HX. In both cases, amines or ethers, the ion-pair extraction is sustained by Coulombic attraction forces with little contribution from other sources. Ion-pair complexation by crown ethers is another example of a cation coordination governed process, by strict topochemical requirements. It is of course of considerable interest to establish whether the metal coordination by polymeric pseudocrown ether is driven by cation coordination, similar to amines, ethers, and crown ethers, or more significantly by anion coordination.

The experimental evidence in this work follows.

(a) PPCE coordinate ion pairs of the type H_yMX_4 (y = 1, 2) e.g., $HAuCl_4$ and $HFeCl_4$, as insoluble polymeric oxonium salts (see Experimental Section) forming a 1:1 type complex (with PPCE ⟨14⟩).

(b) The coordination process is independent of the total hydrogen ion concentration; only an equivalent amount of H^+ is required (see Figure 8).

(c) No other cations besides hydrogen ions take part in the coordination (even when present in 500-fold excess).

(d) The coordination is directly related to the concentration of MX_4^- or MX_4^{2-} anions in solution. For cations like Fe^{3+} and Zn^{2+}, which form weak halide complexes, this means strong dependency on halide solution concentration (see Figure 7).

(e) No evidence was found for halide anion competition with the coordination.

(f) The coordination of Zn^{2+} and Fe^{3+} halide complexes is in the order of respective stability constants, i.e., $[FeI_4^-] > [FeBr_4]^- > [FeCl_4]^-$ and $[ZnI_4]^- > [ZnBr_4]^{2-} > [ZnCl_4]^{2-}$, for reasons discussed in (d).

(g) The coordination is related to the crown ether cavity size. Dibenzo-18-crown-6, with a cavity diameter of 2.6–3.2 Å,[1,2] does not coordinate $[ZnCl_4]^{2-}$ anions (ionic diameter 9.62 Å). Polymeric pseudocrown ethers which show a good compatibility with anionic dimensions of the metal complex coordinate with them very efficiently. Others, which do not encompass the metal anion, fail to coordinate, in spite of their high concentration of oxygen ligands (12.29 mmol 0 per g polymer; see Table IV).

(h) Polymeric ethers which contain noncyclic ether structures (as a result of large distance between anchoring groups, such as polymers no. 11 and 12) show a low coordination ability.

It is interesting to compare the binding of transition-metal anions by polymeric pseudocrown ethers to other works on inclusion of simple halide anions. The works of Lehn[16] and Schmidtchen[17] on the inclusion of anions in macrotricyclic quaternary ammonium salts have shown that three-dimensional binding of halide ions with complete inclusion in a topologically optimal receptor for spherical anions is possible. The quaternary cryptates show definite preference for halide anions by a size selection. Compounds with a cavity of 1.96 Å bind[17] only chloride (ionic radius 1.18 Å) and bromide (r = 1.96 Å), but the cryptate with ionic radius of 3.8 Å binds also iodide (r = 2.28 Å).

The stability constants order for anion inclusion by the quaternary ammonium cryptates is $I^- > Br^- > Cl^-$, which is inverse to the solvation order of these anions in water and is a measure to the contribution of the hydrophobic interactions in the "molecular cavity" to the overall stability of the anion (no. 17). Small anions form inclusion complexes also with biprotonated macrobicyclic diamines[39] $^+HN(CH_2)_n]_3NH^+$ by ionic hydrogen bonds of the kind $N^+{-}H\cdots X^-$, and also with the neutral α- and β-cyclodextrins.[40]

The coordination of transition-metal halide anions by polymeric pseudocrown ethers involves the formation of an oxonium salt. The basicity of pseudocrown ⟨14⟩ in chloroform[18] is an order of magnitude larger than that of dibenzo-18-crown-6 and stochiometric coordination, 13.6 mmol HBr/g polymer, is achieved in benzene.

In water, the protonation of PPCE ⟨14⟩ starts at 1-2 M HCl.[18] The formation of oxonium-type complexes at only 10^{-4} M H^+ (Zn^{2+} salts) to 10^{-2} M H^+ (Au^{3+}, Fe^{3+} salts) suggests that the anion coordination is the driving force in the formation of polymeric pseudocrown ether transition metal complexes.

The stability of the polymeric pseudocrown-MX_4^- or MX_4^{2-} complex depends on optimal size fitting as in the case of halide complexation by the cryptates. When the cavity dimensions of the pseudocrown ether fit the anion's topological requirements, the coordination process will be accomplished, and, as in the case of biprotonated diamines, the anion is held by electrostatic attraction and polar hydrogen bonds.

VIII. Experimental Section

Polymers. Amberlite XE-305 was obtained by courtesy of Rohm & Haas. The polymer was washed with 1 N HCl, H_2O, 1 N NaOH, DMF, and methanol, then dried at 80 °C for 24 h. No nitrogen or chlorine could be detected in polymer samples after this washing procedure.

Polyethers. The lower glycols up to tetraethylene glycol were purchased from Fluka (purum grade). The higher glycols were synthesized by procedures of Bradshaw et al.[36] and Newcomb et al.[37] Alternatively they were isolated by distillation of the following commercial polyethylene glycols: PEG-200 (pentaglycol), PEG-300 (heptaglycol), PEG-400 (decaglycol), and PEG-600 (tridecaglycol). All the synthetic glycols were pure by TLC (silica 30% CH_3OH-70% EtOAc) and had the characteristic 3.6-3.8 ppm band of the $-OCH_2CH_2O$ protons. In addition the bis(dinitrophenyl) derivatives were prepared (all oils) and characterized by NMR, TLC, and nitrogen analysis.[38] The physical properties of the synthetic glycols are given.

Pentaethylene Glycol: bp 178-182 °C (1.5 Torr), R_f 0.24. Bis-DNP: Anal. Calcd for $C_{22}H_{26}O_{14}N_4$: N, 9.82. Found: N, 9.80. R_f 0.14 (EtOAc).

Heptaethylene Glycol: bp 200-208 °C (0.3 Torr), R_f 0.15. Bis-DNP: Anal. Calcd for $C_{26}H_{36}O_{16}N_4$: N, 8.51. Found: N, 8.02. R_f 0.61 (20% MeOH-EtOAc).

Decaethylene Glycol: bp 272-280 °C (0.7 Torr), R_f 0.09. Bis-DNP: Anal. Calcd for $C_{32}H_{48}O_{19}N_4$: N, 7.07. Found: N, 6.74. R_f 0.175 (20% MeOH-EtOAc).

Dodecaethylene Glycol: bp 310-325 °C (0.5 Torr), R_f 0.05. Bis-DNP: Anal. Calcd for $C_{36}H_{56}O_{24}N_4$: N, 6.37. Found: N, 6.17. R_f 0.035 (20% MeOH-EtOAc).

The glycols were dried by azeotropic distillation with toluene, which was later distilled off.

Chloromethylation. In Chlorodimethyl Ether at 50 °C, after Warshawsky.[20] Dry XE-305 (100 g) was allowed to swell for 30 min in 400 mL of chlorodimethyl ether (Fluka, CP grade) in a three-necked round-bottom flask, equipped with a condenser and moisture protected. Anhydrous stannic chloride (30 mL) (BDH AR grade) dissolved in 200 mL of chlorodimethyl ether was added dropwise until spontaneous reflux occurred. The reflux was continued for 20 h in a 50 °C constant-temperature bath. The polymer was filtered and washed with dioxane, dioxane-H_2O (1:1), dioxane, and methanol, then dried at 50 °C under vacuum to constant weight, typical crop 138.3 g of colorless product containing 21.84% Cl.

Polymeric Pseudocrown Ether Synthesis. General Procedure (Tables I and II). Chloromethylated XE-305 (100 g) was placed in a three-necked, 3-L flask, immersed in a thermally controlled oil bath. One liter of distilled dioxane, predried over anhydrous sodium sulfate, was charged, followed by 1 mol of the polyethylene glycol. Sixty grams of 50% NaH in oil (Fluka, CP grade) was washed rapidly with dry ether and added slowly to the reaction mixture. The temperature was allowed to rise spontaneously to 100 °C. In an alternative method, the disodium salt was prepared first, and only then the polymer was added. After 24-36 h, the reaction mixture was cooled to room temperature and methanol added slowly to destroy excess of sodium hydride. The polymer was filtered and washed successively with distilled water, methanol, water, and ethanol, then dried at 50 °C under vacuum to constant weight. Samples which were washed further for 24 h in a Soxhlet thimble did not release any organic matter.

The polymeric pseudocrowns do not hold free water, as estimated from azaetropic distillation with water.

The polymers contain between 0 and 0.2 mmol of chlorine and 0-0.015 mmol of sodium per g of polymer. They are characterized by a broad -C-O-C- band absorption in the 1100-cm^{-1} region (KBr pellets).

The elemental analyses for the polymeric pseudocrown ethers, besides calculated values for recurring PPCE unit, are given. No correction was made for 4% divinylbenzene.

The reaction with ethylene glycol failed several times, even though absolute ethylene glycol was used. No attempt was made to push this reaction to completion under more exhaustive conditions.

Polymer No. 1 (AD-215). Anal. Found: C, 74.47; H, 6.16; Cl, 17.06.

Polymer No. 2 (AD-217). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.10; H, 7.69; O, 14.20. Found: C, 75.16; H, 7.88; O, 15.35; Cl, 0.18.

Polymer No. 3 (AD-219). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.30; H, 7.85; O, 16.70. Found: C, 75.56; H, 8.18; O, 16.80; Cl, 0.05.

Polymer No. 4 (AD-431). Anal. Calcd for $C_{26}H_{34}O_5$: C, 73.24; H, 7.98; O, 18.70. Found: C, 70.14; H, 8.10; O, 18.12; Cl, 0.11.

Polymer No. 5 (AD-441). Anal. Calcd for $C_{30}H_{42}O_7$: C, 70.03; H, 8.17; O, 21.7. Found: C, 69.60; H, 8.27; O, 22.41; Cl, 0.13.

Polymer No. 6 (AD-433). Anal. Calcd for $C_{36}H_{54}O_{10}$: C, 66.87; H, 8.36; O, 24.77. Found: C, 68.68; H, 8.85; O, 25.36; Cl, 0.28.

Polymer No. 8 (AD-311). Anal. Calcd for $C_{44}H_{70}O_4$: C, 64.23; H, 8.51; O, 27.25. Found: C, 65.32; H, 8.27; O, 26.65; Cl, 0.43.

Polymer No. 9 (AD-439). Anal. Calcd for $C_{39}H_{60}O_8$: C, 71.34; H, 9.15; O, 19.51. Found: C, 71.72; H, 9.10; O, 18.12; Cl, 0.75.

Determination of OH Groups. PPCE samples (1.0 g) were dried over P_2O_5 at 80 °C for 24 h. The polymers were then reacted with 10 mmol of freshly crystallized 3,5-dinitrobenzoyl chloride (mp 68-69 °C) in 10 mL of ethanol-free chloroform at reflux temperature for 1 h. The polymers were filtered, washed with chloroform and acetone, and dried at 50 °C for 24 h, then weighed and analyzed. The percent benzoylation was determined from weight increase and nitrogen content. The number of hydroxyl groups M_{OH} is presented in Table II. The method was checked by determination of OH groups on a polybenzyl alcohol polymer prepared from chloromethylated XE-305 (5.29 mmol Cl/g) by acetylation, followed by alkaline hydrolysis. OH recoveries were 90% or better.

Dihexylpolyoxypropylene (7). Polypropylene glycol, mol wt 425 (212 g, 0.5 mol), was dissolved in 400 mL of dry dioxane, and 48 g of 50% sodium hydride in oil was added gradually until evolution of hydrogen ceased. Then 230 g (1 mol) of *n*-hexyl bromide was added dropwise at 100 °C within a 3-h period. After 20 h at 100 °C, the mixture was cooled, diluted with 1 L of $CHCl_3$, washed with water, 3 × 200 mL of 6 N HCl, and water again to neutrality, dried over anhydrous Na_2SO_4, and filtered and solvent was removed. After evacuation, 300 g of colorless liquid was obtained, insoluble in water. Anal. Calcd for $C_{33}H_{68}O_8$: C, 66.89; H, 11.48. Found: C, 67.40; H, 11.65; Br, 0.53.

Coordination of Anionic Transition Metal Complexes. A. Solutions. Solutions of AR grade chloride salts (10^{-3}–10^{-1} M) were prepared in varying HCl (AR grade) and sodium chloride concentrations.

B. Metal Anion Coordination with Polymeric Pseudocrown Ethers at Equilibrium General Procedure (Figures 7–11). Polymeric ethers (5 g) were equilibrated with 10–50 mL of 0.05 M metal solutions in 100-mL volume stoppered Erlenmeyers, by shaking on a Griffin-type shaker in a thermostated room (25 ± 1 °C) for 24 h. Aliquots of the equilibrated solution were titrated with EDTA or analyzed by atomic absorption spectrophotometry. The metal uptake was calculated by difference.

C. Metal Uptake at Maximum Polymer Capacity. This occurred essentially under the same conditions as described in B, 0.05 M metal salt, 5 M NaCl, pH 1.4. The polymers were reimmersed in original metal solutions and equilibrated further, until the solution concentration did not change. The metal uptake for polymeric pseudocrown-14 is 1.42 mmol of $FeCl_4^-$, 1.24 mmol of $AuCl_4^-$, and 0.90 mmol of $ZnCl_4^{2-}$ per g of polymer.

Determination of the Metal Complex Composition. Polymeric pseudocrown-14 was placed in a Soxhlet thimble and washed with water continuously until the pH of the water was 7. This polymer was now used for all stoichiometry determination experiments and in all the pH-dependency experiments.

A. Stoichiometry of $FeCl_4^-$ Coordination. Ferric chloride (40 mL, 0.019 M Fe(III)) in 5 M NaCl adjusted to pH 1.55 with radiometer/type pH meter was equilibrated with 5 g of polymeric pseudocrown-14 for 24 h. The polymer was filtered and centrifuged on a sintered test tube at 5000 rpm for 10 min. The combined filtrate contains 0.0873 g/L of iron and the pH is 2.0. Calculation shows the uptake of 0.70 mmol of Fe(III) and 0.72 mmol of H^+, corresponding to a stoichiometry of $HFeCl_4$ extraction.

B. Stoichiometry of $AuCl_4^-$ Coordination. Gold tetrachloroaurate sodium salt (20 mL, 0.015 M, pH 1.5) in H_2O was equilibrated with 2 g of polymeric pseudocrown-14 for 24 h. The polymer was filtered and centrifuged as previously described. The combined filtrate contains 0.072 g/L of gold and has a pH of 1.75. Calculation shows the uptake of 0.30 mmol of $AuCl_4^-$ and 0.31 mmol of H^+ corresponding to a stoichiometry of $HAuCl_4$ extraction.

Comparison between Polymeric Pseudocrown-8-heptamethyl (Polymer No. 8, Table II) and Dihexylpolyoxypropylene (7) (See Figure 11). The metal uptake was determined in 0.016 M $FeCl_3$ solutions of varying NaCl concentrations (1–5 M) at pH 1.5. The maximum capacity for polymer no. 8 was determined as described previously. The phase transfer of $FeCl_4^-$ was determined as follows. Aqueous solution (10 mL) was mixed in a Vortex apparatus for 60 min with 10 mL of 50% (w/v) dihexylpolyoxypropylene (no. 7) in toluene. After phase separation, the residual metal concentration in the aqueous phase was determined, and metal uptake calculated by difference.

Attempted Anion Complexation by Dibenzo-18-crown-6. A 0.2 M dibenzo-18-crown-6 (130 mL) solution in chloroform was equilibrated vigorously in a Vortex with 150 mL of 0.05 M zinc chloride in 5 M sodium chloride at pH 2.0 for 1 h. After phase separation the aqueous phase was analyzed for its metal content. No change in metal concentration was observed. Same result were obtained upon equilibration with 0.05 M zinc chloride in 5 M HCl for 1 h.

Acknowledgments. We wish to thank Mr. A. Beck for synthetic assistance and Mrs. Bracha Goldner and Mr. R. Heller of the Biophysics Department for the elemental analysis. Special thanks are due to Dr. Sofia Belfer of the Research and Development Authority, Ben Gurion University, for taking the SEM photographs. The oxygen analysis was done by Engineer G. Hesselius at the Microanalytical Laboratory, Agricultural University, Uppsala, Sweden.

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