are quite different, so it seems that studies of M-type proton resonance may be of value for tacticity measurement. Because of coupling effects, rather complex patterns are obtained for the resonance of M-type protons, and it should be a formidable task to unravel the pattern observed for the atactic polymer (Figure 3a). However, studies on polymers of 1,2-poly(1,1,4,4-tetradeuteriobutadiene),[2] with methine protons decoupled should make the task relatively simple.

300-MHz Spectra. After this paper was submitted for publication, we had occasion to record the 300-MHz nmr spectrum of isotactic 1,2-polybutadiene. The spectrum is provided in Figure 4, along with computed spectra. The chemical shifts required to fit calculated spectra (see Figure 4 caption) to experimental spectra are slightly different from those given in Table I. The differences may be due to the fact that the 100- and 300-MHz spectra were recorded at different temperatures.

The 300-MHz spectrum contains unexpected resonances at 1.28 and 1.31 ppm in the methylene region and at 4.86 and 4.91 ppm in the vinyl region. These are attributed to structural imperfections. The resonances at 1.28 and 1.31 are believed to be due to methylene protons in 1,4 units. It is interesting that the methylene resonance observed from 1.15 to 1.27 ppm is more intense than that observed from 1.35 to 1.50 ppm. This indicates that an appreciable concentration (~12%) of racemic placements is present in the polymer. The presence of racemic dyads in the polymer may account for the resonances observed at 4.86 and 4.91 ppm.

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Poly(vinyl macrocyclic polyethers). Synthesis and Cation Binding Properties

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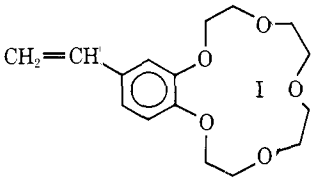
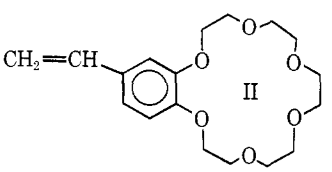
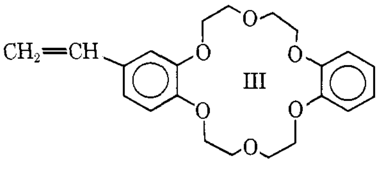
ABSTRACT: The synthesis of the 4′-vinyl derivatives of monobenzo-15-crown-5, of monobenzo-18-crown-6, and of dibenzo-18-crown-6 are described in detail. The monomers can be polymerized to high molecular weight polymers by radical or anionic initiators. The latter method produces living polymers if carried out at low temperatures. The polymers strongly chelate with cations, and their efficiency and selectivities in binding cations are compared with those of their monomeric analogs by using data obtained from salt distribution equilibria in water-methylene chloride and from conductance measurements. For all cations the polymers are found to extract the salt from the aqueous phase more efficiently than the monomers, but this is partially caused by differences in partition coefficients between the respective crown species. However, cation complexation constants for polymers are considerably enhanced in cation-crown systems which form stable 2:1 crown to cation complexes. This is usually the case when the cation diameter exceeds that of the crown ether cavity. The stoichiometries of the various crown complexes were determined from conductance measurements and from distribution equilibria in the presence of excess salt. These measurements also provide information on the maximum number of ions that can be bound per polymer molecule. Viscosity measurements indicate that the neutral poly(crown ethers) in the presence of salts undergo conformational changes resembling those of polyelectrolytes, the reduced viscosity being enhanced as the polymer-salt mixture is diluted.

In a recent communication[1] we reported on the cation binding properties of two neutral macromolecules, *viz.*, the polymers of 4′-vinylmonobenzo-15-crown-5 (I) and of 4′-vinylmonobenzo-18-crown-6 (II). The two polymers were found to be considerably more effective in binding cations than the corresponding monomeric macrocyclic polyethers or crown ethers, a class of compounds recently synthesized and studied by Pedersen[2] and subsequently by many other researchers.[3-12] The ion selectivities of the







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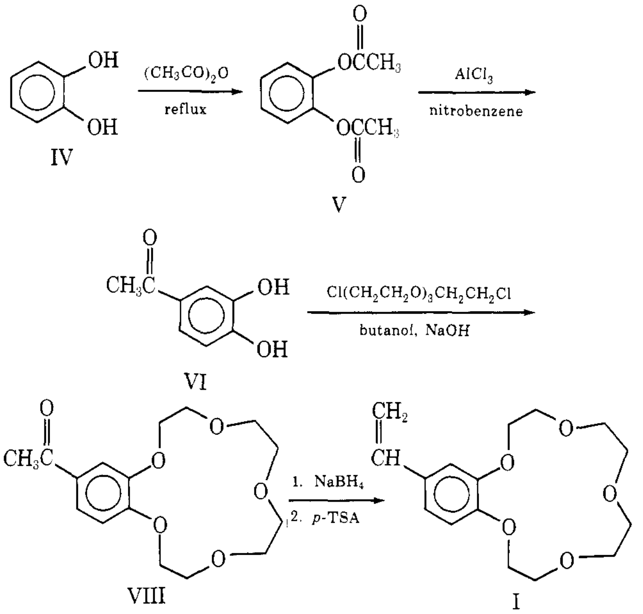
two polymers were also different from that of their monomeric analogs.

In this paper the preparation of the two vinyl monomers is being described in more detail, as well as the polymerization procedures and the properties of the resulting polymers. In addition to the two monomers mentioned above, we also succeeded in synthesizing the 4′-vinyl derivative of dibenzo-18-crown-6 (III). The dibenzo-18-crown-6 ether is known to be one of the most effective crown compounds for binding Na^+ or K^+ ions.[2,3] The vinyl compound like the other two monomers, can be polymerized to a high molecular weight polymer by either a radical or anionic initiator.

The starting material for all three monomers is catechol (IV). This is converted to catechol diacetate (V), followed by a Fries rearrangement which produces 3,4-dihydroxyacetophenone (VI). To obtain the vinyl monomer I, the acetophenone VI is reacted with 1,11-dichloro-3,6,9-trioxaundecane (VII) to form 4′-acetobenzo-15-crown-5 (VIII). For the preparation of monomer II the preceeding reaction is carried out with 1,14-dichloro-3,6,9,12-tetraoxatetradecane (IX), yielding 4′-acetobenzo-18-crown-6 (X)

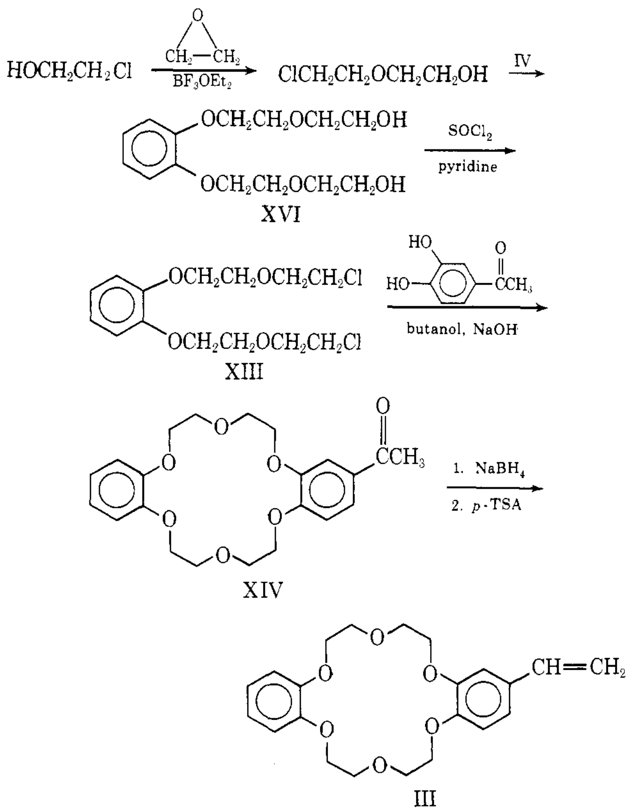
The two crown acetophenones are then reduced with $NaBH_4$ and the resulting alcohols (XI and XII) dehydrated with a trace of *p*-toluenesulfonic acid to form the vinyl crown ethers. The reaction scheme for the 15-crown-5 monomer is depicted in Scheme I.

Scheme I



The dibenzo-18-crown-6 vinyl monomer (III) is prepared by reacting VI with 1,2-bis[2′-(2″-chloroethoxy)ethoxy-]benzene (XIII), which yields 4′-acetodibenzo-18-crown-6 (XIV). This is then reduced and dehydrated to III. To obtain XIII, ethylene chlorohydrin is converted to 2-(2-chloroethoxy)ethanol (XV) with BF_3OEt_2 and ethylene oxide. Compound XV is then converted to 1,2-bis[2-(2″-hydroxyethoxy)ethoxy]benzene (XVI) with catechol. This is followed by reacting XVI with $SOCl_2$, yielding XIII. The preparation of III is shown in Scheme II.

Scheme II



The two vinylmonobenzocrown ethers I and II can be obtained in high purity by treating a benzene solution of the monomers with neutral aluminum oxide. The dibenzocrown ether monomer (III) was purified by sublimation. No special attempts were made to maximize the yields of any of the intermediate products. Polymerization of the monomers by a radical initiator in benzene or toluene, or anionically by a living polymer technique in H_4furan at low temperature proceeds smoothly to high molecular weight polymers (the polymers derived from I, II, and III have been named P15C5, P18C6, and PVDB-18C6, respectively).

Experimental Section

Preparation of Vinyl Monomers. *Catechol Diacetate (V).* A modification of the procedure of Heller *et al.*[13] was used to prepare this compound. A solution of 110 g (1.0 mol) of catechol (obtained from Aldrich) and 189 ml (1.0 mol) of acetic anhydride was refluxed for 4 hr, then cooled to room temperature and poured into 3 l. of stirred ice water. The diacetate was obtained as long white needles (mp 63–64°) after filtration, drying, and recrystallization from *n*-heptane (yield 77%).

3,4-Dihydroxyacetophenone (VI). The acetophenone was synthesized by slightly modifying a procedure outlined by Rosemund and Lohfert.[14] Anhydrous aluminum chloride (84 g) was added to a well-stirred mixture of 60 g (0.309 mol) of catechol diacetate and 250 ml of nitrobenzene (purged with nitrogen). After 4 hr at 75° the reaction mixture was cooled to 40° and poured into a stirred mixture of 750 g of ice and 150 ml of concentrated HCl. Following steam distillation the remaining aqueous solution was extracted for 36 hr with ether in a liquid–liquid extractor. After drying the ether phase with $MgSO_4$, the ether was removed and the residual oily residue was extracted with hot benzene to yield

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the crude product. Recrystallization from benzene afforded pure 3,4-dihydroxyacetophenone (mp 121-123°) in 63% yield.

2,3-(4'-Acetobenzo)-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4'-acetobenzo-15-crown-5 (VIII). This compound was prepared by using method V outlined in Pedersen's paper dealing with the synthesis of crown ethers.[2a] A solution of 34.2 g (0.225 mol) of VI in 477 ml of 1-butanol was purged with nitrogen and charged with 19.2 g of NaOH in 40 ml of water. After several minutes a yellow precipitate formed and 52.2 g (0.191 mol) of 1,11-dichloro-3,6,9-trioxaundecane (VII, bp 95° at 0.4 mm) was added over a 15-min period, after which the mixture was refluxed for 30 hr (the preparation of VII from triethyleneglycol and $SOCl_2$ is described in ref 2a). The mixture, after cooling to room temperature, was then acidified with HCl and filtered, the solids were washed with CH_3OH and the combined filtrate was evaporated to dryness. The oily residue was dissolved in acetone and filtered, the acetone was removed, after which the residue was extracted with *n*-heptane to yield the crude product. Recrystallization from *n*-heptane afforded 31 g (45%) of pure 4'-acetobenzo-15-crown-5 as white flaky crystals: mp 96-97°; nmr ($CDCl_3$) τ 7.45 (s, 3, $-CH_3$), 6.0 (m, 16, CH_2-), 3.10 and 2.48 (d, m, 3, aromatic -CH-). *Anal.* Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 62.07; H, 7.26.

2,3-[4'-(1''-Hydroxyethyl)benzo]-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4'-(1''-Hydroxyethyl)benzo-15-crown-5 (XI). To a well-stirred solution of 20.5 g (0.066 mol) of 4'-acetobenzo-15-crown-5 (VIII) in 400 ml of ethanol was added 3.5 g of $NaBH_4$. The reaction mixture became homogeneous after several minutes. After stirring for 24 hr at room temperature the solution was poured into 400 ml of water, neutralized with dilute acetic acid, and extracted with $CHCl_3$. After washing with water and drying with Na_2SO_4, the chloroform was evaporated and the oily residue was allowed to crystallize. The solid was then suspended in ether and filtered, affording 16.2 g (78.5%) of XI: mp 65-66°; nmr ($CDCl_3$) τ 8.56 (d, 3, J = 6.3 Hz, $-CH_3$), 7.26 (s, 1, -OH), 6.0 (m, 16, $-CH_2-$), 5.2 (q, 1, -CH-), 3.1 (m, 3, aromatic -CH-). *Anal.* Calcd for $C_{16}H_{24}O_6$: C, 61.52; H, 7.78. Found: C, 61.70; H, 7.68.

2,3-(4'-Vinylbenzo)-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4'-Vinylbenzo-15-crown-5 (I). To 6 g (0.0192 mol) of 4'-(1''-hydroxyethyl)benzo-15-crown-5 (XI) in 200 ml of benzene was added a trace of *p*-toluenesulfonic acid. The mixture was refluxed with removal of water for 22 hr and then cooled to room temperature and the benzene was removed by evaporation. The oily residue was then placed on a column of 250 g of neutral aluminum oxide (activity V), prepared in benzene, and then eluted with benzene. Selected fractions were freeze-dried and the melting points were determined. Fractions having melting points between 41 and 44° were combined and freeze-dried. The combined product was further purified by recrystallization from petroleum ether (bp 30-60°), 1 g/50 ml of petroleum ether. This yielded 3.4 g (60%) of pure 4'-vinylbenzo-15-crown-5: mp 43-44°; nmr ($CDCl_3$) τ 6.0 (m, 16, $-CH_2-$), 4.6 (m, 2, vinyl $=CH_2$), 3.4 (m, 1, vinyl $-CH=$), 3.05 (m, 3, aromatic -CH-). *Anal.* Calcd for $C_{16}H_{22}O_5$: C, 65.32, H, 7.53. Found: C, 65.34; H, 7.47.

2,3-(4'-Acetobenzo)-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene or 4'-Acetobenzo-18-crown-6 (X). This compound was prepared from VI and 1,14-dichloro-3,6,9,12-tetraoxatetradecane by a procedure similar to that described for VIII. The pure product was obtained in 32% yield: mp 77.5-78.5'; nmr ($CDCl_3$) τ 7.45 (s, 3, $-CH_3$), 6.0 (m, 20, $-CH_2-$), 3.1 and 2.42 (d, m, 3, aromatic -CH-). *Anal.* Calcd for $C_{18}H_{25}O_7$: C, 61.00, H, 7.40. Found: C, 61.05; H, 7.17.

The compound 1,14-dichloro-3,6,9,12-tetraoxatetradecane (bp 129-134° (0.4 mm) used in the above reaction was obtained in 66% yield from $SOCl_2$ and pentaethylene glycol.[2a] The latter compound was synthesized in 47% yield from 1,2-bis[(2-chloroethoxy)ethane] (Aldrich), ethylene glycol and an aqueous KOH solution.[2a]

2,3-[4'-(1''-Hydroxyethyl)benzo]-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene or 4'-(1''-Hydroxyethyl)benzo-18-crown-6 (XII). The synthesis of this compound was similar to that of XI, using X as starting material. It was obtained in 70% yield: mp 58-59°; nmr ($CDCl_3$) τ 8.56 (d, 3, J = 6.5 Hz, $-CH_3$), 7.3 (s, 1, -OH), 6.0 (m, 20, $-CH_2-$), 4.8 (q, 1, -CH-), 3.1 (m, 3, aromatic -CH-). *Anal.* Calcd for $C_{18}H_{28}O_7$: C, 60.64; H, 7.92. Found: C, 60.45; H, 7.48.

2,3-(4'-Vinylbenzo)-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene or 4'-vinylbenzo-18-crown-6 (II). Prepared by dehydration of XII, similar to that described for I. The product was eluted from neutral aluminum oxide, activity V, with benzene, followed by a mixture of benzene-methylene chloride. The freeze dried product of mp 59-61° was further purified by recrystallization from hexane in 71% yield: mp 61-62°; nmr ($CDCl_3$) τ 6.0 (m, 20, $-CH_2-$), 4.6 (m, 2, $=CH_2$), 3.4 (m, 1, $-CH=$), 3.05 (m, 3, aromatic -CH-). *Anal.* Calcd for $C_{18}H_{26}O_6$: C, 63.88; H, 7.75. Found: C, 64.12; H, 7.71.

2-(2-Chloroethoxy)ethanol (XV). This compound was prepared in 35% yield from ethylene chlorohydrin and ethylene oxide in the presence of BF_3OEt_2.[15]

1,2-Bis[2'-(2''-hydroxyethoxy)ethoxy]benzene (XVI). To a solution of 62 g of catechol in 1500 ml of 1-butanol, purged with nitrogen, was added 40 g of NaOH (dissolved under reflux), followed by dropwise addition of 115 g (1.0 mol) of XV. After 16 hr of reflux the mixture was cooled and acidified, the solvent was removed, and the crude product was vacuum distilled, yielding 97 g (70%) of the desired product, bp 187-194° (0.3 mm); nmr ($CDCl_3$) τ 6.15 (s, 1, -OH), 6.2 (m, 16, $-CH_2-$), 3.15 (s, 4, aromatic -CH-). *Anal.* Calcd for $C_{14}H_{22}O_6$: C, 58.72; H, 7.75. Found: C, 58.42; H, 7.95.

1,2-Bis[2'-(2''-chloroethoxy)ethoxyl]benzene (XIII). To 63.5 g (0.222 mol) of XVI, dissolved in 300 ml of benzene and 23 ml of pyridine, was added dropwise 32 mol (0.23 mol) of $SOCl_2$ at reflux temperature. After 16 hr the solution was cooled to room temperature and 40 ml of HCl in 100 ml of water was added. The benzene layer was twice washed with water, 10% $NaHCO_3$, and again with water, the benzene was removed, and the residue was vacuum distilled, affording 61 g (85%) of the dichloride; bp 165-170° (0.2 mm); nmr ($CDCl_3$) τ 6.1 (m, 16, $-CH_2-$), 3.1 (s, 4, aromatic -CH-). *Anal.* Calcd for $C_{14}H_{20}Cl_2O_4$: C, 52.02; H, 6.24. Found: C, 52.29; H, 6.31.

2,3,11,12-[(4'-Aceto)dibenzo]-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene or 4'-Acetodibenzo-18-crown-6 (XIV). A solution of 15.6 g of (0.1 mol) of 3,4-dihydroxyacetophenone (VI) and 200 ml of 1-butanol was purged with nitrogen, and 8 g of NaOH was added and dissolved at reflux. This was followed by addition of 32.3 g (0.1 mol) of XIII. After 16 hr the mixture was cooled and acidified and the butanol was evaporated. Water was added and the aqueous mixture was extracted with $CHCl_3$. After drying and removal of the $CHCl_3$ the product was isolated by crystallization from benzene-petroleum ether, yielding 22.5 g (55%); mp 169-171°; nmr ($CDCl_3$) τ 7.45 (s, 3, $-CH_3$), 5.9 (m, 16, $-CH_2-$), 2.9 (m, 7, aromatic -CH-). *Anal.* Calcd for $C_{22}H_{26}O_7$: C, 65.66; H, 6.51. Found: C, 65.49; H, 6.28.

2,3,11,12-[4'-(1''-Hydroxyethyl)dibenzo]-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene or 4'-(1''-Hydroxyethyl)dibenzo-18-crown-6 (XVII). To 20.1 g (0.05 mol) of XIV and 500 ml of ethanol was added 2 g of $NaBH_4$, the mixture was stirred for 24 hr, and the excess $NaBH_4$ was destroyed with dilute HOAc. The aqueous solution was extracted with $CHCl_3$, and the extract was washed with water and dried. Upon removal of the $CHCl_3$ an oil was obtained. The desired product was obtained from benzene-petroleum ether, yield 17.6 g (93%); mp 141-143°, nmr ($CDCl_3$) 8.58 (d, 3, $-CH_3$), 7.8 (s, 1, -OH), 6.0 (m, 16, $-CH_2-$), 5.2 (q, 1, -CH-), 3.1 (m, 7, aromatic -CH-). *Anal.* Calcd for $C_{22}H_{28}O_7$: C, 65.33; H, 6.98. Found: C, 65.74; H, 7.01.

2,3,11,12-(4'-Vinyl)dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene or 4'-Vinyldibenzo-18-crown-6 (III). A trace of *p*-toluenesulfonic acid was added to a solution of 6 g of XVII in 300 ml of benzene. After refluxing with removal of water for 24 hr the mixture was cooled and the benzene was removed. The crude product was recrystallized from CH_2Cl_2–petroleum ether to afford 5.0 g of III, mp 142-148°. Analytically pure product was obtained by sublimation at 140° yielding 3.8 g (66.5%), mp 148-149°, nmr ($CDCl_3$) 5.95 (m, 16, $-CH_2-$), 4.6 (m, 2, $=CH_2$), 3.4 (m, 1, -CH), 3.0 (m, 7, aromatic -CH-). *Anal.* Calcd for $C_{22}H_{26}O_6$: C, 68.37; H, 6.78. Found: C, 68.50; H, 6.81.

The 4'-vinyl(4''- or 5''-methyl)dibenzo-18-crown-6 (XVIII) was also prepared, using 4-methylcathecol as the starting material. The overall synthesis is similar to that of III, the boiling or melting points of the *methyl* derivatives of the intermediates being: bp 182-187° (0.03 mm) for XVI, bp 160-167° (0.05 mm) for XIII, mp 151-153° for XIV, and mp 135-139° for XVII. Compound XVIII was purified by sublimation, mp 144-147°, nmr ($CDCl_3$) τ 7.75 (s, 3, $-CH_3$), 5.9 (m, 16, $-CH_2$), 4.6 (m, 2, $=CH_2$), 3.45 (m, 1, $=CH$), 3.15 (m, 6, aromatic -CH-). *Anal.* Calcd for $C_{23}H_{28}O_6$: C, 68.18; H. 7.05. Found: C, 68.20; H, 7.00.

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Table I
Molecular Weights and Softening Points of Poly(vinyl crown ethers)

Polymer	Initiator	Solvent	$\bar{M}_n$	Sp (°C)
P15C5	ABIN	Toluene	27,000	113–117
P15C5	ABIN	Benzene	116,000	122–128
P15C5	Tetramer	H_4furan	30,000	113–118
P15C5	Tetramer	H_4furan	110,000	123–128
P18C6	ABIN	Toluene	33,000	75–83
P18C6	ABIN	Benzene	106,000	91–97
P18C6	Tetramer	H_4furan	31,000	75–81
P18C6	Tetramer	H_4furan	119,000	93–97
PVDB-18C6	ABIN	Benzene	18,000	92–98
PVDB-18C6	Tetramer	H_4furan	25,000	110–117

Table II
Solubilities (S, in g/100 cm^3) and Intrinsic Viscosities of Poly(vinyl crown ethers) at 25°

	P15C5[a]		P18C6[b]		PVDB-18C6[c]
Solvent	S	$[\eta]_0$	S	$[\eta]_0$	S
Acetone	2.6		0.3		Poor
Methanol	0.34		0.73		Poor
Water	0.095		8.1	0.107	Poor
Hexane	0.09		0.06		Poor
Benzene	High		High		Fair
Toluene	High		High		Fair
Chloroform	High	0.41	High	0.37	Good
Methylene chloride	High		High		Good
Tetrahydrofuran	High	0.27	High	0.24	Fair
Nitrobenzene	High		High		

[a] M_n = 116,000. [b] M_n = 106,000. [c] M_n = 18,000.

Polymerization with Radical Initiator. A benzene or toluene solution containing the desired amounts of monomer and initiator (azobis(isobutyronitrile) is thoroughly degassed on a vacuum line, and the ampoule is sealed off and heated for 24 hr at 70°. The polymer solution is then slowly added to 20 times its volume of petroleum ether (for P15C5) or hexane (for P18C6 and PVDB-18C6) and the white precipitate is filtered off. The polymer is reprecipitated once again and finally dried under vacuum. Two different ABIN:monomer ratios (~0.007 and ~0.002 by weight) were used to produce polymers with number-average molecular weights of about 30,000 and 100,000, respectively. A few copolymers with styrene containing different ratios of vinylcrown ether to styrene were also prepared.

Anionic Polymerization. To a vigorously stirred solution of the sodium tetramer of α-methylstyrene[16] in H_4furan is dropwise added a solution of the crown ether monomer in H_4furan. Both solutions must be kept at −80°, and all manipulations are carried out under vacuum. Addition of the first quantity of monomer instantaneously turns the red initiator solution to a light orange color. This color remains stable as long as the temperature is kept below about −50°. Above this temperature the color fades due to termination of the carbanion.

The living polymer solution is terminated with a drop of methanol after about 0.5 hr and the H_4furan was removed. The polymer is then dissolved in benzene and purified as described above. Polymers of different molecular weights (~30,000 and ~100,000) were prepared by adjusting the catalyst to monomer ratio.

Polymer Properties. The melting points and number-average molecular weights of the respective polymers are collected in Table I. The M_n values were obtained in toluene by high-speed membrane osmometry. Solubilities were determined only for the high molecular weight polymers of I and II. The pertinent data are given in Table II, including the intrinsic viscosities of the polymers in some of the solvents. The viscosities were measured with an Ubbelohde viscometer. In a number of experiments, the viscosities of the crown ether polymer solutions were measured in the presence of salts such as KBr and CsCl.

Measurements of Ion Binding. The binding efficiencies of the polymers and their monomeric analogs were evaluated from distribution equilibria of the respective salt complexes between an aqueous phase and an immiscible organic solvent (methylene chloride). The method, developed by Pedersen[2c] and subsequently used by other investigators,[3b,7] involves the transfer of a picrate salt from an aqueous metal hydroxide or salt solution to the organic phase containing the crown ether. In our procedure, a 0.1 or 0.01 M metal hydroxide solution containing a small amount of picric acid (7×10^{-5} M) was vigorously shaken in a separatory funnel with an equal volume of a methylene chloride solution of the crown ether. The organic layer was removed, then filtered to remove any cloudiness, and the picrate concentration was measured by optical spectroscopy, using the extinction coefficients reported by Pederson (λ_m 357 nm, ϵ 1.5×10^4 in water and λ_m 378 nm, ϵ 1.8×10^4 in CH_2Cl_2). For each cation–crown system the measurements were carried out at five different crown concentrations, using picrate:crown ratios of 1:1, 1:3, 1:5, 1:7, and 1:10. We confirmed the observation of Pedersen that no picrate salt is transferred to the organic phase in the absence of crown ether. Also, no metal hydroxide could be detected in the organic phase even in the presence of crown ether. The concentration of crown species in the aqueous phase is very low compared to that in CH_2Cl_2, judging from the values of the partition coefficients (see Discussion) which were determined by a procedure recently reported by Frensdorff.[3b]

Results and Discussion

Polymerization and Polymer Properties. All monomers could be polymerized quantitatively to high molecular weight polymers using either the radical or anionic initiator, with the exception of the 4-methyl derivative of vinyldibenzo-18-crown-6 which did not polymerize radically. A low ceiling temperature due to the presence of the methyl group may cause the failure of this monomer to polymerize at elevated temperatures.

The X-ray patterns of the powdered polymers did not reveal any crystallinity. The softening points of the polymers (Table I) are essentially independent of the polymerization mechanism. Also, as we will see later, there is little difference between the binding efficiencies of the anionic and radical polymers. These observations all indicate that the anionic polymerization apparently does not introduce any unusual regularity in the polymer chain, as has been observed for other monomers such as methyl methacrylate polymerized in H_4furan at −80°.[17]

The solubility behavior of the polymers (see Table II) is about what one would expect. Of interest is the rather high solubility of P18C6 in water. The low intrinsic viscosity of this polymer in water implies that the chains are considerably coiled, with the hydrophilic crown ether rings probably located mostly on the periphery of the coil which facilitates hydrogen bonding to the water molecules. The solubility increases at lower temperature, and the polymer, when dissolved in water at 0°, will partially precipitate as the solution is allowed to stand at room temperature.

The mechanism of the anionic polymerization of the vinyl crown ethers should be of interest to study. The polymerization at −80° in H_4furan is rapidly initiated by the sodium tetramer of α-methylstyrene, as indicated by the immediate color change from red to light orange. The 350-nm absorption maximum of the initiator solution is replaced by a sharper absorption band (less tailing in the visible region) at 345 nm, the maximum being almost identical with that of a poly(styryl)sodium solution in H_4-

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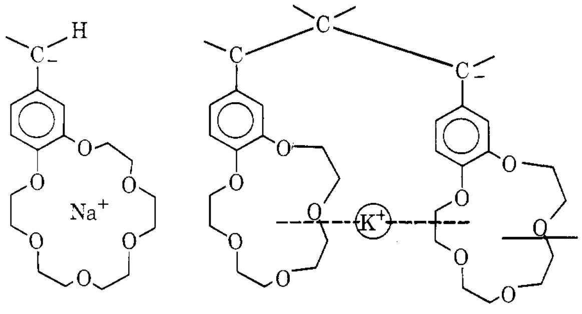
(16) C. Geacintov, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **84**, 2508 (1962).

(17) W. Fowells, C. Schuerch, F. A. Bovey, and F. P. Hood, *J. Amer. Chem. Soc.*, **89**, 1396 (1967).

furan at −80°.[18] As mentioned, the living polymer derived from the vinyl crown ether is unstable in H_4furan above −50°, the lithium salt being less stable than the sodium carbanion salt. The most probable termination reaction is an attack of the carbanion on the PhO-C bond, producing a stable phenoxy ion.

The propagation reaction (as well as the initiation) at −80° in H_4furan appears to be rapid, and is complete in less than 1 min at a catalyst concentration of about 10^{-3} *M*. This is also the case with poly(styryl)sodium, which in H_4furan at −80° contains a large fraction of reactive free ions and loose ion pairs.[18] In the case of the vinyl crown ether the polymerizing carbanion most likely is present as an intramolecular separated ion pair. The cation may be complexed with either one crown moiety (*e.g.*, in the system Na^+ with 18C6 where the 18C6 unit may be the terminal or penultimate unit), or two crown units (*e.g.*, K^+ with 15C5, see ref 1 and 10b). In the latter case this may involve the terminal and penultimate crown moieties.



The possibility of forming stable intramolecular separated ion pairs may considerably reduce the fraction of free ions (similar as in poly(2-vinylpyridine)sodium, see ref 19). Conductance measurements should give more information on the detailed behavior of these ion pair species.

The cation may also play a role in the propagation step by coordinating with the incoming monomer, especially when the cations show a tendency to complex with two crown molecules (*i.e.*, K^+-15C5, or Cs^+-15C5 or -18C6). This could conceivably affect the structure of the resulting polymer. In this respect it may be of interest to study the radical polymerization of the vinyl crown ethers in the presence of excess salt, as one would expect the monomers to be complexed to the cation which in turn may affect the polymerization.

The polymerization in toluene is considerably slower. At −65° the propagation of the sodium living polymer could be followed spectrophotometrically by monitoring the disappearance of vinyl-15-crown-5 at its λ_m of 295 nm. The propagation is first order in monomer, the k_p being 1 M^{-1} sec^{-1} (carbanion concentration 6×10^{-4} *M*, initial monomer concentration 1.2×10^{-2} *M*). No attempt was made to check the dependence of k_p on carbanion concentration. Aggregation of crown separated ion pairs has been observed for fluorenyl salts in ethereal solvents[20] and dimeric living polymer species in toluene at −65° can certainly not be excluded.

Table III
Extraction of Picrate Salts by Poly(vinylbenzo-15-crown-5) and Poly(vinylbenzo-18-crown-6) as Compared to Their Monomeric Analogs. Solvent System: H_2O-CH_2Cl_2 (50:50, v/v)[a]

	% Picrate Salt Extracted[b]			
Cation	15C5	P15C5	18C6	P18C6
Li^+	<1	5.3	<1	3.1
Na^+	2.3	13.1	4.2	11.2
K^+	8.1	68.8	55.5	72.2
Rb^+	4.7	67.8	30.7	68.0
Cs^+	1.6	38.2	20.0	82.2
NH_4^+	<1	6.0	3.8	19.3
Ba^{2+}	<1	14.7	2.1	17.5

[a] [Picric acid] = 7×10^{-5} *M*; [crown units] = 35×10^{-5} *M*; [Metal hydroxide] = 0.01 *M*. [b] Based on total amount of picric salt.

Extraction Equilibria. The evaluation of cation binding efficiencies of crown ethers from partition equilibria was first pursued by Pedersen.[2] The relevant equilibria governing the transfer of the salt from the aqueous to the organic phase have been carefully analyzed by Eisenman[7] and by Frensdorff.[3b] Assuming a 1:1 stoichiometry for the crown complex, the overall extraction equilibrium may be written as

$$M^+ + A^- + Cr^* \overset{K_e}{\rightleftharpoons} M^+,Cr,A^{-*} \qquad (1)$$

where the asterisk denotes species present in the organic phase. Three fundamental equilibria must be considered in the extraction procedure.[3b]

$$M^+ + Cr \overset{K_s}{\rightleftharpoons} M^+,Cr \qquad (2)$$

$$Cr^* \overset{P_e}{\rightleftharpoons} Cr \qquad (3)$$

$$M^+,Cr + A^- \overset{P_c}{\rightleftharpoons} M^+,Cr,A^{-*} \qquad (4)$$

The overall extraction constant K_e is given by $K_e = K_sP_eP_c$, which shows that differences in K_e values may arise from variations in the complex formation constants K_s and/or in the partition coefficients P_e and P_c. The results of a series of extractions carried out at a crown to picric acid ratio of 5:1 with 0.01 *M* base are given in Table III and are expressed as the per cent of total picrate salt transferred to the organic phase. The data demonstrate that the polymers extract the salts more effectively than do the corresponding monobenzo crown ethers, especially in systems where it may be anticipated that two crown moieties are complexed to a cation, *e.g.*, in cases where the cation diameter exceeds that of the crown cavity.

Assuming that $Cr^* \gg Cr + M^+,Cr$ and that the ion pair complex M^+,Cr,A^{-*} is not dissociated in CH_2Cl_2, one obtains the following expression for K_e

$$K_e = \frac{\alpha}{a^+(1-\alpha)([Cr_0]/[A_0] - \alpha)[A_0]} \qquad (5)$$

where a^+ represents the cation activity in the aqueous phase, $[Cr_0]$ and $[A_0]$ are the total concentrations of crown ether and picric acid, respectively, and α denotes the fraction of picric acid transferred as salt to the organic layer. The first assumption is certainly valid for the H_2O-CH_2Cl_2 system (see P_e values reported later in the Discussion). The second assumption is questionable as the picrate concentration in the organic phase under our experimental conditions is always less than 10^{-4} *M*. Taking the dissociation step $M^+,Cr,A^{-*} \rightleftharpoons M^+,Cr^* + A^{-*}$ (K_d) into account, Frensdorff derived a more complicated expression

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(18) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem Soc.*, 89, 796 (1967).
(19) M. Fisher and M. Szwarc, *Macromolecules*, 3, 23 (1970).
(20) U. Takaki, T. E. Hogen Esch, and J. Smid, *J. Phys. Chem.*, 76, 2152 (1972).

Table IV
Apparent K_e Values[a] (K_e') of Poly(vinylbenzo-15-crown-5)[b] and Poly(vinylbenzo-18-crown-6)[b] and Their Monomeric Analogs. Solvents: H_2O-CH_2Cl_2; Base Concentration, 0.01 M

	$K_e' \times 10^{-3}\ M^{-2}$					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
15C5		8.6	35[c]	16[c]	7.6[c]	
P15C5	19	59	1730	1630	260	73
18C6		15	530	170	97	7.2
P18C6	12	50	1160	1000	2150	87

[a] Calculated by assuming that the crown complexed ion pair is not dissociated in CH_2Cl_2. The standard deviation of these values is between 10 and 40%. [b] Data refer to polymers of M_n = 110,000 prepared by radical polymerization. [c] The K^+, Rb^+, and Cs^+-15C5 systems most likely form 2:1 crown cation complexes. The numbers given here are based on a 1:1 stoichiometry.

Table V
Comparison of K_e Values for the System 15C5-K^+, Calculated for a 1:1 and 2:1 Complex with K_d = 0 or 4.0 × 10^{-5} M, Respectively

	1:1 Complex		2:1 Complex	
$[Cr_0]/[A_0]$	$K_d = 0$	$K_d = 4 \times 10^{-5}\ M$	$K_d = 0$	$K_d = 4 \times 10^{-5}\ M$
	$K_e \times 10^{-3}\ M^{-2}$		$K_e \times 10^{-6}\ M^{-3}$	
1	28.8	14.5	431	11.2
3	31.0	22.7	155	11.4
5	32.1	36.1	96	10.8
7	34.1	50.3	73	10.8
10	39.6	79.2	60	11.9

for K_e, and was able to arrive at reasonable estimates of the ion pair dissociation constants using a nonlinear regression fitting procedure for his data. For the dicyclohexyl-18-crown-6 complex of potassium picrate in CH_2Cl_2 the dissociation constant K_d was found to be approximately 4 × 10^{-5} M.[3b] This means that at concentrations less than 10^{-4} M the picrate salt in CH_2Cl_2 is considerably ionized.

A complicating factor in the use of polymeric crown ethers is the possible variation of the dissociation constant with the degree of ion pair binding. As more polymer is added at constant picrate concentration, the macromolecule becomes less saturated with ion pairs, and this is likely to affect the free ion dissociation. Because of this uncertainty in K_d, and because the experiments were all carried out at one picric acid concentration (7 × 10^{-5} M), we calculated an apparent K_e (K_e') by assuming no ion pair dissociation. The data are collected in Table IV and represent in each instance the average of five K_e' values at five different crown to picric acid ratios. The standard deviation is between 10 and 40%, and a trend in the K_e' value with α is often observed, most likely because ion pair dissociation does occur. In spite of this, the K_e' values can be used for a qualitative comparison of the extraction capabilities of the crown ethers and the corresponding polymers.

A 2:1 stoichiometric crown-cation complex is anticipated when the crown cavity cannot accommodate the cation, *e.g.*, in the systems 15C5-K^+,Rb^+,Cs^+,Ba^{2+} and for 18C6-Cs^+. If this is the predominant species, the expression for K_e for the monomeric crown ethers changes to

$$K_e = \frac{\alpha}{a^{+}(1-\alpha)([Cr_0]/[A_0] - 2\alpha)^2[A_0]^2} \tag{6}$$

In the polymeric crown ethers a 2:1 crown cation complexation most likely involves closely neighboring crown moieties, in which case K_e is given by

$$K_e = \frac{\alpha}{a^{+}(1-\alpha)([Cr_0]/[A_0] - 2\alpha)[A_0]} \tag{7}$$

Since 15C5 is known to form a 2:1 complex with K^+,[3a,10b] we calculated K_e by using both eq 5 and 6, assuming first K_d = 0. Then we recalculated K_e, taking ion pair dissociation into account, and using the expressions derived by Frensdorff.[3b] The dissociation constant was varied until a minimum was obtained in the standard deviation of K_e as a function of α. The results, collected in Table V, demonstrate that a constant K_e value of (11.2 ± 0.04) × 10^6 M^{-3} is obtained by assuming a 2:1 15C5-K^+ complex, the dissociation constant of the picrate ion pair complex being 4 × 10^{-5} M. The latter value is nearly identical with that found by Frensdorff for the complex of the same salt with dicyclohexyl-18-crown-6.[3b] A 2:1 complex of 15C5 with K^+ is consistent with spectrophotometric data on interactions of 15C5 with fluorenyl ion pairs in H_4furan, in which solvent this crown ether was shown to form a stable 2:1 complex with the potassium salt.[10b] The low per cent of picrate extraction for Rb^+ and Cs^+ with 15C5 does not permit us to decide with certainty whether 2:1 complexes are formed. However, conductance measurements, to be discussed later, make it likely that at least for Rb^+ and 15C5 such a complex exists.

We have recalculated all K_e values pertaining to the monomeric crown ethers by taking into account ion pair dissociation and varying K_d until a minimum in the standard deviation of K_e was obtained. The data are shown in Table VI, where it was assumed that 2:1 complexes are formed between 15C5 and K^+, Rb^+, and Cs^+, respectively.

The calculated K_d values appear to be reasonable, except that of Na^+-15C5 which seems a bit low. The per cent extraction in the latter system is too low for an accurate determination of K_d. In rationalizing these values it should be realized that the 2:1 complexes are most likely to be loose ion pairs, *e.g.*, Pi^-, 15C5, K^+, 15C5, but the 1:1 complexes may be either tight or loose ion pairs. For example, the fluorenylsodium-18C6 complex is a loose ion pair in H_4furan, but the 15C5 complex is a mixture of tight (F^-, Na^+, 15C5) and loose ion pairs (F^-, 15C5, Na^+), and the ratio changes in favor of the tight ion pair complex in less polar solvents.[10b] The same is found in fluorenylpotassium with 18C6 and with dicyclohexyl-18-crown-6. The tight ion pairs are likely to have lower dissociation constants than the loose ion pairs, and this may well be the reason for the lower K_d values of the K^+-18C6, Rb^+-18C6, and Cs^+-18C6 picrate complexes. Conductance measurements may shed more light on this problem, and one may find that in some systems the ion pair complex contains one crown ether while the free cation is coordinated with two of these molecules.[21] This would further complicate the system.

Calculations were also carried out for the poly(crown ethers), and the results are presented in Table VII. It should be stressed that the reported K_d values are not very accurate, and sometimes no clear minimum in the standard deviation of K_e with α was obtained. This may be due to a dependence of K_d on the number of ion pairs bound per poly(crown ether) chain. The K_d values for the Li^+ complexes and that of Na^+-P15C5 appear too low, but most of the other values seem to be consistent with

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(21) M. Shinohara, J. Smid, and M. Szwarc, *Chem. Commun.*, 1232 (1969).

Table VI
Extraction Equilibrium Constants, K_e, and Complex Dissociation Constants, K_d, for Picrate with 15C5 and 18C6 in H_2O–CH_2Cl_2

Cation	Crown	Complex	$K_e \times 10^{-3}$ M^{-2}	$K_e \times 10^{-6}$ M^{-3}	$K_d \times 10^6$ M
Na^+	15C5	1:1	6.1 ± 0.1		0.2
Na^+	18C6	1:1	1.2 ± 0.1		30
K^+	15C5	2:1		11.2 ± 0.5	40
K^+	18C6	1:1	305 ± 10		10
Rb^+	15C5	2:1		3.0 ± 0.5[a]	40[a]
Rb^+	18C6	1:1	92 ± 2		9
Cs^+	15C5	2:1 (?)		0.45 ± 0.05[a]	40[a]
Cs^+	18C6	1:1	57 ± 3		4
NH_4^+	18C6	1:1	3.8 ± 0.1		0.8
Ba^{2+}	18C6	1:1		26 ± 0.5	3

[a] The per cent extractions in these two cases were too small to obtain a reasonable K_d value. We assumed it to be the same as that for the Pi^-–15C5–K^+–15C5 complex.

Table VII
Extraction Equilibrium Constants, K_e, and Complex Dissociation Constants, K_d, for Picrate with P15C5[a] and P18C6[a] in H_2O–CH_2Cl_2

Cation	Polymer	Complex	$K_e \times 10^{-3}\, M^{-2}$	$K_d \times 10^6$ M
Li^+	P15C5	1:1	13 ± 1	0.4
Li^+	P18C6	1:1	8.7 ± 0.4	0.2
Na^+	P15C5	1:1	45 ± 3	5
Na^+	P18C6	1:1	25 ± 0.1	5
K^+	P15C5	2:1	570 ± 10	20
K^+	P18C6	1:1	720 ± 15	8
Rb^+	P15C5	2:1	540 ± 40	20
Rb^+	P18C6	2:1	580 ± 3	20
Cs^+	P15C5	2:1	150 ± 25	10
Cs^+	P18C6	2:1	1650 ± 430	10
NH_4^+	P15C5	2:1	48 ± 5	2
NH_4^+	P18C6	1:1	51 ± 7	4
Ba^{2+}	P15C5	2:1	[(34 ± 1) × $10^6\, M^{-3}$]	10
Ba^{2+}	P18C6	1:1	[(210 ± 1) × $10^6\, M^{-3}$]	40

[a] Polymer made with radical initiator; M_n = 110,000.

those of the monomeric crown ethers. The highest K_d values are found in systems were 2:1 complexes can be expected, probably because the interionic ion pair distances are larger than for 1:1 complexes.

Using K_e' values one finds the following selectivity sequence for extracting picrate salts with P15C5 (based on Na^+ equal to unity): Li^+:Na^+:K^+:Rb^+:Cs^+:NH_4^+ = 0.3:1:29:28:3.9:1.2, while for P18C6 the ratio is 0.24:1:23:21:43:1.7. Using K_e values (Table VII) one finds the same sequence, although the ratios are slightly different. Actually, a comparison of K_e values does not always give a true picture of the extraction capabilities of the various crown species, since K_e involves the ion pairs only. If the ion pair complexes have different structures (*i.e.*, tight or loose ion pairs) the fraction of complex in the form of free ions may differ considerably from one crown to another, and this in turn affects K_e. The K_e' values, or the fraction of picrate salt extracted, provides us in such a case with a better comparison.

Extractions carried out at 0.1 M base yielded K_e' values that are considerably lower than those obtained at 0.01 M base. Deviations at 0.1 M base concentration were also reported by Frensdorff[3b] and were attributed to possible deviations in the activity coefficient of the metal ion. We also repeated the measurements with polymers prepared anionically, using both 0.1 and 0.01 M base. The results were similar with those found for the radically prepared polymers, possibly indicating that no important structural differences exist between the two kinds of polymers. Data obtained for the lower molecular weight polymers ($M_n \approx$ 30,000) give K_e values which on the average are about 30% higher than those for polymers of M_n = 110,000. This may be caused by differences in the partition coefficients.

As pointed out earlier, differences in K_e values between various crown species (*e.g.*, the more efficient extraction of picrate salts by polycrown ethers as compared to their monomeric analogs) may be due to variations in partition coefficients and/or differences in the actual complex formation constants, K_s. To check this, we measured the partition coefficients, P_e, for the four crown species, and obtained the following values: $P_e = 5.1 \times 10^{-4}$ (15C5), 0.11×10^{-4} (P15C5), 19×10^{-4} (18C6), and 0.073×10^{-4} (P18C6). Not unexpectedly, the P_e values of the polymers are considerably lower than those of the monobenzo crown ethers, with P18C6 having the lowest P_e value. This latter observation is somewhat surprising in view of its high solubility in water (see Table II). The low P_e values of the polymers would render them less effective in extracting the picrate salts.

Formation constants for crown–cation complexes have recently been determined by calorimetry[5,8] and by potentiometry.[3a] Measurements using the latter technique are presently underway to obtain the K_s values for the four crown species used in this investigation.[22] Preliminary data (referring to crown solutions in a mixture of equal volumes of H_4furan and H_2O) indicate that the differences in K_s values between monomer and polymer are the largest in systems that favor 2:1 crown cation complexes. For example, K_s for P15C5–K^+ is about 15 times that of 15C5–K^+. The differences for 1:1 complexes appear to be small. Judging from the available data (to be published elsewhere), it seems that much of the observed differences between the extraction equilibrium constants must be attributed to the P_c factor. Apparently, differences in the partition coefficients of the respective monomer and polymer cation complexes are more pronounced than the variations of the P_e values. The importance of the partition coefficient, P_c, was stressed by Frensdorff,[3b] who also pointed out the strong anion effect, *i.e.*, no hydroxide ions are transferred to the organic phase. He attributed this to the dependence of P_c on the nature of the anion. This may be partially due to different ion pair structures in the organic phase. The delocalized picrate anion has a stronger tendency to form a loose ion pair when its counterion complexes with a crown ether than a hydroxide or halide anion, and the cation–crown binding is likely to be considerably stronger than in a tight ion pair.

A number of experiments were carried out with poly(vinyldibenzo-18-crown-6), all at 0.1 M base concentration. The polymer is more effective in extracting picrate salts than is dimethyldibenzo-18-crown-6, especially for the larger cations, but it is less efficient than P18C6. It has not been established whether this is due to a lower complexation constant or because of an unfavorable partition coefficient.

Maximum Number of Ions Complexed to the Polymer. By increasing the picric acid concentration in the aqueous phase at constant crown concentration, more salt is transferred to the organic phase. If the extraction equi-

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[22] These measurements are kindly being carried out by Dr. E. Eyal in the laboratory of Dr. G. A. Rechnitz, Chemistry Department, State University of New York at Buffalo, Buffalo, N. Y., see also: G. A. Rechnitz and E. Eyal, *Anal. Chem.*, 44, 370 (1972).

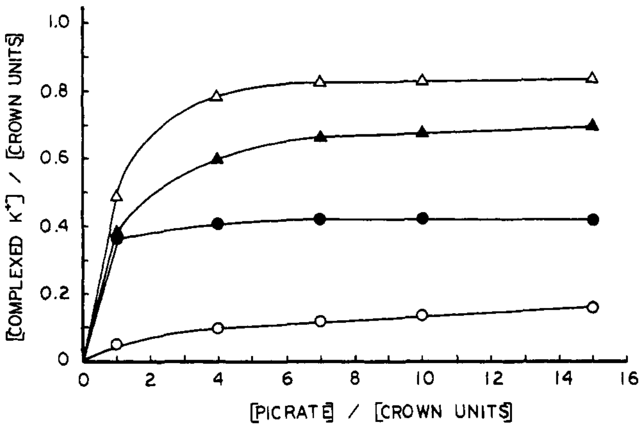

Figure 1. Binding of K+ ions to 15C5 (○), P15C5 (●), 18C6 (△), and P18C6 (▲) as a function of potassium picrate concentration; [crown units] = 7 × 10^{-5} *M*.

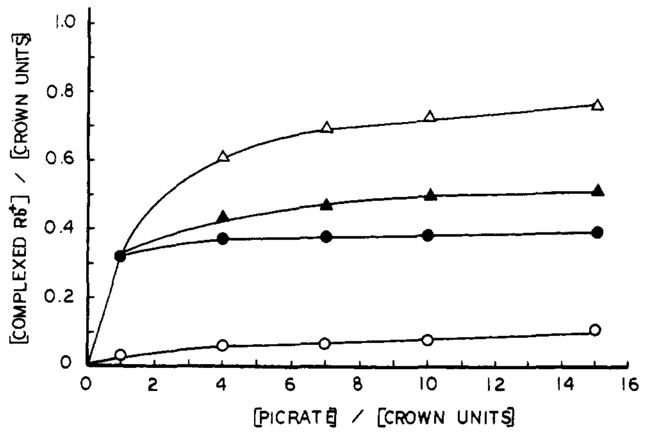

Figure 2. Binding of Rb+ ions to 15C5 (○), P15C5 (●), 18C6 (△), and P18C6 (▲) as a function of picrate concentration; [crown units] = 7 × 10^{-5} *M*.

librium constant is large enough a point will be reached where nearly all the available crown units are coordinated to a cation. The maximum attainable cation to crown ratio may provide information on the stoichiometry of the complexes formed with the monomeric and polymeric crown ethers.

A number of saturation experiments were carried out with K^+, Rb^+, and Cs^+ ions at 0.1 *M* base concentration for the four crown species 15C5, P15C5, 18C6, and P18C6. The results are graphically depicted in Figures 1, 2, and 3, where the ratio of complexed cation to total available crown units is plotted *vs.* $[A_0]/[Cr_0]$, $[Cr_0]$ being 7 × 10^{-5} *M*.

The results for the potassium salt (Figure 1) clearly demonstrate again the more efficient extraction of this picrate salt by P15C5 as compared to 15C5, while P18C6 and 18C6 do not differ to a great extent. More important, the cation to crown ratio rapidly approaches a maximum close to 0.5 (the actual maximum is about 0.42). The ratio found for P18C6 is substantially higher than 0.5 and approaches 0.7. This strongly suggests that with P15C5 two crown units are complexed to a K^+ ion, while 1:1 complexes are prevalent with P18C6. In the latter case the maximum ratio could be unity, but a high degree of cation binding will result in stronger repulsion between the closely packed cations, and additional binding of cations may become increasingly difficult. A similar observation was made in a different kind of experiment, where the number of fluorenylpotassium ion pairs bound per P18C6 molecule in H_4furan was determined spectrophotometrically. The ratio K^+-18C6 was found to be 0.8.[23]

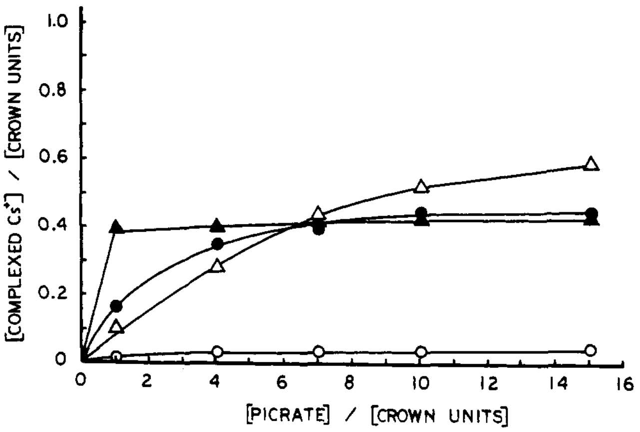

Figure 3. Binding of Cs+ ions to 15C5 (○), P15C5 (●), 18C6 (△) and P18C6 (▲) as a function of picrate concentration; [crown units] = 7 × 10^{-5} *M*.

For the rubidium and cesium ions the cation to crown ratio for both polymers does not exceed 0.5, which again is indicative of a 2:1 complex. The Rb^+-P18C6 system may be a borderline case, as the Rb^+ ion barely fits the 18C6 cavity. Actually, in none of the cases where 2:1 complexes are formed does the cation to crown ratio appear to exceed 0.42. Spectrophotometric measurements on the binding of potassium carbanion salts in H_4furan to P15C5 confirms this observation.[23] Since electrostatic repulsion and also steric factors should be less important in polymers that form 2:1 complexes than in those giving 1:1 complexes, the most probable cause for this lower ratio is a statistical factor. Flory[24] has calculated that in selecting at random pairs of consecutive substituents of a macromolecule made up of structural units CH_2CHX, 13.5% of unpaired substituents are left. This has been substantiated in a number of reactions on polymers.[25] The calculations strictly apply only to irreversible reactions.[24] The binding of cations to polyvinyl crown ethers is a reversible process with a continuous rearrangement of binding sites. Nevertheless, complete saturation *i.e.*, a cation to crown ratio of 0.5 represents a less favorable distribution and a considerably lower entropy that the most probable distribution, and the ratio that is eventually reached depends on the interaction energy between cation and crown. The observed ratio of 0.42 indicates that the statistical ratio of 0.43 is not exceeded.

Conductance Measurements. Frensdorff and Pedersen[4] obtained important information on the stoichiometry of the crown-cation complexes by measuring conductances of salt solutions in the presence of crown ethers. When conditions are such that only free ions are present, the conductance of the salt solution on addition of crown ether may be affected as a result of a change in the mobility of the cation as it becomes complexed to the crown ether. When ion pairs are the predominant species, the formation of crown complexed ion pairs will affect the interionic ion pair distance. This should give rise to a change in the ion pair dissociation constant, especially when, as a result of this binding, a tight ion pair is converted into a loose pair.

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(24) P. J. Flory, *J. Amer. Chem. Soc.*, **61**, 1518 (1939).

(25) See, for example: W. E. Smith, G. E. Ham, H. D. Anspon, S. E. Gebura, and D. W. Alwani, *J. Polym. Sci., Part A1*, **6**, 2001 (1968); F. Shepherd and H. J. Harwood, *J. Polym. Sci., Part B*, **9**, 419 (1971).

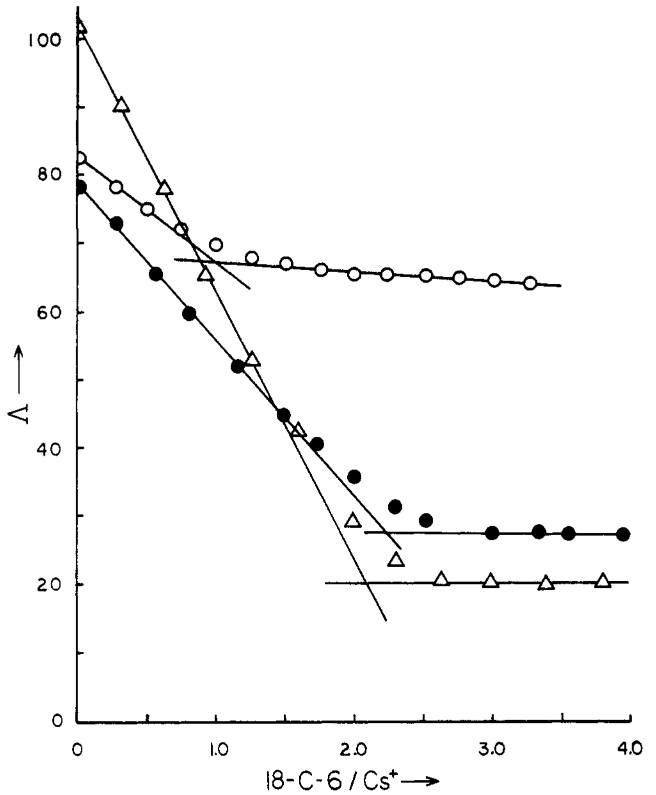

Figure 4. Plot of equivalent conductance Λ *vs.* the ratio of 18C6 units to [cesium salt]; (○) 18C6-CsCl in CH_3OH-$CHCl_3$ (9:1); (●) P18C6-CsCl in CH_3OH-$CHCl_3$ (9:1); (△) P18C6-$CsBPh_4$ in acetone.

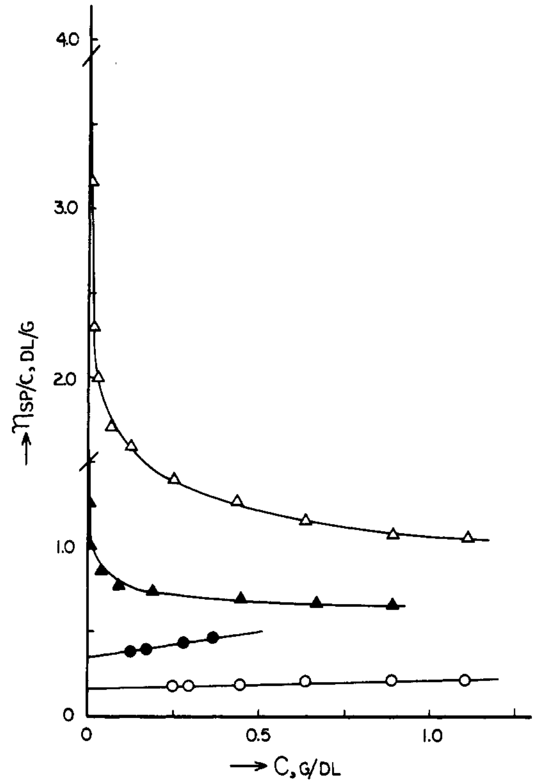

Figure 5. Viscosity of P18C6 in CH_3OH-H_4furan (1:1, v/v) in the presence and absence of salt; (○) no salt present; (▲) with KBr, ratio of crown units to KBr = 1:1; (●) with KBr, constant ionic strength, initial ratio of crown units to KBr = 1:3; (△) with CsCl, ratio of crown units to CsCl = 2:1.

Assuming complete dissociation of the salt and a high complexation constant, it can easily be shown that at constant salt concentration (and assuming that interionic interactions are not affected by the changing solvation shell of the cation) the observed equivalent conductance Λ is proportional to the ratio [crown]:[salt]. A plot of Λ *vs.* this ratio should give a sharp break at a crown to salt ratio equal to the stoichiometry of the complex. Addition of a polycrown ether to the salt solution should reduce Λ more drastically because of the low mobility of the macroion. This mobility may be somewhat affected by the number of ions bound to a chain and by their distribution. Also, the equivalent conductance is likely to change further beyond the stoichiometric crown to cation ratio as addition of more poly(crown ether) will lead to a redistribution of the positive charges. Furthermore, the ion pair dissociation constants are affected by the number of ions bound to the chain, and this becomes important in lower dielectric constant media.

The conductance experiments were carried out at a constant salt concentration (10^{-3} *M*) using alkali halides or tetraphenyl borides dissolved in acetone or a mixture of CH_3OH and $CHCl_3$ (9:1, v/v). The conductances were measured at several crown to salt ratios in a cell provided with platinum electrodes (cell constant 0.00504) using a General Radio Co. 1673 automatic capacitance bridge. Some of the results obtained with CsCl and $CsBPh_4$ in solutions of 18C6 and P18C6 are graphically depicted in Figure 4. The salts are probably completely dissociated in the two solvents. The plot for CsCl-18C6 reveals a rather abrupt break at a crown to Cs^+ ratio of unity, indicating a 1:1 stoichiometry for the Cs^+-18C6 complex. The slight curvature at the equivalence point may be due to a low complexation constant. Addition of P18C6 causes a much bigger drop in Λ, and the break in the curve now occurs at a 2:1 crown to cation ratio, consistent with the observation made on this polymer-cation system in the extraction experiments. Similar plots for potassium salts in acetone yield 1:1 stoichiometries for the complexes of K^+-18C6 and K^+-P18C6, but for 15C5 and P15C5 sharp breaks are observed at 2:1 crown to salt ratios.

In media of lower polarity the increase in conductance is chiefly due to a change in ion pair structure. This is the case in solvents such as H_4furan or $CHCl_3$-CH_3OH (9:1, v/v). Plots of equivalent conductance *vs.* crown to cation ratio in these media usually do not yield straight lines as the dissociation constant increases at higher crown concentration. Generally, however, a sharp break in the plot is observed at stoichiometric crown to cation ratios. The sodium salts show sharp breaks in the conductance plots at 1:1 crown to cation ratios for all four crown species, both in acetone and in the 9:1 $CHCl_3$-CH_3OH mixture. Beyond the equivalence point the conductance in low polarity media may continue to increase, depending on the nature of the complexed ion pair.

Viscosity Behavior in the Presence of Salts. The binding of cations or ion pairs to the poly(vinyl crown ethers) should impart properties to the polymers that are characteristic for polyelectrolytes. For example, conformational changes in the macromolecule are anticipated on addition of salts to a solution of these neutral polymers, and these changes should be reflected in the viscosity behavior of such solutions. To verify this the viscosities of solutions of P15C5 and of P18C6 in a mixture of equal volumes of H_4furan and CH_3OH were measured in the absence and presence of alkali salts. Some of the results obtained with P18C6 are graphically shown in Figure 5. In the absence of salt the familiar reduced viscosity versus concentration plot is found, the intrinsic viscosity of the P18C6 polymer of M_n = 110,000 being 0.15. The reduced viscosity substantially increases on addition of potassium bromide, and, keeping the ratio of crown to salt constant (ratio = 1), dilution of the polymer solution leads to a further enhancement of η_r. The changes are even more pronounced with cesium chloride, with the reduced viscosity going up to about 3.5 by diluting at a constant crown to salt ratio equal to two. This behavior is typical for that observed in many polyelectrolyte solutions.[26] Our results imply that in this solvent mixture a substantial amount of K^+ and Cs^+ ions remain bound to the polymer. The curvature disappears when the ionic strength is kept constant by diluting the polymer with the salt solution (see Figure 5, initial potassium bromide to crown ratio is three). This is also observed for polyelectrolytes and can be used to obtain the intrinsic viscosities as a function of ionic strength.[26] The higher $[\eta]$ value recorded with cesium chloride may be due to the formation of 2:1 complexes between the 18C6 moieties and Cs^+, which tends to extend the chain beyond that due to electrostatic repulsion. This is not so much of a problem with the smaller K^+ ion which fits the 18C6 cavity. It may of course also be due to a higher fraction of cesium ions bound to P18C6. A similar larger increase is found in the system KBr-P15C5, where also 2:1 complexes are formed. No pronounced curvature in the viscosity plot was observed in a mixture of equal volumes of H_4furan and water, although the reduced viscosity is considerably higher than in the absence of KBr. A lower binding constant may be the reason for this.

In conclusion, the poly(vinylbenzo crown ethers), which can be comparatively easily synthesized, represent a class of polymers that appear to be useful in the study of ion or ion pair binding to neutral macromolecules in both aqueous and nonaqueous media. The ion complexation can be investigated by a variety of techniques such as potentiometric titrations, optical spectroscopy, conductance, distribution equilibria, and viscosity, providing information on the stoichiometry of the complexes, the cation binding selectivities of the polymers and the values of the binding constants. We are presently engaged in the synthesis of other crown monomers such as crown esters of methacrylic acid. We are also preparing random and block copolymers of the vinyl crown ethers with various monomers in order to study the cation binding efficiency as a function of the spacing of crown moieties and to determine the extent of intramolecular ion binding in copolymers containing salts of polymeric acids. It should also be of interest to study in more detail the mechanism of anionic polymerization of these vinyl monomers, as well as the radical polymerization in the presence of salts. Furthermore, certain ionic reactions may be accelerated by addition of these neutral polymers if binding of the respective reactants occurs.

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