(22) ATR IR spectra were obtained with a Nicolet 7199 instrument (100 scans) and an MIR stainless steel holder set at an angle of 45°. Films were cut to cover the entire germanium sample faces used. The thickness of the germanium plates was 3 mm.
(23) Compound 2 was prepared by procedures similar to those previously described for related phospholipids: O'Brien, D. F.; Whitesides, T. H.; Klingbiel, R. T. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 95. Johnston, D. S.; Sanghera, S.; Pons, M.; Chapman, D. *Biochim. Biophys. Acta* **1980**, *602*, 57.
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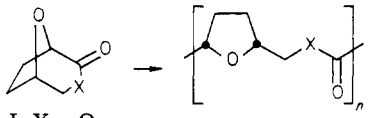
Ion-Binding Properties of Poly(iminomethylene(*cis*-tetrahydro-2,5-furandiyl)carbonyl) and Poly(oxymethylene(*cis*-tetrahydro-2,5-furandiyl)-carbonyl)

In previous publications,[1] we reported the syntheses and ring-opening polymerization of 3,8-dioxabicyclo[3.2.1]octan-2-one (I) and 3-aza-8-oxabicyclo[3.2.1]octan-2-one (II) to polyester III and polyamide IV, respectively. We now



I, X = O
II, X = NH

III, X = O
IV, X = NH

report preliminary data on the ion-binding properties of these materials.

The ion-binding properties of macrocyclic systems such as crown ethers,[2] cryptates,[3] and polymers containing these structures as pendent entities[4] are well-known. However, the ion-binding properties of linear polymers are less defined. Recently, Smith and co-workers[5] prepared *threo*- and *erythro*-poly(tetrahydro-2,5-furandiyl) and found that the threo polymer was an effective binder of lithium, potassium, and barium cations, while the erythro isomer was ineffective. The difference in binding properties was attributed to the ability of the threo isomer to exist in a helical conformation with the oxygen atoms pointed inward. Böhmer and co-workers[6,7] have recently prepared a series of linear, acyclic, ion-binding poly(ether amides) and have reported preliminary ion-binding data.

Picrate extractions[5-7] were used to assay the binding characteristics of polyester III and polyamide IV. The polymer to be tested was dissolved in chloroform at a repeat unit concentration of 10^{-2} M. The solution was allowed to reach thermal equilibrium in a water bath at 25 °C and an aliquot, typically 5 mL, was mixed with an equal volume of an aqueous solution of an alkali metal picrate (10^{-3}–10^{-4} M). The mixture was shaken intermittently, and after 1 h, the lower, organic layer was removed. An aliquot of the lower layer, typically 2 mL, was quantitatively diluted with ethanol to 5 mL, and the picrate concentration was determined spectrophotometrically (λ_{max} = 360 nm, log ϵ = 4.15 determined in chloroform–ethanol solution). The amount of alkali metal picrate extracted was expressed as a percent of the initial picrate concentration. Alkali metal picrate salts were prepared by the reaction of picric acid and alkali metal carbonates or hydroxides.[8] In the absence of polymer, no detectable amount of alkali metal picrate was extracted by chloroform alone.

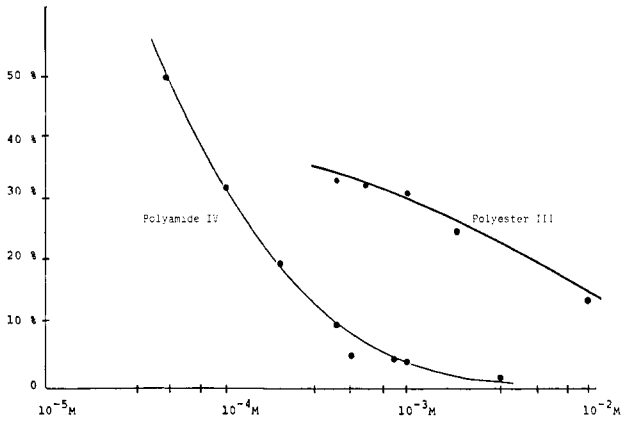


Figure 1. Percent solute extracted vs. log (total solute) for polyester III and polyamide IV. Solute: potassium picrate.

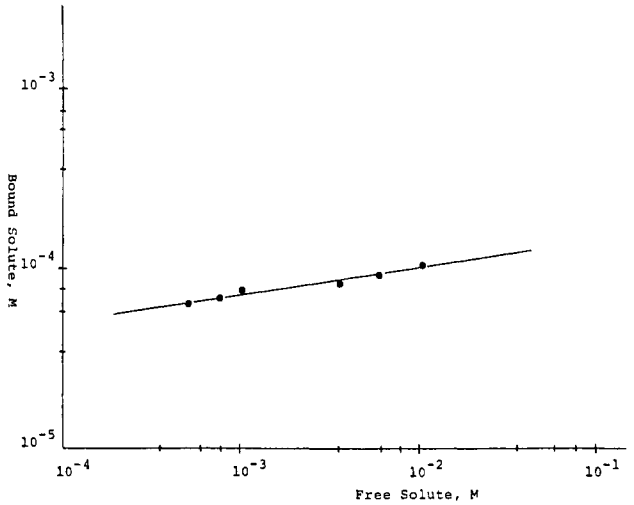


Figure 2. Log (bound solute) vs. log (free solute) for polyamide IV. Solute: potassium picrate.

The results of the ion-binding experiments for polyamide IV, polyester III, and polymers prepared by Böhmer and Smith are presented in Table I. The other data given in the table are for comparison. The amount of solute extracted varies as a function of the total solute concentration, as illustrated in Figure 1. It is apparent that measuring the extent of ion-binding at only one concentration may not be a good measure of the binding capacity of the material. To understand better the ion-binding behavior of polyamide IV and polyester III, plots of log (bound solute) vs. log (free solute) were prepared (Figures 2 and 3, respectively). Bound solute is the amount of picrate extracted into the organic phase, and free solute is that which remains in the aqueous phase. The figures show data for potassium picrate as solute but data for lithium, sodium, and cesium exhibit the same trends.

For polyamide IV (Figure 2), the concentration of bound solute is virtually constant over 3 orders of magnitude of free solute concentration. This observation is in direct contrast to that for polyester III (Figure 3), where changing free solute concentration has a much larger effect on the bound solute concentration. Based on the different

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Table I
Ion-Binding Properties of Selected Ionophores[a]

ionophore	% solute extracted			ref
	Li	K	Cs	
18-crown-6	63	74		5
threo-poly(tetrahydrofurandiyl)	37	53		5
erythro-poly(tetrahydrofurandiyl)		0		5
$-NHCH_2CH_2(OCH_2CH_2)_3NHC(O)RC(O)-$	3	2		6a
$-NHCH_2CH_2(OCH_2CH_2)_4NHC(O)RC(O)-$	5	14		6a
$-NHCH_2CH_2(OCH_2CH_2)_5NHC(O)RC(O)-$	10	21		6a
$-NHCH_2CH_2(OCH_2CH_2)_4NHC(O)R'C(O)-$	15	31	28	6b
polyamide IV	30	32	34	*b*
polyester III	33	33		*b–d*

[a] The ionophore concentration was 10^{-2} M. The solute concentration was 10^{-4} M, except where noted. R = CH_2OCH_2; R′ = $(CH_2)_3$. T = 25 °C. [b] These values were determined in this work. [c] Polyester III was prepared with $(i\text{-Bu})_3Al$. [d] The solute concentration was 10^{-3} M.

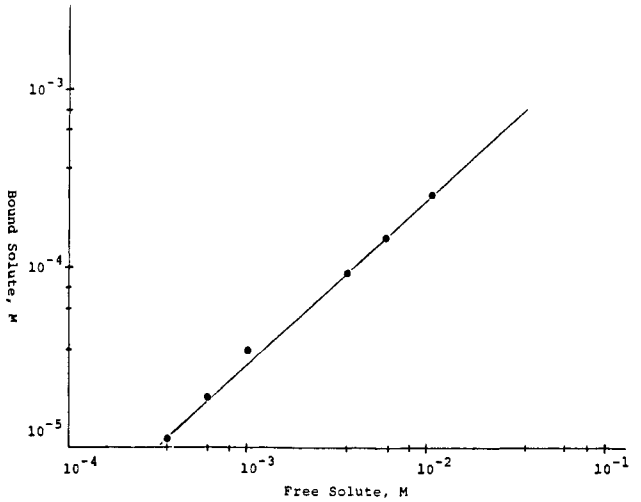

Figure 3. Log (bound solute) vs. log (free solute) for polyester III. Solute: potassium picrate.

binding characteristics of the two polymers, it appears that different modes of binding may be at work.

A tentative binding model would require the polymer to wrap itself around the ion(s) being bound. The absence of selectivity may indicate that both polymers are flexible enough to adjust conformationally to fit ions of different size. However, polyamides are relatively less flexible than polyesters and the polyamide might not be able to encircle ions as easily as the polyester. The lower binding efficiency of the polyamide might reflect the inherent stiffness of the polyamide arising from hindered rotation about the amide link. Work is continuing to try to verify these tentative conclusions and to elucidate further the mechanism(s) of binding.

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Registry No. I homopolymer, 56814-64-3; II homopolymer, 83601-56-3; III, 83693-50-9; IV, 83693-51-0; Li, 7439-93-2; K, 7440-09-7; Cs, 7440-46-2.

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