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NEW POLY- AND BIS(THIACROWN ETHER)S AS EXTRACTION REAGENTS

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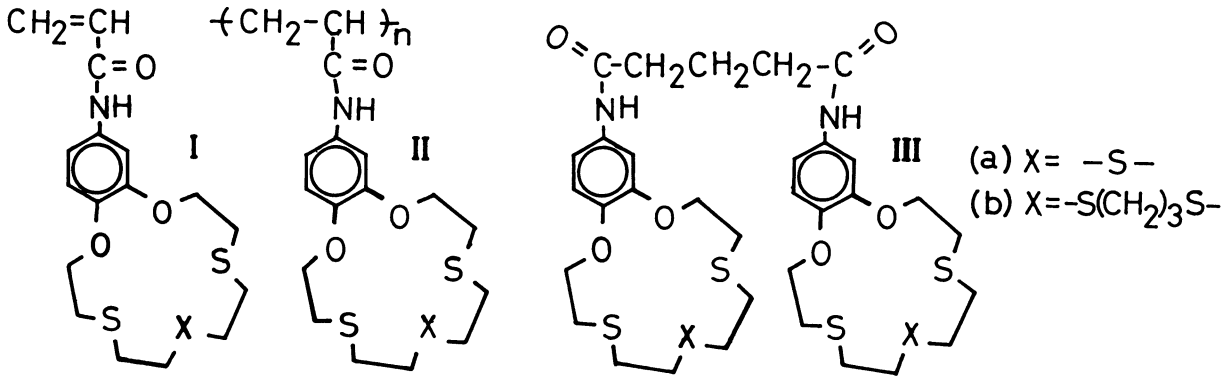
New poly- and bis(thiacrown ether)s containing two oxygen atoms and three to four sulfur atoms in the polyether-polysulfide ring have been synthesized, and they were found to bind silver picrate effectively compared with their monocyclic analogs.

The synthesis of a number of poly- and bis(crown ether)s derived from aromatic vicinal diols and the solvent extraction of alkali and alkaline earth metal picrates with them have been previously reported.[1-3] The results have shown that the extractability of the poly- and bis(crown ether)s are superior to those of their monomeric analogs for alkali and alkaline earth metal picrates. Though there are many reports about the synthesis of " thiacrown ether " ,[4,5] the solvent extraction of poly- and bis(thiacrown ether)s **II**, **III** in which three to four oxygen atom linkages are replaced by sulfur atom linkages has not been reported previously. We prepared poly- and bis(thiacrown ether)s, which contain two oxygen atoms and three to four sulfur atoms in the macrocyclic polyether-polysulfide, from the polymerization of acryloylaminobenzothiacrown ether and the reaction of aminobenzothiacrown ethers with glutaryl chloride, and screened them for the extractability of silver picrate.

The reaction of acrylic anhydride with the appropriate aminobenzothiacrown ethers in dioxane affords acryloylaminobenzothiacrown ether **I**. Radical polymeri-



zation of **I** in DMF gives poly(thiacrown ether)s **II** which were purified by repeated reprecipitation in DMF-diethyl ether system. Bis(thiacrown ether)s **III** are obtained by reaction of the product **I** and glutaryl chloride in benzene in the presence of triethylamine.

I (a) (53%). white crystal; mp 170-172°C; Found:C,52.81;H,5.99;N,3.54%;M^+,385. Calcd for $C_{17}H_{23}NO_3S_3$:C,52.96;H,6.01;N,3.63%;M,385.

(b) (54%). white crystal; mp 137.5-140°C; Found:C,51.96;H,6.34;N,3.00%;M^+,459. Calcd for $C_{20}H_{29}NO_3S_4$:C,52.25;H,6.36;N,3.05%;M,459.

III(a) (63%). white crystal; mp(dec.)265-270°C; Found:C,52.05;H,6.29;N,3.66%; M^+,758. Calcd for $C_{33}H_{46}N_2O_6S_6$:C,52.22;H,6.11;N,3.69%;M,758.

(b) (57%). white crystal; mp 178-181°C; Found:C,51.49;H,6.38;N,3.01%;M^+,906. Calcd for $C_{39}H_{58}N_2O_6S_8$:C,51.62;H,6.44:N,3.09%;M,906.

A stoppered flask, which contained equal volumes (10 ml) of 5×10^{-4} M (for the thiacrown unit) thiacrown ether chloroform solution and 1×10^{-4} M silver picrate aqueous solution, was shaken for 40 minutes at 25 ± 0.1°C. After shaking, the silver picrate concentration of aqueous phase was measured by the visible absorption to determine the concentration of formed complexes or extractability, and the results are shown in Table 1. In the solvent extraction of silver picrate with poly(thiacrown ether)s **IIa**, **IIb** formed precipitation, which might suggest that the complexing ability of the poly(thiacrown ether)s is larger than the others.

Table 1. Distribution ratios and percent extraction

CROWN	D (PERCENT EXTRACTION)
Ia	1.552 (60.82)
Ib	4.083 (80.32)
IIa	--- *
IIb	--- *
IIIa	4.276 (81.05)
IIIb	4.721 (82.53)
PB 15-CR-5	0.043 (4.10)
PB 18-CR-6	0.091 (8.36)

* precipitations are formed

As compared with the distribution ratio of PB 15-CR-5, the values for thiacrown ethers are extremely large, about ten times as much. This may be mainly due to the substitution of the sulfur atoms for the oxygens. And also the thiacrown ether / Ag ratio is equal to unity in their monomer, while in the bis(thiacrown ether)s 2:1 ratios have been found conductometrically. Thus, the cooperative effect of two adjacent crown rings in forming the sandwich-type complexes might be concerned with the increase of the extractability of the poly- and bis(thiacrown ether)s. Further study is currently under way.

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