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NEW POLY- AND BIS(12-CROWN-4)S POSSESSING HIGH SODIUM-SELECTIVITY

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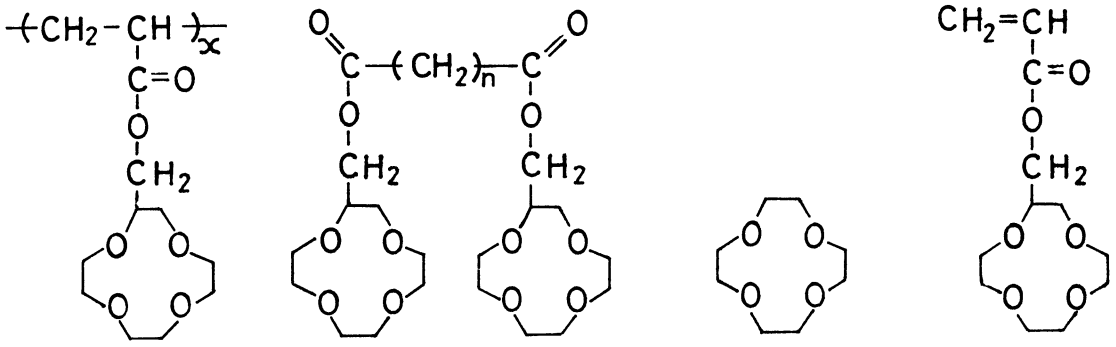
New poly- and bis(crown ether)s containing 12-crown-4 moieties were synthesized. Solvent extraction data suggested that poly-(crown ether) and bis(crown ether) derived from acryloyl chloride and malonyl chloride, respectively, have much larger extractability and selectivity for Na^+ than bis(crown ether) derived from glutaryl chloride and monocyclic analog.

Although 12-crown-4 is known to form stable complexes with Li^+ or Na^+, only a few papers have appeared on solvent extraction of alkali metal cations with 12-crown-4 and its derivatives.[1] In this paper, we would like to report a synthesis of new poly(crown ether) I and bis(crown ether)s II(n=1,3), and solvent extraction of alkali metal picrates with them.

Poly(crown ether) I was obtained by radical polymerization of acryloyloxymethyl-12-crown-4 IV in a similar manner as described previously.[2] Acryloyloxymethyl-12-crown-4 IV and bis(crown ether)s II(n=1,3) were synthesized by esterification of hydroxymethyl-12-crown-4[3] with acryloyl chloride or corresponding dicarboxylic chloride in chloroform in the presence of triethylamine at ambient temperature. Bis(crown ether)s were further purified by GPC.

II(n=1) (22%). Colorless oil; M^+ 480; ^1H NMR($CDCl_3$) δ 3.40(s, CH_2, 2H), 3.50-4.00(m, OCH_2CH_2O, $OCHCH_2O$, 30H), 4.08-4.40(d, $COOCH_2$, 4H).



I II(n=1,3) III IV

Fig. 1. Crown ether derivatives used in this study.

II(n=3) (40%). Colorless oil; M^+ 508; ^1H NMR($CDCl_3$) δ 1.72-2.10(q, CH_2, 2H), 2.20-2.80(t, $COCH_2$, 4H), 3.40-3.95(m, OCH_2CH_2O, $OCHCH_2O$, 30H), 4.00-4.40(d, $COOCH_2$, 4H).

IV(67%). Colorless oil; M^+ 260; ^1H NMR($CDCl_3$) δ 3.40-4.00(m, OCH_2CH_2O, $OCHCH_2O$, 15H), 4.12-4.30(d, $COOCH_2$, 2H), 5.76-6.16(m, $CH_2=$, 2H), 6.24-6.50(m, =CH, 1H).

Solvent extractions were carried out using 8 x 10^{-3}M(for crown ether units) crown ether dichloromethane solution and 5 x 10^{-3}M alkali metal picrate aqueous solution according to the procedure described previously.[4] The values of distribution ratio[5] of alkali metal cations between the two phases(expressed as D) were calculated and listed in Table 1. It is noteworthy that bis(crown ether) II(n=1) has larger extractability and selectivity for Na^+ than bis(crown ether) II(n=3) and monocyclic analog III. Moreover, poly(crown ether) I has much larger extractability for Na^+ than II and III.

In the optical spectral change of the crown ether-sodium cation complexes with increasing crown ether unit concentration in THF, large bathochromic shifts of the main optical absorption band were found from 351 nm to 374 nm for I and 378 nm for II (n=1), although only slight bathochromic shifts nearly to 365 nm were observed for II(n=3) and III. This result suggests that intramolecular 2:1 crown ether unit-cation complexes(sandwich-type compounds) are formed with I and II(n=1), while 1:1 crown ether unit-cation complexes are formed with II(n=3) and III.[6,7]

Taking account of these results, it is safe to say that I and II(n=1) have favorable structures to form intramolecular 2:1 crown ether unit-cation complexes with Na^+, which brings about their large extractability and selectivity for Na^+. Further study is now in progress.

Table 1. Distribution ratio in extraction of alkali metal picrates (25°C)

Crown ether	D (x 10^{-3})			
	Na^+	K^+	Rb^+	Cs^+
I	256.0	67.5	62.5	51.7
II(n=1)	108.3	11.7	8.37	7.39
II(n=3)	44.4	11.6	7.07	6.10
III	31.9	8.06	6.20	6.10

[Picrate] = 5 x 10^{-3}M.
[Crown ether unit] = 8 x 10^{-3}M in CH_2Cl_2.

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