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Tactic Poly(crown ether)s with Pendant Benzocrown Ethers

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Summary

Tactic and atactic poly(crown ether)s, poly(methacryloyloxymethylbenzo-15-crown-5), were synthesized by polymer reaction of the respective poly(methacrylic acid) with chloromethylbenzo-15-crown-5 and radical polymerization of methacryloyloxymethylbenzo-15-crown-5. By solvent extraction of alkali metal picrates with these poly(crown ether)s, the isotactic poly(crown ether) was found to be a little more selective for K^+ and Rb^+ than the syndiotactic and atactic ones.

Introduction

Considerable attention has been given to cation-complexing properties of macrocyclic polyethers, crown ethers. They are known to form cation complexes not only with 1:1 stoichiometry but also with 2:1(crown ether/cation) stoichiometry (PEDERSEN 1970). The stoichiometry is substantially dependent on the relative size of cavity of crown ether and cation. Polymers containing pendant crown ether moieties, so-called poly(crown ether)s, show a lot of attractive properties. For example, they have high extractability in solvent extraction of alkali metal cations, compared with the corresponding monomeric analogs (KOPOLOW et al. 1973, KIMURA et al. 1978). It is remarkable particularly for cations capable of forming the 2:1 complexes, partly because the poly(crown ether)s can form the complexes intramolecularly by cooperative action of two adjacent crown ether moieties. Our attention is concentrated in the effect of tacticity of poly(crown ether)s upon their cation-complexing abilities. We would like to report on the synthesis of tactic and atactic poly(crown ether)s of benzo-15-crown-5 and preliminary screening of their cation-complexing abilities for alkali metals by solvent extraction.

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Experimental

Synthesis of tactic and atactic poly(crown ether)s III *by polymer reaction*

The reaction of hydroxymethylbenzo-15-crown-5 (KOPOLOW et al. 1973) with dry hydrogen chloride in chloroform affords the chloromethyl derivative I, which was purified by recrystallization from petroleum ether. (mp: 67-68°C; M^+ 316; Anal. Calcd. for $C_{15}H_{21}O_5Cl$: C 56.87 H 6.68 Cl 11.19, Found: C 56.75 H 6.70 Cl 10.92) Poly(methacrylic acid)s with various tacticities were prepared according to the methods described by YUKI et al.(1970). The general procedure for the polymer reaction of the original polymer is illustrated below.
To a solution of a mixture of the appropriate poly(methacrylic acid)(0.25 g, 3 mmol for monomer unit) and chloromethylbenzo-15-crown-5(3.68 g, 12 mmol) in 40 ml of dimethylformamide(DMF), dicyclohexylmethylamine(2.30 g, 12 mmol) was added dropwise in more than 6 hours while stirring at 60°C. The reaction was allowed to continue for 5 days. After the solvent was replaced by a small quantity of chloroform, poly(crown ether) III was isolated by pouring the solution into a large excess of methanol. The conversion, tacticity, and number average molecular weight of the poly(crown ether)s were determined by pH-titration, ^{1}H-NMR spectroscopy, and high speed membrane osmometry, respectively.

Synthesis of atactic poly(crown ether) III *by radical polymerization of methacryloyloxymethylbenzo-15-crown-5* II

Methacryloyloxymethylbenzo-15-crown-5 II was prepared by reaction of hydroxymethylbenzo-15-crown-5 with methacrylic chloride in the presence of triethylamine in chloroform. The crude product was recrystallized from petroleum ether. (mp: 76.5-77°C; M^+ 366; Anal. Calcd. for $C_{19}H_{26}O_7$: C 62.28 H 7.15, Found: C 61.88 H 7.20) The polymerization of the monomer initiated by α,α'-azobisisobutyronitrile(AIBN) was carried out in toluene, using a sealed tube. The polymer obtained was purified by reprecipitation from chloroform in diethyl ether.

Solvent extraction of alkali metal picrates by tactic and atactic poly(crown ether)s III

The procedure for solvent extraction employed here is similar to one developed by PEDERSEN(1968). Chloroform was used as a water-immiscible solvent. Equal volvolume(10 ml) of 3×10^{-4} or 5×10^{-4}M(for crown ether unit) poly(crown ether) chloroform solution and 1×10^{-2} M alkali metal hydroxide aqueous solution containing 7×10^{-5}M picric acid were introduced into a stoppered flask, and then the system was shaken for 40 minutes at 25 ± 0.1°C. After completing the phase separation in a thermostated bath, the picrate concentration in the aqueous phase was measured by optical spectroscopy (λmax: 357 nm, ε: 14600 $cm^{-1}M^{-1}$). The percent picrate salt extracted was then calculated.

Results and Discussion

Tactic and atactic poly(crown ether)s containing benzo-15-crown-5 in the side group, poly(methacryloyloxymethylbenzo-15-crown-5) (iso-, syndio-, and atac-III), were synthesized as shown in SCHEME 1. The polymer reaction of tactic and atactic poly(methacrylic acid) (PMA) with chloromethylbenzo-15-crown-5 I in DMF in the presence of dicyclohexylmethylamine affords the respective poly(crown ether) III. The original polymers were prepared by anionic and radical polymerization of diphenylmethyl methacrylate, followed by treating with dry hydrogen bromide (YUKI et al. 1970). For quantitative conversion to poly(crown ether) III, three- or fourfold excess of chloromethylbenzocrown ether and amine are required. Slow addition of the amine to a DMF solution of a mixture of PMA and chloromethylbenzocrown ether is also of much importance to depress direct quaternization of the amine by the chloromethylbenzocrown ether.
An attempt was also made to prepare tactic poly(crown ether) III by anionic polymerization of methacryloyloxymethylbenzo-15-crown-5 II with various initiators, but it failed. For comparison, another atactic poly(crown ether) (rad-III) was prepared by radical polymerization of the monomer. Since the monomer is highly polymerizable, high yield (>80%) and molecular weight of poly-

SCHEME 1.

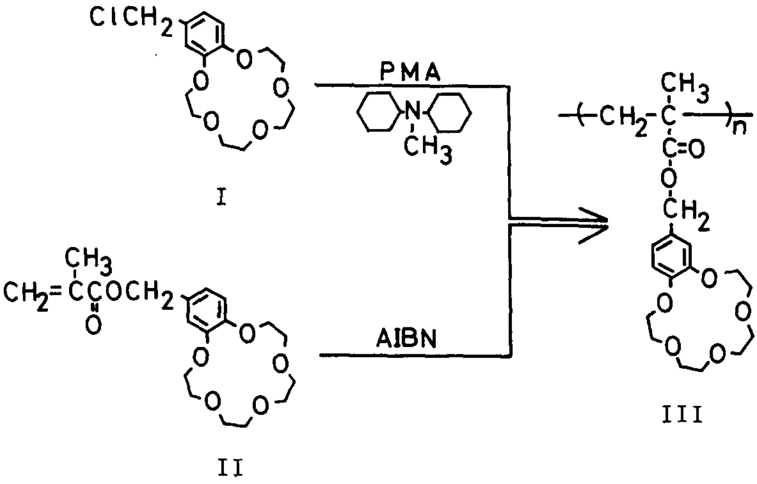

TABLE 1. Tacticity, conversion, and molecular weight of poly(crown ether)s III

Poly-(crown ether)	Tacticity(%)[a]			Conversion(%)[b]	$\overline{M}_n$ ($\times 10^4$)[c]
	I	H	S		
(iso-III)	94	4	2	98	10.7
(syndio-III)	4	12	84	96	4.7
(atac-III)	7	33	60	97	9.8
(rad-III)	7	34	59	100	8.0

a. tactic triads from ^{1}H-NMR spectra of α-CH_3 proton in nitrobenzene-d_5 at 150°C

b. determined by pH-titration in aqueous methanol

c. number average molecular weight measured by high speed membrane osmometry in dichloroethane

TABLE 2. Solvent extraction of alkali metal picrates by tactic and atactic poly(crown ether)s III

Poly-(crown ether)	Picrate salt extracted (%)			
	Na^+	K^+	Rb^+	Cs^+
(iso-III)	5 (8)	76 (88)	47 (61)	5 (7)
(syndio-III)	5 (8)	59 (70)	29 (36)	3 (6)
(atac-III)	3 (7)	65 (79)	28 (40)	4 (7)
(rad-III)	2 (3)	63 (75)	28 (38)	4 (6)

solvent system: $CHCl_3/H_2O$(10/10); [metal hydroxide]: 1×10^{-2}M, [picric acid]: 7×10^{-5}M in H_2O; [crown ether unit]: 3×10^{-4}M or 5×10^{-4}M(in parentheses) in $CHCl_3$

(crown ether) III were attained readily.

The tacticity, conversion, and molecular weight of four kinds of poly(crown ether)s III obtained here are listed in TABLE 1. The tactic poly(crown ether)s, (iso-III) and (syndio-III), have 94% isotacticity and 84% syndiotacticity in tactic triads, respectively. The tacticities of (atac-III) and (rad-III) are almost the same, which resemble those of usual radical polymers.

Preliminary solvent extraction was carried out from alkali metal picrate (Na^+, K^+, Rb^+, and Cs^+) aqueous solution with poly(crown ether) chloroform solution, in order to estimate cation-complexing abilities of poly(crown ether)s III with various tacticities. High cation-complexing ability of crown ethers generally brings about high extractability of them for cations (PEDERSEN 1968). The results of the respective systems are shown in TABLE 2. For all poly(crown ether)s employed here, the extractability is in the following order, $K^+ > Rb^+ > Na^+ \approx Cs^+$. Taking account into the fact that K^+ and Rb^+ are able to form 2:1(crown ether/cation) complexes with benzo-15-crown-5 (PEDERSEN 1970, MALLINSON et al. 1972), the high extractability for these cations could be derived from a sort of cooperative effect of poly(crown ether) in formation of the 2:1(crown ether unit/cation) complexes (KOPOLOW et al. 1973, KIMURA et al. 1978). It should be noted that the extractability of (iso-III) for K^+ and Rb^+ is significantly larger than those of three other poly(crown ether)s, although little difference among the poly(crown ether)s was observed in the extractability for Na^+ and Cs^+. That is to say, (iso-III) is a little more selective for K^+ and Rb^+ than the other poly(crown ether)s. Thus, the effect of the microstructure of poly(crown ether)s on the cooperative action of two adjacent crown ether moieties might be reflected in their extractability and cation-complexing ability.

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