

mpound which is much higher than 3 or 4, but still lower than that of MAP. Although the original goal has not been achieved yet, this study demonstrates the importance of the orientation of molecules in the crystal lattice in determining second-order NLO properties of crystalline materials. Further work is under way to improve the SHG efficiency of MAP by structural modifications.

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Polymer-Supported Crown Ethers(IV) Synthesis and Phase-transfer Catalytic Activity

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Immobilization method of lariat azacrown ethers, containing hydroxyl group in the side arm of crown ring, on the polymer matrix and the phase-transfer catalytic activity of thus obtained immobilized lariat azacrown ethers were studied. Polystyrene resins with crown ether structures and hydroxyl groups adjacent to the macrorings were prepared by the reaction of crosslinked polystyrene resins containing epoxy groups with monoaza-15-crown-5 or monoaza-18-crown-6. Microporous crosslinked polystyrene resins containing epoxy group for the syntheses of these immobilized lariat crown catalysts were prepared by suspension polymerization of styrene, divinylbenzene (DVB 2%) and vinylbenzyl glycidyl ether. The immobilized lariat catalysts with 10-20% ring substitution exhibited maximal activity for the halogen exchange reactions of 1-bromooctane with aqueous KI or NaI under triphase heterogeneous conditions. Immobilized catalyst exhibited higher activity than corresponding catalyst without the hydroxyl group and this result was suggested that the active site have a structure in which the K^+ ion was bound by the cooperative coordination of the crown ring donors and the hydroxyl group in the side arm.

Introduction

Polymer-supported quaternary ammonium and phospho-

onium ions, crown ethers, and cryptands are phase-transfer catalysts for reactions between water-soluble salts and water-insoluble organic substrates^{1,2}. When the polymer is inso-

luble, the reaction mixture is triphase, and the catalyst can be separated from the reaction products by simple filtration³. Ease of separation in batch reactions, suitability for use in flow reactors and reuse of the catalyst make polymer-supported catalysts attractive for new industrial chemical processes.

One drawback to polymer-supported catalysts is that their activity may be substantially lower than that of analogous soluble phase-transfer catalysts because reaction rates are limited by diffusional processes⁴. Recently, the introduction of a spacer arm between the catalytic moiety and the polymer support was carried out to improve these disadvantages⁵. Attempts to improve the activity of polystyrene-supported crown ethers, this paper reports the syntheses and the phase-transfer catalytic activities of polystyrene resins containing crown ether moieties and hydroxyl groups adjacent to the macrorings.

Resins I are expected to have high catalytic activity results from the cooperative action of the crown ether unit and the adjacent hydroxyl groups.

Experimental

Materials. Chloromethylstyrene was purchased from Seimi chemical, Japan, as a mixture of meta- and para-isomers (6:4, technical 91%). Monoaza-15-crown-5 and monoaza-18-crown-6 were prepared by Gokel's method as described before⁶. N-Methylpyrrolidone (NMP) was refluxed and distilled over CaH₂ under reduced pressure. Other reagents and solvents obtained commercially were used without further purification.

Measurements. IR spectra were taken using a Shimadzu FTIR-4000 spectrophotometer. ¹H-NMR spectra were recorded on a 60 MHz instrument (JNM-PMX60) using CDCl₃ as solvent and tetramethylsilane as internal standard. Epoxide content was determined by the HCl-dioxane method⁷. A 10 ml Erlenmeyer flask with a stopper was charged with 300 mg of the resin and 0.1 M of HCl in 1,4-dioxane (100 ml). The mixture was stirred by a magnetic bar at room temp. for 2 h and titrated with 0.1 M methanolic NaOH, using cresol-red as indicator. Hydroxyl content was determined by acetylation with an acetic anhydride-pyridine mixture⁸. A 15 ml culture tube with a Teflon-lined screw cap was charged with 0.1 g of the resin was swelled for 0.5 h, 1 ml of 1:3 (v/v) acetic anhydride-pyridine was added into the tube. The tube was heated for 3 h at 80°C, cooled to room temperature, and 2 ml of H₂O was added to the mixture. Then, the tube was heated for 0.5 h at 80°C and cooled to room temperature. The contents were transferred into an Erlenmeyer flask using 30 ml of H₂O. The mixture was titrated with 0.1 N methanolic NaOH using phenolphthalein as indicator.

Bromide ion content was determined as follows: A sample of resin (0.20 g) was held in 5 ml of N,N-dimethylformamide for 2 h and 5 ml saturated aqueous NaNO₃ was added. After 20 h the mixture was diluted with 100 ml of water and titrated by the Volhard method⁹.

Crown ether content was determined by adsorption of KSCN¹⁰. A 10 ml vial with a cap was charged with polymer-supported crown (30-150 mg) and a 2.2×10⁻²M solution of potassium thiocyanate in a dioxane-methanol (92:8 by vol)

mixture (5 ml, ca. 2 mol equiv. on the basis of the supported crown). The mixture was shaken and then allowed to stand for 20-22 h at room temperature. Next 2.0 ml of the liquid was diluted with 100 ml of water and 0.1 N of aqueous silver nitrate (1.0 ml) was added to the solution. The excess of silver ion was titrated with ammonium thiocyanate. The crown content was calculated from the thiocyanate concentrations of the original and resulting solutions.

The weight of imbibed solvent was determined as follows: Dry catalyst (0.02 g) was weighed into a tared fritted tube and soaked at room temperature for 20 h in toluene or methanol. Excess liquid was removed by centrifugation (3,000 rpm) and the tube was weighed. The amount of imbibed solvent in the catalyst was determined from its gain in weight.

Phase-transfer reactions were followed by GLC on a Shimadzu 4C-PT thermal conductivity instrument with a 2 m glass column of Silicone GE SF-96 on Chromosorb W AW DMCS at 170°C. The temperature of the oil bath used for kinetic experiments was controlled (±0.1°C) by use of a Yamato Model BF-61 heat controller.

Synthesis of 2,3-Epoxypropyl vinylbenzyl ether. A 1,000 ml three-necked flask was charged with sodium acetate (3.0 mol), water (170 ml), chloromethylstyrene (1.0 mol), benzene (150 ml), tetrabutylammonium hydrogen sulfate (0.05 mol), and hydroquinone (1.0 g). The mixture was stirred mechanically at 60°C for 15 h. After cooling, the organic layer was separated, washed with water, dried over anhydrous MgSO₄, and concentrated. The resulting residue was distilled under reduced pressure, in the presence of 1,1-diphenyl-2-picrylhydrazyl (DPPH), to give acetoxymethyl styrene in 80% yield; bp. 74-80°C (1 mbar) (Lit.¹¹: bp. 136-139°C (20 mbar)); IR (neat): 1730 (C=O), 1620 cm⁻¹ (C=C).

A 500 ml four-necked flask was charged with aqueous 50 wt.% NaOH (64 g: 0.80 mol), 240 ml of ethanol, and 0.20 g of hydroquinone. Acetoxymethylstyrene (0.80 mol) was added dropwise, over a period of 3 h, to the stirring mixture at reflux temperature, and the mixture was stirred for additional 1 h at the same temperature. After the reaction mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with benzene. The organic layer, combined with the benzene extract, was dried over anhydrous MgSO₄ and concentrated. The resulting viscous oil was distilled i.vac. in the presence of DPPH, to give hydroxymethylstyrene in 80% yield; bp. 79-84°C (2 mbar) (Lit.¹²: bp. 132-137°C (20 mbar)); IR (neat): 3300 (OH), 1630 cm⁻¹ (C=C); ¹H-NMR (CDCl₃): δ=4.04 (1H, s; OH), 4.44 (2H, s; benzylic CH₂), 5.10-5.82 (2H, m; CH₂=), 6.42-6.90 (1H, m; CH=), 7.20-7.43 (4H, m; phenylene) A 500 ml four-necked flask was charged with aqueous 50 wt.% NaOH (180 g: 2.3 mol), epichlorohydrin (1.3 mol), and tetrabutyl ammonium hydrogen sulfate (0.01 mol). Hydroxymethylstyrene (0.25 mol) was added dropwise, over a period of 1 h, to the stirred mixture at 25°C. The reaction mixture was poured into water, and the organic layer was separated. The aqueous layer was extracted with benzene and the extract combined with the organic layer was dried over anhydrous MgSO₄. After evaporating benzene the residue was distilled twice i.vac. to give ether in 55% yield; bp. 100-104°C (0.15 mbar) (Lit.¹³: b.p. 100°C (0.15 mbar)); IR (neat): 1630 (C=C), 1100 (C-O-C), 910 cm⁻¹ (epoxy); ¹H-NMR CDCl₃: δ=2.52-2.85

(2H, m; CH₂ of epoxy), 3.08-3.28 (1H, m; CH of epoxy), 3.44-3.85 (2H, m; CH₂-epoxy), 4.57 (2H, s; benzylic CH₂), 5.14-5.83 (2H, m; CH₂=), 6.50-6.95 (1H, m; CH=), 7.19-7.34 (4H, m; phenylene).

Synthesis of 4-Bromobutylstyrene. A solution of vinylbenzyl magnesium chloride (0.33 mol) in ether (200 ml) was added dropwise to a stirred solution of 1,3-dibromopropane (0.33 mol) in tetrahydrofuran (THF, 300 ml) that contained lithium tetrachlorocuprate¹⁴ (3 mmol) in the temperature range of 5-10°C in a nitrogen atmosphere. After the addition was completed the mixture was stirred for an additional 5 h at room temperature and 10 ml of methanol was added dropwise to the mixture. The reaction mixture was concentrated i.vac., poured into water, and extracted with benzene. The benzene layer was dried over anhydrous MgSO₄, concentrated, and the residue was distilled i.vac. in the presence of DPPH to give 4-bromobutylstyrene in 58% yield; bp. 105°C (0.13 mbar); IR (neat): 1610 (C=C), 1250 (CH₂Br), 560 cm⁻¹ (CH₂Br); ¹H-NMR (CDCl₃): δ=1.63-1.83 (4H, m; CH₂), 2.40-2.67 (2H, m; benzylic CH₂), 3.23-3.47 (2H, m; CH₂Br), 4.97-5.78 (2H, m; CH₂=), 6.40-6.67 (1H, m; CH=), 6.87-7.30 (4H, m; phenylene).

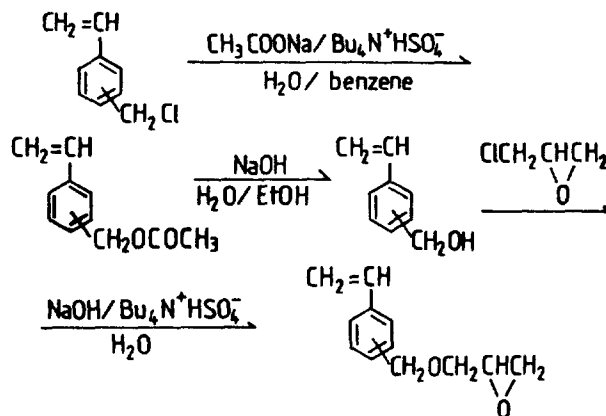
Synthesis of a Microporous Polystyrene Resin Containing 2,3-epoxy Propoxymethyl Groups.

A solution of 1 g of gelatin, 10 g of polyamino-sulfone A (from Nittobo, Japan), and 3.7 g of boric acid and 0.1 g of sodium nitrite in 300 ml of water was adjusted to pH 8.5 with 25 wt.% aqueous NaOH and added to a 500 ml three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer. A solution of monomer, styrene, divinylbenzene (DVB) (technical, 55 wt.%; 2 mol), and 2,2'-azobisisobutyronitrile (AIBN) was added into the flask. The flask was purged with nitrogen for 0.5 h, and the mixture was stirred (~380 rpm) at 70°C for 20 h. The insoluble polymer was isolated by using a fritted glass funnel, washed thoroughly with water and acetone and dried i.vac. at 60°C for 20 h. The yield of microporous polystyrene, crosslinked with 2 mol% of DVB, was 66%. By use of the same procedure 4-bromobutylated polystyrene was prepared in 86% yield. The control of ring substitution (RS) can be easily carried out in this copolymerization method.

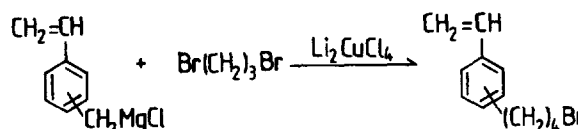
Reaction of Glycidyl-containing Polystyrene with Monoazacrown Ethers.

A typical run is as follows. A 50 ml three-necked flask was charged with 4.40 g of epoxy-propoxymethylated polystyrene resin (epoxide content: 2.26 meq/g; crosslinked with 2 mol% of DVB), monoaza-15-crown-5 (6.6 g, 30 mmol) and 1,4-dioxane (20 ml). The mixture was stirred at 80°C for 5 days under nitrogen. After cooling, polymer beads were separated using a fritted glass funnel, washed thoroughly with acetone, THF, dichloromethane, and dried i.vac. at 60°C. Yield (of product): 6.66 g. The hydroxyl and crown ether contents were 1.60 and 1.52 meq/g, respectively. The degree of loading determined from gain in weight was 1.47 meq/g.

Reaction of Br-containing Polystyrenes with Monoazacrown Ethers. A 50 ml three-necked flask was charged with 4.1 g of 4-bromobutylated polystyrene (Br content: 1.7 meq/g; crosslinked with 2 mol% of DVB), NaHCO₃ 2.28 g (27.2 mmol), monoaza-15-crown-5 3.1 g (13.6 mmol) and NMP (30 ml). The mixture was stirred at 90°C for 5 days under nitrogen. After cooling, polymer beads collected



Scheme 1



Scheme 2

in a fritted glass funnel were washed thoroughly with water-dioxane (1:1 v/v), methanol-dioxane (1:1 v/v), dioxane, THF, and dichloromethane, and dried i.vac. at 60°C. Yield (of product): 4.98 g. The crown ether content was 1.26 meq/g. The degree of loading determined from gain in weight was 1.29 meq/g.

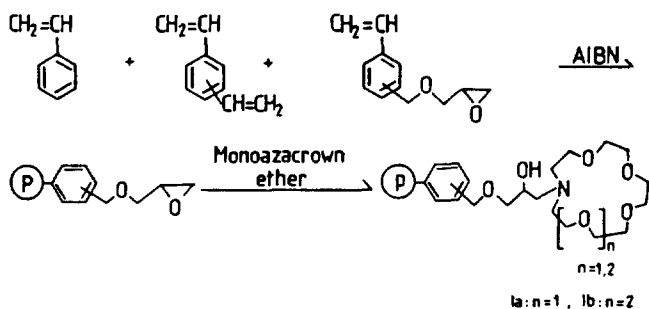
Phase-transfer Reactions. Halogen exchange reactions were studied at 90°C. A 100 ml three-necked flask was charged with 0.02 mol equiv. of the catalyst (based on 1-bromooctane), 20 ml of an organic solvent, 0.10 mol of NaI or KI, 15 ml of water, and 0.5 g of *p*-cymene (internal standard for GLC). The mixture was stirred mechanically at 200 rpm for 1h to condition the catalyst. 1-Bromooctane (20 mmol) was added at time=0, the stirring speed was increased to 500-550 rpm, and samples of the organic phase were analyzed periodically by GLC.

Results and Discussion

The reaction of hydroxymethylstyrene with 1-chloro-2,3-epoxypropane (epichlorohydrin) proceeds smoothly under phase-transfer conditions¹⁵ (Scheme 1). The structure was confirmed by ¹H-NMR and IR spectral data. This monomer can be easily prepared and copolymerized with a variety of vinyl monomers¹⁶. In comparison with previous method¹⁷, this is a convenient route to polystyrene derivatives carrying epoxy group. 4-bromobutylstyrene was prepared by cross coupling¹⁴ of vinylbenzyl magnesium chloride with 1,3-dibromopropane in reasonable yields (Scheme 2). The structure of the monomer was confirmed by its ¹H-NMR and IR spectral data.

Because vinylbenzyl chloride and α, ω -dibromoalkanes are readily available commercially, this is a convenient route for the preparation of ω -bromoalkylstyrene¹⁸.

Preparation and Characterization of Polystyrenes Containing Hydroxyl Groups and Monoazacrown Ether Units. Microporous polystyrene resins having hy-

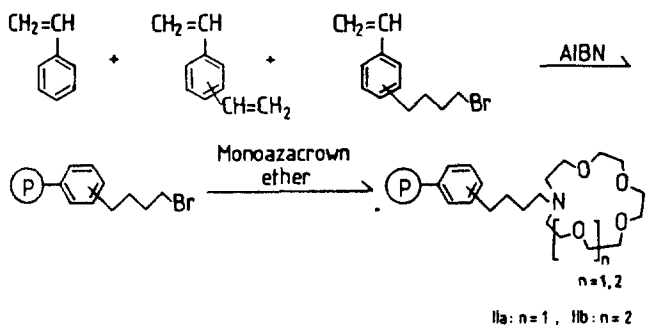


Scheme 3

Table 1. Characterization of Polystyrene Resins with OH and Monoazacrown Structure

Polymer-supported crown	Monoazacrown unit	Loading(mequiv/g)		Ring substitution(%)
		crown ^a	OH ^b	
Ia	15-crown-5	0.46	—	5
		0.65	0.54	9
		1.22	1.20	20
		1.52	1.60	28
		1.71	1.81	38
Ib	18-crown-6	0.77	—	9
		1.07	—	18
		1.44	—	27

^aCrown ether determined by KSCN adsorption method. ^bHydroxyl group content determined by acetylation method.



Scheme 4

hydroxyl groups and monoazacrown ethers units were successfully prepared by the reaction of monoazacrown ethers with epoxide-containing polystyrene resins crosslinked with 2 mol% of divinylbenzene (Scheme 3). The ring-opening reaction of the epoxide predominantly affords polymer with secondary hydroxyl groups and monoazacrown units¹⁹. The results are summarized in Table 1. The IR spectra of polymer showed a strong absorption band at 3400 cm⁻¹ due to the hydroxyl group and a very weak absorption due to the epoxy group at 905-910 cm⁻¹. The analysis of epoxide contents indicated the negligible (<3%) presence of the unreacted epoxy groups in the product resins. These results conclude that polymer contains equimolar amounts of the secondary hydroxyl group and the crown ether structure.

Polymer-supported crown ethers II were prepared from ω-bromoalkylated polystyrene resins and monoazacrown

Table 2. Characterization of Polymer-supported Crown Ethers

Polymer-supported crown	Spacer	Monoazacrown unit	Crown content ^a (mequiv/g)	Ring substitution (%)
IIa	(CH ₂) ₄	15-crown-5	0.60	7
			1.26	22
			1.59	26
IIb		18-crown-6	1.30	23

^aDetermined by adsorption of KSCN.

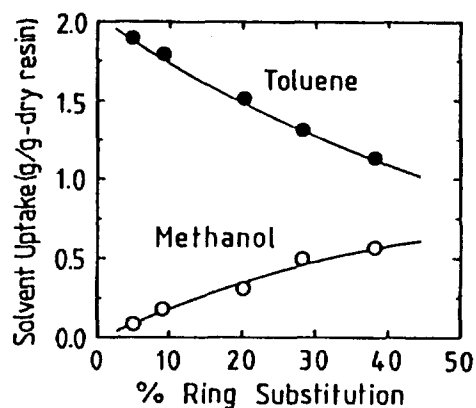


Figure 1. Swellability of polystyrene resins Ia containing monoaza-15-crown-5 unit and hydroxyl group. The amount of solvents imbibed into resins was determined on the basis of weight of dry resins (60-100 mesh) at room temperature.

ethers (Scheme 4). The IR spectrum of polymer II, compared with the 4-bromobutylated polystyrene, show a new absorption at 1100 cm⁻¹ due to the ether group, and a decreased absorption at 1250 cm⁻¹ due to the Br group.

Table 2 lists the polymer-supported crown ethers prepared and their loadings of crown moiety.

The affinity of polymer Ia for toluene and methanol is reported in Figure 1. The amounts of toluene and methanol imbibed into polymer beads correlate with the lipophilicity and hydrophilicity, respectively, of the beads^{20,21}; these parameters are convenient to examine the relative characteristics among a series of polymers with similar functional groups, though they may not always indicate the inherent lipo- and hydrophilicity under tri-phase conditions²².

The hydrophilicity of polymers Ia with monoaza-15-crown-5 structure increased with increasing RS and the lipophilicity showed an opposite tendency. This result can be attributed to the increased hydroxyl group and crown ether unit in the polymers.

Phase-transfer Catalytic Activity in Halogen Exchange Reaction. The phase-transfer catalytic activity of I and II was examined using the conversion of 1-bromooctane to iodoctane under tri-phase conditions as a typical reaction, and was evaluated by using pseudo-first-order rate constants (k_{obsd}). Figure 2 reports the effect of the structure of active site on the activity of catalyst I and II. Catalyst Ia with both OH group and monoaza-15-crown-5 unit had higher activity than corresponding catalyst IIa, without OH group. A particularly large difference in activity was observed

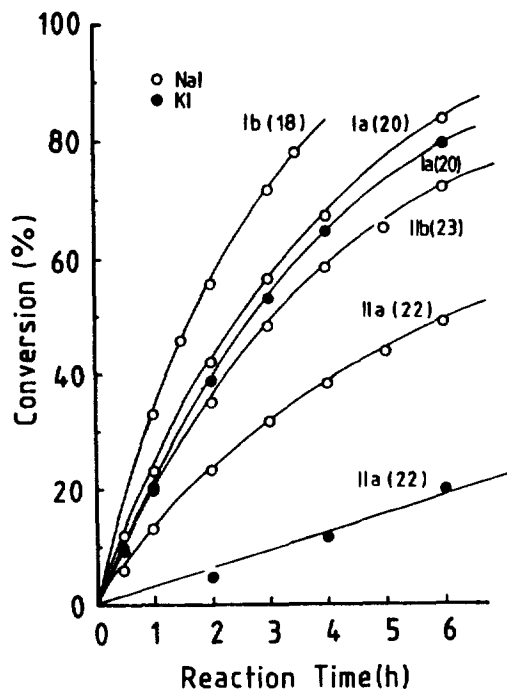
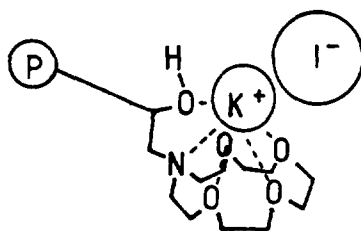


Figure 2. Dependence of catalytic activity of polystyrene resins with OH and crown ether unit in the halogen exchange reaction of 1-bromooctane on active site structure.



Scheme 5

for the reaction with KI. These results suggest that the high activity of catalyst Ia results from the cooperative action of the crown ether unit and the adjacent hydroxyl group (Scheme 5).

The structure of the complex was expected to resemble that of lariat crown ether complexes such as K^+ complex of N-(2-methoxyethyl)-monoaza-15-crown-5²³.

Catalyst with monoaza-18-crown-6 structure had increased catalytic activity for the halogen exchange reaction. An increment in activity, however, was smaller than that in the case of the catalyst with monoaza-15-crown-5 structure.

Table 3 and Figure 3-5 reports the dependence of the activity of catalyst I and II on the percentage of RS.

The catalyst Ia with 10-20% RS exhibited maximal activity for the halogen exchange reaction. Such a dependence has been observed for other immobilized phase-transfer catalyst^{10,20,21}.

The low activity of low ring-substituted (5-10%) catalysts is due to the low hydrophilicity or high lipophilicity of the catalyst (Figure 1). The reduced hydrophilicity results in slow intraparticle diffusion of reagent KI or NaI and hence the depressed formation of active site, which should be less

Table 3. Dependence of k_{obsd} in the Reaction of 1-Bromooctane on the Percent of Ring Substitution

Polymer-supported crown ether	Monoazacrown unit	Ring substitution(%)	$10^5 k_{obsd}(s^{-1})$	
			NaI	KI
Ia	15-crown-5	5	6.44	1.00
		9	11.30	4.19
		20	7.73	7.07
		28	3.42	4.21
		38	—	2.79
Ib	18-crown-6	9	9.54	9.87
		18	11.42	10.07
		27	3.46	4.04
IIa	15-crown-5	7	1.76	0.40
		22	4.00	0.96
		26	3.25	0.50
IIb	18-crown-6	23	6.00	11.00

^aReaction conditions: 1-Bromooctane, 20 mmol; Reagent, 100 mmol; Crown unit, 0.40 mmol; Catalyst particle size, 60-100 mesh; H_2O (15 ml)-toluene (20 ml); 90°C; stirring speed, 500-550 rpm.

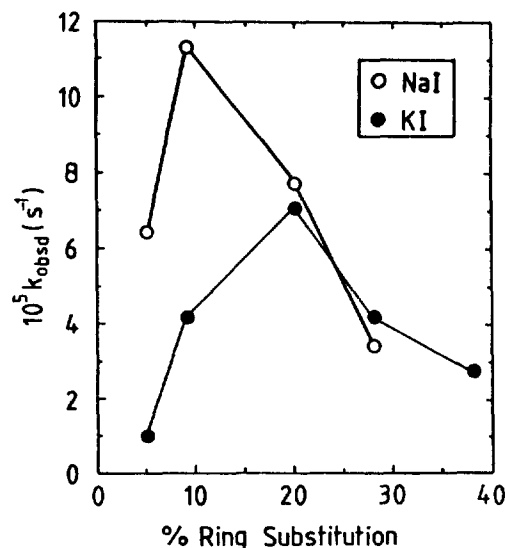


Figure 3. Dependence of activity of catalyst Ia with monoaza-15-crown-5 unit for the reaction of 1-bromooctane with NaI or KI on % ring substitution.

hydrated species with high intrinsic reactivity. The low activity of the high ring-substituted (20-40%) catalysts is attributed to the low reactivity of the more hydrated iodide anion in the catalyst with high hydrophilicity.

The catalysts having a proper hydrophile-lipophile balance, which results from RS of ca. 10-20% in this case, have eventually maximal apparent activity.

The relatively high activity of low ring-substituted catalysts was observed for the reaction using NaI instead of KI. This suggests that the active site produced from NaI is more highly hydrated than that produced from KI and a better hydrophile-lipophile balance is attained for the catalyst with

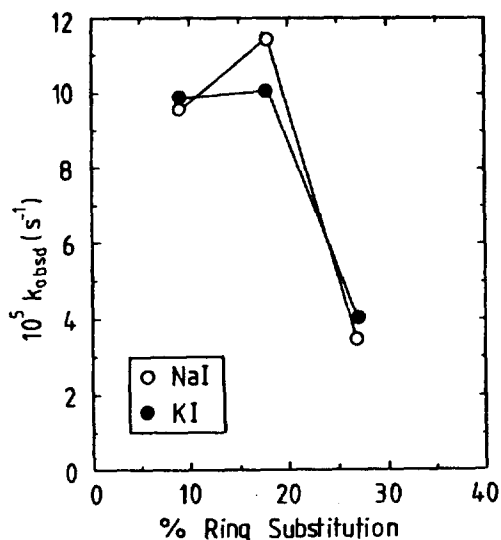


Figure 4. Dependence of activity of catalyst Ib with monoaza-18-crown-6 unit for the reaction of 1-bromooctane with NaI or KI on % ring substitution.

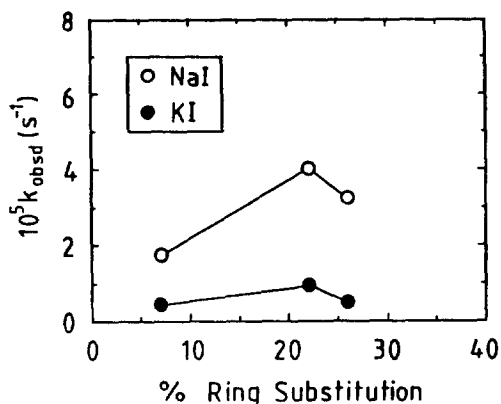


Figure 5. Dependence of activity of catalyst IIa with monoaza-15-crown-5 unit for the reaction of 1-bromooctane with NaI or KI on % ring substitution.

lower RS; this is on the basis of the fact that the order of hydration numbers of alkali metal cations is $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.²⁴

It is well-known that the size of potassium ion is suited to the cavity size of 18-membered crown ethers²⁵. It has been also reported that the activity of polymer-supported monoaza-18-crown-6 for halogen exchange reactions with KI is higher than that of immobilized monoaza-15-crown-5. Catalyst IIb showed the same tendency.

In conclusion, polystyrene-supported crown ethers with hydroxyl groups adjacent to the macrorings were prepared by the reaction of monoazacrown ethers with polystyrene resins containing epoxide groups. The polymer-supported catalyst with 15- or 18-membered crown rings and OH adjacent to the ring exhibited higher activity for halogen-exchange

reaction under tri-phase conditions than corresponding catalysts without OH group in the side arm.

The active site is considered to have a structure in which the crown ring and the OH bind alkali metal ion by the cooperative coordination.

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