Polymer (Korea) Vol. 16, No. 3, pp 285－290 (1992)

고분자 물질로 지지된 크라운 에테르류 : 5. Lariat Azacrown Ether의 합성

심 재 후 · 정 광 보 · 마사오 도모이*
동국대학교 공과대학 화학공학과 · *일본 橫浜국립대학 공학부 물질공학과
(1992년 1월 6일 접수)

Polymer-Supported Crown Ethers : 5. Syntheses of Lariat Azacrown Ethers

Jae Hu Shim, Kwang Bo Chung, and Masao Tomoi*
Dept. of Chemical Engineering, Dongguk University, Pil-Dong, Joong-Gu, Seoul 100-715, Korea
**Dept. of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama 240, Japan*
(Received January 6, 1992)

요 약 : Crown 환 측쇄부에 oxyethylene쇄를 갖는 lariat형 monoazacrown 구조를 고분자상에 고정화하는 방법에 대해 검토하였다. Oxyethylene쇄에 의해 polystyrene에 결합된 crown ether는 2-hydroxyethoxy기나 2-(2-hydroxyethoxy)ethoxy기 함유 가교 polystyrene의 수산기를 tosyl화 하여 얻은 2-tosyloxyethoxy 또는 2-(2-tosyloxyethoxy)ethoxymethyl화 polystyrene 수지와 monoazacrown ether와의 반응에 의하여 합성하였다. 이는 여러 종류의 crown ether를 poly(oxyethylene)쇄에 의해 polystyrene 담체에 고정화시킬 수 있는 일반적인 방법을 제공할 것이다. 이들 lariat azacrown ether에 대응하는 측쇄에 산소를 갖지않는 단순한 고정화 crown ether는 ω-Br함유 가교 polystyrene과 monoazacrown ether와의 반응에 의하여 합성하였다.

Abstract : Immobilization methods of lariat azacrown ether, containing oxyethylene spacer in the sidearm of crown ring, on the polymer matrix were studied. Crown ethers bound to polystyrene resins by oxyethylene spacer were obtained by the reaction of monoazacrown ether with 2-tosyloxyethoxy- or 2-(2-tosyloxyethoxy)ethoxy methylated polystyrene resins, derived from tosylation of 2-hydroxyethoxy- or 2-(2-hydroxyethoxy)ethoxymethylated polystyrene resins. This method presented a convenient route to immobilize various crown ether structure on polystyrene supports by poly(oxyethylene) spacers. Polymer supported simple crown ethers without oxygen donors in the spacer chain corresponding to the above lariat azacrowns were obtained by the reaction of crosslinked ω-bromoalkylated polystyrene resins with monoazacrown ether.

INTRODUCTION

Crown ether moieties immobilized on polymeric supports are effective catalysts for aqueous-organic two-phase reaction.[1~11]

Crown ethers with additional donor atoms in the side arms of the macrorings are called as lariat crown ethers.[12~15]

The lariat ethers can bind alkali metal cations by cooperative coordination of the crown ring donors and the side chain donors : The binding ability of the lariat crowns is generally higher than that of crown ether with simple alkyl side chains.

This paper reports on the syntheses of crown ethers attached on polystyrene supports by oxyethylene spacers.

EXPERIMENTAL

Materials

Monoaza-15-crown-5 and monoaza-18-crown-6 were prepared by Gokel's method.[16] Crosslinked polystyrene resins containing hydroxyl groups were prepared by suspension polymerization of styrene, divinylbenzene (DVB)(2mol%), and hydroxyl-containing styrene derivatives as described previously.[16]

Polystyrene-supported monoazacrown ethers with heptamethylene spacers were prepared by the method described previously.[16] Other reagents and solvents obtained commercially were used as received.

Measurements

IR spectra were taken using a Shimadzu FTIR-4000 spectrophotometer. ^{1}HNMR spectra were recorded on a 60 MHz instrument (JNM-PMX 60) using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Hydroxyl content was determined by acetylation with an acetic anhydride-pyridine mixture.[16] Crown ether content was determined by adsorption of KSCN.[8,16] The amount of imbibed solvent into catalysts was determined from gain in weight of the catalysts by using a fritted tube at room temperature.[16,17]

Synthesis of 2-(vinylbenzyloxy)ethanol[18]

A 1L four-necked flask was charged with 3.4 mol of ethylene glycol, 2 mol of sodium hydroxide and 2 g of hydroquinone. After the mixture was stirred at 80℃ for 2 h, 1 mol of chloromethylstyrene (a mixture of meta- and para-isomers (6 ; 4), technical, 91%) was added dropwise over a period of 30 min to the stirring mixture at 80℃. The reaction system was stirred at the same temperature for an additional 20 min. After cooling, the mixture was poured into a brine (ca. 15%), and the organic layer was separated. The aqueous layer was extracted with toluene and extract, combined with the organic layer, was washed with a brine and dried over anhydrous $MgSO_4$. After evaporation of toluene the residue was distilled under reduced pressure, in the presence of 1,1-diphenyl-2-picrylhydrazyl : b.p. 100-105℃ (0.35-0.40 torr) ; yield, 69%.

IR(neat) : 3400(OH), 1630(C=C), 1100 cm^{-1} (C-O-C)

^{1}HNMR($CDCl_3$) : δ=2.50(s ; OH), 3.52-3.84 (m ; OCH_2CH_2O), 4.54(s ; benzylic CH_2), 5.17-5.91(m ; CH_2=), 6.54-7.04(m ; CH=), 7.24-7.38 (m ; phenylene)

2-(2-Vinylbenzyloxyethoxy)ethanol was prepared in a similar manner from diethylene glycol and chloromethylstyrene : b.p. 116-120℃ (0.30-0.40 torr) ; yield, 54%

IR(neat) : 3400(OH), 1625(C=C), 1100 cm^{-1} (C-O-C)

^{1}HNMR($CDCl_3$) : δ=3.32(s ; OH), 3.53-3.70 (m ; OCH_2CH_2O), 4.67(s ; benzylic CH_2), 5.30-6.03(m ; CH_2=), 6.63-7.17(m ; CH=), 7.34-7.57 (m ; phenylene)

7-Bromoheptylstyrene was prepared in a similar manner from vinylbenzyl magnesium chloride (60/40 meta/para) and 1,6-dibromohexane by the procedure described[16] : b.p. 118-120℃ (0.3 torr) ; yield, 35%

IR(neat) : 1610(C=C), 1250(CH_2Br), 560 cm^{-1} (CH_2Br)

^{1}HNMR($CDCl_3$) : δ=1.37-1.92(m ; CH_2), 2.47-2.70(m ; benzylic CH_2), 3.23-3.47(m ; CH_2Br),

5.10-5.90(m ; CH_2=), 6.63-6.93(m ; CH=), 6.93-7.43(m ; phenylene)

Tosylation of Hydroxyl-containing polystyrene resins[19]

A 100 mL three-necked flask was charged with 4.50 g of 2-hydroxyethoxymethylated polystyrene beads (OH content, 2.23 mequiv/g ; crosslinked with 2 mol% of DVB), *p*-toluenesulfonyl chloride (94.07 g, 20.1 mmol), di-isopropylamine (4.07 g, 40.2 mmol), and carbon tetrachloride (40 mL). The mixture was stirred at a reflux temperature for 6 h under nitrogen. After cooling, the separated polymer beads were washed thoroughly with methanol/dioxane(1 : 1 v/v), dioxane, tetrahydrofuran(THF), and dichloromethane, and dried at 60℃ in vacuo ; yield of tosylated product, 4.46 g(92%)

Immobilization of Crown Ether Structures on Polystyrene Resins

A 50 mL three-necked flask was charged with 5.50 g of 2-tosyloxyethoxymethylated polystyrene resin (tosyl content, 1.16 mequiv/g), monoaza-15-crown-5(7.0 g, 31.8 mmol), and acetonitrile (20 mL). The mixture was stirred at 80℃ for 5 days under nitrogen. After cooling, polymer beads were separated using a fritted glass funnel, washed thoroughly with dioxane/water(1 : 1 v/v), dioxane/methanol (1 : 1 v/v), dioxane, THF, and dichloromethane, and dried at 60℃ in vacuo : yield of crown-containing polymer Ia, 5.84 g ; degree of loading, 1.34 mequiv/g.

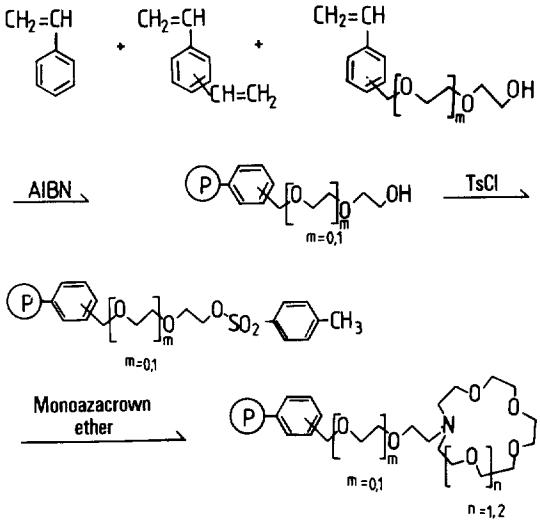
RESULTS AND DISCUSSION

Microporous polystyrene resins containing lariat azacrown ether moieties were successfully prepared by the reaction of monoazacrown ethers with 2-tosyloxyethoxymethylated or 2-(2-tosyloxyethoxy)ethoxymethylated polystyrene resins crosslinked with 2 mol% of DVB(Scheme 1). The tosylated resins were obtained by tosylation of polystyrene resins having ethylene or diethylene glycols moieties according to the method of Darling and Frechet.[19] The tosylation and the immobilization of the azacrowns proceeded in high yields : In the

Table 1. Characterization of Polymer-supported Lariat Crown Ethers

Polymer-supported lariat crown	Oxyethylene spacer	Monoazacrown unit	Crown content[a] (mequiv/g)	Ring substitution(%)
Ia	$CH_2OCH_2CH_2$ (m=0)	15-crown-5 (n=1)	0.62	8
			0.98	14
			1.34	22
			1.57	29
			1.95	44
Ib	〃	18-crown-6 (n=2)	0.92	14
			1.28	23
			1.55	32
IIa	$CH_2OCH_2CH_2OCH_2CH_2$ (m=1)	15-crown-5 (n=1)	0.84	12
			1.24	22
			1.53	31
			1.75	42
			1.95	54
IIb	〃	18-crown-6 (n=2)	0.76	11
			1.24	23
			1.46	32

[a] Determined by adsorption of KSCN



Ia : m=0, n=1 IIa : m=1, n=1

Ib : m=0, n=2 IIb : m=1, n=2

Scheme 1

comparison of IR-spectrum, tosylated resin, compared with the original one, shows a new absorption due to tosyl group, and a decreased absorption at 3400 cm^{-1} due to the hydroxyl group. In the immobilized crowns I and II, absorption at 1100 cm^{-1} due to the ether group was appeared.

Table 1 list the polymer-supported lariat azacrown ethers prepared. The loading of crown residues could be controlled with ease by changing the hydroxyl content of the starting polystyrene beads. This is a convenient route to immobilize various crown ether structures on polystyrene supports by poly(oxyethylene) spacers, though the immobilized lariat crown ethers can be also synthesized by the reaction of hydroxyl-containing crowns and chloromethylated polystyrenes.[20]

Table 2 list the polymer-supported monoazac-

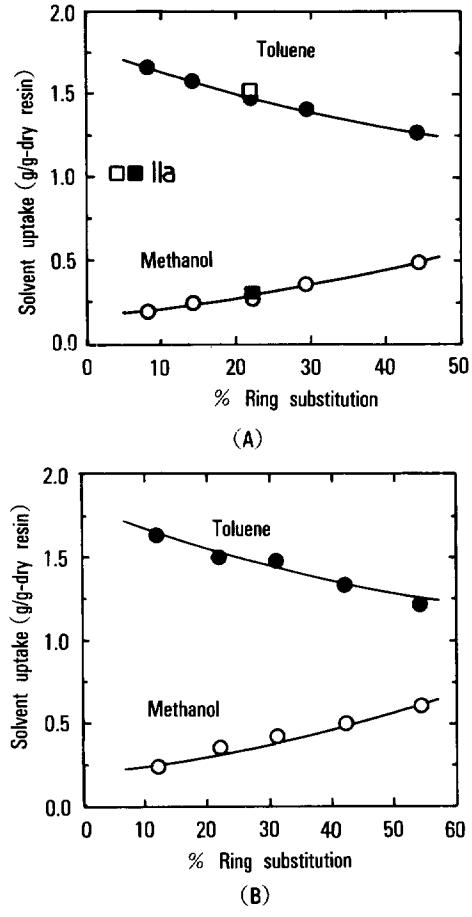


Fig. 1. Effect of percentage of ring substitution on the amount of solvents imbibed into immobilized catalyst with monoaza-15-crown-5 unit. (A) : catalyst Ia with oxyethylene spacer of m=0. (B) : catalyst IIa with oxyethylene spacer of m=1. The amount was determined on the basis of weight of dry catalyst(60-100 mesh) at room temperature. Fig. (A) also contains data for IIa with tetramethylene spacer (□, ■), presented in a previous paper.[16]

Table 2. Characterization of Polymer-supported Crown Ethers

Polymer-supported crown	Spacer	Monoazacrown unit	Crown content[a] (mequiv/g)	Ring substitution(%)
	$(CH_2)_7$	15-crown-5	1.19	20
		18-crown-6	1.21	22

[a] Determined by adsorption of KSCN

rown ethers with heptamethylene spacers prepared.

Fig. 1 and 2 reports the dependence of the amount of toluene or methanol, imbibed into catalysts I and II at room temperature, on the percentage of ring substitution (RS).

The affinity of supported catalysts with similar active sites for toluene and methanol corresponds to the lipophilicity and hydrophilicity, respectively, of the catalysts.[16,21,22]

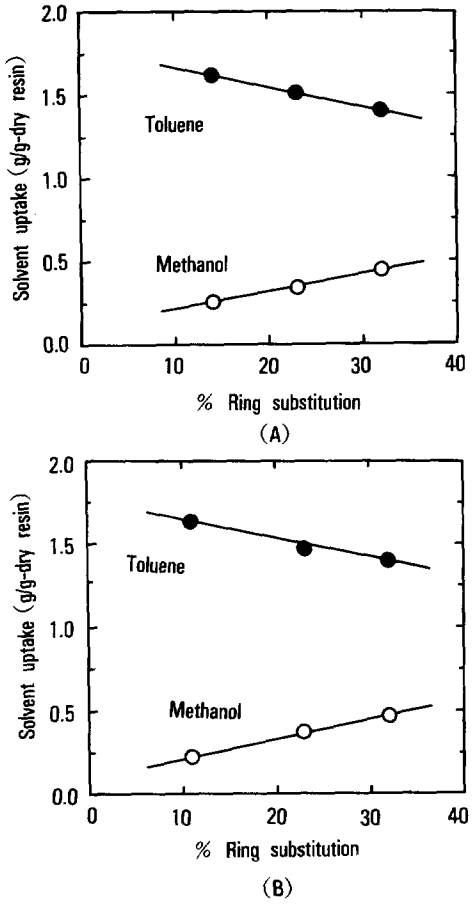


Fig. 2. Effect of percentage of ring substitution on the amount of solvents imbibed into immobilized catalyst with monoaza-18-crown-6 unit. (A) : catalyst Ib with oxyethylene spacer of m=0. (B) : catalyst IIb with oxyethylene spacer of m=1. The amount was determined on the basis of weight of dry catalyst(60-100 mesh) at room temperature.

The decreased lipophilicity or increased hydrophilicity with increasing RS is due to an increase in the content of the hydrophilic crown ether unit in the supported catalysts. It is interesting that the affinity hardly depends on the structure of the spacer chain : catalysts Ia and IIa containing one oxygen and two oxygens, respectively, in the spacer chain were similar in the affinity, which was analogous to that of catalyst IIa with no oxygen in the spacer, presented in a previous paper[16] (see Fig. 1A).

The catalysts with monoaza-15-crown-5 structure exhibited the lipo- and hydrophilicity similar to those of the catalysts with monoaza-18-crown-6 structure(Fig. 2). This must be attributed to the similar amphiphilic nature of both the crown structures.

In conclusion, polystyrene-supported lariat azacrown ethers were prepared by the reaction of monoazacrown ethers with polystyrene resins containing ω-tosyloxylated groups. This synthetic method presented a more general route to immobilize various crown ether structures on polystyrene supports by poly(oxyethylene) spacers than a traditional method, synthesized by the reaction of hydroxyl-containing crowns and chloromethylated polystyrene.

REFERENCE

1. S. L. Regen, *Angew. Chem. Int. Ed. Engl.*, **18**, 421 (1979).
2. F. Montanari, D. Landini, and F. Rolla, *Top. Curr. Chem.*, **101**, 147 (1982).
3. W. T. Ford and M. Tomoi, *Adv. Polym. Sci.*, **55**, 49 (1984).
4. J. Smid and R. Sinta, *Top. Curr. Chem.*, **121**, 105 (1984).
5. M. Tomoi and W. T. Ford, in Syntheses and Separations Using Functional Polymer, D. C. Sherrington and P. Hodge, Eds., Wiley, Chichester, 1988.
6. A. van Zon, F. de Jong, and Y. Onwezen, *Recl. Trav. Chim. Pays-Bas*, **100**, 429 (1981).
7. G. Manecke and A. Kramer, *Makromol. Chem.*,

182, 3017 (1981).
8. M. Tomoi, N. Yanai, S. Shiiki, and H. Kakiuchi, *J. Polym. Sci. Polym. Chem. Ed.*, **22,** 911 (1984).
9. P. L. Anelli, B. Czech, F. Montanari, and S. Quici, *J. Am. Chem. Soc.*, **106,** 861 (1984).
10. F. Montanari, S. Quici, and P. L. Anelli, *Brit. Polym. J.*, **16,** 212 (1984).
11. M. J. Pugia, A. Czech, B. P. Czech, and R. A. Bartsch, *J. Org. Chem.*, **51,** 2945 (1986).
12. G. W. Gokel and S. H. Korzeniowski, Macrocyclic Polyether Syntheses, Springer-Verlag, Berlin, 19 82.
13. G. W. Gokel, et al., "New Chemistry, Catalysis, and Application", in "Phase-Transfer Catalysis", C. M. Starks, ed., ACS Symp. Ser., 326, Am. Chem. Soc., Washington, D. C., 1987.
14. E. Weber, "Crown Ether and Analogs", S. Patai, Z. Rappoport, eds., Wiley, New York, 1984.
15. G. W. Gokel and J. E. Trafton, "Cation Binding by Macrocycles", Y. Inoue, G. W. Gokel, eds., Marcel Dekker, New York, 1990.
16. Submitted to *Bulletin of The Korean Chemical Society*.
17. M. Tomoi and W. T. Ford, *J. Am. Chem. Soc.*, **103,** 3821 (1981).
18. M. Tomoi, H. Oda, and H. Kakiuchi, *Makromol. Chem.*, **189,** 277 (1985).
19. G. D. Darling and J. M. J. Frechet, *J. Org. Chem.*, **51,** 2270 (1986).
20. B. Valter, V. Janout, H. Hrudkova, P. Cefelin, N. G. Lukyanenko, S. S. Basok, and E. Y. Kurigina, *Polym. Bull.*, **22,** 261 (1989).
21. M. Tomoi, E. Ogawa, Y. Hosokawa, and H. Kakiuchi, *J. Polym. Sci. Polym. Chem. Ed.*, **20,** 3421 (19 82).
22. M. Tomoi, T. Suzuki, and H. Kakiuchi, *React. Polym.*, **10,** 27 (1989).