

LINEAR POLYSILOXANE WITH DIBENZO-18-CROWN-6 MOIETIES AS LIQUID MEMBRANE CARRIER*

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ABSTRACT

A modified method of preparing crown functionalized linear polysiloxane has been described. 4'-Allyldibenzo-18-crown-6 was subjected to hydrosilylation with methylchlorosilane, followed by polycondensation with silanol-terminated polydimethylsiloxane to give the title crown functionalized linear polysiloxane. The transport properties of sodium, potassium, and ammonium salt through a bulk liquid membrane system using the new type of crown functionalized linear polysiloxane as a carrier were investigated. It is worthy to point out that the carrier can be used repeatedly at least six runs with no apparent change in the transport rate of potassium ion.

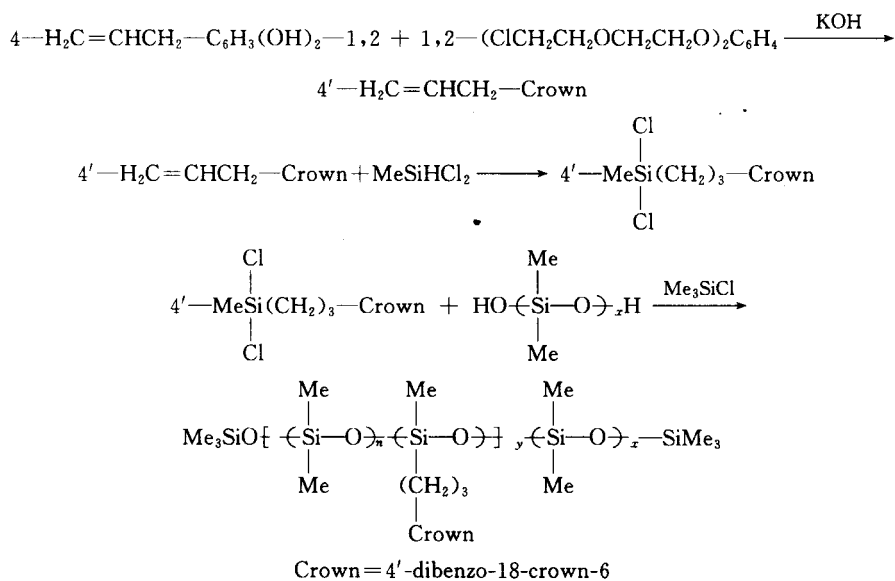
Crown ether is one of the best carriers using in the liquid membrane system. However, its lipophilicity is not enough to satisfy the need of stable liquid membrane in general, as it is not so soluble in the membrane phase and easy leaching out from the membrane phase. The increased lipophilicity was accomplished by introduction of alkyl, aryl, or aralkyl groups onto the ring of crown ether, but the lifetime of these membrane is still limited. Attaching the crown ethers to the polymer backbone is another feasible route, although often accompanying the decrease of solubility in the membrane phase. Recently, Wienk et al. synthesized polysiloxane-coupled crown ethers via coupling hydroxymethyl crown ethers with 4-bromobutyl-terminated polydimethylsiloxane and used them as carriers in supported liquid membrane, and found that the stability of the membrane was

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improved considerably^[1]. However, the application of this synthetic method is limited, and the density and the distribution of the crown ether moieties in the polymer can not be adjustable.

There are several routes for the preparation of crown functionalized polysiloxanes. Besides the above mentioned one, we have obtained them by hydrosilylation of 3'-or 4'-allylbenzo-15-crown-5 with methyldichlorosilane, followed by hydrolysis of the obtained silicon monomers with water directly^[2]. As far as we know, these are the first examples of crown functionalized linear polysiloxane. In 1987, Bayona et al. adopted a modified route, i. e. hydrosilylation of allyloxymethyl-18-crown-6 with polymethylhydrosiloxane^[3]. However, the solubilities of the polymers obtained by the above methods in organic solvents are often small, and not suitable to use as the carriers in liquid membrane^[4]. In this paper, we wish to report a new modified route for the preparation of crown functionalized linear polysiloxane, which has enough solubility in the organic solvent, and also, the density and distribution of crown ether moieties in polymer are adjustable. The synthetic scheme is shown below:



The transport properties of the above polymer as carrier in the bulk liquid membrane system were investigated in detail.

EXPERIMENTAL

PMR, IR, and UV spectra were obtained on EM-360-L spectrometer,

Nicolet 170 SX FT-IR spectrometer, and UV-240 spectrometer, respectively. Elemental analysis was carried out on a MOD 1106 elemental autoanalyzer. 4-Allylcatechol and 1, 2-bis (β -(β' -chloroethoxy) ethoxy)-benzene were synthesized according to Refs. [5] and [6], respectively.

Synthesis of 4'-allyldibenzo-18-crown-6

1, 2-Bis (β -(β' -chloroethoxy) ethoxy) benzene (9.6 g, 0.03 mol) was added slowly to a mixture composed of 4-allylcatechol (4.5 g, 0.03 mol), iso-pentanol (90 mL), water (6 mL), and potassium hydroxide (3.5 g, 0.064 mol) at reflux temperature under nitrogen atmosphere. Stirring was continued for 30 h. The cooled mixture was filtered, and the filtrate was distilled under reduced pressure. The residue was dissolved in dichloromethane, and then 200 g of activated alumina was added. After the solvent was evaporated, the solid residue was transferred to Soxhlet apparatus and extracted with carbon tetrachloride for 24 h. A slightly yellow solid was obtained by evaporation of the solvent from the extract. The crude product was recrystallized from benzene. 6.0 g of 4'-allyldibenzo-18-crown-6 was obtained as colourless crystal. The yield was 50%. Calcd. for $C_{23}H_{28}O_6$: C 68.98, H 7.05; Found: C 69.05, H 7.09. PMR: 6.8—6.2 (m, 7H, ArH), 6.0—4.5 (m, 3H, $H_2C=CH$), 4.3—3.7 (m, 16H, OCH_2), 3.3—3.0 (d, 2H, $=C-CH_2$) ppm. IR: 3078, 1646, 1594, 1508, 1258, 1233, 1137, 1050, 991, 908, 860, 738 cm^{-1} . MS: m/z 400 (M^+).

Hydrosilylation of 4'-allyldibenzo-18-crown-6

A mixture of 4'-allyldibenzo-18-crown-6 (2.0 g, 5 mmol), methyldichlorosilane (2.3 g, 20 mmol), 20 mL of THF, and 2 drops of 0.1 mol $\cdot$ L $^{-1}$ $H_2PtCl_6 \cdot i\text{-PrOH}$ solution was stirred at ambient temperature for 2 h, and then at reflux temperature for 20 h. After removing THF and unreacted methyldichlorosilane, a viscous oil was obtained in 96.5% yield. Its PMR spectra showed that no peak of protons attached to double bond appeared and a new triple peak around 0.5 ppm due to the protons of Si— CH_2 appeared. The obtained 4'-methyldichlorosilylpropyl-dibenzo-18-crown-6 was used directly in the next step without further purification.

Synthesis of dibenzo-18-crown-6 functionalized linear polysiloxane

Five mmol of 4'-methyldichlorosilylpropyl-dibenzo-18-crown-6 was dissolved in 20 mL of benzene and added dropwise, with stirring, to a solution of silanol-terminated polydimethylsiloxane (6.0 g, 10.5 mmol) in 20 mL of benzene under nitrogen atmosphere. Stirring was continued for 10 h.

1.5 mL of trimethylchlorosilane was added to this system, and the reaction was continued for 10 h. Benzene and excess of trimethylchlorosilane were removed by distillation under reduced pressure. The residue was dissolved in dichloromethane, washed with water until the rinsed water remained neutral. A solid product (7.5 g, 82%) was obtained after distilling off the solvent. $\bar{M}_n = 3060$ (VPO). IR: 2962, 2862 (ν_{C-H}), 1563, 1517 ($\nu_{C_6H_5}$), 1093—1022 ($\nu_{Si-O-Si}$ and ν_{C-O-C}) cm^{-1} . According to the analytical data of UV spectroscopy, the crown ether content was 4.85×10^{-4} mol of polysiloxane/g.

Liquid membrane transport experiment

The liquid membrane experiments were performed at $25 \pm 0.2^\circ C$ in the vessel described in Ref. [7]. The volume of the receiving phase (a), source phase (b), and membrane phase (c) was 10.0, 10.0, and 30.0 mL, respectively. The interfaces between a and c, b and c were 5.31 and 7.89 cm^2 . Various kinds of salt solution were used as source phase, and doubly distilled water was used as receiving phase. The amount of salt through the bulk membrane was monitored by measuring the conductivity of the receiving phase using DDS-II A conductivity meter and electrode with a cell constant of $9.8\ cm^{-1}$.

RESULTS AND DISCUSSION

1. *Effect of salt concentration on transport rate*

Various concentrations of potassium chloride aqueous solution were used as source phases to investigate the effect of salt concentration on the transport rate through bulk liquid membrane. A plot of salt concentration in receiving phase versus time was made as shown in Fig. 1. It shows that the transport rate increases with the increasing of salt concentration.

2. *Influence of the crown ether concentration*

The transport rate is very sensitive to the variation of crown ether concentration as shown in Fig. 2. The larger the crown ether concentration, the higher the transport rate, and the shorter the induction period.

3. *Influence of the kind of cation*

Potassium chloride, ammonium chloride, and sodium chloride were

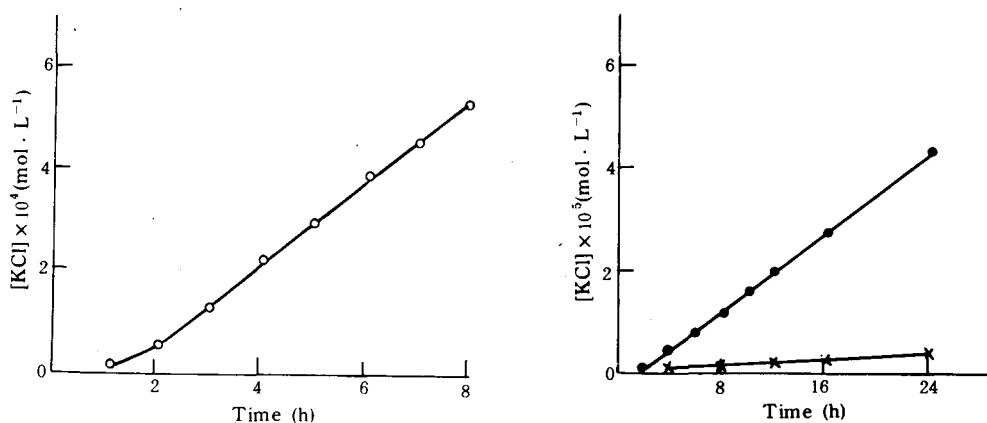


Fig. 1 Plot of $[KCl]$ in receiving phase vs. time with various concentrations of KCl in source phase
 (○) 1.0; (●) 0.10; (×) 0.05 $\text{mol} \cdot \text{L}^{-1}$
 Conditions: $[\text{Carrier}] = 0.01 \text{ mol} \cdot \text{L}^{-1}$; Solvent: HCCl_3

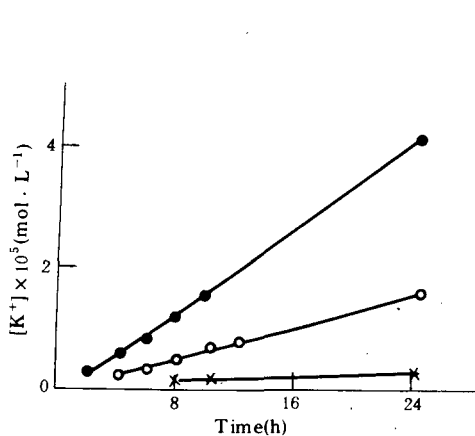


Fig. 2 Plot of K^+ concentration in receiving phase vs. time with various concentrations of carrier
 (○) 5.0×10^{-3} ; (●) 1.0×10^{-2} ;
 (×) $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$
 Conditions:
 $[KCl] = 0.01 \text{ mol} \cdot \text{L}^{-1}$;
 Solvent: HCCl_3

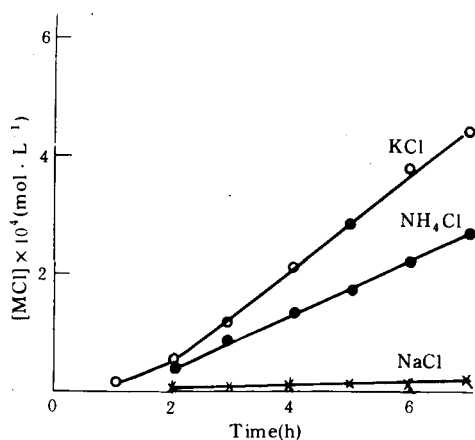


Fig. 3 Plot of salt concentration in receiving phase vs. time for KCl, NH_4Cl and NaCl
 Conditions:
 $[\text{Carrier}] = 0.01 \text{ mol} \cdot \text{L}^{-1}$;
 $[\text{Salt}] = 1.0 \text{ mol} \cdot \text{L}^{-1}$

used as probe to examine the influence of the kind of cation on transport

rate. As it can be seen from Fig. 3, the title crown ether exhibits high selectivity for transport K^+ in comparison with Na^+ . This can be explained as size effect, i. e. the ionic radius of K^+ (13.8 nm) is almost identical to the radius of 18-crown-6 cavity (14.0 nm).

4. Influence of the kind of anion

Fig. 4 shows that the differences of transport rates among various potassium salts are remarkable. These can be rationalized due to the difference of Gibbs free energies of hydration of various anions. The smaller Gibbs free energy of hydration, the faster transport rate^[7].

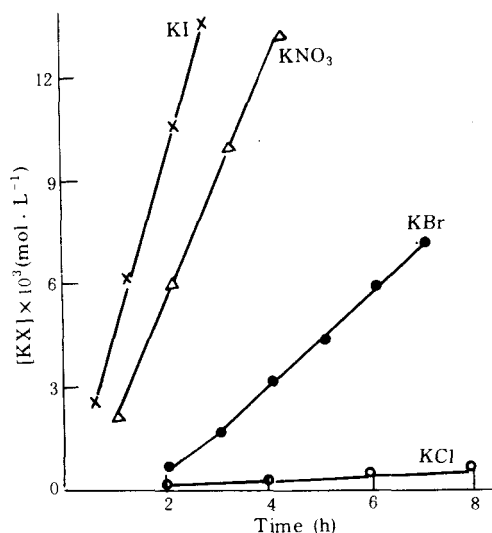


Fig. 4 Plot of salt concentration in receiving phase vs. time for potassium iodide, nitrate, bromide, and chloride
Conditions:
[Carrier] = 0.01 mol · L⁻¹;
[Salt] = 1.0 mol · L⁻¹; Solvent: HCCl₃

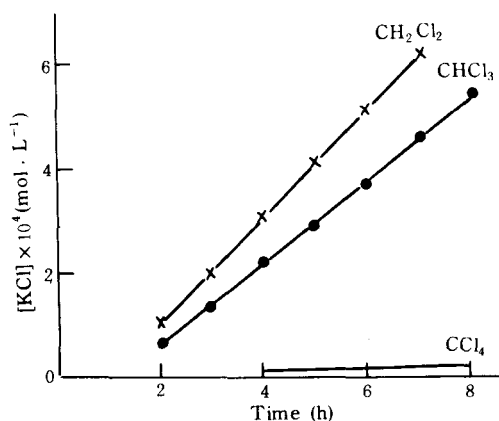


Fig. 5 Plot of KCl concentration vs. time using CH₂Cl₂, CHCl₃ and CCl₄ as solvent respectively
Conditions:
[Carrier] = 0.01 mol · L⁻¹;
[KCl] = 1.0 mol · L⁻¹

5. Influence of the kind of solvent

It is known that the polarity of solvent influences the transport rate of salts through a bulk liquid membrane containing crown ethers as carriers^[8]. This is also true for the title polymer-mediated transport. The transport rate increases remarkably with the increase of solvent polarity, as shown in Fig. 5.

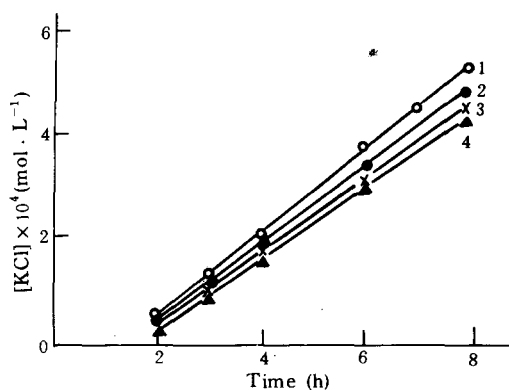


Fig. 6 Plot of KCl concentration vs. time in sequential run (1)1st, (2)2nd, (3)3rd—5th, (4)6th
Conditions: $[\text{Carrier}] = 0.01 \text{ mol} \cdot \text{L}^{-1}$; $[\text{Salt}] = 1.0 \text{ mol} \cdot \text{L}^{-1}$; Solvent: HCCl_3

6. Stability of the liquid membrane system

In order to estimate the stability of the title liquid membrane system, experiments were carried out in such a way. After 8 h measurement, the source phase and the receiving phase were renewed, and the membrane phase was washed with twice distilled water throughout, and then the transport experiment was repeated. The experiment results were shown in Fig. 6. From it, we can see that the transport rate of potassium chloride has no apparent change with the increasing run. The stability of the liquid membrane is enhanced in comparison with that of simple crown ethers as expected.

Keywords:

Liquid membrane; Crown ether; Polysiloxane; Ion transport; Ionophore

REFERENCES

- [1] Wienk, M. M. ; Stolwijk, T. B. ; Sudhölter, E. J. R. , et al. , *J. Am. Chem. Soc.* , **1990**, *112*, 797.
- [2] Chen, Y. Y. and Yuan, G. P. , 2nd China-Japan-USA Symposium on Organometallic and Inorganic Chemistry, Shanghai, China, B Ilc, **1982**, p. 135.
- [3] Bayona, J. M. ; Tarbet, B. J. ; Chang, H. C. , et al. , *Intern. J. Environ. Anal. Chem.* , **1987**, *28*, 263.
- [4] Brisdon, B. J. ; England, R. ; Reza, K. , et al. , *Tetrahedron* , **1993**, *49*, 1103.
- [5] Chen, Y. Y. and Yuan, G. P. , *Chem. J. Chin. Univs.* (in Chinese), **1983**, *4*, 458.
- [6] Liu, B. S. , *Org. Chem.* (in Chinese), **1990**, *10*, 255.
- [7] Lamb, J. D. ; Christensen, J. J. ; Izatt, S. R. , et al. , *J. Am. Chem. Soc.* , **1980**, *102*, 3399.
- [8] Tian, X. M. and Xue, T. J. , *Membrane Separation Science and Technology* (in Chinese), **1983**, *3*(4), 14.