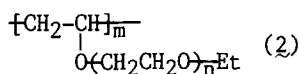# Transport of alkali metal ions by comb-like poly(vinyl ethers) with pendant poly(oxyethylene) chains*

Toshinobu Higashimura**, Takayuki Nakamura, and Sadahito Aoshima

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto, 606 Japan

SUMMARY

    Comb-like poly(oxyethylenes) ($\underset{\sim}{2}$), prepared by the HI/I_2-initiated living cationic polymerization of vinyl ethers carrying a poly(oxyethylene) pendant, were found to transport alkali metal ions (Li^+, Na^+, K^+, and Cs^+) through a dichloromethane liquid membrane at 25°C. Polymer $\underset{\sim}{2}$ with four oxyethylene units per pendant (n = 4) transported all the four cations (best for K^+), and more effective as an ion carrier than its non-polymeric counterpart (tetraglyme), whereas $\underset{\sim}{2}$ with n = 0 [poly-(ethyl vinyl ether)] was virtually ineffective. The observed polymeric effect indicates an enhancement of ion transport via a cooperative action of the neighboring poly(oxyethylene) pendants. Related vinyl ether co-polymers consisting of poly(oxyethylene) (n = 4) and hydrophobic phenoxyl pendants were inferior to $\underset{\sim}{2}$ as ion-transport carriers, but introduction of hydrophilic alcoholic pendants into $\underset{\sim}{2}$ (n = 4) facilitated the transport of the smaller cations (Li^+ and Na^+).

$$\begin{array}{c} +CH_2-\underset{\underset{\textstyle O(CH_2CH_2O)_{\overline{n}}Et}{|}}{CH}\overline{}_m \end{array} \quad (\underset{\sim}{2})$$
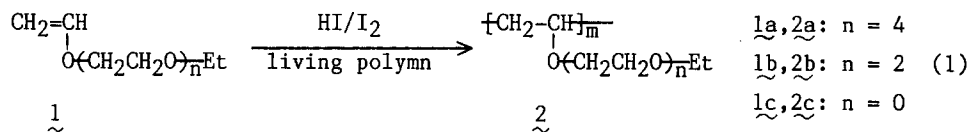
INTRODUCTION

    Long before the discovery of crown ethers and their binding and transport of ionic solutes, non-cyclic poly(oxyethylenes) were known to bind cations of alkali metals and alkali earth metals (2). Detailed knowledge is available for their ion binding properties as a function of the number of oxyethylene units per molecule and the structure of the end groups (3). Poly(oxyethylene)-containing compounds have been designed and examined as carriers for metal-ion transport and as phase-transfer catalysts; recent examples include a telechelic poly(oxyethylene) capped with strongly coordinating end groups ("non-cyclic crown ether") (4) and "polypode ligands" that carry 3 - 6 poly(oxyethylene) chains in one molecule (5,6). Although these compounds are unique in structure and show interesting properties, they are difficult to synthesize, requiring a multistepped synthesis.
    Recently, we prepared comb-like poly(oxyethylenes) ($\underset{\sim}{2}$) by a single step synthesis based on the living cationic polymerization of vinyl ether $\underset{\sim}{1}$ with a poly(oxyethylene) chain (n = 1 - 4) in the pendant (eq 1) (1); see $\underset{\sim}{5}$ below for a schematic illustration of the comb-like structure of $\underset{\sim}{2a}$ (n = 4). The living nature of the polymerization enabled us to control the

---

$$CH_2=CH \xrightarrow[\text{living polymn}]{HI/I_2} \ \overline{+CH_2-CH\frac{}{}}_m$$

CH$_2$=CH
  O$+$CH$_2$CH$_2$O$\overline{)_n}$Et $+$CH$_2$-CH$\overline{)_m}$
               O$+$CH$_2$CH$_2$O$\overline{)_n}$Et

1a,2a: n = 4
1b,2b: n = 2   (1)
1c,2c: n = 0

1   2

molecular weight of the poly(vinyl ether) backbone and thereby the number of the anchored poly(oxyethylene) side chains per molecule; the molecular weight distribution of the backbone is almost monodisperse. The synthesis of monomer 1 is also straightforward (1); the length of the poly(oxy-ethylene) moiety can thus be predetermined.

    In this study, noting the facile structural control of 2, we investigated the binding and transport of alkali metal ions by the comb-like poly-(oxyethylene) through a liquid membrane. The ion transport property of 2 was evaluated as a function of the chain length (n) of the pendant and further compared with those of its non-polymeric counterparts (glymes) and copolymers of 1a with a vinyl ether carrying a hydrophobic (phenoxy) (3) or a hydrophilic (hydroxyl) pendant (4). The structure of the carrier polymers employed in this study is shown in Figure 1. The ion binding to poly(oxyethylene) ligands anchored to poly(methyl methacrylate) has been studied (7), but our ion-binding/transport study is the first for the combination of a poly(vinyl ether) backbone and poly(oxyethylene) side chains.
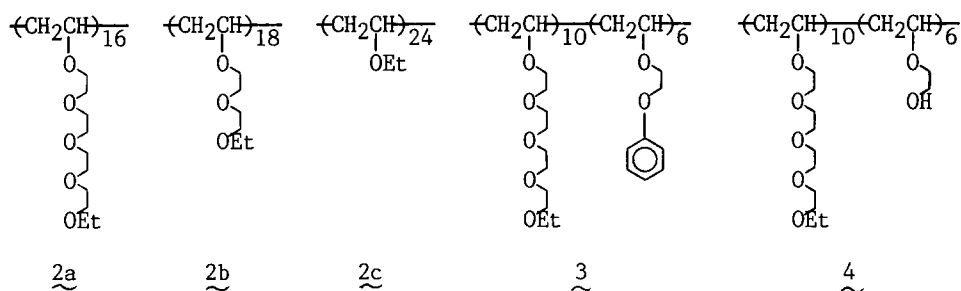
Figure 1. Structure of carrier polymers.

RESULTS AND DISCUSSION

Effects of the Chain Length of Poly(oxyethylene) Pendants

    As carriers for the transport of alkali metal ions, comb-like poly-(oxyethylenes) (2a - 2c) with different chain lengths (n = 0 - 4) were prepared by the living cationic polymerization of 1 initiated by the hydrogen iodide/iodine system (Table 1) (1); 2c [poly(ethyl vinyl ether)] was employed as a reference polymer that has the same backbone as 2a and 2b but lacks a poly(oxyethylene) legand. All the samples shown in Table 1 have nearly the same degree of polymerization ($\overline{DP}_n \sim 20$) and a very narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n \cong 1.1$), so that the effects of polymer molecular weight and its distribution upon ion transport can safely be ignored.

Table 1

Synthesis of Carrier Polymers[a]

$([HI]_0/[I_2]_0 = 10/2$ (mM), toluene, $-40^{\circ}C)$

Polymer	$\bar{M}_n$[b]	$\overline{DP}_n$	$\bar{M}_w/\bar{M}_n$[b]
2a (n = 4)	4500	16	1.13
2b (n = 2)	2900	18	1.11
2c (n = 0)	1800	24	1.07
3	3700	16	1.14
4	3500	16	1.22

a) See Figure 1 for structural details.
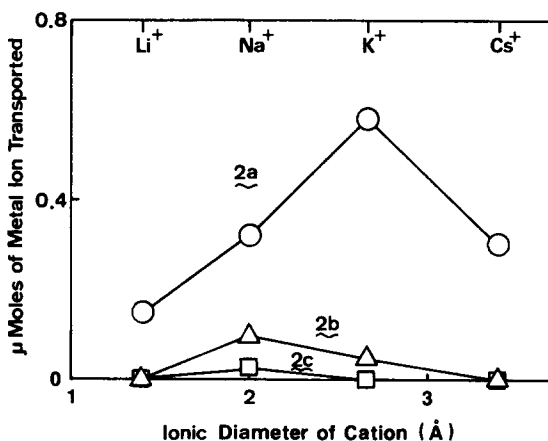b) By size exclusion chromatography; polystyrene calibration.

Figure 2. Transport of alkali metal ions by polymeric carriers 2a-2c: effects of ionic diameter and the length (n) of poly(oxyethylene) pendants. [carrier] = 1.0 mM, [metal nitrate] = 1.0 M, at 25°C for 5 hr.

The transport of ionic solutes by carrier polymer 2 was studied for four alkali metal cations (Li+, Na+, K+, and Cs+) in a three-phase system in a U-shaped tube where a solution (liquid membrane) of 2 in dichloromethane was placed between layers of an aqueous solution of an alkali metal nitrate (phase I) and pure deionized water (phase II) (see Experimental). Figure 2 shows the amount of the metal ions transported from phases I to II through the liquid membrane in 5 h, as a function of their ionic diameters.

For all metal cations, the ion transport increased in the order: 2c (n = 0) < 2b (n = 2) < 2a (n = 4). 2a was more or less selective for K^+, ca. 12 times more effective than 2b, whereas 2b and 2c showed almost no selectivity for the ion size. The virtual absence of ion delivery by 2c shows that the pendant poly(oxyethylene) moiety, rather than the ether oxygen adjacent to the main chain, plays a critical role in binding and transporting metal ions.

Polymeric versus Monomeric Carriers: Polymeric Effects

Figure 3 compares the ion transport by 2a (n = 4; $\overline{DP}_n$ = 16) and that by tetraethylene glycol dimethyl ether [tetraglyme; $CH_3(OCH_2CH_2)_4OCH_3$] as its nonpolymeric counterpart having the same poly(oxyethylene) moiety. The comparison was made for carrier solutions containing the same number of ether oxygens. Under these conditions, polymeric carrier 2a transported all the ions better than tetraglyme; in particular, the difference was considerable for the larger cations like K^+ and Cs^+. Such polymeric effects indicate a cooperative action of the neighboring poly(oxyethylene) pendants in binding (and transporting) a metal cation, as schematically illustrated in 5, which may be more important for a larger ion that is too large to be bound to a single tetraglyme molecule.

Separate experiments, however, showed that 2a is inferior as an ion carrier to the corresponding crown ether (18-crown-6; 1,4,7,10,13,16-hexaoxacyclooctadecane).
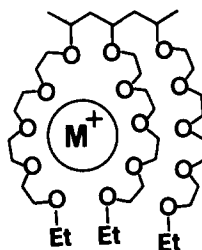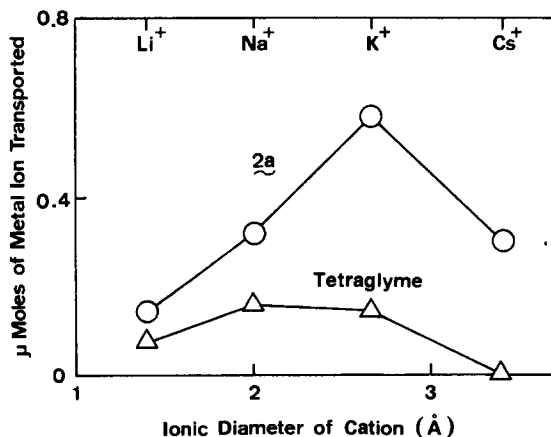

5

Figure 3. Transport of alkali metal ions by polymer 2a and tetraglyme: polymeric effects. [2a] = 1.0 mM, [tetraglyme] = 16 mM, [metal nitrate] = 1.0 M, at 25°C for 5 hr.

Under the conditions for the ion transport experiments (Fig. 2), the amounts of metal ion delivery for 18-crown-6 and 2a were as follows (in 10^{-8}mol, for 5 hr):

	Li^+	Na^+	K^+	Cs^+
18-crown-6	14.4	102	1260	523
2a	14.4	32.1	58.1	30.1

The crown ether was comparable to polymer 2a for the transport of Li^+, but was much more effective for the larger ions like K^+ and Cs^+.

The interaction (binding) of the potassium cation with 2a or tetraglyme was further studied by measuring the apparent extraction constant (K_{ex}) (8) for the water/dichloromethane system, which is defined by eq 2 with the assumption that tetraglyme or each poly(oxyethylene) pendant of 2a forms a 1:1 complex with the potassium nitrate ion pair in the organic solvent:

$$K_{ex} = \frac{[K^+NO_3^-\cdot L]_{org}}{[K^+]_{aq}[NO_3^-]_{aq}[L]_{org}} \qquad (2)$$

where L indicates a carrier and $K^+NO_3^-\cdot L$ the 1:1 complex with potassium nitrate; the subscripts aq and org mean the concentrations in the aqueous and organic solutions, respectively. The extraction experiments gave the following K_{ex} values (in M^{-2}): 2a, 4.53×10^{-2}; tetraglyme, 0.962×10^{-2}. The larger value for 2a shows a better binding of K^+ to the polymeric carrier, which most likely arises from a cooperative effect of neighboring polyether pendants, because we assumed a 1:1 complex between the cation and each poly(oxyethylene) chain of 2a on calculation of K_{ex}.

Copolymers 3 and 4: Effects of Hydrophilic or Hydrophobic Comonomer Units

Copolymer 3, containing hydrophobic phenoxyl pendants, was obtained by living copolymerization between 1a (n = 4) and 2-phenoxyethyl vinyl ether initiated by the HI/I_2 system. The synthesis of copolymer 4 with hydrophilic alcoholic repeat units involved living copolymerization of 1a with 2-benzoyloxyethyl vinyl ether, followed by saponification of the ester pendants into hydroxyl groups (9). As shown in Table 1, both copolymer samples have nearly the same $\overline{DP}_n$ ($\sim$16) as that of the parent homopolymer 2a, as well as a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n \le 1.2$).

Table 2 presents a comparison of the ion-transport properties of 2a, 3, and 4. For all four metals, 3 was much less effective than 2a, which indicates that the introduction of hydrophobic phenoxyl pendants into 2a disturbs the transport (and/or binding) of the cations. In contrast, copolymer 4 with alcoholic comonomer units exhibited an interesting ion-transport propeties when compared with 2a: Although 4 is slightly less effective than 2a as carrier for K^+ and Cs^+, it transported the smaller cations (Li^+ and Na^+) much more than 2a did. Interestingly, 4 showed a selectivity towards Na^+, whereas 2a toward K^+.

Table 2

Transport of Alkali Metal Ions

by Polymeric Carriers[a]

Polymer[b]	Ion Transport (10^{-8}mol)			
	Li$^+$	Na$^+$	K$^+$	Cs$^+$
2a	14.4	32.1	58.1	30.1
3	0.0	19.8	25.6	0.0
4	49.0	229	44.8	20.5

a) [alkali metal nitrate] = 1.0 M;
   [carrier] = 1.0 mM; at 25°C, for 5 hr.
b) See Table 1 and Figure 1.

EXPERIMENTAL

Synthesis of Carrier Polymers

Homopolymers 2a – 2c were prepared by the living cationic polymerization of the corresponding vinyl ethers (1a – 1c) initiated by the HI/I$_2$ system in toluene at –40°C; [HI]$_0$ = 10 mM, [I$_2$]$_0$ = 2.0 mM, [monomer]$_0$/ [HI]$_0$ = 20, conversion ca. 100% (Table 1). Copolymer 3 was synthesized by copolymerizing 1a and 2-phenoxyethyl vinyl ether (10) under similar conditions as for 2. 4 was obtained by alkaline hydrolysis of a copolymer between 1a and 2-benzoyloxyethyl vinyl ether, which was prepared by the HI/I$_2$-initiated copolymerization of the two comonomers in toluene at –40°C (9). Tetraglyme and 18-crown-6 were used as commercially supplied.

Ion Transport Measurement (11)

In the bottom of a U-shaped glass tube was placed a solution of a carrier polymer (1.0 mM) in 20 ml of doubly distilled dichloromethane. On one side of this liquid membrane was then placed 8 ml of a 1.0 M aqueous solution of an alkali metal nitrate (phase I), and on the other side was 8 ml of pure deionized water (phase II). Each phase was gently stirred magnetically or mechanically, so that the two interfaces were kept undisturbed. After stirring for 5 hr at 25°C, the metal ion concentration in phase II was determined by atomic absorption spectrometry on a Jarrel Ash AA780.

Ion Extraction Measurement

An aqueous solution of potassium nitrate (1.0 M, 5 ml) and a carrier solution in doublly distilled dichloromethane (1.0 mM, 5 ml) were vigorously stirred at 25°C for 1 hr, and then allowed to stand for an additional 1 hr for phase separation. The organic layer was separated and subjected to atomic absorption specroscopy to determine the the concentration of the extracted potassium ion.

REFERENCES

1. T. Nakamura, S. Aoshima, and T. Higashimura, <u>Polym. Bull.</u>, <u>14</u>, 515 (1984).
2. As a review, J. Smid, <u>Angew. Chem. Internat. Ed. Engl.</u>, <u>11</u>, 112 (1972).
3. See, for example, J. G. Heffernan, W. M. MacKenzie, and D. C. Sherrington, <u>J. Chem. Soc.</u>, <u>Perkin II</u>, 514 (1981).
4. B. Tummler, G. Maass, F. Vogtle, H. Sieger, U. Heimann, and E. Weber, <u>J. Am. Chem. Soc.</u>, <u>101</u>, 2588 (1979).
5. R. Fornasier, F. Montanari, G. Podda, and P. Tando, <u>Tetrahedron Lett.</u>, 1381 (1974).
6. F. Vogtle and E. Weber, <u>Angew. Chem. Internat. Ed. Engl.</u>, <u>13</u>, 814 (1974).
7. W.-Y. Xu, B. Roland, and J. Smid, <u>Macromolecules</u>, <u>18</u>, 2061 (1985).
8. K. H. Wong, K. Yagi, and J. Smid, <u>J. Membrane Biol.</u>, <u>18</u>, 379 (1984).
9. T. Higashimura, S. Aoshima, and M. Sawamoto, <u>Makromol. Chem.</u>, <u>Macromol. Symp.</u>, <u>3</u>, 99 (1986).
10. J. V. Crivello and D. A. Conlon, <u>J. Polym. Sci.</u>, <u>Polym. Chem. Ed.</u>, <u>21</u>, 1785 (1983).
11. S. Kimura and Y. Imanishi, <u>Biopolymers</u>, <u>23</u>, 563 (1984).