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ION-TRANSPORT ACROSS A MEMBRANE PREPARED BY GLOW DISCHARGE PLASMA POLYMERIZATION OF DICYCLOHEXYL-18-CROWN-6

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Dicyclohexyl-18-crown-6 was "polymerized" on an acetylcellulose membrane by a glow discharge plasma. The membrane prepared under proper conditions showed the K^+ selectivity in ion-transport.

Since the unexpected discovery of dibenzo-18-crown-6 by Pedersen in 1967,[1] the chemistry of crown compounds has rapidly been established as a new field and is steadily increasing. Because of their ability to take up ions and to transfer them across a lipophilic medium, they have widely been used in organic synthesis, in ion-extraction into nonpolar solvents, as chiral complexing agents, etc. The survey of past literatures manifests, importantly, that most materials presently in practical use for these purposes are "polymerized" or "immobilized" crown ethers.[2-7] The crown polymers have been prepared so far by the traditional polymerization methods such as vinyl polymerization, polycondensation, polymer reaction, etc.[8] In these methods one has to synthesize the crown compounds bearing polymerizable functional groups, the synthesis of which is frequently troublesome. It occurred to us that simple crown compounds may be derived to corresponding polymers by plasma polymerization.[9,10] Here, we wish to report a new, convenient method to immobilize crown ethers by a glow discharge plasma. We have found that the membranes prepared under proper conditions retain the structure of the original crown compounds enough to recognized metal ions.

The apparatus of plasma polymerization of dicyclohexyl-18-crown-6(DC18C6) consists of a pyrex glass bell jar and a pair of parallel electrodes connected to an RFG-200 radio frequency generator operating at 13.56 MHz(Samco International Inc.). Polymerization was carried out by evaporating DC18C6 sample at elevated temperature. For this purpose a tungsten filament was specially equipped in the reactor between a pair of electrodes. DC18C6 was heated by two different methods. One is the direct evaporation of the sample from a tungsten basket in which DC18C6 was placed(method A). Another is the indirect heating of the sample with the aid of radiant heat emitted from the filament(method B). In the latter case DC18C6 was placed in a ceramic boat set just below the filament at a distance of 20 mm.

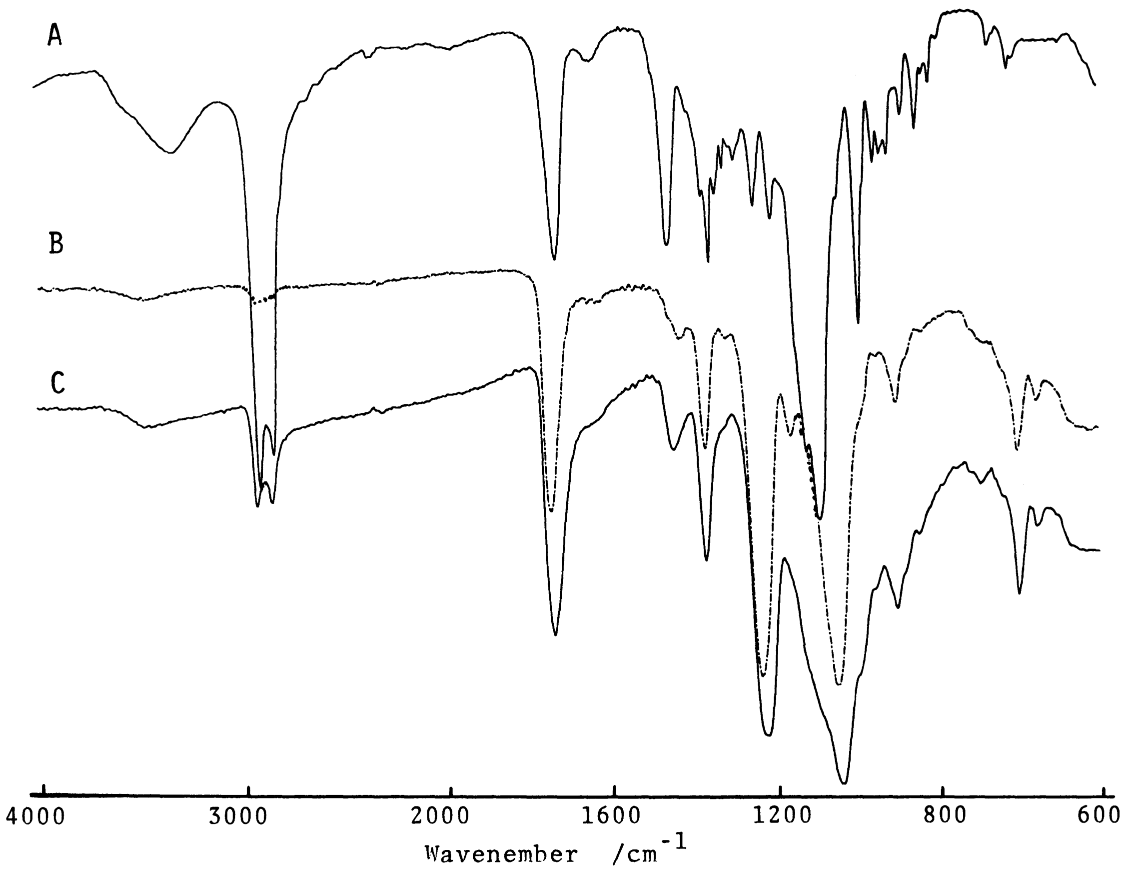

Fig. 1. IR spectra of the monomer and the polymerized membrane.

A: IR of DC18C6

B: ATR-IR of acetylcellulose membrane

C: ATR-IR of plasma-polymerized acetylcellulose membrane (membrane-1)

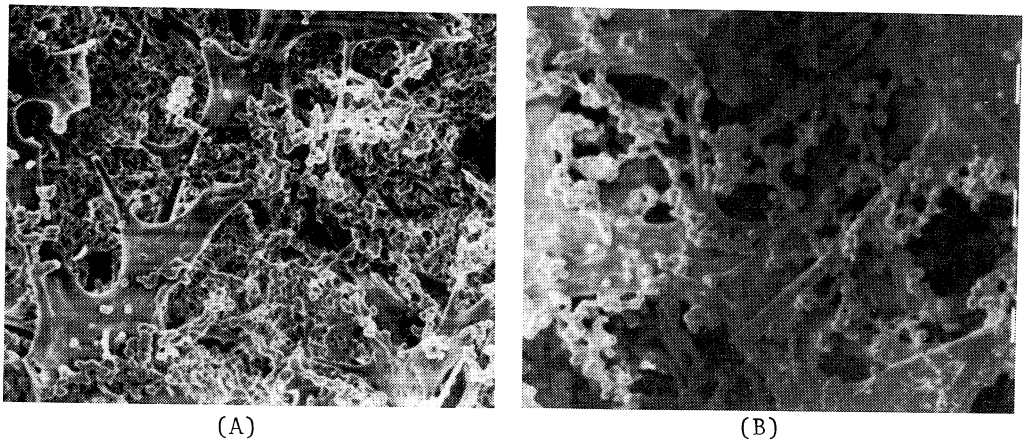
(A) (B)

Fig. 2. Scanning electron micrographs of (A) acetylcellulose membrane (B) membrane-1 (x2000 as provided).

Table 1. Rate of ion-transport across membranes

Membrane	$10^4 \cdot v$/mol h^{-1}		
	Li^+	K^+	Cs^+
Membrane-1	15.4	4.4	63.8
Membrane-2	7.9	8.4	35.6
Liquid membrane + DC18C6[a)]	(<0.2)	116	75.0
Liquid membrane[b)]	21.6	25.2	33.8

a) [DC18C6]=3.00×10^{-3} M in 40 mL o-dichlorobenzene.

b) o-dichlorobenzene:1-butanol=80:20 v/v.

Substrate(acetylcellulose filter, Fuji prefilter FP, 142 mm diameter, 160 μm thick, 5 μm pore size) was placed on the lower electrode and the plasma polymerization was carried out for 60 s. During this time DC18C6 was evaporated completely and the substrate was coated with the polymer layer. The composite membranes thus obtained were stirred and washed in a large amount of ethanol to remove unreacted DC18C6 and soluble products and then dried in vacuo. The membranes prepared by methods A and B(abbreviated as membrane-1 and membrane-2 hereafter) were 165 and 160 μm thick, respectively. Figure 1 shows the IR spectra of DC18C6, membrane-1, and acetylcellulose membrane.[11)] It is seen from Fig. 1 that the IR spectrum of membrane-1 is very similar to that of acetylcellulose membrane itself but has new peaks at 2856 and 2932 cm^{-1} and strengthened peaks at 1220 and 1444 cm^{-1}, which are all characteristic peaks of DC18C6. The scanning electron micrographs of the surface of the plasma-polymerized membranes (Fig. 2) showed the appearance of new small-grained fibrils. These IR and electron micrographic data support the immobilization of DC18C6 on the surface of acetylcellulose membranes.

Ion-transport was carried out in a U-tube(membrane area 3.46 cm^2) immersed in a thermostated water-bath(30 °C): IN aqueous phase(40 mL), [LiOH]=[KOH]=[CsOH]=1.25×10^{-3} M(1 M=1 mol dm^{-3}), [picric acid]=3.75×10^{-3} M; OUT aqueous phase (40 mL), pure water. Membranes-1 and -2 were immersed in o-dichlorobenzene for one day and then set in the U-tube while they were "wet". For comparison we carried out ion-transport across a liquid membrane(o-dichlorobenzene) in the absence and the presence of DC18C6. The rate in the absence of DC18C6 was so slow that we mixed 20 vol% of 1-butanol into the o-dichlorobenzene phase. The concentration of metal ions transported to the OUT aqueous phase was evaluated by atomic absorption spectroscopy. The results are summarized in Table 1.

The transport studies in the liquid membrane system established that (i) the rate of ion-transport across the liquid membrane is in the order $Li^+<K^+<Cs^+$ and (ii) DC18C6 can carry K^+ most efficiently. The transport order in the absence of DC18C6 is parallel to the solubility order of these metal salts. The K^+ selectivety in the presence of DC18C6 is a typical spherical recognition pattern of DC18C6. Ion-transport across membrane-2, which was prepared by means

of the indirect heating of DC18C6, resulted in an ion-selectivity similar to the liquid membrane system in the absence of DC18C6(i.e., $Li^+<K^+<Cs^+$). In contrast, permeation of K^+ ion was selectively suppressed in ion-transport across membrane-1 which was prepared by means of the direct heating of DC18C6: v_{K^+}/v_{Li^+} and v_{K^+}/v_{Cs^+}(ratio of ion-permeation rates) for membrane-1 are smaller by factors of 3.7 and 3.4, respectively, than those for membrane-2. These results support that membrane-1 retains the DC18C6-like structure which can selectively interact with K^+ ion. Hence, membrane-1 dipped with o-dichlorobenzene serves as a reverse-osmotic membrane effective for K^+ ion. We believe, therefore, that this is the first successful example for the immobilization of crown ethers by plasma polymerization. Further applications are now continued in these laboratories.

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11) Commercially-available DC18C6 showed a peak attributable to $\nu_{C=O}$ at 1736 cm^{-1}. This is probably due to the partial oxidation of DC18C6. We used this sample without further purification.

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