Membranes of Novel Crown Ether Polymers for Proton-driven Cation Transport

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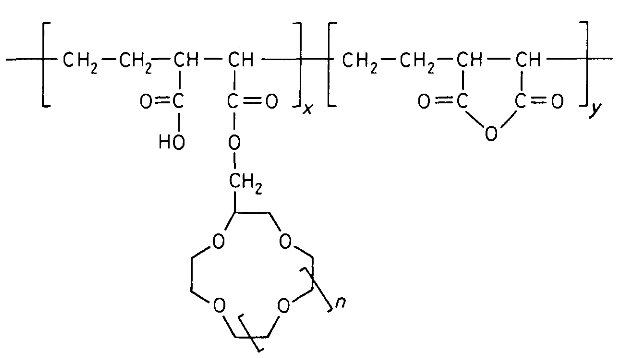
Proton-driven transport of alkali metal ions through a membrane formed from crown ether polymers (**1**; *n* = 1—3), which are derived from an alternating copolymer of ethylene and maleic anhydride, is reported.

Membrane transport of metal ions has been extensively investigated using crown ether derivatives. Of particular interest are crown ether compounds bearing an ionisable functional group at the periphery, which permit active transport of alkali metal ions when used in combination with a proton concentration gradient.[1] Immobilization of a crown ether-carboxylic acid on a polymeric film has also been attempted by coating on a commercially available membrane filter.[2] It occurred to us that poly(ethylene-*co*-maleic anhydride) (PEMA) which is capable of forming polymeric films may be modified by a crown ether moiety to yield crown ether polymers (**1**; *n* = 1—3). It was hoped that membranes of such polymers would induce proton-driven cation transport of alkali metal ions.

Polymers incorporating 12-crown-4, 15-crown-5, and 18-crown-6 rings can be synthesized by the condensation reaction of PEMA and an appropriate hydroxymethylcrown ether derivative[3] in acetone, the crown ether content of the resulting polymer being controlled by the initial concentration of the crown ether. It should be noted that the polymer reaction process accomplishes both the immobilization of the crown ether moiety and the introduction of one carboxylic group per crown ether moiety, which could lead to the possibility of active cation transport. Casting of the crown ether polymers from dimethyl sulphoxide gave transparent polymeric films, and blending of the polymers with poly(vinyl alcohol) (1/5, w/w) improved the mechanical strength of the films. The blended polymer films were made insoluble for use in the transport experiments by treatment with an aqueous solution of formaldehyde containing sulphuric acid.

Proton-driven transport of alkali metal ions (Na^+, K^+, and Cs^+) was studied at 25 °C, using a glass cell which was separ-



(1) $n = 1$–3

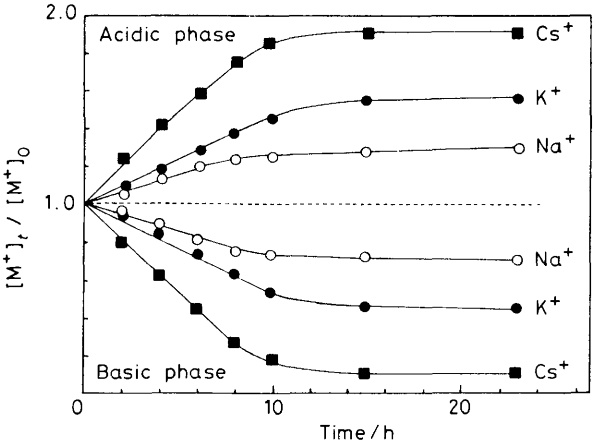


Figure 1. Proton-driven transport of alkali metal ions through a membrane formed from 12-crown-4 polymer (**1**; $n = 1$) (crown ether content of about 30%). $[M^+]_t$ and $[M^+]_0$ refer to metal ion concentrations at time = t and 0, respectively.

ated into two compartments by the polymeric membrane.† The transport was followed by flame-photometric determination of metal ions in both the acidic and basic phases. Figure 1 illustrates the results for the 12-crown-4 polymer (**1**; $n = 1$) (crown ether content of about 30%), showing efficient cation transport. The membranes formed from 15-crown-5 (**1**; $n = 2$) and 18-crown-6 polymers (**1**; $n = 3$) exhibited the similar transport properties. However, the three crown ether polymers showed distinctly different ion-selectivities for transport, as depicted in Figure 2.

It is well known that polymers bearing pendant crown ether moieties are capable of forming intramolecular sandwich-type complexes with particular cations which are slightly larger in size than the crown ether cavity, by the co-operative action of two neighbouring crown ether moieties.[4,5] Also, the ion-selectivities of the crown ether polymers often differ from those of the corresponding monocyclic crown ethers. Thus, poly(12-crown-4),[5] poly(15-crown-5),[4] and poly(18-crown-6)[4] derivatives show their most powerful binding ability with the alkali metal ions Na^+, K^+, and Cs^+, respectively. In the proton-driven cation transport behaviour of the crown ether polymers, (**1**; $n = 1$—3), there seems to be transport retardation of these particular cations owing to powerful binding to the crown ether polymers.

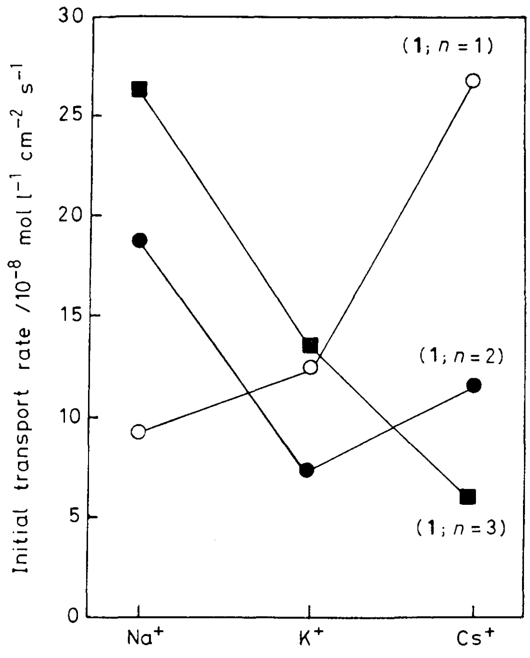


Figure 2. Comparison of crown ether polymers (**1**; $n = 1$—3) in ion-selectivity for proton-driven cation transport. The crown ether content of the polymers is almost the same in each case (about 30%).

In conclusion, polymeric membranes based on this new type of crown ether polymer, which are accessible from PEMA, function as effective proton-driven alkali metal ion pumps, and the transport behaviour of the polymeric membranes reflects the cation-binding abilities of the crown ether polymers themselves.

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† Basic phase: tris(hydroxymethyl)aminomethane–hydrochloric acid buffer, pH 9, [alkali metal chloride] = 10^{-2} M; acidic phase: triethanolamine–phosphoric acid buffer, pH 2; stirring rate in both phases: 400 r.p.m. The exposed area and the thickness of the membranes were 1 cm^2 and 140 μm, respectively.