

Polymer/liquid crystal composite membranes: a new membrane system for crown-mediated ion transport

Seiji Shinkai¹ and Tisato Kajiyama²

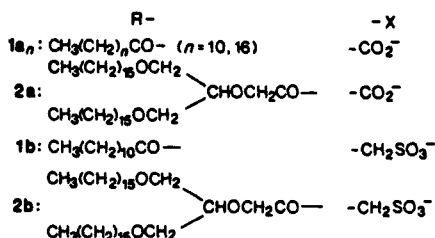
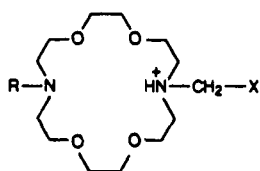
¹Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan and ²Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

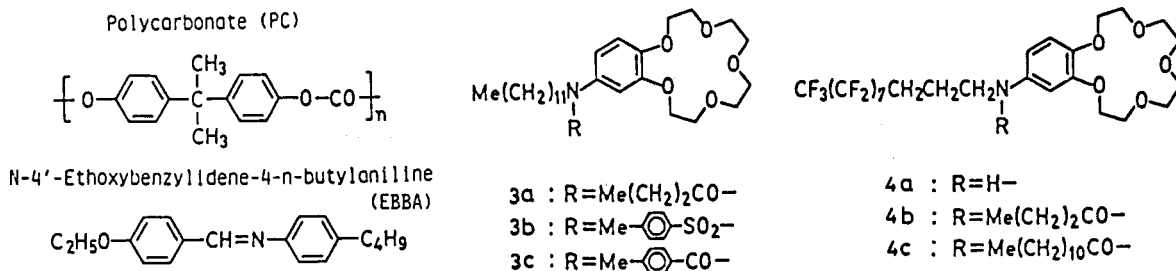
Abstract - Composite membranes composed of polymer (polycarbonate, PC)/liquid crystal [N-(4-ethoxybenzylidene)-4'-butylaniline, EBBA]/crown ethers have been prepared. Crown-mediated K⁺ transport through the PC/EBBA/crown membranes was very fast above T_{KN} (crystal-nematic liquid crystal phase transition temperature of EBBA) owing to the high fluidity of EBBA forming a continuous phase in the composite membranes. K⁺ transport was very slow below T_{KN} where the thermal molecular motion of EBBA is frozen. In particular, K⁺ transport is "completely" suppressed when the crown carriers form microheterogeneous, phase-separated aggregates in the membranes. This is the first example for "complete" thermocontrol of ion transport through the polymer composite membranes.

INTRODUCTION

In the past two different types of membranes have been used in membrane transport systems: liquid membranes and polymeric membranes. Each type of membrane has advantages and disadvantages. A liquid membrane is very convenient and can provide a large transport flux, but the system is not necessarily useful for practical applications. On the other hand, a polymeric membrane is more useful for practical applications, but is often hampered by a low transport flux. If one could develop a new membrane which would compensate for these disadvantages, it would be very useful not only for laboratory-scale transport experiments but also for practical membrane separations. The polymer/liquid crystal composite membrane, in which the liquid-crystalline material is embedded in a polymer matrix, can satisfy these requirements. It is apparently a polymeric solid membrane but can provide a relatively large transport flux above the crystal-liquid crystal phase-transition temperature (T_{KN}) (ref. 1-6). This is due to the high fluidity of the liquid-crystalline material which forms the continuous phase in the polymer matrix (ref. 1-6). It could be called "a liquid membrane in polymer clothing" or "an immobilized liquid membrane". Another interesting feature of the polymer/liquid crystal composite membrane is related to thermocontrol of permeation rates. Thermal molecular motion of the liquid-crystalline material changes drastically at T_{KN}, so that the permeation efficiency across this membrane changes discontinuously at this temperature. It is known that a distinct increase in the thermal molecular motion at T_{KN} causes a rapid increase in water or gas permeability coefficients (ref. 1, 2). One may consider, therefore, that polymer/liquid crystal composite membranes possess biomembrane-mimetic properties with respect to the phase-transition phenomena.

We here report the temperature regulation of crown-mediated ion transport through ternary composite membranes composed of polymer (polycarbonate, PC), liquid crystal [N-(4-ethoxybenzylidene)-4'-butylaniline, EBBA], and crown ethers. The crown ethers used in this study are amphiphilic crown ethers (1a₁₀, 1a₁₆, 1b, 2a, 2b), hydrocarbon-(3a, 3b, 3c) or fluorocarbon-





containing crown ethers (4a, 4b, 4c). We have found that the rate of ion transport is profoundly related to the fluidity of the EBBA phase and also to the dispersion state of the crown ethers in the membrane (ref. 3-6). In particular, when the crown ethers (2a, 2b, 4b, 4c) which form microheterogeneous, phase-separated aggregates were used as ion carriers, ion transport below T_{KN} was suppressed "completely" (ref. 4-6).

DISPERSION STATE OF CROWN ETHERS IN COMPOSITE MEMBRANE

The composite membrane is a blend film prepared by casting a 1,2-dichloroethane solution of PC (40 wt%), EBBA (60 wt%), and crown ether. In the composite membrane EBBA forms a continuous phase across the polymer matrix and exhibits a crystal-nematic liquid crystal phase-transition at 304-305 K. One of the main objectives of this investigation is to clarify a potential relation between the ion transport ability and the dispersion state of the carriers in a composite membrane. In order to change the "solubility" of crown ethers in the membrane, we synthesized amphiphilic crown ethers illustrated above. The DSC study established that 1a₁₆ (mp 388-340 K) is homogeneously dispersed in the composite membrane whereas 2a and 2b (mp 317 K and 309 K, respectively) exist as phase-separated aggregates in the composite membrane. Because of the structural similarity 1a₁₆, 1a₁₀ (oil) would be dispersed homogeneously.

The solubility of crown ethers can be also changed by introducing a fluorocarbon chain. When 1,2-dichloroethane solutions of 3 (4.3 mol% of EBBA), PC, and EBBA were cast on a glass plate, transparent, homogeneous membranes suitable for membrane transport experiments were obtained. In contrast, 4a (4.3 mol% of EBBA) gave a phase-separated white layer above the PC/EBBA membrane because of the lipophobic nature of the fluorocarbon chain. To enhance the miscibility, we synthesized 4b and 4c which possess an additional hydrocarbon chain. As expected, 4b and 4c gave "apparently" homogeneous membranes when cast from 1,2-dichloroethane solutions. The DSC study established, however, that 4b and 4c form microheterogeneous, phase-separated aggregates in the composite membrane. The phase separation should be caused by the poor miscibility of the fluorocarbon chain. On the other hand, hydrocarbon-containing crown ethers (3a, 3b, 3c) dissolve homogeneously in the composite membrane.

TEMPERATURE REGULATION OF ION TRANSPORT RATES

Transport experiments were conducted in a U-tube immersed in a thermostated water-bath. In the PC/EBBA/1 (or 2) membranes, the pH's of IN (containing 0.03 M MSCN) and OUT aqueous phases were adjusted to 10.0 and 7.0 with K₂CO₃ (0.015 M)-HCl and Me₄NOH-H₃PO₄ (0.010 M), respectively. Figure 1 shows plots of P_{K^+} vs. transport temperature for 1a₁₀, 1a₁₆, and 2a. Permeation of K⁺ ion through PC/EBBA/1a₁₀ and PC/EBBA/1a₁₆ was observed below and above T_{KN} and the plots had break points at around T_{KN} . In fact, the Arrhenius plots consisted of two straight lines intersecting at T_{KN} . Carrier-mediated K⁺ permeation through the PC/EBBA composite membrane must thus be directly affected by the molecular motion of the liquid crystal phase. In contrast to the permeation behavior of these membranes, K⁺ permeation through PC/EBBA/2a (and also PC/EBBA/2b) was "completely" suppressed below T_{KN} and increased with increasing transport temperature above T_{KN} (Fig. 1). This indicates that ion permeation below T_{KN} is largely governed by the dispersion state of the carriers and that the ion flux can be "completely" stopped by separating the carriers in aggregate domains.

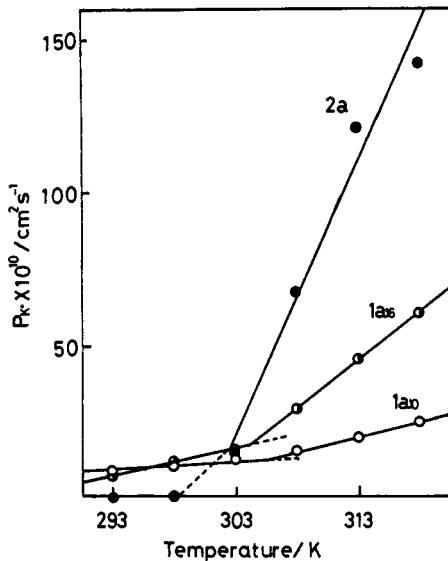


Fig. 1. Temperature dependence of K^+ transport for PC/EBBA/crown ternary composite membranes.

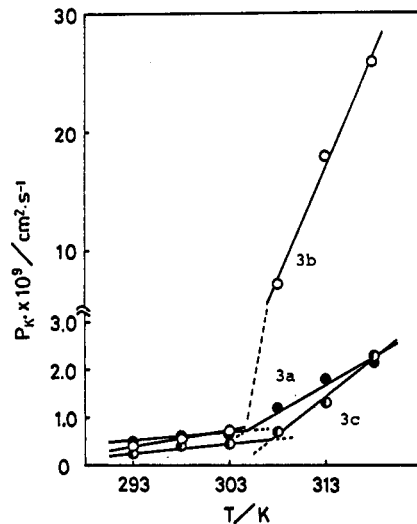


Fig. 2. Temperature dependence of K^+ transport for PC/EBBA/crown ternary composite membranes.

In the PC/EBBA/3 (or 4) membranes, the source aqueous phase (IN phase) contained 0.30 M potassium p-toluenesulfonate and the concentration of transported K^+ in the receiving aqueous phase (OUT phase) was measured as a function of time by atomic absorption spectroscopy. Figure 2 shows plots of the permeability coefficients for K^+ (P_{K^+}) vs. transport temperature for the PC/EBBA/3 membranes. Transport of K^+ across the PC/EBBA/3 membrane was observed below and above T_{KN} and was faster above T_{KN} resulting in a clear break point near T_{KN} . Thus, carrier-mediated K^+ transport is directly affected by the molecular motion of EBBA and becomes more advantageous in the fluid liquid crystal phase. The PC/EBBA/3b membrane gave the largest P_{K^+} above T_{KN} . Arrhenius plots (not shown here) consisted of two straight lines intersecting at T_{KN} . The thermodynamic parameters (E_a and $\log A$) and typical P_{K^+} values are summarized in Table 1.

Table 1 shows that the liquid crystal phase (above T_{KN}) gives E_a and $\log A$ values which are greater than those for the crystal phase (below T_{KN}). As shown in Fig. 2, ion transport rates are considerably enhanced above T_{KN} . This result implies that P_{K^+} increases because of a favorable enhancement in $\log A$ in spite of the unfavorable E_a increase. In fact, P_{K^+} is correlated (although approximately) with the increase in the $\log A$ term and almost inversely with the increase in the $-E_a/RT$ term. The observation that the transport rate is governed by the entropy term suggests that diffusion of the crown-metal complexes is a main rate-limiting step in the present transport system. In contrast, association-dissociation of the complexes which should be reflected in the enthalpy term would be less important.

TABLE 1. Permeability Coefficients (P_{K^+}) and Arrhenius Thermodynamic Parameters (E_a and $\log A$) for K^+ Transport

membrane	$10^9 \cdot P_{K^+} (\text{cm}^2 \text{ s}^{-1})$		$E_a (\text{kJ mol}^{-1})$		$\log A$	
	at 298 K	at 318 K	below T_{KN}	above T_{KN}	below T_{KN}	above T_{KN}
PC/EBBA/3a	0.616	2.12	34.4	42.2	-3.16	-1.74
PC/EBBA/3b	0.564	26.0	45.1	105	-1.39	9.72
PC/EBBA/3c	0.464	2.30	45.6	97.4	-1.38	7.38
PC/EBBA/4b	0	49.7	-	186	-	23.4
PC/EBBA/4c	0	44.6	-	172	-	20.9

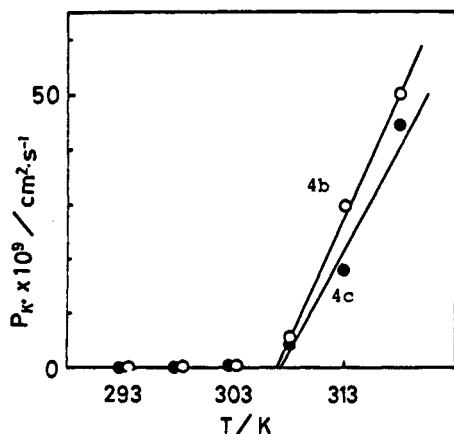


Fig. 3. Temperature dependence of K^+ transport for PC/EBBA/3 ternary composite membranes.

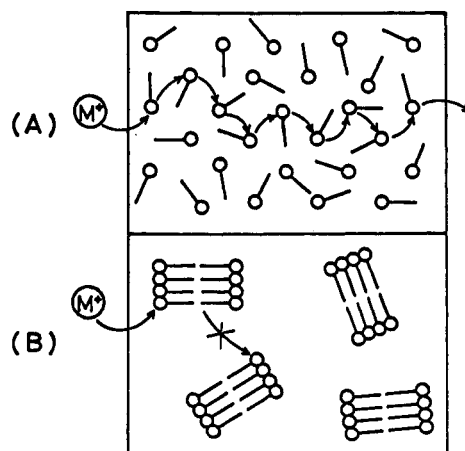


Fig. 4. Schematic representation of ion transport below T_{KN} : (A) a site-to-site jump mechanism for homogeneously dispersed membranes, (B) an aggregate-to-aggregate (inter-aggregate) jump mechanism for phase-separated membranes.

The PC/EBBA/4 membranes provide two novel transport properties (Fig. 3). First, K^+ transport through these membranes is "completely" suppressed below T_{KN} . This finding indicates that ion transport through the crystal phase is profoundly influenced by the dispersion state of ion-carriers and that the ion flux can be stopped "completely" by forming microheterogeneous carrier domains. Secondly, the fluorocarbon-containing 4 transports K^+ much faster than the hydrocarbon-containing 3 above T_{KN} (Table 1). Comparison of the thermodynamic parameters indicates that above T_{KN} the log A values for 4b and 4c are markedly increased (by 25.1 and 22.6, respectively, compared with that of 3a) but at the same time the E_a values increase 4.1-4.4 fold. However, the transport rate is actually governed by the log A term but not by the E_a term. Therefore, the remarkable enhancement of the P_K values of 4b and 4c must result from the "favorable entropy term". This suggests that 4b and 4c, which are barely dispersed in the membrane, are not "wet" by the EBBA molecules and are relatively "desolvated". Furthermore, they may disorder the liquid crystal structure of EBBA because of the aggregate formation. These situations would allow the rapid diffusion of the fluorocarbon-containing crown ethers through the membrane phase. This effect would be reflected by the entropy term.

COMMENTS ON THE TRANSPORT MECHANISM

It is very interesting to consider why K^+ transport was suppressed "completely" below T_{KN} in the PC/EBBA/2 and PC/EBBA/4 membranes. Above T_{KN} the continuous EBBA phase is fluid, so that crown ethers can diffuse in the membrane phase as those in a liquid membrane system. This is the so-called carrier-mechanism. Below T_{KN} , on the other hand, the carrier-mechanism is no longer operative because crown ethers are fixed in the frozen, crystalline lattice of EBBA and cannot diffuse in the membrane. However, Fig. 2 shows how K^+ transport still can take place across such a frozen membrane below T_{KN} when the crown ethers are homogeneously dispersed. In this case, ions are transported according to a site-to-site jump mechanism (Fig. 4A) which is generally proposed for crown-immobilized polymeric membranes (ref. 7). When the carrier sites are dispersed homogeneously in the membrane (i.e. with PC/EBBA/1 (or 3)), the jump mechanism can easily occur because a metal cation complexed by a crown can easily find an adjacent crown for the jump. In contrast, when the carriers form the phase-separated aggregates in the membrane (i.e. with PC/EBBA/2 (or 4)), the distance is too far to jump and an aggregate-to-aggregate (inter-aggregate) jump becomes almost impossible (Fig. 4B). This would result in the "complete" suppression of ion transport below T_{KN} . Thus, one can conclude that the ion transport phenomena in the polymer/liquid crystal composite membrane are profoundly related to the dispersion state of carrier molecules.

NEW APPLICATIONS OF POLYMER/LIQUID CRYSTAL COMPOSITE MEMBRANES

Since the K^+ transport rates in PC/EBBA/4 membranes are remarkably rapid, it is of interest to evaluate the ion selectivity of these membranes. The permeability coefficients (P_{M^+}) determined for four alkali metal cations under identical conditions are illustrated in Fig. 5. Examination of these transport data reveals that the PC/EBBA/3a membrane gives almost the same transport rates for Na^+ and K^+ , whereas the PC/EBBA/4b membrane gives a maximum rate value for K^+ and (ii) the transport of Rb^+ and Cs^+ across the PC/EBBA/3a membrane was not detected, but the efficient transport of these metal cations still takes place in the PC/EBBA/4b membrane. Finding (ii) that large alkali metal cations such as Rb^+ and Cs^+ can permeate through the PC/EBBA/4b membrane but not through the PC/EBBA/3a membrane could be related to the dispersion state of the ion-carriers. It is known that monobenzo-15-crown-5 shows a high selectivity for Na^+ or K^+ and binds Rb^+ and Cs^+ only weakly. This is probably the case for the PC/EBBA/3a membrane in which 3a is dissolved homogeneously. On the other hand, bis(crown ethers) and polymeric crown ethers exhibit selectivity toward large alkali metal cations because of the formation of 1:2 metal/crown sandwich complexes (ref. 8, 9). Probably this is the case for the PC/EBBA/4b membrane in which 4b forms the phase-separated crown-aggregates. We believe that Rb^+ and Cs^+ are extracted into the membrane phase because of the formation of such sandwich complexes. The fact that the PC/EBBA/4b membrane shows the K^+ selectivity rather than the Na^+ selectivity can also be rationalized in terms of the contribution of the 1:2 K^+ /crown complexes.

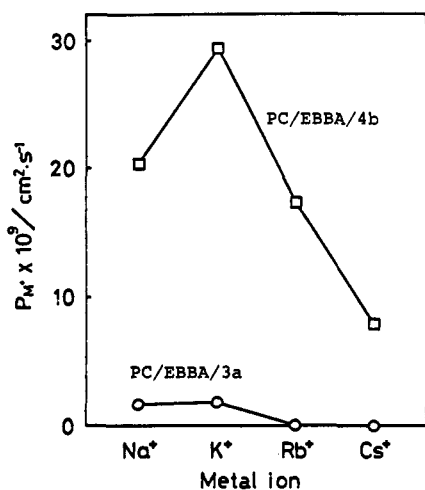


Fig. 5. Ion selectivity for transport of alkali metal cations through the PC/EBBA/3a membrane and the PC/EBBA/4b membrane.

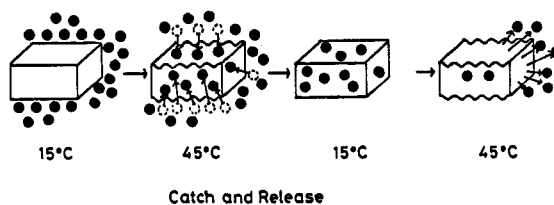


Fig. 6. Schematic illustration of catch-and-release. The wavy pieces denote the membrane above the T_{KN} .

The temperature-dependent release of ions and organic molecules (especially, drugs) has been widely investigated. We here tested an application of the PC/EBBA/2a composite membrane to the "catch-and-release" of alkali metal cations (Fig. 6: $M^+ = K^+$ and Cs^+). The PC/EBBA/2a membrane (0.138 g, 2a 8.00×10^{-6} mol) was stirred in an aqueous solution (50 mL, pH 10.0 with 0.015 M M_2CO_3-HCl) containing 0.39 M of MSCN at 318 K for 10 h. During this period M^+ should permeate into the membrane. The solution was kept at 288 K for 4 h and then the membrane was washed with cold water (ca. 5°C). This membrane was put into an aqueous solution (50 mL, pH 7.0 with 0.010 M phosphate- Me_4NOH). The solution was stirred at a constant speed (ca. 150 rpm) and the increase in the M^+ concentration was followed by atomic absorption spectroscopy. As shown in Fig. 7, the metal ions are scarcely released from the membrane at 288 K. The metal concentrations begin to increase immediately after the temperature change to 318 K and reach an equilibrium value after about 30 min. This equilibrium value corresponds to 70 mol% of 2a. Since the crown ring of 2a possibly forms a 1:1 metal/crown complex with K^+ , this value is quite reasonable in the K^+ uptake. However, it becomes unreasonable in the Cs^+ uptake if the crown ring forms a 1:2 metal/crown sandwich complex with Cs^+ : that is, the equilibrium value should not exceed 50 mol%. This dilemma would be accommodated in terms of the formation of an n:n+1 metal/crown "poly-sandwich" complex. Crown ethers can form not only 1:2 metal/crown sandwich complexes but also 2:3 metal/crown club-sandwich complexes with large alkali metal cations. Therefore, an n:n+1 metal/crown "poly-sandwich" complex could be formed when crown ethers are properly aligned. Provided that 2a forms the bilayer-like aggregates in the membrane phase, stacks of the crown ethers would be composed on the surface of the aggregates. The

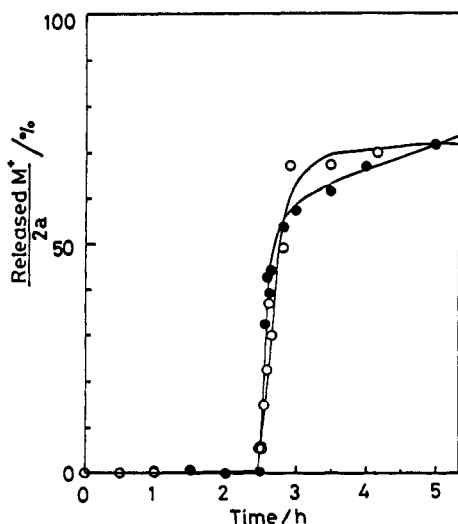


Fig. 7. Temperature regulation of ion release from the PC/EBBA/2a membrane: ○ K⁺, ● Cs⁺.

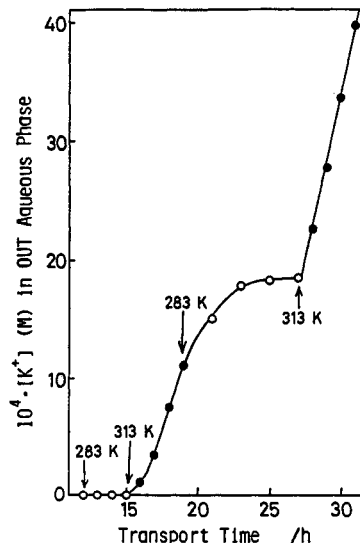


Fig. 8. Thermocontrol of K⁺ transport through the PC/EBBA/2a composite membrane.

stacks would possibly form the $n:n+1$ metal/crown "poly-sandwich" complex with Cs⁺. Anyhow, the temperature dependence in Fig. 7 indicates that the PC/EBBA/2a membrane exhibits a complete "catch-and-release" function.

Figure 8 shows the reversible thermocontrol of K⁺ permeation through the PC/EBBA/2a composite membrane. In response to a temperature change in the water bath (283 K → 313 K → 283 K → 313 K), the rate of K⁺ permeation showed an all-or-nothing change. The response (i.e., K⁺ concentration in the OUT aqueous phase) for the change from 283 K to 313 K is fast, whereas that for the change from 313 K to 283 K is relatively slow, taking about 4 h to stop K⁺ permeation completely. This slow response is attributed either to a leakage of K⁺ dissolved in the membrane phase during the 313 K period or to an induction period for reorganization of the crystal phase. As described above, we tested the K⁺ release from the composite membrane below and above T_{KN} . As a result, we confirmed that the K⁺ leakage does not occur from the K⁺-containing membrane below T_{KN} . One may conclude, therefore, that the transient leakage for the change from 313 K to 283 K stems from slow reorganization of the liquid crystal phase to the crystal phase in the polymer matrix.

CONCLUSION

The present study demonstrated that ion transport through the polymer/liquid crystal/crown ternary composite membranes is directly affected by the molecular motion of the liquid crystal phase. Further important is the finding that when the amphiphilic crown ethers and the fluorocarbon-containing crown ethers form phase-separated aggregates, the ion flux can be stopped completely. This novel phenomenon is readily applicable to the reversible thermocontrol of ion permeation and to the temperature-dependent catch-and-release. We expect that further elaborations of this concept might lead to a more generalized method to control the ion permeability by an on-off temperature-switch.

REFERENCES

1. T. Kajiyama, Y. Nagata, S. Washizu and M. Takayanagi, *J. Membr. Sci.* **11**, 39-52 (1982).
2. S. Washizu, I. Terada, T. Kajiyama and M. Takayanagi, *Polym. J.* **16**, 307-316 (1984).
3. S. Shinkai, S. Nakamura, S. Tachiki, O. Manabe and T. Kajiyama, *J. Am. Chem. Soc.* **107**, 3363-3365 (1985).
4. S. Shinkai, S. Nakamura, N. Ohara, S. Tachiki, O. Manabe and T. Kajiyama, *Macromolecules* **20**, 21-28 (1987).
5. S. Shinkai, K. Torigoe, O. Manabe and T. Kajiyama, *J. Chem. Soc., Chem. Commun.* 933-935 (1986).
6. S. Shinkai, K. Torigoe, O. Manabe and T. Kajiyama, *J. Am. Chem. Soc.* in press.
7. E. Shchori and J. Jagur-Grodzinski, *J. Appl. Polym. Sci.* **20**, 773-788 (1976).
8. J. Smid, *Makromol. Chem. Suppl.* **5**, 203-215 (1981) and references cited therein.
9. K. Kimura, T. Maeda and T. Shono, *Makromol. Chem.* **182**, 1579-1586 (1981).