Bilayer Coated Capsule Membranes. Part 2.[1,2] Photoresponsive Permeability Control of Sodium Chloride across a Capsule Membrane

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Two types of photoresponsive nylon capsules coated with synthetic bilayer membranes were prepared. In one system, the azobenzene chromophore is incorporated in the bilayer component (System I); the other system contains the azobenzene moiety as part of the polyamide chain (System II). Release of NaCl from nylon capsules coated with photoresponsive bilayer membranes (System I) was reversibly regulated by alternate irradiation with u.v. or visible light. Thus, permeation of NaCl was enhanced due to the distorted *cis*-configuration of the azobenzene unit in bilayers, and reverted to the original rate by recovery of the *trans*-configuration. NaCl release was also affected by the phase transition of the coating bilayer membrane. The permeation mechanism is discussed from the activation energy data. Permeation of the System II capsule, in which the azobenzene unit is linked covalently, was not changed by photoirradiation.

Nylon capsule membranes have been described by Chang *et al.*[3-5] and Kondo *et al.*[6,7] in connection with their studies on artificial cells by trapping enzymes in the inner aqueous phase. Capsule membranes, however, are semipermeable and therefore have the disadvantage that they cannot trap low-molecular-weight substances in the inner core.[3,6] Chang *et al.*[5,8] prepared the egg-lecithin-coated capsule membrane in order to overcome this disadvantage. On the other hand, the trapping of various water-soluble substances in the inner water phase of synthetic bilayer vesicles [9-12] has been examined by several groups.[13-16] These synthetic bilayer vesicles as well as liposomes of natural lipids, however, have several disadvantages in trapping; very small inner aqueous phases, easily breakable bilayer walls against the osmotic pressure difference, and difficulty in the separation of vesicles from the outer phase.

To remove the respective weak points of both membranes, functional nylon capsules whose porous membranes were coated with synthetic dialkyl bilayers were prepared.[1,17,18] The capsule is formed by physically strong nylon membranes and the coating shows the characteristics of bilayer vesicles. For example, the release of water-soluble substances was controlled by the phase transition of the coating dialkylammonium bilayers,[1,17] and by the interaction of added divalent cations from outside with the coating dialkyl phosphate bilayers.[18]

In aiming at the photoresponsive permeability control of capsule membranes, we prepared two types of azobenzene-containing nylon capsules coated with synthetic bilayer membranes. A schematic illustration of two types of capsules is shown in Figure 1. In System I, an ordinary nylon-2,12 capsule membrane was coated with photoresponsive bilayers of C_{12}-Azo-C_4-N^+ or C_{16}-,C_{12}-Azo-C_4-N^+, and/or $2C_{14}N^+$-$2C_1$ (see Figure 1). The distorted bilayer structure of the *cis*-azobenzene chromophore which is formed by photoirradiation is expected to increase the permeability across the membrane. In System II, the photoresponsive unit was covalently bonded to the nylon capsule membrane (nylon-2,Azo) which was coated with ordinary dialkylammonium ($2C_{14}N^+2C_1$) bilayers. The *cis–trans* configurational change of the azobenzene unit in a capsule membrane is expected to change the pore size of the membrane.

The azobenzene system was selected as the photoresponsive unit since its photoisomerization behaviour has been studied in detail in various systems: polymer solutions,[19-23] polymer membranes,[24-27] crown ethers, [28,29] cyclodextrins,[30] liquid crystals,[31] and bilayer membranes.[32-35]

Experimental

Materials.—Preparations of the amphiphiles ditetradecyldimethylammonium bromide ($2C_{14}N^+2C_1$) [36] and *p*-dodecyloxy-*p*′-(ω-trimethylammoniobutoxy)azobenzene bromide (C_{12}-Azo-C_4-N^+) [37] have been reported elsewhere. *p*-Dodecyloxy-*p*′-(ω-dimethylhexadecylammoniobutoxy)-azobenzene bromide (C_{16}-,C_{12}-Azo-C_4-N^+) was prepared from *p*-dodecyloxy-*p*′-(ω-bromobutoxy)azobenzene and dimethylhexadecylamine, according to the literature.[38] 1,10-Bis(chlorocarbonyl)decane, b.p. 150 °C at 0.5 mmHg, 4,4′-bis(chlorocarbonyl)azobenzene, m.p. 160 °C [from n-hexane and benzene (1 : 1)], and trimesoyl chloride, b.p. 130 °C at 3 mmHg, were prepared from the corresponding acids and thionyl chloride according to the ordinary procedure. These acid chlorides were redistilled just before use.

Preparation of Capsules.—Large, semipermeable nylon capsules were prepared from the corresponding diacid chloride and ethylenediamine in the presence of 5 mol% of crosslinking agent (trimesoyl chloride) by interfacial polymerization using a drop technique, as described previously.[1,7,17,18] The presence of the crosslinking agent gave strong, tensile capsule membranes.[1,17,18] Nylon-2,12 and nylon-2,Azo capsules, which were prepared from ethylenediamine and 1,10-bis(chlorocarbonyl)decane or 4,4′-bis(chlorocarbonyl)-azobenzene, respectively, had an ultra-thin membrane thickness (5 μm) and a large diameter (2.5 mm). Both nylon-2,12- and -2,Azo capsules were proved by scanning electron microscopy (s.e.m.) to have a porous and semipermeable membrane structure, as shown in Figure 2A. They were dialysed in 0.2M-NaCl aqueous solution for 2—3 days to obtain capsules containing NaCl in the inner aqueous phase.

Amphiphile-coated capsules were prepared as follows.[1,17,18] Ten pieces of NaCl-trapped capsules were transferred to a dodecane solution (3 ml) of amphiphile (50 mg) and kept at 50—60 °C for 10 min. After cooling slowly, amphiphile-coated capsules were picked up and rolled on a filter paper to remove excess of dodecane solution. It was proved by s.e.m. that amphiphile-coated capsule membranes were entirely covered with plates of amphiphile including pores, and clear pores observed in the uncoated capsule (Figure 2A) were not seen in the intersection of the coated capsule. For example, the intersectional s.e.m. of nylon-2,12 capsule membrane coated with a mixed bilayer of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1) is shown in Figure 2B. Similar results were obtained from other amphiphile-coated capsules.

The amphiphile content on the capsule was estimated to be

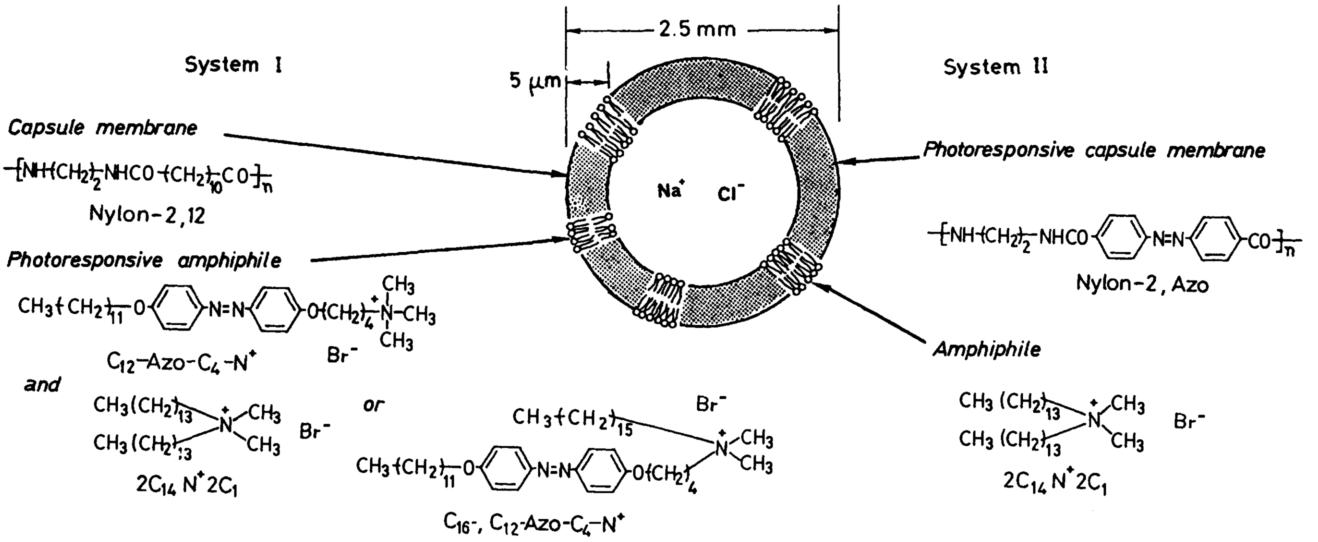


Figure 1. A schematic illustration of two types of photoresponsive nylon capsule membranes coated with synthetic amphiphile bilayers In System I, an ordinary nylon-2,12 capsule membrane is coated with photoresponsive bilayers of C_{12}-Azo-C_4-N^+ or C_{16}-,C_{12}-Azo-C_4-N^+ and/or $2C_{14}N^+2C_1$. In System II, the photoresponsive unit is covalently bonded to the nylon capsule membrane (nylon-2,Azo) which is coated with ordinary dialkylammonium bilayers ($2C_{14}N^+2C_1$). Amphiphile bilayers on the capsule exist as multiple-lamellar structures, although they are drawn as single wall bilayers

0.01—0.02 mg per capsule from elemental analysis. The surface area of capsules are calculated to be 0.30 ± 0.03 cm^2.

Measurements.—Permeation of NaCl from the inner aqueous phase across the capsule membrane was measured by detecting increases in the electrical conductance of the outer water phase. It was started by dropping one capsule into 50 ml of the deionized water in a constant temperature cell.

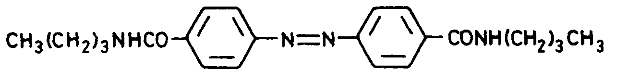
trans–cis-Photoisomerization of the azobenzene unit in capsule membranes (Systems I and II) was carried out in dodecane by irradiating with 360 nm (a HOYA U 360 glass filter) or >400 nm light (a HOYA L38 glass filter), respectively, from an Ushio 500 W super high-pressure lamp.

The gel-to-liquid crystalline phase transition of coating amphiphile-bilayers was measured with a Daini–Seikosha model SSC-560 differential scanning calorimeter. Five crushed amphiphile-coated capsules were sealed with 50 μl of water in silver sample-pans and heated from 2 to 90 °C at a rate of 2 °C min^{-1}.

Results and Discussion

Photoisomerization Spectra.—Figure 3A shows progressive spectra changes when the nylon-2,12 capsule membrane coated with a mixed bilayer of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+$-$2C_1$ (5 : 1) (System I) was irradiated in dodecane with 360 nm light. The absorption spectra clearly showed the formation of the *cis*-isomer within 10 min; adsorption peaks at 239 and 358 nm due to the *trans*-azobenzene unit disappeared and a new peak for the *cis*-isomer appeared at 450 nm. This spectral change due to photoisomerization is consistent with those of C_{12}-Azo-C_4-N^+ amphiphiles embedded in liposomal membranes[33] and C_{12}-Azo-C_4-N^+ bilayer aggregates.[32] It is estimated from the spectral change that >80% of *trans*-C_{12}-Azo-C_4-N^+ was converted into the *cis*-isomer at a photostationary state. Upon irradiation with >400 nm light, *ca.* 90% of the *cis*-isomer on the capsule reverted to the *trans*-isomer without other photochemical processes. The photochemical behaviour of the capsule membrane coated solely with C_{12}-Azo-C_4-N^+ or C_{16}-,C_{12}-Azo-C_4-N^+ was virtually identical with that of Figure 3A.

In the case of both $2C_{14}N^+2C_1$-coated and uncoated nylon-2,Azo capsule membranes in which the azobenzene unit was incorporated covalently (System II), the spectral change of *trans*-azobenzene unit ($\lambda_{max.}$ 338 nm) was hardly observed upon irradiation of 360 nm light for >1 h (Figure 3B). When tetrahydrofuran solutions of nylon-2,Azo or the monomeric analogue (1) were irradiated with 360 nm light, the isomerization proceeded within 1 min to >80% *cis*-isomer (Figure 3C). This indicates the nylon-2,Azo capsule membrane prepared from interfacial polymerization is not suitable for the photoisomerization, because the nylon membrane is slightly cross-linked (5 mol%). A cast film of nylon-2,Azo can be to some extent photoisomerized under the same conditions.



(1)

Permeation of NaCl.—Permeation of NaCl from the inner aqueous phase was followed by detecting increases in the electrical conductance in the outer water phase. Figure 4 shows typical time courses for release of NaCl to the outer water phase.

The permeability constant P can be calculated from equation (1) where k, V, and A are the slope of Figure 4, the volume of

$$P = kV/AC = kd/6\Delta C \qquad (1)$$

the outer water phase, and the surface area of the capsule, respectively. C denotes the concentration of NaCl trapped in the inner phase and is substituted by ΔC (the change of the electric conductance after crushing the capsule). Thus, P/cm s^{-1} depends on only the capsule diameter (d/cm), the slope (k/μS cm^{-1} s^{-1}), and the electric conductance change at infinite time (ΔC/μS cm^{-1}). From the ΔC values, the concentration of the NaCl incorporated in the inner core was esti-

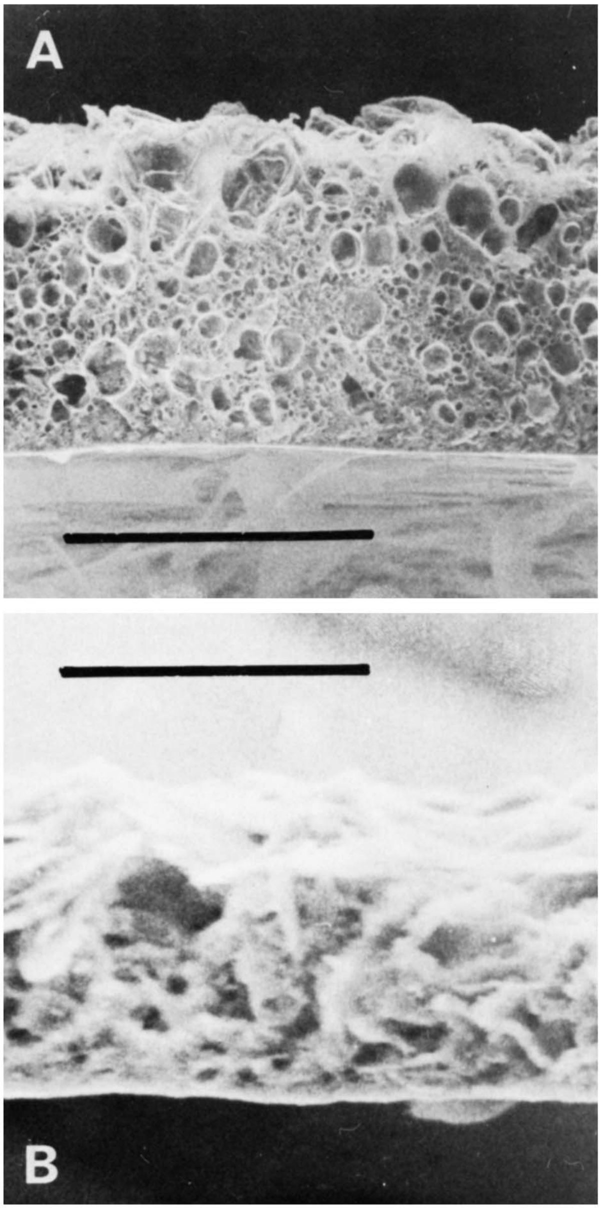


Figure 2. Scanning electron micrographs of intersectional view of the nylon-2,12 capsule membrane (A) uncoated, and (B) coated with a mixture of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ amphiphiles (5 : 1). The scale is 5 μm

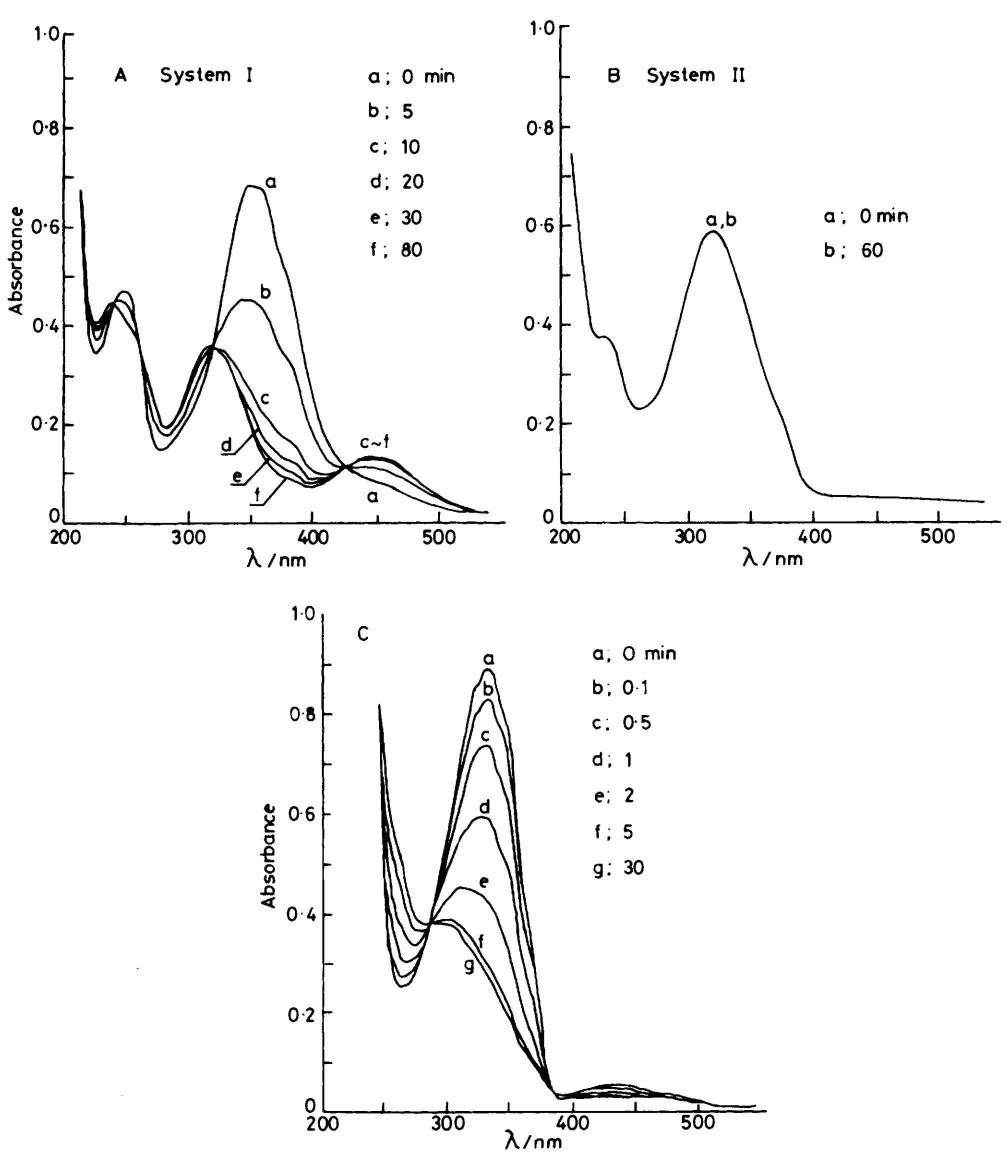


Figure 3. Progressive absorption spectral changes of (A) nylon-2,12 capsule membrane coated with a mixture of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1), (B) nylon-2,Azo capsule membrane coated with $2C_{14}N^+2C_1$, and (C) a tetrahydrofuran solution of nylon-2,Azo polymer, during irradiation by 360 nm light at 25 °C

mated to be 0.19 ± 0.01M which was nearly equal to that of the dialysis solution (0.2M). Permeability constants calculated from equation (1) are summarized in Table 1. When uncoated, semipermeable capsule membranes (nylon-2,12 or nylon-2,Azo) were employed, complete release of NaCl was achieved within 10 min (see Figure 4), and the permeability was not affected by photoirradiation (P 5.0—5.6 × 10^{-5} cm s^{-1}). On the other hand, a marked decrease in NaCl release was observed when capsules were coated with azobenzene-containing amphiphiles and/or dialkyl amphiphiles (P 1.3—2.4 × 10^{-6} cm s^{-1}) except for the C_{12}-Azo-C_4-N^+-coated nylon-2,12-capsule.

When a capsule coated with a mixed bilayer of *trans*-C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1) was picked from the cell, irradiated with 360 nm light in dodecane for 10 min, and returned to the cell, the permeability of NaCl was enhanced 3.2 times (P 6.0 × 10^{-6} cm s^{-1}). Upon reirradiation with >400 nm light in dodecane for 10 min, the permeability was reduced nearly to the original size (P 2.0 × 10^{-6} cm s^{-1}). This permeability control by u.v. and visible light irradiation could be repeated more than five times (see Figure 4). A capsule coated with the single-chain amphiphile (C_{12}-Azo-C_4-N^+) did not show a detectable permeability change by photoirradiation. The permeation constant P was not markedly reduced in the C_{12}-Azo-C_4-N^+-coated capsule compared with those of other bilayer-coated capsules (Table 1). This means the covering bilayers of single-chain amphiphiles do not have enough barrier ability. Therefore, the effect of photoisomerization (the formation of the distorted *cis*-isomer) is not clearly detected. The large permeability change was not either observed (1.3—1.7 times), when the capsule was coated with the dialkyl-type azobenzene-amphiphile (C_{16}-,C_{12}-Azo-C_4-N^+) or coated with a mixed bilayer containing a small amount of the chromophore (C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (1 : 4). In the latter case, since the content of azobenzene-amphiphile in the bilayer is relatively small (20 mol%), the effect of the distorted *cis*-isomer on the permeability seems not to appear clearly. These results indicate that the combination of dialkylammonium-amphiphile with a large amount of azobenzene-amphiphile produces the most suitable coating

Table 1. Permeability constants of NaCl across capsule membranes under irradiation with light (25 °C) [a]

Capsules	10^6 P/cm s^{-1} Dark	U.v. light	Visible light	U.v. light / Dark
Uncoated nylon-2,12	50	51	51	1.0
Uncoated nylon-2,Azo	55	56	55	1.0
System I (nylon-2,12) coated with a mixture of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1)	1.9	6.0	2.0	3.2
(1 : 4)	1.3	1.7	1.3	1.3
coated with C_{12}-Azo-C_4-N^+	11	12	10	1.0
coated with C_{16}-,C_{12}-Azo-C_4-N^+	2.4	4.0	2.6	1.7
System II (nylon-2,Azo) coated with $2C_{14}N^+2C_1$	1.8	1.9	1.9	1.0

[a] A capsule was picked from a cell, irradiated with u.v. (360 nm) or visible (>400 nm) light in dodecane, and returned to the cell.

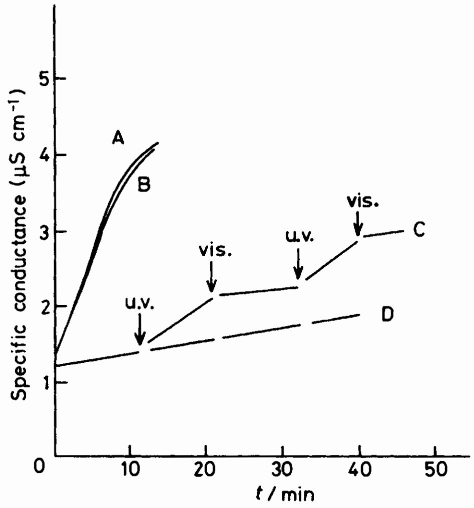


Figure 4. NaCl permeation from nylon capsules at 25 °C. One capsule trapped *ca.* 0.19M-NaCl in the inner aqueous phase was dropped into distilled water (50 ml). A capsule was picked from a cell, irradiated with u.v. (360 nm) or visible light (>400 nm) in dodecane, and returned to the cell. (A), uncoated nylon-2,Azo capsule; (B), uncoated nylon-2,12 capsule; (C), nylon-2,12 capsule coated with a mixture of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1) (System I); (D), nylon-2,Azo capsule coated with $2C_{14}N^+2C_1$ (System II)

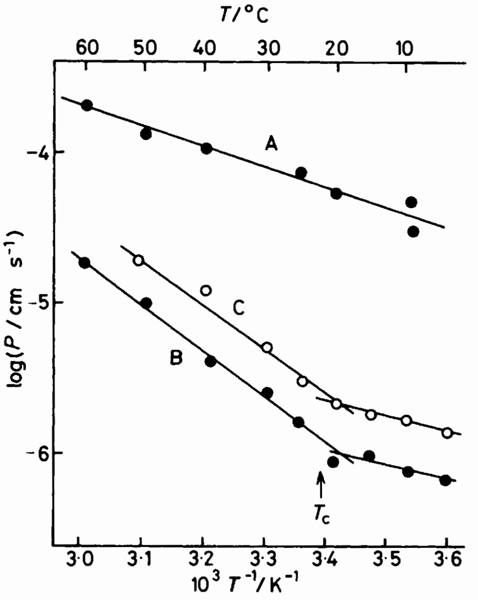


Figure 5. Arrhenius plots of NaCl permeation across (A) uncoated nylon-2,12 capsule membrane, and nylon-2,12 capsule membrane coated with a mixture of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1), (B), *trans*-isomer and (C), *cis*-isomer. Arrow shows T_c obtained from d.s.c. measurements

for the bilayer, having both higher barrier ability and a large effect on photoisomerization.

On the other hand, the permeability was not affected when the $2C_{14}N^+2C_1$-coated nylon-2,Azo capsule (System II) was photoirradiated in the same way (Table 1 and Figure 4). In System II, since the azobenzene unit exists as part of the slightly crosslinked nylon capsule membrane, it did not undergo photoisomerization (Figure 3B).

It has been observed that the permeation of water molecules across the liposomal membrane (dipalmitoyl-lecithin bilayer vesicle) with embedded C_{12}-Azo-C_4-N^+ amphiphile increases with the photoisomerization of *trans*- to *cis*-form.[33] It was not mentioned, however, whether the permeability can revert to the original rate by re-photoisomerization from *cis*- to *trans*-isomer in the liposomal membrane. The photoirradiation of the chromophore-containing liposome seems to cause photobleaching of lipid bilayers or morphological change of the liposomes such as vesicle fusion. On the other hand, the bilayer-coated capsule membrane is not damaged by repeated photoisomerization because of the physically strong capsule wall and the chemically stable synthetic amphiphiles.

Effect of Temperature.—It is important to confirm whether the coating amphiphiles form bilayer structures on the capsule membrane or not. The liquid crystalline property is one of the fundamental physicochemical characteristics of the synthetic bilayer membrane.[39-42] The presence of the phase transition between gel and liquid crystal has been inferred or proved for the synthetic bilayers on the capsule membrane by differential scanning calorimetry (DSC),[1,17,18] as in the case of aqueous bilayer vesicles [39-41] and bilayer-polymer blends.[42]

The capsule membrane coated with a mixture of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1) showed the phase transition temperature (T_c) at 22 °C (endothermic peak, ΔH 17 kcal mol^{-1}). $2C_{14}N^+2C_1$ bilayer- and C_{12}-Azo-C_4-N^+ bilayer-coated capsules coincidentally have T_c 22 °C and the transition enthalpy was 25 and 1.0 kcal mol^{-1}, respectively. Therefore the enthalpy change at T_c of the mixed bilayer should be largely attributed to the $2C_{14}N^+2C_1$ component. T_c of aqueous vesicles of $2C_{14}N^+2C_1$ and C_{12}-Azo-C_4-N^+ and their mixed vesicles appeared at 22, 25, and 22 °C, respectively, and the

Table 2. Activation energies above and below T_c for NaCl permeation through the capsule membrane

Capsule (nylon-2,12)	E_a/kcal mol^{-1} [a] above T_c	below T_c
Uncoated	2.8	
Coated with $2C_{14}N^+2C_1$ [b]	12	5.4
Coated with a mixture of C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1)		
trans-isomer	5.8	2.4
cis-isomer	5.8	2.1

[a] 1 kcal = 4.184 kJ. [b] Ref. 1.

enthalpy change at T_c of single-chain bilayers was also much smaller than those of dialkyl-chain bilayers.[37,39]

It is expected that the permeability of NaCl across the capsule membrane may change near T_c of the coating bilayers. Permeability constants of capsule membranes coated with the *trans*- and *cis*-isomer of a mixed bilayer [C_{12}-Azo-C_4-N^+ and $2C_{14}N^+2C_1$ (5 : 1)] were obtained at various temperatures (2—60 °C), together with those of the uncoated capsule. This mixed-bilayer-coated capsule was chosen because of the largest effect of photoisomerization. Arrhenius plots are shown in Figure 5.

In the case of the uncoated capsule, the plot of log P *versus* T^{-1} gave a straight line. On the other hand, Arrhenius plots gave inflections near 22 °C in the case of capsules coated with the *trans*- and *cis*-isomers. The *cis*-isomer-coated capsule showed about three-fold enhancement of the permeability, compared with the *trans*-isomer-coated one over the whole temperature range. The inflection points agree with T_c obtained from d.s.c. measurements (T_c is shown by the arrow in Figure 5). Activation energies E_a calculated from Arrhenius slopes above and below T_c are summarized in Table 2 together with data for the capsule coated with $2C_{14}N^+2C_1$.[1]

When a hydrated electrolyte such as NaCl permeates through the hydrophobic bilayer membrane, large E_a values will result. E_a Values of the permeation of Na^+ and Cl^- through egg lecithin vesicles have been reported to be 14—27 kcal mol^{-1}.[43,44] E_a Values above T_c are larger than those below T_c in both the *trans*- and *cis*-isomer-coated membrane. At temperatures above T_c, NaCl may permeate through the fluid, a hydrophobic bilayer matrix with relatively high activation energy (E_a 5.8 kcal mol^{-1}). When the bilayer is in the rigid gel state below T_c, permeation through the hydrophobic matrix becomes difficult and NaCl may permeate through defective pores in the coated capsule membrane, instead. E_a Values below T_c, then, become similar to that of the uncoated capsule (E_a 2.8 kcal mol^{-1}), in which NaCl permeation mainly proceeds by a diffusion process (E_a 2—4 kcal mol^{-1}).[45-47] The same phenomenon was also observed in the capsule membrane coated with a series of dialkyldimethylammonium bilayers ($2C_nN^+2C_1$, n = 12—18).[1]

E_a Values both above and below T_c of the *cis*-isomer-coated capsule are nearly equal to those of the *trans*-isomer-coated one and only the permeation rate is accelerated. Photoisomerization from *trans*- to *cis*-C_{12}-Azo-C_4-N^+ in the mixed bilayer is expected to give a smaller E_a value, because NaCl can permeate through the defective pores of the distorted *cis*-configuration. Judging from E_a values, the formation of the distorted *cis*-isomer in bilayers, however, seems to make bilayers more fluid and the permeability increases without a change in E_a values.

Conclusions.—We prepared two types of photo-responsive capsule membranes (Systems I and II) aiming at 'on-off light switch' permeability control. The permeability of water-soluble substances such as NaCl can be *reversibility* controlled in the case of a capsule coated with a large amount of azobenzene-amphiphile containing dialkyl bilayers (System I). The configurational change due to *trans–cis* photoisomerization of the azobenzene unit enables the perturbation of the coating bilayers to result in the increase of the permeability. This is the first example of a *reversibly* photoresponsive capsule membrane. We are also studying other, new, signal-receptive capsule membranes, which respond to stimuli from outside such as temperature,[1,17] metal ion interaction,[18] electric field, ultrasound,[48] *etc.*

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References

1 Part 1, Y. Okahata, H.-J. Lim, G. Nakamura, and S. Hachiya, *J. Am. Chem. Soc.*, 1983, **105**, 4855.

2 Preliminary report, Y. Okahata, H.-J. Lim, and S. Hachiya, *Makromol. Chem. Rapid Commun.*, 1983, **4**, 303.

3 For a review see T. M. S. Chang, 'Artificial Cells,' Thomas, Springfield, 1972.

4 T. M. S. Chang, *Science*, 1964, **146**, 524.

5 Y. T. Yu and T. M. S. Chang, *FEBS Lett.*, 1981, **125**, 94.

6 For a review see T. Kondo, ' Microencapsulation, New Techniques and Application,' Techno, Tokyo, 1979.

7 A. Arakawa and T. Kondo, *Can. J. Physiol. Pharmacol.*, 1980, **58**, 183.

8 A. M. Rothenthal and T. M. S. Chang, *J. Memb. Sci.*, 1980, **6**, 329.

9 T. Kunitake and Y. Okahata, *J. Am. Chem. Soc.*, 1977, **99**, 3860.

10 T. Kunitake and Y. Okahata, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1877.

11 Y. Okahata, S. Tanamachi, M. Nagai, and T. Kunitake, *J. Colloid Interface Sci.*, 1981, **82**, 401.

12 T. Kunitake, Y. Okahata, and S. Yasunami, *J. Am. Chem. Soc.*, 1982, **104**, 5547.

13 C. D. Tran, P. L. Klahn, A. Romero, and J. H. Fendler, *J. Am. Chem. Soc.*, 1978, **100**, 1622.

14 R. A. Mortana, F. H. Quina, and H. Chaimovich, *Biochem. Biophys. Res. Comm.*, 1978, **81**, 1080.

15 T. Kunitake, Y. Okahata, and S. Yasunami, *Chem. Lett.*, 1981, 1397.

16 R. McNeil and J. K. Thomas, *J. Colloid Interface Sci.*, 1980, **73**, 522.

17 Y. Okahata, S. Hachiya, and G. Nakamura, *Chem. Lett.*, 1982, 1719.

18 Y. Okahata, H.-J. Lim, and G. Nakamura, *Chem. Lett.*, 1983, 755.

19 J. L. Houben, O. Pieroni, and A. Fissi, *Biopolymers*, 1978, **17**, 789.

20 (*a*) A. Ueno, J. Anzai, T. Osa, and Y. Kodama, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2995; (*b*) A. Ueno, K. Takahashi, J. Anzai, and T. Osa, *ibid.*, 1980, **53**, 1998.

21 G. Veen, R. Honquest, and W. Prins, *Photochem. Photobiol.*, 1974, **19**, 197.

22 (*a*) M. Irie and K. Hayashi, *J. Macromol. Sci., Chem.*, 1979, **A13**, 511; (*b*) M. Irie, A. Menju, and K. Hayashi, *Macromolecules*, 1979, **12**, 1176.

23 D. T. Chen and H. Morawetz, *Macromolecules*, 1976, 9, 463.

24 A. Kumano, O. Niwa, T. Kajiyama, M. Takayanagi, K. Kano, and S. Shinkai, *Chem. Lett.*, 1983, 1327.

25 C. D. Eisenbach, *Macromolecules*, 1978, **179**, 2489.

26 S. Shinkai, H. Kinda, and O. Manabe, *J. Am. Chem. Soc.*, 1982, **104**, 2933.

27 K. Ishihara, N. Negishi, and I. Shinohara, *J. Appl. Polym. Sci.*, 1982, **27**, 1897.

28 (*a*) S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano, and O. Manabe, *Tetrahedron Lett.*, 1976, 4569; (*b*) S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa, and O. Manage, *J. Am. Chem. Soc.*, 1980, **102**, 5860; (*c*) S. Shinkai, T. Ogawa, Y. Kusano, and O. Manabe, *Chem. Lett.*, 1980, 283; (*d*) S. Shinkai, T. Ogawa, T. Nakaji, and Manabe, *J. Chem. Soc., Chem. Commun.*, 1980, 375; (*e*) S. Shinkai, T. Nakaji, T. Ogawa, K. Shigemitsu, and O. Manabe, *J. Am. Chem. Soc.*, 1891, **103**, 111; (*f*) I. Yamashita, M. Fujii, T. Kaneda, S. Misumi, and T. Otsubo, *Tetrahedron Lett.*, 1980, **21**, 541; (*g*) S. Shinkai, T. Ogawa, Y. Kusano, O. Manabe, K. Kikukawa, and T. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 1960; (*h*) S. Shinkai, T. Minami, Y. Kusano, and O. Manabe, *ibid.*, p. 1967.

29 M. Shiga, M. Takagi, and K. Ueno, *Chem. Lett.*, 1980, 1021.

30 (*a*) A. Ueno, H. Yoshimura, R. Saka, and T. Osa, *J. Am. Chem. Soc.*, 1979, **101**, 2779; (*b*) A. Ueno, R. Saka, and T. Osa, *Chem. Lett.*, 1979, 841.

31 (*a*) G. Pelzl, *Z. Chem.*, 1977, **17**, 294; (*b*) C. Leier, and G. Pelzl, *J. prakt. Chem.*, 1979, **321**, 197.

32 T. Kunitake, N. Nakashima, M. Shimomura, Y. Okahata, K. Kano, and T. Ogawa, *J. Am. Chem. Soc.*, 1980, **102**, 6642.

33 (*a*) K. Kano, Y. Tanaka, T. Ogawa, M. Shimomura, Y. Okahata, and T. Kunitake, *Chem. Lett.*, 1980, 421; (*b*) K. Kano, Y. Tanaka, T. Ogawa, M. Shimomura, and T. Kunitake, *Photochem. Photobiol.*, 1981, **34**, 323.

34 Y. Okahata, H. Ihara, M. Shimomura, S. Tawaki, and T. Kunitake, *Chem. Lett.*, 1980, 1169.

35 M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.*, 1982, **104**, 1757; *Chem. Lett.*, 1981, 1001.

36 (*a*) T. Kunitake, Y. Okahata, K. Tamaki, F. Kumamaru, and M. Takayanagi, *Chem. Lett.*, 1977, 387; (*b*) Y. Okahata, R. Ando, and T. Kunitake, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3647.

37 T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami, and K. Takarabe, *J. Am. Chem. Soc.*, 1981, **103**, 5401.

38 M. Shimomura, K. Iida, and T. Kunitake, *Polym. Preprints Jpn.* 1981, **20**, 1208.

39 Y. Okahata, R. Ando, and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 789.

40 T. Nagamura, S. Mihara, Y. Okahata, T. Kunitake, and T. Matsuo, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 1093.

41 K. Kano, A. Romero, B. Djermouni, H. Aehe, and J. H. Fendler, *J. Am. Chem. Soc.*, 1979, **101**, 4030.

42 T. Kajiyama, A. Kumano, M. Takayanagi, Y. Okahata, and T. Kunitake, *Chem. Lett.*, 1979, 645.

43 D. Papahadjopoulous, S. Nir, and S. Ohki, *Biochim. Biophys. Acta*, 1971, **266**, 561.

44 F. T. Schwarz and F. Poltanf, *Biochemistry*, 1977, **16**, 4335.

45 H. D. Price and T. E. Thompson, *J. Mol. Biol.*, 1969, **41**, 443.

46 S. B. Hldaky and D. H. Haydon, *Biochim. Biophys. Acta*, 1972, **274**, 294.

47 S. Kranse, G. Eisenman, and G. Szabo, *Science*, 1971, **174**, 412.

48 Y. Okahata and H. Noguchi, *Chem. Lett.*, 1983, 1517.

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