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PHOTOSENSITIVE ARTIFICIAL MEMBRANES BASED ON AZOBENZENE AND SPIROBENZOPYRAN DERIVATIVES

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1. INTRODUCTION

Much effort has recently been devoted to developing artificial membranes the chemical and physical properties of which can be regulated in response to external stimuli such as temperature, electric field, light and ions and molecules.[1–5] The functions of these artificial systems are closely related to those of biological membranes and often mimic directly their highly sophisticated functions and even structure. Stimulus-sensitive membranes would find applications in energy conversion and storage, electric devices such as transducers and sensors, separation and purification of chemicals, and in other fields.

Among the stimuli-sensitive membranes, the present Report deals with some topics in the recent progress of photosensitive artificial membranes prepared using organic materials. Photosensitive membranes are currently attracting much attention because of the many possible applications in diverse fields of science and technology. Additionally, the mechanistic study of the photoresponsive behaviour of membranes can provide us with valuable information concerning the mechanisms of naturally occurring systems sensitive to light, such as photosynthesis, phototropism, and vision. The membrane-forming materials (e.g., polymers and natural or synthetic lipids) are usually insensitive to light by themselves. Therefore, to endow the membrane with photosensitivity, it needs to be modified with suitable photosensitive molecules which can receive and convert the light signal appropriately. Figure 1 illustrates typical photosensitive molecules and their photochemical

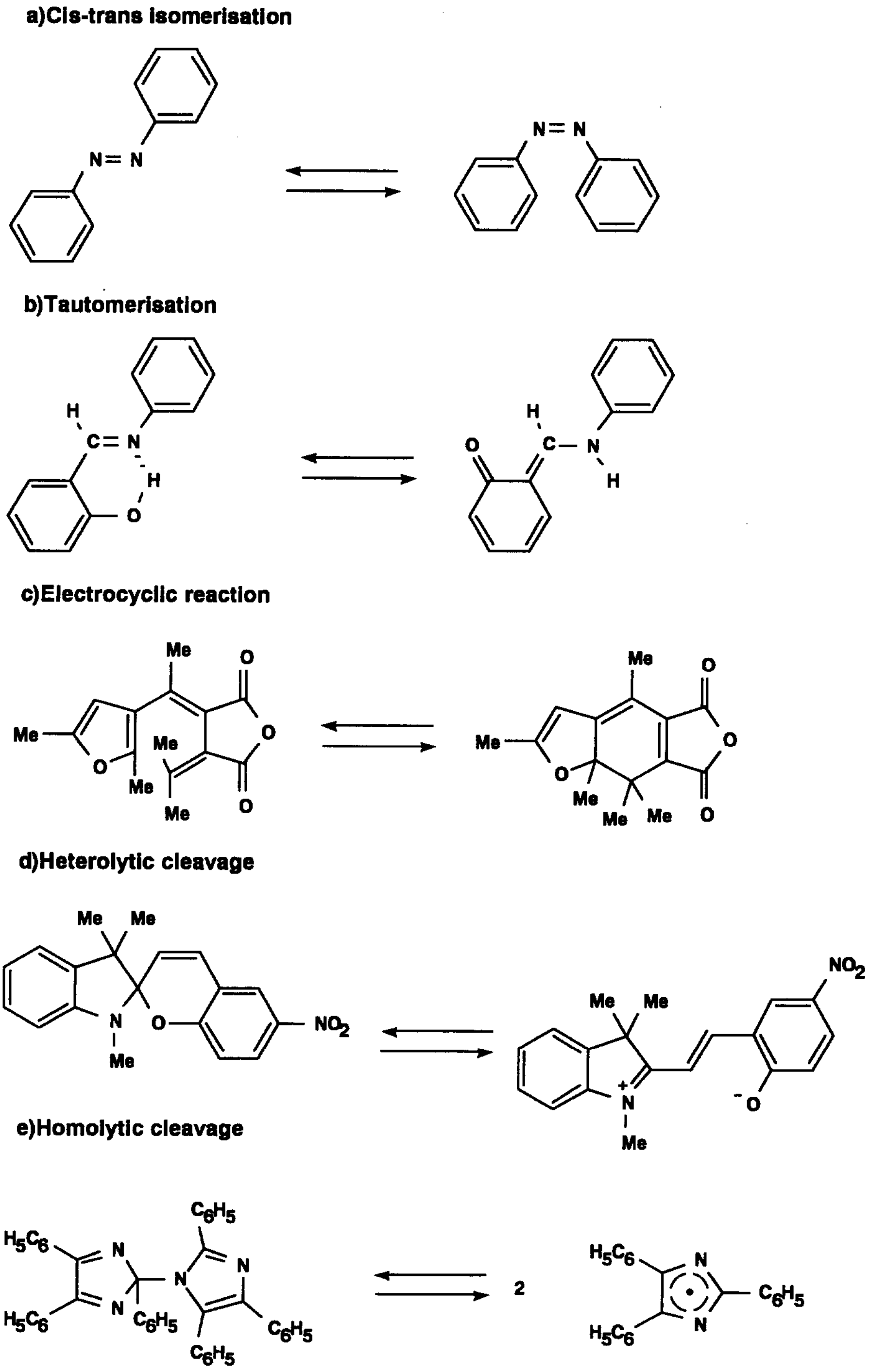

Fig. 1. Typical photo-sensor molecules and their photochromic reactions.

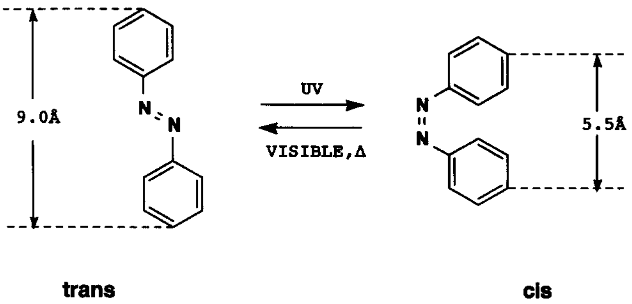

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Fig. 2. Photoisomerisation of azobenzene **1**.

reactions. It is common to all such molecules that they exhibit reversible changes between two states having considerably different optical and electrical properties. The types of photoinduced reactions include *cis–trans* isomerism, tautomerism, homolytic and heterolytic cleavage and dimerization. The present report concentrates upon photosensitive membranes using azobenzene and spirobenzopyran derivatives as photo-sensors.

2. PHOTOCHEMISTRY OF AZOBENZENE AND SPIROBENZOPYRAN

2.1. *Photoisomerism of azobenzenes*

Azobenzene **1** and its derivatives can undergo *cis–trans* isomerisation as shown in Fig. 2.[6] Azobenzene derivatives generally assume the *trans* configuration under dark conditions: i.e., the *trans* form is thermodynamically more stable than the *cis* form. The *trans* isomer is converted into the *cis* form by UV light irradiation, and the resultant *cis* isomer can return to the original *trans* form photochemically in visible light or thermally in the dark. Thus, UV or visible light irradiation yields a photostationary mixture of *cis* and *trans* isomers, the composition of which is dependent upon the wavelength and intensity of light, temperature, solvent, etc.

The *cis–trans* isomerisation of azobenzene derivatives is characterized by monitoring the intense UV absorption (at 320 nm for azobenzene, Fig. 3) which is attributable to the π–π^* transition of

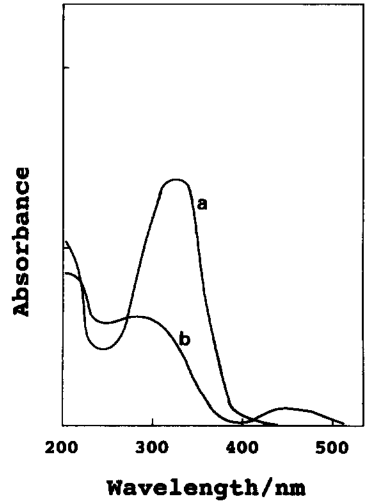


Fig. 3. Absorption spectra of azobenzene before (a) and after (b) UV light irradiation.

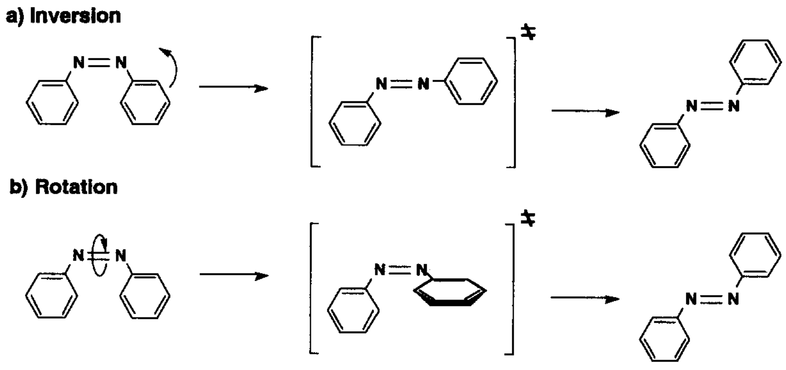


Fig. 4. Mechanisms of thermal *cis–trans* isomerisation of 1.

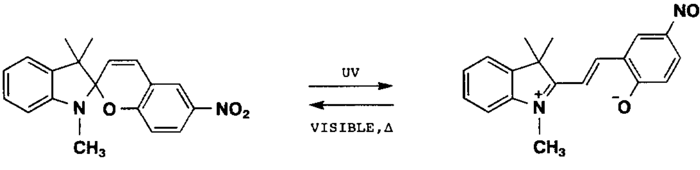
the *trans* isomer and the weak band at longer wavelength (at 430 nm for azobenzene) arising from the n–π^* transition of the *cis* isomer.[7] The wavelengths of the π–π^* and n–π^* transitions depend upon the positions and types of substituent on the azobenzene framework. The photochemical and thermal interconversion between *trans* and *cis* forms is almost reversible and involves no competing reaction of significance. Quantum yields for the photochemical reactions are generally high, and the thermal isomerisation follows first-order kinetics in solution. Most azobenzene derivatives are inherently photochromic; however, in some cases the *cis* isomers are difficult to detect by conventional equipment on account of the extremely short half-life of the *cis* isomer.

There has long been controversy over the mechanism of the thermal *cis–trans* isomerisation of azobenzene derivatives: the rotation mechanism[8–10] and the inversion mechanism[11–16] (Fig. 4).

It is important, in relation to the development of photosensitive membranes, to note that the photoisomerism of azobenzene derivatives is accompanied by a significant change in stereochemistry. The *trans* isomers assume a planar configuration, whereas one of the benzene rings of the *cis* isomers occupies a plane tilted 56° from the plane of the other ring. Thus, the distance between the *para* carbon atoms in the azobenzene framework decreases to ca. 5.5 Å in the *cis* form as compared with ca. 9.0 Å in the *trans* form.[17] These changes in geometry have been successfully utilized to regulate the structure and function of azobenzene-based photosensitive membranes.

2.2. *Photo-cleavage of spirobenzopyrans*

The photochromic behaviour of spirobenzopyran derivatives has been investigated by many researchers.[18–22] It is well established that 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] **2**, as a prototype of a photochromic spirobenzopyran, exhibits a photochromism as shown in Fig. 5. The compound is stable in its closed form and its solution is colourless. UV irradiation produces a metastable open form which absorbs intensely at 550–600 nm (purple) (Fig. 6). The original colourless form can be restored by visible light irradiation or thermally. The remarkable



2

Fig. 5. Photochromic reaction of spirobenzopyran **2**.

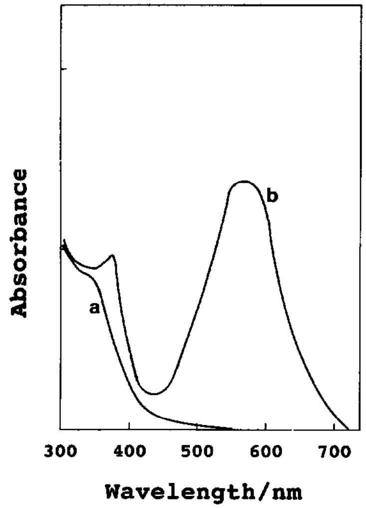


Fig. 6. Absorption spectra of spirobenzopyran **2** before (a) and after (b) UV light irradiation.

photoinduced colour change can be explained by the extension of the conjugated system in the open form as compared with the nonplanar structure of the original spirobenzopyran which is contained in orthogonal planes connected by a spiro carbon.

Another interesting feature of the photoinduced reaction is that UV irradiation induces electric charges in the open form of the molecule: that is, a positive charge at the tertiary amine group and negative at the phenolate group. This implies that spirobenzopyran derivatives can be used to regulate the electrical properties of artificial membranes as well as their optical properties.

The photochromic properties of spirobenzopyran derivatives are known to be modified drastically depending upon the position and type of substituents. A typical example is shown in Fig. 7.[23] The carboxy-substituted spirobenzopyran (1′,3′,3′-trimethylspiro[indoline-2,2′-benzopyran]-8′-carboxylic acid, **3**) shows 'reverse photochromism', in which the coloured open form is more stable than the closed form. The compound exhibits a deep colour in organic solution and the colour is bleached by photoirradiation. The open form is considered to be stabilized by proton transfer from the COOH group to the adjacent phenolate residue. Likewise, the solvent polarity significantly influences the photochromism of spirobenzopyrans. Polar solvents generally stabilize the charged structure of the open form, by which effect the absorption spectrum, the kinetics of the thermal back reaction, etc. are modified. As a result of the stabilization effects, polar solvents tend to facilitate 'reverse photochromism'. For example, compound **2** exhibits reverse photochromism in methanol, while normal photochromism is observed in chloroform.[21]

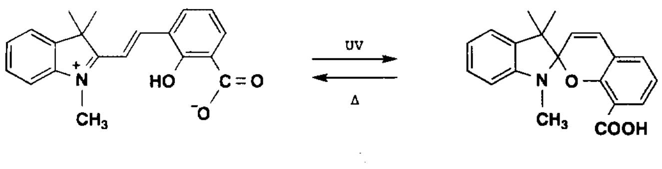


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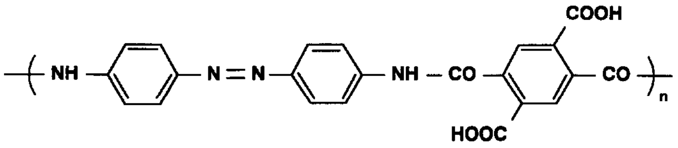
Fig. 7. Reverse photochromism of carboxy substituted spirobenzopyran **3**.

3. AZOBENZENE-MODIFIED MEMBRANES

3.1. *Polymer membranes*

Early studies of azobenzene-modified polymer systems were carried out to clarify the effects of chemical and physical properties of the polymer matrix upon the photochromic behaviour of azobenzenes. Azobenzenes were covalently incorporated in the backbone[24–27] and in the side chain[28–31] of many kinds of polymers, and the kinetics of *cis–trans* photoisomerization of azobenzene residues were discussed in relation to the molecular weight and flexibility of the polymer chains, phase transition between rubbery and glassy states, distribution of free volume, etc.

On the other hand, it is relatively recently that attention has been devoted to the development of photosensitive polymers whose structures and functions can be controlled by photoirradiation. These systems include the reversible control of conformation and viscosity, conductivity, solubility, hydrophobicity and the mechanical properties of polymers in solution and in the solid. In these photosensitive polymers, the azobenzene groups act as the photo-sensor which mediates the transfer of light energy into a change in the chemical and physical properties of the polymers. Some typical polymers are briefly discussed. Irie *et al.* prepared polyamides **4–8** (Fig. 8) having azobenzene units in the backbone to control the solution viscosity.[32] They found that viscosity changes were induced by photoirradiation of the polymer solutions of the polymers (photo-viscosity effect). The viscosity changes were larger in the polymer **5** in which azobenzene units were connected by rigid phenyl groups, as compared with the other polymers (**6–8**) with relatively flexible $-CH_2-$ chains. Photo-induced changes in pH and conductivity were also observed for these polymers. Several authors have reported photo-viscosity effects using azoaromatic polymers or polymer/azobenzene composites.[33–37] The photo-viscosity effects may be caused by the conformational changes of the polymer chains in solution. However, it is rather difficult to identify each conformation responsible for the observed viscosity changes.



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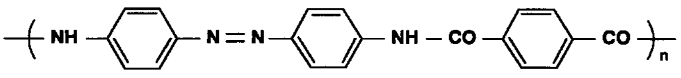

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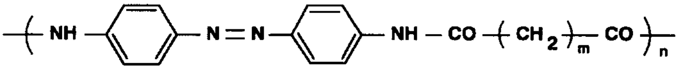
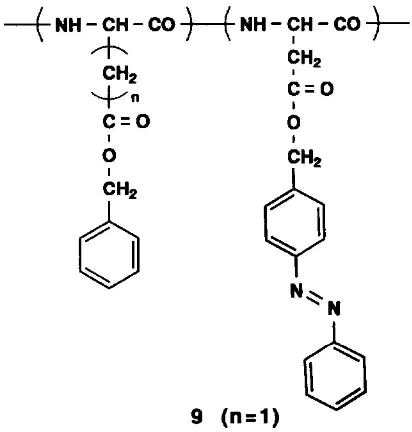


6 (m= 4)
7 (m= 8)
8 (m=12)

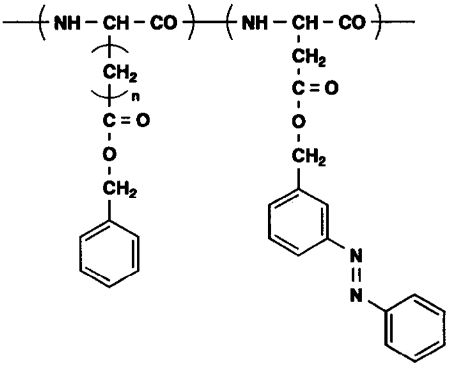
Fig. 8. Azobenzene-containing polyimides **4–8**.

Clear evidence for the photoinduced conformational changes was reported using α-helical polypeptides modified with azobenzene residues.[38–47] Ueno *et al.* prepared a series of polyaspartates **9**–**12** containing an azobenzene residue in the side chains (Fig. 9) and measured IR, NMR, and CD spectra to elucidate the secondary structure (helix or coil) of the polypeptides. They observed a variety of conformational changes including left-handed helix ⇄ right-handed helix, left-handed helix ⇄ random coil, and random coil ⇄ right-handed helix, depending upon the monomer composition of the polypeptides. In contrast, photoirradiation did not induce any conformation change for these polypeptides in solid membranes.[48] Polypeptides composed of phenylalanine, glutamic acid, and lysine were also modified with azobenzenes to study their photoresponse in solution.[49–53]

Kinoshita *et al.* have studied the photoregulation of membrane properties of azobenzene-modified polypeptides **13** and **14** (Fig. 10).[54–58] They measured ionic permeability through the polypeptide membranes, which were prepared by coating a porous Millipore filter with a 0.2% chloroform solution of **13**. UV light irradiation enhanced ionic permeability of the membrane. The results were explained in terms of increased water uptake by the membrane and the resultant higher degree of dissociation of –COOH groups in the side chains. The membrane potential across the

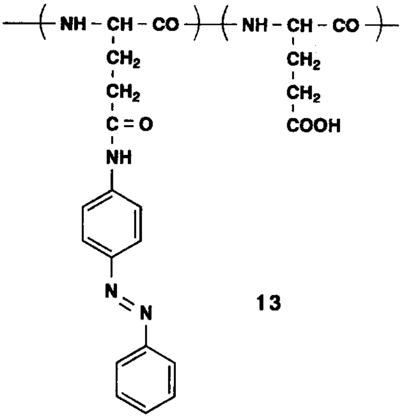


9 (n=1)
10 (n=2)

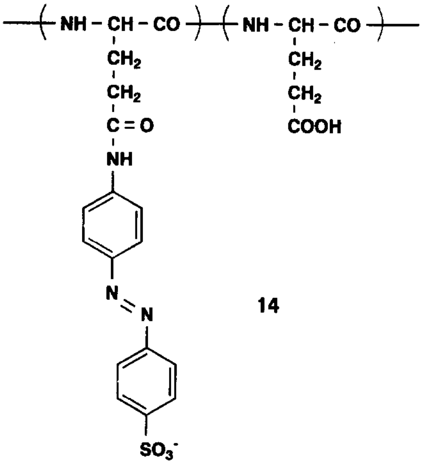


11 (n=1)
12 (n=2)

Fig. 9. Photosensitive poly(aspartate)s having azobenzene side chains 9–12.



13



14

Fig. 10. Poly(glutamate)s having azobenzene side chains **13** and **14**.

polypeptide **13** membrane was also induced upon irradiation. Photoinduced membrane potential was observed in pH 6.2 solution while no response was induced at pH 9.0, indicating the important role of the dissociation equilibrium –COOH $\rightleftarrows$ –COO$^-$ in the membrane. They explained the results on the basis of the fact that the water content of the membrane was enhanced by photoirradiation due to the hydrophilic nature of *cis*-azobenzene residues. The enhanced water content probably increased the dissociation of –COOH residues to increase the negative fixed charges in the membrane. Porous filters coated with polypeptide **14** were also photoirradiated to examine the permeability in relation to the helix–coil transition of the polypeptide. The hydrodynamic permeability of the membrane was dependent upon pH and photoirradiation, showing a key role of the helix–coil transition in determining the permeability of the membrane. UV light irradiation induced permeability changes of the membrane in the pH range 3–7, where the conformation of the polypeptide is sensitive to light. It can be supposed that the effective pore size of the filter membrane is regulated by the conformational transition of the polypeptide chains adsorbed on the pore wall.

The polypeptide **14** was cross-linked with diaminodiphenylmethane to prepare insoluble membranes (Fig. 11), and the conformation of **14** in the membrane, the hydration and the membrane potential were studied under photoirradiation. The CD spectra of the membrane **14** (the azo-

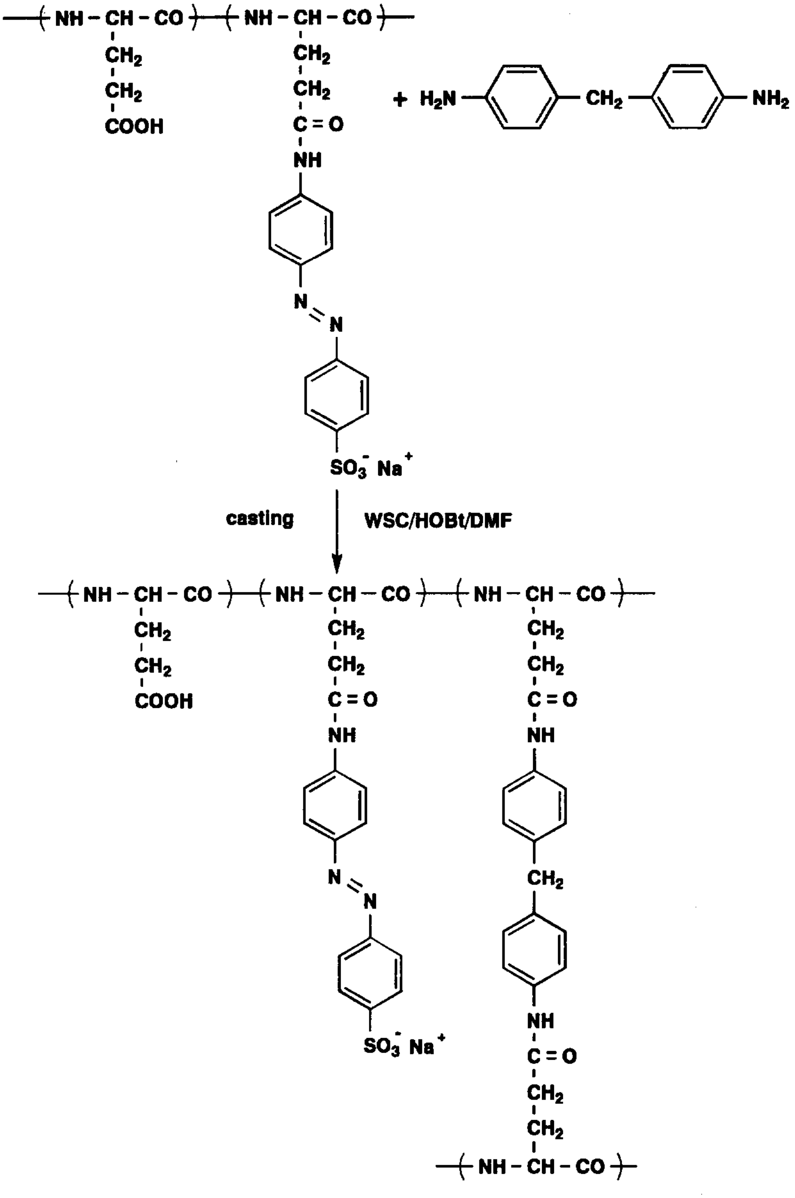


Fig. 11. Preparation of photosensitive membrane from **14**.

benzenesulfonate content was 14.1%) showed that the helix content of the membrane decreased from 76% to 46% upon UV irradiation at pH 7.5. The photoinduced conformational changes occurred in the limited pH range (pH 5.0–9.0) where the –COOH group in glutamic acid can dissociate in part. These results suggest that the conformational changes of the membrane arise from the increase in the electrostatic repulsion between sulfonate anions and carboxylate anions in the side chains, which may result from the formation of the *cis* form of azobenzenesulfonate. It is conceivable that *trans–cis* isomerization of azobenzenesulfonate induces rearrangement of the charge distribution in the membrane. The membrane potential was induced across the polypeptide **14** upon photoirradiation in the pH region where the helix content is sensitive to light. The results were discussed in relation to the change in hydration of the membrane. Unfortunately, the photoinduced changes in conformation, hydration and potential of the membrane **14** were not reversible. Triphenylmethane dyes have also been employed by Kinoshita *et al.*[59–62] to prepare photosensitive polypeptide membranes.

The conformational versatility of azobenzene-modified polypeptides **9–12** in solution was first demonstrated by Ueno *et al.* (Fig. 9).[38–48] The polypeptide **9** was grafted to a copolymer composed of styrene and butyl methacrylate to prepare solid membranes which have microdomains of the polypeptide **9** (Fig. 12).[63] Inoue *et al.* showed that the premeability of the membrane can be controlled reversibly by UV and visible light irradiation. The permeability changes were discussed in relation to the photoinduced conformational changes of polypeptide **9** forming microdomains in the membrane.

Shinohara and co-workers prepared several kinds of azoaromatic polymers and studied the photoresponse in binding and transporting abilities of the polymers in solid membranes.[64–72] It was demonstrated that the hydrophobicity of the membrane surface can be regulated by *cis–trans* isomerisation of azoaromatic residues in the membrane. They proposed 'photocontrolled adsorption chromatography' for the purification of some drugs[65] and proteins[66]. It was also possible to control

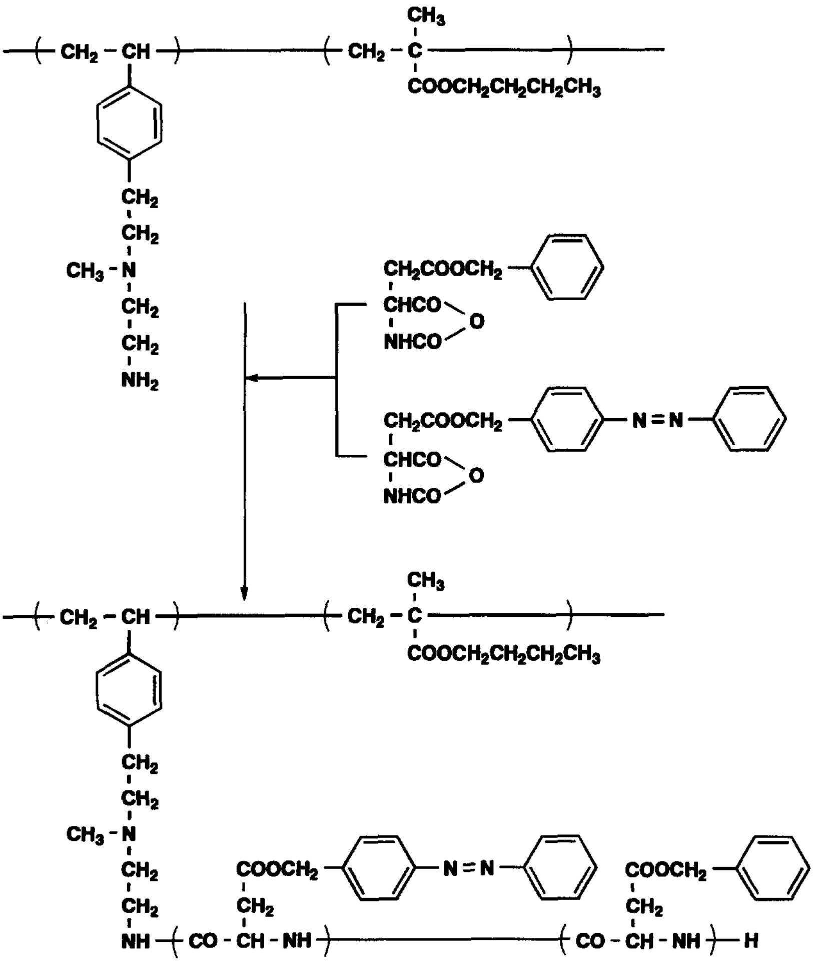
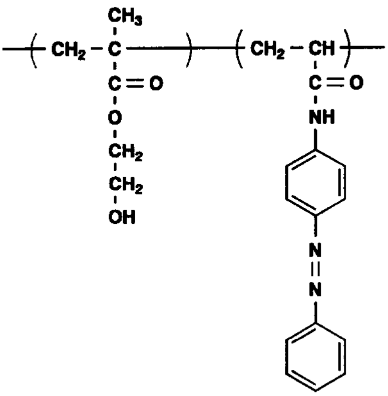


Fig. 12. Polymer membranes having photosensitive channel.



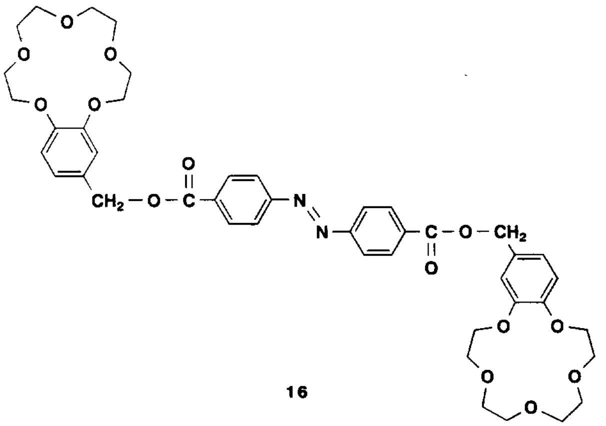
15

Fig. 13. Azobenzene-modified poly(2-hydroxyethyl methacrylate) **15**.

the permeability of proteins through membranes composed of poly(2-hydroxyethyl methacrylate) having azobenzene side chains **15** (Fig. 13), based on the contraction of the swollen membrane caused by a photoinduced polarity change of the azobenzene residues.[67,72]

The photocontrolled permeability of the azobenzene-modified polymer membranes discussed above is mainly based upon the change in the size and structure of the membrane pores. On the other hand, it would be possible for artificial membranes to use a carrier for the selective transport of ions and molecules. In fact, in biological membranes, a carrier mechanism is an important process in selective permeation, as well as channel or pore mechanisms. The photocontrol of the membrane permeability may be realized for artificial membranes by the use of carrier molecules which are modified with an appropriate photo-sensor group. Based on this strategy, ion carriers (crown ether) were modified with photosensitive groups.[73-80] Modified crown ethers have been used extensively for ion transport through liquid membranes.

We have prepared photosensitive poly(vinyl chloride) (PVC) membranes in which azobenzene-modified bis(crown ether) **16** (Fig. 14) is entrapped as an ion carrier.[81,82] The **16**-entrapped PVC membrane was prepared typically by pouring a mixture of 235 g of PVC, 0.54 ml of dibutyl phthalate (plasticizer), and 2.5 mg of **16** in 20 ml of tetrahydrofuran onto a 9.2 cm diameter rimmed glass plate (or flat Petri dish) and allowing the solvent to evaporate at ambient temperature. This



16

Fig. 14. Azobenzene-bridged bis(crown ether) **16**.

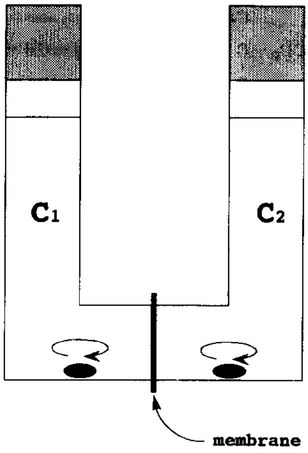


Fig. 15. A U-shaped glass cell for ion transport.

procedure gave a transparent membrane of ca. 0.1 mm thickness. A U-shaped glass cell (Fig. 15) was used for the permeation experiment of alkali-metal picrates.

It is reasonable to assume that, in this system, a large portion of alkali-metal picrate diffuses across the hydrophobic membrane in an electrically-neutral ternary complex composed of metal cation, picrate anion and crown ether, which forms according to Eq. (1) at the membrane/solution interface:

$$M^+ + Pi^- + CR \rightleftharpoons (CR \cdot M^+ \cdot Pi^-) \qquad (1)$$

where M^+, Pi^-, and CR denote metal cation, picrate anion and crown ether, respectively, and $(CR \cdot M^+ \cdot Pi^-)$ is the ternary complex (Fig. 16). Therefore, the binding constant of the crown ether to the cation should directly determine the concentration of the ternary complex in the membrane and hence the flux of the ion across the membrane. For these reasons, it would be possible to regulate the ion permeation across the membrane if the ion binding constant can be switched by photoirradiation. Table 1 lists the rates of permeation of alkali-metal picrates before and after photoirradiation. From the data the following conclusions may be reached: (1) UV light irradiation facilitates the permeation of K^+ picrate, but not the permeation of the other cations, (2) the permeation selectivity of the membrane is in the order of $K^+ > Rb^+ > Na^+ > Cs^+$, and (3) the permeation rate of the cations depends almost linearly upon the density of **16** in the membrane. The results can be explained in terms of the enhanced binding ability of **16** to K^+ ion selectively by

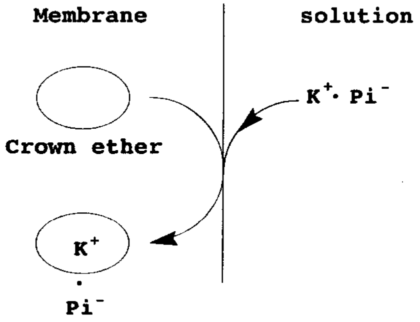


Fig. 16. Ion binding by crown ether at the membrane/solution interface.

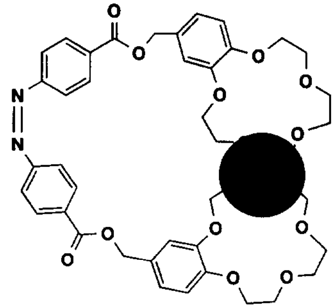


Fig. 17. Intramolecular 2 : 1 complex of **16** with large cations (bis-crown effect).

UV light irradiation. This is often called "bis-crown effects" (Fig. 17). Table 2 shows the ion binding ability of **16**, assessed by a liquid–liquid extraction technique. The data clearly shows the enhanced ion binding of **16** to K^+ ion in the *cis* form.

Kajiyama *et al.* employed polymer/liquid crystal/azobenzene-modified crown ether composite membranes to control ion permeation by light irradiation. They reported that the facilitated and up-hill transport of alkali-metal ions can be induced by light as a driving force.[83]

Because of the selective binding to alkali- and alkaline earth-metal cations, crown ethers are currently finding many scientific and industrial applications, including as solubilizers of metal ions in organic media, in catalysis in organic synthesis, in extraction and purification of metal ions, and as ion carriers in membrane electrodes. The membranes containing crown ethers are also attracting much attention with a view to developing selective separation systems. However, comparatively few studies have reported on the membrane potential of the crown ether membranes.

We have found that the membrane potential can be induced by photoirradiation to the plasticized

Table 1. Effect of UV light upon ion permeation through PVC/**16** membrane with various **16** content[a)]

Membrane	Permeation rate (10^{-9} mol h^{-1} cm^{-2})			
	Na	K	Rb	Cs
In dark				
A	3.5	9.4	4.6	1.7
B	4.7	13	9.4	2.8
C	8.7	20	21	5.9
Under UV light				
A[b)]	4.3	12	4.7	1.9
B[b)]	5.7	18	10	2.8
C[b)]	10	29	20	6.9

a)The contents of **16** in the membranes are 0.02 (A), 0.08 (B), and 0.16 mg/cm^2 (C).

b)<u>Cis</u> isomer, 50%.

Table 2. Effect of photoirradiation upon ion binding ability of **16**[a)]

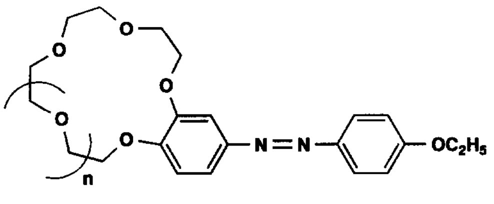
	Extracted picrate (%)			
	Na	K	Rb	Cs
Trans **16**	24	40	25	27
Irradiated **16**[b)]	24	53	38	34

a)Ion binding was assessed by liquid/liquid extraction. Organic phase (dichloromethane):[**16**]=1×10^{-4} M. Aqueous phase:[picrate]=1×10^{-5} M and [metal chloride]= 1×10^{-3} M.

b)Cis isomer, 36%.

PVC membranes doped with azobenzene-modified crown ethers **16**, **17**, and **18** (Figs. 14 and 18).[84] The experimental setup for the potential measurements is shown in Fig. 19. The membrane was irradiated with a xenon lamp from the c_2 solution side. As discussed already, *trans–cis* isomerisation of the azobenzene moiety occurs upon photoirradiation, and therefore their conformations can be switched in an on–off fashion. More important is the fact that the binding ability for cations is perturbed by the conformational changes induced by photoirradiation. It is reasonable to assume that, if adsorption/desorption equilibria of ions at the membrane/solution interface is altered by irradiation, surface potential changes can be induced, due to the changes in the structure of the electric double layer at the membrane/solution interface. As discussed later, the photoresponse of the membrane potential could be explained successfully in terms of the surface potential changes associated with the adsorption and/or desorption of ions upon irradiation.

Figure 20a illustrates the time–response of the potential change of the PVC/**16** membrane induced by alternating UV and visible light irradiation.[84–87] After a steady-state potential is set up in the dark, a negative shift of the membrane potential was induced by UV light irradiation. About 3 min sufficed to attain a second steady-state potential under UV light and the initial potential was recovered rapidly by visible light irradiation. The potential changes are thought to arise from the *trans–cis* isomerization of **16** in the membrane in view of the fact that the potential change is synchronized with the absorption change at 331 nm of the membrane, i.e., *trans–cis* isomerisation of **16** (Fig. 20b).



17 (n=1)
18 (n=2)

Fig. 18. Azobenzene-substituted crown ethers **17** and **18**.

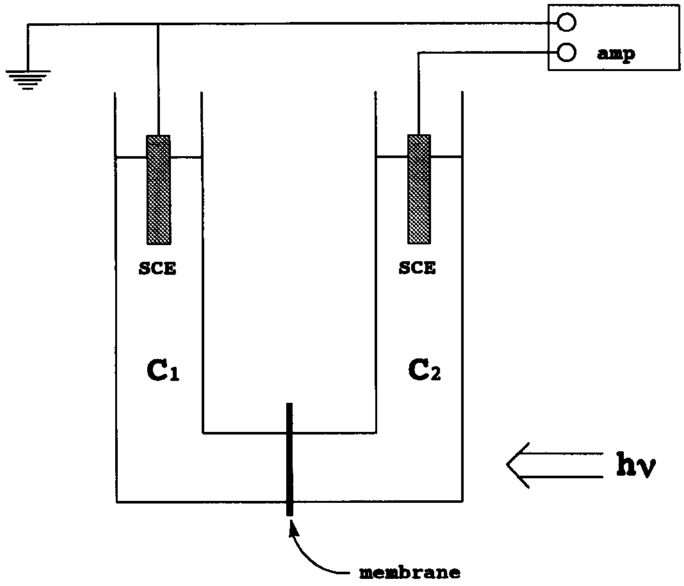


Fig. 19. Experimental setup for the measurement of membrane potential of photosensitive membranes.

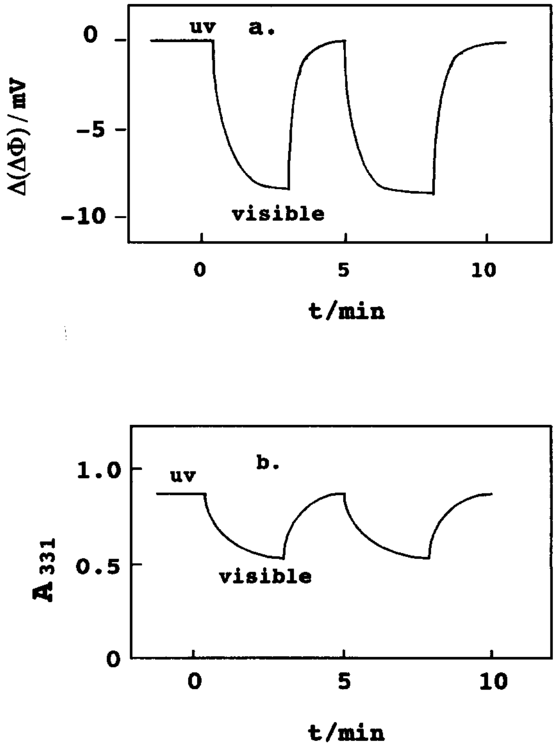


Fig. 20. Photoresponse of membrane potential (a) and absorption (b) of PVC/16 membrane.

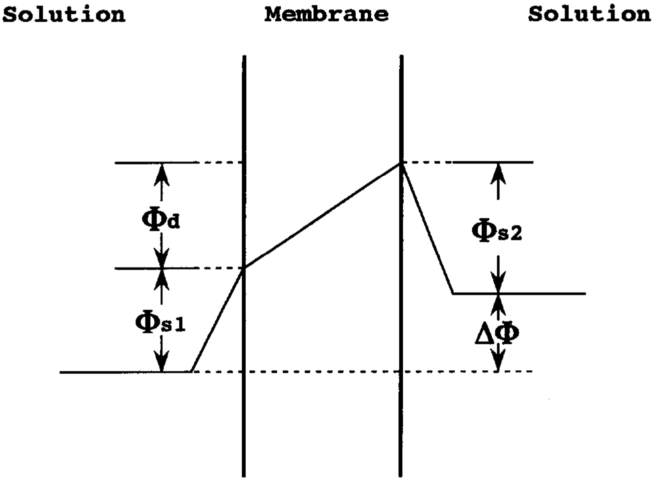
Table 3. Photoinduced potential across PVC/**16** membrane[a)]

Electrolyte	Photoinduced potential (mV)				
	Ion concentration in C_2 side (mM)				
	1	10	100	500	1000
LiCl	-0.5	-0.5	-1.5	-2.0	-2.5
NaCl	0	0	0	0	0
KCl	-2.0	-6.5	-10	-12	-13
RbCl	-2.5	-6.5	-11	-13	-14
CsCl	-1.5	-4.5	-6.5	-8.0	-8.5

a)The ion concentration in C_1 side was 1 mM.
The light was irradiated from C_2 side.

Table 3 describes the effects of the type of cations and the ionic concentration in the solutions upon the photoinduced potential change. A marked dependence of the magnitude of photoresponse upon the cation species was observed. UV irradiation resulted in the large potential shift in the presence of KCl and RbCl, while the response was 2.5 mV or less in the presence of LiCl and NaCl. These observations strongly suggest that the potential changes stem from the enhanced binding ability of **16** for the larger cations at the membrane/solution interface. A 2 : 1 sandwich-type complex formation between *cis*-**16** and the cations seems to be the origin of the enhanced ion binding.

In general, the potential difference ($\Delta\phi$) across a charged membrane (i.e., membrane potential) is given as an algebraic sum of the surface potential differences at the membrane/solution interfaces and the diffusion potential inside the membrane (Fig. 21).[88,89] In the case of the PVC membranes,



$$\Delta\Phi = \Phi_{s1} + \Phi_{d} + \Phi_{s2}$$

Fig. 21. Potential profile across a charged membrane.

the contribution of the diffusion potential to the membrane potential is considered to be always small irrespective of the electrolyte concentration, because the ions diffuse across the membrane mainly in the electrically neutral form of ternary complexes composed of cation, anion, and crown ether due to the highly hydrophobic nature of the plasticized PVC membrane.

In the PVC/**16** membrane system, we can assume that the distribution equilibrium holds with regard to the alkali-metal cation at the membrane/solution interface and that the main factor governing the equilibrium constant is the binding ability of **16** for the cations. Since there is apparently no fixed charge in the PVC membrane, the charge density at the membrane surface is determined by the amount of alkali-metal cation bound to **16** at the membrane surface. As is obvious from the above discussion, *trans–cis* isomerization of **16**, by which the binding ability for larger cations is enhanced, increases the charge density, that is, the surface potential. This mechanism of the potential change reasonably agrees with the result that high response was observed in the region of higher salt concentration. Another interesting aspect is that, even when $c_1 = c_2$ (1 mM), a photoinduced potential was observed. It is generally established that the membrane potential should be zero when the charged membrane is placed between two electrolyte solutions of the same activity.[88,89] This discrepancy may be explained in terms of the formation of an asymmetric membrane on UV irradiation. In other words, the *cis*-**16**:*trans*-**16** ratios on the two surfaces of the membrane are different under UV light. It seems that the *trans–cis* photoisomerisation reaction of **16** proceeds more efficiently on the irradiated surface of the membrane than on the opposite surface. This means that the charge density at the irradiated surface is higher than that at the opposite surface under UV light (Fig. 22).

Figure 23 shows the photoresponse of the membrane potential across the PVC/**18** membrane.[90] The photoresponsive behaviour of the membrane potential was almost the same as that of the PVC/**16** membrane, except for the polarity of the potential shift. Table 4 lists the values of photoinduced potential changes across the PVC/**17** and PVC/**18** membranes. The most remarkable feature is that the membrane potential shifted positively in all cases. We can find the reverse tendency in the case of PVC/**16** membrane (Table 3). The photoinduced uptake of cations from the solution onto the membrane surface was the origin of the negative shifts of the membrane potential for the PVC/**16** membrane. On the other hand, the positive shifts of the potential for the PVC/**17** and

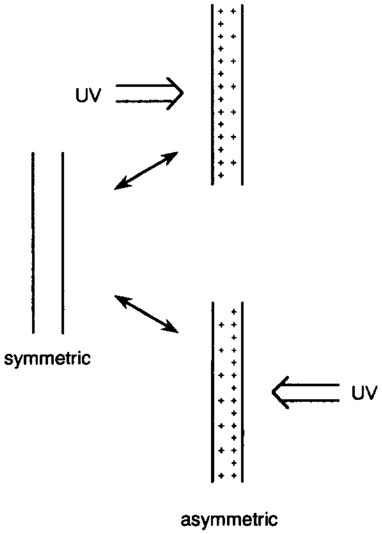


Fig. 22. Photoinduced asymmetric membrane.

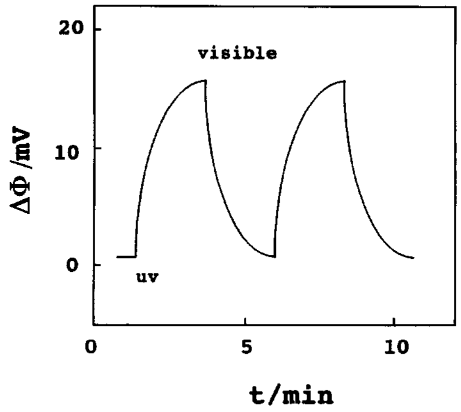


Fig. 23. Photoinduced membrane potential across PVC/**18** membrane. Solution : $c_1 = c_2 = 1$ mM KCl.

PVC/**18** membranes can be explained reasonably on the basis of the photoinduced release of cations from the membrane surface into the solution, in view of the fact that the cation binding abilities of **17** and **18** decrease upon UV light irradiation (Table 4). The ethoxy side chain in *cis*-**17** and *cis*-**18** may interfere with the complexation of the crown ether moiety with cations.

The cation selectivity in the photoresponse was relatively small because the photoresponse of **17** and **18** does not involve a mechanism with cation-size dependence such as 'bis-crown effects', which operated in the case of **16**.

3.2. *Monolayer, bilayer and multilayer membranes*

Recently, thin membranes composed of monolayer, bilayer and multilayers of organic compounds such as natural lipids and fatty acids or their synthetic alternatives have been attracting the attention of scientists in the fields of biology, chemistry, and even electronics. It is envisaged that

Table 4. Effect of photoirradiation upon ion binding abilities of **17** and **18**[a)]

	Extracted picrate (%)			
	Li	Na	K	Rb
Trans **17**	2.8	25	34	18
Irradiated **17**[b)]	1.4	22	20	10
Trans **18**	2.0	23	91	78
Irradiated **18**[c)]	1.5	19	88	74

a)Ion binding was assessed by liquid/liquid extraction.
Organic phase (dichloromethane):[**17**] or [**18**]=5×10^{-5} M.
Aqueous phase:[picric acid]=1×10^{-4} M and [metal hydroxide]= 5×10^{-1} M.

b)Cis isomer, 65%.

c)Cis isomer, 72%.

the physical and chemical properties of the thin membranes can be switched upon photoirradiation, by modifying the membrane with photosensitive molecules.

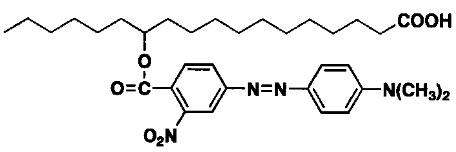
Several groups have reported the synthesis of azobenzene-modified lipids and fatty acids with the intention of developing photosensitive monolayers and multilayers. Möbius first suggested the possibility of the construction of designed monolayer assemblies by the use of monolayer membranes containing such functional groups as dyes, fluorophores and electron donors and acceptors.[91] The azobenzene-modified lipids **19**–**27** (Fig. 24) were prepared by Heesemann[92,93] and Morgan and co-workers.[94,95] They studied monolayer properties of the lipids on a water surface and the deposition of the membranes. However, the effects of *trans–cis* photoisomerisation upon the structure and functions of the monolayers were not reported.

Kunitake and Fukuda and their co-workers have studied the synthesis, membrane formation and spectroscopic properties of several types of azobenzene-containing amphiphiles.[96–103] The azobenzene-containing amphiphiles formed stable monolayers, bilayers and multilayers due to the stacking interaction between the rigid azobenzene residues. They reported an important result that, in the closely-packed membranes, the isomerisation of the azobenzene residues from *trans* to *cis* form is significantly restricted due to the lack of free volume in the membrane phase.[103] In the case of the expanded monolayers at lower pressure, the photoisomerisation occurred to some extent.

Bilayer membranes have been made subject to modification with azobenzene derivatives to control the permeability of the membranes. Kano *et al.* prepared a photosensitive bilayer membrane by doping dipalmitoyl phosphatidylcholine liposomes with the amphiphile **28** (Fig. 25). The *trans–cis* photoisomerisation of **28** perturbed to the ordered structure of the bilayer, and induced an increase of its permeability towards water and bromothymol blue.[104] Recently Sato *et al.* have reported a detailed study on the photochemical control of ion permeability of liposomal membranes containing the azobenzene amphiphile **29** (Fig. 26).[105] The liposomes composed of L-α-dimyristoyl phosphatidylcholine and dicetyl phosphate were doped with **29**, and the ion permeation was monitored in UV and visible light. The liposomal membranes showed higher ion permeability under UV irradiation (permeability coefficient: $P = 10^{-8}$ cm/s at 288 K), as compared with values in the region of $P = 10^{-12}$–10^{-13} cm/s in the dark. The photo-enhanced permeation of ions may arise from the formation of transient pores, as a result of the strain of the membrane around the *cis*-**29** molecule, which has a larger occupied volume than *trans*-**29**. The photoresponse of the liposomal membrane was fully reversible. However, prolonged irradiation with UV light induced deformation and/or fusion of the liposomes.

Liposomes and synthetic bilayer vesicles have been extensively used to simulate the functions of biological membranes, including the photoresponse of cell membranes. The lipid bilayers are generally unstable and fragile against external stimuli such as ambient pH, ionic strength, temperature and osmotic pressure. These drawbacks of lipid bilayers sometimes interfere with the kinetic study of the membrane permeability and its control. In order to solve these problems, Okahata *et al.* employed lipid bilayer-coated nylon capsule membranes and developed photosensitive systems.[106,107] They prepared the nylon capsules with an ultra-thin membrane thickness of 1.0 ± 0.2 μm and a large diameter of 2.5 ± 0.5 mm by the interfacial polycondensation reaction of ethylenediamine and 1,10-bis(chlorocarbonyl)decane. The nylon membrane was porous and asymmetric in structure across the membrane: the highly dense and thin inner layer (pore size 1–2 nm) and the outer porous sponge layer (pore size 0.1–0.3 μm). The pores of the nylon capsules were covered with a lipid bilayer composed of dialkylammonium and azobenzene-modified synthetic lipid **30** (Fig. 27). The permeability of NaCl was increased upon UV irradiation by a factor 3.2 ($P = 6.0 \times 10^{-6}$ cm/s) relative to that in the dark ($P = 1.9 \times 10^{-6}$ cm/s). The disordered structure of the bilayer membrane originating from *cis*-**30** may be responsible for the enhanced permeation of NaCl. The lipid bilayer-covered nylon capsules were used further to develop controlled permeation systems sensitive to pH, temperature, ions and electric field.[107]

The reversible adhesion of vesicles was observed by Kinoshita and coworkers, by the use of a



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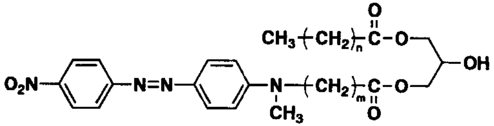
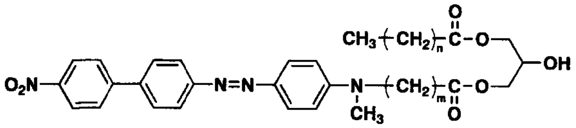
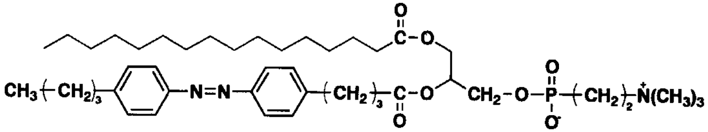


20 (n=18, m=5), **21** (n=18, m=2)
22 (n=14, m=5), **23** (n=14, m=2)



24 (n=16, m=2)



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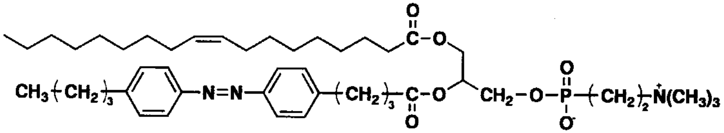

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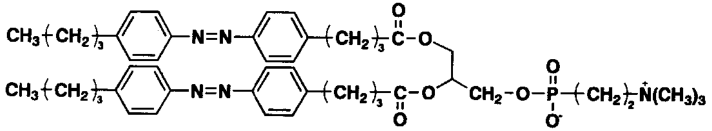

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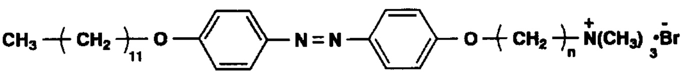
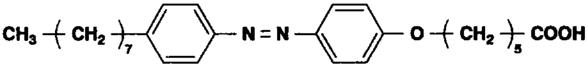
Fig. 24. Azobenzene-modified lipids **19**–**27**.



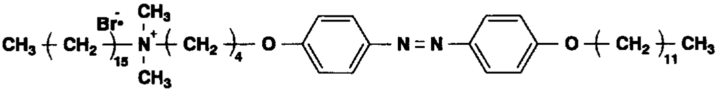
28 n=2 or 4

Fig. 25. Photosensitive amphiphiles **28**.



29

Fig. 26. Photosensitive amphiphile **29**.



30

Fig. 27. Photosensitive amphiphile **30**.

dialkylammonium chloride vesicle doped with azobenzene-modifed polypeptide **31** (Fig. 28).[108] UV light irradiation to the vesicle induced a transfer of the polypeptide from the bilayer membrane interior to the hydrophilic surface of the membrane, which resulted in a decrease of ion permeability across the membrane and of intervesicular adhesion. This process was photochemically irreversible, that is, the ion permeability and the adhesion of the vesicles remained unchanged upon visible light irradiation. However, by increasing the temperature above the transition temperature from gel to liquid crystal, 40°C, of the vesicle, the original permeability and dispersed vesicle structure could be recovered.

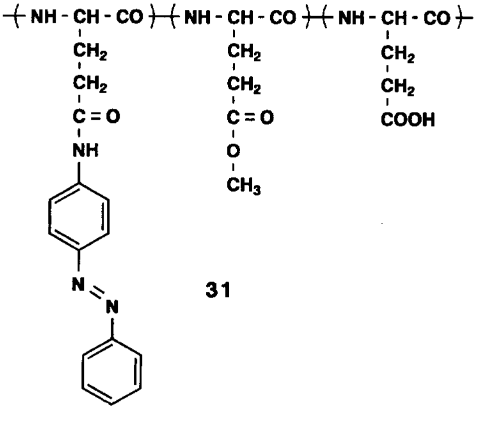


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Fig. 28. Azobenzene-modified polypeptide **31**.

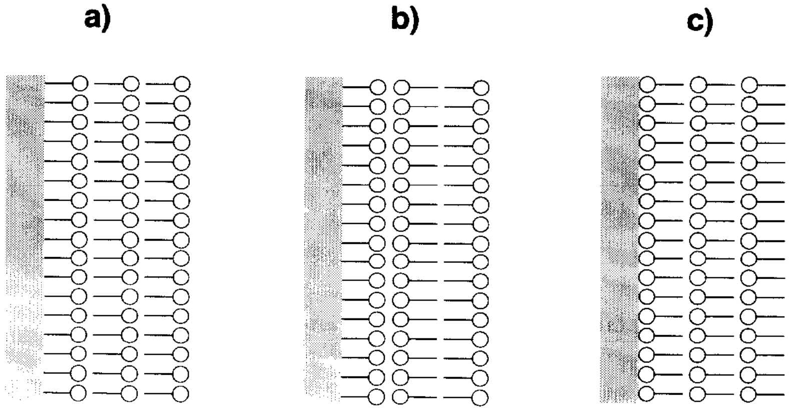
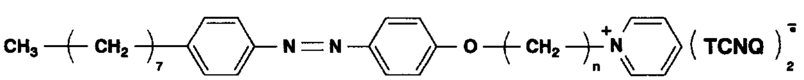


Fig. 29. Structures of deposited LB membranes (a) X-type, (b) Y-type, and (c) Z-type deposition.

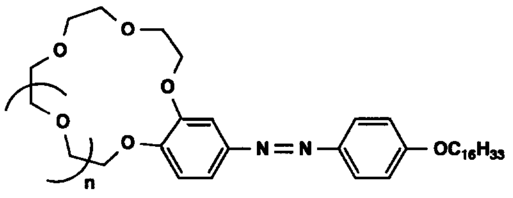
The lipid multilayers prepared on the surface of solid supports are called Langmuir–Blodgett (LB) membranes. The LB membranes are deposited on the solid support by dipping and raising the support vertically through the monolayer which is prepared on a water surface. This procedure gives three possible kinds of structure in the built up multilayers (Fig. 29). The deposition mode depends not only upon the chemical structure of the molecules but also upon the ionic composition of the water phase, the temperature, and even the speed of dipping and raising of the support.[109] The amphiphilic molecules, which have a structure composed of hydrophilic and hydrophobic portions, are most widely utilized for LB membrane formation. Fatty acids and lipids are prototypes of this class of molecules.

It has been established that the photoisomerisation of azobenzene residues from *trans* form to *cis* form is generally retarded in the LB membrane due to the lack of free volume for the conformational change.[103] In order to develop photosensitive LB membranes containing the azobenzene unit as a photo-sensor, the composites of LB membranes have recently been studied and the *trans–cis* photoisomerisation was observed for the systems composed of an amphiphilic cyclodextrin[110] and a polyion complex of poly(allylamine).[111] More recently, the photochromic behaviour of pure LB membranes without any additives has been studied for the azobenzene amphiphiles **32–34** (Fig. 30). The content of the *cis* isomers of **32**, **33**, and **34** at the photostationary state is reported to be 22%, 25%, and 56%, respectively, in the pure LB membranes deposited at a surface pressure of 25 mN/m.[112,113] The bulky head group in the hydrophilic part in **32–34** probably supplies a sufficient free volume for the *trans–cis* isomerisation. It was shown that the conductivities of the LB membranes of **32–34** are regulated by photoirradiation.



32 (n= 6)
33 (n=12)
34 (n=14)

Fig. 30. Azobenzene amphiphiles with bulky head group **32–34** TCNQ : 7,7,8,8-tetracyanoquinodimethane.



35 (n=1)
36 (n=2)

Fig. 31. Azobenzene-substituted lipophilic crown ethers **35** and **36**.

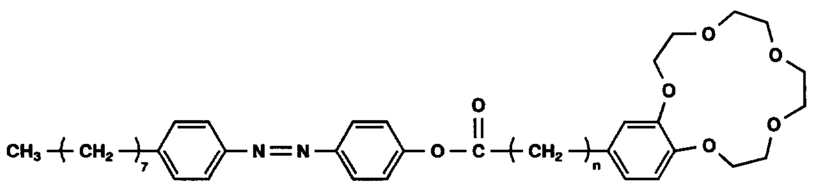
We prepared **35**–**38** for developing crown ether LB membranes sensitive to light.[114] The LB membranes of **35** and **36** (Fig. 31) can be prepared on a glass plate as a Y-type structure. Unfortunately, the photoisomerisation of **35** and **36** was severely retarded in these membranes, the content of *cis* isomers in the photostationary state being 10–15% for both **35** and **36**. This is probably the result of strong interaction caused by intermolecular stacking of the adjacent azobenzene residues in the LB membranes. On the other hand, the LB membranes prepared from **37** and **38** (Fig. 32) exhibited photoresponse. The absorption spectra of the LB membranes showed that the compounds **37** and **38** can isomerise reversibly upon photoirradiation. The contents of *cis* isomers of **37** and **38** were 42% and 55%, respectively, in the photostationary state at room temperature (ca. 20°C). Sufficient free volume may be available in the membranes due to the bulky head group of the crown ether moiety. This result, together with the data for the LB membranes of **32**–**36**, implies that the photoisomerisation proceeds more efficiently when the azobenzene moiety is more isolated from the hydrophilic head group. The azobenzene-containing amphiphiles **37** and **38** would be expected to be used for developing LB membranes sensitive to light and ions.

As reported by Fukuda and coworkers,[103] the *trans–cis* isomerisation of azobenzene residues is usually suppressed or, in some cases, inhibited in the LB membranes. The Fujishima group, however, have found that the amphiphile **29** (Fig. 26) isomerises from *trans* form to *cis* form to some extent in its pure LB membrane after a pretreatment with UV light.[115] They have proposed a novel photoelectrochemical system for photon-mode information storage using the **29** LB membranes.[116–119]

4. SPIROBENZOPYRAN-MODIFIED MEMBRANES

4.1. *Polymer membranes*

The photoregulation of the conformation of polymer chains has been studied in solution for spirobenzopyran-modified polymers including poly(methacrylate),[120] poly(tyrosine),[121] poly



37 (n=0)
38 (n=2)

Fig. 32. Azobenzene amphiphiles with crown ether head group **37** and **38**.

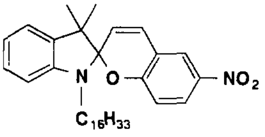
(lysine),[122] and poly(glutamate).[123] Photo-viscosity effects were found for the spirobenzopyran-modified poly(methacrylate).[124] In these systems, the electrostatic repulsion between the open form of spirobenzopyran in the side chains is responsible for the conformational changes and the photo-viscosity effect of the polymers.

Few reports have appeared on solid membranes prepared from spirobenzopyran-modified polymers. Irie *et al.* reported that the solid membranes prepared from poly(methacrylate) having spirobenzopyran side chains exhibit photoresponse in membrane potential. They observed ca. 10 mV of photoinduced potential for the membranes.[125]

On the other hand, the composite membranes of polymer materials and spirobenzopyrans have been extensively studied to control membrane potential. Suzuki and coworkers first demonstrated that membrane potential can be regulated by photoirradiation using spirobenzopyran-doped acetyl cellulose membranes.[126–128] They entrapped spirobenzopyran **2** in an acetyl cellulose membrane, and showed that the membrane potential can be changed upon irradiation. Bellobono *et al.* studied the photoresponse of cellulose 2,4-diacetate membranes incorporating spirobenzopyran derivatives with the intention of constructing photoresponsive devices for optical data storage.[129,130]

Recently, photoresponse of the spirobenzopyran-containing membrane has been highly improved by us by the use of a plasticized poly(vinyl chloride) (PVC) as a membrane matrix.[131–134] Figure 33 shows a typical photoresponse of the membrane potential across the PVC/1′-hexadecyl-3′,3′-dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2′-indoline) **39** membrane. After a steady-state membrane potential had been obtained in the dark, a remarkable negative shift of the potential was induced by UV light irradiation. A photoinduced potential of more than 100 mV was attained with rapid response time (ca. 1 min). The highly hydrophobic environment in the membrane phase, in which there is no apparent fixed charge except for the open form of **39**, may be favourable for the enhanced photoresponse. This is not the case for cellulose and poly(methacrylate) membranes.

From the viewpoint of mechanistic study of the photoresponse of the PVC/**39** membrane, it is important to analyse the data obtained under conditions of equal NaCl concentrations on both



39

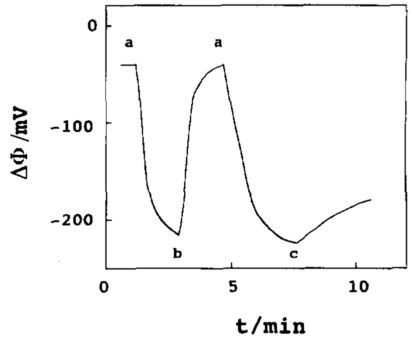


Fig. 33. Photoinduced potential across the PVC/**39** membrane (a) UV light on, (b) visible light on, and (c) light off. Solution : c_1 = 1 mM KCl and c_2 = 10 mM KCl.

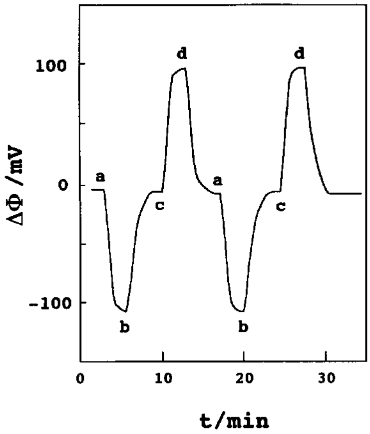


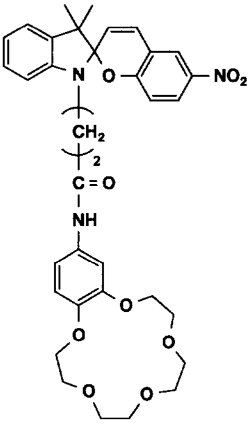
Fig. 34. Photoresponse of the PVC/**39** membrane. The membrane was irradiated with UV light from c_2 (a) and c_1 (c) sides and with visible light (b and d). Solution: $c_1 = c_2 = 1$ mM KCl.

sides of the membrane. Figure 34 illustrates the photoresponse observed when UV and visible light were irradiated from each side of the membrane alternately. Even under $c_1 = c_2$ conditions, the membrane potential shifted upon UV light irradiation positively or negatively, depending upon the direction from which the membrane was irradiated. The membrane potential always has a value of ca. 0 mV under visible light. These results suggest that the charge densities at both surfaces of the membrane are not equal when irradiated with UV light. The unequal distribution of the electric charges between both surfaces of the membrane is because the open form of **39** is generated more efficiently at the irradiated surface than at the opposite surface. In other words, the PVC/**39** membrane has an asymmetric structure only under UV light with respect to the charge density, or the content of open-**39** (Fig. 22).

It is evident that the generation of membrane potential can be attributed to the photochemically produced open form of **39**. However, the correct structure of the open form, which is directly concerned with the potential generation at the membrane/solution interfaces, is not fully obvious. Some authors refer to the significant role of the protonation of the open form of spirobenzopyran. In this regard, the effects of pH of the solution were examined. The photoresponse depended drastically upon the pH of the aqueous solutions at both sides of the membrane, and the higher response was obtained when the membrane surface facing an acidic solution was exposed to UV light. These data suggest the importance of the protonated form of the spirobenzopyran in inducing the membrane potential. The protonated form of the open **39** is likely to be the origin of the net positive charge in the irradiated membrane.

We have also studied the photoresponse of the PVC/**40** membranes (Fig. 35).[135] Since the crowned-spirobenzopyran **40** contains a selective binding site for alkali metal cations, we may expect ion selective behaviour in the photoinduced membrane potential. According to the liquid/liquid extraction of alkali metal cations, the ion binding selectivity of **40** was in the order of $K^+ > Na^+ > Rb^+ > Cs^+$ in both closed and open forms of the spirobenzopyran moiety. The closed **40** can bind ions more strongly than in the open **40** (Table 5). Table 6 lists the magnitude of photoinduced potential in the membrane. The magnitude and sign of the photoinduced potential depended upon the type of cation. The photoresponse was discussed in terms of the change in charge density originating from the photochemical reaction of the spirobenzopyran moiety and on the ion binding equilibrium by the crown ether moiety of **40**.

The PVC/**39** membrane is applicable to construct photosensitive electrodes and cells whose electromotive force can be switched upon irradiation. The devices exhibited photoresponsive poten-



40

Fig. 35. Crown ether-substituted spirobenzopyran **40**.

tial changes of 100–200 mV.[136] These devices could be useful as photosensors and phototransducers.

It is possible to apply these photosensitive membranes to a sensitive layer of ion sensors and biosensors. By using the PVC/**39** membrane doped with nonactin and valinomycin, ion sensors sensitive to ammonium and potassium ions, respectively, were fabricated.[137,138] The magnitude of the photoresponse of these sensors depended upon the ion concentration in the solutions in contact with the irradiated surface of the membrane. These sensors were useful for measuring the concentration of ions at μM levels.

Another example of the use of a PVC/**39** membrane-based sensor is in fabrication of enzyme sensors for determining urea, amino acids, and creatinine.[139,140] These sensors were constructed by covering the sensitive layer of the PVC/**39** membrane-based ammonium ion sensor with an immobilized enzyme membrane. A typical calibration graph is illustrated for the urea sensor in Fig. 36. The magnitude of photoresponse depended upon the urea concentration. These ideas can be extended to the construction of immunosensors by immobilizing antigen or antibody molecules on the surface of the membrane.[141,142]

Table 5. Effect of photoirradiation upon ion binding ability of **40**[a)]

	Extracted picrate (%)			
	Na	K	Rb	Cs
In dark	38	58	31	24
Under UV light	35	52	28	18

a)Ion binding was assessed by liquid/liquid extraction.
Organic phase (dichloromethane):[**40**]=1x10^{-4} M.
Aqueous phase:[picrate]=1x10^{-5} M and [metal chloride]=1 M.

Table 6. Photoinduced potential across PVC/**40** membrane

	Photoinduced potential (mV)		
Electrolyte	Ion concentration in c_1 and c_2 sides (mM)		
	10	100	1000
NaCl	-33	-10	17
KCl	4	10	39
RbCl	2	3	19
CsCl	-21	-4	2

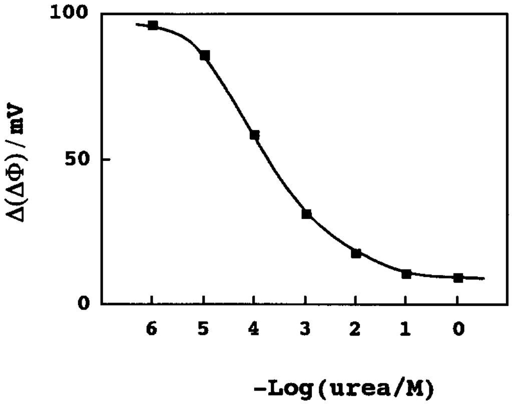


Fig. 36. Typical calibration curve of the PVC/**39**-based urea sensor.

4.2. *Monolayer, bilayer and multilayer membranes*

The spirobenzopyran molecule itself cannot form a stable monolayer on the air/water interface. Therefore, in order to prepare monolayer spirobenzopyran membranes, a hydrophobic side chain was attached to the framework. The spectroscopic and photochromic properties were then studied for the spirobenzopyran monolayers.[143–145]

The photoresponse of the monolayers prepared from poly(methacrylate) having spirobenzopyran side chains was studied in detail by Rondelez and coworkers.[146,147] They spread a monolayer of the spirobenzopyran polymer on the water surface and observed the photoinduced changes in the surface pressure. The photo-generated open form of the spirobenzopyran residues seems to be strongly attracted by the water and to penetrate the monolayer more deeply, resulting in enhanced strain in the membrane phase. Holden *et al.* studied the influence of irradiation on the spreading behaviour of spirobenzopyrans at the air/water interface.[148]

Spirobenzopyran-doped bilayer membranes have also been prepared to study the effects of the membrane environment upon the photochromic properties and to regulate the membrane properties by the photochemical reaction of the spirobenzopyran. Sunamoto *et al.* prepared **2**-doped lipid liposomal membrane to control the permeability of a bilayer membrane.[149] The open form of **2** served as a carrier to transport amino acids by forming complexes with the amino acids through ionic interactions (Fig. 37). Thus the photoregulated transport of amino acids was observed.

Recently, Toyama *et al.* reported the photo-switching of electric current through bilayer lipid membranes containing **39**.[150] The photo-enhanced electric current was explained on the basis of the lowered energy barrier for ion migration as a result of defects formed around the open-**39** in the

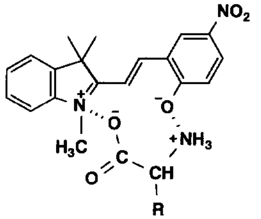
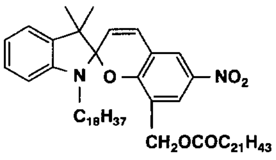


Fig. 37. Complex between amino acid and open-**2**.

membrane. The photochemical reaction and the subsequent diffusion of **39** in the membrane may induce a disordered alignment of the bilayer membrane. On the other hand, it was shown that the kinetic parameters for the thermal decolouration of open spirobenzopyrans incorporated in a bilayer membrane are significantly affected by the phase transition from crystalline to liquid crystal state.[151] The results were rationalized in terms of the fluidity changes of the bilayer matrix above and below the phase transition temperature.

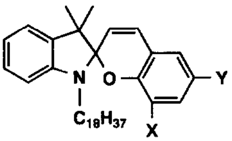
The photochromic behaviour of LB membranes composed of spirobenzopyrans has been studied for application to high-density optical memories. Ando *et al.* reported the monolayer and multilayer properties of amphiphilic spirobenzopyrans having single and double side chains.[152,153] The single-chain spirobenzopyran **39** could not form a stable monolayer in its closed form, while in the open form **39** formed a stable monolayer on the water surface. The charge-separated open-**39** may have a hydrophobic/hydrophilic balance suitable for forming a stable monolayer. In contrast, the double-chain derivative **41** (Fig. 38) can form a stable monolayer by itself on the water surface. Both the single- and double-chain compounds were deposited on a glass plate as LB membranes. The LB membranes of **39** and **41** showed the photochromic reaction in a similar way to that in solutions, in spite of the fact that the ring-opening reactions of the spirobenzopyrans are accompanied by an increase in the occupied volume. This behaviour of the spirobenzopyrans in LB membranes is in contrast with the suppressed isomerisation of azobenzenes in the LB membranes. More interesting is the fact that the LB membrane of **41**, under UV light irradiation at above 35°C, exhibited a sharp and intense absorption band at ca. 620 nm, which can be attributed to the formation of a so-called J-aggregate[154] of the open-**41**. The J-aggregate of **41** was extremely stable in the dark at room temperature and the half-life was 10^{14} times larger than that of the normal open form of **41**. The possible use of the J-aggregates for three-dimensional high-density optical memory was suggested.

The LB membranes exhibit a well-ordered structure along the thickness of the membrane. The in-plane molecular orientation, however, is usually difficult to control by the LB technique. Unuma and Miyata succeeded in regulating the in-plane molecular orientation in the LB membrane composed of the J-aggregates of **41**, by irradiation with a linearly polarized visible laser and unpolarized UV light.[155] They found that linearly polarized He–Ne laser irradiation caused the selective de-



41

Fig. 38. Amphiphilic spirobenzopyran bearing double side chains.



42 (X=H, Y=OH)
43 (X=CH_2OH, Y=NO_2)
44 (X=OH, Y=NO_2)

Fig. 39. Hydroxyl group-substituted spirobenzopyrans **42–44**.

composition of the J-aggregates having the transition dipole moment parallel to the polarization of the laser. After the selective decomposition of a part of the J-aggregates, the LB membrane was exposed to unpolarized UV light to reform the J-aggregates, in which the in-plane molecular reorientation was facilitated by the crystal growth of the J-aggregates induced by the remaining J-aggregate. Thus repeated irradiation gave well-ordered in-plane orientation in the **41** LB membrane. This technique may be useful to control three-dimensional molecular ordering. Miyata *et al.* also studied the aggregation properties of –OH group containing spirobenzopyrans **42–44** (Fig. 39) in the LB membranes.[156] It was concluded that the aggregated structure was stabilized by hydrogen bonding between the open forms of **42–44**.

There are few reports which describe the photocontrol of the permeability of the spirobenzopyran-based LB membrane. In this connection the mixed LB membrane composed of **39** and methyl arachidate was used photochemically to control the accessibility of ions to the electrode surface.[157] Up to five layers of the mixed monolayer of **39** and methyl arachidate (1 : 3) were deposited on an optically transparent gold electrode. Electrochemical monitoring of the redox current showed that the LB membrane was permeable to Fe^{3+}/Fe^{2+} ions in the dark or in visible light, while UV irradiation blocked the permeation of the ions. The results were explained in terms of 'loose' and 'compact' structures of the LB membrane, which can be switched by photoirradiation.

5. CONCLUSIONS

Increasingly numerous examples have firmly demonstrated that the physical and chemical properties of artificial membranes, modified appropriately by photosensitive molecules such as azobenzenes and spirobenzopyrans, can be controlled by photoirradiation. Such systems include a variety of monolayer, bilayer, multilayer and polymer membranes. There remains the interesting question of how these systems can find practical application to isolation, purification, energy conversion, signal transduction and other fields. There is no doubt that these processes will greatly benefit by the use of photosensitive membranes.

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