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POLY(VINYL CHLORIDE)/AZOBENZENE-LINKED BIS(15-CROWN-5) MEMBRANES. PHOTOINDUCED POTENTIAL CHANGES ACROSS ASYMMETRIC MEMBRANES

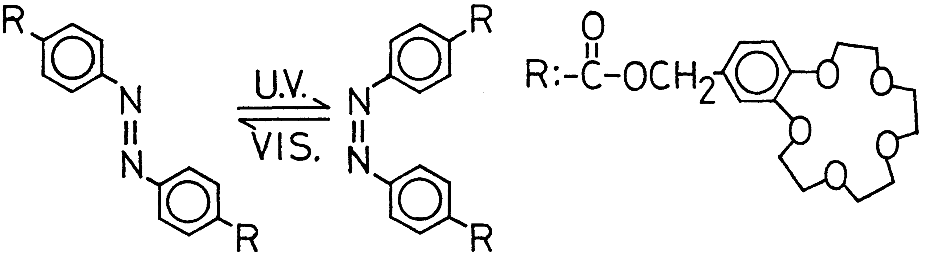
Jun-ichi ANZAI, Hiroshi SASAKI, Akihiko UENO, and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University,
Aobayama, Sendai 980

An azobenzene-linked bis(15-crown-5) (1) was entrapped in the plasticized poly(vinyl chloride) (PVC) membranes in order to regulate their membrane potential by photoirradiation. The membrane potential changed synchronously with trans-cis isomerization of 1 by UV and visible light irradiation even when no concentration gradient of electrolyte existed between the two external solutions separated by the membrane. The results were explicated in terms of the formation of asymmetric membranes, i.e., the surface potential of the irradiated side of the membrane was different from that of the opposite side.

Photochemical trans-cis isomerism of azobenzene derivatives has been widely utilized to photoregulate such chemical and physical properties as conformations of polypeptides[1)] and vinyl polymers,[2)] membrane permeability,[3)] binding ability of cyclodextrin,[4)] and hydrophobicity of synthetic polymers.[5)]

We[6)] and Shinkai et al.[7)] independently have studied the photocontrol of alkali metal ion binding and transporting properties of azobenzene-modified crown ethers. Recently, we have reported that the potential changes across a PVC/1 membrane were induced significantly by photoirradiation when a large concentration gradient of KCl existed across the membrane.[8)] The purpose of this paper is to describe the photoinduced potential changes across PVC/1 membranes in the case that there is no concentration gradient between the external solutions separated by the membrane.

Synthetic and analytical details of 1 were reported previously.[6)] The membrane of ca. 0.1 mm thickness was prepared by pouring a solution, which contained 235 mg of PVC, 0.54 ml of di-n-butyl phthalate, 1.3 mg of 1, and 20 ml of tetrahydrofuran, onto a flat petri dish (9.2 cm diameter). To obtain the



trans-1 cis-1

thicker membranes (0.2 and 0.4 mm thickness), twice and 4-times of the materials were used, respectively. Crown ether 1 was found to undergo trans-cis isomerization reversibly in the membrane in a similar manner as in the solution. The half life of cis-1 in the membrane was about 45 h at 25 °C under dark condition. The composition of the electrochemical cell for the membrane potential measurements was as follows; Hg_2Cl_2(s), Hg|KCl(sat.)|0.1 M NH_4NO_3|KCl solution 1|membrane|KCl solution 2|0.1 M NH_4NO_3|KCl(sat.)|Hg_2Cl_2(s), Hg. The KCl concentrations in the solutions 1 and 2 were equal in this study. The electrorode in compartment 1 was earthed (Fig. 1). The light source was 500 W xenon lamp and Toshiba UV-D35 and Corning 3-74 glass filters were used for isolating UV and visible light, respectively.

The membrane potential changes induced by UV and visible light irradiation in the presence of KCl are illustrated in Fig. 2. After a steady state potential difference, $\Delta\Phi_{dark}$, had been attained in the dark, a negative shift of the membrane potential was induced by UV irradiation (320 nm$< \lambda <$400 nm). About 3 min was enough to obtain a steady state potential under UV irradiation , $\Delta\Phi_{UV}$, and the initial potential was recovered rapidly by visible irradiation (λ >400 nm) (Fig. 2-a). The membrane potential under visible irradiation, $\Delta\Phi_{vis}$, read the same value as $\Delta\Phi_{dark}$. It should be noted here that the potential changes were synchronized with the absorption changes at 331 nm of the membrane (Fig. 2-b). Another important aspect is that no significant potential change, $|\Delta(\Delta\Phi)|<0.2$ mV, was induced by photoirradiation when KCl was replaced by NaCl. The effects of membrane thickness and KCl concentration in the solutions on the membrane potential changes, $\Delta(\Delta\Phi) = \Delta\Phi_{UV} - \Delta\Phi_{vis}$, are listed in Table 1. The KCl concentration, over the range of 10-1000 mM, had no significant influence on the photoresponse of the membrane potentials. On the contrary, the $\Delta(\Delta\Phi)$ values were markedly dependent on the membrane thickness, larger $\Delta(\Delta\Phi)$ values being observed for the thicker membrane.

It is well established that the membrane potential should be zero when the membrane is placed between two 1:1 electrolyte solutions having same activity.[9)] Indeed, in the case of PVC/1 membrane, the membrane potentials were almost zero under dark or visible light irradiation, where 1 assumed trans form. Some authors,[10)] however, reported that the potential differences were observed across the collodion and lipid membranes separating two identical 1:1 electrolyte solutions. The origin of the membrane potentials was ascribed to the differences between charge densities of two surfaces of the membrane, i.e., the differences between the two surface potentials. These are called an asymmetric membrane potential. The photoinduced potentials across PVC/1 membranes observed in the two identical KCl solutions may also be explained based on the asymmetric membrane formation under UV irradiation. The charge density of the membrane surface of the irradiated side is considered to be different from that of the other side, which originates from the concentration difference of K^+ ion between two surfaces of the membrane. This explanation inevitably postulates that, under UV irradiation, the cis-1/trans-1 ratios of the two surfaces of the membrane are different from each other since the K^+ binding ability of cis-1 is better than that of trans-1.[6)]

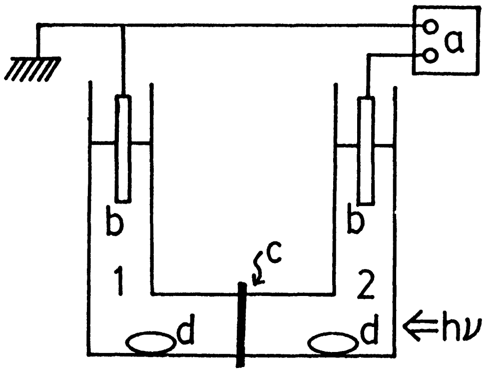


Fig. 1.
Schematic sketch of the cell for membrane potential measurements.
a) Potentiometer,
b) saturated calomel electrode,
c) membrane,
d) stirring bar.

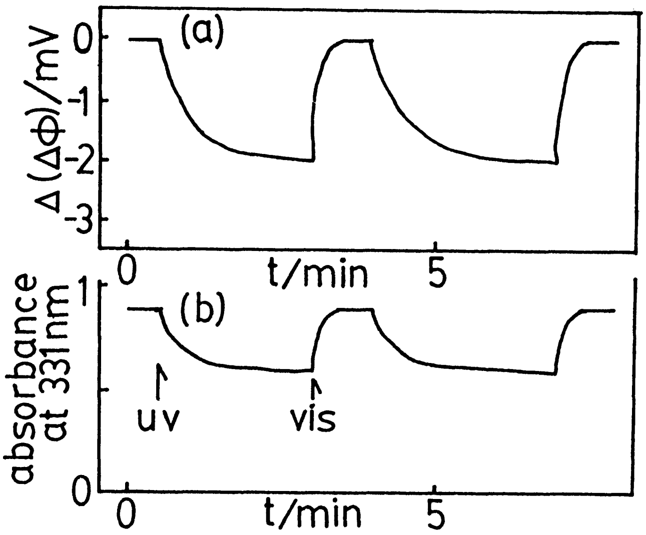


Fig. 2.
(a) Photoresponse of the membrane potential. Membrane thickness, 0.1 mm. KCl concentration in solutions 1 and 2 is 100 mM.
(b) Change in absorbance of the membrane.

Table 1. Effects of KCl concentration and membrane thickness on the photoresponse of the membranes

Membrane	Thickness/mm	Photoinduced potential change[a] /mV			
		KCl concentration/mM			
		10	100	500	1000
A	0.1	-1.5	-2.0	-2.5	-2.0
B	0.2	-4.0	-3.5	-3.5	-4.0
C	0.4	-5.0	-4.0	-5.5	-5.5

a) Photoirradiation was conducted from the compartment 2 side.

The time course of the photochemical trans-cis isomerization of 1 in the membrane was checked to reveal the cis-1 contents of two sides of the membrane (Fig. 3). The absorbance of the membrane at 331 nm decreased markedly at the initial stage of UV irradiation and declined to reach stationary-state trans/cis ratio after about 5 min. On the other hand, when the membrane, after the photostationary trans/cis ratio was attained by UV irradiation from one side of the membrane, was exposed to UV light, in turn, from the opposite direction after 10 or 60 min, a further decrease of the absorbance (ca. 5%) was observed. On this treatment the membrane potential also shifted to the positive direction synchronously with the absorption change. These facts imply that cis-1 content in the membrane is not uniform in the direction of membrane thickness when irradiated from one side of the membrane. It is clear that cis-1 content of the irradiated surface of the membrane is higher than that of the other surface. These observations reasonably support our interpretation that the photoinduced potential differences across PVC/1 membrane were ascribable to the difference between the surface potentials of two sides of the membrane, which stems from

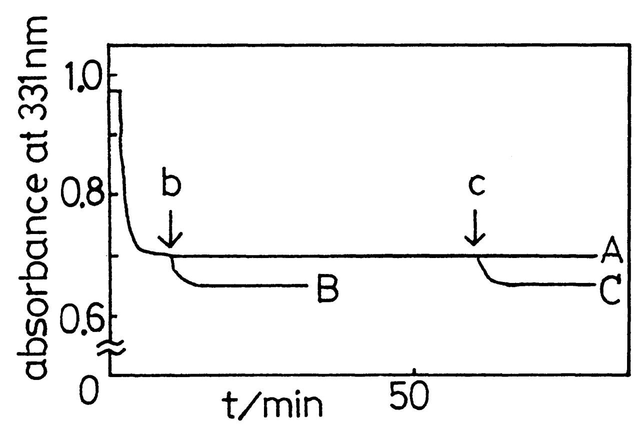


Fig. 3.
Time course of photoisomerization of 1 in the membrane (thickness, 0.1 mm) under UV irradiation.
A) irradiated from one side of the membrane.
B, C) irradiated from the opposite side of the membrane after 10 min (b) and 60 min (c), respectively.

the unequal distribution of cis-1 between the irradiated and non-irradiated sides of the membrane. The remarkable dependence of $\Delta(\Delta\Phi)$ values on the membrane thickness (Table 1) is also compatible with this interpretation as one can easily understand that cis-1 content of the non-irradiated side of the thicker membrane is suppressed at lower level than that of the thinner membrane.

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