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Photoinduced Resistance Change across Poly(vinyl chloride)/ Spirobenzopyran Membrane

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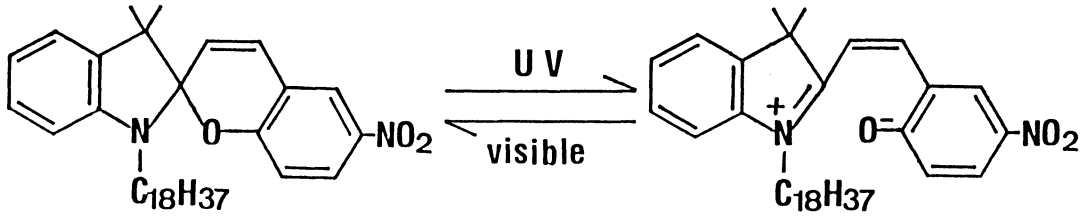
Membrane resistance across poly(vinyl chloride) entrapping spirobenzopyran was reversibly controlled by UV and visible light irradiation. After UV light irradiation, the magnitude of the membrane resistance became less than 1/1000.

Spirobenzopyran derivatives are well known photoresponsive compounds, and in recent years, many attempts have been made to use these compounds as photo- chemical switches for controlling various molecular phenomena.[1,2] We have already shown that photoinduced changes of membrane potential can be attained with poly(vinyl chloride) (PVC) membranes containing spirobenzopyran derivatives.[3-6] Here, we report on the photoinduced resistance change across the PVC/spirobenzopyran (1) membrane which occurs reversibly and quickly with UV and visible light irradiation. Recently study of photoinduced resistance change was published with using azobenzene unit.[7] The resistance change of our system is faster and larger than that of their report.



1 1'

Compound 1 was obtained by the condensation reaction of 5-nitrosalicylaldehyde with 1-octadecyl-2,3,3-trimethylindolenium bromide according to the reported procedure.[8] Yield: (66%). Mp: 81 °C. Found: C,76.76; H,9.45; N, 4.67. Calcd for $C_{36}H_{52}N_2O_3$: C,77.10; H,9.35; N,5.00. ^{1}H-NMR ($CDCl_3$) δ= 0.9, 1.2 (3H, s, 3H, s, $C(CH_3)_2$), 1.0 (3H, m, $(CH_2)_{16}CH_3$), 1.3(32H, m, $(CH_2)_{16}CH_3$), 3.1 (2H, b, $-NCH_2$), 5.8, 6.7 (1H, s, 1H, s, pyran ring), 6.4-7.2, 7.9-8.2 (4H, m, 3H, m, aromatic ring). The PVC/1 membrane was prepared by pouring a mixture of PVC (200 mg), dibutyl phthalate (480 mg), 1 (57 mg), and tetrahydrofuran (12 ml) onto a flat petri dish (7.7 cm diameter) and allowing the solvent to evaporate. The prepared membrane had a thickness of ca. 0.1 mm. All measurements were carried out at 20 °C.

The system used for the membrane resistance measurements is shown in Fig. 1. The composition of the system was as follows: Ag, AgCl|KCl (sat.)|NaCl solution (c)|PVC/1 membrane|NaCl solution (c)|KCl (sat.)|Ag, AgCl. Resistance measurement was performed with digital multimeter (model TR-6843, Takeda Riken Inc.). Electrolyte concentrations (c) in both a and b chambers were the same in all measurements. The electrolyte solution of the a (anode) side was earthed. Photoirradiation was performed with a 500 W xenon lamp using cut off filters Toshiba UV D-35 and Y-45 for isolating UV (320 nm < λ < 400 nm) and visible (450 nm < λ) light, respectively. From the absorption spectrum we confirmed that 1 could be photoisomerized to 1'.[9]

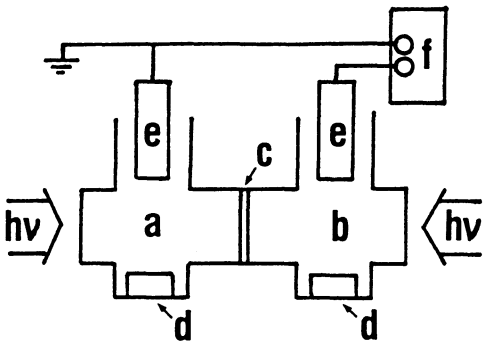


Fig. 1.
Schematic representation of the cell for membrane resistance measurements.

a: NaCl solution (20 ml)
b: NaCl solution (20 ml)
c: PVC/1 membrane (effective membrane area; 2 cm^2)
d: stirring bars
e: Ag-AgCl electrodes
f: Digital multimeter

Figure 2 illustrates the changes of the membrane resistance induced by alternating UV and visible light irradiation. Before UV irradiation, the membrane resistance was 1.3 MΩ. When the membrane surface facing the b phase was exposed to UV light, the membrane resistance was increased. Ten seconds later the membrane resistance reached ca. 3 MΩ, and then returned to the initial resistance after visible light irradiation. On the other hand, when the a phase was exposed to UV light, the membrane resistance was decreased. Ten seconds later the membrane resistance was less than 1 kΩ. The original resistance

value was recovered after visible light irradiation. For UV irradiation longer than 10 seconds, the membrane resistance increased gradually. When the surface of the membrane was changed, the membrane resistance showed same behavior.

Figure 3 shows the effect of the concentration of NaCl solutions (c) on the membrane resistance. Before UV irradiation the resistance depended slightly upon the concentration of NaCl. With increasing concentration, the resistance decreased, which might be ascribed to a small amount of NaCl soaking into the membrane. After the UV irradiation from the b side, the resistance was twice as much as that of the initial value. For UV irradiation from the a side, the minimum membrane resistance was less than 1 kΩ for any NaCl concentration. Such a low membrane resistance can be attributed to a new ion pair which was produced in the membrane, namely compound 1', upon UV irradiation. As a result of our earlier study on the photoinduced membrane potential across the PVC/spirobenzopyran membrane, we suggested that UV induced potential change reflected the addition of a proton in the NaCl solution to the phenolate ion of the open-form spirobenzopyran on the UV irradiated surface in the membrane.[3] So UV was irradiated on the membrane, polarization occurred due to the charge separation into two sides; i. e. the inside of the membrane was positive, and the outside was negative. When UV was irradiated from the b side, we think, movement of electrons was obstructed by the polarization in the b side of the membrane. In the case of irradiation from the a side, the electrons might move smoothly. As the a side was exposed to UV light for a long time, compound

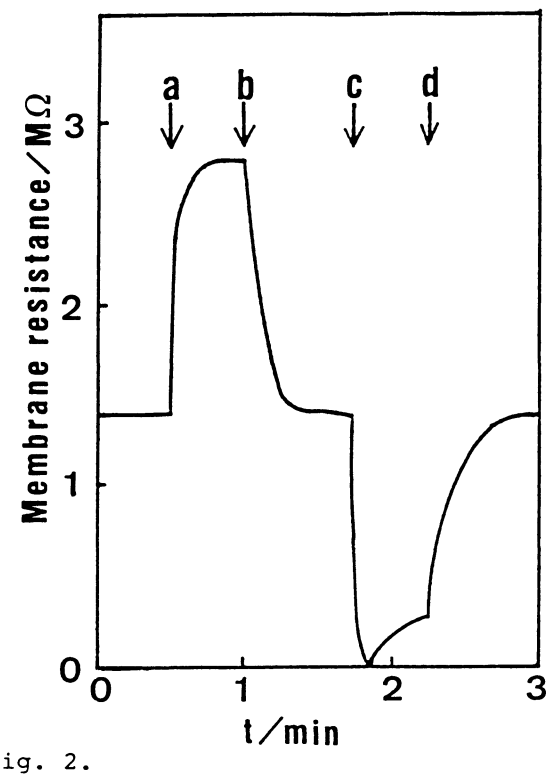


Fig. 2.
Photoresponse of the membrane resistance upon UV and visible light irradiation.
NaCl concentrations (in a and b phases) are 10 m mol dm^{-3} for both solutions.
a) UV irradiation from b side
b) visible light irradiation from b side
c) UV irradiation from a side
d) visible light irradiation from a side

1 near the b side was also isomerized. Therefore the membrane resistance gradually increased. We are carrying out further work on the exact mechanism of the photoinduced system.

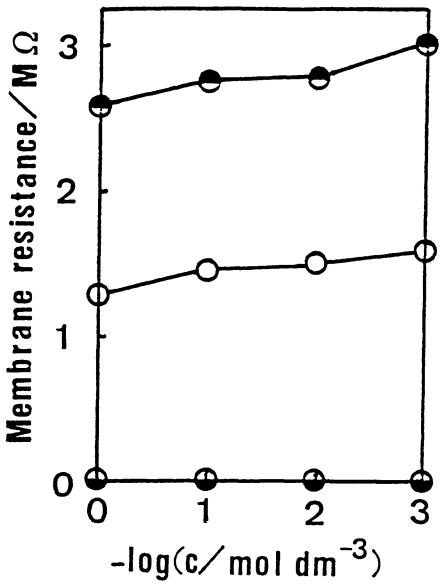


Fig. 3.
Dependence of the membrane resistance on NaCl concentration.
○: In the dark or under visible light irradiation
◒: UV irradiation from a side
◓: UV irradiation from b side
(minimum value)

References
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9) In our earlier study of spirobenzopyran derivative we obtained the absorption spectrum indicating the photoisomerized open-form.[3] The photoinduced spectrum change of compound 1 in the PVC membrane is similar to this spectrum.

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