

High and Rapid Response in Photo-induced Potential Changes across a Poly(vinyl chloride)/Spirobenzopyran Membrane

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Photo-induced potential changes of more than 100 mV were attained with rapid response time (about 20 s) across a poly(vinyl chloride)/spirobenzopyran membrane.

The development of photoresponsive membranes which change their potentials by photoirradiation is currently a focal subject in the fields of biological and artificial membranes. To date pigmented lipid membranes have been intensively studied as model systems for biological photo-receptor cell membranes.^{1,2} Few reports, however, have appeared on polymer membrane systems of practical use.³ In this connection, Kato *et al.* have attempted photoregulation of the membrane potential with polymer/lipid composite membranes entrapping a spirobenzopyran compound, but the potential shifts obtained are relatively small (20 mV or less) and the response time slow (10 min or more).^{4,5} We report here some preliminary data on the highly improved response in photo-induced membrane potential changes obtained using a plasticized poly(vinyl chloride) (PVC) membrane entrapping the spirobenzopyran (**1**) as a photoresponsive dye.

Closed-(**1**) was prepared by condensation of 1-hexadecyl-2,3,3-trimethylindolenium bromide with 5-nitrosalicylaldehyde according to the reported procedure (69%).^{6†} A membrane of *ca.* 0.1 mm thickness was prepared by pouring a solution, which contained 250 mg of PVC, 0.5 ml of di-*n*-butyl phthalate, 20 mg of closed-(**1**), and 20 ml of tetrahydrofuran, onto a flat Petri-dish (9.2 cm diameter) and allowing the solvent to evaporate. After immersing the membrane (0.1 mm thickness) in 0.1 M NaCl solution for 12 h under dark conditions, the d.c. resistance measured *ca.* $1 \times 10^8 \Omega \text{ cm}^2$. The composition of the electrochemical cell for the membrane potential measurements was as follows; Hg₂Cl₂ (s), Hg|KCl(sat.)|0.1 M NH₄NO₃|NaCl solution (*c*₁)|membrane|NaCl solution (*c*₂)|0.1 M NH₄NO₃|KCl (sat.)|Hg₂Cl₂ (s), Hg. The electrode in the lower concentration compartment was earthed. A 500 W xenon lamp was used as a light source. All measurements were carried out at 25°C.

The spirobenzopyran (**1**) exhibited normal photochromism in the membrane: a closed-form (colourless) under visible light irradiation and an opened-form (purple) under u.v. light irradiation. The isomerization of (**1**) in the membrane was fairly reversible and the absorption maximum of the opened-(**1**) in the membrane was found at 578 nm, Figure 1(b).

The membrane potential changes induced by irradiation are illustrated in Figure 1(a). After a steady state potential difference, $\Delta\Phi$, had been reached under visible light irradiation, a remarkable negative shift of the membrane potential was induced by u.v. irradiation (280 nm < λ < 400 nm). By switching the u.v. light to the visible one, (410 nm < λ), the

initial potential was recovered rapidly. The reversible potential shift should be ascribable to the charge-density changes in the membrane, which, in turn, originate from the photo-generated opened-(**1**).^{4,5} This is also supported by the fact that the potential changes are entirely synchronized with the absorption change at 578 nm of the membrane.

We can emphasize two important aspects with regard to the photoresponsive behaviour of the membrane. First, the potential shifts are remarkably enhanced, $\Delta(\Delta\Phi) > 100 \text{ mV}$, by use of the highly hydrophobic membrane material, a plasticized PVC. The absence of the fixed charge except for opened-(**1**) in the membrane, which is not the case for lipid membranes, may be favourable for the large potential shifts. Secondly, the time-response of the potential changes is markedly fast. Only about 20 s suffices to attain steady state potential in our case while the lipid/spirobenzopyran membranes required about 10 min or more.^{4,5} It is clear that the rapid response in the membrane potential stems from the rapid photoisomerization of (**1**) in the membrane.

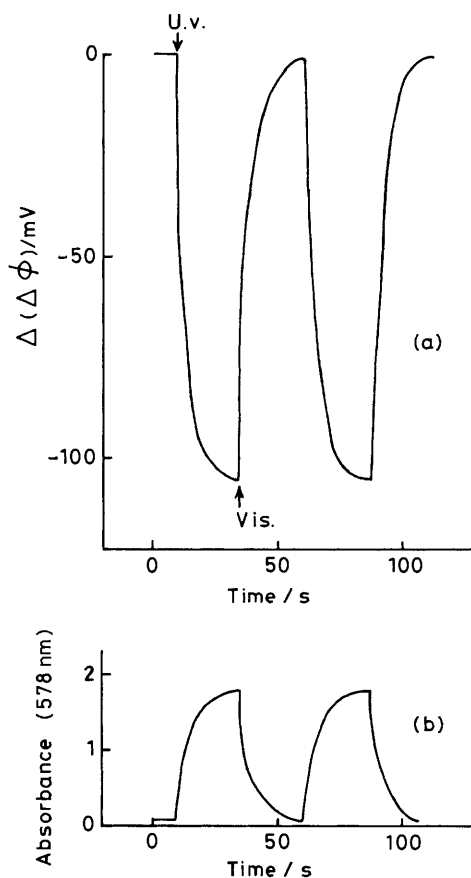
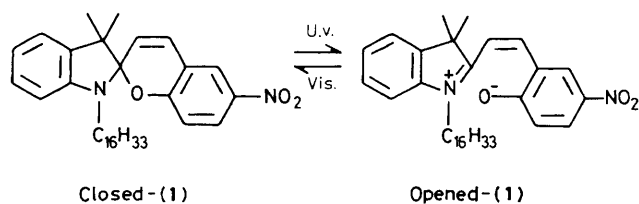


Figure 1. (a) Photoresponse of the membrane potential; alternate u.v. and visible light irradiation (*c*₁ 10 mM, *c*₂ 100 mM NaCl). (b) Change in absorbance (at 578 nm) of the membrane.

† Satisfactory elemental analysis and spectral data were obtained for (**1**).

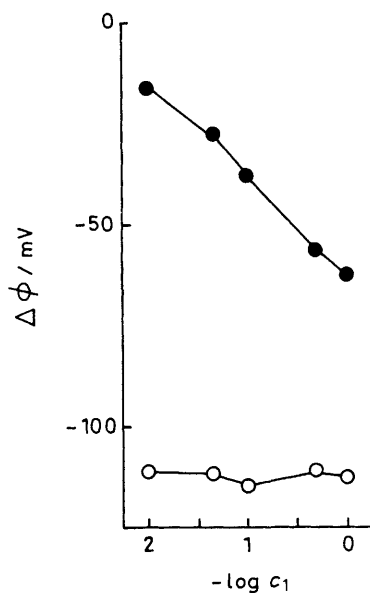


Figure 2. Dependence of membrane potential on NaCl concentration at $c_2 1 \times 10^{-3}$ M. ●: In darkness or under visible light. ○: Under u.v. light.

Effects of c_1/c_2 ratios on the dark and irradiated potential differences across the membrane were also examined (Figure 2). Though the c_1/c_2 ratios had scarcely any influence on the membrane potentials under u.v. light irradiation, the potential differences were linearly dependent on $-\log c_1$ values under dark or visible light irradiation. In the low c_1/c_2 regions, the photoinduced potential changes were large.

Thus, we have shown that the photoresponse in membrane potential can be highly improved by use of hydrophobic PVC/spirobenzopyran membranes. Such membranes may serve as sensor membranes which transduce a light signal into electric output.

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