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PHOTOINDUCED ION PERMEATION THROUGH TERNARY COMPOSITE MEMBRANE COMPOSED OF POLYMER/LIQUID CRYSTAL/AZOBENZENE-BRIDGED CROWN ETHER

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Azobenzene-bridged crown ether(AZO-CR) in the ternary composite membrane exhibits *trans-cis* photoisomerization by irradiation of ultraviolet and visible lights. The K^+ ion permeation through the ternary composite membrane is facilitated by photoirradiation. The facilitated transport of K^+ ion is in strong relation to an altered affinity of AZO-CR for K^+ ion due to the *trans-cis* configurational change of AZO-CR induced by photoirradiation. The cation permeation is remarkably influenced by the magnitude of solubility of counter-anion to the composite membrane.

Crown ether compounds incorporate alkali metal ions into their cavities, forming complexes. Permselectivity for alkali metal ions had been investigated by the use of polymer-liquid crystal/crown ether composite membrane.1) One of authors succeeded in synthesis of an azobenzene-bridged crown ether (AZO-CR).2) Azobenzene derivatives exhibit photoinduced reversible *trans-cis* isomerization.3) The *trans*-AZO-CR is transformed to the *cis*-isomer upon irradiation of light with the wavelength of 360 nm, and the latter to the former upon irradiation of light with the wavelength longer than 460 nm or heating. Ion trapping ability of AZO-CR for alkali metal ion is controlled by photoisomerization. *Trans*-AZO-CR extracts effectively Na^+ ion 5.6 times as much as *cis*-AZO-CR, whereas *cis*-AZO-CR extracts selectively K^+ ion 47.5 times as much as *trans*-AZO-CR.2) *Cis*-AZO-CR is able to form sandwich-type 1:1 cation/AZO-CR complex and extracts more effectively larger metal cations such as K^+ ion than the magnitude of cavity corresponding to 15-crown-5.2)

The purpose of this paper is to investigate the photoresponsive and facilitated transport of K^+ ion through the polymer/liquid crystal/AZO-CR ternary composite membrane, utilizing the configurational change upon irradiation of light.

The chemical structures of polymer, liquid crystal and AZO-CR are shown in Fig. 1. Poly(vinyl chloride)(PVC) was used as the membrane matrix, and either 4-cyano-4'-n-pentylbiphenyl(CPB) or N-(4-ethoxybenzylidene)-4'-n-butylaniline (EBBA) was used as the liquid crystalline material. The compatibility between PVC and liquid crystals is remarkably good. In case of polymer/liquid crystal composite membrane, it was confirmed that polymer fibrils were present as the three dimensional network and liquid crystals were present as the continuous domain.[4] Futhermore, a leakage of liquid crystals from composite membrane was not observed because of the network structure of polymer matrix.

The ternary composite membrane was prepared by evaporating solvent from a tetrahydrofuran solution of PVC, CPB(or EBBA) and AZO-CR at 313 K. A weight ratio of PBC/CPB/AZO-CR or PVC/EBBA/AZO-CR is 40/60/2.6 or 40/60/2.7, respectively. A molar ratio of liquid crystal and AZO-CR is 52/1. A thickness of ternary composite membrane was 100 μm. The dispersion state of AZO-CR molecules in the composite membrane was investigated by differential scanning calorimetry(DSC) study. Figure 2 shows the DSC curves of AZO-CR, liquid crystals and ternary composite membrane. AZO-CR exhibited melting behavior at 468 K(T_{KI}). In case of the ternary composite membrane, the crystal-liquid crystal phase(nematic) transition temperatures, T_{KN} shifted to a lower temperature side by 3∿4 K compared with those of liquid crystal themselves. Furthermore, the melting behavior of AZO-CR was not observed in the ternary composite membrane. It was confirmed from the DSC results that AZO-CR molecules were almost dispersed molecularly in the ternary composite membrane.

The *trans*-*cis* photoisomerization of AZO-CR was confirmed from the variation of the ultraviolet (UV) absorption spectra upon irradiation of UV light. Figure 3 shows the irradiation time dependence of the UV absorption spectra for the PVC/CPB/AZO-CR ternary composite membrane in a solid state upon irradiation of 360 nm light. The composite membrane cast on a quartz glass plate was irradiated by 360 nm light. The absorption maximum corresponding to *trans*-AZO-CR was observed at about 380 nm. PVC and CPB have no interfering UV absorption of AZO-CR molecules in the wavelength region about 380 nm . The absorption peak intensity of *trans*-AZO-CR decreased with increasing the irradiation time of 360 nm light. Also, its absorption peak returned to the original magnitude

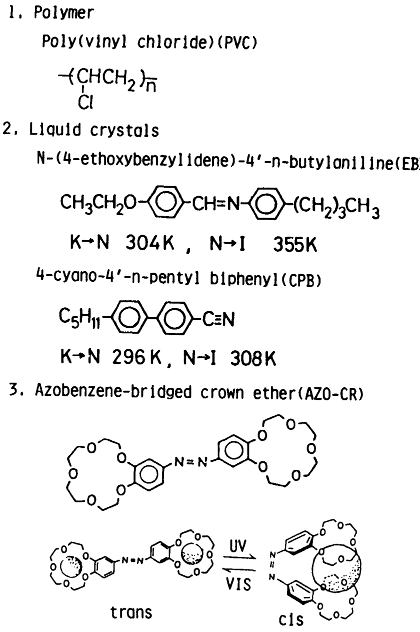

Fig. 1. Chemical structures of constituents for composite membrane.

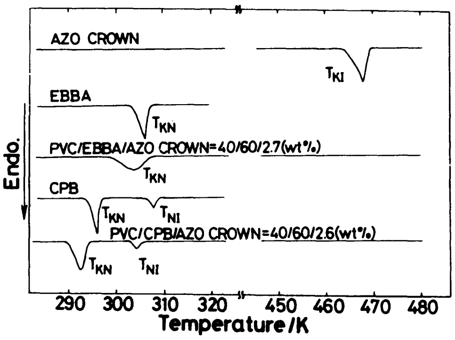

Fig. 2. DSC curves of AZO-CR, liquid crystal and ternary composite membrane. T_{AB}:transition temperature from A to B phases. K:Crystal, N:Nematic, I:Isotropic.

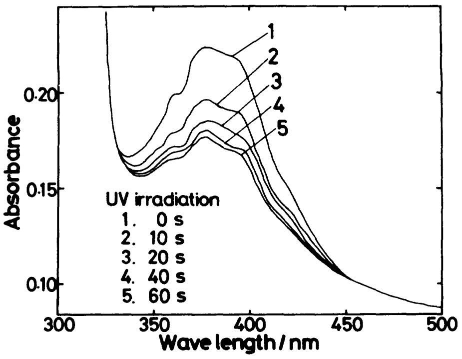

Fig. 3. UV absorption spectra of PVC/CPB/AZO-CR ternary composite membrane upon irradiation of 360 nm light.

upon irradiation of visible(VIS) light with longer wavelength than 460 nm. The UV absorption behaviors upon UV and VIS irradiation indicate that the *trans-cis* photoisomerization of AZO-CR occurred even in the ternary composite membrane in a similar manner to that in dilute solution.

The permeability of K^+ ion was measured by a normal osmosis method. Figure 4 shows a permeation cell attached to the irradiation system of UV and VIS lights. Aqueous solution of either KCl or potassium p-toluenesulfonate and distilled water were separated by the composite membrane. The membrane area was 9.0 cm^2. The concentration of permeated K^+ ion was evaluated by the atomic absorption spectrophotometry. In order to investigate the photoresponsive permeation control, the UV and VIS lights were simultaneously irradiated perpendicular to the membrane surface from the salt solution (up-stream) and distilled water (down-stream) sides, respectively. The lights were irradiated to overall membrane surface.

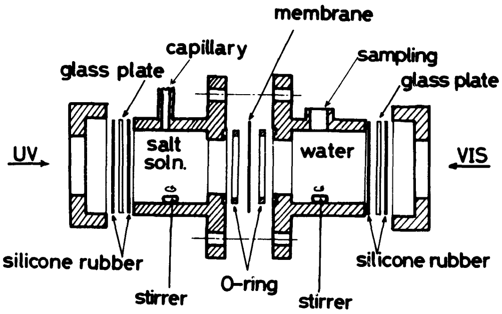

Fig. 4. Cell for K^+ ion permeation measurement.

Figure 5 shows the time dependence of a relative increase of K^+ ion concentration in the permeation side through the PVC/CPB/AZO-CR composite membrane upon irradiation of UV and VIS lights at 310 K, in other words, the increment of K^+ ion due to the facilitated transport upon light irradiation. The relative increase of K^+ ion concentration was calculated as the difference between permeated K^+ ion concentration with and without light irradiation. KCl was used as salt in Fig. 5. At this temperature, CPB is in an isotropic state and takes a role of the transporting phase for AZO-CR molecules. It is apparent that the UV and VIS light irradiations facilitate or activate permeation of K^+ ion through the PVC/CPB/AZO-CR ternary composite membrane. After light irradiation was stopped, the permeation rate of K^+ ion returned to the same order as the starting condition.

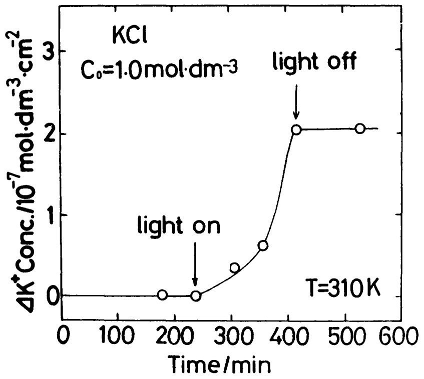

Fig. 5. Photoisomerization effect on relative K^+ ion permeation through PVC/CPB/AZO-CR composite membrane at 310 K.

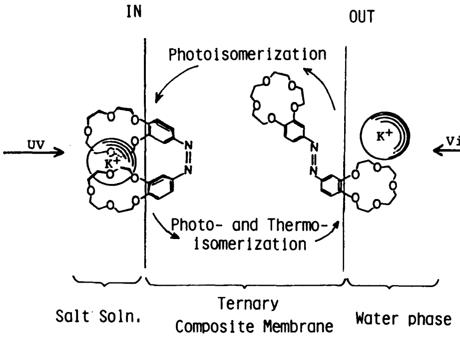

Fig. 6. Schematic representation of light-driven ion transport across composite membrane.

Figure 6 shows a schematic representation of the permeation mechanism through the PVC/CPB/AZO-CR ternary composite membrane. Around the contacting surface of the composite membrane with salt solution, *trans*-AZO-CR transforms to the *cis*-isomer upon irradiation of UV light so that 1:1 K^+ ion/AZO-CR complex is formed. Then this complex diffuses to the opposite side owing to the gradient of the *cis*-configurational concentration in the composite membrane. Around the membrane surface of the opposite side (down-stream), the cis-AZO-CR containing

K^+ ion transforms to the *trans*-isomer upon irradiation of VIS light, so that *trans*-AZO-CR releases K^+ ion into the water phase. Furthermore, *trans*-AZO-CR returns to the side of salt solution phase owing to the gradient of the *trans*-configurational concentration in the composite membrane. It seems reasonable to consider that the photoinduced carrier with the *cis*- or *trans*- configuration diffuses or transports in the isotropic liquid phase of CPB due to their concentration gradients. Affinity of AZO-CR for K^+ ion must be strikingly altered on the each side of the composite membrane due to the configurational change of AZO-CR induced by irradiation of light. That is, the complex formation of K^+ ion-(*cis*-AZO-CR) is more predominant in the side of salt solution phase than that of K^+ ion-(*trans*-AZO-CR) in the side of water phase. In the case of ordinary crown ether compounds, their affinities for cations do not change on both sides of the membrane.$^{1)}$ Therefore, this AZO-CR system is one of the advantageous methods for the facilitated transport of metal ions in carrying out the permselective experiment.

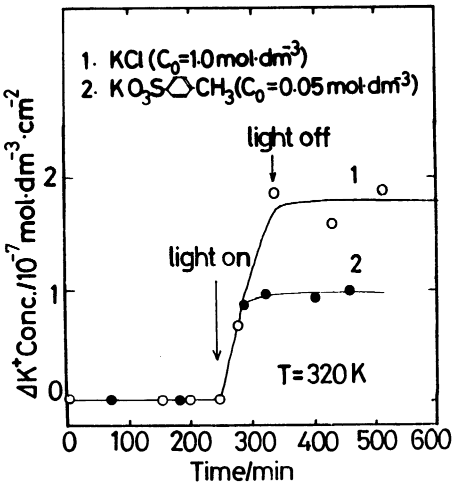

Fig. 7. Photoisomerization effect on relative K^+ ion permeation through PVC/EBBA/AZO-CR composite membrane at 320 K.

Figure 7 shows the time dependences of permeated K^+ ion concentration through the PVC/EBBA/AZO-CR composite membrane upon irradiation of UV and VIS lights at 320 K. Aqueous solution of KCl of 1 mol·dm^{-3} and potassium p-toluenesulfonate of 0.05 mol·dm^{-3} were used as salt solutions (1) and (2) in Fig. 7, respectively, in order to investigate the counter-anion effect for the facilitated transport of cation. Though their light-driven behaviors on K^+ ion permeation by light irradiation are similar, the effect of facilitated permeation of K^+ ion in Fig. 7(2) is about 10 times as much as that shown in Fig. 7(1), in consideration of the initial and permeated K^+ ion concentrations. These results indicate that the counter-anion remarkably affects the cation permeability. Since the p-toluenesulfonate anion is more hydorphobic than chloride anion, the p-toluenesulfonate anion may be greatly dissolved in the hydrophobic domain of the liquid crystal than Cl^-. Cations diffuse in pairs with counter-anions in electrically neutral state within the composite membrane. Therefore, K^+ ion with p-toluenesulfonate is effectively incorporated into AZO-CR in the liquid crystalline phase. It may suggest that cation permeability would be increased by suitable selection of counter-anion which has stronger affinity to the membrane.

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