PHOTOINDUCED PHASE TRANSITION OF AZO BENZENE BILAYER MEMBRANES IMMobilIZED BY POLYION COMPLEX TECNIQUE

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In this communication, we report a large memory effect and photochemical switching of absorption spectra of azobenzene-containing bilayer membranes based on a peculiar solid-solid phase transition in the cast films immobilized with anionic polymers. Thermal stability of on- and off-state in the memory is required for the recording devices of the organic materials. Phase transition with a large thermal hysteresis is available for making the thermal bistability of two different physical states. We have already reported that an immobilized cast bilayer film of an azobenzene amphiphile 1 showed a peculiar solid-solid phase transition with a large thermal hysteresis.

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\text{CH}_3\text{(CH}_2\text{)}_7\text{O-}
\text{N=Q-}
\text{O(Ch}_2\text{)}_1\text{6-N^2CH}_2\text{CH}_2\text{OH Br}^- \]

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A large spectral shift from 300nm to 370nm was found when the molecular orientation of the azobenzene amphiphile was transformed by the thermal transition of the immobilized film cast from water solution. An X-ray structural analysis ascribed this transition to solid-solid phase transition. Two crystalline states, 300nm and 370nm, were found to be very stable in dry atmosphere even at room temperature. A very fast spectral shift from 370nm to 300nm was observed when the film was kept in humid condition. Repeating couples of the thermal transition...
and the isothermal moisture treatment conducted reversible switching of the spectral shift.

In order to use the bilayer membranes as recording materials, mechanical properties and film preparation process should be improved. Polymerization of bilayer membranes\(^3\) and composite formation with polymeric compounds\(^4\) are well known to be useful techniques for materialization of the bilayer membranes. Polyion complex technique is one of useful methods to prepare polymeric cast films of the bilayer membranes\(^5,6\). Polymer composites with anionic polymers were prepared as precipitates on mixing the aqueous solutions. An optically transparent film was cast on quartz substrates from chloroform by spin coating method.

Molecular orientation of the azobenzene chromophore in the as-cast films of the polyion complexes is very similar to that of the immobilized bilayer membranes without polymer, because absorption maxima are located around 300nm. Spectral shift by the thermal phase transition is dependent on the chemical structure of the polymers. A drastic spectral shift from 311nm to 346nm was observed at 79°C on heating the cast film of the composite with dextran sulfate 2. Similar spectral transition (from 307nm to 342nm at 101°C) was found in the film with poly(styrene sulfonate) 3. Spectral state of 340nm is attributed to liquid crystalline phase\(^7\). In the case of the complex film with copolymer of vinylsulfate and acrylamide 4 (m/n=8), transition from 302nm to 359nm was observed at 112°C.

Spectral bistability at room temperature was also found in the polyion complex films in the dry atmosphere. Liquid crystalline phase in the macroscopically oriented lamella structure is seemed to be quenched at room temperature in the complex films with 2 and 3, since an amorphous halo indicating disordered packing of the hydrophobic alkyl chain was found in the wide angle X-ray diffraction as well as strong sharp diffractions in the low angle region.

Isothermal phase transition triggered by moisture treatment is also observed in the polyion complexed films. Speed of the phase transition is also affected by the polymer structure. Figure 1 shows absorption change at \(\lambda_{\text{max}}\) of cast films annealed at 130°C in the constant humidity( RH =62%) at room temperature. \(A_0\) and \(A_{\infty}\) are absorbance of the film after and before annealing, respectively. \(A_t\) is absorbance at time \(t\) after moisture treatment. The moisture triggered
isothermal transition of the complex film with dextran sulfate is strongly suppressed than the original cast bilayer film without polymer. While in the complex film with poly(vinylsulfate-co-acrylamide), the transition is faster than the original film.

The moisture treatment is not, however, an actual process for recording or erasing. Azobenzene chromophore is well known photochromic compound showing trans-cis photoisomerization. Reaction rate of the isomerization of the azobenzene amphiphile was strongly affected by molecular orientation and molecular distribution in the aqueous bilayer membranes. Photoreaction was completely depressed in the phase separated cluster of amphiphile 1 in the bilayer matrix of dioctadecyldimethylammonium bromide, where the absorption maximum was located at 300 nm.

The as-cast films of the polyion complexes showing a large hypsochromic shift in the absorption spectrum showed no spectral change on UV light irradiation (low pressure Hg lamp with UV-D35 cut filter). On the other hand, large spectral changes on photoirradiation were found in the annealed films. As shown in Figure 2a, new absorption band at 450 nm attributed to cis isomer clearly appears concomitant with decreasing the absorption of trans isomer at 346 nm in the polyion complex film with dextran sulfate. On further irradiation, however, the absorption at 450 nm decreases and another new peak at 310 nm appears. Similar photoresponse of the absorption spectrum is found in the complex film with poly(vinylsulfate-co-acrylamide) (Fig. 2b). The photoinduced spectral change is very similar to that of the moisture treatment. Since the films were sealed
with desiccant in the quartz cells, relative humidity was estimated to be less than 12%. Spectral change due to the moisture triggered phase transition was not found at this humidity condition.

These results strongly indicate that the bilayer membranes immobilized by polyion complex technique are available to the erasable memory materials based on the phase transition triggered by thermal and photochemical processes. Details of photo- and moisture induced phase transition are now investigating.

References