Polymer Journal, Vol. 16, No. 2, pp 187—190 (1984)

NOTES

Immobilization of Synthetic Bilayer Membranes as Multilayered Polymer Films[†]

Masatsugu SHIMOMURA and Toyoki KUNITAKE*

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka-shi 812, Japan

(Received October 25, 1983)

KEY WORDS Bilayer Membrane / Immobilization / Polymer Film / Dialkylammonium Salt /

The synthetic bilayer membrane is prepared from a large variety of amphiphiles which include single-chain, double-chain, triple-chain, and polymeric compounds, and possess physicochemical characteristics common to the bilayer membrane of biolipids.[1] The combination of unique physicochemical properties and the structural versatility makes the synthetic bilayer membrane promising as novel functional material. However, functional applications have been limited since synthetic bilayers are usually obtained as *aqueous* dispersions. This paper shows that by proper combinations with polymers, it is possible to produce immobilized bilayers which though not soluble in water, still possess the bilayer characteristics common to those of an aqueous dispersion.

We showed recently that transparent films remain on glass by casting aqueous bilayers.[2,3] These films, however, tend to dissolve on prolonged contact with water, and dried films are often devoid of dynamic physicochemical properties characterizing aqueous bilayers. Similar situations more or less arise for a bilayer aggregate loaded in porous polymer membranes,[4] although it is well protected in the nonpermeable poly(vinyl chloride) matrix.[5]

Bilayer membranes, being stable aggregates of very large molecular weight, may be protected from disintegration in water by covering them with thin layers of water-insoluble, permeable films. Cellulose acetate (CA) is a polymer of choice since only water readily permeates the CA membrane. Aqueous bilayers of dialkylammonium salts[6] can be cast on a CA film, whereas CA in acetone cannot, owing to the solubility of the bilayer components in acetone. To avoid dissolution, acetone-insoluble polymers were used as binders. Poly(vinyl alcohol) (PVA) was suitable for this purpose, since the bilayer structure is retained in this matrix.[7]

Three-layered films (a PVA-bilayer composite layer sandwiched between two layers of CA) were prepared by two different procedures. In the first procedure, cast films of the PVA-bilayer composite were dipped in an acetone solution of CA and dried at room temperature under saturated acetone vapor. The film became opaque, when drying was too quick. The thickness of the CA layer was not easy to control by this procedure.

[†] Contribution No. 710 from Department of Organic Synthesis.

[*] Address correspondence to this author.

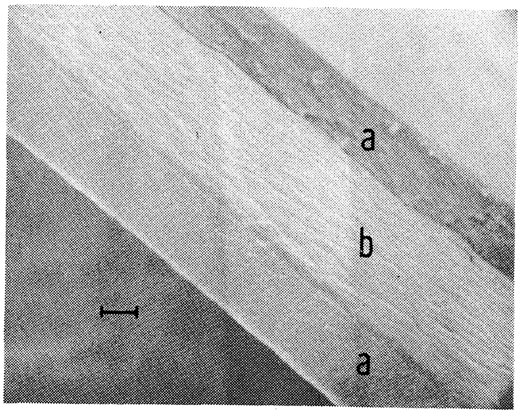
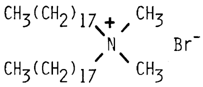


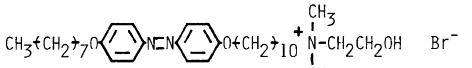
Figure 1. Scanning electron micrograph of a cross-section of a three-layered film. bar, 10 μm; a, CA layer; b, PVA-bilayer composite layer. The vertical shades are artifacts.

In the other procedure, an aqueous PVA-bilayer composite was cast on a CA film; this composite was then topped with a casting of CA. An aqueous solution (1 ml) of 50 mg of bilayer components (the mole ratio of $2C_{18}N^+2C_1$ and $C_8AzoC_{10}N^+$ was 10 : 1) and aqueous PVA (200 mg in 4 ml) were gently mixed, placed on a pre-cast film of cellulose acetate (300 mg from 6 ml acetone), and dried *in vacuo*. Cellulose acetate (300 mg) in 6 ml acetone was placed on the double-layered film and cast slowly under saturated acetone vapor.

Figure 1 is a scanning electron micrograph of a cross-sectional view of the film prepared by the second procedure from a mixed bilayer of $2C_{18}N^+2C_1$ and $C_8AzoC_{10}N^+$.[8] The three-layer structure can be clearly seen. The bilayer-composite layer (b, *ca.* 30 μm) is sandwiched between two CA layers (a, 10 and 20 μm). The possible release of the bilayer component from between the two CA layers was tested by measuring the absorbance of film-bound $C_8AzoC_{10}N^+$. Only 5% of the bilayer component was released following incubation in water for 1 h at 60°C. This release could probably be more effectively repressed by an improved casting procedure.



$2C_{18}N^+2C_1$



$C_8AzoC_{10}N^+$

The dynamic bilayer characteristics could be easily examined on the basis of the phase separation behavior. The phase separation behavior of azobenzene amphiphiles in a bilayer matrix has been studied extensively, along with its application to functionalized membranes.[9,10] Blue shifts of the azobenzene chromophore are observed when amphiphile $C_8AzoC_{10}N^+$ forms clusters in the matrix.

Figure 2 shows spectral changes in a sandwiched film containing a bilayer mixture of $2C_{18}N^+2C_1$ and $C_8AzoC_{10}N^+$ in the 10 : 1 molar ratio. The three-layer film prepared on a quartz plate was immersed in water in a quartz cell. At 10°C, λ_{max} was located at 305 nm, indicating the presence of azobenzene amphiphile clusters.[9] On raising the temperature, the peak at 305 nm diminished and a new peak appeared at 355 nm (monomeric species). These changes are schematically shown in the figure. Figure 3 illustrates a differential scanning calorimetry (DSC) curve and the temperature dependence of the 360-nm absorbance of the sandwiched film immersed in water. Polymer films (10—20 mg) were cut into pieces and placed in Ag sample pans with and without water (50 μl). The experimental details are given elsewhere.[11] The heating curve in Figure 3b corresponds to the spectral change in Figure 2 and the increase in monomeric absorbance levels off at 45°C which is close to T_c of $2C_{18}N^+2C_1$ (peak top in Figure 3a, 44°C). The spectrum does not revert completely in the cooling process.

When measurement was conducted without immersion in water (Figure 4), T_c moved to 68°C, and the monomer spectrum increased

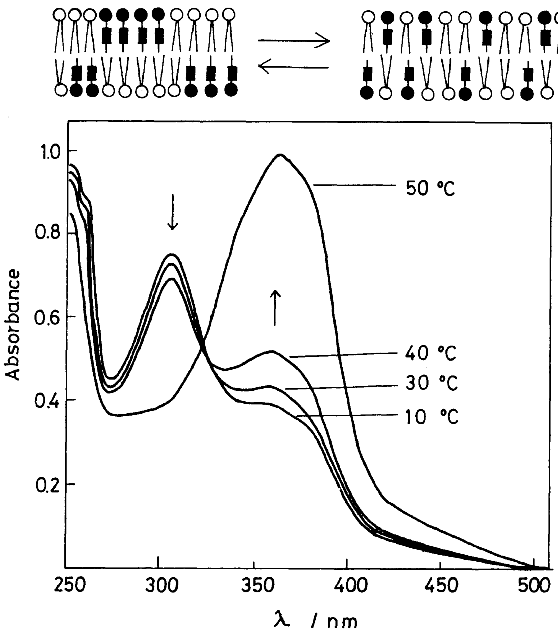
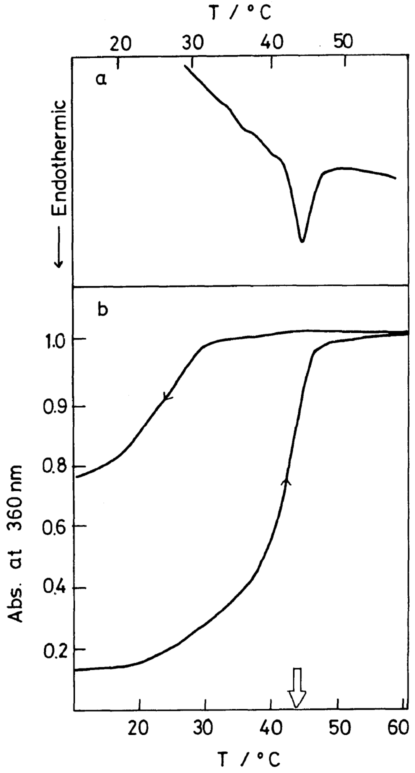


Figure 2. Absorption spectra of a sandwiched film immersed in water. Film prepared in a manner similar to that of Figure 1.



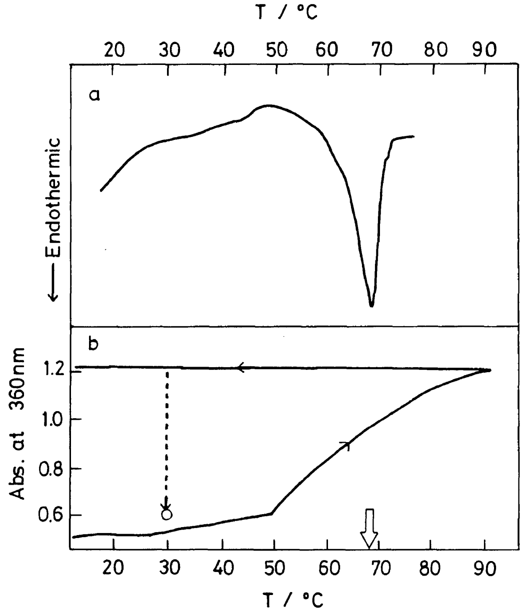


Figure 4. DSC thermogram (a) and temperature dependence of the absorbance at 360 nm (b) of the air-dried film.

Figure 3. DSC thermogram (a) and temperature dependence of the absorbance at 360 nm (b) of the sandwiched film immersed in water. Instrument, Daini-Seikosha SSC/560. The arrow in b indicates the direction of temperature change (2°C min^{-1}).

gradually from at *ca.* 50 to 90°C. The spectrum did not change with temperature in the cooling process. The homogeneous mixing attained at high temperatures remained intact in the dry film at all temperatures. However, the cluster species were capable of being regenerated in 10—20 min on immersing the film in water at temperatures below 30°C, as indicated by the dotted line.

It was established from these results that the sandwiched film described in this paper maintain the dynamic bilayer characteristics on contact with water. This immobilization procedure will be useful in the development of bilayer-based functional materials.

Acknowledgement. We are grateful to Prof. M. Takayanagi for the use of a scanning electron microscope. This work was supported in part by Special Coordination Funds for Promoting Science and Technology (Science and Technology Agency of Japan).

REFERENCES AND NOTES

1. T. Kunitake and Y. Okahata, *J. Am. Chem. Soc.*, **99**, 3860 (1977) and the subsequent publications.
2. N. Nakashima, R. Ando, and T. Kunitake, *Chem. Lett.*, 1577 (1983).
3. M. Shimomura, R. Ando, and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, **87**, 1134 (1983).
4. Y. Okahata, S. Hachiya, and G. Nakamura, *Chem. Lett.*, 1719 (1982).
5. T. Kajiyama, A. Kumano, M. Takayanagi, Y. Okahata, and T. Kunitake, *Chem. Lett.*, 645 (1979).
6. T. Kunitake, Y. Okahata, K. Tamaki, M. Takayanagi, and F. Kumamaru, *Chem. Lett.*, 387 (1977).
7. S. Hayashida, H. Sato, and S. Sugawara, *Chem. Lett.*, 625 (1983).
8. A piece of the three-layer film was immersed in liquid nitrogen and fractured. Gold was sputtered on the fractured surface and observed by Hitachi S-450 scanning electron microscope.
9. M. Shimomura and T. Kunitake, *Chem. Lett.*, 1001 (1981).
10. M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.*, **104**, 1757 (1982).
11. Y. Okahata, R. Ando, and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, **85**, 789 (1981).