

SHORT COMMUNICATIONS

**Immobilization of Cast Bilayer Films by  $^{60}\text{Co}$   $\gamma$ -Irradiation and Other Means<sup>†</sup>**

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The unique characteristics of synthetic bilayer membranes become applicable to many hitherto-difficult purposes upon immobilization. This has been accomplished by using water-insoluble polymers as solid matrices.<sup>1,2</sup> It was shown recently that bilayer characteristics are maintained in cast bilayer films with and without added poly(vinyl alcohol) (PVA).<sup>3-5</sup> Unfortunately, these composite (bilayer/PVA) films cannot be used in aqueous solutions, because they disintegrate in water. This disadvantage can be avoided in the case of three-layered films of cellulose acetate/bilayer-PVA/cellulose acetate.<sup>6</sup>

We report in this communication that insoluble bilayer films are readily obtainable without losing the bilayer characteristics when the PVA matrix is cross-linked by chemical and radiation treatments.

PVA can be rendered insoluble by chemical treatment (formalization etc.),<sup>7,8</sup> by thermal treatment,<sup>9</sup> and by irradiation.<sup>10,11</sup> We used  $^{60}\text{Co}$   $\gamma$ -irradiation mainly in this study, because this process appeared to give least damages to the composite film. The amphiphiles used are shown below and are typical double-chain ammonium salts which are capable of bilayer formation.<sup>12,13</sup> They were dis-

persed in water by sonication (Bransonic Cell Disrupter 185, sonic power 40, 1 min), and mixed with aqueous PVA (molecular weight, 154,000). The aqueous mixtures were cast in glass Petri dishes at room temperature, and dried *in vacuo*. Transparent films were obtained as follows:  $2\text{C}_{16}\text{N}^+$ /PVA, thickness  $35\ \mu\text{m}$ , 31 wt% bilayer;  $2\text{C}_8^{\text{F}}\text{C}_3\text{-de-C}_2\text{N}^+$ /PVA, thickness  $49\ \mu\text{m}$ , 83 wt% bilayer. Part of these films were placed in sealed ampoules under nitrogen, and irradiated from a  $^{60}\text{Co}$  source (2475 curie) at a dose rate of  $7.59 \times 10^5\ \text{rad h}^{-1}$ .

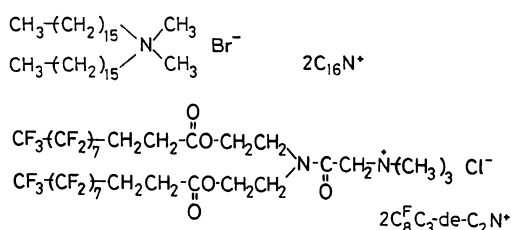
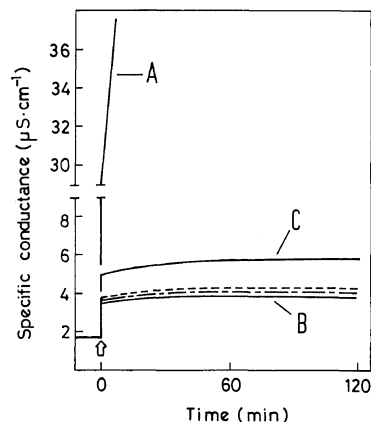


Figure 1 illustrates the conductivity change of the aqueous phase upon immersion of the composite films: instrument, TOA Electronics Ltd. CM-7B; cell, CG-7001 PL. When an unirradiated film of  $2\text{C}_{16}\text{N}^+$ /PVA was immersed, a very rapid increase in the specific conductivity ( $\kappa$ ) was observed (Figure 1A). This indicates very fast dissolution of the

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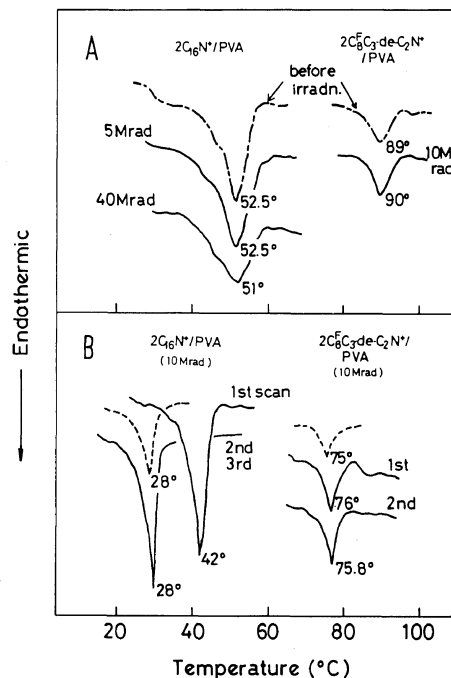


**Figure 1.** Conductivity change due to amphiphile released from composite films immersed in water. A: unirradiated  $2C_{16}N^+$ /PVA film,  $25^\circ C$ . B: irradiated  $2C_{16}N^+$ /PVA films,  $25^\circ C$ , —, 5 Mrad; ---, 10 Mrad; ----, 20 Mrad. C: irradiated  $2C_8^F C_3\text{-de-}C_2N^+$ /PVA film,  $25^\circ C$ , 10 Mrad.

ionic amphiphile into the bulk aqueous phase. On the other hand,  $\kappa$  increased very slowly for an irradiated film of  $2C_{16}N^+$ /PVA except for the initial burst. The change in the total dose (5 to 20 Mrad) did not cause significant differences. A similar result was found for an irradiated film of  $2C_8^F C_3\text{-de-}C_2N^+$ /PVA (Figure 1C). The time course of  $\kappa$  did not change after the film was immersed in water at  $100^\circ C$  for 30 min. These results clearly show that the bilayer membranes are immobilized in cross-linked PVA very efficiently. The initial small rise of  $\kappa$  is probably attributed to dissolution of bilayers near the film surface.

The IR spectral patterns before and after irradiation were identical, particularly in the  $\nu_{C=O}$  (ester, amide) and  $\nu_{C-F}$  regions which are sensitive to irradiation. Therefore, the bilayer components do not undergo detectable radiation damages by this method.

Figure 2 displays differential scanning calorimetry (DSC) thermograms of the cast films. Temperature was raised from 0 to  $100^\circ C$  at a rate of  $2 K \text{ min}^{-1}$ , as described elsewhere.<sup>14</sup> Cast films were cut into small pieces and



**Figure 2.** DSC thermograms. Solid line: A, air-dried films; B, films immersed in water. Dotted line: aqueous bilayer dispersions.

placed in Ag sample pans in the presence and absence of water. As shown in Figure 2A, endothermic patterns of the dry composite films were virtually not altered after irradiation. The phase transition of cast bilayers occurs at temperatures higher than that of aqueous dispersion, as discussed before.<sup>4</sup> Figure 2B gives thermograms of the bilayer film immersed in water. The endothermic peaks are sharper than those of the dry films. The irradiated  $2C_{16}N^+$ /PVA film exhibits a sharp peak at  $42^\circ C$  in the first scan and at  $28^\circ C$  in the 2nd and 3rd scans. The latter peak is exactly the same as that observed for an aqueous dispersion of  $2C_{16}N^+$  bilayer. These results indicate that the cast bilayer films absorb water gradually during the DSC scan, and that the physical state of the bilayer in the swollen films is the same as that of the corresponding aqueous dispersions. The irradiated  $2C_8^F C_3\text{-de-}C_2N^+$ /PVA film in the

presence of water gives a peak identical to that of aqueous  $2\text{C}_8\text{F}_3\text{C}_3\text{-de-C}_2\text{N}^+$  from the very first scan, probably because of the large bilayer content.

Immobilization of the composite film can be also accomplished by formalization of PVA. The composite films were immersed in an aqueous mixture of formaldehyde, sulfuric acid and sodium sulfate at *ca.* 70°C for 15 min.<sup>15</sup> The conductivity measurement showed that the bilayer components are not released from the treated film.

In conclusion, it is established that bilayer/PVA composite films can be made water-insoluble by  $^{60}\text{Co}$   $\gamma$ -ray irradiation and other means. The bilayer characteristics are maintained in the immobilized film. The present finding will greatly accelerate the use of the bilayer film as new functional materials.

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