Effect of Lipid Structure on the Formation of Ordered Cast Films of Polydiacetylenes

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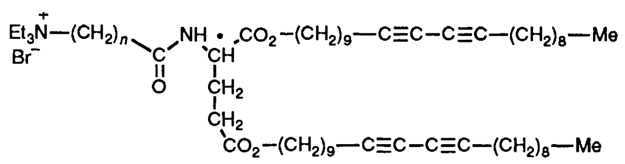
The efficient formation of polydiacetylenes in cast films demonstrates that a well-ordered multilayer structure can be readily formed by the casting of hydrated bilayer membranes onto solid supports.

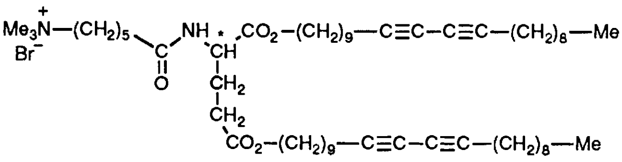
Langmuir–Blodgett techniques are widely used to prepare well-ordered multilayer films of amphiphiles for scientific studies and for potential applications in electronic and photonic materials. Recently Kunitake and co-workers described a potentially attractive alternative procedure for the preparation of multilayer films.[1] An aqueous dispersion of amphiphilic bilayer vesicles was allowed to dry slowly onto a solid support. The dried film was readily removed from the substrate, and the free-standing film was examined by *X*-ray scattering (edge-on) and differential scanning calorimetry. Both methods indicate the presence of a lamellar arrangement of the amphiphiles. In order to test the extent of retention of lamellar characteristics upon the conversion of hydrated bilayers into dried multilayers, we have designed and synthesized new diacetylenic lipids and evaluated polydiacetylene (PDA) formation in both bilayers and cast films composed of these lipids.

The formation of PDAs is a valuable test of molecular order, because the photopolymerization is acutely sensitive to the molecular packing and order of monomeric diacetylenes in crystals or supramolecular assemblies. Monolayers of fatty acid diacetylenes are polymerizable in the condensed phase.[2] Bilayers of lipid diacetylenes are polymerizable at temperatures below the lipid phase transition temperature in the solid-analogous phase, but not in the more disordered liquid-analogous phase.[3] The disordering of lipid chain packing that occurs upon the sonication of bilayer membranes, to form small sonicated vesicles, inhibits PDA formation.[4]

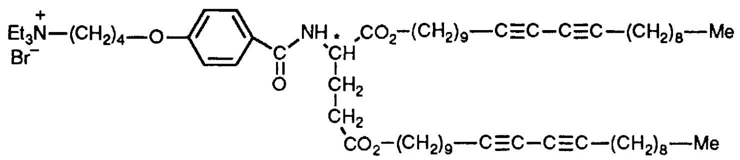
We previously reported the synthesis and characterization of lipid (**1**).[5] Bilayer membranes and cast films from vesicles of (**1**) were photosensitive and readily gave highly-coloured PDAs, which strongly indicates that the lipids are arranged in multilayers throughout the films.[5] However the absorption maxima of PDAs formed in bilayer vesicles was at 640 nm, whereas the peak occurred at 610 nm for the PDAs formed in the cast film. Since the absorption maxima of PDAs are indicative of the polymer chain length and/or order of the polymer structure, the observed hypsochromic shift suggests the PDA-(**1**) chains in cast films are less ordered or shorter than those formed in the bilayers. To test whether the apparent difference in PDA structure was an inherent consequence of the casting procedure or specifically related to lipid (**1**), three additional diacetylenic glutamate lipids (**2**)—(**4**) were investigated. Each of these new lipids were designed to raise the lipid phase transition temperature, T_m, to above the room temperature casting conditions. Since the T_m shifts to higher temperatures as the water content of the bilayers is decreased,[6] the casting of lipids, *e.g.* (**1**), whose T_m is below room temperature will cause the membranes to undergo a



(1) *n* = 5 (2) *n* = 10



(3)



(4)

dehydration induced transition from the liquid-analogous phase to the solid-analogous phase. This dehydration induced excursion of the phase transition may be responsible for the observed differences between the bilayers and cast films of (**1**).

The T_m is sensitive to lipid chain packing and is usually modulated by the structure and length of the lipid chains. It was clearly undesirable to modify the lipid chains in this instance. Therefore the original lipid structure was altered only in the head group. The T_m was increased by using a longer spacer between the glutamate backbone and the triethylammonium group [lipid (**2**), T_m 30.5 °C], by the substitution of the smaller trimethylammonium group [lipid (**3**), T_m 26.0 °C] for the Et_3N^+, and by the incorporation of an aromatic ring into the spacer link [lipid (**4**), T_m 35.5 °C). Bilayer membranes of each new lipid were prepared by hydration (Milli-Q water) of a thin lipid film, followed by brief sonication at temperatures above T_m. The lipid bilayers of (**2**), (**3**), or (**4**) at room temperature are photosensitive to 254 nm light, and rapidly form purple–blue PDAs. The absorption maxima are reported in Table 1.

Cast films were formed at room temperature from unpolymerized bilayers of each of the lipids. A few drops of the hydrated diacetylene bilayers were spread on a clean glass slide and allowed to dry slowly over two days to yield thin transparent films, which were then vacuum dried. Irradiation (254 nm light) caused the films to immediately become uniformly highly coloured. The absorption maxima of the PDAs formed in the cast films are shown in Table 1. There is good agreement for the PDAs formed from lipids (**2**)—(**4**) in bilayers and in cast films. In addition, each cast film shows reversible thermochromic behaviour from room temperature to 50 °C. The characteristics of this thermally induced spectral change are similar for the PDAs formed in bilayers and in cast films for each of the three new lipids (**2**)—(**4**).

Table 1. Absorption maxima (nm) of the polydiacetylenes formed in lipid bilayer vesicles and in cast multilayer films.

Temperature: 22 °C

Lipid	Bilayer $\lambda_{max.}$	Cast film $\lambda_{max.}$
(**1**)	640	610
(**2**)	610, 570	610, 570
(**3**)	610, 570	610, 570
(**4**)	590	590

Temperature: 50 °C

Lipid	Bilayer $\lambda_{max.}$	Cast film $\lambda_{max.}$
(**2**)	545	540
(**3**)	555	540
(**4**)	540	540

In summary the ease of the polymerization reaction and the absorption characteristics of the PDAs in both bilayer membranes and cast films indicate that the molecular order of the lipid bilayers was retained during the casting procedure. The especially close similarity of the characteristics for the PDAs formed in bilayers and cast films for lipids (**2**)—(**4**), indicates that the casting technique is most successful at retaining the molecular order of the original bilayer, if the experiment is always below the T_m of the hydrated lipids.

Under these conditions the cast film technique appears to be a convenient procedure for the preparation of multilayer films.

Finally, particular note should be paid to the effect of changing the lipid head group from a choline (Me_3N^+) to a triethylammonium group. This relatively small change provides a potentially useful way to modulate the T_m by approximately 10 °C without modifying the hydrophobic region of the bilayer forming lipid. Therefore when circumstances prevent structural modification of the lipid chains, the T_m may be lowered by increasing the size of the quaternary ammonium head group.

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