apparent intensity distortions, and the phase of the whole enzyme spectrum could be corrected by the usual small linear frequency-dependent correction. *No base line correction of any kind was performed.* The "1331" sequence[4,5] produced hopelessly distorted base lines after phase correction under the same conditions.

To obtain this spectrum the usual precautions in obtaining solvent-peak suppressed spectra were followed. The probe was first detuned to avoid radiation damping and the water line shimmed carefully down to a width at half-height of about 1 Hz. The probe was retuned for the suppression experiment. A small "trim" pulse, with phase 270°, was added at the end of the sequence, and the suppression was optimized by empirical adjustment of this pulse together with slight variation of the two center pulses so as to correct for residual errors. However, we found that because of the absence of a large spectral phase correction, quite strong residual water signals could be tolerated as long as saturation of preamplifier or receiver were avoided. We conclude that at least on instruments that are equipped with digital phase shifters, stable radio-frequency amplifiers, and a resonance coil providing good radio-frequency homogeneity, NERO-2 may be the method of choice for suppressing the solvent peak without introducing large phase distortions.

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Polymerizable Dienoyl Lipids as Spectroscopic Bilayer Membrane Probes

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It is well known that dienoates and other α,β unsaturated carbonyl compounds are sensitive to solvent polarity.[1] Here we summarize the spectral properties of unpolymerized dienoyl lipids in isotropic media and molecular assemblies and demonstrate that the chromophore absorption maxima are sensitive to lipid chain packing as well as to media polarity. These characteristics provide a spectroscopic probe of the immediate environment of the chromophore in lipid bilayer membranes prior to polymerization.

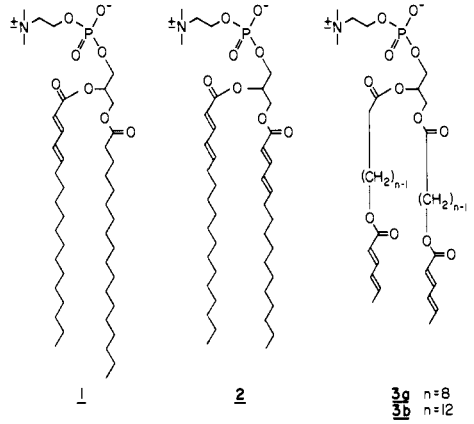
The monomeric amphiphilic membrane probes described here are also useful as polymerizable lipids[2] for the modification of bilayer physical properties, e.g., increasing colloidal stability[3] and decreasing membrane permeability.[4] Photopolymerization of reactive groups, e.g., methacryloyl,[5] dienoyl,[6] or styryl,[7] offers a general route to polymerized vesicles.

Table I. Absorption Maxima for Lipids in Isotropic and Smectic Media at 22 °C

	in CH_3CN		in H_2O	
lipid	λ_{max}, nm	log ϵ_{max}	λ_{max}, nm	log ϵ_{max}
1	260	4.32	260	4.20
2	260	4.63	260	4.49
3a	257	4.61	262	4.54
3b	257	4.56	242 (257)[a]	4.15 (4.56)[a]
4	260	4.69	237	4.48
5	260	4.75	232	4.52
6	257	4.70	260	4.54

[a] The values in the parentheses were determined at 40 °C.

Lipids form supramolecular bilayer structures when hydrated in aqueous buffers with close packing of the lipid chains. The area per lipid molecule is usually about 70 A^2.[8] In this study lipid dienoates based on three phosphatidylcholines **1**, **2**, and **3**,[3,9] a long chain sulfoethylamine **4**,[3] and a dialkyldimethylammonium salt **5**,[10] were prepared, and their absorption determined in organic solution and hydrated assemblies. A micelle-forming shorter chain compound **6**[10] was prepared for comparison.



1 **2** **3a** n=8 **3b** n=12

The dienoylphosphatidylcholines (PC) **1** and **2** in acetonitrile solution absorb at 260 nm (Table I). The extinction coefficients for these compounds are 1.5–2 × 10^4 per dienoyl group per molecule. The lipid conformations in isotropic media minimize the ground-state interactions between the two chain chromophores. Bilayer assemblies of both the mono **1** and didienoyl PC **2** in water show absorption maxima at 260 nm, the same as observed in acetonitrile. Therefore, the two chromophores in **2** are not favorably arranged to form dimers or higher aggregates in the bilayer. Note also that the polarity of the chromophoric environment is similar in the bilayer and acetonitrile.

In contrast the absorption maxima of the chain terminal, disorbyl PC **3a**, is different in acetonitrile solutions (257 nm) and water assemblies (262 nm). This effect is similar to the absorption reported for sorbic acid in ethanol (254 nm) and hexane (261 nm)[11] and reflects the more hydrophobic nature of the interior of the bilayer, where the chromophore resides. Again in this case, as for **1** and **2**, the absorption spectra indicate that the chromo-

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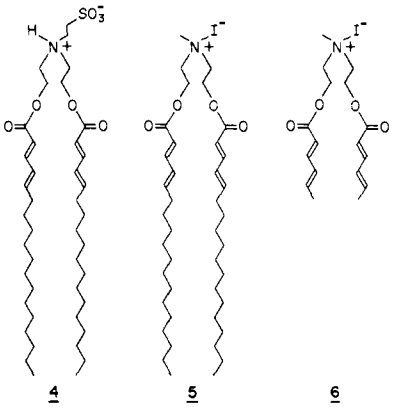
phore is not aggregated. The lipid phase transition is 11 °C for bilayers of **3a**;[12] therefore, the membranes were in the liquid analogous phase during the measurement at room temperature.

The longer chain disorbyl PC **3b** forms bilayer membranes with a phase transition at 33 °C.[12] The absorption maxima (room temperature) of **3b** in acetonitrile is the same as **3a**, 257 nm. However, in water the **3b** vesicles absorption shows a hypsochromic shift to 242 nm with a diminished extinction coefficient. This indicates the chain terminal sorbyl group is aggregated in the bilayer solidlike phase. When the vesicles are warmed above the phase transition temperature, 40 °C, the absorption shifts to 257 nm with a doubling of the extinction coefficient.

Previously we reported a 6000-fold difference in photosensitivity of lipid diacetylene bilayers as a function of the lipid structure.[13] The reactivity of the phospholipid and dialkyl dimethylammonium halide analogues was interpretable based on the conformational preferences of these molecules. The glycerol backbone of phospholipids is approximately perpendicular to the plane of the bilayer with the two alkyl chains extending unequal distances into the bilayer membrane.[14] The synthetic lipid dialkyl dimethylammonium salts[15] have planes of symmetry, which suggest that both hydrocarbon chains penetrate equally into the bilayer membrane.

Indeed, the molecular assemblies of the symmetrical molecules **4** and **5** in water show a pronounced hypsochromic shift from the



4 **5** **6**

monomer absorption maxima at 260 nm to approximately 235 nm ($\Delta\nu$ = 4000 cm^{-1}). This spectral effect is similar to that observed upon the formation of dimers and higher aggregates of dye molecules in monolayers and adsorbed on surfaces.[16] The size of the shift indicates the aggregates in these vesicles are larger than dimers. We propose that the spectral shift is due to the bilayer induced close packing of the chromophores in these symmetric molecules. A test of this hypothesis is provided by the absorption of aqueous dispersions of **6**, which forms micelles in water. In contrast to the longer chain bilayer former, **5**, the absorption maximum of **6** in water is not shifted. Consequently, the chromophores have more freedom of motion in the micelle and are not constrained in a structure that favors aggregation. This is consistent with the view that amphiphile chain packing is looser and more disorganized in micelles than bilayers. In contrast to micelles, tightly organized assemblies of dienoyl-containing amphiphiles such as monolayers and multilayers should show short wavelength absorption due to aggregate formation. This prediction has recently been confirmed.[17]

In summary, the unsymmetrical dienoyl PCs do not show evidence of bilayer-induced aggregation, whereas the symmetrical dimethyldialkylammonium halides favor chromophore aggregation with a pronounced hypsochromic absorption shift. These data demonstrate the utility of dienoyl lipids as probes of lipid chain packing in lipid assemblies.

Hydrogen Atom Transfer Reactions of Transition-Metal Hydrides. Utilization of a Radical Rearrangement in the Determination of Hydrogen Atom Transfer Rates

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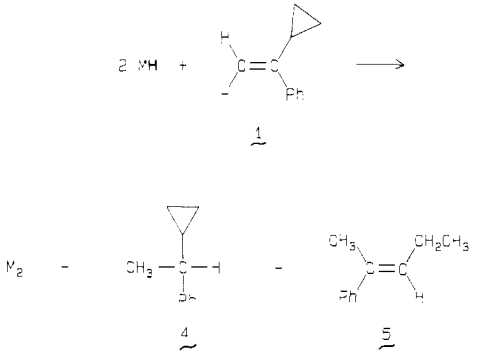
The reaction of a transition-metal hydride with an unsaturated substrate is a critical step in several catalytic reactions. Commonly accepted mechanisms[1] for homogeneous hydrogenation and hydroformylation have traditionally involved even-electron intermediates conforming to the 16- and 18-electron rule.[2] Recently, kinetic and spectroscopic (CIDNP) evidence has been reported in support of odd-electron pathways for reactions of metal hydrides with substituted styrenes,[3] anthracenes,[4] allenes,[5] and conjugated dienes,[6] all of which form stabilized (benzylic or allylic) radicals. We report a new approach, in which metal hydrides are reacted with vinylcyclopropanes, which contain a radical clock.[7]

The reaction of α-cyclopropylstyrene (**1**, 0.052 M) with $HCr(CO)_3(C_5H_5)$ (0.155 M) in benzene at room temperature resulted in hydrogenation of the carbon–carbon double bond as the predominant reaction and produced 1-cyclopropyl-1-



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4 **5**

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