

Alternation of Absorption Maxima in Helical Superstructures of Chiral, Single-chain Ammonium Amphiphiles

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The absorption maxima of azobenzene-containing amphiphiles, which self-organize into helical superstructures, alternate with the number of carbon atoms in the hydrophobic chain.

The bilayer membrane, which is a spontaneous assemblage of amphiphiles in water, has been extensively studied to elucidate the mechanisms of biological processes and to constitute new functionalized molecular architecture systems.¹ However, there has been no investigation into bilayer membranes composed of amphiphiles which possess an odd number of carbon atoms in their hydrophobic chain. Here we describe some differences between bilayers of amphiphiles containing even and odd numbers of carbons.

The series of amphiphiles, **(1)**, used in the work contain an azobenzene chromophore as its spectrum provides information on molecular orientation within the bilayer membrane.² The amphiphiles with an odd number of carbons were prepared in the same manner as described for amphiphiles containing an even number of carbons.^{3†} The amphiphiles

thus obtained were dispersed in water by vortexing at a temperature close to the boiling point of water. The dispersions were examined by transmission electron microscopy after staining with uranyl acetate or by optical microscopy using darkfield illumination.

After dispersion the amphiphile of [**(1)**, $n = 12$] immediately formed fibrous aggregates in abundance, however they were transformed into helical superstructures within 24 h at room temperature as described previously.⁴ Other amphiphiles were found to form helical superstructures in the same way. Another amphiphile of [**(1)**, $n = 10$] formed needle-like aggregates, which are known to grow from the helical superstructures.⁵ The helical superstructure is therefore a general feature of the bilayers of these amphiphiles. On the other hand, the phase-transition temperature alternates with the number of carbon atoms in the hydrophobic chain (Figure 1).

The even-odd-chain effect is also observed in the spectral behaviour. We reported previously that a morphological change in the bilayer of [**(1)**, $n = 12$] was accompanied by a

† All compounds gave the expected IR, NMR, and microanalytical data. Differential scanning calorimetry (DSC) was performed by the method described elsewhere.⁶ T_c (°C): 57 ($n = 6$), 76 ($n = 10$), 73 ($n = 11$), 83 ($n = 12$), and 85 ($n = 13$).

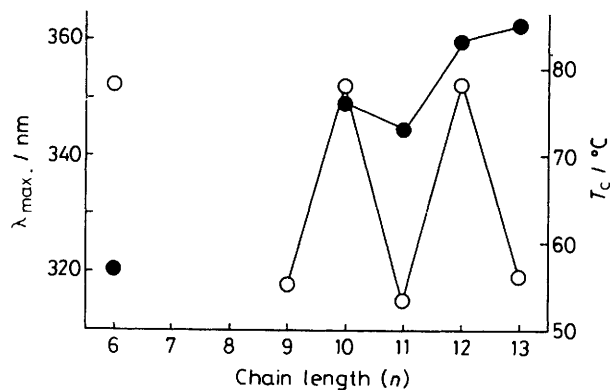
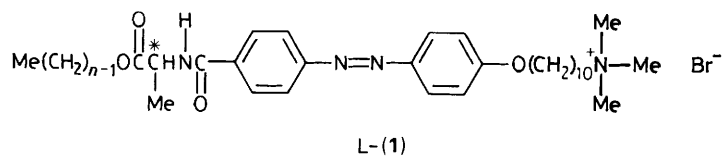


Figure 1. T_c (●) and λ_{\max} (○) as a function of the chain length of (1). Absorption spectra were measured for well incubated (usually 24 h at room temp.) aqueous dispersions of (1) (0.05 mM).

λ_{\max} shift from 321 to 352 nm.⁴ The same red shift was observed in the bilayer membranes of the amphiphiles containing an even number of carbons [(1), $n = 6, 10$], whereas the bilayer membranes of the amphiphiles containing an odd number of carbons [(1), $n = 9, 11, 13$] absorbed at about 320 nm, and displayed no spectral changes even if a morphological transformation occurred. Thus, the absorption maximum of (1) is located at approximately 350 nm when the amphiphiles possess an even number of carbon atoms in the hydrophobic chain (Figure 1). The azobenzene chromophore is either in the H (parallel stacking) or J (tilted stacking) aggregation, as reflected by λ_{\max} shifts in absorption spectro-

scopy.² Therefore, the chromophore orientation is rather more tilted in the helical superstructure of the amphiphile containing an even number of carbons compared to the orientation of the amphiphile containing an odd number of carbons. The result of the DSC measurement suggests that the hydrophobic chain is more tightly packed when the chromophore is in the tilted stacking, because the T_c of the bilayers of amphiphiles containing an even number of carbons are higher than those estimated from the bilayers of amphiphiles containing an odd number of carbons.

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