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ENHANCED CIRCULAR DICHROISM AND FLUIDITY OF DISK-LIKE AGGREGATES OF A CHIRAL, SINGLE-CHAIN AMPHIPHILE[1)]

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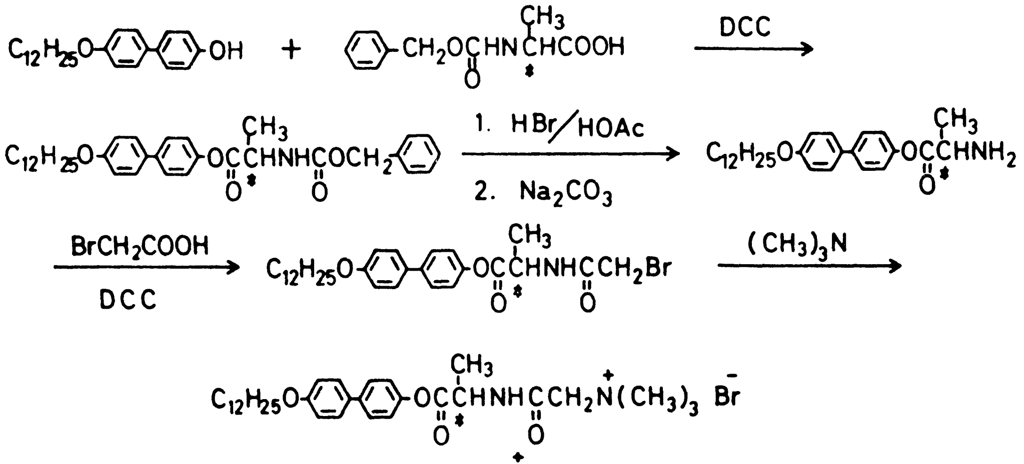
Chiral, single-chain ammonium amphiphiles which possess the alanine unit formed disk-shaped bilayer aggregates in water. Circular dichroism of the chiral aggregate was much enhanced at temperatures below the phase transition.

It has been reported from these laboratories that a variety of single-chain amphiphiles produce stable, membrane-forming aggregates spontaneously when dispersed in water.[2-4)] The presence of a rigid segment such as biphenyl or diphenylazomethine moiety was required for the membrane formation. We describe in this letter the introduction of the chiral center to a single-chain amphiphile and the enhanced optical activity due to the aggregate formation.

A chiral single-chain amphiphile(L-1) and its racemate(DL-1) were synthesized from alanine and dodecyloxyhydroxybiphenyl according to Scheme 1.

Scheme 1.



C_{12}-Bph-Ala-C_2-$\overset{+}{N}$ (1)

The final products were recrystallized two times from methanol and ether, and their purities were confirmed by thin layer chromatography, NMR and IR spectroscopies and elemental analysis.5)

These amphiphiles gave clear aqueous solution upon sonication(Bransonic 12, bath type). Electron microscopy indicates the formation of disk-like structures for both L-1(Fig. 1a) and DL-1(Fig. 1b). The thickness of the disk is 60 - 70 Å, in accordance with the bilayer structure. Differential scanning calorimetry(DSC) of aqueous solution(30 mM; instrument, Daini-Seikosha, Model SSC-560) showed the presence of the phase transition(35°C for L-1 and 21°C for DL-1), which is characteristic of the liquid crystalline property.

The circular dichroic(CD) spectrum of the L-1 bilayer is strongly dependent on the temperature and the amphiphile concentration. The temperature dependence is shown in Fig. 2. At low temperatures of 5 - 10°C, the spectrum possesses a maximum at 273 nm($[\theta] = 15\pm1 \times 10^4$ deg cm^2dmol^{-1}) and a trough at 252 nm($[\theta] = 3.6 \times 10^4$). With elevating temperature, the spectrum becomes smaller in magnitude gradually at 15 - 20°C and drastically at 25 - 30°C. The magnitude becomes constant again at temperatures above 35°C($[\theta]$ = +15,000). The λ_{max} in the UV spectrum is located at 260 nm, and much less sensitive to the temperature change. The temperature dependence of the CD spectrum is more clearly seen in Fig. 3, in which $[\theta]_{273}$ is plotted against temperature. The large reduction of $[\theta]_{273}$ at 20 - 30°C is apparent. A shallow minimum exists at 35°C which exactly corresponds to the phase transition temperature observed by DSC.

The concentration dependence of $[\theta]_{273}$ at 10°C is shown in Fig. 4. A 1 mM solution was prepared by sonication and diluted in portions. A rapid decrease in $[\theta]_{273}$ starts at 1×10^{-4} M. The light scattering experiment(instrument, Toyo Soda LS-8) showed that the aggregate weight of L-1 was $(3 - 4) \times 10^6$ at $(1 - 5) \times 10^{-4}$ M, but decreased to one-tenth ($(1 - 2) \times 10^5$) at 5×10^{-5} M. Apparently, the CD change in Fig. 4 is related to the critical micelle(aggregate) concentration.

When CTAB was added, the CD spectrum did not change up to 5.8×10^{-4} M, but at higher concentrations it started to decrease and $[\theta]_{273}$ reached a minimal value of -3000 at [CTAB] = 1.2×10^{-3} M. This concentration is close to the cmc of CTAB and the $[\theta]_{273}$ value is in the same range as that observed in CH_3OH. The CTAB micelle undoubtedly destroyed the highly chiral structure of the L-1 aggregate.

In conclusion, the experiments described above indicate that the highly enhanced circular dichroism is derived from molecular fixation of the chiral surfactant in the rigid, disk-like bilayer assembly. This phenomenon may be a general one, since chiral

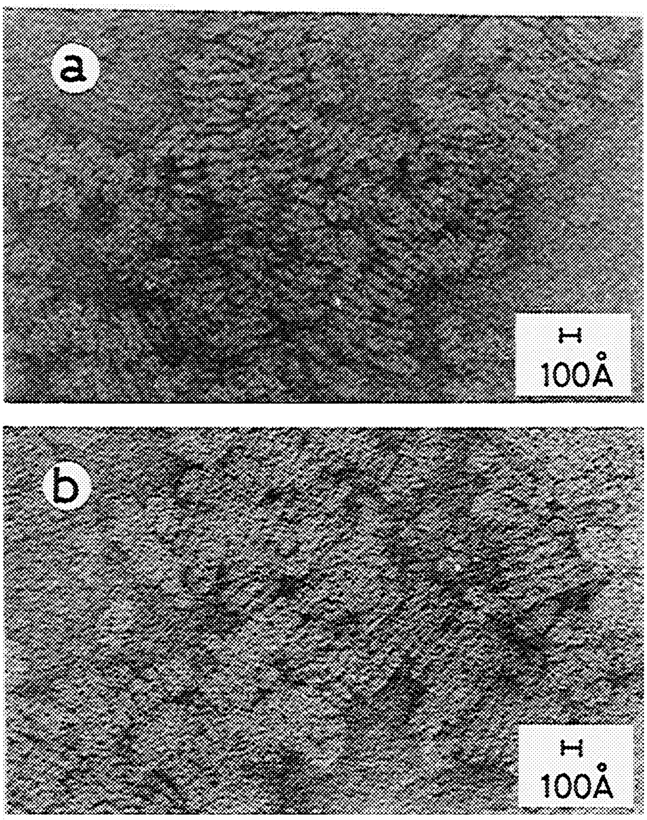


Fig. 1 Electron Micrograph
Stained by Uranyl Acetate
a. L-1, 10 mM. magnification × 300,000.
b. DL-1, 10 mM. magnification × 300,000.

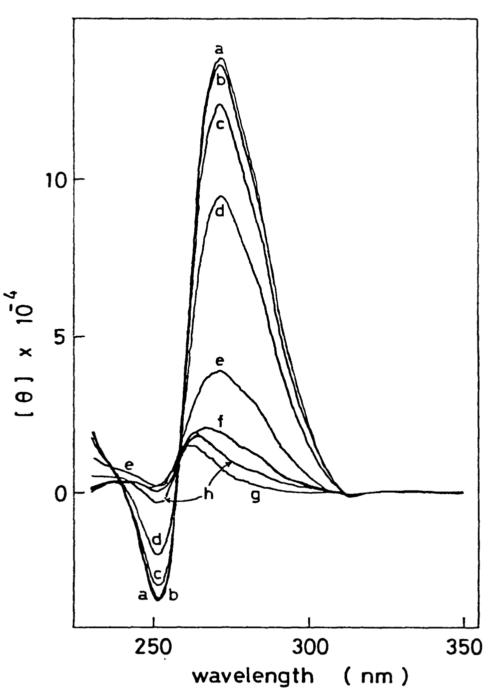


Fig. 2 Temperature Dependence of CD Spectrum
$[L\text{-}1] = 1 \times 10^{-3}$ M.
Temperature: a, 10°; b, 15°; c, 20°; d, 25°; e, 30°; f, 32°; g, 35°; h, 40°.

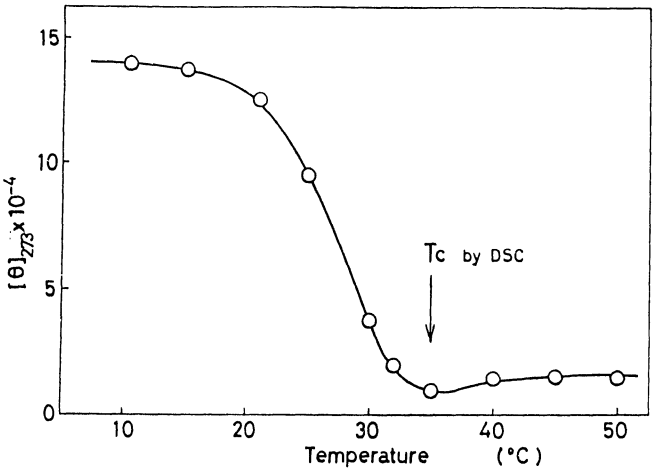


Fig. 3 Temperature Dependence of $[\theta]_{273}$
$[L\text{-}1] = 1 \times 10^{-3}$ M.

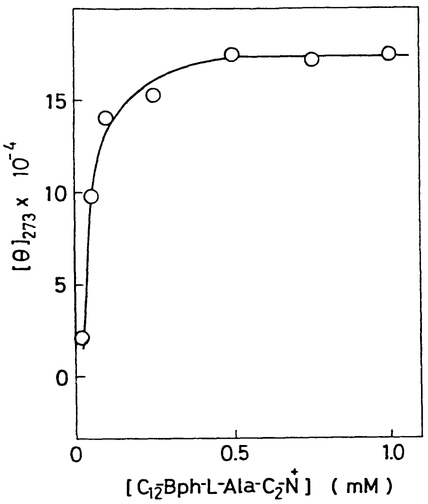
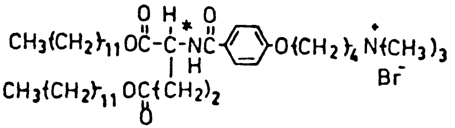


Fig. 4 Concentration Dependence of $[\theta]_{273}$ at 10°C.

dialkylammonium membranes have been prepared[6)] and large CD enhancement observed for a chromophore-containing bilayer of dialkylammonium amphiphile 2.[7)] Enhanced CD spectra have been observed for lyotropic liquid crystals[8,9)]; however no large influences of the phase transition on CD have been reported. These bilayer assemblies will provide highly chiral microenvironments which are useful for developing new physical and chemical functions.



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References and Notes

1) Contribution No. 595 from Department of Organic Synthesis.
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4) Y. Okahata and T. Kunitake, Ber. Bunsenges. Phys. Chem., 84, 550(1980).
5) L-1: mp 213 → 221°C(the liquid crystalline region indicated by the arrow); $[\alpha]_D^{20}$ -81.5°(c = 0.99, $CHCl_3$); found, C 63.09, H 8.08, N 4.52 %. calcd for $C_{32}H_{49}BrN_2O_4$, C 63.46, H 8.16, N 4.62 %. DL-1: mp 200 → 210°C; found, C 63.28, H 8.07, N 4.57 %. calcd for $C_{32}H_{49}BrN_2O_4$, C 63.46, H 8.16, N 4.62 %.
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