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Giant Helical Superstructures Formed by Cationic Cholesterol-Containing Polymers

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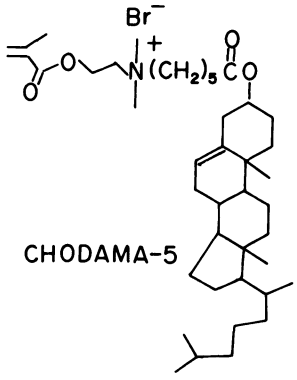
Giant fibrous right-handed helical superstructures were formed in aqueous solution by a cholesterol-containing polymeric amphiphile, poly(CHODAMA-5). The ordered packing of tubular structures formed by vesicle-fusion mechanism is considered to be prerequisite for the formation of these giant superstructures. The vesicle-fusion was controlled by addition of Ca^{2+} and/or with aging time control at phase transition temperature.

Recently, it was reported that the direct observations of aqueous dispersions of synthetic bilayer membranes by optical microscopy showed not only vesicles but a variety of dynamically changing morphologies such as fibers, tubules, etc.[1] And more recently, the helical superstructures were formed from bilayer membranes of amino acid-derived chiral amphiphiles.[2-4] It is to be noted in these reported studies that the morphological transformations are closely related to the function of biological membranes such as fusion and fission of natural cells. Focusing our attention on these fusions of natural cell membranes, we have designed a structure of synthetic polymeric amphiphile, poly(CHODAMA-5),[5] containing cholesterol and investigated the growth of the polymeric bilayer vesicles to stable giant fibrous superstructures via vesicle-fusion mechanism, and we now wish to report the preliminary results in this report.

The monomer, coded CHODAMA-5, was synthesized from cholesteryl ω-bromohexanoate by reacting with 2-(dimethylamino)ethyl methacrylate. The structure and purity of CHODAMA-5 was identified by spectroscopic data, elemental analysis, and TLC: mp 82→105 °C. Found: C,67.0; H,9.72; N,1.76%. Calcd for $C_{41}H_{70}BrNO_4$: C,68.3; H,9.78; N,1.94%. R_f=0.44 (CH_3Cl:CH_3OH=3:1).



CHODAMA-5

CHODAMA-5 was soluble in water and formed well developed polymeric bilayer vesicles upon polymerization.[6] CHODAMA-5(0.28 mM in water, M=mol/l) was mixed with $CaCl_2$(1wt% to CHODAMA-5), sonicated at 60 °C for 15 min(Branson bath type B-52, 240w), aged at a phase transition temperature(62 °C) of CHODAMA-5 solution for 1 day and then polymerized by $K_2S_2O_8$ at 60 °C for 24 h. Figure 1 shows an electron micrograph(recorded on a JEOL JEM 100-CX) of the resulting dispersion of poly(CHODAMA-5) stained

by 2% uranyl acetate. Tubular(or ribon-like) structures(length, ≈10 μm; diameter, 0.7-1 μm) and large extended ordered aggregates(diameter, 0.3-1 μm) were observed (Fig. 1). These structures were assumed to be formed by successive fusions of vesicles. When the poly(CHODAMA-5) solution was aged for 4 more days, the large fibers were resulted and could be observed even by naked eyes. The solution was then stained with uranyl acetate and the fibers were observed by optical microscope(American Optical Co Thomas Model-40). As shown in Figs. 2-a and 2-b, the fibers(length, ≈1000 μm; diameter, 10 μm) possess right-handed helical structures (pitch, 32 μm). These helical superstructures were thermally stable up to 90 °C, but were easily destroyed by the mechanical force such as pressure. We assume that these giant helical aggregates are formed by the ordered packing of tubular(or ribon-like) structures as those shown in Fig. 1, and the growth of vesicles by fusion was assumed to be required step for the formation of these giant fibrous structures. However, the detailed molecular arrangement of poly(CHODAMA-5) chains in the helices are not clear, and the morphological studies of these helices are now in progress.

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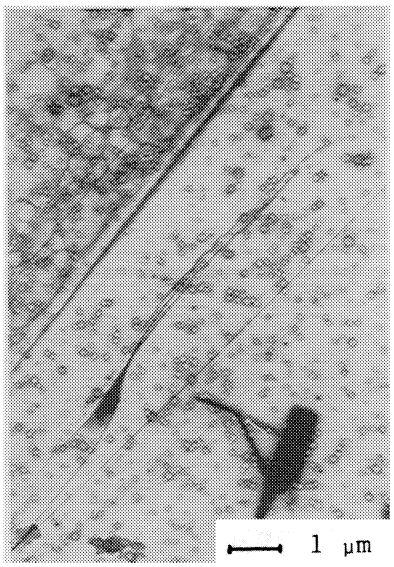

Fig. 1. Electron micrograph of aqueous dispersion of poly(CHODAMA-5). magnification, x8800

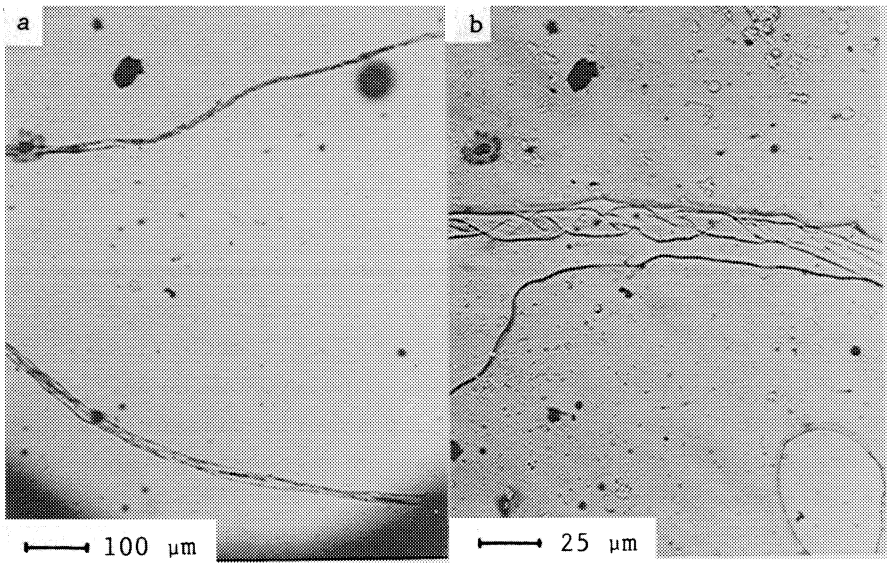

Fig. 2. Optical micrographs of fibers formed by poly (CHODAMA-5). (a) magnification, x100; (b) magnification, x400.

References

1) N. Nakashima, S. Asakuma, T. Kunitake, and H. Hotani, Chem. Lett., 1984, 227.
2) N. Nakashima, S. Asakuma, J.-M. Kim, and T. Kunitake, Chem. Lett., 1984, 1709.
3) N. Nakashima, S. Asakuma, and T. Kunitake, J. Am. Chem. Soc., 107, 509(1985).
4) K. Yamada, H. Ihara, T. Ide, T. Fukumoto, and C. Hirayama, Chem. Lett., 1984, 1713.
5) The original chemical name of CHODAMA-5 is cholesteryl-oxycarbonyl-hexamethyl-2-(methacryloyl)ethyl dimethyl ammonium bromide.
6) Iwhan Cho and Kwang-Choon Chung, Macromolecules, 17, 2937(1984).

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