

Research on Supramolecular Assemblies of Synthetic Glycolipids

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Amidic glycolipids, 1,5-bis-*O*-alkyl-*N*-maltooligonoyl-*L*-glutamate (**1**), having various lengths of two hydrocarbon chains (carbon number, *m*: 14, 16, 18) and maltooligotose (glucose unit, *n*: 3, 5, 7) and *N*-glycosidic lipid; 1,5-bis-*O*-octadecyl-*N*-maltopentaonosyl-*L*-glutamate **2** were synthesized. The assembling structures were analyzed by microscopic observation such as negatively stained TEM, cryo-TEM, and AFM. The glycolipid **1a** (*m,n*: 14,5) showed a fiber-like structure, while **1b** (16,5) showed a fiber-like structure when the hydrating temperature was above the gel-to-liquid crystalline phase transition temperature (T_c) and a large disk-like structure when incubated below the T_c . The glycolipid **1c** (18,5) took a large disk-like structure by hydrating the powder above the T_c . The glycolipids **1d** (18,3) and **1e** (18,7) showed the mixture of large disks and large vesicles and the mixture of small disks and micelles, respectively. While, *N*-glycoside lipid **2** made vesicular structure only.

Preparation procedure using high shear stress such as extrusion or sonication converted the large disk of **1c** to the smaller assemblies such as small disk-, cone-, and granule-like assemblies, having low molecular packing states. The glycolipid molecules in the plane part of the disk were packed so tight that the segmental mobility was very low even above the T_c , and the reactivity of the saccharide chain against *Concanavalin A* (*ConA*) was also very low. These data indicate that high reactivity should come from the loose packing of saccharide chains around the edge part of the assemblies.

The disks make a unique supramolecular assembling structure by complex formation with *ConA*. The stacking of several disks forms a rouleaux-like structure, and the structures further assemble to construct hyperbranched three-dimensional aggregates. This supramolecular assembly would be a model of an extracellular matrix, an effective matrix to keep bound water, or a material which releases hydrophilic or hydrophobic substances with controllable rates.