

Structure and phase behavior of synthetic sphingomyelin analogue: 1,2-dimyristamido-1,2-deoxyphosphatidylcholine

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Introduction

Acylamino-phospholipid, 1,2-dimyristamido-1,2-deoxyphosphatidylcholine (DDPC) has two amide bonds, instead of two ester bonds in dimyristoylphosphatidylcholine. The DDPC was synthesized as an analogue of sphingomyelin [1]. Recently, sphingomyelin, one of the most abundant sphingolipids in biological membrane, has been recognized as an important molecule for the formation of functional lipid domains, so-called "lipid rafts". The lipid raft domains are thought to play important roles in many biological processes. Masserini and Ravasi [2] have proposed a hypothesis that an intermolecular hydrogen bond between hydroxyl and amide groups of the ceramide moiety of sphingolipids is one of the main driving forces of lipid raft formation.

The aim of this study is to get basic knowledge on the physical properties that is needed to discuss the function of the lipids having amide bonds in the raft formation. To this end, we investigated the structure and phase behavior of hydrated DDPC bilayers by means of differential scanning calorimetry (DSC) and X-ray diffraction.

Materials and Methods

DDPC was synthesized from a starting material, diaminopropanol. The detailed methods of the synthesis and purification have been reported elsewhere [1]. Simultaneous X-ray diffraction and differential scanning calorimetry (DSC) measurements with synchrotron radiation were performed at the station BL9C of Photon Factory at KEK, Tsukuba, Japan. Normal small angle X-ray diffraction measurements were also performed at the station BL15A.

Results and Discussion

Figure 1 shows a typical data obtained by simultaneous X-ray diffraction and DSC measurements. From these data, we found that hydrated DDPC bilayer samples exhibits a metastable phase behavior. By cooling from a chain-melted state at the rates of greater than 4 °C min⁻¹, hydrated DDPC bilayers form a metastable gel phase. In the gel phase, the hydrophobic chains are tilted with respect to the bilayer normal. By heating, the metastable gel phase is transformed into a stable phase associated with an exothermic heat event at 18.3 °C and then the stable phase is transformed into a liquid-crystalline phase at 25.6 °C. The incubation at 17 °C for more than 1 hour also induces the formation of the stable

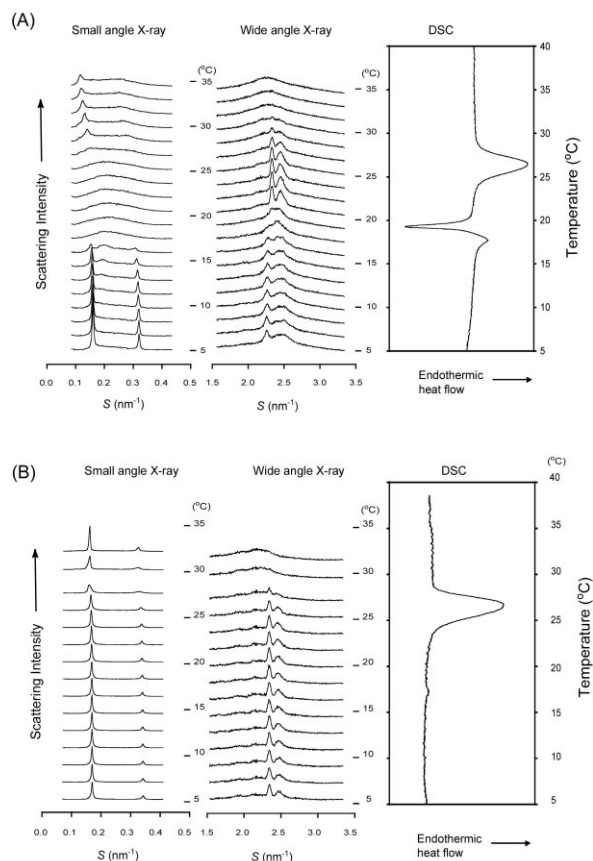


Fig.1 Comparison among small- and wide-angle X-ray diffraction and DSC data obtained simultaneously for hydrated DDPC samples. The scanning rate was 2.0 °C min⁻¹. (A) Heating scan after cooling from 40 °C to 0 °C. (B) Heating scan after cooling from 17 °C to 0 °C following more than 1hr incubation at 17 °C. For the DSC data, the horizontal and vertical axes represent heat flow and temperature, respectively.

phase. The further detail results and discussion are described elsewhere [3].

References

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