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Kinetics of Lyotropic Liquid Crystal Phase Transitions: A Time Resolved X-Ray Diffraction Study†

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Phase transitions in the fully saturated monogalactosyldiacylglycerol in water system have been studied using time resolved x-ray diffraction. Three mechanisms for phase transitions are identified in these studies and can be correlated with the transit times involved in the transformations. The relationship between these observations and previous reports on phospholipid and surfactant phase transitions is discussed.

Keywords: lyotropic phase change, x-ray diffraction, lyotropic kinetics

INTRODUCTION

Time resolved x-ray diffraction has recently been used to examine a variety of phase transitions in lyotropic liquid crystal systems of biological interest.[1–4] In these studies, the extreme brilliance of synchrotron sources for x-rays is exploited to monitor phase transitions in real time. The determination of the transit time and the identification of short-lived metastable states or intermediate states of a

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phase transition are accessible by this technique. The aforementioned studies have examined phase transitions between bilayer phases, or between bilayers and hexagonal arrays of cylinders. We have focussed our attention on describing the phase transitions in the monogalactosyldiacylglycerol/water system.[5-7]

Saturated monogalactosyldiacylglycerol (MGDG) in water has been characterized by a variety of techniques.[8-12] Four phases have been identified: a crystalline bilayer phase (LC_2) which is the eventual stable phase at room temperature; an intermediate crystalline bilayer phase (LC_1); a gel bilayer phase (L_β); and a liquid crystalline phase (alpha). Phase transitions have been inferred between the LC_2, LC_1 or L_β and the alpha phases, between the L_β and LC_1 phases, between the alpha and the L_β phases, and reversibly between the LC_2 and LC_1 phases. Phases and phase transitions can be identified using x-ray diffraction by examining the small angle x-ray scattering characteristic of the mesophase structure (30–150Å), and the wide angle x-ray scattering characteristic of the acyl chain subcell packing (3–6Å). The packing within the mesophase or subcell can be determined by indexing the diffraction lines and comparing these with the expected ratios of the distances for these diffraction lines from the various possible structures.

In this report, we discuss our observations related to the transit times for the various MGDG/water phase transitions, and the mechanisms for the phase transitions. We have observed three types of mechanisms: coexistence of initial and final phases, intermediate phases, and continuous changes in the dimensions of the initial unit cell. These observations are related to previous reports involving the phospholipids phosphatidylcholine[1,3] and phosphatidylethanolamine[4] in water.

MATERIALS AND METHODS

A mixture of fully saturated monogalactosyldiacylglycerol (75% stearoyl (by weight) and 25% palmitoyl residues) was prepared as described previously (5–7). Samples were prepared by mixing the lipid with a five-fold excess (by weight) of distilled water and allowing the mixture to equilibrate at 20°C for over 3 days. The samples were then mounted between mica sheets 1 mm apart in an x-ray sample holder.

The x-ray experiments were carried out at station 7.3 of the Daresbury Synchrotron Laboratory using a Keele flat plate camera and linear detector. The characteristics of the beam and detector have been reported previously.[5-7] The analysis of data was done using the

OTOKO program. Corrections for detector response and the calibration for the scattering angle have been discussed previously. Temperature jumps or scans were produced by water baths connected internally to the sample mount of the x-ray camera. The temperature of the sample was monitored internally using a thermocouple placed adjacent to the sample in the x-ray sample holder.

RESULTS

The various phases for our mixture of fully saturated monogalactosyldiacylglycerol in water have been previously characterized during our examination of the appropriate phase transitions using time resolved x-ray diffraction.[5-7] The high temperature phase in this system is an isotropic array of vesicles[6,7] denoted by I_α. The diffraction patterns obtained as a function of time while the sample was driven by a slow (10°C/min) or fast (~1.5°C/sec) temperature change have also been reported.[5-7] We have observed three mechanisms involved in the MGDG/water phase transitions. The LC_1 to I_α and LC_2 to I_α (slow rate of temperature change) phase transitions occur via a gradual change in the dimensions of the acyl chain or head group subcells.[5,6] In each case, the dimensions of the subcells are gradually broadened due to a disruption in the long range packing order until a single diffraction peak characteristic of an hexagonal packing of the subcell is present. The reversible L_β to I_α, the L_β to LC_1, and the LC_1 to LC_2 phase transitions involve a coexistence of phases over the temperature induced transformations.[6,14] Finally, the LC_2 to I_α phase transition produced with a fast rate of temperature change involves the presence of a variety of intermediate phases.[5]

In Table I, we catalog the available transit times for phase transitions in MGDG/water determined from our time resolved x-ray diffraction studies. The relaxation of the LC_1 to LC_2 phase occurs over the course of days and was not determined from our measurements. The majority of transit times have been determined for temperature jumps of ~1.5°/sec. We, along with other investigators, have noted that lowering the rate of temperature change slows the kinetics of the phase transition. The L_β to LC_1 phase transition was induced isothermally. All the driven phase transformations studied, except the LC_2 to I_α phase transition occur over 2 to 3 seconds. Previous studies on transformations in phospholipid systems (i.e. phosphatidylcholine or phosphatidylethanolamine in water) indicate that the transit times for transitions between bilayer states or between bilayers

TABLE I

Transit times for liquid crystal phase transformations in saturated monogalactosyldiacylglycerol mixtures in water. These times were determined for samples undergoing temperature changes of approximately 1.5°C sec^{-1} except for the isothermal L_β to LC_1 transition at 20°C

Phase transition	Transit time
LC_2 to I_α	20s
LC_1 to I_α	3s
L_β to I_α	2 to 3s
I_α to L_β	2 to 3s
L_β to LC_1	<6s

and cylinders are 1 to 2 seconds or less.[1,2,4] The reported values were limited by the temporal resolution of the experiment. In these studies,[1,2,4] intermediate states were not observed. The LC_2 to I_α phase transition is at least an order of magnitude slower than the other phase transitions studied at equivalent temperature jumps. The appearance of intermediate phases thus causes the transition to require more time for completion. The L_β to LC_1 transition occurred isothermally[14] while the temporal resolution of our experiment was 6 seconds. The transition was observed between recorded frames and thus occurred in 6 seconds or less.

CONCLUSIONS

We have catalogued our observations of changes in the diffraction pattern for lyotropic liquid crystal systems undergoing phase transitions driven by fast rates of temperature change to three mechanisms. Transitions such as the isothermal LC_1 to LC_2 which is the slow hysteretic transition in this system usually require days for completion and evolve by the final phase nucleating and growing in the initial phase. Slow rates of temperature change influence the transit time required for the completion of a phase transition. The LC_2 to I_α phase transition, when driven by a slow rate of change of temperature, evolves by the gradual change in the acyl chain unit cell. This transition also has a long transit time (on the order of minutes) inherent to the process of slowly changing the temperature. Perdeuterated potassium palmitate in D_2O also undergoes bilayer transitions using a temperature scan of 10°/min involving a disordering of a unit cell over the course of minutes.[14]

Samples of MGDG in water driven by fast rates of temperature change have been shown[5–7] to produce phase transitions involving three general processes. Transitions with transit times of 1 to 2 seconds occur either by the nucleation and growth of the final phase in the initial phase (i.e. L_β to I_α, I_α to L_β, and perhaps L_β to LC_1) or by the gradual disordering of the initial phase's two dimensional unit cell (LC_1 to I_α). These transit times are in the range of those which occur when phospholipids undergo thermotropic phase transitions involving a change in mesophase structure[4] or acyl chain packing.[1,3] Phase transitions can also occur via the formation of intermediate phases. In our system, the LC_2 to I_α transition proceeds by this mechanism over a transit time of 20 seconds. The appearance of intermediate phases increases the time required for the transition to go to completion by an order of magnitude. These observations may eventually be related to the actual order of the transition when a more detailed analysis of the structures involved in the transitions can be made.

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