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New Phase Formation of Dimyristoylphosphatidylglycerol Bilayer-Assembly with Sodium or Ammonium Ions: Gelation Phenomena in the Lamellar Liquid Crystals Aged in Water

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The thermal properties of lamellar phases of dimyristoylphosphatidylglycerol (DMPG) bilayer-assemblies with counter ions of Na+ and NH4+ are remarkably different. However, these lamellar phases of NaDMPG and NH4DMPG in water have been found to undergo a new gelation in common when they are aged for a couple of weeks below 40 °C. The new gel phases named Gel-2 reversibly change to the corresponding liquid crystal phases (LC-2) at transition temperatures (T*) of 40 ºC for NaDMPG and 44 ºC for NH4DMPG, respectively.

Figure 1. DSC charts for NaDMPG (a) and NH4DMPG (b) dispersions incubated overnight at various temperatures.

However, when NH4DMPG dispersions were aged for a long period at respective temperatures, the peaks at Tm shifted toward higher temperatures with time, and finally reached 44.0 ºC (the Tl temperature of NH4DMPG). These results are summarized in Figure 2. The dotted lines are charts for the dispersions incubated overnight, and the solid lines are those for the dispersions in equilibrium after about two-week aging. The small peak at 53 ºC in the bottom curve may be identified with myristic acid produced by the hydrolysis of NH4DMPG after further aging (15 days at 40 ºC).

Figure 2. DSC charts for NH4DMPG dispersions. Dotted lines: incubated overnight, solid lines: equilibrium (Gel-2).

In order to compare the thermal properties of NaDMPG and NH4DMPG dispersions, DSC measurements were made for these dispersions incubated overnight at various temperatures as shown in Figures 1a and 1b. The DSC charts for NaDMPG obviously depend on the incubation temperatures. Namely an endothermic peak was observed at the T* temperature (31.7 ºC) for the dispersions incubated below T*, while no peak was observed for the dispersions incubated above T*. In this regard, we have thought that NaDMPG bilayers take a nematic liquid crystal state above T* (31.7 ºC)2. In the case of NH4DMPG, the charts did not exhibit endothermic peak at T* at any incubation temperatures, though the gel (Gel-1) – liquid crystal (LC-1) transition at 23.5 ºC (Tm) was observed. These aspects for NH4DMPG are similar to DMPC. Thus, the results in Figures 1a and 1b indicate that a difference in counter ions of DMPG bilayers brings about obviously different thermal properties.
Figure 3 shows XRD patterns for the lamellar phases of NH4DMPG incubated overnight at respective temperatures (dotted lines) and the patterns for resulting Gel-2 phases (solid lines). These data indicate two features: (1) the bilayer distances of Gel-1 (15 °C) and LC-1 (25 °C, 40 °C) are almost the same as corresponding Gel-2 (d = 5.33 ± 0.03 nm); (2) the d values do not vary with temperature, in contrast to NaDMPG2 or DMPC.7 Thus, we suppose that the bilayer distances observed for the NH4DMPG dispersions are almost constant.

![Figure 3. XRD patterns for NH4DMPG dispersions. Dotted lines: incubated overnight, solid lines: equilibrium (Gel-2).](image)

As for NaDMPG dispersion, we have reported on a similar gelation phenomenon at 40 °C,7 and on the properties of Gel-2 phase as an emulsifier.9 Thus, thermal characters of NaDMPG dispersion below 40 °C were further investigated. Figure 4 shows the time dependence of DSC charts for the dispersions incubated at 15 °C and 25 °C, together with the previous data at 40 °C.7 While, at the initial stage of aging, the peak at T* (31.7 °C) was observed for the dispersion incubated at 15 °C or 25 °C, after a couple of days, the peak at T* diminished gradually. Concurrently, a small peak emerged at lower temperature, grew, shifted to higher temperatures, and finally converged at 40 °C after about 2-week aging. These results indicate that NaDMPG dispersions incubated at 15 °C, 25 °C, and 40 °C are all transformed isothermally with time into a new gel phase (Gel-2), the T* temperature of which is 40 °C.

![Figure 4. DSC charts for NaDMPG dispersions. Dotted lines: incubated overnight, solid lines: equilibrium (Gel-2).](image)

Table 1 summarizes the transition temperatures for NaDMPG and NH4DMPG bilayer-assemblies, together with their zeta-potential at various states. Remarkably different characters between NaDMPG and NH4DMPG bilayers described above may be explained in terms of the zeta-potential that primarily reflects the degree of counter ion dissociation from DMPG bilayers. For example, the incredibly large zeta-potentials for NaDMPG bilayers at 40 °C shown in Table 1 seem to cause so much disturbance in bilayer arrangement that no peak could be detected in XRD measurement at 40 °C,7 while we could observe XRD peak for NH4DMPG bilayers, regardless the incubation temperatures and aging times (Figure 3).

The molecular mechanism for gelation of both Gel-2 phases of Na+ and NH4+ salts may be explained in terms of changes in conformation of the terminal glycerol moiety of DMPG molecules. The hydrogen bonds in or between terminal glycerol groups are more stabilized by taking an extended structure induced by hydration of solvent water. As a result of enhanced lateral interactions between hydrocarbon chains, the lamellar phase of DMPG bilayers would start to change into Gel-2 phase so long as the incubation temperature is below T*, DMPG bilayers that had reached Gel-2 state will be reversibly transformed into a new liquid crystal state (LC-2) at T*.

In conclusion, we have the following results: (1) The thermal properties of NH4+ and Na+ salts of DMPG bilayer-assembly after overnight aging are remarkably different. (2) The Tm temperature of bilayer-assemblies that is independent of counter ions increases with aging time up to the T* temperature indicating the formation of a new gel phase (Gel-2). (3) The gelation from lamellar LC states is caused by change in hydration of the terminal glycerol moiety in each molecule followed by entire rearrangement of the bilayer-assembly. (4) The transitions of Gel-2 to LC-2 at the T* temperatures are reproducible for two weeks, and then myristic acid was observed as a result of hydrolysis of DMPG molecules.

Table 1. Thermal properties for DMPG bilayer-assemblies.

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<th>Counter ions</th>
<th>Transition temperature/°C</th>
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<tr>
<td>Na+</td>
<td>Tm</td>
<td>T*</td>
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<tr>
<td>NH4+</td>
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References