

Supplementary Material

A Facile Synthesis of Discoidal Lipid Bilayer Nanostructure by Association of a Cationic Amphiphilic Polyelectrolyte

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Received March 5, 2012, Accepted March 28, 2012

Further Discussion on the Structure of the Lipid Bilayers Made with the Anionic and Cationic Amphiphilic Polyelectrolytes. For the bilayer nanostructures made with poly(methacrylic acid-co-SA), the microcalorimetry studies (Figure 4(b)) showed that the two types of the gel to fluid transition temperatures of liposomes co-existed: the one at 50 °C is due to the pure lipid bilayer and the other at 45 °C is likely due to the lipid bilayers associated with poly(methacrylic acid-co-SA). With increasing the concentration of the polymer, the fraction of pure lipid was rapidly decreased whereas the fraction of the bilayers associated with the polymer was increased. At 30 wt % of poly(methacrylic acid-co-SA), all the lipid bilayers were associated with the polymer. The conclusion above was based on the followings. The hydrodynamic sizes of the nanostructures, measured from the photocorrelation spectroscopy (PCS; Malvern Instruments 3000HS), were more or less the similar (105–120 nm). In addition, they were all vesicular forms (Figure 4(a)) regardless of polymer concentration. As such, it is possible to exclude the possibilities that the change in the thermograms of the lipid bilayer nanostructures was due to the size or shape of the bilayers.

It is worth comparing the thermogram at 10 wt % of the anionic amphiphilic polyelectrolyte (Figure 4(a)) with that at 8.5 wt % of the cationic amphiphilic polyelectrolyte (Figure 3(a)). For the anionic amphiphilic polyelectrolyte, the intensity of the new peak, due to the association of the polymer with the bilayer, was clearly developed and separated from the peak of pure bilayer. Meanwhile, for the bilayer nanostructures with the cationic amphiphilic polyelectrolyte, a new peak around 43–45 °C was developed, too. However, the new peak was shown as a shoulder and it was not clearly separated from the peak of pure lipid bilayer. As a result, the peak became broader with the concentration. The broadening of the peak might indicate that there existed various lipid bilayers differently associated with the cationic amphiphilic

polyelectrolyte. In addition, the way of association of the lipid bilayers with the cationic amphiphilic polyelectrolyte was different from the way with the anionic amphiphilic polyelectrolyte. It is thought that the development of the new peak should be clear as in the case of the anionic amphiphilic polyelectrolyte if the stearyl group in the cationic polymer was uniform and well associated with the lipid bilayer. However, the current results suggest that the association of the stearyl group in the cationic amphiphilic polyelectrolyte with the lipid components be poorer than the case with the anionic polymer.

For the nanostructures with the anionic amphiphilic polyelectrolyte, the anisotropy ratio was decreased with concentration of the polymers, thereby increasing the mobilities of the bilayers with the concentration of polymer. This was quite contrasted with the mobility of the nanostructures with the cationic amphiphilic polyelectrolyte. The anisotropy ratio of the lipid bilayers was decreased from 0.375 to 0.360 at 5 wt % and to 0.357 at 10 wt % of the anionic amphiphilic polyelectrolyte. In contrast, at 8.5 wt % of the cationic amphiphilic polyelectrolyte, there was essentially no change in the anisotropy ratio of the bilayers. From this result, it is speculated that the addition of the cationic amphiphilic polyelectrolyte did not affect the mobilities of the bilayer nanostructures, probably due to the poor association of the stearyl group with the lipid bilayers.

The surfaces charges of the bilayers with the anionic amphiphilic polyelectrolyte became negative and the negative charges were increased with the concentration of the polymer. However, the rate of increase in the surface charge was not as high as in the case of the lipid nanostructures with the cationic amphiphilic polyelectrolyte (see Figure 3(b)). More importantly, at 8.5 wt % of the cationic amphiphilic polyelectrolyte, the surface charges were fairly high, indicating that the cationic polymer mostly covers the surface of the lipid bilayers even at low concentration.