Thermal isomerization process in benzene gels of l-glutamic acid-derived lipids with spiropyran head groups

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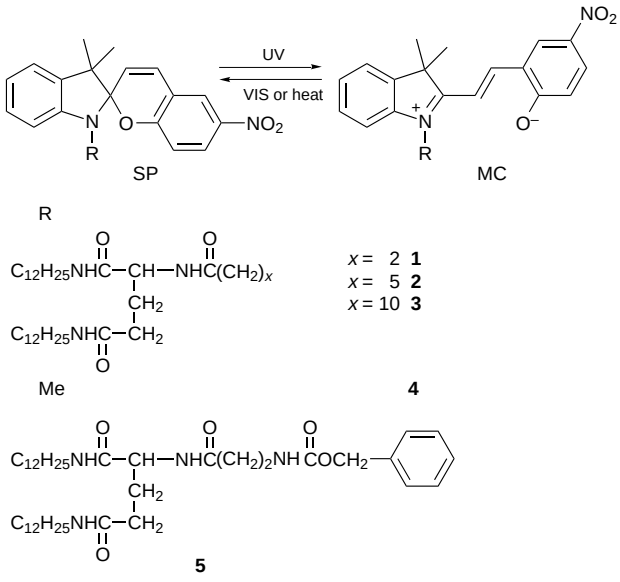
First-order kinetic behaviour during the thermal isomerization process of lipids with photochromic spiropyran head groups in benzene strongly depends on the dispersion state of the lipids and this enables the determination of their critical aggregation concentrations.

In recent years, organic gels arising from the formation of highly organized lipid assemblies in organic media have been attracting wide attention.[1–4] It is necessary to evaluate the critical gelling concentration (c.g.c.), at which the solution begins to form gels, as a measure of the stability of the aggregates of self-assembling lipids. In general, gelation has been considered successful if the cooled solution forms a nearly transparent mass that can be inverted without apparent flow.[4] However, this method is not applicable to fluid solutions containing fragmentary gels. On the other hand, the critical aggregation concentration (c.a.c.), at which lipids begin to aggregate, is believed to be almost identical to the c.g.c. However, this has not been verified because of the difficulty in direct evaluation of the c.a.c. in organic solutions (gels) by using conventional evaluation methods for aqueous solutions.† Therefore, an establishment of a direct evaluation method of c.a.c. in organic systems is very important.

On the other hand, it is well known that spiropyran (SP) shows reversible photochromism. Upon UV irradiation, a colourless and non-ionic SP is converted to a coloured and zwitterionic merocyanine (MC). This MC is reconverted to the SP thermally or upon exposure to visible light. We have previously reported that an l-glutamic acid-derived lipid **5** and related lipids with three amide bonds form organic gels through fibrous aggregates composed of a lipid membrane-like highly oriented structure.[1] Our present attention is focused on the application of photochromic behaviour of highly oriented aggregates of the SP-containing lipids **1**–**3** in organic media. Here, we propose an evaluation method for the c.a.c. of the l-glutamic acid-derived lipids with SP head groups, using MC–SP thermal isomerization (decolouration) behaviour in organic media.

SP-containing lipids **1**–**3** form transparent organic gels in benzene at concentrations of 2.0×10^{-2} m. Differential scanning calorimetry (DSC) measurements of these gels (heating rate, 2 °C min^{-1}; temperature range, 5–100 °C) revealed that these lipids **1**–**3** showed sharp and single endothermic peaks‡ due to a gel-to-sol transition in the heating process in benzene, indicating that these SP-containing lipids self assemble into highly oriented structures in the gel state. Scanning electron micrographs of the cast film of **2** from a benzene solution revealed that the gel was composed of a network structure of fibrous aggregates with diameters of 300–2000 Å, close to those of aggregates of lipid **5** in benzene.[1]

SP-containing lipids **1**–**3** dissolved in benzene at 70 °C were gradually cooled to 20 °C to form gels. When the gels were exposed to UV light for 5 min at room temp. using a high-pressure mercury lamp in conjunction with a Toshiba UV-D35 colour filter ($330 < \lambda < 380$ nm), visible absorption spectral changes due to SP–MC conversion were observed. Fig. 1 shows a typical decolouration process of the UV-exposed lipid **2** in the benzene gel. Similar decolourations were observed in the gels of lipids **1** and **3**. The absorption maxima (λ_{max} in benzene) of the



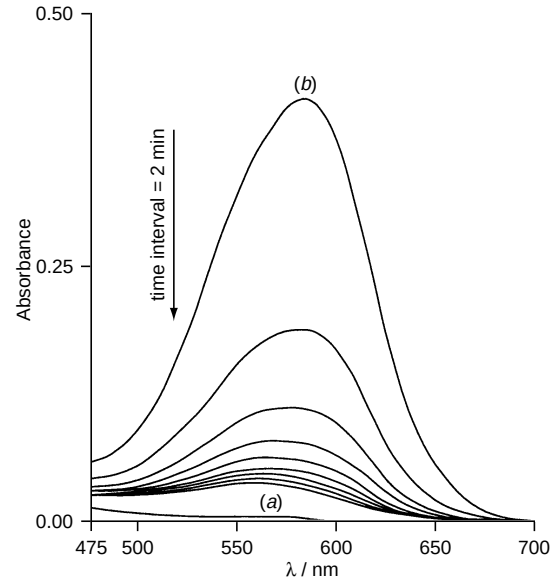


Fig. 1 Visible absorption spectra of UV-irradiated **2** in benzene. [lipid] = 2×10^{-2} m, 20 °C, path length of quartz cell 0.1 mm. (*a*) Before UV-irradiation; (*b*) measured immediately after UV irradiation for 5 min.

resulting MC species depended on the chemical structure of the *N*-substituents (R): 595, 585 and 571 nm for **1**, **2** and **3** respectively. The MC–SP thermal isomerizations were evaluated by first-order kinetic analyses. The plots of the MC–SP conversion process of lipids **1**– **3** in the gel states (2.0×10^{-2} m in benzene) did not obey simple first-order kinetics, whereas good linearities were obtained in the solution state (1.0×10^{-3} m in benzene). Similar deviations from linearity are, in general, observed in many other systems.[5] The first-order rate constants (k_1)§ for the MC–SP thermal isomerization for lipids **1**–**3** in benzene were calculated from the slope of these plots and are plotted against lipid concentrations as shown in Fig. 2. The k_1 values were remarkably dependent on the lipid concentrations. The critical concentrations shown by the dotted lines in Fig. 2 correspond closely to the critical gelling concentration (c.g.c.) determined by the inversion method.[4] Similar phenomena were observed in toluene. On the other hand, the thermal isomerization rate of the non-gelling SP **4** in benzene was slightly accelerated by increasing the concentration as shown in Fig. 2 and obeyed simple first-order kinetics. This difference can be explained by the fact that lipids **1**–**3** show lipid membrane-like highly oriented aggregation and SP **4** is in a molecularly dispersed state.¶ Fig. 1 shows the hypsochromic λ_{max} shift from 585 to 560 nm at the later stage of the decolouration process. This species at 560 nm is ascribable to the H-like aggregates[7] of MC species with head-to-head stacking. These results indicate that the thermal MC–SP isomerization behaviour of the SP-containing lipids is sensitive to the aggregation of the lipid molecules. Therefore, it is concluded that the critical concentrations in Fig. 2 correspond to the c.a.c. of lipids **1**–**3**, respectively. This finding enabled us to detect the c.a.c. directly using first-order kinetics of thermal isomerization instead of *via* an indirect method through evaluation of the c.g.c. by conventional gelation tests, *e.g*. the inversion method.[4] Values of the c.a.c. determined from Fig. 2 were 3×10^{-3}, 2×10^{-3} and 1×10^{-2} m for **1**, **2** and **3** respectively. By comparison the corresponding c.g.c. values determined by the inversion method were 4×10^{-3}, 2×10^{-3} and 1×10^{-2} m.

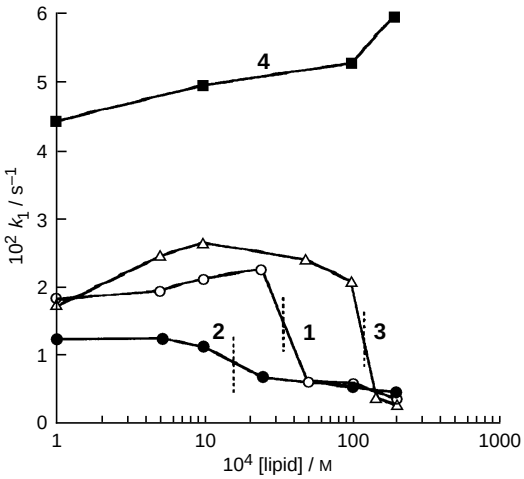


Fig. 2 Concentration dependence of first-order rate constant (k_1) for MC–SP thermal isomerization of lipids **1**–**3** in benzene. 20 °C. Dotted lines indicate the c.a.c. values determined by this method. The error limits of k_1 values are within ±10%.‖

In conclusion, we have established a direct method to determine the critical aggregation concentration of organic gels by using first-order kinetic analyses for the thermal MC–SP isomerization process of the component lipids with SP head groups. This finding will also help in clarification of the detailed aggregate structures of a series of organic gel-forming lipids.[1]

Footnotes

† Surface tension, conductivity, fluorescence (using a fluorescent dye as a microenvironmental probe) and visible absorption spectral measurements (using a solvatochromic dye as a microenvironmental probe), *etc*. are used for the evaluation of c.a.c. in aqueous solution.

‡ Peak-top temperatures: 36 °C for **1**; 39 °C for **2**; 28 °C for **3** in benzene.

§ In the case of deviation from linearity, *e.g*. at 2×10^{-2} m in benzene, k_1 values were calculated from the first two points and are plotted in Fig. 2.

¶ It has been reported that the thermal MC–SP isomerization is suppressed by aggregation of MC species.[6] Therefore, the retardation of the thermal isomerization rates of **1**–**3** and deviation of their first-order plots from linearity are ascribed to the existence of aggregated MC species.

‖ However, the error limits are much less than the change of k_1 values at the critical concentrations; therefore, the c.a.c. is not affected by the error of the of k_1 values and the method is safely applied to the determination of c.a.c. (c.g.c.) of the lipids.

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Received, 17th September 1996; Com. 6/06386A