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Thermal Isomerization Rate of a Long Chain Spiropyran in Bilayer Matrix. Dependence of Aggregate Dimension of Bilayer Formed by Dioctadecyldimethylammonium Bromide

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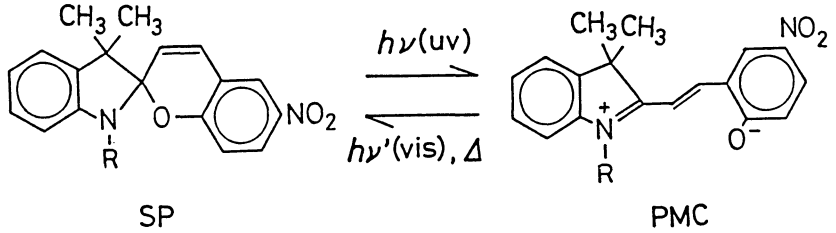
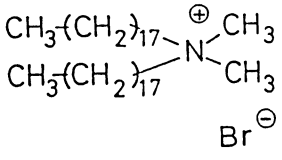
The thermal isomerization rate from UV-induced merocyanine to spiropyran is observed in an ammonium bilayer membrane of varied aggregate dimension. In smaller bilayer aggregates, the reaction rate is retarded due to increase of polarity around the chromophore possibly as the result of larger penetration of water molecules into the bilayer matrix having the greater membrane curvature.

We have recently reported photochromic behaviors of spiropyrans in dioctadecyldimethylammonium ($2C_{18}N^+2C_1$) bilayer membrane.[1,2] In this bilayer matrix, a distinct discrepancy is observed in the kinetics of thermal decoloration observed with two spiropyrans. The thermal decoloration (from photomerocyanine (**PMC**) to spiropyran (**SP**), the scheme is shown below) of a compound (1) in the bilayer obeyed the first order, but that of a long chain compound (2) showed deviation from the monoexponential nature. In the meantime we have found that the reaction rate is largely dependent on the sonication time in the preparation of bilayer suspension which varies the dimension of bilayer aggregates. The present paper describes the correlation between the thermal decay rate of PMC and dimension of the bilayer aggregates (possibly vesicles[3-5]), and indicates that the distribution of aggregate size is in large part responsible for the heterogeneity of the thermal decoloration of 2.





$2C_{18}N^+2C_1$

R = $-CH_3$ 1
= $-(CH_2)_{17}-CH_3$ 2

Bilayer solutions were prepared in a standard sonication method. $2C_{18}N^+2C_1$ bilayer containing a spiropyran compound (the mixing molar ratio to the amphiphile, R = 0.005) was sonicated with a probe-type disrupter (Tomy Seiko UR-200P) at 45 - 50 °C, above T_c of $2C_{18}N^+2C_1$ bilayer, in distilled water as described earlier,[2] the sonication time being varied from time 0 to 60 min. The concentration of dispersed $2C_{18}N^+2C_1$ was 5 x 10^{-3} mol dm^{-3}. Hydrodynamic diameters were determined by the dynamic light scattering (DLS) measurements using a laser particle analyzer LPS3000/3100 (Otuka Electric. Co.). With this instrument, photon correlation functions of scattered He-Ne laser light (633 nm) were determined. An 1-cm square cell was used to observe 90° scattering. The photon correlation functions were accumulated 100 times for final analyses. The bilayer solutions were passed through 0.4 μm milipore filter before DLS measurements. In this procedure dispersed metal particles of the probe tip on the sonicater did not interfere the measurements. Filtered samples were incubate at 20 °C for 10 min, and diluted with ca. 10-folds amount of distilled water for DLS measurements. The experimental procedure of kinetic measurements has been described previously.[2] Determination of aggregate dimensions and kinetic measurements[2] were carried out at 30 °C.

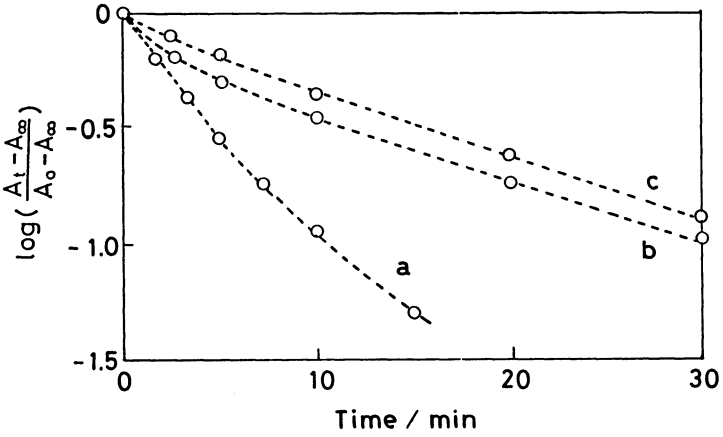


Fig. 1. First-order plots of PMC→SP decoloration of 2 in $2C_{18}N^+2C_1$ bilayer at 30 °C for samples prepared with 0 min (a), 2 min (b), and 30 min (c) sonication.

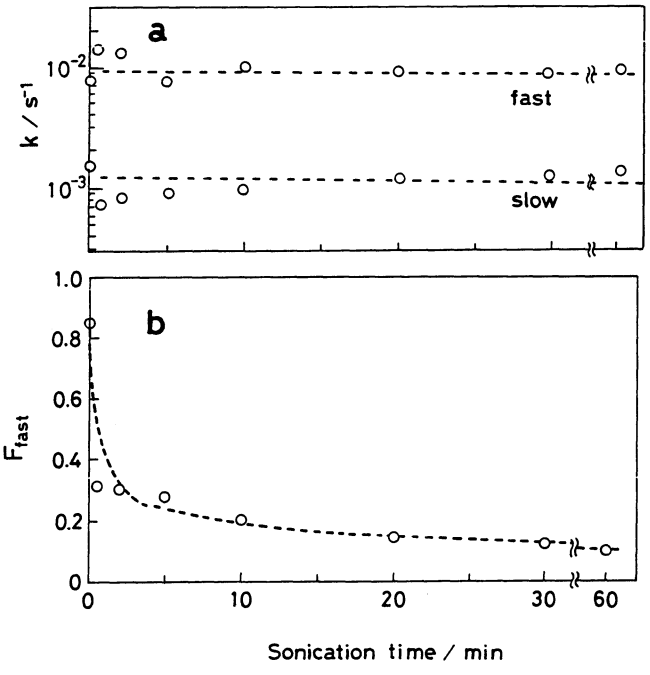


Fig. 2. Changes in k_{fast} and k_{slow} (a), and F (b) analyzed by Eq. (1) using 2 at 30 °C during the course of sonication.

Figure 1 shows the first-order plots of the decoloration reaction observed at varied sonication time. Before sonication the rate was relatively high approximately obeying the first order kinetics up to 80% conversion. Upon short time sonication deviation from the linearity became obvious as has been previously reported.[1,2] After prolonged sonication PMC decayed almost monoexponentially again, in this case, with a slower rate. The kinetics was analyzed with an assumption of two simultaneous exponential decays according to the

following equation,

$$(A_t - A_\infty)/(A_o - A_\infty) = F \exp(-k_{fast}\, t) + (1 - F) \exp(-k_{slow}\, t) \qquad (1),$$

where A_t, A_o, and A_∞ are absorbances at λ_{max} at time t, zero, and infinite time, respectively, k_{fast} and k_{slow} are the first-order rate constants ($k_{fast} > k_{slow}$), and F is the fraction of k_{fast} component. k_{fast} and k_{slow} were almost constant irrespective of sonication time, ranging around 1 x 10^{-2} s^{-1} and 1 x 10^{-3} s^{-1}, respectively (Fig. 2a). Instead the apparent kinetic change regarding to sonication time was mainly due to the change of parameter F in the above equation (Fig. 2b), namely, the sonication increased the fraction of slowly decaying process.

The mean hydrodynamic diameters (D/nm) of $2C_{18}N^+2C_1$ aggregate obtained in Cumulant calculation[6] as a function of sonication time is indicated in Fig. 3. As clearly shown, the sonication procedure decreased the particle size which agrees with the obserbation of electron microscopy.[5] A sample prepared only with stirring above T_c without sonication gave the aggregate dimension in the range of micrometers. Upon sonication D decreased abruptly and fell into a constant value of approximately 100 nm after 10 min. Further sonication did not noticeably reduce D. In the figure are also shown data obtained by Herrmann and Fendler[7] (x) which are in good agreement with our results. This profile has a good correlation with the change of F in the kinetic analyses.

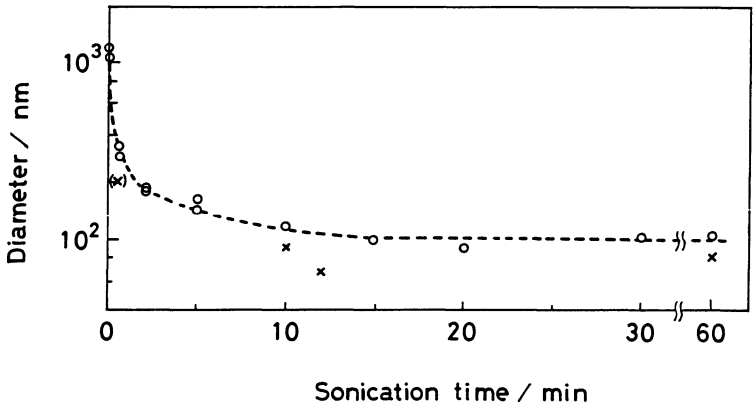


Fig. 3. Mean hydrodynamic diameter of $2C_{18}N^+2C_1$ bilayer aggregate at 30 °C obtained by DLS measurements as a function of sonication time. (x) are the data reported by Herrmann and Fendler.[7]

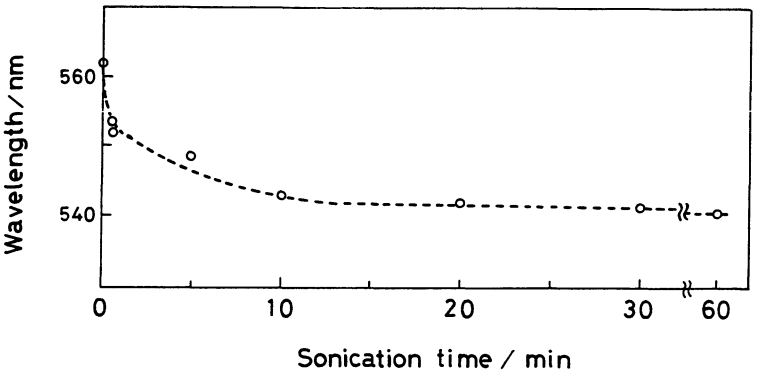


Fig. 4. Visible absorption maximum of PMC of 2 at 30 °C as a function of sonication time.

Visible absorption maximum of PMC of 2 is plotted as a function of the sonication time, in Fig. 4. Sonication led to a hypsochromic shift of the absorption maximum (λ_{max}). The shape of this profile agrees also well with those for F and the aggregate dimension. Before sonication λ_{max} positioned at 565 nm and after prolonged sonication (30 min) it shifted to 540 nm.

This shift can be regarded as the consequence of increased micropolarity surrounding PMC in the bilayer.[8] In contrast, when 1 was employed, λ_{max} stayed at 522 nm without spectral shift during the course of sonication, indicating that PMC of 1 is located at highly polar sites, likely near the head group region of the bilayer, irrespective of the aggregate size. In the case of 2, on the other hand, PMC is located in less polar environments that are susceptible to the morphology of the bilayer aggregate.

From these observations one can reasonably understand the kinetic change influenced by the bilayer aggregate size as follows. Smaller bilayer vesicles have the greater membrane curvature and are likely to have more open or disordered sites in the bilayer structure than larger aggregates (schematic illustration is shown in Fig. 5). This could lead to larger penetration of water molecules into the solubilized site of PMC and increase the micropolarity, which brings about the blue shift in the PMC spectrum and retardation of the thermal decoloration rate.[2,9] It should be noted that these results do not necessarily give direct information on the polarity of the pure bilayer matrix because bulky and rather polar PMC could induce large disorder of the bilayer structure and may drag water into the matrix. Uznański and Kryszewski[10] have reported homogeneous nature of this thermal process using other spiropyran compounds in dimiristoylphosphatidylcholine bilayer membrane. The inconsistency may arise both from difference in the process of sample preparation and characteristics of the bilayer formed by each amphiphiles.

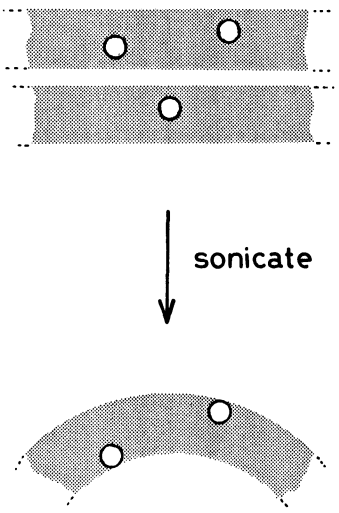


Fig. 5. Schematic illustration of the morphological change of bilayer aggregates by sonication.

References

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