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Properties of lipid bilayer membranes examined with time-resolved fluorescence and Raman spectroscopies

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Abstract

Biomembranes host a large number of chemical reactions that are vital for biological activities. It is therefore important to examine the mechanism of biochemical reactions that proceed at the biomembranes. The biomembranes are formed by lipid bilayer membranes of phospholipids, having two saturated or unsaturated hydrocarbon chains with typically 12 to 18 carbons in each chain. Membrane proteins, often acting as enzymes, and cholesterol are major constituents of the biomembranes as well. We study artificial lipid bilayer membranes as simple and good model structures for biomembranes by characterizing their properties with spectroscopic experiments. The lipid bilayer membranes for this purpose are a thin layer of bilayers with a thickness of 5 nm. The thin sheet of oil assembled in water is not commonly used as a reaction medium for chemical syntheses. It should act differently from ordinary solvents when it hosts chemical reactions. We try to estimate the viscosity, polarity and thermal diffusivity, which usually characterize the properties of bulk solvents, of the lipid bilayer membranes with time-resolved fluorescence and time-resolved Raman spectroscopies.

When *trans*-stilbene is photoexcited to the first excited singlet (S_1) state, it changes the configuration to the perpendicular form in the S_1 state. The rate constant of this photochemical reaction is well correlated with the viscosity of the solvent. We embed the *trans*-stilbene molecule in the non-polar portion of the liposome bilayer membranes and determine the rate constant of the photoisomerization reaction by measuring the fluorescence lifetime of *trans*-stilbene. The liposome lipid bilayer membranes are formed by a single phospholipid of DLPC, DMPC, DPPC, DSPC, or DOPC. The diameter of the liposome is changed from 50 and 1000 nm. Three-component membranes formed by various mixtures of DPPC, DOPC, and cholesterol are also prepared for the spectroscopic experiments. *Trans*-stilbene embedded in the liposome lipid bilayers is photoexcited at 300 nm. The fluorescence from the sample is analyzed by a spectrograph and is detected by a streak camera.

The result from the time-resolved fluorescence spectroscopy reveals that there are at least two environments present in the liposome lipid bilayer membranes with viscosities different by 30 to 290 times. The heterogeneity is recorded not only for the three-component membranes but also for single-component membranes. Presence of nanodomains along the lateral direction is strongly suggested from the time-resolved fluorescence measurements of stilbene derivatives.

We have constructed a time-resolved Raman spectrometer by using a new picosecond light source with improved power stability. Results of picosecond time-resolved Raman spectroscopy on lipid bilayer membranes will also be reported in the presentation.

Keywords: lipid bilayer membranes, lipid raft, time-resolved fluorescence, time-resolved Raman

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