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Dielectric study on restricted molecules of liquid crystal and liposome

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We performed dielectric relaxation measurements for 5CB/benzene mixtures in the frozen state at frequencies from 40Hz to 10GHz and for liposome/water dispersion systems at frequencies from 300MHz to 20GHz. When 5CB/benzene mixtures take Nematic (N) phase from Isotropic (Iso) phase with increasing concentration, the relaxation time distribution parameter, β, becomes smaller. On the other hand, gel – liquid crystal (LC) phase transition for liposome/water system is characterized by a change in the parameter β . The β value in the LC phase is smaller than that in the gel phase. It is considered that the larger fluctuation of water molecules is realized by interaction between water and lipid molecules in the LC phase with higher mobility. Therefore, dynamical behaviors of LC and liposome in the LC phase are reflected by smaller β values with respective molecular mechanisms.
Key words: liquid crystal, liposome, dielectric relaxation

1. INTRODUCTION

The liposome is researched as a typical biomembrane model formed with phospholipids. It is well known that the structure and phase transition of liposome have been investigated by various measuring systems viz. NMR, X-ray diffraction and dielectric measurements [1-4]. We already reported TDR (Time Domain Reflectometry) studies on human erythrocyte ghost and total lipid membranes to clarify how water behaves on the biomembranes [3, 4]. Lipid molecules of biomebranes interacting with water molecules can control the transport phenomena and protein functions with the anisotropic flow ability. Though dynamics of molecules restricted in those alignments have also been investigated for liquid crystals (LCs), the anisotropic behaviors of intermolecular interactions have not been enough analyzed yet. TDR is very useful to observe complex permittivity in the frequency range from 1MHz to 10GHz and to clarify changing water structure around the lipid membranes. Additionally, these observations of dynamics of lipid molecules and water structures are effective to understand real biomembranes and can be applied to Drug Delivery System (DDS).

The LC molecule has a rod or disc shape and makes particular alignments in the liquid crystal phase, which has a character of flowable like liquids and form birefringence like crystals. Due to those characters, the LC phase and the optical anisotropy occur. Molecular interactions in LCs are researched from both sides of theory and experiment [7-11]. In this study, we report TDR measurements on cyanobiphenyl LCs in solvent benzene on widely concentration range and consider the molecular interaction from relaxation parameters, and inspect relationship of the dynamics and the phase transition. The intermolecular interaction working between polar molecules becomes weak when benzene is dissolved in the polar molecules, and the interaction can be controlled by the concentration. Thus this work for solutions is also effective to study restricted systems.

2. EXPERIMENTAL

2.1 5CB/benzene mixture

4'-pentyl-4-biphenylcarbonitrile (5CB, molecular weight M_w=249) and benzene were purchased from SIGMA-ALDRICH JAPAN and WAKO Pure Chemical Industries, Ltd., respectively. 5CB is LC that takes only a Nematic (N) phase between 22.4°C and 34.7°C. Dielectric measurements of 5CB/benzene mixtures were performed by TDR system (HEWLET PACKARD, HP54124A) and Impedance Analyzer (IA, Agilent technology, 4294A) in a frequency range of 40Hz to 10GHz and in a temperature range from -25°C to 40°C.

2.2 Liposome/water dispersion

1,2-dipalmitoyl-sn-glycero-3-phosphacholine (DPPC, molecular weight M_w=734) was purchased from SYGENA. Liposome/water dispersions are made from DPPC powder and distilled and de-ionized water prepared by Milli-Q-Lab (Millipore). 10ml of pure water about (70°C) was put in 0.30g DPPC powder, and the mixture was shaken by a vortex mixer at 70°C for one hour as the first dispersion. The dispersion was passed through polycarbonate membrane filters of Extruder (Nichiyu Liposome Co. Ltd.) three times by high-pressure N_2 gas, after the dispersion was kept at 70°C for one hour. The pore size of the filter used was 0.4μm for the first filtration and 0.05μm for the second and third filtrations, as the liposome vesicle size is adjusted less than 0.05μm. Gel-LC phase transition was observed at around 41.0°C for DPPC-liposome/water dispersion systems. TDR system having a frequency range of 300MHz - 20GHz, was used to investigate the dielectric relaxation and the gel-LC phase transition of DPPC-liposome/water dispersion system in the temperature range of 25°C-50°C.

3. RESULTS AND DISCUSSION

3.1 5CB/benzene mixtures

Figure 1 shows the dielectric dispersion and absorption spectra for 5CB/benzene mixtures with different concentrations at fixed temperature of 25°C. The relaxation peak frequency shifts towards the lower frequency side with increasing concentration. Two dielectric relaxation processes due to molecular rotations around major and minor axes are expressed by the Cole-Cole relaxation functions [12] and DC conductivity as

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_{min}}{1+(j\omega\tau_{min})^{\beta_{min}}} + \frac{\Delta\varepsilon_{maj}}{1+(j\omega\tau_{maj})^{\beta_{maj}}} + \frac{\sigma}{j\varepsilon_0\omega}, \quad (1)$$

where $\Delta\varepsilon$ is the relaxation strength, τ is the relaxation time, β is the relaxation-time distribution parameter ($0 < \beta \leq 1$), ω is the angular frequency, j is the imaginary unit, ε_∞ is the high frequency limit of the dielectric constant, ε_0 is the dielectric constant of vacuum, σ is the electric conductivity, and subscripts, *min* and *maj*, indicate relaxation processes due to the rotation of 5CB molecular around minor and major axes, respectively. Figure 2 shows the two processes in a typical fitting result for a 5CB/benzene mixture. Figure 3 shows the concentration dependences of the relaxation strength $\Delta\varepsilon$, the logarithm of relaxation time, τ, and the shape parameter, β, thus obtained for 5CB/benzene mixtures at 25°C. $\Delta\varepsilon_{min}$ is larger than $\Delta\varepsilon_{maj}$, and τ_{min} is slower than τ_{maj}. These reasons are that, when the total dipole moment of 5CB molecule is divided into the minor axis and the major axis components, i.e., a rod like shape is assumed for a molecule, the dipole moment of major axis component is larger than the minor axis. The dynamics around the minor axis need larger space in comparison with those around major axis one. It is considered that the molecular interaction is separated into 3 stages of the concentration in Fig.3. The first stage in the concentration range, 0wt% < c ≤ 80wt%5CB (① in Fig.3), exhibits Iso phase. In this range, $\Delta\varepsilon$, increases monotonous, τ decreases, and β indicates no change from unity with increasing concentration. Both relaxation processes are described by Debye functions. The second stage in, 80wt% < c < 96wt%5CB (②), molecular interaction set to work and 5CB molecules restrain to another 5CB molecules. The third stage above 96wt%5CB (③), takes N phase. In this range, $\Delta\varepsilon$ is decreasing, since 5CB molecules take anti-parallel dimer and decrease in the apparent dipole moment. 5CB/benzene mixture takes N phase from Iso phase with increasing concentration, and the parameter of the relaxation-time distribution, β, becomes smaller. It is considered that the larger fluctuation of LC occurs with interaction between 5CB molecules in LC phase under the higher restriction. Figure 4 shows τ–β diagram for the process the around minor axis for 5CB/benzene mixture at 25°C. Here ①, ②, and ③ indicate stages of the molecular interaction. This downward curve indicates slow dynamics on the stage ② in the restricted process with the interaction, and discontinuously changes into N phase ③. On the 5CB/benzene mixtures in the frozen state, the relaxation parameters for the process around minor axis changed in a discontinuous manner with phase transition. It is considered that 5CB molecules were restricted among frozen domains and those local domains of LC took high concentration, over 80wt%5CB.

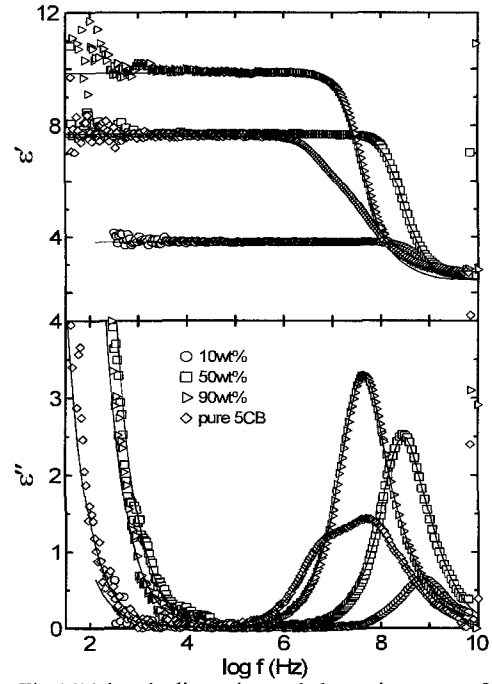

Fig.1 Dielectric dispersion and absorption curves for 10wt%, 50wt%, 90wt%5CB/benzene mixtures and pure 5CB

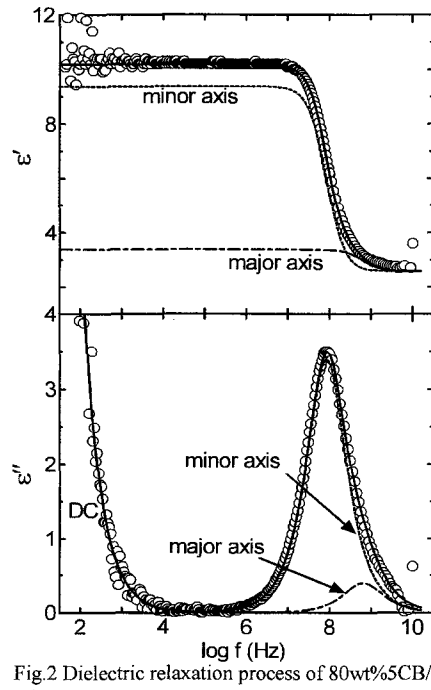

Fig.2 Dielectric relaxation process of 80wt%5CB/benzene mixture

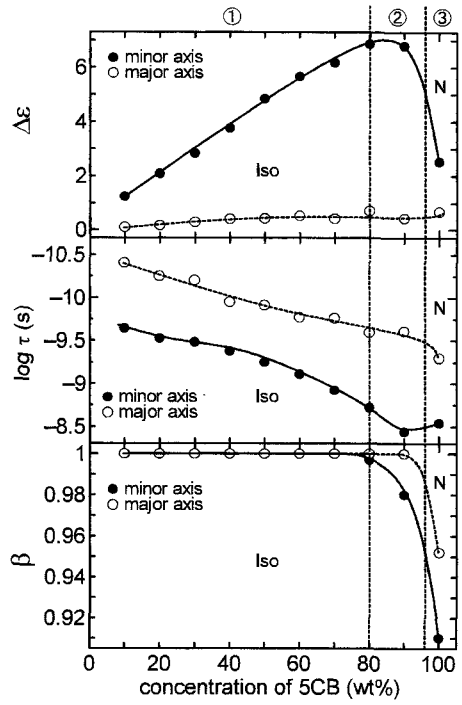

Fig.3 Concentration dependence of the dielectric strength, Δε, the logarithm of relaxation time, τ, and the shape parameter, β, for 5CB/benzene mixture at 25°C

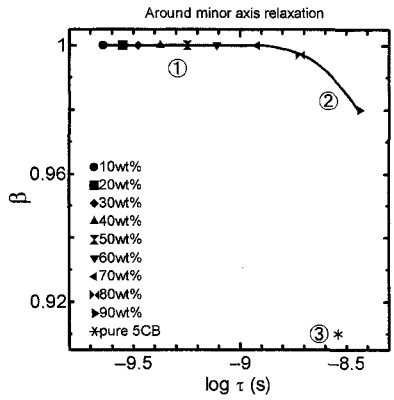

Fig.4 τ–β diagram of minor axis relaxation process for 5CB/benzene mixture at 25°C

3.2 DPPC-liposome/water dispersion

Figure 5 shows dielectric constant and loss spectra for 3wt%DPPC-liposome/water dispersion. The permittivity of DPPC-liposome dispersion is smaller than pure water. Dielectric relaxation curves are expressed by a Cole-Cole relaxation function and the DC conductivity as

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(j\omega\tau)^\beta} + \frac{\sigma}{j\varepsilon_0\omega}. \qquad (2)$$

Figure 6 shows temperature dependences of the relaxation strength, Δε, the logarithm of the relaxation time, τ, and the shape factor, β, for 3wt%DPPC-liposome/water dispersion. The values of Δε and β become smaller with increasing temperature. The Gel-LC phase transition can be easily described from the shape factor, β. In the gel phase, the β value was almost unity, but the β value becomes smaller in the LC phase. It is considered that interactions between water and lipid molecules in LC phase with higher mobility of lipid molecules bring about the larger fluctuation of water molecules. The relaxation time, τ, for the liposome dispersion is obtained as smaller values than those for pure water. But in principle, the relaxation time, τ, should be nearly similar to that of pure water. Since we fit the low frequency tail, the precision of TDR measurement for high frequency side, should be improved to make sure. The values of Δε and β changed in a discontinuous manner with gel-LC phase transition, especially changing shape factor, β, reflected anisotropic molecular interaction in LC phase.

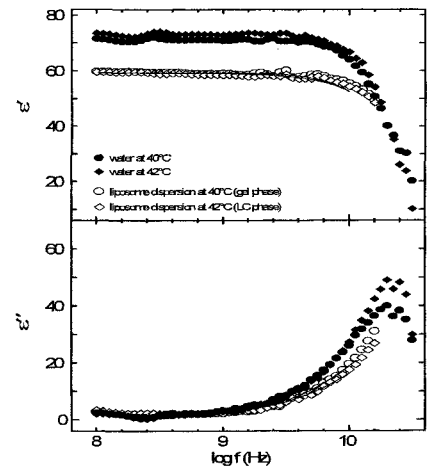

Fig.5 Dielectric constant and loss spectra for pure water and 3wt%DPPC-liposome/water dispersion at 40°C and 42°C

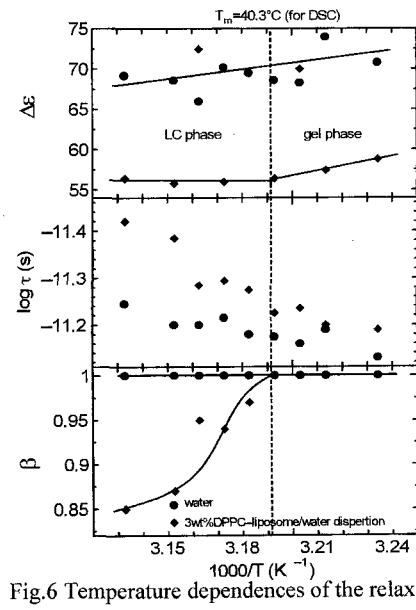

Fig.6 Temperature dependences of the relaxation strength, Δε, the logarithm of relaxation time, τ, and the shape factor, β, for 3wt%DPPC-liposome/water dispersions

4. CONCLUSION

We observed dielectric relaxation of 5CB/benzene mixtures and 3wt%DPPC-lipoome/water dispersion by TDR system. 5CB/benzene mixtures indicated two relaxation processes, which were molecular rotations around the minor and major axes, respectively, and the molecular interaction was separated into 3 stages with changing concentration. For 3wt%DPPC-lipoome/water dispersion, the values of relaxation parameter changed in a discontinuous manner with gel-LC phase transition. The dynamic behaviors of LC and liposome in the LC phase are characterized by smaller β values with respective mechanisms. The molecule was restrained and anisotropic behaviors occurred in the molecular alignments.

5. ACKNOWLEDGEMENTS

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