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Light Scattering Study of the 12-Hydroxyoctadecanoic Acid and Benzene Mixture in the Gel State

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The structure of the 12-hydroxyoctadecanoic acid–benzene gel was studied by the use of the light scattering spectrometer. The scattering angular dependence of the scattering intensity and the time correlation function of the electric field were measured. It was found that the coarse mesh network and the fine mesh network coexist in this gel. The former was detected by the intensity measurement, while the latter was detected by intensity-fluctuation spectroscopy. The usefulness of the light scattering technique was emphasized.

A measurement of light scattered by the fluctuation of a dielectric constant is a preferred method for studying a molecular arrangement in a dimension of several hundred or several thousand angstroms. Gels are interesting objects to study by the light scattering method, as has been shown by the reports of Prins *et al.*[1)] and Tanaka *et al.*[2)] on the structure determination of the agarose or polyacrylamide gel.

In the present work, we study a gel made of 12-hydroxyoctadecanoic acid (12HOA hereafter) and benzene in order to examine the structure utilizing the features of the light scattering method. The 12HOA–benzene gel has already been studied in detail by Tachibana *et al.* using the X-ray diffraction method, circular dichroic spectroscopy, an electron microscope, and other methods.[3)] According to their conclusions, the 12HOA molecules construct fiber-like crystallites in which 12HOA molecules are aligned to form a chiral smectic structure. These fiber-like crystallites enmeshing the gel may be thinner than 10—100 nm, as estimated from the observation of the dried gel (the solvent having been evaporated) under an electron microscope.

The purpose of the present study is to get direct information about the structure of network constructed by the fiber-like crystallites. Using the light scattering method, we can study the structure of the gel state without evaporating the solvent. We measured the angular dependence of the scattered light intensity and the time correlation function of the electric field of the scattered light. The light is scattered essentially by the crystallites in this gel.

Experimental

A schematic diagram of the light scattering spectrometer constructed in this laboratory is shown in Fig. 1. The light source is an argon-ion laser (Spectra-Physics Model 165-09). The scattering angle, θ, is varied by adjustable mirrors, M_1 and M_2, and is defined by two pinholes, P_1 and P_2, with a diameter of 1 mm. P_1 and P_2 are approximately 50 cm apart from each other. The incident light is focused into a sample cell ($12\times15\times16$ mm^3) made of fused quartz.

The photomultiplier tube, PM, has a S-20 response (Hamamatsu TV, R-374) and is operated at 840 V at room temperature. The photomultiplier, and the output power is integrated at a time constant of 1 s and is read out on an oscilloscope. The autocorrelation function of the photocurrent is observed by means of a 400-channel correlation and probability analyzer (KANOMAX, SAI 43A).

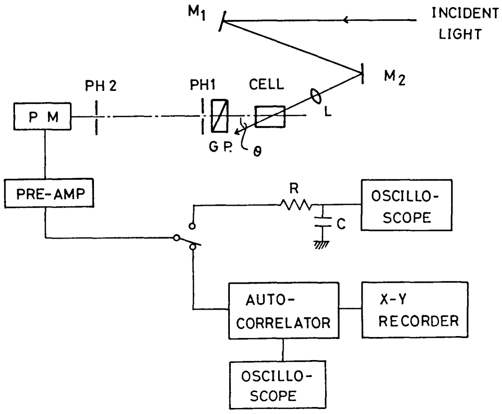

Fig. 1. The block diagram of the light-beating spectrometer.

All the measurements were performed at 24 ± 1 °C. The power of the incident light was controlled within 60—15 mW by the use of ND filters in order to avoid any temperature elevation in the sample.

12HOA was purified from commercial products following the method described in the literature.[4)] The purity was ascertained to be more than 99% by observing the presence of the methyl ester by gas chromatography. The concentration of 12HOA in this gel was about 33 mmol dm^{-3}.

12HOA was dissolved in benzene at 50 °C. Then, it was made dust-free by the use of a millipore filter FG of 0.1 μm pore size and was injected into the sample cell. This sample was cooled down from 50 °C to 24 °C with the cooling rate of 2 °C/h. Further, the sample was left for about one day at 24 °C. The gel finally obtained was an aggregate of spherulitical domains, as has been reported by Tachibana *et al.*[3)] For the actual measurement, we used a gel whose spherulitical domains were larger several centimeters in diameter so that we could avoid the reflection effect at the boundaries of these domains. This gel was transparent to the human eye.

For the polarization measurements, Glan-Thompson prisms (1×1 cm^2 in section) were used to define the polarization direction of the light.

Results and Discussion

The power spectrum of the light scattered from the gel corresponds to the fluctuation of the dielectric constant in space and time, as expressed by these relations:[5)]

$$I(\tilde{q},\ \omega) = \frac{1}{2\pi}\int\langle\tilde{\boldsymbol{E}}_{\mathrm{s}}(\tilde{\boldsymbol{q}},\ t)\tilde{\boldsymbol{E}}_{\mathrm{s}}(\tilde{\boldsymbol{q}},\ 0)\rangle \mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}t$$

$$= \frac{A}{2\pi}\int\left\{\int_V <\Delta\varepsilon_{\mathrm{si}}(\tilde{\boldsymbol{r}},\ t)\Delta\varepsilon_{\mathrm{si}}(\boldsymbol{O},\ 0)\mathrm{e}^{\mathrm{i}\tilde{\boldsymbol{q}}\cdot\tilde{\boldsymbol{r}}}\mathrm{d}^3r\, \mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}t\right.$$

$$= \frac{A}{2\pi}\int\gamma(\tilde{\boldsymbol{q}},\ t)\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}t, \tag{1}$$

with

$$\Delta\varepsilon_{\mathrm{si}} = \tilde{\boldsymbol{n}}_{\mathrm{s}}\cdot\Delta\varepsilon\cdot\tilde{\boldsymbol{n}}_{\mathrm{i}}, \tag{2}$$

$$\gamma(\tilde{\boldsymbol{q}},\ t) = \int_V\langle\Delta\varepsilon_{\mathrm{si}}(\tilde{\boldsymbol{r}},\ t)\Delta\varepsilon_{\mathrm{si}}(\boldsymbol{O},\ 0)\rangle\mathrm{e}^{\mathrm{i}\tilde{\boldsymbol{q}}\cdot\tilde{\boldsymbol{r}}}\,\mathrm{d}^3r, \tag{3}$$

and

$$A = k_{\mathrm{s}}^4E_0^2V/16\pi^2R^2\varepsilon_0^2, \tag{4}$$

where $E_{\mathrm{s}}(\tilde{\boldsymbol{q}},t)$ is the electric field of the scattered light at time t and for a scattering vector, $\tilde{\boldsymbol{q}}$, $\Delta\varepsilon_{\mathrm{si}}$ the element of the dielectric-constat fluctuation tensor, $\Delta\varepsilon$; $\tilde{\boldsymbol{n}}_{\mathrm{s}}$ and $\tilde{\boldsymbol{n}}_{\mathrm{i}}$, the directions of the electric field of the scattering and incident light respectively; V, the scattering volume; $\tilde{\boldsymbol{k}}_{\mathrm{s}}$, the wave vector of the scattered light in the medium; E_0, the electric field of the i-component of the incident light; R, the distance between the scattering volume and the detector, and ε_0, the macroscopic dielectric constant; the suffixes i and s identify the polarization directions of the incident and scattered lights respectively.

Integrating Eq. 1 over the frequency, one gets:

$$I(\tilde{q}) = A\int_V\langle\Delta\varepsilon_{\mathrm{si}}(\tilde{\boldsymbol{r}})\Delta\varepsilon_{\mathrm{si}}(\boldsymbol{O})\rangle\mathrm{e}^{\mathrm{i}\tilde{\boldsymbol{q}}\cdot\tilde{\boldsymbol{r}}}\,\mathrm{d}^3r, \tag{5}$$

which shows that the integrated intensity of a Rayleigh line can afford information about the dielectric-constant fluctuation.

On the other hand, the photo-current correlation function, $\langle i(t)i(0)\rangle$, is related to the field correlation function by this formula:[5)]

$$\langle i(t)i(0)\rangle \propto \langle|\boldsymbol{E}(\tilde{q},\ 0)|^2\rangle + |\langle\boldsymbol{E}(\tilde{q},\ t)\cdot\boldsymbol{E}(\tilde{q},\ 0)\rangle|^2 \tag{6}$$

so long as the optical field obeys Gaussian statistics. A comparison of Eqs. 1 and 6 leads to the conclusion that it is possible to obtain the square of the field correlation function experimentally, because we can observe the photocurrent correlation function with the use of our instrument, in which an analog correlator is installed.

Angular Dependence of the Intensity of the Scattered Light. We consider here only the intensity of the light scattered from the isotropic fluctuation of the dielectric constant, because the intensity of the depolarized component is only about 8% that of the polarized one in this gel. Although several kinds of fluctuations can cause the dielectric-constant fluctuation, the existence of the fiber-like crystallites of 12HOA has the decisive effect. Other fluctuations—for example, the thermally excited density fluctuation of a solvent and the density and orientation fluctuation of 12HOA in each crystalline, have negligibly small effects on the fluctuation of the dielectric constant.

If we expand the exponential term in the right-hand side of Eq. 5 and neglect the terms higher than cubic, we obtain these relations:

$$I(\tilde{q}) = A\int_V\langle\Delta\varepsilon(\tilde{\boldsymbol{r}})\Delta\varepsilon(\boldsymbol{O})\rangle\mathrm{d}^3r\left(1-\frac{1}{6}q^2R_{\mathrm{c}}^2\right) \tag{7}$$

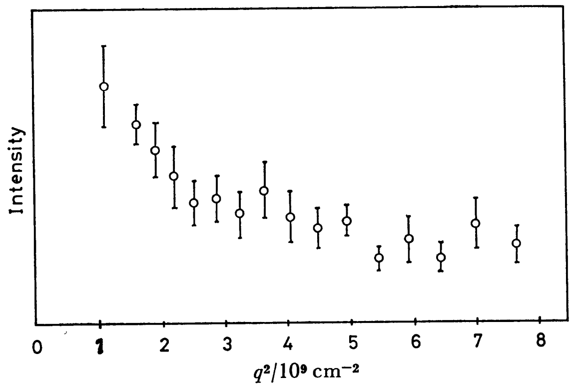

Fig. 2. The scattering intensity against q^2 for the 33 mmol dm^{-3} 12HOA–benzene gel at 24 °C.

with

$$R_{\mathrm{c}}^2 = \int_V\langle\Delta\varepsilon(\tilde{\boldsymbol{r}})\Delta\varepsilon(\boldsymbol{O})\rangle r^2\mathrm{d}^3r\Big/\int_V\langle\Delta\varepsilon(\tilde{\boldsymbol{r}})\Delta\varepsilon(\boldsymbol{O})\rangle\mathrm{d}^3r. \tag{8}$$

R_{c} is called a correlation length of the fluctuation and corresponds to the mean size of the mesh of the gel network, made of 12HOA in the present system. R_{c} can be estimated by using Eq. 7 if we measure the intensity of the scattered light as a function of $\tilde{\boldsymbol{q}}$.

The observed intensities are plotted against q^2 in Fig. 2. The scattered-light intensity is nearly constant in the range of $3.0\times10^9<q^2<8.0\times10^9$ and then increases as q^2 increases in the range of $3.0\times10^9>q^2$ (see Fig. 2). We have to put a large uncertainty in the final "correlation length" value because we could not measure $I(\boldsymbol{O})=A\int_V\langle\Delta\varepsilon(\boldsymbol{O})\Delta\varepsilon(\tilde{\boldsymbol{r}})\rangle\mathrm{d}^3r$ with sufficient accuracy. This arises from the existence of the stray light which is inevitable for small-angle measurements. In addition, the neglections of the higher-order terms of Eq. 7 can be a source of considerable uncertainty for the R_{c} value. However, it may be reasonable to conclude that the "correlation length of fluctuation" or the size of mesh in this gel is in the order of a few thousand angstroms.

Intensity Fluctuation Spectroscopy of the Scattered Light. The intensity fluctuation of the light scattered from the gel originates from various types of motions: (1) the relative motions between the solvent and the fiber-like crystallites which construct the gel network; (2) the relative motions of the 12HOA molecules in the crystallites, and (3) the relative motions of the solvent molecules. The correlation functions, $\gamma(\tilde{\boldsymbol{q}},t)$, of the dielectric constant fluctuation caused by these relative motions can be expressed by this relation:[5)]

$$\gamma(\tilde{q},\ t) \propto \exp(-q^2Dt), \tag{9}$$

where $\tilde{\boldsymbol{q}}$ is the scattering vector and D is the parameter describing the rapidity of the motion, the dimension of which is $[L]^2/[T]$. In the case of the relative motion of Type (3), D is estimated from the thermal diffusivity of liquid benzene, to be in the order of 10^{-3} cm^2/s.[6)] In the case of the relative motion of Type (2), D can be in the order of 10^{-6} cm^2/s, which is estimated from the elastic constant, K, and the

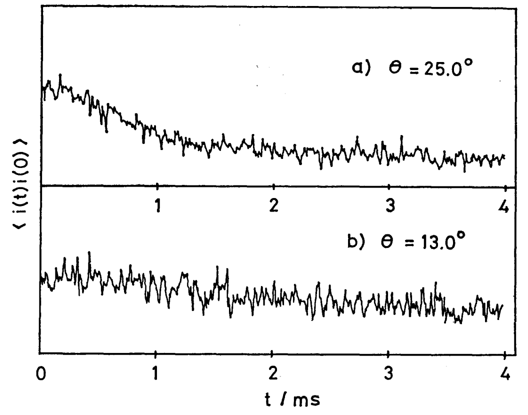

Fig. 3. The observed correlation function for the 33 mmol dm^{-3} 12HOA–benzene gel at 24 °C. The scattering angles are: a) 25° and b) 13°.

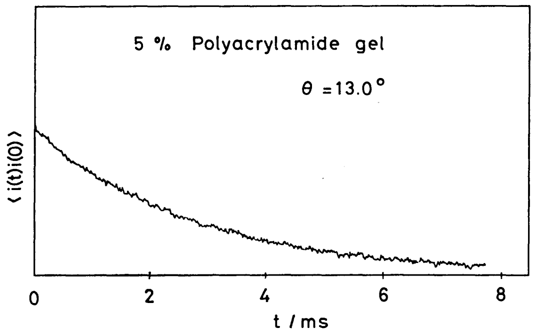

Fig. 4. The observed correlation function of the 5% w/w aqueous polyacrylamide gel at 24 °C with the scattering angle of 13°.

viscosity, η, for the ordinary smectic A-type liquid crystal through the relation: $D \simeq K/\eta$.[7] Furthermore, the scattered light strongly depolarized in this case, because this fluctuation is caused by the orientation of the mesophase molecules. On the other hand, the D-value for Type (1) has been known to be in the order of 10^{-7} cm^2/s, as estimated from the longitudinal compressional modulus, G, and the friction constant, f, observed for polyacrylamide gel through the relation: $D = G/f$.[2] Therefore, these three different modes can be observed separately if we adopt an appropriate experimental set-up for the actual measurement of the correlation function.

Figure 3 shows some typical examples of the actually observed current correlation function, which corresponds to the electrical field of the polarized component of the light scattered from the 12HOA–benzene gel. The correlation function of the depolarized component could not be observed in this case, because the intensity of the depolarized component was negligibly small in comparison with that of the correlation function in the aqueous polyacrylamide gel (5% w/w). One of the results is illustrated in Fig. 4. In the case of the aqueous polyacrylamide gel, we could observe the correlation function with a good reproducibity from any scattering volumes in the sample. From Eqs. 1, 6, and 9 it can be seen that the time-dependent part of the current correlation function is related to the correlation function of the dielectric constant as:

$$\langle i(t)i(0)\rangle_t \propto \exp(-2q^2Dt). \qquad (10)$$

The D-value was obtained for the polyacrylamide system as $(2.2\pm0.2)\times10^{-7}$ cm^2/s from the least-squares fitting to Eq. 9, which agrees well with the observation of Tanaka *et al.* ($D = (2.4\pm0.1)\times10^{-7}$ cm^2/s).

In the case of the 12HOA–benzene gel, D was obtained as $(0.97\pm0.24)\times10^{-7}$ cm^2/s. The relatively large uncertainty attached to the D-value arises from the poor S/N ratio of the observed correlation function. As the magnitude of D is as large as that of the polyacrylamide gel, we can conclude that the scattered light from the 12HOA–benzene gel reflects the relative motions of Type (1), that is, the relative motion between the solvent and the crystallites. The mesh of the network made from the crystallites should be much finer than the wavelength of the incident light. It must be emphasized that the correlation function was not always observed in the 12HOA–benzene gel; that is, the appearance of the correlation function was dependent on the position of the scattering volume. This may reflect the situation that the network with the fine mesh is not dispersed homogeneously in the sample, quite different the situation in the aqueous polyacrylamide gel.

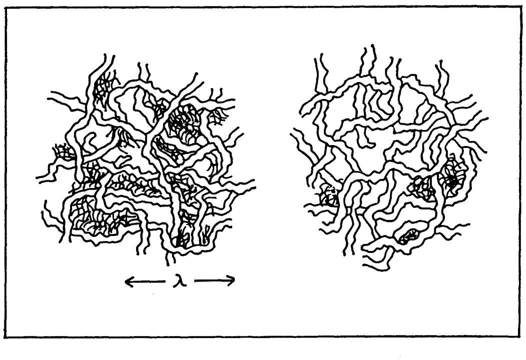

Fig. 5. The structure of the netweork constructed in the 12HOA–benzene gel (schematic). λ is several thousand Ångstroms which corresponds to the wavelength of the incident light.

Concluding Discussion. According to the results reported in the previous paragraphs, a network with rather complicated structures is formed in the 12HOA–benzene gel. The integrated intensity data and the current correlation function show that there are two kinds of networks in this gel. One is a network with a mesh of a few thousand angstroms (obtained from the intensity data), and the other is one with a much finer mesh (from the correlation function).

Tachibana *et al.* observed fiber-like crystallites whose thickness was 10—100 nm in the dried gel (the solvent being evaporated) under an electric microscope. The network with a mesh of a few thousand angstroms may be constructed from such fiber-like crystallites. As the thickness of the fiber-like crystallites is 10—100 nm, and as those crystallites contain no solvent,[3] the fiber might be very hard. Therefore, they cannot entangle themselves with each other densely, thus forming a rather coarse network. These fibers which form the coarse network are linked together here and there by smaller networks with a fine mesh. These fine networks are dispersed inhomogeneously in the gel: that is, there might be some areas in which the fine networks are stretched densely and others in which the fine networks are not stretched. In Fig. 5 we visualize the structure of the network formed in the 12HOA–benzene gel schematically. The existence of the fine network has not been noticed before in the 12HOA–benzene gel. We believe the existence of this fine network is essential for the formation of the gel phase, because the solvent molecules can be trapped in this fine network much more easily than in the coarse network.

Incidentally, the present work has emphasized the importance of the light scattering study for the determination of complicated structures in materials, because we are able to choose appropriate regions of time and space for the measurements of the intensity and the correlation function of the electric field of the scattered light.

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