

Pretransitional Phenomena in the Isotropic Phase of a Lyotropic Liquid Crystal of Bacterial Virus fd

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Measurements of transient magnetic birefringence are reported for isotropic solutions of a biological rodlike macromolecule, bacterial virus fd. A steep increase of the birefringence and a slowing down of the relaxation process are observed just below the concentration at which the liquid-crystalline phase appears. These pretransitional phenomena are considered to be due to the short-range order effects, and a Landau-de Gennes-type approach based on the Onsager theory describes our results semiquantitatively.

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It is known that the nematic-isotropic phase transition in a thermotropic liquid crystal is weakly of first order, and in the vicinity of the transition point there occur many anomalies as if it were of second order. Just above the transition temperature in the isotropic phase, there is no long-range order in the direction of alignment of the molecules, but locally they are still parallel to each other due to the critical fluctuation in the orientational order. The pretransitional phenomena associated with this short-range order effect are successfully interpreted by the so-called Landau-de Gennes theory.¹

However, similar pretransitional phenomena have not yet been reported for a lyotropic liquid crystal, in which the phase transition is induced most naturally by a change in concentration of solute molecules. In this Letter, we examine whether these types of short-range order effects exist or not in the lyotropic liquid crystal of solutions of biological rodlike particles. We carried out measurements of a transient magnetic birefringence (TMB) of solutions of bacterial virus fd in the concentration range just below the critical concentration at which the liquid-crystalline phase appears. As a result, we have found deviations from what is expected from the individual behavior of rods, and these can be interpreted as due to the collective behavior of rods associated with the "short-range order effects."²

Bacterial virus fd is a semiflexible rod 890 nm in length and 8.5 nm in diameter, and the molecular weight is 1.58×10^7 .³ For the study of physical phenomena of a rod particle, this biological macromolecule has an advantage that it is monodisperse in length and diameter. It has been found that concentrated solutions form liquid-crystalline structures spontaneously⁴ and the particles are ordered by external fields (Kerr

effect^{5,6} and Cotton-Mouton effect⁷). So, we first made a phase diagram of the solution by observation using a polarizing microscope, and have found the critical concentration agrees rather well with the predicted value by Onsager considering only the excluded-volume effect.⁸ Second, the TMB measurements, in which we observe a relaxation process of the magnetically induced birefringence after cutting off the field, were carried out analogously to the usual transient electric birefringence (TEB) measurements. Since this macromolecule is an electrolyte and should be shielded adequately with counter ions so as to preclude electrostatic interactions, TMB is more adequate than TEB⁶ for concentrated solutions with large conductivity.

In order to describe the short-range order effects, let us introduce the tensor order parameter $Q_{\alpha\beta}$,¹

$$Q_{\alpha\beta} = \frac{3}{2}S(n_{\alpha}n_{\beta} - \frac{1}{3}\delta_{\alpha\beta}), \quad (1)$$

where S is the scalar order parameter and \vec{n} is the local direction of alignment of rods. We then invoke de Gennes's phenomenological kinetic equation for $Q_{\alpha\beta}$,⁹

$$-\frac{\partial Q_{\alpha\beta}}{\partial t} = \mu\gamma_{\alpha\beta} + \nu\frac{\partial Q_{\alpha\beta}}{\partial t}, \quad (2)$$

where $\gamma_{\alpha\beta}$ is the shear rate tensor and μ and ν are the kinetic coefficients having the dimension of the viscosity. F is the free-energy density of the rod-particle solution.

In the immediate neighborhood of the critical concentration, F can be expanded as a power series in $Q_{\alpha\beta}$. In the presence of external magnetic field \vec{H} , the Landau-type free-energy density is given by retaining only the harmonic term;

$$F = F_0 + \frac{1}{2}A Q_{\alpha\beta}^2 - \chi_a Q_{\alpha\beta}(H_{\alpha}H_{\beta} - \frac{1}{3}H^2\delta_{\alpha\beta}). \quad (3)$$

The anisotropy of the diamagnetic susceptibility

χ_a is given by

$$\chi_a = c\Delta\chi, \quad (4)$$

where $\Delta\chi$ is the anisotropy of one rod and c is the number of rods per unit volume. Solving Eq. (2) with Eq. (3) under the external field of \vec{H} , we obtain

$$\begin{aligned} \vec{H} &= \text{const} \equiv \vec{H}_0 \quad (t < 0) \\ &\equiv 0 \quad (t > 0). \end{aligned} \quad (5)$$

One can readily obtain the time evolution of birefringence $\Delta n(t)$ by neglecting the backflow effect,

$$F = F_0 + ckT \left[\frac{\Gamma}{2} \left(1 - \frac{\Gamma}{5} \right) S^2 - \frac{\Gamma^3}{105} S^3 + \frac{\Gamma^4}{700} S^4 + \dots \right], \quad (9)$$

$$\Gamma = \frac{5}{16}\pi cDL^2, \quad (10)$$

where D and L are the diameter and the length of the rod, respectively. Comparing Eq. (3) with Eq. (9), A is described as a function of the volume fraction φ (total volume of the particles per unit volume);

$$A(\varphi) = \frac{5}{6\pi} kT \frac{L}{D^4} \varphi^2(\varphi^* - \varphi), \quad (11)$$

$$\varphi^* = 4D/L. \quad (12)$$

Since both ϵ_a and χ_a are proportional to φ , Eq. (7) leads to a relation

$$\Delta n_0 \propto H_0^2/(\varphi^* - \varphi). \quad (13)$$

The critical volume fraction φ_c , where the liquid-crystalline phase appears, is given by Onsager⁸ as

$$\varphi_c = 3.3D/L. \quad (14)$$

φ_c is a little smaller than φ^* .

The bacterial virus fd was prepared and purified following the procedures of Marvin and Schaller¹⁰ and Yamamoto *et al.*,¹¹ and ultracentrifuged (35 000 rpm \times 24 h at 15 °C) with CsCl density gradient. The solvent condition was all 50 mM tris buffer (pH 8.1); the Debye screening length was then 2.0 nm. All the measurements were carried out at a room temperature of 24 \pm 1 °C. The concentrations of the solutions were determined by measurements of ultraviolet absorption at 260 nm. The observed critical concentration was 13.8 \pm 0.8 mg/ml ($\varphi_c = 2.7\%$) and the concentration for TMB measurements varied from 1.25 to 12.7 mg/ml. \bar{n} was observed to be 1.333 \pm 0.002 for all the solutions.

The optical setup of the TMB was a standard one for a usual TEB technique,¹² including a 1

as follows:

$$\Delta n(t) = \Delta n_0 \exp(-t/\tau) \quad (t > 0), \quad (6)$$

$$\Delta n_0 = \epsilon_a \chi_a H_0^2 / 4A\bar{n}, \quad (7)$$

$$\tau = \nu/A, \quad (8)$$

where ϵ_a is the anisotropy in the dielectric permittivity tensor, and \bar{n} is the mean refractive index.

On the other hand, the concentration dependence of the coefficient A is given by expanding Onsager's mean-field free-energy density⁸ in the scalar order parameter S ;

mW He-Ne laser, two linear polarizers, a $\lambda/4$ plate, and a photodiode detector. The magnetic field, up to 10 kG, was produced by an electromagnet (Mitsubishi-steel-magnetics; EM1103A) with a steady-current power supply. The field was monitored almost simultaneously with a calibrated Hall-effect Gauss meter (Siemens; FA22e). By use of a diode-clamping technique, an exponential decay time of 70 ms after cutting off the current was attained for a 9.1-kG field. The sample cell was made of acrylic acid resin with two quartz windows. The light path length was 1 cm and the cell was fixed in the 0.6-cm gap between pole pieces of the magnet. The light intensity at the detector $I(t)$ was recorded by a transient recorder (Iwatsu-Electronics; DM305) and analyzed by a microcomputer (NEC; PC8000). In order to reduce the effect of residual magnetism in the magnet, the direction of the field was alternately reversed, and $I(t)$ was averaged. Since the decay time of the magnetic field was not fast enough, $I(t)$ was deconvoluted and the relaxation time τ of the birefringence $\Delta n(t)$ was determined.¹³ It was difficult to determine τ for dilute solutions below 3 mg/ml. The resolution of the birefringence was 10^{-9} by the present measuring system, and uncertainty of $\pm 5\%$ for τ was unavoidable.

In order to study pretransitional phenomena, we first examined H_0^2 dependence of Δn_0 (Cotton-Mouton effect) for concentrated solutions and Δn_0 were found to be proportional to H_0^2 below 10 kG.¹⁴

The results of TMB measurements at 9.1 kG are shown in Figs. 1 and 2. As seen in Fig. 1(a),

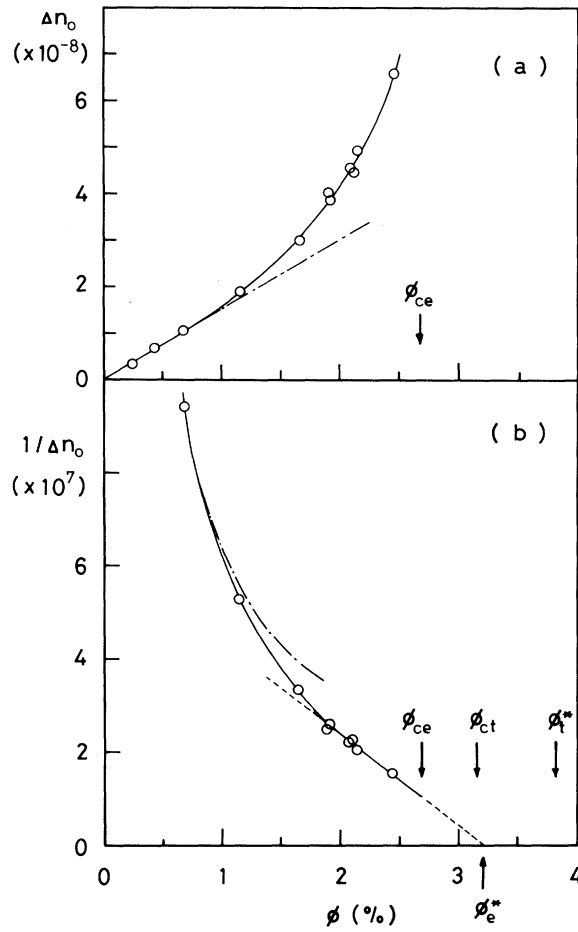


FIG. 1. (a) The intensity of the magnetic birefringence Δn_0 at 9.1 kG is plotted against the volume fraction ϕ . The dash-dotted line indicates a linear relation of $\Delta n_0 \propto \phi$, which holds for dilute solutions. (b) The reciprocal of Δn_0 . The dotted line is a fit to Eq. (13). The dash-dotted line indicates the same linear relation as in (a). ϕ_{ce} and ϕ_e^* are observed values of ϕ_c and ϕ^* , respectively, and ϕ_{ct} and ϕ_t^* are theoretical values with $D = 8.5$ nm.

below $\phi = 1\%$ Δn_0 is proportional to ϕ as a characteristic of dilute solutions, and above 1% Δn_0 obviously increases steeply as ϕ approaches the observed ϕ_c . In Fig. 1(b), we plot $1/\Delta n_0$; above 1.8% the concentration dependence is linear in agreement with Eq. (13). The experimentally obtained ϕ^* is 3.2% . Figure 2(a) shows the relation between τ and ϕ^2 . Below 1.8% , τ is nearly proportional to ϕ^2 , which may be explained as a rotational relaxation of Doi-Edwards theory for semidilute solutions.^{6,15} Above 1.8% , τ increases much faster than ϕ^2 . Since the Doi-Edwards theory says $\nu \propto \phi^3$, τ should be proportional to $\phi/(\phi^* - \phi)$ by Eq. (8). Figure 2(b) indicates this

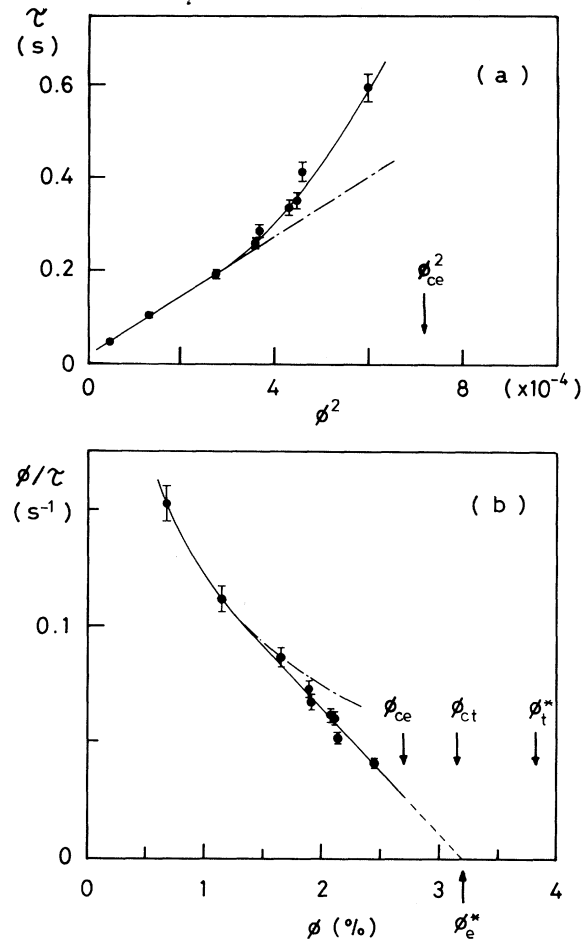


FIG. 2. (a) The relaxation time τ of the TMB at 9.1 kG vs the square of the volume fraction ϕ^2 . The dash-dotted line is a fit to the Doi-Edwards relation. (b) ϕ/τ vs ϕ , by replotting (a). The dashed line is a fit to the mean-field theory, if one assumes the rotational relaxation obeys the Doi-Edwards relation (dash-dotted line).

relation holds above 1.8% and ϕ^* is found to be 3.2% , the same as in Fig. 1(b).

In view of the approximate nature of the Onsager theory, we may not expect a strict quantitative agreement between theory and experiment, but some part of the discrepancy of each value of ϕ_c and ϕ^* may be due to the estimation of D . We have taken the value of 8.5 nm, which was determined from x-ray analysis with 98% humidity.³ Considering the screened electrostatic effect, D as it appears in Eqs. (10)–(14) should be a little larger than 8.5 nm. When we take 10.1 nm instead, the observed values of ϕ_c and ϕ^* just agree with the theoretical values (3.8 and 4.5% , respectively). In what follows, we use 10.1 nm temporarily, and ϕ in Figs. 1 and 2 should be

1.4 times larger and is represented as φ' . Using the values of ϵ_a and χ_a from recently published data for dilute solutions⁷ ($3.9 \times 10^{-2} \varphi'$ and $5.9 \times 10^{-9} \varphi'$ erg G⁻² cm⁻³, respectively), we may estimate A from the slope of the dotted line in Fig. 1(b) (1.4×10^9), as $A = 5.1 \times 10^6 \varphi'^2 (\varphi'^* - \varphi')$ erg cm⁻³. From Eq. (11), the coefficient of A is calculated to be 9.3×10^5 erg cm⁻³, about $\frac{1}{5}$ of the experimental value.¹⁶ Previously we have measured steady flow viscosities η for the same sample,¹⁷ and η at zero shear can be approximated as $6.6 \times 10^3 \varphi'^{2.2}$ P around $\varphi' \approx 3\%$. When we take $A = 9.3 \times 10^5 \varphi'^2 (\varphi'^* - \varphi')$ erg cm⁻³ and assume $\nu = a\eta$, $\varphi'/\tau = 140 \varphi'^{0.8} (\varphi'^* - \varphi')/a \approx 8.5 (\varphi'^* - \varphi')/a$ s⁻¹. The slope of the dotted line in Fig. 2(b) (3.8 s⁻¹) indicates $a \approx 2.2$.

In conclusion, we have observed TMB for concentrated solutions of the bacterial virus fd, just below the critical concentration, and found pretransitional phenomena in both static and dynamic aspects of the birefringence. These phenomena are considered to be due to the short-range order effects in the same way as in the case of a thermotropic liquid crystal just above the clearing point. A Landau-de Gennes-type approach based on the Onsager theory can semiquantitatively interpret the observed effects.

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thermotropic liquid crystals is by P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, London, 1974).

²The short-range order effects in the phage solution are actually fairly long range, because it can be shown that the correlation length of the short-range order ξ_s near φ_c is of the order of the length of the rod L , and L is as long as $1 \mu\text{m}$.

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¹⁴We have observed that τ is independent of H_0 .

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