Time-transient process of magnetically induced growth of nematic domains in a biological macromolecular liquid crystal

M. Hirai,[1,*] T. Takizawa,[1] S. Yabuki,[1] T. Hirai,[2] T. Ueki,[3] and Y. Sano[4]
[1]*Department of Physics, Gunma University, Maebashi 371, Japan*
[2]*Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan*
[3]*Division of Biophysics, The Institute of Physical and Chemical Research, Wako 351-01, Japan*
[4]*National Food Research Institute, Tsukuba 305, Japan*
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A lyotropic nematic liquid crystal of biological macromolecules was investigated at a nonequilibrium state induced by a magnetic field. By using synchrotron radiation, an x-ray scattering method, and a specially designed magnetic circuit, we have succeeded in observing a time-transient process of a drastic change of the scattering profile from the macromolecular assembly. We can describe this process by a magnetically induced orientation of nematic liquid crystal domains along the field which is equivalent to a growth of nematic domain from polycrystalline to a single liquid crystal. We can estimate the growth rate constant, the longitudinal relaxation time, and the dimension of the nematic microdomains.

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I. INTRODUCTION

The behavior of biological macromolecular assemblies under magnetic field has been attracting scientific concern, and has been studied intensively from various viewpoints such as electromagnetic characteristics of molecular structure [1–5] relating widely to physiological function [6,7] and cooperative phenomena of polyelectrolytes concerning about liquid crystal phase transitions [8,9]. On the other hand, from the discovery of polymer liquid crystals, some biological macromolecular colloidal suspensions are known to form lyotropic liquid crystals [10]. Many theoretical works have been done to predict and explain the self-ordering mechanism of liquid crystals, especially those composed of rod-shaped colloidal particles, by assuming some repulsive or attractive interaction between them [11–15]. Although some experimental works were done for biological macromolecular colloids of hard rods under magnetic field [8,9], there is little direct evidence to show a dynamic orientational process of those solute components or to show an effect of magnetic field on the formation of those liquid crystals. By using a highly intense synchrotron radiation x-ray beam we have succeeded in observing a time-transient process for a drastic change of the scattering profile of a hard-rod assembly, which evidently shows a transient phenomenon of a lyotropic liquid crystal at an unequilibrium state induced by applying a weak perturbation such as a magnetic field.

II. EXPERIMENT

The sample used for the present experiments was a tobacco mosaic virus (TMV), which has a cylindrical structure 300 nm in height and 18 nm in diameter, known to be a typical system of hard rods [16]. The TMV used was the Japanese common strain [17], and its purification method was shown elsewhere [18]. The virus was suspended in a 10-mM sodium phosphate buffer adjusted at 7.2 *p*H. TMV suspensions with three different solute concentrations of 34.5, 56.5, and 87.9 mg/ml were used for the present scattering experiments. TMV concentrations of the suspensions were determined spectrophotometrically by using an absorption coefficient of $e^{1g/l}_{260\,nm}=3.0$ for the virus [19]. The suspensions were confirmed to be monodisperse by using both analytical ultracentrifugation and dynamic light scattering methods.

X-ray scattering experiments were carried out with a small-angle scattering spectrometer installed at the 2.5-GeV storage ring in the Photon Factory, Tsukuba, Japan. The scattering intensity was detected by using a one-dimensional position sensitive proportional counter (PSPC). The wavelength used was 1.49 Å, and the sample-to-detector distance was 195 cm. TMV samples were contained in a quartz cell with a 1-mm path length. The details of the optics were explained elsewhere [20]. Time-resolved measurements were done at 25 °C on a programmed time-interval setting. Each measuring exposure time for every time frame was 60 s and the integrated exposure time for one sample was 780 s, which is short enough to avoid radiation damage on the samples. A compact permanent magnetic circuit developed for the present experiments has various characteristics, such as a magnetic field strength adjustable from 0.7 to 2.0 T, with high uniformity at a sample position in volume of $4\times10\times10$ mm^3, avoiding an artifact caused by a magnetic field heterogeneity such as translational migration of macromolecules [21]. The direction of the applied magnetic field was perpendicular to the incident x ray. To observe an anisotropy of the scattering profile induced by applying magnetic field, the PSPC anode wire was placed perpendicular or parallel to the direction of the magnetic field.

*Corresponding author. FAX: INT+81 272-20-7405.
Electronic address: hirai@la.gunma-u.ac.jp

III. RESULTS AND DISCUSSION

A. Time-transient change of scattering profiles

At the TMV concentrations of 34.5 and 56.5 mg/ml, we could not observe any changes of the scattering profiles up to a magnetic field strength of 1.7 T, whereas the 87.9-mg/ml TMV suspension became very sensitive to the application of magnetic field. Figure 1 shows the time course of changes to the scattering profile of the 87.9-mg/ml suspension under different conditions. The time when the sample is placed in the sample holder is defined as $t=0$. The abrupt decrease of the scattering intensity at very small angle is attributed to the beam stopper. Figure 1(a) corresponds to the case without the magnetic field, and Figs. 1(b) and 1(c) to the cases with a magnetic field strength of 1.4 T when the magnetic field directions to the PSPC anode wire were perpendicular and parallel, respectively. In Fig. 1(a) any spontaneous orientation of the TMV particles did not occur, even, at this concentration. In contrast, Figs. 1(b) and 1(c) show drastic changes of the scattering profiles and intensities depending on time. On the above two different experimental alignments in scattering measurement direction against magnetic field, we can see two opposing tendencies, namely a systematic increase in Fig. 1(b) and a decrease in Fig. 1(c). Both these opposing tendencies are compensated for by each other, thus showing the conservation rule of the total scattering power. As an elongated cylindrical particle like TMV is well known to cause a fairly asymmetric scattering profile in different measurement directions [22], the difference between the final scattering profiles in Figs. 1(b) and 1(c) is evidently attributed to the intrinsic structural anisotropy of the TMV particle, suggesting the gradual orientation of the TMV long axes along the applied magnetic field. Alternatively,

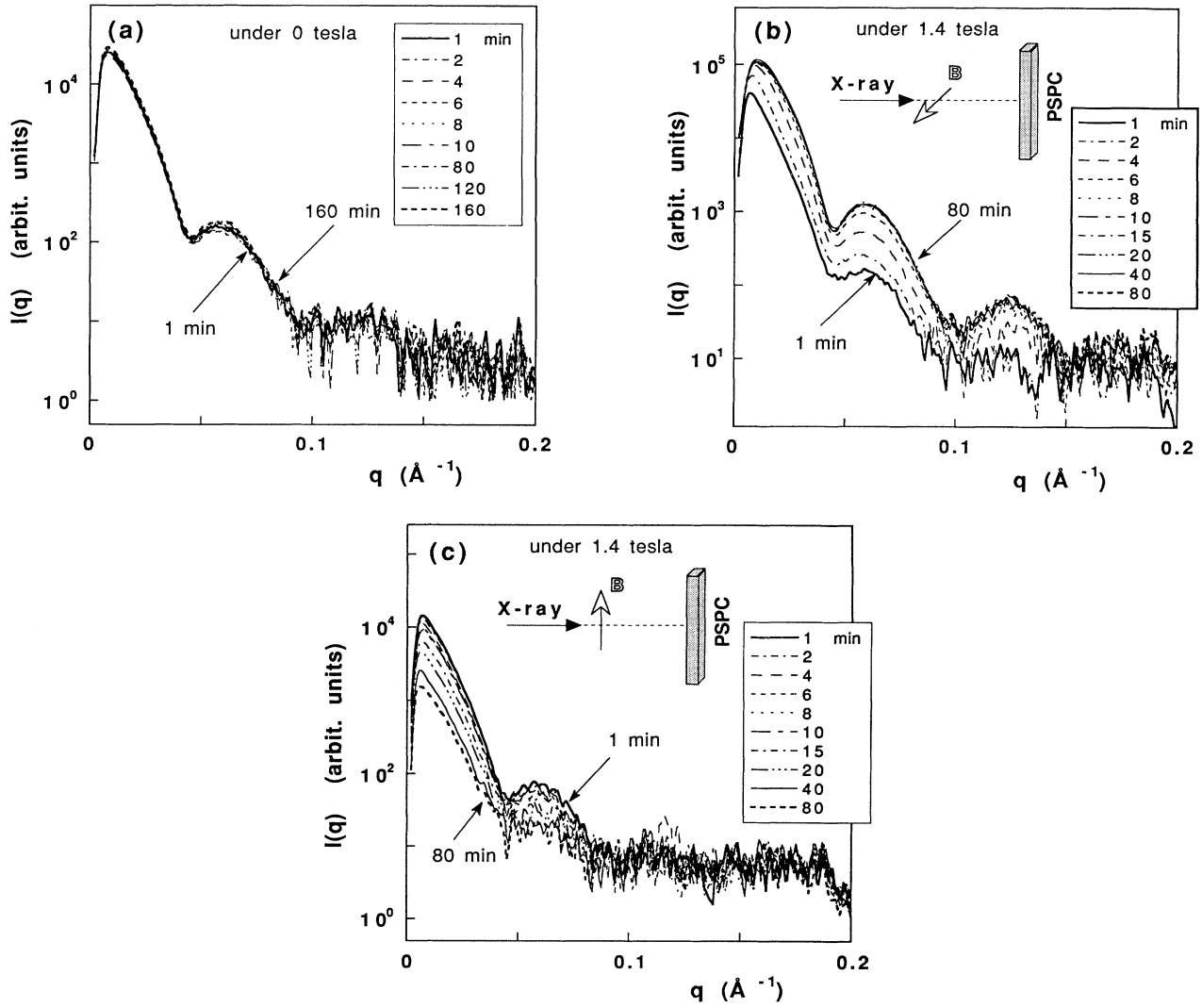

FIG. 1. Time-resolved scattering curves of the 87.9-mg/ml TMV suspension in the nematic liquid crystal phase. (a) corresponds to zero magnetic field, (b) and (c) to a magnetic-field strength of 1.4 T, where the magnetic-field directions to the PSPC anode were perpendicular and parallel, respectively. The insets show the experimental alignments.

this means that, owing to the presence of the diamagnetic anisotropy of the TMV particles, the application of magnetic field induced a highly anisotropic rotational order, resulting in the scattering profile changing to a thermal equilibrium one.

B. Estimation of growth rate constant of nematic domains

By a conventional method using crossed polarizers, we confirmed that the 34.5- and 56.5-mg/ml TMV suspensions were in the isotropic phase, that the suspension of 66.9 mg/ml separated into upper and lower phases (isotropic and liquid crystal phases with equal volume ratio), and that the suspension of 87.9 mg/ml was mostly in the nematic liquid crystal phase. No evidence of a long-range order in the smectic phase was observed. As shown in many previous works on other lyotropic biopolymer liquid crystals using polarizing micrographs [10,23,24], those crystals contained in a thick sample cell generally take polydomain structures such as the polycrystalline structure in crystal. The suspension of 87.9 mg/ml was composed of randomly oriented nematic domains. This we can assume that the magnetic field induces the rearrangement of randomly oriented nematic domains to form a uniaxial single nematic domain with some orientational distribution of the TMV particle axes inside. As the cross section of the incident x-ray beam on the sample was collimated to be about 3 mm^2, the maximum volume V_0 of the total nematic domains contributing to an observable total forward scattering intensity is limited by this cross section. The variation of the volume $V_s(t)$ of the nematic domains with axes parallel to the magnetic field, which we have measured as a change of the scattering intensity, can be described by

$$\frac{dV_s(t)}{dt}=\frac{V_0-V_s(t)}{\tau} .$$

Then,

$$V_s(t)=V_0\{1-\exp(-t/\tau)\} , \tag{1}$$

where $1/\tau$ is the growth rate constant of the volume $V_s(t)$ equivalent to that of a single nematic domain. Compared with the case of the smectic liquid crystal, the nematic liquid crystal is known to have only an orientational order and not to have an order in the center of the gravity, i.e., a translational order. The overall scattering density distribution function $\rho(\mathbf{r})$ composed of identical particles is generally given by the convolution of the scattering density distribution function of a single particle $\rho_s(\mathcal{R}(\omega)\mathbf{r})$, and the translational distribution function $w(\mathbf{r})$ of the particles as

$$\rho(\mathbf{r})=\sum_{i=1}^{N_0}\rho_i(\mathcal{R}(\omega)\mathbf{r})*\delta(\mathbf{r}-\mathbf{r}_i)=\rho_s(\mathcal{R}(\omega)\mathbf{r})*w(\mathbf{r}) , \tag{2}$$

where $*$ means the convolution integral, $\int w(\mathbf{r})d\mathbf{r}\equiv N_0$, $\delta(\mathbf{r})$ is the Dirac delta function, and $\mathcal{R}(\omega)$ is the rotational operator which rotates the particle from the arbitrarily defined initial position $\rho_s(\mathbf{r})$ to another orientation [25]. Thus the scattering function $I(\mathbf{q})$ (magnitude of scattering vector $q=4\pi\sin\theta/\lambda$, scattering angle 2θ, and wavelength λ) is given by square of the Fourier transform of $\rho(\mathbf{r})$ as

$$I(\mathbf{q})=\left|\int\rho(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}\right|^2=\{I_s(\mathbf{q})f(\Omega)\}W(\mathbf{q}) , \tag{3}$$

where $I_s(\mathbf{q})$ is the scattering function of the particle, and $f(\Omega)$ and $W(\mathbf{q})$ are Fourier-transformed orientational and translational functions, respectively. $W(\mathbf{q})$ contributes to the appearance of the peaks (Bragg peaks for crystal), and for a random translational arrangement of the particles, such as a nematic liquid crystal, $W(\mathbf{q})$ becomes constant expect at a very small angle. Then the time-dependent scattering intensity $I_t(q)$ measured at a defined scattering angle is given by averaging $I_s(\mathbf{q})f(\Omega)$ over the defined solid angle $\Delta\omega$ determined by the aperture of the detector window of 2 mm in width:

$$\begin{aligned} I_t(q)&\propto\int_{\Delta\omega}I_s(\mathbf{q})f(\Omega,t,H)d\Omega \\ &=\alpha_t I_{\text{init}}(q)+(1-\alpha_t)I_{\text{final}}(q) , \end{aligned} \tag{4}$$

where $f(\Omega)$ is replaced by the function $f(\Omega,t,H)$; Ω is an arbitrary solid angle, $I_{\text{init}}(q)$ and $I_{\text{final}}(q)$ are the initial and final scattering functions observed which correspond to the isotropic and anisotropic scattering functions contributing to the solid angle $\Delta\omega$, alternatively; and $I_{\text{init}}(q)$ and $I_{\text{final}}(q)$, respectively, represent the scattering function of the randomly oriented nematic domains and that of the nematic domains aligned along the magnetic field. α_t is the ratio between them ($\alpha_t\leq 1$). At the lowest scattering angle region, we observed no evident peak or hump caused by the presence of a translational correlation, suggesting that TMV particles retained homogeneous dispersion in the nematic phase even under magnetic field. As the scattering intensity from a homogeneous scattering object is proportional to its volume, Eq. (4) can relate to Eq. (1) directly. Thus $I_t(q)$ is given as

$$I_t(q)\propto I_{\text{final}}(q)\left[1-\frac{I_{\text{final}}(q)-I_{\text{init}}(q)}{I_{\text{final}}(q)}\exp(-t/\tau)\right] . \tag{5}$$

Equation (5) indicates the change of the scattering profile from a thermal equilibrium state without magnetic field to a thermal equilibrium state with magnetic field. In Fig. 2, we can determine the growth rate constant $1/\tau$ by applying Eq. (5) to the scattering profiles in Fig. 1(b), using least-squares fittings. In Table I the values obtained at various magnitude of scattering vector q are about 0.25 min^{-1} and are independent of q. The absence of a q dependence means the present scattering process is an elastic one, since in the case of small-angle x-ray scattering (in the present experiments, the scattering angle 2θ is below 2.7°, 8.3×10^3 eV for 1.5 Å) an elastic scattering process generally occurs and a q dependence of $1/\tau$ caused by low energy excitation such as a rotational or translational motion of molecules ($\sim k_BT\sim2.5\times10^{-2}$ eV at room temperature) cannot be observed, except for cases using other inelastic or quasielastic scattering methods such as neutron scattering (thermal and cold neutron: ~0.1–0.001 eV) or dynamic light scattering. On the other hand, Eq. (5) is evidently equivalent to the

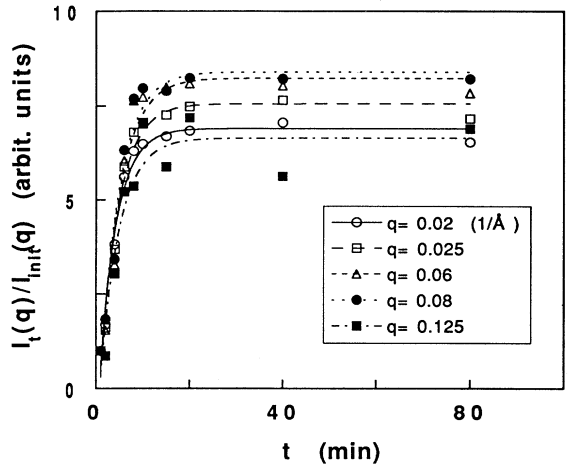

FIG. 2. Determination of the growth rate constant of the uniaxial nematic domain using least-squares fittings based on Eq. (5). Scattering intensities at arbitrary angles in Fig. 1(b) were used after normalization by those initial ones to avoid overlap in plots. Table I lists the values obtained.

solution of Bloch equations for $M_x = M_y = 0$ that describe phenomenologically the motion of the magnetic moment under magnetic field [26]. Therefore the term τ can correspond to the longitudinal relaxation time in the Bloch equations, which is 243±22 s.

C. Phenomenological model

The above analysis suggests that we can describe the observed time course of the change of the scattering intensity by an analogy with the orientational motion of the magnetic moment under magnetic field, as shown below. To advance a phenomenological analogy, the present time-transient process may be similar to a superparamagnetic behavior in magnetically diluted systems [27,28], where ferromagnetic microclusters usually orient randomly, and by applying magnetic field to those clusters oriented along the field to show a large magnetic moment. The change of the scattering profile is described well by a single exponential equation, suggesting the presence of components with identical orientational time constants. Therefore, if we suppose that the growth of the nematic domains aligned along the magnetic field is dominated by the orientation of identical components, we can estimate the dimension of such identical components, namely nematic domains. The magnetic potential energy ΔE of a component in competition with the Brownian motion is given by $\Delta E = |\Delta\chi| H^2/2$ ($\Delta\chi$ is the diamagnetic anisotropy of the component). The energy ΔE per TMV particle at 1.4 T is 2.3×10^{-24} J ($\Delta\chi$ of the TMV particle is equal to 2.3×10^{-24} J/T^2) [29], which is too small to compete with the thermal motional energy $k_B T$ (4.1×10^{-21} J at 25 °C) per arbitrary particle. Thus the component must be an assembly of oriented TMV particles, namely a nematic domain. For a complete alignment by magnetic field, $\Delta E/k_B T$ needs to be more than 20 [30], and in that case the domain turns out to include over 3.6×10^4 oriented TMV particles (the domain radius is above 1.1 μm for 87.9-mg/ml TMV at 1.4 T). As has been justified in the studies of macromolecular rotational diffusion using the saturation transfer electron paramagnetic resonance method [31,32], the rotational correlation time τ_c for a spherical particle is given by $\tau_c = 4\pi a^3\eta/3k_B T$ (particle radius a, solvent viscosity η). Based on the present picture assuming the presence of nematic domains with identical dimensions under magnetic field, we can regard the relaxation time τ as τ_c. To explain the experimental relaxation time of 243 s the domain radius turns out to be 4.0 μm, where $\eta = 3.76\times10^{-3}$ Pa s at 25 °C. Although the above discussion seems to be too simplified to take into account the dependence of the orientational order $f(\omega,t,H)$ on the magnetic field strength, and temperature or other factors, it is noteworthy that the size estimated is comparable with one magnetic coherence length of 4.3 μm at 1.4 T [23].

TABLE I. Growth rate constant $1/\tau$ of the uniaxial nematic liquid crystal domain determined from Fig. 2.

q (Å^{-1})	$1/\tau$ (min^{-1})
0.020	0.27±0.03
0.025	0.25±0.04
0.030	0.24±0.04
0.040	0.23±0.04
0.050	0.25±0.03
0.060	0.23±0.04
0.070	0.23±0.04
0.080	0.24±0.04
0.090	0.27±0.07
0.100	0.27±0.20
0.125	0.24±0.07

IV. CONCLUSION

As the present scattering data show an evident exponential kinetic response to magnetic field, another interpretation may be possible in terms of the slow motion of a domain wall induced by a symmetry breaking field. In such a model the Bloch wall moves by flipping individual spins, namely TMV particles in the present case; therefore the time constant obtained should relate to individual TMV particles. Under weak magnetic field the domains oriented along the field grow by a smooth motion of the domain walls, and this process is reversible. Under strong magnetic field this process becomes irreversible due to the presence of a defect such as a kind of impurity, and begins to show a hysteresis. This model may be more standard and cannot be ruled out, but it seems not to be enough to explain the order of the experimental values. Owing to a use of a permanent magnet and to a limitation of experimental settings, we did not directly observe the decay process in zero field; however, by an analogy with the superparamagnetic model we can de-

scribe qualitatively the present experimental result that the application of magnetic field on the TMV lyotropic nematic liquid crystals induced the growth of a large nematic domain by an orientation of microdomains comparable to one magnetic coherence length. In a nematic liquid crystal order the application of magnetic field may effectively induce a higher long-range orientational fluctuation relating to magnetic coherency at some critical condition.

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