# Diffusion Process of a Liquid Crystal Probed by the Transient Grating Method

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Translational diffusion of MBBA (*N*-(4-methoxybenzylidene)-4-*n*-butylaniline) in the nematic and isotropic phases is investigated by the transient grating (TG) method. The origin of the TG signal due to the population grating is attributed to the spatial variation of the order parameter and, as a result, the time dependence of the signal reflects the diffusion of the cis form of MBBA, not of the trans form. In the nematic phase, the diffusion constant parallel to the director orientation, $D_{\|}$, is always larger than the perpendicular one, $D_{\perp}$. The obtained values are 2.2—2.5 times larger than previously reported ones measured by using a photosensitive probe molecule in the liquid crystal. The anomaly previously reported near the nematic–isotropic phase transition temperature is not observed, and the diffusion constant in the isotropic phase is close to the average value of the both components, $1/3(D_{\|}+2D_{\perp})$. The experimental values are also compared with the ones calculated from two theoretical expressions by Franklin, and Chu and Moroi.

A translational diffusion constant ($D$) is one of the important parameters for elucidating the dynamic properties of liquid crystals. Numerous studies have been made by employing various methods, such as dye tracer,[1] NMR,[2] and neutron scattering methods.[3] However different values have been obtained depending on which methods and what probe molecules were used for the measurements. One of the convenient, less time consuming and accurate methods to measure $D$ is the transient grating (TG) method. In this method, spatially modulated concentration of chemical species is created by an optical interference pattern and the diffusion processes of these species are monitored as the temporal dependence of the TG signal. Because of various advantages of this method, it has been applied to a variety of systems, such as short-lived radicals[4] and ions,[5] dye molecules in polymer solutions,[6] in polymer glasses,[7] in a gel,[8] in a organic solvent,[9] and in a supercritical fluid.[10]

The TG method was first applied to the liquid crystal by Hervet et al.[11] They measured binary diffusion of Methyl Red (MR) in MBBA (*N*-(4-methoxybenzylidene)-4-*n*-butylaniline). In the nematic phase, by choosing the direction of the grating wave vector against the director of the liquid crystal, an anisotropic diffusion constant could be obtained and they found that the diffusion constant parallel to the director ($D_{\|}$) is larger than the perpendicular one ($D_{\perp}$). Systematic studies of the binary diffusion processes of MR in various liquid crystals were performed by Takezoe, Fukuda, and co-workers.[12] They suggested that the binary diffusion constant might be nearly identical with the self diffusion constant because of similar shapes and sizes of MR to those of the liquid crystal molecules. Later Urbach et al.[13] investigated the self diffusion of MBBA and the binary diffusion of MR in MBBA at room temperature. They obtained diffusion constants different from those of binary diffusion and suggested that the interaction between the probe molecule and the liquid crystal has a large influence on the diffusion process.

Even after a series of these works, there have been two unresolved questions which we would like to answer based on the results of the TG measurement. First, the reported TG signal due to the mass diffusion always decayed single exponentially. However, according to the theoretical analysis of the TG signal, which will be presented in a latter section, the temporal profile of the TG signal of binary system (MR/liquid crystal) should be expressed by a sum of two exponential functions whose lifetimes are determined by the diffusion of two photoisomers. In the previous works they considered only one component of the diffusion constants to analyze the TG signal, which means that they assumed $D$'s of the cis and trans forms of MR are equal. However the two isomers have quite different shapes and sizes, so that their assumption seems to be rather unrealistic. Furthermore, they found a discontinuity in $D$ near the nematic–isotropic phase-transition temperature. This discontinuity is difficult to be explained with molecular dynamic theories of liquid crystals.

In this paper, we study the self diffusion constant of MBBA at various temperatures by the TG method with the photoexcitation of MBBA itself and compare our results with those obtained by the same method using MR as a probe molecule. The origin of the TG signal and the difference of the self and binary diffusion constants, particularly near the phase-transition temperature between the nematic and isotropic phases, are discussed. We also compare our results with those calculated from two different theoretical expressions by Franklin, and Chu and Moroi.

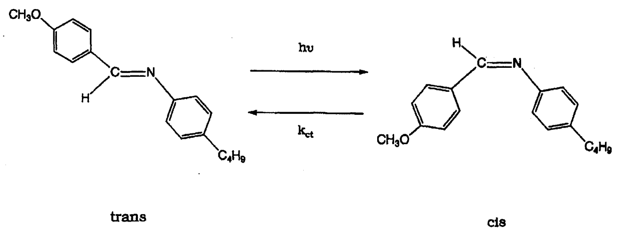
## Experimental

The experimental setup was described in detail previously.[14)] Briefly, the laser beam from an excimer laser pumped dye laser (Lumonics Hyper 400, Lumonics Hyper Dye 300, energy≈10 μJ) was split into two with a beam splitter and intersected inside a sample to produce a transient grating. The excitation wavelength was 390 nm which is on a long wavelength tail of the absorption spectrum of MBBA. Due to the small absorbance, MBBA was excited nearly uniformly across the sample thickness. The repetition rate of the excitation pulse was 3—4 Hz and its pulse width was ca. 20 ns. A He–Ne laser (632.8 nm; random polarization) was brought into the crossing region at the Bragg condition for probing the grating. The diffracted signal was detected by a photomultiplier (Hamamatsu R928) and averaged by a digital oscilloscope (Tektronix 2430A) and a microcomputer. By choosing the direction of the grating wave vector parallel or perpendicular to the director, $D_{\parallel}$ and $D_{\perp}$ were determined. The fringe spacing $\Lambda$ was calibrated from the decay of the thermal grating signal of benzene containing a small amount of MR ($D_{th}=1.1\times10^{-7}$ m$^2$ s$^{-1}$).[9)] The sample was temperature-controlled by a heated aluminum holder. The temperature was measured by a copper–constantan thermocoupler. The fluctuation of the temperature was within ±0.2 K.

MBBA was purchased from Tokyo Kasei Co. and used without further purification.. The nematic–isotropic transition temperature was 46.5 °C. For the measurement in the nematic phase, the sample was sandwiched between two glass plates. These plates were coated with a thin film of poly(vinyl alcohol) and rubbed unidirectionally back and forth to achieve a homogeneous alignment. The sample thickness was 100 μm. For the measurement in the isotropic phase, the sample was contained in a 1 mm-path quartz cell to achieve a good $S/N$ ratio because the TG signal was weaker compared with that in the nematic phase.

## Analysis

The principle for the measurement of the self diffusion constant is similar to that of the binary diffusion of MR in liquid crystal.[12)] Here we briefly describe the method. Two laser beams are crossed in a sample to produce an optical interference pattern. Due to the azo linkage of MBBA, the photoexcitation of this molecule causes isomerization from the cis form to the trans form within the excitation pulse width and the cis form gradually returns back to the trans form by the thermal process (Scheme 1). Hence, the interference pattern that induces the isomerization creates periodic changes of the refractive index ($\delta n$) and the absorption coefficient ($\delta k$). In this case, we can neglect the contribution of $\delta k$ because the peaks of the absorption spectra of cis and trans MBBA are located at shorter wavelengths than that of the He–Ne laser. Hereafter only the contribution of the refractive index is considered. Not only the concentration changes of the cis and trans forms of the molecule (population grating) but also the thermal expansion of the medium contributes to $\delta n$. This thermal component (thermal grating) always appears in the TG signal because heat is generated by the nonradiative relaxation of the photoexcited state of the molecule.



Scheme 1. Molecular structures of cis and trans MBBA.

These spatial modulations are smeared out by the thermal and mass diffusion processes. The time dependences of the TG signal are governed by the thermal and mass diffusion equations including the back transfer process from the cis form to the trans form. By solving the diffusion equations combined with a coupled wave theory in optics,[15)] the time dependence of the TG signal in the weak diffraction limit and the thick grating condition is given by[9)]

$$I_{TG} = \alpha\{\delta n_{th}\exp(-D_{th}q^2t) + \delta n_1\exp(-D_tq^2t) + \delta n_2\exp[-(D_cq^2t+k_{ct})t]\}^2, \tag{2}$$

where $\alpha$ is a proportional constant that depends on the excitation and probe laser intensities as well as the experimental configuration, $D_{th}$ the thermal diffusion constant, $D_t$ and $D_c$, respectively, the mass diffusion constants of the trans and cis forms of MBBA, and $q$ the grating wave vector which is given by

$$q = \frac{2\pi}{\Lambda}. \tag{3}$$

$\Lambda$ is the fringe spacing which is related to the wavelength of the excitation laser ($\lambda_0$) and the crossing angle ($\theta$) by

$$\Lambda = \frac{\lambda_0}{2\sin\left(\frac{\theta}{2}\right)}. \tag{4}$$

$\delta n_{th}$ is the refractive index change due to the thermal expansion. $\delta n_1$ and $\delta n_2$ are given by

$$\delta n_1 = -[\Delta c]\delta n_t\frac{D_cq^2 - D_tq^2}{D_cq^2 - D_tq^2 + k_{ct}}, \tag{5}$$

and

$$\delta n_2 = [\Delta c](\delta n_c - \delta n_t\frac{k_{ct}}{D_cq^2 - D_tq^2 + k_{ct}}), \tag{6}$$

where subscripts t and c are the trans and cis forms, respectively and $[\Delta c]$ is the concentration change of the cis form created by the photoexcitation. $\delta n_t$ and $\delta n_c$ are the refractive index changes due to the depletion of the trans form and the creation of the cis form, respectively. Since $D_{th}$ and $D_{c(t)}$ are different each other by 2—3 orders of magnitude, both contributions can be easily separated. After the complete decay of the thermal grating signal, the square root of the diffracted intensity is given by

$$\sqrt{I_{\mathrm{TG}}(t)} \propto \delta n_1 \exp\left(-D_{\mathrm{t}} q^2 t\right) + \delta n_2 \exp\left\{-(D_{\mathrm{c}} q^2 + k_{\mathrm{ct}})t\right\} \quad (7)$$

Since absorption spectra are generally just shifted by the trans-cis isomerization, the magnitude of $\delta n_1$ and $\delta n_2$ should not be different dramatically.[9] Therefore, if the diffusion constants of the cis and trans forms of MR in liquid crystal are different each other, the TG signal is expected to decay biexponentially.

## Results and Discussion

**Origin of the TG Signal.** First we should identify the origin of the TG signal. Otherwise it is impossible to discuss the quantity we measure by this technique. A typical TG signal of MBA is shown in Fig. 1. After the thermal grating decays in the microsecond time scale, the signal due to the population grating is observed. As clearly seen from the log $I_{\mathrm{TG}}{}^{1/2}$ vs. $t$ plot, the population grating can be fitted by a single exponential function almost perfectly within our experimental uncertainty (Fig. 1b). This observation is consistent with the previously reported TG signal of MR in MBBA[12] and we also confirmed that the TG signal after the photoexcitation of MR in MBBA gives a single exponential decay.

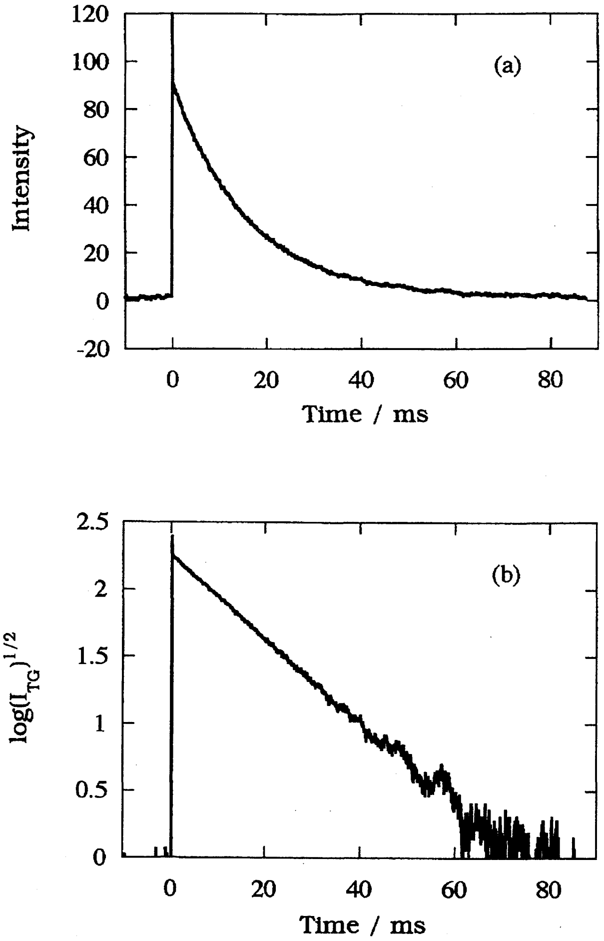


Fig. 1. (a) A typical time profile of the TG signal of MBBA at $q^2 = 8.3 \times 10^{11}$ m$^{-2}$ and 299 K. (b) Log$(I_{\mathrm{TG}})^{1/2}$ vs. $t$ plot of the TG signal due to the population grating.

If the origin of the TG signal is determined by only the optical properties of the cis and trans isomers of MR, the decay should show a biexponential form (Eq. 6). (Since the back transfer rate $k_{\mathrm{ct}}$ is of the order of a second, we can neglect the contribution in this time scale. This point will be discussed later.) But the results show that the decay can be expressed by a single exponential function, as shown in Fig. 1.[12,13] In order to explain the discrepancy, the simplest way is to assume that the cis form diffuses at about the same speed as the trans form. Under this condition, Eq. 6 reduces to

$$\sqrt{I_{\mathrm{TG}}(t)} \propto \exp\left\{-(D_{\mathrm{c}} q^2 + k_{\mathrm{ct}})t\right\}. \quad (8)$$

This situation actually found in nonviscous simple liquids. However in an anisotropic medium like the nematic phase of the liquid crystal, the diffusion is sensitive to the molecular shape and its environment. Indeed in many cases, $D_{\parallel}$ is different from $D_{\perp}$. Moreover, Terazima et al.[9] reported that even in normal liquids such as alcohols and aldehyde solutions, the square root of the TG signal slightly deviates from a single exponential decay and it was attributed to the different $D$ of the cis and trans forms. Therefore, it is very unlikely that $D_{\mathrm{c}}$ is nearly equal to $D_{\mathrm{t}}$ to give the single exponential decay in the range of more than two orders of magnitude in the case of a well-aligned medium of rod-like molecules such as the liquid crystal. We must seek another explanation for the decay of the TG signal. Here we propose the following model for the appearance of the TG signal to explain the single exponential decays.

When the cis form of MBBA is created in the bright region of the grating, the order parameter, which is defined by $S = 1/2\langle 3\cos^2\theta - 1\rangle$, in the bright region of the grating is changed because a small change of the molecular structure greatly influences the alignment. Therefore this photoisomerization causes the modulation of the order parameter and it leads the modulation of the refractive index because of the anisotropic polarizability of MBBA, in other words, the TG is created as a periodic change of the order parameter. This situation is schematically shown in Fig. 2

Since the TG signal of this component appears within ca. 100 μs after the photoexcitation of MBBA, the change of the order parameter in the presence of *cis*-MBBA should be sufficiently fast. Therefore, this grating disappears by the diffusion of the cis form. On the basis of these considerations, the time dependence of the TG signal reflects only the diffusion process of the cis form. Under this circumstance, the decay of the TG signal is expected to be a single exponential form.

The above assumption is supported by the fact that

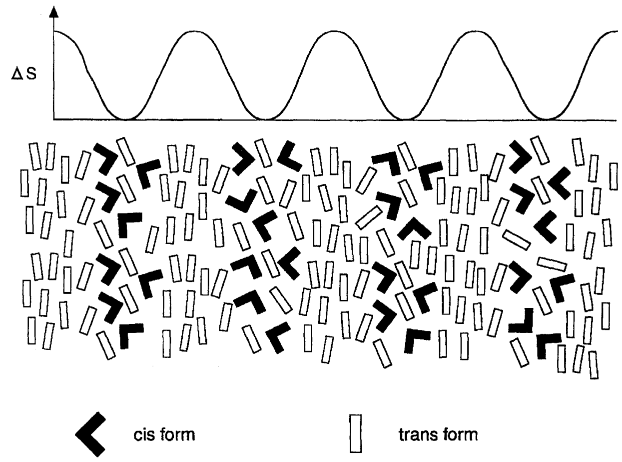


Fig. 2. Schematic representation of the spatial variation of the order parameter due to the creation of the cis form. This grating disappears by the diffusion of the cis form. $\Delta S$ is the variation of the order parameter.

the radiation of UV light induces the phase transition between the nematic and isotropic phases in some azobenzene-doped liquid crystal systems.[16] Furthermore, to confirm this interpretation, we compare the TG signal intensities of the homogenously aligned and randomly oriented samples. If the TG signal comes from the periodic disturbance of the spatial alignment of the liquid crystal, the signal intensity should be very weak for the randomly oriented sample. We prepare the randomly oriented sample which is sandwiched between two untreated glass plates. The domain structure of the sample is examined by the polarizing optical microscope to check the random alignment. The intensity of the TG signal of this sample (A) is compared with that of the sample with the homogeneous alignment (B) under the same experimental conditions (Fig. 3). We found that the intensity of (A) is much weaker than that of (B). This result is what we expect from our model because, for the sample with the random alignment, the change of the order parameter by the creation of the cis form must be quite small. Therefore we conclude that the origin of the TG signal comes mainly from the grating due to the variation of the order parameter.

The change of the order parameter is also created by the heat releasing process (nonradiative relaxation of the photoexcited state) because the order parameter also depends on the temperature. To investigate this effect, we try to observe the appearance of the population grating component after the photoexcitation of 5CB (4′-pentyl-4-cyanobiphenyl) which does not isomerize in the excited state. However, after the photoexcitation of 5CB at 340 nm, only the thermal grating component is observed and there is no trace of the population grating signal. Therefore we find that the change of the order parameter by rising the temperature can be negligible, probably because the temperature rise under our experimental conditions is very small (ca. 0.1 K) and also because the thermal diffusion is much faster than the mass diffusion time.

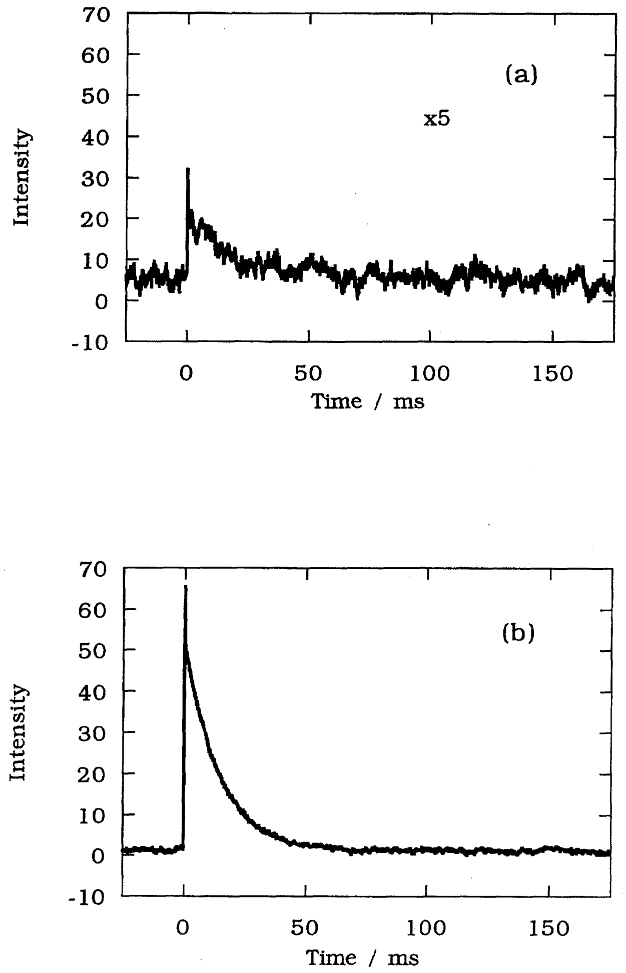


Fig. 3. Observed TG signal after the photoexcitation of MBBA of the random alignment (a) and the homogeneous alignment (b).

Moreover, we observe the diffraction efficiency increases divergently as the temperature is approached to the phase-transition temperature from the nematic phase region and it drops suddenly by more than one order magnitude in the isotropic phase. The same behavior was observed in the case of the binary diffusion of MR in MBBA.[12] Odulov et al.[17] have performed the self diffraction experiment of MBBA. They also observed an anomalous increase in the diffraction efficiency near the phase-transition temperature and interpreted the results by a photostimulated change of the phase-transition temperature. They suggested that the photoisomerization of MBBA caused the change of the order parameter and it led to the shift of the phase-transition temperature. The fluctuation of the order parameter becomes larger as the temperature approaches to the phase transition, so that the diffraction efficiency increases divergently. This explanation is consistent with our interpretation that the variation of the order parameter is the cause of the TG signal.

**Temperature Dependence of the Diffusion Constant.** Based on the procedure described in the section of the analysis and the interpretation in the previous section, we conclude that the diffusion constant of the cis form of MBBA can be determined from the measurement of the decay of the population grating at various fringe spacings. The decay rate is plotted against $q^2$ in Fig. 4. For both of the parallel and perpendicular components, the decay rates show good linear relations with $q^2$. From the slopes of these plots, $D_{\parallel}$ and $D_{\perp}$ are determined. The intercept with the ordinate is very small, which means that $k_{ct}$ is negligible in Eq. 7. Using the above fact, we can determine the diffusion constant from the single data point at a certain $q$-value by the relation of $D=k/q^2$.

The temperature dependence of the diffusion constant determined in this way is shown in Fig. 5. It is of the Arrhenius type

$$D = D_0 \exp\left(-\frac{E}{RT}\right), \tag{9}$$

where $E$ is the activation energy, $D_0$ is the preexponential factor, and $R$ is the gas constant. The diffusion constant parallel to the director ($D_{\parallel}$) is always larger than that perpendicular to the director ($D_{\perp}$). $E$ and $D_0$ are determined by the least-squares fitting method and shown in Table 1.

At room temperature (22 °C), both $D_{\parallel}$ and $D_{\perp}$ are in good agreement with the values obtained by Urbach et al.[13] However, both self diffusion constants are always 2.2—2.5 times larger than the binary ones in the nematic phase obtained by Hara et al. using MR as a probe molecule.[12] In the isotropic phase, the self diffusion constant $D_{\text{iso}}$ is nearly identical with the binary one. This suggests that there exists a strong interaction between MR and the liquid crystal at all temperatures in the nematic phase. In contrast with the diffusion constants, our obtained activation energies are almost consistent with those for the binary diffusion.

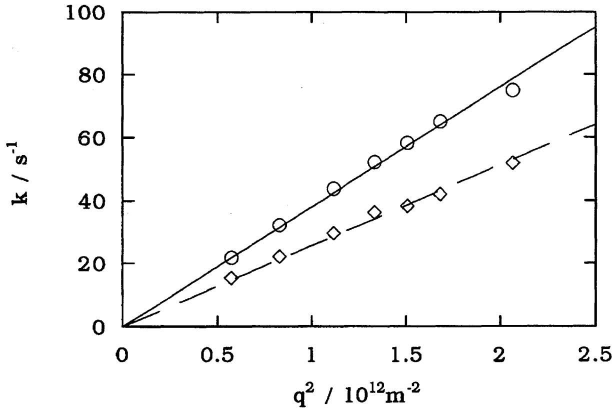


Fig. 4. Plot of the decay rate constants of the TG signal under the parallel (○) and perpendicular (◇) conditions against $q^2$.

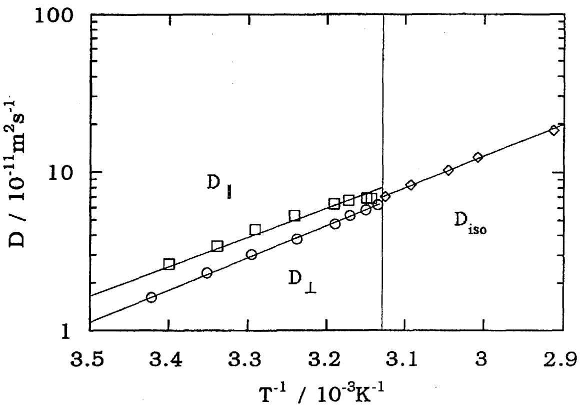


Fig. 5. Temperature dependence of the self diffusion constants of MBBA.

Near the phase transition between the nematic and isotropic phases, the self diffusion data shows that $D_{\text{iso}}$ is nearly equal to $1/3(D_{\parallel}+2D_{\perp})$. This observation is sharply in contrast to the results of the binary diffusion of MR, which shows that there is an anomalously discontinuous jump between them. Our observation is reasonable in view of the dynamics of the liquid crystal because the diffusion in the isotropic phase can be regarded as the average process of the anisotropic diffusion in the nematic phase.

**Difference of *D* between the Self and Binary Diffusions in the Nematic Phase.** In this section, the difference between $D$ obtained in this work and $D$ determined by the MR probe experiment previously in the nematic phase is explained based on the interpretation described in the previous section. In the case of the binary diffusion, the creation of the cis form of MR causes the periodic modulation of the order parameter to produce the transient grating. This grating disappears due to the diffusion of the cis form of MR. This suggests that the diffusing molecule which is monitored

Table 1. The Preexponential Factors and the Activation Energies of the Diffusion Constants of MBBA and MR in MBBA (Ref. 12)

| | Preexponential factor | | | Activation energy | | |
|---|---|---|---|---|---|---|
| | m$^2$ s$^{-1}$ | | | kJ mol$^{-1}$ | | |
| | $D_{\parallel 0}$ | $D_{\perp 0}$ | $D_{\text{iso}0}$ | $E_{\parallel}$ | $E_{\perp}$ | $E_{\text{iso}}$ |
| MBBA | $1.1\times10^{-5}$ | $3.5\times10^{-5}$ | $9.5\times10^{-5}$ | 32 | 35 | 38 |
| MR in MBBA | $5.2\times10^{-7}$ | $1.3\times10^{-5}$ | $9.2\times10^{-4}$ | 26 | 35 | 44 |

as the TG signal is not an isolated MR itself but MR which is affected by the strong interaction between MR and the liquid crystalline host. Therefore it seems to be reasonable that the binary diffusion constant is expected to be different from the self one. However in the isotropic phase, the origin of the population grating is attributed to the difference of the refractive indices between the cis and trans species. Thus the diffusion process is mainly governed by the parameters, such as the radius of the molecule, the viscosity of the solution, and temperature. In this case, since MR and MBBA have similar sizes and shapes, the binary diffusion constant is considered to be similar to the self one. Therefore, we can understand an anomalous behavior of $D$ at the phase-transition temperature in the case of the binary diffusion. In the nematic phase, the interaction between the probe molecule and the liquid crystalline host makes the diffusion of the probe molecule slower than that of the liquid crystal itself and in the isotropic phase, the dynamics is governed by the motion of the free probe molecule. The difference in $D$ between these phases may cause the unexpected discontinuous jump in the $\log D$ vs. $1/T$ plot, which has been observed before.

**Comparison with the Theory.** Franklin[18] has developed a theory of the diffusion in the nematic phase based on the Kirkwood–Risemann theory of the mass diffusion in polymer solutions. He obtained the following expression for the diffusion constants.

$$D_\parallel = kT[\frac{1}{\mu f} + \frac{2+S}{6\pi\mu^2\Phi\alpha_\parallel}], \tag{10}$$

and

$$D_\perp = kT[\frac{1}{\mu f} + \frac{5-S}{12\pi\mu^2\Phi\alpha_\perp}], \tag{11}$$

where k is Boltzmann's constant, $f$ is the scalar friction constant, $S$ is the order parameter, $\mu$ and $\Phi$ can be obtained by the molecular structure and bond length (See Ref. 13). $\alpha_\parallel$ and $\alpha_\perp$ are given by

$$\alpha_\parallel = 4\alpha_1 + \frac{1}{2}\alpha_2 + \frac{11}{2}\alpha_3 + 2\alpha_4 + 6\alpha_5, \tag{12}$$

$$\alpha_\perp = -\frac{13}{2}\alpha_2 + \frac{7}{4}\alpha_3 + 6\alpha_4 - \frac{3}{2}\alpha_5 \tag{13}$$

where $\alpha_1$—$\alpha_5$ are the Leslie coefficients. Since $f$ cannot be calculated directly, we compare the difference between $D_\parallel$ and $D_\perp$ with that of the experimental values. Using the reported values,[19] $D_\parallel - D_\perp$ is plotted against the temperature in Fig. 6. The calculated values are in poor agreement with the experimental ones except near the phase-transition temperature $T_{NI}$.

Chu and Moroi[20] derived another expression for the diffusion constant by using a properly parameterized form of the velocity autocorrelation function. The two components $D_\parallel$ and $D_\perp$ are given by

$$D_\parallel = \overline{D}[1 + \frac{2(1-\gamma)S}{2\gamma+1}], \tag{14}$$

and

$$D_\perp = \overline{D}[1 - \frac{(1-\gamma)S}{2\gamma+1}], \tag{15}$$

where $\gamma=\pi d/4L$ is a structural factor ($\alpha$: the diameter of the molecule, $L$: the length of the molecule), $S$ is the order parameter and $D$ is the average diffusion constant which is given by

$$\overline{D} = \frac{1}{3}(D_\parallel + 2D_\perp). \tag{16}$$

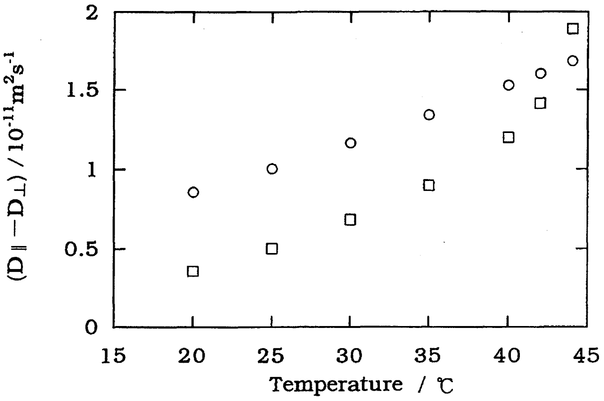


Fig. 6. Comparison of $D_\parallel - D_\perp$ calculated from Franklin theory (□) and the experimental ones (○) at various temperatures. Experimental values are estimated by Eq. 8 using the fitted values of $D_0$ and $E$.

To compare these theoretical expressions to the experimental values, it is convenient to use the ratio $D_\parallel/D_\perp$ because of the cancellation of $D$. For MBBA $L$=19 Å and $d$=5 Å and therefore $\gamma$=0.21 is obtained. The ratio $D_\parallel/D_\perp$ is plotted against the temperature in Fig. 7. The theoretical value is always larger than the experimental one. The Chu and Moroi's equation does not provide a good expression for our results. One of reasons for the disagreement between the theoretically calculated values and the experimentally obtained ones may be that $D$ measured by the TG signal is the 'binary' diffusion of the cis forms of MBBA in the trans

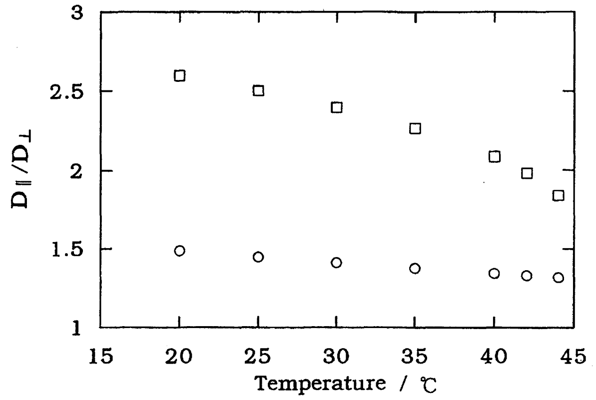


Fig. 7. Comparison of $D_\parallel/D_\perp$ calculated from Chu–Moroi theory (□) and the experimental ones (○) at various temperatures. Experimental values are estimated by Eq. 8 using the fitted values of $D_0$ and $E$.

forms, while $D$ calculated by these theories should be that of the trans form.

## Conclusion

The self diffusion constants of MBBA are measured at various temperatures by the transient grating (TG) method. Since MBBA has two isomers, cis and trans forms, we expect to observe a biexponential decay in the time dependence of the TG signal. Contrary to this expectation, the observed TG signal can be fitted by a single exponential function almost perfectly. We interpret this result by assuming that the population grating signal appears due to the spatial variation of the order parameter in the presence of the cis form. One the basis of this interpretation, the diffusion coefficient determined by the TG method should be $D$ of cis form. In the nematic phase, the diffusion constant parallel to the director orientation, $D_{\|}$, is always larger than the perpendicular one, $D_{\perp}$. The temperature dependences of the diffusion constants follow the Arrhenius-type equation. Compared with the binary diffusion constants of MR in MBBA measured by the same method, both parallel and perpendicular components of the self diffusion constants are 2.2—2.5 times larger than those of binary ones in the whole temperature range, while in the isotropic phase, self diffusion constants are almost the same as the binary ones. This indicates that there exists a strong interaction between the probe molecule and the liquid crystal. The previously observed discontinuous anomalous jump of $D$ at $T_{\mathrm{NI}}$ in the case of the binary diffusion is not observed. $D_{\mathrm{iso}}$ has the value between $D_{\|}$ and $D_{\perp}$ near the phase-transition temperature. We compare the experimental values with the theoretical calculated ones. Both Franklin theory and Chu and Moroi theory cannot explain our results.

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### References

1) F. Rondelez, *Solid State Commun.*, **14**, 815 (1974); H. Hakemi and M. M. Labes, *J. Chem. Phys.*, **61**, 4020 (1974).

2) G. J. Krüger, *Phys. Rep.*, **82**, 229 (1982), and references therein.

3) V. Dimic, L. Barbič, and R. Blinc, *Phys. Status Solidi B*, **54**, 121 (1972).

4) M. Terazima and N. Hirota, *J. Chem. Phys.*, **98**, 6257 (1993); M. Terazima, K. Okamoto, and N. Hirota, *J. Phys. Chem.*, **97**, 13387 (1993).

5) M. Terazima, T. Okazaki, and N. Hirota, *J. Photochem. Photobiol.*, in press.

6) C. H. Wang and J. L. Xia, *J. Phys. Chem.*, **96**, 190 (1992); J. A. Lee and T. P. Lodge, *J. Phys. Chem.*, **91**, 5546 (1987); T. P. Lodge, J. A. Lee, and T. S. Frick, *J. Polym. Sci., Part B*, **28**, 2607 (1990).

7) S. S. Gong, D. Christensen, J. Zhang, and C. H. Wang, *J. Phys. Chem.*, **91**, 4505 (1987); J. Zhang, B. K. Yu, and C. H. Wang, *J. Phys. Chem.*, **90**, 1299 (1986).

8) J. A. Wesson, H. Takezoe, H. Yu, and S. P. Chen, *J. Appl. Phys.*, **53**, 6513 (1982).

9) M. Terazima, K. Okamoto, and N. Hirota, *J. Phys. Chem.*, **97**, 5188 (1993); M. Terazima, K. Okamoto, and N. Hirota, *Laser Chem.*, **13**, 169 (1994).

10) Y. Kimura, D. Kanda, M. Terazima, and N. Hirota, *Ber. Bunsenges. Phys. Chem.*, in press.

11) H. Hervet, W. Urbach, and F. Rondelez, *J. Chem. Phys.*, **68**, 2725 (1978).

12) H. Takezoe, S. Ichikawa, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.*, **23**, L78 (1984); M. Hara, S. Ichikawa, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **23**, 1420 (1984); H. Takezoe, M. Hara, S. Ichikawa, and A. Fukuda, *Mol. Cryst. Liq. Cryst.*, **122**, 169 (1985); M. Hara, H. Tenmei, S. Ichikawa, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **24**, L777 (1985); M. Hara, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **25**, 1756 (1986); T. Nishikawa, J. Minabe, H. Takezoe, and A. Fukuda, *Mol. Cryst. Liq. Cryst.*, **231**, 153 (1993).

13) W. Urbach, H. Hervet, and F. Rondelez, *J. Chem. Phys.*, **83**, 1877 (1985).

14) M. Terazima and N. Hirota, *J. Chem. Phys.*, **95**, 6490 (1991).

15) H. Kogelnik, *Bell Syst. Tech. J.*, **48**, 2909 (1969).

16) S. Tazuke, S. Kurihara, and T. Ikeda, *Chem. Lett.*, **1987**, 911.

17) S. G. Odulov, Yu. A. Reznikov, M. S. Soskin, and A. I. Khizhnyak, *Sov. Phys. JETP* (*Engl. Transl.*), **58**, 1154 (1983).

18) W. Franklin, *Phys. Rev. Sect. A.*, **11**, 2156 (1975).

19) S. T. Wu and C. S. Wu, *Phys. Rev. Sect. A*, **42**, 2219 (1990).

20) K. S. Chu and D. S. Moroi, *J. Phys.* (*Paris*) *Colloq.*, **36**, 99 (1975).