

# Steady-State and Time-Resolved Fluorescence Analysis for a Cyanobiphenyl Mesogen in Polymer-Dispersed Liquid Crystal Films

Shinji Kato,<sup>†</sup> Feng-Qi Chen,<sup>†</sup> Tetsuya Shimada,<sup>‡</sup> Tomoyuki Yatsushashi,<sup>‡,§</sup> Haruo Inoue,<sup>‡</sup> and Chyongjin Pac<sup>\*,†</sup>

Kawamura Institute of Chemical Research, 631 Sakado, Sakura, Chiba 285-0078, Japan, and Department of Applied Chemistry, Graduate Course of Engineering, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan

Received: October 18, 1999; In Final Form: January 3, 2000

Steady-state and time-resolved fluorescence behavior of 4-cyano-4'-pentylbiphenyl (5CB) in polymer-dispersed liquid crystal (PDLC) films sandwiched between two quartz substrates was characterized by the *surface-limited excitation* (SLE) and *through-film excitation* (TFE) methods, which were used to discriminate the emissions from the interface layer with the substrate and from the interior domain. Although PDLC films showed both the monomer and excimer emissions of 5CB, SLE gave a substantially greater contribution of the former in the fluorescence than TFE. By contrast, a neat nematic film of 5CB showed exclusively the excimer emission independently of the excitation methods. Time-resolved analysis of the excimer emission from PDLC films revealed double-exponential decay profiles with shorter-lived (1.5–1.8 ns) and longer-lived (12–17 ns) components, in which the former is dominant for the excimer emission obtained by SLE, while the latter takes a major part for that obtained by TFE. By contrast, the excimer emission from a neat nematic film of 5CB showed a single-exponential decay with a  $\sim 17$  ns lifetime independently of the excitation methods. The unique fluorescence behavior of the PDLC films has been discussed in terms of different molecular aggregation features of 5CB in the interface layer and in the interior domain.

## Introduction

Heterogeneous composite films of polymer-dispersed liquid crystal (PDLC), which have LC droplets in polymer matrixes, are of considerable current interest in scientific fields as well as for electrooptic applications.<sup>1</sup> The fabrication of PDLC composite films can be conveniently achieved by photopolymerization-induced phase separation of homogeneous LC/pre-polymer mixtures sandwiched between two solid substrates.<sup>2</sup> However, it can be easily predicted that the photopolymerization-induced phase separation should proceed under complex mutual interactions of LC molecules, growing polymer chains, and the substrate surface accompanied by progressive changes in molecular aggregation features of LC. Consequently, LC domains in the resultant composite films should have microscopic inhomogeneities in molecular alignments and mobilities, especially in interface layers with substrates and with polymer matrixes. Unique molecular features in the interface layers should exert important effects on the electrooptic functions of PDLC thin films. Nevertheless, little has been investigated on the physicochemical behavior of LC molecules in microscopic regions of PDLC.

We have been investigating the fluorescence behavior of 4-cyano-4'-pentylbiphenyl (5CB) in PDLC films in order to explore microscopic features of 5CB. In a previous paper, it has been demonstrated that the *surface-limited excitation* (SLE) and the *through-film excitation* (TFE) methods provide a

potentially useful and convenient diagnosis for the evaluation of molecular alignments and/or mobilities of 5CB in the interface layer with the substrate surface compared with those in the interior domain.<sup>3</sup> In SLE, PDLC films are excited by the light around the absorption maximum of 5CB ( $\approx 280$  nm) where the optical densities are extremely high to limit the light absorption only within a very thin interface layer ( $\leq 60$  nm), so that the fluorescence emission can occur from this limited layer. The selective excitation of the interface layer was confirmed by a comparative study with a total-internal-reflection (TIR) excitation method<sup>4</sup> using a particular semicylindrical sapphire prism.<sup>3</sup> On the other hand, the TFE method utilizes the excitation light at  $\geq 320$  nm where the optical densities are low ( $< 0.2$ ) enough for the light beam to pass through the film. As the consequence, therefore, one can observe the fluorescence that dominantly comes from the interior domain of the film.

On the basis of the SLE and TFE techniques, we have performed extensive studies on steady-state and time-resolved fluorescence behavior of PDLC films to explore possible unique aggregation features of 5CB molecules in the interface layer with substrate, which might be related with surface anchoring phenomena of LC molecules.<sup>5</sup> In the present investigation, the fluorescence behavior of PDLC films having different LC feeding ratios was carefully characterized and compared with that of a neat thin film of 5CB with no polymer component. We wish to report herein that the fluorescence characteristics of 5CB molecules located in the interface layer of PDLC films are unique, significantly different from those of the typical 5CB nematic phase extensively distributing in the interior bulk.

## Experimental Section

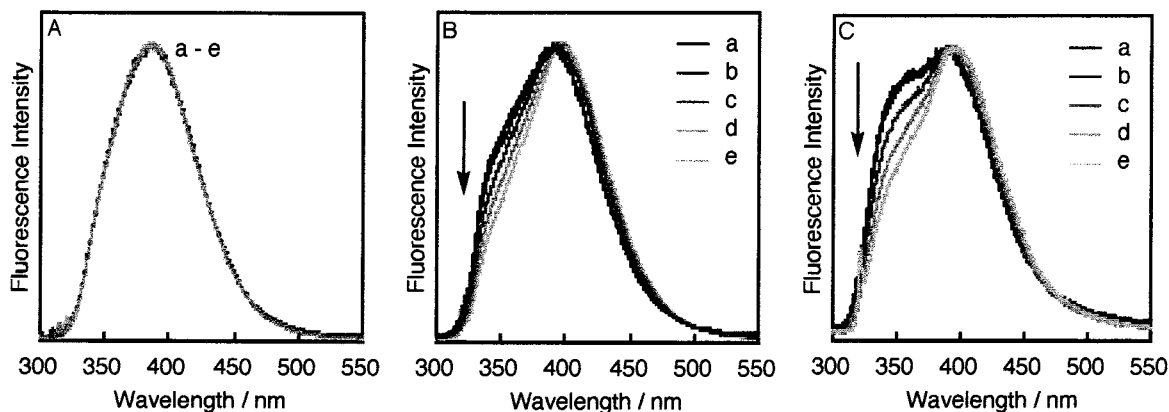
**Materials.** 5CB was donated from Lodic Co. Ltd. and used as-received. The diacrylate monomer (Nippon Kayaku) and the

\* Author to whom correspondence should be addressed. Tel: (+81)43-498-2111. Fax: (+81)43-498-2202. E-mail: j90085@simail.ne.jp.

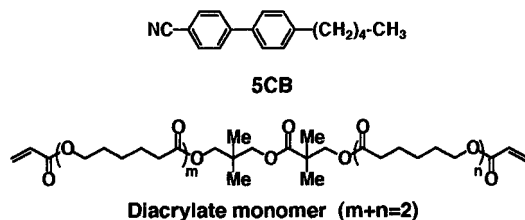
<sup>†</sup> Kawamura Institute of Chemical Research.

<sup>‡</sup> Tokyo Metropolitan University.

<sup>§</sup> Present address: Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan.



**Figure 1.** Normalized fluorescence spectra of (A) neat 5CB film and of PDLC films containing (B) 77 wt % 5CB and (C) 30 wt % 5CB; the films were sandwiched between two quartz substrates with 11  $\mu\text{m}$  thickness and excited at (a) 290 nm, (b) 300 nm, (c) 310 nm, (d) 315 nm, and (e) 320 nm.



photoinitiator (Ciba Geigy Irgacure 184) were purchased and used as-received. Optically flat, nonfluorescent quartz plates ( $25 \times 25 \text{ mm}^2$ , 1.0 mm thick) purchased from Eikohsha Co. Ltd. (Osaka, Japan) were washed with detergent (Merck Extran MA02) solution and then several times with deionized water in an ultrasonicator bath prior to use.

**Preparation of PDLC Films.** A homogeneous mixture of 5CB, the diacrylate monomer, and the photoinitiator ( $\sim 1 \text{ wt } \%$  of the monomer) was sandwiched between two quartz plates with 11  $\mu\text{m}$  thickness and was photoirradiated at  $\geq 310 \text{ nm}$  through the both sides of the two substrates at  $25^\circ\text{C}$  using a high-pressure mercury arc ( $2.3 \text{ mW cm}^{-2}$  at 366 nm) combined with a neutral glass filter and a cutoff glass filter ( $< 310 \text{ nm}$ ). The feeding ratio of 5CB was fixed at 30 wt % or 77 wt %. For comparison, a 11  $\mu\text{m}$  thick film of neat 5CB with no polymer component was also prepared.

**Fluorescence Measurements.** Steady-state fluorescence spectra were obtained on a Hitachi F-4500 spectrofluorimeter. The PDLC and neat 5CB films sandwiched between two quartz substrates were excited with an angle of  $45^\circ$ , and the fluorescence emitted in a direction orthogonal to the excitation light beam was picked up from the front surface. Details of the measurements are essentially identical with those described in a previous paper.<sup>3</sup>

For fluorescence decay analysis, the fourth harmonic (266 nm, fwhm 30 ps, 5 Hz) of a mode-locked  $\text{Nd}^{3+}$ :YAG laser (EKSPLA-Tokyo Instruments, PL2143B) was used as the light source for SLE, and the decay profiles were monitored by a picosecond fluorescence lifetime measurement system (Hamamatsu C4334 streak scope connected with a CHROMEX 250IS polychromator). Under TFE conditions, on the other hand, the films were excited by the second harmonic of a dye laser (320 nm, fwhm 13 ps, 10 Hz), synchronously pumped by the second harmonic of a mode-locked  $\text{Nd}^{3+}$ :YAG laser (Quantel, Picochrome YG-503C/PTL-10), and time-resolved analysis of the fluorescence was carried out with a streak camera (Hamamatsu C2830 temporal disperser with H2547 fast scan unit). The power densities of the excitation laser pulses were set at  $< 1 \mu\text{J cm}^{-2}$ ,

weak enough to avoid possible multiphoton-induced processes. The decay profiles were monitored at 330 nm for the monomer emission of 5CB and at 450 nm for the 5CB excimer emission.

## Results and Discussion

**Steady-State Measurements.** Excited-singlet 5CB strongly emits the fluorescence at  $\sim 340 \text{ nm}$  with a lifetime of  $\sim 1 \text{ ns}$  in dilute solution, whereas the neat material in either the isotropic or nematic phase exclusively gives the highly emissive excimer whose emission appears at  $\sim 400 \text{ nm}$  with a lifetime of 10–20 ns.<sup>6,7</sup> Figure 1 shows the normalized fluorescence spectra of the neat 5CB and PDLC thin films (77 wt % and 30 wt % 5CB) taken by excitation at 290, 300, 310, 315, and 320 nm. The neat film exclusively gave the excimer emission with no contribution of the monomer fluorescence independently of the excitation wavelengths. In the cases of PDLC films, on the other hand, the monomer emission significantly appeared along with the dominant excimer emission, becoming higher in relative intensity upon excitation at shorter wavelengths.<sup>8</sup>

The excitation-wavelength dependence of the fluorescence spectra for the PDLC films can be reasonably explained in terms of the penetration depth of the excitation light beam. As already mentioned, the excitation light at 290 nm used for SLE should be completely absorbed by 5CB in a very thin interface layer ( $\leq 60 \text{ nm}$ ) to give the fluorescence from this interface layer. On the other hand, the absorbance sharply drops at  $\geq 300 \text{ nm}$  so that the excitation light penetrates into a deeper region of the film at longer wavelengths and, finally, can pass through the film at 320 nm to give the emission dominantly from the interior bulk.<sup>9</sup> It is therefore reasonable to consider that the excimer formation should be less favorable in the interface layer than in the interior bulk. Since the excimer formation should be associated with the nematic phase of 5CB in phase-separated droplets, it is strongly suggested that the nematic phase should be dominant in the interior bulk but is significantly disturbed in the interface layer with the substrate surface.<sup>10,11</sup>

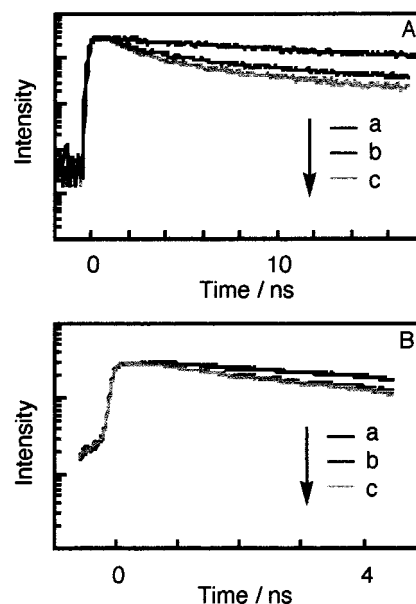
It should be noted that relatively high contributions of the monomer emission in the interface layer of the PDLC films show a sharp contrast to the exclusive appearance of the excimer emission even in the interface layer of the neat film. This clearly indicates that the nematic phase of 5CB is not disturbed solely by interactions of 5CB molecules with the substrate surface. Presumably, the photopolymerization-induced phase separation in the interface layer might proceed under mutual interactions between 5CB molecules, growing polymer chains, and the substrate surface to give unique, complex morphologies of

droplets unlike the phase separation in the interior bulk. Under the presumption, the unique fluorescence behavior in the interface layer of the PDLC films might be attributable to unique molecular aggregations different from the nematic phase. Alternatively, the monomer emission of the PDLC films would come from 5CB molecules dissolved in the polymer matrixes. If this were the case, the stronger monomer emission in the interface layer compared with the interior bulk would require the assumption that the dissolved 5CB in the polymer should be present in greater amount in the interface layer than in the interior bulk. It is, however, more realistic to assume that both of the monomer emissions from the interface layer and from the interior bulk might equally involve the fluorescence of the dissolved 5CB, in part if any. At any rate, the contribution of the fluorescence from the dissolved 5CB should be minor, because the fluorescence dynamic studies again demonstrated unique molecular aggregation features of 5CB in the interface layer (vide infra).

Another interesting observation in Figure 1 is that the contribution of the excimer emission is greater for the 77 wt % 5CB PDLC film than for the 30 wt % 5CB film at each of the excitation wavelengths. This can be easily attributed to different LC domain sizes in the PDLC films. It was recently reported that the LC phase in PDLC films fabricated by photopolymerization at  $\sim 25^\circ\text{C}$  is not continuous even at high LC content ( $\sim 80$  wt %) but forms spherical LC droplets whose sizes are larger at higher feeding ratios of LC component.<sup>12</sup> It is therefore expected that the LC droplet size in the 77 wt % 5CB PDLC film should be larger than that in the 30 wt % 5CB case. Larger-size LC droplets should contain a greater amount of nematic domains but with less contributions of interfaces with the polymer matrixes. This is probably a major reason the excimer emission is more notable for the 77 wt % 5CB PDLC film. In other word, interfacial interactions of 5CB with the polymer matrixes might disturb the nematic phase to give unique molecular aggregation of 5CB.

**Decay Dynamics.** The fluorescence decay analysis for the neat 5CB and PDLC films were performed with the fourth harmonic (266 nm, fwhm 30 ps, 5 Hz) of a mode-locked Nd<sup>3+</sup>:YAG laser for SLE and with the second harmonic of a dye laser (320 nm, fwhm 13 ps, 10 Hz), synchronously pumped by the second harmonic of a mode-locked Nd<sup>3+</sup>:YAG laser for TFE. The monomer emission was analyzed at 330 nm where the excimer emission is negligible and the 5CB excimer emission at 450 nm where the monomer emission has little contribution. The observed time dependences of the emissions for the PDLC films were successfully analyzed on the basis of the triple-exponential function,  $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$ , whereas the excimer emissions from the neat 5CB film exactly follow the double-exponential kinetics (i.e.,  $A_3 = 0$ ).

Typical rise and decay profiles are shown in Figure 2 for the excimer emissions from the neat 5CB and PDLC films excited at 266 nm (SLE) and at 320 nm (TFE). Table 1 summarizes the rise and decay components of the excimer and monomer emissions. The monomer emission showed a major rapid decay ( $<200$  ps) and minor second component of  $\sim 1$  ns and third one of 6.9 ns or 16–17 ns. The first should be due to the excimer formation, corresponding to the 100–200 ps rise of the excimer emission.<sup>7,13,14</sup> The second  $\sim 1$  ns component can be mainly attributed to the decay of excited-singlet 5CB that has occurred without the excimer formation.<sup>13,14</sup> On the other hand, the excited-singlet 5CB regenerated from the long-lived excimer might be responsible for the last decay component of 16–17



**Figure 2.** Decay profiles of 5CB excimer emissions at 450 nm taken by (A) SLE at 266 nm and (B) TFE at 320 nm for (a) neat 5CB film and for PDLC films containing (b) 77 wt % 5CB, and (c) 30 wt % 5CB sandwiched between two quartz substrates.

**TABLE 1: Fluorescence Rise and Decay Components of 5CB in Thin Films<sup>a</sup>**

excitation method	sample	$\lambda_{em}/\text{nm}^b$	$\tau_1/\text{ns}$	$\tau_2/\text{ns}$	$\tau_3/\text{ns}$
SLE	neat 5CB	330	0.05 (0.94)	0.97 (0.03)	16 (0.03)
		450	0.18 (−0.20)		17 (0.80)
	77 wt % 5CB	330	0.12 (0.86)	0.87 (0.13)	6.9 (0.01)
		450	0.20 (−0.26)	1.7 (0.52)	14 (0.22)
	30 wt % 5CB	330	0.12 (0.87)	1.0 (0.12)	6.9 (0.01)
		450	0.17 (−0.37)	1.5 (0.55)	12 (0.08)
TFE	neat 5CB	330	0.10 (0.90)	1.0 (0.09)	17 (0.01)
		450	0.12 (−0.11)		17 (0.89)
	77 wt % 5CB	330	0.08 (0.85)	0.92 (0.10)	17 (0.05)
		450	0.12 (−0.11)	1.5 (0.16)	17 (0.73)
	30 wt % 5CB	330	0.18 (0.78)	0.90 (0.21)	17 (0.01)
		450	0.10 (−0.11)	1.8 (0.19)	17 (0.70)

<sup>a</sup> Values in parentheses are the pre-exponential factors ( $A_1$ ,  $A_2$ , and  $A_3$ ). <sup>b</sup> Emission wavelength to monitor decay profiles.

ns. The very minor component of 6.9 ns was observed only for the emissions under the SLE of the PDLC films, so it might be appropriate to assume the participation of an unknown species in the interface layer of the PDLC films.

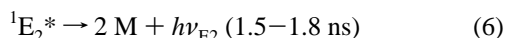
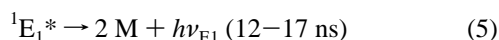
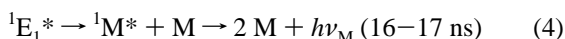
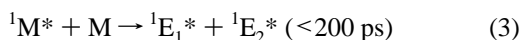
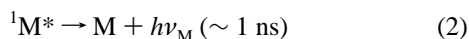
The decay profiles of the excimer emission reveal some interesting features related with molecular aggregations of 5CB. In the case of the PDLC films, it is of particular significance to note that the excimer emission showed double-exponential decays consisting of shorter-lived (1.5–1.8 ns) and longer-lived (12–17 ns) components. This is in sharp contrast to the excimer decay behavior of the neat 5CB film that exactly follows a single-exponential decay kinetics with a 17 ns lifetime. Another prominent observation for the PDLC films is that relative contributions of the shorter-lived and longer-lived excimer components remarkably depend on the excitation wavelengths, i.e., the shorter-lived emission is dominant when excited at 266 nm (SLE), but the longer-lived one takes a major part when excited at 320 nm (TFE). In the case of the neat film, on the other hand, the excimer emission showed no excitation-wavelength dependence at all but the common single-exponential decay of 17 ns.<sup>7</sup>

In general, 5CB and related alkyl- and alkoxy-cyanobiphenyl LCs in the nematic phase exclusively give the excimers of 10–

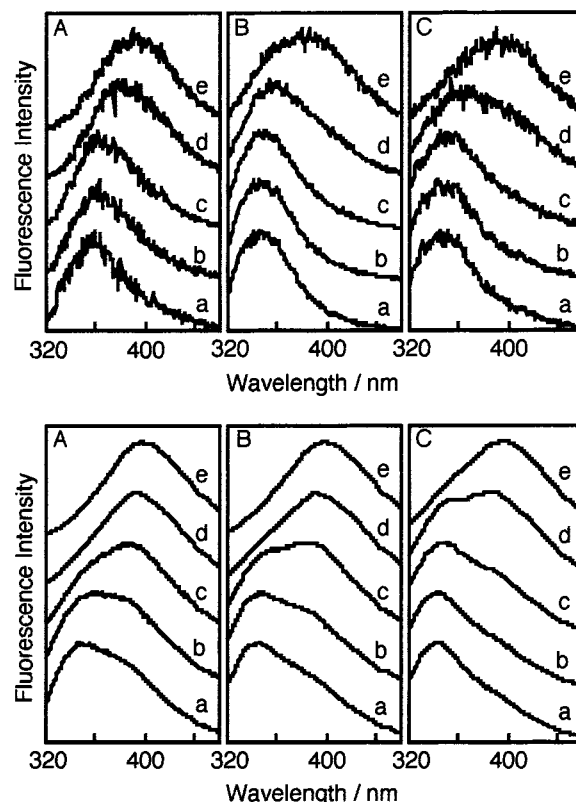


20 ns lifetimes,<sup>7,13–15</sup> which are assumed to take a fully overlapped antiparallel arrangement of the chromophores associated with the molecular alignment in the nematic phase. On the other hand, it was reported that some cyanobiphenyl LCs with longer alkyl chains than 5CB reveal a short-lived decay component (2.6–3.4 ns) in the excimer emission, even to minor extents, though long-lived decay components (14–21 ns) are still dominant.<sup>13</sup> For the short-lived excimer, a partially overlapped arrangement of the chromophores has been proposed by taking into consideration the characteristic molecular alignment of LC molecules in the smectic A phase,<sup>16</sup> while the TICT excited state of the cyanobiphenyl chromophore as a possible candidate for the short-lived emission has been rigorously ruled out by analysis of the fluorescence from an alkylcyanofluorene compound incapable of taking a twisted conformation.<sup>14</sup>

According to these precedents, we attributed the shorter-lived and longer-lived excimer components for the PDLC films to partially overlapped and fully overlapped excimers of 5CB, respectively. In this regard, it should be noted that 5CB does not form the smectic A phase and gives only the long-lived excimer in the isotropic and nematic phases.<sup>7</sup> This is exactly true for the neat 5CB film but apparently contradicts the dominant or significant formation of the *unusual* shorter-lived excimer in the case of PDLC film. A possible interpretation for the short-lived excimer formation in the interface layer can be made by assuming that 5CB molecules take restricted geometries in a specific molecular aggregation different from the nematic phase, probably because of unique microscopic inhomogeneity in the morphology of LC droplets in the interface layer. In the interior domain, on the other hand, nematic LC droplets should be mainly formed, but partial disturbances in molecular association might occur, perhaps at the interface with the polymer matrixes, as suggested by the minor but significant contribution of the shorter-lived excimer. It should be noted that the relative contribution of the short-lived excimer was greater for the 30 wt % 5CB PDLC film than for the 77 wt % 5CB film in both the interface layer and the interior domain, indicating that a greater disturbance of the 5CB aggregation occurs for the former. This molecular picture depicted for the droplets of the PDLC films can reasonably explain the steady-state fluorescence results described above. An equational representation proposed from the fluorescence dynamics is shown below, where M is 5CB, and  $^1M^*$ ,  $^1E_1^*$ , and  $^1E_2^*$  denote the excited-singlet state of 5CB, long-lived excimer, and short-lived excimer, respectively.



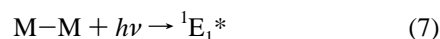
**Time-Resolved Spectra.** Figure 3 shows time-resolved fluorescence spectra in the wavelength range 320–460 nm for the neat 5CB and PDLC films, taken by SLE at 266 nm and by TFE at 320 nm. For all the samples, the monomer emission with the maximum at ~340 nm dominantly appears immediately after the pulse excitation ( $t = 0$ ), followed by time-progressive



**Figure 3.** Time-resolved fluorescence spectra taken by SLE at 266 nm (top) and TFE at 320 nm (bottom) for (A) neat 5CB film, and for PDLC films containing (B) 77 wt % 5CB and (C) 30 wt % 5CB sandwiched between two quartz substrates; the delay times after pulse excitation are (a) 0 ps, (b) 41 ps, (c) 165 ps, (d) 450–550 ps, and (e) 1.46–1.66 ns.

changes to reach common excimer spectra with the maximum at ~400 nm after delay times of 1.46–1.66 ns. The time-dependent spectral changes clearly indicate that the excimer formation is dynamic in nature to occur through a bimolecular process between excited-singlet and ground-state 5CB molecules (eq 3).

It is of significance to note that the intensity of the excimer emission at an early stage depends on the excitation methods as well as on the films. The time-resolved spectra at  $t = 0$  taken by SLE showed negligible contributions of the excimer emission for all the films. In the case of TFE, on the other hand, the excimer emission can be observed at  $t = 0$  even in low intensities to vary from film to film, being maximum with the neat 5CB film but minimum with the PDLC film containing 30 wt % 5CB. The *spontaneous* appearance of the excimer emission at  $t = 0$  was already reported for neat 5CB.<sup>7</sup> It was assumed that 5CB forms a ground-state dimer ( $M-M$ ) in the nematic phase which has a face-to-face chromophore arrangement favorable for the excimer formation without molecular reorientation (eq 7):



According to the precedent, the dimer formation might contribute, at least in part, to the excimer formation in the interior bulk of all the films, but it is certainly unlikely to occur in the interface layer even for the neat 5CB film since the excimer formation occurs exclusively through the bimolecular process (eq 3). Since the preformed dimer might be formed only in the nematic phase,<sup>7</sup> the lack of the excimer emission at  $t = 0$  in the interface layer again indicates that 5CB molecules

should be distributed in a manner different from the nematic molecular alignment. At any rate, however, possible contributions of the presumed dimer to the observed excimer formation should be minor if any.

If the ground-state dimer would have the characteristic absorption at  $>300$  nm, the excitation at  $>300$  nm (TFE) would give the excimer emission more than that at  $<300$  nm (SLE). In a previous work, however, it was demonstrated that the absorption spectra of the PDLC thin films reveal no indication for the possible formation of a discrete dimer having light absorption at  $>300$  nm.<sup>3</sup> It is therefore realistic to understand that the *dimer* is not a discrete species with intermolecular electronic interactions but a particular mobile assembly of 5CB that can give excimer  $E_1$  with least motion upon excitation. In the interface layers, on the other hand, interactions of 5CB molecules with either or both of the substrate surface and polymer wall should give unique molecular aggregations in which 5CB molecules are less aligned and less mobile than in the typical nematic phase. As the consequence, the excimer formation proceeds via the dynamic process (eq 3) with no participation of eq 7 in the interface layers. In the case of the neat film, interactions of 5CB molecules with the substrate surface might not largely disturb the nematic phase but should more or less freeze the molecular motion to disfavor the *dimer* formation. In the case of the PDLC films, complex environments in the interface region of droplets should affect not only the molecular mobilities but also the molecular alignments so that  $E_2$  is dominantly formed.

## Conclusions

On the basis of the steady-state and time-resolved fluorescence measurements utilizing the SLE and TFE techniques, we have demonstrated that the interface layer of the PDLC films has unique molecular alignments and mobilities of 5CB substantially different from those in the interior bulk as well as from those of neat nematic 5CB. Moreover, it has been suggested through the unique excimer-formation behavior that the molecular aggregation of 5CB at the interface of the droplets is partially disturbed by the interaction with the polymer matrixes. These findings are of crucial significance related with essential roles of interface in LC-based devices. The dominant formation of the short-lived excimer in the interface layer of the PDLC films is unusual, because its formation is generally minor or negligible in neat and solution materials of cyanoaromatic LCs even in the interface layer with the substrate. This is, therefore, of photophysical interest associated with environmental-controlled dynamics of excimer formation.

**Acknowledgment.** We are grateful to Professors Tadashi Okada and Yoshinori Hirata of Osaka University for helping us in measurements of the fluorescence decay profiles under TFE conditions and also for useful comments.

## References and Notes

- (1) (a) Doane, J. W.; Vaz, N. A.; Wu, B.-G.; Zumer, S. *Appl. Phys. Lett.* **1986**, *48*, 269. (b) Doane, J. W.; Golemme, A.; West, J. L.; Whitehead, J. B., Jr.; Wu, B.-G. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511. (c) Coates, D. *J. Mater. Chem.* **1995**, *5*, 2063. (d) Bouteiller, L.; LeBarny, P. *Liq. Cryst.* **1996**, *21*, 157, and references therein.
- (2) (a) Vaz, N. A.; Smith, G. W.; Montgomery, G. P. *Mol. Cryst. Liq. Cryst.* **1987**, *146*, 1. (b) Kim, J. Y.; Cho, C. H.; Palfy-Muhoray, P.; Mustafa, M.; Kyu, T. *Phys. Rev. Lett.* **1993**, *71*, 2232. (c) Russell, G. M.; Paterson, B. J. A.; Imrie, C. T.; Heeks, S. K. *Chem. Mater.* **1995**, *7*, 2185. (d) Rajaram, C. V.; Hudson, S. D.; Chien, L. C. *Chem. Mater.* **1995**, *7*, 2300.
- (3) Kato, S.; Lee, B.; Pac, C. *Liq. Cryst.* **1997**, *22*, 595.
- (4) (a) Lok, B. K.; Cheng, Y.-L.; Robertson, C. R. *J. Colloid Interface Sci.* **1983**, *91*, 87. (b) Masuhara, H.; Tazuke, S.; Tamai, N.; Yamazaki, I. *J. Phys. Chem.* **1986**, *90*, 5830. (c) Itaya, A.; Yamada, T.; Tokuda, K.; Masuhara, H. *Polym. J.* **1990**, *22*, 697. (d) Rumbles, G.; Brown, A. J.; Phillips, D. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 825.
- (5) For recent reviews see: (a) Jérôme, B. *Rep. Prog. Phys.* **1991**, *54*, 391. (b) Abbott, N. L. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 76.
- (6) David, C.; Baeyens-Volant, D. *Mol. Cryst. Liq. Cryst.* **1980**, *59*, 181.
- (7) Ikeda, T.; Kurihara, S.; Tazuke, S. *J. Phys. Chem.* **1990**, *94*, 6550.
- (8) No significant shifting of the maximum wavelength of the fluorescence spectra was observed as the excitation wavelength varied. These results apparently indicate that the spectral distributions of the fluorescence mostly depend on the relative contribution of the monomer and excimer emissions of 5CB. The participation of possible preformed aggregates which would absorb and emit should be negligible even in such condensed media in this work.
- (9) The penetration depth of the excitation light was estimated by characterizing the correlation between the absorbance and the film thickness for the particularly thin PDLC films. Details are described in a previous paper.<sup>3</sup>
- (10) The emitted light passing through such condensed inhomogeneous materials as PDLC films would be scattered, depending on the wavelength of the light as well as on the droplet sizes. This is, however, not important for the PDLC films. In a previous work, we demonstrated that any optical effects including scattering as well as reabsorption of the emitted light are negligible or are not important in the fluorescence study based on the SLE and TFE methods.<sup>3</sup> Presumably, possible optical effects on the fluorescence are spatially randomized and canceled to be negligible in spectral distributions of the fluorescence for the PDLC films.
- (11) It was confirmed that the photopolymerized films prepared from the diacrylate and Irgacure 184 in the absence of 5CB show little fluorescence upon excitation at 275–320 nm. It is therefore indicated that Irgacure 184 and its benzoyl fragments virtually exerted no effect on the observed fluorescence spectra of the PDLC films. This is in line with the well-known fact that aromatic ketones generally reveal no or only negligibly weak fluorescence from the excited-singlet  $n, \pi^*$  state.
- (12) (a) Serbutoviez, C.; Kloosterboer, J. G.; Boots, H. M. J.; Touwslager, F. J. *Macromolecules* **1996**, *29*, 7690. (b) Serbutoviez, C.; Kloosterboer, J. G.; Boots, H. M. J.; Paulissen, F. A. M. A.; Touwslager, F. J. *Liq. Cryst.* **1997**, *22*, 145. (c) Miyajima, M.; Anazawa, T. *RadTech Asia 1997*, Proceedings p 76 (S3-2).
- (13) Markovitsi, D.; Ide, J. P. *J. Chim. Phys.* **1986**, *83*, 97.
- (14) Klock, A. M.; Rettig, W.; Hofkens, J.; van Damme, M.; DeSchryver, F. C. J. *Photochem. Photobiol. A: Chem.* **1995**, *85*, 11.
- (15) (a) Subramanian, R.; Patterson, L. K.; Levanon, H. *Chem. Phys. Lett.* **1982**, *93*, 578. (b) David, C.; Baeyens-Volant, D. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 45. (c) Tamai, N.; Yamazaki, I.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1984**, *104*, 485.
- (16) Jaffrain, M.; Lacrampe, G.; Martin, G. *J. Physique Lett.* **1984**, *45*, L-1103.