A Study on Fluorescence Behavior of Pyrene at the Interface of Polymer Langmuir–Blodgett Films

Jun Matsui, Masaya Mitsuishi, and Tokuji Miyashita*

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Katahira 2-1-1, Aoba, Sendai 980-8577, Japan

This study describes the fluorescence behavior of the pyrene chromophore, which was incorporated into polymer Langmuir–Blodgett (LB) films, from the viewpoint of molecular motion and molecular orientations in the LB film matrix. 1-Pyrenylmethyl acrylate (PyMA) was copolymerized with a long alkylacrylamide [*N*-dodecylacrylamide (DDA)] and a short, branched alkylacrylamide [*tert*-pentylacrylamide (*t*PA)]. Copolymers (p(DDA/PyMA) and p(*t*PA/PyMA)) formed stable monolayers on the water surface, and monolayers were transferred onto solid substrates, yielding polymer LB films. Photophysical properties of the pyrene chromophore placed in polymer LB films were studied by UV–vis spectroscopy, steady-state fluorescence spectroscopy, and time-resolved fluorescence spectroscopy. Molecular motion of the pyrene molecule was highly restricted in both LB films, so that pyrene fluorescence lifetimes were longer than those in tetrahydrofuran (THF) solution and excimer emission was from a partially overlapped conformation. Excimer intensity in LB films is smaller than that in THF solution and cast films. Moreover, capping layers on LB films drastically affected emission behavior of the pyrene chromophore in the p(*t*PA/PyMA) LB film, although emission behavior of the pyrene chromophore in p(DDA/PyMA) was not influenced by capping layers. This can be explained by the fact that the pyrene chromophore is exposed to the surface in the p(*t*PA/PyMA) LB monolayer, whereas it is surrounded by long alkyl chains in p(DDA/PyMA).

Introduction

Ultrathin films such as the Langmuir–Blodgett (LB) film, self-assembled monolayer (SAM), and layer-by-layer film have potential use in construction of molecular devices.[1–3] Especially, the LB technique enables simplified arrangement of molecular assemblies regularly at the molecular scale.[4–7] For instance, Kuhn and co-workers showed that photochemical and photophysical processes such as energy transfer and electron transfer in LB multilayers can be controlled by changing the layer structure.[4] Yamazaki et al., using picosecond time-resolved fluorescence spectroscopy, observed layer-to-layer sequential excitation transport in a long alkyl fatty acid LB film containing an energy donor and acceptor.[8] In general, however, it is difficult to distribute chromophores uniformly in low molecular weight fatty LB films because the chromophore molecules form aggregate species of even a few percentages in LB films.[9] To overcome this disadvantage, chromophores were often fixed into LB films by chemical reaction or polymerization. It is reported that the chromophore incorporated in poly(vinyl alkanal) LB films by copolymerization is distributed uniformly in LB films.[10]

Chromophores incorporated into ultrathin films can also be utilized for a luminescent probe to characterize film properties.[11,12] For example, change of layer structure of LB films by heat treatment was clearly observed by change in pyrene excimer emission.[13] Moreover, thermal stability of polymer LB films was discussed using an energy migration method.[14] Karpovich et al., using the fluorescence anisotropy method, studied the mobility of a pyrene molecule that was incorporated into a 1-octadecanethiol SAM.[15] Wu et al. discussed stability and

mobility of cadmium arachidate LB bilayer films; and it can be concluded that capping of the top of the bilayer with another layer increases the stability and decreases the mobility of lateral diffusion.[16]

We have reported that a series of *N*-alkylacrylamide polymers have excellent properties for forming LB films,[17–21] and various functional groups can be incorporated into polymer LB films as a sort of copolymer.[22,23] We also have found that with selecting side alkyl chain length of alkylacrylamide polymers, not only the molecular orientation of the functional group but also the molecular environment can be controlled.[24]

The current study focuses on photophysical behavior of an emission probe in polymer LB films to discuss precisely the molecular environment in an LB film matrix. We prepared two types of polymer LB films labeled with a pyrene probe (Figure 1); one contains a long alkyl side chain, and the other contains a short, branched alkyl side chain. Pyrene chromophore mobility in these LB film monolayers and the effect of probe position in LB films on photophysical properties were examined. We also investigated the influence of capping LB layers upon pyrene emission in the LB films.

Experimental Section

By a similar procedure described elsewhere, 1-pyrenylmethyl acrylate monomer (PyMA) was synthesized.[24] Poly(*N*-dodecylacrylamide) (pDDA), poly(*tert*-pentylacrylamide) (p(*t*PA)), and copolymers of PyMA with DDA and with *t*PA were prepared by free radical polymerization initiated by 2,2′-azobis(isobutyronitrile) (AIBN) in toluene at 60 °C. Mole fractions of the pyrene chromophore in copolymers were determined with UV–vis spectroscopy using the molar extinction coefficient for

Study on Fluorescence Behavior of Pyrene

J. Phys. Chem. B, Vol. 106, No. 10, 2002 **2469**
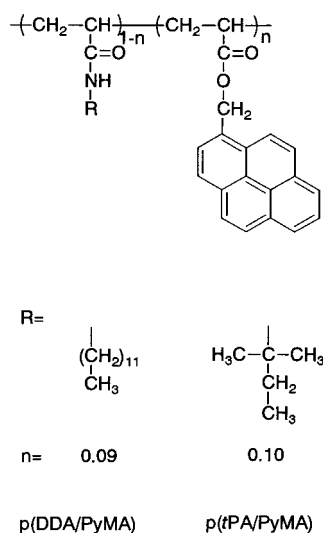
Figure 1. The molecular structure of p(DDA/PyMA) and p(*t*PA/PyMA).

**TABLE 1: Characterization of p(DDA/PyMA) and p(*t*PA/PyMA) Copolymers**

	PyMA (mol %)	$M_w \times 10^{-4}$	M_w/M_n	deposition pressure (mN/m)
p(DDA/PyMA)	9.4	5.69	1.63	30
p(*t*PA/PyMA)	10.2	5.00	1.61	15

1-pyrenylmethyl acrylate ($\epsilon = 4.6 \times 10^4$ M^{-1} cm^{-1}) at 345 nm in chloroform. Molecular weights were determined by gel permeation chromatography using a polystyrene standard (Table 1). Measurements of π−A isotherms and deposition of monolayers were carried out with an automatic Langmuir trough (USI, LB lift controller FSD-51 using a Wilhelmy-type film balance). Stable monolayers were prepared on a Langmuir trough in pure water (>17 MΩ cm, Millipore Milli-QII) by spreading a 1 × 10^{-3} M chloroform solution at 15 °C and compressed at a rate of 15 cm^2/min. Quartz slides used as deposition substrates were cleaned in boiling HNO$_3$ solution and made hydrophobic by immersing them into a chloroform solution of octadecyltrichlorosilane (Tokyo Chemical Industry). Monolayers were transferred onto substrates at a surface pressure of 30 mN/m for p(DDA/PyMA) and 15 mN/m for p(*t*PA/PyMA) with a dipping speed of 10 mm/min. Transfer ratios were almost unity through the dipping process.

Fluorescence spectra and UV−vis absorption spectra were measured with a Hitachi F-4500 spectrofluorophotometer and a Hitachi U-3000 UV−vis spectrophotometer, respectively. Fluorescence lifetimes and time-resolved fluorescence spectra were measured using a single-photon-counting apparatus (C4780, Hamamatsu Photonics). A nitrogen gas laser (LN120C, Laser photonics, 337.1 nm and 300 ps pulse fwhm) was used as an excitation source. Fluorescence decay data were obtained with a Hamamatsu streak scope system (C4334).

Results and Discussion

Fluorescence Behavior of the Pyrene Chromophore in Polymer LB Films. Before discussion of the photophysical properties of the pyrene chromophore in polymer LB films, fluorescence of pyrene-labeled polymers in solution was investigated. Figure 2 shows steady-state fluorescence spectra excited at 315 nm for p(DDA/PyMA) and p(*t*PA/PyMA) in tetrahydrofuran (THF). The solution (10^{-6} M) was bubbled with argon flow to remove oxygen for at least 20 min before measurement.
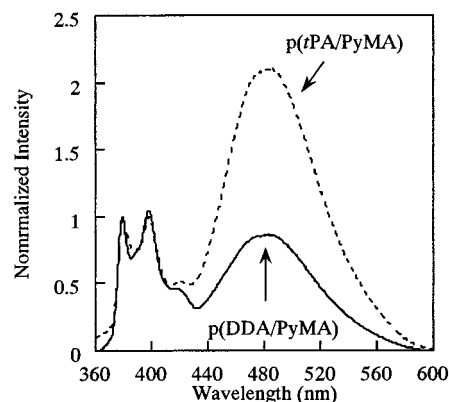
Figure 2. Fluorescence emission spectra for p(DDA/PyMA) and p(*t*PA/PyMA) in tetrahydrofuran solution.
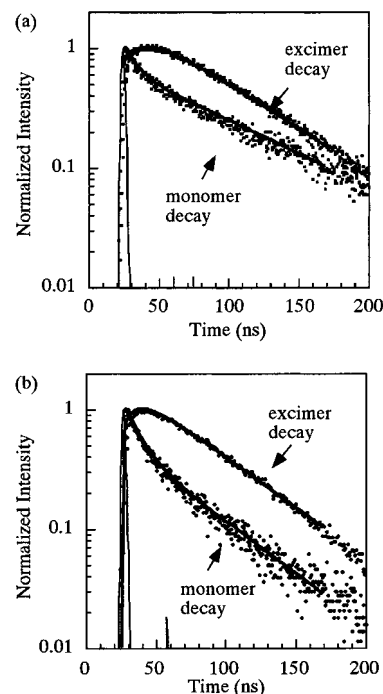
Figure 3. Fluorescence decay curves of copolymers in tetrahydrofuran solution: (a) p(DDA/PyMA); (b) p(*t*PA/PyMA). The solid line is a fitting result.
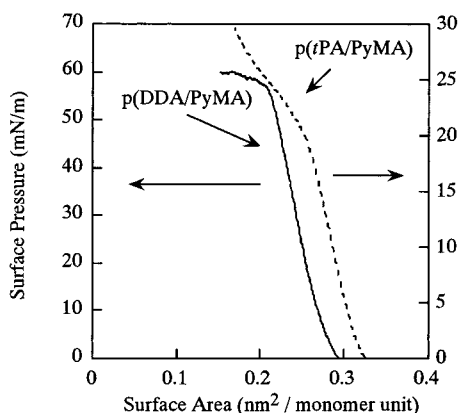
Fluorescence spectra consist of a structured band of pyrene monomer between 370 and 400 nm and a broad structureless band of excimer around 480 nm. The ratio of the excimer and monomer emission (I_E/I_M) was smaller for p(DDA/PyMA) than for p(*t*PA/PyMA), whereas pyrene contents are nearly the same in both copolymers (ca. 10%). Low excimer emission in p(DDA/PyMA) would be caused by the long alkyl chain.

Subsequently, fluorescence decay curves for p(DDA/PyMA) and p(*t*PA/PyMA) monitored at the monomer region (370−400 nm) and the excimer region (450−500 nm) in THF solution were measured (Figure 3a,b). Decay curves observed at the monomer region spanned more than a single exponent. This is partially due to intramolecular energy migration. Time-resolved profiles of excimer emission in both copolymers show a rising in initial time. The rise time for the excimer in p(DDA/PyMA) is longer than that in p(*t*PA/PyMA) (Table 2). Because the long alkyl side chain restricts movement of polymer segments, it takes a longer time for the pyrene chromophore to take the excimer conformation. Monomer emission decay time of p(*t*PA/PyMA) is shorter than that of p(DDA/PyMA). This corroborates with more efficient excimer formation in copolymers. From studies

TABLE 2: Decay Fitting Parameters[a] for the Copolymers Measured in THF

| copolymer		τ_1 (ns)	τ_2 (ns)	a_1	a_2	χ^2
p(DDA/PyMA)	monomer	7.8	73.6	0.069	0.079	1.13
	excimer	16.2	54.0	−0.142	0.232	1.12
p(tPA/PyMA)	monomer	7.9	47.6	0.081	0.055	1.12
	excimer	11.4	50.6	−0.097	0.176	1.28

[a] The experimental decay curves were analyzed using the equation $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, where $I(t)$ is the emission decay function, a_i is the preexponential factor, and τ_i is the decay parameter.

Figure 4. The π−A isotherm for p(DDA/PyMA) and p(tPA/PyMA).

Figure 5. Fluorescence spectra of LB monolayer films: (a) p(DDA/PyMA); (b) p(tPA/PyMA).

Figure 6. Fluorescence decay curves of LB monolayer films monitored at excimer region (450−500 nm): (a) p(DDA/PyMA); (b) p(tPA/PyMA). The solid line is a fitting result.

for steady-state fluorescence spectra and fluorescence lifetime, it can be concluded that the alkyl side chain affects excimer formation largely in THF solution.

Copolymers were spread onto a water surface from a chloroform solution to examine the monolayer property of copolymers by measurement of surface pressure (π)-area (A) isotherms at 15 °C. The π−A isotherms for both copolymers showed a steep rise in surface pressures (Figure 4). Furthermore, we observed no significant decrease in surface area due to structural relaxation when the barrier was kept at surface pressure forming a condensed monolayer. These observations indicate that copolymer monolayers are stable and densely packed at the air/water interface. Orientation of the pyrene chromophore in monolayer films was discussed in previous work by comparing the limiting surface area of the pyrene chromophore at the air/water interface with calculated values based on the Corey−Pauling−Koltun (CPK) model. It was concluded that the pyrene ring in p(tPA/PyMA) takes a parallel orientation to the monolayer plane at the air/water interface, while pyrene orients vertically to the water surface in the case of the p(DDA/PyMA) monolayer.[24]

Copolymer LB films for measurement of pyrene fluorescence were prepared as follows: first, non-pyrene-labeled polymer LB films, N-dodecylacrylamide homopolymer LB film with five layers (p(DDA) 5 layers), were deposited on the quartz plate as a primary layer to prevent substrate quenching; then, only one layer of the pyrene-labeled copolymer monolayer was deposited. Steady-state fluorescence spectra of p(DDA/PyMA) and p(tPA/PyMA) monolayer films measured under an argon atmosphere are shown in Figure 5. Broad emission around 470 nm is assigned as excimer fluorescence because excitation spectra monitored at monomer fluorescence (380 nm) and at excimer fluorescence (470 nm) are identical. It is very interesting that values of I_E/I_M in copolymer LB films are smaller than values in THF solution and cast films (data not shown). In general, excimer formation is enhanced in polymer films compared with that in solution because interpolymer chain aggregation and energy migration occurs in condensed media
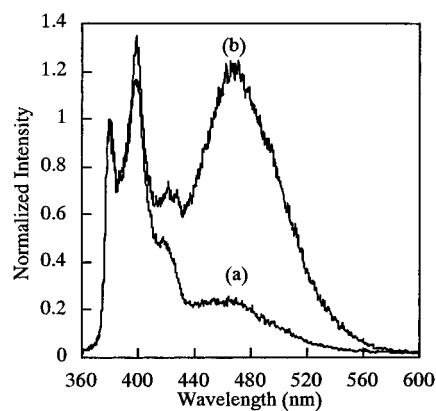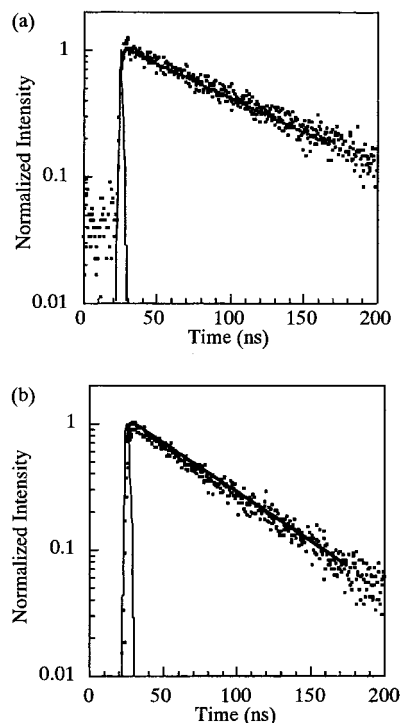
(film).[25] In present polymer LB films, pyrene chromophores are highly oriented from the chains, so interlayer chain aggregation and energy migration are suppressed. Moreover, because the pyrene chromophore in polymer LB films is placed among tightly packed alkyl chains, movement to take an excimer conformation is also restricted. As a result, excimer intensity becomes small in LB films. Excimer emission maxima (λ_{max}) are about 10 nm shorter in LB films than those in THF solution. The blue shift of excimer emission is often observed for chromophores in a rigid matrix, and the higher energy excimer is attributed to a partially overlapped conformation of the excimer.[26] Dynamic properties of emission behavior of the pyrene in LB films were investigated by using time-resolved fluorescence spectroscopy. Figure 6 shows fluorescence decay curves for LB monolayers of p(DDA/PyMA) (a) and p(tPA/PyMA) (b) monitored at the excimer region (450−500 nm). Contrary to decays measured in THF solution, no rising in excimer emission profiles was observed. This fact suggested that pyrene chromophores exist in a rigid molecular environment

Study on Fluorescence Behavior of Pyrene

J. Phys. Chem. B, Vol. 106, No. 10, 2002 **2471**

TABLE 3: Decay Fitting Parameters[a] for the Copolymer LB Films

copolymer	film structure		τ_1 (ns)	τ_2 (ns)	a_1	a_2	χ^2
p(DDA/PyMA)	no capping	monomer	6.4	101.1	0.063	0.086	1.04
		excimer	84.7		0.124		0.967
	p(DDA) capping	monomer	5.1	100.1	0.040	0.092	1.07
		excimer	83.3		0.111		0.902
p(tPA/PyMA)	no capping	monomer	5.9	55.5	0.071	0.093	1.04
		excimer	55.5		0.118		1.06
	p(DDA) capping	monomer	7.7	75.7	0.066	0.063	0.935
		excimer	58.9		0.118		1.12
	p(tPA) capping	monomer	7.4	66.7	0.069	0.055	1.08
		excimer	54.5		0.110		1.08

[a] The experimental decay curves were analyzed using the equation $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, where $I(t)$ is the emission decay function, a_i is the preexponential factor, and τ_i is the decay parameter.
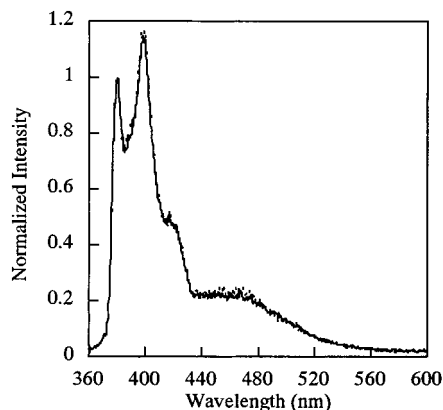

Figure 7. Fluorescence spectra for p(DDA/PyMA) LB monolayer films with different film structure: (—) no capping; (⋯) p(DDA) capping.

Figure 8. Fluorescence spectra for p(tPA/PyMA) LB monolayer films with different film structure: (a) no capping; (b) p(DDA) capping.

in LB films.[27] This condition was further confirmed by fluorescence depolarization measurement.[28] Excimer emissions were fitted by a single exponential decay function with the decay parameters shown in Table 3. Longer emission lifetimes in LB films compared with those in THF solution suggest that pyrene chromophores in LB films exist in a different polarity from the environment or take different packing of the excimer compared with those in THF solution or both. Moreover, the excimer emission lifetime in p(DDA/PyMA) was apparently longer than that in p(tPA/PyMA). This difference is caused by different molecular environments of the pyrene chromophore between p(DDA/PyMA) and p(tPA/PyMA) LB films. In the previous paper, we reported that the pyrene chromophores are surrounded by dodecyl side chains in p(DDA/PyMA) LB film, while they are exposed to their surroundings at the p(tPA/PyMA) surface.[24] This indicates that the pyrene chromophore is more stable in the inner site of the LB film than at the interface.

Influence of Capping Layers on Pyrene Emission. The influence of capping layers on pyrene emission properties in LB films was investigated to confirm differential placement of the pyrene chromophore in the DDA copolymer and tPA copolymer LB films. The emission spectrum of the p(DDA/PyMA) LB monolayer was not changed by capping with p(DDA) LB film (4 layers) (Figure 7), whereas the spectrum in the p(tPA/PyMA) LB film was drastically changed by capping (Figure 8). Because in p(tPA/PyMA) LB films the pyrene chromophore is exposed to the surface of the LB film, the capping layer appears to influence pyrene emission in the p(tPA/PyMA) LB film. We investigated these effects with time-resolved fluorescence spectra. Figure 9 shows fluorescence decay curves for monomer emission in the p(tPA/PyMA) LB film with and without capping layers, respectively. Fitting kinetic parameters for emission decay (Table 3) indicate that decay lifetimes became longer with capping layers. In the case of the
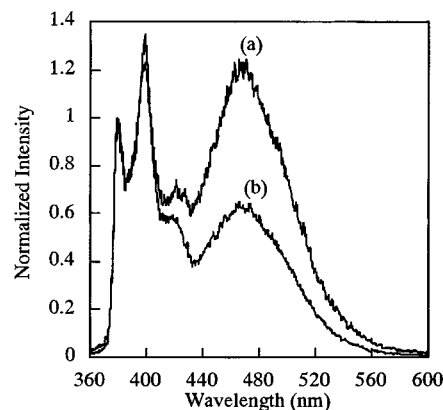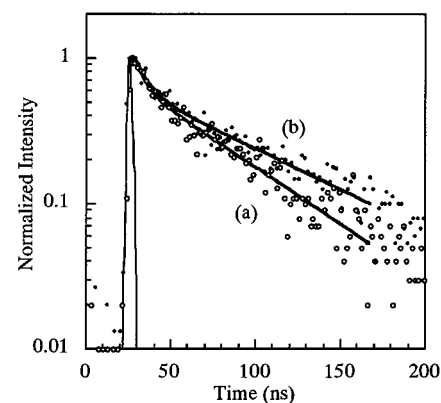

Figure 9. Decay curves for p(tPA/PyMA) LB films with different structure monitored at the monomer region (370−400 nm): (a) no capping; (b) p(DDA) capping. The solid line is a fitting result.

p(tPA/PyMA) LB film capped with p(DDA) layers, the long alkyl side chains can penetrate into the pyrene chromophore as a "needle", so it can be considered that the molecular environment of pyrene chromophore approximates that in the p(DDA/PyMA) LB film, resulting in the longer lifetime.

In the previous section, it was found that capping with p(DDA) layers influences emission properties of the pyrene chromophore in the p(tPA/PyMA) LB monolayer. Here, we investigated the effect of capping with different LB films: poly-*tert*-pentylacrylamide (p(tPA)), the short, branched type, and p(DDA) LB film. Figure 10 shows fluorescence spectra for three different layer structures of p(tPA/PyMA) LB films. Excimer emission of LB films decreases by capping of p(tPA) or p(DDA) LB film. In the LB film capped with p(tPA), the shape of the emission around 420 nm is different from that in the uncapped LB film. This indicates that additional emissive species are
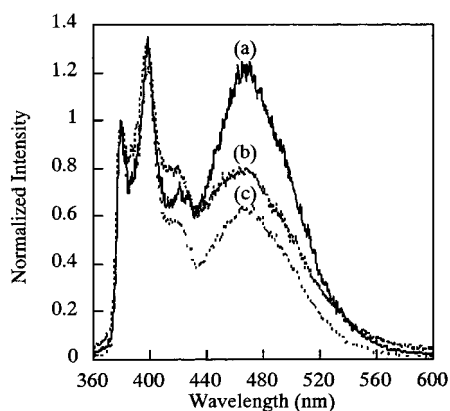
Figure 10. Fluorescence spectra for the p(*t*PA/PyMA) LB monolayer: (a) no capping; (b) p(*t*PA) capping; (c) p(DDA) capping.
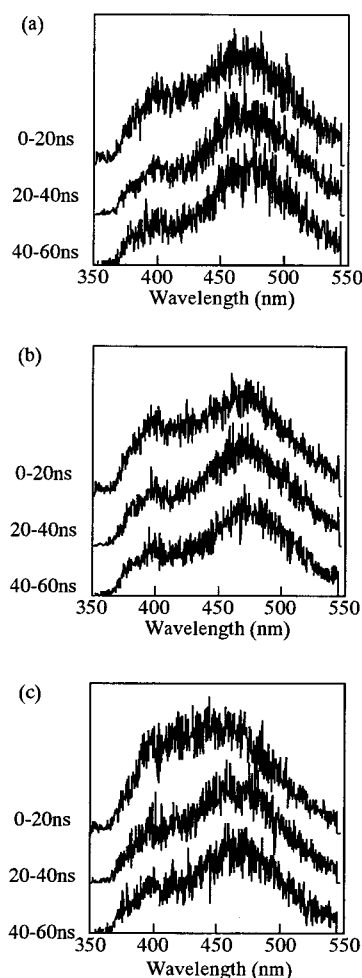
Figure 11. Time-resolved fluorescence spectra of p(*t*PA/PyMA) LB monolayer films: (a) no capping; (b) p(DDA) capping; (c) p(*t*PA) capping. The time zero corresponds to the time at which the excitation laser pulse reaches maximum intensity.

produced by p(*t*PA) capping. To obtain information about additional species in more detail, we examined time-resolved fluorescence spectra of LB films. Figure 11 shows time-resolved fluorescence spectra of p(*t*PA/PyMA) LB films with no capping, p(DDA) capping, and p(*t*PA) capping. The LB films capped by a p(*t*PA) LB film show a different shape of the spectrum at a time region of 0−20 ns from the spectra at a longer time region (Figure 11c), whereas the LB film with no capping and p(DDA) capping did not show such a difference. Fluorescent species observed at 420 nm with a quite-short lifetime can be

assigned to a partially overlapped dimer or excimer. Taniguchi et al. reported that the broad fluorescence band at 420 nm is formed by a parallel small overlapping pair of pyrene chromophores.[29] Yamazaki et al. assigned the broad band as a partially overlapped excimer.[27] On the other hand, Tsuchida et al. ascribed the broad band to the preformed partially overlapped dimer.[30] Considering these works and the present result that only the p(*t*PA/PyMA) LB film capped with p(*t*PA) layers shows the emission band at 420 nm, fluorescence at 420 nm will be from a partially overlapped dimer. The ground-state dimer formation often originates from forces imposed by the external medium, such as crystal defect sites or hydrophobic interaction in water.[31] In this case, the external medium is the bulky side chain of p(*t*PA); this presses surface pyrene molecules to form a partial-overlap conformation.

Conclusion

Photophysical properties of the pyrene chromophore in p(DDA/PyMA) and p(*t*PA/PyMA) LB films were studied from the viewpoint of differences in the molecular environment. Molecular motion of the pyrene molecule was highly restricted in both LB films so that excimer emission arises from the partially overlapped conformation. The pyrene fluorescence lifetime was longer in the p(DDA/PyMA) LB film than in the p(*t*PA/PyMA) LB film. Moreover, capping layers on LB films drastically affected emission behavior of the pyrene chromophore in the p(*t*PA/PyMA) LB film, although emission behavior of the pyrene chromophore in p(DDA/PyMA) was not influenced by capping layers. These results indicate that the pyrene chromophore is more stable and less sensitive to change in the surrounding molecular environment in the p(DDA/PyMA) LB film than in the p(*t*PA/PyMA) LB film because the pyrene chromophore in the p(DDA/PyMA) LB film is buried in the side alkyl chain while in the p(*t*PA/PyMA) LB film it is exposed to the surface.

References and Notes

(1) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir−Blodgett to Self-Assembly*; Academic Press: New York, 1991.
(2) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210/211*, 831.
(3) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21* 319.
(4) Kuhn, H.; Möbius, D.; Bücher, H. In *Physical Methods of Chemistry*; Weissberger, A, Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. 1, part 3B, p 577.
(5) Hsu, Y.; Penner, T. L.; Whitten, D. G. *J. Phys. Chem.* **1992**, *96*, 2790.
(6) Fujihira, M. In *Thin Films*; Ulman, A., Ed.; Academic Press: San Diego, CA, 1995; Vol. 29, p 239.
(7) Pevenage, D.; Van der Auweraer, M.; DeSchryver, F. C. *Langmuir* **1999**, *15*, 4641.
(8) Yamazaki, I.; Tamai, N.; Yamazaki, T.; Murakami, A.; Mimuro, M.; Fujita, T. *J. Phys. Chem.* **1988**, *92*, 5035.
(9) Jensen, K. K.; Albinsson, B.; Van der Auweraer, M.; Vuorimaa, E.; Hemmetyinen, H. *J. Phys. Chem. B* **1999**, *103*, 8514.
(10) Ohmori, S.; Ito, S.; Yamamoto, M. *Macromolecules* **1990**, *23*, 4047.
(11) Tedeschi, C.; Möhwald, H.; Kirstein. S. *J. Am. Chem. Soc.* **2001**, *123*, 954.
(12) Caminati, G.; Gabrielli, G.; Ricceri, R.; Turro, C.; Turro, N. J. *Thin Solid Films* **1996**, 718.
(13) Murakata, T.; Miyashita, T.; Matsuda, M. *Langmuir* **1986**, *2*, 786.
(14) Mabuchi, M.; Kawano, K.; Ito, S.; Yamamoto, M. *Macromolecules* **1998**, *31*, 6077.

Study on Fluorescence Behavior of Pyrene

J. Phys. Chem. B, Vol. 106, No. 10, 2002 **2473**

(15) Karovich, D. S.; Blanchard, J. G. *Langmuir* **1996**, *12*, 5522.

(16) Wu, H.; Foster, D. M.; Ross, A. S.; Mattice, L. W.; Matties, A. M. *Langmuir* **1996**, *12*, 3015.

(17) Miyashita, T. *Prog. Polym. Sci.* **1993**, *18*, 263.

(18) Miyashita, T.; Mizuta, Y.; Matsuda, M. *Br. Polym. J.* **1990**, *22*, 327.

(19) Taniguchi, T.; Yokoyama, Y.; Miyashita, T. *Macromolecules* **1997**, *30*, 3646.

(20) Feng, F.; Aoki, A.; Miyashita, T. *Chem. Lett*. **1998**, 205.

(21) Li, X.; Aoki, A.; Miyashita, T. *Langmuir* **1996**, *12*, 5444.

(22) Miyashita, T.; Mizuta, Y.; Matsuda, M. *Langmuir* **1993**, *9*, 1110.

(23) Miyashita, T.; Yatsue, Y. *J. Phys. Chem.* **1995**, 99, 16047.

(24) Matsui, J.; Mitsuishi, M.; Miyashita, T. *Macromolecules* **1999**, *32*, 381.

(25) Fox, B. R.; Price, R. T.; Cozzens, F. R.; McDonald, R. J. *J. Chem. Phys.* **1972**, *57*, 534.

(26) Todesco, V. R.; Basheer, A. R.; Kamat, V. P. *Macromolecules* **1986**, *19*, 2390.

(27) Yamazaki, T.; Tamai, N.; Yamazaki, I. *Chem. Phys. Lett*. **1986**, *124*, 326.

(28) Matsui, J.; Mitsuishi, M.; Miyashita, T. *Stud. Surf. Sci. Catal*. **2001**, *132*, 573.

(29) Taniguchi, Y.; Mitsuya, M.; Tamai, N.; Yamazaki, I.; Masuhara, H. *Chem. Phys. Lett.* **1986**, *132*, 516.

(30) Tsuchida, A.; Ikawa, T.; Yamamoto, M. *Polymer* **1995**, *36*, 3103.

(31) Winnik, M, F. *Chem. Rev*. **1993**, 93, 587.