Polymer Langmuir–Blodgett Films Containing Photofunctional Groups. 4.[1] A Photophysical Study of Copolymers Containing a Carbazole Chromophore in a Monolayer and Langmuir–Blodgett Multilayers

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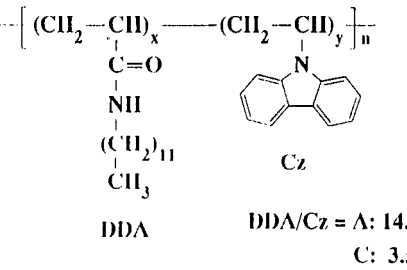
ABSTRACT: Copolymers of *N*-dodecylacrylamide (DDA), which form LB multilayers, and *N*-vinylcarbazole (Cz) with various copolymer compositions were prepared to investigate the photophysical behavior of the carbazole chromophore in a monolayer and LB multilayers. In LB multilayers, the emission spectra changed with the number of layers deposited. The excimer emission increases in the LB multilayers of a Y-type LB structure which have a head-to-head arrangement, due to effective energy migration between Cz chromophores. Inter- and intralayer energy transfer in the LB multilayers is suggested by the increase in the excimer emission up to the deposition of six layers. The emission decay profiles in the LB films (monolayer and multilayers) containing only a few percent of Cz are nearly single exponential. More importantly no rapid decay in an initial stage is observed, which is often found for dyes incorporated into conventional LB layers when aggregates are formed. The analysis supports that the Cz chromophores in the copolymer LB films are dispersed more or less uniformly.

Introduction

The Langmuir–Blodgett technique is known to be an attractive method to prepare ultrathin films with a controlled thickness and well-defined molecular orientation.[2,3] Recently, LB films consisting of some amphiphilic polymers have been investigated as it could be expected that this would improve the poor thermal and mechanical stability of conventional LB films of long-chain fatty acids.[4–7] We have reported that preformed *N*-dodecylacrylamide (DDA) polymer forms LB multilayers[4] and have proposed a method to introduce chromophores into the polymer LB films as a comonomer of DDA.[1] Chromophores in LB films are expected to have a regular orientation. The amphiphilic chromophores, however, in the conventional LB films of long-chain fatty acids quite often form aggregates,[8] and the distribution of the chromophores in those LB films is often not uniform. Although the uniform distribution of chromophores is often difficult to obtain in LB films of low molecular weight compounds, the actual tendency to form aggregates depends on the chemical structure of the dyes and the matrix; incorporation of, e.g., surfactants with unsaturated chains in the matrix reduces the aggregation of tetraphenylporphyrins in LB films.[9] The photophysical properties of chromophores in solid matries are known to be strongly influenced by the distribution of the chromophores. In a previous study, we succeeded in the preparation of the polymer LB film having a carbazole chromophore (Cz) dispersed uniformly.[1] In the present paper, multilayers are investigated with various Cz mole fractions (Chart 1). Their emission spectra and fluorescence decay were measured and compared with analogous data in cast films and in a homogeneous solution.

Chart 1



Experimental Section

Materials. The copolymers (DDA/Cz) were prepared by free-radical polymerization of *N*-dodecylacrylamide (DDA) with *N*-vinylcarbazole (VCz) in benzene at 60 °C. The copolymers were purified by dissolution in chloroform, followed by filtration and precipitation in a large excess of acetonitrile. The molar ratios of the carbazole chromophore, incorporated in the copolymers, were determined by nuclear magnetic resonance (NMR) and UV–visible absorption spectroscopy. The number-average molecular weights, measured by gel permeation chromatography (GPC), for the copolymers with the compositions of DDA/Cz = 14.7/1 (A), 7/1 (B), 3.5/1 (C), and 2/1 (D) are 1.6, 1.0, 3.0, and 7.0 × 10^4, respectively.

Preparation of Langmuir–Blodgett Films. An automated Langmuir trough (Kyowa Kaimen Kagaku HBM-AP with a Wilhelmy-type film balance) was used for the measurement of surface pressure–area isotherms (π–A isotherms) and the preparation of LB films. All copolymers were dissolved in chloroform (spectroscopic grade) at a concentration of about 10^{-3} M (monomer unit) and spread on a water surface. Distilled water was used (Millipore Milli-QII). The quartz slides used for the deposition of monolayers were previously cleaned in a boiling H_2SO_4–HNO_3

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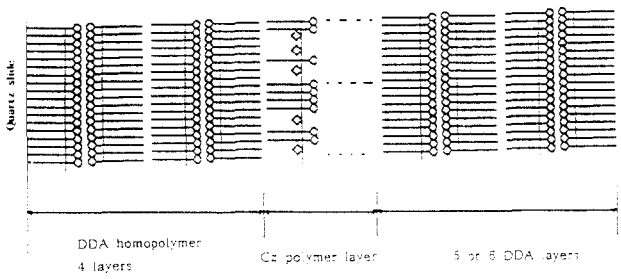
Chart 2



(2:1) solution, made hydrophobic with dichlorodimethylsilane, and coated in advance by four layers of poly(*N*-dodecylacrylamide) to prepare a uniform surface (Chart 2).

Measurements. Fluorescence spectra and UV–visible absorption spectra were measured with a Hitachi 850 spectrofluorophotometer and a Shimadzu UV-160 UV–visible spectrophotometer, respectively. Fluorescence decays were obtained by time-correlated single-photon counting using a setup described previously.[10]

Results and Discussion

Steady-State Fluorescence Spectra. The DDA/VCz copolymers with various VCz contents (DDA/Cz = 14.7/1 (A), 7/1 (B), 3.5/1 (C), 2/1 (D)) were prepared by the usual free-radical copolymerization of DDA and VCz. The emission spectra of the A–D copolymers in a dichloromethane solution consisted of the structured emission characteristic of the locally excited state of the carbazole chromophore at 350 nm (Figure 1), and no excimer emission at 420 nm[11,12] was observed. Only for copolymer D with a Cz content of 33 mol % does the emission intensity around 420 nm increase slightly. The absence of an appreciable excimer intensity indicates that the amount of the nearest Cz–Cz pairs (excimer-forming sites) is very small in the copolymers. From the Q and e values of DDA[13] (Q = 0.51 and e = 0.73) and VCz[12] (0.41 and −1.4, respectively), the r_1 times r_2 value, which indicates the alternation tendency in the copolymers, is calculated to be 0.01. This small r_1 times r_2 value indicates a high alternation and is consistent with the observed emission spectra.

The copolymers (A–D) were spread onto a water surface from a chloroform solution. The surface pressure–area isotherms indicate the formation of a stable condensed monolayer, characterized by a steep rise in surface pressure and a high collapse pressure (Figure 2).[1] The average limiting surface areas per monomer unit in the copolymers were determined to be 0.28–0.30 nm^2/monomer by extrapolating the steep region of the isotherms to zero surface pressure. The surface area for the carbazole moiety could be calculated from the average areas by assuming the area of DDA to be 0.28 nm^2/monomer.[5] The obtained area for the carbazole moiety was almost constantly 0.34 ± 0.02 nm^2/molecule regardless of the mole fraction of carbazole in the copolymers. This suggests that the carbazole chromophores are dispersed having their own surface area in the copolymer monolayer and that the copolymer chains are closely packed in a stretched conformation. The surface area is consistent with the value estimated from the CPK molecular model. The LB assemblies used in the determination of the emission spectrum were built in the following way: the condensed monolayers of the sample copolymers were transferred onto the PDDA LB films (four layers) which are coated previously onto a quartz slide, and the sample copolymer LB films were finally coated again with the PDDA monolayers (five or six layers) (Chart 2).

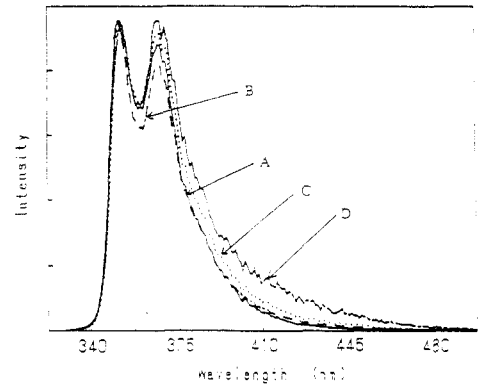


Figure 1. Fluorescence spectra of the copolymers (A–D) in a dichloromethane solution.

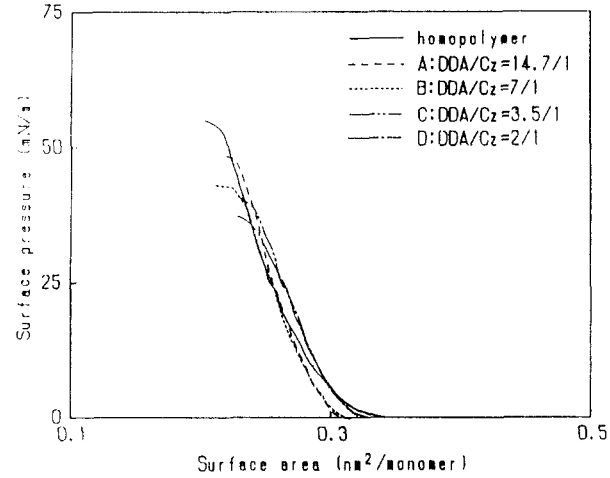


Figure 2. Surface pressure–area isotherms of DDA/Cz copolymer monolayers at 19 °C.

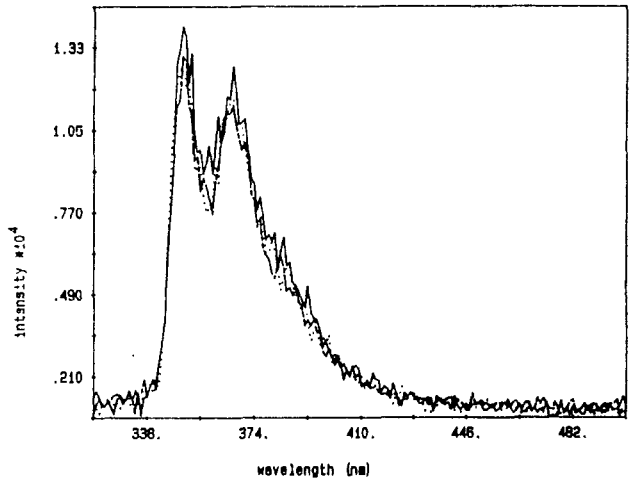


Figure 3. Emission spectra of a LB multilayer of DDA/Cz copolymer (A copolymer) in air (—), in vacuo (· · ·), and in air after in vacuo (– · –).

The fluorescence spectrum of the "copolymer A" monolayer was measured in air and in vacuum (Figure 3). Since both spectra are nearly identical, quenching by oxygen is negligible; therefore, subsequent measurements were carried out in air. Figure 4 shows the emission spectra of the copolymers in LB multilayers. Apparently, the excimer emission intensity of copolymer D LB film increased compared with that in a homogeneous solution of the same polymer. The excitation spectra for the emission monitored at 350 nm and at 420 nm were identical and in agreement in the absorption spectrum of the copolymer. The increase in the relative intensity of the excimer

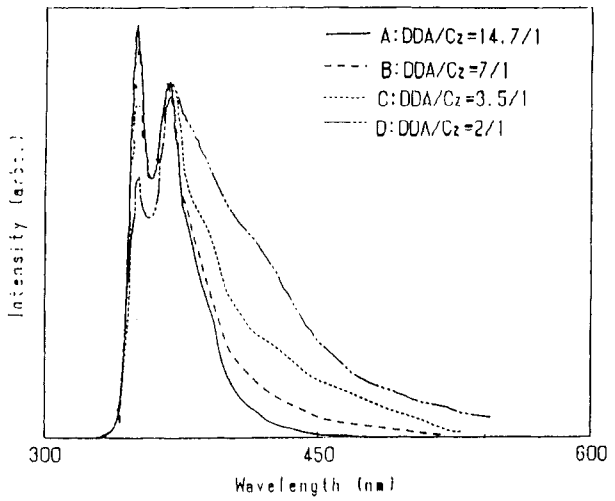


Figure 4. Emission spectra of DDA/Cz copolymers in LB multilayers.

Table 1. Relative Ratios of the Excimer to the Monomer Fluorescence Intensity for Copolymer D in Various Media

			LB film	
	solution	cast film	monolayer	multilayer
I_e/I_m	0.13	0.46	0.29	0.9

emission around 420 nm in the LB films could be due to an effective energy migration to excimer-forming sites which are due to a small percentage of the nearest-neighbor Cz–Cz pairs in the carbazole sequences. The relative intensity ratios of the excimer to the local excited-state emission of copolymer D in various media, that is, solution, cast film, LB monolayer, and LB multilayer, are reported in Table 1. The most intense excimer emission was observed in the LB multilayer, suggesting the most effective energy migration between carbazole chromophores in a LB multilayer.

The emission spectra were measured as a function of the number of layers in LB multilayers in order to clarify the effectiveness of energy migration (Figure 5). The excimer emission intensity around 420 nm apparently increases with the number of deposited layers, as shown in Figure 5. The increment of the intensity, however, is not constant. The excimer emission intensity increases significantly from monolayer to bilayers, whereas the increment from bilayers to three-layers is very small. Again the increment from three layers to four layers is larger. Finally no increase in the excimer emission for the LB multilayers over six layers was observed. The emission spectrum no longer changed with the number of deposited layers. This interesting observation is attributable to the Y-type structure of the LB multilayers and the effective interlayer energy transfer to the excimer site through energy migration between Cz chromophores (Figure 6). The interlayer energy transfer in the head-to-head structure occurring for an even number of deposited layers (Figure 6b) is very effective. The transfer, however, in the LB multilayers with an odd number of layers is not so efficient, considering that the critical distance for energy transfer (Förster type) between carbazole chromophores (22 Å)[14] is shorter than the interlayer distance of Cz–Cz in the tail-to-tail structure (ca. 36 Å) (Figure 6c). Therefore, the excimer formation is more efficient in LB multilayers with an even number of deposited layers. The excimer emission increasing up to the deposition of six layers indicates that a long-distance energy transfer (through several steps of energy migration) can occur. These changes in emission spectra are characteristic of

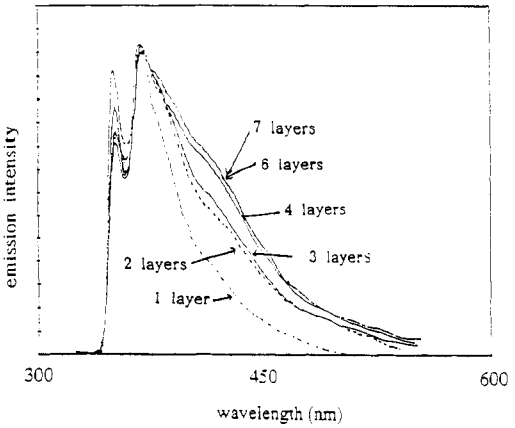


Figure 5. Emission spectra of copolymer D in LB multilayers with various deposited layers.

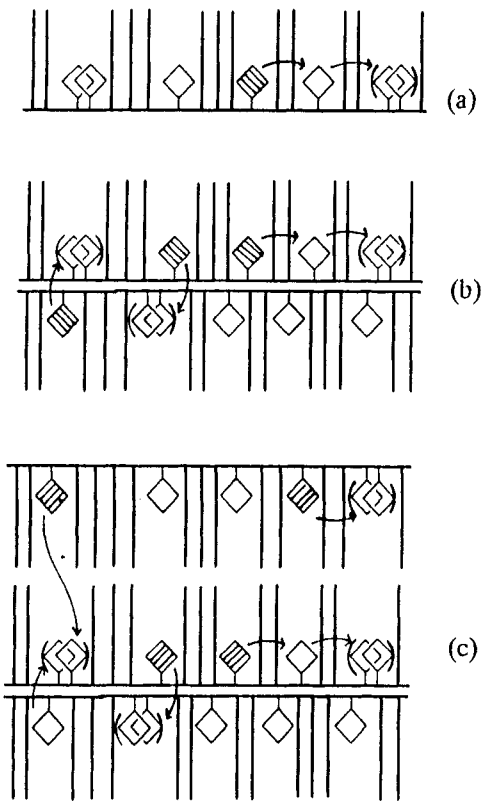


Figure 6. Schematic illustration of energy transfer between Cz chromophores in (a) a monolayer, (b) bilayers, and (c) three layers.

the DDA/Cz copolymer LB multilayers.

In a separate study, we have prepared the polymer LB multilayer containing naphthalene chromophores which have a shorter critical distance of Förster-type transfer (7.3 Å). The results show that the emission spectrum in the LB bilayer was identical with that of a LB multilayer with 4 layers, suggesting no or substantially less interlayer energy transfer.[15]

Emission Decay Kinetic Analysis. The fluorescence decay of the carbazole was measured using the time-correlated single-photon-counting method. First the emission decays of the copolymers were measured in a CH_2Cl_2 solution. The emission decay of copolymer A with a 6.4% Cz content in a CH_2Cl_2 solution could be described by a single-exponential decay with a decay time of 10 ns (Table 2). The decay gradually deviates from single exponential with increasing Cz content in the copolymers. Global analysis of the fluorescence decay[16] across the local and excimer band allows a description of the decay by the sum of three exponents (eq 1, Table 2). However, in view

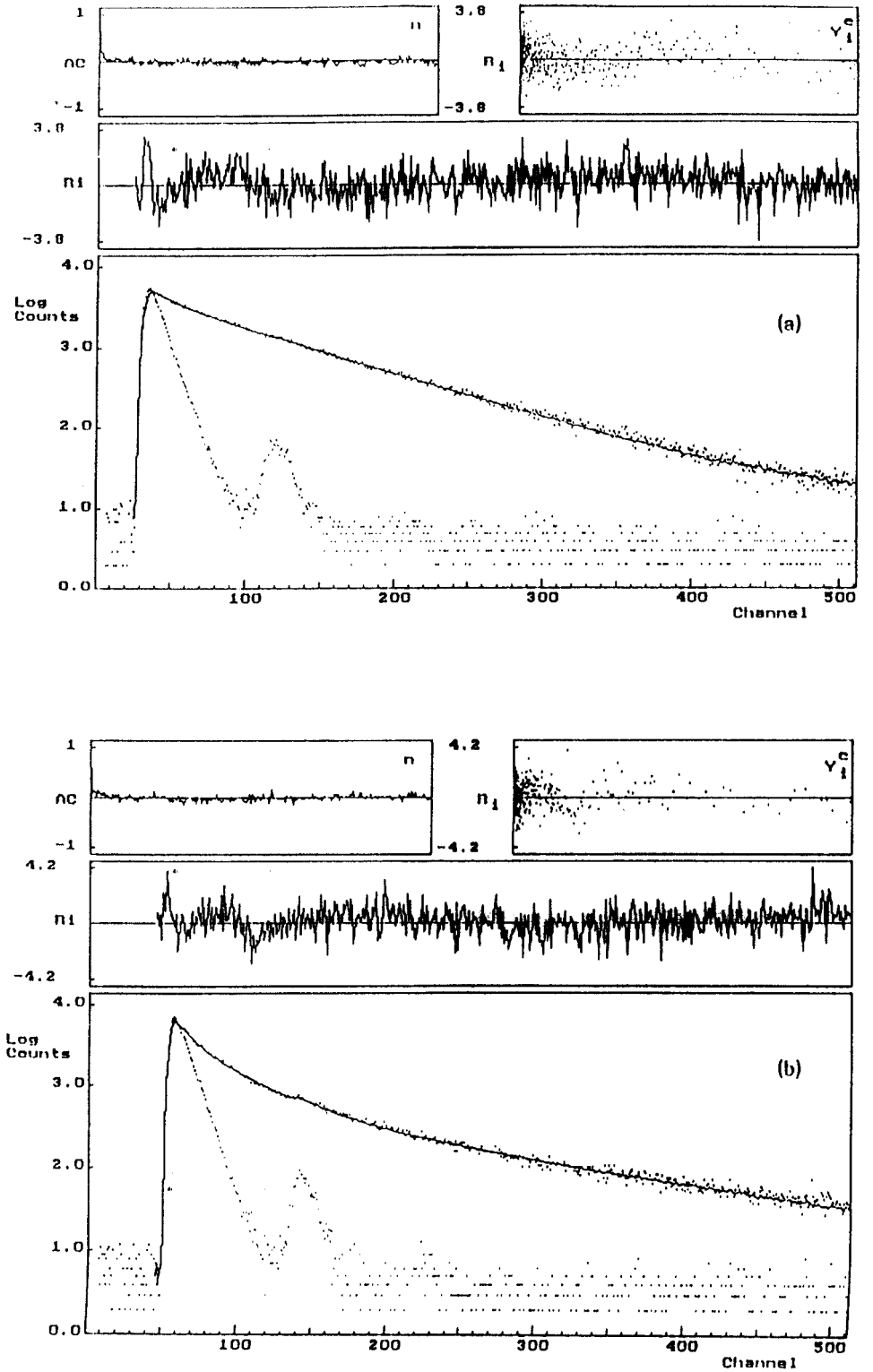


Figure 7. Emission decay profile at 350 nm of copolymer A in a monolayer (a) and at 420 nm of copolymer D in a monolayer (b). Time increment: 0.174 ns.

of the complexity of the system no physical correlation can be made between the decay times and emitting species present in the system.

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \quad (1)$$

The emission decay profile for copolymer A in the monolayer on a quartz slide is shown in Figure 7, where the decay slightly deviates from single exponentially just like the decay for copolymer D in a homogeneous solution, which in view of the stationary emission data could be due to energy migration within a monolayer. It has been reported that the emission decays of a dye compound incorporated in conventional fatty acid monolayers and LB films show an initial rapid decay due to the formation of aggregated species even at a few percent of dye contents.[10] In the present case, no such fast-decaying component in the initial stage was observed. This suggests that the carbazole chromophores in the polymer monolayer are dispersed more uniformly than in conventional fatty acid monolayers and LB multilayers. The emission profiles and the decay analysis in monolayers (Table 3) are not essentially different from those in solution, except that the contribution of energy migration in the monolayer is more significant. In LB multilayers with over six layers,

Table 2. Decay Parameters of the Monomer Emission (350 nm) and Excimer (420 nm) of Carbazole Copolymers in a CH_2Cl_2 Solution

copolymer	τ_1/ns (A_1)	τ_2/ns (A_2)	τ_3/ns (A_3)
	Monomer Emission (350 nm)		
A	10.0		
B	10.2		
C	11.3 (0.42)	6.2 (0.13)	
D (global)	10.5 (0.39)	3.7 (0.16)	24.9 (0.01)
	Excimer Emission (420 nm)		
C	9.73 (0.44)	9.75 (0.11)	22.51 (0.09)
D (global)	10.5 (0.39)	3.7 (0.16)	24.9 (0.01)

Table 3. Decay Parameters of the Monomer Emission (350 nm) and Excimer (420 nm) for Carbazole Copolymers in a Monolayer

copolymer	τ_1/ns (A_1)	τ_2/ns (A_2)	τ_3/ns (A_3)
	Monomer Emission (350 nm)		
A	12.8 (0.46)	2.53 (0.18)	
B	8.12 (0.39)	1.76 (0.33)	30.8 (0.02)
C	6.71 (0.19)	1.18 (0.12)	22.7 (0.02)
	Excimer Emission (420 nm)		
C	7.62 (0.31)	2.36 (0.17)	23.11 (0.04)
D	5.43 (0.37)	1.33 (0.32)	23.55 (0.06)

the decay of the monomer emission becomes more rapid due to the effective interlayer (vertical) energy migration in addition to intramonolayer energy migration.

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References and Notes

(1) Part 3: Mizuta, T.; Matsuda, M.; Miyashita, T. *Macromolecules* **1991**, *24*, 5459. Part 2: Miyashita, T.; Yatsue, T.; Matsuda, M. *J. Phys. Chem.* **1991**, *95*, 2448.
(2) Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964.
(3) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.
(4) (a) Miyashita, T.; Saito, H.; Matsuda, M. *Chem. Lett.* **1991**, 859. (b) Miyashita, T.; Konno, M.; Matsuda, M.; Saito, S. *Macromolecules* **1990**, *23*, 3531.
(5) Miyashita, T.; Mizuta, Y.; Matsuda, M. *Br. Polym. J.* **1990**, *22*, 327.
(6) (a) Hodge, P.; Khoshdel, E.; Tredgold, R. H.; Vickers, A. J.; Winter, C. S. *Br. Polym. J.* **1985**, *17*, 368. (b) Tredgold, R. H. *Thin Solid Films* **1987**, *152*, 223.
(7) (a) Ohmori, S.; Ito, S.; Yamamoto, M. *Macromolecules* **1990**, *23*, 4047; **1991**, *24*, 2377.
(8) (a) Yamazaki, I.; Tamai, N.; Yamazaki, T. *J. Phys. Chem.* **1987**, *91*, 3572. (b) Yamazaki, T.; Tamai, N.; Yamazaki, I. *Chem. Phys. Lett.* **1986**, *124*, 326.
(9) Gust, D.; Moore, T. A.; Moore, A. L.; Luttrull, D. K.; DeGraziano, J. M.; Boldt, N.; Van der Auweraer, M.; De Schryver, F. C. *Langmuir* **1991**, *7*, 1483.
(10) Khalil, M. M. H.; Boens, N.; Van der Auweraer, M.; Ameloot, M.; Andriessen, R.; Hofkens, J.; De Schryver, F. C. *J. Phys. Chem.* **1991**, *95*, 9375.
(11) Solaro, R.; Galli, G.; Ledwith, A.; Chiellini, E. In *Polymer Photophysics*; Phillips, D., Ed.; Chapman and Hall: New York, 1985; p 377.
(12) Murakata, T.; Miyashita, T.; Matsuda, M. *Macromolecules* **1988**, *21*, 2730.
(13) Mizuta, Y.; Miyashita, T.; Matsuda, M. *Polym. J.* **1991**, *23*, 1387.
(14) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973.
(15) Miyashita, T.; Sakai, J.; Mizuta, Y.; Matsuda, M. *Thin Solid Films*, in press.
(16) Janssens, L. D.; Boens, N.; Ameloot, M.; De Schryver, F. C. *J. Phys. Chem.* **1990**, *94*, 3564.