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# Thermal Relaxation of Langmuir–Blodgett Films of Poly(vinyl alkylals) Studied by the Interlayer Energy-Transfer Method

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ABSTRACT: Ultrathin polymer films of poly(vinyl alkylals) with a spatial order of multilayers were made by the Langmuir–Blodgett (LB) technique. The structural relaxation was examined by energy-transfer phenomena between phenanthrene (P) labeled and anthracene (A) labeled layers. The energy-transfer efficiency began to increase markedly with the first rise in temperature. Once the sample was heated to 100 °C, the increased efficiency was maintained during successive cooling and heating cycles, and the value was independent of the spatial arrangement at the initial stage. The efficiency resembled that of spin-coated films containing the P and A polymers with the same compositions. The layered structure was irreversibly disordered and mixed by the thermal treatment. The structural changes could not be detected by a macroscopic measurement such as ellipsometry but could be sensitively observed by the energy-transfer method.

## Introduction

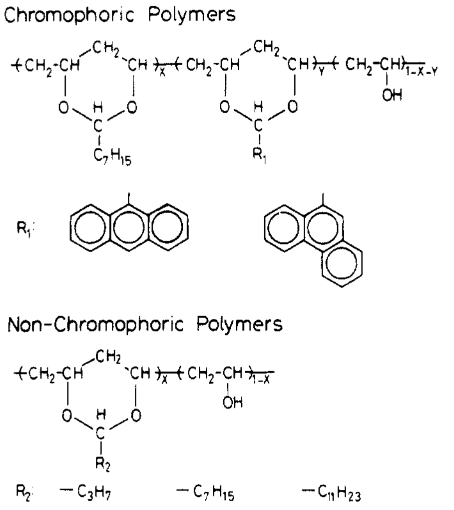
Deposition of a monolayer on a substrate by the Langmuir–Blodgett (LB) technique[1,2] yields layered films with a thickness of a few nanometers. Fabrication of supermolecular structures could be valuable in making functionalized organic films. A new LB material, polymer LB, overcomes the drawbacks of conventional fatty acid films with its amorphous character.[3-13]

For application of the LB films, the stability of the layered structure is critical. Small-angle X-ray scattering is a powerful method for elucidating the layered structure and its stability. Ringsdorf et al. reported the structural stability of LB films prepared from a macrolipid which consists of two-chain surfactants interconneted by hydrophilic polymer chains.[8] By use of an appropriate length of spacer units between lipid monomers, the X-ray reflection was retained at high temperatures; i.e., the thermal stability was improved markedly by the adjustment of the molecular flexibility. Rabolt et al. also studied the stability of polymer LB films by polarized infrared spectroscopy.[9] The hydrophobic side chains attached to a hydrophilic main chain showed a high degree of orientation to the substrate. The orientation was disordered by heating, but cooling back to ambient temperature resulted in a significant recovery of the initial order. These samples are made from polymeric materials, but the polymer chains act merely as a hydrophilic spacer. The main structure of the LB films consists of long alkyl side chains or highly hydrophobic fluorocarbon chains which form crystallike domains.

Measurement of the microscopic disordering is indispensable for structural studies on layered thin films. X-ray scattering is a powerful tool for crystalline materials but is not appropriate for determining the diffraction pattern of many LB films made from amorphous polymers. We have used the fluorescence method to detect the structural disordering in the nanoscale order.[14] A pair of energy donor and acceptor layers incorporated in spectroscopically inert layers give information on the distance of separation. Sensitive detection is possible even for the weak fluorescence from a monolayer containing fluorescent probes with a fluorescence quantum yield of only a few percent.[15] In the present study, the structural changes of polymer LB films with the rise of temperature were examined in situ by the interlayer energy-transfer method.

## Experimental Section

**Sample Preparation.** Poly(vinyl alkylals) were synthesized by acetalization of commercial poly(vinyl alcohol) (dp = 2000) with alkylal, according to the procedure of Ogata et al.[6] (see formula).



Three kinds of poly(vinyl alkylals) (PVB, PVO, and PVD) having different side chain lengths were prepared from butanal, octanal, and dodecanal, respectively. With the coexistence of aldehyde chromophores and alkyl aldehyde, some polymers were labeled with fluorescent probes: phenanthrene (P) and anthracene (A) chromophores. The details are described elsewhere.[13,14]

Table I shows the compositions of the synthesized polymers. Unlabeled polymers (PVB, PVO, and PVD) were used as the spacing layer while the polymers labeled with P and A were for the energy donating and accepting layers, respectively. The fractions of alkyl units (X) and chromophoric units (Y) in the polymers were calculated from the UV absorbance of chromophores and carbon fractions measured by elementary analysis. The extinction coefficient of the anthracene unit to determine the fraction of anthracene unit was determined to be 8880 L mol$^{-1}$ cm$^{-1}$ at 364 nm by dissolving the isomers of 4,6-dimethyl-2-(9-anthryl)-1,3-dioxane (a model compound of anthracene unit) in dichloromethane.[14] The extinction coefficient of the phenanthrene group was also determined to be 11750 L mol$^{-1}$ cm$^{-1}$ at 298 nm by using 9-phenanthrenemethanol. The fractions of chromophoric units in the polymers were adjusted to Y = 0.12 (PVO-P) and 0.07 (PVO-A). These labeled polymers were transferable to solid substrates as well as unlabeled ones, and

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**Table I**
**Compositions of Synthesized Polymers, Surface Pressures at the LB Deposition, and Glass Transition Temperatures ($T_g$) of Polymers**

| sample | X, % | Y, % | Y/(X + Y) | surface pressure, mN m$^{-1}$ | $T_g$, °C |
|---|---|---|---|---|---|
| PVB | 70 | 0 | 0 | 20.0 | 63 |
| PVO | 73 | 0 | 0 | 25.0 | 25 |
| PVD | 66 | 0 | 0 | 27.5 | 12 |
| PVO-P | 57 | 12 | 0.17 | 22.5 | 50 |
| PVO-A | 55 | 7 | 0.11 | 21.0 | 48 |

showed no photophysical interaction either in the ground state or in the excited state.

LB films were prepared in the following way. Water in the subphase was ion-exchanged, distilled, and passed through a water purification system (Barnstead Nanopure II). The benzene solution of each polymer (0.01 wt %) was spread on the pure water in a trough (Kenkosha Model SI-1). The temperature of the subphase was 19 °C for PVO and PVD and 7 °C for PVB. The surface film was compressed at the rate of 10 mm min$^{-1}$, and the surface pressure–area isotherm was recorded using a Wilhelmy type film balance (Shimadzu ST-1). A nonfluorescent quartz plate, which is a solid substrate for the fluorescence measurements, was cleaned in oxidative sulfuric acid, rinsed repeatedly with pure water, and then made hydrophobic by dipping it in a 10% solution of trimethylchlorosilane in toluene. Silicon wafers (Shin-etsu Chemical Industries, Ltd.) were used as substrates for the ellipsometry. At the surface pressures listed in Table I, the LB films were prepared by dipping the substrate vertically at a rate of 15 mm min$^{-1}$. For the hydrophobic quartz plate, the deposition was possible in up–down modes from the first dip, yielding a Y-type built-up film.

Figure 1 shows the structure of the PVO film for energy-transfer measurements. At first, four layers of PVO were deposited on a quartz plate in order to prevent the interface effect of the substrate. Next, two layers of PVO-P as energy-donating layers, *n* layers (*n* = 0–8) of PVO as the spacer for the chromophores, and two layers of PVO-A as energy accepting layers were transferred. Finally, PVO layers were again deposited to make the total number of LB layers 18. At this stage we consider that the phenanthrene and anthracene chromophores are distributed more or less homogeneously over the double layers. All samples have the same number of layers and the same compositions of PVO-P, PVO-A, and PVO polymers. These were hereafter called PVO-P*n*A. In the same way, PVB-P*n*A and PVD-P*n*A LB films were pepared. Besides these, PVO was deposited on silicon substrates to measure its thickness by ellipsometry. Before the fluorescence measurements, the samples were allowed to stand for 1 week in a desiccator in order to remove the structural instability at an early stage after the deposition.

A spin-coated film, which has the same compositions with PVO-P*n*A, was also prepared on a quartz plate from a 5 wt % solution of a mixture of PVO, PVO-P, and PVO-A in toluene. The film was dried under vacuum for 12 h. Its thickness was ca. 400 nm.

**Measurements.** The fluorescence spectra were recorded by a Hitachi 850 fluorescence spectrophotometer. The fluorescence measurements at high temperatures were carried out in a thermostated sample chamber. Heating and cooling rates were 0.5 deg min$^{-1}$ in the range 20–100 °C. Thermal treatments of the LB films on silicon wafers and the spin-coated film were done at 100 °C for 2 h. Fluorescence decay curves were measured by a single photon counting method using a picosecond laser system as the excitation light pulse. The details have been described elsewhere.[16,17] The fwhm of the instrumental response function was 500 ps. The thickness of the multilayered films was measured by an ellipsometer (Mizojiri Kogaku). The glass transition temperatures ($T_g$) of the prepared polymers were measured with a Mettler thermosystem Model FP-85.

## Results and Discussion

The energy-transfer method was applied as a probing technique for the structural relaxation of polymer LB films.

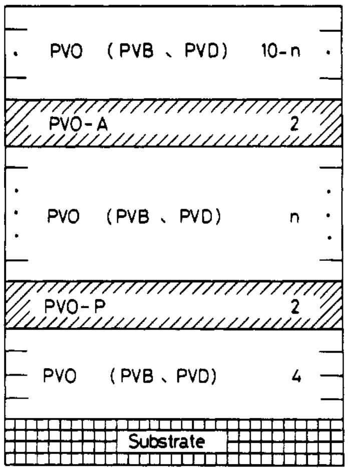

**Figure 1.** Schematic illustration of PVO-P*n*A LB films.

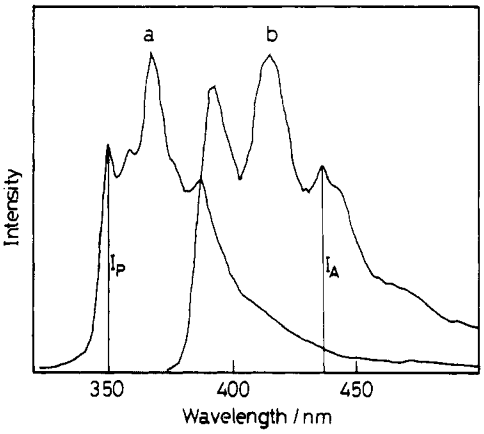

**Figure 2.** Fluorescence spectra of two-layer LB films: (a) PVO-P; (b) PVO-A. Spectra are recorded with a band width of 3 nm and the excitation wavelengths are (a) 298 nm and (b) 348 nm.

Phenanthrene (P) and anthracene (A) were used as an energy donor and an acceptor probe, respectively. These chromophores were separately incorporated into poly(vinyl octylal), as shown in the previous formula. The pair of P and A is quite appropriate for the energy-transfer experiments for the following reasons.

(1) P units have a strong absorption band at 298 nm (the molar extinction coefficient is 11 750 L mol$^{-1}$ cm$^{-1}$). Since this value is ca. 35 times larger than that of the A unit (340 L mol$^{-1}$ cm$^{-1}$), one can selectively excite the P moieties at this wavelength.

(2) A large overlap integral on the fluorescence spectrum of P (donor) and the absorption spectrum of A (acceptor) results in a long energy-transfer distance. $R_o$ = 2.12 nm was calculated by the Förster formula.[18,19]

Figure 2 shows the fluorescence spectra of two-layer LB films of PVO containing P or A moieties. The emission of PVO-P at 350 and 367 nm is the monomer fluorescence of the phenanthrene unit, and the emission at 393, 416, and 438 nm is the monomer fluorescence of the anthracene unit. Each spectrum shows no specific chromophore interaction such as excimer formation. Sufficient separation of the emission bands of these chromophores also makes it easy to evaluate energy-transfer efficiencies. In principle, the efficiency is given by $(I_{P0} - I_P)/I_{P0}$, where $I_P$ is the fluorescence intensity of the P emission and $I_{P0}$ is that in the absence of energy transfer to the A layers. However, the intensity measurements from film to film involve an error of about 5%. Therefore, the intensity ratio, $I_A/I_P$, on the spectrum ($I_A$ is the intensity of A

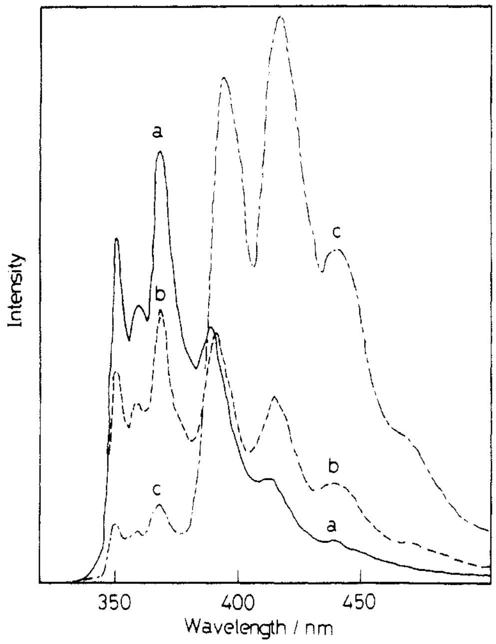

**Figure 3.** Fluorescence spectra of PVO-P*n*A films: (a) PVO-P8A; (b) PVO-P4A; (c) PVO-P0A. Spectra are recorded with the excitation wavelength of 298 nm and the band width of 3 nm.

emission at 438 nm and $I_P$ is the intensity of P at 350 nm) is conveniently indicative of the transfer efficiency.

As shown in Figure 1, spectroscopically inert layers (unlabeled PVO) were sandwiched between the P and A layers. The number of the spacer layers, *n*, was varied from 0 to 8. Figure 3 shows the fluorescence spectra of the multilayered LB films thus prepared, where the P chromophores were selectively excited at a wavelength of 298 nm. As the number of spacer layers is reduced from 8 to 0, the intensity of the P emission decreases. In place of it, the sensitized A emission increases at 393, 416, and 438 nm. This indicates that the excitation energies on the P moieties transfer to the A layers beyond the spacer layers and that the efficiency can be controlled by the layer thickness. However, quantitative analysis based on a theoretical simulation of the energy-transfer phenomena revealed that the chromophores do not stay in the original two-dimensional plane on which the chromophores would be deposited.[14] From a slight increase in the transfer efficiency with the elapse of time after deposition, we concluded that a partial relaxation of the layered structure takes place for a few days in a newly made sample. Therefore, the fluorescence measurements were carried out 1 week after the deposition.

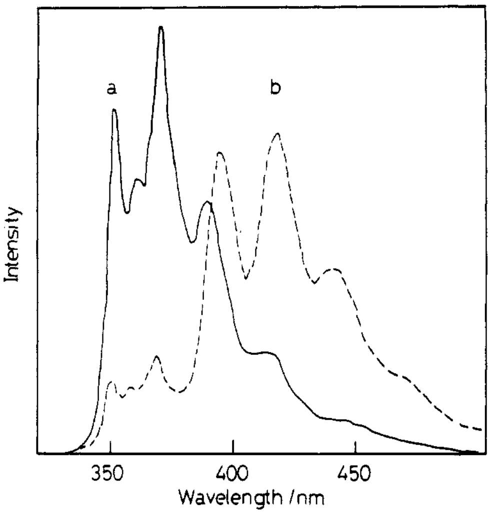

**Figure 4.** Spectral change of a PVO-P8A film by thermal treatment: (a) before heating; (b) after heating.

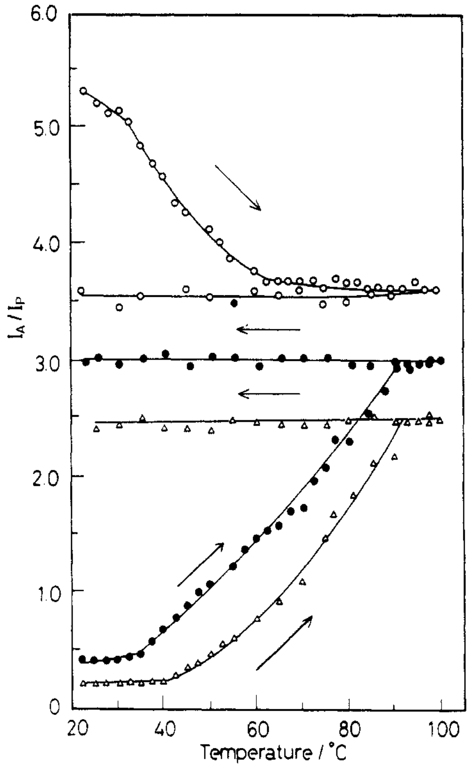

**Figure 5.** Effect of heating on $I_A/I_P$; (○) PVO-P0A, (●) PVO-P4A; (△) PVO-P8A.

Thermal treatment of the LB films causes drastic changes in the fluorescence spectra. Figure 4 shows the fluorescence spectra of PVO-P8A recorded at room temperature before and after the heating. A marked change in the fluorescence spectra occurred during the first rise of temperature, and once the samples were heated up to 100 °C, no appreciable changes were observed in the subsequent cooling and heating cycles. Surprisingly, all the samples gave quite similar fluorescence spectra after the heating, regardless of the number of spacer layers, that is, regardless of the spatial arrangement at the initial stage. This means that the final structure for all the samples is the same, which is determined only by the polymer compositions of PVO-P, PVO-A, and PVO. As mentioned in the Experimental Section, the samples were prepared so as to have the same number of chromophoric layers and PVO layers. These findings indicate that the layered structure is irreversibly disordered and the chromophores are mixed by the heating process. Figure 5 shows the $I_A/I_P$ in the process of the thermal treatment. The structural relaxation starts at about 40 °C and the disordered distribution of the chromophores is kept in the cooling process. In the samples, P4A, P6A, and P8A, the energy-transfer efficiency increased due to the thermal treatment. This shows that a part of the donor–acceptor pairs takes distances of separation shorter than those for the initial locations. In the case of P0A, $I_A/I_P$ decreased in the process of heating, that is, the average distance of P–A pairs increases because the chromophores are initially arranged to the nearest position.

The critical temperatures, at which the rapid increase of transfer efficiencies starts, $T_c$, are listed in Table II. PVO layers begin disordering at around 40 °C, but PVB films show higher critical temperatures than PVO. Compared with the glass transition temperatures ($T_g$) of the polymer bulk (see Table I), the difference between PVO

**Table II**
**Thickness of Total Spacer Layers and Critical Temperatures ($T_c$) of LB films**

| sample | thickness of total spacer layer, nm | $T_c$, °C |
|---|---|---|
| PVB-P6A | 5.1[a] | 55 |
| PVB-P8A | 6.8[a] | 60 |
| PVO-P6A | 6.1 | 38 |
| PVO-P8A | 8.2 | 40 |
| PVD-P6A | 8.3[a] | 48 |

[a] Reference 6.

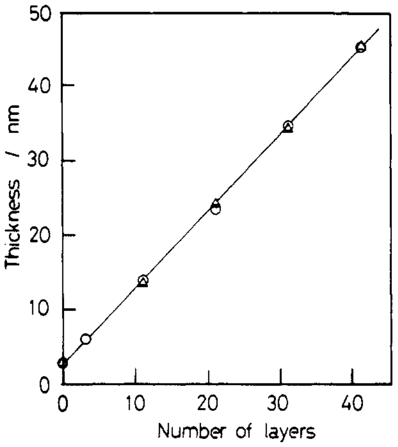

**Figure 6.** Film thickness of PVO LB films as a function of the number of layers: (○) before heating; (△) after heating.

and PVB is probably due to the intrinsic mobilities of the polymer chains. As the length of the side chain becomes longer from PVB to PVD, the value of $T_g$ decreases by the flexibility of the alkyl chains. However, the critical temperatures of the PVD LB films are still higher than those of PVO. This behavior cannot be explained by the difference in $T_g$. This suggests that the $T_g$ value for the polymer bulk is not always applicable to the films having a highly ordered structure. In this case, the long alkyl chains of PVD may assist in the formation of ordered structures at the air–water interface.

The structural relaxation of layered LB films can be well detected by the energy-transfer phenomena. Next, the thickness of the multilayered LB films was checked by ellipsometry before and after heating. Figure 6 shows the relation between the number of layers and the thickness of the LB films deposited on a silicon wafer. The ordinate value at the 0 layer shows the thickness of an oxidized silicon layer located on the surface of the wafer. From the slope of the line, one can obtain the thickness per layer, which was constant (1.02 nm) through the thermal treatment. This means that during the heating there is no disruptive change in the film structure such as peeling off, thermal decomposition, and evaporation. Fluorescence behavior, however, clearly indicated the relaxation of the internal structure. The disordering of layered structure is not reflected in the film thickness. The energy-transfer method is a useful measurement for the microscopic structure of an LB film, even if no change is detected by a macroscopic measurement such as ellipsometry.

Next, the final distribution of chromophoric polymers was considered from the value of $I_A/I_P$ (see Table III). As a reference sample, a spin-coated film having the same polymer compositions as the PVO–P$n$A LB films, was prepared from a mixed solution of PVO-P, PVO-A, and PVO in toluene. The film was heated at 100 °C for 2 h. The fluorescence spectra of the spin-coated film were independent of the thermal treatment. This means that an equilibrium distribution of polymer segments has already been attained in the as-cast film prepared by the spin-coating method. As listed in Table III, the LB films after heating show values of $I_A/I_P$ similar to that of the spin-coated film, irrespective of the initial values. This shows that the layered structure of the LB films is completely disordered and mixed by the thermal treatment.

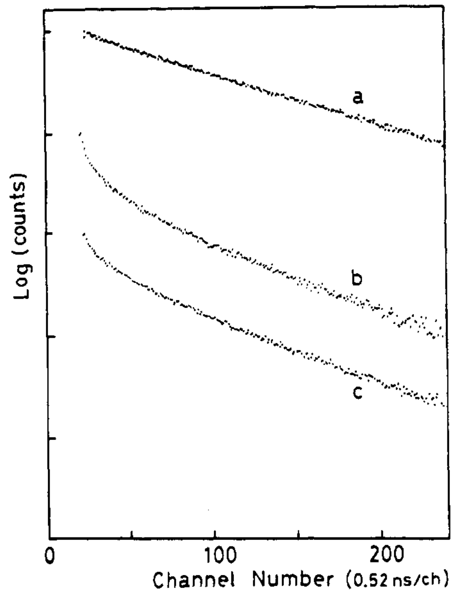

**Figure 7.** Fluorescence decay curves of phenanthrene emission observed at 357 nm: (a) PVO-P8A film before heating; (b) PVO-P8A after heating; (c) spin-coated film.

**Table III**
**$I_A/I_P$ for PVO-P$n$A Films before and after Heating**

| sample | $I_A/I_P$ before heating | $I_A/I_P$ after heating |
|---|---|---|
| PVO-P0A | 5.3 | 3.6 |
| PVO-P2A | 1.2 | 3.2 |
| PVO-P4A | 0.5 | 3.0 |
| PVO-P6A | 0.4 | 2.5 |
| PVO-P8A | 0.1 | 2.5 |
| cast film | 2.4 | 2.5 |

Fluorescence decay curves of the donor emission give more direct information on the transfer processes. Figure 7 shows the semilogarithmic plot of fluorescence intensity versus time after a pulsed excitation at 298 nm. The P8A film before heating shows a nearly straight line, i.e., a single-exponential decay curve with a slight fast component. This is because most of the donor and acceptor chromophores are distributed uniformly in the plane and with small fluctuations of the in-plane concentration. The film thickness of PVO is ca. 1 nm/layer. Therefore, the donor and acceptor probes are separated by an 8-nm-thick spacer. The uniform distance of separation gives a constant energy-transfer rate for each donor, resulting in a single-exponential decay as an ensemble average. On the other hand, if the system contains molecules under various situations, as in this case, different locations and different distances of separation between the P–A pairs, the donor probes exhibit a multiexponential decay as the sum of different transfer rates. Such a case is the P8A film after heating and the spin-coated film. Both films show quite similar decay profiles that are ascribed to the mixed polymer structure. We have already reported quantitative analysis of curve a in Figure 7 (P8A before heating).[14] However, the analysis of curves b and c cannot be performed at the present stage. This problem has been frequently discussed in the field of compatibility of polymer blends.[20-24] If the acceptor molecules take a statistically random distribution around a donor molecule, the decay curve can be expressed by Förster's equation.[18] However, our system has to be considered as a solid film containing random coils of donor and acceptor polymers. To the best of our knowledge, there is no mathematical formula describing such a distribution of donor–acceptor distances. At the present stage, it can be safely said from the decay profiles that the heated LB films take a segment distribution similar to that of a simple mixture of these polymers.

## Concluding Remarks

The fluorescence method is a very powerful tool for determining the structural relaxation. The layered structure of polymer LB films is easily disordered and mixed by heating. Mechanical and thermal stabilities are critical for application. This means that the current data give a negative result for polymer LB films. Amorphous polymers, however, have many advantages as LB materials compared with conventional long-chain fatty acids: variety of the chemical structures, easy introduction of functional groups to the base polymer, uniform distribution of the guest moieties, thinness of one layer, and fewer pinholes. These characters are attributed to the intrinsic characters of the polymeric materials. Development of new LB films with these advantages and improved structural stability is awaited.

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