Photoregulation of Molecular Orientation of Stearic Acid in a Polyion Complex LB Film Containing Azobenzene Derivative

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Polyion complex of stearic acid-d_{35} (St-d_{35}) and 4-octyl-4′-(5-carboxypentamethyleneoxy)azobenzene (8A5) with polyallylamine has been prepared, and orientational regulation of St-d_{35} by trans−cis photoisomerization of 8A5 in the Langmuir−Blodgett films has been studied by means of infrared reflection absorption (RA) spectroscopy. The RA spectra revealed that irradiation with UV light in the temperature range 45−65 °C leads to an orientation change in St-d_{35} by 8A5 isomerization from the trans form to the cis form, and that irradiation with visible light returns 8A5 and St-d_{35} to the initial states. However, below 35 °C and above 75 °C, the performance of the photoregulation of St-d_{35}'s orientation considerably decreased.

1. Introduction

Much research attention has been directed at studying organized photochromic thin films due to their attractive applications as optical information storage media.[1−21] One particular area of interest involves controlling the orientation of liquid crystals using photoisomerizing photochromic films,[1−6] with Ichimura et al.[1−5] having demonstrated that the orientation of nematic liquid crystals a few micrometers thick can be photochemically regulated by modifying the surface of an amphiphilic polymer or a silylating reagent containing an azobenzene moiety. Such photoregulation systems typically consist of a liquid crystal layer coated onto a photochromic thin layer, which functions as the command layer. If, however, long-chain amphiphiles could be used rather than liquid crystals, this would then open the door to a broad range of new applications in information storage systems.

In a micrometer-thick copolymer film consisting of chromophores and nonchromophores, Anderle et al.[14,15] reported that reorientation of the nonchromophores is induced by photoisomerization of the chromophores in liquid crystalline states. Further, Stumpe et al.[16−21] demonstrated that in copolymer film systems photoorientation of the chromophore results in reorientation of rodlike chromophores even in the glassy state. In a previous study,[22] we used Fourier transform infrared (FT-IR) reflection−absorption (RA) spectra to examine the molecular orientation of a liquid crystal mixed with stearic acid in Langmuir−Blodgett (LB) films coated onto an azobenzene derivative, ultimately showing that the orientation of both the liquid crystal and stearic acid can be controlled by photoisomerizing the derivative.

Here, after preparing LB films of a polyion complex of stearic acid and long-chain azobenzene derivative with polyallylamine, we irradiate them with UV or visible light and use the same spectroscopic technique to show that the molecular orientation of stearic acid can be controlled by photoisomerization of the adjacent azobenzene derivative. In addition, we clarify the effect of temperature on orientation regulation.

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2. Experimental Section

We used photochromic molecules of 4-octyl-4′-(5-carboxypentamethyleneoxy)azobenzene (8A5) (Dojindo Laboratories) and stearic acid-d_{35} (St-d_{35}) (Euriso-Top) without further purification. Cationic polymer of polyallylamine (PAA) with an average molecular weight of about 10 000 was donated by Nitto Boseki Co., Ltd.

A polyion complex (8A5+St-d_{35}/PAA) comprised of 8A5, St-d_{35}, and PAA was prepared by mixing in methanol such that the molar ratio of 8A5, St-d_{35}, and PAA (monomer unit) was 1:1:2. To obtain a monolayer of the polyion complex, a chloroform solution of the complex, prepared by evaporating the methanol, was spread onto pure water and the surface pressure−area (π−A) isotherm was measured at 20 °C using a Wilhelmy balance (Kyowa Interface Science Co. Ltd., HBM). It was then transferred to plates of Al (IR RA and UV−vis measurements) or ZnSe (IR transmission measurements) at a surface pressure of 15 mN/m to prepare nine-monolayer LB films of 8A5+St-d_{35}/PAA. The vertical dipping method was used to deposit the first monolayer, and the horizontal lifting method was used for further depositions.

Infrared spectra were obtained using an FT-IR spectrometer (Nicolet, 510M) with a resolution of 4 cm^{-1}. For RA measurements, while subjecting the LB film to continual irradiation by UV or visible light, the p-polarized IR beam was directed incident to the sample plane at 80° from the surface normal.

After 10 min of irradiation, UV−vis spectra were obtained using a spectrophotometer (JASCO, V-500). Probe light for UV−vis measurements was incident to the LB film at an angle of 45°.

Light from a 500-W Xe lamp was passed through either Toshiba UV-360 or L-42 optical glass filters to respectively produce selected-wavelength UV or visible light. The sample was placed on a mount whose temperature was controlled by a refrigerated bath circulator. Temperature was monitored by a copper−constantan thermocouple.

Differential scanning calorimetric (DSC) measurements were taken with a thermal analyzer (Seiko Instruments Inc., DSC 220) using a heating rate of 2.5 °C/min.
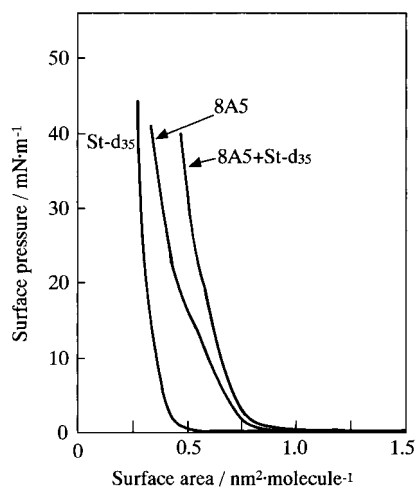
Figure 1. Surface pressure−area isotherms of 8A5+St-d_{35}/PAA, 8A5/PAA, and St-d_{35}/PAA on pure water at 20 °C.
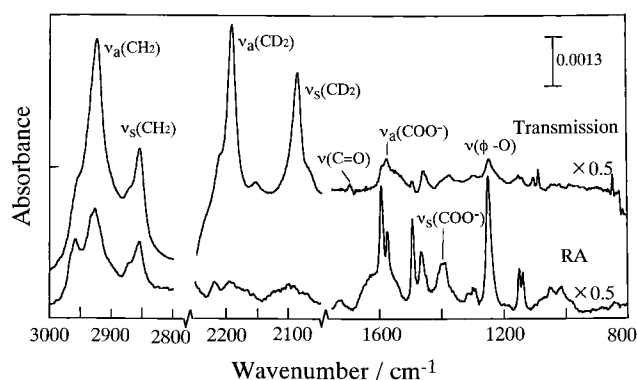

Figure 2. FT-IR transmission and RA spectra of nine-monolayer 8A5+St-d_{35}/PAA LB film.

TABLE 1: Major Infrared Absorption Bands of Nine-Monolayer LB Films of 8A5+St-d_{35}/PAA

wavenumber/ cm^{-1}	assignment[a]	wavenumber/ cm^{-1}	assignment[a]
2959	$\nu_a(CH_3)$	1581	benzene ring
2925	$\nu_a(CH_2)$	1501	benzene ring
2871	$\nu_s(CH_3)$	1473	benzene ring
2854	$\nu_s(CH_2)$	1468	$\delta(CH_2)$
2194	$\nu_a(CD_2)$	1400	$\nu_s(COO^-)$
2088	$\nu_s(CD_2)$	1252	$\nu(\phi\text{-O})$
1704	$\nu(C=O)$	1153	$\nu(\phi\text{-N})$
1604	benzene ring	1142	$\nu(\phi\text{-N})$
1586	$\nu_a(COO^-)$	1088	$\delta(CD_2)$

[a] ν, stretching mode; δ, bending mode; a, asymmetric; s, symmetric.

3. Results

3.1. $\pi-A$ Isotherm. Figure 1 shows $\pi-A$ isotherms of polyion complexes of 8A5+St-d_{35}/PAA, 8A5/PAA, and St-d_{35}/PAA on pure water, where the limiting area of each isotherm is respectively 0.62, 0.52, and 0.33 nm^2. As the value for the 8A5+St-d_{35}/PAA system is larger than the sum of those of 8A5/PAA and St-d_{35}/PAA (i.e., 0.85 nm^2), this indicates that the 8A5 and St-d_{35} molecules in the mixed polyion complex system have a condensed packing configuration.

3.2. Molecular Orientation of LB Film of 8A5+St-d_{35}/PAA. Figure 2 shows the transmission and RA spectra of a nine-monolayer LB film of 8A5+St-d_{35}/PAA on ZnSe and Al plates, respectively. Table 1 summarizes the assignments of the absorption bands.[22−24] When comparing the transmission and

TABLE 2: Spectroscopic Data and Orientation Angle φ in Nine-Monolayer 8A5+St-d_{35}/PAA LB Film

assignment	wavenumber/ cm^{-1}	A_T/A_R	m_z	m_x	φ/ deg
$\nu_a(CH_2)$	2925	1.37	4.81	0.06	75
$\nu_s(CH_2)$	2854	1.00	4.83	0.06	73
$\nu_a(CD_2)$	2194	4.53	4.92	0.04	82
$\nu_s(CD_2)$	2088	3.26	4.97	0.03	81
$\nu(\phi\text{-O})$	1252	0.03	5.04	0.01	29

RA spectra, note that the former shows stronger peaks for the antisymmetric and symmetric CH$_2$ and CD$_2$ stretching bands at 2925 and 2854 cm^{-1} and 2194 and 2088 cm^{-1}, respectively. However, the RA spectrum shows relatively stronger peaks for the in-plane vibration bands of the benzene ring at 1604, 1581, 1501, and 1473 cm^{-1}, the symmetric COO$^-$ stretching band at 1400 cm^{-1}, the ϕ-O stretching band at 1252 cm^{-1}, and the ϕ-N stretching bands at 1153 and 1142 cm^{-1}. When considering such contrastive spectra along with the fact that the electric field of the IR beam is parallel to the film in the transmission measurements and perpendicular to it in the RA measurements, this indicates that the 8A5 and St-d_{35} molecules in the mixed polyion complex system have a regular orientation relative to the film surface.[25−27]

When there exists, as in our case, uniaxial orientation of a transition moment around the surface normal z, the tilt angle φ of the transition moment relative to z can be determined by[27]

$$\frac{A_T}{A_R} = \frac{\sin^2 \varphi}{2m_z \cos^2 \varphi + m_x \sin^2 \varphi} \tag{1}$$

where A_T and A_R are measured absorbance in the transmission and RA spectra, respectively, and m_x and m_z are the x and z components of the spectra intensity enhancement factors (RA versus transmission). Using eq 1, φ for each main absorption band can be solved, since A_T and A_R are known and since m_z and m_x can be precisely calculated using Hansen's equations for optics of thin multilayer films; that is, they are functions of the complex refractive indices of the LB film and substrate, vibrational frequency, angle of incidence in RA measurements, and film thickness.[28]

For major bands, Table 2 summarizes the values of A_T/A_R and φ relative to z. To determine the tilt angle of the carbon chain axis, γ, we use the orthogonal relation

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \tag{2}$$

where α and β are tilt angles of the antisymmetric and symmetric CH$_2$ (or CD$_2$) stretching modes, respectively.[28] Values of γ for 8A5 and St-d_{35} were respectively calculated as 23° and 12°; results indicating that both chain axes tend to be oriented perpendicular to the film surface.

3.3. Effect of Irradiation by UV or Visible Light. Figure 3 shows the absorption spectra of a nine-monolayer LB film of 8A5+St-d_{35}/PAA when irradiated by visible or UV light. Note that irradiation by UV light results in relatively decreasing the $\pi-\pi^*$ transition band of the trans isomer at 332 nm and the appearance of a characteristic cis isomer band at around 450 nm.[20,29,30] These results confirm that, even in the presence of St-d_{35}, UV irradiation causes 8A5 to isomerize from the trans to the cis form. However, since the extent of the intensity change at 332 nm is unfortunately ca. 20%, only part of 8A5 is transformed to the cis isomer.

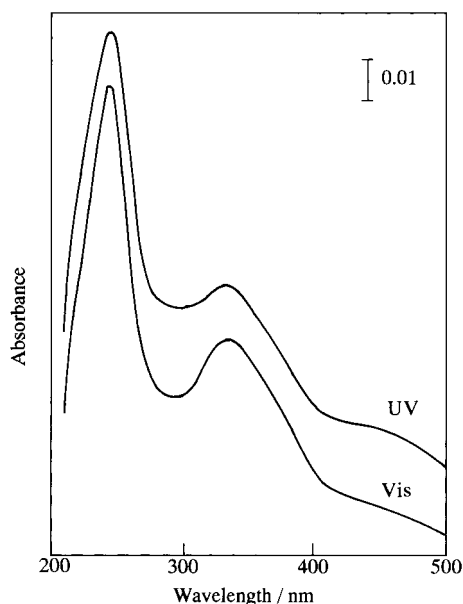**3.4. Effect of Irradiation on FT-IR RA Spectra.** Measured at 25 and 55 °C, respectively, Figures 4 and 5 show the RA

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Figure 3. UV-vis spectra of nine-monolayer 8A5+St-d_{35}/PAA LB film when irradiated by visible (vis) or UV light.
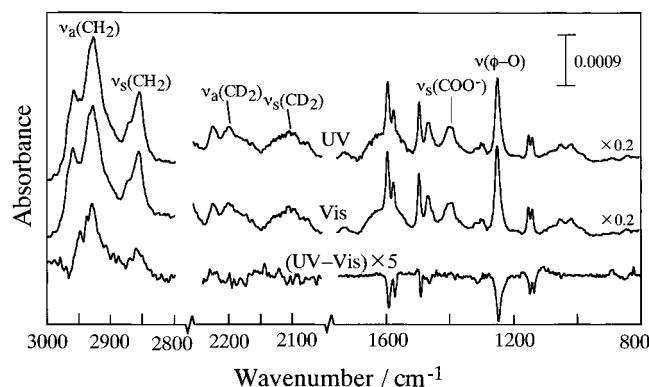

Figure 4. FT-IR RA spectra of nine-monolayer 8A5+St-d_{35}/PAA LB film at 25 °C when irradiated by visible (vis) or UV light. The difference spectrum (UV−vis) is also shown.
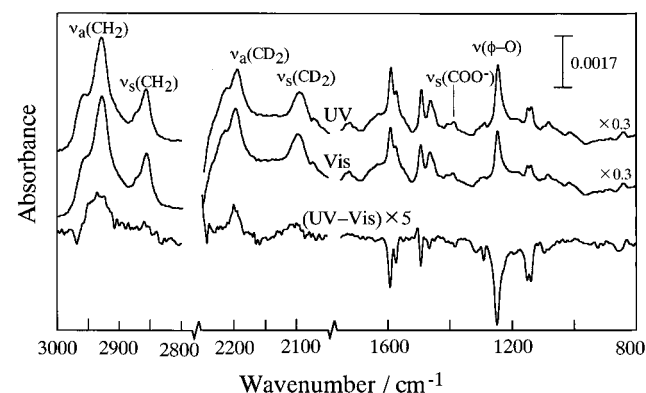

Figure 5. FT-IR RA spectra of nine-monolayer 8A5+St-d_{35}/PAA LB film at 55 °C when irradiated by visible (vis) or UV light. The difference spectrum (UV−vis) is also shown.

spectra of a LB film of 8A5+St-d_{35}/PAA when irradiated by visible or UV light. Also shown are the difference spectra (UV−vis), where at 25 °C, UV irradiation produces intensity changes in 8A5 bands, i.e., a decrease in the intensity of the CH$_2$ stretching bands at 2925 and 2854 cm^{-1} and an increase in that of the benzene-ring, ϕ-O, and ϕ-N stretching bands. In contrast, however, unaffected by UV irradiation were the intensities of the (i) CD$_2$ stretching bands of St-d_{35} at 2194 and 2088 cm^{-1}

TABLE 3: Changes in Absorbance of Major Bands upon Irradiation with UV Light

temperature/ °C	$\Delta A = |A_{vis} - A_{UV}|/10^{-5}$		
	$\nu_a(CH_2)$	$\nu(\phi\text{-}O)$	$\nu_a(CD_2)$
25	22.3	91.1	2.8
35	24.8	123.4	4.7
45	24.3	136.4	13.6
55	28.9	161.7	25.7
65	18.7	110.3	15.0
75	9.8	75.0	4.2

and (ii) COO$^-$ stretching bands of the headgroup of 8A5 and of St-d_{35} at 1400 cm^{-1}. At the higher temperature of 55 °C, however, in addition to similar UV light induced intensity changes in the CH$_2$, ϕ-O, and ϕ-N stretching bands, the COO$^-$ and CD$_2$ stretching bands were also affected. Moreover, the increase in temperature-produced absorbance increases in the CD$_2$ stretching bands and COO$^-$ symmetric stretching band; changes which clarify the inclinations relative to the film surface of the chain axis of St-d_{35} and the bisecting axis of the COO$^-$ group.[26,27]

Of most interest, irradiation by visible light after that by UV light showed that the RA spectra had spectral features that closely correspond with the original spectral features; that is, a cyclic reversible effect occurs.[31] Table 3 summarizes for major bands the intensity differences between UV and visible light irradiation systems maintained at various temperatures, where the antisymmetric CD$_2$ and CH$_2$ stretching bands and the ϕ-O stretching band indicate a measure of change in orientation of the corresponding functional groups, i.e., the carbon chains of St-d_{35} and 8A5 and the azobenzene moiety, respectively. Since all values are greatest at 55 °C, this temperature is accordingly most effective for producing the apparent orientation changes in functional groups. In particular, the value of the CD$_2$ stretching band shows remarkable temperature dependence, being smaller at lower and higher temperatures. On the other hand, the values of the CH$_2$ and ϕ-O stretching bands below 65 °C showed only slight temperature dependence and were considerably smaller at 75 °C. This completely different behavior between 8A5 and St-d_{35} suggests that temperature governs the regulation of St-d_{35}'s orientation.

4. Discussion

4.1. Molecular State of 8A5 and St-d_{35}. The presence of COO$^-$ stretching bands at 1400 and 1586 cm^{-1} (Figure 2, Table 1) confirms the formation of a polyion complex of 8A5 and St-d_{35} with PAA in an LB film;[23,24] that is, both molecules are hanging from the polymer chains of PAA. However, the weak carbonyl stretching band at 1704 cm^{-1} (Figure 2) indicates that free 8A5 and St-d_{35} are present as well, while a value of the limiting area of 8A5+St-d_{35}/PAA is smaller than the sum of 8A5/PAA and St-d_{35}/PAA (Figure 1) indicates that 8A5 and St-d_{35} molecules are randomly mixed in the monolayer film; that is, most St-d_{35} are adjacent to 8A5 precluding the existence of larger domain structures of 8A5 or St-d_{35}. We believe that with such molecular packing, the change in molecular orientation of 8A5 directly affects that of St-d_{35}; an effect which enhances the realization of regulating St-d_{35}'s orientation by the photoisomerization of 8A5.

Table 4 compares the limiting area, peak position of the π−π* band of azobenzene chromophore, and tilt angle of the carbon chain axis for 8A5 and St-d_{35} with corresponding values in other reference systems,[23,24,27,32,33] where it should be noted that the tilt angle of 8A5 in the 8A5+St-d_{35}/PAA system closely approximates those in polyion complex systems of 8A5/PB and

TABLE 4: Limiting Area, Tilt Angle of the Chain Axis γ, and Wavelength of the $\pi-\pi^*$ Transition Band in Various Monolayer Systems

|	limiting area/ nm^2	γ/ deg	wavelength/ nm
8A5+St-d_{35}/PAA	0.85	23, 12	332
8A5/PB^a	0.53	23	317
8A5/PVP^a	0.50	28	322
8A5Ba^b	0.32	18	295
StCd^c	0.20	7	

^{a} PB, 1,5-dimethyl-1,5-diazaundecamethlenepolymethobromide; PVP, poly(1-methyl-4-vinylpyridinium iodide).[18] ^{b} 8A5Ba, barium salt of 8A5.[17] ^{c} StCd, cadmium stearate.[21]

8A5/PVP; which suggests that the orientation of 8A5 in polyion complex systems is not affected by incorporating St-d_{35}. Another noteworthy feature is that the orientation of 8A5 and St-d_{35} is more inclined than that in corresponding metal salts, i.e., 18° for barium salts of 8A5[23] and 7° for cadmium stearate;[27] a finding in good agreement with the fact that limiting areas in polyion complex systems are larger than the sum of the area of corresponding metal salts (0.52 nm^2 = 0.32 (8A5Ba) + 0.20 (St-d_{35})).[32,33]

Another advantage arises due to a larger limiting area in that it provides sufficient free space to allow conformation changes in 8A5.[22,30] As evident from Figure 2, 8A5 in a polyion complex system assuredly photoisomerizes from the trans to the cis form, although the transformation efficiency is low. Such low efficiency is surmised to be due to the formation of an H-aggregate[34] of 8A5 in the LB film, being supported by the fact that there occurs a shorter wavelength shift of the $\pi-\pi^*$ band from its peak in an isotropic solution at 360 nm.[32,35] However, based on the magnitude of the wavelength shift, the degree of H-aggregate forming in the polyion complex system is much lower than that in 8A5Ba, which is strongly restrained from trans−cis isomerization.[30]

4.2. Changes in Molecular Orientation by Light Irradiation. The observed intensity changes in the CH$_2$, benzene ring, ϕ-O, and ϕ-N stretching bands upon UV irradiation (Figures 4 and 5) indicate changes in the orientation of the alkyl chain and azobenzene moiety of 8A5 caused by trans−cis photoisomerization. Since (i) a decrease in band intensity in RA measurements indicates a greater tilt of the transition moment relative to the surface normal and (ii) the transition moments of symmetric and antisymmetric CH$_2$ stretching modes and the chain axis have a mutual orthogonal relation (eq 2),[27] an increase in intensity of the CH$_2$ stretching bands upon UV irradiation at 25 and 55 °C (Figures 4 and 5) can reasonably be interpreted as an inclination of the chain axis of 8A5.[27]

UV irradiation induced photoisomerization of 8A5 at 25 °C, however, does not affect the orientation of the headgroup of COO$^-$ nor the St-d_{35} molecule as indicated by the nearly constant intensities of the COO$^-$ and CD$_2$ stretching bands. At 55 °C, however, UV light produces inclinations of the chain axis of St-d_{35} and the bisecting axis of the COO$^-$ group; inclinations confirmed by increases in the CD$_2$ stretching bands and a decrease in the COO$^-$ stretching band (Figure 5). Thus, it becomes clear that controlling the orientation of St-d_{35} molecules at 55 °C is realized by photoisomerization of the adjacent 8A5, although the number of St-d_{35} molecules changing their orientation is limited since only a portion of the 8A5 molecules can photoisomerize as mentioned in the previous section. Obviously then, further research is needed to allow quantitative estimation of respective molecular orientation changes.
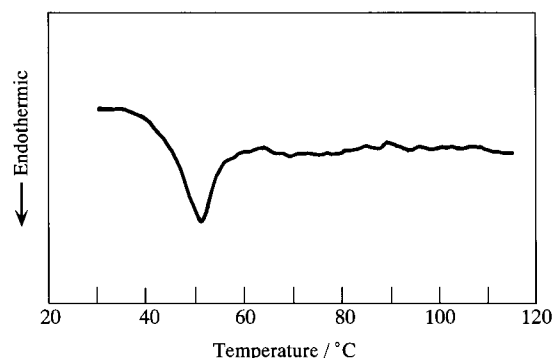
Figure 6. DSC thermogram of bulk 8A5+St-d_{35}/PAA obtained at a heating rate of 2.5 °C/min.

Regarding temperature dependence of molecular orientation changes of 8A5 and St-d_{35} produced by UV irradiation, as shown in Table 3, the orientation of St-d_{35} can be effectively regulated from 45 to 65 °C, with the most effective temperature being 55 °C; whereas below 35 °C and above 75 °C, regulation is relatively impossible. This molecular orientation temperature-dependent behavior of St-d_{35} confirms that temperature plays a critical role in the presented orientation regulation system.

We note from Table 3 that below 35 °C the CH$_2$ and ϕ-O stretching bands have larger values, which indicates that the carbon chain of 8A5 has sufficient potential to change its orientation by trans−cis photoisomerization. The CD$_2$ value, on the other hand, would be smaller owing to no change in the molecular orientation of St-d_{35}. Such insensitivity below this temperature is considered to be due to the St-d_{35} molecule being in a solid state such that the mechanical force generated by 8A5 isomerization is insufficient to alter St-d_{35}'s orientation. In other words, molecular control above 45 °C is highly efficient due to St-d_{35} molecules being in a fluid state similar to liquid crystals. Such a difference in the molecular state of St-d_{35} is confirmed by a broad peak at ca. 50 °C in the DSC chart of bulk 8A5+St-d_{35}/PAA (Figure 6).

On the other hand, when heated to 75 °C or higher, the degree of change in the orientation of 8A5 and St-d_{35} is significantly reduced. Generally, an increase in temperature decreases the orientation order of carbon chains of long-chain alkyl compounds such that at higher temperatures carbon chains are in a completely disordered state mimicking a liquid. The flexibility of carbon chains in 8A5 and St-d_{35} is therefore considerably greater at 75 °C, thus the mechanical force generated by trans−cis isomerization of 8A5 cannot be transferred from 8A5 to St-d_{35}.

In summary, we believe that orientational regulation in LB films of long-chain fatty acids such as St-d_{35} incorporated with photochromic molecules is effectively governed by the molecular state of the long-chain molecules, a hypothesis in good agreement with previous findings by Anderle et al.,[14,15] who reported that controlling the orientation of nonchromophores by photoisomerization of the neighboring chromophore in the side chain of a copolymer system is possible in the nematic but not in the glassy state. Thus, if the molecular state of polyion complexes consisting of 8A5 and another compound vice stearic acid can be controlled by temperature, etc., this could easily lead to the realization of a molecular orientation based photoregulation system that can ultimately be widely applied in optical information storage systems.

5. Conclusions

Using FT-IR RA measurements, we investigated orientation control of St-d_{35} molecules by UV light induced photoisomer-

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ization of the adjacent 8A5 molecule in polyion complex 8A5+St-d_{35}/PAA LB films. This unique photofunctional thin-film system exhibited photoregulation by trans−cis photo-isomerization of 8A5 in the temperature range from 45 to 65 °C, although not below 35 °C nor above 75 °C; a behavior indicating that system temperature, i.e., the states of 8A5 and St-d_{35} molecules, plays a critical role in the photoregulating St-d_{35}'s orientation. These results are of great interest as they demonstrate that, in addition to thermotropic liquid crystal molecules, long-chain fatty acids of St-d_{35} can also be used in a molecular orientation based photoregulation system that is expected to have high application potential as optical memory storage media.

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