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Communications

Control of Molecular Aggregation Features in Polymer-Dispersed Liquid Crystal Films Utilizing a Boronate-Terminated Self-Assembled Monolayer

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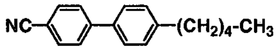
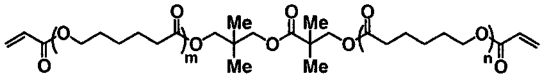
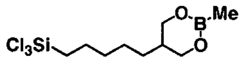
Polymer-dispersed liquid crystal (PDLC) films comprising LC droplets in polymer matrixes are materials of considerable current interest in scientific fields as well as for electro-optic applications to, for example, a new type of LC display panels that do not need alignment films nor polarizers nor backlight.[1] The fabrication of PDLC films can be achieved with relative ease, typically by photopolymerization-induced phase separation (PIPS) of homogeneous LC/prepolymer mixtures sandwiched between two solid substrates.[2] For such heterogeneous PDLC films, however, it can be easily conceived that complex interface layers should be formed by specific interactions of LC molecules with either or both of the substrate surface and polymer chains to bring about unexpected effects on physical properties and electro-optic functions of relevant devices. In previous works,[3] we demonstrated through fluorescence analysis that PDLC films of 4-cyano-4′-pentylbiphenyl (5CB), a typical nematic LC, have a thin interface layer in contact with the substrate surface, where 5CB molecules take unique molecular alignments and mobilities substantially different from those in the interior nematic LC domain. The PIPS process in contact with the substrate surface should proceed under complex interactions of both LC molecules and growing polymer chains with the substrate surface, thus giving a particular interface layer different from the interior bulk. In other words, it can be predicted that controlled chemical modifications of the substrate surface might be able to tune molecular features in the interface layer of PDLC films.



5CB



Diacrylate monomer (m+n=2)



BPS

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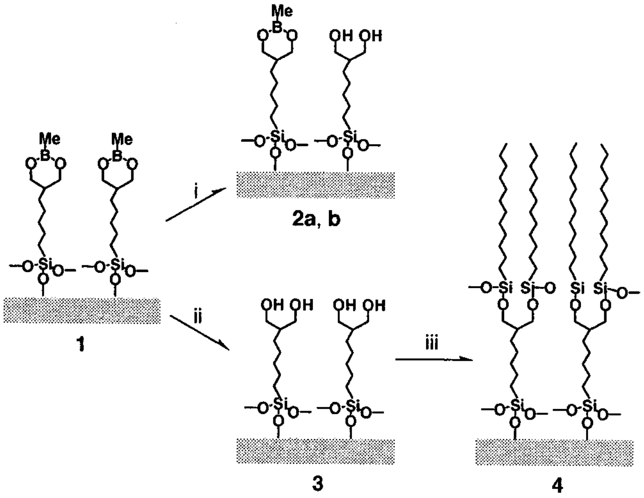

Figure 1. Tuning of the chemical nature on the SAM surfaces; the boronate surface of BPS SAM (**1**), the partially hydrolyzed surfaces (hydrolysis yield, 38% for **2a** and 57% for **2b**), the fully hydroxylated surface (**3**), and the hydrocarbon surface (**4**). (i) Immersion of **1** into 3:7 water/ethanol (v/v) at room temperature for 30 min (**2a**) or for 1 h (**2b**), (ii) three cycles of repetitive immersion of **1** into fresh 3:7 water/ethanol (v/v) at room temperature for 1 h, and (iii) immersion of **3** into a 3 mM toluene solution of dodecyltrichlorosilane in the presence of triethylamine (9 mM) at room temperature for 3 h.

A typical way for surface modifications is the deposition of self-assembled monolayers (SAMs).[4] To obtain important molecular insights into surface effects on PDLC films, we have employed the SAM of a particular boronate-terminated silane compound, BPS,[5] in an attempt to tune surface properties of substrates by controlled hydrolysis of the boronate termini of the SAM. In this communication, we wish to report that the molecular aggregation features in 5CB PDLC films using the SAM-deposited substrates reveal systematic changes depending upon the hydroxy densities on the SAM surfaces.

The boronate-terminated SAM **1** was fabricated on quartz substrates and was hydrolyzed under controlled conditions.[6] As a typical run (Figure 1), the immersion of **1** into a water/ethanol mixture for 30 min or for 1 h gave the 38% or 57% hydrolyzed surface **2a** or **2b** each, whereas the fully hydroxylated SAM (**3**) was obtained by three cycles of repetitive immersion for 1 h into a fresh water/ethanol mixture. The hydrolysis yields for **2a** and **2b** were estimated from relative areas of the XPS B_{1s} signals combined with their advancing contact angles for water.[7] As a counterpart of **3**, a less polar hydrocarbon surface **4** was fabricated by a self-assembly coupled reaction of dodecyltrichlorosilane with the hydroxylated surface **3**.[5,8]

With these modified quartz substrates, PDLC films were constructed by the PIPS procedure for a mixture of 30 wt % 5CB and a diacrylate monomer. Figure 2 shows the normalized fluorescence spectra of the PDLC films taken by excitation at 290, 310, and 320 nm. It is well-known that excited-singlet 5CB emits the fluorescence at ≈340 nm and competitively forms an excimer that emits at ≈400 nm.[9] The fluorescence spectra taken by *excitation at ≤310 nm* substantially vary from film to film, whereas *excitation at 320 nm* gives nearly identical excimer-rich spectra common for all the films. It is of significance to note that when excited at 290 nm, the intensity ratios of the monomer and excimer emissions are systematically changed from the dominant appearance of the excimer emission for the aliphatic hydrocarbon surface **4** to comparable contributions of the monomer and excimer emissions for the polar boronate surface **1,** to a higher intensity of the monomer emission compared with the excimer one for the partially hydroxylated surface **2a**, to a further increase of the monomer emission for the more hydroxylated surface **2b**, and finally to the exclusive appearance of the monomer emission for the fully hydroxylated surface **3**.

Another interesting observation is the excitation-wavelength dependence of the fluorescence spectra. The longer the excitation wavelength from 290 to 310 nm, the greater the relative intensity of the excimer emission commonly becomes with one exception (**4**). In the case of **4**, on the other hand, the excimer emission is exclusive when excited at 290 nm, but the monomer emission appears even in a low relative intensity upon excitation at 310 nm and still more upon excitation at 320 nm (Figure 2E). As demonstrated in previous papers,[3] the excitation light at 290 nm is completely absorbed by 5CB in a very thin interface layer (≤60 nm) due to the extremely high optical density to give the fluorescence from this limited interface layer. We call this the *surface-limited excitation* (SLE). On the other hand, the absorbance of 5CB sharply drops at ≥300 nm so that the excitation light penetrates into a deeper region of the film at longer wavelengths and can pass through the film at 320 nm to give the emission dominantly from the interior bulk. We call this the *through-film excitation* (TFE). Accordingly, the observed excitation-wavelength dependencies clearly indicate that the excimer formation occurs with dominant contributions in the interior domain commonly for all the films, but with remarkably variable contributions in the interface layer depending

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(4) For studies focusing on the interactions of LC molecules with SAMs, see: (a) Yang, J. Y.; Mathauer, K.; Frank, C. W. In *Microchemistry: Spectroscopy and Chemistry in Small Domains*; Masuhara, H., DeSchryver, F. C., Kitamura, N., Tamai, N., Eds.; North-Holland: Amsterdam, 1994; p 441. (b) Ondris-Crawford, R. J.; Lander, L. M.; Frank, C. W.; Twieg, R. J. *Mater. Res. Soc. Symp. Proc.* **1997**, *424*, 311. (c) Drawhorn, R. A.; Abbott, N. L. *J. Phys. Chem.* **1995**, *99*, 16511. (d) Abbott, N. L.; Gupta, V. K.; Miller, W. J.; Shah, R. R. *ACS Symp. Ser.* **1998**, *695*, 81. (e) Mino, N.; Nakajima, K.; Ogawa, K. *Langmuir* **1991**, *7*, 1468. (f) Peek, B.; Ratna, B.; Pfeiffer, S.; Calvert, J.; Shashidhar, R. *Proc. SPIE* **1994**, *2175*, 42.

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(6) Analysis of the XPS C_{1s} signals and ellipsometric measurements of thickness for the resulting hydrolyzed SAMs demonstrated that the boronate linkage is selectively hydrolyzed with no significant destruction of the SAMs. The results are available as Supporting Information.

(7) The data of XPS B_{1s} signals and advancing contact angles for water in the partial hydrolysis experiments for the SAM **1** are provided as Supporting Information. The formation of the fully hydrolyzed SAM **3** was proved by the disappearance of the XPS B_{1s} signal as well as by the low advancing contact angle (≈30°) for water, a typical value for a uniformly hydrophilic surface.

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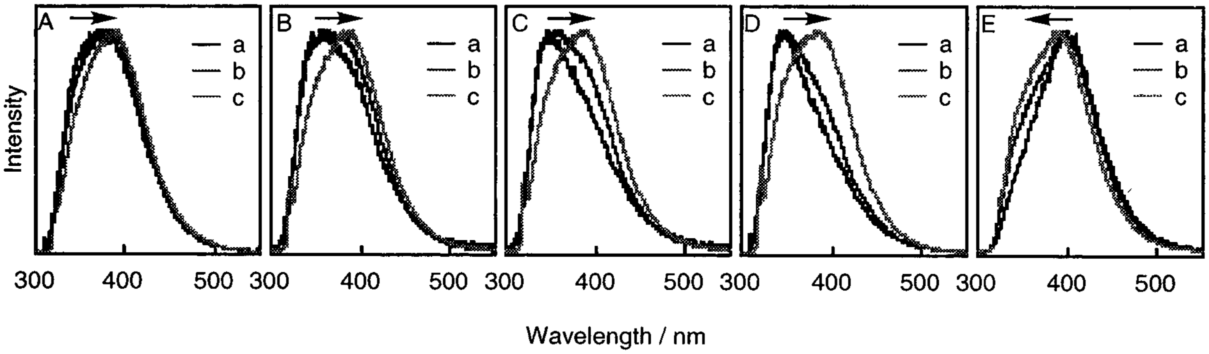

Figure 2. Normalized fluorescence spectra of 30 wt % 5CB PDLC films taken by excitation at (a) 290 nm, (b) 310 nm, and (c) 320 nm at room temperature; the films were sandwiched between the quartz substrates modified with the SAMs (A) **1**, (B) **2a**, (C) **2b**, (D) **3**, and (E) **4**.

Table 1. Electro-Optic Parameters of 77 wt % 5CB PDLC Devices[a]

SAM modification	T_{min} (%)	T_{max} (%)	V_{10} (V)	V_{90} (V)	CR	γ
1	33.7 ± 0.5	83.2 ± 0.5	4.5 ± 0.2	17.9 ± 0.3	2.47 ± 0.05	3.96 ± 0.03
2a	30.4 ± 0.4	83.1 ± 0.5	6.4 ± 0.3	20.1 ± 0.3	2.73 ± 0.04	3.13 ± 0.03
2b	26.1 ± 0.4	81.6 ± 0.4	8.1 ± 0.3	24.5 ± 0.4	3.12 ± 0.04	3.03 ± 0.02
3	20.5 ± 0.5	77.2 ± 0.4	9.8 ± 0.3	29.2 ± 0.3	3.76 ± 0.06	2.98 ± 0.02
4	39.8 ± 0.2	84.6 ± 0.3	3.2 ± 0.2	13.1 ± 0.3	2.12 ± 0.04	4.09 ± 0.03
none[b]	29.4 ± 0.4	78.8 ± 0.4	6.7 ± 0.3	24.8 ± 0.2	2.68 ± 0.05	3.69 ± 0.02

[a] T_{min} and T_{max} are the minimum and maximum transmittances, respectively, V_{10} and V_{90} the voltages at 10% and 90% transmittances, respectively, CR indicating the contrast $T_{\mathrm{max}}/T_{\mathrm{min}}$, and γ representing the susceptibility of the $T-V$ response corresponding to V_{90}/V_{10}. [b] Bare ITO electrodes.

on the hydroxy densities of the surfaces as well as on the surface polarity.

It has been well documented that molecular alignments of 5CB and related LCs nicely fit the excimer formation in the nematic phase but are less favorable in the isotropic and smectic A phases.[9,10] Therefore, the fluorescence results demonstrate that the nematic phase dominates in the interior bulk commonly for all the films, but is substantially disturbed in the interface layer with the polar boronate surface **1** and still more with the hydroxylated surfaces **2** and **3**. As the extreme, it appears that the surface **3** should “freeze” 5CB molecules in the interface layer to prevent the excimer formation. It is probable that the mesogenic interaction of 5CB molecules might be disturbed by interactions with the surface hydroxy or polar boronate groups. In the case of **4**, on the other hand, nematic domains should be favorably formed with little disturbance in the interface layer in contact with the surface **4**. The purely nematic behavior of the fluorescence in the interface layer might be interpreted in terms of a well-established anchoring effect of the long aliphatic chain[11] to facilitate a homeotropic orientation of 5CB even in the LC/polymer composites. Thus, the present observations clearly demonstrate that the molecular aggregation features of 5CB in the interface layer have been widely and systematically tuned by utilizing the boronate-terminated SAM **1** through its controlled hydrolysis and the second aliphatic layer lamination.

Interestingly, electro-optic functions of PDLC devices were also affected by the surface modifications of indium−tin oxide (ITO) transparent electrodes. The PDLC devices of 77 wt % 5CB were constructed by using ITO-coated glass substrates, which had been modified with the SAMs in a manner essentially identical to that described above. The transmittance−voltage ($T-V$) responses of the devices were measured upon application of 1-kHz sinusoidal voltage using a photomultiplier at room temperature. Table 1 summarizes the electro-optic parameters determined from the $T-V$ responses for the PDLC devices. The ratios of the minimum and maximum transmittances representing the contrast (CR) are commonly increased in the order **4** < **1** < **2a** < **2b** < **3**, whereas the susceptibilities of the $T-V$ responses (γ) are enhanced in the opposite order.[12]

This finding suggests that the electro-optic functions of the PDLC devices are controlled by the chemical nature of the electrode surface. As already demonstrated by the SAM effects on the fluorescence behavior, interface layers in contact with the different surfaces should have different molecular alignments of 5CB, that is, from an exclusive homeotropic alignment in the case of **4** to a highly disordered phase in the case of **3**. It can be therefore speculated that such unique molecular alignments of 5CB in the interface layers might cooperatively affect the molecular order in the interior PDLC containing a high content of 5CB. For instance, disordered molecular alignments of 5CB in the interface layer with the hydroxy surface of **3** would induce a substantially disordered nature in the interior LC domains to cause a high degree of light scattering, while the slow response of the device against an applied electric field would arise from low mobilities of 5CB molecules. On the other hand, it might be envisaged that the long aliphatic chains of **4** induce the growth of well-oriented phases not only in the interface layer but also in the

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(12) It was found that electro-optic behavior of a PDLC device with *unmodified bare ITO electrodes* is similar to that of the **2a** or **2b** device.

interior bulk, thus giving rise to an easy cooperative change of the LC ordering upon application of a relatively modest voltage.

Alternatively, the surface modifications would affect relative concentrations and distributions of the LC and polymer domains in the interface region depending on the relative affinities,[13] thus leading to different bulk properties associated with the electro-optic functions of the PDLC devices. Work is now in progress to explore in detail the SAM effects on the electro-optic functions of PDLC devices in association with the molecular features in the interface layers.

Acknowledgment. We are indebted to Dainippon Ink & Chemicals Co. Ltd. for precious technical information on electro-optic measurements of PDLC devices.

Supporting Information Available: Experimental section on 5CB PDLC films, table of film thickness and XPS elemental ratio for SAM **1** and its derivatives **2**−**4**, and figures of the plots of the B_{1s} ratio and advancing contact angle for water vs the time of immersion of the boronate-terminated SAM **1** in water/ethanol, of the normalized fluorescence spectra of 30 wt % 5CB PDLC films taken by excitation at 290 nm at room temperature, and of optical transmittances through 77 wt % 5CB PDLC devices vs an applied 1-kHz voltage at room temperature (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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