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Diacetylenic monolayers containing a boronic acid moiety form a chemically and thermally stable poly(diacetylene) film on water

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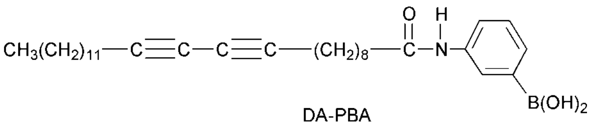
Polymerization and characterization of the monolayers composed of a boronic acid-carrying diacetylenic compound, *m*-(10,12-pentacosadiynamide)phenylboronic acid (DA-PBA), have been performed at the air–water interface and on solid substrates. *m*-(10,12-Pentacosadiynamide)anisole (DA-An), which has a methoxy group in place of the boronic acid group, has also been prepared and used for comparison. DA-PBA formed a stable monolayer on water. Photopolymerization of the monolayer proceeded successfully on water at both 5 and 20 °C and gave a highly conjugated blue polymer with absorption maxima at 600 and 645 nm. The DA-PBA LB film transferred from the surface monolayer onto a quartz plate also provides such a blue polymer upon UV irradiation. This polymerized DA-PBA LB film was found to display completely reversible thermochromism between 20 and 70 °C, and the boronic acid groups located at the surface of the LB film did not interact with poly(vinyl alcohol) at all. Therefore, the spontaneous dehydration among boronic acid groups was supposed to occur, accompanied by polymerization of the diacetylene moiety. The formation of borate glass was supported by FT-IR and XPS spectroscopies.

Introduction

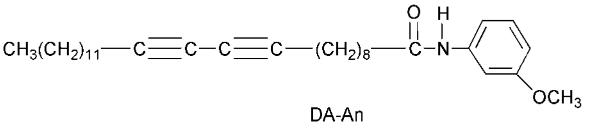
This paper describes studies on the polymerization and characterization of monolayers composed of the boronic acid-carrying diacetylenic compound, *m*-(10,12-pentacosadiynamide)phenylboronic acid (DA-PBA), at the air–water interface.The topotactic polymerization of diacetylene is generally known to be acutely sensitive to the molecular order of molecular assemblies.[1] O'Brien and Kuo have demonstrated that the photopolymerization of cast films from bilayer dispersions of a diacetylenic lipid successfully proceeds below the membrane phase transition temperature (in the crystalline state).[2] Recently, some reports have appeared on the polymerization characteristics of a new type of ultrathin poly(diacetylene) film prepared by self-assembly techniques.[3,4] The resultant poly(diacetylene) films have unique chromatic properties; the conjugated backbone of alternating double and triple bonds causes intense absorptions in the visible spectrum. In single crystals[5] and mono-[6] and multi-layer films,[7,8] these materials are known to undergo blue to red color transitions due to environmental perturbations such as heating and the addition of chemical substances. Charych *et al.* have reported the development of a direct colorimetric detection method for the influenza virus based on the chromatic change of poly(diacetylene) LB films.[9] However, most reports of these chromatic studies describe irreversible behavior. Recently, we have achieved the reversible color change of poly(diacetylene) assemblies with polyion-complexation.[10,11] In this case, the polyion bound to the surface of the poly(diacetylene) assemblies would play an important role in bringing about such a reversibility.

Boronic acids are interesting groups to incorporate into the surface of molecular assemblies. In solution, boronic acids form stable complexes with diol compounds including poly(vinyl alcohol), glucose, and sorbitol.[12–15] In dry hydrocarbon solvent, boronic acids dehydrate readily and form cyclic trimers. Dehydration of boronic acid groups constrained in position on the surface of a two-dimensional monolayer assembly would form a surface comprising cross-linked boronic anhydrides (a borate glass). In fact, Whitesides *et al.* have prepared, on the surface of gold substrates, self-assembled monolayers of ω-mercaptoalkylboronic acids, and have found that the boronic acid groups dehydrate rapidly and form a cross-linked borate glass in dry isooctane.[16]

In the present study, we have prepared fresh DA-PBA, and described the photopolymerization behavior of pure DA-PBA monolayers and laterally diluted DA-PBA monolayers with *m*-(10,12-pentacosadiynamide)anisole (DA-An) at the air–water interface. DA-An has a methoxy group, which is inactive for diol compounds and dehydration, in place of the boronic acid group. The resultant monolayers were then examined in light of their interaction with poly(vinyl alcohol), a typical diol compound, and their thermochromism. Finally, we report the formation of a borate glass due to dehydration accompanied by the topochemical polymerization of the diacetylenic moiety.



DA-PBA



DA-An

Experimental

Synthesis of diacetylenic compounds (DA-PBA and DA-An)

m-Aminophenylboronic acid, *m*-anisidine and 10,12-pentacosadiynoic acid were purchased from Wako Chemical Co. (Japan). DA-PBA and DA-An were synthesized by the reaction of *m*-aminophenylboronic acid and anisidine, respectively, with 10,12-pentacosadiynoyl chloride, which was prepared from 10,12-pentacosadiynoic acid by treatment with oxalyl chloride.

Oxalyl chloride (4.1 g, 32.7 mmol in benzene) was added dropwise to a solution of 10,12-pentacosadiynoic acid (4.0 g, 10.7 mmol) in benzene. The reaction was allowed to proceed at room temperature over 12 h. Removal of the solvent and the unreacted oxalyl chloride gave an oily product; yield 3.5 g (83%). An IR spectrum of this oil showed the appearance of a peak for the C=O stretching band (COCl) at 1790 cm^{-1} and the disappearance of that for COOH at 1715 cm^{-1}.

10,12-Pentacosadiynoyl chloride (3.5 g, 32.7 mmol in THF) was added dropwise to a solution of *m*-aminophenylboronic acid (0.5 g, 15.4 mmol) at 0 °C in THF, and the reaction mixture was then stirred for 1 day. After filtration of the triethylamine·HCl salt produced and removal of the solvent and the excess triethylamine *in vacuo*, the residue was recrystallized from acetone to give a white powder; yield 0.7 g (44%); TLC ($CHCl_3$–CH_3OH = 9 : 1) $R_f = 0.63$, single spot. The structure of DA-PBA was confirmed by means of IR and ^1H NMR spectroscopies.

DA-An was prepared in a similar way by using *m*-anisidine in place of *m*-aminophenylboronic acid. The final product was purified by recrystallization from hexane to give a white powder; yield 88%; TLC ($CHCl_3$–CH_3OH = 9 : 1) $R_f = 0.74$, single spot.

Spreading experiments

The monolayers were obtained by spreading a benzene–dimethylformamide (8 : 2 in vol.) solution (about 1 mg ml^{-1}) of the diacetylenic compound on water that was purified ($\rho > 18$ MΩ cm) using a Milli-Q system (Millipore Ltd.). Ten minutes after spreading, the monolayer was compressed continuously at a rate of 0.25 cm^2 s^{-1}. Wilhelmy's plate method and a Teflon-coated trough with a microprocessor-controlled film balance, FSD-220 (USI systems Ltd., Japan) with a precision of 0.01 mN m^{-1}, were used for surface pressure measurements. The pH in the subphase was adjusted with aqueous HCl and NaOH.

The LB films were prepared by transferring the corresponding monolayers onto solid substrates such as a CaF_2 plate, an Au-coated glass plate and a hydrophobically-treated quartz plate at a constant surface pressure *via* the horizontal lifting method using the FSD-220.

Polymerization and measurements

Polymerization experiments on the monolayers and the LB films were performed in a thermostatted subphase and in a thermostatted air bath, respectively, by irradiation with a low-pressure Hg lamp at a distance of 10 cm. Polymerization processes were monitored by reflection–absorption spectroscopy with a multichannel photodetector, MCPD-100 (Otsuka Electronics Ltd., Japan) and by UV-vis spectroscopy with a UV-2100 spectrophotometer (Shimadzu Co. Ltd., Japan).

The transmission FTIR spectra of the LB films were measured by a Nicolet System 800 using an MCT detector (resolution, 4 cm^{-1}; number of scans, 1024).

X-Ray photoelectron spectra (XPS) for the LB films were measured with a Shimadzu ESCA-1000 system with a Mg-Kα X-ray source at a take-off angle of 5°. The charging shift was corrected with the C_{1s} line emitted from the neutral hydrocarbon.

Results and discussion

Photopolymerization of DA-PBA in surface monolayers and in deposited LB monolayer states

Surface pressure (π)–area (A) isotherms of DA-PBA were first measured at different pHs, and 5 and 20 °C. At pH 5.8 (pure water), DA-PBA provided a stable monolayer with a collapse pressure of 35 mN m^{-1}. The π–A isotherm of DA-PBA measured at 20 °C (pH 5.8) was completely superposed on that at 5 °C. The limiting molecular area, estimated by extrapolating the solid-like region to $\pi = 0$ mN m^{-1}, about 0.30 nm^2 molecule^{-1} was slightly larger than that (0.26 nm^2 molecule^{-1}) for the 10,12-pentacosadiynoic acid monolayer with a collapse pressure of 15 mN m^{-1} (pH 5.8, 23 °C) measured by Wang *et al.*[17] The relatively hydrophilic group of DA-PBA would stabilize the monolayer and also increase the area of the molecule. When the π–A curve was measured at pH 10.3, 5 °C, the monolayer was considerably expanded compared to that at pH 5.8, due to the ionization effect of the boronic acid groups. The electrostatic repulsion among boronic acid moieties must cause such a marked increase in the area of the molecule since the boron atom changes from sp^2- to sp^3-hybridized (tetrahedral anion, $B(OH)_3^-$), which is achieved at high pH.[18] Subsequently, the photopolymerization behavior of DA-PBA was examined in the monolayer state on water. Fig. 1 depicts absorption spectral changes of the monolayer on water (pH 5.8) upon UV irradiation at 5 °C and a constant surface pressure of 20 mN m^{-1}. The appearance of the absorption peaks indicates that the polymerization took place, since there is no absorption peak for the monomeric DA-PBA monolayer in the wavelength range 400–700 nm. The absorption maxima of poly(diacetylene) are indicative of the effective conjugation length of the polymer chain and/or the order of the polymer structure. In studies of poly(diacetylene) LB films, two major absorption maxima are usually recognized.[19] One is found between 600 and 640 nm that corresponds to the so-called blue polymer, and the other is between 500 and 550 nm that corresponds to the shorter or less conjugated red polymer. It should be noted that the polymerized DA-PBA monolayer yields a highly conjugated blue polymer with a remarkable absorption peak at 645 nm and a weak broad shoulder at around 600 nm, which are assigned to the π–π transition (excitonic absorption) and the phonon sideband of poly(diacetylene), respectively.[20] The absorbances at 645 and 600 nm increase rapidly in the early stages of irradiation and saturate after 300 s irradiation. These results imply that the molecular order within the DA-PBA monolayer under these conditions would be well-controlled and suitable for the topotactic polymerization of diacetylene to provide the blue polymer. It is important to elucidate the

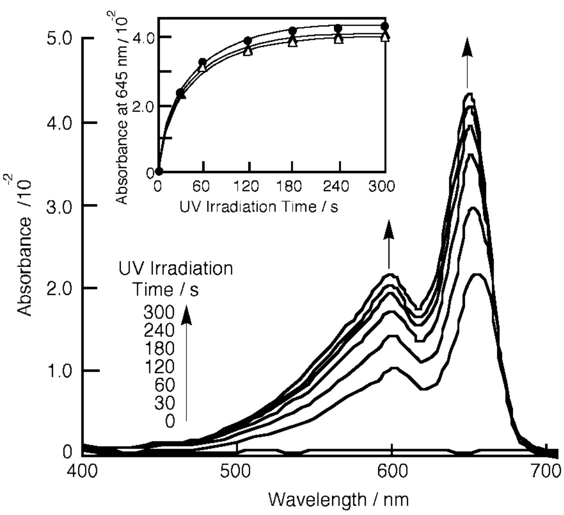


Fig. 1 Absorption spectral change of the DA-PBA monolayer on pure water (pH 5.8) upon UV irradiation at 5 °C. The surface pressure, π, was kept constant at 20 mN m^{-1} throughout the irradiation. The inset shows changes in the absorbance at 645 nm upon UV irradiation for the monolayers at $\pi = 5$ mN m^{-1} (△) and 20 mN m^{-1} (▲), 5 °C and at $\pi = 20$ mN m^{-1}, 20 °C (●).

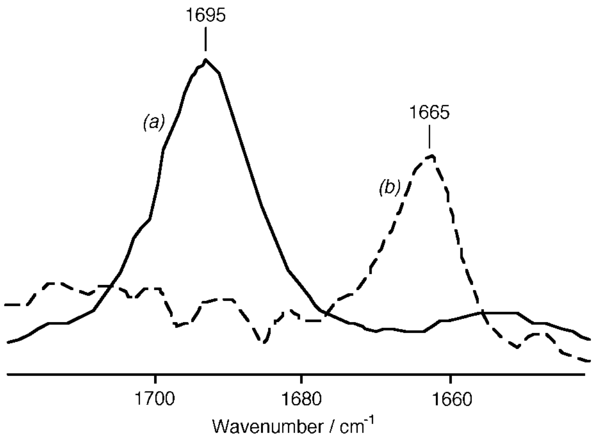


Fig. 2 FTIR spectra of DA-PBA (a) in THF and (b) in LB film on a CaF_2 plate.

surface pressure dependence of polymerization. The inset in Fig. 1 shows the relation between the absorbance at 645 nm and the irradiation time for the monolayer at a constant surface pressure of 5 mN m^{-1} at 5 °C. The polymerization proceeded smoothly, accompanied by the formation of blue polymer, similar to that for the monolayer at $\pi = 20$ mN m^{-1} at 5 °C. In this figure, the data obtained at a higher temperature of 20 °C, $\pi = 20$ mN m^{-1} is also attached. The time course of absorbance is also very similar to that observed at a lower temperature of 5 °C, and the resulting polymer gave a blue phase. These observations correspond well to the results of the π–A isotherms for DA-PBA, and demonstrate that the DA-PBA monolayer has considerable stability, probably due to a strong interaction among the polar head groups including the amide bond. Fig. 2 displays the FTIR spectra of DA-PBA in the LB film and in THF at the C=O stretching band of the amide bond. The LB film was prepared by transferring the monolayer onto a CaF_2 plate by a horizontal lifting method at $\pi = 20$ mN m^{-1}, pH 5.8 and 5 °C. It can be clearly seen that the absorption peak at 1695 cm^{-1} observed in THF shifts drastically to a lower wavenumber of 1665 cm^{-1} in the LB film. Such a shift must be due to formation of hydrogen bonding among the amide groups that would suppress the C=O stretching vibration bringing about a lowering of the stretching energy.

The polymerization of this LB film was also carried out at 20 °C in the same way. The absorption peaks at 645 and 600 nm appeared immediately upon UV irradiation and increased rapidly with irradiation time, and then saturated at 60 s irradiation (data not shown). Such a polymerization profile and formation of blue polymer is very similar to that observed for the surface monolayer before transferrance. Therefore, the results again demonstrate that the molecular order in the monolayer state, which is suitable for topotactic polymerization of the diacetylene moiety, is maintained even in the LB film state in spite of the mechanical transfer, probably because of the existence of hydrogen bonding among the amide groups.

Thermal and chemical stability of poly(DA-PBA) monolayers

Thermochromic behavior of the polymerized DA-PBA monolayer film was examined spectroscopically. Fig. 3 displays the absorption spectral change of the film upon heating. The spectra were measured for the polymerized film-deposited on a quartz plate in pure water. When the temperature was raised from 20 to 70 °C, the absorbance at 645 nm, for the blue polymer, decreased whilst that at 560 nm, for the red polymer, increased. When the temperature was lowered to 20 °C, the spectrum returned to the original one *via* an isosbestic point at 580 nm. The inset in Fig. 3 shows the temperature dependence of the ratio of the absorbance at 645 nm to that at 560 nm (A_{645}/A_{560}). It is clear that there is no hysteresis between the heating and cooling processes. These results imply that the thermochromism of the polymerized DA-PBA [poly(DA-PBA)] LB film is fully reversible under these conditions. Thermochromic phenomena have been observed in poly(diacetylene) assemblies,[5–8] however, most of these reports, except for O'Brien 's cast multilayer films,[2] describe irreversible behavior. Thus the observed reversible thermochromism should be noted. We have previously found that a polyion-complexed poly(diacetylene) assembly displays reversible thermochromism. In this case, poly(styrene sulfonate), as a polyion that reinforces the assembled structure, would play an important role in causing such reversibility in the thermochromism. Therefore, in the case of the polymerized DA-PBA LB film, there must be strong interactions among the boronic acid groups including hydrogen bonding of the amide groups.

As mentioned earlier, the boronic acid group can form stable complexes with diol compounds, and in particular such a complexation is enhanced when the boron atom is an sp^3-hybridized tetrahedral anion, which is achieved at high pH. The absorption spectra of the poly(DA-PBA) LB film before and after immersion into aqueous poly(vinyl alcohol), a typical diol compound, solution (1×10^{-3} M, here M is the molar concentration of poly(vinyl alcohol) as a repeating unit, pH 13, 20 °C) show no considerable differences even after 5 h immersion. This suggests that boronic acid groups were not

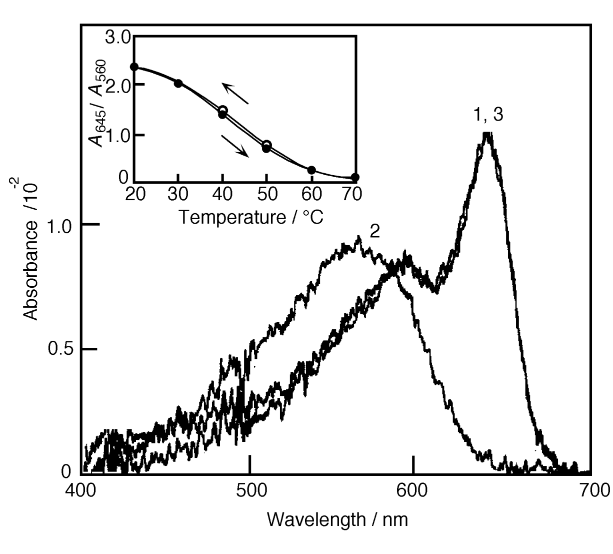


Fig. 3 Absorption spectra of a polymerized DA-PBA/DA-An (1 : 1) mixed monolayer-deposited quartz plate, which was placed in pure water (pH 5.8): curve 1, 20 °C; 2, 70 °C; 3, after cooling back to 20 °C.

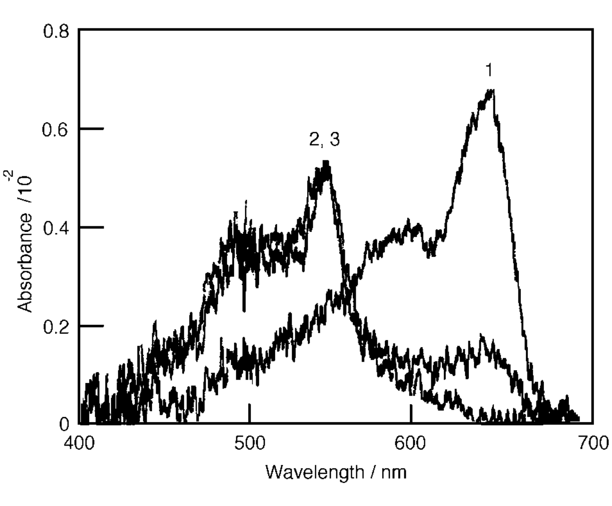


Fig. 4 Absorption spectra of a polymerized DA-PBA/DA-An (1 : 1) mixed monolayer-deposited quartz plate, which was placed in pure water (pH 5.8): curve 1, 20 °C; 2, 70 °C; 3, after cooling back to 20 °C.

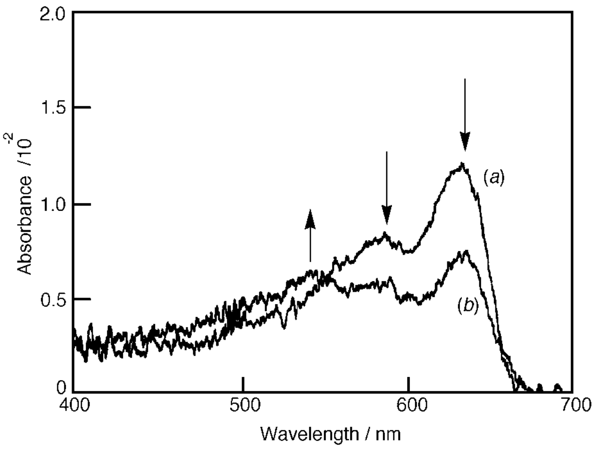


Fig. 5 Absorption spectra of a polymerized DA-PBA monolayer-deposited quartz plate (a) before and (b) after immersion into a poly(vinylalcohol) solution (1×10^{-3} M, here M is the molar concentration of poly(vinyl alcohol) as a repeating unit, pH 13.5) for 5 h.

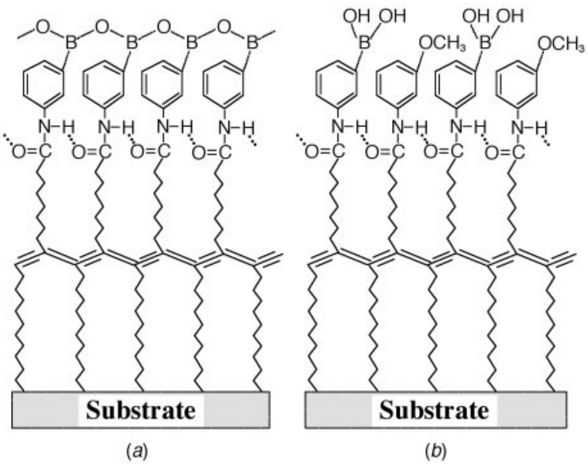


Fig. 7 Possible illustration for poly(diacetylene) assembled monolayers for (a) polymerized monolayer of pure DA-PBA and (b) that of a DA-PBA/DA-An (1 : 1) mixture.

free, but dehydrated. To confirm such a dehydration among boronic acid groups, the same experiments were performed for the attenuated monolayer of DA-An having a methoxy group in place of the boronic acid group. It is expected that the boronic acid groups would be isolated separately in such a mixed monolayer.

The π–A curve for the 1 : 1 binary mixture of DA-PBA and DA-An was measured at pH 5.8, 5 °C and is displayed in Fig. 1. This binary mixture also provided a dense, stable monolayer with a collapse pressure of 34 mN m^{-1} and a limiting molecular area of 0.3 nm^2 molecule^{-1}, values which are very close to those of pure DA-PBA. The photopolymerization of the single-layer LB film on a quartz plate of the mixed monolayer at 5 °C proceeded smoothly and gave only a blue polymer with an absorption maximum at 645 nm. Fig. 4 shows the spectral change of this polymerized LB film upon heating or cooling in water. It can be clearly seen that with heating up to 70 °C from 20 °C, the blue polymer with an absorption maximum at 645 nm completely transforms to the red polymer with an absorption maximum at 540 nm. On cooling to 20 °C, the spectrum remains showing red polymer at 540 nm. This spectral profile demonstrates an irreversible thermochromic process for the mixed monolayer, different from that for the pure poly(DA-PBA) LB film. Fig. 5 shows the spectral change when the polymerized mixed LB film was immersed in aqueous poly(vinyl alcohol) solution. The absorbance at 645 nm due to the blue polymer surely decreases with an increase in the absorbance at 540 nm based on the red polymer, strongly suggesting that poly(vinyl alcohol) would interact with boronic acid groups and then perturb the effective conjugation length of the poly(diacetylene). From these results, it can be concluded that boronic acid groups in the pure poly(DA-PBA) LB film are not free but exist in dehydrated form *i.e.* in borate glass (or boronic anhydride) that would bring about the enhanced thermal and chemical stability.

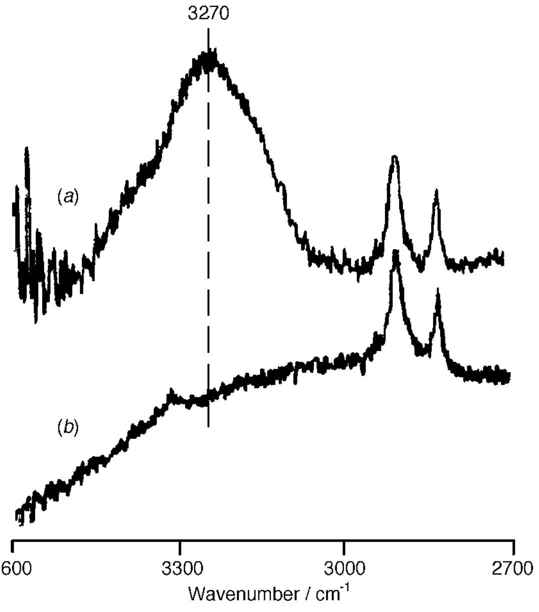


Fig. 6 FTIR spectra of (a) polymerized DA-PBA/DA-An (1 : 1) mixed monolayer and (b) polymerized DA-PBA monolayer on CaF_2 plates.

To obtain more direct evidence to prove the formation of borate glass, FT-IR and XPS spectroscopies were applied for the polymerized LB film. Fig. 6 compares FT-IR spectra in the OH stretching band region between the pure DA-PBA LB film and the binary LB film (1 : 1) of DA-PBA and DA-An. The former film is found to have no OH group probably because of dehydration (Fig. 7a). The XPS spectra for four separate samples of the pure poly(DA-PBA) LB film (data not shown), in which the boronic acid moiety was located at the surface, had an average value of 2.0 ± 0.1 for the ratio of oxygen to boron. The DA-PBA molecule contains one boron atom and three oxygen atoms. Therefore, the obtained value suggests that the species present on the surface was indeed the anhydride and not the boronic acid, for which one would expect a ratio of oxygen to boron of 3.0.

Conclusions

The *m*-(10,12-pentacosadiynamide)phenylboronic acid, DA-PBA, forms a stable monolayer on water. Photopolymerization of the monolayer proceeds successfully on water at both 5 and 20 °C and yields a highly conjugated blue polymer. The transferred DA-PBA LB film from the surface monolayer onto a quartz plate also provides such a blue polymer upon UV irradiation. Interestingly, this polymerized DA-PBA LB film is found to display completely reversible thermochromism between 20 and 70 °C, and the boronic acid groups on the surface of the LB film do not interact with poly(vinyl alcohol). Therefore, the spontaneous dehydration among boronic acid groups is supposed to occur, accompanied by polymerization of the diacetylene moiety. The formation of borate glass is also supported by FT-IR and XPS spectroscopies. At present, we have not determined at exactly which stage the dehydration takes place. Further studies will be needed to clarify such a process.

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