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Effect of Position of Butadiyne Moiety in Amphiphilic Diacetylenes on the Polymerization in the Langmuir−Blodgett Films

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ABSTRACT: We synthesized a series of amphiphilic diacetylenes with the same total length of the alkyl chains but with the butadiyne moiety at different positions in the molecules. These molecules formed monolayers, which were transferred on solid substrates to fabricate Langmuir−Blodgett (LB) films. UV−vis absorption spectra of the LB films changed on polymerization by the irradiation with UV light. The LB films were categorized into blue-red, red, and yellow phases on the basis of the spectral change. These different behaviors on polymerization were explained in terms of the tilt angle of the butadiyne moiety and the distance between the adjacent molecules. Surface pressure−area isotherms showed that the intermolecular distance was ca. 5 Å for all the LB films. This value was almost the same with the typical one for polymerizable diacetylenes in crystals. The tilt angle of the butadiyne moiety was estimated using IR spectroscopy, XRD, and the CPK model. The value for blue-red phase was similar to the typical one for polymerizable diacetylenes in crystals. The tilt angle for the red phase was larger than that for the blue-red phase, while the butadiyne moiety in the yellow phase was almost perpendicular to the film surface.

Introduction

Diacetylenes (DA) are known to polymerize in the solid state on irradiation with UV light or γ-rays.[1,2] The polymerization behaviors have been studied in crystals,[3−7] Langmuir−Blodgett (LB) films,[8−14] self-assembled monolayers,[15−18] vacuum-deposited films,[19] cast films,[20,21] liquid crystals,[22] and bilayer membranes dispersed in water.[23−26] The LB technique is an attractive method for constructing ultrathin films with structures defined at the molecular level. This feature has initiated many investigations on the fabrication of monolayers and LB films of amphiphilic diacetylene derivatives, especially from the viewpoint of polymerization behaviors of the monomers as well as thermochromic behaviors of the resulting polydiacetylenes.[10,11,14]

Polymerization behavior of diacetylenes in crystals has been explained by the following two parameters: one is the distance between the centers of the neighboring butadiyne moieties, and the other is the inclination angle between the butadiyne axis and the stack direction.[27,28] These parameters should also be applied to the polymerization of diacetylenes in the LB films. However, to the best of our knowledge, few studies have investigated directly the effect of these parameters on the polymerization in the LB films.[14]

The purpose of this study is to examine the effect of varying the position of the butadiyne moiety in amphiphilic diacetylenes on the polymerization as well as to investigate the correlation between the polymerization behavior and the molecular arrangement. We have synthesized a series of amphiphilic DA($m-n$) with the position of the butadiyne moiety varied systematically. The spacer length, “n”, represents the length of the alkyl chain connecting the butadiyne and carboxyl groups in DA($m-n$). The number “m” means the length of the alkyl chain attached to the other end of the butadiyne group. The total length of the alkyl chains is kept constant to exclude any differences in the molecular properties such as film-forming ability and molecular length. The polymerization behavior of DA($m-n$) LB films was investigated using UV−vis absorption spectroscopy. We have studied the orientation of DA($m-n$) molecules using IR spectroscopy, XRD, and the CPK model. The relationship between the molecular arrangement and the polymerization behavior is discussed.

$$\mathbf{CH_3(CH_2)_{m\text{-}1}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_n\text{-}COOH}$$

$$\mathbf{DA(\ m\ \text{-}\ n\ )\ (\ m + n = 20\ )}$$

Experimental Section

Materials. DA($m-n$) with various spacer lengths ($m + n = 20$; m, $n = 2$, 4, 6, 8, and 10) were synthesized in a similar way as reported in the literature.[8,29,30] UV spectroscopic grade chloroform (Dojin) was used as a spreading solvent. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) was purchased from Nacalai Tesque, Inc.

Preparation of Monolayers and LB Films. The measurements of the surface pressure−area ($\pi-A$) isotherms and the deposition of LB films were carried out using a Lauda film balance. Chloroform solution of DA($m-n$) was spread at 17 °C onto Cd^{2+} buffer solution (0.4 mM $CdCl_2$ and 0.05 mM $KHCO_3$) at pH = 6.3, which was prepared with the water distilled after passing through a mill-Q filter. DA($m-n$) molecules were converted into their cadmium salts on this subphase. Monolayers were transferred at a surface pressure of 25 mN m^{-1} onto the substrates by the vertical dipping method.

Polymerization and Characterizations. UV−vis absorption spectra were measured using a Shimadzu UV-265FS spectrophotometer. Quartz plates hydrophobized with HMDS were used as the substrates for UV−vis absorption measurements. The LB films were set on a rotating table and polymerized by the irradiation with UV light for various irradiation times. The irradiation times depended on the DA($m-n$) species and were in the range 60−200 min until the

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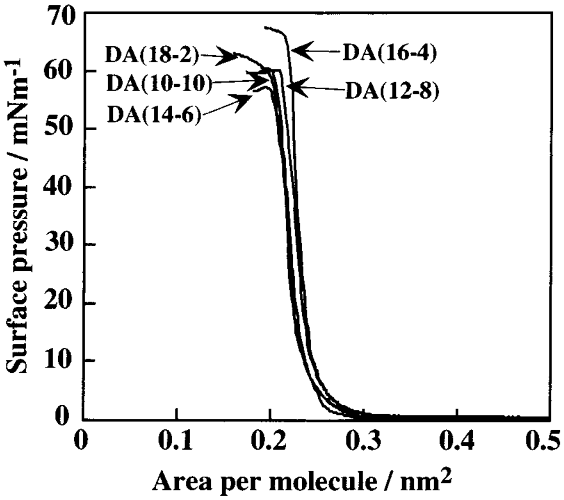

Figure 1. Surface pressure−area isotherms of DA(*m*−*n*) on Cd^{2+} buffer (0.4 mM $CdCl_2$ and 0.05 mM $KHCO_3$) at 17 °C.

spectral change became saturated. A 50 W low-pressure mercury lamp was used as the source of UV light for the polymerization. The distance between the Hg lamp and the film surface was 19 cm. X-ray diffraction (XRD) measurements of the LB films were made on a Phillips PW1800 X-ray diffractometer with the Cu Kα line, $\lambda = 1.54$ Å. FT-IR spectra of the LB films were recorded on a Perkin-Elmer Spectrum 2000 FTIR. The spectra were recorded with a 4 cm^{-1} resolution. CaF_2 plates were used as the substrates for transmission measurements. Reflection−absorption (RA) spectra were measured at an incident angle of 80°. Gold substrates with a thickness of 500 Å for RA measurements were prepared by vacuum evaporation of gold on clean glass plates hydrophobized with HMDS.

Results and Discussion

Monolayers at the Air−Water Interface. The π−A isotherms of DA(*m*−*n*) are shown in Figure 1. All the monolayers show similar isotherms with similar molecular areas and are stable up to 60 mN m^{-1} irrespective of the spacer length. By assuming that the DA(*m*−*n*) molecules are hexagonally packed in the monolayers, the intermolecular distance was estimated to be 5.1−5.2 Å on the basis of the area per molecule at the transfer pressure of 25 mN m^{-1}. These values coincide with the value of ca. 5 Å for polymerizable DAs in crystals.[27,28]

Polymerization of DA(*m*−*n*) in the LB Films. UV−vis absorption spectra of DA(*m*−*n*) LB films changed on irradiation with UV light. Polymerization behaviors can be categorized into three classes on the basis of the spectral change. A typical spectral change of the LB films belonging to class 1 is shown in Figure 2a. Two absorption bands at 590 and 640 nm appear and develop with increasing irradiation time. On prolonged irradiation, these bands are replaced by two new bands at 500 and 540 nm. The LB films of DA(10−10), DA(12−8), and DA(14−6) belong to this class, which is referred to as the blue-red phase. Figure 2b shows the change in the absorption spectrum of DA(16−4) LB film in class 2. This class is referred to as the red phase. An absorption band at 540 nm develops with the irradiation time until the spectrum shows a saturating behavior. Class 3 is the yellow phase. Spectral change is shown in Figure 2c. No distinct band appears, and absorption in the lower wavelength region increases slightly, indicating that the polymerization by 1,4-addition does not proceed to a large extent. DA(18−2) belongs to this class.

The results show that the polymerization manner is almost the same when the spacer length is equal to or longer than 6. This is further supported by the fact that the maximum absorbance in the saturated state is essentially the same for the molecules in class 1. However, for the molecules with shorter spacer lengths, the polymerization shows different behaviors. To study the different polymerization behaviors, molecular arrangement in the LB films was investigated.

Molecular Arrangement of DA(*m*−*n*) in the LB Films. The polymerization of diacetylenes in crystals has been explained in terms of the intermolecular distance and the relative orientation of the adjacent molecules.[27,28] Because the intermolecular distance of DA(*m*−*n*) in the LB films is essentially the same irrespective of the spacer length, the different phases of the polymers in the LB films should be ascribed to the different molecular orientation.

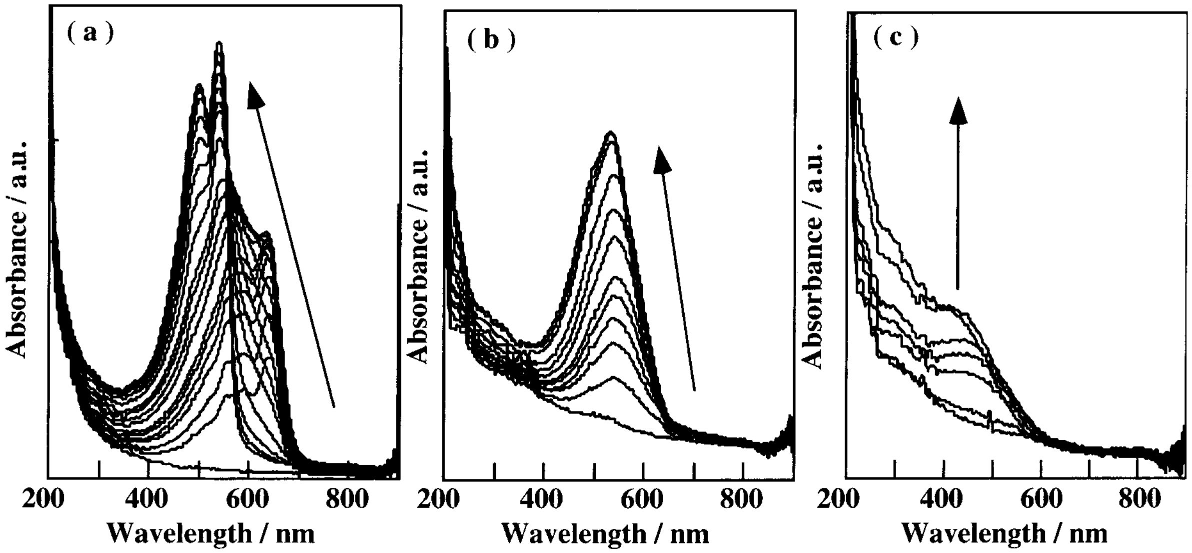

Figure 2. Changes in UV−vis absorption spectra of DA(*m*−*n*) LB films on irradiation with UV light. (a) DA(12−8): blue-red phase, irradiation time of 0−160 min; (b) DA(16−4): red phase, irradiation time of 0−60 min; and (c) DA(18−2): yellow phase, irradiation time of 0−90 min.

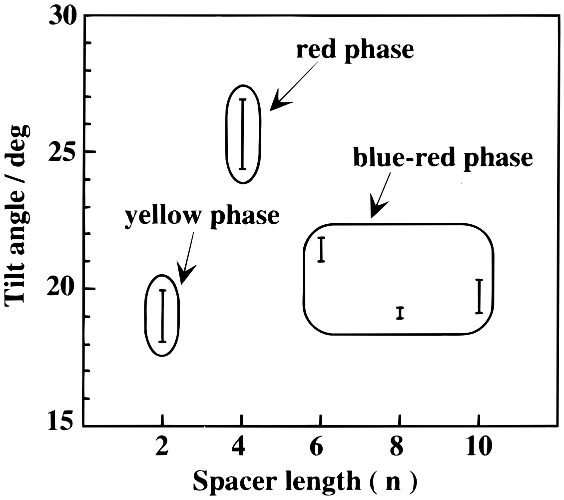

Figure 3. Tilt angle of the alkyl chain of DA($m-n$) in the LB films plotted against spacer length.

First, the orientation of the alkyl chains of DA($m-n$) in the LB films was investigated using FT-IR spectroscopy. This is because the small intensity of the vibrational bands of the butadiyne moiety did not allow for the direct estimation of the orientation of the butadiyne moiety. The CH_2 antisymmetric ($\nu_a(CH_2)$) and symmetric ($\nu_s(CH_2)$) stretching bands, which appear at ca. 2850 and 2920 cm^{-1}, respectively, can be used to determine the orientation of the alkyl chains in the LB films since the transition moments of the two bands are perpendicular to the alkyl chain axis and are orthogonal to each other.[31,32] By comparing the intensities of the two bands in the transmission and RA spectra, the tilt angle of the alkyl chain of DA($m-n$) from the surface normal was estimated.[33,34]

Figure 3 shows the tilt angle of the alkyl chain of DA($m-n$) in the LB film as a function of spacer length. The three phases are located in different regions in this figure. In particular, the tilt angle of the alkyl chain of DA(16−4), belonging to the red phase, is significantly larger than those of the other DA($m-n$). This suggests that the orientation of the butadiyne moiety of DA(16−4) is significantly different from those of the other DA($m-n$), which may be the reason that DA(16−4) is in a different phase from the others. However, DA($m-n$) molecules belonging to the blue-red and yellow phases have almost the same tilt angle of the alkyl chain.

XRD measurements of the LB films were carried out to obtain information on the orientation of the butadiyne group. The thickness per layer of the LB film was 28.4, 24.1, 26.7, 26.7, and 27.1 Å for DA(18−2), DA(16−4), DA(14−6), DA(12−8), and DA(10−10), respectively. The monolayer thickness is essentially the same for the LB films in the blue-red phase, while those in the other phases have different thicknesses. Figure 4 shows the relationship between the tilt angle of the alkyl chain and the monolayer thickness. Each phase is positioned in a separate region. The larger thickness per layer for the yellow phase compared with the blue-red phase indicates that the butadiyne moiety in the yellow phase is less tilted with respect to the surface normal.

The orientation of the butadiyne moiety in the LB films was further studied using the above results. We estimated the length of the butadiyne moiety and that of the rest as 5 and 25 Å, respectively, using the CPK model. These values, combined with the tilt angles of the alkyl chains and the monolayer thicknesses, give the tilt angles of the butadiyne moieties in the LB films. The results are summarized in Table 1. Different phases correspond to different tilt angles of the butadiyne moieties. The angle between the butadiyne axis and the line connecting the centers of the adjacent butadiyne moieties has been reported to be ca. 45° for polymerizable DAs in crystals.[27,28] The value for the blue-red phase is almost the same with this value, which is consistent with the finding that the polymerization proceeds in the LB films belonging to this phase. The tilt angle together with the distance between the adjacent molecules for the red phase have no counterparts for DAs in crystals reported so far. Therefore, the direct comparison of the polymerization behavior of the red phase with those of DAs in crystals is not possible. For the yellow phase, the butadiyne moiety is almost perpendicular to the film surface, which suggests that the molecules are not in a favorable position for the polymerization via 1,4-addition. The slight increase in the absorption in the lower wavelength region may be due to the polymerization through 1,2-addition reaction.

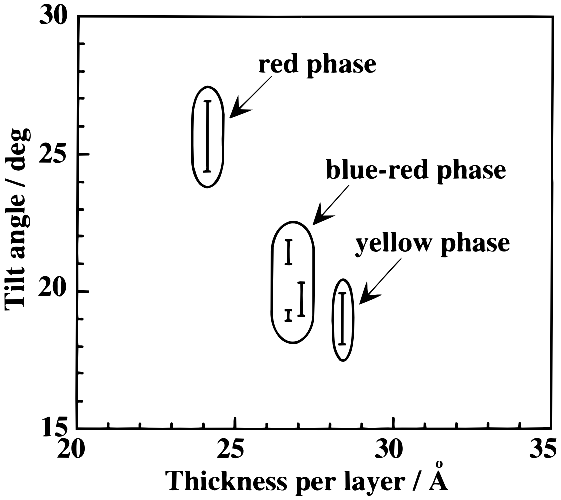

Figure 4. Tilt angle of the alkyl chain of DA($m-n$) in the LB films as a funtion of thickness per layer.

Table 1. Tilt Angle of the Butadiyne Moiety of DA($m-n$) in the LB Films for the Blue-Red, Red, and Yellow Phases

	phase				
	blue-red			red	yellow
spacer length (n)	6	8	10	4	2
tilt angle (deg)	42.0−43.7	37.5−37.7	43.9−47.1	15.9−19.3	67.4−75.2

These results show that the orientation of the butadiyne moiety of DA($m-n$) in the LB films is almost the same when the spacer length is sufficiently long. With decreasing the spacer length, the orientation of the butadiyne moiety changes significantly, which affects the polymerization behavior strongly.

Conclusions

The present work has shown the effect of the position of the butadiyne moiety in DAs on the polymerization in the LB films. The DA($m-n$) LB films can be categorized into three classes on the basis of the spectral change during the polymerization. The intermolecular distance is almost the same for all the films. However, the tilt angle of the butadiyne serves as a measure for the different phases. It should be noted that the variations in spacer length of amphiphilic DAs may give completely different polymerization behaviors in the LB films even when the molecular lengths and the $\pi-A$ isotherms are essentially the same.

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