

Langmuir–Blodgett Membranes of 13-Aryltrideca-10,12-diyonic Acids

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ABSTRACT: To study the formation and properties of Langmuir–Blodgett membranes of aromatic diacetylenes, 4 novel diacetylenic amphiphiles were synthesized, and their multilayer membranes were prepared and photopolymerization was carried out. 13-Phenyl-10,12-tridecynoic acid did not give a stable isotherm, and the structure appeared not proper for topochemical polymerization of the diacetylenic group, but substitution on the *para*-position of the acids stabilized the isotherm giving multilayer Y type membranes whose diacetylene groups readily polymerized on irradiation of UV light. There was a clear relationship between electronic density of aromatic groups, absorption maxima of polydiacetylene films and resistance to radiation.

KEY WORDS Aromatic Diacetylenes / Langmuir–Blodgett Membranes / Photo-Polymerization /

Polydiacetylenes (PDAs) belong to a class of polymers which consist of a unique conjugation of single–double–single–triple linkages, and because of their crystalline nature and third order nonlinear optical properties, they attract much attention. However, PDAs are polymers whose processing to desired forms is not at all simple, and various methods have been attempted. One conventional method is the Langmuir–Blodgett (LB) membrane technique. A variety of diacetylenic amphiphiles has been synthesized and studied systematically. Tieke and Wegner's group extensively studied the diacetylene polymerization in LB films.^{1–4} They discuss mainly the relationships between the chemical structure, polymerizability of the diacetylenic groups, stability of the LB films, orientation of the molecules and packing of the hydrophobic chains.

However, all amphiphilic diacetylenes so far studied are aliphatic diacetylenes. In these cases the conjugation range is limited only to PDA back bones. If aromatic diacetylenes (DAs) are used, the resulting PDAs have more extended conjugation and nonlinear optical (NLO) properties may be improved. The present authors for the first time reported the synthesis and formation of LB membranes of aromatic diacetylenes.⁵ Thus, blue films of PDAs were obtained by irradiation of UV light from *m*-alca-1,3-diynylbenzoic acids.

In this work, a series of novel amphiphilic aromatic diacetylenes were synthesized, and the formations of LB membranes were investigated as well as polymerizability.

EXPERIMENTAL

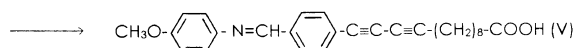
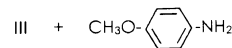
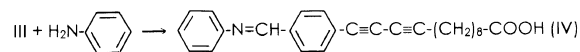
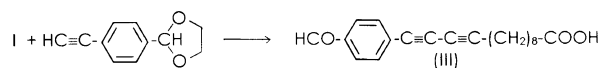
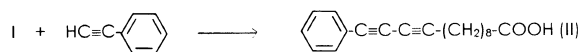
Materials

The amphiphilic DA monomers were synthesized according to the reactions shown in Scheme 1. The synthetic procedures of the compounds are described below:

11-Bromo-10-undecynoic Acid (I). 3.10 g (48 mmol) of

bromine were added to 30 ml of aqueous sodium hydroxide solution (0.110 mol NaOH) at 5–10°C and then 5 g (27.5 mmol) of 10-undecynoic acid dissolved in 50 ml of aqueous sodium hydroxide solution (27.5 mmol) were added at room temperature, and the mixture was stirred for 24 h. 7 g of Na₂SO₃ dissolved in 100 ml of water, were added to the solution to eliminate BrO[−]. The solution was acidified with dilute hydrochloric acid, and the precipitate was filtered, washed with water and dried in vacuum; yield 90%, mp 40°C.


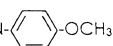
13-Aryltrideca-10,12-diyonic Acids. Under nitrogen atmosphere were mixed 10.34 mmol of phenyl acetylene, excess (200%) 50% aqueous solution of butylamine, 10 ml ethanol, catalytic amount of copper(I) chloride, and small amount of hydroxylamine hydrochloride. The mixture was stirred at room temperature for 5 min, and 11.49 mmol of I dissolved in excess ethanol were added dropwise with stirring. The reaction was exothermic and the reaction flask was cooled occasionally with an ice bath to avoid excess temperature rise. The mixture was stirred at room temperature for 24 h. The mixture was then poured into 200 ml water, and acidified with dilute hydrochloric acid. The insoluble product was filtered,



Scheme 1. Synthetic route to 13-aryltrideca-10,12-diyonic acids.

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Table I. 13-Aryltrideca-10,12-diynoic acids

Compound		mp °C	Elemental analysis	
R	Code		Found %	Calcd %
-H	ϕ DA	81	C: 80.58 H: 8.12	C: 80.56 H: 8.13
-CHO	ϕ DACHO	76	C: 76.91 H: 7.60	C: 76.92 H: 7.69
-CH=N- 	ϕ DAC=N	70	C: 81.23 H: 6.76 N: 4.50	C: 81.25 H: 6.77 N: 4.49
-CH=N- 	ϕ DAC=NOCH ₃	65	C: 78.08 H: 7.00 N: 3.37	C: 78.07 H: 6.99 N: 3.37

washed with water, and dried in vacuum, yield 91%. Under nitrogen atmosphere were mixed 10.34 mmol of 2-[4'-(ethynyl)phenyl]-1,3-dioxolane, an excess (200%) 50% aqueous solution of butylamine, 10 ml ethanol, catalytic amount of copper(I) chloride, and small amount of hydroxylamine hydrochloride. The mixture was stirred at room temperature for 5 min, and 11.49 mmol of **I** dissolved in excess ethanol were added dropwise with stirring. The reaction was exothermic and the reaction flask was cooled occasionally with an ice bath. The mixture was stirred at room temperature for 24 h and poured into 200 ml water, and acidified with dilute hydrochloric acid. The insoluble product was filtered, washed with water, and dried in vacuum, yield 70%.

5 mmol of (**III**) were dissolved in 20 ml ethanol, and 5 mmol of aniline were added dropwise with stirring. The mixture was stirred at room temperature for 4 h. The insoluble product was filtered, washed with ethanol, and dried in vacuum, yield 75%.

5 mmol of (**III**) were dissolved in 20 ml ethanol, and 5 mmol of *p*-anisidine were added dropwise with stirring. The mixture was stirred at room temperature for 4 h. The insoluble product was filtered, washed with ethanol and dried in vacuum; yield 75%.

Results of elemental analysis are shown in Table I.

Formation of LB Films

Monolayers were spread from a CHCl₃ (HPLC grade, Aldrich) solution (1 mg ml⁻¹) on the surface of the subphase. Subphase water was triply distilled, and CdCl₂ (1 × 10⁻⁴ M) was added to stabilize the monolayer and pH of the subphase became 6.0. Pressure-area isotherms were measured at a compression speed of 5 mm min⁻¹, using a Miyata-type moving wall LB film deposition apparatus, Model NL-LB240-MWA, manufactured by Nippon Laser & Electronic Laboratory.

The monomolecular films were successively transferred by LB technique onto ultra-pure quartz plates previously treated⁶ with mixture of sulfuric acid–nitric acid (1 : 1) for 30 min at a temperature of about 370 K and neutralized with 2.5 × 10⁻⁴ M solution of sodium hydroxide, rinsed thoroughly with triply distilled water and dried in a desiccator. Deposition was carried out at room temperature by up-and-down trips to form Y-layers under a constant surface pressure of 10 mN m⁻¹ for ϕ DA, and 35 mN m⁻¹ for ϕ DACHO, ϕ DAC=N, and

ϕ DAC=NOCH₃ at a deposition rate of 5 mm min⁻¹ for the four cases.

Polymerization

Polymerization of diacetylenic groups was carried out by UV irradiation using a 450 W medium-pressure mercury lamp supplied by Ace Glass Inc., at a distance of 30 cm from the light source under air atmosphere.

Multilayer Characterization

Membrane thickness was calculated from ellipsometry data. Ellipsometry was performed with an Auto EI-III automated ellipsometer manufactured by Rudolph Research. With this instrument, elliptically polarized 6328 Å wavelength light strikes the sample at an angle of 70° from vertical. The accuracy of the readings was enhanced using the two-zone averaging.

FT-IR spectra of the films deposited onto a germanium plate were taken using a Perkin-Elmer 1600 using Attenuated Total Reflection (ATR) mode. The spectra were collected by scanning each sample 256 times with a resolution of 4 cm⁻¹.

UV-VIS absorption spectra were recorded using a Perkin-Elmer 553 Fast Scan spectrometer.

RESULTS AND DISCUSSION

Monolayers

Figure 1 shows surface pressure-area isotherms of the compounds which require cadmium ions in the subphase to form a stable condensed monolayer. The addition of cadmium ion to the aqueous subphase had different results as shown in Figure 1. In the absence of cadmium ions, stable monolayers could not be obtained. A gradual increase of the surface pressure was observed for ϕ DA, over the area from 25 to 40 Å² molecule⁻¹, indicating the monolayer to be stable as compared with the case where the subphase was only pure water. Stable monolayers with good condensed phase were obtained for ϕ DACHO, ϕ DAC=N, and ϕ DAC=NOCH₃, and extrapolated areas to zero pressure had 20–23 Å² molecule⁻¹, whereas ϕ DA had an area of 32 Å² molecule⁻¹. In all four cases there were observed collapse pressures, being 15 mN m⁻¹ for ϕ DA, and 55–60 mN m⁻¹ for ϕ DACHO, ϕ DAC=N, and ϕ DAC=NOCH₃. In all the cases, deposition could be satisfactorily carried out at a transfer ratio of 0.95–1.00, which indicates the formation of Y-type membranes.

The ellipsometry results are shown in Table II. Although there is a certain inherent error in the ellipsometry, the observed thickness was considered acceptable.

Photopolymerization of Membranes

Figure 2 shows the absorption spectra of a 40-layers membrane of ϕ DA with different irradiation times. The absorbance of the broad peak at around 540 nm increased with advance of polymerization. The broad shape of the absorption spectra indicates that the crystalline structure of the DA molecules in the layer is not ideal for topochemical polymerization, and this is quite different from aromatic diacetylenic membranes where the aromatic ring is on the water surface.⁵ However, since the unirradiated membrane had no absorption over the

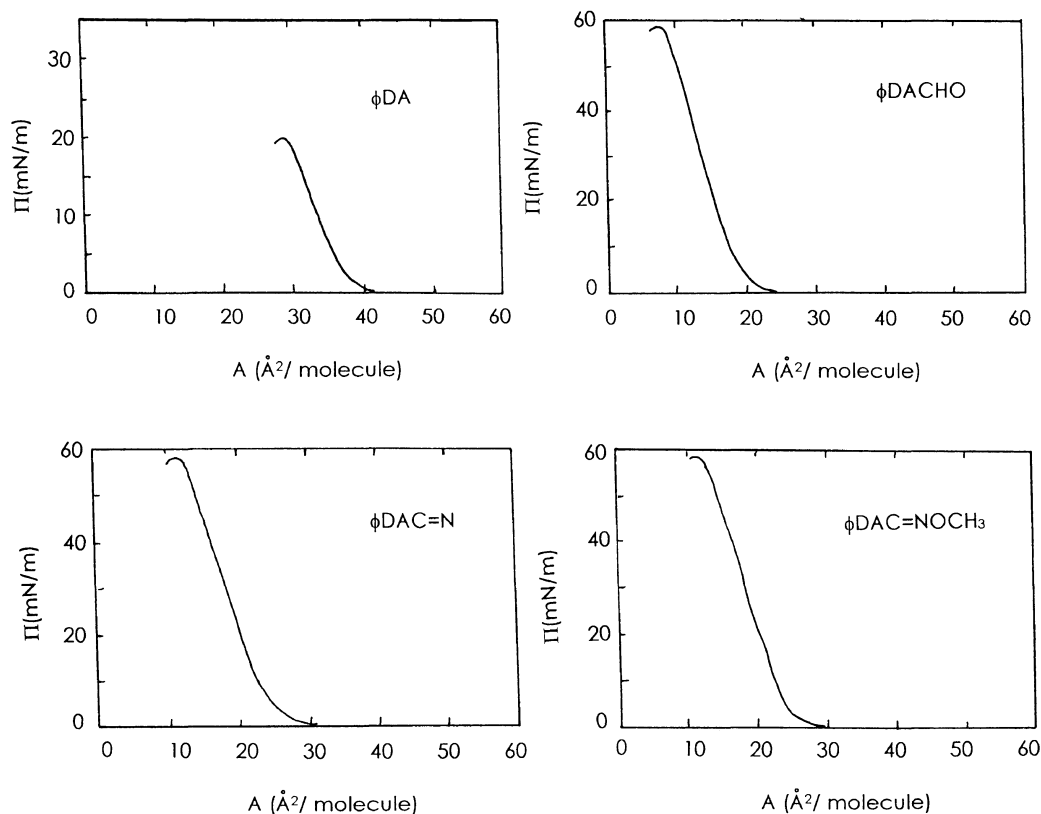


Figure 1. Surface pressure-area isotherms of 13-aryltrideca-10,12-diyynoic acids for aqueous solution of CdCl_2 (1×10^{-4} M; pH 6.0).

Table II. Monolayer thickness

Code	Thickness per layer/Å
ϕDA	25.1 ± 3
ϕDACHO	26.9 ± 2
$\phi\text{DAC=N}$	28.7 ± 5
$\phi\text{DAC=NOCH}_3$	30.9 ± 4

visible region, the polymerization apparently took place.

Figure 3 illustrates the dependence of absorption spectra of a 40-layer membrane of ϕDACHO on UV-lamp irradiation time. The unirradiated membrane had no absorption in the visible region. Contrary to the ϕDA case, two absorption peaks typical of topochemically polymerized PDAs, appeared at 568 and 610 nm. It seems that the carbonyl group significantly contributes to the formation of crystal structures favorable for topochemical polymerization. The absorption maxima of poly(ϕDACHO) were somewhat lower compared to those of other PDA LB membranes reported previously^{2,4,5} (at around 600 and 640 nm), and this is probably due to the electron withdrawing aldehyde group. Polymerization appeared to be completed with 60 min of irradiation (Figure 4), and absorption intensity began to decrease, indicating that the polymer film is possibly photodegraded by oxidation. This phenomenon of oxidation during irradiation was observed for diacetylenic benzoic acids.^{1,5}

Figure 4 shows the FT-IR spectra of ϕDACHO before and after UV irradiation, at the region where acetylenic and diacetylenic stretching appear. Two bands corresponding to the diacetylenic groups before the UV irradiation disappeared completely, and a new acetylenic

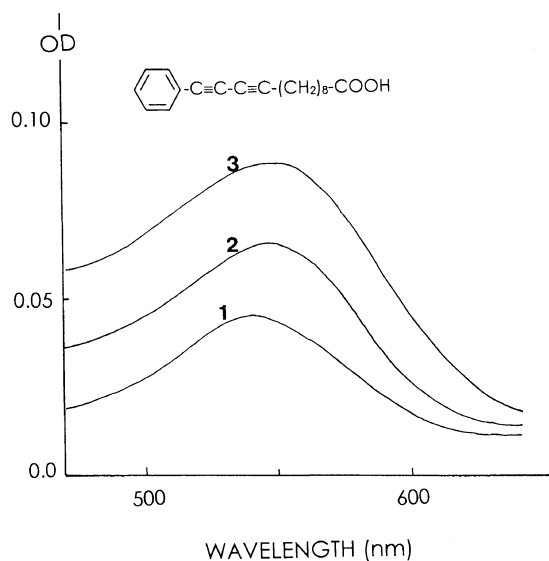


Figure 2. Visible absorption spectra of 40-layer LB membranes of ϕDA irradiated with UV light for different periods. 1, 5 min; 2, 10 min; 3, 30 min.

band appeared at 60 min irradiation. Therefore, topochemical polymerization took place.

Figure 5 shows changes in the absorption spectrum for the 40-layer membrane of $\phi\text{DAC=N}$ irradiated for different periods. No absorption was observed in visible region for the unirradiated membrane. Two absorption peaks appeared as usual at 600 and 640 nm, as the carbonyl group was changed to the less electron-withdrawing azomethyn group. The absorbance intensity of the film increased with irradiation time until 60 min,

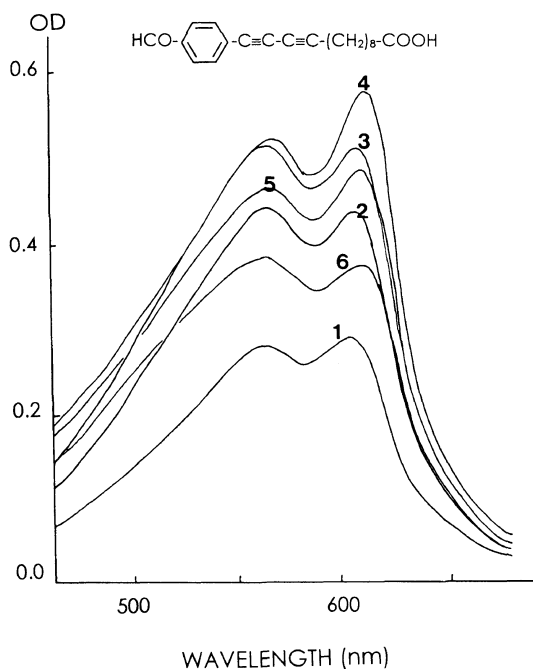


Figure 3. Visible absorption spectra of 40-layer LB membranes of ϕ DACHO irradiated with UV light for different periods. 1, 10 min; 2, 20 min; 3, 30 min; 4, 60 min; 5, 100 min; 6, 120 min.

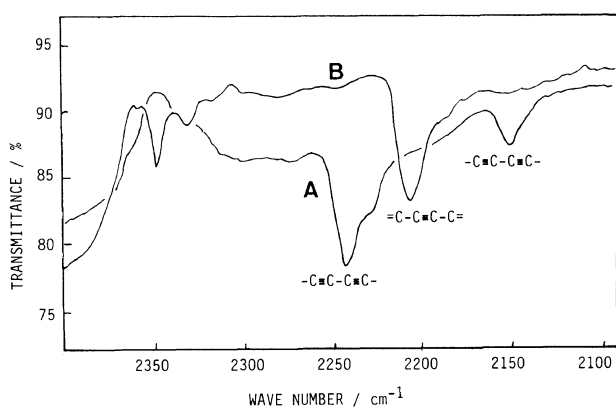


Figure 4. FT-IR spectra of 40-layer membranes of ϕ DACHO before and after UV irradiation for 60 min. A, before; B, after irradiation.

but after 60 min, absorbance peaks started to blue shift and became broader, indicating photodegradation of the conjugated chains of polydiacetylene by oxidation.

Figure 6 illustrates changes of absorption spectra of 40-layers membrane of ϕ DAC=NOCH₃ with irradiation time. Two absorption peaks characteristic of polydiacetylenes, appeared at 645 and 685 nm. This red shift is due to the methoxy group which increases electronic density in the PDA chains. The absorbance of the multilayer increased with irradiation time up to 40 min, and with irradiation for more than 40 min, absorption maxima decreased as seen in the previous cases, indicating that the polymer is photodegraded due to oxidation. This PDA is more vulnerable to oxidation than others which have less electronic density.

The blue shift of the absorption peaks with prolonged irradiation is thought due to oxidation. The photo-crosslinking of polydiacetylene chains cannot be eliminated. However, a powerful UV lamp forms ozone of

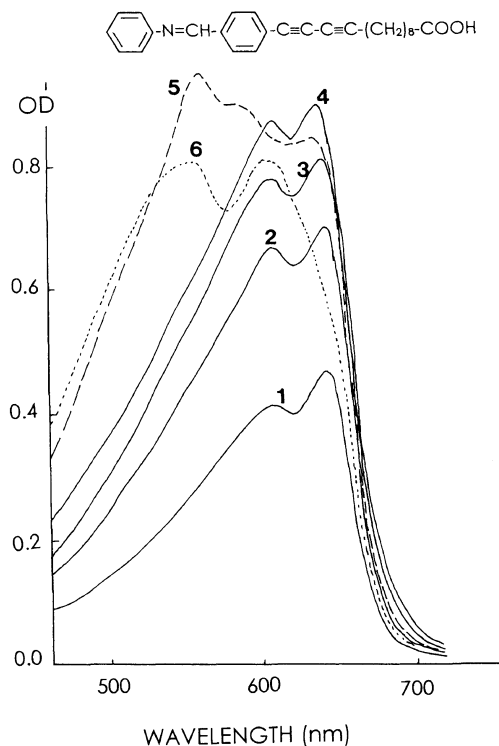


Figure 5. Visible absorption spectra of 40-layer LB membranes of ϕ DAC=N irradiated with UV light for different periods. 1, 10 min; 2, 20 min; 3, 30 min; 4, 60 min; 5, 100 min; 6, 150 min.

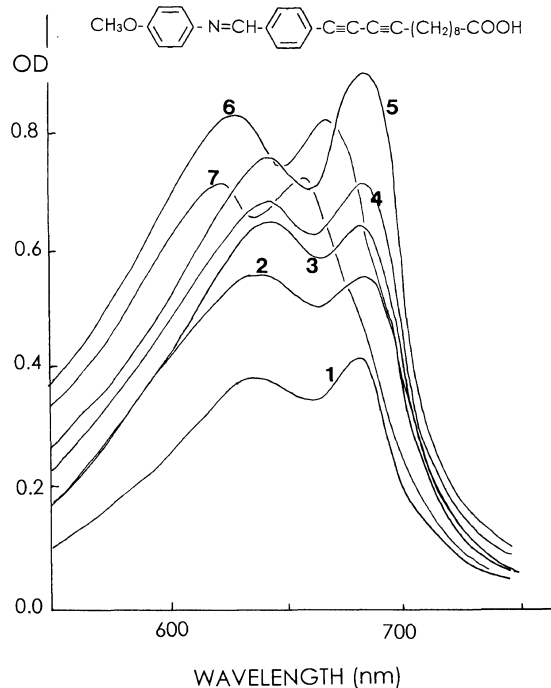


Figure 6. Visible absorption spectra of 40-layer LB membranes of ϕ DAC=NOCH₃ irradiated with UV light for different periods. 1, 5 min; 2, 10 min; 3, 20 min; 4, 30 min; 5, 40 min; 6, 60 min; 7, 100 min.

irradiated area, and photo-excited polydiacetylene molecules may contribute to formation of singlet oxygen. Therefore, oxidation is thought a more probable reason for degradation. The resistance toward photodegradation seemed to depend on the electron density of polydiacetylene chains; the higher the electron density, the lower the resistance.

Third order non-linear optical susceptibility, $\chi^{(3)}$, values reported in literature for LB membranes of polydiacetylenes are quite low, around 10^{-12} esu.⁷ The multilayer films of diacetylenic benzoic acids⁸ also gave a low $\chi^{(3)}$ of the same order as reported.⁷ The low observed $\chi^{(3)}$ values may be due to damage caused by laser beam during determination of $\chi^{(3)}$.

CONCLUSIONS

These results indicate that substitution on the terminal benzene ring stabilize the layer probably by the dipole-dipole interaction (CHO or CH=N groups), and this also gives rise to favorable orientation of the diacetylenic groups for topochemical polymerization. The donor group on the *para*-position of the terminal benzene ring shifts absorption maxima of polydiacetylenes towards the longer wavelength region (red shift): Phenyl-CHO-(568 and 610 nm) < Phenyl-N=CH-(600 and 640 nm) < CH₃O-Phenyl-N=CH-(645 and 685 nm). At the same time resistance to oxidation decreased with electron donor groups. Irradiation under an inert atmosphere is being carried out and results will be reported in the future together with third order NLO

properties of these films.

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