

Langmuir-Blodgett Membranes of *m*-Alca-1,3-Diynylbenzoic Acids

María del Pilar CARREÓN, Guillermina BURILLO, Vladimir AGABEKOV,*
and Takeshi OGAWA**†

*Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México,
Circuito Exterior, Ciudad Universitaria, México, D.F. 04510, México*

**Institute for Physical Organic Chemistry Belorussian Academy of Sciences,
220072 Minsk, Belorussia*

***Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Circuito Exterior, Ciudad Universitaria, México, D.F. 04510, México*

(Received April 1, 1996)

ABSTRACT: Meta-alca-1,3-diynylbenzoic acids with different chain lengths were synthesized and the formation of Langmuir-Blodgett (LB) membranes was studied. Benzoic acids with alkyl chain length greater than 8 formed stable monolayers while those with 4 and 6 did not form good condensed phases. Multilayer films were irradiated with UV light and the diacetylenic groups polymerized to give polydiacetylene LB films having absorption maxima at around 640 nm.

KEY WORDS Langmuir-Blodgett Membranes / Aromatic Diacetylenes / Topochemical Polymerization /

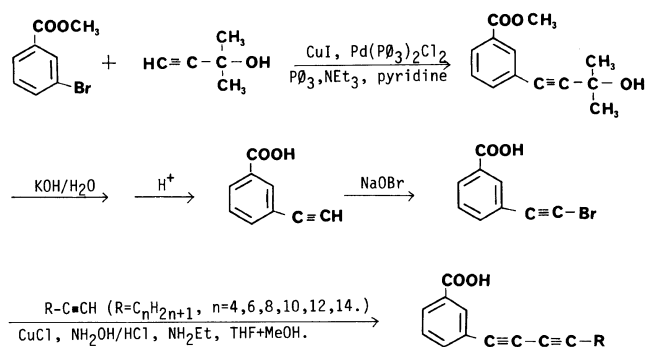
Polydiacetylenes (PDAs) have attracted much attention as possible candidates for ultrafast nonlinear optical signal processing systems,¹ and many studies have been reported.^{2,3} However, the processing of PDAs into high optical quality films is not easy, and various methods are used including large single crystal formation, vapor phase epitaxy, solution casting and Langmuir-Blodgett (LB) membrane technique. The LB membrane technique is a useful method to obtain ultra-thin films although there exist various technical problems to be solved. There are a number of studies on the LB membranes containing diacetylene (DA) groups. Tieke and Wegner extensively studied DA polymerization in LB films, discussing chemical structures, stability of the LB films and orientation of the molecules.^{4–6} Third harmonic generation (THG) behavior of such PDA-containing LB membranes has been investigated by Kajzar *et al.*^{7,8} and Okada *et al.*⁹ $\chi^{(3)}$ of the PDA-containing LB membranes are listed in the literature.¹⁰

The DA-containing LB membranes so far studied are aliphatic amphiphiles,^{11,12} and no aromatic DA-containing membranes has been reported. The authors are studying various PDA-containing polymeric systems,¹³ and previously synthesized a series of DA-containing benzoic acid derivatives.¹⁴ These unsymmetric DAs do not undergo topochemical polymerization due to crystal packing unfavorable for the solid state polymerization. It is interesting to find whether DA groups of LB membranes of these benzoic acids forced to orientate in an unsymmetrical manner, have topochemical polymerizability, and if so, whether the PDAs thus obtained will give higher $\chi^{(3)}$ than the aliphatic analogues. Therefore a series of *m*-alca-1,3-diynylbenzoic acids having different length of alkyl chains were prepared and their isotherms were studied, and the results are reported.

EXPERIMENTAL

Synthesis of Diacetylenic Benzoic Acids

m-Alcadiynylbenzoic acids were synthesized from *m*-bromomethylbenzoate and 1-alkynes according to the following reactions (Scheme 1). 100 g (0.465 mol) of *m*-bromomethylbenzoate prepared from *m*-bromobenzoylchloride (Aldrich) and methanol and 43 g (0.512 mol) of 2-methyl-3-butyn-2-ol (Aldrich) were dissolved in a mixture of 200 ml triethylamine and 300 ml pyridine. After bubbling nitrogen into the solution 1 g each of copper(I) iodide, triphenylphosphine and bis(triphenylphosphine) palladium(II) chloride was added and the solution was refluxed under nitrogen for 24 hours. The precipitated triethylamine hydrobromide was filtered and washed with triethylamine. The mother liquors were evaporated under reduced pressure, and the concentrated reaction product was poured into dilute hydrochloric acid. The organic layer was extracted with ether and washed with water. After adding activated carbon powders and anhydrous magnesium sulfate which were then filtered off, ether was evaporated. A pale brown viscous liquid was obtained with 80% yield. This was dissolved in methanol and the solution was added dropwise into 2 liters of water containing 100 g of potassium hydroxide heated at 85°C. The mixture was heated for 24 hours. After cooling to room temperature,



Scheme 1. Synthetic route to *meta*-alca-1,3-diynylbenzoic acids.

† To whom correspondence should be addressed.

insoluble matter was filtered off, and the solution was acidified with hydrochloric acid. The precipitate was filtered, washed well with water and dried in vacuum. The yield was 90%. The *m*-ethynylbenzoic acid (**II**) thus obtained was recrystallized from benzene, and a pale yellow powder melting at 146°C was obtained. 5.43 g (0.034 mol) of bromine were added to 30 ml aqueous sodium hydroxide solution (0.137 mol NaOH) at 5–10°C and then 5 g (0.034 mol) of **II** dissolved in 50 ml sodium hydroxide solution (0.04 mol) were added at room temperature and the mixture was stirred for 24 hours. The solution was then acidified with dilute hydrochloric acid, and the precipitate was filtered, washed with water and dried in vacuum; yield 91% mp 152°C, the peak at 3350 cm⁻¹ due to the H–C≡C– disappeared.

Under nitrogen atmosphere were mixed 0.0143 mol of an *n*-alkyne, excess (180%) 70% aqueous solution of ethylamine, 1 ml of tetrahydrofuran, 1 ml of methanol, a catalytic amount of copper(I) chloride, and a small amount of hydroxylamine hydrochloride. The mixture was stirred at room temperature for 5 minutes, and then 0.013 mole of **III** dissolved in a small amount of triethylamine was added dropwise with stirring. The reaction was exothermic and the reaction flask was cooled occasionally with an ice bath during the addition of **III** to avoid temperature rise. The mixture was stirred at room temperature for 24 hours. A small amount of potassium cyanide was added, and the mixture was poured into 200 ml of water, the insoluble product was filtered, washed with water, and dried in vacuum. Recrystallization from methanol gave colorless crystalline powders. The yield of this Cadiot–Chodkiewicz coupling reaction was 60–80%. Results of elemental analysis are shown in Table I.

Preparation of LB Films

A Miyata-type moving wall LB film deposition apparatus, NL-LB240-MWA, manufactured by Nippon Laser & Electronic Laboratory, was used for this work. Chloroform and *n*-hexane of HPLC grade supplied by Aldrich were used as solvents for spreading. Water for the subphase was triply distilled, and pH was set by

0.1 M hydrochloric acid. Barrier speed was varied from 0.5 to 6.0 cm/min with 0.5 cm intervals. Ultra-pure quartz slides supplied by Nippon Laser & Electronics Lab. were used as substrates, and they were treated with a mixture of sulfuric and nitric acids (1/1) for 30 minutes at 370 K, then with 2.5 × 10⁻⁴ M solution of sodium hydroxide, and finally rinsed thoroughly with triply distilled water and dried in a desiccator.¹⁵

After repeated preliminary experiments the optimum concentration for these benzoic acids to be spread was found to be 1 × 10⁻³ M in chloroform, and a dipping speed of 1.0 cm min⁻¹ and a pH of 2 were found to be adequate. The deposition was made by up and down trips, and thus Y-layers were obtained under a constant surface pressure of 30 m Nm⁻¹ at room temperature.

Multilayer Characterization

Film thickness was measured by ellipsometry using an Auto El-III ellipsometer of Rudolph Research Inc. in which, elliptically polarized 6328 Å wavelength light strikes the sample at an angle of 70° from the vertical. The accuracy of the readings was enhanced using the two-zone averaging technique.

FT-IR spectra of the films deposited on 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.

Polymerization

The films were irradiated in air using a 450W medium pressure mercury lamp supplied by Ace Glass Inc.

RESULTS AND DISCUSSION

Figure 1 shows the pH dependency of spreading behavior for C10. The monolayer was more stable with pH 2, at which the benzoic acid exists as undissociated form. Therefore pH 2 was chosen throughout this study. The stability of the monomolecular films in the condensed state increased with increase in the number of chain carbon atoms. C4 and C6 formed a liquid analogous state, which was indicated by the slow rise of surface pressure upon compression of the monolayer surface. These compounds are unable to form stable

Table I. *meta*-Alcadiynylbenzoic acids

Compound		mp °C	Elemental analysis	
R	Code		Found	Calcd
<i>n</i> -C ₄ H ₉ -	C4	143	C: 79.60 H: 6.22	C: 79.65 H: 6.19
<i>n</i> -C ₆ H ₁₃ -	C6	127	C: 80.29 H: 7.10	C: 80.31 H: 7.09
<i>n</i> -C ₈ H ₁₇ -	C8	118	C: 80.87 H: 7.83	C: 80.85 H: 7.80
<i>n</i> -C ₁₀ H ₂₁ -	C10	106	C: 81.32 H: 8.37	C: 81.29 H: 8.39
<i>n</i> -C ₁₂ H ₂₅ -	C12	98	C: 81.69 H: 8.89	C: 81.66 H: 8.87
<i>n</i> -C ₁₄ H ₂₉ -	C14	85	C: 82.00 H: 9.25	C: 81.97 H: 9.29

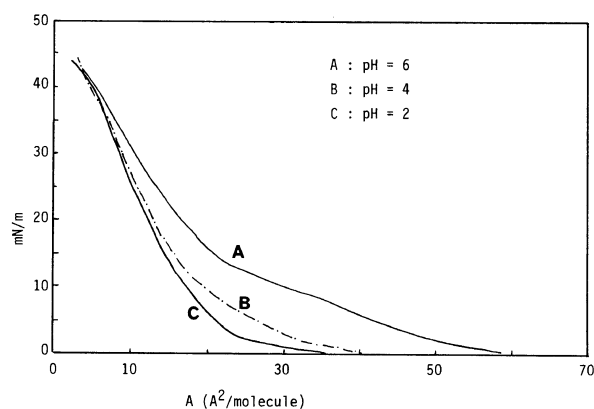


Figure 1. Surface pressure-area isotherms of C10 at different pH.

monolayers and it was difficult to observe a condensed state, in particular for C4. This behavior suggests that C4 membranes cannot be transferred onto substrates, and a minimum of 8 carbons in the hydrophobic chain is necessary in order to form a stable monolayer with a satisfactory condensed phase. Thus, in the case of C4, it was not possible to evaluate the limiting area because the Π - A curve did not show a linear section and therefore there is no evidence of the condensed phase formation. Π - A isotherm of C6 showed a small linear section in the condensed phase but it was not stable enough for reasonable deposition.

The benzoic acids C8—C14 formed very fine condensed states as indicated by the steep rise of the isotherms upon compression and A values of these acids were found to be 20—23 Å² per molecule. The collapse

pressure largely depended on the number of carbon atom of the aliphatic chain as can be seen from the Figures 2c, 2d, and 2e. No collapse point was observed for C14 (Figure 2f) under these conditions probably because it forms a very stable monolayer. The deposition of C8—C14 monolayers was satisfactory, transfer ratio being 0.95—1.00 for the first upward transversal and also for the subsequent up-and-down strokes (Y-type deposition).

The ellipsometry results are shown in Table II. Taking into account the inherent error of ellipsometry technique, the values observed for the benzoic acids are thought to be reasonable for the diacetylenic acid monolayer. Figure 3 shows a linear relationship between the number of layers and multilayer thickness for C14. The linear characteristic of the thickness plot is indica-

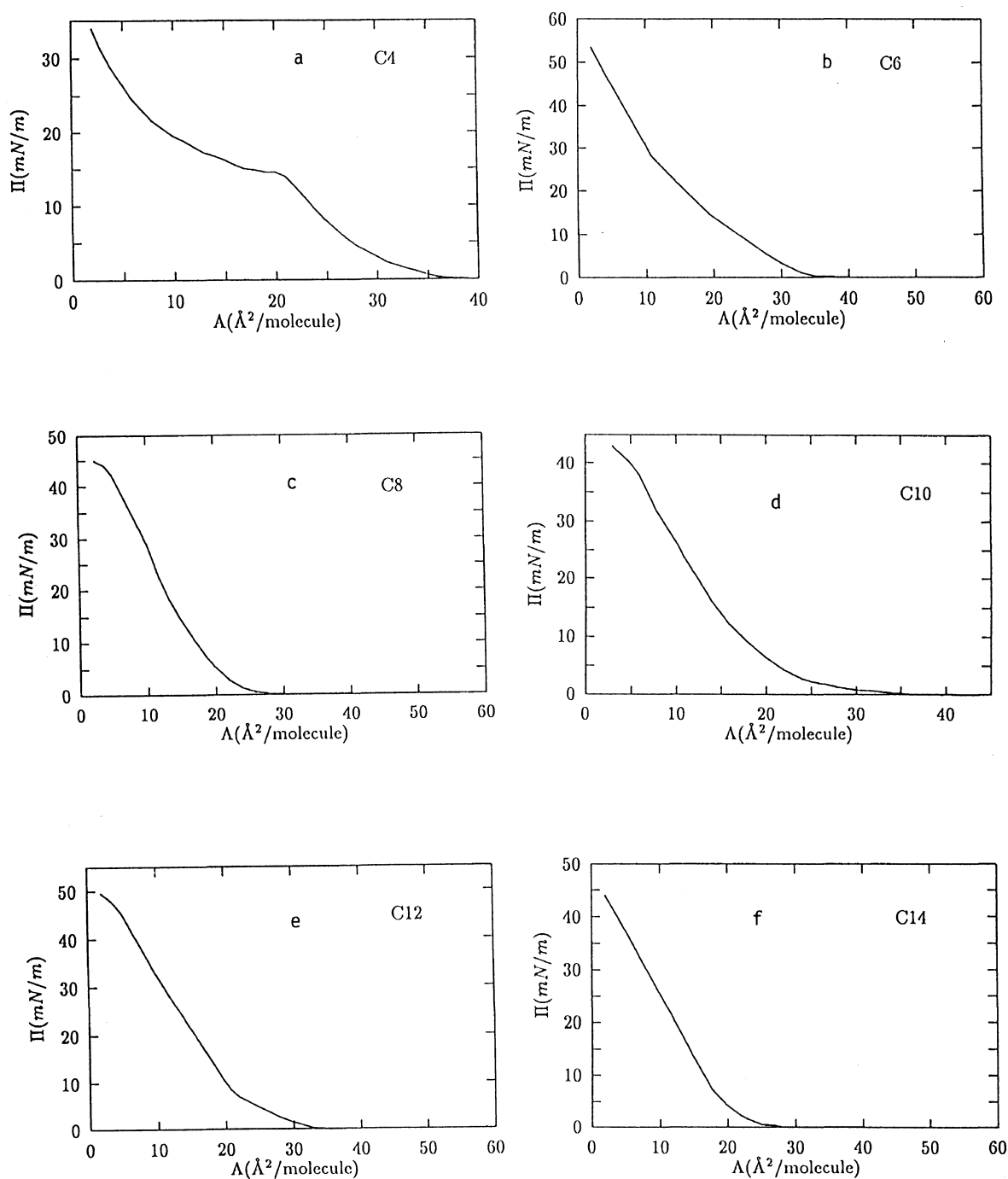
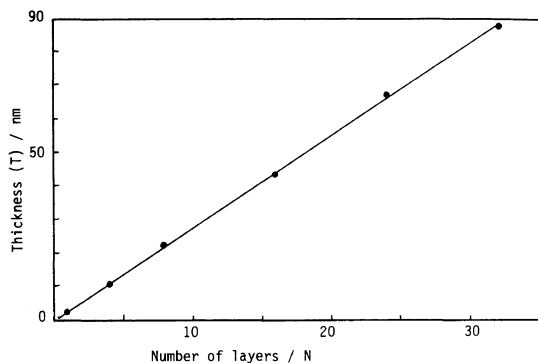
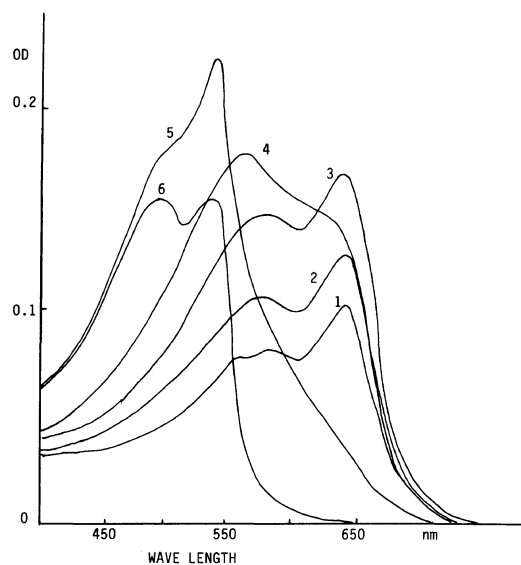


Figure 2. Surface pressure-area isotherms of 6 benzoic acids.

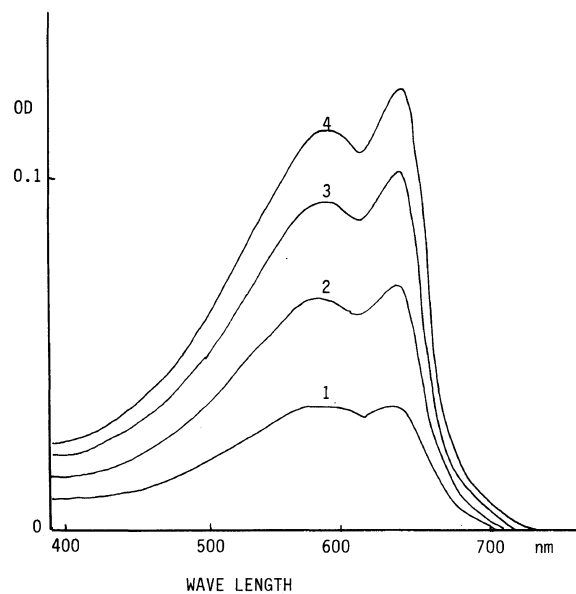
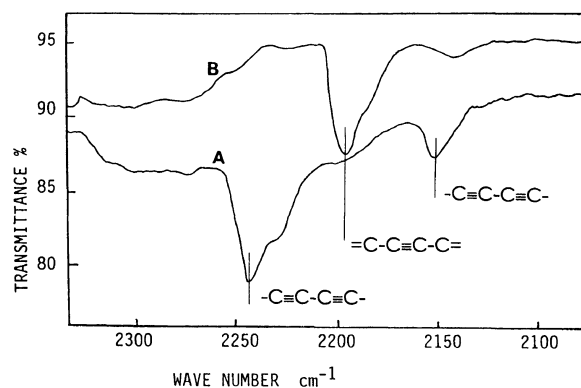
Table II. Monolayer thickness

No. of <i>n</i> -alkyl chains	Thickness per layer/Å
4	16.1 ± 6
6	18.7 ± 3
8	20.9 ± 2
10	23.4 ± 3
12	25.3 ± 5
14	27.6 ± 3

**Figure 3.** Film thickness (T) as a function of the number of layers (N) of C14 acid.**Figure 4.** VIS absorption spectra of C14 films with 28 layers with different irradiation time. 1, 5 min; 2, 10 min; 3, 20 min; 4, 30 min; 5, 40 min; 6, 70 min.

tive of the reproducibility of the transferred film.

These benzoic acids do not undergo topochemical polymerization in the solid state¹⁴ due to unfavorable crystal packing for the polymerization. However, in the form of LB films the topochemical polymerization took place. Figure 4 shows the visible absorption spectra of 28-layer film of C14 acid irradiated with UV light at room temperature. It can be seen that the optical density increased with irradiation time, indicating the polymerization taking place. The absorption maxima at around 600 and 640 nm are those typical of polydiacetylenes. Broadening and shifts toward shorter wave length of the absorption maxima after prolonged irradiation, *i.e.*, over 30 minutes, are due to the oxidation of polyDA chains as the film was irradiated in air.

**Figure 5.** Relationship between the number of layers and absorption intensity for the C14 films with 20 minutes irradiation. 1, 8 layers; 2, 16 layers; 3, 24 layers; 4, 28 layers.**Figure 6.** FT-IR spectra of 33 layer films of C10 acid before and after UV irradiation for 20 minutes. A, before; B, after irradiation.

This type of oxidation has been also reported by other workers^{9,16,17} for diacetylenic LB membranes. The surface of the cast films of a DA-containing polyamide irradiated under atmospheric air is gold in color while that under inert atmosphere is deep blue.¹⁸ This is a common phenomenon for the topochemical polymerization of DAs. Figure 5 shows the relationship between the optical density and number of layers for C14 acid. A linear relationship is clearly observed between the absorption intensity and the number of layers as shown in Figure 5. This behavior was also observed for C8, C10, and C12.

Figure 6 shows the FT-IR spectra of C10 before and after UV irradiation, at the region where acetylenic and diacetylenic stretching appear. The spectra showed that the topochemical polymerization took place, as the spectrum of the irradiated film was that of typical polydiacetylene, and it was completed within 20 minutes indicating that the DA groups of the benzoic acid are reactive.

The results of UV irradiation for C10 and C4 acids are shown in Figures 7 and 8, respectively. The polymerization behavior of C10 is similar to that of C14, but C4 did not demonstrate the polymerization. This is

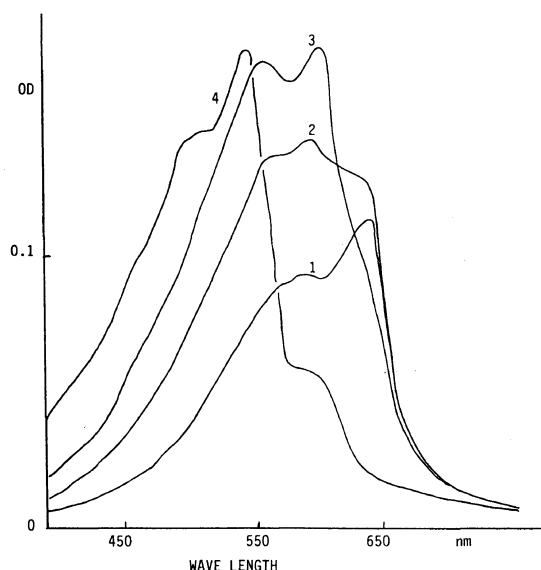


Figure 7. VIS absorption spectra of 28 layer films of C10 acid irradiated with UV light. 1, 20 min; 2, 30 min; 3, 40 min; 4, 90 min.

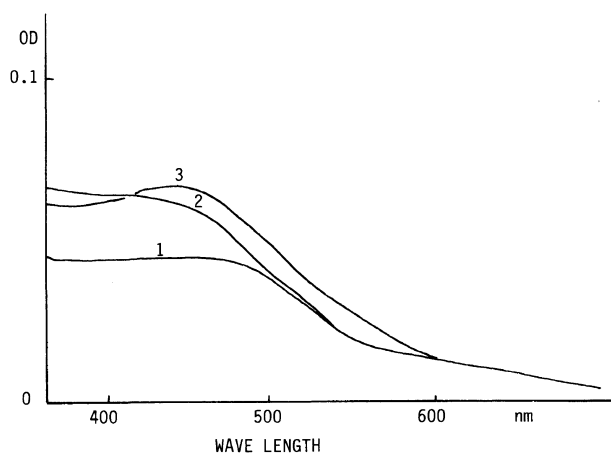


Figure 8. VIS absorption spectra of 28 layer film of C4 acid irradiated with UV light. 1, 10 min; 2, 40 min; 3, 20 min.

probably because that C4 membrane did not form a crystal structure favorable for topochemical polymerization.

The LB-films of the corresponding *para*-isomers did not undergo polymerization although they gave stable monolayers, probably because they do not form a membrane crystal structure favorable for topochemical polymerization.

CONCLUSION

Aromatic diacetylenic amphiphilic compounds were made into LB membranes for the first time. These benzoic acids form stable monolayers independently of alkyl chain length when the alkyl chain is greater than C8. The multilayer films having alkyl chains greater than C8 underwent topochemical polymerization by irradiation of UV light. More detailed studies on the characterization are being made.

Acknowledgments. This work was partially supported by the grant from DGAPA-UNAM with grant number IN-101793. Thanks are also due to the scholarship given by DGAPA to M. P. Carreón, and PADEP (Project number 05313), UNAM.

REFERENCES

1. P. W. Smith, *Bell Sys. Tech. J.*, **61**, 1975 (1982).
2. D. S. Chemla and J. Zyss, Ed., "Nonlinear Optical Properties of Organic Molecules and Crystals," Vol. 2, Academic Press, Orlando, Florida, 1987.
3. D. J. Sandman, Ed., "Crystallographically Ordered Polymers," ACS Symposia Series 337, The American Chemical Society, New York, N.Y., 1987.
4. B. Tieke and G. Lieser, *J. Colloid Interface Sci.*, **88**, 471 (1982).
5. G. Lieser, B. Tieke, and G. Wegner, *Thin Solid Films*, **68**, 77 (1980).
6. B. Tieke and G. Lieser, *Macromolecules*, **18**, 327 (1985).
7. F. Kajzar, J. Messier, J. Zyss, and I. Ledoux, *Opt. Commun.*, **45**, 13 (1983).
8. F. Kajzar and J. Messier, *Thin Solid Films*, **132**, 11 (1985).
9. S. Okada, H. Matsuda, H. Nakanishi, and M. Kato, *Thin Solid Films*, **179**, 423 (1989).
10. J. L. Brédas and R. Silby, Ed., "Conjugated Polymers," Kluwer Academic Publishers, Dordrecht, 1991, Chapter by F. Kajzar and J. Messier "Third Order Nonlinear Optical Effects in Conjugated Polymers," p 541.
11. A. Ulman, "An Introduction to Ultrathin Films from Langmuir-Blodgett to Self Assembly," Academic Press, New York, N.Y., 1991, p 182.
12. H. Bader, K. Dorn, B. Hupfer, and H. Ringdorf, *Adv. Polym. Sci.*, **64**, 1 (1985).
13. T. Ogawa, *Prog. Polym. Sci.*, **20**, 943 (1995).
14. G. Burillo, S. Torres, M. P. Carreón, M. E. Aguirre, and T. Ogawa, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **49**, 1 (1991).
15. G. L. Gaines, Jr., *J. Colloid Interface Sci.*, **54**, 430 (1976).
16. J. P. Fouassier, B. Tieke, and G. Wegner, *Israel J. Chem.*, **18**, 227 (1979).
17. G. Lieser, B. Tieke, and G. Wegner, *Thin Solid Films*, **68**, 77 (1980).
18. S. Fomine and T. Ogawa, *Polym. J.*, **26**, 93 (1994).