500, 930 nm. Anal. Calcd for $(C_{38}H_{54}NiS_4)_n$: C, 65.41; H, 7.80. Found: C, 64.77; H, 7.63.

Acknowledgment. This work was supported by grants from the Defense Advanced Research Projects Agency monitored by the Office of Naval Research and the Robert A. Welch Foundation.

References and Notes

(1) Reynolds, J. R.; Karasz, F. E.; Lillya, C. P.; Chien, J. C. W. *J. Chem. Soc., Chem. Commun.* **1985**, 268.
(2) Reynolds, J. R.; Chien, J. C. W.; Lillya, C. P. *Macromolecules* **1987**, *20*, 1184.
(3) Reynolds, J. R.; Jolly, C. A.; Krichene, S.; Cassoux, P.; Faulmann, C. *Synth, Met.* **1989**, *31*, 109.
(4) Engler, E. M.; Nichols, K. H.; Patel, V. V.; Rivera, N. M.; Schumaker, R. R. U.S. Patent 4,111,857, 1978.
(5) Poleschner, H.; John, W.; Hoppe, F.; Fanghanel, E. *J. Prakt. Chem.* **1983**, *325*, 957.
(6) Vicente, R.; Ribas, J.; Cassoux, P.; Valade, L. *Synth. Met.* **1986**, *13*, 265.
(7) Gotzfried, F.; Beck, W.; Lerf, A.; Sebald, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 463.
(8) Rivera, N. M.; Engler, E. M.; Schumaker, R. R. *J. Chem. Soc., Chem. Commun.* **1979**, 164.
(9) Ribas, J.; Cassoux, P. *C. R. Acad. Sci., Ser. 2* **1981**, *293*, 665.
(10) Teo, B. K.; Wudl, F.; Hauser, J. J.; Kruger, A. *J. Am. Chem. Soc.* **1977**, *99*, 4862.
(11) Dirk, C. W.; Bosseau, M.; Barrett, P. H.; Moraes, F.; Wudl, F.; Heeger, A. J. *Macromolecules* **1986**, *19*, 266.
(12) Wang, F.; Reynolds, J. R. *Macromolecules* **1988**, *21*, 2887.
(13) Friedman, L.; Shani, A. *J. Am. Chem. Soc.* **1974**, *96*, 7101.
(14) Neville, G.; Mahoney, W. *J. Appl. Polym. Sci.* **1967**, *11*, 2029.
(15) (a) Von Hopff, H.; Wandaler, R. *Helv. Chim. Acta* **1962**, *45*, 982. (b) Mueller-Westerhoff, U. T.; Nazzal, A.; Cox, R. J.; Giroud, A. M. *Mol. Cryst. Liq. Cryst. Lett.* **1980**, 249.
(16) Reynolds, J. R. Ph.D. Dissertation, University of Massachusetts, 1985.
(17) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 3585.
(18) Ahmad, M. M.; Underhill, A. E. *J. Chem. Soc., Dalton Trans.* **1983**, 165.
(19) Herman, Z. S.; Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T.; Nazzal, A.; Zerner, M. C. *Inorg. Chem.* **1982**, *21*, 46.
(20) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483.
(21) Tabushi, I.; Vamamura, K.; Nonoguchi, H. *Chem. Lett.* **1987**, 1373.
(22) Olson, D. C.; Mayweg, V. P.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1966**, *88*, 4876.
(23) Suzuki, Y.; Hayashi, G. U.S. Patent 4,763,966; Aug 16, 1988.
(24) Umehara, M.; Abe, M.; Oba, H. *Yuki Gosei Kagaku Kyokai Shi* **1985**, *43*, 334.
(25) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K. *Inorg. Chem.* **1983**, *22*, 1208.
(26) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253.
(27) Underhill, A. E.; Ahmad, M. M. *J. Chem. Soc., Chem. Commun.* **1981**, 67.
(28) Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Underhill, A. E.; Ahmad, M. M. *J. Chem. Soc., Chem. Commun.* **1982**, 390.
(29) Ahmad, M. M.; Underhill, A. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1062.
(30) Simons, J. K. U.S. Patent 2,396,893; March 19, 1946; *Chem. Abstr.* **1946**, *40*, 3779.
(31) Howell, W. C.; Cott, W. J.; Pattison, F. L. M. *J. Org. Chem.* **1957**, *22*, 255.
(32) *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 109.
(33) Badger, G. M.; Cheuychit, P.; Sasse, W. H. F. *J. Chem. Soc.* **1962**, 3235.
(34) Jefferson, A.; Sargent, M. V.; Wangchareontrakul, S. *Aust. J. Chem.* **1988**, *41*, 19.
(35) Ishizawa, A.; Yamamura, M.; Goto, R. *Nippon Kagaku Zasshi* **1969**, *90*, 806; *Chem. Abstr.* **1969**, *71*, 101376y.
(36) Higgins, J.; Jones, J. F.; Thornburgh, A. *J. Polym. Sci., Part A-1* **1971**, *9*, 763.
(37) Miyahara, Y.; Inazu, T.; Yoshino, T. *J. Org. Chem.* **1984**, *49*, 1177.

Synthesis and Properties of Diacetylenic Glutamate Lipid Monomer and Polymer: Thermochromic Polydiacetylene Free-Standing Films

Thauming Kuo and David F. O'Brien*

C. S. Marvel Laboratories, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received July 31, 1989; Revised Manuscript Received December 29, 1989

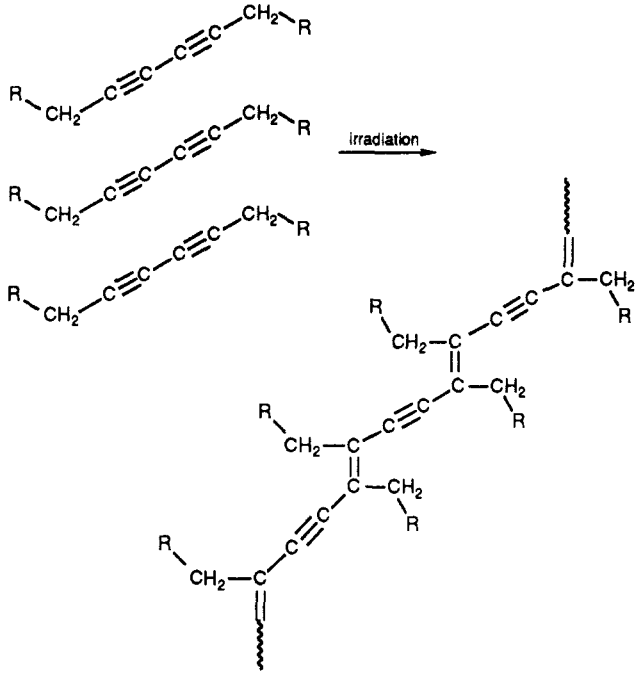
ABSTRACT: A novel double-chain diacetylene lipid based on a glutamate backbone, bis(docosa-10,12-diynyl) *N*-[6-(triethylammonio)hexanoyl]-L-glutamate bromide, was prepared by a multistep synthesis. Vesicles were formed by room-temperature sonication of the hydrated lipid. At 0 °C, the vesicles were readily polymerized by UV irradiation and the polydiacetylene (PDA) vesicles showed a two-stage thermochromic phase transition as the temperature was elevated. In the first irreversible stage, the PDA vesicles turned from blue to orange-red on warming to room temperature; in the second reversible stage, they turned from orange-red to yellow-orange on warming to 50 °C. Ordered multilayer films of the diacetylene lipid were cast from unpolymerized bilayer vesicles. Photopolymerization of these cast multilayer films yield highly colored polydiacetylenic films, thereby demonstrating that the molecular order inherent in the bilayer vesicles is retained during the casting procedure. The cast, polymerized films of PDA could be stripped from the support to give free-standing thin films of PDA, which were not disrupted by treatment with organic solvents. The PDA films showed reversible thermochromic phase transitions. Treatment of the PDA films with iodine vapors increased the electrical conductivity to 6×10^{-4} Ω^{-1} cm^{-1}.

Introduction

The polymerization of diacetylenes has been of great interest since it was reported[1,2] that the solid-state reaction proceeds by a topochemical 1,4-addition. The reaction is controlled by the packing of monomers in the crystal lattice and leads to the formation of polymeric single crystals. As illustrated, the UV-initiated polymeriza-

0024-9297/90/2223-3225$02.50/0

tion causes the molecules to tilt along the array without moving the center of gravity, so that the lattice symmetry and the packing of the side groups R are retained throughout the reaction.



The molecular order of monomers in many supramolecular assemblies is sufficient to allow topotactic polymerization of diacetylenes. Thus, lipid diacetylenes may be photopolymerized in monolayers at the air–water interface,[3,4] in Langmuir–Blodgett multilayers,[5] or in lipid bilayer vesicles.[6-8] Chapman and co-workers have published extensive studies on phosphatidylcholine diacetylenes. These data include the synthesis of monomers,[6a] formation of polymerized lipids,[6a] absorption characteristics of the polymers,[6a,b] optical activity of chiral polymers,[6c] as well as phase behavior of bilayers of the monomers.[6a,d] The fully conjugated structure exhibited in polydiacetylenes (PDAs) has also been utilized as a unique model for the studies of the electronic structure and chain conformation of polyconjugated systems.[9,10]

It is well-known that the topotactic photopolymerization of diacetylenes is acutely sensitive to the molecular order of crystals and supramolecular assemblies. Monolayers of diacetylenic fatty acids are polymerizable only in close-packed solidlike monolayers.[3,11] Bilayer membranes of lipid diacetylenes are photopolymerizable neither above the lipid phase-transition temperature (T_c) of the membrane[7] nor in small sonicated vesicles where the lipid chain packing is disordered by the sharp radius of curvature of the membrane.[8] The stringent requirements for efficient photopolymerization of diacetylenes provide an excellent chemical test of the ordering in supramolecular assemblies.

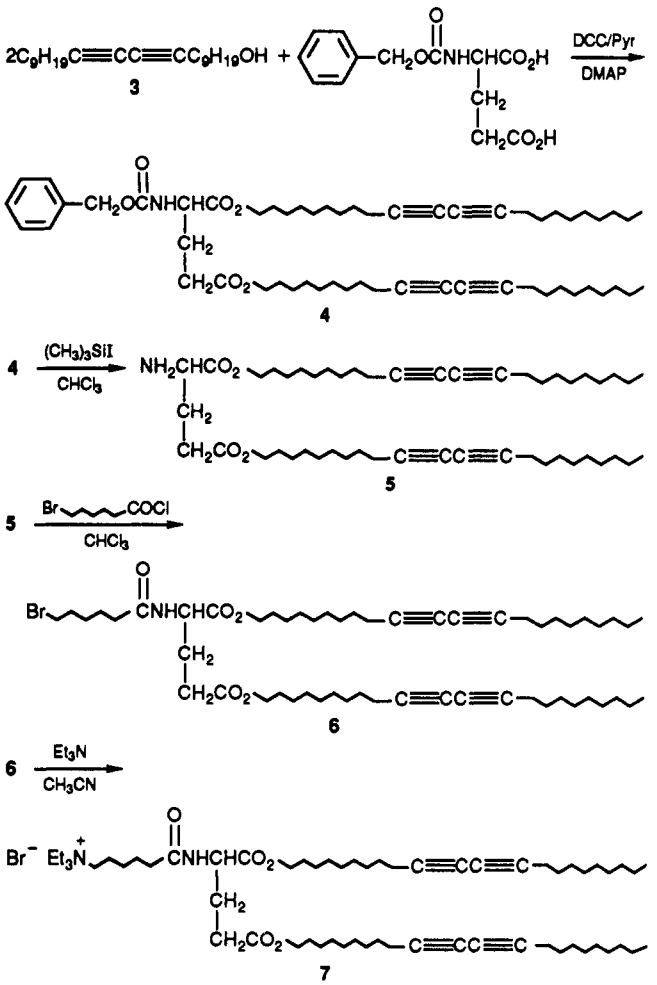
Previously we reported the synthesis of symmetrical and unsymmetrical lipids and studied the effect of structure and symmetry on the photopolymerization of bilayer membranes.[7,8] We now report the synthesis and polymerization of a new unsymmetrical diacetylenic lipid based on a glutamate rather than a glycerol backbone.[12] The glutamate lipid is similar in structure to those used by Kunitake and co-workers[13-15] to form ordered multilayers by the casting of aqueous dispersions of bilayer vesicles onto solid supports. Monolayers and multilayers are frequently prepared by Langmuir–Blodgett techniques. The casting technique may be an attractive alternative to L–B methods, if the molecular order present in bilayers is retained in the multilayer films formed during the casting technique. We describe here the polymerization behavior of both bilayer vesicles and cast multilayer films composed of the new diacetylenic glutamate lipid. Under appropriate circumstances, each type of assembly may be converted to polydiacetylenes. Furthermore, the PDA multilayer films may be removed from the support to yield free-standing PDA films.[12]

In addition, the conducting and thermochromic properties of these new PDAs are described. It is well-known that the electrical conductivity of conjugated polymers can be greatly enhanced by treatment with suitable oxidizing agents (e.g., I_2, AsF_5) or reducing agents (e.g., sodium naphthalide).[16] Although polydiacetylenes possess a unique ene–yne conjugated structure, they only show moderate conductivity upon doping, presumably due to the diffusion barrier caused by the nearly perfect crystal lattice and to the effect of bulky side groups. Upon doping, PDAs have shown semiconducting properties in single crystals,[17,18] monolayers,[19] multilayers,[20] and films.[21,22] Semiconducting PDA films were obtained previously from only a few soluble PDAs (i.e., poly-3BCMU, poly-4BCMU).[21,22] The free-standing PDA films reported here show a conductivity of 6×10^{-4} Ω^{-1} cm^{-1}, when treated with I_2 vapors.

Results

Synthesis. Docosa-10,12-diynoic acid (**2**) was synthesized by the oxidative coupling of 1-iodo-1-undecyne (**1**) and 10-undecynoic acid according to the literature method.[23,24] The acid **2** was reduced to the corresponding diacetylenic alcohol, docosa-10,12-diyn-1-ol (**3**), with lithium aluminum hydride. In this step, reaction time and temperature were crucial to the success of the reaction; longer reaction time (>3 h) or higher temperature (>65 °C) can cause partial reduction of the diacetylene groups, and the resulting product is difficult to crystallize or purify. The diacetylenic alcohol **3** was reacted in situ with *N*-carbobenzoxy-L-glutamic acid with dicyclohexylcarbodiimide (DCC) as a dehydrating agent and subsequently condensed with the catalytic aid of 4-(dimethylamino)pyridine (DMAP) to give bis(docosa-10,12-diynyl) *N*-carbobenzoxy-L-glutamate (**4**). The use of 1-hydroxybenzotriazole hydrate in this reaction reduced the reaction time from 18 to 3 h and increased the yield of **4** by 10%.[25] The deprotection of **4** to the corresponding amine, bis(docosa-10,12-diynyl) L-glutamate (**5**), was complicated by the presence of the diacetylene groups; catalytic hydrogenation by Pd/C caused the reduction of diacetylene groups; while the reaction with a strong protonic acid, CF_3CO_2H, or Lewis acid, BBr_3, afforded products that might be caused by the cationic chain polymerization of the diacetylene. The desired reaction was achieved with iodotrimethylsilane in chloroform at room temperature. Reaction of **5** with 6-bromohexanoyl chloride gave bis(docosa-10,12-diynyl) *N*-(6-bromohexanoyl)-L-glutamate (**6**). The final product, bis(docosa-10,12-diynyl) *N*-[6-(triethylammonio)hexanoyl]-L-glutamate bromide (**7**), was obtained by amination of **6** with triethylamine as shown in this scheme.

The diacetylenic glutamate lipid **7** showed thermotropic liquid-crystal behavior on a hot-stage polarizing microscope (Thomas) in the temperature range 35–85 °C. Examination by DSC (Perkin-Elmer 4) revealed a sharp peak at 39 °C (t_m), but a clearing temperature (t_i) was not observed.



Solid-State Polymerization. The final diacetylenic lipid, and the diacetylene intermediates were white solids until exposed to ultraviolet light. Each compound could be photopolymerized in the solid state by a low-pressure mercury lamp (Pen Ray, 254 nm) at a distance of 8 cm. The relative reactivity and PDA colors are shown in Table I.

The observed relative reactivities of various synthesized diacetylenes were consistent with the established theory of topochemical solid-state polymerization.[2] The reactivity of diacetylenes is determined by the substituents. Only those molecules that can form hydrogen bonds or possess a high dipole moment will favor an arrangement of monomer molecules in a crystal lattice suitable for efficient topochemical polymerization. The greater reactivity of **2**, **4**, **6**, and **7**, than that of **3** and **5**, is due to the strong hydrogen bonding of the carboxylic acid or amide groups. Stronger intermolecular interactions facilitate the crystal-lattice packing necessary for topochemical polymerization.

Vesicles. Vesicles were prepared by sonication of hydrated bilayers of **7** for 30 s at room temperature in a thermostated cup-horn sonicator. The vesicles were clear or opalescent, depending on the concentration. The midpoint of the phase-transition temperature (T_m) of the hydrated bilayers of **7** was determined to be 18.5 °C by differential scanning calorimetry (Figure 1).

It is known that polymerization of bilayers of lipid diacetylenes occurs only below the phase-transition temperature, where the diacetylene-containing chains are in a crystalline-like state.[7] Thus, aqueous suspensions of vesicles of **7** could not be polymerized at temperatures above the phase-transition temperature. When a sample of **7** was cooled in an ice bath, the bilayer vesicles became

Table I
Relative Reactivity of the Synthesized Diacetylenes

diacetylene	reactivity	PDA color
2	*b*	blue
3	*a*	light blue
4	*b*	red
5	*a*	light pink
6	*b*	black
7	*b*	black

[a] Color change observed only after prolonged irradiation (>$^1/_2$ h). [b] Color change observed after a 1-s UV irradiation.

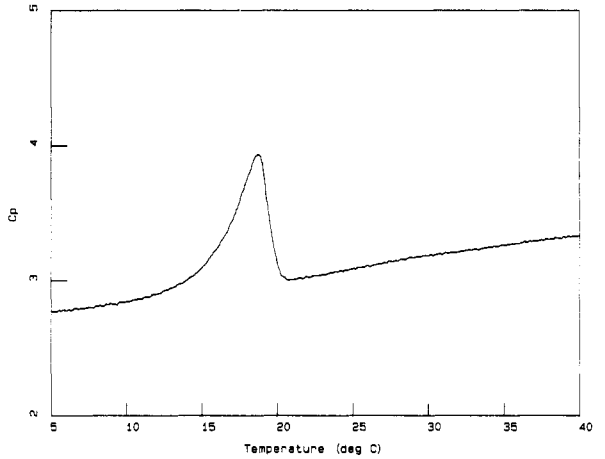


Figure 1. Main phase transition for hydrated bilayers of **7** (1 mg/mL).

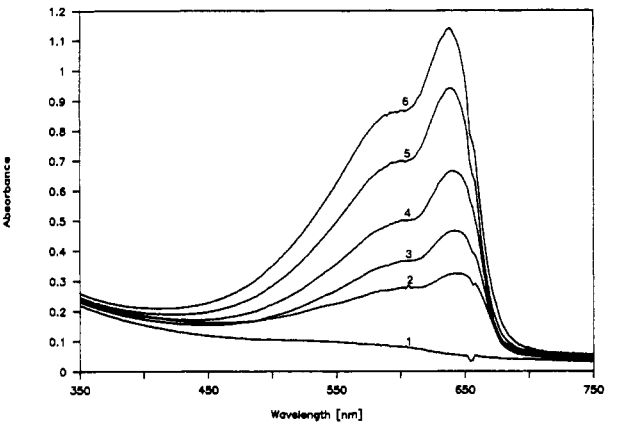


Figure 2. Absorption spectra of bilayer vesicles of **7** (0.25 mM) in a 1-cm cuvette at 0 °C. The spectra were recorded after exposure to 254-nm light for the following times: 0 s, curve 1; 30 s, curve 2; 60 s, curve 3; 120 s, curve 4; 300 s, curve 5; 600 s, curve 6.

sensitive to UV irradiation and quickly turned blue upon UV exposure. The polymerization process was conveniently followed by the increase in visible absorption, which is characteristic of PDAs (Figure 2).

The sample color remained blue when the polymerized vesicles were kept near 0 °C. However, the vesicle suspension underwent an irreversible thermochromic transition to orange-red when warmed up to room temperature, which is reflected in the visible absorption spectra (Figure 3). It was also observed that the polymerized vesicles underwent another stage of thermochromic transition from orange-red to yellow-orange when heated to above room temperature. At 50 °C, the spectrum is bimodal with the maxima at 500 and 540 nm; however, as the temperature is elevated to 80 °C, the spectrum becomes unimodal and broad with the maximum at 500 nm. When the sample was cooled to 22 °C, the orange-red absorption spectrum was restored. Differential scanning cal-

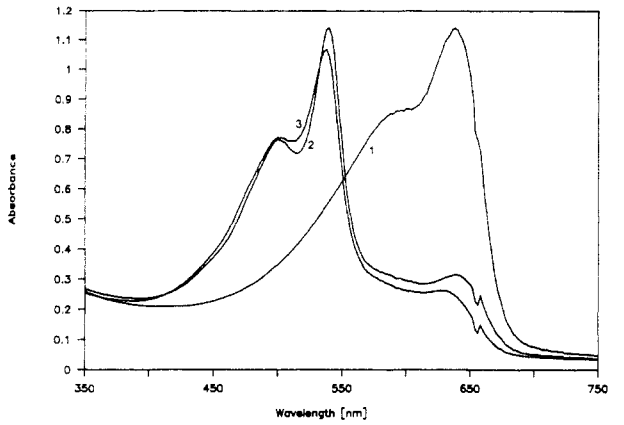


Figure 3. Effect of temperature on the absorption spectra of polymerized bilayer vesicles of **7** (0.25 mM) in a 1-cm cuvette. The sample temperature was as follows: 0 °C, curve 1; 22 °C, curve 2; cooled back to 0 °C, curve 3.

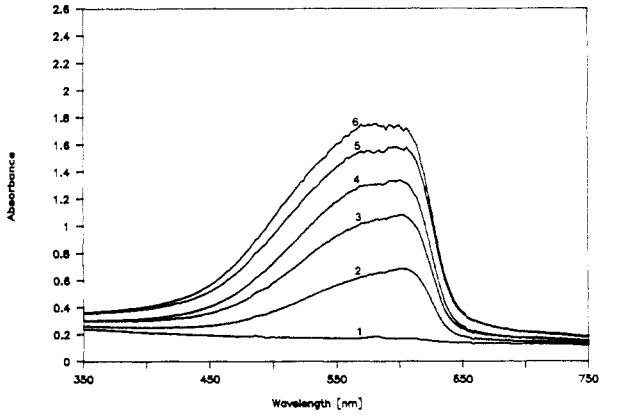


Figure 4. Absorption spectra of a cast multilayer film of **7**. The spectra were recorded after exposure to 254-nm light for the following times: 0 s, curve 1; 1 s, curve 2; 30 s, curve 3; 60 s, curve 4; 120 s, curve 5; 180 s, curve 6.

orimetry of the PDA bilayers did not show a sharp thermotransition in the temperature range from 5 to 70 °C.

Cast Multibilayer Film. A few drops of the bilayer membranes of **7** (5 mM in lipid) were spread on a clean glass slide (75 × 25 mm) and allowed to dry slowly. After 2 days a thin transparent film was formed. The colorless film on glass was further dried under vacuum for 2 h. It was then irradiated at room temperature by a low-pressure mercury lamp at a distance of 8 cm (flux of about 10^{14} photons/s). The film immediately became blue, and the color intensified with continued irradiation in a manner typical of diacetylene polymerizations. After irradiation, the PDA film was stripped off the glass to give a 10-μm-thick, dark purple-blue, flexible free-standing film. The absorption was too intense for spectrophotometric measurement; therefore, a thinner film was prepared from 0.25 mM lipid. Figure 4 shows the absorption spectra obtained by irradiation of this film with 254-nm light for various times.

The film showed a distinct reversible thermochromic phase transition. It changed from dark purple-blue to red when heated to about 50 °C and returned to the original color when cooled. The effect of temperature on the visible absorption spectra of a multilayer film of **7** is shown in Figure 5. At room temperature, the spectrum has a maximum at 620 nm, which shifts to 534 nm when the temperature was increased to 50 °C.

The extent of polymerization of the lipids was estimated to be 75–80% after 3-min exposure. Approximately 20% monomeric lipid could be extracted from

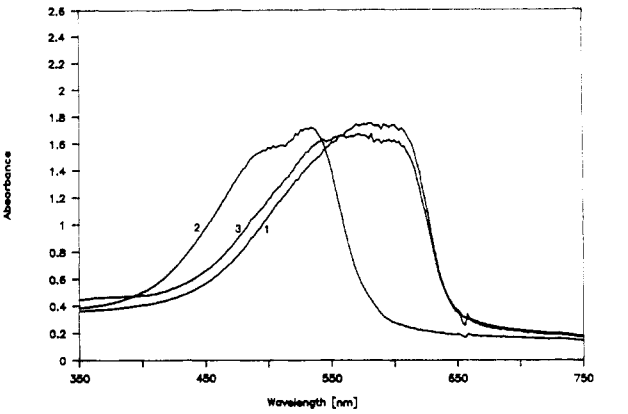


Figure 5. Absorption spectra of a polymerized case multilayer film of **7**: 22 °C, curve 1; 50 °C, curve 2; after cooling back to 22 °C, curve 3.

the polymerized film. Even after the extraction, the free-standing PDA film was not disrupted by treatment at room temperature with any of the following solvents: chloroform, chlorobenzene, THF, DMF, and DMSO.

A multilayer film was also cast from polymerized vesicles of **7**. An aliquot of the polymerized vesicles was spread on a glass slide and slowly dried. The resulting red-purple PDA film was significantly less stable to organic solvents than the previously described film. In fact, solvent stability could only be achieved by additional UV irradiation after casting of the film.

The purple-blue PDA film of **7** was an insulator with a conductivity less than $10^{-9}\ \Omega^{-1}\ cm^{-1}$. The film was treated in a chamber under vacuum by oxidizing iodine vapors as described in the Experimental Section. The conductivity, monitored by a multimeter, increased steadily when the sample was exposed to iodine vapors and reached a maximum after 22 h. The resultant film was black with metallic luster and showed an electrical conductivity of $6 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$.

The doped PDA films were environmentally sensitive; they gradually lost conductivity on exposure to air. Comparison of the films cast from both methods shows they both became black with metallic luster after doping. However, the PDA films cast from monomeric vesicles remained flexible, while those cast from polymerized vesicles became sticky and very brittle, presumably caused by the presence of a greater fraction of unreacted monomers. If the film from polymerized vesicles was further irradiated before I_2 treatment, it had similar properties as the film prepared from unpolymerized vesicles.

Discussion

By using techniques pioneered by Kunitake and co-workers,[13-15] we have obtained free-standing PDA films from two methods: one is to cast a film from monomeric vesicles first and then polymerize the film after it has been dried; the other is to cast the film from polymerized vesicles. The PDA films cast by using the first method have significantly better quality. Presumably, the polymerization was more complete in dehydrated bilayers than in vesicles. This was indicated by placing films obtained from both methods in chloroform. The PDA films cast from monomeric vesicles followed by polymerization remained intact, while those cast from polymerized vesicles did not. TLC of each of the above chloroform solutions showed that the latter had a larger fraction of unreacted monomer than the former (approximately 50% vs 20%). Moreover, when the film from polymerized vesicles was further irradiated by UV, it turned dark purple and appeared to be similar to the former film in quality.

When heated, PDA films cast from monomeric vesicles showed distinct reversible thermochromic phase transition as evidenced by the color change and red shift of absorption maxima. Thermochromic behavior of solution-cast films of urethane-substituted PDAs (poly-3BCMU and poly-4BCMU) was also observed by Chance et al.[26] They suggested that color changes were caused by the disruption of intramolecular hydrogen bonding and the destabilization of the planar polymer conformation.

The observation that cast multilayer films of **7** readily undergo photopolymerization indicates the films have sufficient molecular order to allow the topotactic polymerization to proceed. Therefore, the casting procedure successfully retains a high degree of the molecular order present in the original bilayer membranes. The absorption maxima of PDAs are indicative of the length of the polymer chain and/or the order of the polymer structure. Longer and/or more highly ordered PDAs, e.g., fatty acid diacetylene monolayers, exhibit absorption maxima at 650 nm (blue form),[5] whereas shorter and/or less ordered PDAs, e.g., phosphatidylcholine diacetylene bilayers, show absorption maxima near 540 nm (red form).[27] The absorption maximum of poly-**7** in extended bilayers at 0 °C is at about 640 nm and shifted to somewhat shorter wavelength (620 nm) for poly-**7** formed in cast multilayers. The shorter wavelength absorption found in the films as compared to that of the bilayers (see Figures 4 and 2, respectively) indicates the polymer chain lengths are longer in the bilayers than in the multilayer films. On the other hand, the increased solvent stability of films prepared by casting followed by polymerization suggests that the multilayer films are more highly cross-linked than the polymerized bilayer vesicles of **7**. This apparent tendency to give highly cross-linked PDA in cast multibilayer films may result in the shorter polymer chain lengths.

Thermochromic phenomenon has been observed in PDA crystals,[26,28] solutions,[29,30] monolayers,[3] multilayers,[5,31] vesicles,[32,33] and films.[26] Most of the studies were done in a solution system (i.e., $CHCl_3$/hexane), where the addition of a nonsolvent to PDA solutions or the decrease in temperature changed the color from yellow to blue or red. Chance et al.[28,34] first suggested that this phenomenon was due to a nonplanar to planar "visual conformational transition" and that the color change was caused by changes in the effective conjugation length. Heeger et al.[35] proposed a coil-to-rod model and suggested a possible cis configuration existed in the yellow phase. While they both agreed the color change was a single-chain phenomenon, Wegner et al.[36] suggested that the blue phase was caused by the aggregation of several individual chains (≈150). Although the nature of thermochromic phase transitions shown in our studies has not yet been studied in detail, it is notable that the thermochromism of the cast films of **7** is fully reversible. Most reports of PDA thermochromism describe irreversible behavior. Therefore, the thermochromism of cast films requires continued investigation.

In summary, we have prepared a novel diacetylenic lipid based on a glutamate, rather than a glycerol, backbone. Both bilayer vesicles and cast multilayer films prepared from this lipid could be readily polymerized. The formation of PDAs in cast films shows that these methods of forming multilayer assemblies retain a significant degree of molecular order. The data suggest that cast films can be an attractive alternative to L–B techniques for the formation of repeating multilayer assemblies. The films are readily removed from the support to give free-standing PDA films, which display reversible thermochromism.

Experimental Section

Methods. All the experiments were carried out under yellow light. Melting points were taken on a Mel-Temp apparatus except otherwise indicated. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. NMR spectra were taken on a 250-MHz Bruker WM250 spectrometer. Visible absorption spectra were recorded on a Hewlett-Packard 8452A spectrophotometer. Elemental analyses were performed by Desert Analysis, Tucson, AZ. Chloroform and acetonitrile were dried over P_2O_5. Distilled water was further purified by a Milli-Q water system, Millipore.

Synthesis. Docosa-10,12-diynoic acid (2): [23,24] mp 47–49 °C; IR (KBr) 2919, 2848, 2180, 2140, 1694, 1465, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, CH_3C), 1.20–1.66 (m, 26 H, CH_2), 2.23 (t, 4 H, $CH_2C{\equiv}$), 2.34 (t, 2 H, CH_2CO_2). Anal. Calcd for $C_{22}H_{36}O_2$: C, 79.52; H, 10.84. Found: C, 79.03; H, 11.30.

Docosa-10,12-diyn-1-ol (3):[24] mp 43–45 °C; IR (KBr) 3350, 2918, 2848, 2184, 2139, 1466, 1414, 1350, 1061, 1044, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3 H, CH_3C), 1.26–1.51 (m, 28 H, CH_2), 2.24 (t, 4 H, $CH_2C{\equiv}$), 3.64 (t, 2 H, CH_2O). Anal. Calcd for $C_{22}H_{38}O$: C, 83.02; H, 11.95. Found: C, 82.13; H, 11.98.

Bis(docosa-10,12-diynyl) *N*-Carbobenzoxy-L-glutamate (4). A solution of 0.067 g (0.24 mmol) of *N*-carbobenzoxy-L-glutamic acid (Chemalog) in 5 mL of pyridine was treated with 0.103 g (0.5 mmol) of dicyclohexylcarbodiimide. The mixture was stirred at room temperature for 15 min under nitrogen atmosphere; a white precipitate was formed. The above mixture was subsequently mixed with 0.16 g (0.5 mmol) of docosa-10,12-diyn-1-ol (**3**), 0.034 g (0.25 mmol) of 1-hydroxybenzotriazole hydrate, and a catalytic amount of 4-(dimethylamino)pyridine. The reaction mixture was then stirred overnight. The resulting precipitate was filtered and washed with chloroform. The filtrate was taken up in chloroform and extracted with dilute HCl, and the organic layer was separated. The solution was dried over sodium sulfate, and the solvent was removed. The resulting residue was recrystallized from methanol to give 0.13 g (61%) of **4**: mp 38–40 °C; IR (KBr) 3316, 2922, 2848, 2180, 2140, 1742, 1728, 1685, 1525, 1463, 1285, 1202, 1175, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 6 H, CH_3C), 1.26–1.70 (m, 56 H, CH_2), 2.0 (m, 2 H, CH_2), 2.24 (t, 8 H, $CH_2C{\equiv}$), 2.40 (t, 2 H, CH_2CO_2), 4.05 (t, 2 H, CH_2O), 4.15 (t, 2 H, CH_2O), 4.40 (m, 1 H, CH), 5.11 (s, 2 H, CH_2Ph), 5.40 (d, 1 H, NH), 7.35 (s, 5 H, C_6H_5C). Anal. Calcd for $C_{57}H_{87}NO_6$: C, 77.64; H, 9.88; N, 1.59. Found: C, 77.49; H, 10.24; N, 1.39.

Bis(docosa-10,12-diynyl) L-Glutamate (5). A solution of 0.5 g (0.57 mmol) of **4** in 15 mL of dried chloroform was treated with 0.23 g (1.2 mmol) of iodotrimethylsilane. The reaction mixture was stirred at room temperature for 2 days. A total of 10 mL of distilled water was then added, and the reaction mixture was stirred for 15 min. The mixture was transferred into a separatory funnel and neutralized with 10% sodium bicarbonate. The organic layer was separated and dried, and the solvent was removed to give a colorless oil, which crystallized on standing. The crude product was purified by flash chromatography over silica gel (eluent: chloroform/ether 100:7): yield 0.35 g (82%); mp 31–33 °C; IR (KBr) 3397, 3322, 2915, 2849, 2180, 2140, 1731, 1714, 1468, 1260, 1201, 1174, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 6 H, CH_3C), 1.26–1.90 (m, 58 H, CH_2), 2.24 (t, 8 H, CH_2), 2.46 (t, 2 H, $CH_2C{\equiv}$), 3.45 (m, 1 H, CH_2CO_2), 4.06 (t, 2 H, CH), 4.11 (t, 2 H, CH_2O). Anal. Calcd for $C_{47}H_{81}N$: C, 78.71; H, 10.84; N, 1.87. Found: C, 78.04; H, 10.98; N, 2.04.

Bis(docosa-10,12-diynyl) *N*-(6-Bromohexanoyl)-L-glutamate (6). A solution of 0.1 g (0.13 mmol) of **5** in 20 mL of dried chloroform was mixed with 56 mg (0.26 mmol) of 6-bromohexanoyl chloride and 16 mg (0.13 mmol) of 4-(dimethylamino)pyridine and then stirred at room temperature for 30 min. After the reaction, the mixture was extracted with dilute HCl and 10% sodium bicarbonate. The organic layer was separated and dried, and the solvent was removed to give a colorless oil, which was crystallized from methanol to give 0.11 g (92%) of a white powder **6**: mp 33–34 °C; IR (KBr) 3298, 2923, 2850, 2180, 2140, 1751, 1730, 1644, 1532, 1464, 1195, 1174, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 6 H, CH_3C), 1.26–2.05 (m, 66 H, CH_2), 2.24 (t, 8 H, $CH_2C{\equiv}$), 2.40 (t, 2 H, CH_2CO_2), 3.41 (t, 2 H, CH_2Br), 4.06 (t, 2 H, CH_2O), 4.13 (t, 2 H, CH_2O), 4.60 (m,

1 H, CH), 6.20 (d, 1 H, NH). Anal. Calcd for $C_{55}H_{90}NO_5Br$: C, 71.43; H, 9.74; N, 1.52. Found: C, 71.99; H, 9.85; N, 1.43.

Bis(docosa-10,12-diynyl) *N*-[6-(Triethylammonio)hexanoyl]-L-glutamate Bromide (7). A stirred solution of 0.16 g (0.17 mmol) of **6** in 20 mL of dried acetonitrile was refluxed for 1 day with an excess of triethylamine. The solvent was then evaporated under reduced pressure, and the resulting oil was taken up in a small amount of chloroform for silica gel column chromatography (eluent: subsequently using 5%, 10%, and 20% of methanol in chloroform): Yield 0.12 g (69%); mp t_m 35 °C, t_i 85 °C (thermotropic liquid crystal); IR (KBr) 3302, 2922, 2849, 2180, 2140, 1726, 1644, 1532, 1463, 1203, 801, 723 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.88 (t, 6 H), 1.26–1.85 (m, 66 H, CH_2), 2.24 (t, 8 H, $CH_2C\equiv$), 2.53 (t, 2 H, CH_2CO_2), 3.55 (q, 8 H, CH_2N), 4.04 (t, 2 H, CH_2O), 4.06 (t, 2 H, CH_2O), 4.45 (m, 1 H, CH), 7.92 (d, 1 H, NH). Anal. Calcd for $C_{61}H_{105}N_2O_5Br$: C, 71.41; H, 10.24; N, 2.73. Found: C, 71.64; H, 10.77; N, 2.74.

Vesicle Preparation. The diacetylenic glutamate lipid **7** (2 mg, 2 μmol) was dissolved in chloroform and then dried on a rotary evaporator to form a thin film. The film was further dried with a vacuum pump and then was hydrated with 2 mL of purified water and subsequently sonicated at room temperature for 30 s with a cup–horn type sonicator (Heat Systems, W-380) to yield a slightly opalescent suspension of vesicles (1 mM in **7**).

Photopolymerization of the Vesicles. A total of 1 mL of the vesicles (0.25 mM in **7**) was introduced into a 1-cm quartz cell; the water suspension was then purged with argon and capped tightly. The sample was irradiated in an ice–water bath (using a quartz container) with a low-pressure mercury lamp (Pen Ray) at a distance of 4 cm for selected times. The polymerization process was monitored spectrophotometrically by the appearance of absorption bands in the visible region.

Calorimetry. Calorimetric data were obtained with a Microcal, Inc., MC-2, differential scanning microcalorimeter. A heating rate of 10 °C/h was used. Lipid suspensions were prepared by vortexing the dry lipid **7** (2 mg, 2 μmol) under argon in purifed water (2 mL) and subsequently transferred to the calorimeter via a calibrated syringe.

Film Casting and Polymerization. A few drops of the unpolymerized vesicles (5 mM in **7**) were spread on a portion of glass slide (75 × 25 mm). A thin transparent film was formed after drying in air for 2 days. The film on glass was further dried under vacuum for 2 h and irradiated by the low-pressure mercury lamp at a distance of 8 cm for selected times. The polymerization process was followed spectrophotometrically. After the polymerization, the film could be peeled off the glass.

A few drops of blue polymerized vesicles (5 mM) were spread on a piece of glass slide. A red-purple film was formed after the glass slide was dried in air for 2 days and subsequently under vacuum for 2 h. The PDA film was then peeled off the glass.

Iodine Treatment of Films. A type II apparatus reported by Chien[37] was used. A strip of the diacetylene film was mounted on the four probes with the aid of Electrodag (Acheson 502). After the system was evacuated for 1 h, the iodine vapors were admitted into the sample chamber. The conductivity, monitored by a multimeter (Fluke Model 8024B), increased steadily and reached its maximum after 22 h.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

References and Notes

(1) Wegner, G. *Naturforsch.* **1969**, *24B*, 824.
(2) Wegner, G. *Makromol. Chem.* **1972**, *154*, 35.
(3) Day, D. R.; Ringsdorf, H. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 205.
(4) Thomas, H. T.; Drexhage, K. H.; O'Brien, D. F., unpublished observations.
(5) Tieke, B.; Liester, G.; Wegner, G. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1631.
(6) (a) Johnston, D. S.; Sanghera, S.; Pons, M.; Chapman, D. *Biochim. Biophys. Acta* **1980**, *602*, 57. (b) Pons, M.; Johnson, D. S.; Chapman, D. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 513. (c) Pons, M.; Johnson, D. S.; Chapman, D. *Biochim. Biophys. Acta* **1982**, *693*, 461. (d) Leaver, J.; Alonso, A.; Durrani, A. A.; Chapman, D. *Biochim. Biophys. Acta* **1983**, *732*, 210.
(7) O'Brien, D. F.; Whitesides, T. H.; Klingbiel, R. T. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 95.
(8) Lopez, E.; O'Brien, D. F.; Whitesides, T. H. *J. Am. Chem. Soc.* **1982**, *104*, 305.
(9) Bloor, D., Chance, R. R., Eds. *Polydiacetylenes*; Martinus Nijhoft Publishers: Boston, 1985.
(10) Cantow, H.-J., Ed. *Advances in Polymer Science. 63. Polydiacetylenes*; Springer-Verlag: New York, 1984.
(11) Hub, H. H.; Hupfer, B.; Koch, H.; Ringsdorf, H. *J. Macromol. Sci., Chem.* **1981**, *A15* (5), 701.
(12) A preliminary account of this research appeared in: Kuo, T.; O'Brien, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 7571.
(13) Nakashima, N.; Ando, R.; Kunitake, T. *Chem. Lett.* **1983**, 1577.
(14) Nakashima, N.; Kunitake, M.; Kunitake, T. *Macromolecules* **1985**, *18*, 1515.
(15) Highashi, N.; Kajiyama, T.; Kunitake, T.; Prass, W.; Ringsdorf, H.; Takahara, A. *Macromolecules* **1987**, *20*, 29.
(16) Frommer, J. E.; Chance, R. R. *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., etc., Eds.; John Wiley & Sons: New York, 1985; Vol. 5, p 462.
(17) Nakanishi, H.; Mizutani, F.; Kato, M. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 983.
(18) Sakamoto, M.; Wasserman, B.; Dresselhaus, M. S.; Wnek, G. E.; Elman, B. S.; Sandman, D. J. *J. Appl. Phys.* **1986**, *60*, 2788.
(19) Day, D. R.; Lando, J. B. *J. Appl. Polym. Sci.* **1981**, *26*, 1605.
(20) Bloor, D.; Hubble, C. L.; Ando, D. J. *Molecular Metals*; Hatfield, E. W., Ed.; Plenum: New York, 1979; p 243.
(21) Se, K.; Ohnuma, H.; Kotaka, T. *Macromolecules* **1983**, *16*, 1581.
(22) Ohnuma, H.; Inoue, K.; Se, K.; Kotaka, T. *Macromolecules* **1984**, *17*, 1285.
(23) Tieke, B.; Wegner, G.; Nagele, D.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 764.
(24) Singh, A.; Schur, J. M. *Synth. Commun.* **1986**, *16*, 847.
(25) We thank Dr. U. Liman for this suggestion.
(26) Chance, R. R.; Patel, G. N.; Witt, J. D. *J. Chem. Phys.* **1979**, *71*, 206.
(27) Lopez, E.; O'Brien, D. F.; Whitesides, T. H. *Biochim. Biophys. Acta* **1982**, *693*, 437.
(28) Chance, R. R.; Baughman, R. H.; Muller, H.; Eckhardt, C. J. *J. Chem. Phys.* **1977**, *67*, 3616.
(29) Patel, G. N.; Chance, R. R. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 607.
(30) Chance, R. R.; Sowa, J. M.; Eckhardt, H. *J. Phys. Chem.* **1986**, *90*, 3031.
(31) Tieke, B.; Enkelmann, V.; Kapp, H.; Lieser, G.; Wegner, G. *J. Macromol. Sci., Chem.* **1981**, A15(5), 1045.
(32) Pons, M.; Johnston, D. S.; Chapman, D. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 513.
(33) Singh, A.; Thompson, R. B.; Schnur, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 2785.
(34) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *70*, 4387.
(35) Kim, K. C.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 522.
(36) Wenz, G. W.; Muller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837.
(37) Chien, J. C. W. *Polyacetylene: Chemistry, Physics and Materials Science*; Academic Press: Orlando, FL, 1984; p 327.