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Synthesis and Characterization of a Novel Amphiphilic Polydiacetylene

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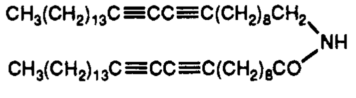
Introduction

Surfactants containing diacetylene units, which form sufficiently stable monolayers at the air–water interface to be transferred as Langmuir–Blodgett (LB) films on solid substrates, can subsequently polymerize when exposed to UV radiation or heat.[1,2] This results in stable, ordered monolayers.[2,3] Such polymeric LB films have interesting applications in microelectronic devices, in microlithography, and in nonlinear optics.[4–8]

The most commonly researched diacetylene surfactant contains the carboxylic acid head group. A number of studies in the last 2 decades have described properties such as surface activity, polymerizability, fluorescence, and nonlinear optical capacity.[9–12]

However, little research has been performed on other structural variations of diacetylene surfactants. For example, diacetylenes with polar groups such as the amine or amide functionality have rarely been examined. This type of study is warranted, since such variations in structure will affect and possibly improve the surface activity, the degree of polymerization, and the ability of the molecules to assemble as LB layers. The resulting polydiacetylenes may also exhibit improvements in properties such as conductivity and solubility.

We report the synthesis and characterization of a new diacetylene amphiphile, *N*-heptacosa-10,12-diynylheptacosa-10,12-diynamide (HDDA), with the structure:



HDDA

Two significant differences in this compound from previously studied surface-active diacetylenes are that the amide functionality acts as the hydrophilic unit and that the double-tail structure renders this compound structurally similar to naturally occurring phospholipids, making this molecule attractive for potential biochemical applications in vesicles and membranes. Thus, this particular compound represents a novel class of diacetylenes. We describe the synthetic route to the monomer, determine its spreadability at the air–water interface and its ability to transfer as LB layers, investigate the polymerizability of the monomer in these structures, and characterize the resulting polydiacetylene by UV/visible and resonance Raman spectroscopy.

Experimental Section

Materials. Water was purified to a resistivity of 18 MΩ·cm by a Millipore Milli-Q filtration apparatus. Solvents used in the monolayer studies were HPLC grade and were used without further purification. All other reagents were used as received.

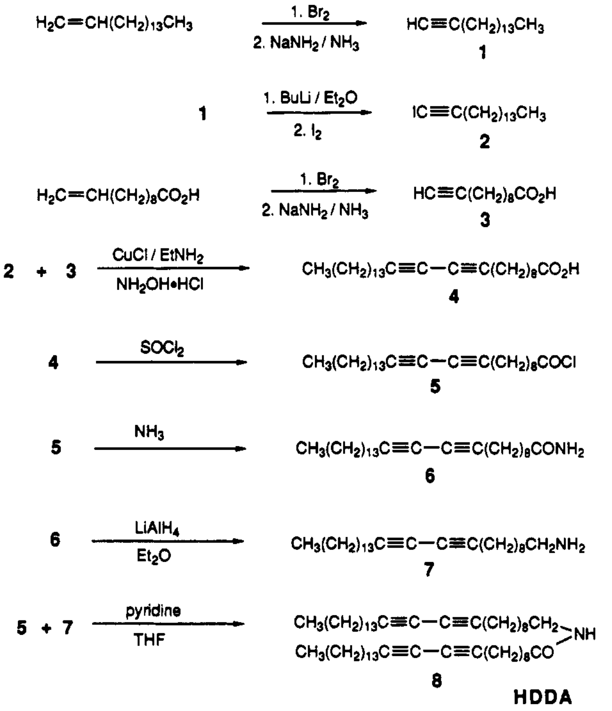
Techniques. Monolayer studies were performed on a Langmuir balance. Surface pressures were measured by the Wilhelmy plate method, using a 1 cm by 1 cm square of filter paper as the plate. An IBM XT microcomputer was utilized for data acquisition and instrument control. Monolayers and LB layers were irradiated by an overhead mantle at a height of 20 cm with six 10-W Hg lamps emitting at 254 nm. Irradiations were performed in air for periods of approximately 30 s.

Monolayers were transferred to quartz disks via a Lauda Filmlift FL1 apparatus, moving the substrates vertically at a rate of 1.25 cm/min. Monolayers were compressed to a surface pressure of 20 mN/m prior to transfer, and all transfers were done from a pure water subphase.

A Varian Cary 118 spectrophotometer was used to obtain UV/visible spectra. A Dilor Omars 89 instrument equipped with an argon ion laser, focused on the sample through a microscope attachment, was used for Raman spectroscopy. Excitation was at 488 nm.

Synthesis. The synthesis utilizes the method of Cadiot and Chodkiewicz[13] for the cupling of terminal alkynes as well as a modification of the procedures of Rygas.[14] The synthetic steps are shown in Scheme I. The synthesis of compounds **1**–**7** has been well-described in the above references.

Scheme I
Synthetic Steps for the Preparation of *N*-Heptacosa-10,12-diynylheptacosa-10,12-diynamide (HDDA)



***N*-Heptacosa-10,12-diynylheptacosa-10,12-diynamide (8).** Approximately 1.0×10^{-3} mol of the acyl chloride **5** was dissolved in dry THF and added dropwise to a THF solution of 9.8×10^{-4} mol of **7** and 0.1 g of pyridine. After the addition, the mixture was stirred at room temperature for 24 h and then cooled to −10 °C to precipitate the product (**8**). The product was further purified by recrystallization from THF. Yield: 52%. Mp: 90–92 °C. IR: 3300 (N–H str), 1640 cm^{-1} (C=O str). ^{1}H NMR (in $CDCl_3$): δ 0.9 (t, $-CH_3$), 1.2–1.6 (m, $-CH_2-$), 2.1–2.25 (m, $-CH_2C{\equiv}C-$ and $-CH_2CO-$), 3.2 (m, $-CH_2NH-$), 5.4 (s, –NH–). ^{13}C NMR ($CDCl_3$): δ 14.1 ($-CH_3$), 19.2 ($-CH_2C{\equiv}C-$), 22–32 ($-CH_2-$), 36.9 ($-CH_2CO-$), 39.5 ($-CH_2NH-$), 65.2 and 65.3 ($-C{\equiv}CC{\equiv}C-$), 172.9 (–CO–). TLC: On silica plate with eluting solvent of benzene/ethyl acetate (2:1); one spot visible with R_f = 0.76.

Results and Discussion

HDDA was surface-active at the air–water interface, forming a stable monolayer. A typical surface pressure–

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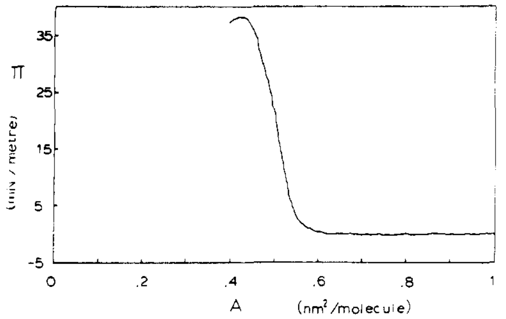

Figure 1. Surface pressure versus area isotherm of HDDA on a subphase of 1 g/L of $MgCl_2$.

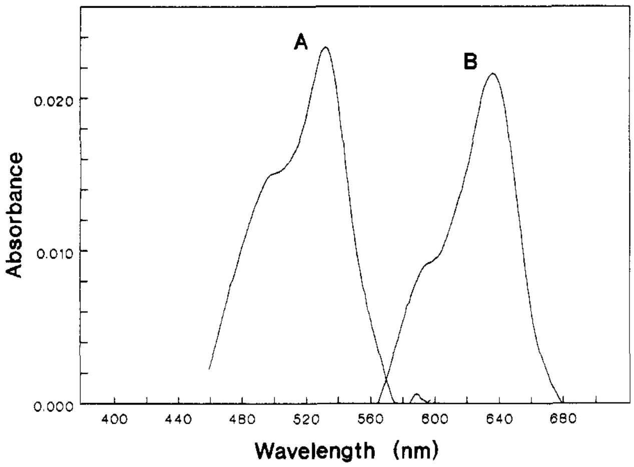

Figure 2. Visible spectra of poly(HDDA): (A) Polymer obtained after UV irradiation of HDDA on a pure water subphase. (B) Polymer obtained after UV irradiation of four LB layers of HDDA.

area isotherm of this compound on a subphase containing $MgCl_2$ is shown in Figure 1. The cross-sectional area of the monomer, calculated by extrapolating the isotherm back to the base line, is approximately 0.56 nm^2/molecule. The value is similar to values previously reported for double-chain amphiphiles.[15]

It is well-known that monolayers with collapse pressures of approximately 20 mN/m or higher are stable enough to permit assembly into LB layers.[16] Figure 1 shows that HDDA has a collapse pressure of 38 mN/m, making it an excellent candidate for constructing LB films.

Isotherms were also obtained for this compound on subphases of pure water. These were virtually identical with that of Figure 1; thus, the addition of the ionic $MgCl_2$ species to the subphase has no influence on the nature of the monolayer.

Irradiation of HDDA monolayers on all subphases resulted in a red polydiacetylene film on the water surface. Figure 2 shows the visible spectrum obtained for this polymer when transferred to a quartz substrate. Maxima occur at 480 and 540 nm, as observed previously for other polydiacetylenes.[17]

Solid-state polydiacetylenes generally exist in a blue or red phase. The difference between these phases is thought to be due to a transition from an ordered state (blue) to a disordered state (red) with a corresponding change in effective conjugation lengths along the polymer backbone.[18] However, crystalline structural differences may also exist between, for example, the blue-state polymer derived from an ordered monolayer and that derived from the bulk monomer. A polymer formed from the monomer multilayer would have the same structure as the monolayer, whereas in bulk the monomer may crystallize in an extended form. Nevertheless, we conclude that poly(HDDA) exists in a disordered conformation when polymerized on the air–water interface.

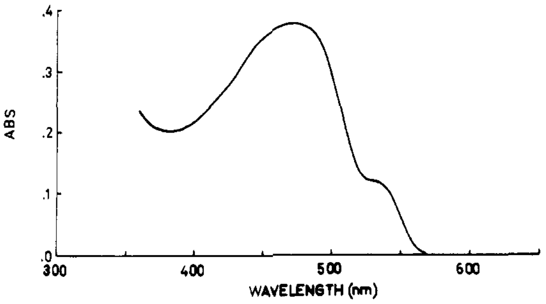

Figure 3. Visible spectrum of a solution of poly(HDDA) in chloroform.

The monolayers on the water surface polymerized readily when compressed, but they also polymerized prior to any compression. This suggests that existence of islands or ordered domains of monomer in the expanded state, where the molecules are in close enough proximity to polymerize when irradiated. Thus, HDDA does not form a truly spreadable monolayer, as has often been observed for diacetylenes and other amphiphiles.[19] The existence of such islands at low surface pressures has also been ascertained by free energy calculations of nucleation at the air–water interface.[20]

Several layers of HDDA were transferred to a quartz disk by a vertical dipping process, forming Y-type monolayers. These layers were irradiated to form a blue poly(HDDA) film. This indicates that the monomer transferred to the disk with retention of molecular order. The visible spectrum of the blue film is also shown in Figure 2, with maxima at 590 and 640 nm, which concur with literature values for blue-phase polydiacetylenes.[17]

Raman spectra of the LB poly(HDDA) film showed peaks at 1520 and 2124 cm^{-1} from the excitation line due to the symmetric stretching modes of the backbone double and triple bonds, respectively. These peak positions agree very well with those observed previously for polydiacetylenes upon resonance excitation at low frequencies.[18]

An unexpected result from this work was that poly(HDDA) was found to be soluble in chloroform. A small bulk portion of the monomer, approximately 20 mg, was irradiated at 254 nm for 1 min to obtain the blue-phase polymer. The observed behavior of this diacetylene, which only polymerizes to the ordered blue form when in multilayers or in bulk, may be due to a decrease in the mobility of the polymer chains compared to the relative freedom of movement at the air–water interface, where the disordered red-phase polymer is formed. When this polymer was added to 5 mL of $CHCl_3$, it assumed the red phase and formed a fine suspension. Upon gentle heating, a clear orange-red solution resulted. The solution was filtered through a 450-nm syringe filter and the color persisted. The visible spectrum of this solution shown in Figure 3 shows peaks at 450 and 500 nm with a shoulder at 540 nm. This is similar to the spectrum obtained for a chloroform solution of poly(4-BCMU) by Xu and Chu, who determined that the polymer chains were in a wormlike conformation.[21] Thus, our polydiacetylene is assumed to exist in a similar conformation. Of course, the solubility of the polymer is likely dependent on the degree of polymerization, and the poly(HDDA) chains produced here may simply be short enough to be highly soluble.

The behavior of this polymer is presumably dependent on its crystal structure and the crystal structure of the monomer from which it is prepared. It would be useful to perform X-ray and electron diffraction studies of the monolayers, multilayers, and bulk samples. Such a study would further enhance the understanding of the various structural phases of this polymer.

Conclusions

The diacetylene amphiphile *N*-heptacosa-10,12-diynylheptacosa-10,12-diynamide was synthesized and was found to be surface active at the air–water interface. The resulting monolayers were stable on subphases of both pure water and dilute solutions of $MgCl_2$. These monolayers polymerized upon UV irradiation to the red-phase polydiacetylene and were also transferrable as Langmuir–Blodgett layers to solid substrates. Irradiation of Langmuir–Blodgett layers of HDDA results in the blue-phase polydiacetylene. Finally, poly(HDDA) was shown to be soluble in chloroform.

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