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Laser Raman Optical-Wave-Guide Study of Mono- and Multilayer Langmuir–Blodgett Films of Poly(diacetylenes) Containing a Carboxylic Acid Group

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ABSTRACT: Coherent mono- and multilayer polymer films of the 11-8 diacetylenic fatty acid $CH_3(CH_2)_{11}C{\equiv}CC{\equiv}C(CH_2)_8COOH$ were formed by the Langmuir–Blodgett technique. The films thus formed were characterized by traditional force–area isotherms while on a pure water subphase. Molecular organization in both mono- and multilayer films was investigated by the resonance Raman optical-wave-guide method. Our results show that the molecular organizations in both the monolayer and multilayer films are the same and also show no dependence on the nature of the substrate. Furthermore, both monolayer and multilayer films can be prepared in either blue or red forms. The study of the Raman spectral change as a function of the blue-to-red polymer-form conversion reveals that the phase transformation involves a two-phase heterogeneous process.

Introduction

Diacetylenes have received considerable attention because of their ability to form highly ordered polymers by topochemical polymerization in the solid state.[1] Poly(diacetylenes) are highly conjugated linear polymers that exhibit anisotropic optical properties as well as strong third-order nonlinear interactions. Potential applications of poly(diacetylenes) as ultrathin resins, as protective coatings, or as integrated optical devices have been discussed.[2-6]

One special group of diacetylenes has the general formula

$$C_mH_{2m+1}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_n{-}COOH$$

These amphiphilic diacetylenes form traditional mono- and multilayer Langmuir–Blodgett (abbreviated as L–B) films. Photopolymerizations have been observed in these L–B films to produce highly oriented polymer films.[7-9] It has been reported that the polymers formed in the L–B films are initially in a blue (nonfluorescing) form but subsequently transform to a red form that is highly fluorescent.[10,11] The exact nature of this transformation is not established, although it is agreed that the π-electron conjugation in the red form is reduced.

All past studies of structural characterization have dealt with multilayer films. Only very recently, a surface-enhanced Raman scattering study of monolayer L–B films of a poly(diacetylene) with $m = 12$ and $n = 8$ in the above formula has been reported.[12] This work reports that the polymer in a monolayer L–B film deposited on silver is of a different form than that in multilayer films and in a bulk state. These authors attribute this difference as being due to a more delocalized backbone when more than one layer is deposited.

In the present paper, we report the structural studies of mono- and multilayer L–B films of a specific poly(diacetylene) with $m = 12$ and $n = 8$ by using the technique of Raman optical wave guide. The Raman optical-wave-guide technique has successfully been used in the vibrational study of many polymer films.[13] The technique does not rely on any specific enhancement from the surface of the substrate, such as is the case when the film is deposited on silver. In addition, the study of poly(diacetylene) films in an optical-wave-guide system is also of interest from the point of view of its application in integrated optical devices. These films are deposited on several different kinds of optical wave guides to examine the effect of the substrate. Mono- and multilayer films are compared to investigate if indeed the monolayer structure is different from that of multilayer L–B films. Finally, we discuss the formation of both blue and red forms in monolayer and multilayer L–B films.

Experimental Section

L–B Experiments. The diacetylenic fatty acid used in this study was $CH_3(CH_2)_{11}C{\equiv}CC{\equiv}C(CH_2)_8COOH$. From here on the monomer will be abbreviated as 11-8 DA and the corresponding polymer as 11-8 PDA. It was obtained from Dr. D. Chapman (Royal Free Hospital, School of Medicine, London, England) and was used without further purification. Prior to L–B film formation, bulk material was stored in a dark container at about 0 °C to avoid polymerization and thermal decomposition. The water used for the subphase was first distilled and subsequently filtered to remove trace organics and ions. This water of resistivity more than 15 MΩ cm was then quadruply distilled, first from a slightly

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alkaline stage, next from a slightly acidic stage, and finally twice from itself through an all-quartz still. The resulting water had a pH of 5.6. The customized L–B setup used in our study consisted of a Teflon (TFE grade) trough and two Teflon barriers for containing and compressing the film. The motorized dipping mechanism (vertical dip) allowed smooth and reproducible rates of immersion (or emersion) of about 5 mm/min. This arrangement was kept in a double-wall Plexiglas box through which constant-temperature water was circulated, maintaining the desired temperature inside the box within ±0.5 °C. In our experiment the subphase temperature was 18 °C. During film spreading, compression, and transfer, the surface pressure, $\pi = \gamma^0 - \gamma$, was continuously monitored with the Wilhelmy plate method, which consisted of a glass slide connected via a quartz thread to a Cahn nulling electrobalance and an analogue recorder. With this method an error of ±0.5 dyn/cm was associated with surface pressure measurements. Film formation in the L–B trough was performed by spreading 100 μL of the solution of 1 mg of 11-8 DA in 10 mL of a hexane/ethanol mixture (9:1 by volume) onto the air/water interface by means of an Agla micrometer syringe. Sufficient time of 10 min was then allowed for solvent evaporation.

Cover microscope slides (24 mm × 40 mm × 100 μm) were used as substrates for L–B film transfer. These substrates were carefully cleaned in a chromic–sulfuric acid bath for 12 h, rinsed thoroughly with distilled water, finally rinsed with quadruply distilled water, and dried in air just prior to film transfer. We also used polymer-coated quartz substrates in this experiment; however, we were not as successful in maintaining them as clean as the glass substrates.

The glass slides were immersed in the subphase prior to film spreading and compression. After the desired surface pressure was achieved (usually between 6 and 8 dyn/cm), the slides were emersed through the water/air interface, resulting in a single monolayer being transferred. When necessary, slides were subsequently dipped one or more times in order to produce a L–B multilayer. When polymer-coated (PMMA or PS) quartz substrates were used, two layers of 11-8 DA (or PDA) were transferred to the substrate (one during the immersion, the second during the emersion). The monomer polymerization was carried out by exposing the slide to UV radiation, this usually being done after the film had been transferred to the substrate. However, for the sake of comparison, we also polymerized the monomer at the air/water interface in the film balance (the observed decrease in surface pressure was ~10%) and then transferred the 11-8 PDA monolayer to the various substrates in the same manner. Samples prepared in this way were used for spectroscopic Raman studies.

Spectroscopic Experiment. The experimental procedure used in this work basically is a standard wave-guide coupling method.[13-15] Laser light is directed onto the coupling prism (Schott Glass LASF-9) after passing through a polarizer and focusing lens, as shown in Figure 1. Two types of light-guiding media were used: (i) ~5-μm-thick films of polystyrene or poly(methyl methacrylate) deposited by doctor blading or by spinning methods, and (ii) a cover-glass slide of average thickness 90–100 μm. The cover glass was found to be most convenient for two reasons: (i) the greater ease of Langmuir–Blodgett (L–B) film preparation, and (ii) its low refractive index.

We find the use of the cover glass as a wave guide for the Raman work specially suited for films of materials that cannot be used as a wave guide because, for example, of high absorption in the visible region. Since the cover glass is much thicker (~100 μm) than the wave guides normally used (~2 μm), the experimental arrangement for coupling the light through the prism does not need to be that precise and tedious for the cover glass. Furthermore, cover glasses are readily available commercially (Fisher Scientific), whereas planar wave guides of several micron dimensions must be fabricated.

The glass substrate was easily cleaned for L–B mono- and multilayer deposition. Our experience with polymer wave guides like polystyrene (PS) or poly(methyl methacrylate) (PMMA) showed that it is really difficult to avoid contamination of the polymer-coated glass substrate. During the dipping process in the L–B trough we observed an increase in the surface pressure, possibly due to the contaminants coming off the polymer substrate. Moreover, in the case of PS, the polymer tended to peel off the substrate. A further complication in the case of the polymer wave guides was observed when the polymers were found to decompose under the UV radiation used to polymerize the diacetylene L–B films. In all cases the Raman spectra of L–B diacetylene mono- and multimolecular layers obtained from either kind of arrangement (L–B film deposited on a cover glass or on the polymer wave guide) showed no difference except for the blue-to-red transition of the polymer (discussed below). The glass substrate with the L–B-deposited diacetylene film was placed in a prism/substrate assembly.

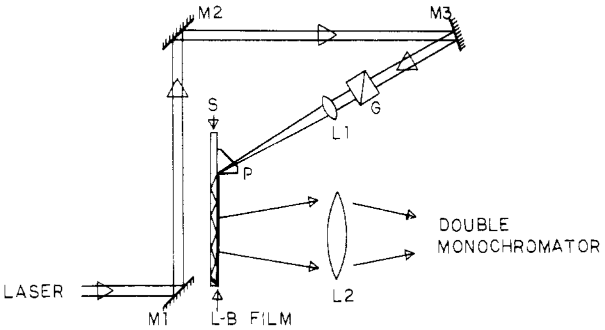

Figure 1. Schematic representation of the experimental geometry. M1, M2, M3, reflecting mirrors; G, Glan type prism polarizer; P, coupling prism; L1, L2, focusing and collecting lens, respectively; S, cover microscope slide (substrate) with deposited L–B film. M2, G, and L1 are mounted firmly on the arm attached to the X-ray goniometer wheel, which allows precise control of the angle of incidence on the prism face. The coupling prism, P, is set at the goniometer axis. Support assembly for the prism and the wave guide consists of a prism holder and an *xyz* translater for fine adjustment. M2 is placed on a rotating goniometer axis. When M2 rotates by an angle α, the corresponding rotation of M3 is 2α. For clarity, M2 is shown in a different place.

The UV irradiation of diacetylene films was carried out either in the L–B trough or on the glass substrate. The prism/substrate assembly was demounted for the heating process. This allowed us to take spectra of a monomer and the blue and red forms of the polymer from the same sample without additional alignments.

Two different sources of the excitation radiation for Raman spectra were used: (1) the 532-nm line of the CW mode-locked Nd-YAG laser Model 3000 or the 587-nm line of the Model 375 synch-pumped dye laser (both Spectra Physics); (2) the 488- or 475-nm line of the Model FL 2002 dye laser pumped by an excimer laser Model EMG 201MSC (both Lambda Physik). The output power of the laser was adjusted between 5 and 50 mW, and a TE polarization was used in all experiments. Scattered light was focused onto the entrance slit of a Spex double monochromator Model 1401. The dc output of the electrometer was fed into a Nicolet signal averager, from where it was read by a Micronova Data General computer and subsequently stored on floppy disks for data processing.

Results and Discussion

Force-Area Isotherm. A typical force–area isotherm for an 11-8 DA film at 18.4 °C is shown in Figure 2. It can be seen that a condensed film of 11-8 DA forms over the surface pressure range 3–15 dyn/cm. The film starts collapsing at ~18 dyn/cm. At temperatures above 20 °C, the stability of the film decreases and the collapse pressure shifts to lower values. The films used for the Raman investigation were formed at 18.4 °C with a surface pressure of ~8 dyn/cm, well below the collapse point.

Raman Spectra of Monolayer Films. The Raman spectra of a monolayer film deposited on the quartz substrate are shown in Figure 3 before and after the film's exposure to UV light. As is typical of diacetylenes, only the polymer backbone modes, i.e., C=C and C≡C motions of the polymer, are observed because of the resonance enhancement. As a result, only transitions due to the in-plane stretching and bending C=C and C≡C modes are observed. No transitions due to the side groups are observed. The Raman spectra of these monolayer films are of excellent quality in S/N ratio. We focus on two

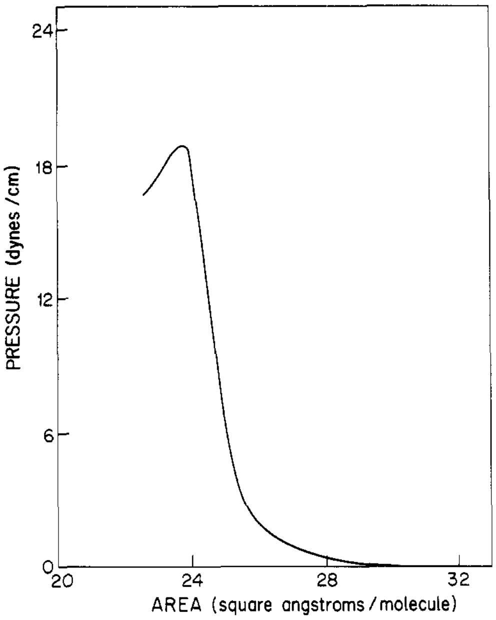

Figure 2. Surface pressure-area isotherm for 11-8 DA at 18.4 °C.

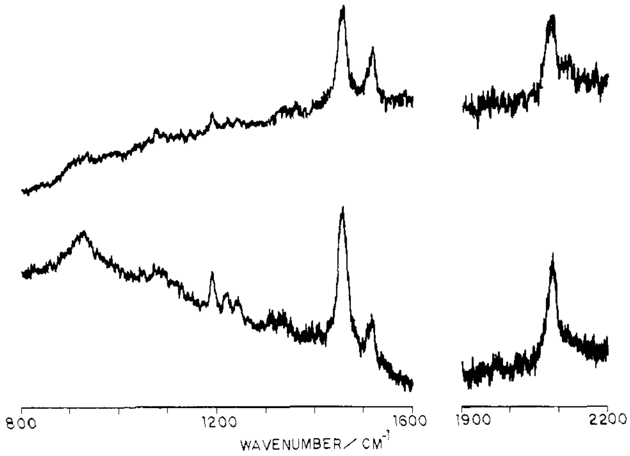

Figure 3. Raman spectra of the 11-8 PDA monomolecular L-B film deposited on a glass substrate: bottom spectrum, sample before UV exposure; top spectrum, after exposing the sample to the UV radiation for ca. 5 min. Excitation wavelength is 532 nm, power used is 30 mW, and the spectral resolution is 3 cm^{-1}.

sharp transitions at 1456 cm^{-1} (ν_2) due to C═C stretch and at 2081 cm^{-1} (ν_1) due to C≡C stretch. Even in a sample containing less than 1% polymer (color only very faint blue) only polymer bands are observed. As a result of UV exposure, the film turns blue because of further polymerization. However, the position of these bands does not change. This is in contrast to what is observed for poly(diacetylenes *p*-toluenesulfonate) (PTS). In the case of the latter compound, the frequencies of these modes change continuously with the extent of polymerization.

In the spectra of the monolayer films we also see a weak peak at 1517 cm^{-1}. Initially, the relative intensity of this peak grows as a function of UV exposure time. The growth in intensity of this peak is accompanied by an increase of the fluorescent background. We assign this peak to the red form. The blue-to-red transformation is discussed below. However, upon prolonged UV irradiation for ca. 40 min at 150 W, the 1517 cm^{-1} band intensity decreases and only changes in the background fluorescence can be observed.

In our study of the monolayer we do not see any difference in the Raman spectra if the film is deposited on the substrate as a monomer and polymerized or if the film is polymerized on the water subphase and then transferred to the substrate.

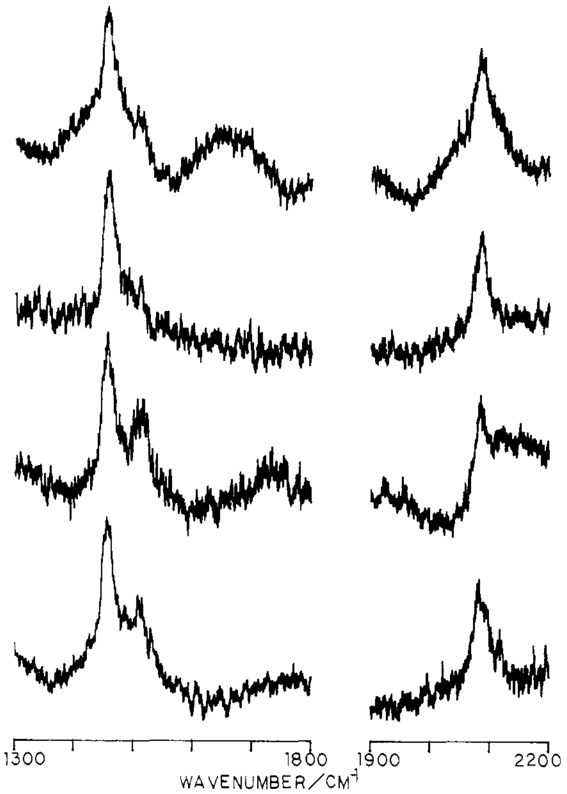

Figure 4. Raman spectra of 11-8 PDA. A three-layer L-B film after different times of UV irradiation: 0 min, 10 min, 30 min, and 60 min from the bottom to the top, respectively. Excitation wavelength is 532 nm, the power level is 30 mW, and the spectral band-pass is 3 cm^{-1}.

Monolayer vs. Multilayer. The Raman spectra of the three layer L-B film after various UV exposure times are shown in Figure 4. This film was again deposited on the glass substrate. It can be seen that the spectra correlate very well with those of a monolayer (Figure 3). We, therefore, conclude from our study that the monolayer and multilayer films have the same molecular organization. We have studied bilayer and multilayer films deposited on polystyrene and PMMA substrates (wave guides). Again, the spectra are the same, provided all samples are in the blue form. Therefore, no dependence of the Raman spectra either on the number of layers deposited or on the nature of the substrate was observed.

Our result is different from that obtained by Chen et al.[12] These authors reported differences in the spectra of bilayer and multilayer L-B films of 15-8 PDA deposited on silver-coated glass slide. They report a shift of the C≡C and C═C stretching modes from 2123 and 1521 cm^{-1} in bilayer films to 2078 and 1456 cm^{-1} in multilayer films. They assign this shift as being due to a difference in the conjugation length for bilayer and multilayer films. Our experimental results showed that, irrespective of whether the monomer monolayer is transferred to the substrate and subsequently polymerized by UV irradiation or the monolayer is polymerized on the water surface and then transferred to the substrate, the polymer film on the substrate is in the blue form. The Raman spectra of both the mono- and multilayer L-B films show bands at 2081 and 1456 cm^{-1}, characteristic of the blue polymer form. The red form in either the monolayer or the multilayer was only obtained by heating the blue form when the bands now shift to 2119 and 1517 cm^{-1}. We did not however investigate if a red-form monolayer would turn blue when

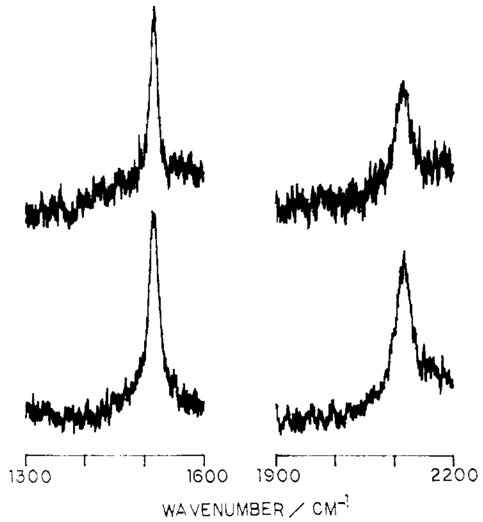

Figure 5. Raman spectra of an 11-8 PDA monolayer (top) and a three-layer (bottom) film after thermal conversion of the polymer into the red form. Excitation wavelength is 488 nm, the laser power is 5 mW, and the band-pass is 6 cm^{-1}.

successively dipped to form a multilayer film.

Blue-to-Red Transition. The irreversible transition from the blue form to the red form of the polymer is thermally induced in the bulk phase. We have found that such a thermal transition occurs in both monolayer and multilayer films deposited on quartz, polystyrene, or PMMA. The Raman spectra of a monolayer and a three-layer polymer film in the red form are displayed in Figure 5. It can be seen that the frequencies of the $C{=}C$ and the $C{\equiv}C$ bands shift to higher values, indicating a reduced conjugation of the polymer backbone. This reduced conjugation is also supported by the electronic spectra of these forms. The transformation can readily be introduced by heating. We have observed that a monolayer film when irradiated with the 532-nm line of power >100 mW (from a frequency-doubled CW mode-locked Nd–YAG laser) gives the same spectra as that of the red form. Also, if a multilayer monomer film is exposed to a strong UV light from an excimer laser, it produces only the red form. We believe that these results are derived from heating of the film due to nonradiative relaxation of the light absorbed. If care is taken to choose a Raman excitation wavelength where absorption is not strong or to reduce the power level, the blue form is photostable. However, here we must add that the red form of the polymer generated by the strong collimated laser beam (e.g., 532 nm) and that by the heating process differ somewhat from each other. Although both show backbone transitions at the same frequency, fluorescence from the laser-beam-induced red form is of much less intensity. We were still able to record Raman spectra of this form using a 532-nm excitation source, whereas the thermally generated form showed extremely intense fluorescence that obscured completely the Raman spectrum, for the same wavelength. This observation may indicate that two different mechanisms of phase transition can lead to the same form of the polymer. Although the final structure of the polymer backbone appears the same in both cases, either the side-group arrangement is different or "byproducts" of the phase transition such as structural defects can cause changes in the fluorescence profile. While we cannot rule out any of these explanations, the IR spectra (see below) make the former one unlikely.

As we discussed above, the Raman spectra of these polymers contain only resonance-enhanced motion of the conjugated backbone. In contrast, the IR spectra are dominated by the side-group motions. The IR spectra of both the blue and red forms in the KBr pellet showed no difference between them. However, reported X-ray crystallographic and electron microscopic data of the multilayer cadmium salt of several diacetylene monocarboxylic acids[18] indicate that the blue-to-red polymer form transformation in their case involves a rearrangement of the side group and a small translation of the polymer chains. The resulting structure of the red form crystallites differs significantly from that of a blue form, which, being better organized, shows greater electron conjugation within the polymer chain. Nonetheless, even this kind of structural transformation would not be expected to contribute to the infrared spectral changes. However, to verify this conclusion, additional experiments are required. Because of the highly anisotropic properties of the L–B poly(diacetylene) films, the IR spectra of the bulk material and that of the L–B films may differ somewhat.[17]

The spectral changes monitored as a function of the extent of conversion from the blue to the red form reveal that as conversion proceeds the peaks due to the blue form decrease in intensity while those due to the red form grow in intensity. No frequency changes of the bands due to the blue or red forms are observed in the intermediate conversion range. Our observation is different from that of Tieke and Bloor, who have reported that the Raman spectra of a multilayer 10-8 PDA cadmium salt L–B film showed a continuous shift of the ν_1 and ν_2 vibrations from the blue form, via an intermediate purple form, to the final red form.[16] We, therefore, conclude that the pure acid L–B films behave differently than the salt L–B films. The process of the blue-to-red transformation in the acid may be a heterogeneous two-phase process, while that in the salt form may involve a one-phase homogeneous transformation.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research contract No. F49620855C0052. D.A.C. thanks Professor D. Chapman for generously providing the sample of 11-8 DA.

Registry No. Poly(10,12-pentacosadiynoic acid) (homopolymer), 66990-33-8.

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