Polymeric Self-Assembled Monolayers. 2. Synthesis and Characterization of Self-Assembled Polydiacetylene Mono- and Multilayers

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Received October 13, 1994[⊗]

Abstract: We report the synthesis and characterization of self-assembled mono- and multilayers of ω-functionalized diacetylenic thiols. We used the carboxylic acid-terminated alkanethiol diacetylene $HS(CH_2)_{10}C{\equiv}CC{\equiv}C(CH_2)_{10}COOH$ as a block for preparing multilayers. Individual layers are covalently bonded through a thioester linkage. These two orthogonal polymerization steps yield a highly structured three-dimensional, surface-confined polymer. The results of infrared external reflectance spectroscopy and ellipsometry clearly indicate layer-by-layer growth up to at least 6 layers. The multilayers can be polymerized by UV irradiation either after the deposition of each individual layer or after all layers are deposited. The appearance of bands attributable to C=C vibrational modes in resonance Raman spectra confirms polymerization. Transmission UV–vis spectroscopy indicates the films consist of the highly conjugated blue polydiacetylenic polymer, and that polymerization is complete within 5 min of initial irradiation.

Introduction

We report the synthesis and characterization of self-assembled mono- and multilayers of ω-functionalized diacetylenic thiols. Self-assembled monolayers (SAMs) of organomercaptans confined to Au surfaces have found wide use as substrates for fundamental studies as well as a few technological uses.[1] However, most SAMs are relatively fragile since their total adsorption energy is thought to be in the range of 30–50 kcal/mol.[1] We have found that diacetylenic SAMs can be polymerized in the plane parallel to the substrate with UV light, and once polymerized they are extremely rugged.[2] Surprisingly, the polymerized SAMs are better barriers to transfilm mass transfer than the unpolymerized monolayers.[2] In this report, we discuss the first example of the formation of monomeric and polymeric diacetylenic mercaptan-based SAMs and then the formation of polymerized multilayers based on a covalent thioester linkage between layers. These two orthogonal polymerization steps yield a highly structured three-dimensional, surface-confined polymer, and we believe these materials will find use as ordered conducting polymers, third-order nonlinear optical (NLO) materials, and lithographic resists.

Polymerization of diacetylenes in the solid state was first reported by Wegner.[3] In contrast to the extended conjugation found in single crystals, alternative strategies, such as those based on Langmuir-Blodgett methods, usually result in conjugation defects.[4] Cao and Mallouk have shown that the extent of polymerization of the diacetylenic monomers in organometallic crystals depends on the coordinating metal ion; divalent metal ions yield polymers with the greatest extent of conjugation.[5] The similarity between the packing structures of monomeric diacetylene-based SAMs and their polymerized analogs suggests that monolayers and multilayers of these materials should undergo topochemical polymerization to yield films with high structural integrity.[1,5b] There has been one prior report of the polymerization of a monolayer fabricated from methyl-terminated diacetylene disulfides that confirms this prediction.[6]

Since we are interested in preparing oriented polydiacetylene multilayers for optical and electronic applications, we designed and synthesized various ω-functionalized n-alkanethiols containing a diacetylene group. We chose the carboxylic acid-terminated alkanethiol diacetylene $HS(CH_2)_{10}C{\equiv}CC{\equiv}C(CH_2)_{10}COOH$, **1**, as a block for preparing multilayers,[7] since it is conveniently configured for linking individual layers through a thioester bond.[8]

Experimental Section

All chemicals were of reagent grade purity. The synthesis of **1** has been described previously.[7] Gold substrates for FTIR-external reflectance spectroscopy (FTIR-ERS), ellipsometry, and Raman spectroscopy were prepared by thermal evaporation of 2000 Å of Au over a 50-Å Cr adhesion layer confined to Si(100). For UV–vis measurements, transparent substrates were prepared by thermal deposition of 50 Å of Au onto a (3-mercaptopropyl)trimethoxysilane adhesion layer confined to a quartz substrate.[9,10] The substrates were cleaned in piranha solution (30% H_2O_2:concentrated H_2SO_4 = 1:3, freshly prepared. **Caution**: piranha solution is a powerful oxidizing agent and reacts violently with organic compounds. It should be discarded immediately after use in a waste container with a loosely fitting lid.) for 15 s, rinsed, and dried. Monolayers were prepared by soaking the substrate in a 1 mM $CHCl_3$ solution of **1** for 1 h, removing the substrate, and then rinsing it in acetone and deionized water. Multilayers were prepared by thioester coupling of **1** to the base monolayer either before or after polymerization

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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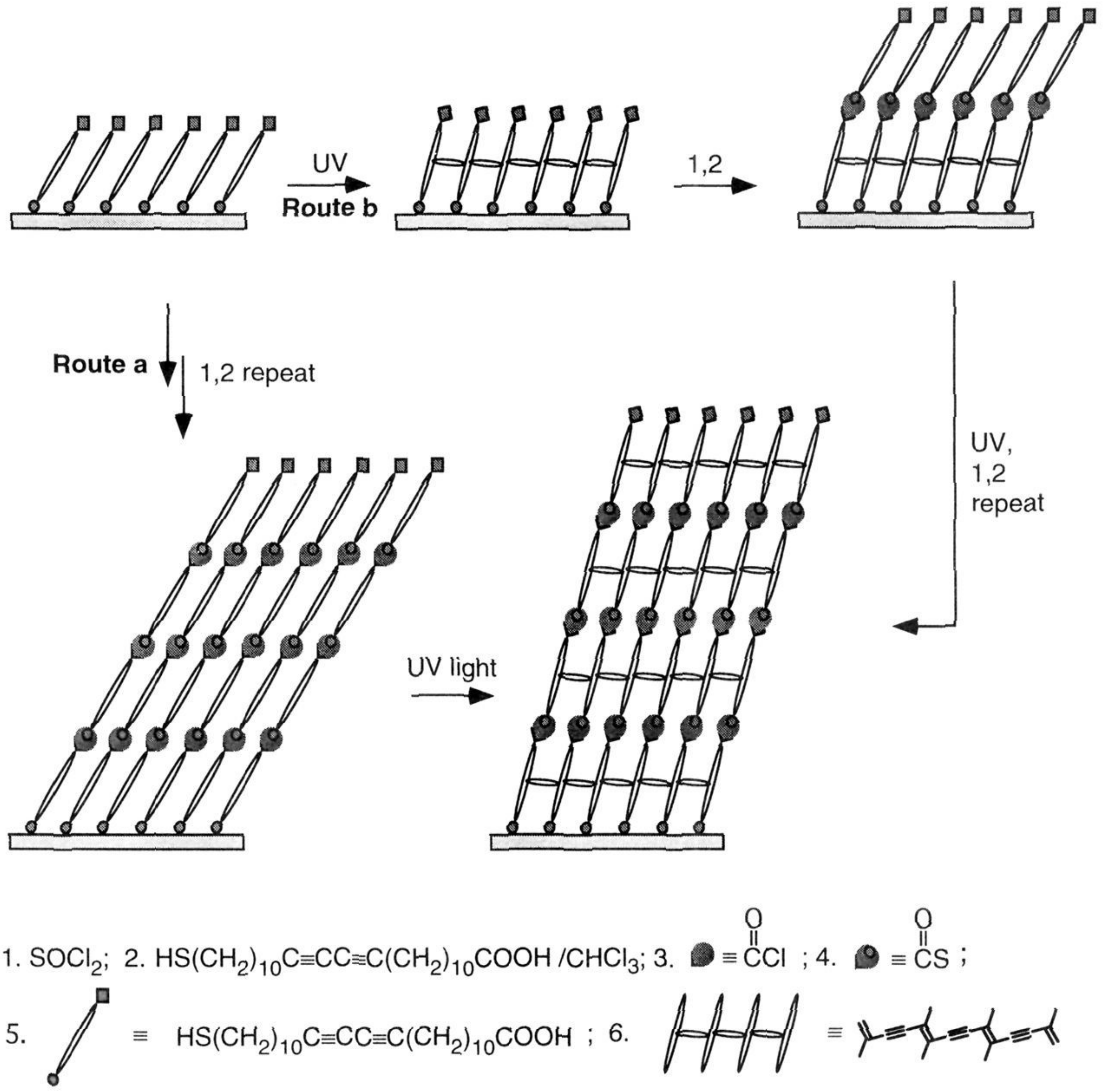
Scheme 1



of the base layer.[8] The carboxylic acid-terminated SAM was positioned in a closed container, and after the container was purged with dry N_2 for 5 min, $SOCl_2$ vapor was introduced for 10 min. Control experiments, which involved monitoring this reaction by FTIR-external reflectance spectroscopy in real time,[11] indicated that the absorbance due to the carboxylic acid carbonyl stretching mode originally present around 1713 cm^{-1} was completely eliminated within 1 min and replaced by an absorbance at 1813 cm^{-1} that we identify as the acid chloride carbonyl mode.[12] The substrate was then transferred to a 1 mM $CHCl_3$ solution of **1**, and thioester formation was complete within 1 h. Complete characterization of this transformation is discussed in the next section. Subsequent layers were prepared similarly.

Except for the UV−vis spectroscopic experiments, which are discussed later, polymerization was performed by placing the substrate into a gas-tight container and irradiating it under a N_2 purge for 5 min with a lamp (Oriel, Model 6035) positioned 1 cm above the substrate.

FTIR-ERS measurements were made using a Digilab FTS-40 FTIR spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid N_2-cooled MCT detector. All spectra were obtained using *p*-polarized light incident on the Au substrate at an angle of 84°.

Thickness measurements of the unpolymerized mono- and multilayers were made using a Gaertner Scientific ellipsometer (Model L116C). The data were obtained using the 488 nm Ar laser line, but the 633 nm He−Ne laser line yielded similar results. A refractive index of 1.46 was assumed for the thickness calculations. Due to optical absorptions it was not possible to measure the thickness of the polymerized multilayer SAMs using ellipsometry.

The UV−vis spectra were recorded on a Hewlett-Packard diode-array spectrometer by first obtaining a background spectrum of a four-layer, unpolymerized film, and then polymerizing it for various lengths of time without removing the substrate from the spectrometer (in these experiments the UV light was maintained 0.5−1.0 cm away from the substrate). Throughout these experiments the substrate was kept under a N_2 purge.

The Raman measurement system consists of a Kr-ion laser (Model Innova 90K, Coherent Laser Group, Santa Clara, CA), a 3-in.-diameter holographic notch filter (Model Notch-Plus, Kaiser Optical System, Ann Arbor, MI), a 0.5-m single-grating Czerny-Turner spectrograph (Model 500M, SPEX Industries, Edison, NJ), a liquid-N_2-cooled 1024-by-256-pixel charge-coupled device (CCD) (Model CCD-1000LF, SPEX Industries), and a data acquisition and analysis system (SPEX Industries). Laser power was measured by a semiconductor detector (Model 840-C and 818-SL/CM, Newport, Irvine, CA). The spectral position, of the horizontal CCD pixels were calibrated using emission

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lines of known wavelengths[13] from a Ne lamp (Model A1A/NE-2, Chicago Miniature Lamp, Buffalo, IL). Typical conditions for Raman scattering were 5 mW 647.1 nm excitation, 200 mm slit width (equivalent to 6.7 cm^{-1} band pass), and 5 s integration time. The spectra were corrected for a slowly varying spectral background using set points more than 200 cm^{-1} apart. The laser was focused to a point on the sample surface using a $f = 250$ mm spherical focusing lens.

Results and Discussion

Scheme 1 illustrates two approaches we have used for layer-by-layer growth of polydiacetylene multilayers.[14] This strategy is conceptually similar to Mallouk chemistry.[5a] Following self-assembly of **1** on the Au surface, we converted the carboxylic acid terminal group to an acid chloride by exposing it to $SOCl_2$ vapor (Scheme 1, Step 1).[12] Subsequent reaction with **1** yields the second layer (Step 2). By repeating Steps 1 and 2, we can fabricate unpolymerized multilayer films of **1**, which are easily polymerized upon exposure to UV light (Route a). We were able to improve ordering of the multilayers using the alternative strategy described by Route b. To confirm the structures shown in Scheme 1,[14] we monitored the formation and polymerization of multilayers using ellipsometry, FTIR-external reflectance spectroscopy (FTIR-ERS), resonance Raman scattering (RRS), and UV−vis absorption spectroscopy.

Figure 1 shows FTIR-ERS spectra of **1** obtained after each of five incremental increases in layer thickness and subsequent polymerization immediately following the addition of each layer (Route b). Figure 1a corresponds to a single, polymerized monolayer of **1**. The spectrum is composed of three prominent peaks: methylene asymmetric and symmetric C−H stretches at 2926 and 2854 cm^{-1}, respectively, and the carboxylic acid C=O stretch at 1713 cm^{-1}. The positions of the methylene bands are in general agreement with previous studies, and they indicate that the hydrocarbon portions of the chains probably exist in a liquid-like state.[15−18] As discussed later, the absorbance of the methylene bands in the second and subsequent layers is greatly attenuated following polymerization due to a change in orientation of the hydrocarbon backbone relative to the Au substrate.

After obtaining the spectrum in Figure 1a, we reacted the terminal acid groups with $SOCl_2$ to convert them to the acid chloride, which reacts with **1** to form a thioester-bound bilayer.[8] Exposure to UV light polymerizes the second layer. Figure 1b shows that this treatment increases the absorbance due to both the methylene and carbonyl groups. We anticipated that the methylene band intensity would double, but it only increased by about 30%. We attribute this smaller-than-anticipated increase to a difference in orientation of the first two layers. The infrared surface selection rule dictates that the absorbance due to the methylene groups is related to the tilt angle between the substrate and the hydrocarbon backbone: when the backbone is oriented more parallel to the surface the methylene and carbonyl absorbances are enhanced.[19] This view is consistent with subsequent layering steps (Figure 1c,d,e), which show the same incremental increase in absorbance observed for the second layer (inset of Figure 1). From these data we conclude that the first polymerized layer is significantly tilted with respect to the surface normal, perhaps as much as 35° based on the ellipsometric data discussed later, but subsequent polymerized layers are oriented more perpendicular to the surface—perhaps about 20° from the surface normal based on ellipsometry data and the difference in the maximum IR absorbance.[19]

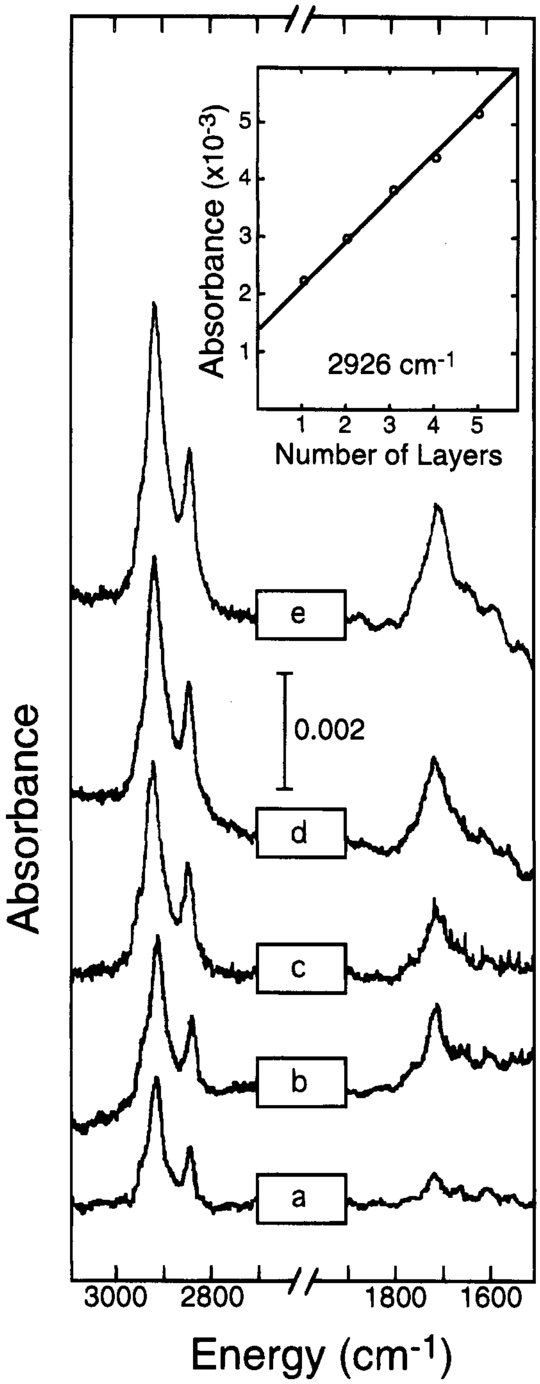

Figure 1. (a−e) FTIR-ERS spectra of 1−5 layers, respectively, of **1** prepared by Route b (Scheme 1). The inset shows the relative increase in absorbance of the asymmetric C−H methylene band (2926 cm^{-1}) as a function of the number of polydiacetylenic layers.

Addition of polydiacetylene layers also promotes an increase in the band at 1713 cm^{-1}, which we believe is composed of two overlapping bands in the spectra of multilayers: one band is due to the terminal acid carbonyl and the other is due to the

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(14) Note that Scheme 1 is an idealized depiction of the multilayer surface. We have no cyrstallographic data to support this highly organized structure, but circumstantial evidence described herein does support the general features of the scheme.

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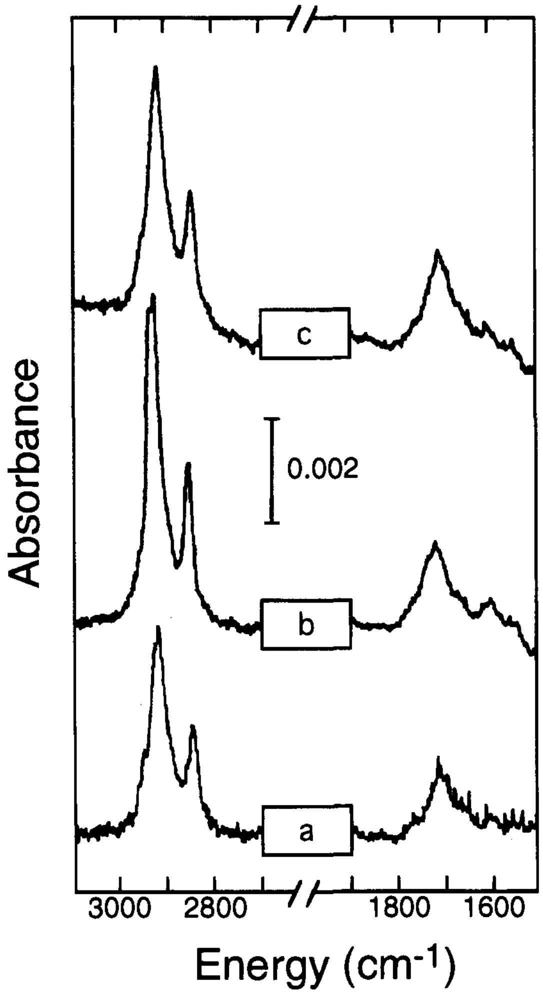

Figure 2. FTIR-ERS spectra: (a) three polymerized layers of **1** prepared by Route b (Scheme 1); (b) after addition of a fourth layer prior to polymerization; (c) immediately after polymerizing the fourth layer.

thioester carbonyl. Aliphatic thioesters normally have a carbonyl stretching frequency around 1700 cm^{-1},[20] but a slight shift of the band to higher energy for the surface-confined species is not too surprising. Importantly, we see no evidence for an anhydride band at 1800 cm^{-1}, which would result from acid chloride–acid rather than acid chloride–thiol coupling. We are able to form the thioester exclusively using low pH reaction conditions, but at high pH we do observe a significant fraction of the anhydride.[8,21] Subsequent addition of layers, followed by polymerization, yields the spectra shown in Figure 1, spectra c, d, and e for layers 3, 4, and 5, respectively. The important points are the linear increase in methylene stretching absorbance and the sequential increase in the combined acid–thioester peak at 1713 cm^{-1}.

Data confirming the change in orientation of the hydrocarbon backbone upon polymerization are illustrated in Figure 2. Figure 2a, which is the same as Figure 1c, is a spectrum of a three-layer polydiacetylene film. Figure 2b is the spectrum that results from coupling a fourth unpolymerized layer to the multilayer of Figure 2a. The large change in absorbance in the hydrocarbon region is consistent with the addition of the fourth layer. However, upon polymerization (Figure 2c) the magnitude of these peaks decreases significantly. This result suggests that the methylene bonds are oriented more parallel to the substrate after polymerization and confirms the structural change mentioned earlier.[19]

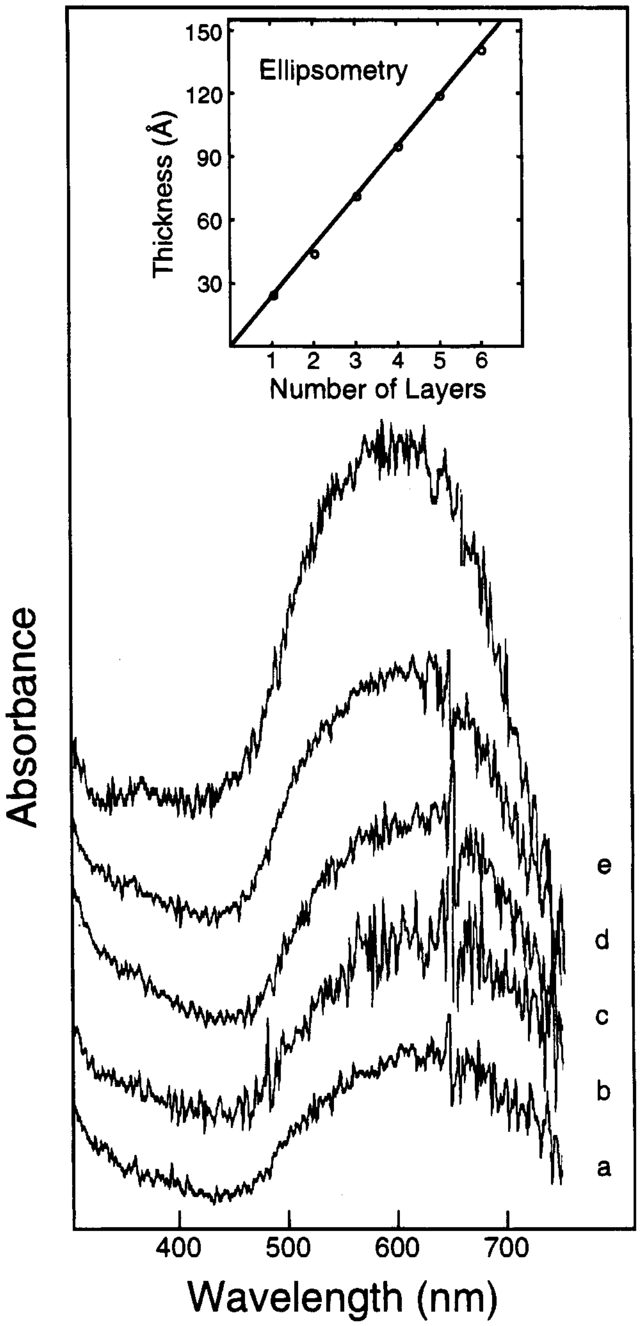

Figure 3. UV–vis spectra of an initially unpolymerized, 4-layer film of **1** prepared by Route a (Scheme 1) as a function of UV irradiation time: (a) 1 min, (b) 2 min, (c) 3 min, (d) 4 min, (e) 5 min. The inset shows the increase in ellipsometrically-measured film thickness for an unpolymerized multilayer (Route a, Scheme 1) as a function of the number of layers.

To better understand this orientational change, we used ellipsometry to measure the layer-by-layer thickness change of a film prepared according to Route a. The inset of Figure 3 shows that each unpolymerized layer adds about 24 Å to the film thickness and that film growth is uniform up to at least 6 layers. An unpolymerized monolayer of **1** oriented normal to the surface and in an all-trans extended configuration has a theoretical thickness of 30 Å. Since the measured thickness of each unpolymerized layer is 24 Å, this implies a 35–40° tilt of the hydrocarbon chains with respect to the substrate surface

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[21] In preliminary experiments we observed coupling through both the acid and the thiol groups, which resulted in formation of the anhydride and thioester, respectively. We confirmed the presence of the anhydride by observing a peak in the IR at 1800 cm^{-1}. We were able to eliminate anhydride coupling using the procedure given in ref 8.

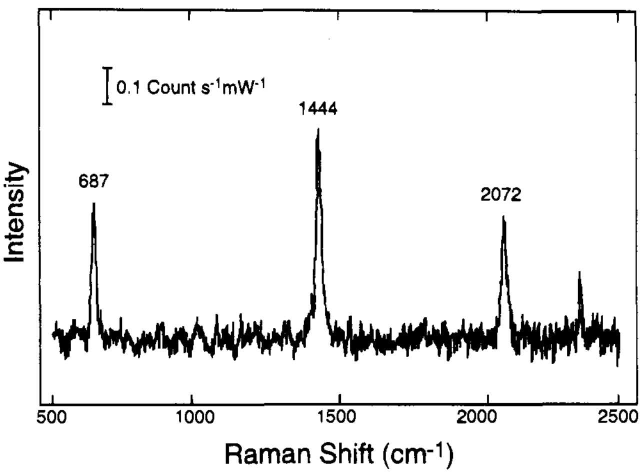

Figure 4. The surface resonance Raman spectrum of a 5-layer, polymerized SAM of **1** obtained on an unroughened Au surface obtained using laser irradiation at 647.1 nm. The peaks at 687, 1444, and 2072 cm^{-1} are due to a bending mode of the polydiacetylene backbone, the $\mathrm{C{=}C}$ stretching mode, and the $\mathrm{C{\equiv}C}$ stretching mode, respectively.

before polymerization. This value is physically reasonable and consistent with the geometry necessary for topochemical polymerization.[7] Following polymerization we measure essentially the same ellipsometric layer thickness (24 Å), but the molecule itself is somewhat shorter (28 Å). This result, which is consistent with the FTIR-ERS data shown in Figure 2, implies that the molecules in the second and subsequent layers are less tilted in their polymerized form: probably about 20 ± 5° with respect to the surface normal.

Figure 3 also shows *in situ* UV–vis transmission spectra as a function of polymerization time for a 4-layer film made according to Route a (Scheme 1). The data indicate that polymerization is complete within 5 min. Exposure of the film to UV light for times up to 8 min revealed no further change in the intensity or position of the absorption maximum, which occurs at 620 nm. In studies of polydiacetylene Langmuir–Blodgett films, two absorption maxima are usually observed.[22] One is found between 600 and 640 nm, which corresponds to the so-called blue polymer, and the other is between 500 and 550 nm, which corresponds to the shorter or less conjugated red polymer. It is significant that the self-assembly approach yields only the more highly conjugated blue polymer.

The surface Raman spectrum of the same substrate used to obtain the data shown in Figure 1 confirms polymerization (Figure 4). Three major peaks located at 687, 1444, and 2072 cm^{-1} all originate from vibrations of the polydiacetylene backbone, which contains conjugated and alternating double and triple bonds. The peak at 687 cm^{-1} has previously been assigned to a bending mode of the backbone,[23] and peaks at 1444 and 2072 cm^{-1} correspond mainly to the $\mathrm{C{=}C}$ and $\mathrm{C{\equiv}C}$ stretching vibrations, respectively.[24] These frequencies are significantly lower than those observed for isolated $\mathrm{C{=}C}$ and $\mathrm{C{\equiv}C}$ stretching modes (approximately 1620 and 2260 cm^{-1}, respectively).[20,25,26] The decrease in both frequencies is due to extensive electronic delocalization in the backbone of the polymerized diacetylene groups.[23–26]

We could not detect surface Raman scattering from a 5-layer, unpolymerized SAM of **1** prepared by Route a; however, prolonged irradiation at 647.1 nm leads to polymerization of the multilayer. The surface Raman spectrum obtained after this treatment is essentially the same as that of the UV-polymerized multilayer (Figure 4). This result is consistent with two recent studies: one by Batchelder et al., who observed that a He–Ne laser operating at 632.8 nm can initiate diacetylene polymerization,[6] and the other by Angkaew, who observed similar phenomena using a 750.7-nm titanium–sapphire laser.[26]

We explain the large difference between the Raman scattering intensity of a polymerized multilayer and that due to an unpolymerized film by resonance Raman scattering: surface Raman scattering from a polymerized multilayer is resonantly enhanced, while scattering from the unpolymerized multilayer is not. This observation is consistent with the UV–vis spectrum shown in Figure 3.[23] This explanation is also consistent with our observation that only those vibrational modes that are associated with the polydiacetylene backbone show prominent intensities.

Conclusion

To summarize, we have successfully fabricated multilayers of the blue form of polydiacetylenes on Au in which all layers are covalently linked to each other. The combination of two distinct linear polymerization steps—first the intralayer diacetylene polymerization and then the interlayer thioester polymerization—is to our knowledge the first example of such a high level of control over a covalently-linked, surface-confined, three-dimensional polymer, and it will be important for fabricating oriented polymeric materials in the future.

Acknowledgment. T.K. and R.M.C. gratefully acknowledge the National Science Foundation (CHE-9313441) and the Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC04-76DP00789 for supporting this research. This work was also funded in part under contact from Sandia National Laboratories, supported by the U.S. Department of Energy under contract No. DE-AC04-94AL85000. We also thank Prof. Marcetta Darensbourg for the use of the UV–vis spectrometer. L.S. acknowledges financial support from the University of Minnesota in the form of start-up funds and a summer fellowship.

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