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Self-Assembled Monolayers Containing Polydiacetylenes

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Abstract: The formation of self-assembled dialkyl disulfide-functionalized monolayers containing diacetylenes is reported for the first time. The diacetylene derivative used was $[S(CH_2)_2COO(CH_2)_9C{\equiv}CC{\equiv}C(CH_2)_{13}CH_3]_2$ and was seen to form well-ordered monolayers when adsorbed on gold from THF. The monomer was readily converted to the polymeric form by a short exposure to UV radiation. A "blue" polymer was formed which was stable against further irradiation; that is, it did not become "red". During the polymerization the alkyl side chains displayed some reorganization.

Introduction

Recently a large amount of interest has been generated in using alkylthiol and dialkyl sulfide derivatives to form well-ordered monolayers on noble metal surfaces.[1] Such interests range from their use as "model" systems for understanding fundamental problems in surface and interfacial science to more technologically oriented goals.[2] In this study we have investigated the possibility of forming self-assembled monolayers (SAMs) with molecules containing diacetylene units, and their subsequent polymerization. The ability to form monolayers which may photopolymerize is of potential interest for creating patterned surfaces, photolithography, and understanding factors affecting polymerization in two dimensions.

It has been well established that disulfide- and thiol-functionalized alkyl chains adsorb onto the $(\sqrt{3}\times\sqrt{3})R30°$ 3-fold hollow site on a gold ⟨111⟩ surface and tilt toward the next nearest neighbor.[3-5] Typically this requires that the alkyl chains are tilted, on average, by approximately 30–35° to the surface normal in order to achieve maximum packing density. Recently, we have demonstrated that the introduction of a rigid phenyl group into the alkyl chain does not disrupt the order found within such monolayers and leads one to expect that the formation of diacetylene-containing films should be possible.[6]

To date there has, to our knowledge, been no work reported on the formation of monolayers from diacetylene-containing disulfides or thiols. In contrast, however, there has been a large amount of effort exerted in the study of Langmuir and Langmuir–Blodgett (LB) monolayers of molecules containing diacetylenes. In particular films of 10–12 pentacosadiynoic acid (12-8 PDA) have received a great deal of attention as a model system for understanding behavior of diacetylenes and their polymerization.[7-12] It has been established that the monomers will only polymerize if they are in a highly-ordered assembly and if certain steric conditions are met. From the outset, we expect the molecules in a self-assembled film to yield films containing regions with a high degree of local ordering, suitable for polymerization. Yet these films have quite different geometries from their LB counterparts, in which the alkyl chains are oriented nearly perpendicular to the substrate, i.e. the diacetylene groups tilted at ~30–35° to the surface normal. Further, it is not envisaged that the molecules in a SAM have the same degree of freedom to alter their conformation, due to the binding to the gold surface, as their LB counterparts. This raises the question of whether a topochemical polymerization would occur, and if so, will there be the same variety of phases as found for LB films. It is thought that polymerization occurs by linking the C1 and C4 carbon atoms of adjacent molecules, Figure 1, and that this can only occur if there is a minimum of distortion between the monomer and polymer lattices and if the adjacent 1,4 carbons are less than 4 Å apart in the monomer monolayer.[13] This has specific implications for the ordering within the monolayer. (Unlike the situation in LB films in SAMs, the thiol/disulphide head groups are strongly bound to the substrate (gold) surface. Thus, we also must address the question of the mechanism of the polymerization for this system and the role of the substrate–adsorbate interaction.)

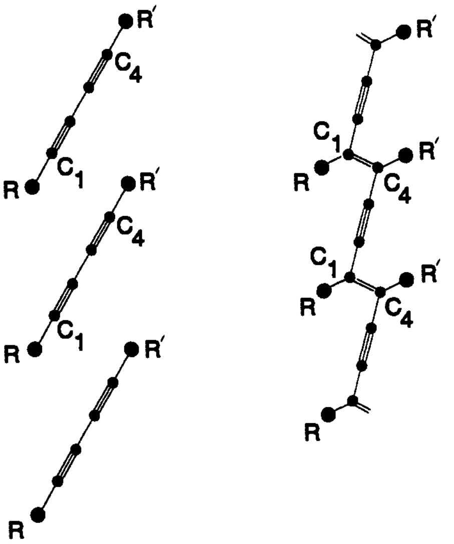

Figure 1. Scheme for solid-state polymerization of diacetylene units.

Experimental Section

Substrate Preparation. The substrates used were prepared by evaporating gold onto polished silicon wafers, with a chromium underlayer

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to ensure good adhesion of the gold. The silicon wafers were cleaned by first ultrasonicating them in propanol for 30 min and then immersing them in "piranha" solution (H_2SO_4:H_2O_2 7:2) at 90 °C for 5–10 min. The wafers were then rinsed thoroughly in Millipore Milli-Q filtered water, dried in a stream of nitrogen, and placed directly into the evaporator. The evaporator used was an Edwards Auto 306 Turbo. A vacuum of $<5 \times 10^{-6}$ mbar was used, and 150 Å of chromium was evaporated onto the wafer, followed by 800–1000 Å of gold (99.99%). Once prepared, the gold slides were cleaned again immediately before use in piranha solution for 5 min at 90 °C, rinsed in Milli-Q water, and dried in nitrogen to form a hydrophilic surface.

Monolayer Preparation. Monolayers were formed by the spontaneous adsorption of the disulfide onto the gold surface. The cleaned gold slides were immersed in a 1 mM diacetylene solution, with dichloromethane or THF (both Aldrich, HPLC grade) as the solvent. The solution was stored in darkness and filtered, through a 0.2-μm PTFE filter, before use. Adsorption times varied between 2 and 15 h, the various times not affecting the monolayer quality. Substrates removed from the solution were immediately rinsed in large amounts of chloroform (Aldrich, HPLC grade) or THF and dried in nitrogen.

Polymerization of the Monolayers. Monolayers of the unpolymerized diacetylene were stored in darkness until use. Polymerization of these slides was effected by exposure to 254-nm UV light from a UV pencil lamp source, nominally 50 W, with the sample–source distance of approximately 2 cm.

Contact Angle Measurements. Advancing and receding contact angles of water were taken, using Milli-Q filtered water. Advancing angles were formed by growing a small drop on the surface via a Rame–Hart micrometer syringe, with a square cut needle. The drop was illuminated from behind and the image viewed through a Hamamatsu C3077 CCD camera on a screen. The volume of the liquid was increased until the edge of the drop just began to advance along the surface, and the image was captured using Accuware software. The angles at both edges of the drop were measured using the same software, and the average angle was taken. Receding angles were measured in the same way, capturing the image as liquid is withdrawn from the drop via the syringe.

FTIR Measurements. Grazing angle FTIR spectra were taken at an angle of incidence of 80° using a Bruker IFS-48 spectrometer. Spectra were taken after purging in dry air for at least 16 h and were background subtracted from a reference sample of freshly cleaned gold, under the same conditions. Spectra were run for 2000 scans at a resolution of 2 cm^{-1}.

Raman Spectroscopy. Raman spectra were obtained with the Renishaw raman imaging microscope using either a 25-mW He–Ne laser of wavelength 632.8 nm or a 25-mW Ar^+ laser (λ = 514.4 nm). Due to the high efficiency of this instrument, low-power laser light is incident on the sample, thus preventing any significant heating effects. Spectra of polymerized samples were taken with exposure times of 10 s. Spectra taken to investigate changes in spectra with UV exposure during polymerization were taken with 2-s exposures. These spectra were taken at the same point on the sample each time and irradiated in-situ. The shorter exposure time is to minimize the polymerization due to exposure to the laser beam. Consecutive spectra taken on an unpolymerized sample show an increase in the size of the bands associated with the carbon–carbon double and triple bonds, indicating that the incident beam can initiate polymerization.

SPR Measurements. Surface plasmon measurements were made to estimate the thicknesses of the films formed. For these experiments gold, 400 Å thick, was evaporated onto a BK7 glass slide (n = 1.5105), which was index matched to a BK7 prism. The real and imaginary parts of the dielectric constant and the thickness of the gold layer were determined by fitting the associated Fresnel equations to the experimental results. The values obtained from this were then used to evaluate the thickness of the adsorbed overlayers. A refractive index of 1.5 for the overlayers was assumed for use in thickness calculations.

Synthesis. 3,3′-Dithiodipropionic acid bis(heptacosa-10,12-diynyl ester) was prepared from heptacosa-10,12-diyn-1-ol and 3,3′-dithiodipropionic acid. 3,3′-Dithiodipropionic acid was purchased from Fluka and used as received. Heptacosa-10,12-diyn-1-ol was synthesized according to the procedure described earlier.[14] The alcohol (2.0 g, 5.2 mmol), 0.4 g (2.6 mmol) of 3,3′-dithiodipropionic acid, and 30 mg of (dimethylamino)pyridine (Fluka) as a base were dissolved in 25 mL of dichloromethane and 4 mL of DMF and cooled with an ice bath. Dicyclohexylcarbodiimide (2.1 g, 10 mmol) (Fluka), dissolved in 15 mL of dichloromethane, was slowly added through a funnel. After the addition of the carbodiimide the reaction mixture was stirred at room temperature over night and after that 8 h under reflux. The crude product was purified by flash chromatography with dichloromethane (R_f 0.75). The yield was 990 mg (40%). Analysis: ^{1}H-NMR δ (ppm) ($CDCl_3$, 200 MHz) 0.85 t (CH_3, t, 6H); 1.1–1.7 (CH_2 aliphat, m, 76H); 2.22 ($CH_2C{\equiv}C$, t, 8H); 2.71 (CH_2COO, t, 4H); 2.90 (CH_2S, t, 4H); 4.06 (CH_2O, t, 4H). Anal. Calcd for $C_{60}H_{102}O_4S_2$ (951.8): C, 75.71; H, 10.82; S, 6.74. Found: C, 76.07; H, 11.12; S, 7.10.

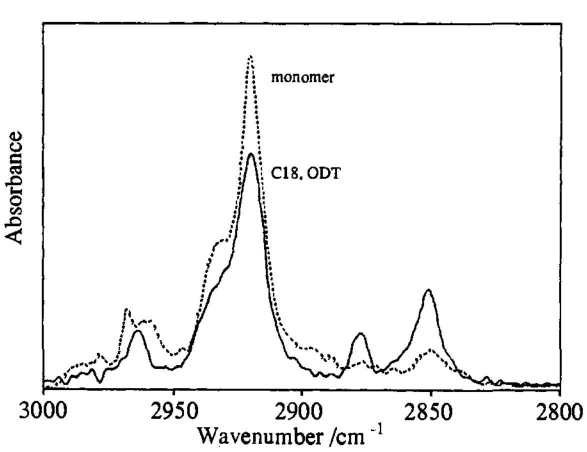

Figure 2. FTIR grazing angle spectra of the CH_3 and CH_2 stretching region for monolayers of octadecylthiol (ODT) and the monomer.

Results and Discussion

Monolayer Formation. Molecules of the monomer were adsorbed from THF solutions which had been filtered immediately prior to use using a 0.2-μm PTFE filter. Estimates of the monolayer thickness from surface plasmon resonance (SPR) measurements give thicknesses of 29 ± 2 Å and are indicative of a monolayer in which the net average molecular tilt is approximately 43 ± 5° to the surface normal, assuming uniform coverage.

From water contact angle measurements we find that the monomer gives an advancing angle of close to 107° and a receding angle of 92°. The degree of hysteresis, 15°, indicates that the monolayer surface is to some extent disordered. This may be expected if one considers the monomer molecules as being in three parts: (i) the lower alkyl chain fixed between the sulfur/gold and the rigid diacetylene chromophore, (ii), and (iii) the upper alkyl chain, fixed at one end to the chromophore but free at the other. Disorder at the monolayer surface may have contributions from each of these segments as well as contributions from domain structures within the monolayer film (vide supra). Additional information on the order within these films can be obtained from FTIR. Figure 2 shows the "high-frequency" region for a diacetylene-containing monomer and for a C18, straight-alkane-chain thiol, octadecylthiol (ODT). The position and full width at half-maximum (fwhm) of the d^- (CH_2 antisymmetric stretch, ν_{as}) mode are particularly noted for their sensitivity to changes in the molecular environment.[15-17] Comparison of the spectra from the monomer-containing films with that of ODT shows that this peak, 2919 cm^{-1}, occurs at a similar position in both, and comparison with KBr and solution spectra indicates that these monolayers have a high degree of local order. This is further confirmed by a comparison of the fwhm, which are 14 and 13 cm^{-1} for the ODT and diacetylene-containing monomer, respectively. It is noted that samples prepared from more dilute solvents did not form complete monolayers and gave spectra in which the CH_2, ν_{as}, contained several peaks, one similar to that

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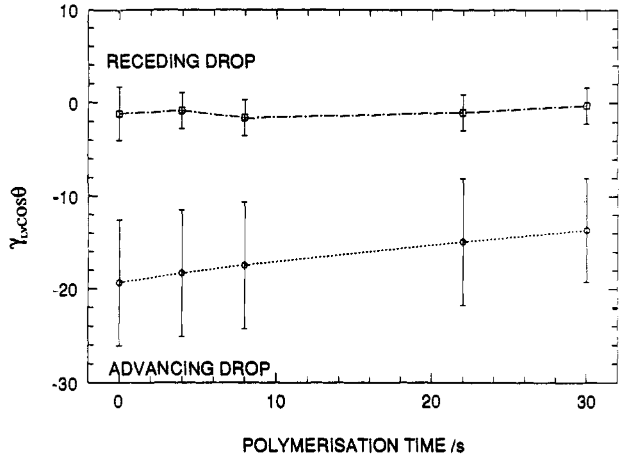

Figure 3. Water contact angles as a function of exposure time. (Circles represent advancing contact angles, and squares represent receding ones.)

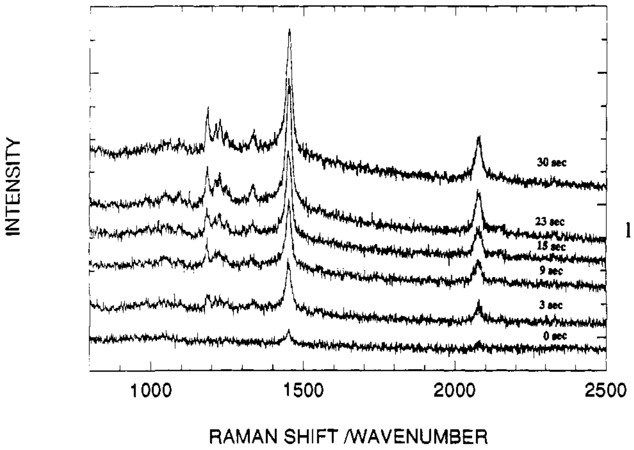

Figure 4. Raman spectra as a function of exposure time. Spectra were obtained using a He-Ne λ = 632.8 nm, 25-mW laser (N.B. the power was reduced such that only ~12.5 mW was reaching the sample).

found for the ordered monolayer films (2921.8 cm^{-1}) and the others shifted toward higher wavenumbers (2927, 2932 cm^{-1}). This would appear to indicate that even for partial coverage the film formation proceeds via the growth of domains with a high degree of local order, between which regions of disorder exist. The most significant difference between the spectra of the diacetylene-containing monomer and ODT is for the CH_3 and CH_2 symmetric vibrations, ν_s, which are of much lower intensity for the diacetylenes. This is indicative of a preferred tilt direction of the alkane chains, due to the presence of the diacetylene group. From the surface selection rule we infer that the ν_s stretch must lie nearly in the plane of the substrate surface.

Polymerization. The monomeric (monolayer) film was polymerized by irradiation with a low-powdered UV light (λ = 254 nm) at a distance of 2–3 cm. Films were exposed for successively longer periods. Between each exposure the advancing and receding contact angles were measured and Raman spectra were taken. The water contact angles, Figure 3, shows only a slight decrease with increasing exposure, indicating that there has been no gross-deterioration of the film quality on polymerization. Figure 4 shows Raman spectra of a monolayer as a function of exposure time. The bands associated with the double and triple carbon–carbon bonds, at 1455 and 2074 cm^{-1}, respectively, are seen to emerge for short exposure times. Polymerization is complete after approximately 30 s of exposure, Figure 5. The band positions are indicative of the monolayer being in the more ordered "blue" phase.[13] Typically, it is found that irradiation of LB films in the "blue" phase drives the films to a more disordered "red" phase; here however we see no such effect. It would seem that this is due to the strong binding of disulfide group to the gold surface.

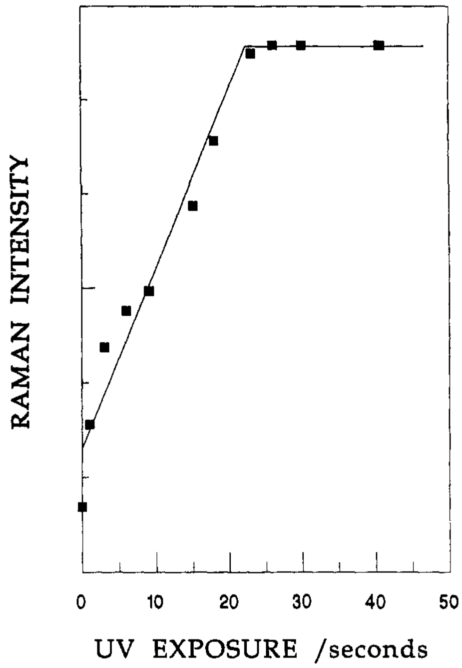

Figure 5. Raman intensity of the C–C double bond versus exposure time.

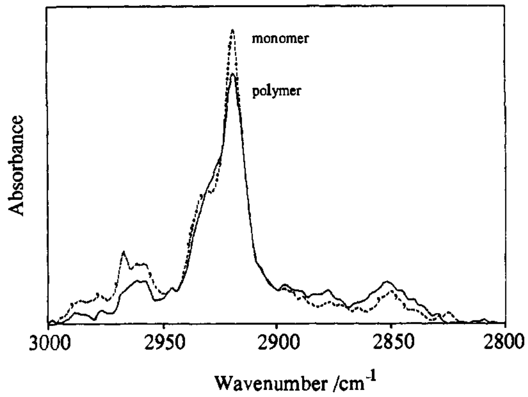

Figure 6. FTIR grazing angle spectra showing the "high-frequency" region of the monomer and polymerized SAMs.

Indeed, these samples are stable to washing with solvents such as chloroform. Upon polymerization, there is no shift in the position of the d$^-$ (Ch_2, $\nu_{as,}$ stretch) mode (in the FTIR), although there is a slight decrease in its intensity presumably due to a decrease in the tilt of the alkyl chains, Figure 6, confirming the high degree of local order within the film. This is further supported from the Raman results, which show the bands associated with the CH_2 rocking and wagging modes, indicative of the high degree of alignment within the CH_2 side chains close to the polymer backbone.[18] The midfrequency range in the FTIR shows the C=O stretch at ~1725 cm^{-1}. This is a weak peak relative to the background noise level, implying that the C=O vibration is near to the plane of the substrate. Upon polymerization, no change in peak position or intensity is seen to occur.

Raman spectra taken using an Ar$^+$ ion laser (λ = 514 nm) show that the monolayers probably contain fractions of the more disordered "red phase". A more detailed investigation using Raman is underway.

We have mentioned above that incomplete monolayers have several contributions to the CH_2 ν_{as} stretch and seem to indicate the presence of both locally disordered and ordered phases. This is corroborated in the Raman, where it is found that for such films polymerization can still be achieved, implying a high degree of order, and further can be seen from the presence of the CH_2

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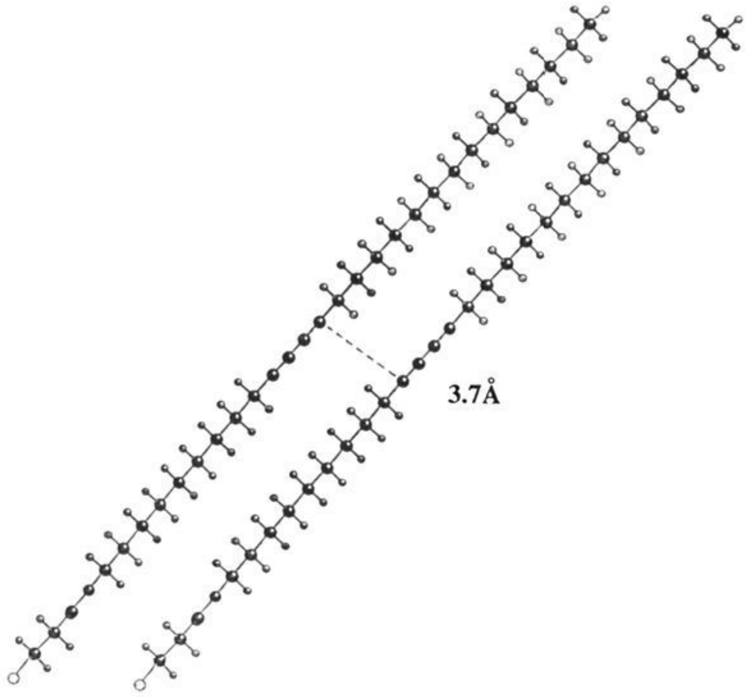

Figure 7. Possible monolayer configuration for the monomer.

rocking and wagging modes even in these spectra. There appears to be little difference between these and films which give only the "ordered" FTIR spectra. All films show small peaks in the Raman spectra at 1061 and 1125 cm^{-1}, indicative of trans links in the chains and a peak at 1093 cm^{-1}, indicative of gauche bonds, most likely due to the aforementioned disorder in the upper chain segments.[19] The results suggest that the film formation proceeds via the island growth, where molecules within the islands display a high degree of local order and are able to undergo topochemical polymerization and the interisland regions contain amorphous/disordered material, which will not easily polymerize. The FTIR results primarily give information regarding the alkyl chains and are thus sensitive to both regions, while the Raman, which gives information on the polymer backbone, is only sensitive to the regions displaying high local order, as these are the only regions that will be polymerized.

In order to understand the possible scheme of polymerization more fully, let us consider a model in which the disulfide bond is cleaved on adsorption and each molecule sits in the 3-fold hollow site of the gold ⟨111⟩ surface. The sulfur groups will thus have a hexagonal packing, with the S···S separation being 4.97 Å. Using hard-sphere models in association with the data from SPR and FTIR, i.e. that the molecules exhibit a net tilt to the surface normal of 42° and that the symmetric stretches must be close to lying in a plane parallel to the substrate surface, we can estimate the molecular orientation. Figure 7 shows the simplest model which meets the requirements above. From this the measured distance between the C1 and C4 carbons on neighboring monomer units is 3.7 Å. Previous studies on the polymerization of diacetylene units have shown that for polymerization to occur the C1–C4 distance should be between 3.5 and 4 Å and that the angle between the polymerization direction and the monomer units should be between 40 and 50°. A molecular orientation as depicted in Figure 7 meets these requirements and also agrees with the results from FTIR and SPR.

Conclusions

In this paper we have presented results which show that diacetylene-containing molecules can be used to form SAMs and that the resulting structures are ordered. The molecular orientation of the diacetylene monomer units is such as to permit topochemical polymerization of these units. The resulting polymers appear to be composed of mainly blue-phase material and are extremely stable. Once complete, the polymer cannot be forced into the red phase by further UV-irradiation or by exposure to organic solvents. It seems that this is most likely due to the binding of the sulfur groups to the gold surface, thus reducing the ability of the polymer to undergo large structural changes. The combination of FTIR and Raman spectroscopies has yielded direct evidence that the films form via the growth of islands, in which the molecules display a high degree of local order and between which the molecules are in an amorphous state. Presumably, the size of the islands increase during monolayer formation at the expense of the intermediary amorphous material and may be envisaged as a kind of two-dimensional nucleation process, until one is left with films mainly consisting of ordered regions with small islands of disorder. The model proposed here is intermediate to previously described models of monolayer formation and may also be supported by STM results reported by Dürig *et al.*[20–23] One may also expect to find grain boundaries between films starting from different nucleation sites. At present it is not clear whether this growth mechanism is the same for all SAMs or whether it is due to the incorporation of the rigid chromophore into the alkyl chains.

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