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Polymeric Self-Assembling Monolayers. 1. Synthesis and Characterization of ω-Functionalized *n*-Alkanethiols Containing a Conjugated Diacetylene Group.

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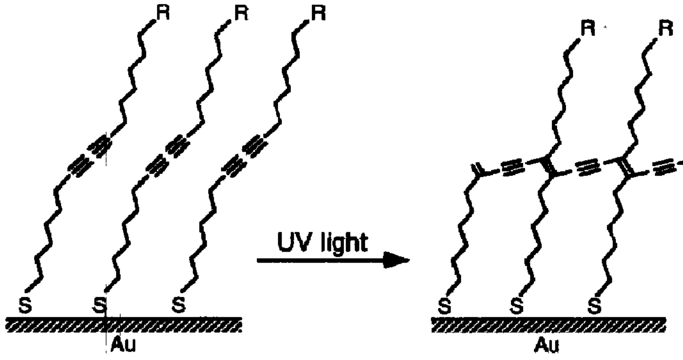
Abstract: ω-Functionalized alkanethiols containing a conjugated diacetylene were synthesized. These molecules spontaneously self assemble onto gold surfaces and they can be polymerized by UV irradiation.

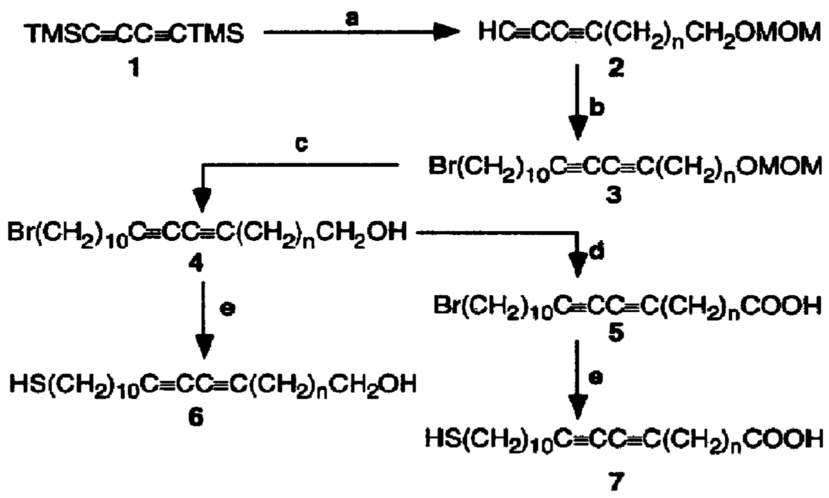
We are interested in developing new types of self-assembling monolayer films for applications in the fields of chemical sensing, lubrication and wear, adhesion, electronics and photonics, and lithography.[1-5] Molecules that undergo self assembly from a liquid or vapor phase must have a strong interaction with the substrate onto which they self assemble and the magnitude of the intramonolayer cohesive energy must be significant. Many classes of self-assembling monolayers (SAMs) are known, but one that has received tremendous attention during the past decade are the organomercaptans.[1,2,6] In their simplest incarnation, these are *n*-alkanethiols of the form $HS(CH_2)_nX$, where n ranges from 9-21 and X is CH_3, COOH, OH, or other functional groups. When a dilute ethanolic solution of an appropriate organomercaptan is exposed to an Au(111)-textured surface, each sulfur atom forms a weak covalent bond with three Au atoms; this results in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer structure. Once anchored to the Au surface, which also serves as a template for self assembly, the hydrocarbon tails rely on van der Waals interactions to arrange themselves in an extended all-trans configuration. By this means, a single, ordered monolayer forms on the Au surface. Since *n*-alkanethiols are so easy to ω-functionalize, they have found broad applications as highly crystalline, model organic surfaces. In many environments organomercaptan SAMs are quite robust; for example, in water or air at room temperature their packing arrangements and surface coverages do not change over periods of months. This is a reflection of the Au-S bond energy (40-45 kcal/mol), the cohesive energy between the alkane chains, and the hydrophobic effect.[2,7] However, there are many applications that require harsher ambients, and these result in either monolayer desorption or molecular disintegration. For example, use of *n*-alkanethiols at either elevated temperatures or in solvents that are able to penetrate the SAM and compete with sulfur for Au binding sites are precluded. To address these problems, we have synthesized ω-functionalized *n*-alkanethiols, which contain conjugated diacetylene groups. On the basis of the previously reported solid-state chemistry of conjugated diacetylenes, the results of studies of Langmuir and Langmuir-Blodgett thin films, and the fortuitous geometrical properties of Au-confined SAMs, we believed such molecules would undergo topochemical polymerization.[8-11] In the present paper we discuss a general synthesis of ω-functionalized organomercaptans, and in the second paper in this series we demonstrate that these molecules self-assemble onto a wide variety of Au substrates and that they can be polymerized by UV radiation to yield highly-stable polymer films (Scheme 1) that many have useful electronic and photonic properties.



Scheme 1. Illustration of photoinduced polymerization of a self-assembling monolayer of a conjugated diacetylene.

Batchelder et al.[12] recently reported the synthesis and characterization of the methyl-terminated disulfide $[S(CH_2)_2COO(CH_2)_9C{\equiv}C\text{-}C{\equiv}C(CH_2)_{13}CH_3]_2$, and they showed that this molecule spontaneously forms a single monolayer when exposed to a Au surface. We believed it was important to extend this important first example of a polymerizable monolayer subunit for two important reasons. First, the ester linkage, which will prevent formation of a close-packed SAM, may lead to organizational defects within the monolayer structure. Second, we believe that a general synthesis of ω-functionalized, diacetylene-containing mercaptans will lead to technologically useful SAMs.[12] However, it turns out to be quite difficult to simultaneously introduce both conjugated diacetylene and mercaptan functional groups to alkyl chains using conventional methods.[13-15] To the best of our knowledge, this is the first report of a simple and efficient strategy for synthesizing ω-functionalized *n*-alkanethiols which contain conjugated diacetylene moieties.

The synthesis of the diacetylene-containing alkanethiols is shown in Scheme 2. Selective deprotection of 1,4-bis(trimethylsilyl)-1,3-butadiyne **1**, subsequent reaction with primary alkylbromides, and deprotection of the remaining trimethylsilyl group gave moderate to high yields (60-90%) of diacetylene **2**.[16] The lithium diacetylenide of **2** reacted with 5 equiv of 1,10-dibromodecane to give functionalized alkylbromide **3**. Alcohol **4** was obtained by deprotection of **3** in acidic media (conc. HCl in a 1:1 mixture of methanol and THF).[17] Oxidation of alcohol **4** was completed by PDC in DMF solution overnight. Because diacetylenes are very sensitive to heat and basic conditions, conventional methods were not useful for converting diacetylenic bromides **4** and **5** to corresponding thiols of purity sufficient for subsequent work up.[16] Using protected thiols instead of dibromodecane in step **b** gave byproducts only. However, sonication (4-8 h) of the diacetylenic alkylbromides in the presence of a large excess of anhydrous sodium hydrogen sulfide (3 equiv) in a minimum amount of ethanol at 50-55 °C led to successful conversion of the alkanethiols. Crude products could be purified by recrystalization in hot methanol solution.[18]



Scheme 2. Synthesis of ω-functionalized, diacetylenic *n*-alkanethiols. **a**. 1 equiv of 1.5 M MeLi/LiBr, THF, -78 °C; $Br(CH_2)_nCH_2OMOM$/HMPA; KF/DMF, rt. **b**. 1-equiv of 1.6 M BuLi, THF, 0 °C; 5 equiv of $Br(CH_2)_{10}Br$/HMPA, rt. **c**. conc. HCl/MeOH, rt. **d**. excess PDC/DMF, rt. **e**. 6 equiv of NaSH/EtOH, 50-55 °C, 4-8 h, sonicated. MOM = CH_2OCH_3; **n** = 2, 10.

In conclusion, we have successfully synthesized diacetylenic *n*-alkanethiols having different chain lengths and functional groups. Moreover, diacetylenic thiols (**6** and **7**) yield close-packed self-assembled monolayers on Au, which can be successfully polymerized with UV radiation to yield SAMs with enhanced stability.[19] We are currently working to develop technologically relevant applications of polymerized SAMs.

ACKNOWLEDGMENT

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17. General procedure for alkylation. To a stirred solution of **2** (9 mmol) in 30 mL of THF was added *n*-BuLi (5.9 mL, 1.6 M in hexane) at 0 °C. After 1 h, 1,10-dibromodecane (45 mmol, 13.5 g) was added to the mixture as a solid, followed by addition of 10 mL of HMPA, and the reaction mixture was stirred for an additional 30 min at 0 °C. The alkylated product was extracted from the mixture with 2x200 mL of petroleum ether. The combined organic layers were washed with 2x200 mL of deionized water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crude product, which was purified by flash column chromatography (silica gel, hexanes:ethyl ether=10:1) to give a 60% yield of **3**.
18. General procedure for conversion to alkanethiols: Sodium hydrogen sulfide (NaSH, 0.6 mmol, 6 equiv) was added to a solution of alkylbromide (0.1 mmol) in absolute ethanol (3 mL) and the mixture was warmed to 50-55 °C in a sonicator for 4-8 h. After dilution with 10 mL of CH_2Cl_2 and washing with acidic water (2-3 drops of 3 N HCl in 5 mL water) followed by 2x5 mL water, the organic layer was dried over anhydrous sodium sulfate and the solvent evaporated to give the crude acetylenic alkanethiols , which were purified by dissolving in 5 mL of hot methanol. Subsequent filtration gave about an 80% yield of the purified, slightly yellow solid product: **7** (n=10): ^{1}H NMR ($CDCl_3$) δ: 2.493 (2H, t, J = 7.4), 2.343 (2H, t, J = 7.4), 2.236 (4H, t, J = 6.7), 1.680-1.250 (32H, m), FT-IR (cm^{-1}) 2926, 2855, 1720. **6** (n=10): ^{1}H NMR ($CDCl_3$) δ: 3.621 (2H, t, J = 6.6), 2.483 (2H, t, J = 7.2), 2.226 (4H, t, J = 6.8), 1.770-1.250 (34H, m), FT-IR (cm^{-1}) 3400, 2923, 2854. **7** (n=2): ^{1}H NMR ($CDCl_3$) δ: 2.589 (4H, bs), 2.555 (2H, t, J = 7.4), 2.283 (2H, t, J = 6.6), 1.630-1.330 (16H, m), FT-IR (cm^{-1}) 2926, 2855, 1720. **6** (n=2): ^{1}H NMR ($CDCl_3$) δ: 3.743 (2H, t, J = 6.2), 2.495 (2H, t, J = 6.2), 2.386 (2H, t, J = 7.0), 2.237 (2H, t, J = 6.8), 1.770 (2H, m), 1.510-1.250 (16H, m). HRMS calcd for $C_{17}H_{27}OS$ ($[M-H]^+$) 279.178, found 279.178.
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