

Polymeric Self-Assembled Monolayers. 4. Chemical, Electrochemical, and Thermal Stability of ω -Functionalized, Self-Assembled Diacetylenic and Polydiacetylenic Monolayers

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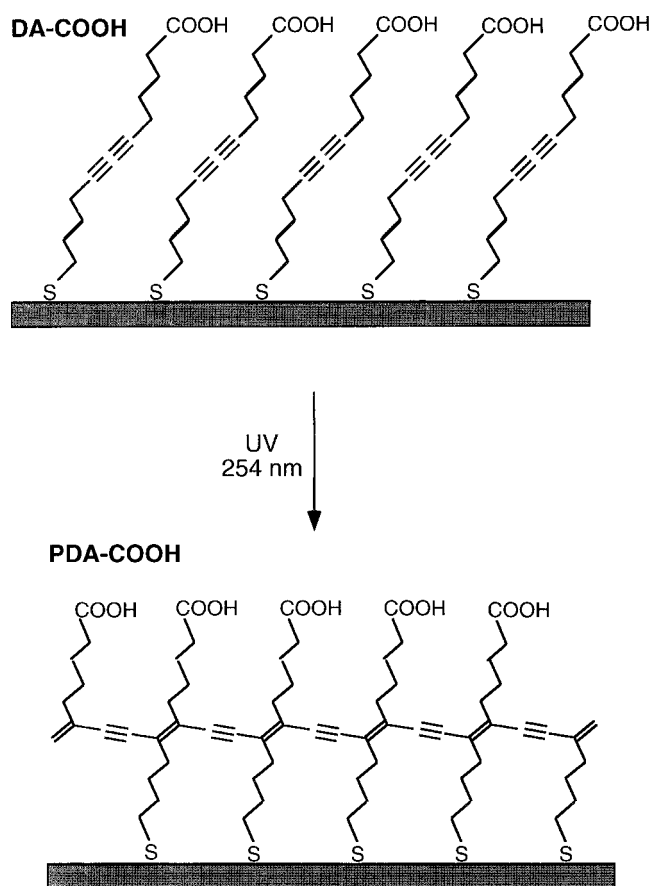
Abstract: Here we contrast the stability of monomeric and photopolymerized self-assembled monolayers (SAMs) containing a diacetylene group ($\text{HS}(\text{CH}_2)_{10}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_{10}\text{COOH}$) with SAMs prepared from simple *n*-alkanethiols. The polymerized SAMs are extremely durable compared to either the *n*-alkanethiol SAMs or the unpolymerized diacetylenic SAMs. For example, they are stable to repeated electrochemical cycling to extreme potentials, thermal excursions to 200 °C, and exposure to hot base (1:1 mixture of ethanol and 1.0 M aqueous KOH at 100 °C). All of these conditions completely strip *n*-alkanethiol SAMs from Au substrates. These high-performance materials are suitable for applications in lubrication, adhesion, corrosion passivation, and chemical sensing.

Introduction

In this paper we discuss the excellent stability of photopolymerizable, self-assembled monolayers (SAMs) that consist of acid-terminated *n*-alkanethiols containing a diacetylene group ($\text{HS}(\text{CH}_2)_{10}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_{10}\text{COOH}$, Scheme 1). These new data follow previous spectroscopic, ellipsometric, and electrochemical results that confirm UV-light-induced polymerization of diacetylenic SAMs.^{1,2} We have also shown that these materials can be used as ultrathin photoresists,³ and as rugged adhesion layers for grafting of bilayer,⁴ multilayer,⁵ and polymeric⁶ composite thin films.

Monolayer and multilayer self-assembly chemistry is useful for preparing well-ordered organic surfaces.^{7–10} A particularly important version of monolayer self assembly occurs when a Au substrate contacts a suitable organomercaptan.^{8,10–12} This treatment results in a surface-adsorbed monolayer possessing well-defined chemical and physical properties, which have been characterized by contact-angle measurements, electrochemical methods, FTIR-external reflection spectroscopy (FTIR-ERS), ellipsometry, scanning probe microscopy, ultrahigh vacuum

Scheme 1



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 (1) Kim, T.; Crooks, R. M. *Tetrahedron Lett.* **1994**, 35, 9501.
 (2) Kim, T.; Ye, Q.; Sun, L.; Chan, K. C.; Crooks, R. M. *Langmuir*. In press.
 (3) Chan, K. C.; Kim, T.; Schoer, J. K.; Crooks, R. M. *J. Am. Chem. Soc.* **1995**, 117, 5877.
 (4) Dermody, D. L.; Crooks, R. M.; Kim, T. *J. Am. Chem. Soc.* In press.
 (5) Kim, T.; Crooks, R. M.; Tsen, M.; Sun, L. *J. Am. Chem. Soc.* **1995**, 117, 3963.
 (6) Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir*. In press.
 (7) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, 1, 513.
 (8) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, 43, 437 and references therein.
 (9) Cao, G.; Hong, H.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, 25, 420.
 (10) Ulman, A. *Introduction to Ultrathin Organic Films from Langmuir Blodgett to Self-Assembly*; Academic Press: New York, 1991.
 (11) Chailapakul, O.; Sun, L.; Xu, C.; Crooks, R. M. *J. Am. Chem. Soc.* **1993**, 115, 12459.
 (12) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, 105, 4481.

(UHV) surface spectroscopy, and other techniques.^{8,10} Organomercaptan SAMs assume a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer structure on Au(111), and are thought to interact with Au via a partial charge transfer between Au and the mercaptan sulfur. The resulting $\text{Au}(\delta^+)/\text{HS}(\delta^-)$ interaction has an energy of about 44 kcal/mol, and the SAM is further stabilized by intermolecular van der Waals interactions.

The factors governing SAM stability are not well understood, but almost certainly involve both the intrinsic cohesive energy

of individual molecules and various types of molecular defects^{13–15} and defects between ordered domains.^{16,17} SAMs are fairly robust under normal laboratory conditions, but at extreme pHs,¹⁸ in many nonaqueous solvents,¹⁹ in the presence of molecules that compete for surface sites (such as Cl⁻, CN⁻, or other thiols),^{20,21} at elevated temperatures,²² or at extreme electrode potentials,^{23,24} SAMs reveal their less-than-covalent binding interaction with the surface. While this instability has not significantly affected fundamental chemical and structural studies of SAMs, it has greatly limited their potential technological applications. Thus, while organomercaptan SAMs are useful for lithographic purposes^{22,25–31} and as chemically sensitive interfaces for chemical sensors,³² some other obvious applications such as corrosion passivation and inhibition,³³ lubrication,³⁴ and adhesion³⁵ have not generally been forthcoming.

To improve substrate adherence and enhance the durability of SAMs, we have prepared diacetylenic SAMs that can be polymerized in the plane parallel to the substrate with UV light. Besides improving durability, we have been surprised to learn that polymerized SAMs are better barriers to transfilm mass transfer than the unpolymerized monolayers,² which suggests that polymerization occurs topochemically, that is, with minimal change in molecular orientation and free volume.

Experimental Section

Chemicals. The synthesis of diacetylenic thiol monomer HS-(CH₂)₁₀C≡CC≡C(CH₂)₁₀COOH has been previously described.^{1,2} The hexadecanethiol was purchased from Aldrich (Milwaukee, WI) and purified by vacuum distillation. Water was purified (resistivity ≥ 18 MΩ·cm) using a Milli-Q reagent water system (Millipore). All other chemicals were used as received.

Preparation of SAMs. Substrate preparation has been described previously.^{2,5} Briefly, about 2000 Å of Au was e-beam evaporated onto Ti-primed (50–100 Å) Si(100) wafers. After being diced into 1.3 × 2.5 cm pieces, the substrates were cleaned in freshly prepared piranha solution (30% H₂O₂:concentrated H₂SO₄ = 1:3; **Caution:** piranha solution is a powerful oxidizing agent and reacts violently with organic compounds and 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 dipping freshly cleaned substrates into 1 mM THF or CHCl₃ (for HS(CH₂)₁₀C≡CC≡C(CH₂)₁₀COOH) or 1 mM ethanol (for hexadecanethiol) solutions of the organomercaptans for 1 h or longer. Following deposition, the modified surfaces were rinsed with solvent and water (additionally, all acid-terminated SAMs were sonicated in 1.0 N HCl for 5 s and then rinsed with water) and then dried under flowing N₂. Polymerization of the diacetylenic SAMs was performed by placing the substrate into a gas-tight polycarbonate container and irradiating it under a N₂ purge for up to 45 min (but typically 10 min) with a Hg(Ar) pencil-type UV lamp (Oriel, model 6035 (~1 W)) positioned 0.5–1 cm above the substrate.

FTIR-External Reflectance Spectroscopy (FTIR-ERS). FTIR-ERS spectra were acquired using a Digilab FTS-40 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific “Seagull” reflection accessory and a liquid-N₂ cooled MCT detector. All spectra were obtained using *p*-polarized light incident on the substrate at an angle of 84° with respect to the surface normal. All spectra were obtained at 2-cm⁻¹ resolution and are the sum of 256 individual spectra. Minimal baseline correction was applied to all spectra.

Electrochemical Desorption. The SAM-modified Au substrates were partially immersed (electroactive area: 2.5 cm²) in a single-compartment electrochemical cell, and their potential was scanned between -0.5 and -1.4 V (vs. Ag/AgCl, NaCl (3 M)) at 50 mV/s in an electrolyte consisting of a 1:1 mixture of 1.0 M aqueous KOH and ethanol using a Pine (Model AFCBP1) potentiostat. Pt gauze was used as a counter electrode. The substrates were scanned for up to 32 cycles and FTIR-ERS spectra were obtained after 2, 4, 8, 16, and 32 cycles. The magnitude of the absorbance in the IR hydrocarbon stretching region (2800–3000 cm⁻¹) was used to determine the extent of reductive stripping of the SAMs.

Thermal Processing. The SAM-modified Au substrates were subjected to thermal processing using a tube furnace consisting of a Pyrex glass tube ~0.5 m in length wrapped with heating tape and Al foil. A type-K thermocouple was used to measure the temperature of the furnace. To assure effective heat transfer to the SAM, the substrate was contained in a small boat prepared from Al foil. Once the temperature was stabilized at the desired temperature (200 ± 5 °C, unless otherwise stated), the boat containing the modified Au substrate was placed inside the tube for varying lengths of time. Throughout these experiments the tube was under an Ar purge. FTIR-ERS spectra were obtained after cooling in air. SAM stability was evaluated as described for the electrochemical desorption experiments.

Exposure to Aggressive Solvents. The SAM-modified Au substrates were exposed to a hot (100 °C) base solution, which consisted of a 1:1 mixture of aqueous 1.0 M aqueous KOH and ethanol contained in a sealed vial for varying lengths of time. FTIR-ERS spectra were obtained after cooling and rinsing the substrates. SAM stability was evaluated as described for the electrochemical desorption experiments.

Results and Discussion

Although several important applications of diacetylenic SAMs were discussed in the introduction, their principal virtue is that they are more durable than SAMs prepared from *n*-alkanethiols since the PDA SAMs are polyodal and have much higher molecular weights. We have already demonstrated that the DA SAMs have many of the same structural characteristics of their *n*-alkanethiol analogs,² which suggests they could be seamless replacements for them if their enhanced durability compensates their more challenging synthesis.¹ We chose to focus our study on SAMs prepared from acid-terminated diacetylenes (HS-(CH₂)₁₀C≡CC≡C(CH₂)₁₀COOH, DAs) and polydiacetylenes (PDAs) because, as a result of their reactive endgroup, they are more synthetically flexible than the methyl-terminated analogs. A brief evaluation of the methyl-terminated PDAs revealed that they are at least as durable as the acid-terminated materials. The stability of the DA and PDA SAMs is compared to methyl-terminated hexadecanethiol since it should be the most stable of the sixteen carbon-containing, ω-functionalized *n*-alkanethiols. We have chosen to focus this study on the electrochemical

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- (13) Chailapakul, O.; Crooks, R. M. *Langmuir* **1993**, *9*, 884.
 (14) Sabatani, E.; Rubinstein, I. *J. Phys. Chem.* **1987**, *91*, 6663.
 (15) Bilewicz, R.; Majda, M. *J. Am. Chem. Soc.* **1991**, *113*, 5464.
 (16) Poirier, G. E.; Tarlov, M. *J. Langmuir* **1994**, *10*, 2853.
 (17) Poirier, G. E.; Tarlov, M. J.; Rushmeier, H. E. *Langmuir* **1994**, *10*, 3383.
 (18) Crooks, R. M. Texas A&M University, unpublished results.
 (19) Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391.
 (20) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Muijsce, A. *J. Am. Chem. Soc.* **1990**, *112*, 4301.
 (21) Zamborini, F.; Crooks, R. M. *Langmuir*. In press.
 (22) Schoer, J. K.; Ross, C. B.; Crooks, R. M.; Corbitt, T. S.; Hampden-Smith, M. J. *Langmuir* **1994**, *10*, 3319.
 (23) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335.
 (24) Walczak, M. M.; Popenoe, D. D.; Deinhammer, R. S.; Lamp, B. D.; Chung, C.; Porter, M. D. *Langmuir* **1991**, *7*, 2687.
 (25) Ross, C. B.; Sun, L.; Crooks, R. M. *Langmuir* **1993**, *9*, 632.
 (26) Huang, J. Y.; Hemminger, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3342.
 (27) Tarlov, M. J.; Burgess, D. R. F.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305.
 (28) Kumar, A.; Whitesides, G. M. *Science* **1994**, *263*, 60.
 (29) Lopez, G. P.; Biebuyck, H. A.; Whitesides, G. M.; Frisbie, C. D. *Science* **1993**, *260*, 647.
 (30) Tiberio, R. C.; Craighead, H. G.; Lercel, M.; Lau, T.; Sheen, C. W.; Allara, D. L. *Appl. Phys. Lett.* **1993**, *62*, 476.
 (31) Kumar, A.; Biebuyck, H. A.; Abbott, N. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9188.
 (32) Kopley, L. J.; Crooks, R. M.; Ricco, A. J. *Anal. Chem.* **1992**, *64*, 3191 and references therein.
 (33) Li, Y.; Chailapakul, O.; Crooks, R. M. *J. Vac. Sci. Technol. B* **1995**, *13*, 1300.
 (34) Tangyonyong, P.; Thomas, R. C.; Houston, J. E.; Michalske, T. A.; Crooks, R. M.; Howard, A. *J. Phys. Rev. Lett.* **1993**, *71*, 3319.
 (35) Thomas, R. C.; Kim, T.; Crooks, R. M.; Houston, J. E.; Michalske, T. A. *J. Am. Chem. Soc.* **1995**, *117*, 3830.

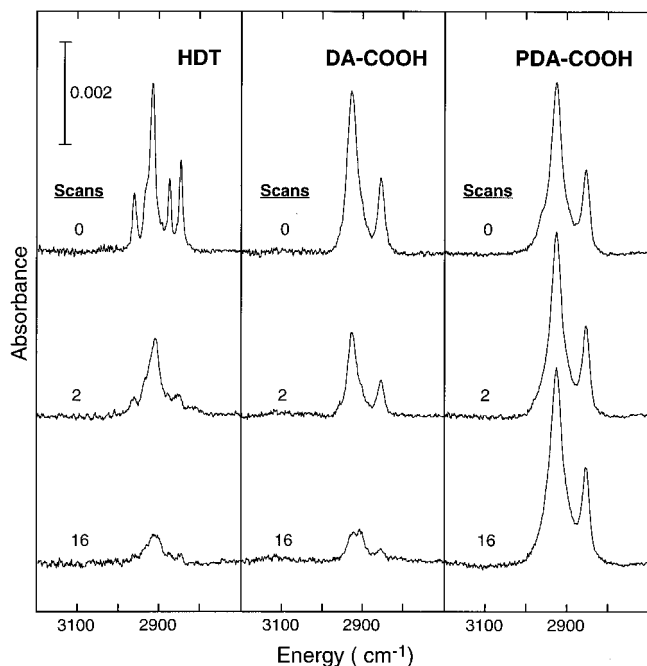


Figure 1. FTIR-ERS spectra for HDT, DA-COOH, and PDA-COOH SAMs on Au electrodes after 0, 2, and 16 reductive desorption cyclic voltammetric scans. All electrodes were scanned between -0.5 and -1.4 V (vs Ag/AgCl (3 M NaCl)) at 50 mV/s in an electrolyte consisting of a 1:1 mixture of 1.0 M aqueous KOH and ethanol.

and thermal stability of the PDA SAMs, and their resistance to aggressive solvents, since these are environments in which SAMs are likely to find technologically significant applications.

Electrochemical Desorption. SAMs may find applications as corrosion passivation layers and as chemically sensitive interfaces for electrochemical-based sensors. However, Porter and co-workers have shown that the SAMs prepared from *n*-alkanethiols are unstable outside of a fairly narrow range of substrate potentials.^{23,24} Their results showed oxidative and reductive desorption occur at about $+0.8$ and -0.8 V (vs Ag/AgCl, saturated KCl), respectively, in aqueous 0.5 M KOH. The exact desorption potential depends on the electrolyte solution, substrate, scan rate, and the thickness of the SAM.^{23,24} Nearly all of the monolayer desorbs from the surface after two voltammetric scans. In a related study, Schneider and Buttry showed that *n*-alkanethiols can be reductively desorbed in acetonitrile and dimethylformamide.¹⁹

We compared the stability of SAMs prepared from *n*-hexadecanethiol ($\text{HS}(\text{CH}_2)_{15}\text{CH}_3$, HDT), the acid-terminated, monomeric DA (DA-COOH), and the acid-terminated PDA (PDA-COOH) by scanning the potential of a monolayer-coated electrode between -0.5 and -1.4 V in an electrolyte consisting of a 1:1 mixture of 1.0 M aqueous KOH and ethanol. These conditions are more aggressive than those used by Porter et al.^{23,24} We evaluated the extent of SAM desorption by examining the electrodes by FTIR-ERS after 0, 2, and 16 cyclic voltammetric scans (Figure 1). Spectroscopic analysis is more quantitative for a broader range of surface coverages than electrochemical methods.^{13,36}

Prior to electrochemical stripping, the spectrum of the HDT-modified Au substrate shows absorbances at 2965 and 2879 cm^{-1} for the methyl stretching modes and 2919 and 2851 cm^{-1} for the methylene stretching modes, which are in accord with previous results.³⁷ After two cyclic voltammetric scans the peak

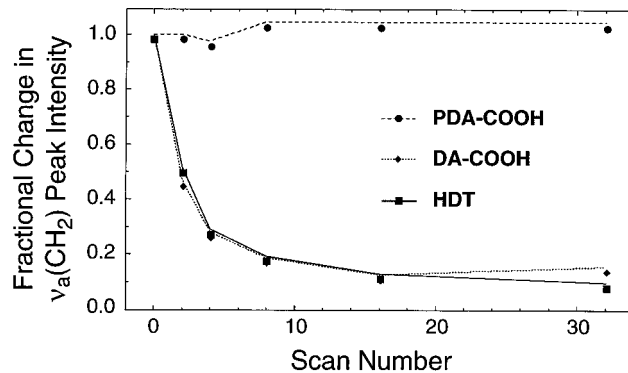


Figure 2. Fractional change in $\nu_a(\text{CH}_2)$ peak intensity vs the number of cyclic voltammetric scans for SAMs composed of HDT, DA-COOH, and PDA-COOH.

at 2878 cm^{-1} disappears completely, and the peaks at 2965 and 2851 cm^{-1} decrease significantly. The peak at 2919 cm^{-1} shifts to 2911 cm^{-1} and also decreases. This result indicates that most of the HDT is stripped from the Au substrate after just two scans in accord with previous reports.^{23,24} The intensity of the HDT hydrocarbon bands decreases continuously until, after 16 voltammetric scans, only a very small peak at 2911 cm^{-1} remains. The material that gives rise to this band may be residual HDT but is more likely adventitious hydrocarbon material that adsorbs to the Au surface during transfer from the electrochemical cell to the spectrometer. Additional scans did not reduce the intensity of these peaks further (Figure 2).

Results similar to those obtained for HDT were obtained for unpolymerized DA-COOH (Figures 1 and 2), indicating that their level of stability is similar. After polymerization, however, the stability of the PDA-COOH SAM is greatly enhanced. As shown in Figure 1, there is no discernible diminution of the hydrocarbon stretching peaks after 16 scans. Even after 32 scans (Figure 2) the PDA-COOH monolayer remains intact, at least as measured by FTIR-ERS. We attribute this result to the fact that PDA-COOH is a macromolecule with attendant high molecular weight, low solubility,¹⁹ and many points of surface attachment per molecule. Some of these attachment points might not survive the potential excursions, but clearly some of them do. Figure 2 summarizes the dramatic results of this important experiment. We also subjected a the methyl-terminated analog of PDA-COOH (PDA- CH_3) SAM to the same electrochemical conditions used for the PDA-COOH experiment and obtained essentially identical results.

Thermal Processing. Organomeraptan SAMs have been used as resists for lithographic applications.^{22,25-31} In some cases, such as those involving chemical vapor deposition (CVD), elevated processing temperatures are required. Other applications such as corrosion passivation, chemical sensing, adhesion, and lubrication might also involve elevated temperatures.

It has been shown that shorter (≤ 10 carbon atoms) *n*-alkanethiol SAMs are thermally stable in vacuum up to about 100 $^\circ\text{C}$, but that even at this temperature there are surface-phase transitions that lead to decreased packing density and attendant loss in SAM barrier properties.^{17,38} For example, results from scanning tunneling microscopy reported by Poirier et al.¹⁷ showed that the surface adlayer structure of *n*-octanethiol and *n*-decanethiol SAMs changed from close-packed $c(4 \times 2)$ to the more open $p \times \sqrt{3}$ phase when annealed at 100 $^\circ\text{C}$ in ultrahigh vacuum (UHV). Heating to 300 $^\circ\text{C}$ leads to monolayer desorption. Scoles et al.³⁸ confirmed these results using x-ray and He diffraction methods by annealing in the temperature

(36) Menon, V. P.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920.

(37) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(38) Li, J.; Liang, K.; Camillone, N.; Leung, T.; Scoles, G. *J. Chem. Phys.* **1995**, *102*, 5012-5028.

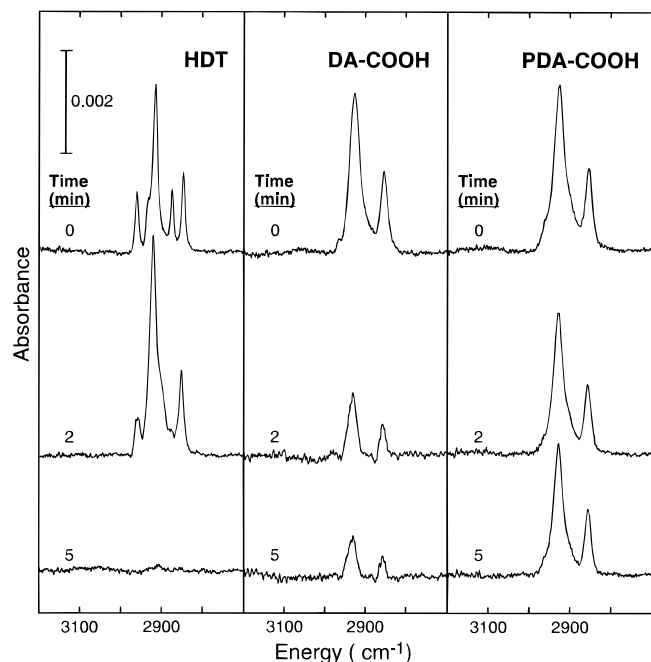


Figure 3. FTIR-ERS spectra for HDT, DA-COOH, and PDA-COOH SAMs on Au electrodes after exposure to flowing Ar at 200 °C for 0, 2, and 5 min.

range 80–135 °C in UHV. However, heating to 200 °C resulted in complete desorption of the monolayer from the surface. McCarley et al. showed that at temperatures less than 100 °C, long-chain SAMs are relatively stable for up to 1 h.³⁹ Our own results indicate that under technologically relevant conditions, for example in the presence of a CVD precursor at atmospheric pressure, the temperature range over which *n*-alkanethiol SAMs are stable is likely to be reduced.²²

We heated SAMs prepared from HDT, DA-COOH, and PDA-COOH to 200 °C for varying lengths of time in an Ar-purged tube furnace and then evaluated the extent of SAM desorption using FTIR-ERS. Figure 3 shows the results of this experiment. Before heating the HDT monolayer has characteristic bands attributable to methyl and methylene modes at the same energies given in the previous section (Figure 1). After heating at 200 °C for only 2 min the spectrum of the HDT SAM changes: the peak at 2879 cm⁻¹ disappears, while the peaks at 2965, 2919, and 2851 cm⁻¹ shift to 2961, 2924, and 2855 cm⁻¹, respectively. Moreover, the absorbance of the peaks at 2924 and 2855 cm⁻¹ becomes larger while that of the peak at 2961 cm⁻¹ is attenuated. From these data we conclude that these conditions lead to a dramatic change in the average molecular orientation of HDT and possibly some desorption.⁴⁰ After heating for 5 min at 200 °C, all the IR peaks disappear implying complete desorption of HDT.

Prior to heating, the DA-COOH SAM has characteristic methylene stretching modes at 2930 and 2856 cm⁻¹ (Figure 3). Upon thermal treatment at 200 °C the absorbance of these bands decrease by about 60%, but even after 5 min they do not disappear completely as they do for HDT SAMs. This may suggest partial thermally-induced polymerization.^{41,42} In contrast to this result, the PDA-COOH methylene peak intensities

(39) McCarley, R. L.; Dunaway, D. J.; Willicut, R. J. *Langmuir* **1993**, *9*, 2775.

(40) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.

(41) Batchelder, D. N.; Bloor, D. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Wiley Heyden: London, 1984; pp 133–209.

(42) Bloor, D.; Denedy, R. J.; Batchelder, D. N. *J. Polym. Sci.: Polym. Phys. Ed.* **1979**, *17*, 1355.

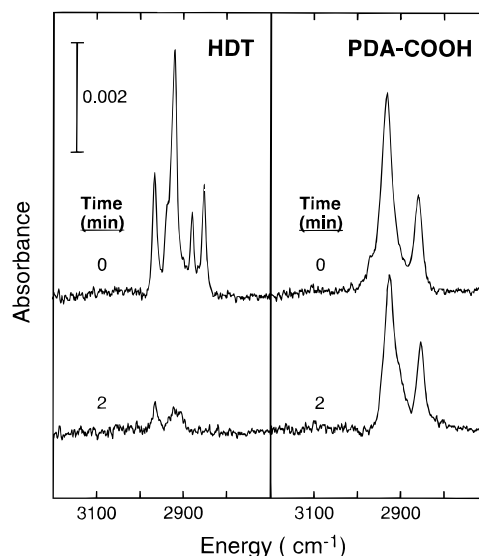


Figure 4. FTIR-ERS spectra for HDT and PDA-COOH SAMs on Au surfaces after exposure to a solution consisting of a 1:1 mixture of ethanol and 1.0 M aqueous KOH at 100 °C for 0 and 2 min.

decrease by only about 15% after the first 2 min of heating. This small change in IR absorbance could easily result from a slight thermally driven structural rearrangement of the hydrocarbon chains,⁴⁰ or it may reflect desorption of DA-COOH present within the PDA film as a result of incomplete polymerization. After the initial decrease in peak intensity at 2 min, there is no further decrease even after 1 h of additional heating at 200 °C. Only after raising the substrate temperature to 300 °C does the PDA-COOH SAM finally desorb. From these results we conclude that the polymerized monolayer is substantially more thermally stable than simple *n*-alkanethiol SAMs, probably for the reasons discussed in the preceding section.

Exposure to Aggressive Solvents. Simple *n*-alkanethiols are quite stable in neutral, aqueous solvents at room temperature, presumably because of the poor solubility of these materials in water. However, in many organic solvents,^{19,43} at extreme pHs, or at elevated solvent temperature unpolymerized SAMs are prone to desorption. This is a particularly troublesome characteristic for many technological applications of SAMs, including lubrication, adhesion, and lithography.

To compare the durability of unpolymerized and polymerized SAMs, we exposed HDT and PDA-COOH to an especially aggressive solvent, a 1:1 mixture of ethanol and 1.0 M aqueous KOH at 100 °C, and then evaluated the effects using FTIR-ERS. Figure 4 illustrates the results of this experiment. Prior to exposure, the HDT SAM has the hydrocarbon IR fingerprint discussed in the two previous sections. After exposure to the hot, basic solvent for 2 min essentially the entire SAM desorbs. In contrast to this result, however, there is little change in the FTIR-ERS spectrum of the PDA-COOH modified substrate after solvent exposure. These results underscore the enhanced stability of the PDA SAMs.

Summary and Conclusions

We have compared the stability of *n*-alkanethiols and unpolymerized and polymerized diacetylenic alkanethiols. The polymerized materials are far more dimensionally stable than either the unpolymerized DAs or simple *n*-alkanethiols. Given the fragility of the latter two materials, we believe they are, in contrast to the PDAs, generally unsuitable for most technological applications. At the present time, we are exploring additional

(43) Groat, K. A.; Creager, S. E. *Langmuir* **1993**, *9*, 3668.

mechanical and structural aspects of the PDAs with a view toward understanding their visco-elastic properties and the length of the individual oligomeric chains. The results of those studies will be reported soon.

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