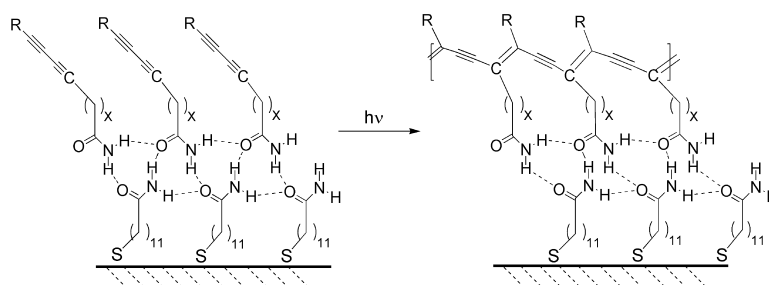


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Polymerization of Diacetylenes by Hydrogen Bond Templated Adlayer Formation

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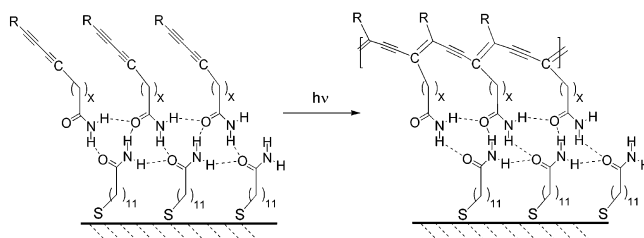
Multilayer films based on covalent or coordination bonding to self-assembled monolayers (SAMs) have been the subject of a number of studies in the last 15 years.^{1–7} Fewer studies have been reported utilizing exclusively hydrogen bonding in SAMs as the organizing principle between multiple layers.^{8–10} This may be due to the fluxional nature of the hydrogen bond under typical film formation conditions. However, as the push for functional nanoscale systems continues, it is likely that the lability of the hydrogen bond will be seen as a strength in the design of functional molecular systems. A classic example of this is templating of polymerization reactions. Hydrogen bonding is the motif of choice in biology for the templating of polymerization reactions, such as DNA replication. Labile bonds such as hydrogen bonds allow easy removal of the product polymer so that the template can be reused. Many attempts to mimic this in solution have been reported.^{11–13} In the monolayer realm, a few studies exist of hydrogen bond templating of polymerization in langmuir troughs using additives within the aqueous phase.^{14,15} To our knowledge no studies exist utilizing hydrogen bond templated polymerization on self-assembled monolayers. This type of system offers advantages in terms of the potential for top-down lithography and control of the polymerization domains, while still allowing for facile removal of the product polymer from the template. By using crosslinkable monomers, it may be a useful route to discrete two-dimensional polymers.¹⁶

We wish to report the system outlined in Scheme 1. It is based on the report of hydrogen bonded adlayers by Laibinis and co-workers⁸ and the well-known properties of diacetylene polymerization in SAMs.^{2,17,18} A base SAM of 12-mercaptododecanamide (12MDA) is first formed under typical monolayer assembly conditions. Then it is exposed to a solution of diacetylene-containing molecules **1**, **2**, or **3**, which form an adlayer through hydrogen bonding. These adlayers exhibit enough ordering to undergo polymerization by exposure to UV light. The compounds **1**, **2**, and **3** were synthesized via a Cadiot–Chodkiewicz based strategy, described in the Supporting Information.¹⁹ Base SAMs of 12MDA were formed from 0.1 mM ethanol solutions on thermally evaporated gold substrates and reliably gave films with advancing water contact angles less than 15°. After base SAM formation, the films were immersed in the adlayer forming solution within 1 h. Adlayers were found to form readily using decalin and toluene/decalin mixtures containing 0.2 to 0.5 mM of **1**, **2**, or **3**.

Table 1 shows selected characterization data for the adlayer films before and after polymerization. All the characterization data for polymerized adlayers of **1**, **2**, and **3** were obtained on films polymerized for 2 min with 254 nm light under nitrogen. The thicknesses, obtained by ellipsometry, are consistent with a high degree of surface coverage for all of the adlayers. We found no difference in measured thickness before or after polymerization. The approximate cant angle for the adlayers based on the experimental thickness and a simple molecular model of the molecules in their fully extended conformation is shown in Table

Scheme 1. Templated Diacetylene Polymerization

- 1**, R = $-(\text{CH}_2)_7-\text{CH}_3$, x = 8
2, R = $-(\text{CH}_2)_7-\text{CH}_3$, x = 9
3, R = $-(\text{CH}_2)_5-\text{C}=\text{C}=\text{C}-(\text{CH}_2)_7-\text{CH}_3$, x = 8



1. The values of 35–42° are similar to previously reported cant angles for diacetylene SAMs.^{2,17} The contact angles (CAs) indicate a disordered surface of methyl and methylene groups, which can be expected given the relatively short “tails” of the monomers, all three of which end in eight carbon chains. The higher water CA of **2** may be an indication of an even/odd effect in the methylene chains.¹⁸ It is interesting that the CAs with water go up after polymerization, particularly in the case of **1**. This may be an effect due to penetration of water into the adlayers before polymerization occurs. Due to the instability of these adlayers in organic solvents, we only report hexadecane CAs after polymerization.

Polymerization was verified by resonance enhanced Raman spectroscopy at 514 nm, shown in Figure 1a. The inset shows the intensity of the alkenyl C=C Raman stretch for polymerization of **1** over time. The polymerization peak grows in over about 2 min, with further exposure to UV light resulting in no increase of the alkenyl signal at 1500 cm⁻¹. No signal is seen before polymerization, as expected for a resonance-enhanced Raman signal originating due to polymer backbone excitation. The Raman data for these adlayers is very similar to previously reported results for diacetylene SAMs.^{17,18} The lower intensity signal for the adlayer of **3** indicates a lower yield of polymer in the adlayer or slower polymerization kinetics, which may be due to a more disordered adlayer structure as indicated by CA and FTIR measurements.

Grazing angle FTIR spectra are shown in Figure 1b for these adlayers. The 12MDA base SAM shows amide peaks at 3500, 1650 (amide I), and 1610 (amide II) cm⁻¹. The methylene C–H stretches are at 2919 (d⁻) and 2850 (d⁺) cm⁻¹, indicative of a well-ordered base SAM.²⁰ Upon adlayer formation, the amide II peak shifts from 1610 to 1625 cm⁻¹. The N–H stretch also shows peaks at 3200 and 3400, characteristic of a hydrogen bonded primary amide. The values for the methylene C–H stretches of each adlayer both before and after polymerization are shown in Table 1. The spectra include both the 12MDA base SAM as well as the adlayer, so the methylene stretching peaks are broadened. SAMs of short alkanethiols such as octanethiol have methylene stretches at 2921 and 2852 cm⁻¹, indicative of less crystalline packing than longer chains such as octadecanethiol which has values of 2917 and 2850 cm⁻¹.²⁰ The

Table 1. Adlayer Characterization

	adlayer thickness ^a (nm)	contact angle ^b H ₂ O before UV (deg)	contact angle ^b H ₂ O after UV (deg)	contact angle ^b HD after UV (deg)	adlayer cant angle (deg)	FTIR CH ₂ C–H stretches before UV (cm ⁻¹)	FTIR CH ₂ C–H stretches after UV (cm ⁻¹)	Raman alkenyl, alkynyl stretches (cm ⁻¹)
1	1.83 ± 0.03	67 ± 2	84 ± 2	40 ± 2	42	2921, 2851	2921, 2851	1499, 2105
2	2.12 ± 0.14	86 ± 3	90 ± 2	35 ± 2	35	2921, 2851	2921, 2851	1503, 2105
3	2.67 ± 0.16	78 ± 3	84 ± 2	30 ± 2	42	2922, 2852	2922, 2852	1495, 2098

^a Thickness measured by ellipsometry. ^b Advancing contact angles are reported; HD is hexadecane.

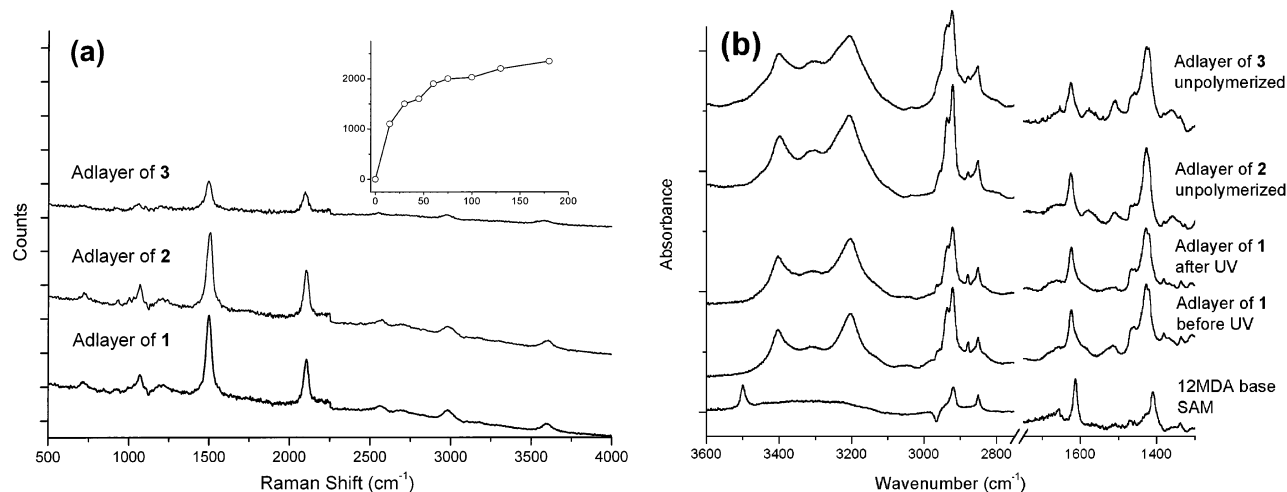


Figure 1. (a) Raman spectra of adlayers after 2 min polymerization. The exciting wavelength was 514 nm, ~ 1.6 mW/cm² power focused through a 50 \times objective. The y origin has been shifted, but relative intensities are maintained. The inset shows a time course of the polymerization for **1**, the y axis showing peak height of the alkene C=C stretch with respect to seconds of UV exposure. (b) Grazing angle FTIR of adlayers. The y origins have been shifted, but relative intensities are the same.

FTIR values for these adlayers are consistent considering they have alkyl chains with nine methylenes or less; also, regular methylene packing is broken by the rigid diacetylene moiety. We have seen no changes in the FTIR spectrum after adlayer polymerization other than a slight shift in the methylene C–H stretches (tenths of a cm⁻¹) to a higher energy.

The polymerized adlayers were more resistant to solvation by hexanes (10–30% thickness loss) than the corresponding unpolymerized adlayers (50–60% thickness loss) as judged by ellipsometry. All three polymerized adlayers could be dissolved upon soaking in solvents such as chloroform or ethyl acetate. AFM studies indicate that these substrates often have steps on the surface of 10 Å or more separating gold grains of from 40 to 50 nm in size. Thus the polymerized adlayers are likely limited to small domains on individual gold grains. We are extending this work to ultraflat gold substrates, which will presumably allow for a greater amount of cross-linking and polymerization to occur in monomers such as **3**.

We have demonstrated the first example of hydrogen bond templated adlayer polymerization on SAMs. This combination of labile adlayer chemistry with crosslinkable monomers may provide a route to single monolayer two-dimensional polymer sheets which can be readily patterned using current lithography techniques and released into solution.

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Supporting Information Available: Experimental details, including syntheses of **1**, **2**, and **3**; AFM images of the adlayer of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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