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# The Synthesis of Conjugated Diacetylene Monomers for the Fabrication of Polymerized Monolayer Assemblies

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**Abstract:** Symmetrical disulfides containing conjugated diacetylene groups for use in forming polymerized self-assembled monolayers have been fabricated using common synthetic techniques. In contrast with previous reports, the proposed synthetic route does not require the use of hexamethylphosphoramide (HMPA) or the incorporation of an ester moiety near the surface attachment site. Overall yields of 20-30% are readily achieved for this four-step synthesis.


It is well known that thiols and disulfides spontaneously self-assemble into monolayer films on gold surfaces through chemisorption of the sulfur atom.[1] The incorporation of polymerizable groups into such monolayer films provides the ruggedness and defined interfacial structure that is of key importance for studies ranging from lubrication/adhesion to photoelectronics and sensor design. The diacetylene class of molecules has been widely investigated[2], and is particularly well suited to these studies because the conjugated triple bonds can be photo-polymerized within the monolayer structure to yield assemblies which are much more robust than typical n-alkane thiol monomolecular films (Figure 1).[3]

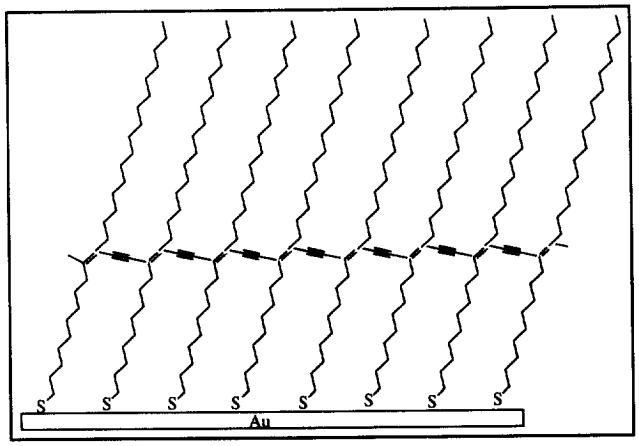



**Figure 1.** An example of a polymerized diacetylene monolayer.

The conjugated polymer backbone inherent in these films also provides unique optical and electronic properties that are not readily attainable within the organic monolayer domain. This unique combination of robustness and optoelectronic properties make such monolayer polymers of significant interest for fundamental studies as well as practical applications.

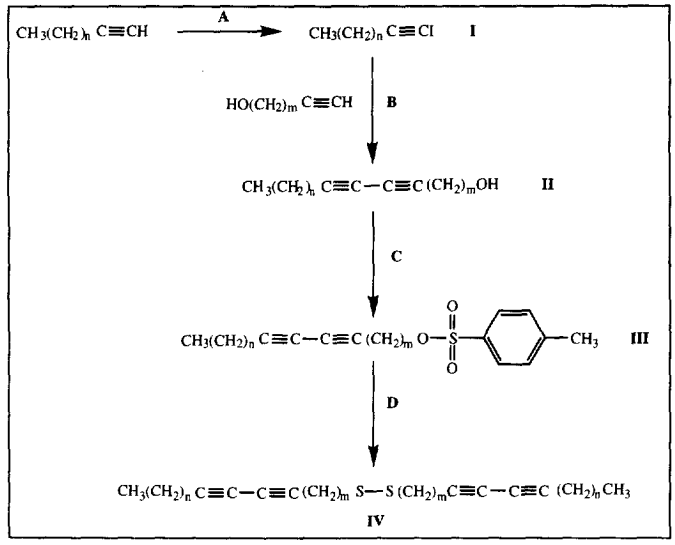
To the best of our knowledge, there exist only two other reports describing the synthesis of diacetylenic

compounds suitable for forming polymerized self-assembled monolayers on gold. The first was the synthesis of long chain disulfides reported by Batchelder *et al.*[3a] Their synthesis was accomplished by reacting two equivalents of 10,12-heptacosadiyn-1-ol with one equivalent of 3,3'-dithiopropionic acid to yield the symmetrical disulfide. Monolayers formed from these compounds contain an ester functional group in the chain extending from the gold surface to the polymer backbone. The role of the ester moiety in disrupting the packing density within the monolayer structure has not yet been determined. However, the possibility exists that the ester group could be a limiting factor in achieving high density monolayers, leading to the formation of defect sites within the film structure. To eliminate this possibility, Crooks and Kim reported the synthesis of diacetylenic thiols of the form

$$HS(CH_2)_{10}C{\equiv}C{-}C{\equiv}C(CH_2)_nX$$

where n = 10 or 2 and X is either $CH_3$, $CH_2OH$, or COOH.[3b,3d] Although this synthetic route is clearly successful, the complexity of the synthesis together with the hazardous nature of hexamethylphosphoramide (HMPA)[4] make this scheme not directly amenable in many laboratory environments. The synthetic approach presented here provides a readily applicable alternative without the need for the repeated use of HMPA.

In an effort to synthesize molecules suitable for our studies, we have developed the synthetic route shown in Scheme 1.




**Scheme 1.** The method for preparing symmetrical disulfides containing conjugated diacetylene groups.

This procedure has the advantage of using relatively simple, well-characterized techniques to synthesize the diacetylenic compounds without the ester functional group and without HMPA, a known mutagen.[4] In Step A, the terminal alkyne is treated with a slight excess of n-butyllithium (1.6 M in hexanes) followed by 1.5 equivalents iodine to yield the iodinated terminal acetylene (product I).[5] Step B involves coupling the iodinated acetylene (I) with a terminal acetylene containing a hydroxyl functional group using the familiar Cadiot-Chodkiewicz method for forming unsymmetrical conjugated diacetylenes.[6-8] This reaction involves dissolving the alcohol in a mixture of 10% aqueous potassium hydroxide and methanol. To this solution is added hydroxylamine hydrochloride, ethylamine (70% aqueous), and a catalytic amount of copper(I) chloride. After

the mixture is cooled in a methanol/dry ice bath, a solution of the iodinated acetylene in THF is added dropwise. The reaction is complete after stirring overnight while gradually warming to room temperature. Step C is a tosylation of the alcohol in a chloroform solution using a 1:2:3 ratio of alcohol - *p*-toluenesulphonyl chloride - pyridine.[9,10] Finally, Step D involves a simple nucleophilic substitution of the tosylate with $^{-}$SH by sonicating at slightly elevated temperatures in ethanol.[3b,11] The product is a mixture of the thiol and corresponding symmetrical disulfide (IV), but prolonged sonication at the elevated temperature drives the reaction toward disulfide formation.

This synthetic route is generally applicable to the fabrication of a wide range of alkyl chain lengths, both above and below the polymer backbone. Diacetylenes have already been successfully prepared with several alkyl chain lengths (m = 9; n = 7,11,15). With slight modification, this synthetic approach is presently being extended to other ω-terminated analogs containing carboxylate and alcohol moieties.

## Acknowledgements

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4. Windows Material Safety Data Sheet Viewers Version 1.01; Aldrich Chemical Co. Inc.; Copyright 1992-1995.
5. Iodination of a terminal alkyne (Step A). n-Butyllithium is added to a solution of the terminal alkyne (30 mmol) in 250 ml hexane cooled in an ice bath. After 20 minutes, 1.5 equivalents of solid iodine is added and the mixture is stirred for four hours. The solution is washed with a saturated aqueous sodium thiosulfate solution to remove residual iodine and the organic phase is collected and dried over sodium sulfate. The iodinated alkyne (product I) is recovered in greater than 90% yield by evaporation of the solvent. The product is used in the coupling reaction without further purification.
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8. The Cadiot-Chodkiewicz coupling of the iodinated alkyne (I) and 10-undecyn-1-ol (Step B). Methanol is added to a mixture of 10-undecyn-1-ol (30 mmol) and 30 ml 10% aqueous potassium hydroxide until the solution becomes homogenous. Hydroxylamine hydrochloride (0.1 equivalent) is then added followed by a solution of copper(I) chloride (0.25 equivalent) in 10 ml ethylamine (70% aqueous). The bright yellow

solution is cooled to <-20°C in a methanol/dry ice bath and a solution of the iodinated alkyne (I) in 20 ml THF is added dropwise. The solution is allowed to stir and warm to room temperature overnight. The solution is then washed with 10% $H_2SO_4$ and extracted four times with diethyl ether. The combined extracts are dried over sodium sulfate. The product is purified by evaporating the solvent and recrystalizing the remaining solid from petroleum ether to produce a slightly yellow solid (product II) in yields ranging from 50-60% depending upon chain length.

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10. Tosylation of the diacetylenic alcohol (Step C). The diacetylenic alcohol formed in Step B (product II) is dissolved in 30 ml chloroform and cooled in an ice bath. Three equivalents of pyridine are added followed by the addition of 3 equivalents *p*-toluenesulphonyl chloride in small portions. The solution is stirred in the ice bath for 5-8 hours and the reaction is monitored for completion by TLC. Upon completion, the solution is added to 30 ml ether and 7 ml water. The organic layer is washed successively with 2 N HCL, 5% aqueous sodium bicarbonate, and water, and the organic phase is dried over magnesium sulfate. Product III is collected in greater than 60% yield by evaporating the solvent and recrystalizing from hexane. $^1$H NMR ($CDCl_3$) for product III with m=9 and n=7: δ(ppm) 7.38 (Ar-H, AA'BB', 4H); 4.02 ($CH_2$-O, t, 2H); 2.46 (Ar-$CH_3$, s, 3H); 2.24 ($CH_2C \equiv C$, t, 4H); 1.70-1.25 ($CH_2$ chain, m, 26H); 0.89 ($CH_3$, t, 3H).

11. Formation of the disulfide (Step D). The tosylated diacetylene (product III) is dissolved in a minimum amount of absolute ethanol. Six equivalents of sodium hydrogen sulfide are added and the mixture is sonicated at 40-45 °C for eight hours. The solution is then diluted with chloroform and washed with 1 N HCl. The organic phase is dried over sodium sulfate. The purified slightly yellow solid (product IV) is obtained by evaporating the solvent and recrystalizing from petroleum ether (overall yield = 20 - 30%).

    Analysis: Product IV with m=9 and n=7: $^1$H NMR ($CDCl_3$) δ(ppm): 2.69 ($CH_2$S-S, t, 4H); 2.25 ($CH_2C \equiv C$, t, 8H); 1.70-1.25 ($CH_2$ chain, m, 52H); 0.89 ($CH_3$, t, 6H).
    FTIR (cm$^{-1}$): 2918 (CH asymm. stretch), 2850 (CH sym. stretch), 1472 (CH scissor), 716 (C-S stretch).

Combustion Analysis:

| | Calculated | | Found | |
|---|---|---|---|---|
| Product IV | C | H | C | H |
| m=9,n=7 | 78.93% | 11.04% | 79.03% | 11.32% |
| m=9,n=11 | 79.93% | 11.54% | 79.80% | 11.56% |
| m=9,n=15 | 80.67% | 11.91% | 80.40% | 11.81% |

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