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# Chemical Surface Modification via Radical C−C Bond-Forming Reactions

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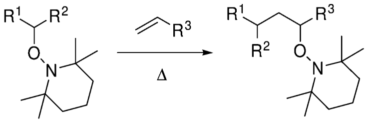
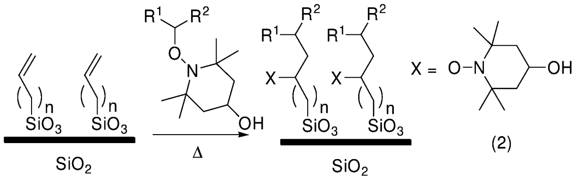
Self-assembled monolayers (SAMs) bearing specific functional groups have gained widespread interest.[1] Functional groups at the surface allow careful tuning of surface properties such as wettability, biocompatibility and corrosion resistance. Many standard organic reactions such as alkene oxidations, amino acylations, imine bond formations, alcohol acylations, and epoxide openings with alcohols and amines have been successfully conducted at SAMs.[1c,e] All these reactions comprise carbon−heteroatom bond formations. However, C−C bond-forming reactions at SAMs are far more difficult to achieve, and only very few reports have appeared to date.[2,3]

Recently, we reported successful thermal radical carboaminoxylations of unactivated olefins (eq 1).[4,5] Radical generation occurs via thermal C−O bond homolysis of the starting alkoxyamine. C-radical addition onto the olefin with subsequent irreversible nitroxide trapping affords the corresponding carboaminoxylation product.[6] Importantly, C−O bond homolysis in the starting alkoxyamine is reversible, and therefore formal long-lived C-radicals result. Generation of radicals can be achieved over days without destroying the C-radical precursor. Therefore, this approach should be particularly suited for radical C−C bond formations at olefin-terminated SAMs which have not been reported to date (eq 2).[7]



(1)



(2)

**Table 1.** Radical Carboaminoxylation of 7-Octenyl SAMs Using HO-TEMPO-malonate at 125 °C in $ClCH_2CH_2Cl$ under Different Conditions[a]

| | *t* [h] | *c* [mol L$^{-1}$] | CA(adv) [deg] | CA(rec) [deg] |
|---|---|---|---|---|
| 1 | 0 | 0 | 95 ± 4 | 63 ± 9 |
| 2 | 5 | 1.0 | 90 ± 3 | 60 ± 3 |
| 3 | 10 | 1.0 | 88 ± 2 | 58 ± 3 |
| 4 | 20 | 1.0 | 76 ± 2 | 46 ± 5 |
| 5 | 40 | 1.0 | 77 ± 1 | 43 ± 1 |
| 6 | 20 | 0.5 | 90 ± 3 | 61 ± 5 |
| 7 | 20 | 0.7 | 85 ± 2 | 54 ± 4 |
| 8 | 10 | 1.5 | 78 ± 5 | 41 ± 2 |

[a] CA(adv) = advancing contact angle; CA(rec) = receding contact angle.

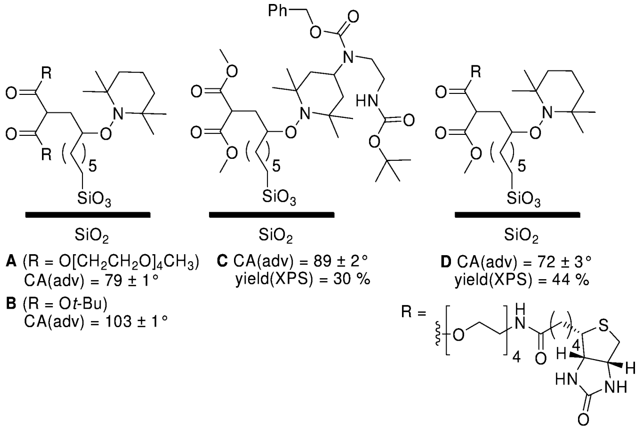


**Figure 1.** Chemically modified Si-wafers **A**, **B**, **C**, and **D**.

Alkene terminated SAMs were prepared using oxidized Si wafers and 7-octenyl or 10-undecenyl trimethoxysilane, respectively (see Supporting Information (SI)). Surface carboaminoxylations were studied using HO-TEMPO-malonate as C-radical precursor (see eq 2, $R^1 = R^2 = CO_2Me$, $n = 6$). Addition reactions were performed by dipping a 7-octenyl-terminated wafer into a solution of the alkoxyamine in $ClCH_2CH_2Cl$ with subsequent heating at 125 °C. Concentration and reaction time were systematically varied, and analysis of the chemically modified surface was performed via contact angle (CA) measurements providing information on the surface polarity (Table 1, 7-octenyl-terminated surface CA(adv) = 95 ± 4°, entry 1). Reaction for 5 h provided a slightly lower CA as one would expect for a successful reaction using HO-TEMPO-malonate (entry 2). Increase of the reaction time to 10 or 20 h led to a further decrease of the CA (entries 3, 4). However, reaction for 40 h did not further increase the polarity of the surface (entry 5). We found that the surface reaction was less efficient under higher dilution (entries 6 and 7). Decreasing the reaction time to 10 h and increasing the concentration (1.5 molar) did not improve the result (entry 8).

Importantly, our method operates under neutral conditions and many functional groups are tolerated. Moreover, functionalized alkoxyamines are readily prepared (see SI). In Figure 1 wafers **A**−**D**, which were successfully chemically modified by using functionalized alkoxyamines, are depicted. Surface polarity can readily be altered upon changing the substituents at the malonate moiety. Carboaminoxylation using an alkoxyamine bearing short polar tetraethyleneglycol tails leads to a surface with a smaller CA (**A**, CA(adv) = 79 ± 1°), whereas di-*tert*-butyl malonyl radical additions provide more hydrophobic surfaces (**B**, CA(adv) = 103 ± 1°). Importantly, the desired functionality can also be introduced via the nitroxide component of the alkoxyamine as documented for wafer **C**.

Even complex molecules with biologically interesting functionalities like TEMPO-biotin conjugates can be added to alkene terminated SAMs (**D**, CA(adv) = 72 ± 3°). Carboaminoxylations

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10.1021/ja0686716 CCC: $37.00

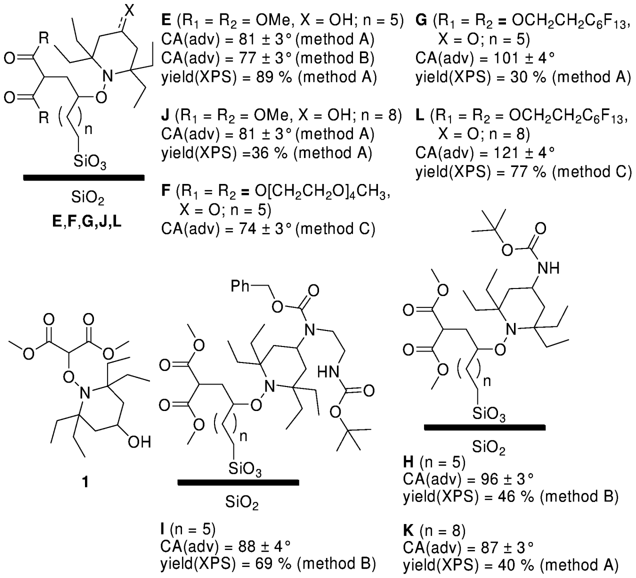

***Figure 2.*** Carboaminoxylation using bulky alkoxyamines.

using alkoxyamines derived from sterically highly hindered nitroxides are far more efficient as compared to the TEMPO-mediated processes.[4c] This is also true for the surface radical chemistry as reaction with the bulky alkoxyamine **1** at 125 °C is completed within 2 h ($ClCH_2CH_2Cl$, 1 M, method A, CA = 81 ± 3°; wafer **E**).[8,9] Surface reaction using **1** can even be achieved at 90 °C (20 h, CA(adv) = 77 ± 3°; wafer **E**, method B). With oily alkoxyamines, radical chemistry at SAMs can be conducted by simply covering the wafer with a film of the alkoxyamine and subsequent heating without using any solvent (90 °C, 15 h, CA(adv) = 74 ± 3°; wafer **F**, method C). Using methods A and B wafers **G**−**I** were successfully prepared showing that various functional groups can readily be introduced. It is known that the alkyl chain length in alkyl trialkoxysilanes influences SAM formation.[1a,10] Therefore, 10-undecenyl covered wafers were modified by radical carboaminoxylations providing wafers **J**−**L**. Generally larger contact angle changes were observed upon C−C bond formation indicating that a higher density of the functional groups at the surface is achieved starting from longer and more densely packed alkene-terminated wafers (see Figure 2).

To further study the surface chemistry, X-ray photoelectron spectroscopy (XPS) was performed. SAM modification with TEMPO-alkoxyamines leading to wafers **C** and **D** was quantified revealing that about 30% (wafer **C**) or 44% (wafer **D**) of the surface bound alkenes underwent reaction (Figure 1). With bulkier alkoxyamines, SAMs can be subjected to radical carboaminoxylation under milder conditions (see above). XPS results show that under these conditions SAM modification proceeds more efficiently. Hence, reaction with **1** leads to very high conversion with respect to the surface bound octene (89%, wafer **E**, method A). Even with sterically hindered alkoxyamines surface modification proceeds smoothly under the described conditions (46%, wafer **H**, method B; 69%, wafer **I**, method B; 40%, wafer **K**, method A). Also fluorination was readily achieved (77%, method C; wafer **L**).

Analysis of the SAM thickness by ellipsometry and angle-resolved XPS further supports the success of the surface reaction. By going from alkenyl terminated wafers (7-octenyl: $d$ = 2.08 nm, ellipsometry; 10-undecenyl: $d$ = 2.10 nm, XPS) to the addition products, a significant increase of SAM thickness was measured (**E**, $d$ = 2.70, ellipsometry; **J**, $d$ = 2.95 nm, XPS; **L**, $d$ = 3.62 nm, XPS; see SI). This indicates that the added functional groups are probably not buried within the monolayer as also supported by the changes of the CAs.

In conclusion we reported first radical C−C-bond forming reactions at SAMs. These reactions can be conducted under neutral conditions and many functional groups are tolerated. This is a major advantage over most of the carbon−heteroatom bond-forming processes at SAMs which are ionic reactions and require often protecting group strategies. We believe that the radical surface chemistry will become an important alternative to the established ionic chemistry for chemical surface modification. The new method can also be used for the immobilization of biologically interesting molecules.

**Acknowledgment.** We thank the Fonds der Chemischen Industrie for a stipend (K.O.S.) and the Deutsche Forschungsgemeinschaft (STU 280/5-1) for supporting our work. Dr. H. Wormeester, MESA+ Research Institute (Enschede, NL) is acknowledged for performing ellipsometry. Wacker Siltronics AG is acknowledged for donation of Si wafers. An anonymous referee is acknowledged for helpful comments. This work is dedicated to Professor Hans J. Schäfer on the occasion of his 70th birthday.

**Supporting Information Available:** Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The same contact angle was obtained if the reaction was run for 20 h.

(9) Reaction of **1** with 7-octenyl trimethoxysilane in solution provides the corresponding carboaminoxylation product which can be covalently bound to the surface by standard SAM formation. A CA(adv) of 81 ± 3° was measured (see SI). The same value is obtained for wafer **E** prepared by surface radical carboaminoxylation showing that the radical C-C bond formation at the surface is indeed a highly efficient process.

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