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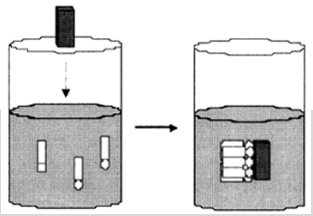
Reactions and Reactivity in Self-Assembled Monolayers**

By *Victor Chechik*, *Richard M. Crooks*, and *Charles J. M. Stirling**



Self-assembled monolayers (SAMs) are excellent models for studying interfacial reactions. Here monolayer chemistry is reviewed, focusing on the features that have no analogues in solution chemistry. The growth of surface-attached polymers, intrafilm reactions, chemistry, photochemistry and reactivity issues are all discussed.

1. Introduction

Interfacial reactions are becoming an increasingly important subject for studies. The ability to control the chemical and structural properties of surfaces is crucial for advancements in selective and environmentally friendly catalysis,[1] electronics,[2] chemical sensing,[3–7] and many other applications.[8–10] Increasing interest in organic synthesis on solid supports and industrial development of combinatorial chemistry methodologies build on the growing knowledge of interfacial chemistry.[11] In parallel, understanding the rules that govern surface reactions provides very important information for fundamental studies in chemistry and biochemistry.[12,13] These considerations, and the availability of numerous analytical techniques capable of detecting chemical changes in films that are just one molecule thick,[8] have made studies of interfacial reactions a viable and important area of modern science.

Self-assembled monolayers (SAMs) are perhaps the best model for such studies. SAMs are defined as monomolecular films of a surfactant formed spontaneously on a substrate upon exposure to a surfactant solution (Fig. 1).[8] The principal driving force for formation of these films is specific interactions between the surfactant head group and the substrate surface. Provided these interactions are strong, SAMs form stable films. Depending on the structure of the surfactant, these films can be disordered (liquid-like) or well-packed, resembling the organization of crystals (Fig. 2a,b). The degree of order in monolayers is a product of many factors, including geometric considerations, electrostatic and dipole–dipole interactions within the monolayers, affinity of the head group of the surfactant to the surface, etc. For instance, gold–thiol monolayers (vide infra) form well-packed, quasi-crystalline structures if the tail group is just a long alkane chain.[9] Incor-

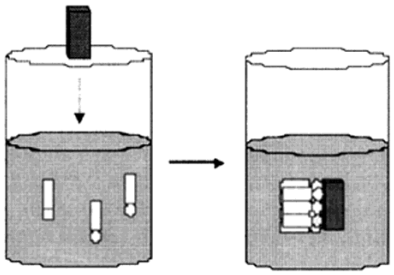


Fig. 1. Exposure of a substrate to a surfactant solution leads to formation of a SAM. The principal driving force for SAM formation is the affinity of surfactant head groups for the surface of the support.

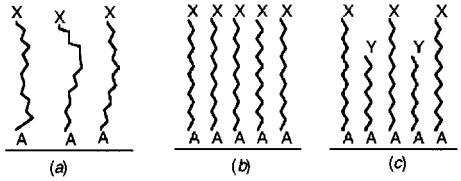


Fig. 2. Disordered (a), well-packed (b), and mixed (c) SAMs. A is the head group, and X and Y are tail groups.

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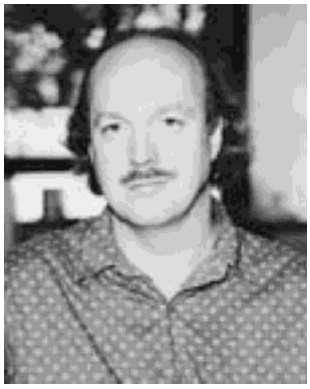
poration of bulky or charged (e.g., quaternary ammonium[14]) groups in the monolayers disrupts the order due to steric/electrostatic repulsion. The presence of polar groups (e.g., sulfones[15]) sometimes enhances order because of dipole–dipole interactions.

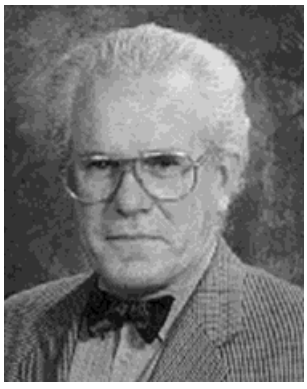
Virtually any functional group can be introduced in these monolayers as a tail group, and this ability to precisely control surface composition makes them an invaluable tool for studying interfacial reactions. Co-adsorption of two different types of surfactants leads to formation of a mixed monolayer (Fig. 2c), thus enhancing control over surface composition. SAMs can also be prepared on highly curved surfaces, such as colloids, which makes it possible to use conventional analytical techniques for characterization.[16]

Two families of SAMs have received the most attention. The first is based on the reaction of trichloro- or trialkoxysilanes with a hydroxylated silicon surface,[17] and the second, conveniently prepared by exposure of gold surfaces to a thiol or disulfide solution, relies on the strength of sulfur–gold interactions[18,19] (Fig. 3). Countless studies have been performed in the last decade that involve chemical modification of such monolayers. However, this review is not intended to cover all available literature comprehensively. Instead, after a brief general discussion of monolayer chemistry we will focus on the unique features of monolayer reactions that have no analogues in solution chemistry. The concluding part of this review will be devoted to reactivity patterns observed in monolayer reactions.

Victor Chechik received his Dipl. Chem. (M.Sc.) and Cand. Sci. (Ph.D.) in St. Petersburg, Russia. In 1995 he moved to the University of Sheffield (UK) for a three year postdoctoral fellowship with Prof. C J. M. Stirling, where he studied reactivity in organized molecular films. After another period of postdoctoral research with Prof. R. M. Crooks (Texas A&M University, USA) on dendrimer-encapsulated metal nanoparticles, he was appointed an Astra-Zeneca Lecturer in Physical Organic Chemistry at the University of York (UK). Research in his group is focused on unique properties of supramolecular assemblies; for example, chemical reactivity in dendrimers and ordered molecular films, selective permeability of monomolecular membranes, and design of functional self-assembled materials.



Richard M. Crooks received his undergraduate degree in chemistry from the University of Illinois in Urbana, Illinois (USA). In 1989 he earned a doctoral degree in electrochemistry with Prof. Allen J. Bard at the University of Texas in Austin, Texas. Following a two-year postdoctoral appointment at MIT with Prof. Mark S. Wrighton, he began his independent career at the University of New Mexico. In 1993, he moved to Texas A&M University in College Station, Texas, where he is now professor of chemistry. Dr. Crooks has broad interests that include chemical and biological sensors, chemical reactions in microfluidic devices, nanomaterials, physical electrochemistry, catalysis and electrocatalysis, and the molecular basis of adhesion and adhesive interactions. He has published more than 100 peer-reviewed research articles and numerous reviews and book chapters.



Charles Stirling is a physical organic chemist now specializing in the formation, structure, and reactivity of very thin organic films. He took the B.Sc. degree of the University of St. Andrews and a Ph.D. on homolytic aromatic substitution with Donald Hey at King's College London. After post-docs at Porton Down and Edinburgh he joined the Faculty at Queen's Belfast and then King's College London before taking the Chair of Organic Chemistry at the University of Wales Bangor in 1969. Since 1990 he has been Professor at Sheffield. He holds the D.Sc. degree of the University of London, was elected FRS in 1986, and received the RSC Award in Organic Reaction Mechanisms and a Millennium Award in 1999. He holds Honorary doctorates from the Universities of St. Andrews and Aix-Marseille.

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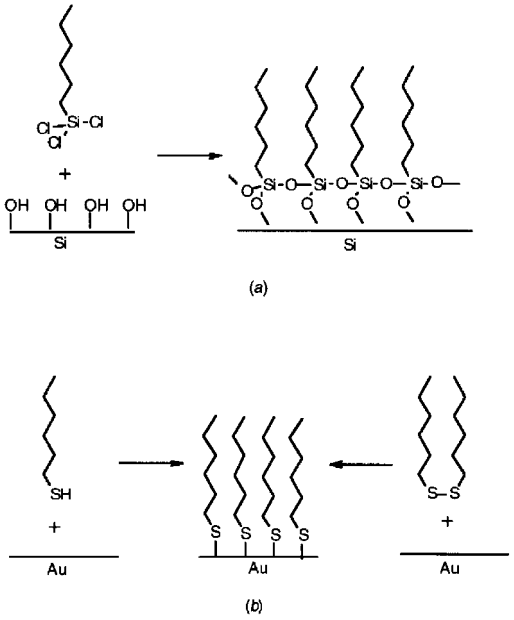
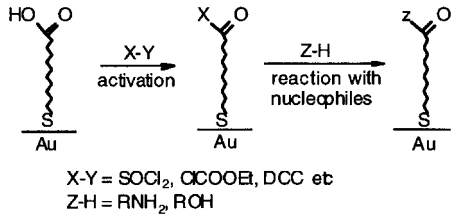


Fig. 3. Formation of trichlorosilane–SiO_2 (a) and gold–thiol (b) monolayers.

2. General Reactions in Monolayers

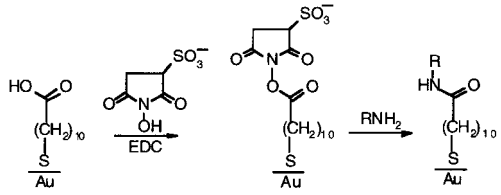
Simple organic reactions such as nucleophilic substitution,[20,21] free radical halogenation,[22] oxidation/reduction,[23,24] etc. can be performed on surfaces in a manner similar to bulk media. In practice, however, most synthetically useful surface reactions are performed on monolayers terminated by carboxyl, amino, or hydroxyl groups. This is mainly due to surface purification issues. While any soluble contaminants can be easily removed from surfaces by rinsing off the solid support, monolayers cannot be purified from by-products or unreacted materials that are attached to the surface. This problem becomes especially acute when monolayers are subjected to a number of successive reactions, as formation of surface-attached by-products at each step leads to accumulation of defects. Only highly specific reactions, which result in a quantitative transformation of functional groups, should be used for clean surface modification. The situation is partly alleviated by the fact that, because of a very small amount of surface-immobilized material, bulk reagents are always present in large excess with respect to the monolayer. These problems are similar to those of solid-phase peptide synthesis, and not surprisingly many of the peptide chemistry motifs are frequently applied to monolayer transformations.

Terminal carboxyl groups in monolayers can be activated by treatment with carbodiimides such as dicyclohexylcarbodiimide (DCC) or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC).[25] Alternatively, conversion to a mixed anhydride can be effected by reaction of a carboxyl-terminated film with ethyl chloroformate.[26] Exposure of the surface to gaseous $SOCl_2$ has been reported to produce carboxyl chloride groups.[27,28] These activated acid derivatives then react smoothly with alcohols or amines to form esters or amides (Scheme 1).



Scheme 1.

Monolayers functionalized with active esters can be prepared by direct deposition of the appropriate thiol/disulfide or by EDC-mediated coupling of acid-terminated films with *N*-hydroxysulfosuccinimide.[29] These structures can be conveniently used for attaching primary amines to the surfaces with very high yield. Similar reactions can also be performed with terminal carboxyl groups of thiol-protected gold colloids, thus enabling attachment of different functional groups to the surfaces of colloids (see Scheme 2).[30]



Scheme 2.

In a similar approach, monolayers with terminal amine groups were reported to react with acylating reagents such as active esters,[31,32] acid chlorides,[33] or quinones.[34] Some studies, however, showed diminished reactivity of the amine groups in the monolayers (vide infra). Monolayers with terminal hydroxyl groups can be acylated by reaction with acid chlorides or anhydrides to produce esters.[35]

Monolayers can also be used to catalyze bulk reactions. Mrksich and co-workers have prepared monolayers of a chiral cinchona alkaloid on the surface of gold colloids. These materials, mixed with OsO_4, showed catalytic activity in Sharpless asymmetric dihydroxylation of olefins.[36] A number of polymerization catalysts incorporated into SAMs will be discussed later.

3. Reactions in the Absence of Solvents

A unique property of SAMs is that the tail groups are generally in contact with the ambient environment. They do not need solvent to become accessible to external reagents, and this makes it possible to study reactions between monolayers and gas-phase reagents. Such solvent-less procedures are especially attractive for technological applications.

Many reactions were found to efficiently proceed in the gas phase. Hydroxy- and amine-terminated monolayers react with volatile silyl chlorides to produce silyl ethers and silylamines, respectively.[37,38] Hydroxyl terminal groups are quantitatively converted to trifluoroacetates by exposure to the vapors of trifluoroacetic anhydride. Reaction with perfluoropropionic and

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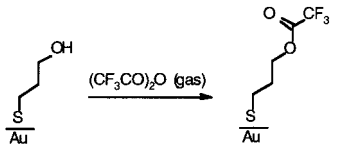
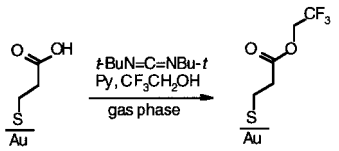
perfluorobutyric anhydrides proceeded similarly, but with ca. 80 % yield. Very high contact angles (>120°) of perfluoro-terminated layers demonstrated formation of esters (see Scheme 3).[39]



Scheme 3.

Interestingly, even carbodiimide coupling can be performed in the gas phase by direct exposure of the acid-terminated monolayer to the mixed vapor of a carbodiimide, an alcohol, and a base (pyridine, see Scheme 4). The reaction does not go to completion; yields are ca. 60 %.[39] Achieving high yields in surface reactions is very important, as surface-attached by-products cannot be removed from the monolayers (vide supra); besides, most analytical methods provide only rough estimates of submonolayer coverage, which makes it difficult to accurately determine yields.



Scheme 4.

Reactivity of OH-terminated monolayers towards acylating reagents in solution and the gas phase was found to be quite similar, although in some instances gas-phase processes also did not lead to complete functionalization.[40,41] The viability of gas-phase reactions makes them promising for industrial fabrication of mono- and multilayers.

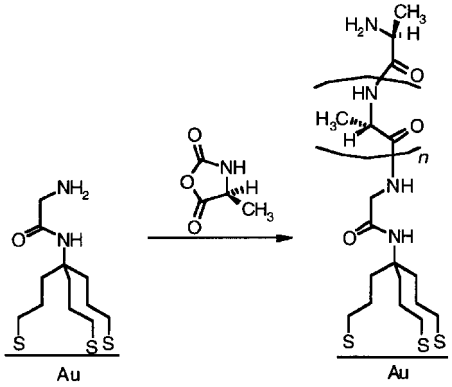
Some reactions, however, do not take place in the gas phase. Exposure of hydroxy- and carboxy-terminated monolayers to the vapors of phenyl isocyanate at pressures up to 60 000 L (1 L = 10^{-6} torr) did not result in any reaction. However, successive cooling of the monolayers to 130 K to condense multilayers of phenyl isocyanate and subsequent heating to 290 K results in almost quantitative formation of mixed anhydride and urethane groups from the acid- and alcohol-terminated films, respectively.[42]

Another interesting example of solvent-less chemistry is based on the microcontact printing techniques.[43] This strategy involves pressing a patterned polymeric stamp inked with a reagent, against the surface. Provided this reagent has a strong affinity for the surface, it is transferred from the stamp to the surface to form a molecular film only in the contact area. This approach was recently found to be applicable to chemical reactions. A stamp inked with an amine was pressed against a self-assembled monolayer with an active ester terminal group. This simple procedure effected immobilization of the amine on the surface via formation of the amide.[44]

4. Growth of Surface-Attached Polymers

Polymer brushes attached to the surfaces find numerous applications in the areas of chemical sensing, nonlinear optical materials, corrosion inhibition, friction and wear, adhesion, and other technologies. SAMs are ideally suited as scaffolds for grafting polymers onto surfaces because of their very high density of the functional groups, small number of defects, and well-defined structure.

Several strategies for growing polymers from SAM surfaces have recently been reported. Ruhe and co-workers[45–47] incorporated azo initiators in the monolayers. Thermal decomposition of these initiators leads to formation of free radicals on the surface, which capture styrene or similar monomers from solution, giving rise to a growing surface-tethered polymer. Alternatively, amine-terminated monolayers initiate polymerization of *N*-carboxyanhydrides of amino acids, thus making it possible to construct orientated layers of polypeptides up to 100 nm thick.[48,49] Polymer films of polypeptides can also be prepared by gas-phase polymerization of *N*-carboxyanhydrides on amine-terminated monolayer surfaces (see Scheme 5).[50]



Scheme 5.

Living polymerization, which provides better control over monodispersity and side reactions during polymer growth, has also been performed on SAMs. Wirth and co-workers prepared a benzyl chloride–terminated monolayer on silicon, and performed a $Cu(bpy)_2Cl$-catalyzed polymerization of acrylamide on this surface.[51–53] The resulting polymer layer had a roughness only 0.1 nm greater than that of the underlying silicon substrate. This is six times smaller than the roughness of the polyacrylamide layer synthesized by conventional surface-initiated radical polymerization. Recently, Sokolov and co-workers have incorporated a lithium biphenyl derivative in gold–thiol SAMs to initiate anionic polymerization of styrene.[54]

Grubbs and co-workers used the ring-opening metathesis polymerization (ROMP) strategy to achieve a living polymerization on the SAM surface. Thiol **1** was adsorbed on the gold surface, and exposure to a ruthenium catalyst **2** and an appropriate monomer (e.g., **3**) started polymerization. The length of

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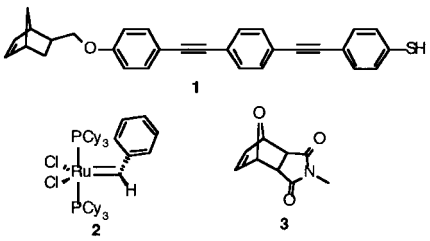
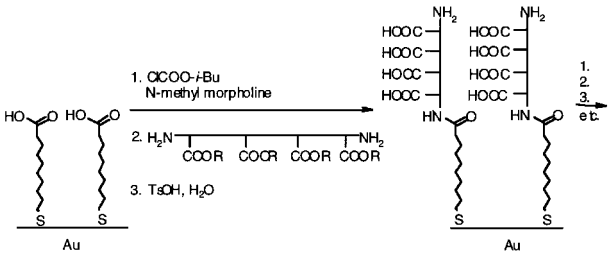


the polymer chains can be easily controlled by varying the exposure time.[55]

An interesting approach to prevent accumulation of defects due to incomplete polymerization on monolayer surfaces relies on grafting of a hyperbranched polymer to the SAMs. In this method, a monomer molecule has at least one branching point so that every polymerization step multiplies the number of reactive sites. Crooks, Bergbreiter, and co-workers used amino-terminated oligomers of protected acrylic acid as a branching unit to grow polymers on SAMs (see Scheme 6).[56,57] Even though the yields of the reactions are likely to be low, this method always results in dense polymer films due to the large number of branching points incorporated within the film. These polymeric films find applications for sensors, tissue engineering and corrosion inhibition.[58]



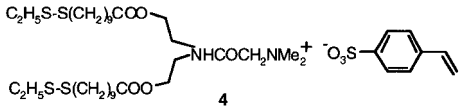
Scheme 6.

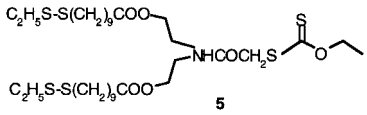
In a related approach, polyamidoamine (PAMAM) dendrimers were synthesized on surfaces using the same chemistry as in bulk dendrimer preparations.[59] Hyperbranched polymer films can also be grown on patterned monolayers using oligoacrylic acid chemistry (vide supra), thus enabling preparation of polymeric features on the micrometer scale.[60] Such patterned polymers can subsequently be capped with a conformal coating of a second polymer.[61] Abbott and co-workers prepared patterned polymeric films by polymerization of ε-caprolactone. Polymerization was initiated by terminal hydroxy groups of the patterned monolayer.[62]

5. "Intrafilm" Reactions

The proximity of adjacent chains in SAMs makes it possible to perform chemical reactions between them, a phenomenon conceptually similar to intramolecular reactions in solution chemistry. An obvious type of such reactions is polymerization of surface-attached unsaturated compounds. For instance, mercaptomethyl styrene was photopolymerized on a gold surface, all monomer being consumed during reaction as evidenced from Raman spectroscopy data.[63]

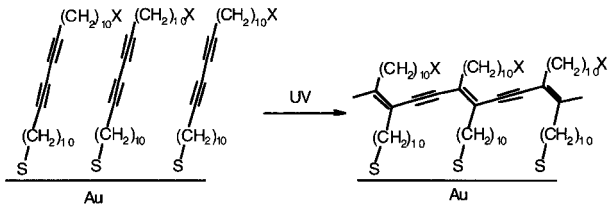
In an elegant experiment, Niwa and co-workers prepared a mixed monolayer by codepositing asymmetrical disulfides **4** and **5** in the ratio 200:1. The xanthate group in disulfide **5** serves as a photoinitiator. Irradiation of the film results in the polymerization of the styrene moieties as seen by cyclic voltammetry. Virtually no polymerization occurs in the single-component monolayer of **4**, which proves the importance of having a photoinitiator in the film.[64,65]





Formation of interchain chemical bonds can also be achieved by electrochemical polymerization of appropriate adsorbates. For example, *N*-pyrrolylalkanethiols can be adsorbed on the surface of a gold electrode. Scanning to +1.3 V in propylene carbonate results in the oxidation of the pyrrole groups to the corresponding radical cations, which then triggers polymerization, similar to bulk polymerization.[66,67] Oxidation rather than polymerization of the same monolayer was observed in acetonitrile.[68]

Diacetylenes containing terminal mercapto groups form monolayers on the gold surface. Irradiation of these monolayers with ultraviolet (UV) light causes polymerization.[69,70] This is a remarkable observation, as polymerization of diacetylenes is only observed in well-ordered systems such as crystals or micelles. The fact that monolayers of diacetylenes can polymerize to give a so-called blue form, characterized by a prolonged conjugation length,[71] indicates a high degree of lateral order in these monolayers. Multilayers of diacetylenes, covalently linked by thioesters, are also sufficiently well-ordered to polymerize.[72] Polymerization of diacetylene and acetylene derivatives on the silica supports have also been reported.[73] Interestingly, even diacetylene monolayers deposited on relatively rough surfaces, such as gold colloids, can be polymerized (see Scheme 7).[74]



Scheme 7.

Another type of polymerization reaction between adjacent chains combines the chemistry of gold–thiol and silane monolayers. Hydrolysis of the monolayers of (3-mercaptopropyl)-

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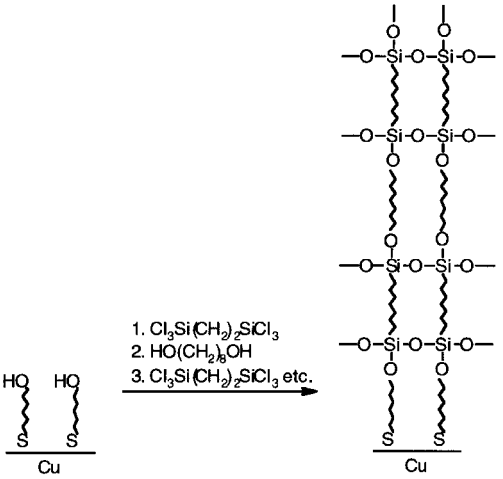
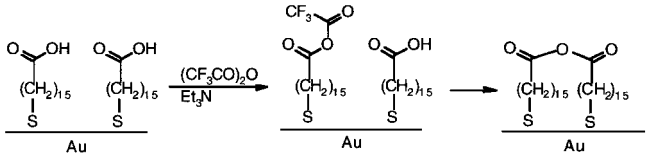
trimethoxysilane, $HS(CH_2)_3Si(OMe)_3$, assembled on a gold surface produces a siloxane polymer. Although vibrational spectroscopy shows the existence of a small number of Si–OH groups on the surface after hydrolysis, the film is highly cross-linked via formation of Si–O–Si bonds with adjacent siloxane groups in the monolayer. The authors estimate that only ca. 3–4 % of the initial monolayer $Si–O–CH_3$ groups produced Si–OH bonds after hydrolysis.[75,76] 3-(Mercaptopropyl)trialkoxysilanes were also deposited and polymerized on the surface of gold and silver colloids to produce silica-coated nanometer-sized metal particles.[77–79]

Repetitive deposition of 1,2-bis(trichlorosilyl)ethane and 1,8-octanediol on the hydroxy-terminated surface leads to formation of multilayers possessing horizontal evenly spaced cross-linked planes of siloxane polymer (see Scheme 8). These coatings were suggested for corrosion inhibition of copper.[80–82]



Scheme 8.

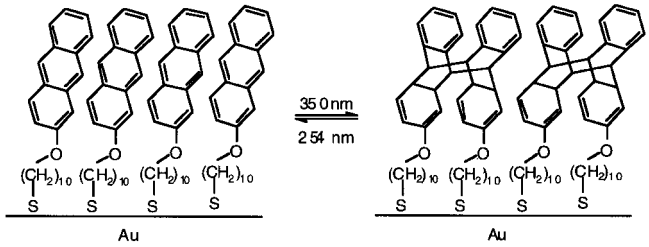
Apart from polymerization, many other reactions can be performed between adjacent chains in monolayers. An elegant recent study described formation of an interchain anhydride from the monolayer of mercaptohexadecanoic acid. Reaction with trifluoroacetic anhydride in dimethylformamide (DMF) in the presence of triethylamine probably leads first to formation of a mixed anhydride intermediate, which then reacts with the adjacent carboxylate group to produce the interchain product (see Scheme 9).



Scheme 9.

Formation of the anhydride was unambiguously shown with Fourier transform infrared (FTIR) spectroscopy. Additionally, no fluorine was detected by X-ray photoelectron spectroscopy (XPS).[83] The monolayer anhydride is quite stable and can survive treatment with water for at least 1–2 min. It can further react with aliphatic amines. The reaction is rapid and quantitative; the ratio of amide and acid in the resultant monolayer is ca. 1:1.

Monolayers of anthracene modified with ω-mercaptoalkane chains undergo photodimerization upon irradiation at 350 nm. This process is confirmed by fluorescence and FTIR measurements. The reaction can be reversed by irradiation at 254 nm, similar to the same process in bulk media. In the reverse reaction, photodecomposition results in a partial loss of anthracene (see Scheme 10).[84]



Scheme 10.

A similar reversible formation of a photodimer from an alkanethiol-substituted coumarin monolayer is described by Fox and co-workers.[85] Irradiation at 350 and 254 nm effects dimerization and dissociation of the dimer, respectively.

6. Photo- and Electrochemistry

Apart from initiating radical polymerizations (vide supra), irradiation of monolayers offers an interesting opportunity to change the orientation of functional groups in the monolayers without subjecting them to the action of external reagents. Azobenzene derivatives undergo cis–trans isomerization when irradiated with light of appropriate wavelength. Such a transformation is sterically demanding, and therefore prohibited in well-packed monolayers. However, loosely packed mixed monolayers, or monolayers prepared on the curved surfaces of gold colloids, permit photoswitching.[86]

Monolayers of *cis*- and *trans*-cyanostilbenes derivatized with a mercaptoalkane chain have different wetting properties. *cis*-Stilbene has a 120° bend between aromatic rings and the surface of its monolayer is probably dominated by the aromatic group; the contact angle with water is 60°. The surface of the linear *trans*-monolayer is dominated by the hydrophilic nitrile group and has a lower contact angle (45°). Irradiation of the monolayer of *cis*-isomer results in decrease of the contact angle to ca. 45°, which implies photoinduced cis–trans isomerization (see Scheme 11). Interestingly, condensation of water droplets on the surface of partially irradiated monolayer makes the boundary between the pristine and irradiated parts visible to the naked eye.[87]

Photo-induced transformations could also be used to pattern monolayers so that detectable chemical modification occurs only in the irradiated area. For example, UV irradiation of a monolayer terminated with aryl azide in the presence of amines results in incorporation of the amines in the monolayer as aze-

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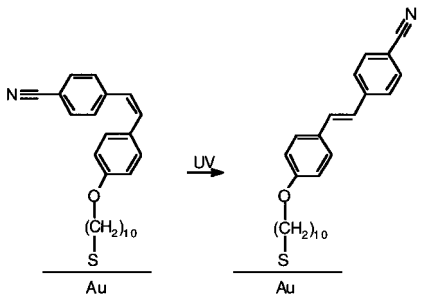

Scheme 11.

pines and hydrazines. No surface attachment takes place without irradiation.[88–91] In a related approach, Workentin and Jocys prepared a monolayer terminated with diazoketone groups. A photo-initiated Wolf rearrangement, in the presence of methanol as a trap for the ketene intermediate, converts the terminal groups into esters.[92] Dressick and co-workers incorporated benzyl chloride chromophores into monolayers on Si surface. Irradiation of these functions at 193 nm converts chloromethyl groups into aldehydes. Metallic Ni features can be created on these selectively irradiated chlorobenzyl-derivatized monolayers in a few simple steps.[93] Another photopatterning technique relies on the oxidation of the thiol head groups of the monolayer upon irradiation with UV light in the presence of air. Rinsing the monolayer with the appropriate solvent achieves removal of the oxidized species in the irradiated area.[94,95] In a related approach, Crooks and co-workers used photopatterning to polymerize diacetylene groups in monolayers. Unpolymerized molecules in the masked regions can then be selectively removed from the surface by electrochemical desorption.[96] These examples illustrate exciting prospects for development of photolithography on the molecular scale.

Thiol monolayers can be conveniently prepared on the surface of gold electrodes, and therefore electrochemical methods offer excellent opportunities for studying or chemically modifying SAMs. The discussion of electrochemistry in monolayers, however, goes beyond the scope of this review; the readers are referred to the excellent review by Finklea.[97]

7. Non-Covalent Interactions

Apart from conventional chemical reactions, numerous non-covalent interactions have been studied in SAMs. The scope of such studies has ranged from simple electrostatic,[98] hydrophobic,[99] or hydrogen bond–driven adsorption[100,101] through molecular recognition phenomena[102] to adsorption of cells and proteins.[13] Unfortunately, space limitations do not allow us to explore this topic in detail. The reader is referred to a review on molecular recognition in SAMs.[103] Discussion of non-covalent interactions in SAMs can also be found in a recent review.[104]

8. Reactivity Issues

Thanks to well-defined structure, low defect density, and chemical stability, SAMs offer unique opportunities to probe the mechanistic details of reactions at interfaces. This largely unexplored area is of great fundamental and applied interest, e.g., because most biological or heterogeneously catalyzed reactions occur at interfaces. One could imagine several factors affecting the reactivity of functional groups placed in the ordered monolayer environment.

- *"Solvent" Effects*: Solvation of functional groups embedded in a monolayer may differ from the bulk. The local concentration of dissolved reagents near the surface can also be different. This is especially true for charged surfaces.
- *"Steric" Effects*: Sterically demanding reactions or reactions requiring penetration of a reagent through a well-packed monolayer may be hindered at surfaces. On the other hand, enforced favorable orientation or conformation of a monolayer-embedded functional group could promote certain reactions.
- *"Electronic" and Anchimeric Effects*: Functional groups adjacent to the reaction center in the monolayer may affect reactivity through field effects, hydrogen bonding, or anchimeric participation.

In this section, we make some general observations about structure–reactivity relationships in monolayers based on a careful analysis of literature data.

8.1. "Solvent Effects" in Monolayers: Surface p$K_{1/2}$ Values

The deprotonation of the surface functional groups (such as COOH, PO_3H_2, NH_3^+) changes the wetting properties of the surface. In general, ionized surfaces are more hydrophilic than their neutral counterparts. A plot of the contact angle of an ionizable surface vs. pH therefore resembles an ordinary titration curve. However, it is usually broadened. The above procedure of measuring pH dependence of the surface wettability is known as "contact-angle titration" and provides the simplest method of determining the acidity of the surface. Surface p$K_{1/2}$ is often defined as the pH of bulk solution at which surfaces are half-ionized.[105]

Table 1 lists some ionization properties of functionalized monolayers along with the corresponding bulk values.[106–123] It can be seen that use of different methods to estimate ionization properties of the same monolayers gives somewhat different results. Some conclusions can, however, be reached. In general, acids and bases on the surface become less acidic and less basic, respectively. The difference between surface p$K_{1/2}$ and bulk pK_a values is usually 2–5 pK_a units. This conclusion is consistent with the data available for other solid–liquid interfaces. Three examples contradict the above trend (Table 1,

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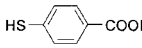
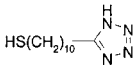
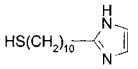
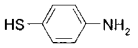
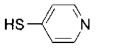
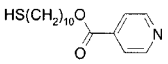
Table 1. Bulk vs. monolayer p$K_{1/2}$ values.

No.	Thiol [a]	Surface p$K_{1/2}$	Bulk p$K_{1/2}$	Reference
Acids				
1	$HS(CH_2)_{15}COOH$	8.0, 6.4	4.5	[106,107]
2	$HS(CH_2)_{10}COOH$	5.5-8.5	4.5	[107–111]
3	$HS(CH_2)_7COOH$	8.0	4.5	[112]
4	$HS(CH_2)_5COOH$	6.0	4.5	[107]
5	$HS(CH_2)_2COOH$	5.8, 8.0	4.5	[107,113]
6		7	5.5	[114]
7	$Cl_3Si(CH_2)_{16}COOH$ [a]	7.5	4.5	[115]
8	$HS(CH_2)_{10}PO_3H_2$	7.0	2.8	[116]
9	$HS(CH_2)_{11}B(OH)_2$	ca. 12	10.7	[117,118]
10		7.5	5.5	[116]
Bases				
11		3.0	8.0	[116]
12		6.9	4.3	[119]
13		4.6, 3.9	1.4	[119,120]
14		5.5	3.26	[121]
15	$(RO)_3Si(CH_2)_3NH_2$ [a]	4.5	10.5	[109]
16	$(EtO)_3Si(CH_2)_3NH_2$ [a]	7.4-7.6	10.5	[122]
17	$Cl_3Si(CH_2)_4NH_2$ [a]	6-8	10.5	[123]

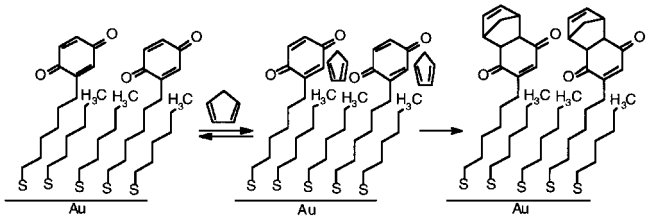
[a] Entry 7 and the last three entries are for alkylsiloxane monolayers on the surface of oxidized Si wafers. All other examples are gold–thiol monolayers.

numbers 12–14). It can be argued, however, that in the two former cases, the electrode potential used could significantly influence surface p$K_{1/2}$ values. Besides, deprotonation of the thiol group during monolayer formation is likely to affect the basicity of the conjugated nitrogen. Interactions between nitrogen functionalities and the surface, which might have altered the surface p$K_{1/2}$ values, also cannot be ruled out.[116]

Ionization of surfaces leads to accumulation of charge and formation of a double layer at the surface. The local concentration of ions in the double layer is known to be different from the bulk solution and can be estimated from the Gouy–Chapman–Stern model. The important conclusion is that the pH in the vicinity of a monolayer is different from the bulk solution due to the presence of the double layer. Thus, the apparent reactivity of the charged surfaces (e.g., their p$K_{1/2}$ values) is inherently different from bulk because of the very existence of the double layer.[110,111,124]

Other factors probably also affect surface acidity. Accumulation of a charge at an interface leads to unfavorable interactions between incipient ionized groups. Contact-angle titration of mixed monolayers of ionizable compounds and appropriate alkanethiols showed, however, that the acid groups become less acidic with a decreased amount of acidic groups in the monolayer. Similarly, basic groups become less basic in the mixed monolayers with alkanethiols.[116] This is in contrast with the expectations that the smaller density of the charged groups in mixed monolayers would lead to the increase of the strength of acid groups. Other reasons that may be responsible for the shift of surface p$K_{1/2}$ values relative to their bulk counterparts include a low interfacial dielectric constant,[116,125,126] the presence of a low dielectric permittivity region surrounding the acidic/basic groups, and changes in the number of degrees of freedom for the immobilized species.[127] Formation of hydrogen bonds between adjacent acid or base groups in the monolayers may also have some effect on their ionization properties,[112] although this effect should decrease in mixed monolayers with alkanethiols.

Mrksich and co-workers studied a Diels–Alder reaction between surface-attached quinone and cyclopentadiene. They found substantial deviations from the second-order kinetics for reactions at hydrophobic surfaces. This led to the suggestion that the diene partitions between the monolayer and the bulk solvent, thus changing its local concentration in the vicinity of the reaction center (see Scheme 12). This model gave an excellent fit to the experimental data.[128,129]



Scheme 12.

To summarize, reactive SAMs are probably best described as a separate solvent phase in which reactions occur. Bulk reactants can partition into this phase, creating local concentrations different from the bulk solution. The acidity scale in SAMs is also different.

8.2. "Steric" Effects in Monolayers

Several reports in the literature have described significant acceleration of reaction rates in monolayers. Such increases in reactivity are usually attributed to either enforced juxtaposition of the reactive functional groups in the ordered environment, or to the favorable orientation of the reactive group. For example, Nakahara and co-workers found that long-chain alkane esters of amino acids polycondense unexpectedly rapidly at the air–water interface, probably because of the close proximity of the amino and ester groups in the monolayer.[130]

$$2n\,NH_2{-}CHR{-}COOR' \longrightarrow [{-}NH{-}CHR{-}CONH{-}CHR{-}CO{-}]_n \qquad (1)$$

Recently, significantly enhanced catalytic activity of a Rh complex used for hydrogenation of C=O bonds was reported

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in Langmuir–Blodgett films. The enforced favorable orientation of the complex within the film is thought to be responsible for the increased reactivity.[131] Similarly, Tremel and co-workers prepared a Ru catalyst on the SAM surface and studied ROMP of norbornene initiated by this catalyst. They found much higher turnover frequencies for the surface-bound Ru catalyst compared to the same catalyst in bulk solution.[132] This phenomenon is tentatively attributed to the favorable orientation of the Ru species, which facilitates their interactions with the growing polymer chain.

Most mechanistic studies in SAMs, however, report diminished reactivity (vide infra), due to partially blocked access of an external reagent to the monolayer-embedded reaction center.

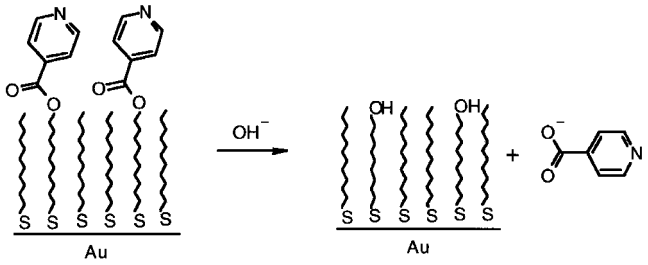
Houseman and Mrksich studied enzymatic glucosylation of *N*-acetylglucosamine immobilized in mixed gold–thiol monolayers. They found that the extent of reaction drops dramatically if the surface concentration of *N*-acetylglucosamine is higher than a certain threshold. These low yields at high coverage are probably due to steric crowding at the surface, which inhibits the enzymatic reaction.[133]

Murray and co-workers studied S_N2 reactivity in monolayers deposited on gold colloids as a function of size of the incoming nucleophile and steric crowding around reaction center. They found that steric effects are important in these reactions, and that the reaction rate is substantially diminished with bulky nucleophiles or in short-chain monolayers on gold colloids, where the density of the reaction centers is expected to be the highest.[134]

Reactivity of surface-attached esters towards base-catalyzed hydrolysis was studied by Stirling and co-workers. They showed that well-packed monolayers of aliphatic esters with the carbonyl group buried well below the surface [$HS(CH_2)_{10}OCO(CH_2)_8CH_3$] are very resistant towards hydrolysis. At the same time esters having their carbonyl function close to the monolayer surface [$HS(CH_2)_{10}OCOCH_3$], hydrolyze more rapidly.[135] In such systems, where access of an external reagent is blocked, the reaction is thought to start at defect sites and domain boundaries, which then grow and coalesce as the reaction proceeds. Rate plots of such reactions show an initial induction period (slow reaction at scarce defect sites) followed by a more rapid process, as the blocking groups are removed from the monolayer by increased conversion.[136]

The above results are consistent with those obtained by van Ryswyk and co-workers. They prepared mixed monolayers of isonicotinate esters and alkanethiols. By varying the relative amount of the alkanethiol and the ester in the deposition solution it is possible to control the surface density of the isonicotinate ester groups. Monolayers of pure ester hydrolyze extremely slowly, probably because of the blocked access to the carbonyl functional group (see Scheme 13).[121]

Mixed monolayers of the isonicotinate ester and nonanethiol that have ca. 25 % of the surface covered with isonicotinate groups are, however, susceptible to hydroxide-mediated hydrolysis. Kinetic plots of this reaction showed



Scheme 13.

clean first-order behavior, implying that access of hydroxide to the reaction center in disordered layers is not hindered.

Similar results were obtained by Chechik and Stirling in the study of aminolysis of surface-confined *p*-nitrophenyl esters. They found that disordered monolayers containing carbonyl groups buried at different levels within the monolayer react with amines at essentially the same rate; moreover, this reaction is actually faster than the corresponding process in the bulk medium. Apparently, disordered monolayers can be easily penetrated by external reagents. Faster reaction in monolayers was tentatively assigned to the higher local concentration of the amine in the vicinity of monolayer as compared to the bulk solution.[137]

Nucleophilic reactivity of amino groups in gold–thiol monolayers was reported to be significantly suppressed as compared to the bulk reactions. This effect was observed in both inter- and intramolecular reactions in monolayers.[138] Failure of the amino-terminated monolayers on the surface of gold colloids to react with isothiocyanate compounds was reported by Buining and co-workers.[77] This unusually low reactivity of the amino group can be tentatively assigned to its interactions with the gold surface.[138]

A detailed study of nucleophilic substitution reactions in silylchloride monolayers on the Si/SiO_2 surface showed results similar to those observed on the Au surface. Well-packed monolayers with Br terminal groups undergo substitution readily with small nucleophiles (such as the N_3^- ion) but with bulky nucleophiles reaction does not go to completion. A sterically undemanding reaction with tin radicals proceeded rapidly and quantitatively. The possibility of condensation between two adjacent chains in the monolayer facilitated by their close proximity, was also discussed.[21]

9. Conclusion

The containment of reactive functional groups within ordered or partially ordered arrays of molecules on surfaces opens intriguing prospects for the preparation of novel materials. Many routine organic reactions can be successfully applied to SAM surfaces. The intimate study of reactions and interactions within such films and with external reagents is sure to widen our understanding of the molecular behavior of such surfaces—an area that has not received sufficient attention from organic chemists. Enforced positioning of functional groups in SAMs has great potential for selective rate enhance-

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ment and inhibition, which may provide links to better understanding of enzymatic reactions.

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