

Self-assembled monolayers on polymer surfaces

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Abstract: The method of forming self-assembled monolayers on polymer surfaces is reviewed. It is shown that the alkylsiloxane monolayers formed on polymer surfaces are structurally similar to the analogous monolayers formed on silicon wafers. These monolayers can be post-derivatized in order to introduce a number of hydrophobic, reactive and polar functionalities, some of which may be useful model systems for studying biological interactions at surfaces.

INTRODUCTION

Self-assembly of organic molecules is a useful method for modifying systematically the chemical properties of solid surfaces in order to control their functions in such processes as wetting, adhesion, friction and biosensing to name but a few. Traditionally, inorganic surfaces have been used as supports for self-assembled monolayers (SAM)¹. By contrast, the technology of modifying the surfaces of organic polymers by SAMs is emerging only recently.^{2–6} SAMs on organic polymers may be useful in cases where the deformability of the support is needed, such is the case with implantable biomaterials that require a certain degree of mechanical flexibility. The scope of this brief review is rather limited — its primary purpose is to introduce this newly emerging technology to the researchers in biomaterials. We hope to show that the self-assembled monolayers can be prepared on organic polymer surfaces with nearly the same level of sophistication as is normally achieved with SAMs on inorganic materials.

METHODS OF PREPARING SAMS ON POLYMERIC SURFACES

Sagiv² first described the adsorption of octadecyltrichlorosilane (and various cyanine dyes) at the surfaces of stretched poly(vinyl alcohol) (PVA) and of polyethylene coated with PVA. Others⁷ have described the preparation of self-assembled multilayers using $\text{Cl}_3\text{SiOSiCl}_2\text{OSiCl}_3$ and PVA. First systematic attempt to form self-assembled monolayers on polymer surfaces was made by Whitesides *et al.*^{3–6}. So far two polymer surfaces have been examined: polyethylene and polydimethylsiloxane. The strategy to modify the surface of polyethylene involves three to four steps. In the first step, polar functionalities are introduced onto the surface of polyethylene by plasma oxidation. In the second step, a thin silicate layer is formed onto this oxidized surface by adsorption and hydrolysis of SiCl_4 . In the third step, this silicate-coated polymer surface is exposed to the vapour of alkyltrichlorosilanes to form the monolayer film. If further modification is required, an olefin functional monolayer may be

reacted with mercapto-functional organic molecules by a free radical process in order to introduce such functionalities as amine, ethylene oxide, carboxylic acid, sulphonate, etc. Formation of self-assembled monolayers on polydimethylsiloxane does not require the second step, because the exposure of the surface to an oxygen plasma readily generates a thin superficial silicate layer (<50 Å), which can be reacted to the vapour of alkyltrichlorosilanes in order to form the monolayer film.⁸

WETTING BEHAVIOUR OF SAMS SUPPORTED ON ORGANIC POLYMERS

Table 1 shows the contact angles of a polar liquid (water) and a non-polar liquid (hexadecane) on several SAM-coated PE and PDMS surfaces. These contact angles compare well with the values obtained on similar SAMs prepared on the surfaces of silicon wafer and the corresponding alkylthiols adsorbed onto gold. This similarity in the wetting behaviour indicates that the SAMs on polymer surfaces are structurally similar to those formed on inorganic substrates.

INFRARED SPECTROSCOPY OF SAMS ON PDMS

The order exhibited by the self-assembled monolayers of alkylsiloxanes adsorbed onto oxidized PDMS surfaces was examined using total internal reflection infrared spectroscopy. For long chain alkylsiloxanes (i.e. C₁₆), the positions of

the asymmetric (2919 cm⁻¹) and symmetric (2850 cm⁻¹) CH₂ stretches indicate that they are at least in a quasicrystalline state.⁵ For short chain alkylsiloxanes (i.e. C₁₀ or lower), infrared spectroscopy ($\nu_a(\text{CH}_2) = 2925 \text{ cm}^{-1}$; $\nu_s(\text{CH}_2) = 2855 \text{ cm}^{-1}$) indicates that the monolayers are in liquid-like state. The adsorbed film produced by long chain alkylsiloxanes can be made more liquid-like by decreasing the amount of surface coverage. Table 2 summarizes the IR and wettability data of hexadecylsiloxane monolayers as a function of surface coverage. With the decrease in surface coverage, the adsorbed film becomes progressively more liquid-like as indicated by the shift of the peak positions of the asymmetric and symmetric CH₂ stretches to higher wavenumbers — consequently, the wettability of these surfaces towards water and hexadecane increases on account of the increase in the concentration of higher energy -CH₂- groups at the surface.

MANIPULATION OF THE WETTABILITY OF MONOLAYER SURFACES BY VARYING THE TERMINAL FUNCTIONALITY

The surface energies of the monolayer coated polymer surfaces can be easily modified by selecting suitable terminal functional groups of the monolayer films, as was done by others¹⁰ for silane monolayers on silicon wafer. X-ray photoelectron spectroscopy⁹ of the C_{1s} region of several PDMS surfaces, which have been modified with the following silanes; Cl₃Si(CH₂)₁₀CH₃, Cl₃Si(CH₂)₂(CF₂)₇CF₃, Cl₃Si(CH₂)₁₁OCH₃, Cl₃Si

TABLE 1 Advancing and receding contact angles (degrees) of water and hexadecane on SAMs supported on various materials.

Material	Θ_a^W	Θ_r^W	Θ_a^{HD}	Θ_r^{HD}
PE[ox]/SiO ₂ /O ₃ Si(CH ₂) ₁₀ CH ₃	113	104	48	40
PE[ox]/SiO ₂ /O ₃ Si(CH ₂) ₁₀ CH = CH ₂	106	100	38	31
PDMS[ox]/O ₃ Si(CH ₂) ₁₀ CH ₃	112	103	46	45
PDMS[ox]/O ₃ Si(CH ₂) ₁₀ CH = CH ₂	104	99	36	35
Si/SiO ₂ /O ₃ Si(CH ₂) ₁₀ CH ₃	112	102	41	39
Si/SiO ₂ /O ₃ Si(CH ₂) ₁₀ CH = CH ₂	101	92	30	24
Au/S(CH ₂) ₁₀ CH ₃	115	105	48	42
Au/S(CH ₂) ₉ CH = CH ₂	107	97	39	33

Θ_a and Θ_r are the advancing and receding contact angles of water (W) and hexadecane (HD). See Ref. 6 for details.

TABLE 2 Phase states of the hexadecylalkoxysilane monolayers adsorbed on oxidized PDMS as a function of surface coverage.

Surface coverage	Phase state	$\nu_a(\text{CH}_2)$	Θ_a^W	Θ_r^W	Θ_a^{HD}	Θ_r^{HD}
100%	Solid	2919	115	100	45	44
80%	Solid-liquid	2922	114	97	40	40
70%	Liquid	2924	110	103	38	35
60%	Liquid	2924	101	92	18	16

$(\text{CH}_2)_{11}\text{OCOCH}_3$, confirmed the presence of the relevant terminal functionalities (i.e. ether, ester, etc.) on the monolayer surfaces.

Contact angles of water^{4,9} showed that the monolayer surfaces containing ether ($\Theta_a = 80^\circ$) and ester ($\Theta_r = 76^\circ$) groups are more polar than the corresponding surfaces constituted of methyl ($\Theta_a = 112^\circ$) and perfluoromethyl ($\Theta_a = 113^\circ$) groups.

CONTACT DEFORMATION EXPERIMENTS

When a curved elastic solid is brought into contact with another flat substrate, specific or non-specific interactions acting between them deform the solids mechanically. The magnitude of the deformation depends on the elasticity of the materials and the intermolecular interactions acting between them. At zero external load, the radius (a) of the contact deformation is related to the radius (R) of the semisphere according¹¹ to the following equation:

$$a^3/R^2 = 6\pi W/K \quad (1)$$

where, W is the work of adhesion and K is the bulk modulus.

For the four different monolayer coated PDMS surfaces, the contact deformations were measured by bringing small semispherical PDMS lenses in contact with flat PDMS sheets under zero loads. Table 3 shows the values of a^3/R^2 as a function of their surface chemical constitutions.

This observation provides a simple example of the conversion of a chemical signal to a mechanical response. It is interesting to note that the mechanical response is sensitive to the 3–4 Å level chemical changes of the monolayer surfaces. The changes observed here are caused by van

TABLE 3 Contact deformation and surface compositions.

System	γ_{SV}^{CA}	a^3/R^2 (μm)
-CF ₃	15.0	1.25
-CF ₃	20.6	1.51
-OCH ₃	30.8	1.89
-CO ₂ CH ₃	36.0	2.34

der Waals forces alone. For stronger specific interactions the magnitude of the response is still higher. For example, for two hydrogen bonding monolayers, the ratio a^3/R^2 is found to be about 4.25.

SELF-ASSEMBLED MONOLAYERS FORMED INSIDE POLYMER TUBES

In this section, we demonstrate that self-assembled monolayers can also be formed on objects that have complex geometries, for example the internal lumens of PDMS tubes. Using special plasma reactors,¹² the internal surfaces of polydimethylsiloxane tubes (1/8" ID) can be oxidized to generate thin silicate films, which can be reacted with the silanes in order to form self-assembled monolayers. Various types of monolayers have been prepared in this manner including one that has terminal olefins. The olefin groups can be further reacted (Scheme 1) with various mercaptans in order to introduce various polar functionalities on the monolayer surfaces.

Scheme 1

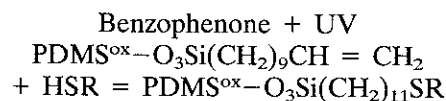


TABLE 4 Water in air contact angles (degrees) on monolayers and their derivatives formed inside PDMS tubes.

Material	Contact angle
PDMS[ox]/O ₃ Si(CH ₂) ₂ (CF ₂) ₇ CF ₃	114
PDMS[ox]/O ₃ Si(CH ₂) ₉ CH ₃	109
PDMS[ox]/O ₃ Si(CH ₂) ₁₁ CO ₂ CH ₃	66
PDMS[ox]/ O ₃ Si(CH ₂) ₁₁ S(CH ₂) ₃ (OCH ₂ CH ₂) ₃ OH	59
PDMS[ox]/ O ₃ Si(CH ₂) ₁₁ S(CH ₂) ₃ (OCH ₂ CH ₂) ₄ OH	53
PDMS[ox]/O ₃ Si(CH ₂) ₁₁ S(CH ₂) ₃ SO ₃ H	50

where, R represents various polar groups (see Table 4).

Contact angles of water on some of these derivatized monolayer surfaces are shown in Table 4.

We will report elsewhere¹² how these surface functionalized PDMS tubes can be used to study biological interactions at surfaces using an *ex-vivo* canine shunt model.

SUMMARY

In this brief review, we have presented a method of modifying the surfaces of polyethylene and polydimethylsiloxane using the technology of self-assembled alkylsiloxane monolayers. Depending upon the chain lengths, the monolayers exhibit crystalline or liquid-like phase states, which are structurally similar to the monolayers formed on silicon wafer. Using functional alkylsiloxanes or chemical derivatization can lead to the formation of monolayers of various hydrophobic, polar and reactive functionalities. Furthermore, monolayers can be formed in complex geometries, such as the internal lumens of polymer tubes, which may be suitable for studying certain types of biological interactions at surfaces.

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