Tailoring Polymer Surface Nanostructure with Surface Modifying End Groups (SMEs): Using SMEs to Create Polymer Surfaces with Covalently Bonded Self-Assembled Monolayers

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Statement of Purpose: Relative to backbone chains, polymer end groups are more mobile, in part because they are often tethered to the backbone by a single, flexible covalent bond. Their mobility allows them to diffuse from the bulk, and assemble in the polymer surface to affect surface composition. This occurs spontaneously if the presence of the end groups in the surface reduces system interfacial energy. Simple *homopathic* hydrophobic end group may diffuse to an air interface, while purely hydrophilic end groups may enrich a polymer surface when exposed to aqueous body fluids. These and more complex *Surface Modifying End Groups* (SME) can be specifically tailored to affect the biologic response of polymers used in medical devices.[1-3] To illustrate: in air, methoxy-terminated PEO SMEs on a polyether-urethane present a surface rich in hydrophobic methyl groups, but one that is devoid of methyl groups in water. This suggests an end group conformation in which hydrated PEO 'arches' project from the surface, and terminal methyl groups are buried below the outermost surface layer accessible by SFG. Other placements of hydrophobic groups and optional reactive groups on hydrophilic end groups could produce more complex surface nanostructures that may be useful in applications, including drug delivery or the binding biologically-active molecules[4]. One body of knowledge useful in the design of polymer SMEs is the literature of Self-Assembled Monolayers (SAM), e.g., from silanes, or thiol monomers on gold. In the present study we use SFG to compare the surface of a polymer with SMEs to a SAM of similar chemistry on a gold substrate. The same alkane chain length and methyl head groups (dodecane) are present on the SME *and* on the SAM thiol monomer.

Methods: The SAM was prepared by the conventional method of adsorption from solution onto a gold substrate. The polymer was synthesized by step growth polymerization using a mono-functional SME analogue of the SAM monomer (dodecanol) as a chain stopper. Films of the SME polymer were spun cast from solution onto acid cleaned quartz substrates under an activated carbon-filtered laminar flow hood, followed by air annealing at various temperatures. Both surfaces were characterized by SFG in air as described below.

Results / Discussion: Figure 1: The SFG spectra for (a) dodecane thiol SAM and (b) dodecane SMEs on Bionate® 55D polycarbonate-urethane are shown. The methyl symmetric and fermi resonance peaks of dodecane are observed at 2875 and 2935 cm^{-1}, respectively. Negative peaks are observed in the SAM spectrum due to the destructive interference of the resonant (methyl) and non-resonant (gold) signals. The bulk dodecane SME concentration in Bionate 55D is only 0.2 wt%. The methyl peaks appear at the surface after annealing at elevated temperatures. Although the methyl peaks do not

dominate the Bionate Spectra, previous results with contact angle goniometry suggest that using a higher concentration of SME will increase the concentration of dodecane at the surface. In both plots the ordinate is SFG Intensity [a.u.] and the abscissa is Frequency [cm^{-1}].
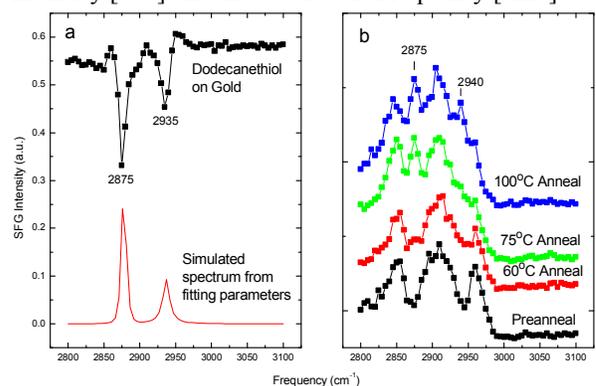
SAM development on gold is characterized by rapid formation of gold-thiol bonds and planar conformation of the alkane chains, followed by slower filling in of the final monolayer, attainment of the characteristic angle of the alkanes relative to the surface, and close packing of head groups. In SME polymers the diffusion of end groups from the bulk 'replaces' the SAM adsorption step, but it is likely that the remaining steps in developing the equilibrium surface are similar. That is, upon arriving at the air interface from the bulk, the SME may initially assume a planar conformation to maximize both the coverage by hydrophobic methylene groups, and the resulting interfacial energy reduction. As more SMEs arrive the alkanes begin to pack more closely in the surface and subsequently allow a tighter packing of very hydrophobic methyl groups, for an additional decrease in interfacial energy. The equilibrium surface structure would then be the closest possible packing of methyl head groups in the air-facing surface.

Conclusions: If additional work continues to support the similarity between fragile gold-thiol SAMs and much more robust SME polymers (or process changes enhance it), the latter could be used in many applications in which SAMs are impractical, e.g., by providing strong structural materials with surface properties of self-assembled monolayers

References: 1. J. A. Jones, et al, *Macrophage behavior on surface-modified polyurethanes,* J. Biomaterial Science Polymer Edition, Vol 15, No. 5, pp. 567 – 584, January 21, 2004
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