Self Assembly of End Group Modifications in Polyurethanes
Bob Ward, Keith McCrea, Yuan Tian, Jim Yang, Shangier Wang, James Parakka, Rob Ward, Nina Harjati
The Polymer Technology Group, Berkeley, CA 94710, www.polymeretech.com

A wealth of information about the effect of surface chemistry and structure on in vitro biological interactions is available from the study of Self Assembled Monolayers (SAMs). However, transfer of SAMs research results to applications is often problematic, in part because of the fragility of model SAM systems. A novel method of producing SAM-like surfaces on structural polymers is presented in this study in which Surface Modifying Endgroups™ (SMEs) are compared to a thiol SAM of similar chemistry on a gold substrate.

Introduction: Relative to backbone chains, polymer end groups are more mobile allowing them to diffuse from the bulk, and assemble at the polymer interface. This can produce a major change in surface composition that 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 exposed to aqueous body fluids. These and more complex SMEs can be specifically tailored to affect the biologic response of polymers used in medical devices. For example: in air, methoxy-terminated PEO SMEs on a polyether-urethane presents 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 Sum Frequency Generation (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 the delivery, or permanent binding of biologically-active molecules.

Methods: The SAM was prepared from octadecanethiol by adsorption from ethanol solution onto a gold substrate. The polymer was synthesized by continuous step growth polymerization using a mono-functional SME analogue of the SAM monomer (octodecanol) as a chain stopper: during bulk polymer synthesis the SME is appended to the polymer backbone by an isocyanate linkage. Film of the SME polymer was cast from solution on a continuous web coater with HEPA filtered oven. Both surfaces were characterized by SFG in air as described below.

Results and Discussion: SME-PCU-SME ultimate tensile properties: Strength = 62 MPa, Elong. = 400%. The SFG spectra for (a) octadecanethiol SAM and (b) octadecane SMEs on Bionate™-55D polycarbonate-urethane (PCU) are shown. The methyl symmetric and Fermi resonance peaks of octadecane are observed at 2875 and 2935 cm⁻¹, respectively. Although the bulk octadecane SME concentration in the PCU is only 0.6 wt%, the methyl peaks dominate the Bionate SFG spectrum, with only a small peak contributed by the methylenes present in the polycarbonate PCU backbone.

In both plots the ordinate is SFG Intensity [a.u.], the abscissa is Frequency [cm⁻¹]. Note: Destructive interference between the non-resonant gold signal and resonant SAM vibrational signal creates negative peaks associated with SAM vibrational modes.

Initial 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 (e.g., methyl) 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 toward surface equilibrium 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 air/polymer interfacial energy. As supported by polarized SFG measurements, 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 ‘SME polymers’ and fragile gold-thiol SAMs, SME polymers could be used in many applications in which SAMs are impractical, e.g., by providing strong structural materials with the surfaces properties of self-assembled monolayers.