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PEG Surface Modification by Thermoreversible Ligand Cleavage in Nanoparticle Composites. RICK BEYER, PHILIP COSTANZO, Army Research Laboratory — The control of surface chemistry is an increasingly important area of research in the polymer science community; a simple example of a need for controlled surface properties can be found in the need for surfaces that are resistant to bacterial growth for medical applications. In this study, we have successfully modified the surface properties of solvent cast poly(ethylene glycol) (PEG) films, triggered by exposure to an elevated environmental temperature. PEG matrices of varying molecular weights have modified with gold nanoparticles functionalized with thiol terminated, poly(styrene)-PEG block copolymer (P(S-*b*-PEG)) ligands. Gold nanoparticles approximately 15 nm in diameter were first synthesized via reduction of $HAuCl_4$ with oleyl amine. Diels-Alder chemistry was then used to create P(S-*b*-EG) ligands that, with increasing temperature, dissociate into simple thiol-terminated PS ligands and PEG oligomers. The ligand-modified gold particles were characterized via small-angle X-ray scattering and TEM. After dissociation occurs, around 90 $^\circ$C, the gold particles are suddenly functionalized with only a PS ligand and thus immiscible in the surrounding PEG matrix. The gold nanoparticles are then driven to the surface of the films, measurably denoted by a change in contact angle. After cooling below 60 $^\circ$C, the Diels-Alders linkages reform, stabilizing the film surfaces with the new morphology trapped both chemically and kinetically.

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