

PHOTOREACTIVE SURFACES AND PARTICLES. EXECUTING MOLECULAR TRANSFORMATIONS AT THE NANOMETER SCALE

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The functionalization of inorganic surfaces by molecular layers, including self-assembled monolayer, is a widely applied and important technique for the fabrication of functionalized and nanostructured materials. By conferring photoreactivity to molecular layers at surfaces, various surface properties can be adjusted by UV illumination. This includes surface polarity, optical properties as well as chemical reactivity, thus enabling follow-up reactions utilizing the photogenerated groups. In combination with lithographic patterning, 2D structures are accessible on various substrates.

It will be demonstrated how photosensitive units can be attached to inorganic surfaces utilizing thiol or trialkoxysilyl anchoring units. Exemplary photoreactions are the thiocyanate – isothiocyanate photoisomerization and the photo-Fries rearrangement, both providing new functional groups and reactivity in the irradiated zones. Follow-up reactions from the liquid phase and the gas phase, yielding 2D nanopatterns, will be reviewed.

In the second part of the presentations surface photochemistry is transferred to inorganic particles, Photoactive fillers have been designed by covalently attaching photoinitiating groups onto silica nanoparticles. A series of tri(alkoxy)silyl functionalized acylphosphine oxides and other Norrish type I photoinitiators have been synthesized and coupled to nanosilica. The modified particles were then incorporated into acrylate resins and thiol-ene resins to study the photoinitiation efficiency of the covalently bound initiators. The concept of using immobilized photoinitiators follows a general strategy towards low-migration photoinitiators as required for UV curable printing inks.

Another approach is related to the immobilization of azidophenyl units onto the surface of inorganic particles. Using this approach, these particles (e.g., silica) can be attached to the surface of chemically inert polymer films and fibres such as polyethylene and poly(ethylene terephthalate) by a photoinduced clic reaction. This paves the way towards inorganic protective layers on polymer surfaces, and also towards the tuning of properties of particle composites: the light induced attachment of nanoparticles to the matrix phase noticeably changes the mechanical properties of the composite, in particular, its brittleness.