

Synthesis

Stimuli-responsive or “smart” polymers refer to a class of macromolecules that undergo physical changes or chemical reactions upon certain stimuli such as temperature, magnetic field, pH or light. Among this class of macromolecules, light-responsive ones have gained increased attention in the design of functional materials, as they allow changes in polymers properties, on demand, and simply by light exposure. For instance, compared to other stimuli, light offers many advantages such as high temporal and spatial control of the photo-triggered reaction, and furthermore the irradiation parameters, such as light intensity, wavelength and irradiation time, can be remotely controlled and easily modulated to adequately comply with the system. For these reasons, in the last years, several photosensitive moieties were introduced in various polymer networks in order to achieve light responsive properties. Among photo-responsive molecules, ortho-nitrobenzyl ester (o-NBE) chemistry has become a common route in the design of polymer networks with photo-responsive properties. Upon UV irradiation, o-NBE groups undergo a cleavage reaction yielding carboxylic acids and o-nitrosobenzaldehyde as primary photoproducts, therefore promoting physical and chemical changes in the polymer networks in which they are applied.

In this thesis, the light responsive properties of o-NBE chemistry were exploited for the fabrication of photo-responsive polymer coatings and silica microparticles. The idea beyond each experimental contribution was to demonstrate how light triggers can be a convenient and a powerful tool for both the synthesis and the post-modification of polymer networks, ensuring high reaction yields and fast reaction rate within mild reaction conditions.

Following this purpose, monomers containing o-NBE groups and with different end functionalities, such as epoxy, vinyl and acrylate, were first synthesized and then polymerized by means of photo-triggered reaction. Once the network was formed, the photo-responsive nature of o-NBE moieties was conveniently exploited for changing bulk and surface properties of the synthesized systems.

In a first work, photo-responsive thiol-epoxy networks were prepared following a photobase-catalyzed nucleophilic ring opening reaction among epoxy monomers with photolabile o-nitrobenzyl ester (o-NBE) groups and tri-functional thiols. In order to not promote the o-NBE cleavage reaction while curing, isopropylthioxanthone derivatives were employed as photosensitizer for shifting the photoinduced curing reaction to visible light region. Once the network has been formed, the o-NBE moieties were used for a well-defined network degradation upon UV exposure. Sol-gel analysis evidenced the formation of soluble species, which were exploited to inscribe positive tone micropatterns by photolithography technique. Along with the localized tuning of network structure, the irreversible o-NBE photoreaction was exploited to change the surface wettability of the thiol-epoxy networks. The water contact angle significantly decreased upon UV exposure due to the photo-induced formation of hydrophilic cleavage products, enabling the inscription of domains with different surface wettability.

In a following work, it was proposed a novel method for the polymer coatings photopatterning, which employed a direct laser beam irradiation of the coatings surface instead of classical photomasking techniques. In this aim, photo-responsive thiol-ene polymer networks containing o-NBE moieties were first photopolymerized upon visible light irradiation, and subsequently cleaved with an UV laser beam. Compared to the commonly used photomasking techniques, direct laser beam

irradiation gave many advantages such as the formation of sharp and defined 2.5D structures, that were developed directly through laser surface ablation and without the use of harsh solvents. Along with the fabrication of dry-developable micropatterns, the chemical surface composition of the exposed areas was conveniently adjusted and different domains with a tailored content of carboxylic groups, as o-NBE reaction products, were obtained simply by modulating the laser energy dose. In a following step, those groups were activated and exploited as anchor points for attaching an Alexa-546 conjugated Protein A, showing high linearity between laser energy dose and the amount of grafted proteins. Therefore, laser writer technique combined with the synthesized light-responsive networks demonstrated to be a convenient method for the fabrication of positive tone patterns, opening also future prospective for a wide range of biosensing applications.

In a last contribution, silica microparticles with light responsive polymer brushes were synthesized. For the polymer brush synthesis, two different procedures were followed and respectively; a photo-grafting from and an amino-epoxy coupling reaction. For the photochemical grafting path, BAPO photo-initiators derivatives with alkoxy-silane ending groups were anchored onto the silanol groups of silica microparticles. Light responsive polymer brushes were then grown upon visible light irradiation, exploiting a radical mediated reaction among the BAPO surface anchored photo-initiators and a synthesized acrylate monomer with o-NBE pendant groups. In a second procedure, the photo-responsive polymer brushes were synthesized through an amino-epoxy coupling reaction among the primary amine of surface anchored trimethoxy silanes and a photo-responsive epoxy monomer containing o-NBE groups. Compared to the amino-epoxy reaction, the photochemical synthesis ensured higher grafting efficiency in terms of grafted polymer (about 3 mg/m²) versus reaction time (4 hours), employing milder reaction conditions. Once the polymer brushes were formed, the o-NBE pending groups were exploited in order to change the particles surface properties upon UV light exposure. Zeta potential measurements and XPS spectroscopy demonstrated that physical and chemical surface properties of the silica particles were successfully modified due to the formation of carboxylic acids groups. Eventually, the presence of the photo-deprotected carboxylic acids onto silica particles were confirmed by conjugating an Alexa-546 fluorescent Protein. Confocal microscopy images proved the selective anchoring of the fluorescent protein only onto the UV irradiated particles, showing how ortho-nitrobenzyl chemistry can be efficiently exploited for the fabrication of light responsive particles.