University of Fribourg/ Faculty of Science and Medicine/Adolphe Merkle Institute

Force responsive block copolymers, amphiphilic co-networks and self-assembled polymer nanoparticles

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This thesis describes the functionalization of block copolymers, amphiphilic polymer co-networks and self-assembled polymer nanoparticles with force responsive motifs for applications in sensors and controlled release systems. Anthracene-maleimide cycloadducts, spiropyrans and anthracene-β-cyclodextrin host-guest inclusion complexes were studied as potential mechanophores in these systems.
The synthesis of a heterobifunctional, mechanophore-initiator based on anthracene-maleimide cycloadducts, was achieved by two different synthesis routes. This initiator was employed for the synthesis of poly(l-lactic acid)-*b*-polystyrene in which the mechanophore sits at the junction of both blocks. The properties of the polymer in response to mechanical tests were assessed. Also, a new synthesis route was developed to make AB type block copolymers with a spiropyran motif at the junction of the blocks. The strategy involves the synthesis of a homopolymer from an indole-based atom transfer radical polymerization (ATRP) initiator followed by its modification to a spiropyran end-functionalized polymer. The spiropyran functionalized polymer is then used as a macro-initiator for the synthesis of a second block by ring opening polymerization (ROP) or for grafting to other polymers by esterification. Stimuli responsive amphiphilic co-networks of poly(ethylene glycol) and polydimethylsiloxane were also prepared by hydrosilylations reactions. The response of the spiropyran functionalized materials to photo and mechanical stimuli were tested and found to exhibit ON and OFF UV-light responsiveness over multiple cycles, still retaining over 80 % of their original activity. Furthermore, polymer nanoparticles built from the self-assembly of anthracene functionalized poly(l-lactic acid) and cyclodextrin functionalized poly(ethylene glycol) were made. These nanoparticles were loaded with enzymes and their potential to function as nanoreactors were also evaluated.

These systems open the road for the study of mechanochemical activation in asymmetrical polymeric systems. Spiropyran functionalized AB block copolymers and amphiphilic co-networks can be very useful building blocks for the preparation of bioinspired and biomimetic nanostructures, such as polymersomes and membranes with switchable permeability. Polymer nanoparticles with anthracene-β-cyclodextrin host-guest inclusion complex mechanophores may be carefully optimized to serve as nano-carriers for controlled release applications such as in drug delivery.

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