

Stimuli-Responsive Polymers with New Mechanophores

Michela Di Giannantonio

Stimuli-responsive polymers are materials with the ability to display a particular property change after an external, predefined stimulus. These materials are characterized by moieties that are integrated into the polymer via weak bonds, to which it is possible to focus the external stimuli in order to provoke a selective scission with a consequent precise physicochemical transformation.

The first project focused on the discovery that ferrocene moieties embedded in the backbone of polymers can act as mechanophores that are preferentially cleaved under mechanical stress (ultrasonication). Thus, polyurethane (PU) with randomly distributed Fc units and poly(methylacrylate)s (PMA) with a single ferrocene unit in the center were successfully synthesized. Kinetic investigations and the corresponding simulations confirmed that the polymers display favorable chain scission of the Fc mechanophore. Reactions with potassium hexacyanoferrate(II) [$K_4Fe(CN)_6$] and potassium thiocyanate, KSCN, were used to demonstrate the presence of Fe(III) through the formation of the pigment Prussian blue ($KFe(II)[Fe(III)(CN)_6]$) and the red thiocyanatoiron complex ($[Fe(SCN)_n(H_2O)_{6-n}]^{(3-n)+}$ ($n = 1-6$)), respectively.

The second part of this work focuses on the development of stimuli-responsive polymers obtained from organoboron polymers, during the NCCR exchange program in the Jäkle group. The novelty of the project lies on the development of a supramolecular polymer where a Lewis acid-Lewis base adduct is formed by the interaction of the end-functionalized organoboron polystyrene and the pyridine-containing polystyrene. This donor-acceptor interaction brings to a luminescence quenching. Depending on the functional groups connected to the boron atom, it is also possible to tune the chemical and physical properties of the material. The project just described is not concluded but promising results are obtained.

Jury:

Prof. Katharina M. Fromm (thesis supervisor)
Prof. Rachel O'Reilly (external co-examiner)
Prof. Andreas Kilbinger (internal co-examiner)
Prof. Marco Lattuada (president of the jury)