Mechanochemistry: a trial from homolytic scission to heterolytic scission

Mechanoreceptors - sensory neurons located within ligaments, tendons, muscles and skin - play an irreplaceable role in the human body. By converting mechanical stimuli into electrical signals to our brain, they give us a clear perception of the surroundings. Scientists have long attempted to mimic the function of mechanoreceptors via the use of artificial materials. Yet, the development of highly sensitive artificial systems mimicking entirely the function of mechanoreceptors remains a critical issue. For his PhD project, Bao Li developed sensory systems (mechanophores) which, upon mechanical stimulation, respond with visible changes in light emission. These artificial systems were proven to be useful for the detection of damages in polymeric systems on a microscopic scale.

Hearing, your ear drums receive an acoustic wave and transform sound into a message for the brain; similarly, when touching with fingers, your skin transfers the applied force to the brain. In both actions, mechanical forces are transformed into nervous signal via the presence of ‘mechanoreceptors’, sensory structures of our body which convert mechanical forces into electrical signals. For long, researchers have been interested in recreating artificial mechanoreceptors, via the development of materials mimicking the role of mechanoreceptors for different applications.

In this PhD project, first attempts focused on the design of the so-called ‘mechanophores’ to investigate, for example, damages in polymeric materials. Mechanophores are sensory systems capable of transforming mechanical forces into chemical reactions. Particularly, the reaction between mechanical force and mechanophores produce luminescent or fluorescent units, which can be employed to map the damage points. Two different mechanophores were employed in this work, and both were successfully employed to detect the damages in materials. Specifically, by deforming these materials faster or slower, or by changing their swelling degree, changes in light emission were observed, which provided a microscopic view of the damage of the materials.

Although multiple groups have spent much time on polymer mechanochemistry, the breakthrough to develop mechanically induced heterolytic scission under which, the reaction will produce two ions instead of two radicals in homolytic scission, has not been overcome yet. Most of researches on mechanochemistry were based on homolytic bond scission, and only few heterolytic bond scission has been reported. Therefore, a pioneering trial on mechanically induced heterolytic scission was launched. Two N-heterocyclic salts-based polymeric materials and a linear bis(phenyl)fluorene-centered polymer were synthesized and used for
the test. It, however, is unfortunate that the targeted heterolytic scission was not observed in all three systems although some bond scission took place as homolytic scission.

An inspiration to develop a system that can undergo the switch of electron spin state by mechanical force was evoked by work reporting host-guest interaction that can switch the electron spin state of diamagnetic form of reduced bis(viologen)s. A family of viologens and bis(viologen)s were prepared and their electrochemical properties were studied, suggesting dimerization takes place in bis(viologen)s systems in polar solvent because of high local concentration, and this conclusion is further supported by temperature-dependent ESR measurements. Although the temperature changes the electron spin state of the reduced bis(viologen)s, the limitation of the characterization prevent us going further to study the effect of mechanical force on switch of electron spin state.

This work shows that mechanically induced homolytic bond scission, to some extent, is easy to reach. There is, however, a long way to go on the study of mechanically induced heterolytic bond scission and its use in mechanochemistry for practical applications.