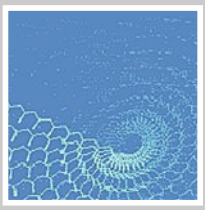
doi:10.2533/chimia.2018.902 Chimia 72 (2018) 902



Polymer and Colloid Highlights

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Metallocene as Mechanophore in Polymers Leads to Metal Ion Release & Oxidation

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Keywords: Mechanochemistry · Organometallic chemistry · Polymers · Stimuli-Responsive Polymers · Ultrasound

Stimuli-responsive polymers are high-performance materials that can change their chemical or physical properties upon exposure to mechanical force, light, heat, or another stimulus or a combination of stimuli.[1,2] This behavior can lead to materials with particular functions, for example self-healing.[3] In a recent study,[4] we investigated mechanoresponsive polymers containing ferrocene as a mechanophore. We, and in the meantime others,[5] demonstrated the mechanical breaking of the sandwich complex, and a related release of metal ions in solution (Fig. 1).

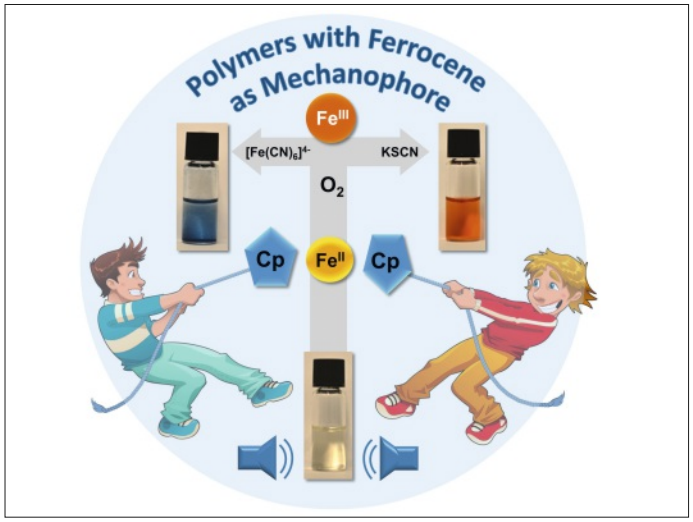

Fig. 1 Mechanoresponsive cleavage of ferrocene-containing polymers.

Although widely investigated in other contexts, ferrocene (Fc) had long remained unexplored as a mechanophore. Based on the low enthalpy of the heterolytic bond dissociation of Fc (40 kcal mol^{-1}), we surmised that this complex should be mechanically responsive and incorporated this motif as a chain-centered breakpoint in poly(methyl acrylate)s (Fc-PMAs) and in a statistically distributed manner in polyurethanes (FC-PUs). We sonicated solutions of these polymers to trigger chain cleavage reactions and studied the molar mass as a function of sonication time of Fc-containing and Fc-free reference polymers (ref-PMA, Ref-PU) to prove preferential cleavage of the Fc motifs (Fig. 2a).

For both series the ultrasound-induced decrease of the molecular weight was analyzed using a recently developed kinetic model. Two competing scission events were discerned and related to the specific scission of the Fc motifs and also non-specific bond cleavage. The data show that the rate of Fc scission is at least 10 times higher than that of unspecific chain cleavage.

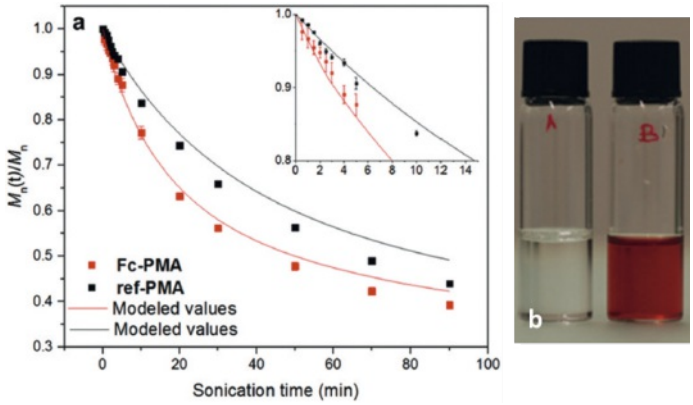

Fig. 2 a) Decrease of the normalized molecular weight ($M_n(t)/M_n$) of ref-PMA (black) and Fc-PMA (red) as a function of sonication time in THF. b) Pictures showing a Fc-PMA solution to which KSCN had been added before (left) and after (right) sonication. The red Fe-thiocyanate complex formed after sonication confirms the release of Fe ions upon sonication. Copyright (2018) Angewandte Chemie International Edition.

As further proof of the preferential cleavage of the Fc-containing polymers at the metal-organic site, the released and oxidized iron ions were detected by addition of KSCN, which generated the red $[Fe(SCN)_n(H_2O)_{6-n})]^{(3-n)+}$ complex (Fig. 2b) or reacted with $K_4[Fe(CN)_6]$ to afford Prussian blue.

Our finding that ferrocence, and possibly other metallocenes, can be used as a mechanophore in polymers that allow the mechanically induced release of metal ions has recently been confirmed by Sha *et al.*, who conducted a similar study with several other polymers and corroborated that the Fe–Cp bond is the favorite cleavage site in ultrasound-induced degradation.[5] The mechanistic studies are consistent with a heterolytic dissociation of ferrocene into Cp^- and $[CpFe]^+$.

Received: November 8, 2018

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