

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Triggered metal ion release and oxidation: Ferrocene as new mechanophore in polymers
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201803524 Angew. Chem. 10.1002/ange.201803524

Link to VoR: http://dx.doi.org/10.1002/anie.201803524 http://dx.doi.org/10.1002/ange.201803524

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Triggered metal ion release and oxidation: Ferrocene as new mechanophore in polymers

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Abstract: The introduction of mechanophores into polymers allows transducing mechanical forces into chemical reactions that can be used to impart functions such as self-healing, catalytic activity, or mechanochromic response. Here, the first example of a mechanically induced metal ion release from a polymer is reported. Ferrocene (Fc) was incorporated as an Fe-ion releasing mechanophore into poly(methyl acrylate)s (PMAs) and polyurethanes (PUs). Sonication triggered the preferential cleavage of the polymers at the Fc units over other bonds, as shown by a kinetic study of the molar mass distribution of the cleaved Fc-containing and Fc-free reference polymers. The released and oxidized Fe²⁺ ions can be detected with KSCN to generate the red-colored [Fe(SCN)_n(H₂O)_{6-n})]⁽³⁻ⁿ⁾⁺ or reacted with K₄[Fe(CN)₆] to afford Prussian blue.

The development of new stimuli-responsive polymers that have the ability to change their chemical or physical properties upon application of an external stimulus such as light.^[1] temperature.^[2] pH.^[3] mechanical force.^[4] or redox potential is receiving considerable attention.^[5] A steadily growing number of polymeric materials has been shown to respond in a useful way to mechanical stress, allowing a wide range of chemical transformations that lead, for example, to a change of color/fluorescence,^[6] the formation of proton catalysts,^[7] the generation of acids^[7-8] and bases,^[9] or the release of small molecules.^[10] Applications of such mechanoresponsive polymeric materials include sensors,^[11] self-healing materials.^[12] drug delivery,^[13] tissue engineering,^[14] and catalysis.^{[15],[16]} They involve mechanophores such as spiropyran, [17] azo, [18] epoxide,^[19] β -lactam,^[20] dioxetane,^[21] or rhodamine moieties,^[22] among others.^[23] Several examples involve non-covalent (supramolecular) motifs,^[24] or coordination bonds.^[25] Sijbesma and coworkers demonstrated the reversible mechanically induced dissociation of a Pd-phosphane bond embedded in a linear polymer using ultrasound.^[26] This result triggered the investigation of other mechanoresponsive polymers containing e.g. Ag-^[26] and Ru-carbene complexes^[15] for catalysis.^[9, 15, 26-27] Further examples include 2,6-bis(1'-methylbenzimidazolyl)-

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pyridine:Eu³⁺,^[27a] and 2,6-bis-(1'-methylbenzimidazolyl)-4-oxypyridine with a penta-(ethylene glycol) core, coordinated with transition metal (Zn^{2+}) and lanthanide (La^{3+}) ions.^[28]

In general, the rate of chain scission upon mechanical stress exerted e.g. by ultrasonication depends on the type of mechanophore incorporated in a polymer backbone. The pre-determined breaking point in a polymer can be preferentially degraded if the bond strength of the weak link is lower than that of all other bonds in the polymer chain.^[29] While there are studies on the production of Fe nanoparticles from the decomposition of ferrocene (Fc) during sonication, surprisingly, the Fc unit has so far remained unexplored as a mechanophore in stimuliresponsive materials.^[30] The enthalpy relative to the heterolytic bond dissociation of this motif (40 kcal/mol)^[31], is about half that of typical covalent single bond values (80 kcal/mol for a C-C bond).^[32] Its high susceptibility to a large number of organic reactions^[33] makes this sandwich complex useful in a wide range of applications, such as molecular sensors, [34],[35] in asymmetrical catalysis,^[36] for electrochemical studies,^[37] and biomedical applications.^[38] Relying on previous strategies for the design of mechanically responsive polymers, we used single-electron living radical polymerizations (SET-LRP)^{[33c],[8]} to prepare poly(methyl acrylate)s having one chain-centered ferrocene motif (Fc-PMA). We further exploited a polycondensation reaction to synthesize polyurethanes, [39] with multiple, statistically distributed ferrocene moieties along the backbone (Fc-PU).^[40] The mechanoresponse of these materials was studied by monitoring the decrease of the molecular weight of these polymers, induced by ultrasonication of dilute solutions.^{[18,} 23e, 26, 41] A mathematical model was used to describe the scission kinetics, while the release and oxidation of Fe²⁺ ions upon ultrasonication was demonstrated by complexation with KSCN or K₄[Fe(CN)₆] to afford the red-colored [Fe(SCN)_n(H₂O)₆- $[n]^{(3-n)+}$ (n = 1-6) or Prussian blue, respectively.



Scheme 1. Syntheses of a) the ferrocene-containing poly(methyl acrylate) (Fc-PMA) and b) the ferrocene-free poly(methyl acrylate) reference (ref-PMA).

For a first proof of principle, a Fc-containing difunctional initiator (**Scheme 1a**) or, for reference purposes, the monofunctional Fcfree initiator methyl α -bromoisobutyrate (**Scheme 1b**), were used to prepare **Fc-PMA** and **ref-PMA** with number-average molecular weights (M_n) of 133 and 119 kDa respectively, and a narrow dispersity of $\mathcal{D} \sim 1.1$ (**Table 1** and **Figure S20**).^[8, 17, 23a, 42] FT-IR spectra (**Figures S1-S2**) confirmed the successful

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preparation of all polymers (with and without ferrocene), which, together with the monomers and initiator, were also fully characterized by ¹H NMR and ¹³C NMR spectroscopy (**Figures S3-S22**), size exclusion chromatography (SEC) (**Figures S23-S25**), and elemental analysis (see SI).

Upon ultrasonication at 0°C under Ar (see SI for details), the M_n of Fc-PMA, determined by SEC, decreases much faster than in the case of ref-PMA, notably during the first minutes of the experiment (Figure 1a). A bimodal profile is observed in the SEC traces (Figure 1b), showing a decrease of the most frequent species in Fc-PMA at an elution time of ca. 12 min (associated with an M_n of 133 kDa) in favor of a peak at an elution time of ca. 12.7 min ($M_n = 52$ kDa) (**Figure 1**)^a. This indicates that the chains are cleaved preferentially at their centers, so that M_n is roughly cut in half, similar to the previously reported PMA samples containing oxime sulphonate or benzocyclobutene as mechanophores.^[8, 12, 17] For **Fc-PMA**, this could be interpreted as preferential cleavage at the ferrocene entity versus the C-C bonds of the remainder of the polymer backbone, as the Fc-unit is placed in the middle of the polymer. With ref-PMA (Figure S23), the result was similar; although the chain scission rate was significantly lower (Figure 1a).



Figure 1. a) Decrease of molecular weight of **ref-PMA** (black) and **Fc-PMA** (red) as a function of time ($M_n(t)$). Results are shown as averages of three experiments (red and black squares) with error bars representing standard deviation at each data point. The inset shows a magnification of the data recorded in the first 15 min; b) Size exclusion chromatography (SEC) traces revealing an increase of the elution time (concomitant with a decrease of the molecular weight) upon ultrasonication of a **Fc-PMA** solution for the time

indicated (in min); c) KSCN (dissolved in a 1:1 v/v mixture of MeOH and THF, 0.53 M) was added to the **Fc-PMA** solution before and after sonication, to show the formation of the red complex FeSCN²⁺ after sonication and the consequent breaking of ferrocene with the releasing of Fe ions. **Fc-PMA** solutions (2 mg/mL in THF) before (pale yellow on the left) and after 90 min sonication (red complex on the right).

Further reference experiments with ferrocene and a short **Fc-PMA2** with a M_n of ca. 40 kDa show that these species do neither dissociate nor release metal ions upon sonication, consistent with the fact that their M_n is below the limiting molecular weight $M_{\rm lim}$ for chain scission of PMA during ultrasonication (see **SI**, **Figures S25-S26**).^{[43],[41b]}

To prove the ultrasound-induced cleavage of **Fc-PMA** at the Fc unit itself (and not at e.g. the ester function), KSCN was added in air to the sonicated solutions, yielding the typical red Fe³⁺ complex [Fe(SCN)_n(H₂O)_{6-n})]⁽³⁻ⁿ⁾⁺ (n = 1-6) (**Figure 2c**).^[44] Similar experiments have been performed also with **Fc-2**, **Fc-PMA2** and **Fc-PMA3** (with one Fc at the chain end, see SI) as further controls. In none of these cases was a color change detected during and after sonication (**Figures S47-S49**).

The detection of Fe³⁺ with KSCN after sonication of Fc-PMA indicates that an oxidative release of the metal ions took place. The cleavage of the Fc unit may occur either homolytically^[45] or heterolytically.^[46] Oxidation of the iron ion can take place in a half-sandwich type complex or after its release into the solution. While thiocyanate is able to act as terminal ligand on monocyclopentadienyl complexes of Fe,^[47] the UV-vis spectrum confirms the presence of [Fe(SCN)_n(H₂O)_{6-n})]⁽³⁻ⁿ⁾⁺ (n = 1-6) (Figure S30).^[44]

To gain insight in the kinetics of the ultrasound-induced chain scission of the polymers investigated, we analyzed the data with a recently developed kinetic model (see SI for details, Figures S33-S45) that allows a distinction between specific chain scission (i.e. cleavage of the mechanophore) and random chain cleavage at other positions.^[48] Considering that the polymer size influences the scission rate (which increases with the molecular weight), the model assumes that the M_n of the polymer decreases by following a pseudo first order kinetic equation, with effective kinetic constants that change with time (see SI), on account of the fact that the polymer chains become shorter during the experiment. The mean values of these constants are compiled in Table 1. Figure 1a shows the results of the model calculations (black and red curves) compared to the experimental evolution of the ratio of the number-average molecular weight $(M_n(t))$ and the initial average molecular weight (M_n) upon ultrasonication of solutions of ref-PMA (black squares) and Fc-PMA (red squares). The data describe the evolution of the entire population of polymer chains in the system, based on a previously tested approach.[49] For the ref-**PMA**, the average rate constant of $k_2 = 0.0086 \text{ min}^{-1}$, derived from the initial slope of the curve, corresponds thus to the unspecific chain scission events. For the Fc-PMA, two average rate constants of $k_1 = 0.058$ (associated with the ferrocene dissociation) and $k_2 = 0.0064 \text{ min}^{-1}$ (corresponding to unspecific chain scission) were found (Table 1), hence the ferrocene cleavage is about 10 times more probable than the unspecific chain scission. The model also permits to evaluate the fraction of ferrocene groups cleaved during the sonication process, which is about 52% in the case of Fc-PMA and less than 4% in the case of Fc-PMA2 polymers.

^a A shoulder appearing after 50 min of sonication at an elution time of ca. 13.5 min (M_n = 33 kDa) seems to be associated with the repeated (non-specific) cleavage of fragments formed by the first cleavage of the population of chains with the highest molecular weight (shoulder at an elution time around 11.2 min corresponding to an M_n of 283 kDa) (details about the correlation between elution time and polymer mass are provided in the **Supporting Information**).

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10.1002/anie.201803524

In order to increase the number of metal ion release events per polymer chain, we also investigated polyurethanes, obtained by a polycondensation reaction (**Scheme 2**), with several ferrocene moieties randomly distributed in the polymer backbone.^[39-40] Thus, **Fc-PU** (M_n =100 kDa, D = 2.03) with an average ferrocene content of 6/chain (3 mol-% Fc), was synthesized and subjected to an ultrasonication experiment. The obtained results were compared with a ferrocene-free **ref-PU** of similar molecular weight and dispersity (see SI, **Figure S21**).



Scheme 2. Synthesis of ferrocene-containing polyurethane (Fc-PU) and ferrocene-free polyurethane (ref-PU) using 1,1'-di(hydroxymethyl)ferrocene (Fc-2) as bifunctional monomer that copolymerize with polytetrahydrofuran (PTHF), methylene diphenyl diisocyanate (MDI) and 1,4-butanediol (BDO) (see SI). (MA = methylacrylate; Me₆TREN = tris[2-(dimethylamino)ethyl]amine; DBTDL = dibutyltin dilaurate).

The scission of **Fc-PU** upon sonication is indicated by a shift of a broad band observed in the SEC trace (**Figure 2a**). Since each **Fc-PU** chain contains several ferrocene mechanophores that are statistically distributed along the backbone, the breaking of a Fc entity can also lead to longer fragments that can then be cleaved again, even multiple times. As a result, the molecular weight distribution remains quite broad, with a wide range of species present. For the ferrocene-free **ref-PU**, the elution peak shifts as well, however slower, and the peak width is decreasing, likely indicating that the polymer breaks into more regular fragments (**Figure S27**). The same behaviour was observed for similar polyurethanes featuring azo motifs as mechanophores.^[50]



Figure 2. a) SEC traces of Fc-PU revealing an increase of the elution time (decrease of the molecular weight; b) KSCN (dissolved in a 1:1 v/v mixture of MeOH and THF) was added to the solution of Fc-PU (0.75 mg/mL in THF), before (left, uncolored solution) and after sonication (right, red solution), to show the formation after sonication of the red complex $Fe[SCN]^{2+}$ (due to the ferrocene breaking and the consequent release of Fe ions).

As a result of the multiple breaking of the chains and the release of more than one Fe-ion per polymer chain, a lower concentration of **Fc-PU** (0.75 mg/mL) as compared to **Fc-PMA** solution (2 mg/mL) was sufficient to detect the oxidative release of iron as red thiocyanate complex after sonication (**Figure 2b**). Again, the formation of the red complex [Fe(SCN)_n(H₂O)_{6-n})]⁽³⁻ⁿ⁾⁺ (n = 1-6) was proven by UV-vis spectroscopy (**Figure S31**).^[44] Videos of the **Fc-PU** color-change and the corresponding reference experiments are available in the Supporting information.

We applied a similar kinetic model to the molecular weight data extracted from the ultrasound-induced chain scission experiments of PU as with Fc-PMA (Figure S46). The larger number of Fc moieties in the Fc-PU, and their random distribution along the chains, increase their probability of being cut by subsequent scission events. The molecular weight decrease observed upon ultrasonication of ref-PU, void of Fc moieties, can be described by a single rate constant of k_2 = 0.0002 min⁻¹, ascribed to the non-specific bond cleavage. This is much lower than for the non-specific bond cleavage in ref-PMA. For Fc-PU, the model reveals the overlay of two types of chain scission events, that are characterized by average rate constants of $k_1 = 1.65$ and $k_2 = 0.00085$ min⁻¹, which can be associated with the dissociation of the (weaker) ferrocene mechanophore and unspecific chain scission, respectively. The difference between the values of k₂ for ref-PU and Fc-PU can be explained by the fact that the constants depend on the initial molecular weight of the polymer and its constitution. It is important to highlight that the value of k_1 determines the initial slope of the molecular weight evolution as function of time, as well as the final consumption as ferrocene moieties. The k_1 value for Fc-PU is thus ca. three orders of magnitude higher than the unspecific rate of scission k_2 (**Table 1**), and confirms the role of Fc groups as effective mechanophores. A comparison of the chain scission data for Fc-PMA and Fc-PU shows that the scission rate constants associated with the cleavage of the Fc moieties are much larger in PU than in PMA, and always much larger than that of non-specific scission rate constants in both polymers (Table 1). This can be accounted for by the larger number of Fc units in Fc-PU that are each preferentially cleaved with respect to the other bonds in the polymer backbone as well as the chemical differences between PMA and PU. The above model also permits to estimate that about 25% of the Fc moieties are cleaved at the end of sonication in the Fc-PU polymer, which is largely confirmed by a titration experiment (see SI).

 Table 1. Description, fitting parameters and cleavage rate constants of the sonicated ferrocene-containing and ferrocene-free polyurethanes Fc-PU and ref-PU and the ferrocene-containing and ferrocene-free poly(methyl acrylate)s, Fc-PMA, ref-PMA1, and ref-PMA2.

Polymer	<i>M</i> n ^ª (kDa)	Đ ^{a,b}	Fc nbr ^c	Cleavage rate constants ^d (min ⁻¹)	
				k 1	k 2 ^e
Fc-PU	100	2.03	6	1.6548	0.00085
ref-PU	119	1.60	0	-	0.0002
Fc-PMA	133	1.10	1	0.0583	0.0064
ref-PMA	129	1.08	0	-	0.0086
Fc-PMA2	43.6	1.12	1	0.0144	0.00098

^aDetermined by size-exclusion chromatography (SEC). ^bThe dispersity (*Đ*) is determined from the ratio of M_w/M_n . ^cAverage number of ferrocene moieties per chain calculated from the measured M_n and the composition of the reaction feed.^[39] ^dObtained by modeling the M_h decrease as shown by SEC data after the sonication experiments (0.75 mg/mL in THF, 10.4 W/cm², 0 °C). ^eThe k_2 values of **Fc-PU** and **ref-PU** are lower than those for **PMA** and **Fc-PU** of similar molecular weight. This may be related to the fact that the **PMA** contains higher substituted carbon atoms in the chain, as well as ester functions instead of urethane groups, which are expected to break more easily than the bonds in **PU**.

Thus, ultrasonication can selectively cleave Fc-containing polymers at the ferrocene moieties, triggering thus oxidative metal ion release that can be evidenced by the formation of the

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red thiocyanate complex (Figures 1c, 2b and supporting movies). Control experiments with KSCN containing solutions of Fc-PU, Fc-PMA and Fc-2 in THF (2 mg/mL) that were heated to reflux for 24 hours without sonication did not lead to color changes, proving that the ferrocene scission is not thermally induced.

Metal ion release was further proven by a possible application, namely the generation of the dark blue pigment Prussian blue on demand, which is used for example in medical applications for the absorption of toxic thallium ions or radioactive cesium. $\ensuremath{^{[51]}}$ To achieve this, we added K₄[Fe(CN)₆] (0.0414 M) to a solution of **Fc-PU2** containing 12% of ferrocene (0.75 g/mol, $M_n = 46$ kDa, D = 2.6), which was prepared by a similar procedure as the Fc-PU with 3% Fc, described above (Figure S15 and Figure S25). During the sonication of Fc-PU2, we observed the formation of a blue colloidal solution (Prussian blue), which confirms the oxidative release of iron ions (Figure 3 (right)). A control experiment with ref-PU or Fc with K₄[Fe(CN)₆] under sonication did not yield the blue pigment (Figures S50 and S51), nor did Fc-PU2 in presence of hexacyanoferrate(II) without sonication (Figure 3a). Although the M_n of Fc-PU2 of 46 kDa is likely close to the limit of M_n allowing to study the molecular weight decrease upon sonication, it was nevertheless shown to work as a further example of color change after the oxidative iron ion release.



Figure 3. Color change of the solution of **Fc-PU2** (containing 12% of ferrocene) before sonication in presence of potassium hexacyanoferrate(II) (a), after sonication in presence of potassium hexacyanoferrate(II) (b) and after sonication with KSCN (c). In the second case the blue color indicates the formation of the Prussian blue. These experiments were carried out after ultrasonication (90 min) of the polymer.

In conclusion, we have used for the first time ferrocene derivatives as mechanophores with the ability to break and to release the central metal under mechanical stress in solution. Two competitive scission events were observed in Fc-containing polymers, the cleavage of the Fc mechanophore (k_1) and the one of random bonds (k_2) . The scission for Fc is at least 10 times more favored than unspecific cleavage. It is thus conceivable to use also other metallocenes as mechanophores for the selective metal ion release.^[52] Furthermore, the triggered oxidative release of the metal ion from ferrocene can be used to induce a color change and/or the formation of a pigment for e.g. analytical and medical applications. It is envisageable to use this unique type of polymer scission also in catalysis, as iron ions are highly active catalysts for different organic reactions, such as hydroalkoxylation intramolecular and hydroamination reactions of allenes.^[53] These materials have the potential to mechano-generate free base in solution, exploiting the cyclopentadienyl anion, formed after the ferrocene breaking, even though we cannot exclude rapid protonation or the formation of Cp, considering that during sonication experiments radical species can also be easily generated.^[8, 46] Further studies are under way to determine the scission mechanism of the metallocene and the use of such a metal-release on demand system for applications in catalysis.

Acknowledgements

This work was supported by the National Center of Competence in Research "Bio-Inspired Materials" (Project 141849) of the Swiss National Science Foundation, the Fribourg Center for Nanomaterials (FriMat), the Adolphe Merkle Foundation, and the University of Fribourg. The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement n° 291490-MERESPO.

The authors thank Prof. Bernd Giese for fruitful discussion.

Keywords: Polymer chemistry, stimuli-responsive polymers, mechanophores, organometallic chemistry.

References

- H. Koshima, N. Ojima, H. Uchimoto, J. Am. Chem. Soc.
 2009, 131, 6890-6891.
- [2] R. P. Wool, *Soft Matter* **2008**, *4*, 400-418.
 [3] O. Azzaroni, B. Trappmann, P. van Rijn, F. Zhou, B. Kong, W. T. Huck, *Angew. Chem. Int. Ed.* **2006**, *45*, 7440-7443.
 [4] J. Li, C. Nagamani, J. S. Moore, *Acc. Chem. Res.*
 - J. Li, C. Nagamani, J. S. Moore, *Acc. Chem. Res.* **2015**, *48*, 2181-2190.
- [5] M. A. C. Stuart, W. T. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, *Nature Mater.* 2010, *9*, 101-113.
- [6] a) M. Rubner, *Macromolecules* 1986, *19*, 2129-2138;
 b) D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martínez, S. R. White, *Nature* 2009, *459*, 68-72.
 [7] C. E. Diesendruck, B. D. Steinberg, N. Sugai, M. N. Silberstein, N. R. Sottos, S. R. White, P. V. Braun, J. S.
- Moore, J. Am. Chem. Soc. 2012, 134, 12446-12449.
 [8] C. Nagamani, H. Liu, J. S. Moore, J. Am. Chem. Soc. 2016, 138, 2540-2543.
 [0] M. Claugh A. Palan, T. L. van Daal, B. D. Sübaama.
- [9] J. M. Clough, A. Balan, T. L. van Daal, R. P. Sijbesma, Angew. Chem. Int. Ed. 2016, 55, 1445-1449.
- a) M. B. Larsen, A. J. Boydston, *J. Am. Chem. Soc.* **2014**, *136*, 1276-1279; b) A. N. Koo, H. J. Lee, S. E. Kim, J. H. Chang, C. Park, C. Kim, J. H. Park, S. C. Lee, *Chem. Commun.* **2008**, 6570-6572.
- [11] J. Hu, S. Liu, *Macromolecules* **2010**, *43*, 8315-8330.
- [12] C. E. Diesendruck, G. I. Peterson, H. J. Kulik, J. A. Kaitz, B. D. Mar, P. A. May, S. R. White, T. J. Martínez, A. J. Boydston, J. S. Moore, *Nature Chem.* **2014**, *6*, 623-628.
- [13] Y. Qiu, K. Park, *Adv. Drug Deliv. Rev.* 2001, *53*, 321-339.
- [14] J. F. Mano, Adv. Eng. Mater. 2008, 10, 515-527.
- [15] A. Piermattei, S. Karthikeyan, R. P. Sijbesma, *Nature Chem.* **2009**, *1*, 133-137.
- [16] Y. Lu, Y. Mei, M. Drechsler, M. Ballauff, Angew. Chem. Int. Ed. 2006, 45, 813-816.
- [17] S. L. Potisek, D. A. Davis, N. R. Sottos, S. R. White, J. S. Moore, J. Am. Chem. Soc. 2007, 129, 13808-13809.
- [18] K. L. Berkowski, S. L. Potisek, C. R. Hickenboth, J. S. Moore, *Macromolecules* **2005**, *38*, 8975-8978.
- [19] Z. S. Kean, A. L. Black Ramirez, Y. Yan, S. L. Craig, J. Am. Chem. Soc. 2012, 134, 12939-12942.
- [20] M. J. Robb, J. S. Moore, J. Am. Chem. Soc. 2015, 137, 10946-10949.

COMMUNICATION

- [21] Y. Chen, A. Spiering, S. Karthikeyan, G. W. Peters, E. Meijer, R. P. Sijbesma, *Nature Chem.* **2012**, *4*, 559-562.
- [22] Z. Wang, Z. Ma, Y. Wang, Z. Xu, Y. Luo, Y. Wei, X. Jia, *Adv. Mater.* **2015**, *27*, 6469-6474.
- [23] a) C. R. Hickenboth, J. S. Moore, S. R. White, N. R. Sottos, J. Baudry, S. R. Wilson, *Nature* 2007, *446*, 423-427; b) Z. a. Li, R. Toivola, F. Ding, J. Yang, P. N. Lai, T. Howie, G. Georgeson, S. H. Jang, X. Li, B. D. Flinn, *Adv. Mater.* 2016, *28*, 6592-6597; c) K. Imato, T. Kanehara, T. Ohishi, M. Nishihara, H. Yajima, M. Ito, A. Takahara, H. Otsuka, *ACS Macro Lett.* 2015, *4*, 1307-1311; d) M. B. Larsen, A. J. Boydston, *J. Am. Chem. Soc.* 2013, *135*, 8189-8192; e) A. L. B. Ramirez, Z. S. Kean, J. A. Orlicki, M. Champhekar, S. M. Elsakr, W. E. Krause, S. L. Craig, *Nature Chem.* 2013, *5*, 757-761.
- [24] A. P. Haehnel, Y. Sagara, Y. C. Simon, C. Weder, in *Polym. Mechanochem.*, Springer, **2015**, 345-375.
- [25] K. M. Wiggins, J. N. Brantley, C. W. Bielawski, Chem. Soc. Rev. 2013, 42, 7130-7147.
- [26] S. Karthikeyan, S. L. Potisek, A. Piermattei, R. P. Sijbesma, *J. Am. Chem. Soc.* **2008**, *130*, 14968-14969.
- [27] a) D. W. Balkenende, S. Coulibaly, S. Balog, Y. C.
 Simon, G. L. Fiore, C. Weder, *J. Am. Chem. Soc.* 2014, 136, 10493-10498; b) R. T. Jakobs, S. Ma, R. P.
 Sijbesma, *ACS Macro Lett.* 2013, 2, 613-616.
- [28] W. Weng, J. B. Beck, A. M. Jamieson, S. J. Rowan, *J. Am. Chem. Soc.* **2006**, *128*, 11663-11672.
- [29] M. Encina, E. Lissi, M. Sarasua, L. Gargallo, D. Radic, J. Polym. Sci. Part C: Polym. Lett. **1980**, 18, 757-760.
- [30] S.-H. Jeong, J.-H. Ko, J.-B. Park, W. Park, *J. Am. Chem. Soc.* **2004**, *126*, 15982-15983.
- [31] E. S. Domalski a. E. D. Hearing, J.A. Martinho Simões, Data compilation copyright by the U.S. Secretary of Commerce on behalf of the U.S.A., National Institute of Standards and Technology (NIST) Chemistry WebBook
- [32] a) N. Cohen, J. Phys. Chem. Ref. Data 1996, 25, 1411-1481; b) J. R. Chipperfield, J. C. Sneyd, D. E. Webster, J. Organomet. Chem. 1979, 178, 177-189; c) F. A. Cotton, G. Wilkinson, J. Am. Chem. Soc. 1952, 74, 5764-5766.
- [33] a) Y. Han, K. Cheng, K. A. Simon, Y. Lan, P. Sejwal, Y.-Y. Luk, *J. Am. Chem. Soc.* 2006, *128*, 13913-13920; b) D. R. Van Staveren, N. Metzler-Nolte, *Chem. Rev.* 2004, *104*, 5931-5986; c) J. Eppinger, K. R. Nikolaides, M. Zhang-Presse, F. A. Riederer, G. W. Rabe, A. L. Rheingold, *Organomet.* 2008, *27*, 736-740.
- [34] F. Otón, A. Espinosa, A. Tárraga, P. Molina, Organomet. **2007**, *26*, 6234-6242.
- [35] M. Nakayama, T. Ihara, K. Nakano, M. Maeda, *Talanta* 2002, 56, 857-866.
- [36] a) R. Gómez Arrayás, J. Adrio, J. C. Carretero, Angew. Chem. Int. Ed. 2006, 45, 7674-7715; b) O. Riant, O. Samuel, H. B. Kagan, J. Am. Chem. Soc. 1993, 115, 5835-5836.
- [37] P. Molina, A. Tárraga, A. Caballero, *Eur. J. Inorg. Chem.* 2008, 2008, 3401-3417.
- [38] a) E. Hillard, A. Vessières, L. Thouin, G. Jaouen, C. Amatore, *Angew. Chem. Int. Ed.* 2006, *45*, 285-290; b)
 X. Peng, H. He, J. Xia, Z. Lou, G. Chang, X. Zhang, S. Wang, *Tetrahedron Lett.* 2014, *55*, 3541-3544; c) E. Hillard, A. Vessieres, F. Le Bideau, D. Plażuk, D. Spera, M. Huche, G. Jaouen, *ChemMedChem* 2006, *1*, 551-559.
- [39] M. A. Ayer, Y. C. Simon, C. Weder, *Macromolecules* **2016**, *49*, 2917-2927.
- [40] B. R. Crenshaw, C. Weder, *Macromolecules* 2006, 39, 9581-9589.
- [41] a) V. Desai, M. A. Shenoy, P. R. Gogate, *Chem. Engin.* J. 2008, 140, 483-487; b) M. M. Caruso, D. A. Davis, Q.

Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755-5798.

- [42] R. Claus, J. P. Lewtak, T. J. Muller, J. C. Swarts, J. Organomet. Chem. 2013, 740, 61-69.
- [43] G. J. Price, P. F. Smith, *Polymer* **1993**, *34*, 4111-4117.
- [44] J. F. Below Jr, R. E. Connick, C. P. Coppel, J. Am. Chem. Soc. 1958, 80, 2961-2967.
- [45] C. R. Kutal, Y. Yamaguchi, Google Patents, 2000.
- [46] Q. M. Phung, S. Vancoillie, K. Pierloot, J. Chem. Theory and Computation **2014**, *10*, 3681-3688.
- [47] a) T. E. Sloan, A. Wojcicki, *Inorg. Chem.* **1968**, 7, 1268-1273; b) D. A. Brown, N. J. Fitzpatrick, W. K. Glass, P. K. Sayal, *Organomet.* **1984**, 3, 1137-1144.
- [48] M. A. Ayer, S. Yoan, C. Weder, *Macromolecules*, 2016, 49(8), 2917-2927.
- [49] M. A. Ayer, E. Verde-Sesto, C. Weder, Y. Simon, Polym. Chem. **2018** (under revision).
- [50] M. A. Ayer, E. Verde-Sesto, C. Weder, Y. Simon, Polym. Chem. **2018** (under revision).
- [51] K. Dunbar, R. A. Heintz, *Progress in Inorg. Chem.* **1997**, *45*, 283-392.
- [52] M. Swart, Inorg. Chim. acta 2007, 360, 179-189.
- [53] M. S. Jung, W. S. Kim, Y. H. Shin, H. J. Jin, Y. S. Kim, E. J. Kang, *Org. Lett.* **2012**, *14*, 6262-6265.

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This work focuses on ferrocene derivatives as new mechanophores embedded in polyurethane and poly(methyl acrylate), able to selectively break under mechanical stress in solution, releasing iron ions in solution.