

Mechanoresponsive Polymers

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Triggered Metal Ion Release and Oxidation: Ferrocene as a Mechanophore in Polymers

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Abstract: The introduction of mechanophores into polymers makes it possible to transduce mechanical forces into chemical reactions that can be used to impart functions such as self-healing, catalytic activity, and mechanochromic response. Here, an example of mechanically induced metal ion release from a polymer is reported. Ferrocene (Fc) was incorporated as an iron 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 iron ions can be detected with KSCN to generate the red-colored $[\text{Fe}(\text{SCN})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ complex or reacted with $\text{K}_4[\text{Fe}(\text{CN})_6]$ 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 have 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 in color/fluorescence,^[6] the formation of proton catalysts,^[7] the generation of acids,^[7,8] and bases,^[9] and the release of small molecules.^[10] Applications of such mechanoresponsive polymeric materials include sensors,^[11] self-healing materials,^[2] drug delivery,^[12] tissue engineering,^[13] and catalysis.^[14] These polymers contain mechanophores such as spiropyran^[6b] and azo units,^[15] as well as epoxide,^[16] β -lactam,^[17] diox-

tane,^[18] and rhodamine moieties,^[19] among others.^[20] Several examples involve noncovalent (supramolecular) motifs^[21] and coordination bonds.^[22] Sijbesma and co-workers demonstrated the reversible mechanically induced dissociation of a Pd–phosphane bond embedded in a linear polymer using ultrasound.^[23] This result triggered the investigation of other mechanoresponsive polymers containing, for example, Ag-^[22] and Ru-carbene complexes^[24] for catalysis.^[10a, 14a, 25] Further examples include metallopolymers based on telechelic cores that were end-functionalized with 2,6-bis(1'-methylbenzimidazolyl)pyridine and assembled with Eu^{3+} ,^[26] Zn^{2+} , or La^{3+} salts.^[27]

In general, the rate of chain scission upon mechanical stress exerted, for example by ultrasonication, depends on the type of mechanophore incorporated in the polymer backbone. The predetermined 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.^[28] 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 stimuli-responsive materials.^[29] The enthalpy of the heterolytic bond dissociation of this motif (40 kcal mol^{-1})^[30] is about half that of a typical covalent single bond (80 kcal mol^{-1} for a C–C bond).^[31] Its high susceptibility to a large number of organic reactions^[32] makes this sandwich complex useful in a wide range of applications, such as molecular sensors,^[33] in asymmetrical catalysis,^[34] for electrochemical studies,^[35] and biomedical applications.^[36] Relying on previous strategies for the design of mechanically responsive polymers, we used single-electron living radical polymerizations (SET-LRP)^[8, 37] to prepare poly(methyl acrylate)s having one chain-centered ferrocene motif (**Fc-PMA**). We further exploited a polycondensation reaction to synthesize polyurethanes^[38] with multiple, statistically distributed ferrocene moieties along the backbone (**Fc-PU**).^[39] The mechanoresponse of these materials was studied by monitoring the decrease of the molecular weight of these polymers, induced by ultrasonication of dilute solutions.^[15, 22, 40] A mathematical model was used to describe the scission kinetics, while the formation of Fe^{3+} ions upon ultrasonication-induced release and oxidation was demonstrated by complexation with KSCN or $\text{K}_4[\text{Fe}(\text{CN})_6]$ to afford the red-colored $[\text{Fe}(\text{SCN})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ ($n = 1-6$) or Prussian blue, respectively.

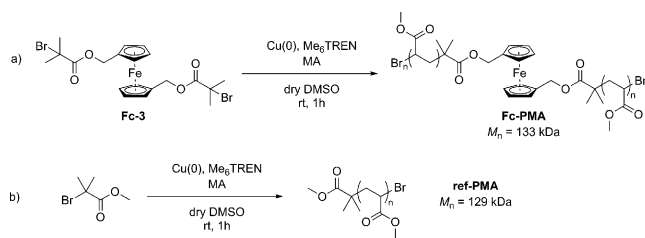
For a first proof of principle, a Fc-containing difunctional initiator (Scheme 1 a) and, for reference purposes, the monofunctional Fc-free initiator methyl α -bromoisobutyrate (Scheme 1 b), were used to prepare **Fc-PMA** and **ref-PMA** with number-average molecular weights (M_n) of 133 and

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Scheme 1. Syntheses of a) the ferrocene-containing poly(methyl acrylate) (**Fc-PMA**) and b) the ferrocene-free poly(methyl acrylate) reference (**ref-PMA**). (MA = methylacrylate; Me₆TREN = tris[2-(dimethylamino)ethyl]amine.)

119 kDa, respectively, and a narrow dispersity of $\mathcal{D} \approx 1.1$ (Table 1 and Figure S20).^[8,37] FTIR spectra (Figures S1 and S2) confirmed the successful preparation of all polymers (with and without ferrocene), which, together with the monomers and initiator, were also fully characterized by ¹H NMR and

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	$M_n^{[a]}$ [kDa]	$\mathcal{D}^{[b]}$	Fc no. ^[c]	Cleavage rate constants ^[d] [min ⁻¹]	
				k_1	k_2
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

[a] Determined by size-exclusion chromatography (SEC). [b] The dispersity (\mathcal{D}) is determined from the ratio of M_w/M_n . [c] Average number of ferrocene moieties per chain calculated from the measured M_n and the composition of the reaction mixture. [d] Obtained by modeling the M_n decrease as shown by SEC data after the sonication experiments (0.75 mg mL⁻¹ in THF, 10.4 W cm⁻², 0 °C).

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 that of **ref-PMA**, notably during the first minutes of the experiment (Figure 1). A largely 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 1b). This indicates that the chains are cleaved preferentially at their centers, so that M_n is roughly halved, similar to the previously reported PMA samples containing oxime sulfonate or benzocyclobutene as mechanophores.^[8,37] For **Fc-PMA**, this could be interpreted as preferential cleavage at the ferrocene entity versus cleavage of the C–C bonds of the remainder of the polymer backbone, as the Fc unit is placed in the middle of the polymer. For **ref-PMA** (Figure S23) the results were similar, although the chain scission rate was significantly lower (Figure 1a).

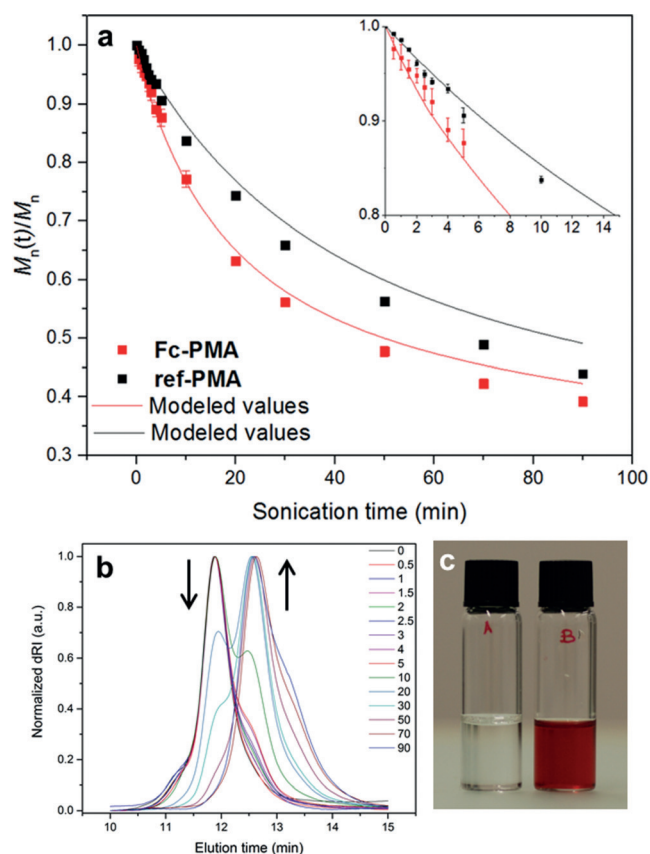


Figure 1. a) Decrease of the normalized molecular weight of **ref-PMA** (black) and **Fc-PMA** (red) as a function of time ($M_n(t)/M_n$). Results are shown as averages of three experiments (red and black squares) with error bars representing the standard deviation at each data point. The inset shows 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). 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 (nonspecific) 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). 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 $[\text{Fe}(\text{SCN})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ after sonication and confirm the release of Fe ions. **Fc-PMA** solutions (2 mg mL⁻¹ in THF) before sonication (sample A, pale yellow, left) and after 90 min of sonication (sample B, red solution). The red Ferriothiocyanate complex formed after sonication confirm the release of Fe ions solely upon sonication.

Further reference experiments with ferrocene and a low-molecular-weight **Fc-PMA2** with an M_n of ca. 40 kDa show that these species neither dissociate nor release metal ions upon sonication, consistent with the fact that their M_n is below the limiting molecular weight M_{lim} for chain scission of PMA during ultrasonication (see SI, Figures S25 and S26).^[40b,41] To prove that the ultrasound-induced cleavage of **Fc-PMA** occurs at the Fc unit itself (and not at, e.g., the ester function), KSCN was added (without protecting the sample

from air) to the sonicated solutions, resulting in the formation of the typical red Fe^{3+} complex $[\text{Fe}(\text{SCN})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ ($n=1-6$) (Figure 2c).^[42] Similar experiments were performed 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).

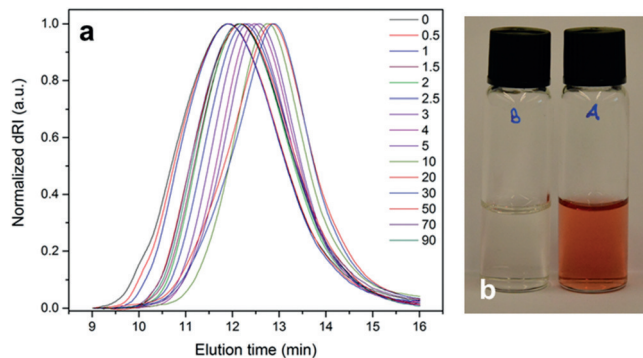


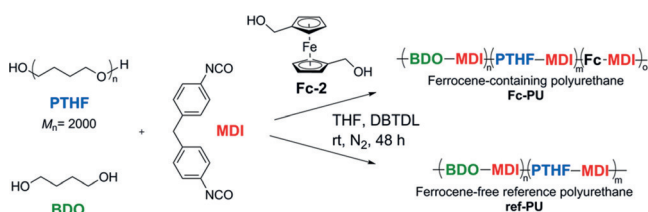
Figure 2. a) SEC traces of **Fc-PU** as a function of ultrasound irradiation time, revealing an increase of the elution time (decrease of the molecular weight); b) KSCN (dissolved in a 1:1 v/v mixture of MeOH and THF) was added to the solution of **Fc-PU** (0.75 mg mL^{-1} in THF), before (left, colorless solution) and after 90 min of sonication (right, red solution), to show the formation after sonication of the red complex $[\text{Fe}(\text{SCN})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ (due to the ferrocene breaking and the release of Fe ions).

The detection of Fe^{3+} with KSCN after sonication of **Fc-PMA** indicates that the release and oxidation of the metal ions took place. The cleavage of the Fc unit may occur either homolytically^[43] or heterolytically.^[44] 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 a terminal ligand on monocyclopentadienyl complexes of Fe,^[45] the UV/Vis spectrum confirms the presence of $[\text{Fe}(\text{SCN})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ ($n=1-6$) (Figure S30).^[42]

To gain insight into 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.^[46] 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 number-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.^[46,47] For **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 **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 can also be used 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 the low-molecular-weight **Fc-PMA2** reference polymer.

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.^[38,39] Thus, **Fc-PU** ($M_n=100 \text{ kDa}$, $\bar{D}=2.03$) with an average ferrocene content of 6 Fc units per chain (3 mol% Fc), was synthesized and subjected to an ultrasonication experiment. The results were compared with those obtained for 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 a bifunctional monomer that was copolymerized with poly(tetrahydrofuran) (**PTHF**), methylene diphenyl diisocyanate (**MDI**), and 1,4-butanediol (**BDO**) (see SI). 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 cleavage of an 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 more slowly, and the peak width decreases, likely indicating that the polymer breaks into more regular fragments (Figure S27). The same behavior was observed for similar polyurethanes featuring azo motifs as mechanophores.^[46]

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^{-1}) as compared to **Fc-PMA** solution (2 mg mL^{-1}) was sufficient in the detection of the release of iron as a red thiocyanate complex after sonication (Figure 2b). Again, the formation of the red complex $[\text{Fe}(\text{SCN})_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ ($n=1-6$) was proven by UV/Vis spectroscopy (Figure S31).^[42] Videos of the **Fc-PU** and the corresponding reference (**ref-PU**, Fc, and KSCN

alone) color-change 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 **Fc-PU** and their random distribution along the chains increase their probability of being cut in 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 $k_2 = 0.0002 \text{ min}^{-1}$, ascribed to the nonspecific bond cleavage. This is much lower than for the nonspecific 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 $k_2 = 0.00085 \text{ min}^{-1}$, which can be associated with the dissociation of the (weaker) ferrocene mechanophore and unspecific chain scission, respectively. The difference between the values of k_2 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 a function of time, as well as the final consumption of 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 nonspecific 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 qualitatively confirmed by a titration experiment (see SI, Titration experiment).

Thus, ultrasonication can selectively cleave Fc-containing polymers at the ferrocene moieties, triggering metal ion release and oxidation that can be evidenced by the formation of the red thiocyanate complex (Figures 1c, 2b and movies in SI). In order to exclude that the metal iron release from **Fc-PU** and **Fc-PMA** was due to a thermal effect upon sonication, control experiments with KSCN-containing solutions of **Fc-PU**, **Fc-PMA** and **Fc-2** were heated to reflux for 24 hours without sonication. In none of the cases did we observe a color change, 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.^[48] To achieve this, we added $\text{K}_4[\text{Fe}(\text{CN})_6]$ (0.0414 M) to a solution of **Fc-PU2** containing 12% Fc (0.75 g mol^{-1} , $M_n = 46 \text{ kDa}$, $D = 2.6$), which was prepared by a procedure similar to that for **Fc-PU** with 3% Fc, described above (Figures S15 and S25). During the sonication of **Fc-**

PU2, we observed the formation of a blue colloidal solution (Prussian blue), which confirms the release and oxidation (but not the sequence of these events) of iron ions (Figure 3). A control experiment with **ref-PU** or **Fc** with $\text{K}_4[\text{Fe}(\text{CN})_6]$ 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 for studying 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.

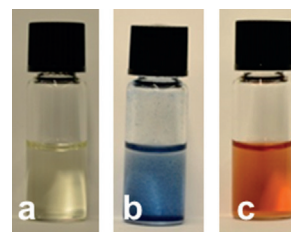


Figure 3. Color change of the solution of **Fc-PU2** (containing 12% Fc) a) before sonication in the presence of $\text{K}_4[\text{Fe}(\text{CN})_6]$, b) after sonication in presence of $\text{K}_4[\text{Fe}(\text{CN})_6]$, and c) after sonication with KSCN. In the second case the blue color indicates 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 in polymers with the ability to break and to release the central metal ion 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 cleavage 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 selective metal ion release.^[49] Furthermore, the triggered release of the metal ion from ferrocene can be used to induce a color change and/or the formation of a pigment for, for example, analytical and medical applications. It can be envisaged to use this unique type of polymer scission also in catalysis, as iron ions are highly active catalysts for different organic reactions, such as intramolecular hydroalkoxylation and hydroamination reactions of allenes.^[50] 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.^[8,44] 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.

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Conflict of interest

The authors declare no conflict of interest.

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