Supporting Information

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

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Experimental section

Materials. Inhibitor free anhydrous tetrahydrofuran (THF, Sigma-Aldrich) was used as the solvent for all polymer syntheses. SEC THF (Romil-SpS™, Super Purity Solvent grade) was used for the ultrasound-induced chain-scission experiments. Poly(tetrahydrofuran) (PTHF, number-average molecular weight, M_n = 2,000 g/mol) was dried *in vacuo* at 100 °C for 1 h before use. 4,4'-Methylenebis(phenyl isocyanate) (MDI) and 1,4-butanediol (BDO) were distilled *in vacuo* and stored in the refrigerator at 5 °C over molecular sieves (4 Å beads, 4-8 mesh) until used. Methyl acrylate (MA) was filtered through a basic alumina column to remove inhibitors. All reagents were obtained from Sigma-Aldrich and used without further purification, except if stated otherwise.

Instrumentation. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Bruker Avance III HD spectrometer. The chemical shifts (δ) are indicated in parts per million (ppm) relative to tetramethylsilane, although referencing relied on the residual solvent protons. An Agilent Technologies 1200 system was used to perform size exclusion chromatography (SEC) analyses. The instrument was equipped with Wyatt Optilab rEX differential refractive index (dRI) and Wyatt miniDAWN TREOS multi-angle laser light scattering (MALLS) detectors. The column system was composed of an Agilent 5 µm MIXED-C guard column and an Agilent PLgel 5 µm MIXED-D (200-400 kDa) column set. The analyses were performed with THF as the solvent at a flow rate of 1 mL/min. The mass-average molecular weight (M_w) and number-average molecular weight (M_n) values were determined by comparison with polystyrene standards. The dispersity ($Đ$) was determined from the M_w/M_n ratio. Elemental analyses (EA) were carried out on a CE Instruments EA 1110 with flash combustion and gas chromatography (GC) separation. To measure Fourier Transform Infrared (FT-IR) spectra, a PerkinElmer Spectrum 65 spectrometer with an attenuated total reflection (ATR) system was used.

Ultrasound-induced chain-scission experiments. A Branson Model 450 digital sonifier bearing a 13 mm tip was used to perform the experiments. To keep the solutions at 0 °C, a VWR MX07R-20 cooling/heating bath containing a mixture of water/ethylene glycol (1:1 v/v) was used. The test solutions contained the polymer dissolved in THF (Romil-SpS™, Super Purity Solvent grade) at a concentration of 0.75 mg/mL (molecular weight decrease experiments) or 2 mg/mL (color change experiments). A Suslick cell containing a volume of 20 mL of the respective test solution was immersed in the cold bath (0 °C) and the solution was purged with argon during 15 min prior to sonication. The solution was then kept under argon during the experiment. The sonication was achieved using pulses of 0.5 s and a power density of 10.4 W/cm^2 intercalated with pauses of 1.0 s, maintaining the argon atmosphere. Several aliquots (400 µL) were taken using syringes at regular time intervals and they were introduced into 1 mL vials. The polymers were then re-concentrated at 1 mg/mL to perform the SEC measurements. For this purpose the solvent was evaporated *in vacuo* at room temperature (rt) and the polymer residues were dissolved in 300 µL of SEC THF.

The polymers have been prepared as dilute solutions in the eluent and injected into the system. The GPC instrument is packed with porous beads of controlled porosity and particle size. For the separation mechanism, polymer molecules elute from the column in order of size in solution. Largest polymers elute first and smallest polymers elute last. The separation is purely a physical partitioning, in fact there are no interactions. The calibration curve describes how molecules with different size elute from the column.

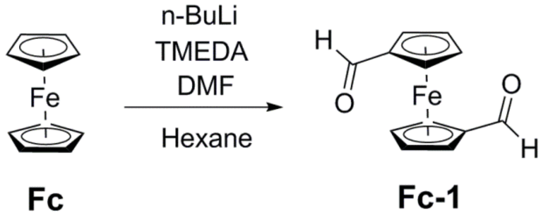
Color-change experiment. An excess (0.3 mL) of KSCN (dissolved in a 1:1 v/v mixture of MeOH and THF, 0.18 M) was added to THF solutions (0.5 mL) of **Fc-PU**, **ref-PU** (2 mg/mL) under stirring, after they had been sonicated for 90 min, until a color change was observed. About the realization of the videos, KSCN (previously dissolved in a 1:1 v/v mixture of MeOH and THF, 0.18 M) was added into the polymer solutions (2 mg/mL in THF) before the sonication experiment was performed, in order to observe the complex formation during sonication. Four different samples were prepared: **Fc-PU** (2 mg/mL in THF) with an excess of KSCN solution; **ref-PU** with an excess of KSCN solution; ferrocene as small molecule (**Fc**) with the same quantity of KSCN solution described previously; the ligand (KSCN) alone, always in the same concentration range. These four samples were then sonicated for 90 minutes and the videos recorded show the color change only for the **Fc-PU** solution, from transparent/yellow to dark red.

The same procedure was used for **Fc-PMA** and the corresponding reference solutions of **ref-PMA, Fc-PMA2, Fc-PMA3 and Fc-2**. An higher concentration of polymer solutions (**Fc-PMA**, **ref-PMA**, **Fc-PMA2** and **Fc-PMA3**) was used (120 mg dissolved in 2 mL of THF, adding 3 mL of KSCN solution (dissolved in a 1:1 v/v mixture of MeOH and THF, 0.53 M).

Titration experiment. In order to quantify the amount of iron released by **Fc-PU** upon sonication, we performed a titration experiment (**Figure S32**). Sulfosalicylic acid (5% solution in water) was used as indicator, EDTA ($1.01 \cdot 10^{-4}$ M) as titrant, **Fc-PU** (2 mg/mL THF, [Fe] = $3.6 \cdot 10^{-4}$ M) as analyte, HCl 1M to acidify the solution. The polymer dissolved in THF, after 90 minutes of sonication, was mixed with 1 mL of HCl and 7.5 mL of sulfosalicylic acid to observe the light red color of the iron(III) sulfosalicylate complex. The EDTA solution was added dropwise to the polymer mixture under stirring, until the color changed from red to pale yellow, which was however difficult to discern. The complex formation of Fe with sulfosalicylic acid was proven by UV analysis (Figure S32). The experiment was repeated three times and the equivalent volume of EDTA added is 14.0 +/- 2,5 mL. This corresponds to a release of 60 % +/- 20 % of the total iron amount contained in the polymer after 90 minutes of sonication, which is higher than predicted by the model.

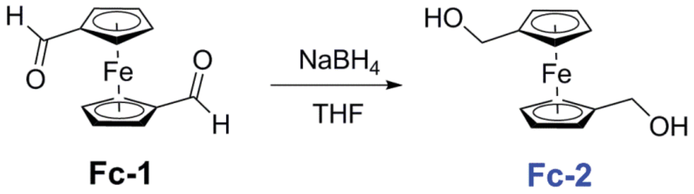
Synthesis of 1,1'- ferrocenedicarboxaldehyde (Fc-1). In a 100 mL flask under argon atmosphere, ferrocene (**Fc**, 1 g, 5.4 mmol) was dissolved in dry hexane (25 mL), then an *n*-butyl lithium solution (7 mL, 1.6 M in hexanes, 10 mmol) was added dropwise to the well-stirred solution. This was followed by the addition of tetramethylene ethylenediamine (TMEDA) (1.90 mL, 12.6 mmol). The reaction mixture was stirred overnight at room temperature and the dilithiated ferrocene derivative formed during this time had precipitated as an orange solid. The suspension was then cooled to 0 °C and anhydrous dimethylformamide (DMF, 0.85 mL, 11 mmol) was added to the mixture. The mixture was allowed to warm up to rt and was stirred at this temperature for a further 2 h. The reaction mixture was quenched by adding ice-cooled 5 M aqueous HCl (200 mL) and the product was extracted with diethyl ether (3x25 mL). The organic fractions were collected and dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford **Fc-1** as a dark-red solid. The product was purified by column chromatography (hexane:dichloromethane 1:1 v/v) and obtained in the form of red crystals upon evaporation (0.660 g, 52%).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 9.87 (s, 2H, C*HO*), 4.92 (ps, 4H, 2 X C_5H_4), 4.75 (ps, 4H, 2 X C_5H_4).
^{13}C NMR (DMSO-d_6, 100 MHz): δ = 193.1 (*C*HO), 80.16 (C_{ipso}), 73.95 (Cp), 70.55 (Cp).



The syntheses of the ferrocene derivatives serving as monomers and initiators (**Fc-2** and **Fc-3**) were performed by adapting the literature procedures.[1]

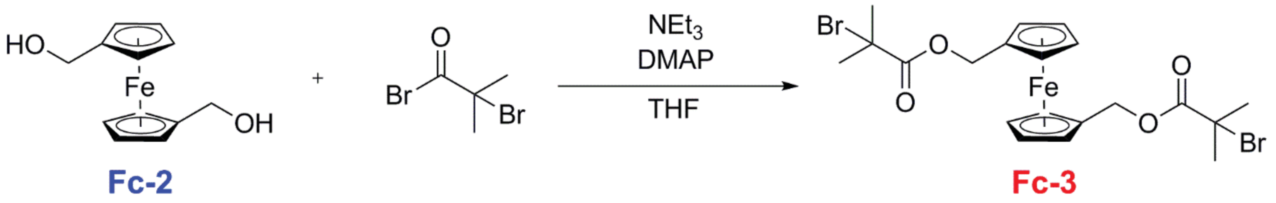
1,1'-Di(hydroxymethyl)ferrocene (Fc-2). In a 25 mL flask under argon atmosphere, $NaBH_4$ (97 mg, 2.5 mmol) was dissolved in dry THF (5 mL) and **Fc-1** (300 mg, 1.2 mmol) was added in small portions. The mixture was stirred at rt for 15 min and $NaBH_4$ (two portions of 59 mg each, 1.56 mmol) was added. The yellow/brownish mixture was filtered through a pad of Celite and then washed with THF (3x10 mL). The organic layers were collected and dried over $MgSO_4$. The fractions were combined and THF was evaporated under reduced pressure to afford **Fc-2** as yellow crystals (0.200 g, 68%).
^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.81 (t, J = 4.81 Hz, 2H, 2X O*H*), 4.20 (d, J = 4.20 Hz, 4H, 2X C*H₂*), 4.12 (t, J = 4.12 Hz, 4H, 2X C_5H_4), 4.07 (t, J = 4.07 Hz, 4H, 2X C_5H_4).
^{13}C NMR (DMSO-d_6, 100 MHz): δ = 88.71 (C_{ipso}), 68.19 (*C*p), 67.74 (*C*p), 58.95 (CH_2).



Synthesis of **Fc-1** and **Fc-2** was performed following a procedure already known in literature.

1,2-Bis(α-bromopropionyloxy)-1,2-dihydroferrocene (Fc-3). Fc-2 (3 g, 12 mmol) was dissolved in anhydrous THF (300 mL) in a dried, two-necked 500 mL round-bottomed flask under nitrogen atmosphere. Distilled trimethylamine (7.5 mL, 54 mmol) and 4-dimethylaminopyridine (DMAP, 0.29g, 2.4 mol) were previously cooled to 0 °C and added to the stirred solution over the course of 10 min. α-Bromoisobutyrylbromide (4.5 mL, 36 mmol) was then added dropwise and a white solid precipitated. The reaction mixture was allowed to warm up to rt overnight, while stirring was maintained. The white precipitate that had formed was filtered off and the filtrate was washed with THF. The solvent was then removed under reduced pressure. The orange solid was dissolved in CH_2Cl_2 and the solution was extracted with 1 M aqueous HCl (3x50 mL), saturated $NaHCO_3$ (3x50 mL), and H_2O (3x50 mL). The organic fractions were collected and the solvent was removed under reduced pressure to obtain a brown paste that was purified by column chromatography (hexane:dichloromethane 1:1v/v) to afford **Fc-3** as a dark-red powder upon evaporation (4.29 g, 66%).

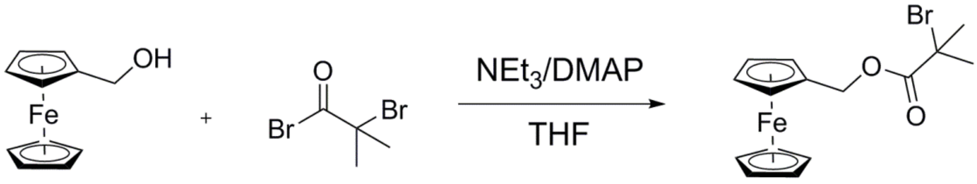
^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.98 (s, 4H, C*H₂*), 4.30 (pt, J = 4.34 Hz, 4H, 2X C_5H_4), 4.21 (pt, J = 4.25 Hz, 4H, 2X C_5H_4), 1.93 (s, 12H, C*H₃*).
^{13}C NMR (DMSO-d_6, 100 MHz): δ = 170.47 (*C*OO), 81.49 (C_{ter}), 69.53 (*C*p), 69.21 (*C*p), 63.78 (CH_2), 57.28 (C_{ipso}), 30.26 (CH_3).



Synthesis of 1,2-bis(α-bromopropionyloxy)-1,2-dihydroferrocene (**Fc-3**)

1-(α-bromopropionyloxy)-1-dihydroferrocene (Fc-4). 1-Di(hydroxymethyl)ferrocene (0.3 g, 1.4 mmol) (Sigma Aldrich) was dissolved in anhydrous THF (35 mL). Net_3 together with DMAP were slowly added, after cooling the solution to 0°C. α-Bromoisobutyrylbromide (0.311 mL, 2.52 mmol) was added dropwise. A precipitate formed quickly. The solution was then filtrate to remove the precipitate and THF was evaporated. The solid obtained was dissolved in DCM and the product was extracted with HCl 1M (3 x 30 mL), $NaHCO_3$ (3 x 30 mL) and H_2O (3 x 30 mL). The organic fractions were collected and dried under $MgSO_4$. DCM was removed under reduced pressure to obtain a dark orange solid (25 %, 50%)

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.97 (s, 2H, CH_2), 4.31 (pt, 2H, C_5H_4), 4.22 (s, 5H, C_5H_5), 4.20 (pt, 2H, C_5H_4), 1.89 (s, 6H, $2xCH_3$).



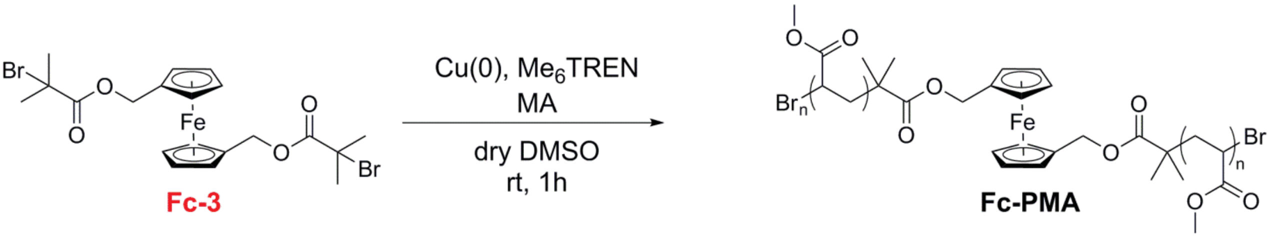
Fc-4

Synthesis of 1-(α-bromopropionyloxy)-1-dihydroferrocene (**Fc-4**)

Synthesis of poly(methyl acrylate)s. The **ref-PMA**, **Fc-PMA** and **Fc-PMA2** were synthesized by single-electron transfer living radical polymerization (SET-LRP) using bifunctional initiators.[1c, 2]

Ferrocene-containing poly(methylacrylate) (Fc-PMA) (containing 1 Fc moiety in the center of the chain) was prepared as follows (**Scheme 2a**): Cu(0) powder (6.1mg, 0.096 mmol), bifunctional initiator **Fc-3** (13.05 mg, 0.024 mmol), tris[2-(dimethylamino)ethyl]amine **(**Me_6TREN, 25.6 µL, 0.096 mmol) and methyl acrylate (MA) (4.32 ml, 48 mmol) were placed in a 25 mL dried Schlenk flask and kept under nitrogen atmosphere. Anhydrous DMSO (2.2 mL) was added and three freeze-pump-thaw cycles were conducted, backfilling with N_2. The reaction mixture was then agitated at 27 °C for 3 h. Finally, the polymerization reaction was quenched by immersing the flask into liquid nitrogen. The crude product was diluted with THF (30 mL) and was passed through a silica column to remove the copper. The mixture was then concentrated, evaporating the solvent under reduced pressure. An excess of MeOH (3x300 mL) was used to precipitate the polymer. The light yellow precipitate obtained was dried *in vacuo* to yield **Fc-PMA** as a yellow solid (2.31 g, 72%).

^{1}H NMR ($CDCl_3$, 400 MHz): 4.23 (ps, 2H, Cp*H*), 4.14 (ps, 2H, Cp*H*), 3.65 (s, $COOCH_3$), 2.30 (m, C*H*), 1.94-1.42 (m, CH_2).^{13}C NMR ($CDCl_3$, 100 MHz): 175.01, 51.86, 41.44, 35.91-34.38. Anal. Calcd for (**Fc-initiator**$_{0.024}$MA$_{48}$)$_n$: C, 53.34; H, 6.56. Found: C, 55.50; H, 7.10. SEC (THF, PS standards): M_n = 133 kDa, $Đ$ = 1.10.



Fc-3

Fc-PMA

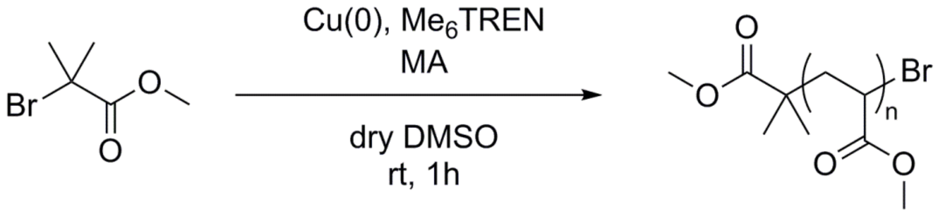
Synthesis of **Fc-PMA** (containing one ferrocene unit in the midchain) obtained with SET-LRP.

Ferrocene-containing poly(methylacrylate) (low molecular weight, Fc-PMA 2) was obtained following the same procedure of **Fc-PMA** (**Scheme 2a)** varying the stoichiometry to obtain a smaller molecular weight: Cu(0) powder (6.1 mg, 0.096 mmol), bifunctional intiator **Fc-3** (13.05 mg, 0.024 mmol), tris[2-(dimethylamino)ethyl]amine **(**Me_6TREN) (25.6 µL 0.096 mmol), and methyl acrylate (MA) (1.28 mL, 14.4 mmol) were added in a 5 mL dried Schlenk flask under nitrogene atmosphere. Anhydrous DMSO (1 mL) was added and three freeze-pump-thaw cycles were conducted, backfilling with N_2. The same procedure previously described for Fc-PMA was used. A light yellow solid (0.80 g, 83%) was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz): 4.24 (ps, 2H, Cp*H*), 4.15 (ps, Cp*H*, 2H), 3.65 (s, $COOCH_3$), 2.30 (m, C*H*), 1.94-1.44 (m, CH_2). ^{13}C NMR($CDCl_3$, 100 Hz): 175.02, 164.37, 51.93, 41.44, 35.07. Anal. Calcd for (**Fc-initiator**$_{0.024}$MA$_{14.3}$)$_n$: C, 53.34; H, 6.56. Found: C, 55.0; H, 7.10. SEC (THF, PS standards) M_n = 40 kDa, $Đ$ = 1.13.

Monofunctionalized ferrocene-containing poly(methylacrylate) (Fc-PMA3) was obtained following the same procedure of **Fc-PMA** (**Scheme 2a**) varying the stoichiometry to obtain a mono-functionalized polymer: Cu(0) powder (7 mg, 0.11 mmol), monofunctional intiator **Fc-4** (20 mg, 0.0055 mmol), tris[2-(dimethylamino)ethyl]amine **(**Me_6TREN) (29 µL 0.11 mmol), and methyl acrylate (MA) (14.7 mL, 165 mmol) were added in a 20 mL dried Schlenk flask under nitrogen atmosphere. Anhydrous DMSO (6.6 mL) was added and three freeze-pump-thaw cycles were conducted, backfilling with N_2. The same procedure previously described for Fc-PMA was used. A light yellow solid (56 %, 60%) was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.65 (s, $COOCH_3$), 2.30 (m, C*H*), 1.94-1.43 (m, CH_2). ^{13}C NMR($CDCl_3$, 100 Hz): 175.02, 51.88, 41.45, 34.98. SEC (THF, PS standards) M_n = 170 kDa, $Đ$ = 1.11.

Reference poly(methylacrylate) (ref-PMA) was synthesized following the same procedure described above (**Scheme 2b**), but using methyl α-bromoisobutyrate (7 µL, 0.048 mmol) as initiator, Cu(0) powder (6.1 mg, 0.096 mmol), Me_6TREN (26µL, 0.096 mmol), MA (12.84 mL, 144 mmol) and anhydrous DMSO (6.6 mL) as solvent. The polymer was obtained as a white solid (3.260 g, 57%) ^{1}H NMR

($CDCl_3$, 400 MHz): 3.65 (s, COOCH_3), 2.30 (m, C*H*), 1.94-1.46 (m, CH_2). ^{13}C ($CDCl_3$, 100 Hz): 175.02, 51.87, 41.44, 35.10. Anal. Calcd for (methyl α-bromoisobutyrate $_{0.048}$MA$_{144}$)$_n$: C, 53.34; H, 6.56. Found: C, 55.50; H, 7.10. SEC (THF, PS standards) M_n = 119 kDa, Đ = 1.08.



Synthesis of **ref-PMA** (ferrocene-free polymer) obtained with SET-LRP.

Syntheses of polyurethanes. The polyurethanes **Fc-PU** and **Ref-PU** were synthesized by adapting previously reported protocols.[3]

Ferrocene-containing polyurethane (Fc-PU) (containing *ca.* 6 Fc motifs per chain) was prepared as follows (**Scheme 2**): PTHF (M_n = 2000 g/mol, 4.960 g, 2.479 mmol) and **Fc-2** (0.102 g, 0.413 mmol) were placed in a dried, two-necked 100 mL round-bottomed flask equipped with a septum. THF (40 mL) was added under N_2 and a solution of MDI (1.8 g, 7.161 mmol, NCO/OH molar ratio of 1.08:1) in THF (10 mL) was rapidly added with a syringe under stirring. Subsequently, dibutyltin dilaurate (DBTDL, 3 drops) was added to the stirred reaction mixture, which was stirred for 3 h at rt to form a yellow solution. After 3 h of reaction, BDO (0.335 g, 3.718 mmol) was added dropwise to the reaction mixture and the homogeneous solution was stirred at rt for another 48 h. A rubbery yellow polymer was recovered after precipitation in EtOH (800 mL) and then washed twice with EtOH (2x800 mL). The resulting polymer was collected by filtration and dried *in vacuo* at 40 °C for 12 h. **Fc-PU** was obtained as a yellow fibrous, rubbery solid (7.00 g, 77%). FT-IR measurements were carried out to confirm the disappearance of the NCO signals at 2282 cm^{-1}, corresponding to the completion of the reaction. ^{1}H NMR (THF-d_8, 400 MHz): δ = MDI residue: 8.58 (s, 2H, N*H*), 8.55 (s, 2H, N*H*), 7.37 (d, 4H, Ar*H*), 7.05 (d, 4H, Ar*H*), 3.82 (s, H, CH_2-Ar); PTHF residue: 4.08 (t, 4H, CH_2-OOC), 3.37 (s, 108H, CH_2-O), 1.59 (s, 108H, CH_2); BDO residue: 4.13 (d, 4H, CH_2-O), 1.73 (4H, CH_2 obstructed); end groups: 4.94 (s, 2H, NH_2); ferrocene residue: 4.29(s, 4H, Cp*H*), 4.17 (ps, 4H, Cp*H*).^{13}C NMR (THF-d_8, 100 MHz): 154.51, 138.76, 136.45, 129.95, 119.08, 71.56, 71.30, 64.87, 41.43, 27.82. Anal. Calcd for ($MDI_{7.1612}BDO_{3.7183}PTHF_{2.4788}Fc_{0.4133}$)$_n$: C, 66.83; H, 9.31; N, 2.77. Found: C, 66.66; H, 9.50; N, 2.40. SEC (THF, PS standards): M_n = 100 kDa, Đ = 2.03.

Reference polyurethane (ref-PU) (without Fc) was synthesized using the same procedure described above, but omitting the addition of **Fc-2**, using the following quantities: PTHF (9.994 g, 4.997 mmol), BDO (0.837 g, 9.284 mmol), MDI (3.945 g, 15.765 mmol), DBTDL (4 drops). **Ref-PU** was obtained as a white fibrous, rubbery solid (13.298 g, 90%). ^{1}H NMR (THF-d_8, 400 MHz): δ = MDI residue: 8.57 (s, 2H, N*H*), 8.54 (s, 2H, N*H*), 7.36 (d, 4H, Ar*H*), 7.03 (d, 4H, Ar*H*), 3.82 (s, 2H, CH_2-Ar); PTHF residue: 4.09 (t, 4H, CH_2-OOC), 3.37 (s, 108H, CH_2-O), 1.69 (s, 4H, CH_2), 1.58 (s, 108H, CH_2); BDO residue: 4.13 (d, 4H, CH_2-O), 1.73 (4H, CH_2 obstructed); end groups: 6.82 (d, 2H Ar*H*), 6.47 (d, 2H Ar*H*), 4.65(s, 2H, NH_2). ^{13}C NMR (THF-d_8, 100 MHz): δ = 154.37, 138.73, 138.64, 136.43, 136.33, 129.83, 119.15, 118.97, 71.45, 71.38, 71.01, 65.00, 64.75, 41.32, 27.70, 27.35, 27.10, 26.80. Anal. Calcd for ($MDI_{15.765}BDO_{9.284}PTHF_{4.997}$)$_n$: C, 66.90; H, 9.27; N, 2.99. Found: C, 66.33; 9.53; N, 2.87. Found: C, 66.33; H, 9.53; N, 2.87 SEC (THF, PS standards): M_n = 119 kDa, Đ = 1.60.

Ferrocene-containing polyurethane2 (Fc-PU2) (containing *ca.* 12 % of Fc motifs per chain) was prepared following the same procedure previously reported for Fc-PU (6 Fc motifs per chain) (**Scheme 2**): PTHF (M_n = 2000 g/mol, 3.251 g, 1.6255 mmol) and **Fc-2** (0.400 g, 1.6275 mmol) were placed in a dried, two-necked 100 mL round-bottomed flask equipped with a septum. THF (40 mL) was added under N_2 and a solution of MDI (1.80 g, 7.214 mmol, NCO/OH molar ratio of 1.08:1) in THF (10 mL) was rapidly added with a syringe under stirring. Subsequently, dibutyltin dilaurate (DBTDL, 3 drops) was added to the stirred reaction mixture, which was stirred for 3 h at rt to form a yellow solution. After 3 h of reaction, BDO (7 g, 3.305 mmol) was added dropwise to the reaction mixture and the homogeneous solution was stirred at rt for another 48 h. A rubbery yellow polymer was recovered after precipitation in EtOH (800 mL) and then washed twice with EtOH (2x800 mL). The resulting polymer was collected by filtration and dried *in vacuo* at 40 °C for 12 h. **Fc-PU** was obtained as a yellow fibrous, rubbery solid (20 g, 26%). ^{1}H NMR (THF-d_8, 400 MHz): δ = MDI residue: 8.57 (s, 2H, N*H*), 8.54 (s, 2H, N*H*), 7.36 (d, 4H, Ar*H*), 7.03 (d, 4H, Ar*H*), 3.82 (s, H, CH_2-Ar); PTHF residue: 4.09 (t, 4H, CH_2-OOC), 3.37 (s, 108H, CH_2-O), 1.58 (s, 108H, CH_2); BDO residue: 4.13 (d, 4H, CH_2-O), 1.73 (4H, CH_2 obstructed); end groups: 4.65 (s, 2H, NH_2); ferrocene residue: 4.29(s, 4H, Cp*H*), 4.17 (ps, 4H, Cp*H*). SEC (THF, PS standards) M_n = 46 kDa, Đ = 2.6.

Fourier transformation infrared (FT-IR) spectra

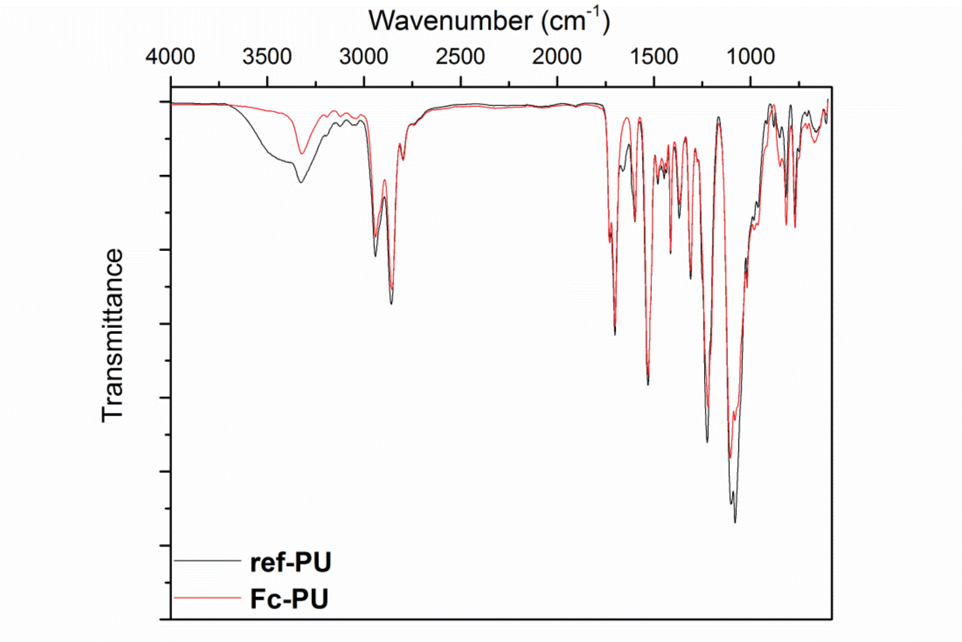


Figure S1. FT-IR spectra of the ferrocene-containing polyurethanes **Fc-PU** (red line) and the reference polyurethane **ref-PU** (black line). The typical signals of the urethane carbonyl group were observed at 1730 cm^{-1} and the bands of the ν(NH) vibration were found at 1520 cm^{-1} and 1210 cm^{-1}. The absence of a signal at 2300 cm^{-1} indicates that all isocyanate groups completely reacted during the polymerization. We can also observe the weak and sharp signal at 1630 cm^{-1} relative to the aromatic overtones of ferrocene. The typical signal of C=C stretching and sp^2 C-H bending were observed at 1400 and 100 cm^{-1} respectively.

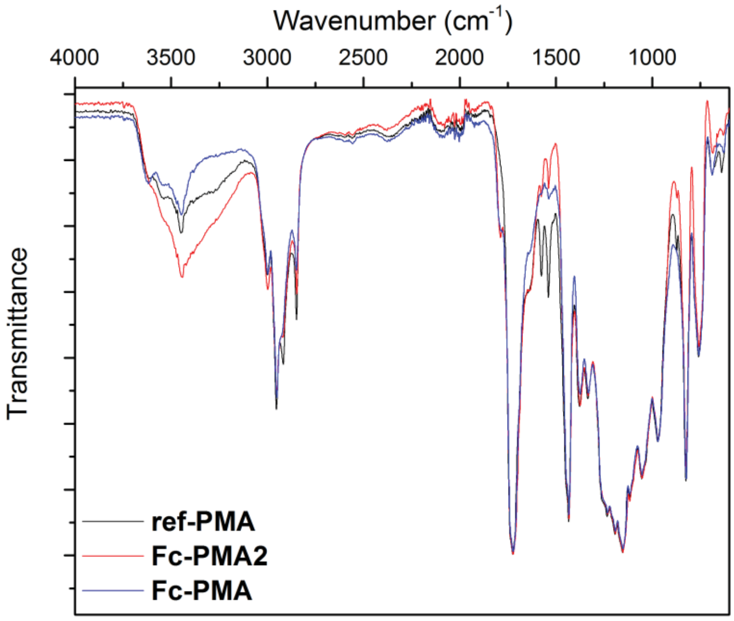


Figure S2. FT-IR spectra of the ferrocene-containing poly(methylacrylate) **Fc-PMA** (blue line), **Fc-PMA2** (red line) and the reference poly(methylacrylate) **ref-PMA** (black line). The typical signal of the C-H stretching was observed at 2954 cm^{-1} and the C=O stretching band was found at 1733 cm^{-1}. Also the signals between 1236 and 1162 cm^{-1} are typical of this polymer, in particular of the C-O-C stretching and O-CH_3 bending, respectively. In this case most of the signals typical of ferrocene are hidden by the overlap with the polymer signals.

Figure S3. 400 MHz ^{1}H NMR spectrum of **ref-PMA** in $CDCl_3$.

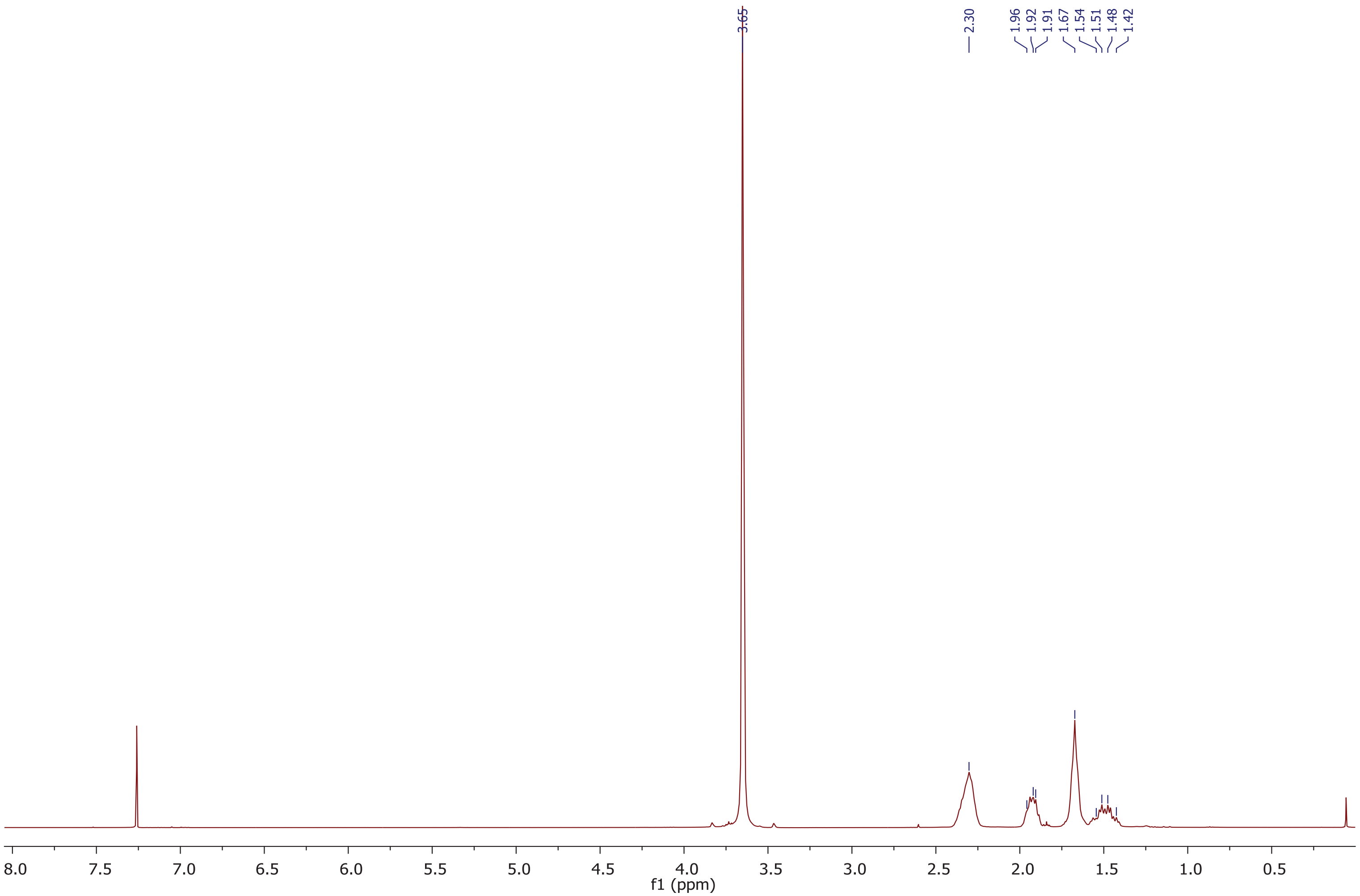


Figure S4. 100 MHz ^{13}C NMR spectrum of **ref-PMA** in CDCl$_3$.

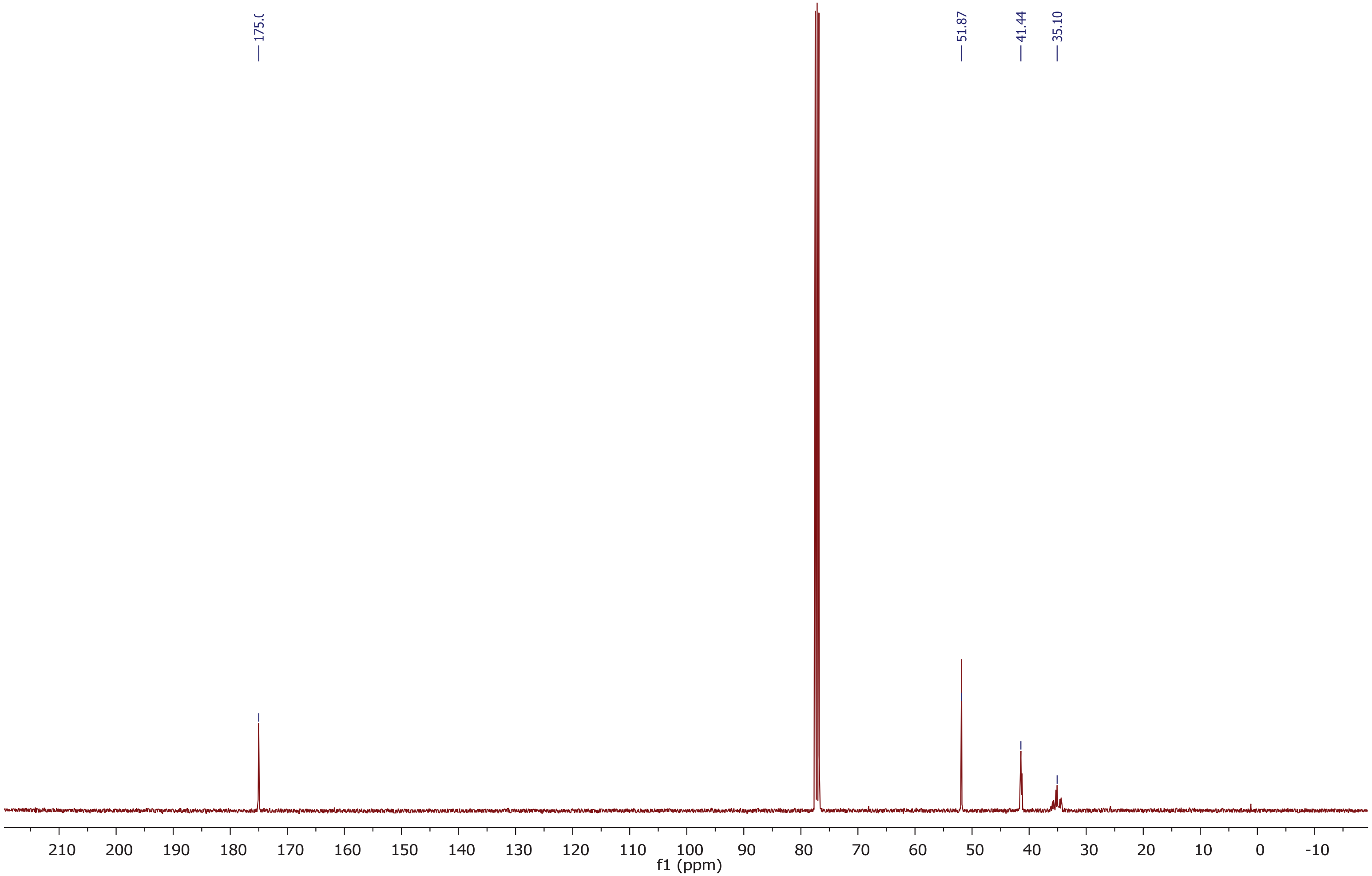


Figure S5. 400 MHz ^{1}H NMR spectrum of **Fc-PMA2** in CDCl$_3$.

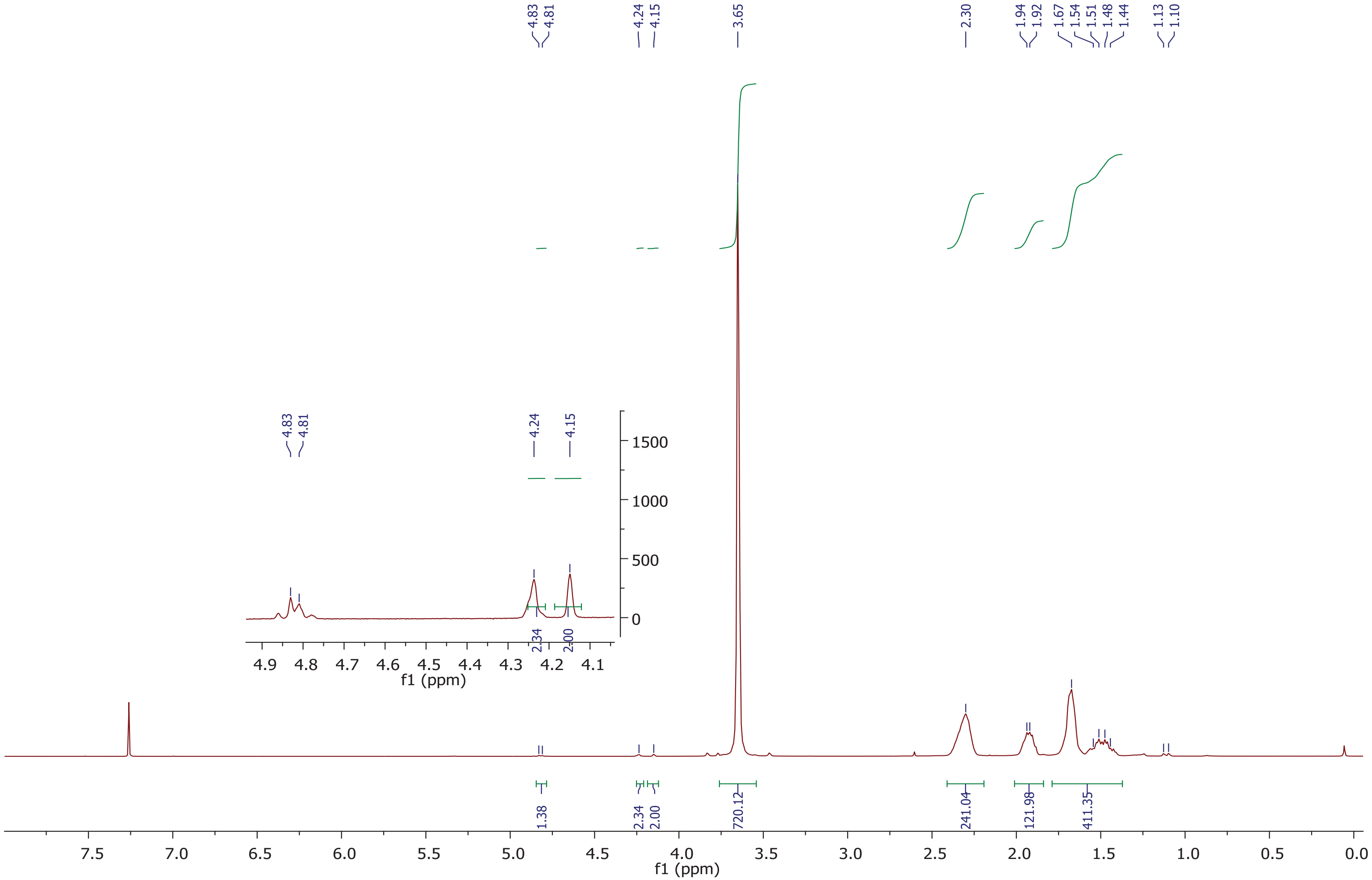


Figure S6. 100 MHz ^{13}C NMR spectrum of **Fc-PMA2**.

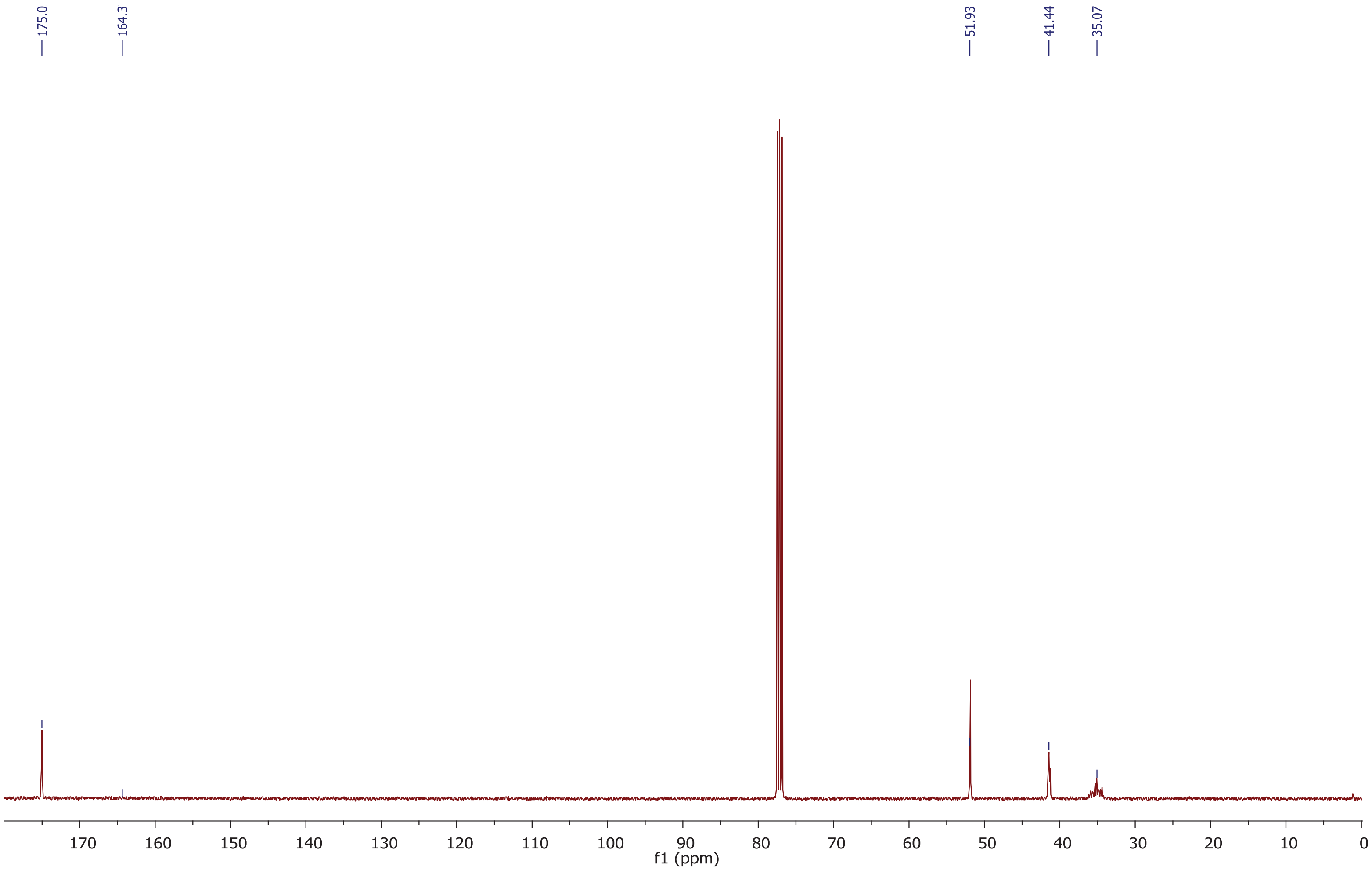


Figure S7. 400 MHz ^{1}H NMR spectrum of **Fc-PMA3**.

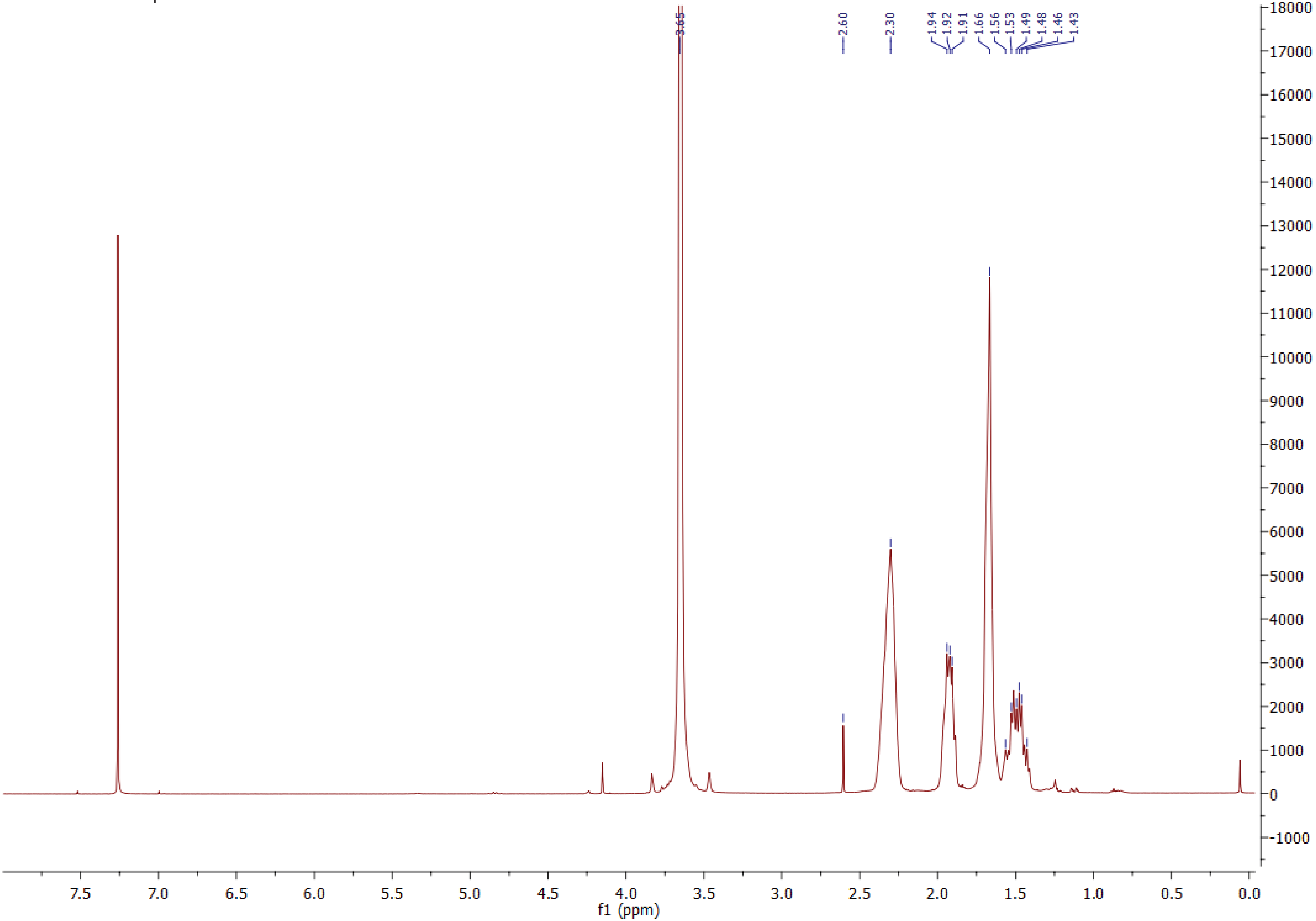


Figure S8. 100 MHz ^{13}C NMR spectrum of **Fc-PMA3**.

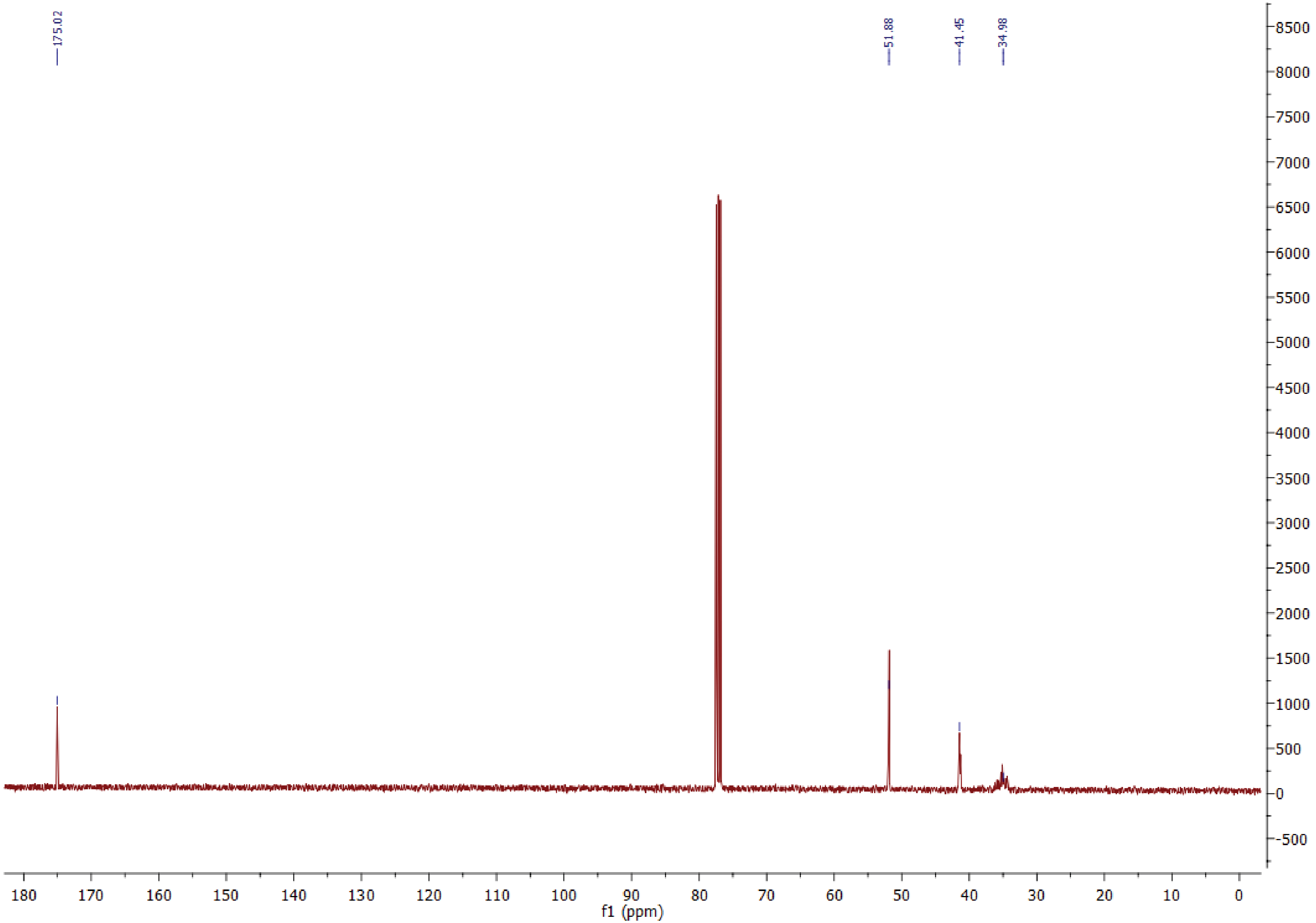


Figure S9. 400 MHz ^{1}H NMR spectrum of **Fc-PMA** in $CDCl_3$.

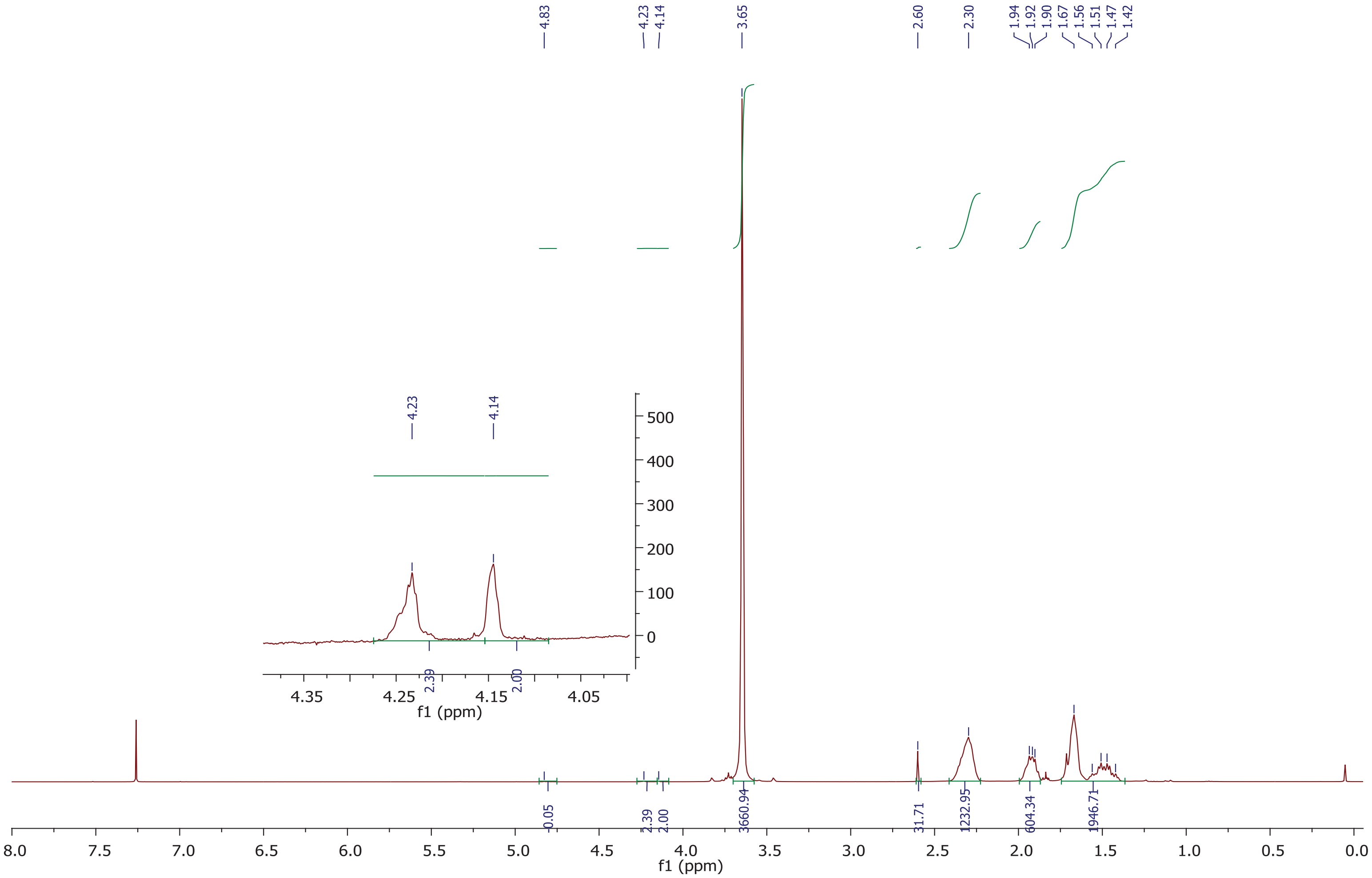


Figure S10. 100 MHz ^{13}C NMR spectrum of **Fc-PMA** in $CDCl_3$.

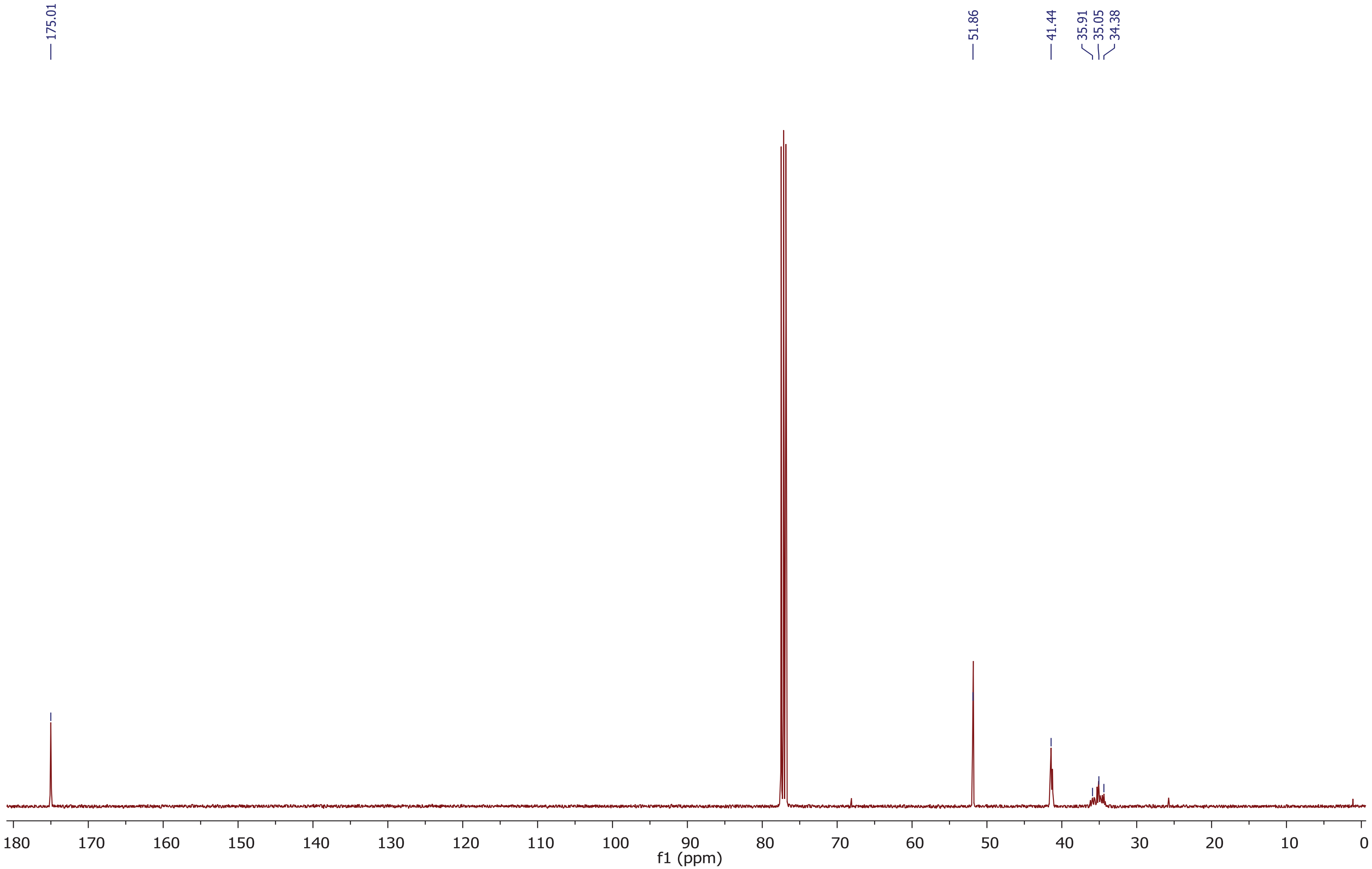


Figure S11. 400 MHz ^{1}H NMR spectrum of **ref-PU** in THF-d_8.

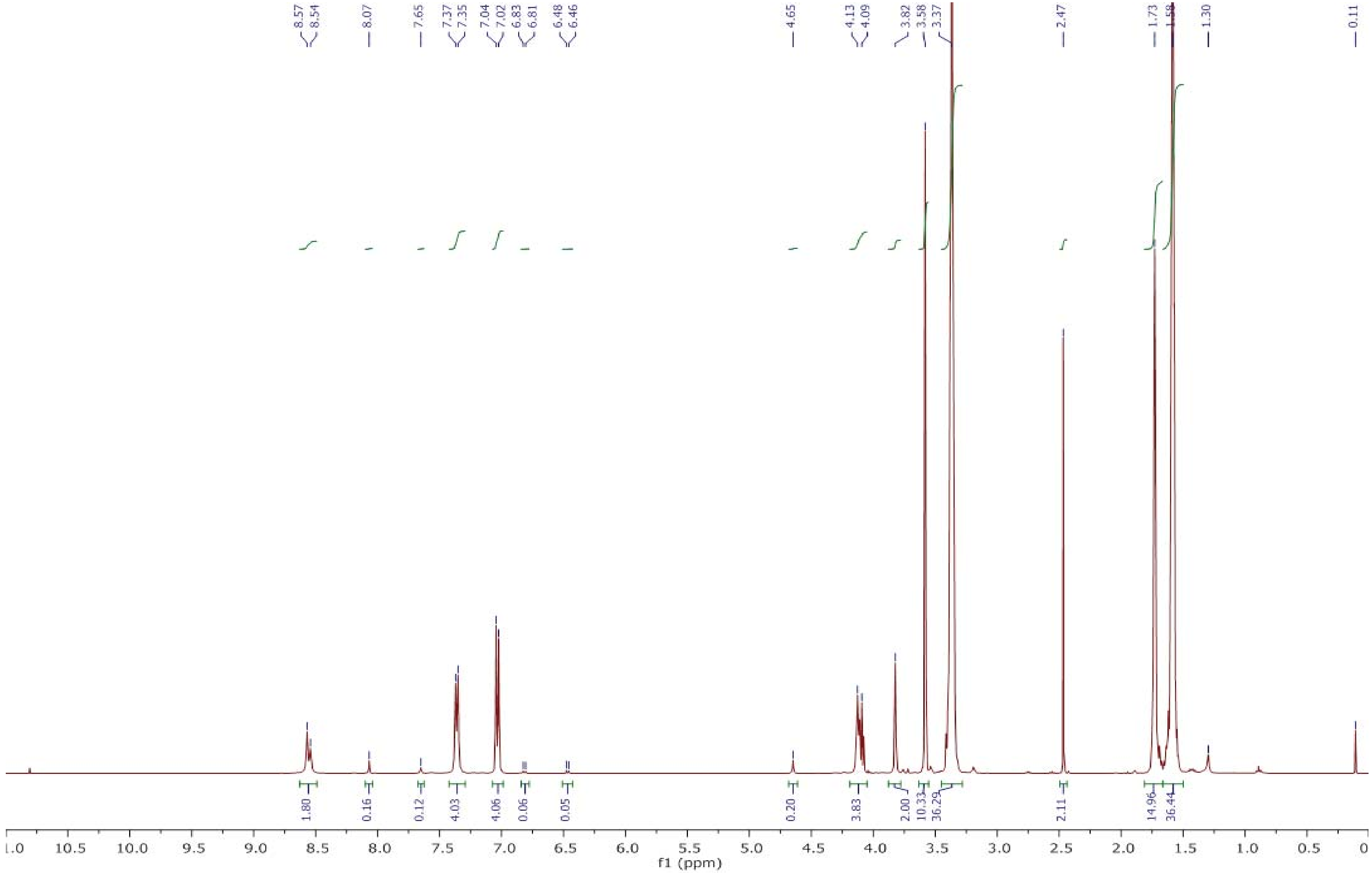


Figure S12. 100 MHz ^{13}C NMR spectrum of **ref-PU** in THF-d_8.

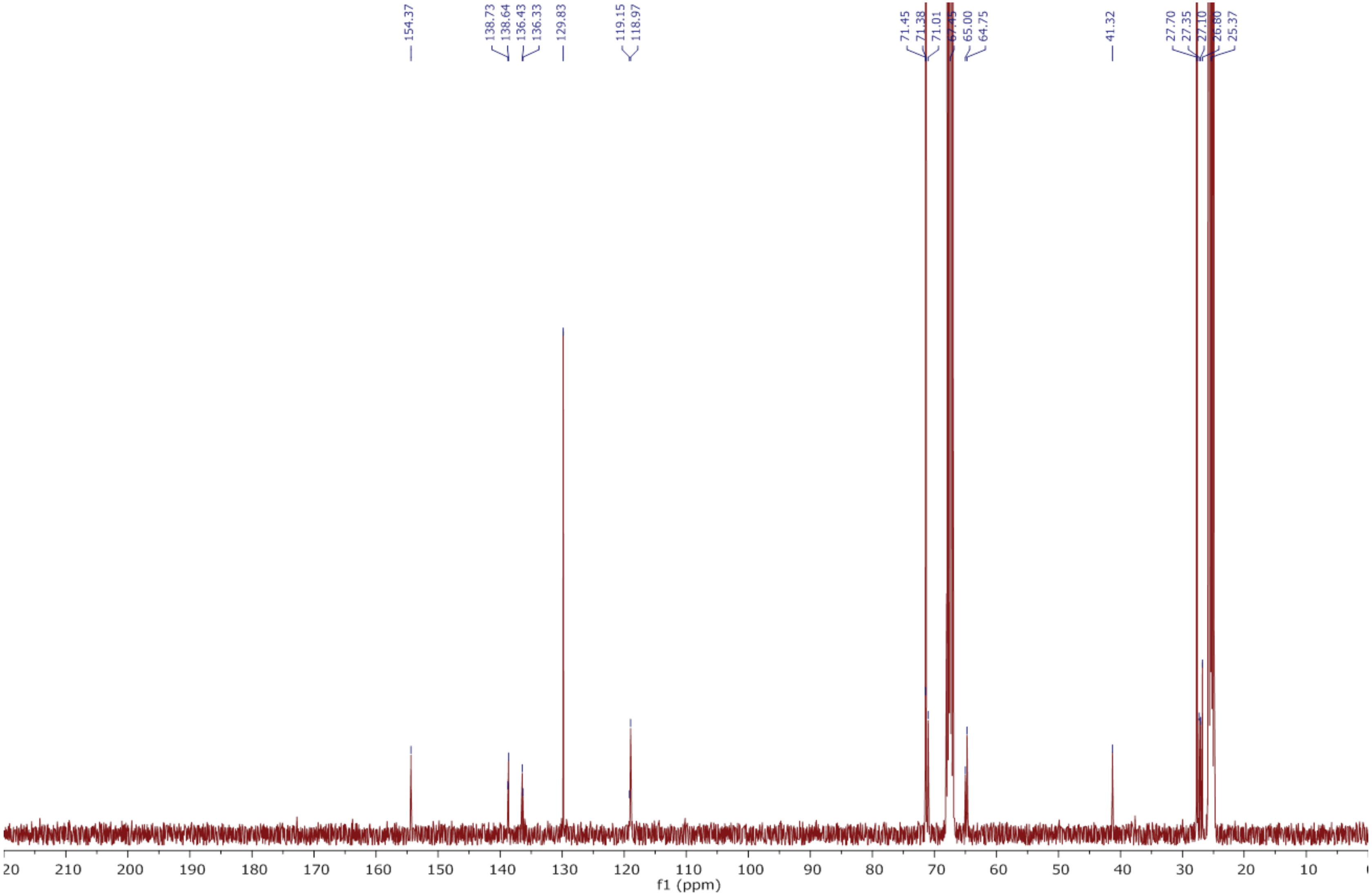


Figure S13. 400 MHz ^{1}H NMR spectrum of **Fc-PU** in THFd$_8$.

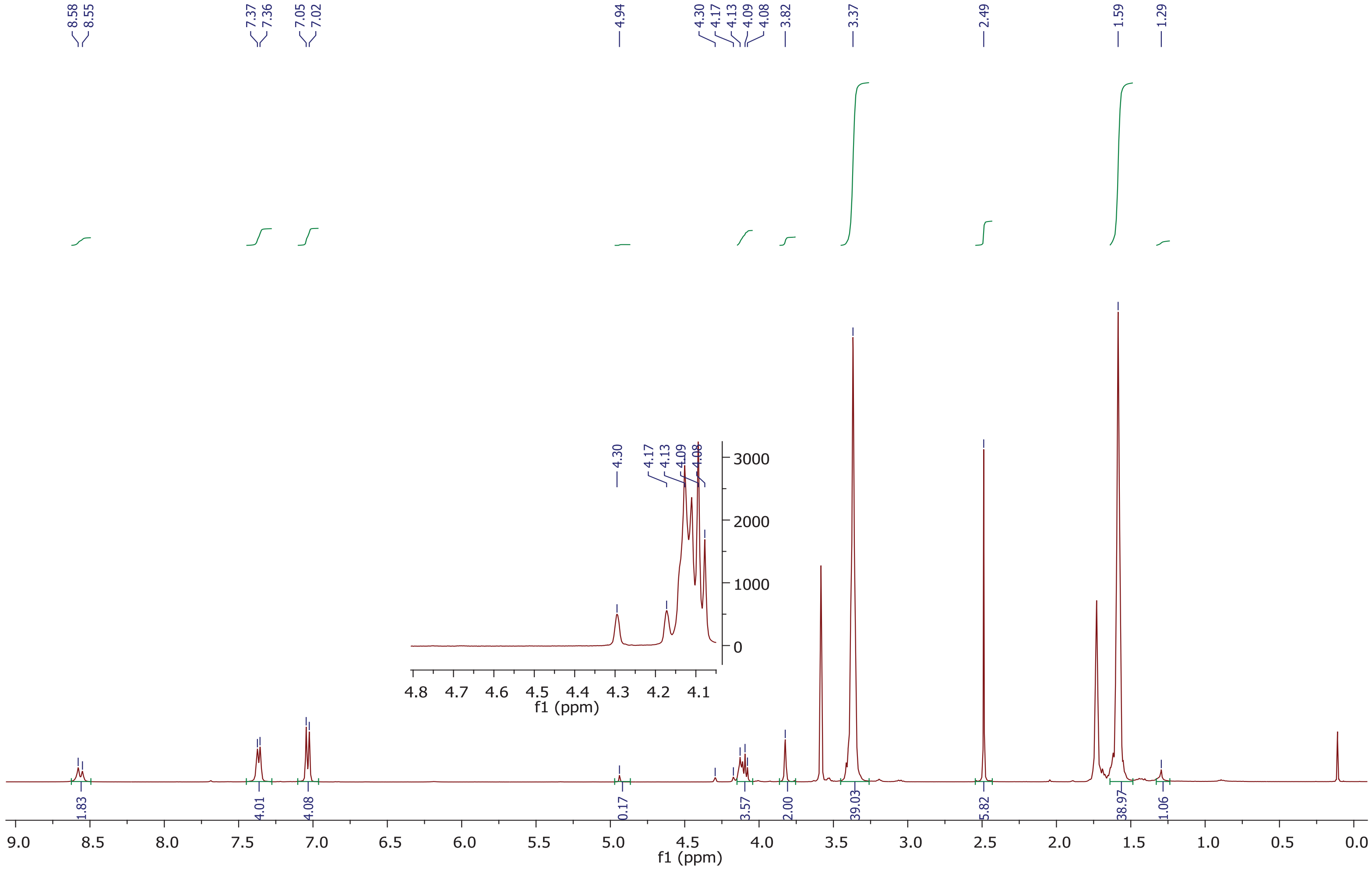


Figure S14. 100 MHz ^{13}C NMR spectrum of **Fc-PU** in THFd$_8$.

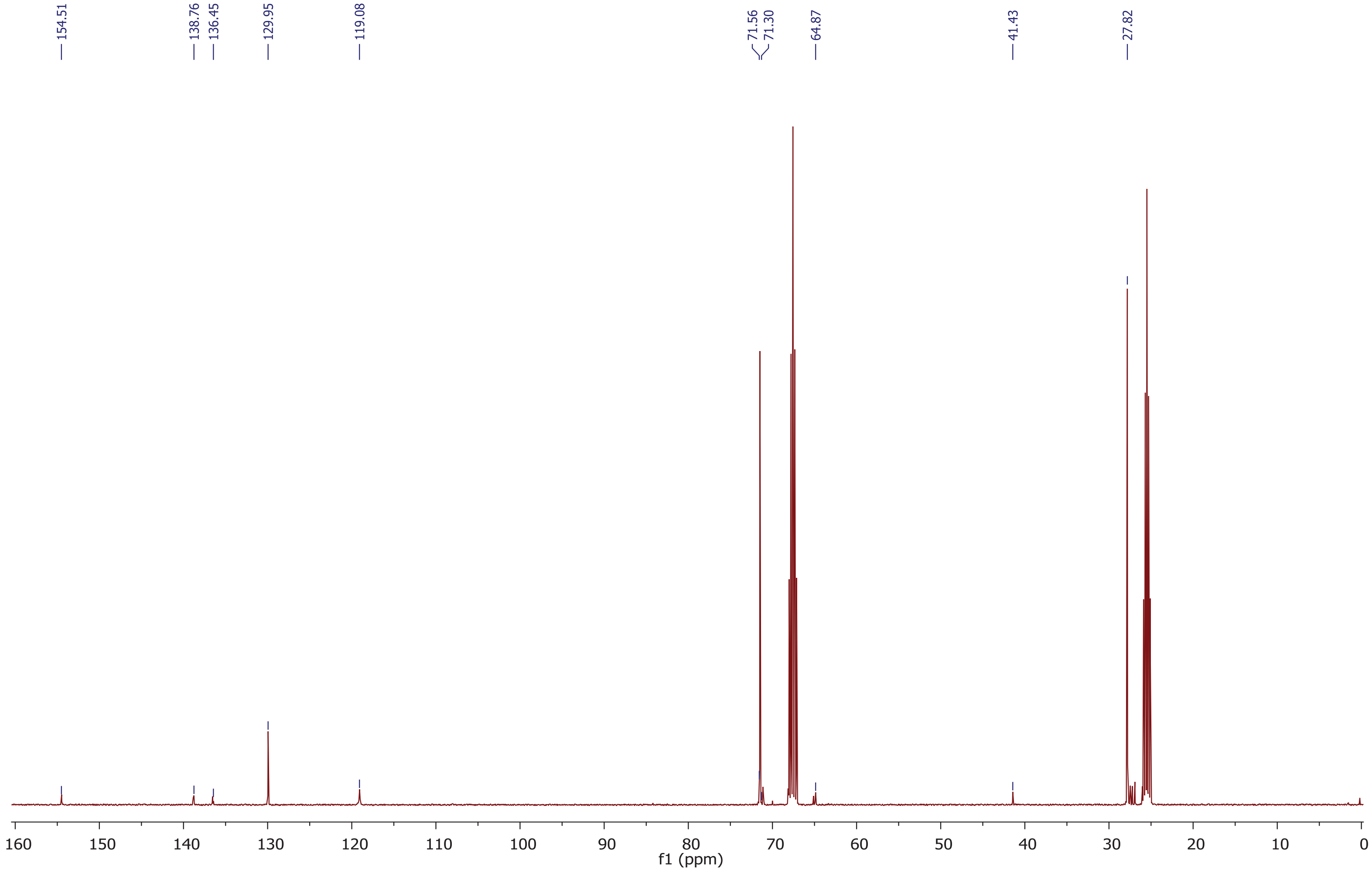


Figure S15. 400 MHz ^{1}H NMR spectrum of **Fc-PU2** in THFd$_8$.

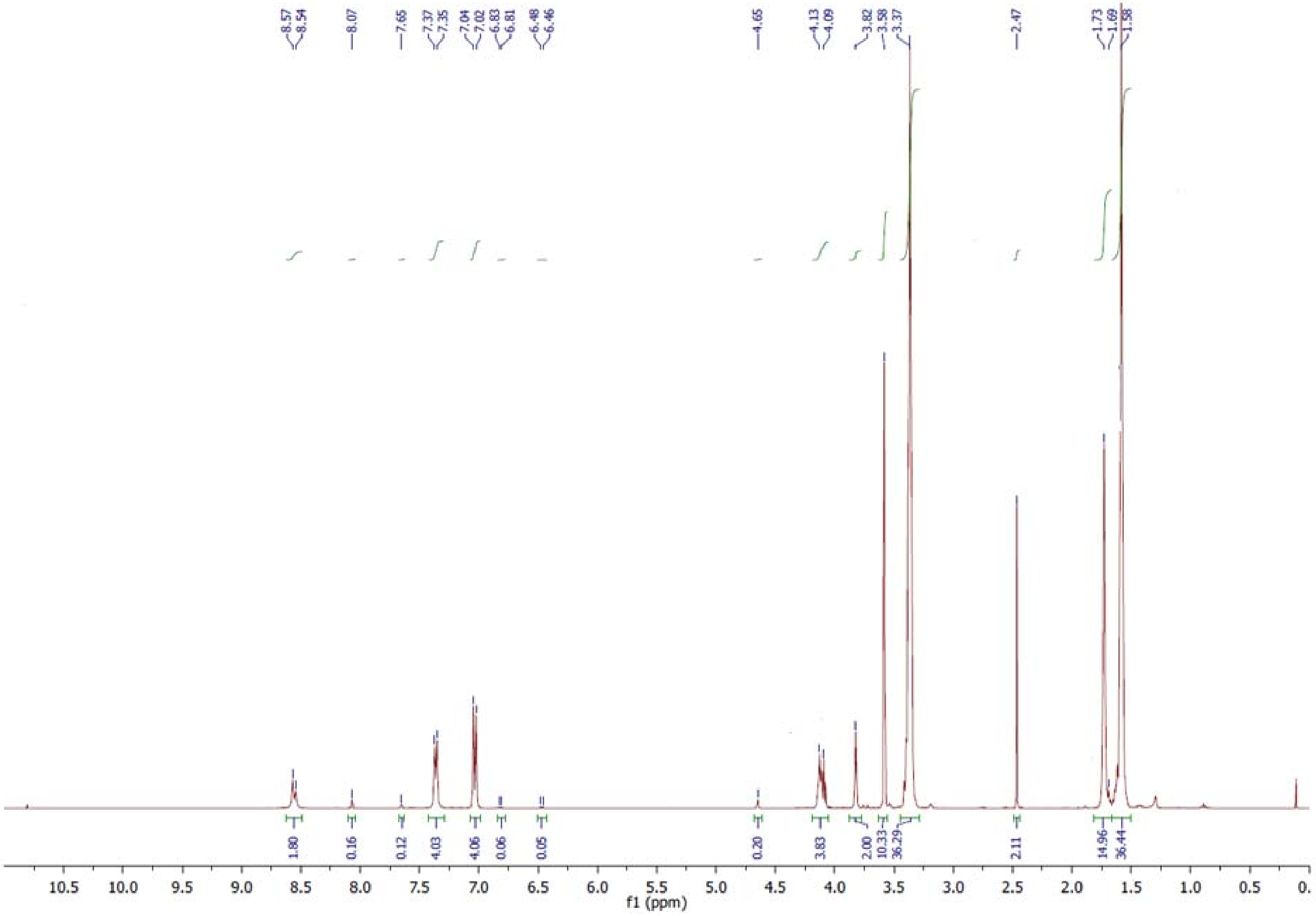


Figure S16. 400 MHz ^{1}H NMR spectrum of **Fc-1** in DMSOd$_6$.

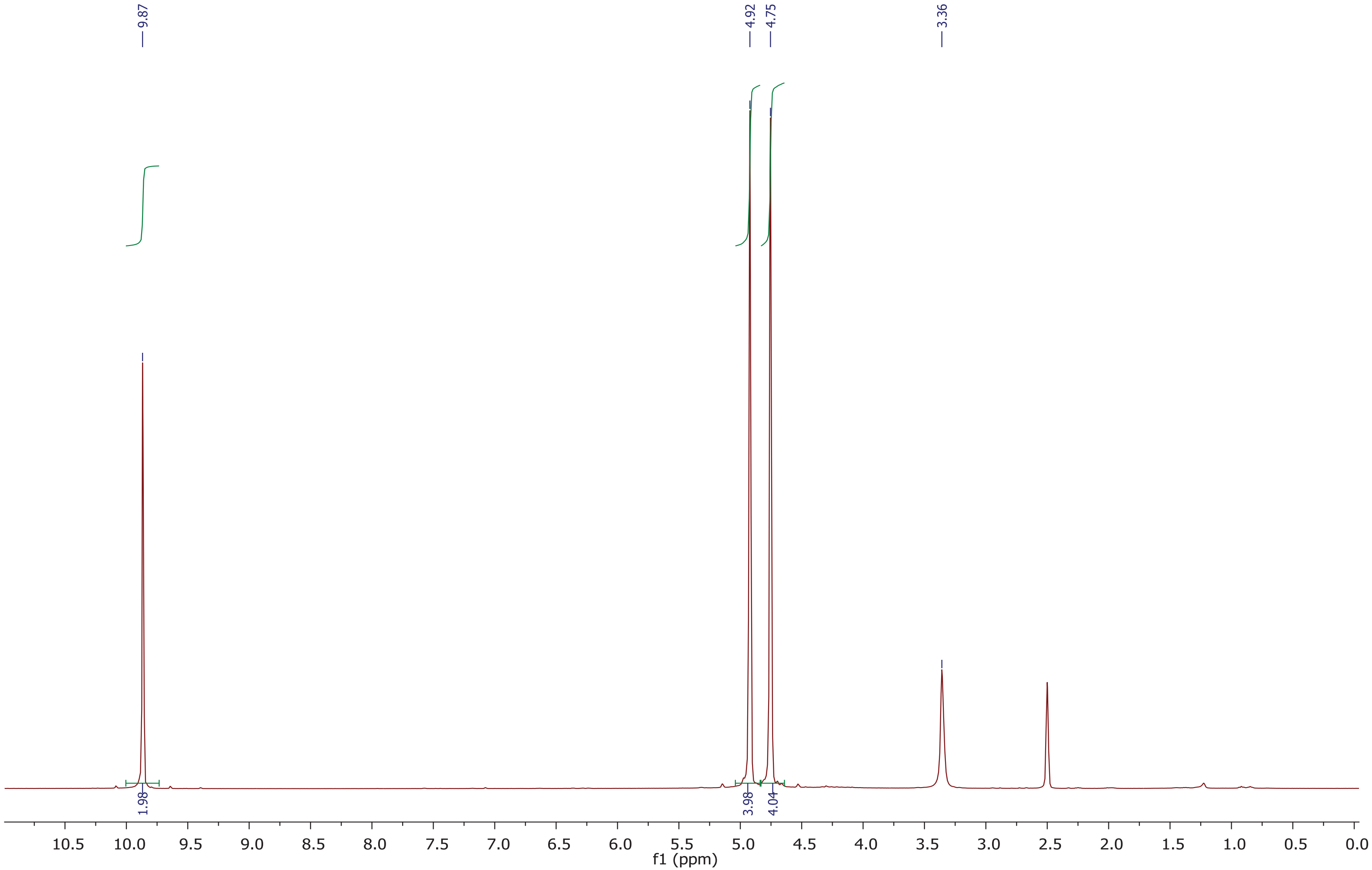


Figure S17. 100 MHz ^{13}C NMR spectrum of **Fc-1** in DMSOd$_6$.

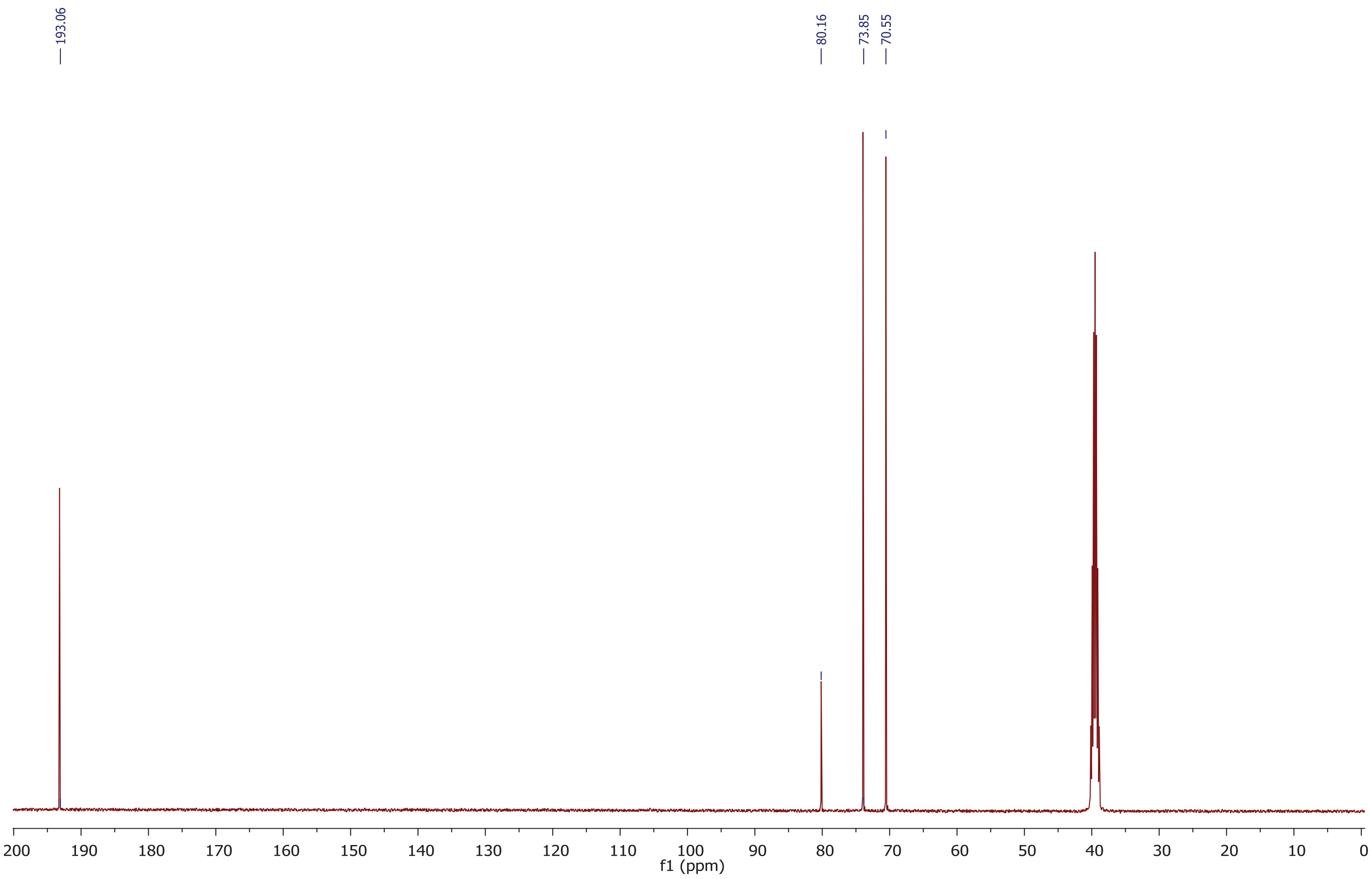


Figure S18. 400 MHz ^{1}H NMR spectrum of **Fc-2** in DMSOd_6.

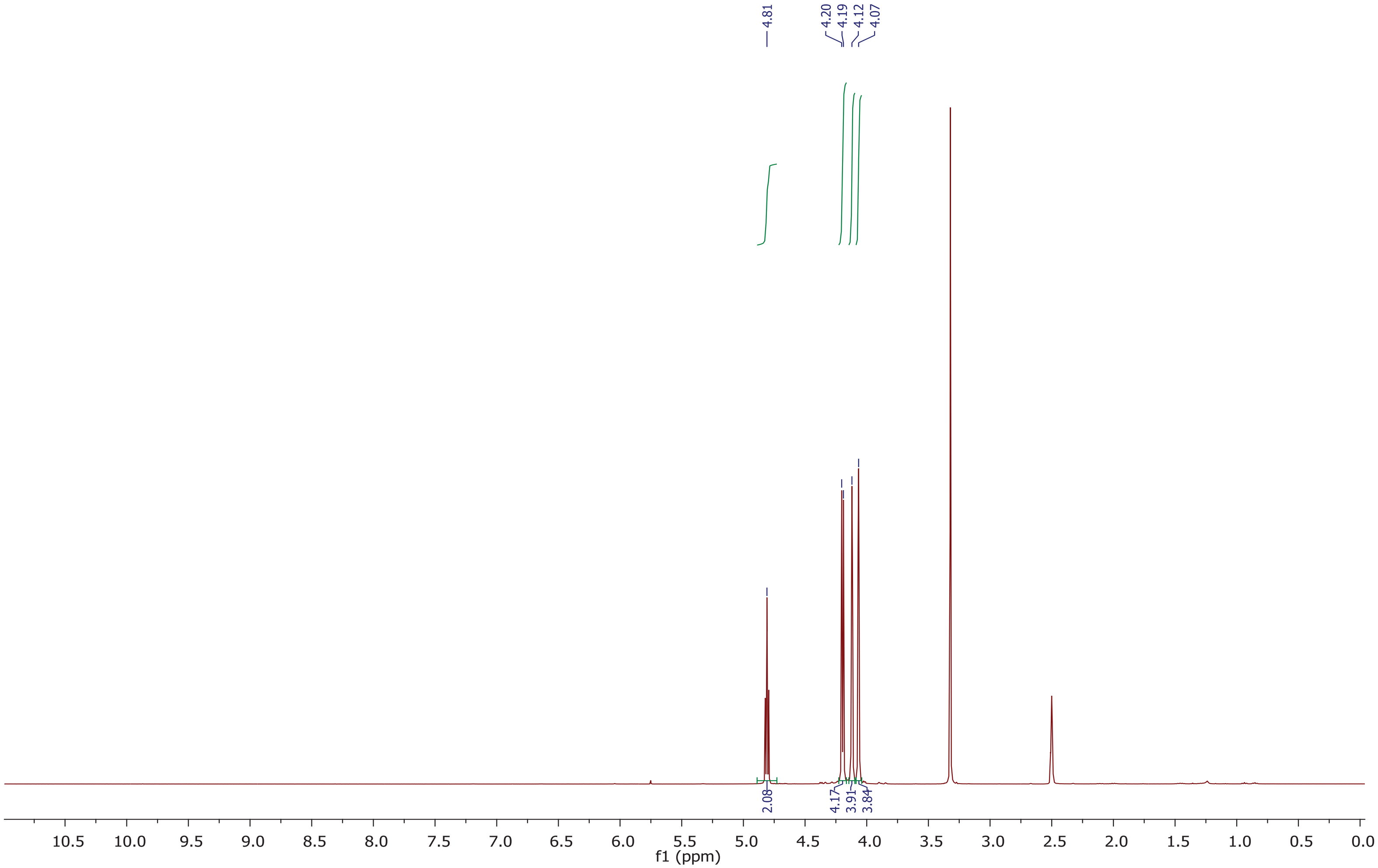


Figure S19. 100 MHz ^{13}C NMR spectrum of **Fc-2** in DMSOd$_6$.

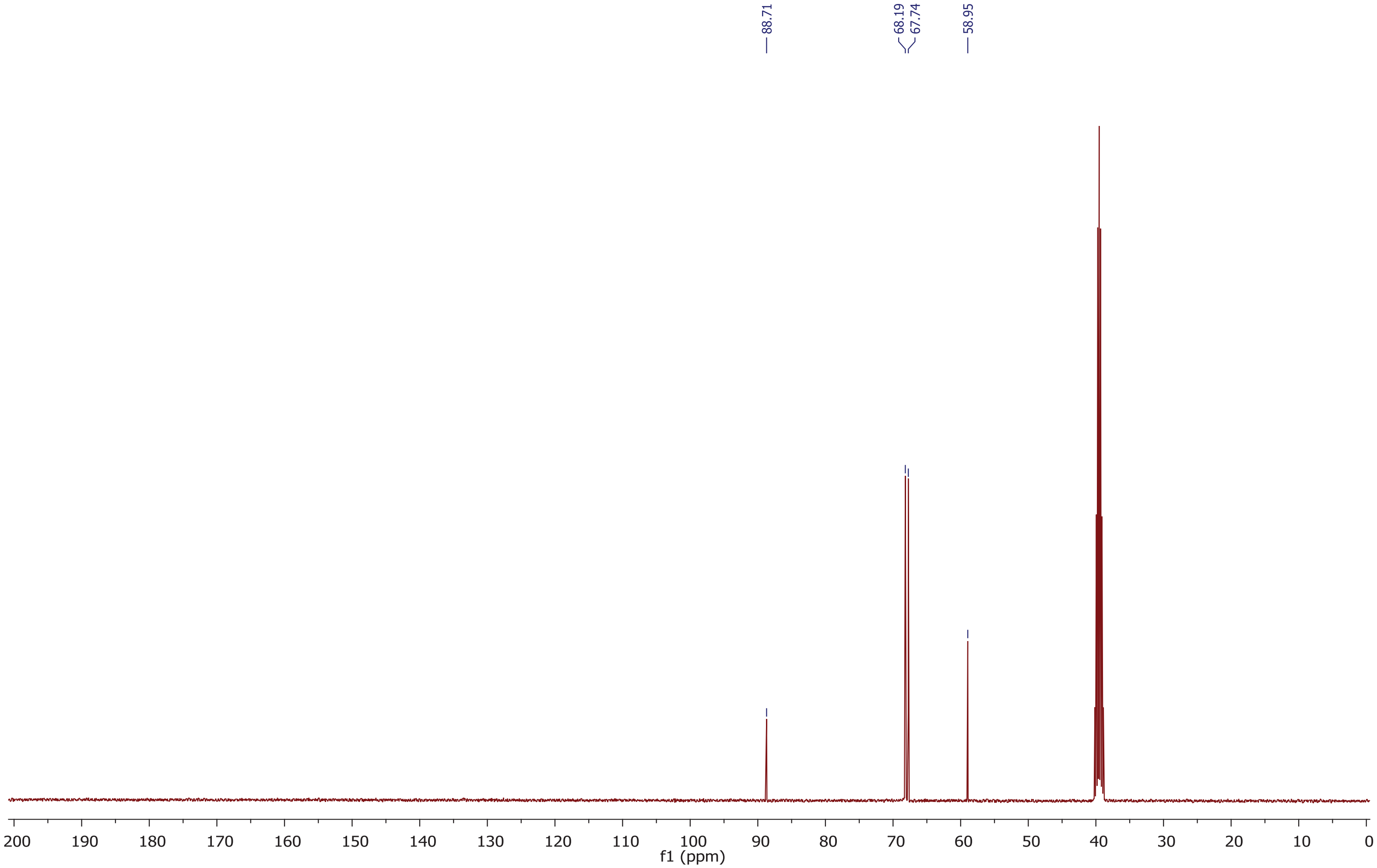


Figure S20. 400 MHz ^1H NMR spectrum of **Fc-initiator** in DMSOd_6.

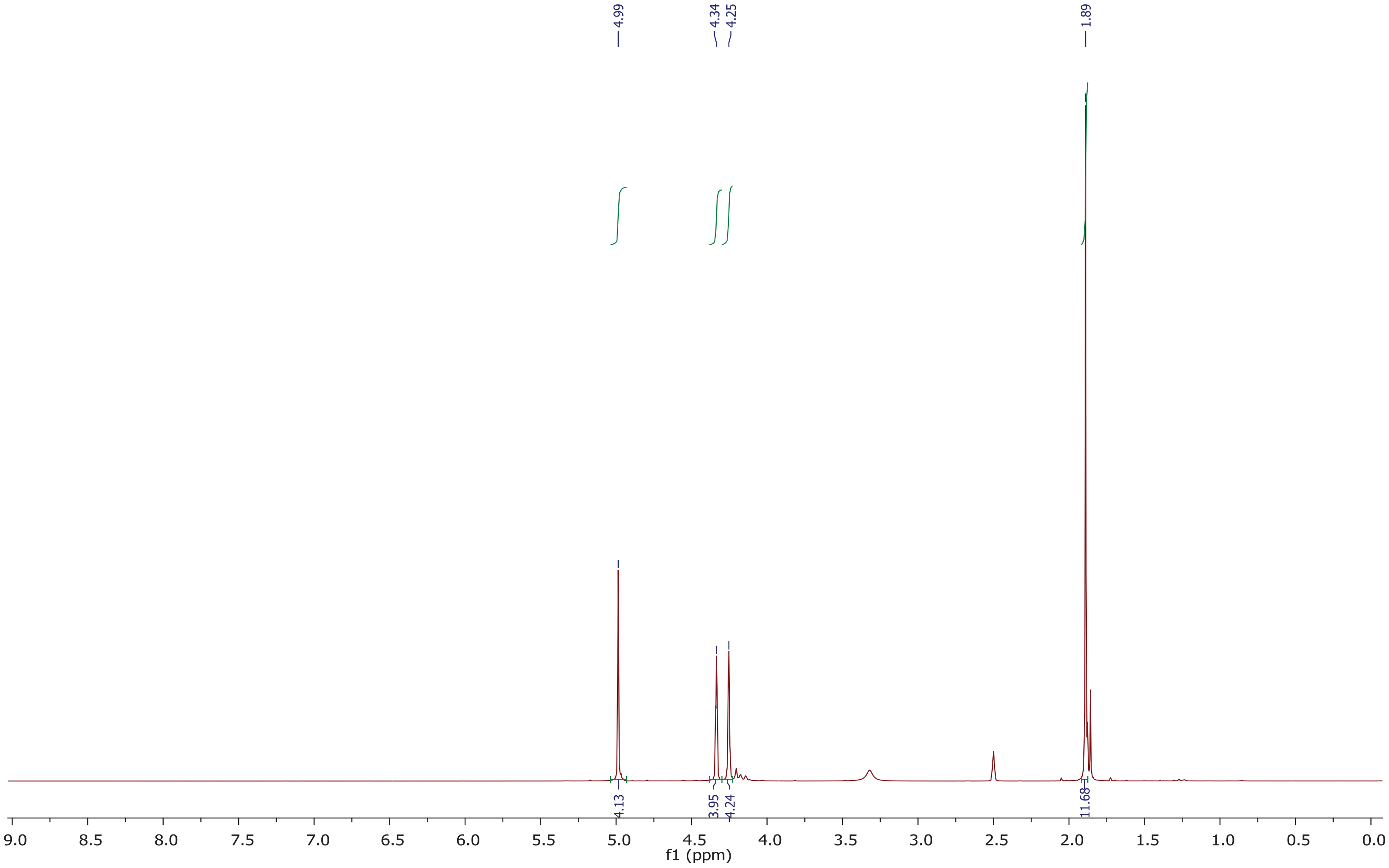


Figure S21. 100 MHz ^{13}C NMR spectrum of **Fc-initiator** in DMSOd_6.

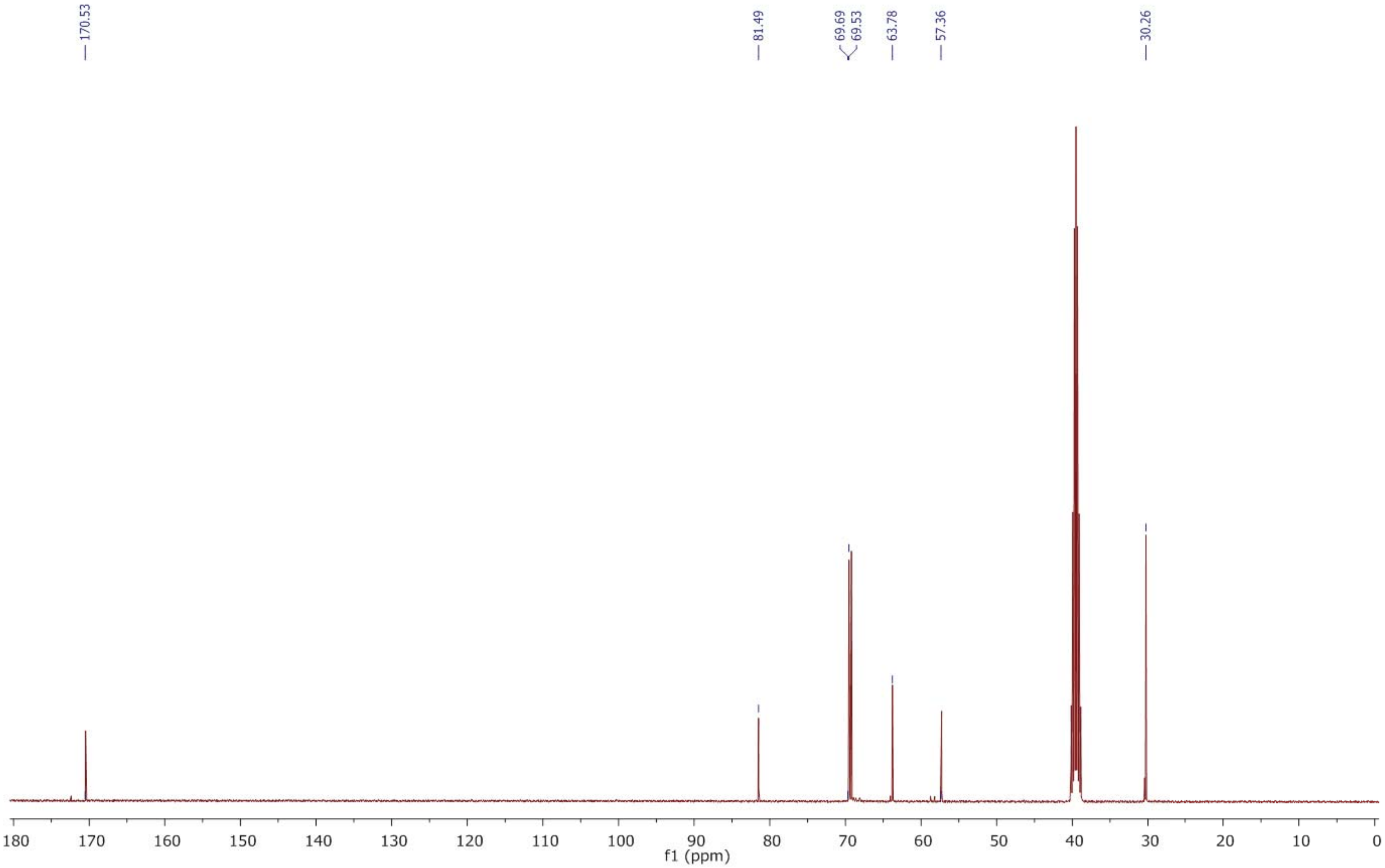
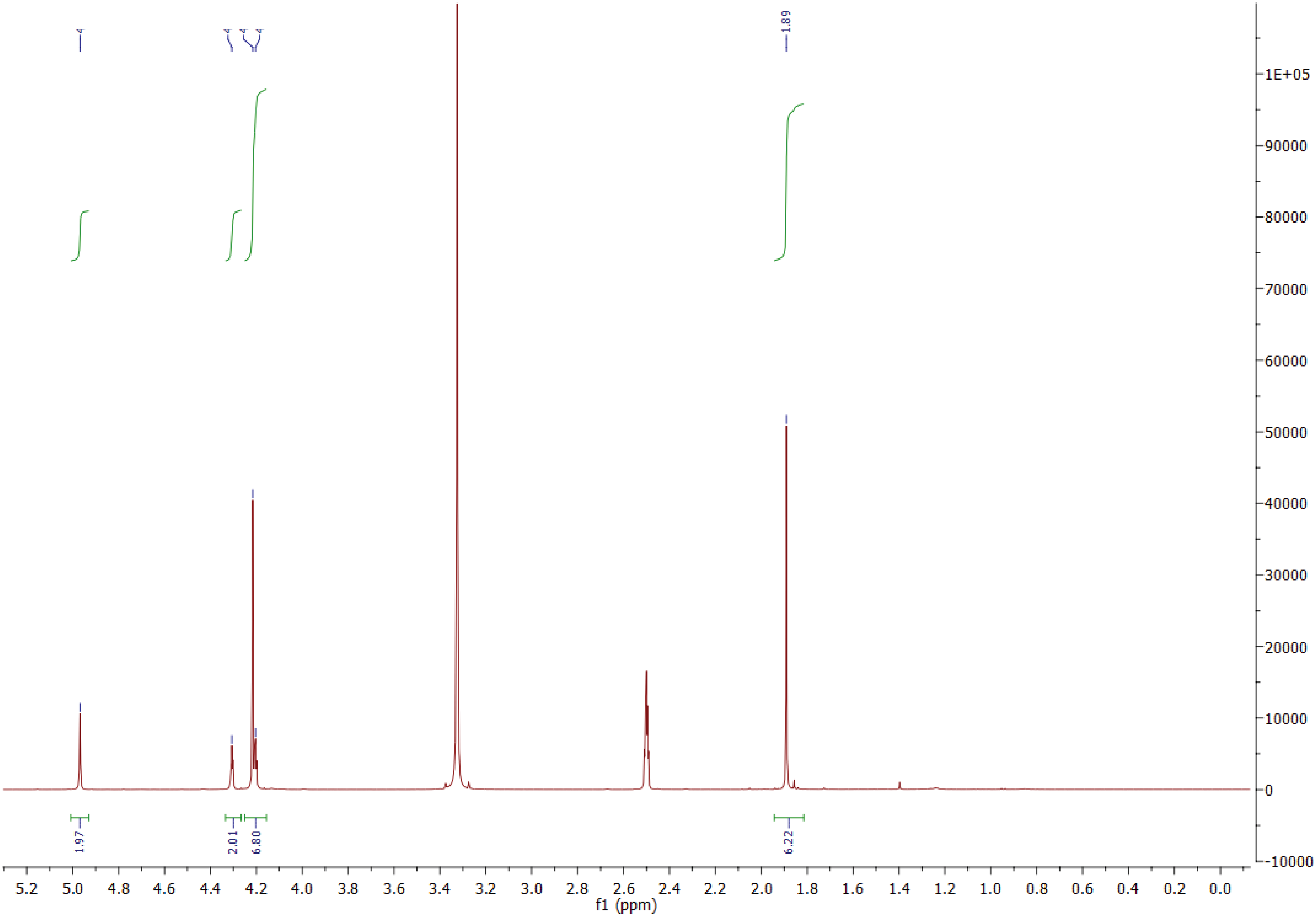


Figure S22. 400 MHz ^{1}H NMR spectrum of **Fc-4** in DMSOd$_6$.



Size exclusion chromatography (SEC) traces of PU and PMA with and without ferrocene

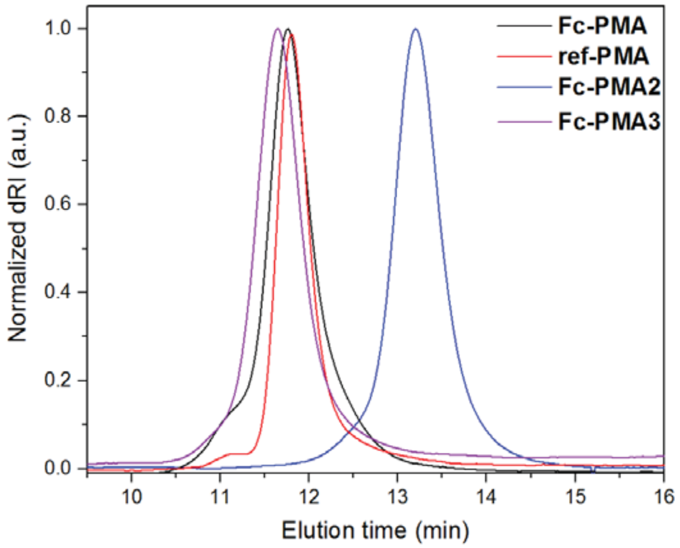


Figure S23. Representative SEC traces of the ferrocene-containing poly(methyl acrylate) **Fc-PMA** (black line), **Fc-PMA2** (blue line)**,** the ferrocene-free reference poly(methyl acrylate) **ref-PMA** (red line) and the mono-functionalized **Fc-PMA3**.

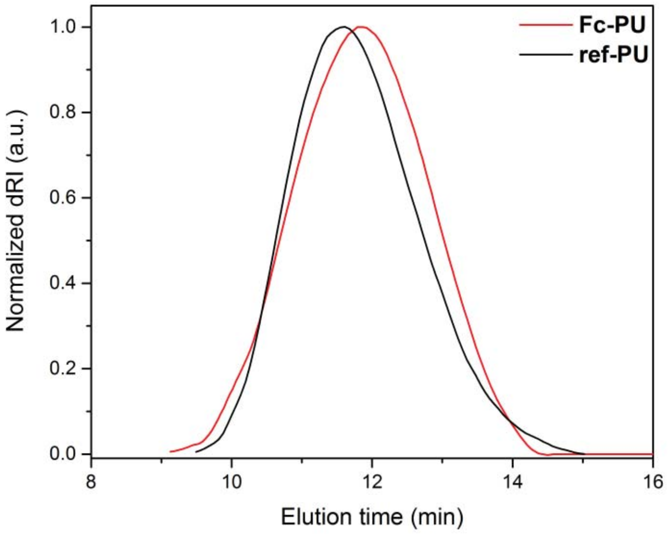


Figure S24. Representative SEC traces of the ferrocene-containing polyurethane **Fc-PU** (red line) and the ferrocene-free reference polyurethane **ref-PU** (black line).

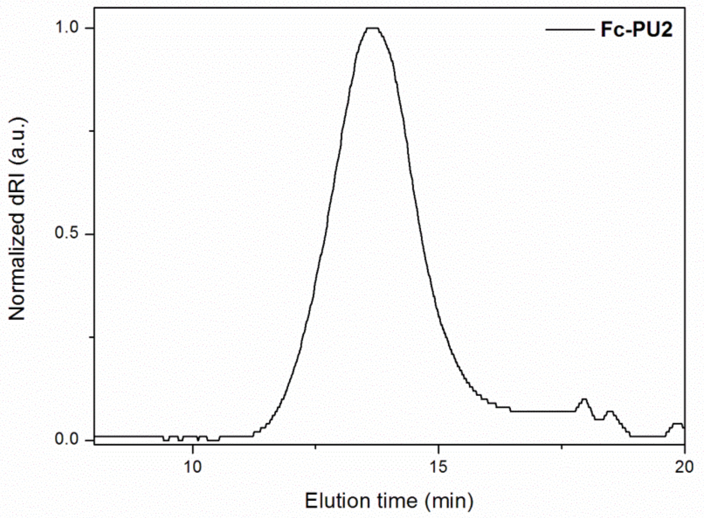


Figure S25. Representative SEC traces of the ferrocene-containing polyurethane **Fc-PU2**.

Ultrasonic degradation by size exclusion chromatography (SEC)

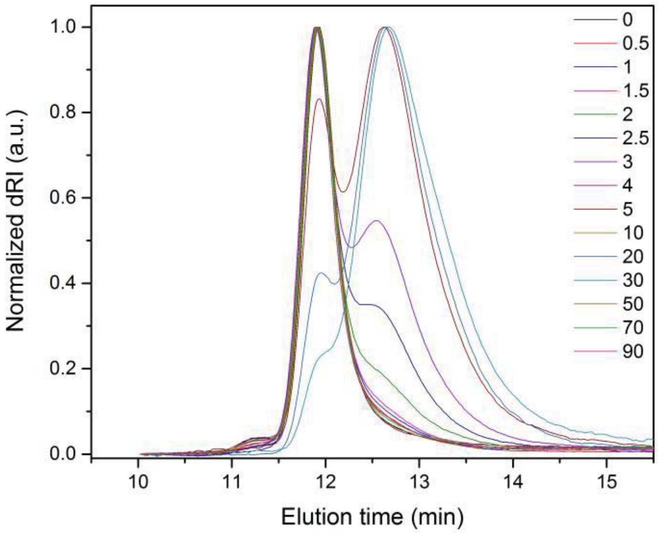


Figure S26. Representative size exclusion chromatography (SEC) traces acquired to monitor the ultrasound-induced degradation of the ferrocene-free reference poly(methyl acrylate) **ref-PMA** (0.75 mg/mL in THF, 10.4 mW/cm^2, 0 °C).

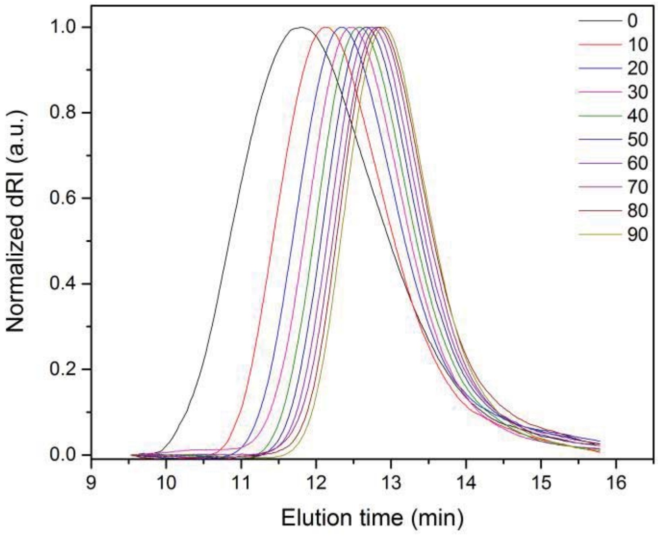


Figure S27. Representative size exclusion chromatography (SEC) traces acquired to monitor the ultrasound-induced degradation of the ferrocene-free reference polyurethane **ref-PU** (0.75 mg/mL in THF, 10.4 mW/cm^2, 0 °C).

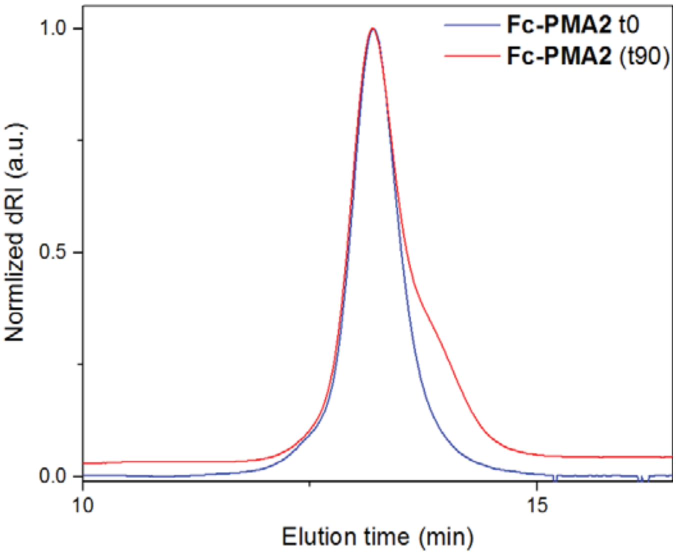


Figure S28. Representative SEC traces of **Fc-PMA 2** before (t0) and after ultrasonication of a degassed polymer solution in THF for 90 min (t90').

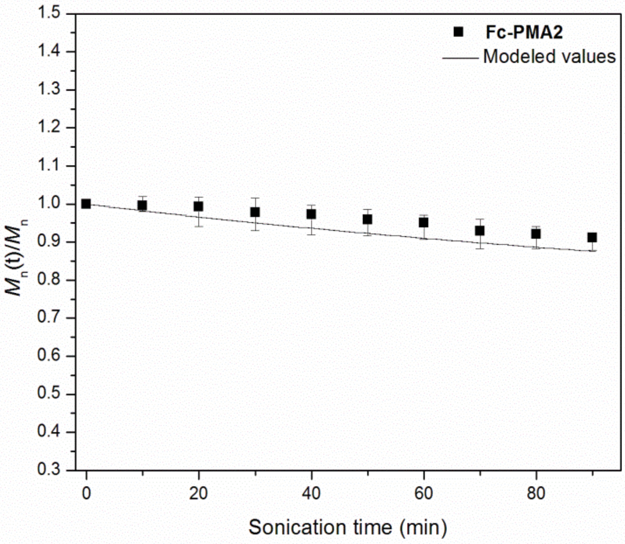


Figure S29. Graph showing the evolution of the ratio of the number-average molecular weight (M_n(t)) and the initial number-average molecular weight (M_n) upon ultrasonication of a solution of **Fc-PMA2** as function of time. The experiment was performed in triplicate and results are shown as average (black squares) with the error bars representing standard deviation of each data point. The squares represent the experimentally determined results. All ultrasonication experiments were conducted at a polymer concentration of 0.75 mg/mL, a sonication power of 10.4 mW/cm^2, and a temperature of 0 °C.

UV/vis absorption

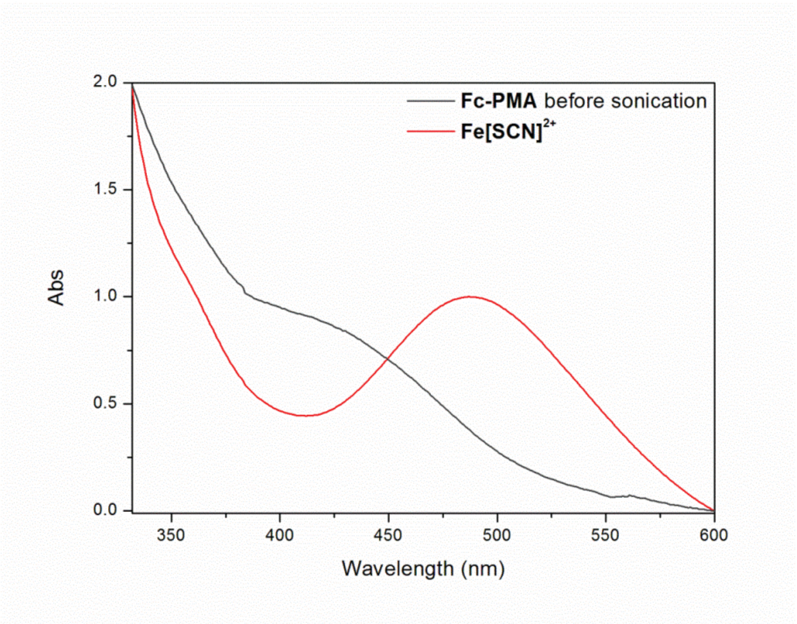


Figure S30. Absorption spectrum of the red complex Fe(SCN)$^{2+}$ in THF (red line) formed after 90 minutes of sonication, after adding the ligand KSCN (1:1 v/v mixture of MeOH and THF, 0.53 M) in the solution of **Fc-PMA** (2 mg/mL). Absorption spectra of **Fc-PMA** (black line) (2 mg/mL) before sonication.

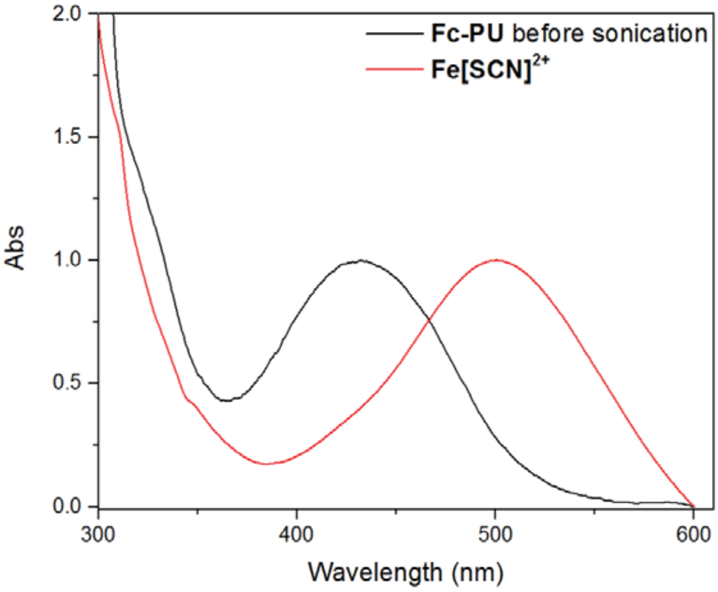


Figure S31. Absorption spectrum of the red complex Fe(SCN)$^{2+}$ in THF (red line) formed after 20 minutes of sonication, after adding the ligand KSCN (1:1 v/v mixture of MeOH and THF, 0.18 M) in a solution of **Fc-PU** (2 mg/mL). Absorption spectra of **Fc-PU** (2 mg/mL) before sonication.

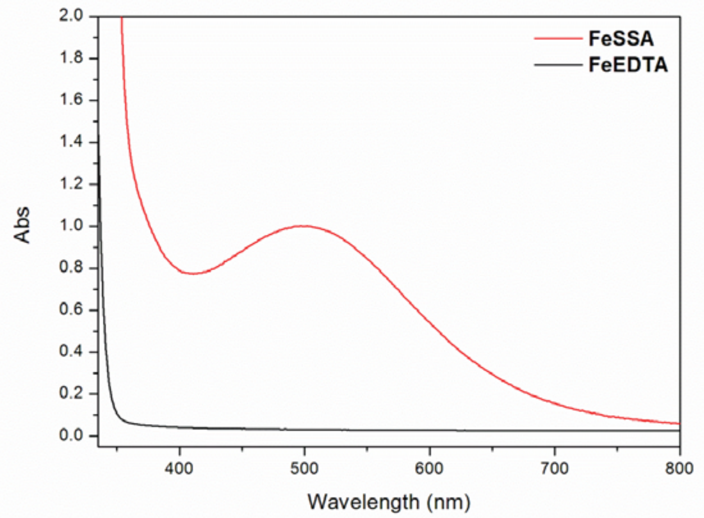


Figure S32. Absorption spectrum of the red complex FeSSA (Fe^{3+} with sulphosalicylic acid) formed during the titration (red line), adding to a solution of **Fc-PU** in THF (2 mg/mL, [Fe] = $3.6 \cdot 10^{-4}$ M), HCl 1M and a solution 5% in water of sulphosalicylic acid. Absorption spectrum of the complex FeEDTA (Fe^{3+} with EDTA) formed after adding EDTA ($1.01 \cdot 10^{-4}$ M) in the solution during the titration (black line). We can observe the disappearance of the red complex with sulphosalicylic acid and the formation of the new complex with EDTA that does not absorb in UV/vis.

Mathematical model of polymer ultrasound-induced scission

Kinetic simulations of polymer degradation have been carried out by adapting an approach already tested in previous works[4]. The model is based on writing detailed kinetic equations for the concentration of polymer chains of all lengths, an approach commonly known as population balance equations[4a].

Two versions of the model have been used for this work. The first one has been utilized to describe the scission of **Fc-PU** polymers, where it can be safely assumed that ferrocene units are randomly distributed in the polymer chains, and it is analogous to the one used in a previous work[4a]. By calling N_n the number of chains containing n breakable units and if ultrasound-induced chain scission is modeled as a first order kinetic process, the following kinetic equations can be written:

$$\frac{dN_n}{dt} = -\left(K_{B,n} \cdot \left(1-p(t)\right) + K_{A,n} \cdot p(t)\right) N_n + \sum_l \left(K_{B,l} \cdot \left(1-p(t)\right) + K_{A,l} \cdot p(t)\right) \Gamma_{l,n} N_l \tag{1}$$

In Equation (1), $K_{A,n}$ and $K_{B,n}$ are the two kinetic constants describing the rate of scission of ferrocene units (A) and of unspecific covalent bonds along the polymer chains (B), and $\Gamma_{l,n}$ represents the fragment distribution function, i.e., the fraction of fragments containing n units obtained from the scission of a longer chain containing l units. The kinetic constants describing scission are a function of the chain molecular weight. As in our previous work, a power law dependence of the constants on the molecular weight is assumed:

$$\begin{aligned} K_{A,i} &= \kappa_A \left(i - c_{off}\right)^{\lambda} \\ K_{B,i} &= \kappa_B \left(i - c_{off}\right)^{\lambda} \end{aligned} \tag{2}$$

The exponent of the power law is set to $\lambda=2$, in agreement with the physical model developed by Kuijpers and coworkers[5], in which it is demonstrated that the force stretching a polymer chain, due to the flow field generated by a collapsing bubble is proportional to the square of the chain length. κ_A and κ_B are the only two adjustable parameters, which values have been tuned to accurately fit the experimental data. It is further assumed that the kinetic constants are different from zero only when $i>c_{off}$, *i.e.*, when the chain length is longer than a critical cutoff value (c_{off}). This is a typical phenomenon observed with ultrasonic scission experiments. In Equation (1), $p(t)$ is the fraction of ferrocene moieties in a chain, which is assumed to be statistically the same for all chains. This fraction is also assumed to be a function of time, decreasing as the scission events progressively consume the ferrocene moieties. The fragment distribution is assumed to be a Gaussian function, centered at the center of the chain. This signifies that the probability of chain to be cleaved by the sonication process is maximal at the chain center, and decreases quickly the further one moves away from said center:

$$\Gamma_{l,n} = Ae^{-\frac{\left(\frac{l}{2}-n\right)^2}{2\left(\sigma\frac{l}{2}\right)^2}} \tag{3}$$

The standard deviation of the Gaussian, σ, is set equal to 0.15 for all the simulations. This function must fulfill the following condition, expressing the conservation of mass of the fragments, *i.e.*, that the sum of the masses of the fragments must be equal to the mass of the original chain:

$$\sum_{n=1}^{l-1} n \cdot \Gamma_{l,n} = l \tag{4}$$

The use of Equation (4) allows on determining the constant A in Equation(3). Clearly, in the case of polymer chains containing no ferrocene, the same approach can be used, with the exception that $K_{A,n}$ are all equal to zero. One additional equation to compute the time evolution of the fraction of Ferrocene (A) units in the chains is necessary:

$$\frac{d\sum_n nN_n p(t)}{dt} = -p(t)\sum_n K_{A,n} \cdot n \cdot N_n \tag{5}$$

This latter equation expresses the conservation of bonds. It can be rearranged as follows:

$$\sum_n n \cdot N_n \frac{dp(t)}{dt} = -p(t)\left[\sum_n K_{A,n} \cdot n \cdot N_n + \sum_n n \cdot \frac{dN_n}{dt}\right] \tag{6}$$

The solution of the kinetic equations requires the knowledge of the initial chain population, which is obtained from the SEC profile of the polymer at time zero. The solution of the equations provides the time evolution of the entire polymer chain distribution as a function of the sonication time. From this solution, any average properties can be calculated, including the number average molecular weight. This can be obtained from the following equation:

$$\frac{dM_n}{dt}=\frac{d}{dt}\left(\frac{\sum_i N_iM_i}{\sum_i N_i}\right)=-\frac{\sum_i N_iM_i}{\left(\sum_i N_i\right)^2}\sum_i\frac{dN_i}{dt}=-\frac{M_n}{\left(\sum_i N_i\right)}\sum_i\left(-\left(K_{A,i}\cdot p(t)+K_{B,i}\cdot(1-p(t))\right)\cdot N_i+\sum_j\left(K_{A,j}\cdot p(t)+K_{B,j}\cdot(1-p(t))\right)\cdot N_j\cdot\Gamma_{j,i}\right)= \quad (7)$$

$$=-\left(K_{A,eff}\cdot p(t)+K_{B,eff}\cdot(1-p(t))\right)M_n$$

The effective rate constants, $K_{A,eff}$ and $K_{B,eff}$ are a function of time, and are defined as:

$$K_{A,eff}=\frac{\sum_i\left[-K_{A,i}\cdot N_i+\sum_j K_{A,j}\cdot N_j\cdot\Gamma_{j,i}\right]}{\left(\sum_i N_i\right)}$$

$$K_{B,eff}=\frac{\sum_i\left[-K_{B,i}\cdot N_i+\sum_j K_{B,j}\cdot N_j\cdot\Gamma_{j,i}\right]}{\left(\sum_i N_i\right)} \quad (8)$$

It follows that the number-average molecular weight follows a pseudo-first order kinetics, with two time-dependent effective rate constants, which are a function of time because of their dependent on the entire polymer molecular weight distribution. The mean values of such time dependent rate constants are reported and discussed in the main text.

In the case of **Fc-PMA** polymer, a slightly different approach has been used. Because these chains have exactly only one ferrocene group located in their middle, any scission even that breaks the ferrocene will lead to fragment chains deprived of all ferrocene groups. Additionally, considering that the scission event occurs preferentially at the middle of the chain, if a chain is broken though a non-specific moiety, the ferrocene group will be located towards the end of the fragment chains. For this reason, such moieties will not be accessible for further cleavage. Therefore, the polymer chains have been divided into two populations: the chains that have a ferrocene group in their middle, and all other chains. The former can undergo scission through both ferrocene group and unspecific bonds, while the latter can only break because of unspecific bond breakage events.

The mass balance of chains containing a ferrocene group, hereafter referred to as A chains, is given by:

$$\frac{dN_{n,A}}{dt}=-\left(K_{A,n}\cdot f_n+K_{B,n}\right)\cdot N_{n,A} \quad (9)$$

The stoichiometric coefficient f_n is defined as:

$$f_n=\frac{1}{\sum_{i=1}^{n-1}e^{-\frac{\left(\frac{n}{2}-i\right)^2}{2\left(\sigma\frac{n}{2}\right)^2}}} \quad (10)$$

These chains can only be broken and cannot be formed from the scission of longer chains because of the hypothesis made before. The chains containing no ferrocene groups, named B chains, instead, obey the following kinetic equations:

$$\frac{dN_{n,B}}{dt}=-K_{B,n}\cdot N_{n,B}+2K_{A,2n}\cdot f_{2n}\cdot N_{2n,A}+2\sum_{i=n+1}^{2n}K_{B,i}\cdot\left(N_{i,A}+N_{i,B}\right)\cdot Ae^{-\frac{\left(\frac{i}{2}-n\right)^2}{2\left(\sigma\frac{i}{2}\right)^2}} \quad (11)$$

The meaning of these equations is that B chains can only be broken by unspecific bond breakage, while they can be formed because of the scission of longer chains, independently of the mechanism responsible for their scission.

The expression for the scission rate constant $K_{B,i}$ is the same reported in Equation (2), while the one for $K_{A,i}$ becomes:

$$K_{A,i} = \kappa_A \left(i - c_{off} \right)^{\lambda} \tag{12}$$

with the same exponent $\lambda=2$ [5a].

Note that in this case the normalization constant A is obtained from the following equation:

$$\sum_{n=1}^{i-1} A e^{-\frac{\left(\frac{i}{2}-n\right)^2}{2\left(\sigma \frac{i}{2}\right)^2}} = 1 \tag{13}$$

On the other hand, the distribution function of fragment chains for unspecific scission is described by Equation (3). The number average molecular weight is given by:

$$\frac{dM_n}{dt} = -\left(K_{A,eff} \cdot f_{eff} + K_{B,eff} \right) M_n \tag{14}$$

where the two effective kinetic constants are defined as:

$$K_{A,eff} = \frac{\sum_j \left(-K_{A,j} \cdot f_j \cdot N_{j,A} + 2K_{A,2j} \cdot f_j \cdot N_{2j,A} \right)}{\left(\sum_i \left(N_{i,A} + N_{i,B} \right) \right) \cdot f_{eff}}$$

$$K_{B,eff} = \frac{\sum_j \left(-K_{B,j} \cdot \left(N_{j,A} + N_{j,B} \right) + 2 \sum_i K_{B,i} \cdot \left(N_{i,A} + N_{i,B} \right) \cdot A e^{-\frac{\left(\frac{i}{2}-j\right)^2}{2\left(\sigma \frac{i}{2}\right)^2}} \right)}{\left(\sum_i \left(N_{i,A} + N_{i,B} \right) \right)} \tag{15}$$

$$f_{eff} = \left\langle f_n \right\rangle$$

$\langle f_n \rangle$ is the mean value of f_n.

The model contains only three adjustable parameters: the cutoff molecular weight (which has been set equal to 30kDa for polyurethanes and to 20kDa for PMA), and the two constant values κ_A and κ_B (the values of which are always identical for a specific polymer: $\kappa_A = 7 \cdot 10^{-10}$ s^{-1} and $\kappa_B = 7 \cdot 10^{-12}$ s^{-1} for the polyurethanes and $\kappa_A = 4 \cdot 10^{-10}$ s^{-1} and $\kappa_B = 6.5 \cdot 10^{-11}$ s^{-1} for the PMA).

Simulated size exclusion chromatography (SEC) traces

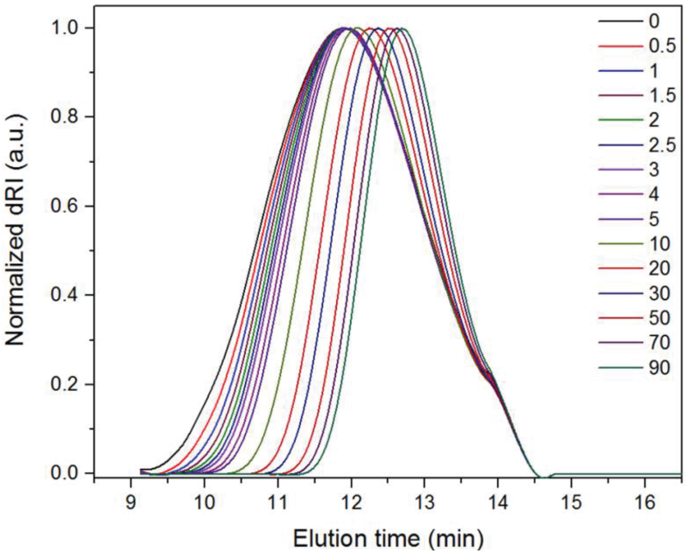


Figure S33. Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation of the ferrocene-containing polyurethane **Fc-PU**.

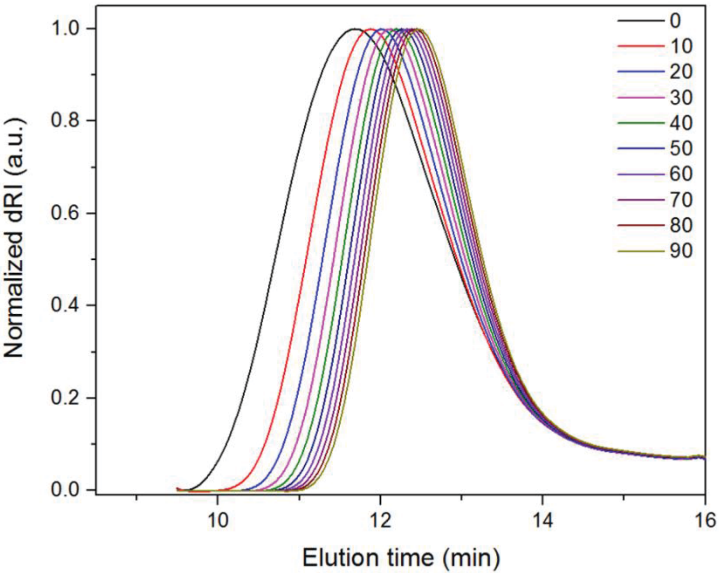


Figure S34. Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation of the ferrocene-free reference polyurethane **ref-PU**.

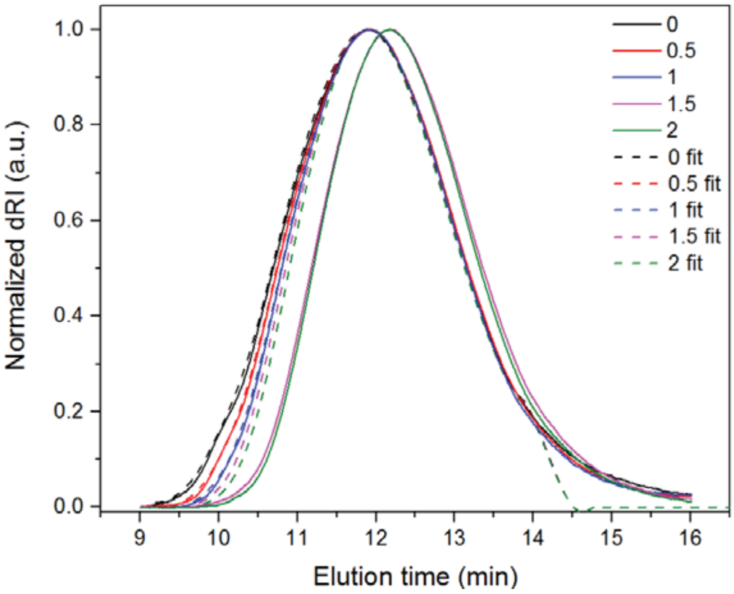


Figure S35. Simulated (dashed line) and experimental (solid line) size exclusion chromatography (SEC) of **Fc-PU**. Overlap from 0 to 2 min.

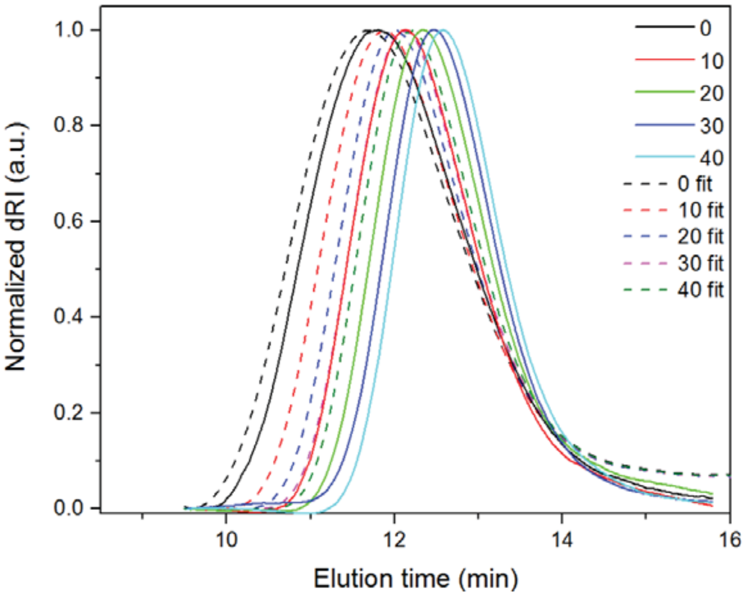


Figure S36. Simulated (dashed line) and experimental (solid line) size exclusion chromatography (SEC) of **ref-PU**. Overlap from 0 to 40 min.

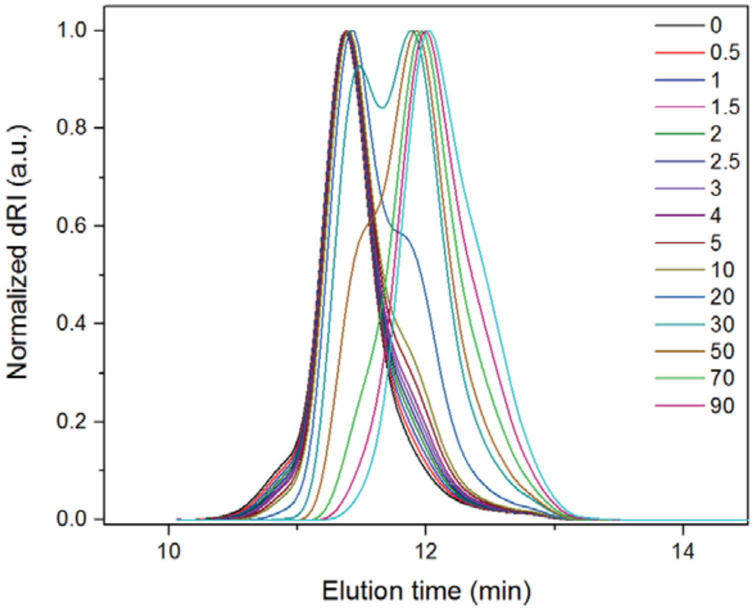


Figure S37. Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation of the ferrocene-containing poly(methyl acrylate) **Fc-PMA**.

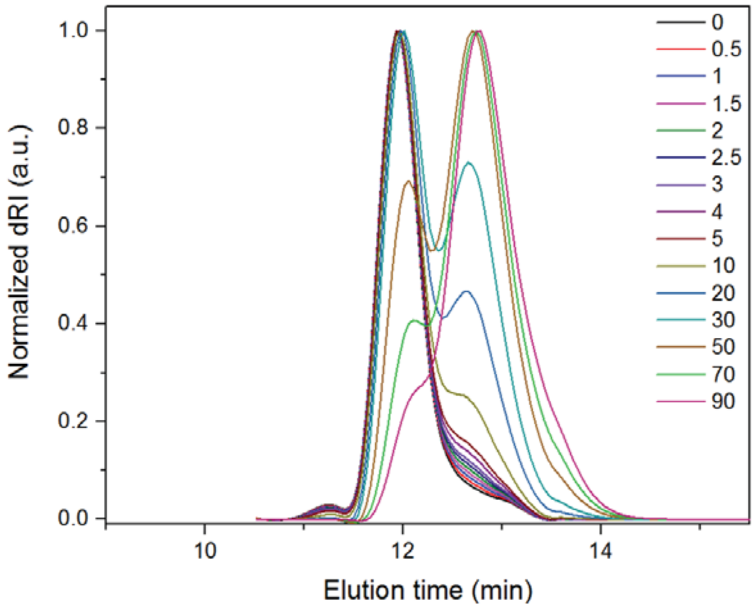


Figure S38. Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation of the ferrocene-free reference poly(methyl acrylate) **ref-PMA**.

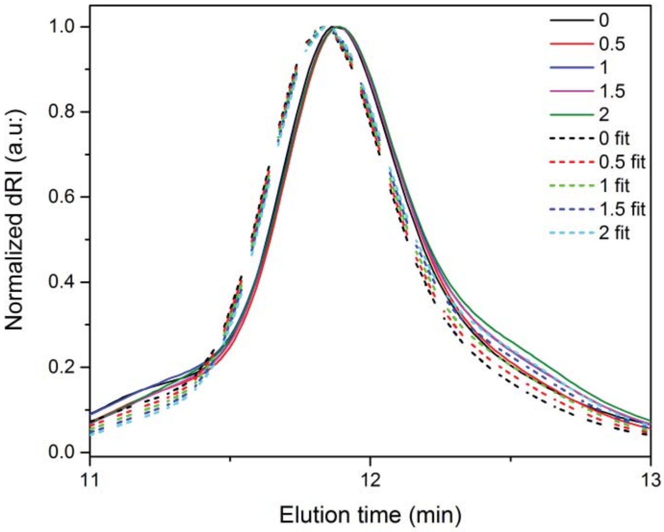


Figure S39. Simulated (dashed line) and experimental (solid line) size exclusion chromatography (SEC) of **Fc-PMA**. Overlap from 0 to 2 min.

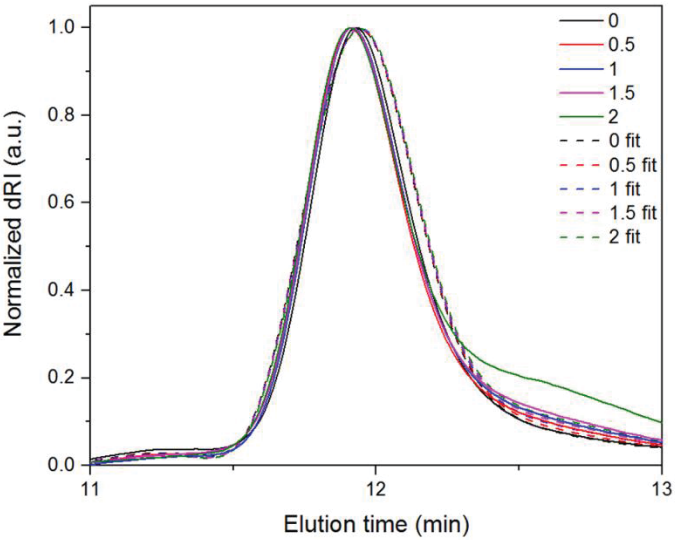


Figure S40. Simulated (dashed line) and experimental (solid line) size exclusion chromatography (SEC) of **ref-PMA**. Overlap from 0 to 2 min.

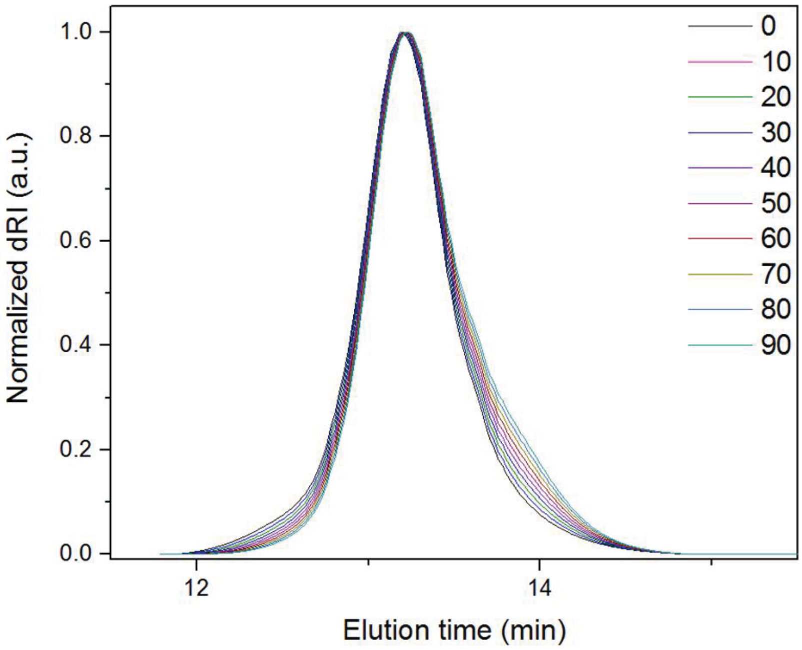


Figure S41. Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation of the ferrocene-containing poly(methylacrylate) **Fc-PMA2**.

Effective scission constants as a function of time

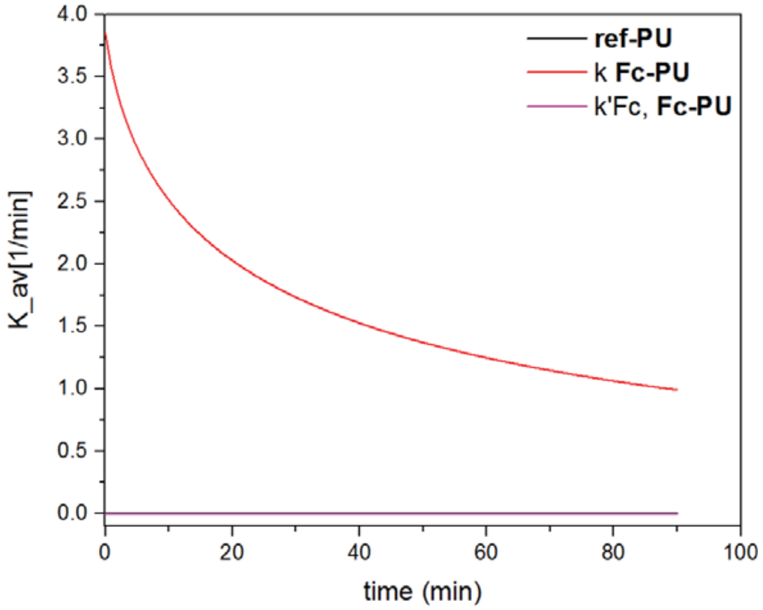


Figure S42. Effective scission rate constants for the ferrocene-containing polyurethane **Fc-PU** and the reference polyurethane **ref-PU** as a function of time.

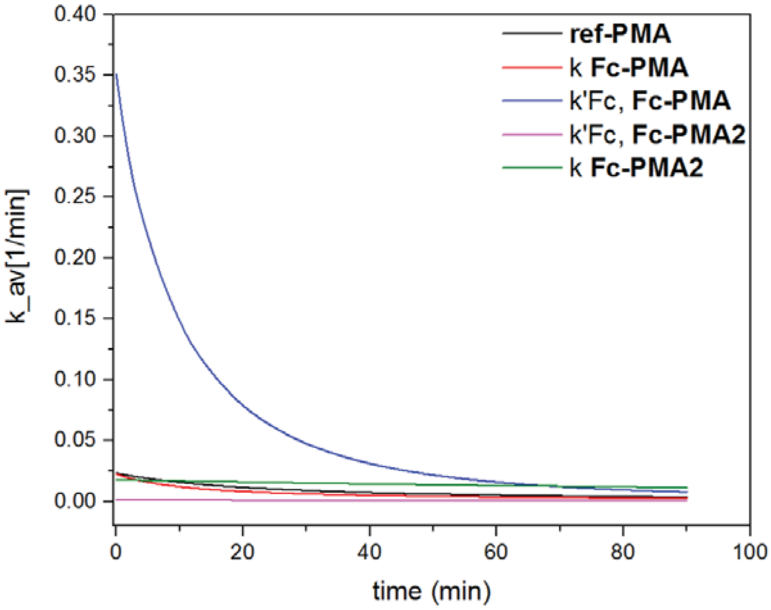


Figure S43. Effective scission rate constants for the ferrocene-containing poly(methyl acrylate) **Fc-PMA** and the reference poly(methyl acrylate) **ref-PMA** as a function of time.

Simulated decrease of the ferrocene moieties content as a function of time

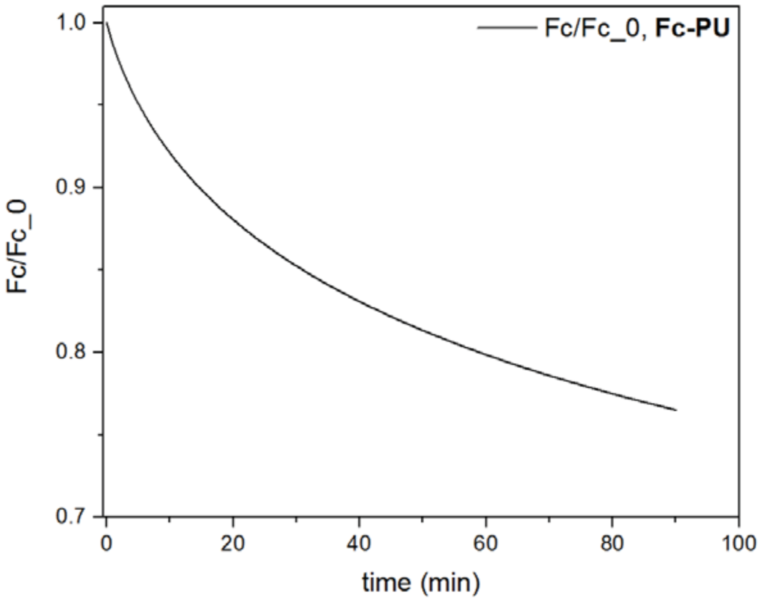


Figure S44. Decrease of the relative ferrocene moiety content as a function of the ultrasonication time for the ferrocene-containing polyurethane **Fc-PU**.

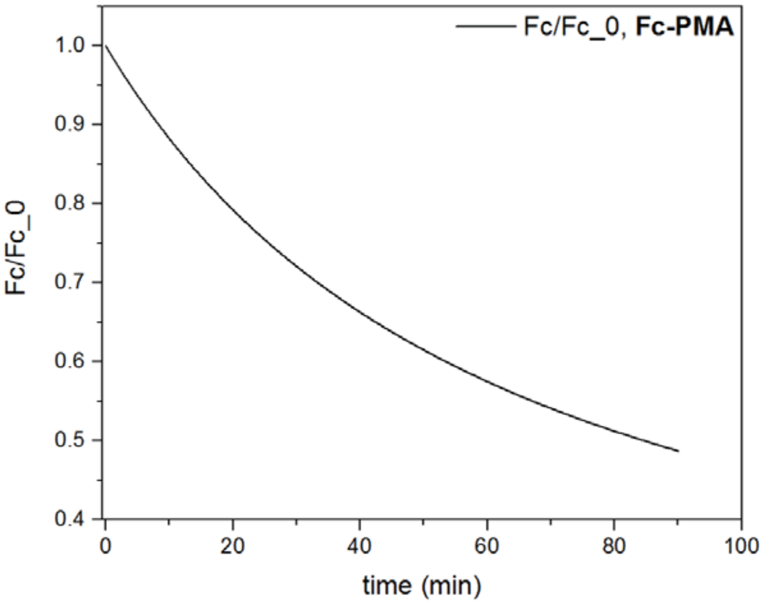


Figure S45. Decrease of the relative ferrocene moiety content as a function of the ultrasonication time for the ferrocene-containing poly(methyl acrylate) **Fc-PMA**.

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 Fc-PMA and ref-PMA

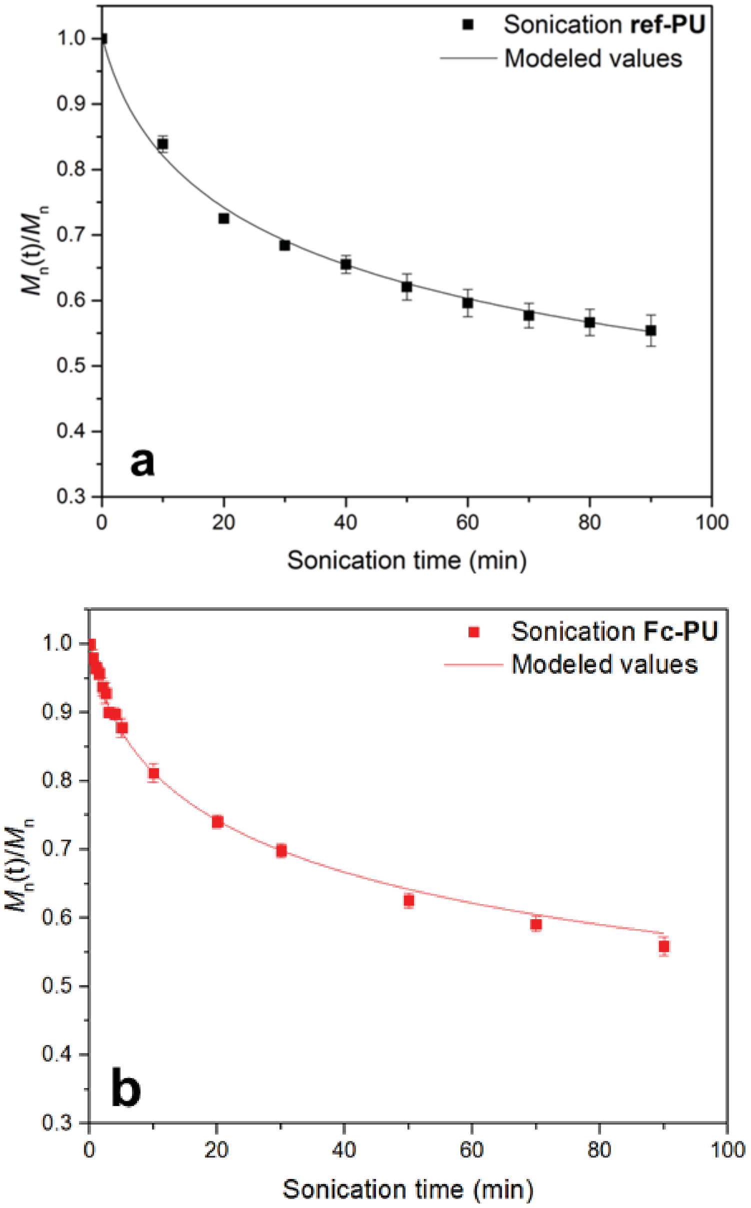


Figure S46. Graphs showing the evolution of the ratio of the number-average molecular weight (M_n(t)) and the initial number-average molecular weight (M_n) upon ultrasonication of solutions of a) the ferrocene-free reference polyurethane **ref-PMA** and b) the ferrocene-containing polyurethane **Fc-PU** as a function of time. The experiments were performed in triplicate at polymer concentrations of 0.75 mg/mL, a sonication power of 10.4 mW/cm^2, and a temperature of 0 °C and results are shown as averages (red and black squares) with the error bars representing standard deviation at each data point. The squares represent the experimentally determined results while the lines are modeled.

Elemental analyses (EA) of polymers

ref-PU

$(MDI_{15.765}BDO_{9.284}PTHF_{4.997})_n$

$(C_{15}H_{10}N_2O)_{15.765}(C_4H_{10}O_2)_{9.284}((C_4H_8O)_{27.486}H_2O)_{4.997}$

Anal. Calcd: C, 66.90; H, 9.27; N, 2.99. Found: C, 66.33; H, 9.53; N, 2.87.

Fc-PU

$(MDI_{7.1612}BDO_{3.7183}PTHF_{2.4788}\mathbf{Fc}_{0.4133})_n$

$(C_{15}H_{10}N_2O_2)_{7.1612}(C_4H_{10}O_2)_{3.7183}((C_4H_8O)_{27.761}H_2O)_{2.4788}(C_{12}H_{10}O_2Fe)_{0.4133}$

Anal. Calcd: C, 66.83; H, 9.31; N, 2.77. Found: C, 66.66; H, 9.50; N, 2.40.

ref-PMA

(methyl α-bromoisobutyrate $_{0.048}$MA$_{144}$)$_n$

$(C_5H_9O_2Br)_{0.048}(C_4H_6O_2)_{144}$

Anal. Calcd : C, 51.00; H, 6.43. Found: C, 55.50; H, 7.10.

Fc-PMA2

(**Fc-initiator**)$_{0.024}$(MA)$_{14.3}$

$(C_4H_6O_2)_{14.3}(C_{20}H_{24}O_4FeBr_2)_{0.024}$

Anal. Calcd : C, 55.66; H, 6.94. Found: C, 55.0; H, 7.10.

Fc-PMA

(**Fc-initiator**)$_{0.024}$(MA)$_{48}$

$(C_{20}H_{24}O_4FeBr_2)_{0.024}(C_4H_6O_2)_{48}$

Anal. Calcd: C, 55.76; H, 6.25. Found: C, 53.5; H, 7.1.

Color change experiments

Figure S47. KSCN (dissolved in a 1:1 v/v mixture of MeOH and THF, 0.53 M) was added to the **Fc-2** solution, before and after sonication. **Fc-2** solutions (2 mg/mL in THF) after 90 minutes of sonication (dark yellow, sample A on the right) and after sonication (pale yellow solution B on the left). Since KSCN interacts only with Fe(III) and not with Fe(II), the darker yellow color of the solution A on the right (after sonication) is probably due to a fragmentation of the polymer in smaller parts that could interact with KSCN. In conclusion the formation of the red complex ($[Fe(SCN)_n(H_2O)_{6-n})]^{(3-n)+}$) was not observed, excluding the breaking of the ferrocene under ultrasonication.

Figure S48. KSCN (dissolved in a 1:1 v/v mixture of MeOH and THF, 0.53 M) was added to the **Fc-PMA2** solution, before and after sonication. **Fc-PMA2** solutions (2 mg/mL in THF) after 90 minutes of sonication (transparent/pinkish, sample A on the right) and after sonication (transparent solution B on the left). In conclusion the formation of the red complex ($[Fe(SCN)_n(H_2O)_{6-n})]^{(3-n)+}$) was not observed, excluding the breaking of the ferrocene under ultrasonication.

Figure S49. KSCN (dissolved in a 1:1 v/v mixture of MeOH and THF, 0.53 M) was added to the monofunctionalized **Fc-PMA3** solution, before and after sonication. **Fc-PMA3** solutions (2 mg/mL in THF) after 90 minutes of sonication (transparent/pinkish, sample A on the right) and after sonication (transparent solution, sample B on the left). In conclusion the formation of the red complex ($[Fe(SCN)_n(H_2O)_{6-n})]^{(3-n)+}$) was not observed, excluding the breaking of the ferrocene under ultrasonication.

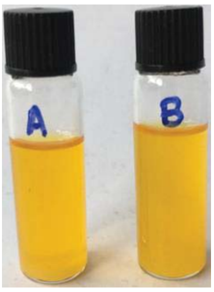


Figure S50. $K_4[Fe(CN)_6]$ (0.0414 M dissolved in H_2O and THF) was added to a solution of **Fc** (ferrocene as small molecule) (0.75 g/mol). The compound was sonicated for 4 hours. After sonication (sample A on the right) and before sonication (sample B on the left) no color change (no Prussian Blue) was observed.

Figure S51. $K_4[Fe(CN)_6]$ (0.0414 M dissolved in H_2O and THF) was added to a solution of **ref-PU** (0.75 g/mol). The compound was sonicated for 4 hours. After sonication (sample A on the right) and before sonication (sample B on the left) no color change (no Prussian Blue) was observed.

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