Supporting Information for

N-Ferrocenylsulfonyl-2-methylaziridine: The First Ferrocene Monomer for the Anionic (Co)Polymerization of Aziridines

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Additional protocols and analysis data:

Materials/ Methods

Instrumentation. ^{1}H NMR spectra (300, 400, 500 and 700 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC300, a Bruker AMX400, Bruker Avance 500 and Bruker Avance III. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in DMF (containing 0.25 g·L^{-1} of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column (106/105/104 g·mol^{-1}), a UV detector (275 nm), and a RI detector at a flow rate of 1 mL·min^{-1} at 50 °C. Calibration was carried out using PEO standards provided by Polymer Standards Service. DSC measurements were performed using a PerkinElmer 7 series thermal analysis system and a PerkinElmer thermal analysis controller TAC 7/DX. Heating rates of 10 K·min^{-1} were employed under nitrogen. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) measurements were performed using a Shimadzu Axima CFR MALDI-TOF mass spectrometer, employing dithranol (1,8-dihydroxy-9(10*H*)-anthracenone) as a matrix.

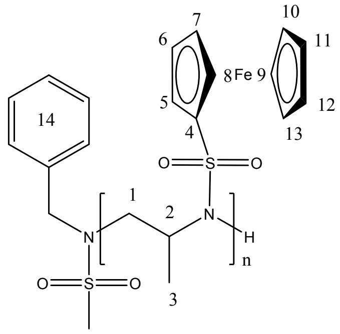
Cyclic voltammetry (CV) was carried out in a conventional three electrode cell using a μ-Autolab Type III potentiostat (Metrohm AG) and dichloromethane as a solvent under argon. The supporting electrolyte was tetrabutylammonium hexafluorophosphate ([0.1 M]). All experiments were performed at 25 °C. A glassy carbon disc served as working electrode and a glassy carbon rod as counter electrode. As reference an Ag/AgCl electrode (silver wire in saturated LiCl/ethanol solution) was employed.

Reagents. Solvents and reagents were purchased from Acros Organics, TCI, Sigma-Aldrich or Fluka and used as received, unless otherwise stated. Deuterated solvents were purchased from Deutero GmbH. TsMAz and MsMAz were synthesized according to the published procedures and dried by azeotropic distillation of benzene to remove traces of water.[1] 2-Methylaziridine was distilled from CaH_2 prior its use.

Polymerization

All glassware was flame-dried prior to the polymerization in vacuo. The monomers were dissolved in ca. 1 mL benzene and dried for ca. 4h *in vacuo* to remove traces of water by azeotropic distillation. The monomers were then dissolved in DMF, DMSO or THF (compare main text, final concentration ca. 10 wt%). If KHMDS was used as initiator, it was used as a DMSO solution and added to the monomer solution at 55°C. BuLi was used as received. If BnNHMs was used as the initiator, the sulfonamide anion was generated in a separate flask by deprotonation with KHMDS and then a calculated amount of this initiator stock solution was added to the monomer solution at 55°C and the reaction was stirred until completion (typically 15h). After the polymerization has reached completion, the living anion was terminated by the addition of methanol and precipitated into a ten-fold excess of methanol. The polymers were recovered by filtration or centrifugation in typically quantitative yield.

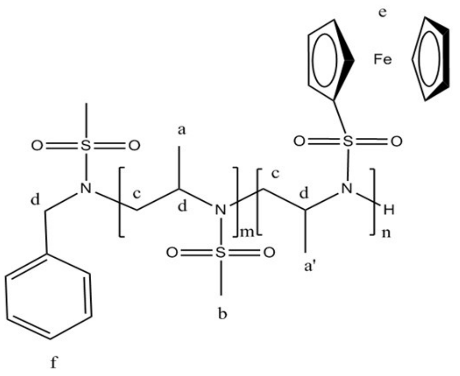
Homopolymerisation, example: PFcMAz33: 100 mg (0.327 mmol) fcMAz, 3 mg (0.016 mmol) BnNHMs and 2,6 mg (0,013 mmol; 0,8 eq.) KHMDS were used. Solvent DMF ca. 1 mL.



^{1}H MAS NMR (700 MHz): δ [ppm] = 8-7 (br, 5H, 14), 7-2 (br, 5-8, 9-13), 4-2 (br, 1, 2), 2-0 (br, 3). ^{13}C CP MAS NMR (700 MHz): δ [ppm] = 130 (14), 90 (4), 75-65 (br, 5-8, 9-13), 60-45 (br, 1, 2), 20-10 (br, 3). Additional polymers have been synthesized, the data is collected in Table 1. IR: $\tilde{\nu}$: 3444 (b), 3104 (m), 2980 (m), 2930 (w), 1643 (m), 1387 (w), 1325 (ss), 1189 (s), 1134 (ss), 1071 (s), 1021 (s), 825 (s), 707 (s), 613 (s) cm^{-1}.

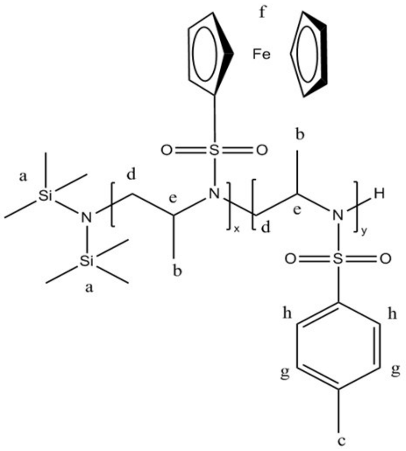
Copolymers. Copolymerization was conducted analogous to the procedure for homopolymers. For block copolymers, first the polymerization of MsMAz or TsMAz was initiated. To the living polymers, then the calculated amount of fcMAz was added after 2 h and stirring was continued overnight.

P(MsMAz)$_{28}$-b-P(fcMAz)$_2$. 19 mg (0.062 mmol) fcMAz, 70 mg (0.518 mmol) MsMAz, 3.4 mg (0.018 mmol) BnNHMs and 2.7 mg (0,014 mmol) KHMDS were used. Solvent DMSO ca 1 mL.



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7,41 (m, 5H, f), 5,21- 4,28 (br, 16H, e), 4,30-3,71 (br, 26H, d), 3,72-3,14 (br, 52H, c), 3,15-2,54 (br, 92H, b), 1,55-0,69 (br, 85H, a), 0,98-0,78 (br, 7H, a‘).

P(TsMAz)$_{22}$-b-P(FcMAz)$_5$. 25 mg (0.082 mmol) FcMAz, 70 mg (0.332 mmol) TsMAz und 2.5 mg (0.013 mmol) KHMDS were used. Solvent DMSO ca 2 mL.



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 8,31-7,62 (br, h), 7,60-7,16 (br, g), 5,25-4,22 (br, f), 4,22-3,86 (br, e), 3,81-2,79 (br, d), 2,74-2,10 (br, c), 1,42-0,75 (br, b), 0,09 (s, a).

^{1}H NMR Kinetics. The monomers and initiator was prepared as described above. In an Argon-filled glovebox the monomers were dissolved in 0.7 mL dry deuterated DMF and added to an NMR tube, which was sealed with a rubber septum. From this solution a 1H NMR spectrum was measured; then the initiator was added (0.1 mL in deuterated DMF, a respective stock

solution was prepared earlier) and the polymerization was monitored over a period of 15h, continuously taking spectra with each 32 scans (404 s).

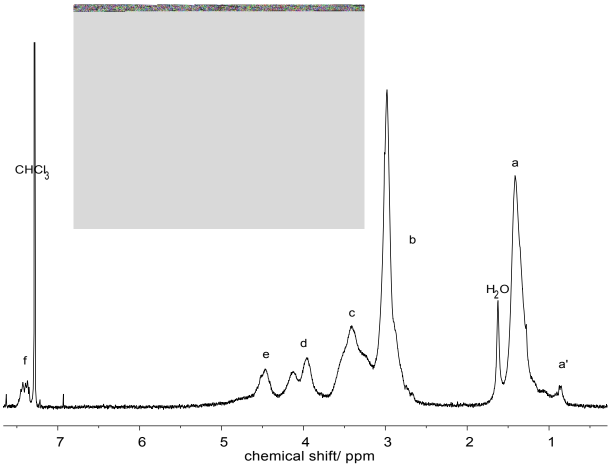
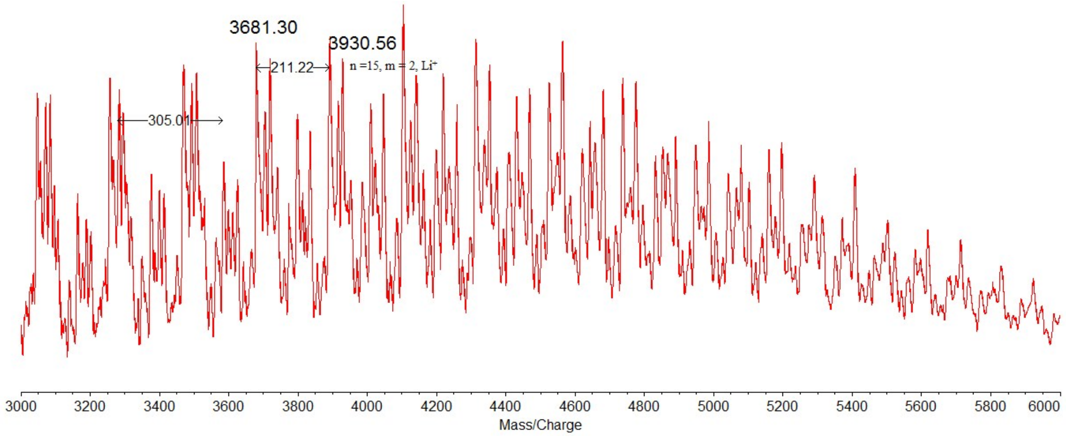


Figure S1: ^{1}H NMR spectrum of P(MsMAz)$_{28}$-*b*-P(FcMAz)$_4$ in CDCl$_3$,300 MHz, 298 K.



Figures S2: Zoom into the MALDI ToF mass spectrum of P(TsMAz)$_{22}$-*b*-P(fcMAz)$_5$.

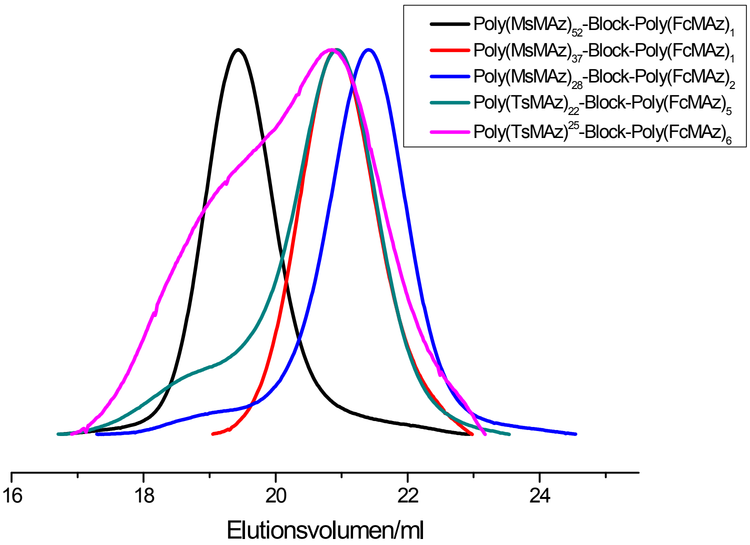


Figure S3: GPC elugrams of block copolymers (DMF, RI detection).

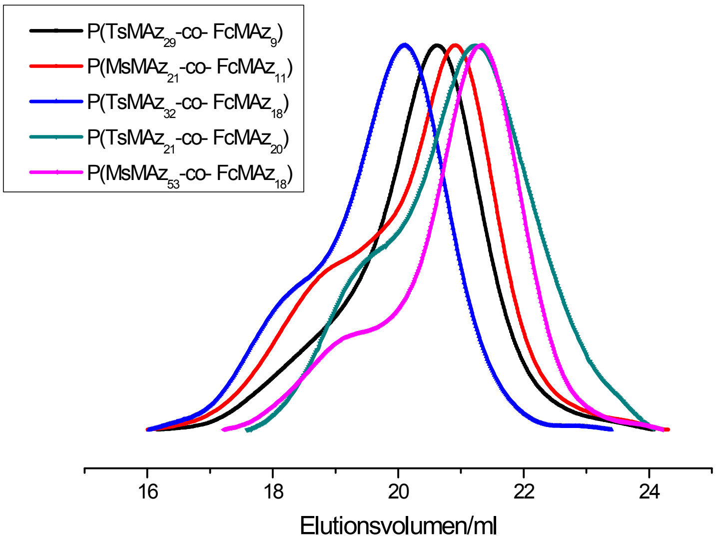


Figure S4: GPC elugrams of statistical copolymers (DMF, RI detection).

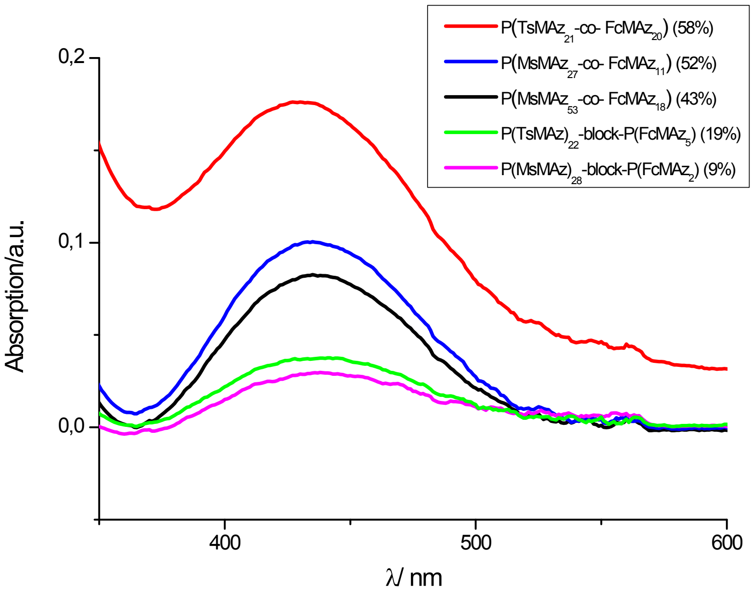


Figure S5: UV/Vis absorption spectra of the fcMAz copolymers with variable fcMAz content in THF.

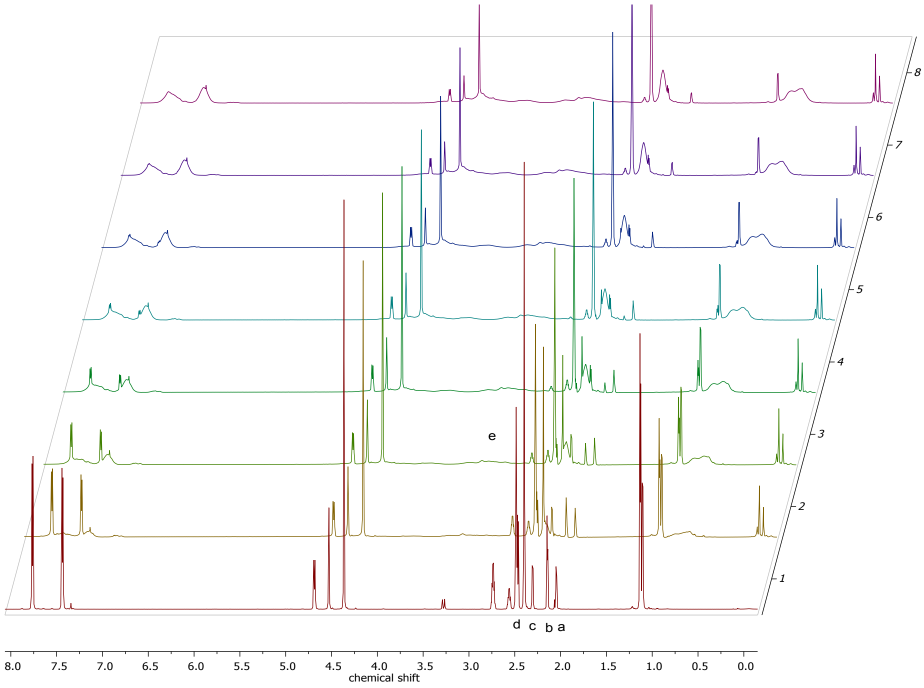


Figure S6 Real-time ^{1}H NMR kinetics of the copolymerization (700 MHz, 303 K) of P(TsMAz$_{30}$-*co*- fcMAz$_{12}$)); time distance between the sprectra 40 min.

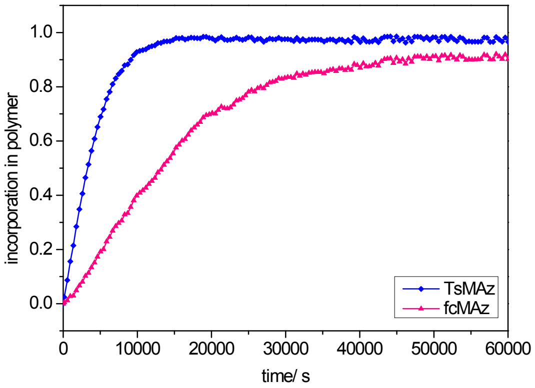


Figure S7: From ^{1}H NMR kinetics: assembly of each monomer in the growing polymer chain *vs.* the reaction time.

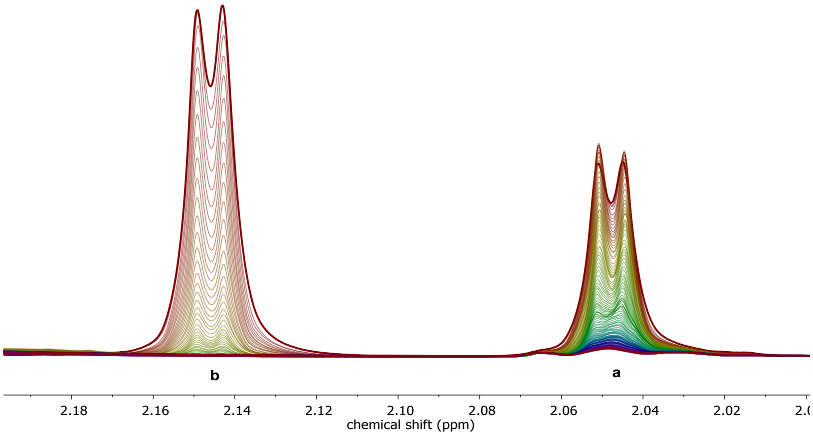


Figure S8: Integrals over the copolymerization of TsMAz (a) and fcMAz (b).

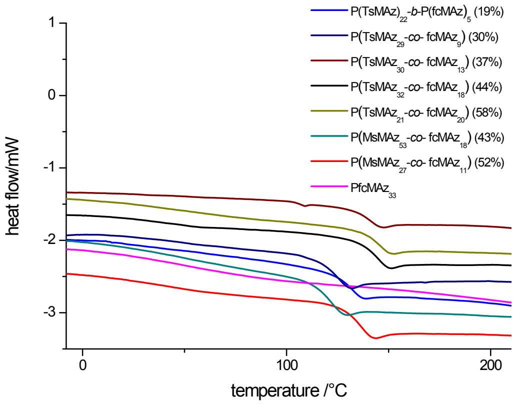


Figure S9: DSC heating curves (2nd heating, 10K/ min) of fcMAz-containing copolymers.

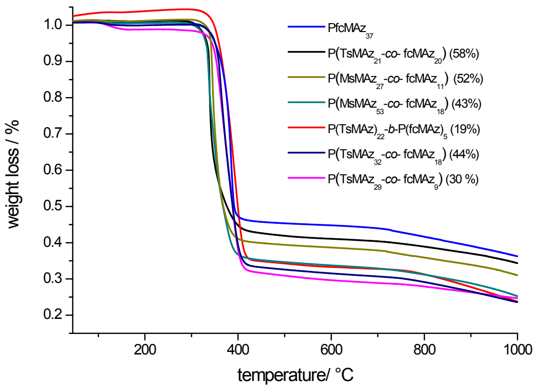


Figure S10: TGA analysis of fcMAz-containing copolymers.

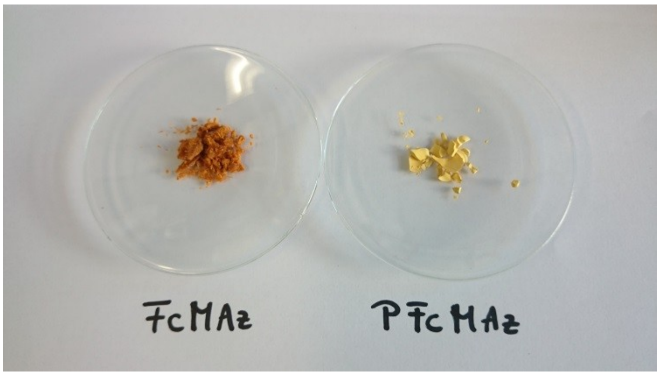


Figure S11: Photograph of **1** and **poly(1).**

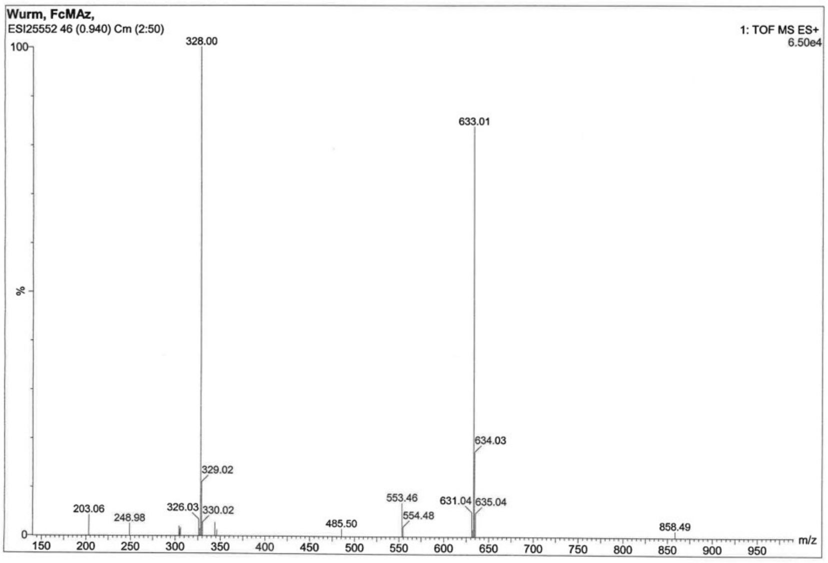


Figure S12: ESI-MS of **1**.

References

1. E. Rieger, A. Alkan, A. Manhart, M. Wagner and F. R. Wurm, *Macromol. Rapid Commun.*, 2016, 37, 833-839.