Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Solvent and catalyst-free modification of hyperbranched polyethyleneimines by ring-opening-addition or ring-opening-polymerization of *N*-sulfonyl aziridines

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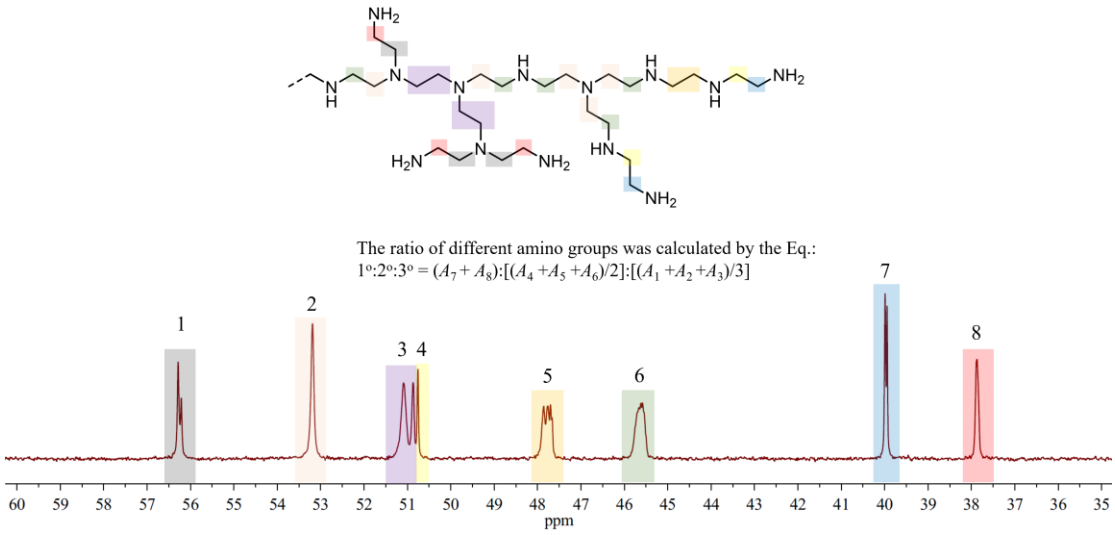
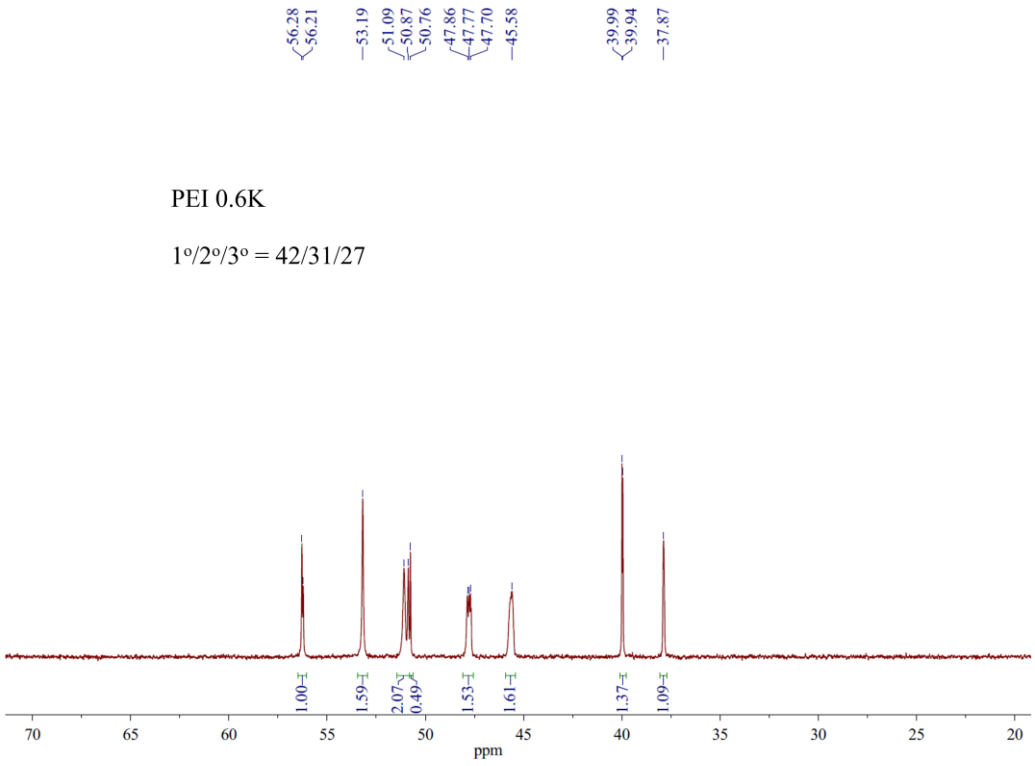
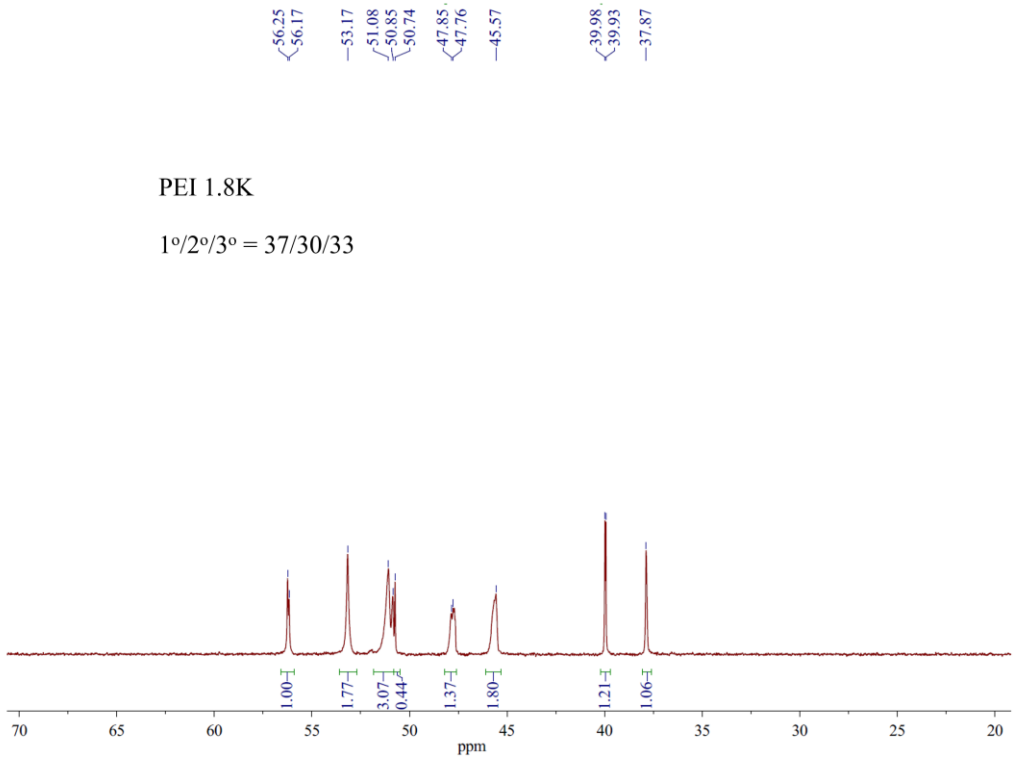


Figure S1. Structure of PEI determined by inverse gated ^{13}C NMR.

(a)



(b)



(c)

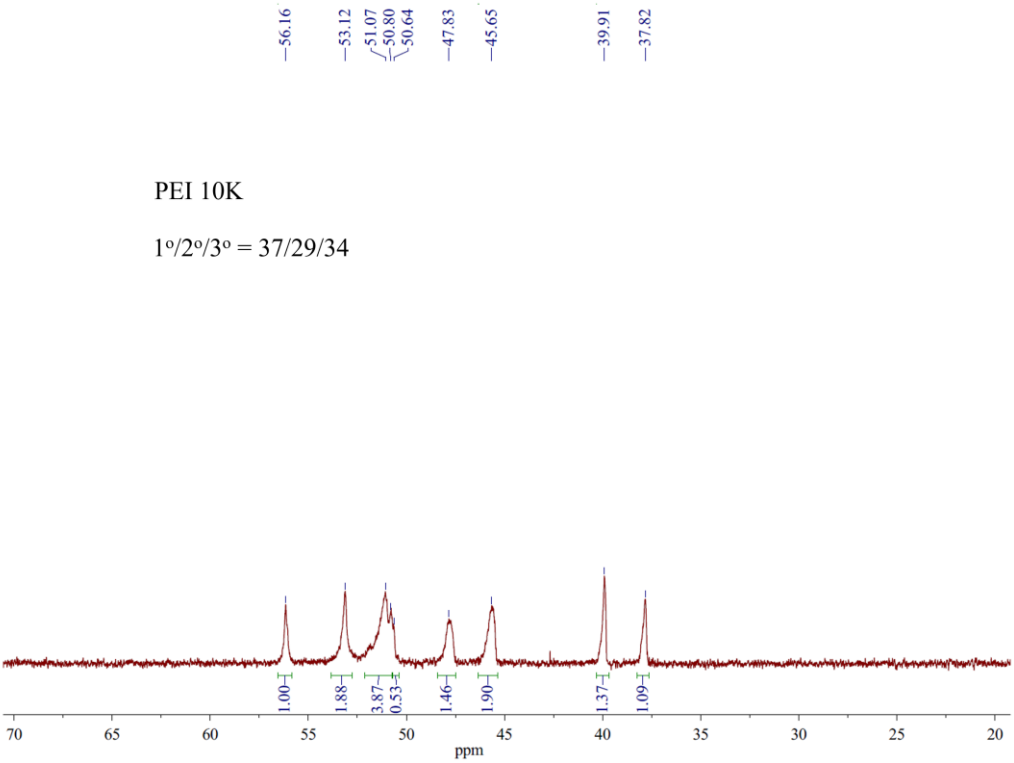


Figure S2. Inverse gated ^{13}C NMR (100 MHz, D_2O, 25 °C) spectra of polyethyleneimine with molecular weight (a) 0.6K, (b) 1.8K, and (c) 10K. The ratio of different amino groups in the polymer is given.

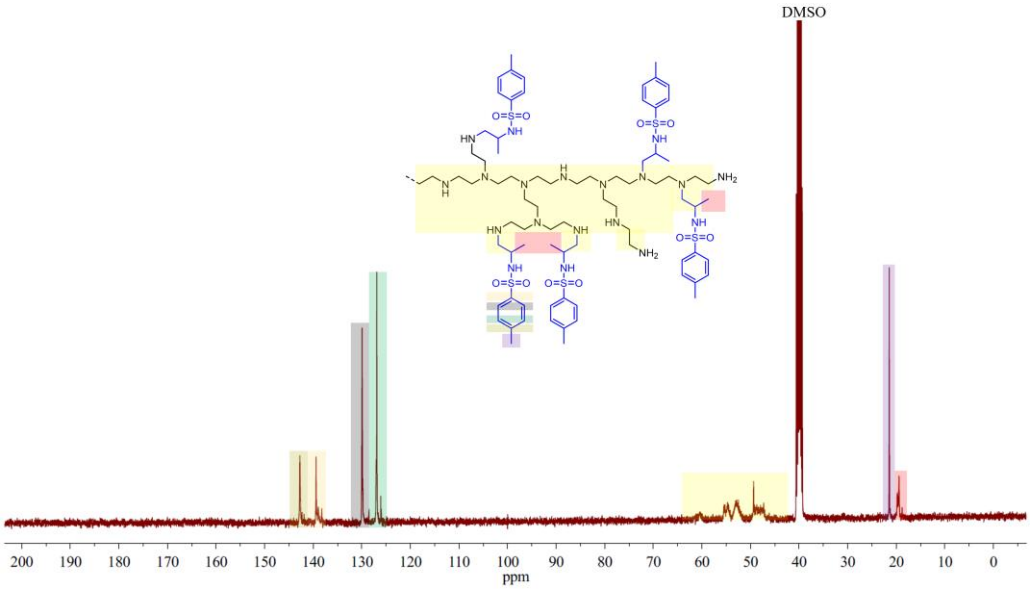


Figure S3. ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C) spectrum of P(EI-SA).

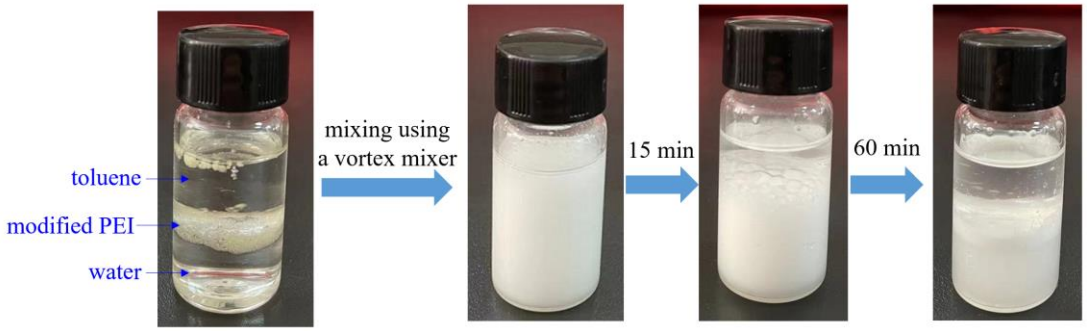


Figure S4. Images of water/toluene emulsions stabilized by P(EI-SA) (sample of entry 2, Table 1) (water 4.0 g, toluene 4.0 g, modified PEI 16 mg).

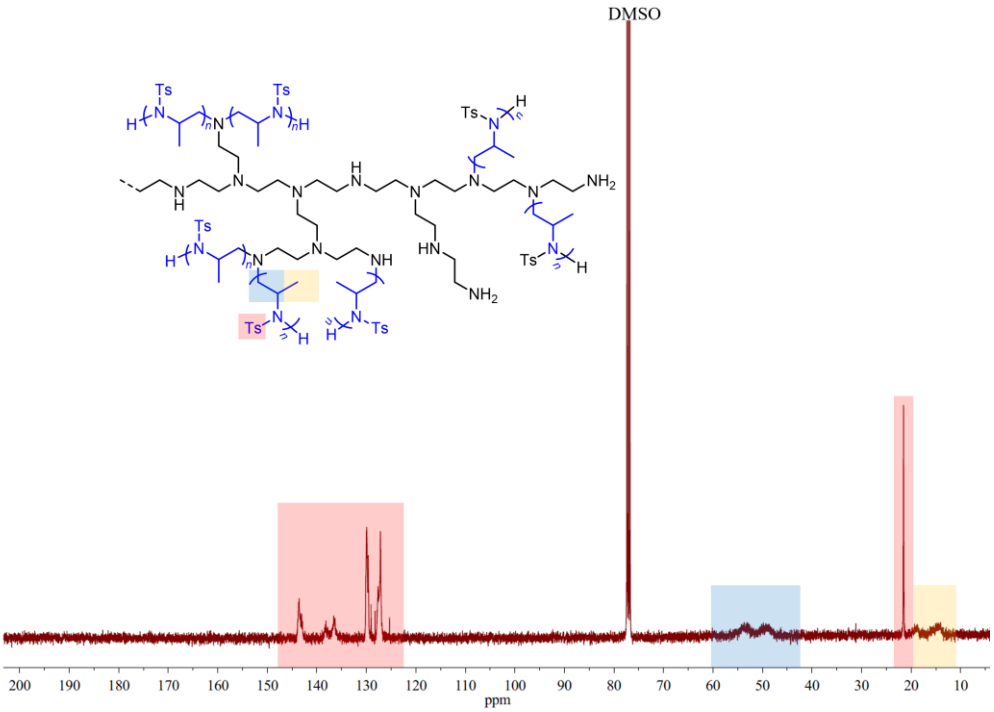


Figure S5. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of PEI0.6K-*g*-P(TsMAz)$_{0.96}$.

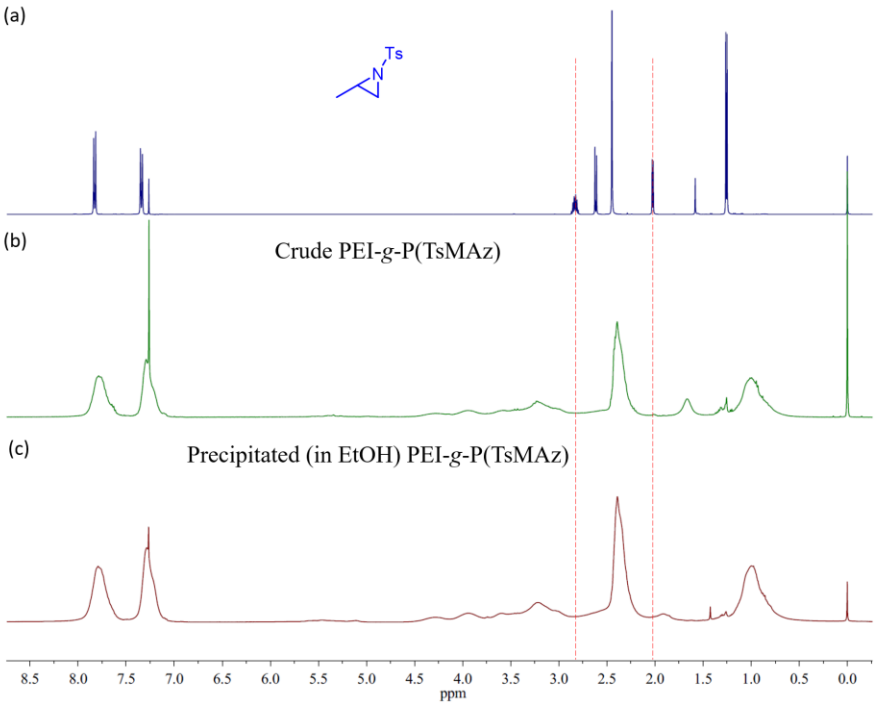


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectra of (a) TsMAz, (b) crude product after reaction (sample of entry 7, Table 1), and (c) precipitated graft copolymer.

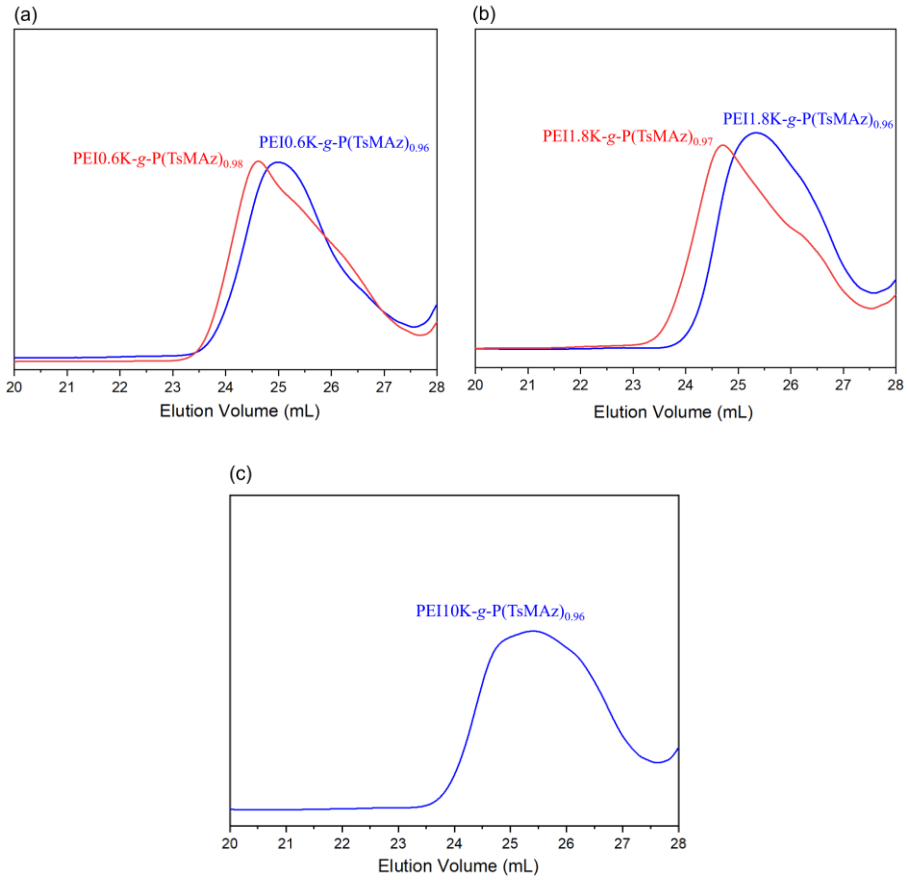


Figure S7. SEC (THF, 35 °C, PS standards) traces of (a) PEI0.6K, (b) PEI1.8K, and (c) PEI10K grafted with P(TsMAz) (Crude polymers without precipitation).

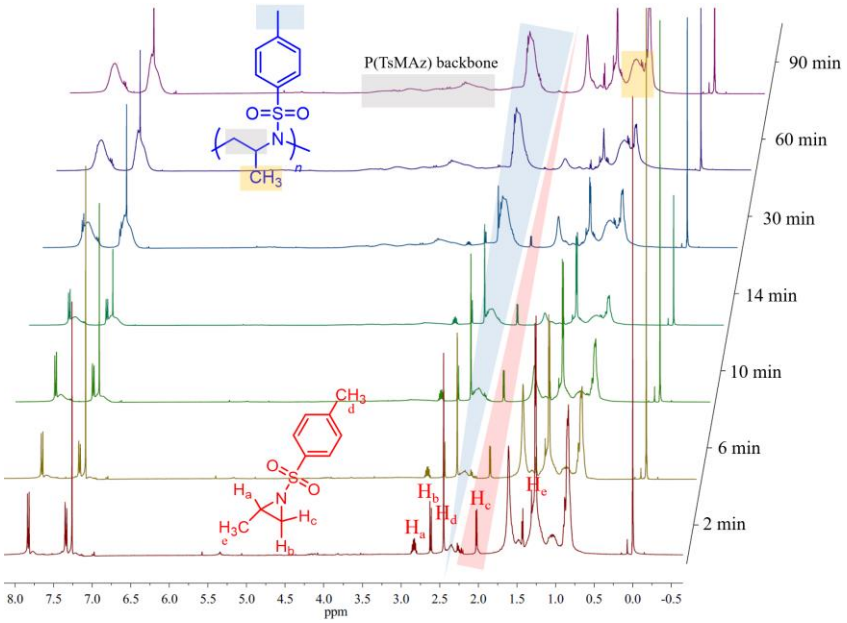


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectra of the reaction mixture of PEI1.8K with TsMAz (solvent-free, 200 °C) took at different time intervals.

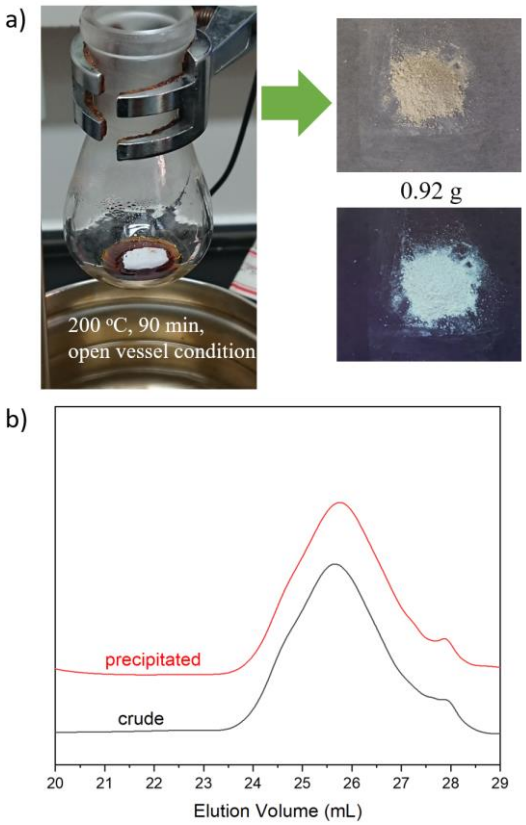


Figure S9. a) Gram-scale synthesis of PEI-*g*-PTsMAz by the reaction of PEI1.8K (0.043 g) with TsMAz (1.06 g, 5.0 equiv.) and the photos of the obtained product under room lighting and 365 nm UV illumination. b) SEC traces of crude (black line) and precipitated (red line) PEI-*g*-PTsMAz copolymers.

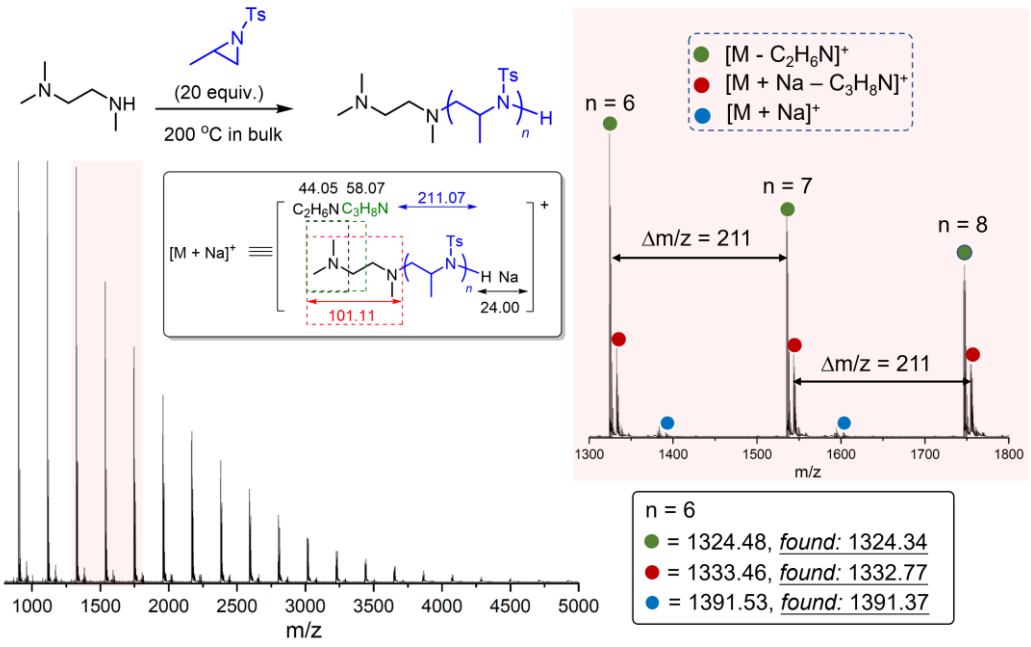


Figure S10. MALDI-ToF MS of P(TsMAz) initiated by *N*,*N*,*N*'-trimethylethylenediamine.

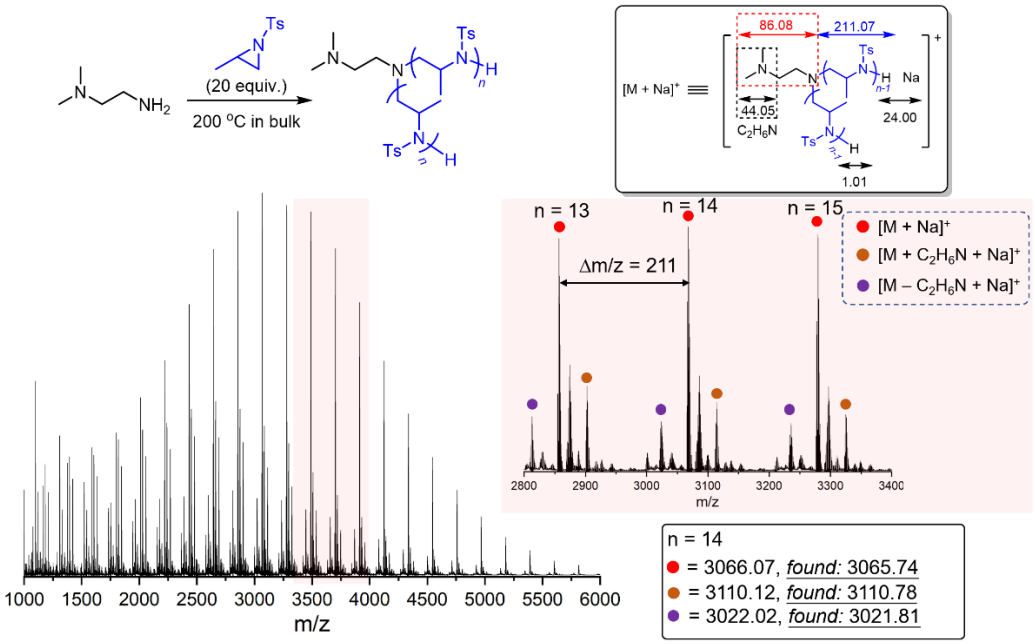
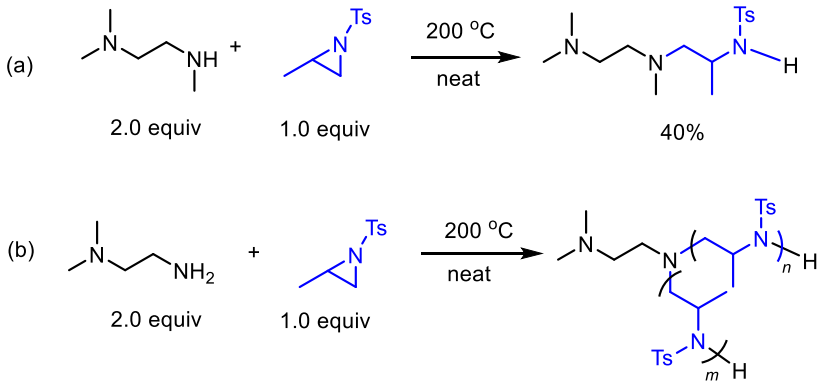


Figure S11. MALDI-ToF MS of P(TsMAz) initiated by *N*,*N*-dimethylethylenediamine.



Scheme S1. Ring-opening reaction of TsMAz with (a) *N*,*N*,*N*'-trimethylethylenediamine, and (b) *N*,*N*-dimethylethylenediamine.

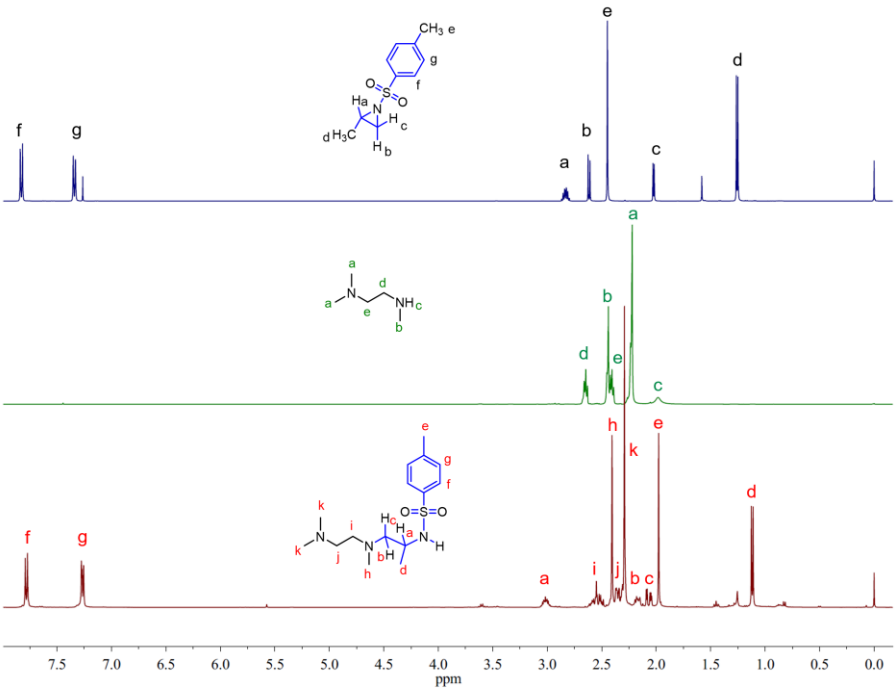


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectra of (a) TsMAz, (b) *N*,*N*,*N*'-trimethylethylenediamine, (c) *N*-(1-((2-(dimethylamino)ethyl)(methyl)amino) propan-2-yl)-4-methylbenzenesulfonamide.

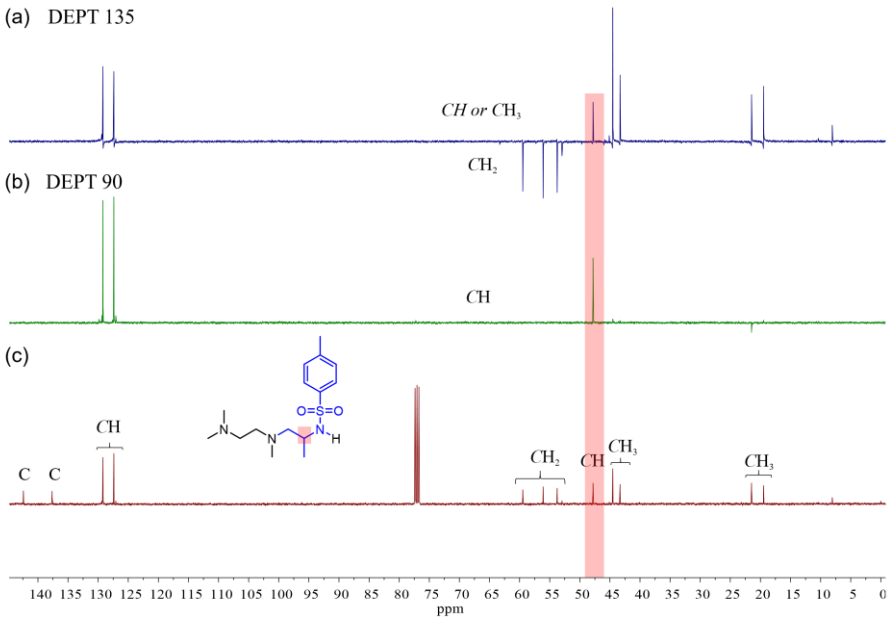


Figure S13. ^{13}C NMR, DEPT135, and DEPT90 (100 MHz, $CDCl_3$, 25 °C) spectra of *N*-(1-((2-(dimethylamino)ethyl)(methyl)amino)propan-2-yl)-4-methylbenzenesulfona mide.

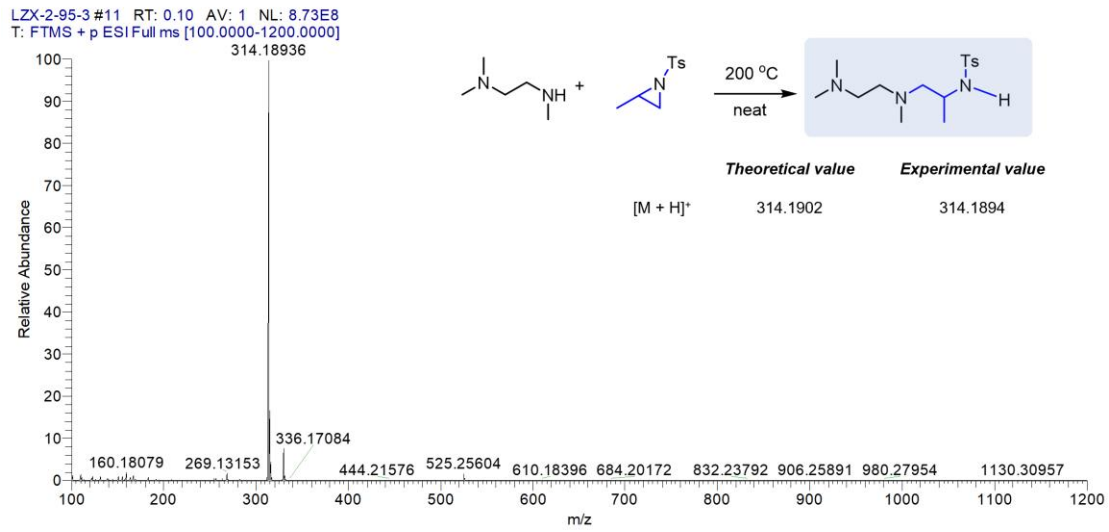
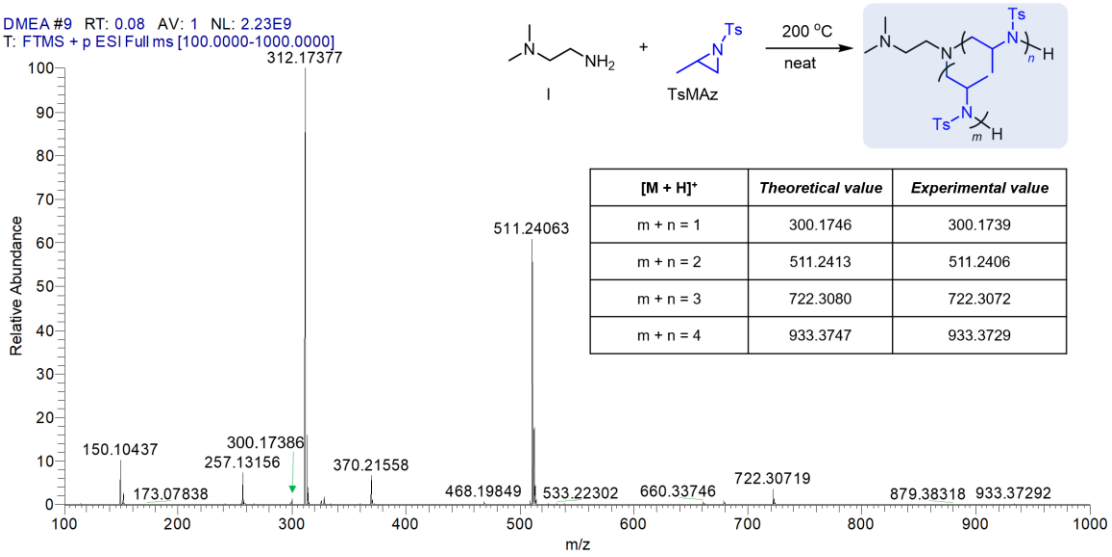


Figure S14. LC-MS of the ring-opened product of TsMAz by *N*,*N*,*N*'-trimethylethylenediamine.



[M + H]+	*Theoretical value*	*Experimental value*
m + n = 1	300.1746	300.1739
m + n = 2	511.2413	511.2406
m + n = 3	722.3080	722.3072
m + n = 4	933.3747	933.3729

Figure S15. LC-MS of the ring-opened crude products of TsMAz by *N*,*N*-dimethylethylenediamine.

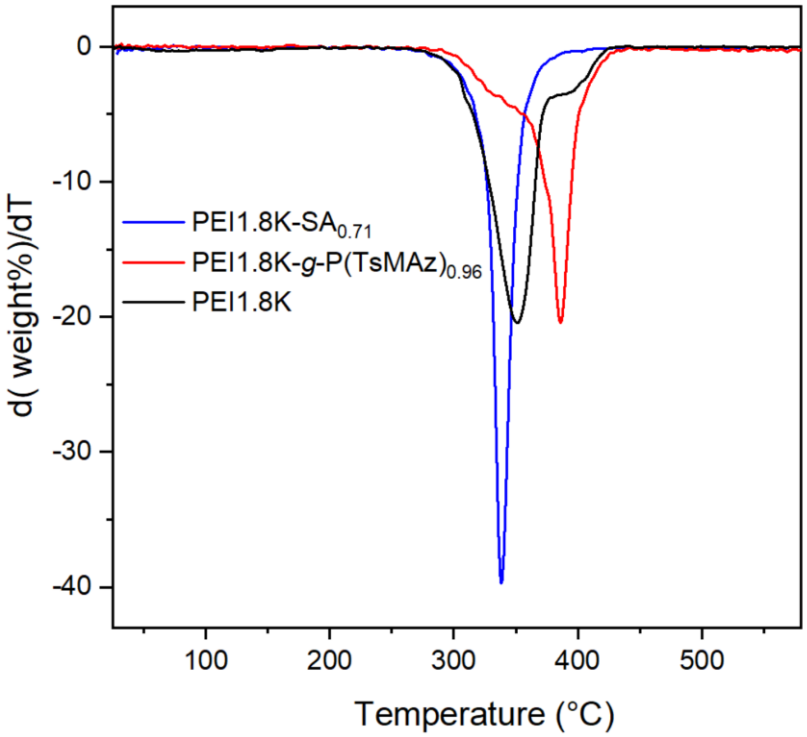


Figure S16. Thermogravimetry curves of PEI1.8K, and modified PEI1.8Ks.

Table S1. Thermostability of PEI1.8K and modified PEIs.

sample	T_{di}[a]/°C	T_{dm}[b]/°C	Residual mass/wt %
PEI1.8K	289	351	0.67
PEI1.8K-$SA_{0.71}$ (29% wt% PEI, sample of entry 2, Table 1)	291	338	12.2
PEI1.8K-*g*-P(TsMAz)$_{0.96}$ (4 wt% PEI, sample of entry 3, Table 2)	307	343, 386	24.6

[a]T_{di} is the initial thermal decomposition temperature, at which the decomposition rate points out a significant weight loss (d(wt%)/dT > 1%/°C). [b]T_{dm} is the maximum decomposition temperature, at which the highest decomposition rate is observed for the corresponding pattern.

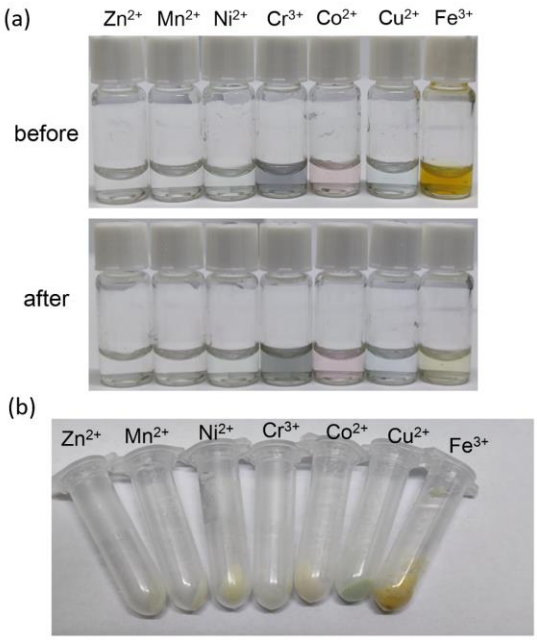


Figure S17. (a) Seven metal ion solutions before and after the treatment with PEI10K-$SA_{0.83}$; (b) PEI10K-$SA_{0.83}$ copolymer after adsorption of metals.

Table S2. Comparison of adsorption behavior of PEI10K-$SA_{0.83}$ with a single metal ion and the mixed metal ions.

metal ion	single metal ion[a]		mixed metal ions[b]	
	adsorption efficiency[c] (%)	adsorption capacity[d] (mg/g)	adsorption efficiency[c] (%)	adsorption capacity[d] (mg/g)
Fe^{3+}	36.65	16.0	36.67	15.2
Co^{2+}	24.05	6.7	26.97	9.5
Ni^{2+}	4.44	1.5	2.82	1.2
Cu^{2+}	32.02	21.3	36.28	15.8
Mn^{2+}	11.54	3.3	10.59	4.9

[a]Carried out in aqueous solution with a single metal ion as in Table 3. [b]Carried out in aqueous solution with the mixed metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} & Mn^{2+}), PEI10K-$SA_{0.83}$ (30 mg) was added into 1.0 mL of mixed metal ions solution, and the mixture was stirred for 4 h. [c]Adsorption efficiency $\eta = (C_0 - C_f)/C_0 \times 100\%$. [d]Adsorption capacity $q = [(C_0 - C_f) \times V]/m$.

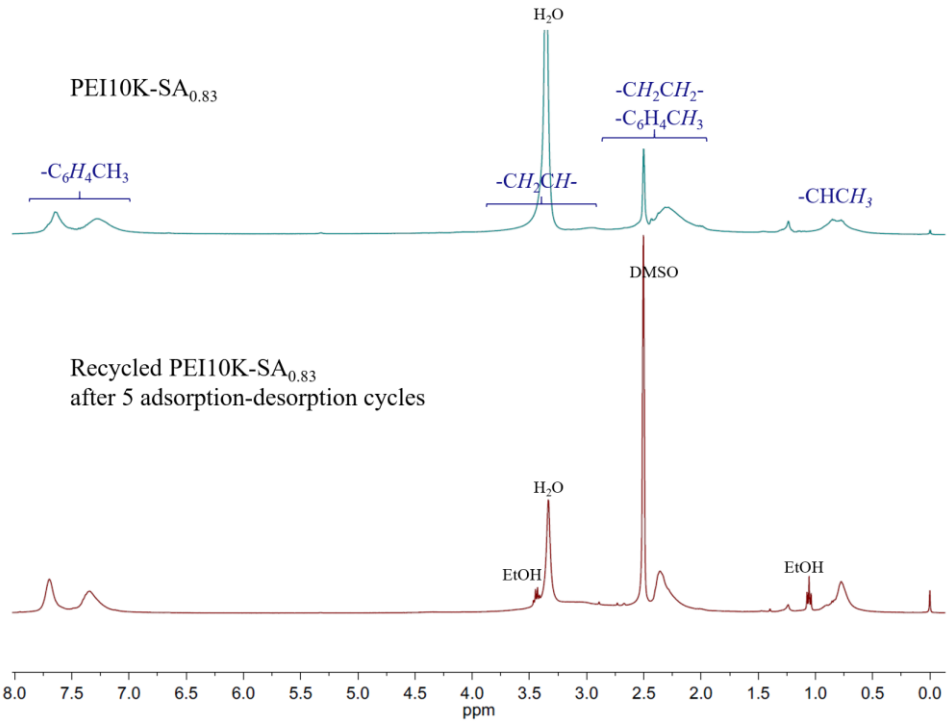


Figure S18. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) spectra of PEI10K-SA$_{0.83}$, and recycled PEI10K-SA$_{0.83}$ after 5 adsorption-desorption cycles.