Supporting Information

Impact of Metal Cations on Thermal, Mechanical, and Rheological Properties of Telechelic Sulfonated Polyetherimides

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^{1}H NMR spectra of SAA-H and SAA-M (M = Li, Na, K, Mg, Ca, Sr)

The proton nuclear magnetic resonance (^{1}H NMR) spectra (Fig. S1) did not reveal peak **c** (-NH_2 group) in SAA-H (H_2N-C_6H_4-SO_3H) due to the proton exchange forming the zwitterion (H_3N^+-C_6H_4-SO^{3-}). After converting SAA-H to SAA-M, a broad peak **c'** appeared, and both peaks **a'** and **b'** shifted upfield because their neighboring groups became less electron-withdrawing (from -NH_3^+ to -NH_2), compared to peaks **a** and **b**. The chemical shifts of peaks **a'** and **b'** were nearly the same for different metal cations. The peak positions matched well with our previous report.[1]

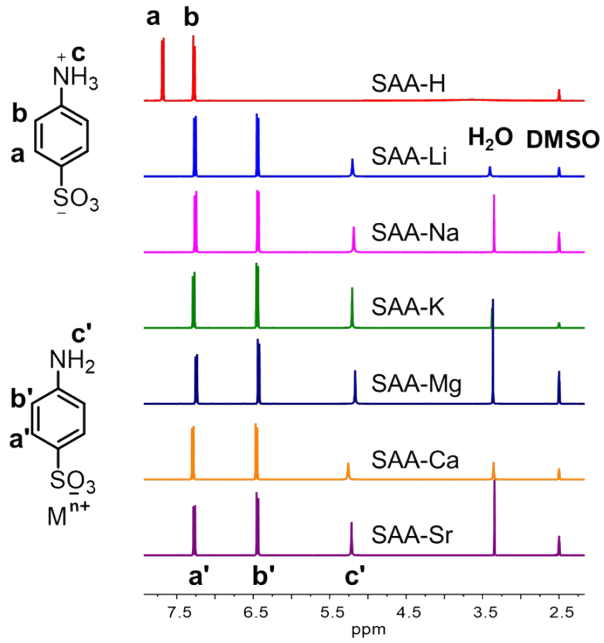

Fig. S1. ^{1}H NMR spectra of SAA-H and SAA-M (M = Li, Na, K, Mg, Ca, and Sr) in DMSO-d_6.

Characterization of number average molecular weight (M_n) of PEI-DA from ^{1}H NMR spectrum

The end group analysis evaluated M_n using integral peak areas associated with the end group and repeating units in the ^{1}H NMR spectrum of PEI-DA (Fig. 1, main text). The M_n is calculated according to the equations shown below, which was described in our previous report.[2]

$$n = \frac{\#\ of\ repeating\ units}{\#\ of\ chains} = \frac{Area\ (a)/2}{Area\ (a')/2} = \frac{Area\ (a)}{Area\ (a')}$$

$$M_n = M_{repeating\ unit} \cdot n + M_{end\ group} = (592.61n + 520.49)\ g \cdot mol^{-1}$$

where the number of repeating units (n) was calculated by normalizing peak **(a)** by a factor of 2 since each unit has two **a** protons in a BPADA moiety. Likewise, the number of chains was evaluated by dividing the peak area of (**a'**) by a factor of 2 because each PEI chain has two **a'** protons in the anhydride end groups. The M_n calculated from NMR ($M_{n,\ NMR}$) roughly matched the theoretical M_n ($M_{n,\ theo}$) (Table 1). The slightly larger $M_{n,\ NMR}$ compared to $M_{n,\ theo}$ results from the error in the integral area of **a'**. As PEI-DA is hygroscopic, it will be more or less hydrolyzed at preparation and the area of peak **a'** becomes smaller than the expected value. Thus, the $M_{n,\ NMR}$ becomes slightly larger than $M_{n,\ theo}$.

Characterization of M_n, weight average molecular weight (M_w), and polydispersity index (PDI) of PEIs by size-exclusion chromatography (SEC)

As the end group signals of PEI-Ph and PEI-SAA-M (M = Li, Na, K, Mg, Ca, and Sr) were not revealed in the spectra (Fig. 1, main text), the M_n, M_w, and PDI of PEI-Ph and PEI-SAA-M were characterized by SEC (Table S1). The PEI-DA was also characterized by SEC. The close M_n and M_w among PEIs with the same targeted molecular weight but different end groups indicated the successful synthesis of PEI-Ph and PEI-SAA-M. The PDIs of PEI-SAA-M were all slightly lower than that of the corresponding PEI-DA or PEI-Ph, as the low-molecular-weight fragments of PEI-SAA-M were removed by water after the precipitation step.

Table S1. M_n, M_w, and PDI of PEI-DA, PEI-Ph, PEI-SAA-M (M = Na, Ca, Zn), and high-MW commercial PEIs (PEI-1 and PEI-2).

Sample	$M_{n,\ theo}$ (kDa)	$M_{n,\ NMR}$ (kDa)[a]	$M_{n,\ SEC}$ (kDa)[b]	$M_{w,\ SEC}$ (kDa)[b]	PDI[b]
8k-PEI-DA	7.6	8.5	8.4	18.7	2.23
10k-PEI-DA	9.4	11.6	9.7	22.7	2.34
12k-PEI-DA	11.8	13.7	11.7	27.7	2.36
8k-PEI-Ph	7.8	-	9.3	22.9	2.46
10k-PEI-Ph	9.6	-	9.7	26.7	2.74
12k-PEI-Ph	11.9	-	15.4	33.7	2.19
8k-PEI-SAA-Li	8.0	-	11.5	20.5	1.79
10k-PEI-SAA-Li	9.7	-	13.2	23.5	1.77
12k-PEI-SAA-Li	12.1	-	15.7	31.1	1.98
8k-PEI-SAA-Na	8.0	-	9.5	18.4	1.92
10k-PEI-SAA-Na	9.8	-	13.8	26.6	1.93
12k-PEI-SAA-Na	12.1	-	17.6	34.4	1.96
8k-PEI-SAA-K	8.0	-	11.9	22.6	1.89
10k-PEI-SAA-K	9.8	-	13.2	25.1	1.91
12k-PEI-SAA-K	12.2	-	14.6	28.2	1.94
8k-PEI-SAA-Mg	8.0	-	11.7	22.2	1.90
10k-PEI-SAA-Mg	9.7	-	12.6	24.0	1.90
12k-PEI-SAA-Mg	12.1	-	15.1	29.3	1.95
8k-PEI-SAA-Ca	8.0	-	10.3	23.4	2.26
10k-PEI-SAA-Ca	9.8	-	12.9	27.2	2.10
12k-PEI-SAA-Ca	12.1	-	15.4	29.3	1.90
8k-PEI-SAA-Sr	8.0	-	11.1	21.5	1.93
10k-PEI-SAA-Sr	9.8	-	12.2	24.1	1.97
12k-PEI-SAA-Sr	12.2	-	14.8	28.4	1.92

[a]$CDCl_3$, ambient conditions. M_n was calculated based on end group analysis. [b]SEC characterization was carried out in DMF with LiBr.

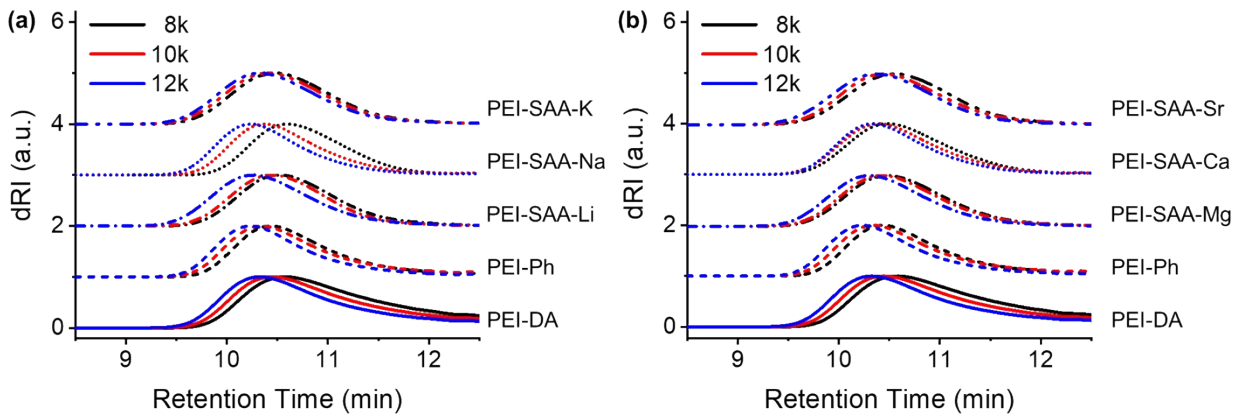

Fig. S2. SEC traces of (a) PEI-SAA-M (M = Li, Na, and K) and (b) PEI-SAA-M (M = Mg, Ca, and Sr) in comparison with those of PEI-DA and PEI-Ph. The targeted M_n are 8, 10, and 12 kDa. DMF was used as the eluent.

TGA thermograms of 10k-PEIs and 12k-PEIs

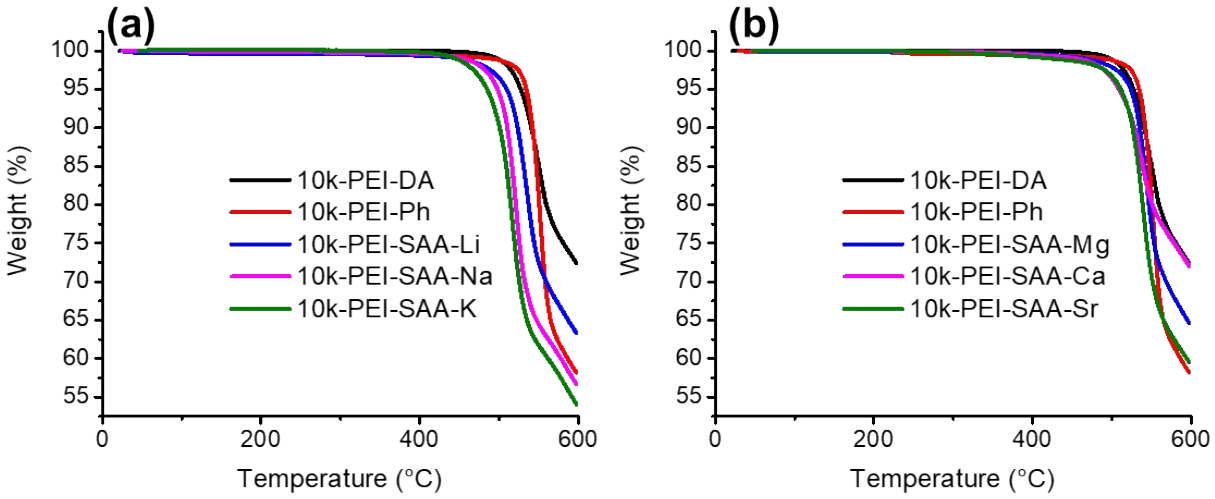

Fig. S3. TGA thermograms of (a) PEI-SAA-M (M = Li, Na, and K) and (b) PEI-SAA-M (M = Mg, Ca, and Sr) compared to PEI-DA and PEI-Ph, respectively. All representative PEIs have a target M_n of 10 kDa.

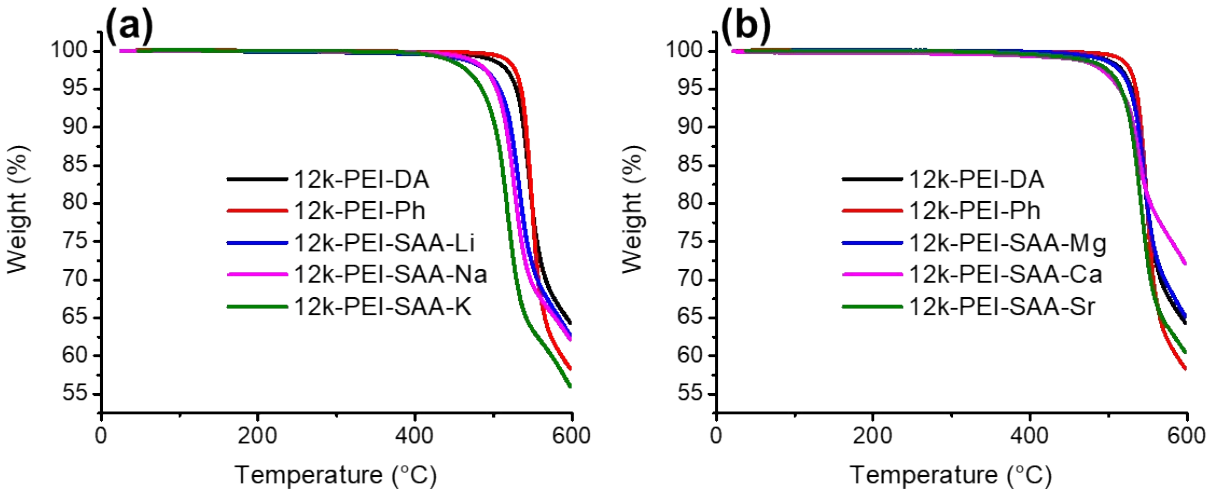

Fig. S4. TGA thermograms of (a) PEI-SAA-M (M = Li, Na, and K) and (b) PEI-SAA-M (M = Mg, Ca, and Sr) compared to PEI-DA and PEI-Ph, respectively. All representative PEIs have a target M_n of 12 kDa.

DSC traces of 10k-PEIs and 12k-PEIs

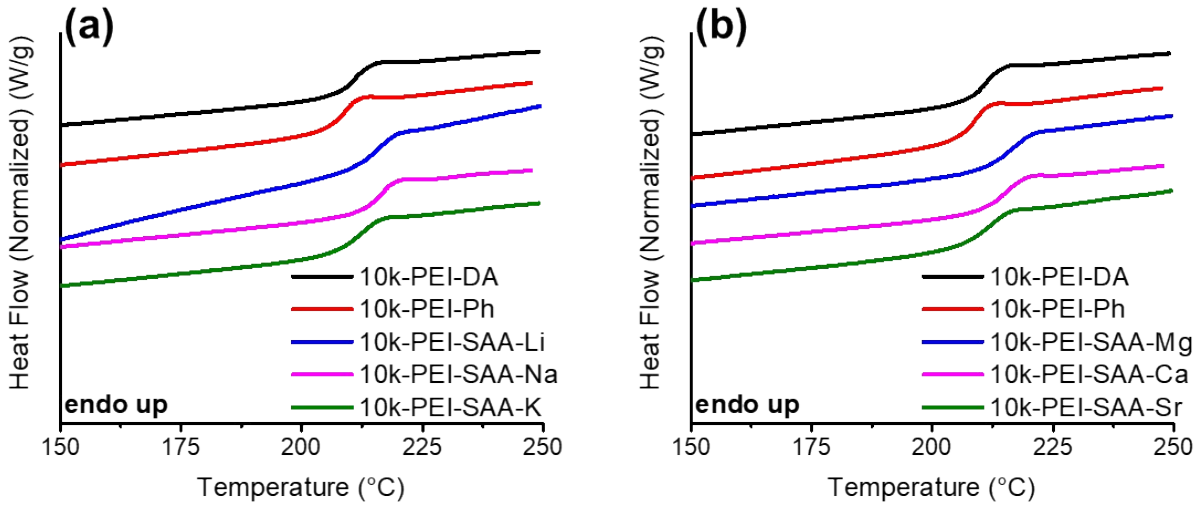

Fig. S5. DSC traces of (a) PEI-SAA-M (M = Li, Na, and K) and (b) PEI-SAA-M (M = Mg, Ca, and Sr) compared to PEI-DA and PEI-Ph, respectively. All representative PEIs have a target M_n of 10 kDa.

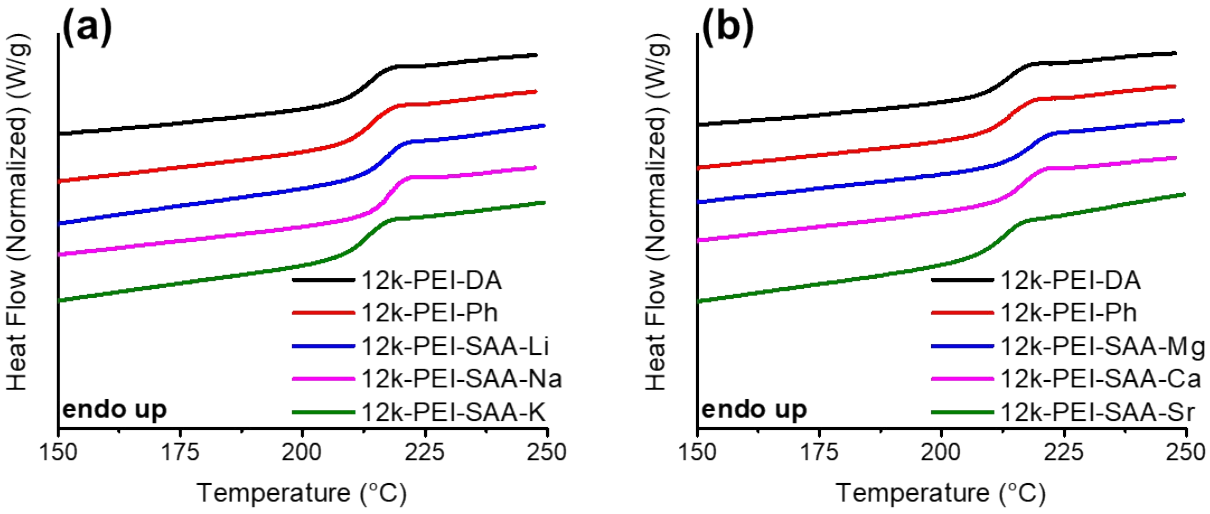

Fig. S6. DSC traces of (a) PEI-SAA-M (M = Li, Na, and K) and (b) PEI-SAA-M (M = Mg, Ca, and Sr) compared to PEI-DA and PEI-Ph, respectively. All representative PEIs have a target M_n of 12 kDa.

References

1. X. J. Yang, X. Wang, D. Y. Chen, J. Yang, L. D. Lu, X. Q. Sun, G. Y. He and J. Chen, *J. Appl. Polym. Sci.*, 2000, **77**, 2363-2369.
2. K. Cao, M. Zhang and G. Liu, *Macromol. Rapid Commun.*, 2018, **39**, 1800045.