

Supporting Information for

Melt-Processable Telechelic Poly(ether imide)s End-Capped with Zinc Sulfonate Salts

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Calculation of the M_n of PEI-DA using ^1H NMR spectroscopy

The number average molecular weight (M_n) and the degree of polymerization (n) of dianhydride-terminated poly(ether imide) (PEI-DA) were estimated using the following equations based on the integral areas of peaks **i** and **j** (Fig. S1).

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

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

where the number of repeating units was calculated by normalizing peak **(a)** by a factor of 2 since each repeating unit has two Type-**a** protons in BPADA. Similarly, the number of chains was calculated by dividing the peak area of **(a')** by a factor of 2 because each chain has two **a'** protons in the dianhydride end groups.

The end-group analysis of M_n becomes less reliable as M_n increases because of a decreasing concentration of the end group. More accurate characterization of M_n can be complemented by size exclusion chromatography (SEC).

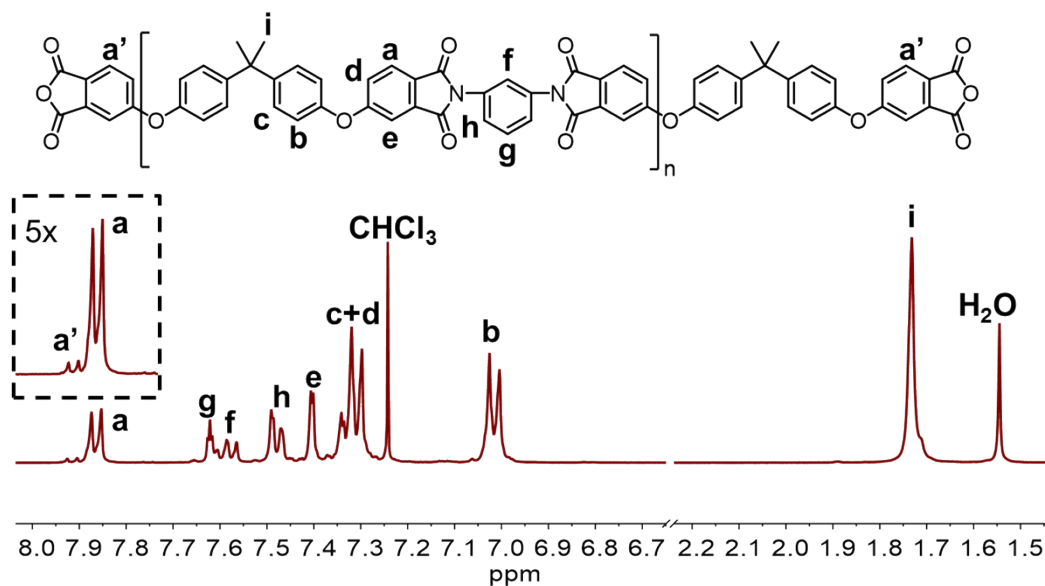


Fig. S1 ^1H NMR spectrum of 8k-PEI-DA in CDCl_3 .

SEC characterization of PEI-Ph, and PEI-SAA-M (M = Na, Ca, Zn)

The M_n and M_w of all PEIs in this work were characterized by SEC in DMF. The SEC traces were shown in Fig. S2. Note that most charged PEIs exhibited PDIs lower than the prepolymer PEI-DA, because the water was used to wash the precipitate during the synthesis of PEI-SAA-M. The water dissolved not only excessive or unreacted end cappers, but also some charged PEIs with short backbone, which had large ionic concentration and thus good solubility in water. As a result, the charged PEIs exhibited low PDIs.

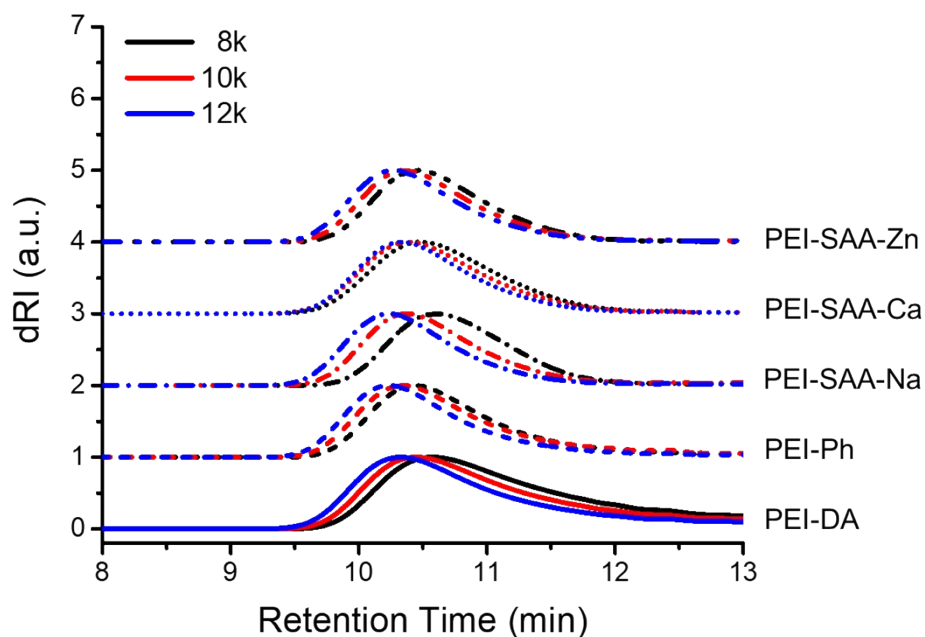


Fig. S2 SEC traces of PEI-DA, PEI-Ph, PEI-SAA-M (M = Na, Ca, Zn) with targeted $M_n = 8, 10$, and 12 kDa. DMF was used as the eluent.

^1H NMR spectra of SAA-M (M = Na, Ca, Zn)

The molecular structures of SAA-Na, SAA-Ca, and SAA-Zn were confirmed by ^1H NMR spectra (Fig. S3). The $-\text{NH}_2$ protons were invisible in the NMR spectrum of SAA-H, suggesting that SAA-H was in the form of zwitterion. In other words, $-\text{NH}_2$ and $-\text{SO}_3\text{H}$ became $-\text{NH}_3^+$ and $-\text{SO}_3^-$ in SAA-H, respectively. After converting SAA-H to SAA-M, the peaks (c) corresponding to $-\text{NH}_2$ appeared and were broad. In addition, peaks (a) and (b) in the NMR spectrum of SAA-H shifted upfield because the electron-donating amine groups lead to increased shielding on protons from the benzene rings. The peak positions matched well with a previous report.²

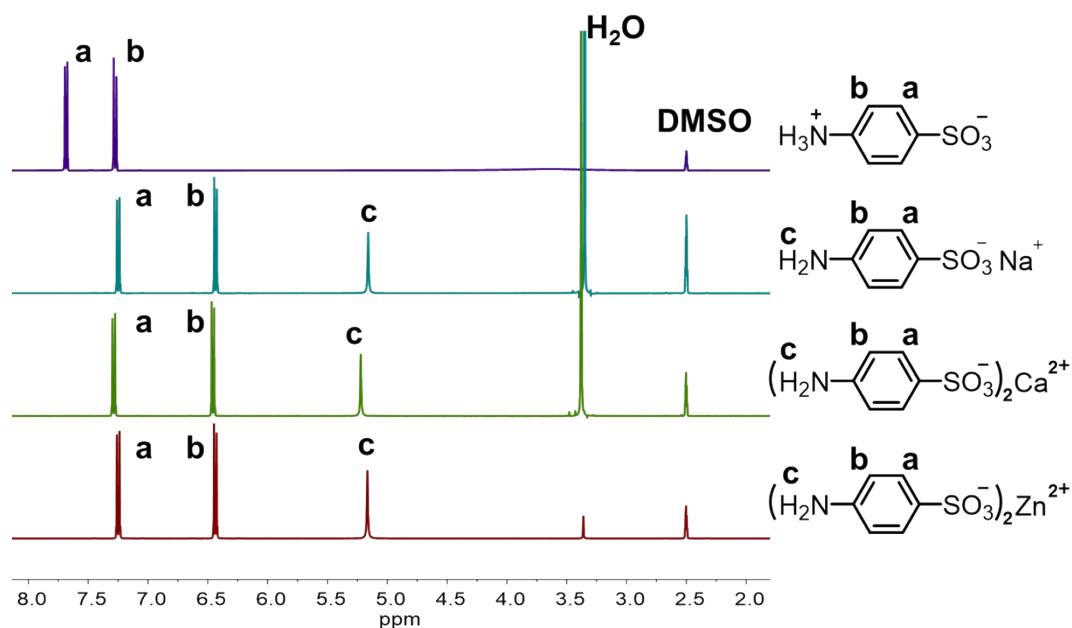


Fig. S3 ^1H NMR spectra of SAA-H and SAA-M (M = Na, Ca, Zn) in DMSO-d_6 .

Thermal stability of SAA-M (M = Na, Ca, Zn)

SAA-M salts are more thermally stable than SAA-H (Fig. S4). Both SAA-Na and SAA-Ca showed a weight loss at ~ 100 °C due to the loss of hydrate water. In contrast, SAA-Zn had no weight loss at ~ 100 °C, indicating that SAA-Zn is not as hygroscopic as SAA-Na and SAA-Ca are. All SAA-M (M = Na, Ca, Zn) exhibited good thermal stability with $T_{d,5\%} > 400$ °C. All $T_{d,5\%}$ values were calculated based on the weight loss of 5% from the plateau above 100 °C.

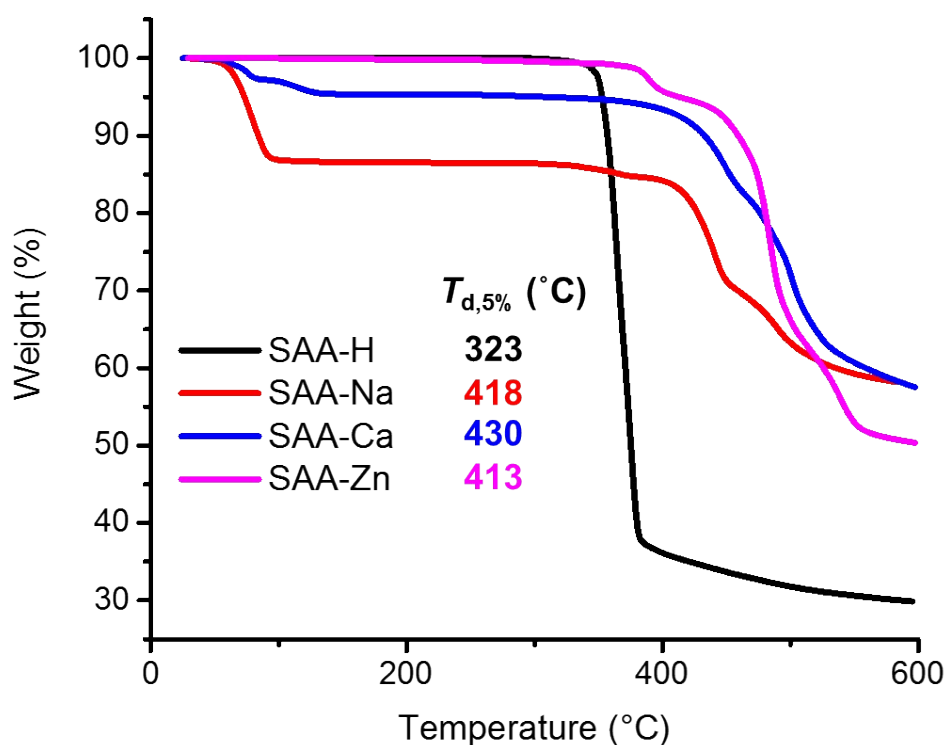


Fig. S4 TGA traces of SAA-H and SAA-M (M = Na, Ca, Zn).

Tensile tests of PEIs

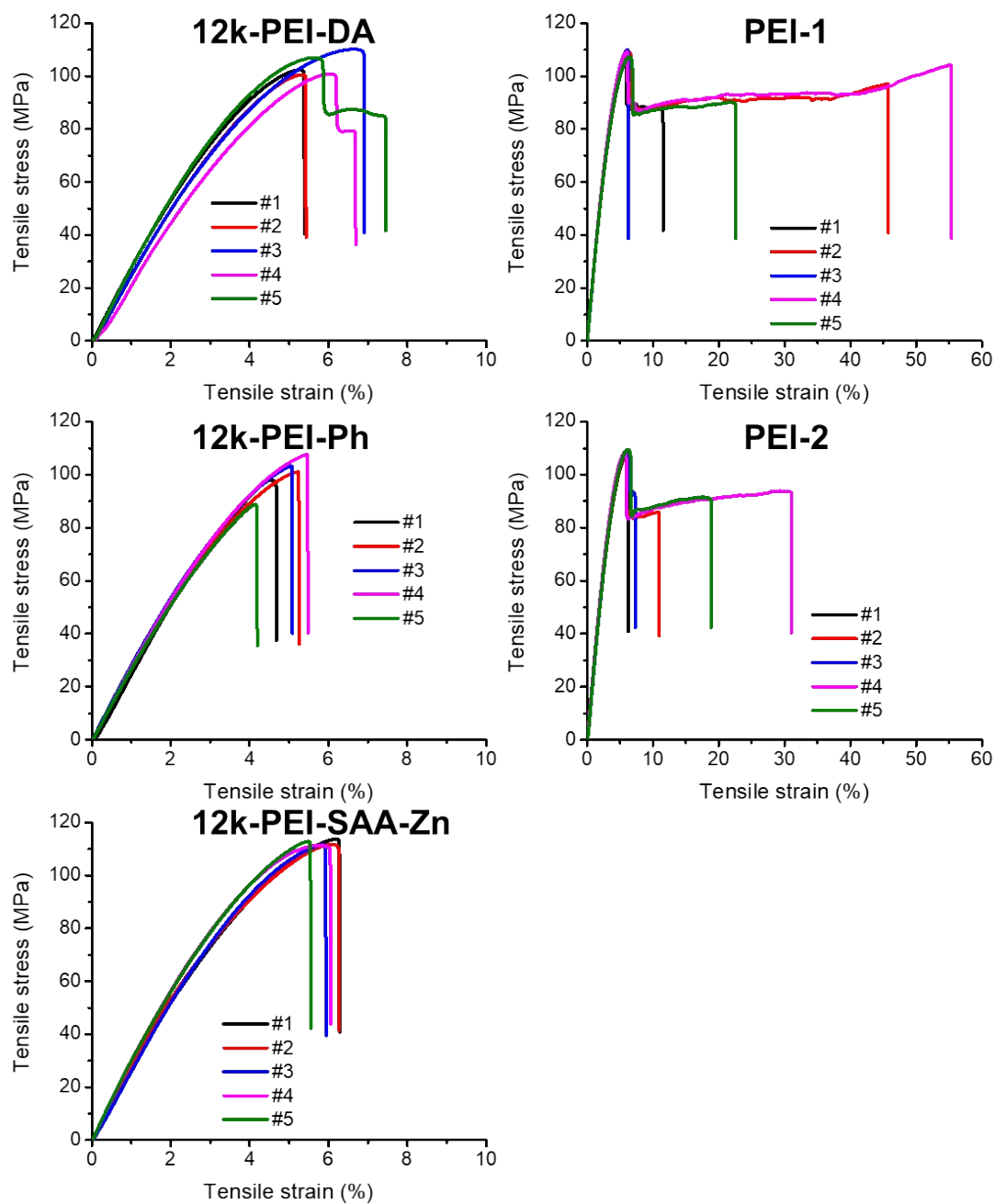


Fig. S5 Stress-strain curves of 12k-PEI-DA, 12k-PEI-Ph, and 12k-PEI-SAA-Zn, in comparison with commercial high-MW PEIs: PEI-1 and PEI-2.

Rheological time sweep of PEI-SAA-Ca

Rheological time sweep of 10k-PEI-SAA-Ca and 12k-PEI-SAA-Ca at 340 °C in air showed the crossover of G' and G'' within the first few minutes. After one hour of rheological time sweep, the two parallel plates stuck together (Fig. S6) and were very difficult to separate. Even after soaking in *N*-methyl-2-pyrrolidone (NMP) for 1 day, the polymers did not dissolve, and the plates remained together, suggesting the strong cross-linking of the polymers.

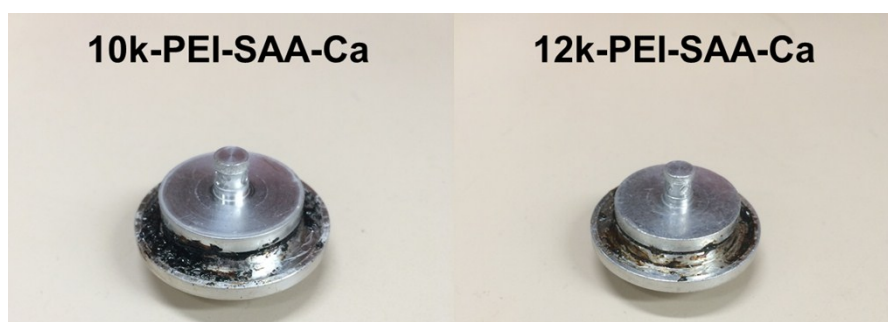


Fig. S6 Rheological time sweep of 10k-PEI-SAA-Ca and 12k-PEI-SAA-Ca at 340 °C. The polymer melts were cross-linked and adhered to the parallel plates. The two parallel plates could not be separated afterwards.

Time-temperature superposition master curves of PEIs

G' , G'' , and η^* are plotted as a function of M_n for PEIs with various end groups, as well as PEI-1 and PEI-2 (Fig. S7).

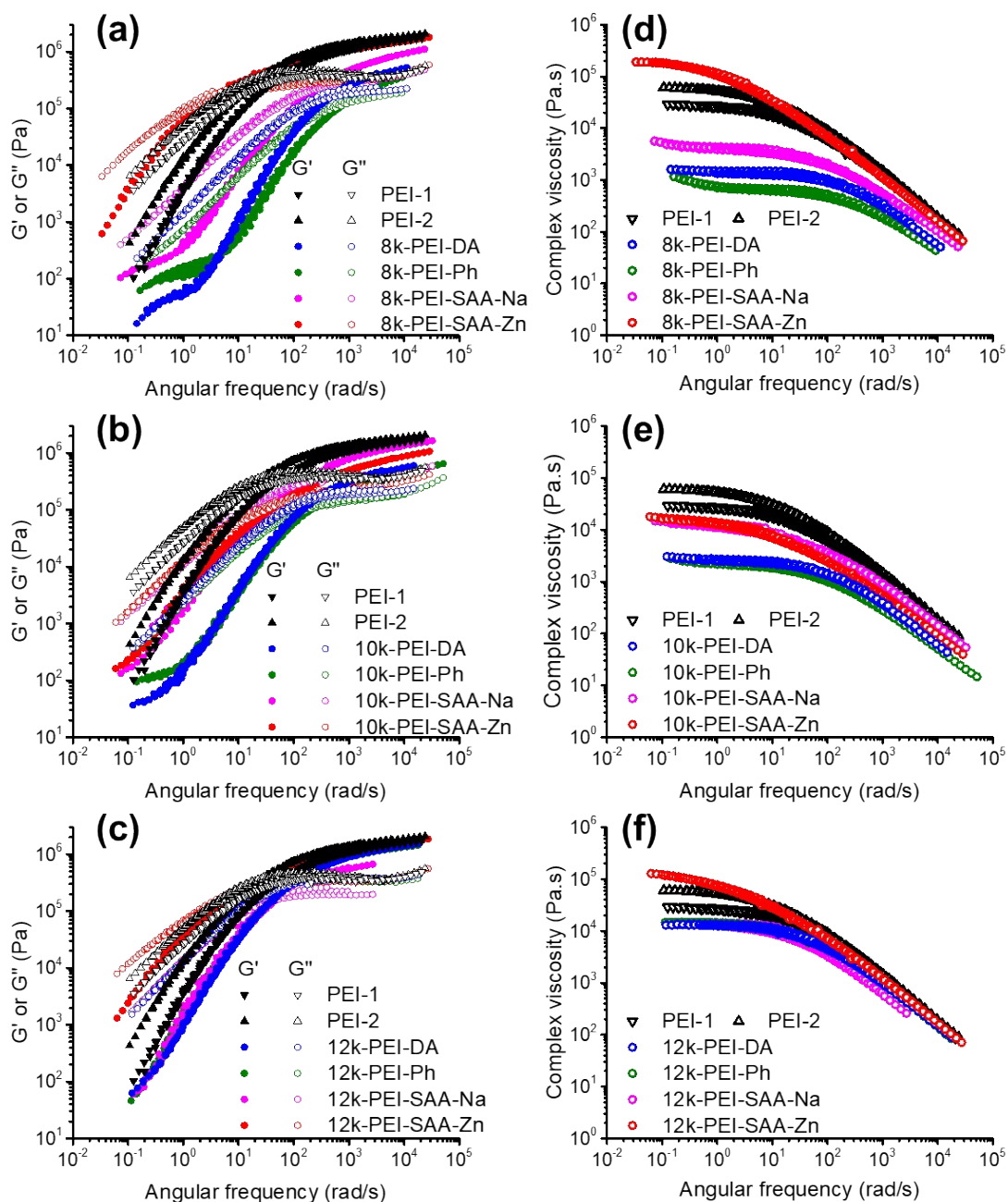


Fig. S7 TTS master curves of G' , G'' , and complex viscosities for 8k-, 10k-, and 12k-PEIs with various end groups, in comparison to PEI-1 and PEI-2 at $T_r = 300$ °C.

The response of viscosity to programed temperature ramps

The possession of pivot temperatures by all PEI-SAA-Zn is attributed to the dissociation of Zn^{2+} from -SAA^- but not from the polymer degradation. To prove it, 12k-PEI-SAA-Zn was subject to repeated heat/cool ramping cycles (Fig. S8). In the absence of a relaxation time between every two heat/cool ramping cycles (Fig. S8a), PEI-SAA-Zn showed a pivot temperature of 322 °C in the first two heating cycles but not in the third cycle due to an insufficient time for Zn^{2+} to re-associate with the -SAA^- end groups (Fig. S8b). However, after preheating PEI-SAA-Zn at 250 °C for 1 h (Fig. S8c), the ion clusters completely dissociated, leading to the disappearance of pivot temperature even in the first rheological heating cycle (Fig. S8d).

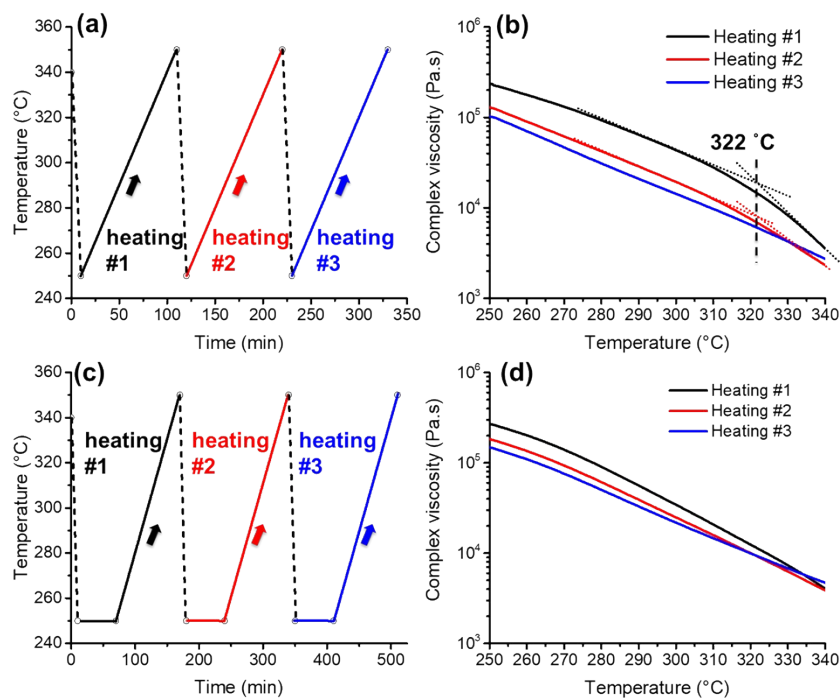


Fig. S8 (a) The heating and cooling cycles during the rheological study (1 °C/min for heating rate and 10 °C/min for cooling rate, 1% oscillatory strain, 1 Hz). (b) Evolution of the complex viscosity of 12k-PEI-SAA-Zn during the three heating cycles in (a). The pivot temperatures became less apparent as the number of heating cycles increased. (c) The heating and cooling

cycles during the rheological study (1 °C/min for heating rate and 10 °C/min for cooling rate with sample isothermal at 250 °C for 1 h, 1% oscillatory strain, 1 Hz). (d) Evolution of the complex viscosity of 12k-PEI-SAA-Zn with the three heating cycles in (c). The pivot temperature was not observed after the 12k-PEI-SAA-Zn polymer melt being isothermal at 250 °C for 1 h ahead of the temperature ramp, and the viscosity decrease behavior became similar to 12k-PEI-SAA-Na (Fig. S9).

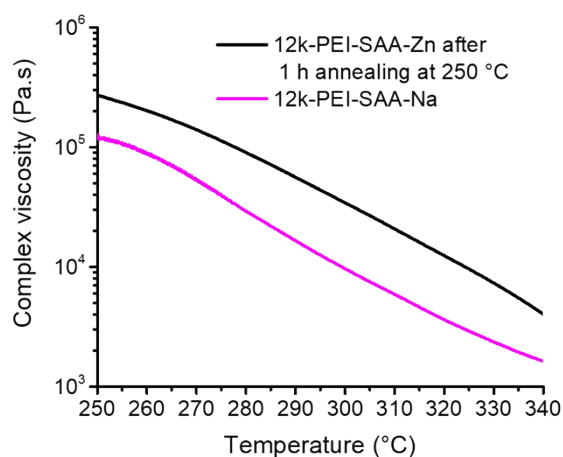


Fig. S9 As the temperature was increased, the viscosity of 12k-PEI-SAA-Zn decreased in the first heating cycle after preheating 12k-PEI-SAA-Zn at 250 °C for 1 h (data replotted from Fig. S8d). The decreasing profile of the viscosity of 12k-PEI-SAA-Zn resembled that of the 12k-PEI-SAA-Na.

Reference

1. Cao, K.; Liu, G. Low-molecular-weight, high-mechanical-strength, and solution-processable telechelic poly(ether imide) end-capped with ureidopyrimidinone. *Macromolecules* **2017**, 50 (5), 2016-2023 DOI: 10.1021/acs.macromol.7b00156.
2. Yang, X. J.; Wang, X.; Chen, D. Y.; Yang, J.; Lu, L. D.; Sun, X. Q.; He, G. Y.; Chen, J. Preparation and characterization of metal-containing aromatic polyimides. *J. Appl. Polym. Sci.* **2000**, 77 (11), 2363-2369 DOI: 10.1002/1097-4628(20000912)77:11<2363::aid-app4>3.0.co;2-1.