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Supporting Information

High-temperature resistant polyetherimides containing a twisted spirane structure for capacitive energy storage

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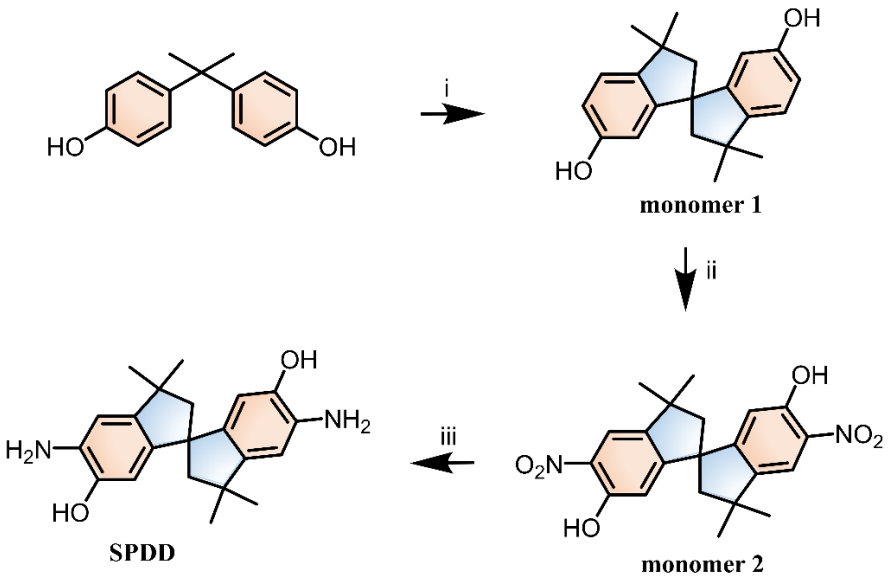
1. The synthesis route of SPDD monomer



(i) methylsulfonic acid, room temperature, 32 h;
(ii) HNO_3 (4N, 2.1 equiv), HAc, 15 h, room temperature;
(iii)Palladium 10% on Carbon, Hydrazine hydrate 80%,ethanol, reflux for 12 h.

Scheme S1. Synthesis process of SPDD monomers.

2. Synthesis of Monomer 1

BAP (20 g, 0.0774 mol), methane sulfonic acid (22 mL) were added to a 50 mL single-necked flask equipped with a magnetic bar. The mixture was stirred at RT for 32 h. Then, the solution was slowly dropped into a mixed solvent of ethanol/water (50/60, w/w), and a large amount of white powder was collected. After washed by boiling water and dried, white needle-like crystals (12 g) were obtained. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.99 (s, 2H), 7.00 (d, 2H), 6.60 (dd, 2H), 6.10 (d, 2H), 2.27 (d, 2H), 2.11 (d, 2H), 1.31 (s, 6H),1.25 (s, 6H).

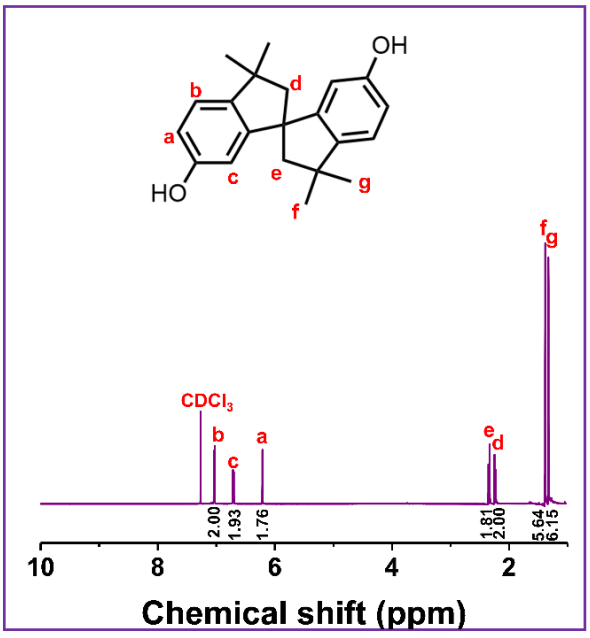


Figure S1. ^{1}H NMR spectrum of the first step of SPDD monomer synthesis. $CDCl_3$ is the solvent.

3. Synthesis of Monomer 2

Monomer I (10 g, 0.03 mol), acetic acid (50 mL) were added to a 250 mL single-necked flask equipped with a magnetic bar. Then, a mixture of nitric acid (4N, 2.1 equiv, 18 mL) and acetic acid (50 mL) was added dropwise and the solution was stirred overnight. After that, the solution was cooled to 6 °C before filtration. Faint yellow powder was collected by acetone/ethanol (10/40, w/w) recrystallization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.60 (s, 2H), 7.91 (s, 2H), 6.53 (s, 2H), 2.43 (d, 2H), 2.28 (d, 2H),1.36 (s, 6H),1.28 (s, 6H).

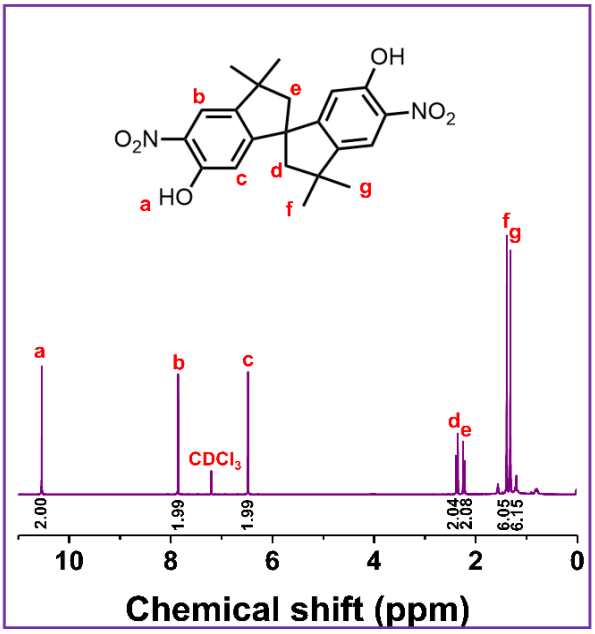


Figure S2. ^{1}H NMR spectrum of the second step of SPDD monomer synthesis. $CDCl_3$ is the solvent.

4. Synthesis of SPDD

Monomer II (12 g, 0.03 mol), Pd/C (0.5 g), ethanol (60 mL) were added to a 250 mL three-necked flask equipped with a magnetic bar. Then, the mixture was heated to 60 °C and hydrazine hydrate (60 mL) was added dropwise later. After stirred for 12 h, Pd/C was removed by centrifugation. The solution was poured into deionized water to precipitate the monomer. After drying, the crude product was dissolved in ethanol and precipitated in hot deionized (DI) water. Finally, the product was dried in a vacuum oven at 100 °C for 12 h.^{1}H NMR (600 MHz, DMSO-d_6): δ 8.59 (s, 2H), 6.30 (s, 2H), 5.96 (s, 2H), 4.26 (s, 4H), 2.06 (d, 2H), 1.91 (d, 2H), 1.18 (s, 6H), 1.13 (s, 6H).

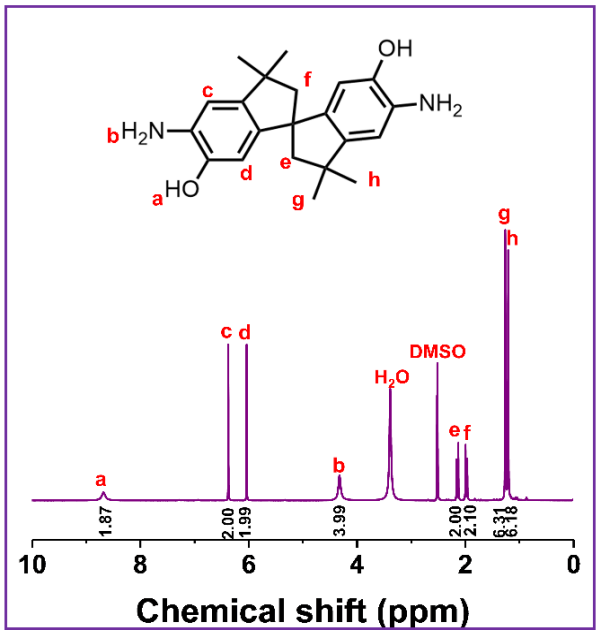


Figure S3. [1]H NMR spectrum of the third step of SPDD monomer synthesis. DMSO-d_6 is the solvent.

5. [1]H NMR spectra of various PEIs polymers

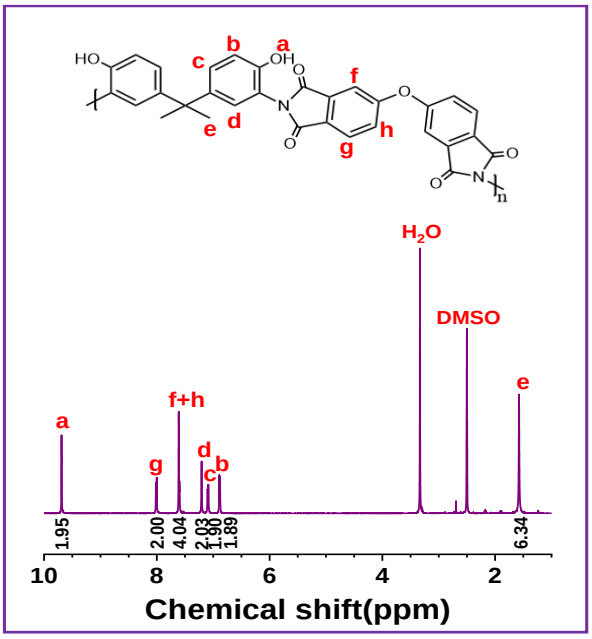


Figure S4. [1]H NMR spectrum of PEI-0. DMSO-d_6 is the solvent.

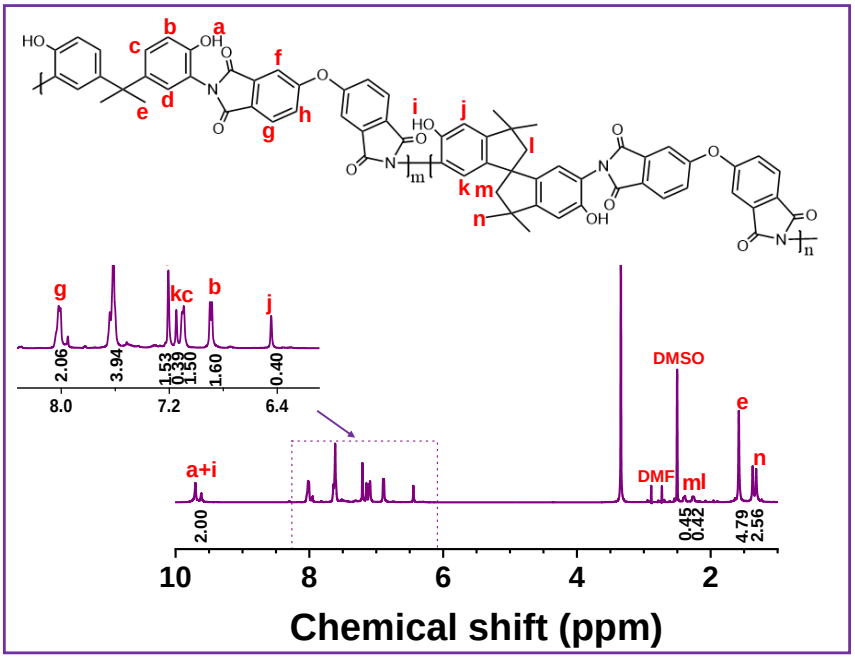


Figure S5. ^{1}H NMR spectrum of PEI-20. DMSO-d_6 is the solvent.

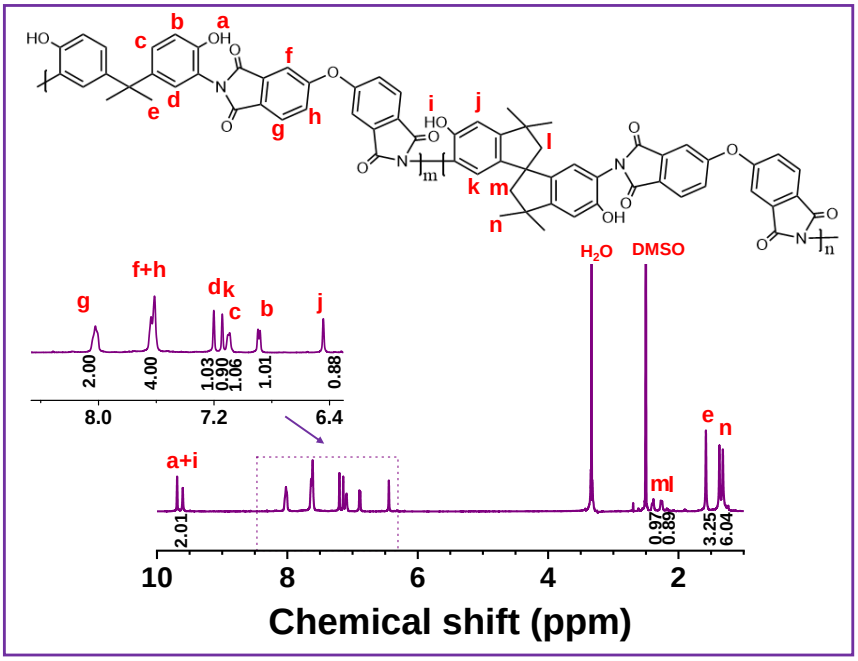


Figure S6. ^{1}H NMR spectrum of PEI-50. DMSO-d_6 is the solvent.

6. Detailed data of TGA tests

Table S1. TGA thermograms of PEI-0, PEI-20 and PEI-50 polymers.

Sample	$T_{d5\%}$/°C	$T_{d10\%}$/°C	Char yield/%
PEI-0	401.5	411.1	35.1
PEI-20	385.5	397.3	38.0
PEI-50	404.3	421.5	43.3

7. BDS of commercial PEI

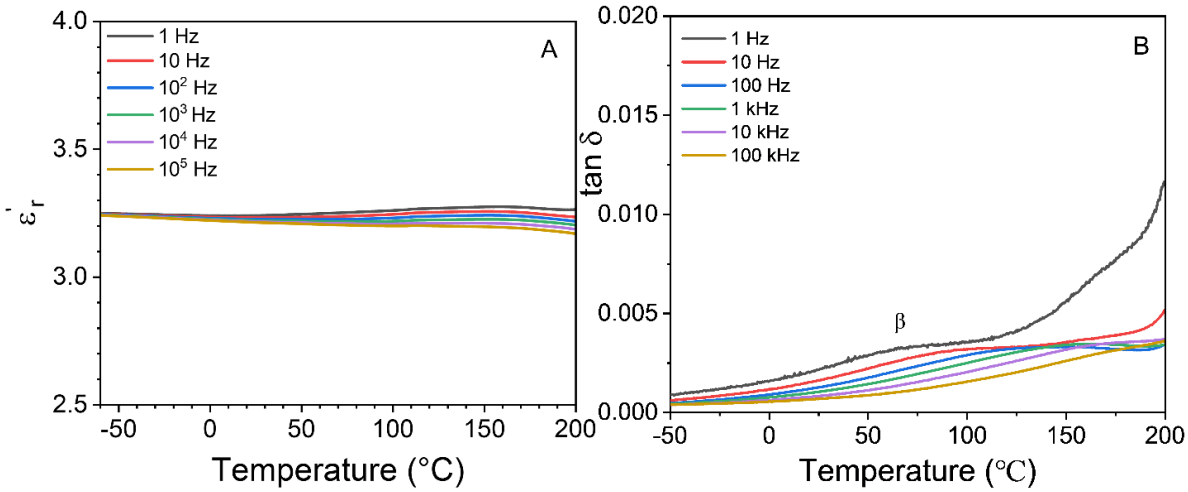


Figure S7. Temperature-scan (A) real part of the relative permittivity (ε_r') and (B) dissipation factor (*tanδ*) at different frequencies for commercial PEI.

8. Bipolar D-E loops for various PEIs polymers

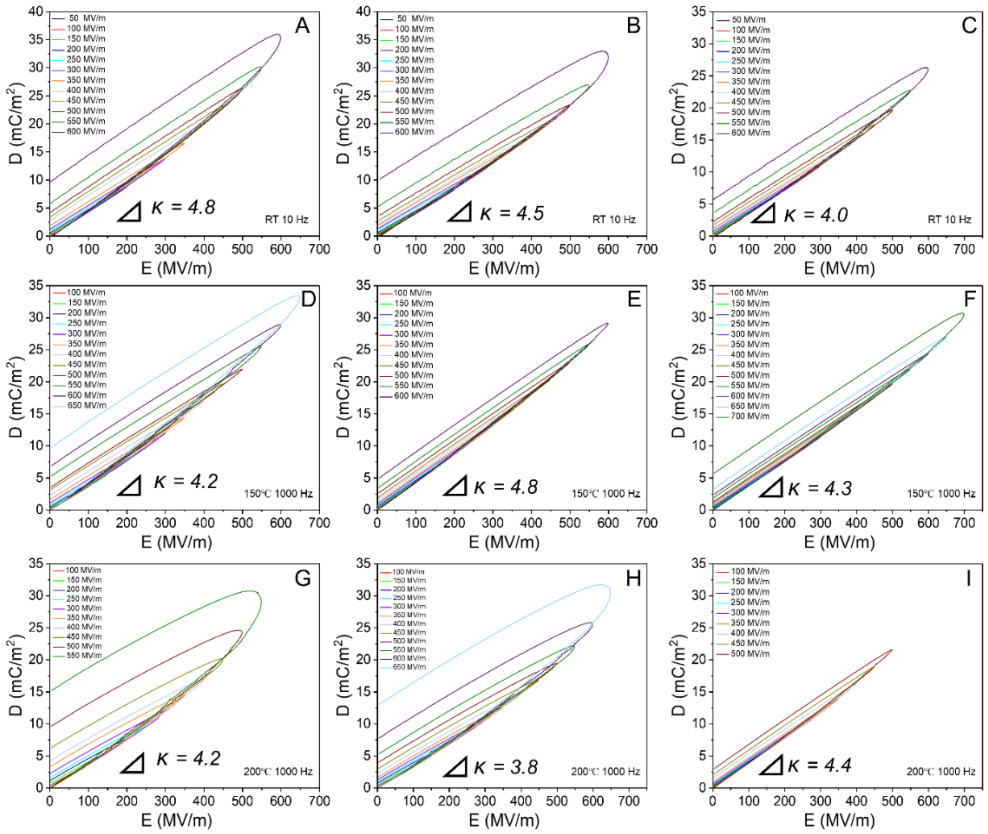


Figure S8. Unipolar D-E loops for solution-cast (A, D, G) PEI-0, (B, E, H) PEI-20, and (C, F, I) PEI-50 films at (A, B, C) room temperature and 10Hz and (D, E, F), (G, H, I) respectively at 150 °C and 200 °C, the poling frequency is 1000 Hz with a sinusoidal waveform.

9. Commercial PEI for unipolar circuits and bipolar circuits

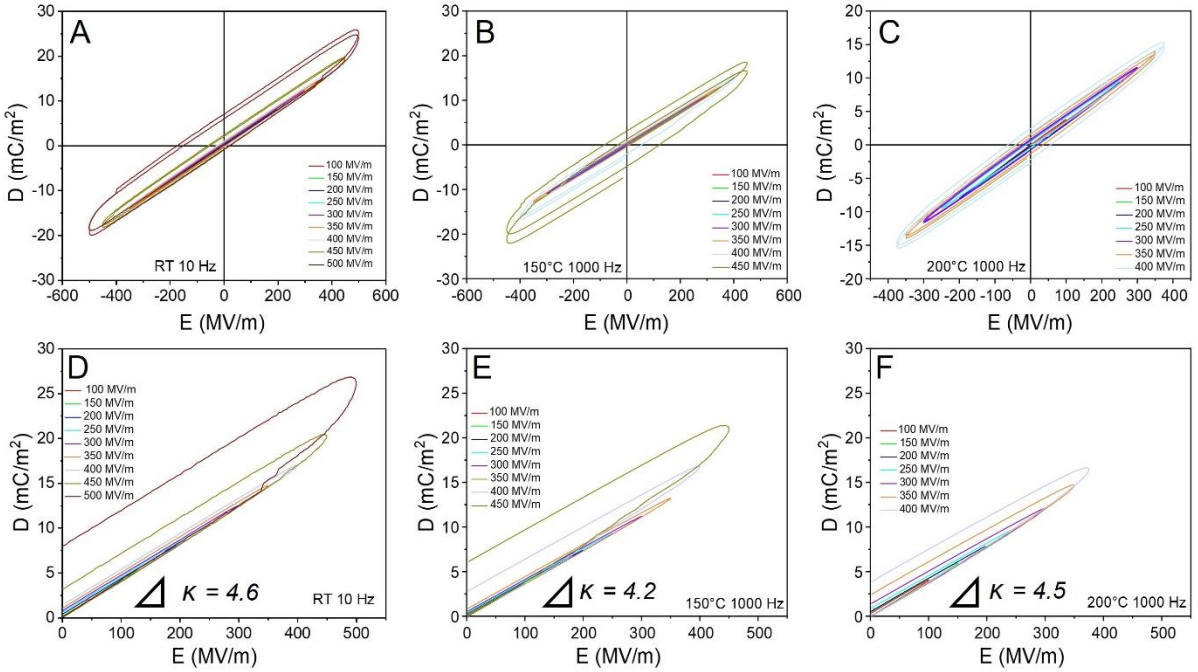


Figure S9. Commercial PEI at room temperature 10 Hz (A, D), 150 °C 1000 Hz (B, E), 200 °C 1000 Hz (C, F) for bipolar and monopolar circuits, respectively.

10. D-E loops of PEIs and commercial PEI after subtracted AC conduction at 150 °C.

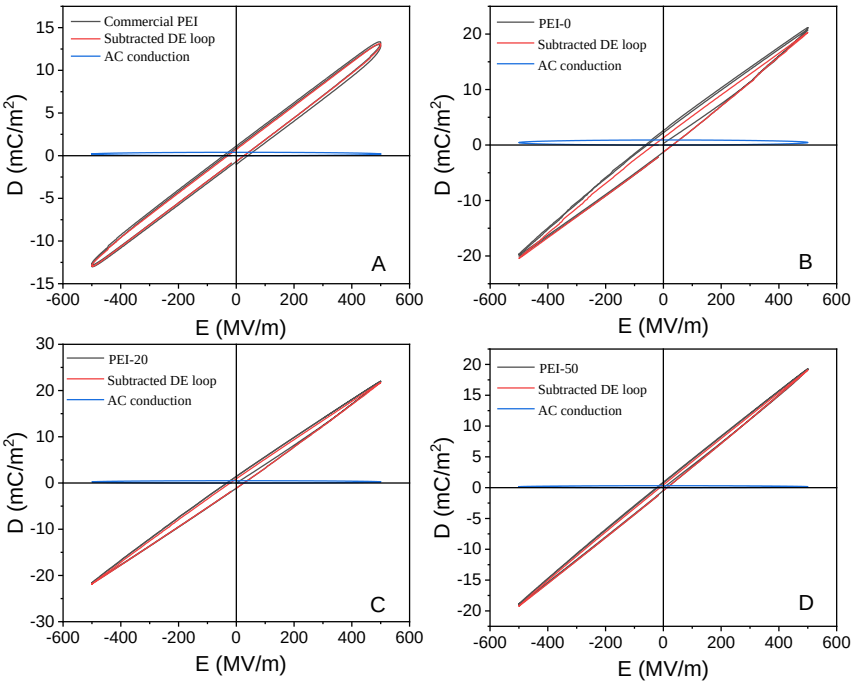


Figure S10. Bipolar D-E loops after subtracting AC conduction for (A) commercial PEI, (B) PEI-0, (C) PEI-20, (D) PEI-50 at 1 kHz and 150 °C.

11. D-E loops of PEIs and commercial PEI after subtracted AC conduction at 200 °C.

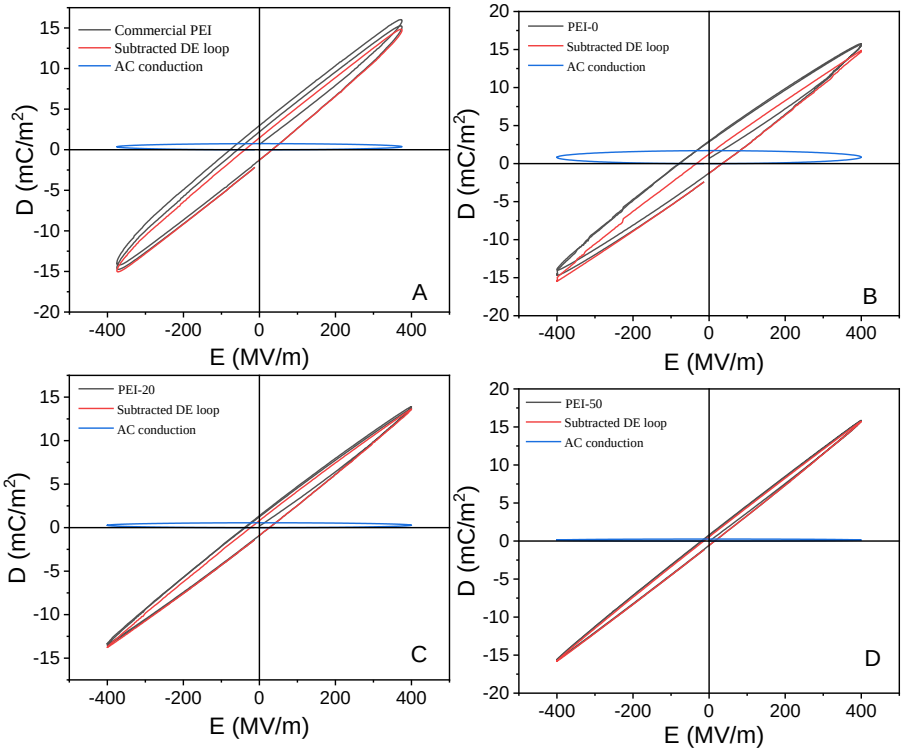


Figure S11. Bipolar D-E loops after subtracting the AC electronic conduction for (A) commercial PEI, (B) PEI-0, (C) PEI-20, (D) PEI-50 at 1 kHz and 200 °C.

12. Leakage current density of PEIs and commercial PEI

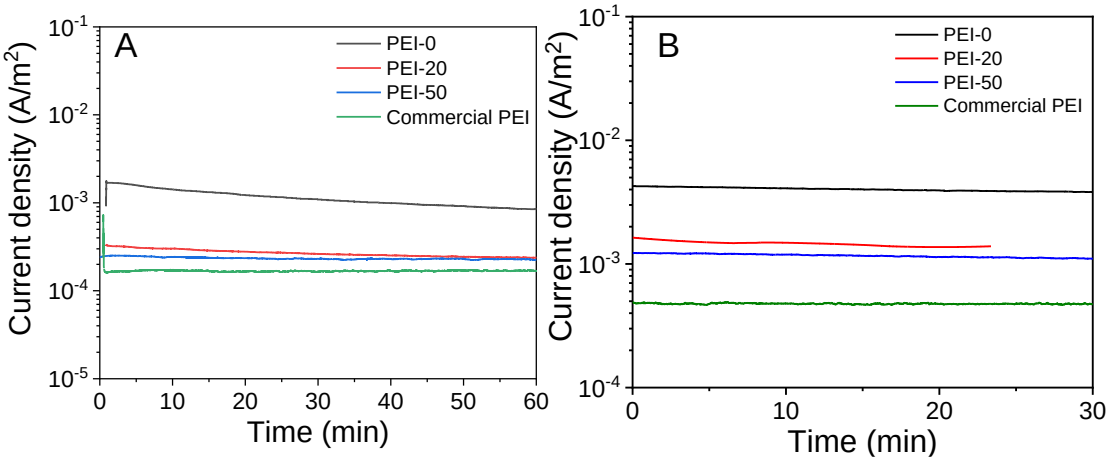


Figure S12. The leakage current density as the function of time at 150 °C for PEIs and commercial PEI at (A) 50 MV/m and (B) 150 MV/m.

13. Breakdown strength of PEIs and commercial PEI at 150 °C.

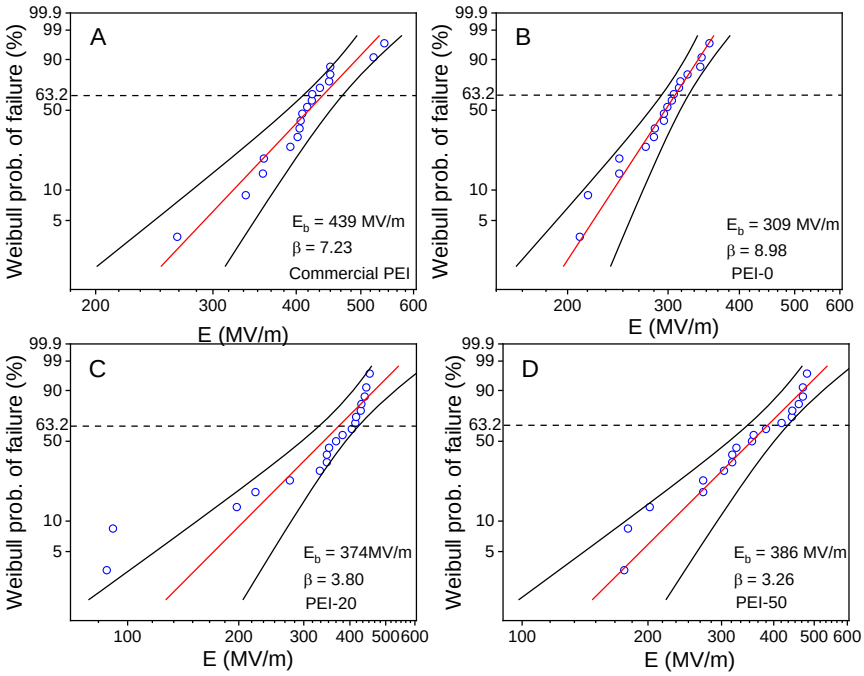


Figure S13. Weibull DC breakdown strengths of (A) the commercial PEI, (B) PEI-0, (C) PEI-20, and (D) PEI-50 films at 150 °C. The voltage ramp rate is 500 V/s.