

## Supporting Information

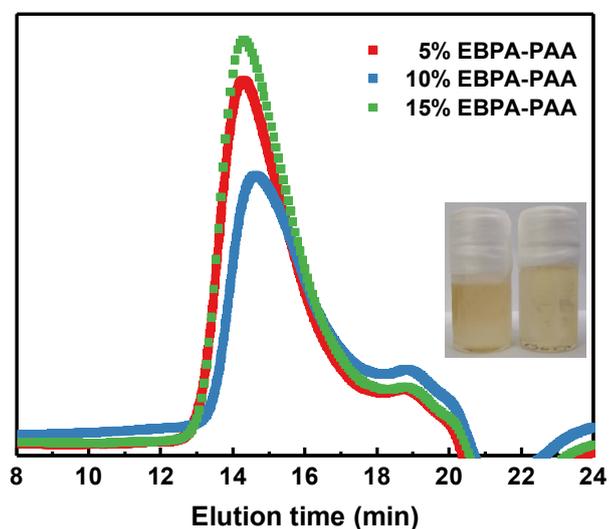
### Thermally self-crosslinkable polyetherimide dielectrics with superior high-temperature energy storage efficiency

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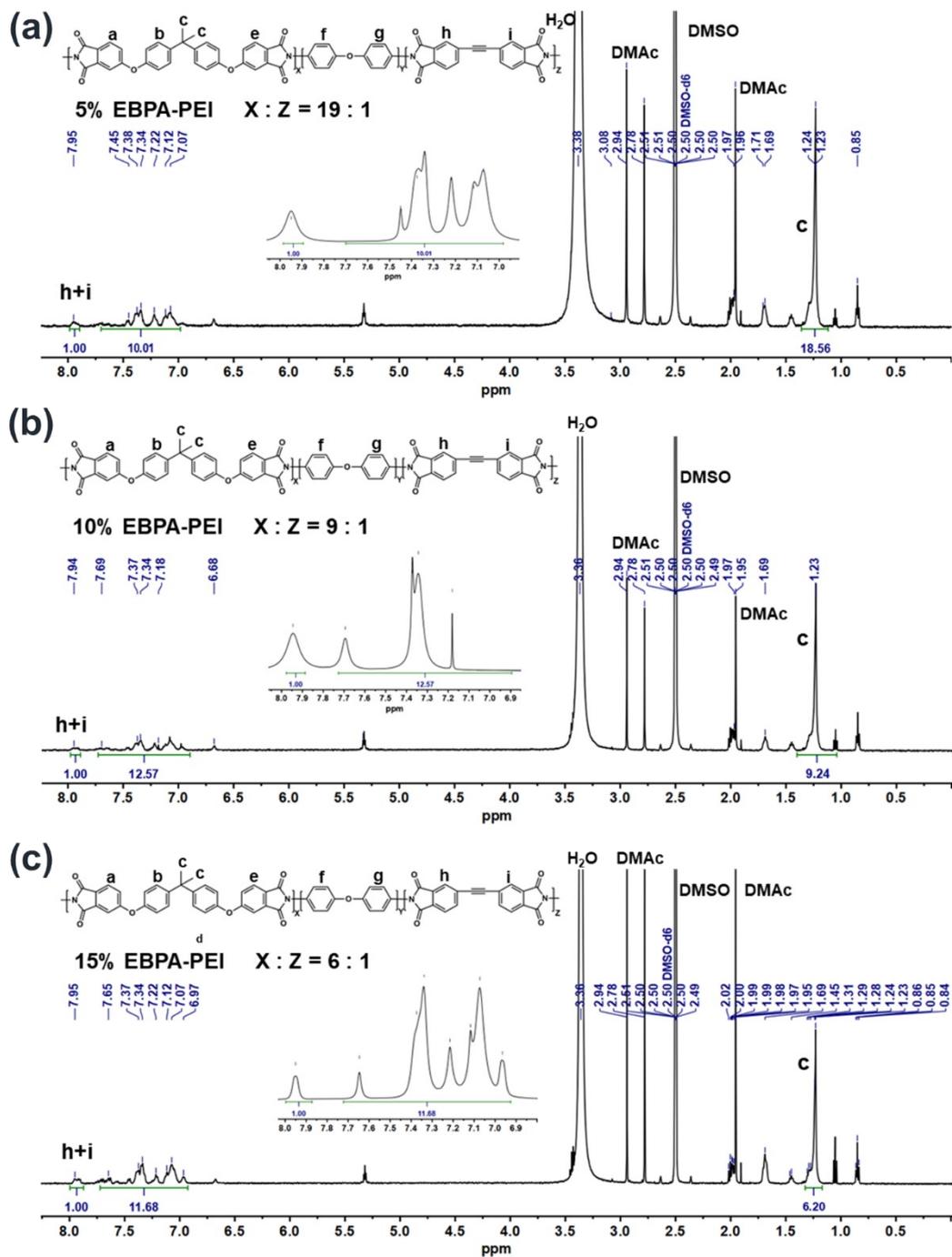
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**Figure S1.** GPC curves of EBPA-PAA samples.

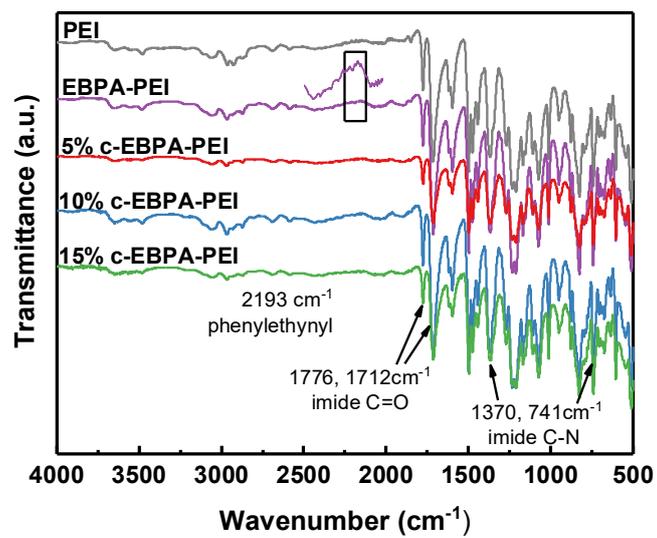
**Table S1.** The molar ratio of monomers and the molecular weight of oligomers with PS as standard.

Oligomers	ODA	BPAD A	EBP A	$\bar{M}_n$ (kDa)	$\bar{M}_w$ (kDa)	PDI
5% EBPA-PAA	50	49.4	2.6	8.70	18.78	2.16
10% EBPA- PAA	50	46.8	5.2	6.93	13.60	1.96
15% EBPA- PAA	50	44.2	7.8	8.24	18.12	2.20

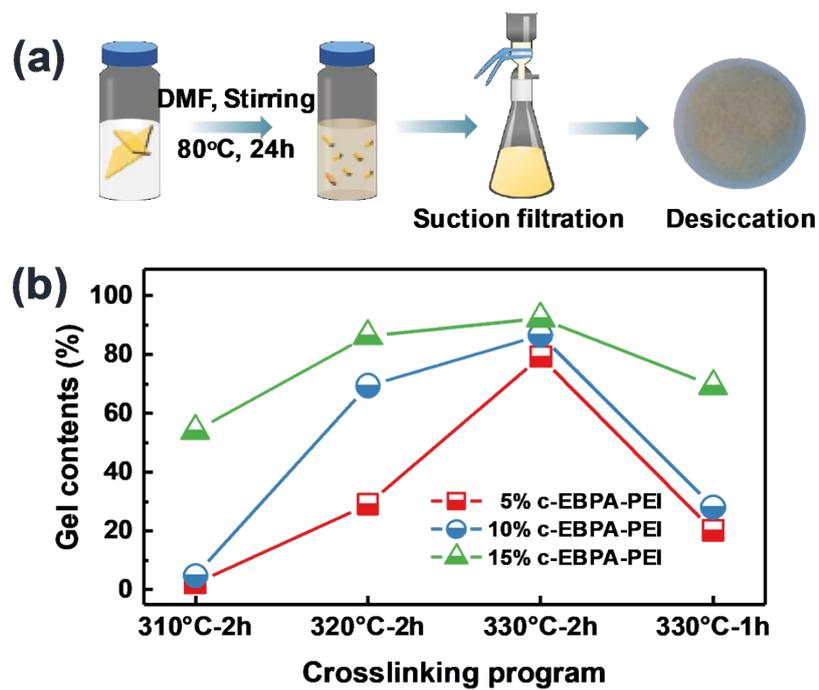


**Figure S2.** <sup>1</sup>H NMR spectrum of (a)5% (b)10% and (c)15% EBPA-PEI.

The peaks of 2.5 and 3.30 ppm are from DMSO-d<sub>6</sub> solvent and water, respectively. The peaks of 2.94, 2.78 and 1.95 ppm are from DMAc solvent.



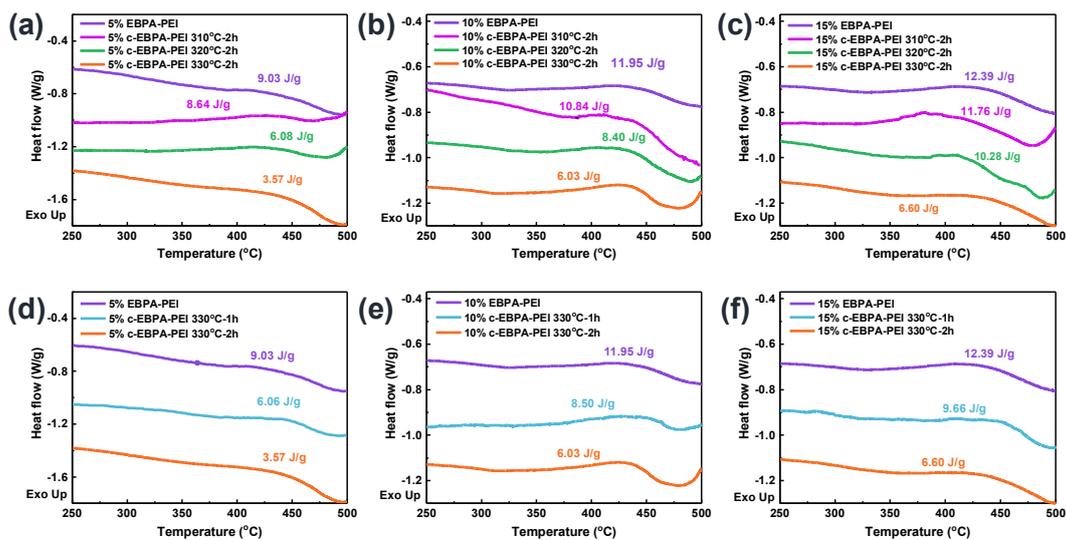
**Figure S3.** FTIR spectra of c-EBPA-PEI films.



**Figure S4.** The gel contents of c-EBPA-PEI films: (a) schematic diagram of gel contents test, and (b) variations of gel contents of films with different heat treatment duration and temperature.

**Table S2.** The gel contents of c-EBPA-PEI films.

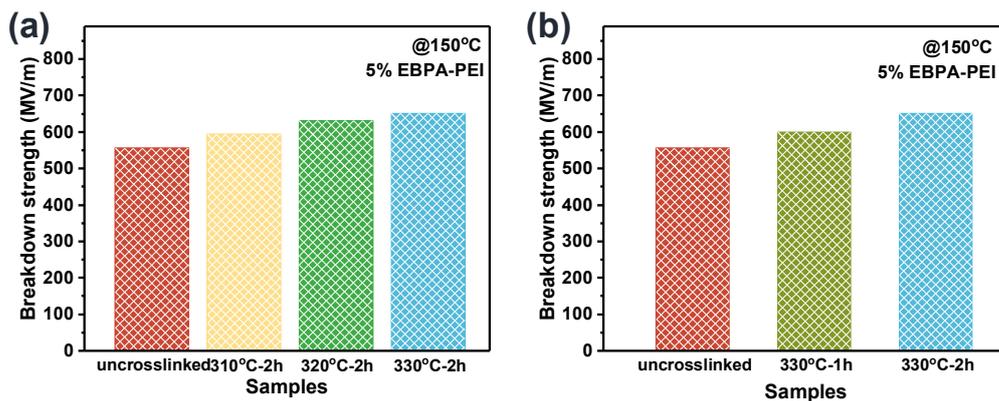
Crosslinking film	Crosslinking program	Gel contents (%)
5% c-EBPA-PEI	310°C-2h	2.21
	320°C-2h	29.12
	330°C-2h	79.24
	330°C-1h	20.09
10% c-EBPA-PEI	310°C-2h	4.94
	320°C-2h	69.43
	330°C-2h	86.61
	330°C-1h	28.14
15% c-EBPA-PEI	310°C-2h	54.03
	320°C-2h	86.36
	330°C-2h	81.48
	330°C-1h	3.31



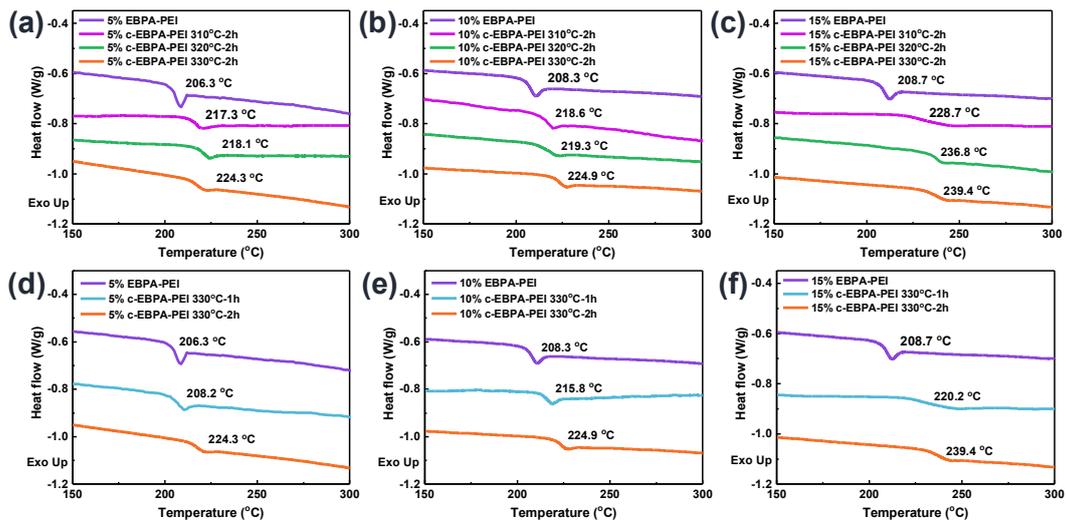
**Figure S5.** DSC curves of c-EBPA-PEI films: (a, b) 5% c-EBPA-PEI, (c, d) 10% c-EBPA-PEI, and (e, f) 15% c-EBPA-PEI.

**Table S3.** The crosslinking density of c-EBPA-PEI film.

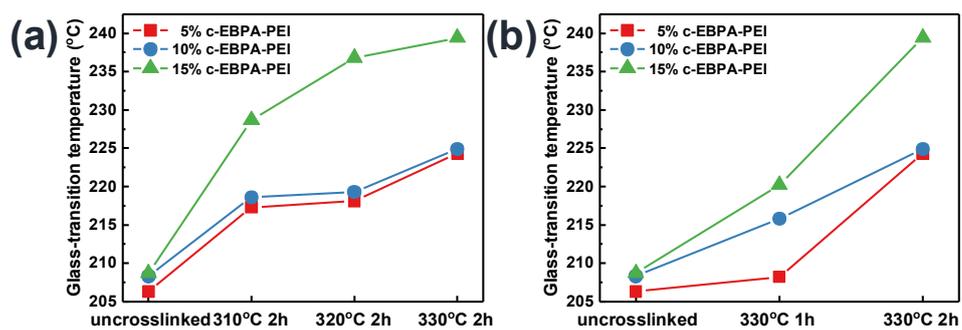
Crosslinking film	Crosslinking program	Crosslinking density (%)
5% c-EBPA-PEI	310°C-2h	0.22
	320°C-2h	1.63
	330°C-2h	3.02
	330°C-1h	1.64
10% c-EBPA-PEI	310°C-2h	0.83
	320°C-2h	2.97
	330°C-2h	4.95
	330°C-1h	2.89
15% c-EBPA-PEI	310°C-2h	0.76
	320°C-2h	3.78
	330°C-2h	7.01
	330°C-1h	3.31



**Figure S6.** Weibull breakdown strength at 150 °C for c-EBPA-PEI films with different heat treatment temperatures (a) and heat treatment times (b).



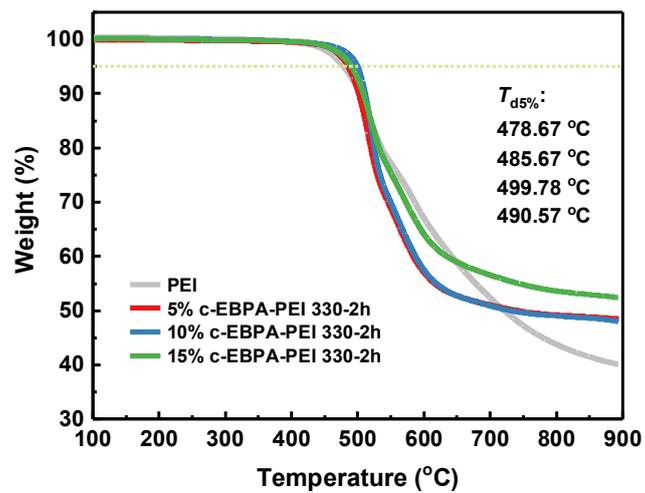
**Figure S7.** Glass transition temperature of c-EBPA-PEI films: (a, b) 5% c-EBPA-PEI, (c, d) 10% c-EBPA-PEI, and (e, f) 15% c-EBPA-PEI with different treatment parameters.



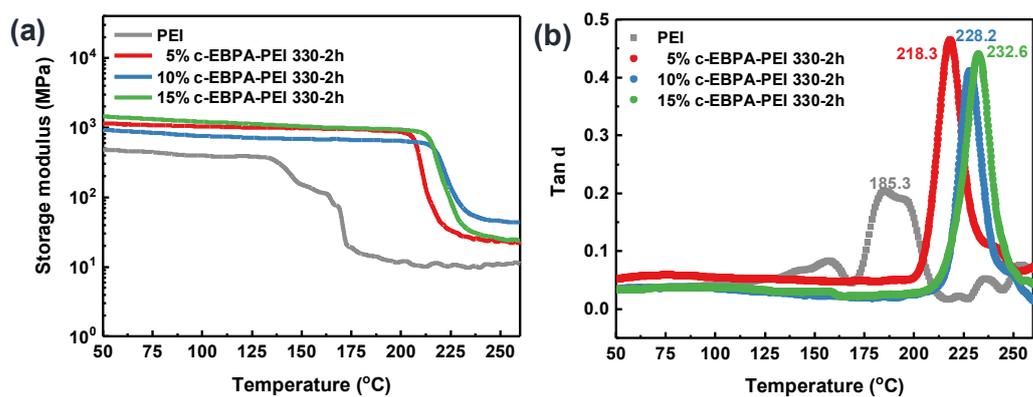
**Figure S8.** Comparison of  $T_g$  for c-EBPA-PEI films: (a) c-EBPA-PEI films with treatment temperatures and (b) c-EBPA-PEI films with different treatment times.

**Table S4.** Glass transition temperature of c-EBPA-PEI films with different contents of crosslinkers.

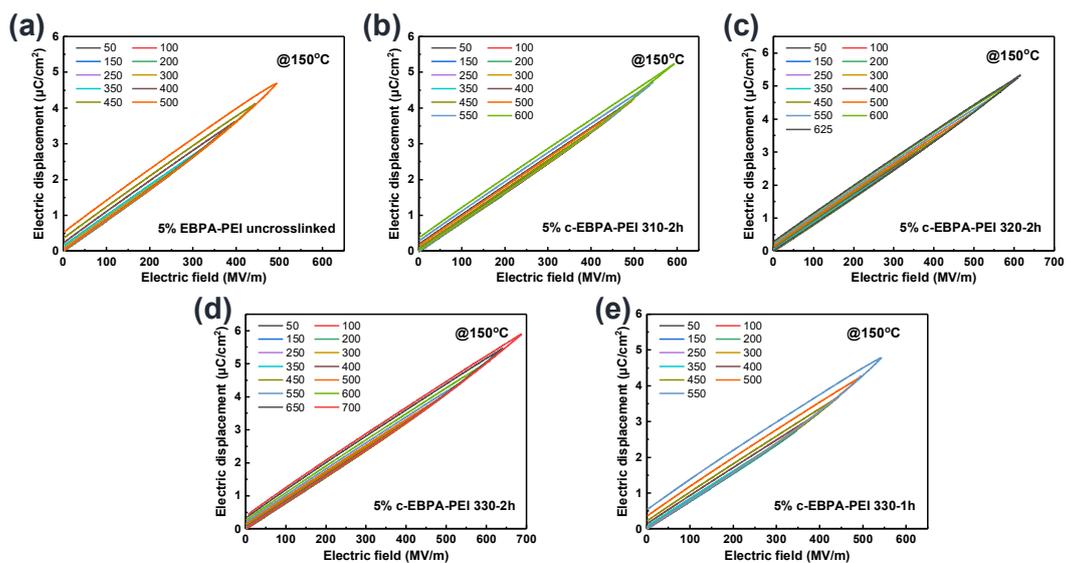
Sample	$T_g$ (°C)				
	Pristine film	310°C-2h	320°C-2h	330°C-2h	330°C-1h
5% c-EBPA-PEI	206.3	217.3	218.1	224.3	208.2
10% c-EBPA-PEI	208.3	218.6	219.3	224.9	215.8
15% c-EBPA-PEI	208.7	228.7	236.8	239.4	220.2



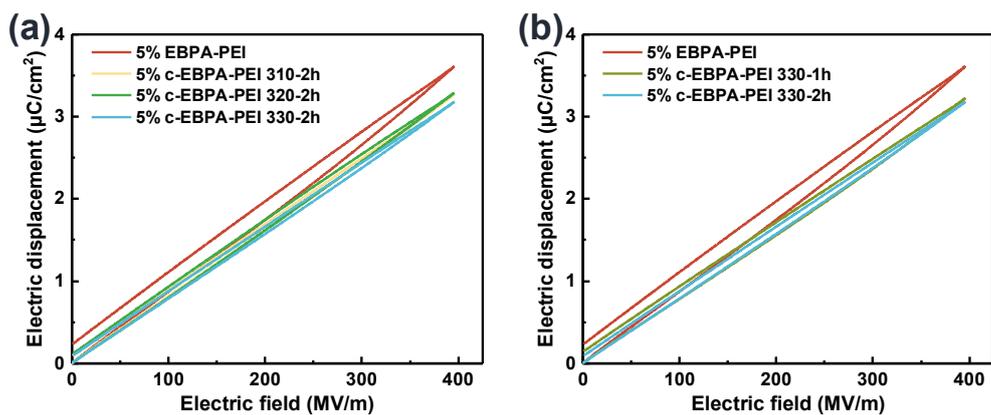
**Figure S9.** TGA curves of c-EBPA-PEI 330-2h films with different contents of crosslinkers.



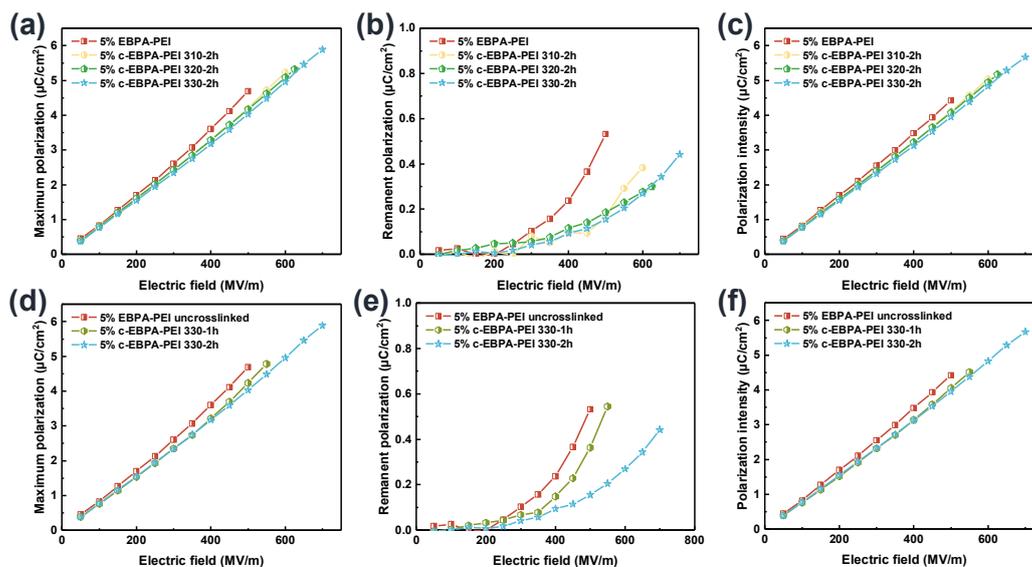
**Figure S10.** DMA curves for c-EBPA-PEI 330-2h films with different contents of crosslinkers: (a) storage modulus and (b)  $\tan \delta$ .



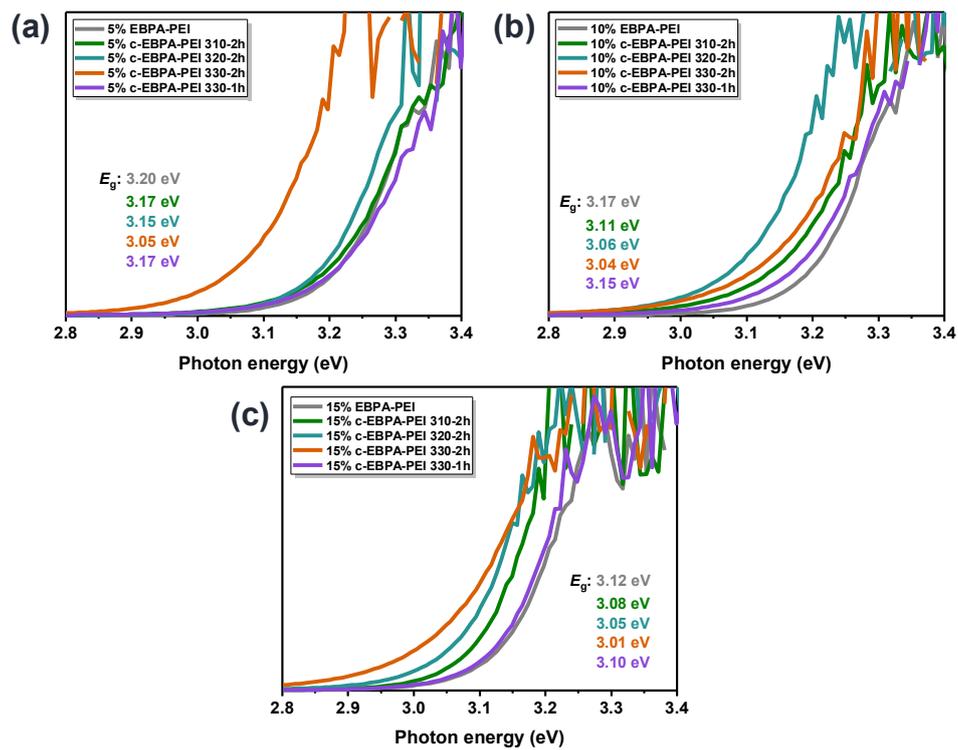
**Figure S11.** Unipolar  $P$ - $E$  loops versus testing fields at 150 °C of c-PEI films: (a) pristine PEI, (b) 310°C-2h, (c) 320°C-2h, (d) 330°C-2h, and (e) 330°C-1h.



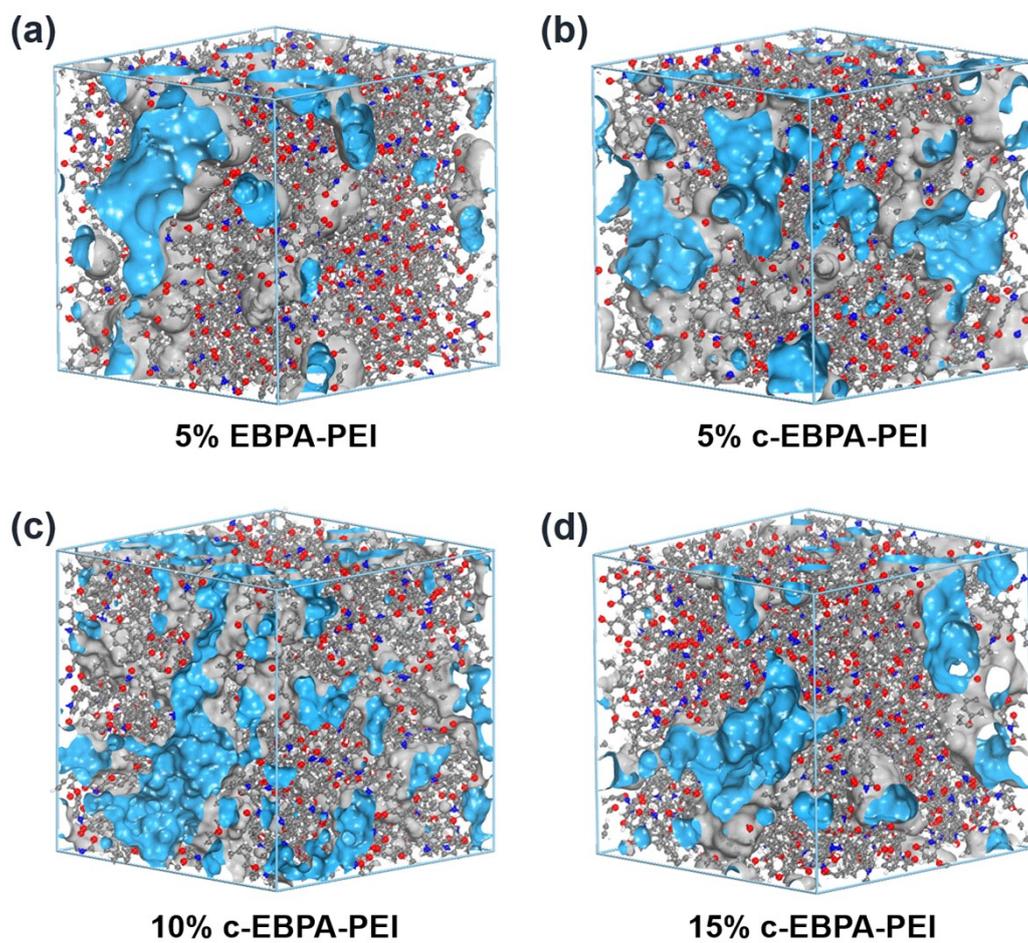
**Figure S12.** Unipolar  $P-E$  loops versus testing fields at  $150\text{ }^\circ\text{C}$  and  $400\text{ MV m}^{-1}$  of c-PEI films with different heat treatment temperatures (a) and heat treatment times (b).



**Figure S13.** Electrical displacements versus testing fields at 150 °C for c-PEI films: (a, b) maximum polarization, (c, d) remanent polarization, and (e, f) polarization intensity.



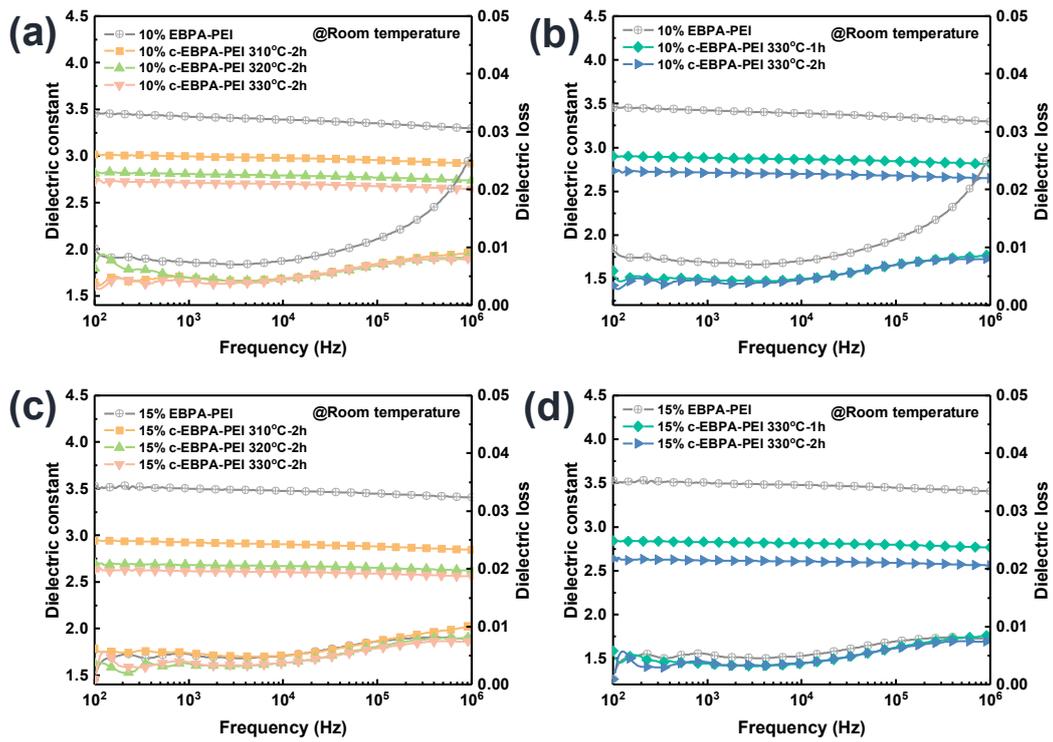
**Figure S14.** Energy band curves derived from UV-vis absorption curves of c-EBPA-PEI films: (a) 5% c-EBPA-PEI, (b) 10% c-EBPA-PEI, and (c) 15% c-EBPA-PEI.



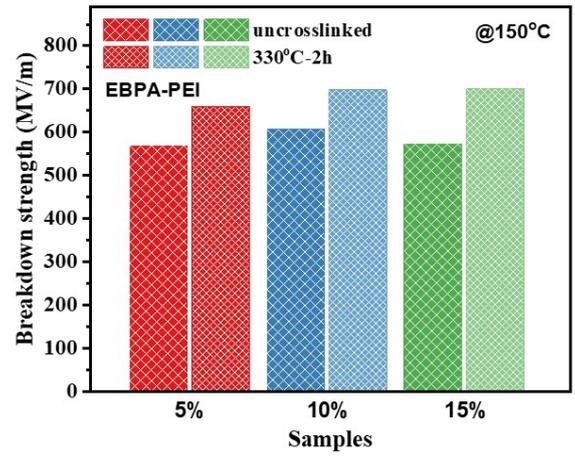
**Figure S15.** Molecular dynamics simulations illustrating polymer structure before and after crosslinking.

**Table S5.** Average interchain spacing of c-EBPA-PEI film.

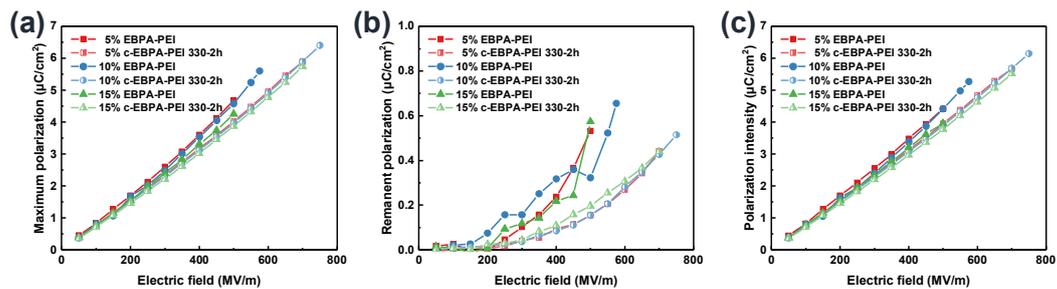
Crosslinking film	Amorphous scattering peak ( $2\theta$ )	Average interchain spacing ( $\text{\AA}$ )
5% EBPA-PEI	17.30	5.126
5% c-EBPA-PAA 310-2h	17.77	4.992
5% c-EBPA-PAA 320-2h	18.07	4.910
5% c-EBPA-PAA 330-2h	19.67	4.514
5% c-EBPA-PAA 330-1h	18.59	4.773
10% c-EBPA-PAA 330-2h	19.92	4.458
15% c-EBPA-PAA 330-2h	20.14	4.409



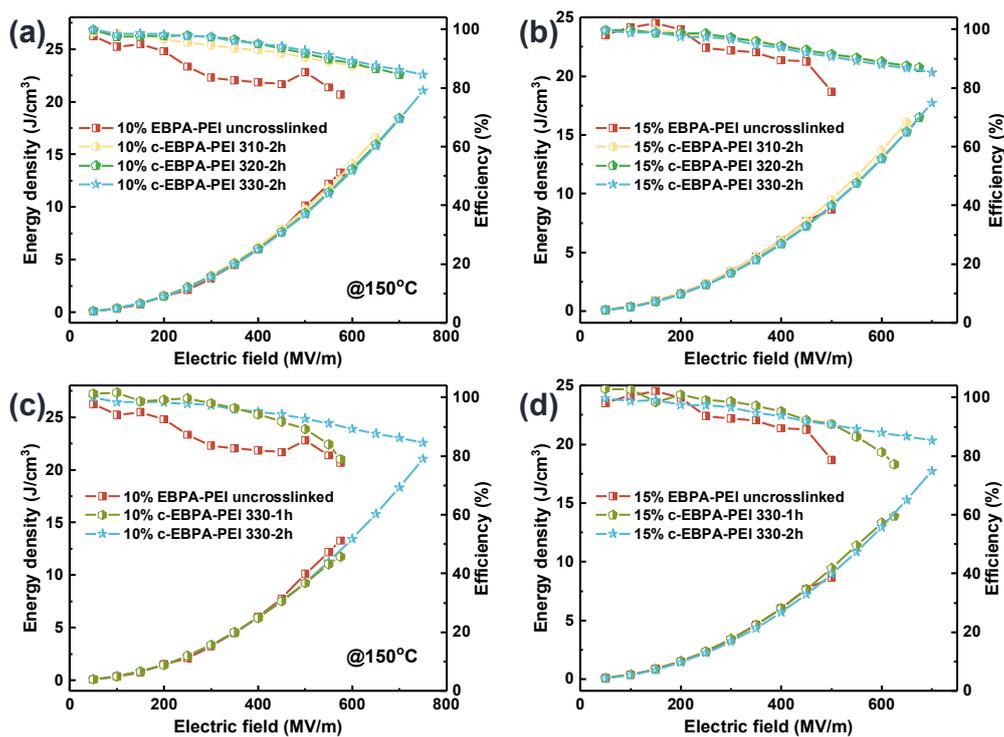
**Figure S16.** Dielectric constant and dielectric loss of c-EBPA-PEI films: (a, b) 10% c-EBPA-PEI and (c, d) 15% c-EBPA-PEI.



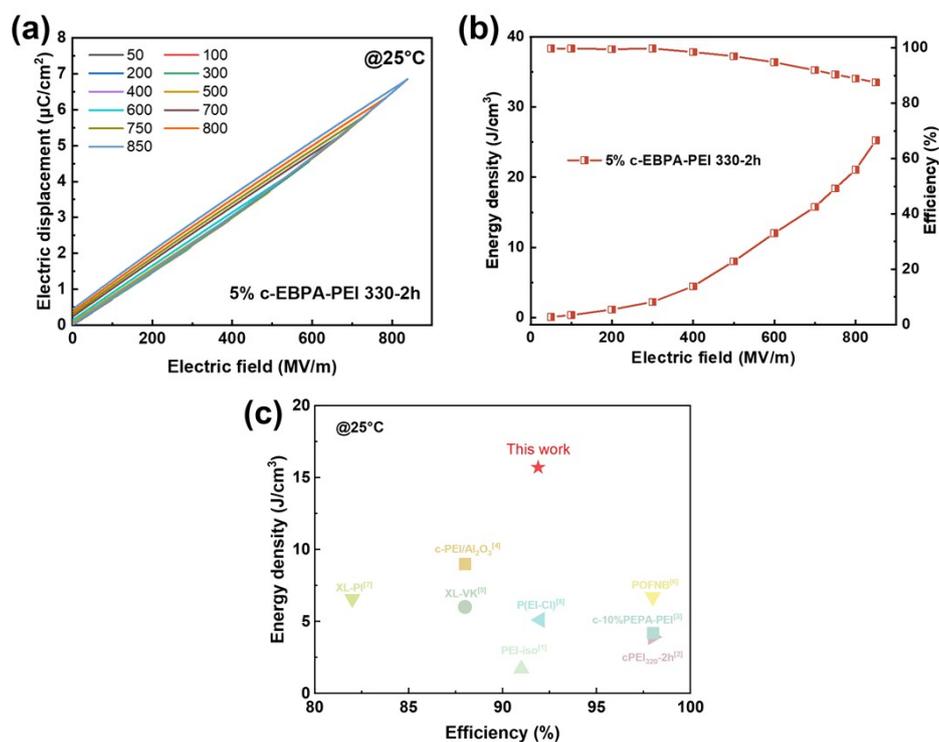
**Figure S17.** Weibull breakdown strength at 150 °C for c-PEI films with different EBPA contents.



**Figure S18.** (a) Maximum polarization, (b) remnant polarization, and (c) polarization intensity of c-PEI films with different EBPA contents. The testing temperature is 150 °C.



**Figure S19.** Energy density and efficiency of c-EBPA-PEI films: (a, b) 10% c-EBPA-PEI and (c, d) 15% c-EBPA-PEI films.



**Figure S20.** (a) Unipolar  $P-E$  loops and (b) energy density and efficiency of 5% c-EBPA-PEI 330-2h film at 25 °C, and (c) comparison of the energy storage capability of the crosslinking structure at 25 °C developed in this work with those reported in previous studies.

## References

1. L. Ren, H. Li, Z. Xie, D. Ai, Y. Zhou, Y. Liu, S. Zhang, L. Yang, X. Zhao, Z. Peng, R. Liao and Q. Wang, *Adv. Energy Mater.*, 2021, **11**, 2101297.
2. L. Zhu, Z. Zheng, W. Xu, Y. Tang, H. Yao, Y. Zhang and Z. Jiang, *Mater. Today Energy*, 2022, **30**, 101145.
3. Y. Zhang, Z. Liu, L. Zhu, J. Liu, Y. Zhang and Z. Jiang, *CCS Chem.*, 2020, **2**, 1169–1177.
4. S. Wang, F. Zhang, Y. Zhang, L. Wang, S. Xiao and J. Wang, *J. Power Sources*, 2025, **632**, 236397.

5. H. Li, M. R. Gadinski, Y. Huang, L. Ren, Y. Zhou, D. Ai, Z. Han, B. Yao and Q. Wang, *Energy Environ. Sci.*, 2020, **13**, 1279–1286.
6. C. Wu, A. A. Deshmukh, Z. Li, L. Chen, A. Alamri, Y. Wang, R. Ramprasad, G. A. Sotzing and Y. Cao, *Adv. Mater.*, 2020, **32**, 2000499.
7. Z. Wu, Y. Peng, Y. Song, H. Liang, L. Gong, Z. Liu, Q. Zhang and Y. Chen, *Mater. Today Energy*, 2023, **32**, 101243.
8. M. Xiao, B. Wan, X. Wang, M.-S. Zheng, Y. Li, Y. Zhang and J.-W. Zha, *Polymer*, 2023, **286**, 126397.