Supporting information

Optimizing high-temperature capacitive energy storage performance by constructing crosslinked structure in self-crosslinkable polyetherimides

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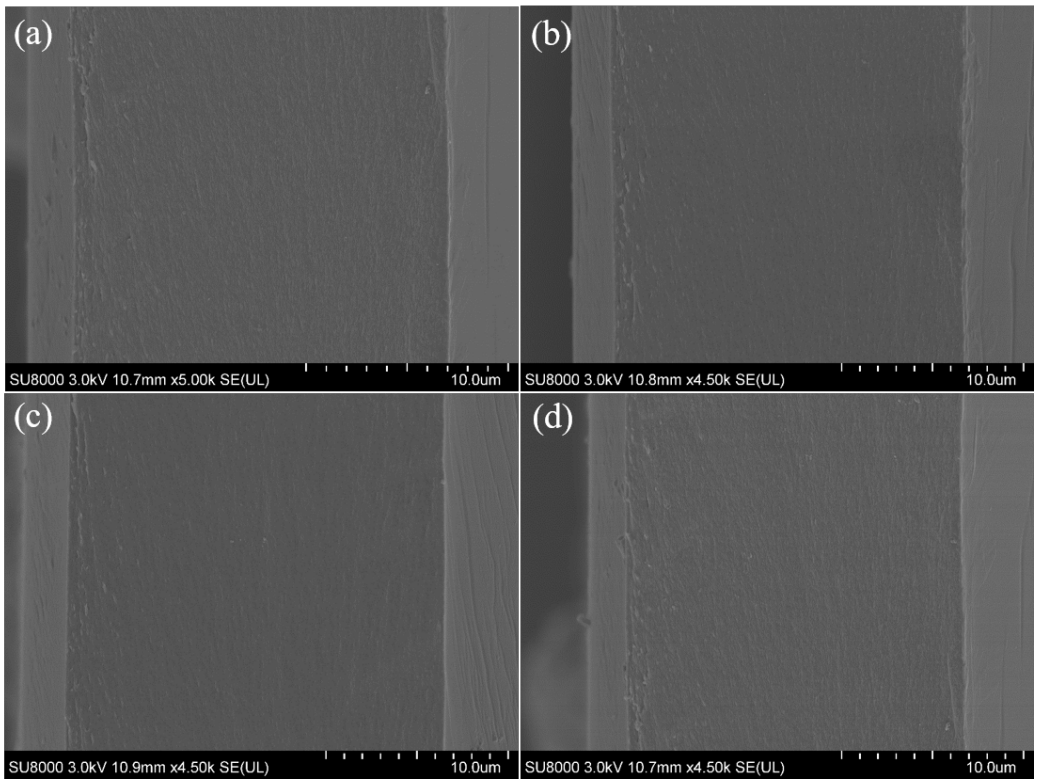

Fig. S1. The cross-sectional SEM images of films with different heating times of (a-d) $cPEI_{320}$-1h ~ $cPEI_{320}$-4h.

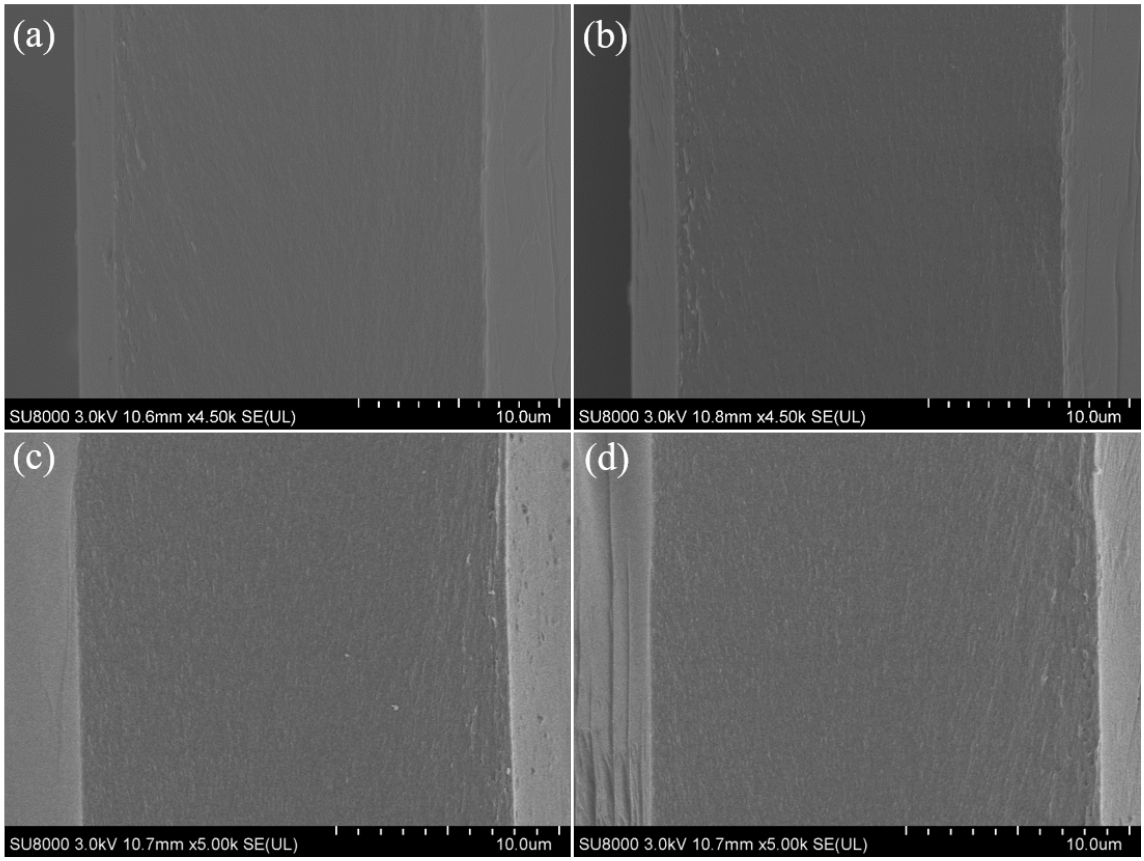

Fig. S2. The cross-sectional SEM images of films with different heating temperatures of (a-d) $cPEI_{310}$-2h ~ $cPEI_{340}$-2h.

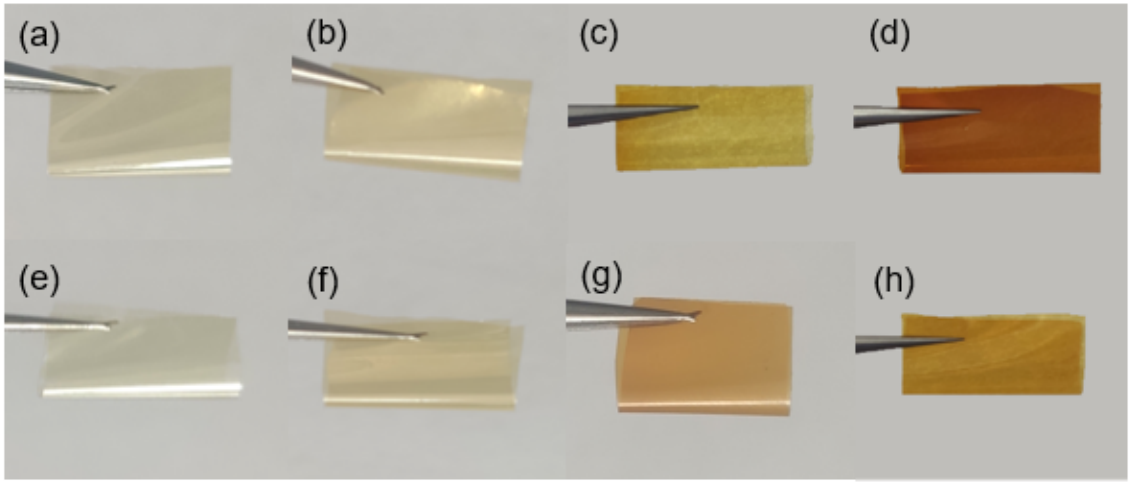

Fig. S3. The digital photos of films with (a-d) different heating times of $cPEI_{320}$-1h ~ $cPEI_{320}$-4h; (e-h) different heating temperatures of $cPEI_{310}$-2h ~ $cPEI_{340}$-2h.

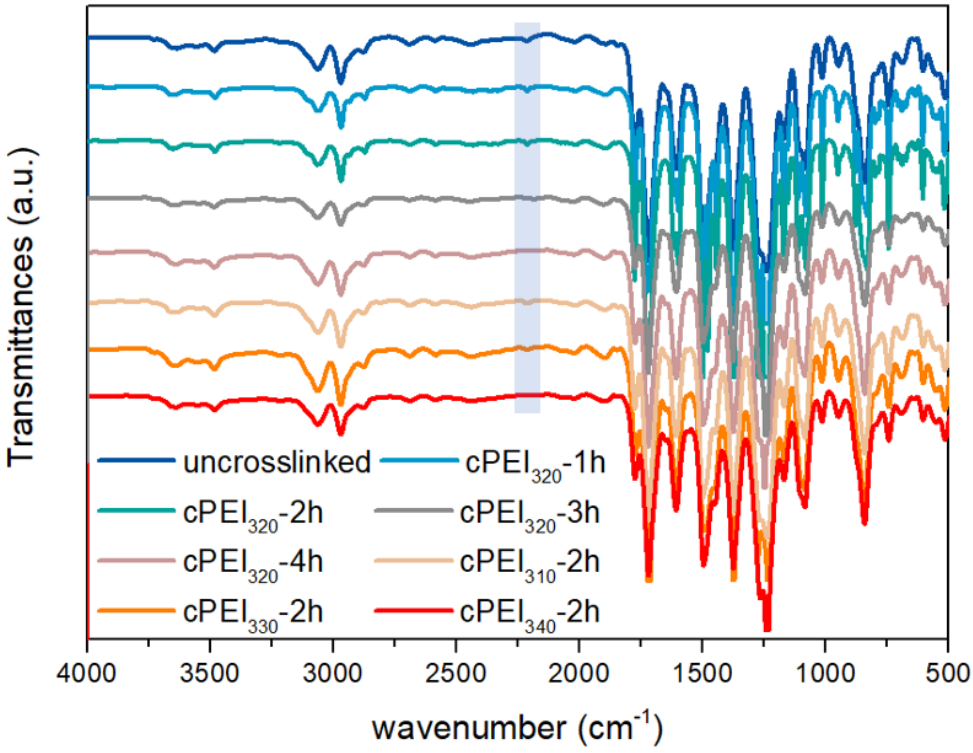

Fig. S4. FT-IR spectrum of uncrosslinked and crosslinked films.

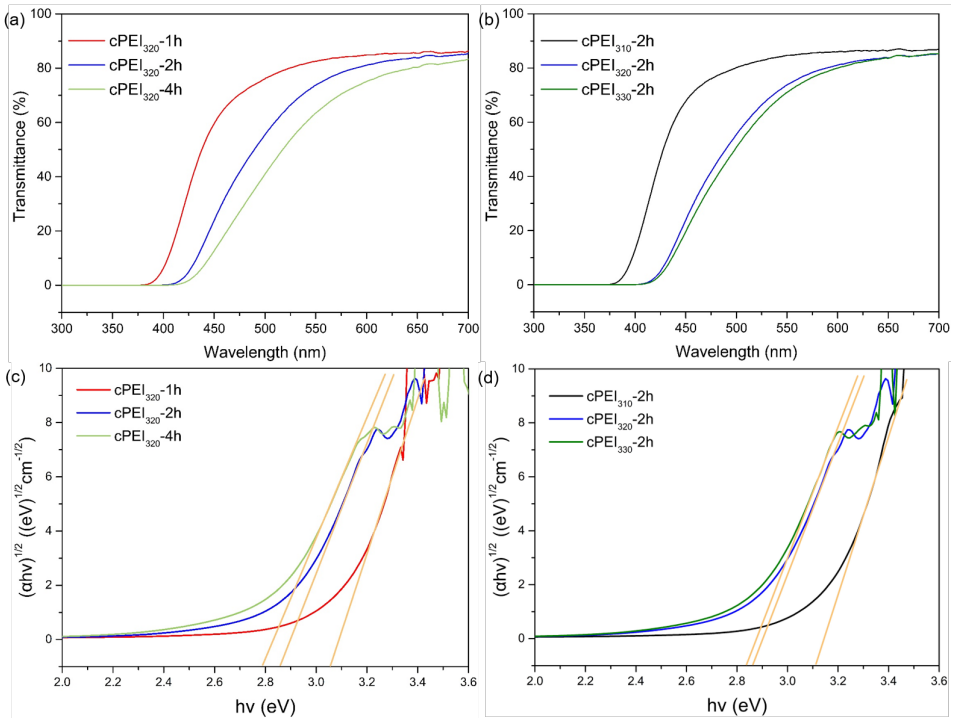

Fig. S5. The average transmittance at different wavelengths of thin films with (a) different heating times and (b) different heating temperatures; Energy band curves derived from UV-vis absorption curves of thin films with (c) different heating times and (d) different heating temperatures.

The energy gap curves were converted from the UV-vis spectra according to the following equations:$(\alpha hv)1/m=A(hv-E_g)$, where α is the absorption coefficient, h is Planck constant, v is the frequency, E_g is the energy gap, A is a constant, and m is assigned a value of 2. The intersection point of the tangent and the X axis is the value of E_g [1]. As the t_h or T_h increases, the experimental results show that the band gap of the polymer film shows a decreasing trend. Specifically, the bandgap of the film changed from 3.05 ev of $cPEI_{320}$-1h to 2.78 ev of $cPEI_{320}$-4h, from 3.11 ev of $cPEI_{310}$-2h to 2.83 ev of $cPEI_{330}$-2h.

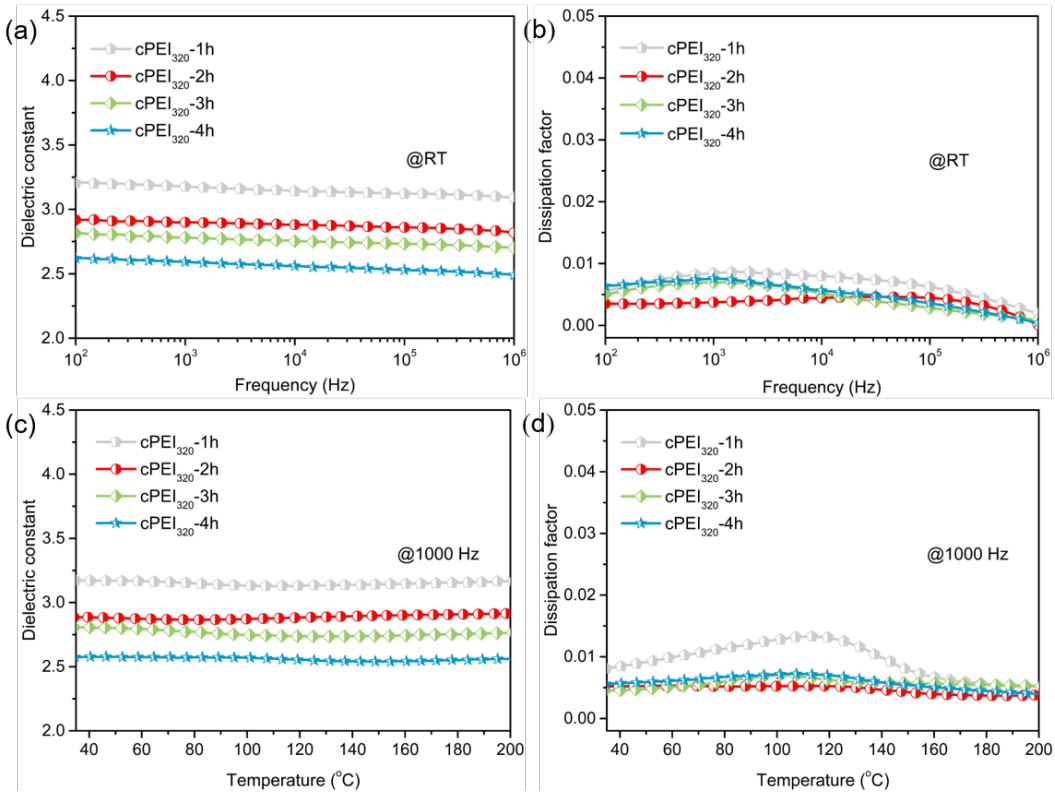

Fig. S6. Dielectric constant and dissipation factor of films with different heating times at room temperature as a function of frequency (a) (b) and as a function of temperature (c) (d) at 1000 Hz.

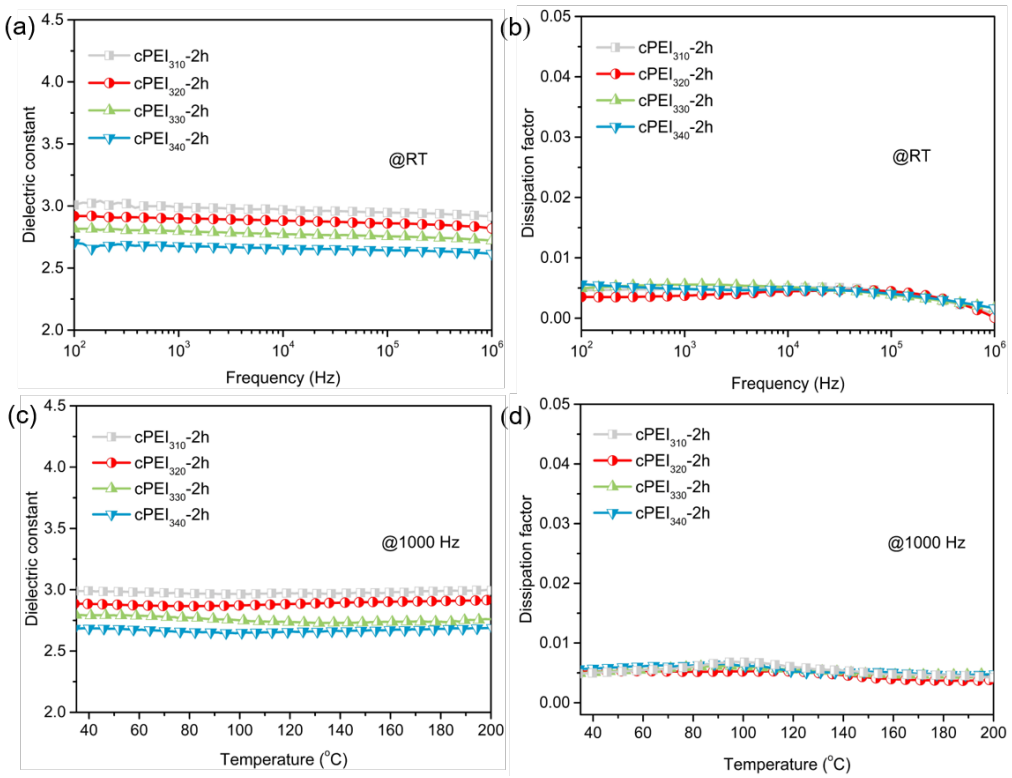

Fig. S7. Dielectric constant and dissipation factor of films with different heating temperatures at room temperature (a) (b) as a function of frequency and (c) (d) as a function of temperature at 1000 Hz.

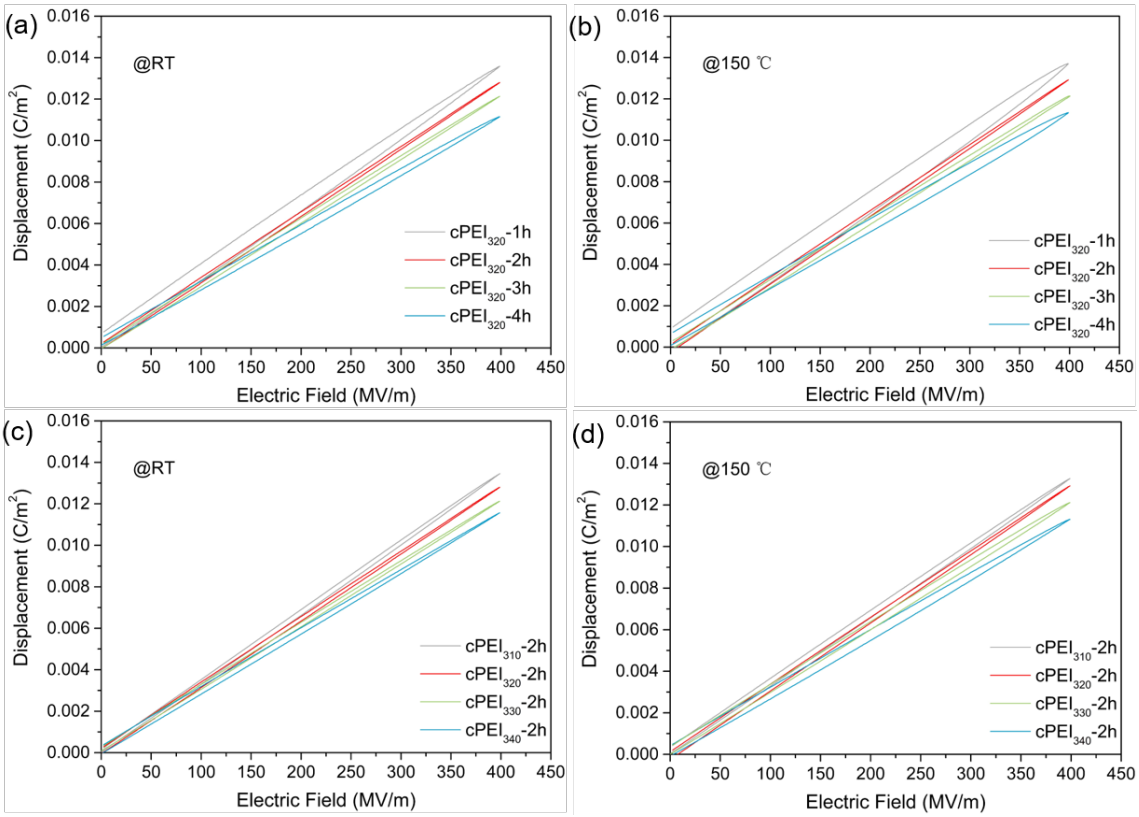

Fig. S8. D-E loops of films with different heating times at 400 MV/m and (a) at room temperature, (b) at 150 ℃. D-E loops of films with different heating temperatures at 400 MV/m and (c) at room temperature, (d) at 150 ℃.

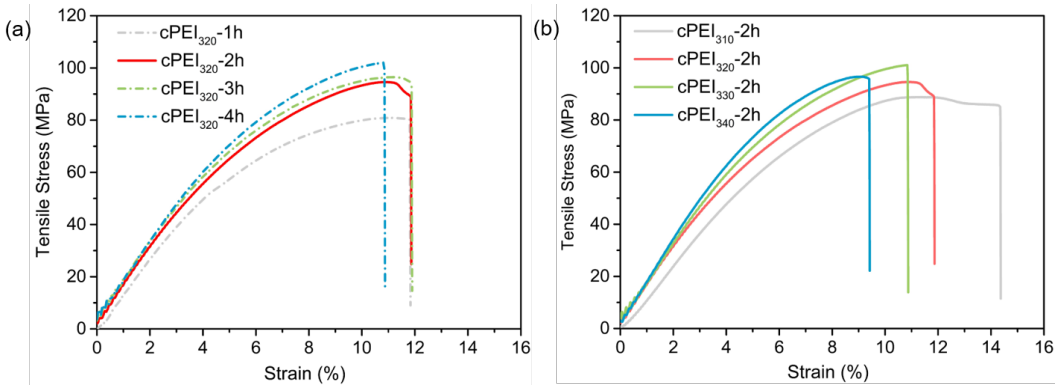

Fig. S9. Tensile stress-strain curves of films with (a) different heating times and (b) different heating temperatures.

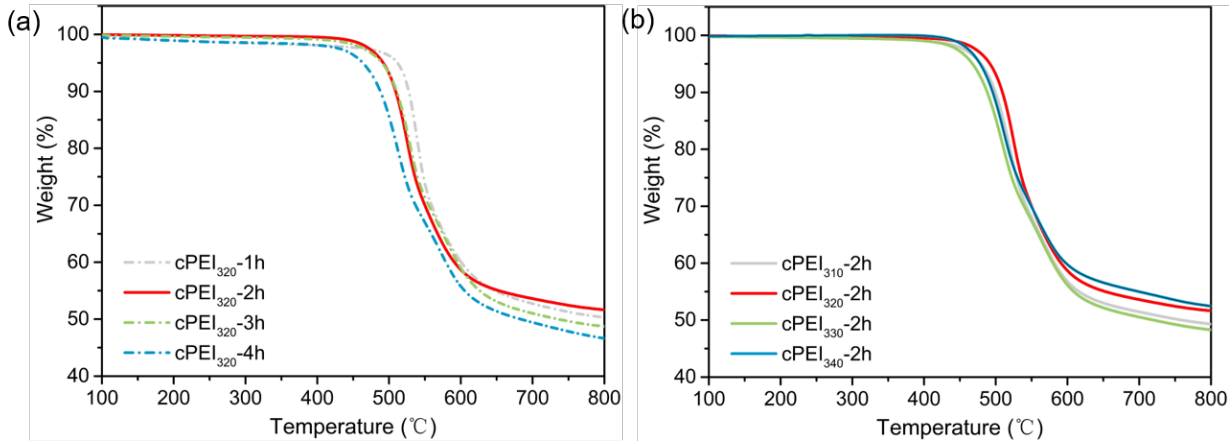

Fig. S10. TGA curves of films with (a) different heating times and (b) different heating temperatures.

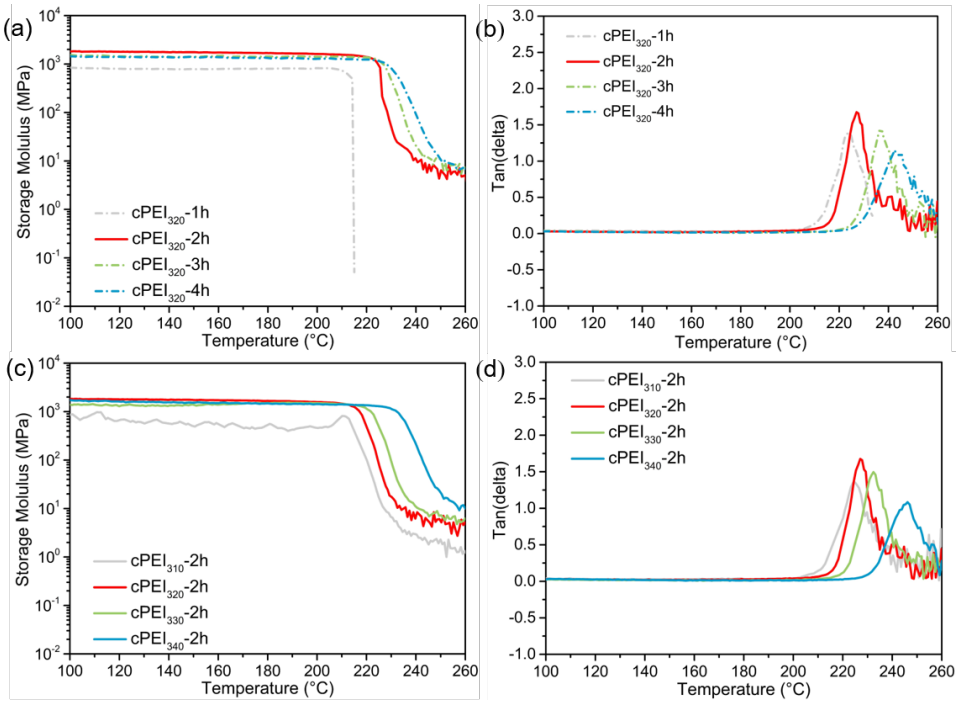

Fig. S11. (a) Storage modulus and (b) tan δ of films with different heating times. (c) Storage modulus and (d) tan δ of films with different heating temperatures.

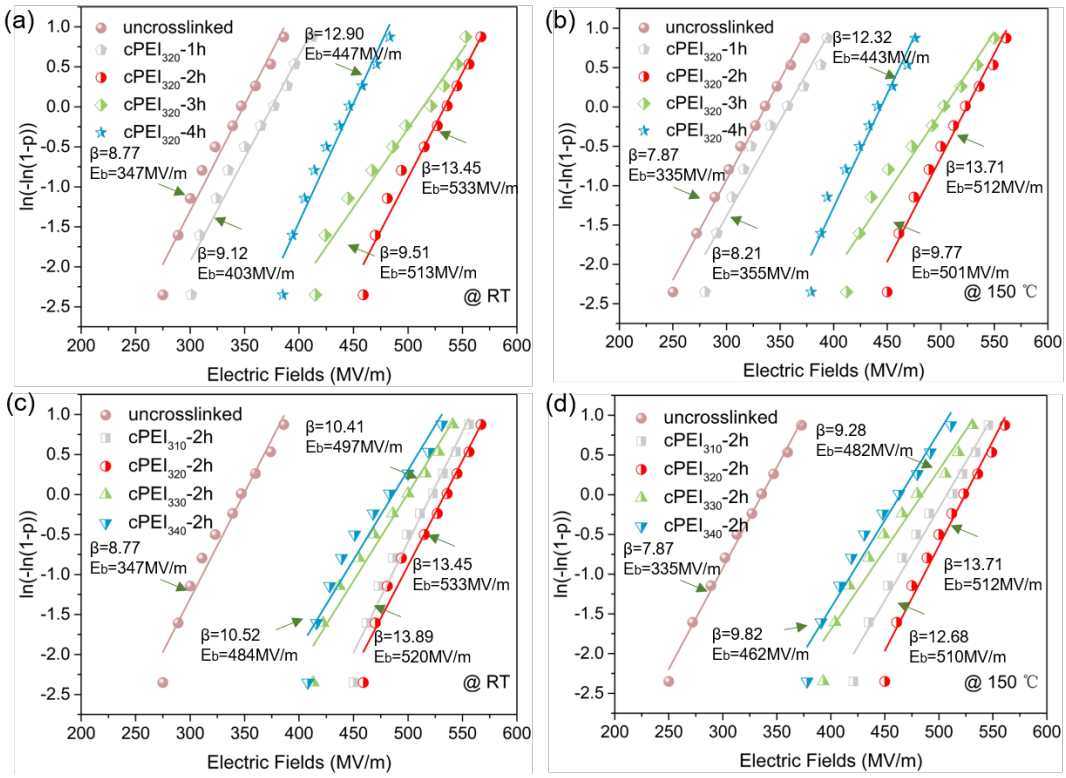

Fig. S12 Weibull breakdown strength of films with different heating times (a) at room temperature and (b) at 150 ℃ as a function of electric fields. Weibull breakdown strength of films with different heating temperatures (c) at room temperature and (d) at 150 ℃ as a function of electric fields.

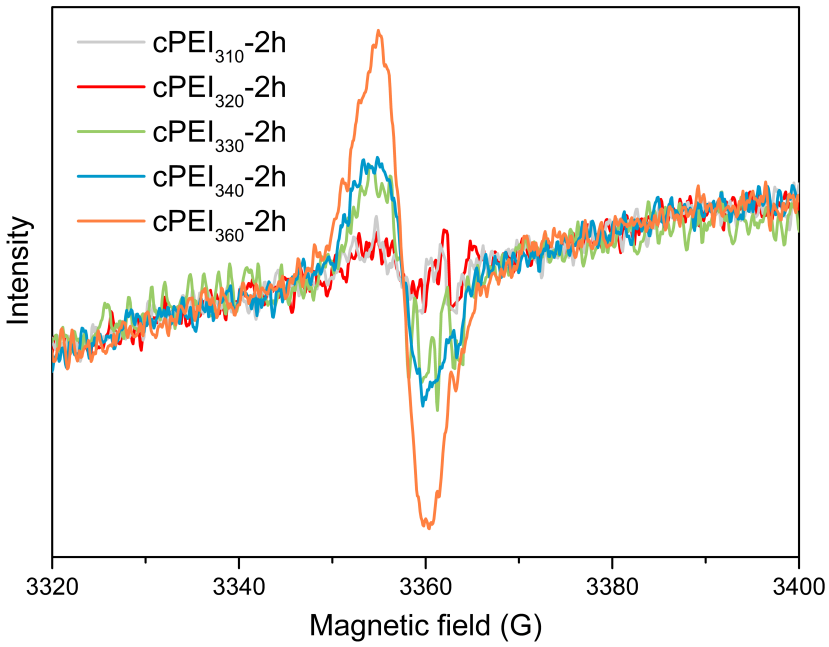

Fig. S13. ESR spectra of films for different heating temperatures.

As shown in **Fig. S13**, all the crosslinked polymer films exhibited a single peak in the ESR spectra (in the observed range), which indicated that a stable free radical was generated after the crosslinking process. The amplitude of the peak of free radical concentration increased with the heating temperature, indicating that free radicals were continuously generated during the heat treatment. It has been reported that the carbon-carbon triple bond in the benzynyl group is broken under thermal induction, and the resulting free radical undergoes complex crosslinking reactions such as chain extension, branching, and cyclization to form conjugated polyene or cyclic structures [2]. In our crosslinking system, we have known from GPC results that the molecular weight increases with the increase of heat treatment temperature (at relatively low temperature) during the crosslinking process involving oxygen under air conditions, and the generated radicals may be RO·. Comparing the spectrum of the films under various heat-treating

conditions on the way, it can be seen that the $cPEI_{310}$-2h film has the lowest peak intensity which mains the lowest free radical content. The free radical concentration in PEI_{320}-2h increases slowly compared with $cPEI_{310}$-2h. The relatively low free radical concentration in PEI_{310}-2h and PEI_{320}-2h may be due to the fact that the generation rate of free radicals is only slightly higher than the consumption rate of the crosslinking reaction under this condition, so that most free radicals are consumed. However, the peak intensities of the $cPEI_{330}$-2h ~ $cPEI_{360}$-2h films increased significantly, and the higher residual free radical concentration may be due to the fact that the rate of free radical generation is much greater than that consumed by the crosslinking reaction. From the GPC results, it is known that with the increase of heating temperature, M_w will decrease at high temperatures, which may be caused by the chain scission to generate additional RO·. Furthermore, with the increase of temperature, we observed a gradual change of the ESR peak type of the crosslinked polymers from asymmetric to symmetric spectrum, which is consistent with the ESR spectral characteristics of RO· with rigid molecular structures [3]. This further confirms the presence of RO· in the crosslinked polymer.

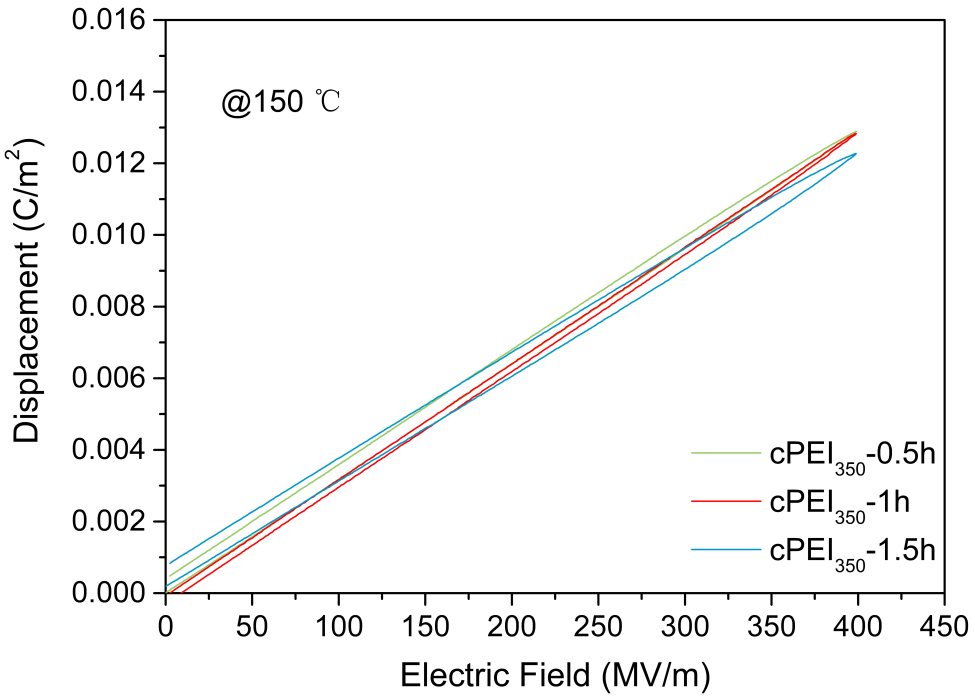

Fig. S14. D-E loops of cPEI$_{350}$-0.5h, cPEI$_{350}$-1h and cPEI$_{350}$-1.5h at 400 MV/m and 150 ℃.

References

[1] C. Yuan, Y. Zhou, Y. Zhu, J. Liang, S. Wang, S. Peng, Y. Li, S. Cheng, M. Yang, J. Hu, B. Zhang, R. Zeng, J. He, Q. Li, Polymer/molecular semiconductor all-organic composites for high-temperature dielectric energy storage. Nat. Commun. **11** (2020) 3919, https://doi.org/10.1038/s41467-020-17760-x.

[2] H. Yao, N. Zhang, K. Shen, N. Song, K. Shi, S. Zhu, Y. Zhang, S. Guan, From a flexible hyperbranched polyimide to a microporous polyimide network: microporous architecture and carbon dioxide adsorption, Polymer 115 (2017) 176-183, https://doi.org/10.1016/j.polymer.2017.03.035.

[3] Y. Niu, G. Wang, S. Zhang, Y. Na, Z. Jiang, F. Dong, Y. Zheng, Thermal crosslinking behavior of poly(aryl ether ketone) copolymers containing naphthalene Moieties, Polym Int. 54 (2005) 180-184, https://doi.org/10.1002/pi.1675.