Supplementary information

Polyacrylonitrile-derived Polyconjugated Ladder Structures for High Performance All-organic Dielectric Materials

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Experimental:

Materials

4,4'-oxydianiline (ODA), p-phenylenediamine (PDA), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China). N, N-dimethylformamide (DMF) was purchased from the Shanghai Chemical Reagents Co. (Shanghai, China). Polyacrylonitrile (PAN, Mw =150,000) powder was purchased from Sigma-Aldrich. All chemicals were used as received.

Preparation of PcLS/PI composites

As shown in Figure S1, the homogeneous polyacrylonitrile/polyamic acid (PAN/PAA) solution was synthesized by *in situ* condensation polymerization. In detail, equimolar diamines (ODA and PDA) and dianhydride (BPDA) were added into PAN/DMF solution, then mechanical stir for 24 h at low temperature (-5 ºC), yielding a homogeneous PAN/PAA solution with solid content about 20 wt%. The PAN/PAA solutions with different weigh ratio of PAA (15, 20, 25, 30 wt%) were used for preparing the PAN/PAA composite films by spin-casting. Then the obtained PAN/PAA films were dried in vacuum oven at 60 ºC for 24 h and followed with the thermal treatment. The thermal treatment includes two steps: 1) heating to 250 ºC (2 ºC /min, in air) and annealing for 1h for the stabilization; 2) then quick heat to a high temperature (300, 350, 400, 450, 480 ºC, 5 ºC /min, in air) and annealing for a short time (5 min).

Characterization

Scanning Electron Microscope (SEM, TESCAN vega3) and Atomic Force Microscopy (AFM, MicroNano D5A, shanghai) were employed to observe the morphologies of the PcLS/PI composites thin films. The chemical structures were studied by using Fourier transform infrared spectroscopy (FT-IR, Bruker tensor 27), Raman (LabRAM HR-800) and X-Ray diffraction (XRD, Siemens D5000). Dielectric properties

were measured using a TH2819-A precision LCR meter (Tong hui Electronic Co., Ltd) at a frequency range from 100 Hz to 100 kHz. The dielectric breakdown strength of the composites was performed on the electric breakdown strength test machine (KP8048, Dongguan, China). Thermal Gravimetric Analysis (TGA) was carried out on a thermogravimetric analyzer (WRT-3P, Shanghai, China) with the heating rate of 10 ºC /min in N_2. Tensile test is carried out using CMT-8102 electromechanical testing machine (Shenzhen, China) with stretching rate of 5 mm/min. The thickness of the samples was measured by screw micrometer.

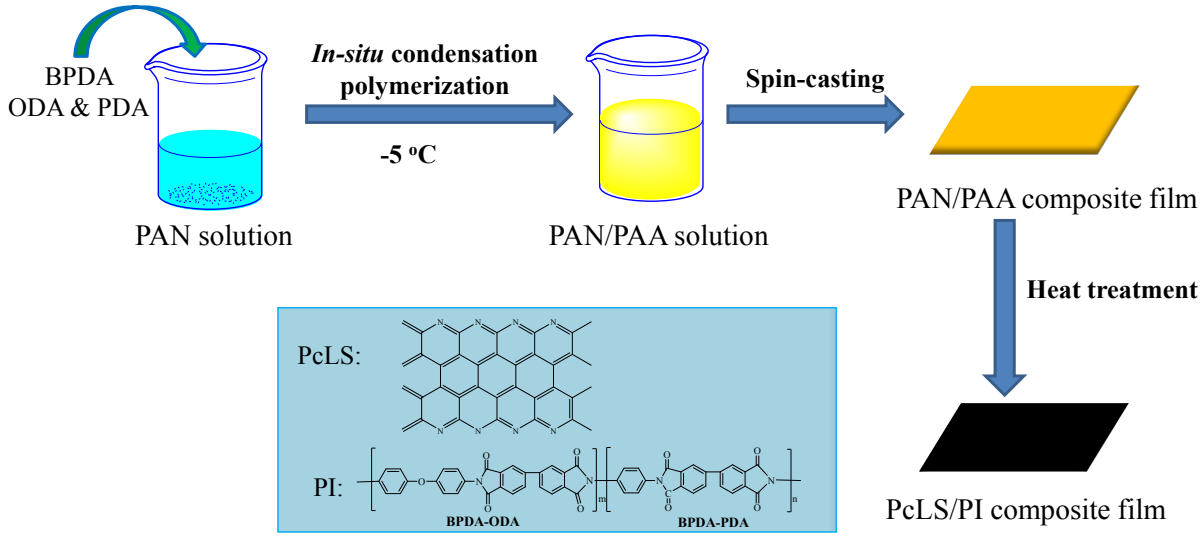

Figure S1 Schematic procedure for the preparation of PcLS/PI composite film.

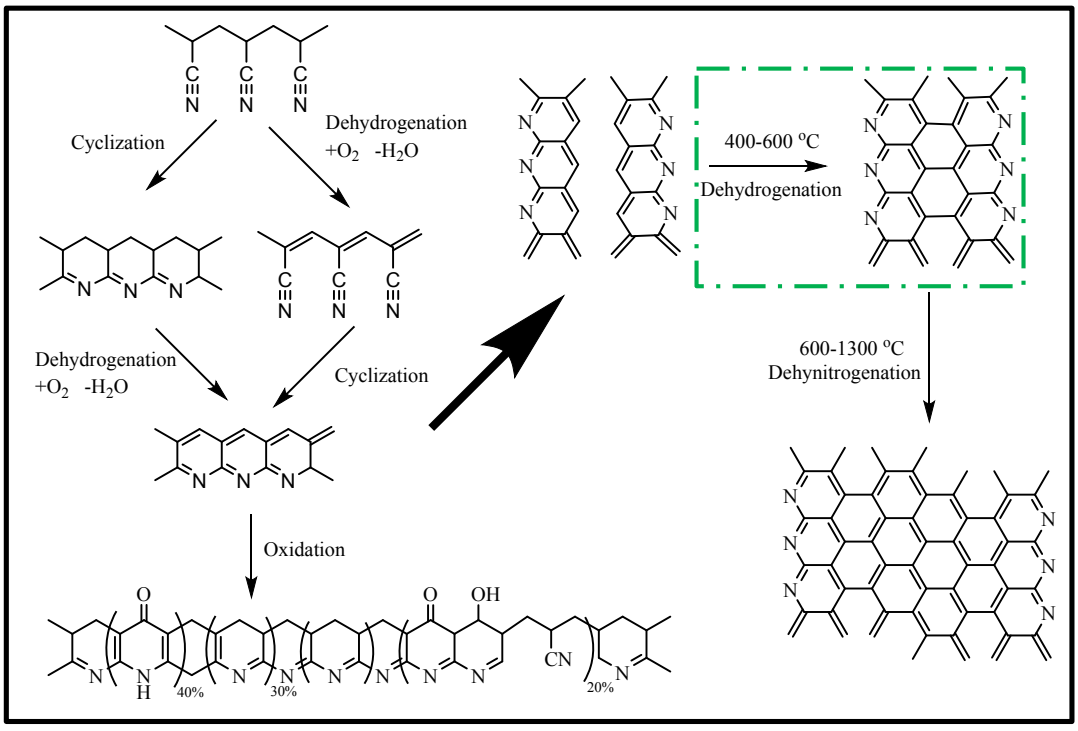

Figure S2 The preparation of carbon fibers from PAN, which generally includes three procedures: stabilization, carbonization, and graphitization. The high temperature treated at 400-600 ºC will yield the polyconjugated ladder structures (PcLS).

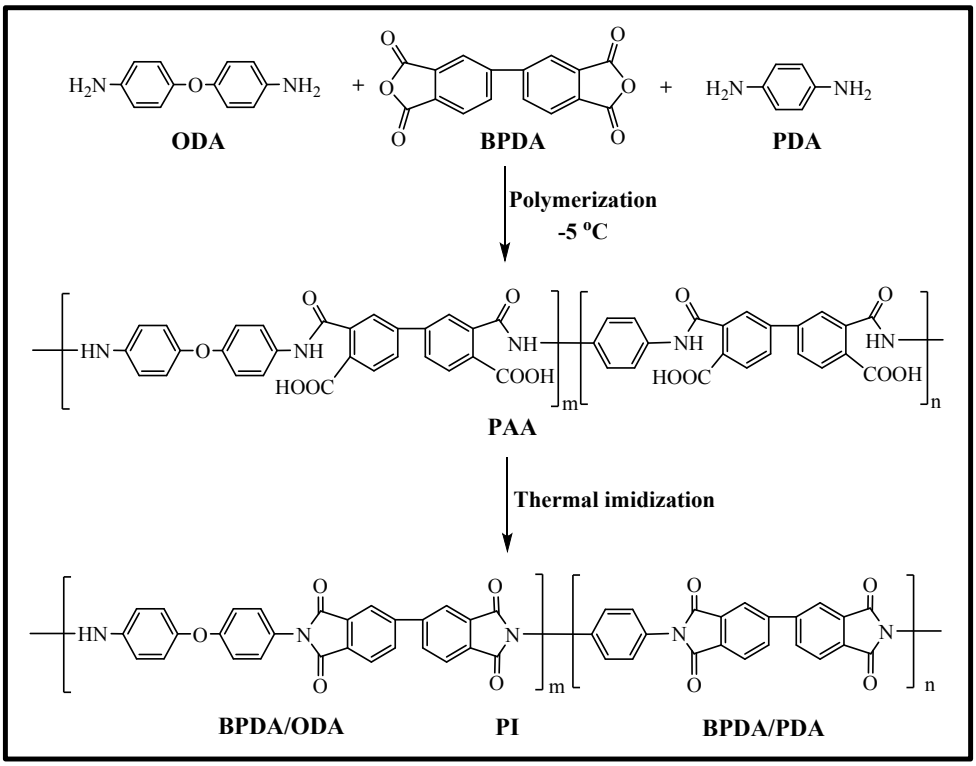

Figure S3 Schematic diagram of the synthsis of polyimide (BPDA/PDA/ODA) by polycondensation between BPDA and diamines, ODA and PDA.

Results:

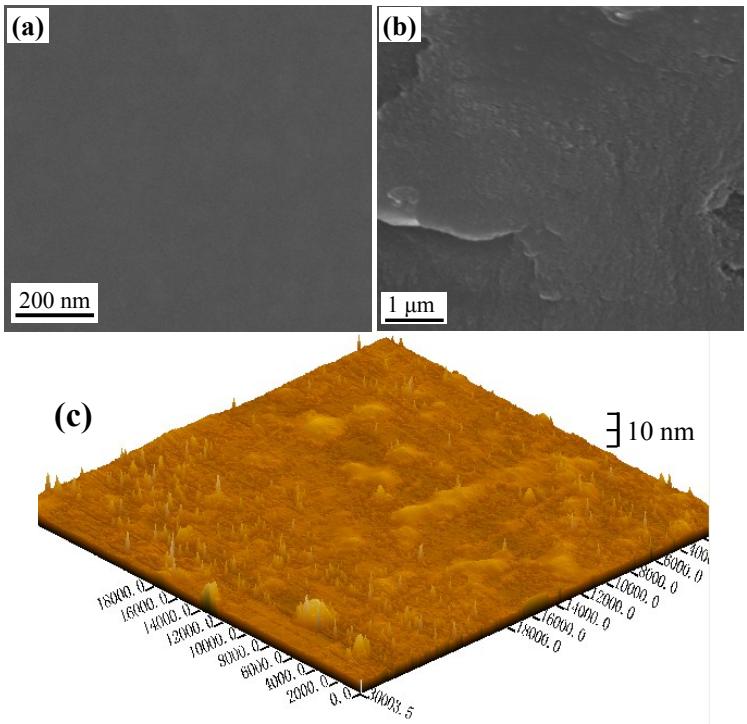

Figure S4 SEM images of the surface **(a)** and cross section **(b)** of the PcLS/PI composite film. **(c)** AFM image of the surface of the PcLS/PI composite film.

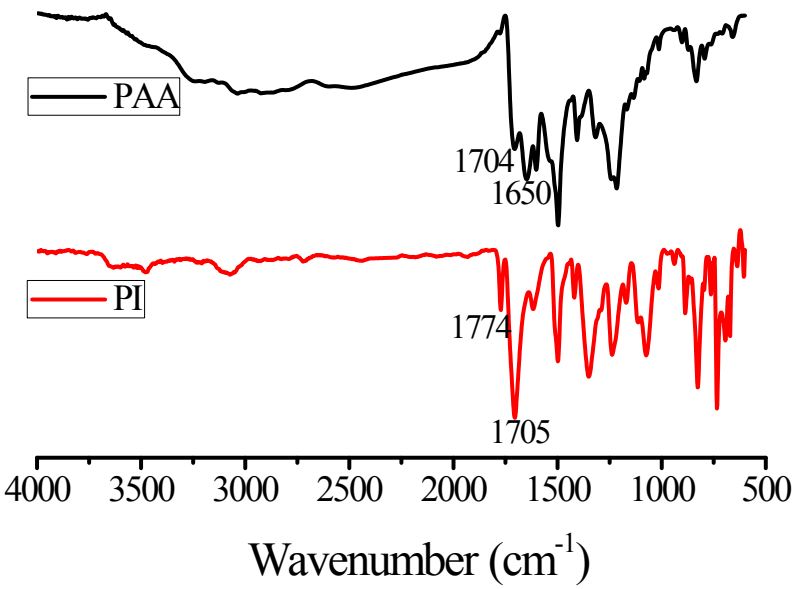

Figure S5 FT-IR spectrum of neat PAA and PI film obtained under 480 ºC treatment.

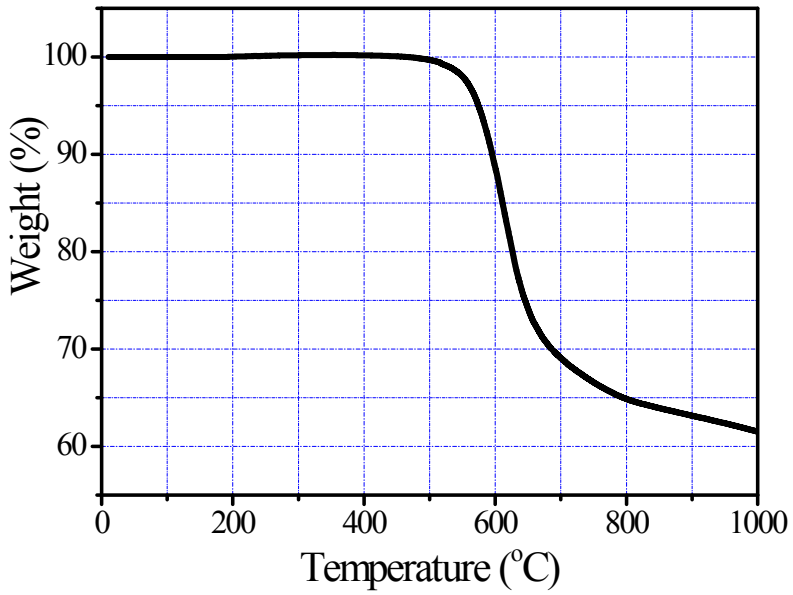

Figure S6 TGA curves of neat PI film obtained under 480 ºC treatment.

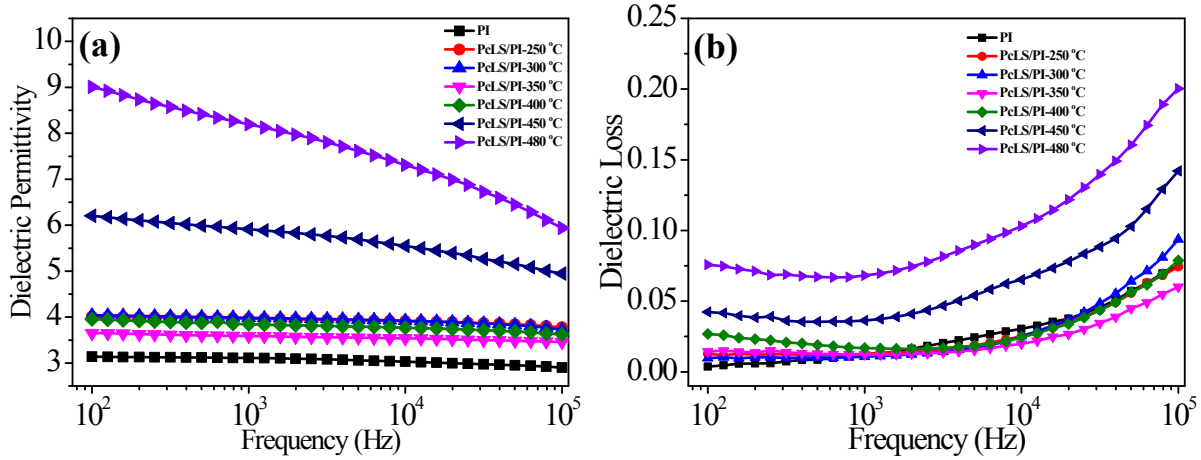

Figure S7 Frequency dependent dielectric permittivity **(a)** and dielectric loss **(b)** of the PcLS/PI composite film derived from the PAN/PI film containing 25 wt% PAN under different high temperature treatment.

Table S1 Dielectric permittivity, breakdown strength, and the maximum energy density of PcLS/PI composite films

Sample	Dielectric permittivity (1 KHz)	Breakdown strength (kV/mm)	Maximum energy density (J/cm^3)
neat PI	3.11	237.5	0.78
PAN 15 wt%	5.01	321.9	2.30
PAN 20 wt%	6.93	374.1	4.29
PAN 25 wt%	8.19	345.7	4.33
PAN 30 wt%	9.19	298.3	3.62

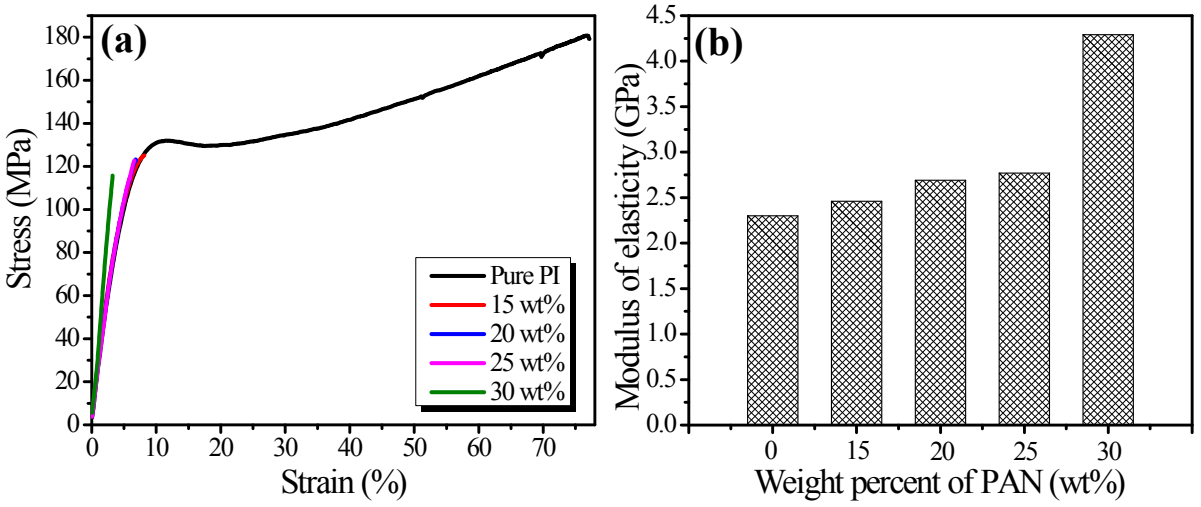

Figure S8 (a) Typical stress–strain curves of mechanical properties of the PcLS/PI composite films with different PAN content in the PAN/PAA precursor. **(b)** Histogram comparison of elastic modulus of the PcLS/PI composite films.

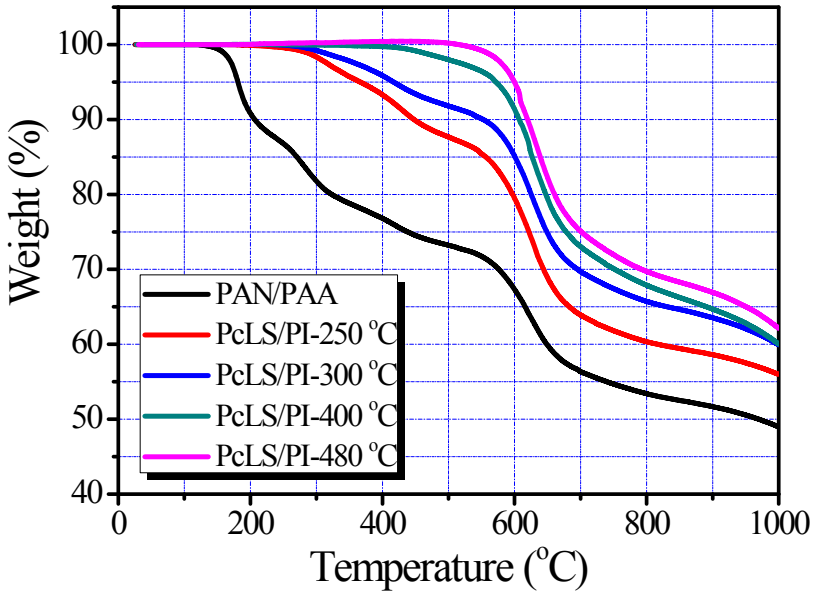

Figure S9 TGA curves of the fabricated PAN/PI film and PcLS/PI composite films obtained from different temperature treatment.

References

1 S. K. Nataraj, K. S. Yang and T. M. Aminabhavi, Progress in Polymer Science, 2012, **37**, 487.

2. T. Kowalewski, E. K. Kim, J. P. Mcgann, K. Matyjaszewski, WO2011022050 A1, Feb 24, 2011.