Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

Rehealable Imide-Imine Hybrid Polymers with Full Recyclability

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1. Materials and methods

All chemical reagents and solvents were provided by commercial suppliers and used as received unless otherwise stated. 2,2-Bis(3,4-dicarboxyphenyl)-hexafluoropropane-dianhydride (6FDA) and 4,4′-diaminodiphenyl ether (ODA) were dried in vacuum at 120 °C overnight before use. *N,N*-Dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were freshly distilled under reduced pressure over phosphorus pentoxide and stored over 4 Å molecular sieves prior to use.

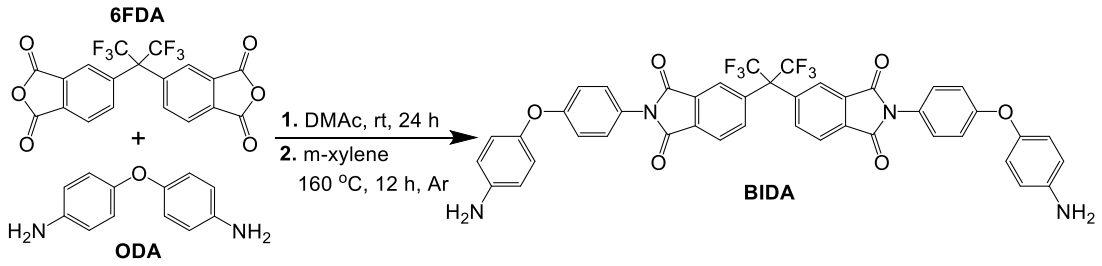
The FT-IR spectra were measured utilizing an Avatar 370 FT-IR Spectrometer. Four scans were averaged for each measurement and the data was analyzed using Omnisec software.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers in deuterated solvents (DMSO-d_6 or CD_2Cl_2). DMSO (2.50 ppm), and CH_2Cl_2 (5.32 ppm) were used as internal references in ^{1}H NMR, and DMSO (39.52 ppm), and CH_2Cl_2 (53.84 ppm) for ^{13}C NMR spectra. ^{1}H NMR data were reported in order: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), and number of protons. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer.

The internal loss factor tan δ was determined on a Q800 DMA instrument (New Castle, DE, USA). The polymer films were cut into 5 × 30 mm^2 rectangular samples for dynamic mechanical thermal analysis. All samples were subjected to the temperature scan mode at a programmed heating rate of 2 °C/min at a single frequency of 1 Hz from room temperature to 300 °C in a tensile mode with strain of 0.1% and preload force of 0.20 N. The glass transition temperature (T_g) was taken from the maximum of the peak in the α-transition region of the tan δ curve.

TGA measurements were carried out on a TA Instruments Q-500 series thermogravimetric analyzer at a heating rate of 10 °C/min under inert atmosphere (**PIIH-2** and **PIIH-5** were measured under argon, all others are under nitrogen) from room temperature to 800 °C.

2. Experimental procedures



Synthesis of BIDA: ODA (40 mmol, 8.01 g) and 6FDA (20 mmol, 8.88 g) were mixed in freshly distilled DMAc (72 mL) with stirring under argon atmosphere at room temperature. After 24 h, *m*-xylene (24 mL) was added and the mixture was heated at 160 °C under argon for 12 h with a Dean-Stark apparatus to remove the water. After cooling to room temperature, the solution was poured into ethanol while stirring. The mixture was left to stand for 5 h to precipitate completely. The precipitate was collected via suction filtration and washed with cold ethanol (3 × 200 mL). Subsequently, the products were extracted with ethanol through Soxhlet extraction for 12 h. The ethanol extract was concentrated and the residue was purified by flash column chromatography (CH_2Cl_2/^{i}PrOH = 40/1, v/v) to yield pure **BIDA** (2.24 g, 14%) as a bright yellow solid (Inset in Fig. S2): ^{1}H-NMR (400 MHz, DMSO-d_6, 25 °C) δ = 8.15-8.17 (m, 2H), 7.94-7.96 (m, 2H), 7.72 (s, 2H), 7.34-7.36 (m, 4H), 6.96-6.98 (m, 4H), 6.82-6.83 (m, 4H), 6.60-6.62 (m, 4H), 5.05 (s, 4H) (Fig. S5); ^{13}C-NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 166.6, 159.5, 147.6, 144.2, 139.2, 136.3, 132.9, 128.4, 125.4, 124.4, 121.8, 117.5, 116.3, 65.6 (Fig. S6); ^{19}F-NMR (300 MHz, CD_2Cl_2, 25 °C) δ = -62.8 (Fig. S7); ESI-MS (*m*/*z*): calcd for $[M + H]^+$ = 809.1835; found: 809.1821.

Preparation of PIIH thin films: Total five different PIIHs were prepared with various monomer types and ratios (Table S1). The preparation of **PIIH-3** was described below as a typical example (Fig. S1). To a solution of **TPA** (0.30 g, 2.24 mmol) and **BIDA** (0.452 g, 0.559 mmol) in DMF (9 mL) were added **DETA** (0.058 g, 0.56 mmol) and **TREN** (0.109 g, 0.746 mmol) dropwise with stirring. The total monomer concentration was kept at about 0.1 g/mL. The above solution was then

poured into a dust-free glass disc (diameter of 10 cm), and the glass disc was placed in a relatively sealed environment to slowly evaporate the solvent through a typical solvent-annealing method. The temperature was gradually raised up from room temperature to 50 °C and held at this temperature overnight, and then gradually heated to 120 °C, holding at 60 °C, 80 °C, 90 °C, 100 °C and 120 °C each for 2 h to yield **PIIH-3** thin film. After slowly cooling to room temperature and soaking in deionized water, the thin film was peeled off from the glass disc. Then the film was heat pressed at 80 °C for 4 h, followed by 1 h at 100 °C, 1 h at 120 °C, and finally 0.5 h at 130 °C using a top platen-heated hand-operated heat press under nominal pressure until achieving constant weight.

Preparation of PI thin films: The PI thin films were prepared following the similar procedure described above. Two different polyimine samples were prepared and the monomer information is listed in Table S1.

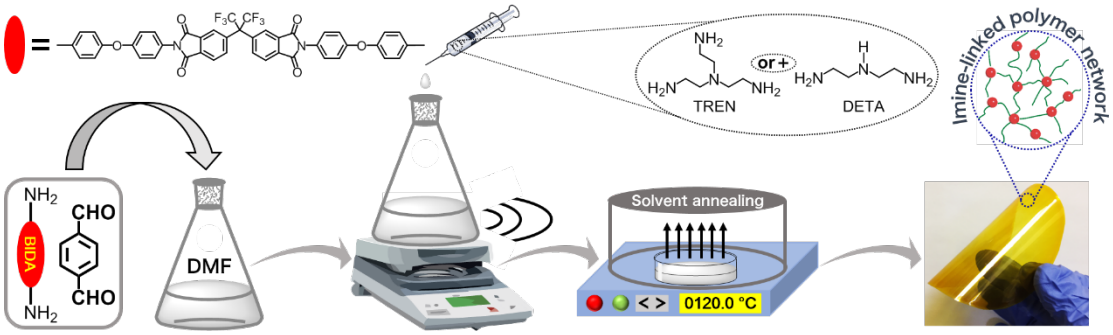


Fig. S1 Schematic representation of the poly(imide imine) hybrid (PIIH) thin film fabrication

Table S1 Recipe for preparing polyimine thin films

Polymer	Imide:imine Mole ratio[a]	TPA (equiv.)	Diamine			TREN Cross-linker (equiv.)	Polymer Density (g/cm^3)[b]
			BIDA (equiv.)	DETA (equiv.)	BAPMA (equiv.)		
PIIH-1	1:1.5	10	6.67	/	/	2.22	1.331
PIIH-2	1:2.2	10	4.5	/	/	3.67	1.293
PIIH-3	1:4	10	2.5	2.5	/	3.33	1.266
PIIH-4	1:4	10	2.5	4.17	/	2.22	1.255
PI-1	0	10	/	5.0	/	3.33	1.141
PIIH-5	1:4	10	2.5	/	2.5	3.33	1.248
PI-2	0	10	0	/	5.0	3.33	1.104

[a]The molar ratio of imide:imine is calculated based on the molar ratio of imide moiety to imine bond within the resulting polymer networks. [b]Film density was measured by a liquid suspension method with a mixture of toluene and tetrachloromethane under ambient conditions.

3. Characterization of PIIH and PI thin films

3.1 FT-IR spectra of starting materials and PIIH and PI thin films

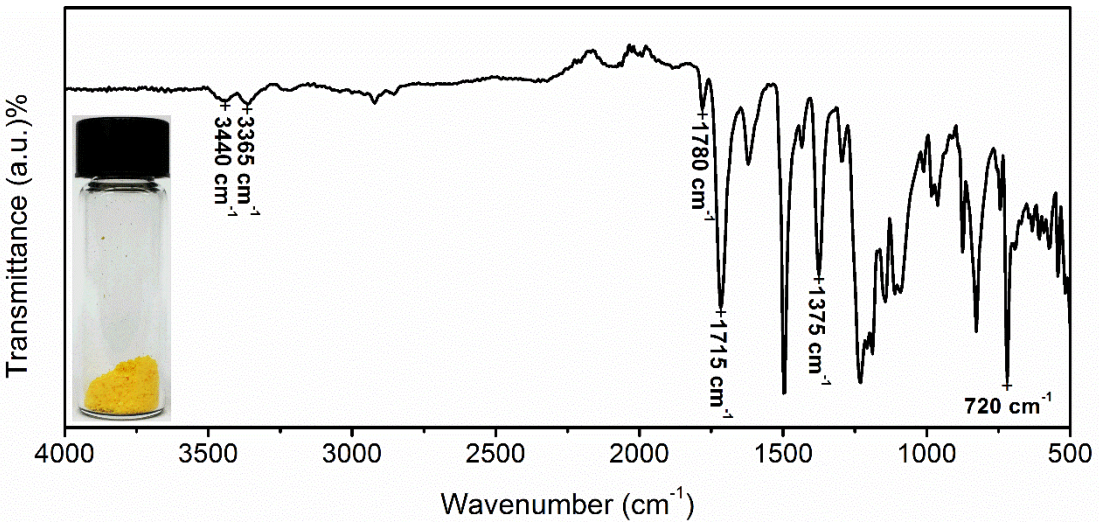


Fig. S2 Digital image (inset) of **BIDA** monomer and its FT-IR spectrum

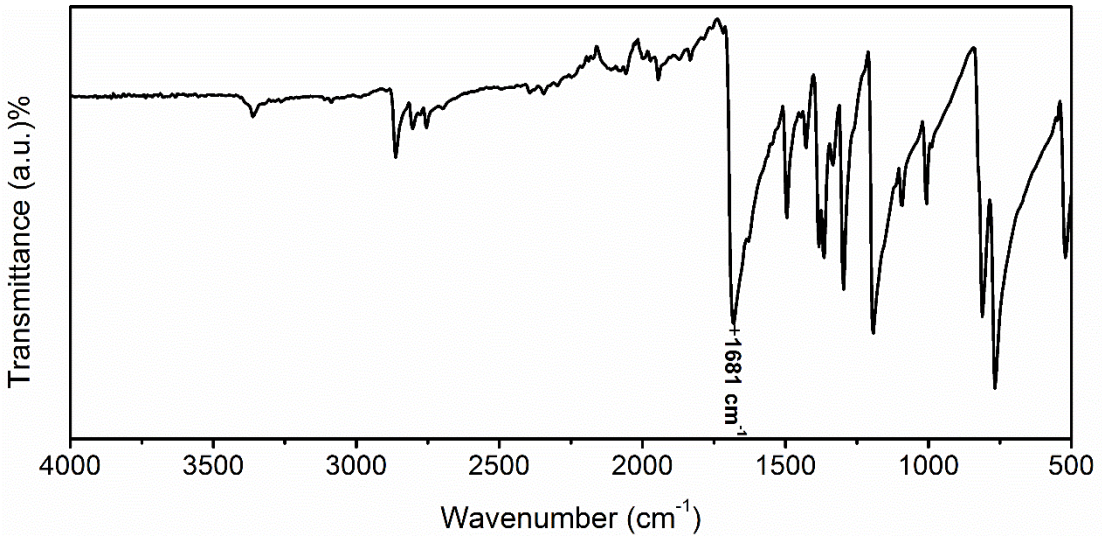
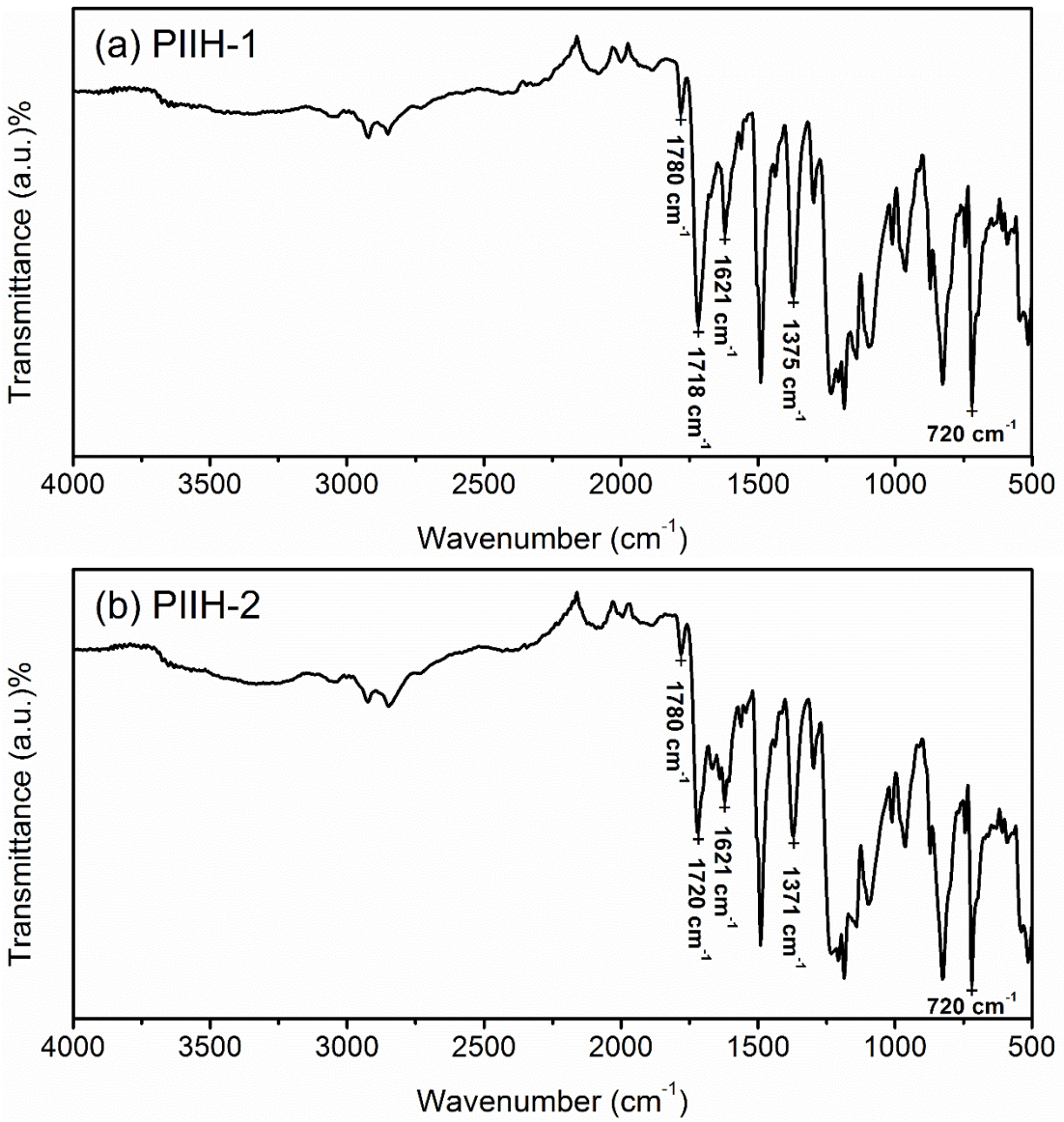
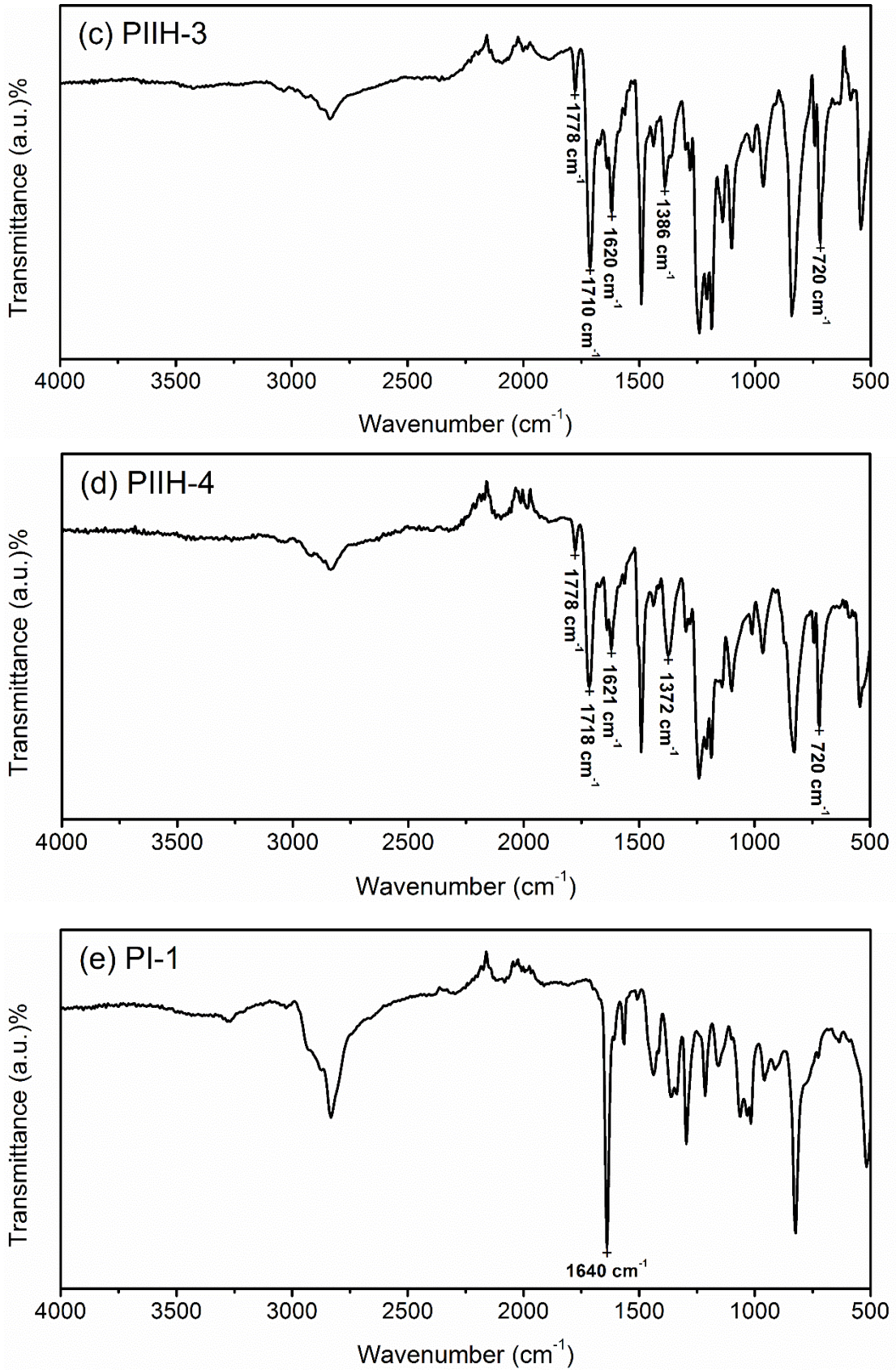


Fig. S3 FT-IR spectrum of terephthalaldehyde (**TPA**)




(c) PIIH-3
Transmittance (a.u.)%
1778 cm-1
1710 cm-1
1620 cm-1
1386 cm-1
720 cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
(d) PIIH-4
Transmittance (a.u.)%
1778 cm-1
1718 cm-1
1621 cm-1
1372 cm-1
720 cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
(e) PI-1
Transmittance (a.u.)%
1640 cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

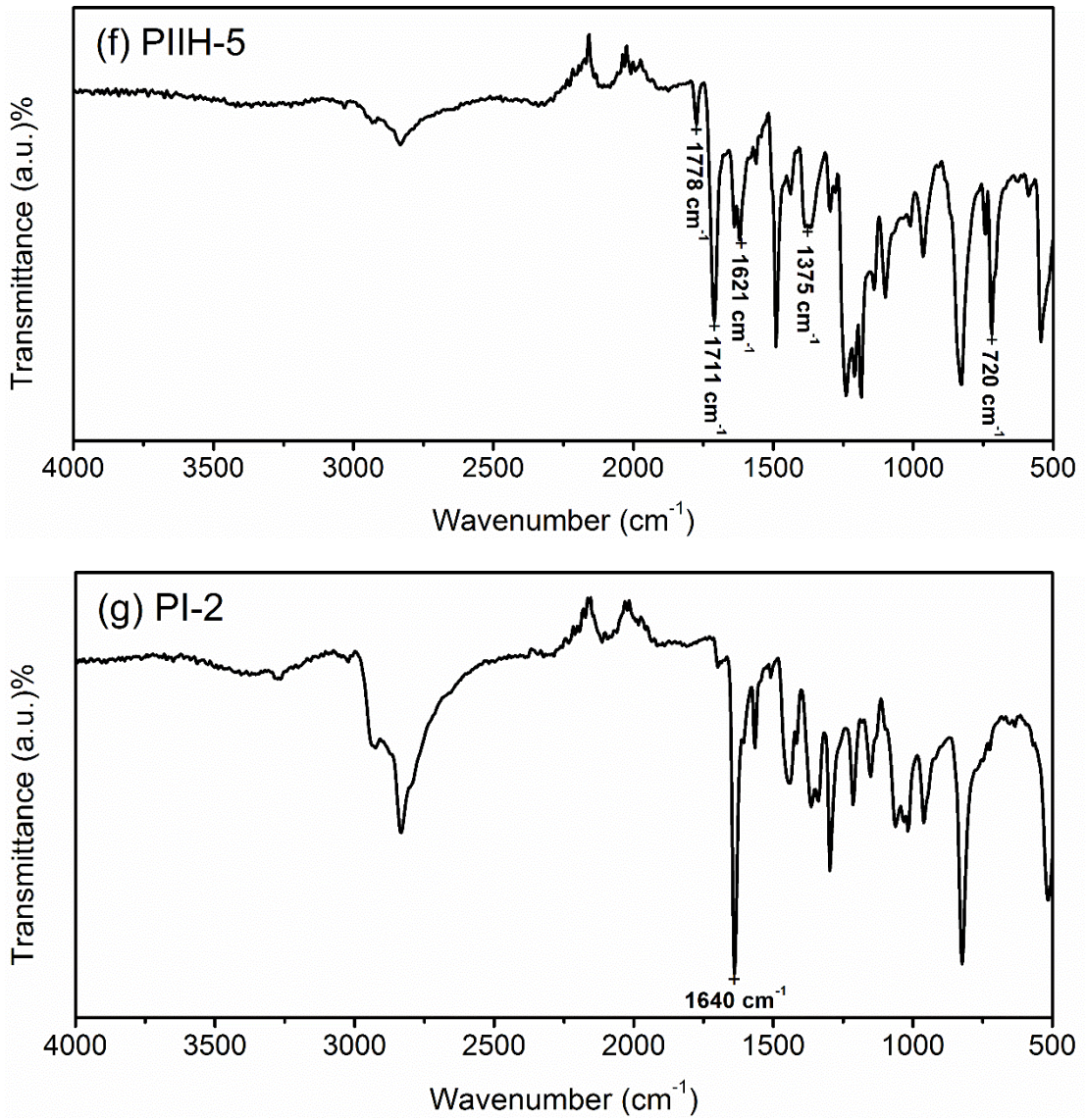


Fig. S4 FT-IR spectra of **PIIH-1** (a), **PIIH-2** (b), **PIIH-3** (c), **PIIH-4** (d), **PI-1** (e), **PIIH-5** (f) and **PI-2** (g)

3.2 Nuclear Magnetic Resonance (NMR) spectra

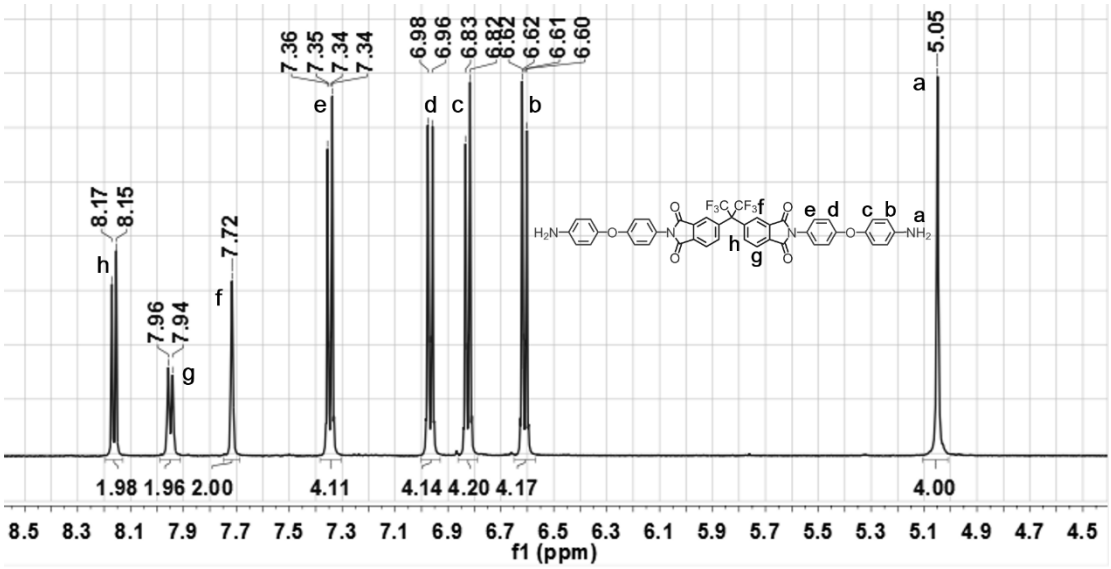


Fig. S5 ^{1}H-NMR spectrum of **BIDA** in DMSO-d_6

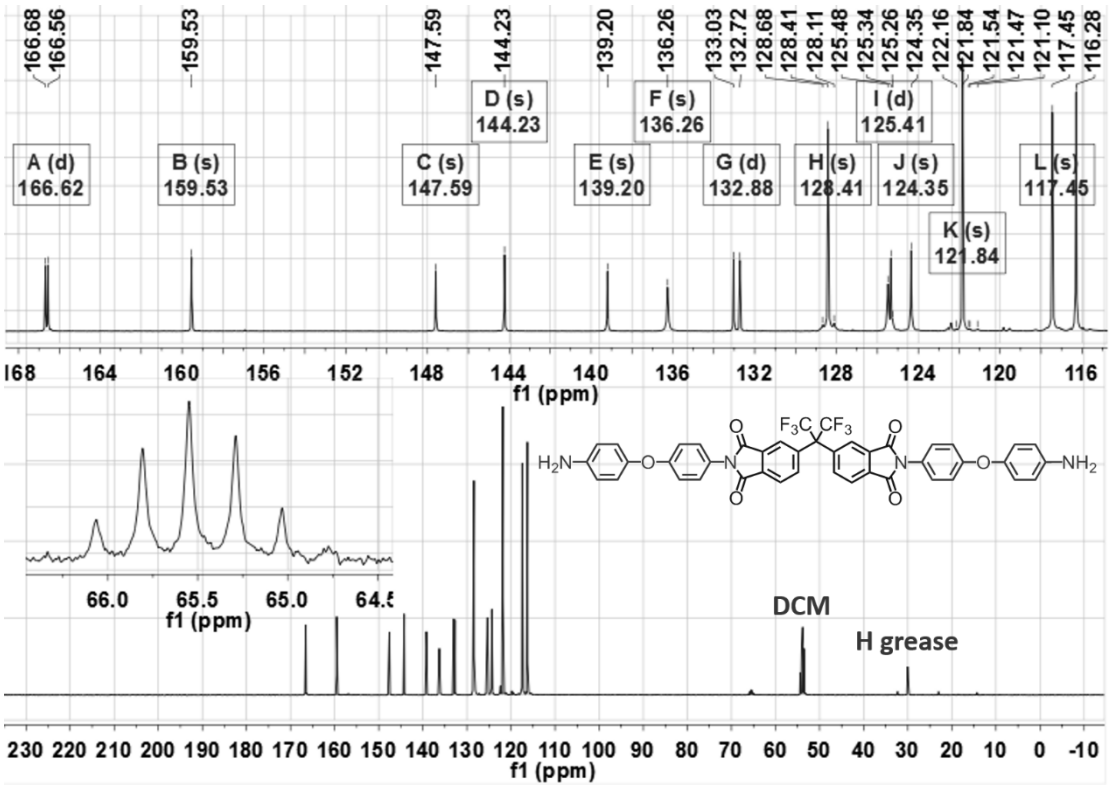


Fig. S6 ^{13}C-NMR spectrum of **BIDA** in CD_2Cl_2

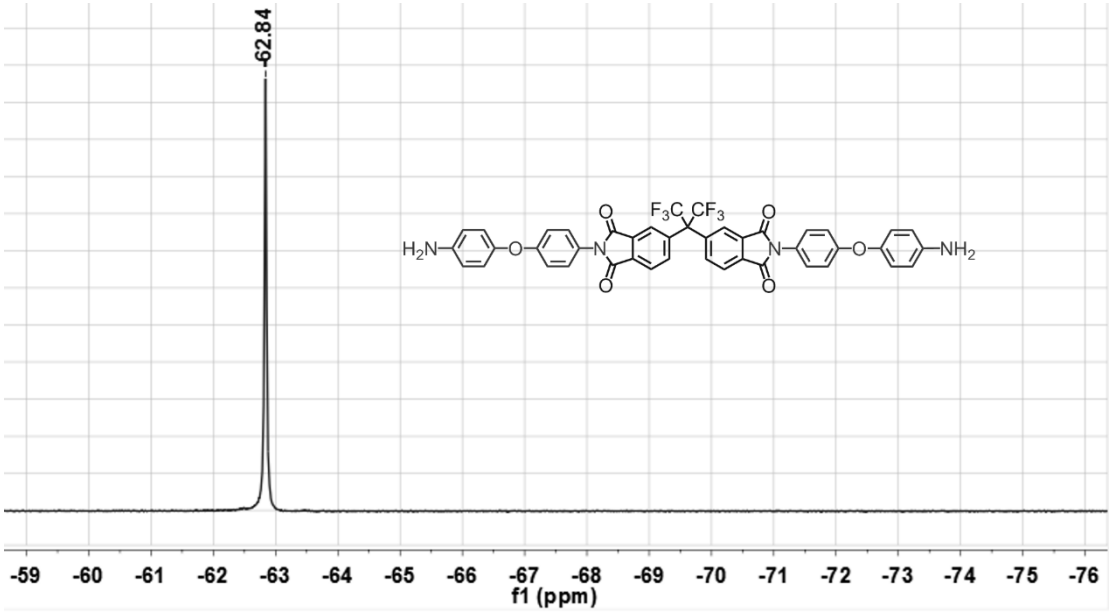
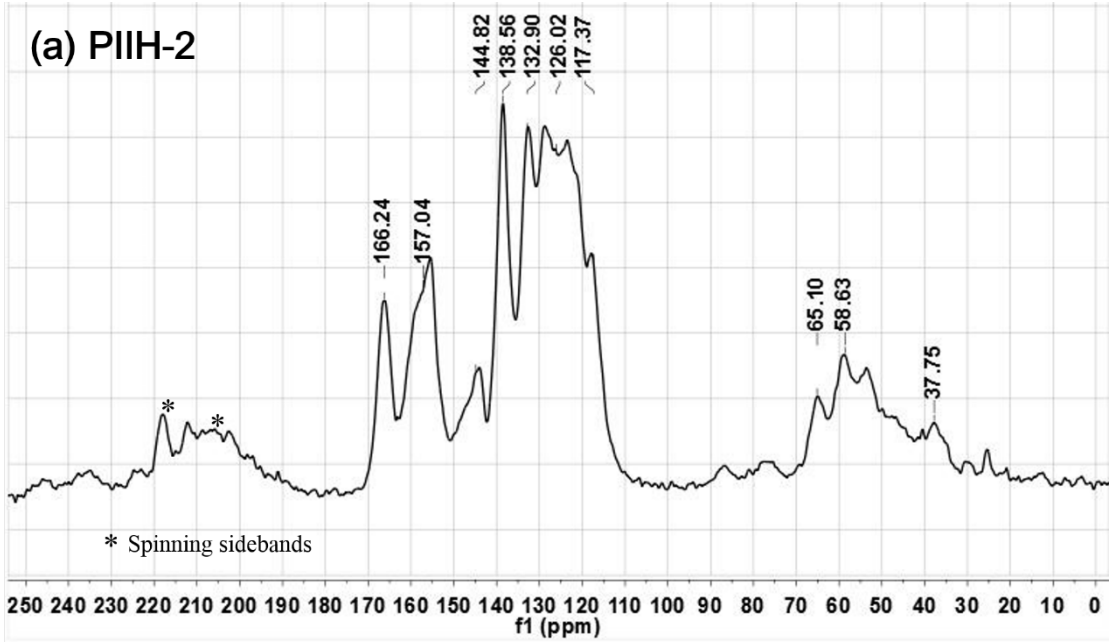
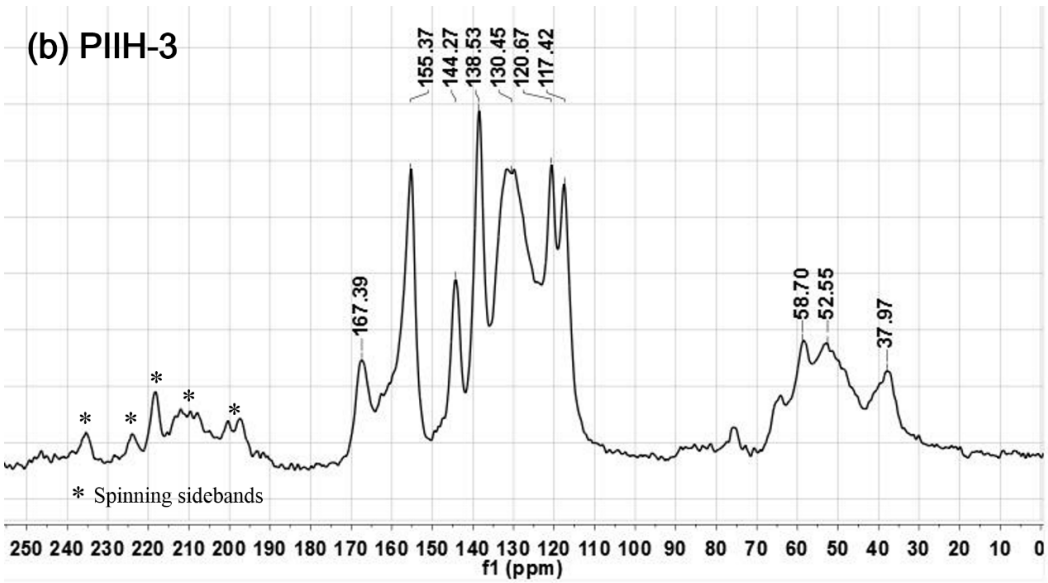
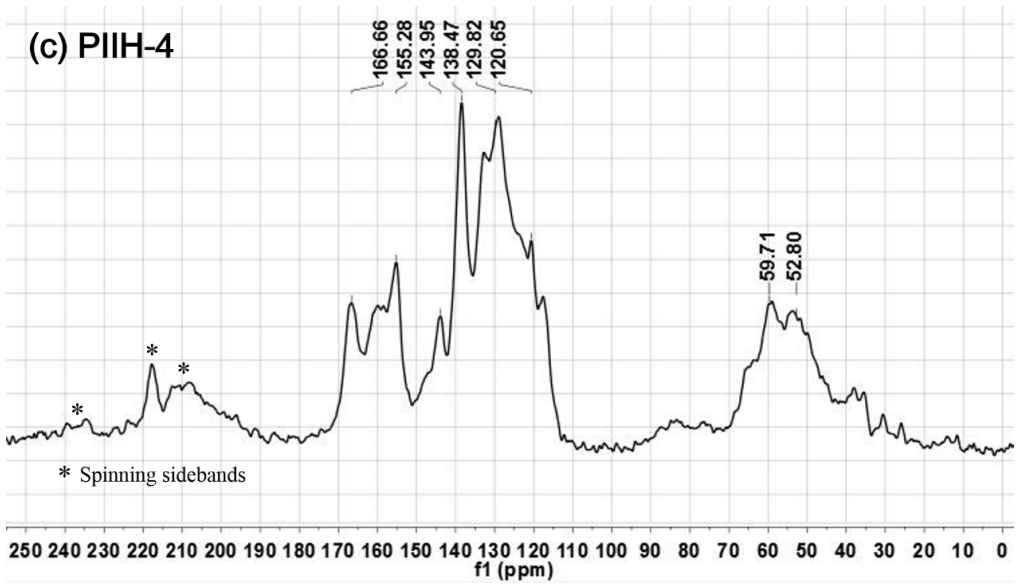
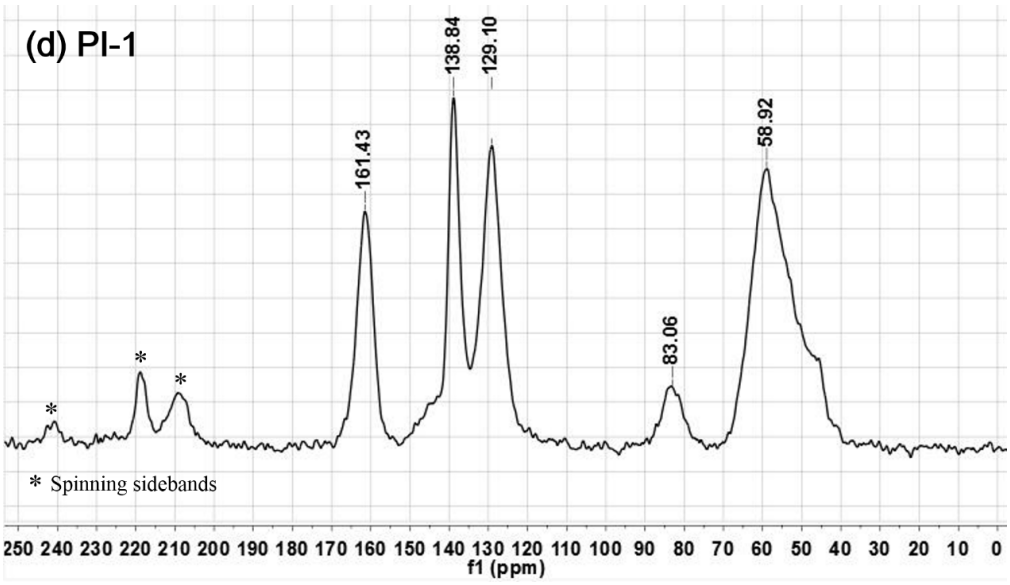


Fig. S7 ^{19}F-NMR spectrum of **BIDA** in CD_2Cl_2




(b) PIIH-3
155.37
144.27
138.53
130.45
120.67
117.42
167.39
58.70
52.55
37.97
* Spinning sidebands
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(c) PIIH-4
166.66
155.28
143.95
138.47
129.82
120.65
59.71
52.80
* Spinning sidebands
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(d) PI-1
138.84
129.10
161.43
58.92
83.06
* Spinning sidebands
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

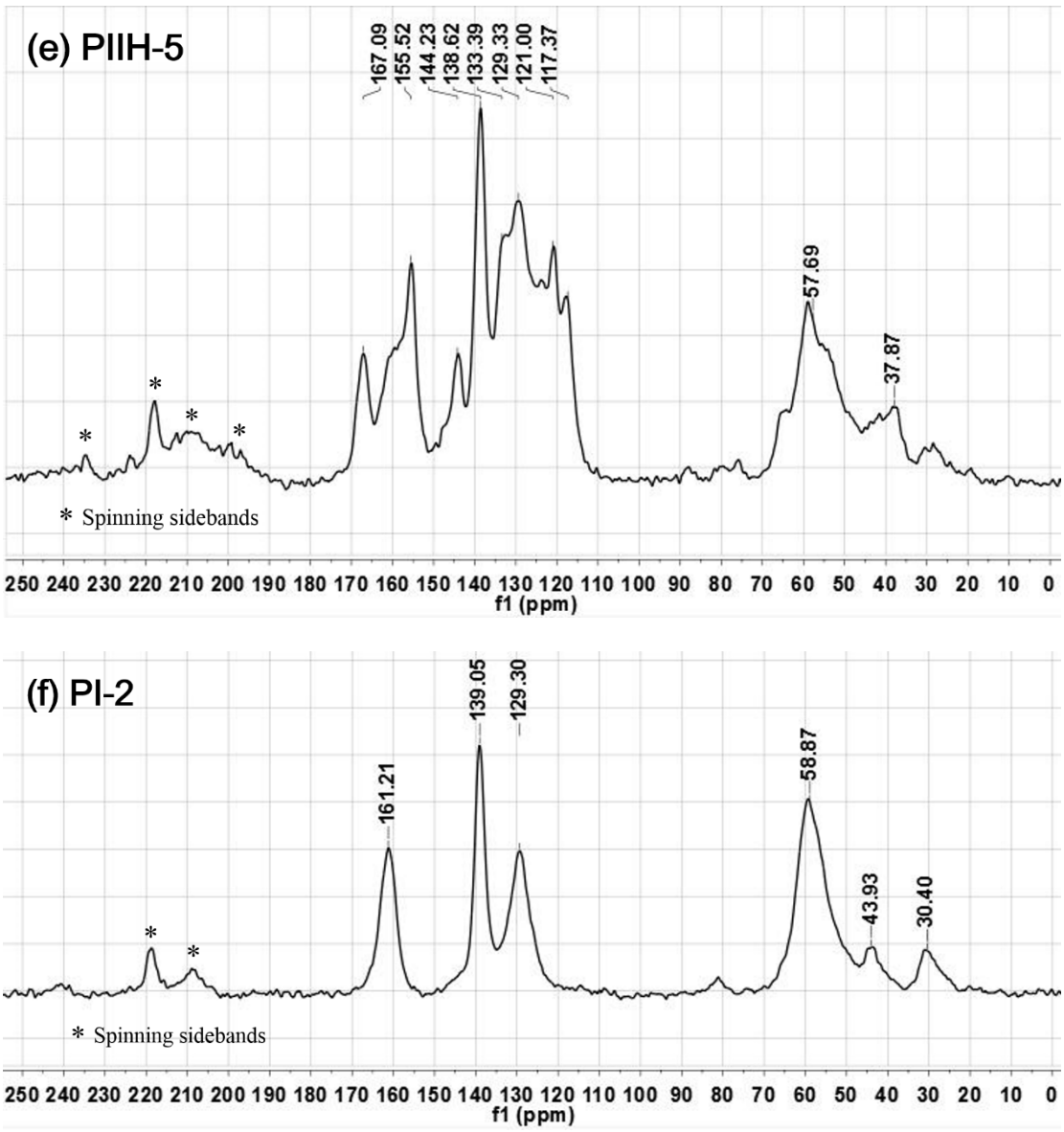


Fig. S8 Solid-state ^{13}C-NMR spectra of **PIIH-2** (a), **PIIH-3** (b), **PIIH-4** (c), **PI-1** (d), **PIIH-5** (e) and **PI-2** (f)

3.3 Dynamic mechanical analysis (DMA) of PIIH and PI thin films

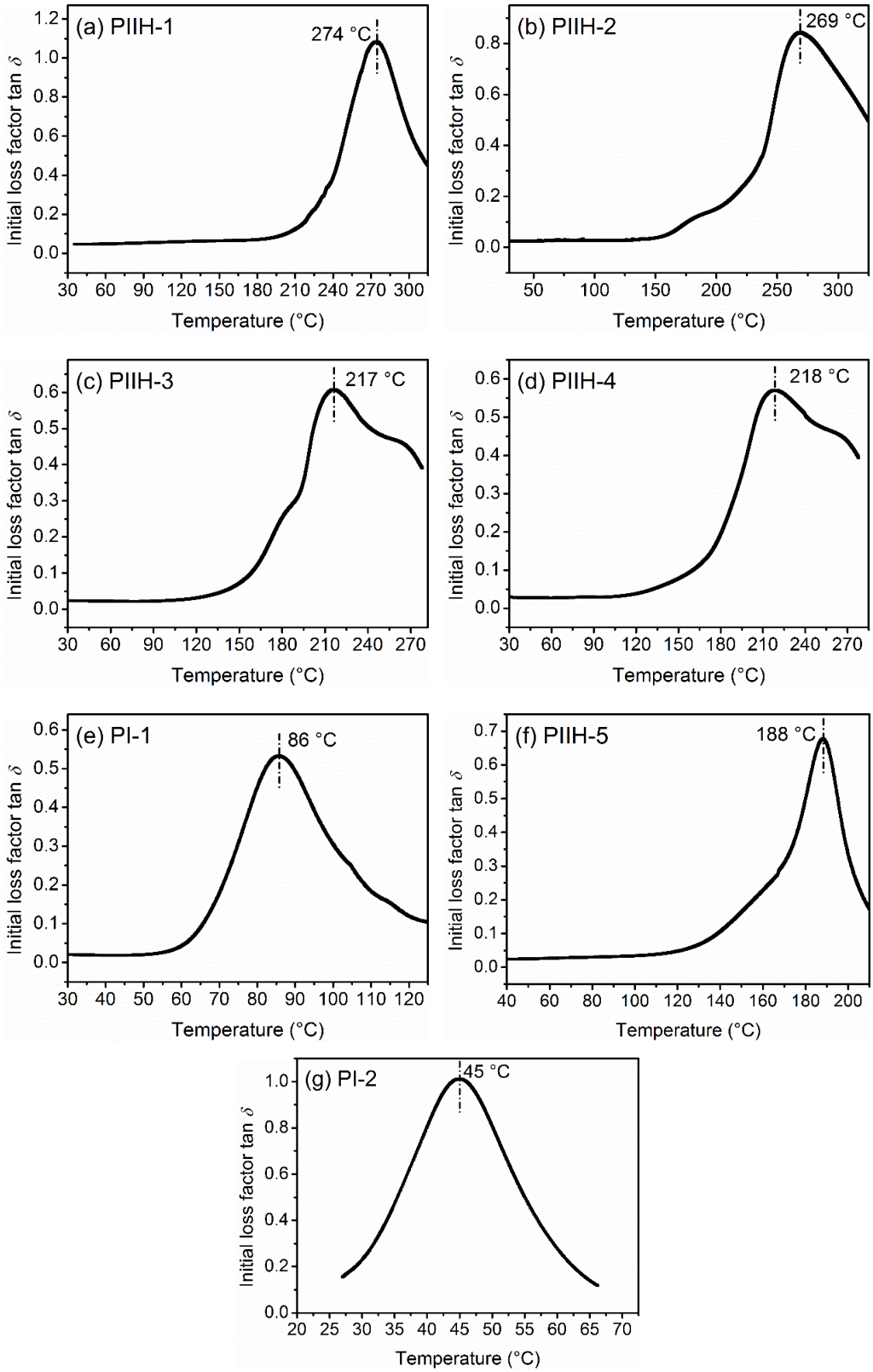


Fig. S9 Initial loss factor tan δ curves of **PIIH-1** (a), **PIIH-2** (b), **PIIH-3** (c), **PIIH-4** (d), **PI-1** (e), **PIIH-5** (f) and **PI-2** (g)

3.4 Thermal gravimetric analysis (TGA)

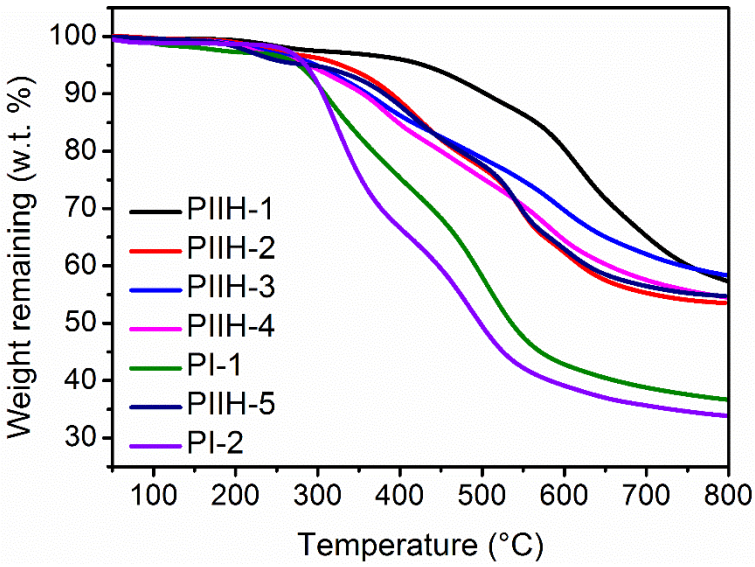


Fig. S10 TGA curves of the PI and PIIH thin films

4. Rehealability test of PIIH thin film

PIIH-3 was used to investigate the re-healable behavior of the PIIH samples. The rectangle film strips ($L \times W = 80 \times 5$ mm^2) were cut into two pieces by a doctor blade, and then the two pieces were overlapped by ca. 10 mm range. One drop of DETA solution (in DMF and acetonitrile: v/v = 1:1, 10 mg/mL) was added to the overlapped position and the film strips were carefully placed on silicon-coated paper and subjected to heat-press treatment. The temperature was gradually raised up from room temperature to 80 °C (held at each of the following temperatures: 50 °C, 60 °C, 80 °C for approximately 2 h) to complete the re-healing process. After slowly cooling to room temperature, the healed strip was subjected to tensile testing and the properties were compared with those of the original sample. The polymers' healing efficiency is defined as the fracture mechanical properties (tensile modulus, tensile strength, elongation at break) of healed sample to those of the pristine sample in tensile experiments.

Table S2 Mechanical properties of the original and healed samples

Sample	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Original sample (PIIH-3)	1.47 ± 0.03	82.7 ± 2.8	8.3 ± 0.6
Healed sample[a]	1.52 ± 0.02	78.2 ± 0.7	7.5 ± 0.5

[a]Tensile measurements for the healed samples were carried out by an Instron instrument on three rectangle film strips ($L \times W = 70 \times 5$ mm^2) with gauge length of 30 mm at room temperature. The crosshead speed was 2 mm/min. Tensile modulus was taken as the initial slope of the stress-strain curves. During tensile test, fracture always took place at a different position from the healed location.

5. Recycling of PIIH thin films

The recycling procedure reported previously was followed.[1] When calculating the molar content of the cured polyimine films, a "dehydrated" molecular weight was used for each monomer. To obtain the dehydrated molecular weight, the atomic weight of 1 oxygen atom is subtracted from each aldehyde moiety, and the atomic weight of 2 hydrogen atoms are subtracted from each primary amine moiety. **PIIH-4** was used in the recycling study. The specific procedure is as follows.

PIIH-4 sample (84 mg) was added to a 20 mL screw cap vial followed by a solution of **DETA** (87 mg, 0.84 mmol), and **TREN** (65 mg, 0.45 mmol) in DMF (9 mL). The mixture was heated at 55 °C for ca. 24 h to completely dissolve the **PIIH-4** and give a clear and homogeneous solution. **TPA** (0.27 g, 2.01 mmol) and **BIDA** (0.41 g, 0.50 mmol) were successively added. After thorough mixing, the above solution was poured into a flat glass disc. The glass disc was placed in a relatively sealed environment to slowly evaporate the solvent through a typical solvent-annealing method as previously described. After slowly cooling to room temperature and then soaking in deionized water, the thin film was peeled off from the glass disc. Then the film was heat pressed at 80 °C for 4 h, followed by 1 h at 100 °C, 1 h at 120 °C, and finally 0.5 h at 130 °C using a top platen-heated hand-operated heat press under

nominal pressure until achieving constant weight. The resulting film was subject to tensile testing by utilizing an Instron instrument and compared with the original sample. This polyimine film was denoted as "1st generation recycled sample". The 2nd and 3rd generation of recycled **PIIH-4** samples were prepared following the similar procedure from 1st generation and 2nd generation recycled **PIIH-4** respectively.

6. References

1 P. Taynton, H. Ni, C. Zhu, K. Yu, S. Loob, Y. Jin, H. J. Qi and W. Zhang, *Adv. Mater.*, 2016, **15**, 2904-2909.