ELECTRONIC SUPPORTING INFORMATION

A Comprehensive Study about the Effect of Molecular Chain Flexibility on the Performance of Low-temperature Curable Polyimide

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Table of Contents

I. Materials

1,4-Bis(4-hydroxy-α,α-dimethylbenzyl)benzene (98%), 1,3-benzofurandione-5-carbonyl chloride (98%), pyridine (99.5%, water ≤ 50 ppm), ethyl acetate (EA, 99.8%, water ≤ 50 ppm) and N-Methyl-2-pyrrolidone (NMP, 99.5%, water ≤ 50 ppm) were provided by Energy Chemical Co., Ltd. *p*-phenylenediamine (*p*-PDA, 97%) were purchased from Aladdin Industrial Corporation. 2,2-Bis(4-aminophenyl)propane (IPDA, 98%) and 4,4'-[p-phenylenebis(propane-2,2-diyl)]bisaniline (BIPDA, 99%) were received from Shanghai Bidepharm Co., Ltd. p-phenylenebis(trimellitate anhydride) (TAHQ, 99.8%) and 5-isobenzofurancarboxylic acid (BPEDA, 99.8%) was obtained from ChinaTech Chemical Co., Ltd. Dimethyl sulfoxide-d_6, (DMSO-d_6, with 0.03% tetramethylsilane) was obtained from Shanghai Acmec Bi°Chemical Co., Ltd. Tetrahydrofuran (THF, 99%), N,N-Dimethylformamide (DMF, 99%), dimethyl sulfoxide, (DMSO, 99%) and N,N-Dimethylacetamide, (DMAc, 99%) were received from Shanghai Lingfeng Chemical Reagent Co., Ltd. All the anhydrides were dried in a 120 °C vacuum oven for 6 hours, and all other materials were used as received without extra treatments.

II. Characterization method

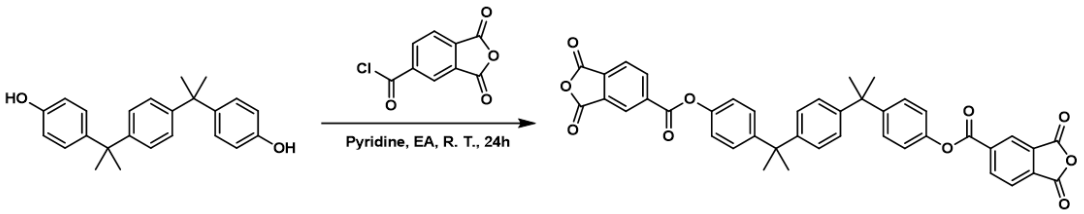
Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE III 400 MHz spectrometer instruments and the compounds (about 20 mg) were dissolved in 600 μL DMSO-d_6 by using residual tetramethylsilane (δH = 0.00 ppm) as internal references. The high-performance liquid chromatography (HPLC) was obtained by Ultimate 3000 to estimate the purity of TABPP. Fourier transform-infrared spectra (FT-IR) were detected from the Bruker Vertex 70 spectrometer with a scan range of 4000-600 cm^{-1} by using the room temperature attenuated total reflection (ATR) testing mode. In-plane orientation of PI films was analyzed by polarized ATR FTIR spectra with the data recorded by a PerkinElmer Frontier Fourier transform spectrometer, and a series of spectra were recorded by every 15° with the polarized angle varied from 0° to 180°. The molecular weight of poly-amide acids (PAAs) and

their polydispersity was measured by gel permeation chromatography (GPC, Waters Alliance e2695) by using DMF as an eluent at a flow rate of 1.0 mL/min at room temperature. The number average molecular weight (M_n) and weight average molecular weight (M_w) were calibrated by the standard curve of polystyrene. The ultraviolet visible (UV-vis) spectra was obtained on a UV-3600 from SHIMADZU (Japan) UV-VIS-NIR spectrophotometer, and the PI film was tightly attached to a 5×5 cm transparent and colorless glass plate. The dielectric constant and dissipation factor of the cured samples at a high frequency of 10 GHz were estimated on the E5071C keysight ENA vector network analyzer at room temperature. The mechanical properties of PI films were characterized by a dynamic mechanical analyzer (DMA Q850, TA Instruments, America) with a procedure of ranging from 1 N to 18 N (2 N/min) at room temperature. Thermomechanical analysis (TMA) was performed with a heating rate of 5 °C/min ranging from 25 °C to 400 °C in nitrogen on the TMA-SDTA2+ (Mettler, Switzerland) instrument. The glass transition temperature (T_g) was detected by DSC 2500 (TA Instruments, America) with a heating rate of 20 °C/min from 30 °C to 350 °C in a nitrogen atmosphere. Thermo-gravimetric analysis (TGA) was performed in the nitrogen atmosphere on a TA SDT Q600 (America) apparatus at a heating rate of 10 °C/min from room temperature to 800 °C. Wide-angle X-ray diffraction (WAXD) was performed on a D8 Advance diffractometer radiated by the CuKα of 0.15418 nm wavelength (Bruker, Germany) with a 2θ ranging from 10° to 70°. The obtaining $d_{spacing}$ values were based on the Bragg's law: $2d \times \sin\theta = n\lambda$. Water contact angel (WCA) was characterized by the Dataphysics-°CA20 with the deionized water. The water absorption was obtained by weighing the mass change before and after 200 mg of dried PI films immersed in deionized water for 24 h. The water absorption of PIs was calculated by the formula: Water absorption (WA) = $(W_b - W_a)/W_a \times 100\%$, where W_a was the mass before immersion and W_b after immersion. The solubility of the synthesized PIs was tested with 5 mg PI film in 8 mL solvent at room temperature for 24 h. If it did not dissolve after 24 h, the film was heated to 60 °C for an additional 24 h to observe the phenomenon.

III. Synthesis of monomers

Synthesis of (1,4-phenylenebis(propane-2,2-diyl))bis(4,1-phenylene) bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) (TABPP)

Under an atmosphere of nitrogen, 1,3-benzofurandione-5-carbonyl chloride (5.00 g, 23.75 mmol) was added to a 100 mL three-necked flask with 20 mL EA. The flask was sealed and kept at 0 °C with magnetic stirring until the solid was completely dissolved. Then a solution of pyridine (5.4 mL) was added to the resulting reaction mixture with 1,4-bis(4-hydroxy-α,α-dimethylbenzyl)benzene (3.92 g, 11.31 mmol) at 0 °C under an atmosphere of dry N_2. Subsequently, the reaction mixture was stirred at 0 °C for 5 h. After the end of the reaction, the reaction mixture was filtered with a Brinell funnel and the white solid was collected in a 100 mL flask. To purify the obtained crude product, 20 mL of acetic acid was added to the flask, and the temperature was raised to 80 °C within a nitrogen atmosphere. Once the white solid had been completely dissolved, the reaction mixture underwent a gradual cooling process to attain room temperature. After the white solid was precipitated, the white solid was filtered and dried in vacuum at 120 °C for 6 h, the product was obtained as a dried white powder with a yield of 55%. The structure of TABPP was confirmed by the nuclear magnetic resonance (NMR) as described in the supporting information (see **Fig. S1** and **Fig. S2**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 - 8.46 (m, 4H), 8.27 (d, J = 7.9 Hz, 2H), 7.35 - 7.17 (m, 12H), 1.67 (s, 12H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.39, 162.97, 162.86, 148.86, 148.58, 147.67, 137.41, 136.28, 135.83, 132.60, 128.15, 128.12, 126.64, 126.36, 126.19, 121.69, 121.60, 42.37, 30.85.



Scheme S1 Synthesis of TABPP.

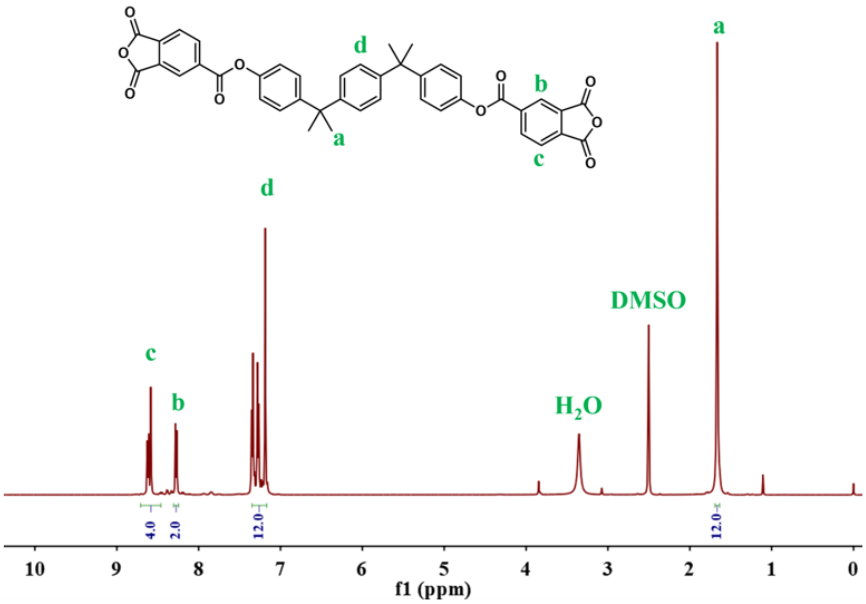


Fig. S1 ^{1}H NMR spectrum of TABPP in DMSO-*d6*.

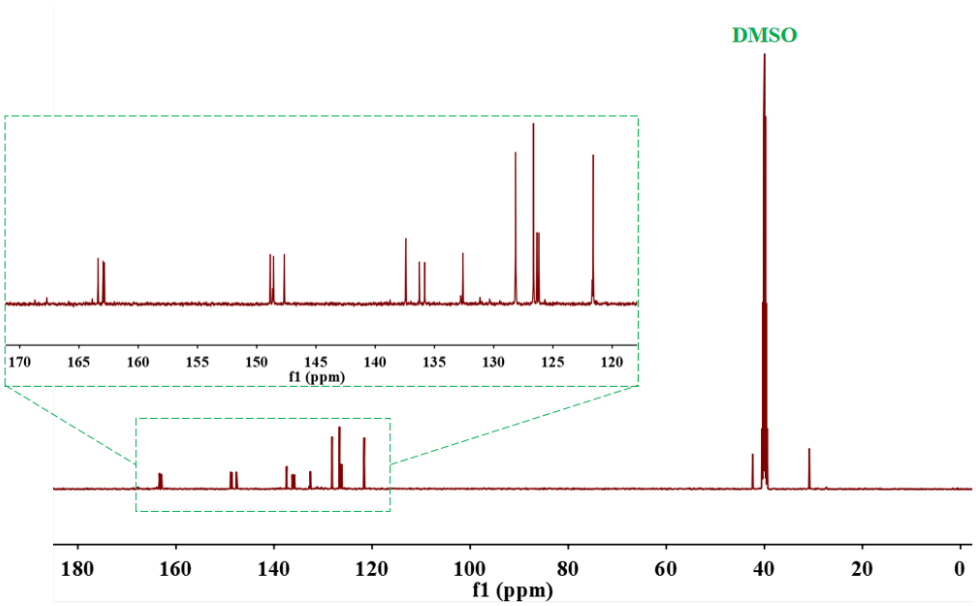


Fig. S2 ^{13}C NMR spectrum of TABPP in DMSO-*d6*.

IV. Additional characterizations of the structure of PI film

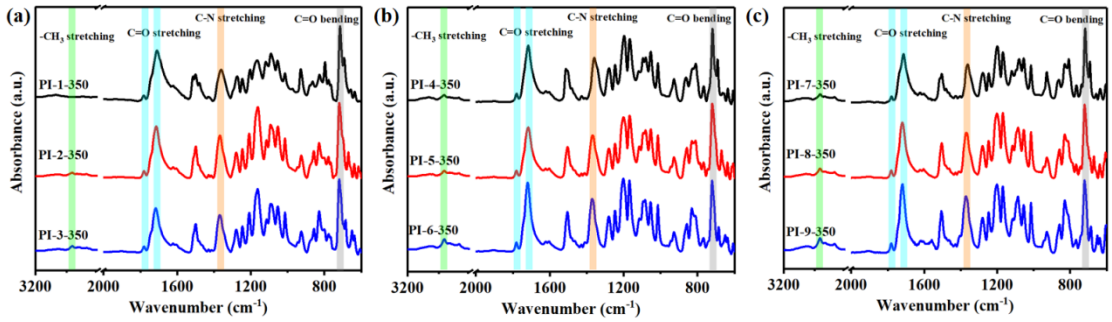


Fig. S3 FT-IR spectra of (a) PI films with anhydride TAHQ cured at 350 ℃, (b) PI films with anhydride BPEDA cured at 350 ℃ and (c) PI films with anhydride TABPP cured at 350 ℃.

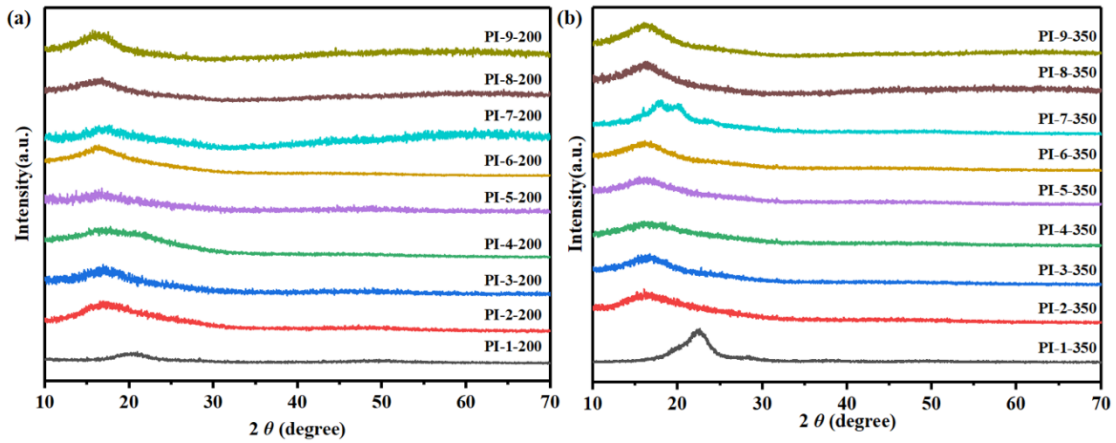


Fig. S4 XRD patterns of (a) PI films cured at 200 ℃ and (b) PI films cured at 350 ℃.

V. Additional thermal properties, mechanical properties and linearly polarized IR spectroscopy of PI films

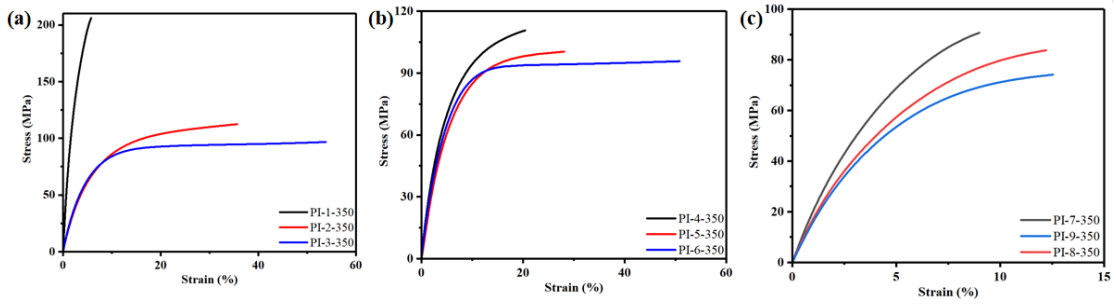


Fig. S5 Typical stress-strain curves of (a) PI films with anhydride TAHQ cured at 350 ℃, (b) PI films with anhydride BPEDA cured at 350 ℃ and (c) PI films with anhydride TABPP cured at 350 ℃.

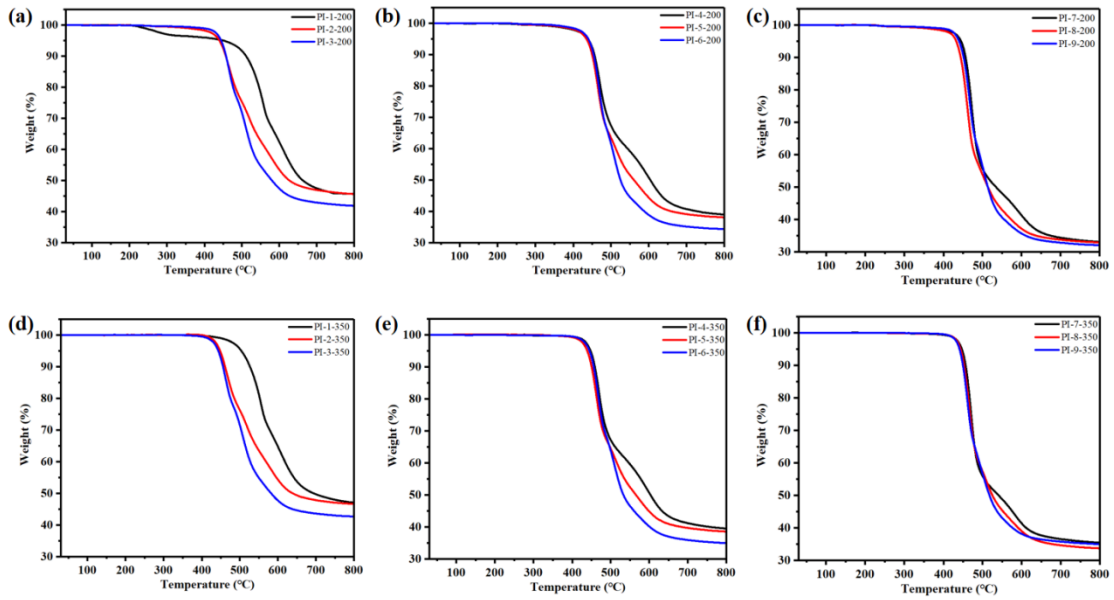


Fig. S6 TGA curves of (a) PI films with anhydride TAHQ cured at 200 ℃, (b) PI films with anhydride BPEDA cured at 200 ℃, (c) PI films with anhydride TABPP cured at 200 ℃, (d) PI films with anhydride TAHQ cured at 350 ℃, (e) PI films with anhydride BPEDA cured at 350 ℃ and (f) PI films with anhydride TABPP cured at 350 ℃.

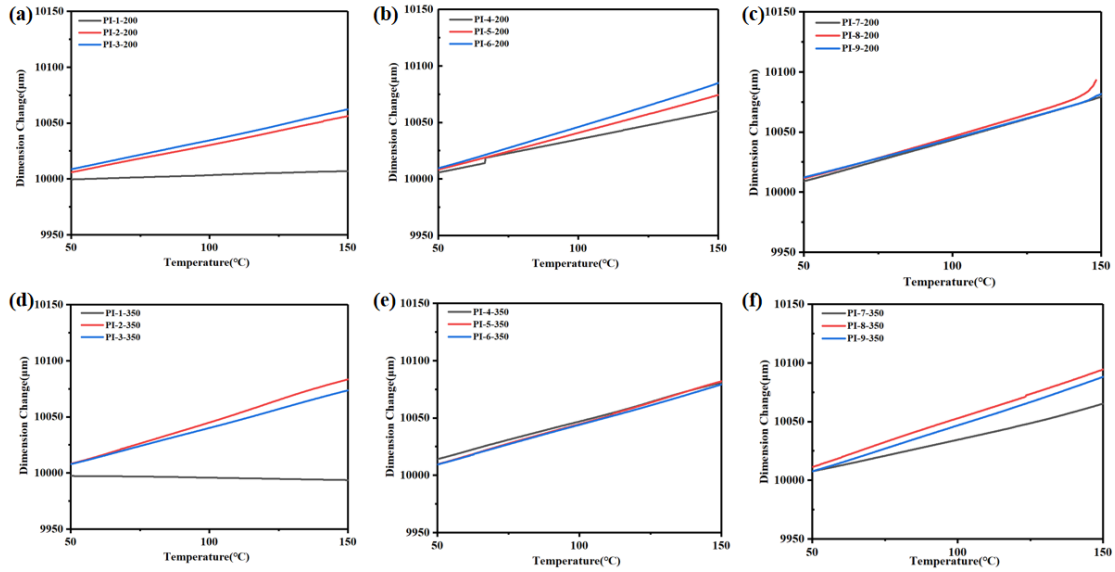


Fig. S7 TMA curves of (a) PI films with anhydride TAHQ cured at 200 ℃, (b) PI films with anhydride BPEDA cured at 200 ℃, (c) PI films with anhydride TABPP cured at 200 ℃, (d) PI films with anhydride TAHQ cured at 350 ℃, (e) PI films with anhydride BPEDA cured at 350 ℃ and (f) PI films with anhydride TABPP cured at 350 ℃.

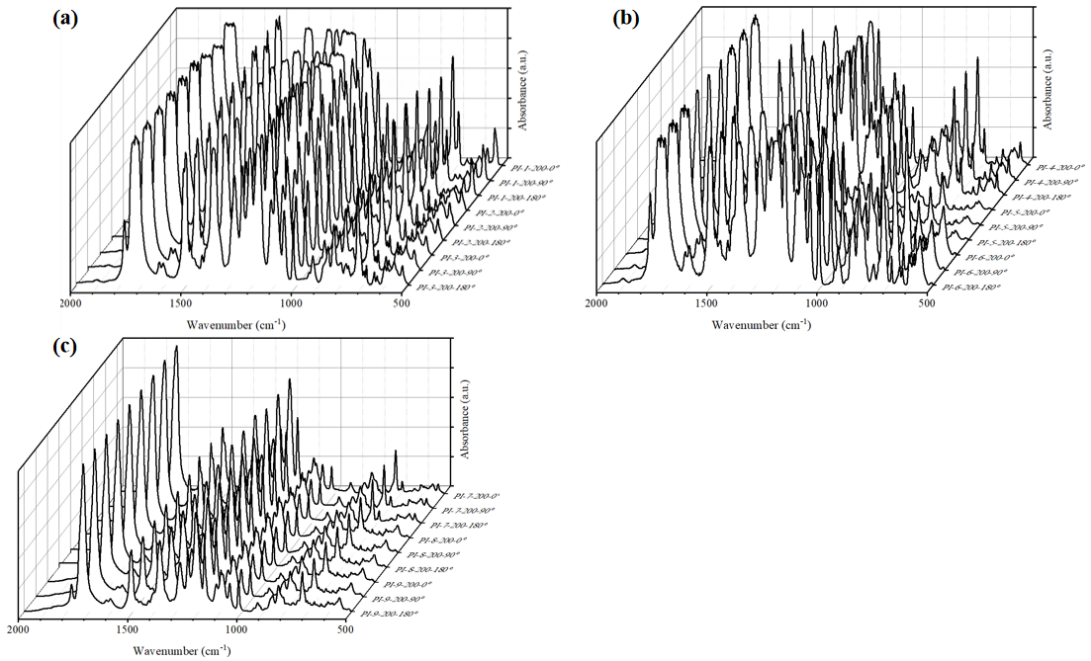


Fig. S8 Linearly polarized IR spectroscopy of (a) PI films with anhydride TAHQ cured at 200 ℃, (b) PI films with anhydride BPEDA cured at 200 ℃ and (c) PI films with anhydride TABPP cured at 200 ℃.

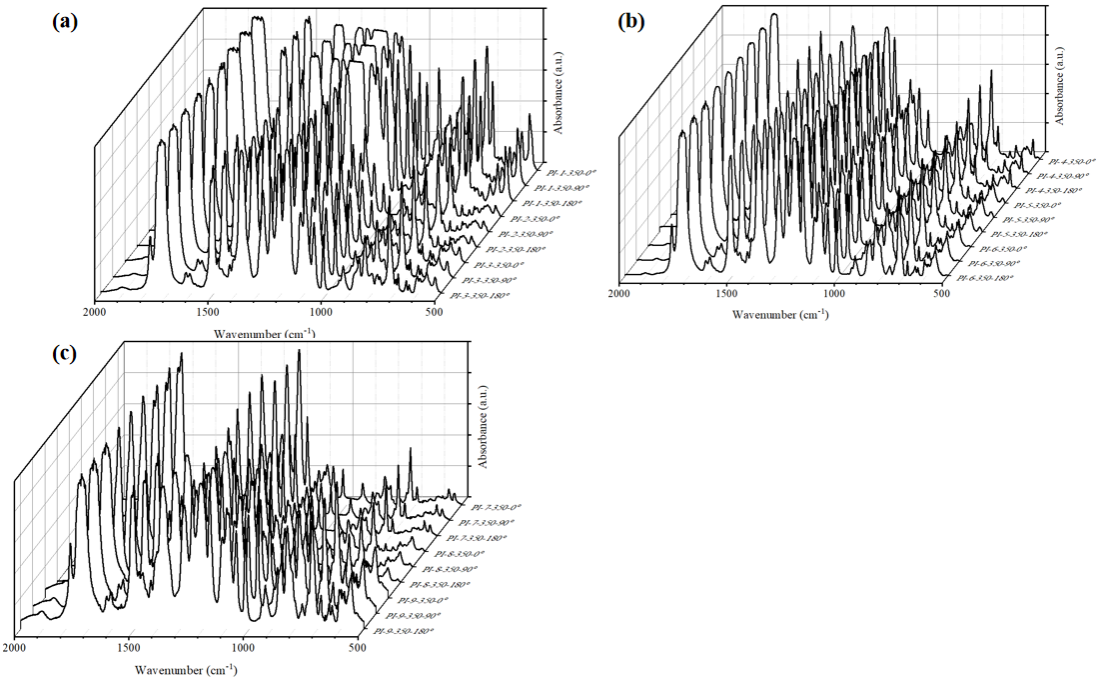


Fig. S9 Linearly polarized IR spectroscopy of (a) PI films with anhydride TAHQ cured at 350 ℃, (b) PI films with anhydride BPEDA cured at 350 ℃ and (c) PI films with anhydride TABPP cured at 350 ℃.

VI. Additional DSC curves of PI films

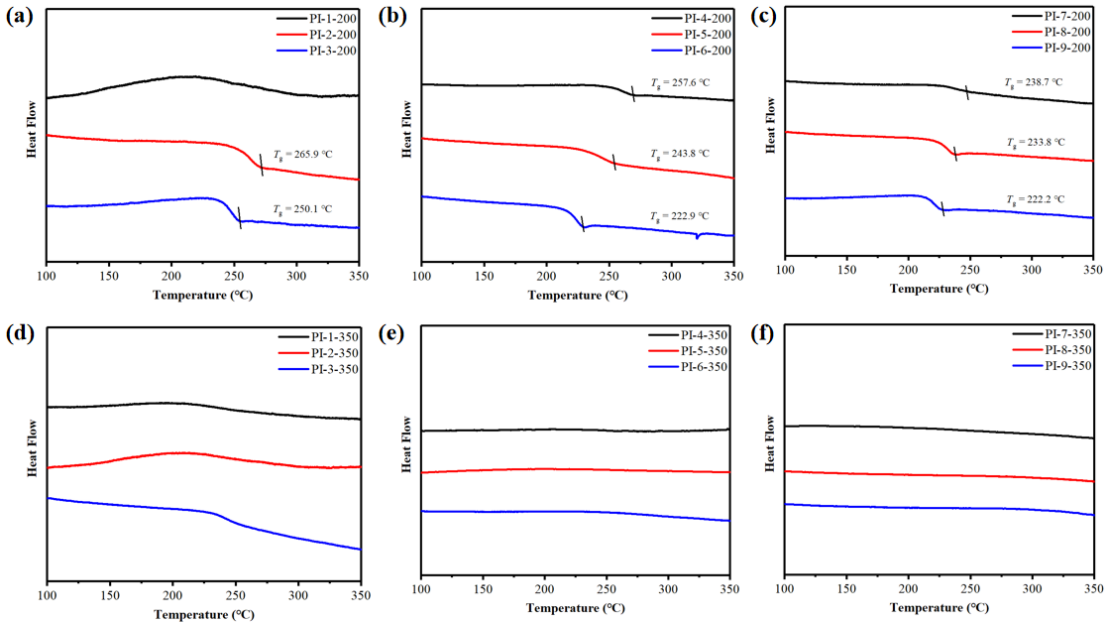


Fig. S10 DSC curves of (a) PI films with anhydride TAHQ cured at 200 ℃, (b) PI films with anhydride BPEDA cured at 200 ℃, (c) PI films with anhydride TABPP cured at 200 ℃, (d) PI films with anhydride TAHQ cured at 350 ℃, (e) PI films with anhydride BPEDA cured at 350 ℃ and (f) PI films with anhydride TABPP cured at 350 ℃.

VII. Additional hydrophobicity and optical properties of PI films

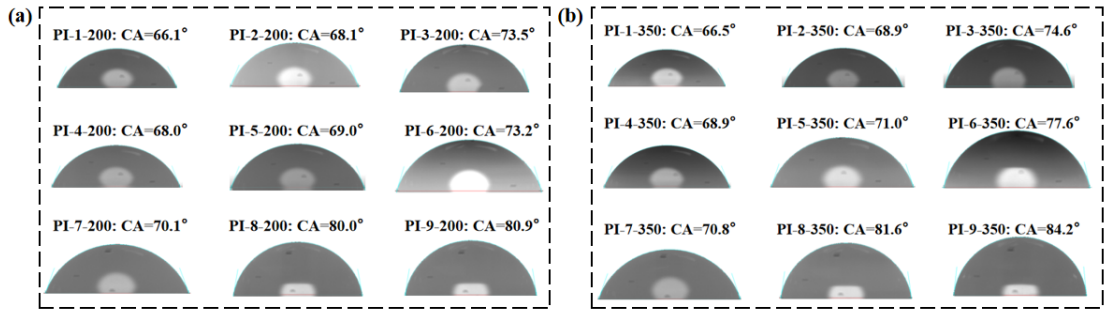


Fig. S11 Water contact angle of (a) PI films cured at 200 ℃ and (b) PI films cured at 350 ℃.

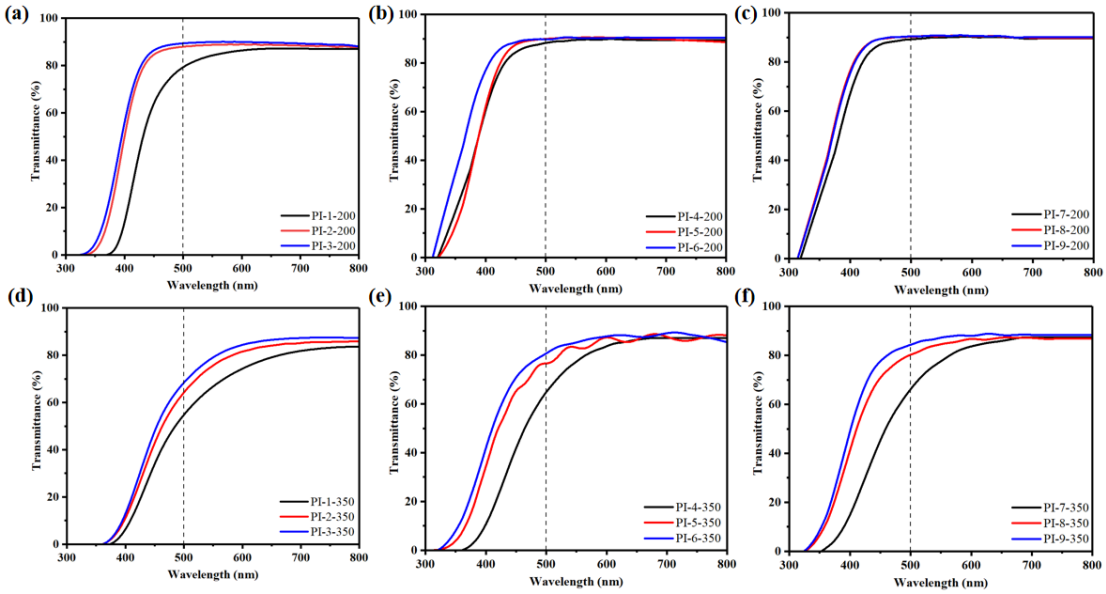


Fig. S12 UV-visible spectra of (a) PI films with anhydride TAHQ cured at 200 ℃, (b) PI films with anhydride BPEDA cured at 200 ℃, (c) PI films with anhydride TABPP cured at 200 ℃, (d) PI films with anhydride TAHQ cured at 350 ℃, (e) PI films with anhydride BPEDA cured at 350 ℃ and (f) PI films with anhydride TABPP cured at 350 ℃.

VIII. Additional detailed data of PI fims

Table S1 The end-to-end distance and total chain length values of the PI segment simulated

Sample name	$L_{end\text{-}to\text{-}end}$	L_o	$L_{end\text{-}to\text{-}end}/L_o$
PI-1	2.49 E+01	25.49	9.76 E-01
PI-2	2.96 E+01	31.41	9.42 E-01
PI-3	3.07 E+01	37.32	8.22 E-01
PI-4	2.75 E+01	31.44	8.75 E-01
PI-5	2.88 E+01	36.91	7.80 E-01
PI-6	2.96 E+01	42.91	6.90 E-01
PI-7	3.24 E+01	37.32	8.68 E-01
PI-8	3.29 E+01	43.24	7.61 E-01
PI-9	3.30 E+01	49.74	6.64 E-01

Table S2 The HOMO/LUMO values of diamine and anhydride monomers

Monomer name	Monomer type	LUMO	HOMO
PDA	diamine	- 0.03 eV	- 4.52 eV
IPDA	diamine	- 0.27 eV	- 5.34 eV
BIPDA	diamine	- 0.31 eV	- 5.47 eV
TAHQ	anhydride	- 3.44 eV	- 7.48 eV
BPEDA	anhydride	- 3.34 eV	- 6.97 eV
TABPP	anhydride	- 3.31 eV	- 6.65 eV

Table S3 Molecular weight of the resulting PAA solutions

Sample Name	*Mn* (Da)	*Mw* (Da)	Polydispersity
PAA-1	83777	151637	1.81
PAA-2	69433	125674	1.81
PAA-3	67794	127454	1.88
PAA-4	76719	137328	1.79
PAA-5	45902	84920	1.85
PAA-6	44458	82692	1.86
PAA-7	53281	97506	1.83
PAA-8	45371	84844	1.87
PAA-9	38159	71359	1.87

Table S4 Detailed data *d*-spacing, CTE and dichroic ratio of the resulting PI films cured at 350 °C

Sample Name	*d*-spacing (Å)	CTE (ppm/K)	Dichroic ratio	Dianhydride	Diamine
PI-1-350	3.93	-3.40	2.114	TAHQ	PDA
PI-2-350	5.36	73.26	2.026	TAHQ	IPDA
PI-3-350	5.24	65.68	2.043	TAHQ	BIPDA
PI-4-350	4.99	63.42	2.046	BPEDA	PDA
PI-5-350	5.29	69.93	2.037	BPEDA	IPDA
PI-6-350	5.40	70.12	2.035	BPEDA	BIPDA
PI-7-350	4.94	59.53	2.055	TABPP	PDA
PI-8-350	5.28	84.77	2.017	TABPP	IPDA
PI-9-350	5.53	81.56	2.020	TABPP	BIPDA

Table S5 Mechanical and thermal properties of the resulting PI films cured at 350 °C

Sample Name	Mechanical properties			Thermal properties			
	σ_{max}	ε_b	E	$T_{d,5\%}$	$T_{d,10\%}$	$T_{d,30\%}$	T_{HRI}
	[MPa]	[%]	[GPa]	[℃]	[℃]	[℃]	[℃]
PI-1-350	206	5.7	8.66	504	526	578	269
PI-2-350	113	35.6	2.30	448	461	522	241
PI-3-350	97	53.8	2.36	444	456	503	235
PI-4-350	111	20.4	2.54	448	459	490	232
PI-5-350	100	28.1	2.16	440	450	480	227
PI-6-350	96	50.8	2.18	445	456	484	230
PI-7-350	91	9.0	2.28	447	456	475	227
PI-8-350	84	12.2	1.89	444	453	473	226
PI-9-350	74	12.5	1.70	441	450	471	224

$T_{HRI} = 0.49 \times [T_{d,5\%} + 0.6 \times (T_{d,30\%} - T_{d,5\%})]$; $T_{d,5\%}$, $T_{d,10\%}$ and $T_{d,30\%}$ were the corresponding decomposition temperature of 5%, 10% and 30% weight loss, respectively.

Table S6 The glass transition temperature of the resulting PI films

Sample name	*Tg*[a]	*Tg*[b]
PI-1-350	-	361.4
PI-2-350	-	282.3
PI-3-350	-	254.2
PI-4-350	-	279.5
PI-5-350	-	275.2
PI-6-350	-	252.6
PI-7-350	-	253.1
PI-8-350	-	250.5
PI-9-350	-	239.8
PI-1-200	-	-
PI-2-200	265.9	254.1
PI-3-200	250.1	234.1
PI-4-200	257.6	246.8
PI-5-200	243.8	-
PI-6-200	222.9	233.0
PI-7-200	238.7	-
PI-8-200	233.8	-
PI-9-200	222.2	-

a: The T_g was measured by DSC, b: The T_g was measured by TMA.

Table S7 Dielectric properties, hydrophilicities and transmittance of synthesized PIs.

Sample Name	Dielectric properties [a]		Hydrophilicity		Transmittance [b] (%)
	D_k	D_f (×10^{-3})	WA (%)	WCA (°)	
PI-1-350	3.47	4.67	1.21	66.5	54.7
PI-2-350	2.94	7.57	1.14	68.9	64.2
PI-3-350	2.83	8.40	1.01	74.6	68.4
PI-4-350	2.92	7.10	0.98	68.9	64.8
PI-5-350	2.86	6.81	0.96	71.0	76.6
PI-6-350	2.67	4.53	0.87	77.6	80.7
PI-7-350	2.82	6.40	0.85	70.8	66.2
PI-8-350	2.73	5.69	0.73	81.6	80.3
PI-9-350	2.68	6.78	0.69	84.2	84.3

a: 10 GHz at room temperature; b: Transmittance at 500 nm.

Table S8 Solubility results of the PI films.

Samples	NMP	DMF	DMAc	DMSO	THF
PI-1-200	+	+	−	+	+
PI-2-200	+	+	+	+	+
PI-3-200	++	++	+	+	++
PI-4-200	+	+	+	+	+
PI-5-200	++	++	+	++	++
PI-6-200	++	++	+	++	++
PI-7-200	++	++	+	+	++
PI-8-200	++	++	+	++	++
PI-9-200	++	++	++	++	++
PI-1-350	−	−	−	−	−
PI-2-350	+	−	−	−	−
PI-3-350	+	+	−	−	−
PI-4-350	+	−	−	−	−
PI-5-350	+	+	−	−	−
PI-6-350	+	+	−	+	+
PI-7-350	+	+	−	−	−
PI-8-350	+	+	−	+	+
PI-9-350	+	+	+	+	+

++: Soluble at R.T. for 24 h; +: soluble at 60 °C for 24 h; −: insoluble at 60 °C for 24 h.