

Supplementary Material

Constructing High Performance Low-temperature Curable PI Materials by Manipulating the Side Group Effects of Diamine

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I. Experimental Section.

Materials

The solvents required for synthesis including *N,N*-Dimethylformamide (DMF) (99.8%), *N,N*-dimethylacetamide (DMAc) (99.8%), dimethyl sulfoxide (99.8%) (DMSO) methylbenzene (PhMe), ethanol (EtOH), and 1,4-dioxane were all commercially available, and used without other pretreatment.. The other raw materials for synthesis including 4-bromoresorcinol, phenylboronic acid, 5-pyrimidinylboronic acid, 85% hydrazine hydrate, 10% Pd/C, potassium carbonate, Pd132 and 4-chloronitrobenzene were commercially purchased and used without any further purification. Pyromellitic Dianhydride (PMDA) (99.0%) and 4,4'-oxydianiline (ODA) (99.9%) were obtained from Tokyo Chemical Industry (TCI) Co., Ltd. Additionally, ODA and PMDA were dried at 60°C and 120°C respectively in a vacuum oven for 10 h prior to use.

Instruments

The NMR spectra were tested by a Bruker AVANCE III 400 MHz spectrometer (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz) to verify the structure of the intermediates as well as the end products. The high-performance liquid chromatography (HPLC) was obtained by Ultimate 3000 to estimate the purity of diamine monomer PhNH₂ and SPMNH₂. The molecular weight of PAAs was measured by gel permeation chromatography (Waters Alliance e2695) at a flow rate of 1.0 mL/min at room temperature and DMF was used as eluent. The Fourier transform-infrared (FT-IR) spectra and polarized attenuated total reflection/Fourier transform infrared spectroscopy were recorded with Vertex 70 (Bruker, Germany) from 4000 cm⁻¹ to 600 cm⁻¹. Wide-angle X-ray data were collected on a Bruker D8 Advance diffractometer (Bruker, Germany) with CuK α radiation at a wavelength of 0.15418 nm with step scanning by 2θ intervals from 5° to 50°. The d -spacing was calculated according to Bragg's equation: $\lambda = 2d \cdot \sin\theta$. The thermal properties such as T_d (thermal decomposition temperature) were tested using a STD Q600 (TA Instruments, America). Coefficient of thermal expansion (CTE) of the PI films and T_g (glass transition temperature) were measured with thermal mechanical analysis (TMA) with

a heating rate of 10°C/min from 30-400°C by NETZSCHTMA 402. The mechanical properties of the samples were also measured using DMA Q800 with a constant stretching speed of 2 N min⁻¹ at room temperature. The high frequency dielectric constant (10 GHz) of PI films was measured by e5071c keysight ENA vector network analyzer, and the samples were pretreated in oven at 150°C for 2 h. Incidentally, most of the general methods are the same as our published paper before.

Calculations

The ground state (S₀) geometries of the three diamines were optimized by density functional theory (DFT) with B3LYP functional 6-31G basis set via Gaussian 16. The pKa values were calculated by B3LYP functional with Def2TZVP basis set. Besides, polarizable continuum model (PCM) with DMAc solvent has been included in pKa calculations. To obtain accurate proton energy under DMAc solvent, proton binding with 7 DMAc molecules have been calculated.

II. Synthesis of monomers.

Synthesis of 4,4'-([1,1'-biphenyl]-2,4-diylbis(oxy))dianiline (PhNH₂)

Synthesis of BrNO₂. As shown in **Scheme S1**, 4-bromoresorcinol (20.00 g, 105.81 mmol), 4-chloronitrobenzene (41.68 g, 264.54 mmol), potassium carbonate (36.56 g, 264.54 mmol), and DMSO (80 mL) were added into a 250 mL three-necked round bottom flask under nitrogen and reacted for 12 h after heating to 150°C. When the reaction was complete, the reaction solution was extracted with deionized water and dichloromethane. The crude product was collected and purified by chromatography on silica gel with petroleum ether (PE)/dichloromethane (DCM) as an eluent. The purified product was yellow powder with a yield of 90%. ¹H NMR (400 MHz, chloroform-*d*) δ 8.30 - 8.23 (m, 4H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.14 - 7.07 (m, 2H), 7.07 - 6.99 (m, 2H), 6.95 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.91 (d, *J* = 2.7 Hz, 1H). HRMS (APCI) *m/z*: [M + H]⁺ calcd for C₁₈H₁₂O₆N₂Br, 430.9811; found, 430.9819.

Synthesis of PhNO₂. The BrNO₂ (10.00 g, 23.19 mmol), phenylboronic acid (2.96 g, 24.35 mmol), potassium carbonate (6.41 g, 46.38 mmol), Pd132 were added into a 500 mL three-necked round bottom flask under nitrogen, and PhMe, EtOH and H₂O were used as reaction solvents, followed by a reaction at 90°C for 14 h. The crude product was extracted and then purified by chromatography on silica gel with petroleum ether (PE)/dichloromethane (DCM) as an eluent. The yield of the purified product was 80%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.30 - 8.25 (m, 2H), 8.18 - 8.12 (m, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.51 - 7.45 (m, 2H), 7.41 - 7.34 (m, 2H), 7.33 - 7.27 (m, 3H), 7.25 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.12 - 7.07 (m, 2H). HRMS (APCI) *m/z*: [M + H]⁺ calcd for C₂₄H₁₇O₆N₂, 429.1030; found, 429.1035.

Synthesis of PhNH₂. Firstly, the PhNO₂ (10.00 g, 23.34 mmol), 10% Pd/C (2.00 g), and 1,4-dioxane (40 mL) were added into a 500 mL three-necked round bottom flask under nitrogen. Then, 6 mL 85% hydrazine hydrate was added slowly dropwise to the reaction solution through a syringe after heating to 100°C with stirring. The reaction was terminated after 20 h under nitrogen atmosphere. Finally, Pd/C was filtered to remove and the crude product was purified by chromatography on silica gel with petroleum ether (PE)/ethyl acetate (EA) as an eluent. The purified product was white powder with a yield of 85%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.55 - 7.49 (m, 2H), 7.39 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.34 - 7.26 (m, 2H), 6.80 - 6.70 (m, 4H), 6.54 (ddd, *J* = 14.1, 8.6, 2.8 Hz, 5H), 6.29 (d, *J* = 2.5 Hz, 1H), 5.01 (s, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 160.74, 159.75, 156.86, 146.14, 146.09, 145.74, 145.43, 137.89, 132.04, 129.47, 128.56, 127.16, 125.18, 121.50, 121.38, 120.86, 115.34, 115.25, 110.41, 105.62. HRMS (APCI) *m/z*: [M + H]⁺ calcd for C₂₄H₂₁O₂N₂, 396.1577; found, 396.1595.

Synthesis of 4,4'-((4-(pyrimidin-5-yl)-1,3-phenylene)bis(oxy))dianiline (SPMNH₂)

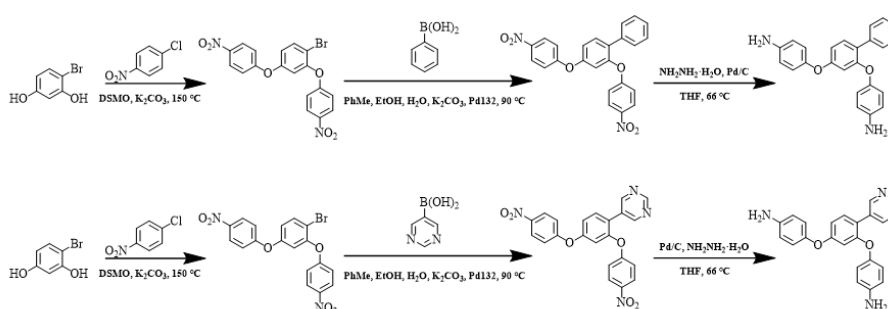
Synthesis of SPMNO₂. The BrNO₂ (10.00 g, 23.19 mmol), 5-pyrimidinylboronic acid

(3.02 g, 24.35 mmol), potassium carbonate (6.41 g, 46.38 mmol), Pd132, PhMe, EtOH and H₂O were added into a 500 mL three-necked round bottom flask to react for 16 h at 90°C, and a nitrogen atmosphere was maintained in the flask. The crude product was treated in the same way as synthesis of PhNO₂. The purified product was yellow powder with a yield of 80%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.14 (s, 1H), 8.98 (s, 2H), 8.33 - 8.27 (m, 2H), 8.22 - 8.15 (m, 2H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.31 (td, *J* = 8.3, 7.2, 2.4 Hz, 3H), 7.25 (d, *J* = 2.4 Hz, 1H), 7.22 - 7.15 (m, 2H). HRMS (APCI) *m/z*: [M + H]⁺ calcd for C₂₂H₁₅O₆N₄, 431.0911; found, 431.0916.

Synthesis of SPMNH₂. The SPMNO₂ (10.00 g, 23.24 mmol) and 10% Pd/C (2.00 g) were added into a 500 mL 3-neck round bottom flask under nitrogen, and 1,4-dioxane (40 mL) was used as the reaction solvent. After heating to reflux with stirring, 6 mL 85% hydrazine hydrate was added dropwise slowly by a syringe. And the reaction time was roughly 20 h. The crude product was treated in the same way as synthesis of PhNH₂. The purified product was yellow powder with a yield of 78%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.12 (s, 1H), 8.99 (s, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 6.83 - 6.72 (m, 4H), 6.62 - 6.51 (m, 5H), 6.32 (d, *J* = 2.4 Hz, 1H), 5.03 (s, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 161.17, 157.46, 156.99, 156.80, 146.33, 146.22, 145.33, 145.02, 132.11, 131.55, 121.49, 121.15, 117.90, 115.29, 115.24, 110.49, 105.04. HRMS (APCI) *m/z*: [M + H]⁺ calcd for C₂₂H₁₉O₂N₄, 371.1483; found, 371.1495.

Synthesis of 4,4'-([1,1'-biphenyl]-2,4-diylbis(oxy))dianiline (PMNH₂)

The diamine monomer was synthesized as reported in our previous research.¹



Scheme S1 Synthesis of PhNH₂ and SPMNH₂.

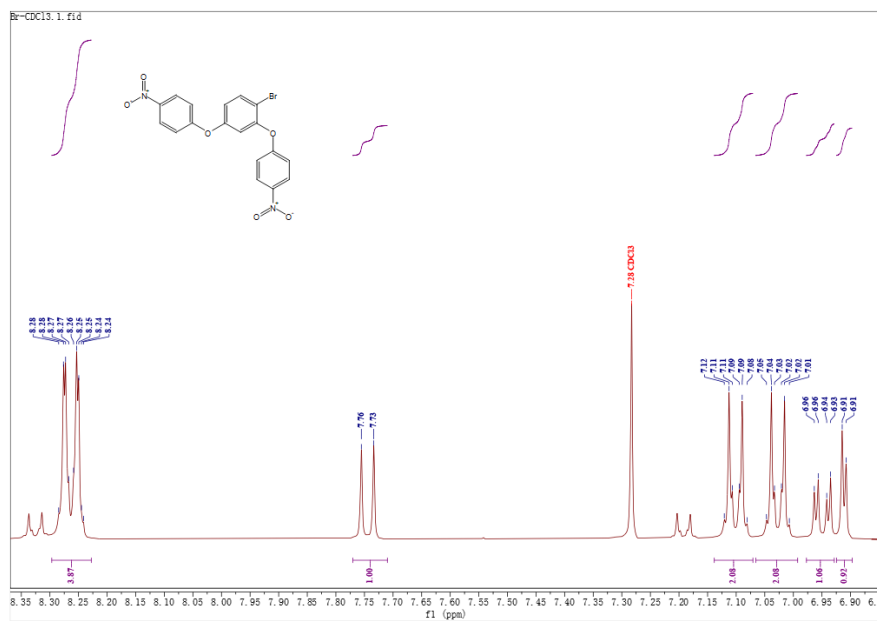


Fig. S1 ¹H NMR spectrum of BrNO₂ in chloroform-*d*.

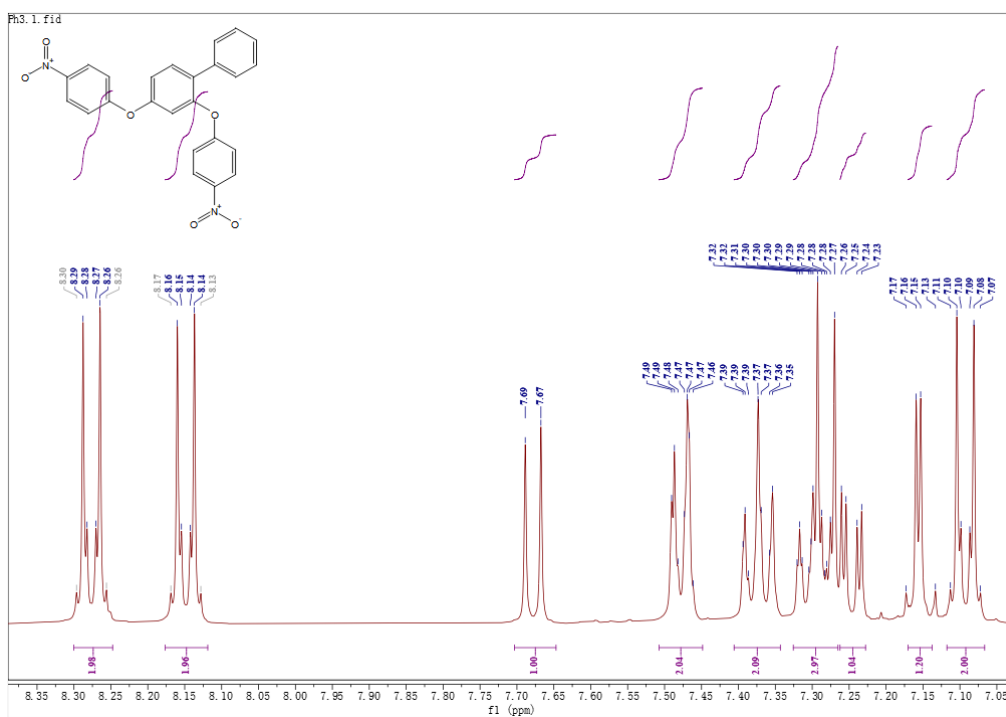


Fig. S2 ¹H NMR spectrum of PhNO₂ in DMSO-*d*₆.

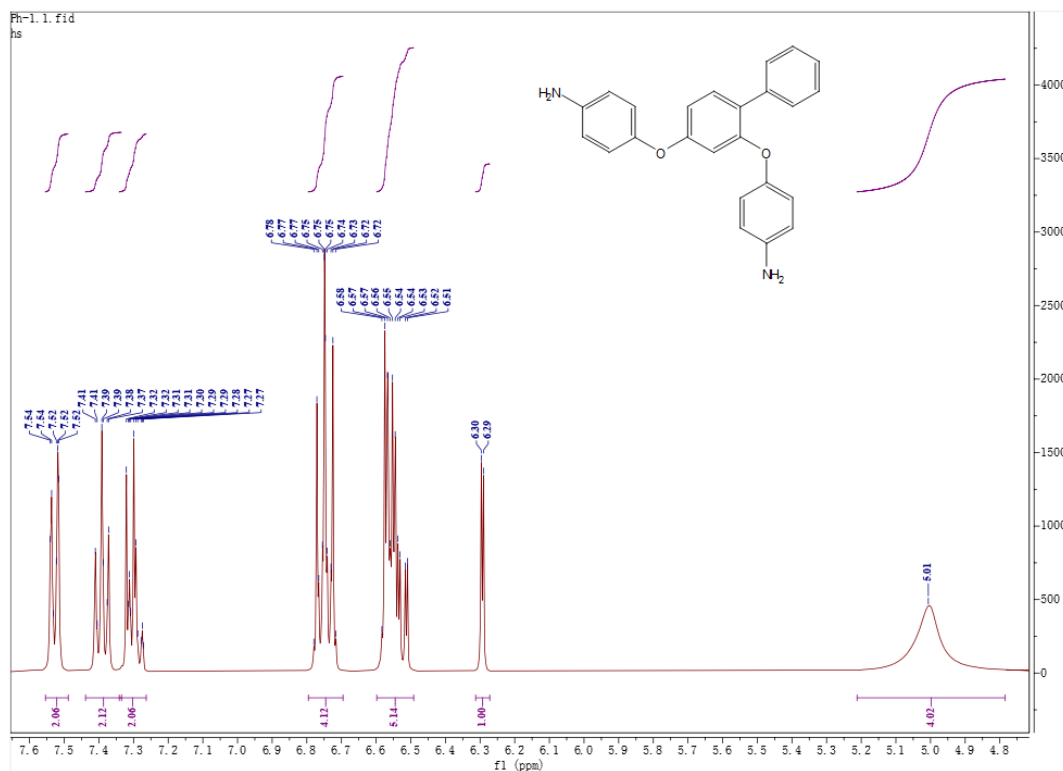


Fig. S3 ¹H NMR spectrum of PhNH₂ in DMSO-*d*₆.

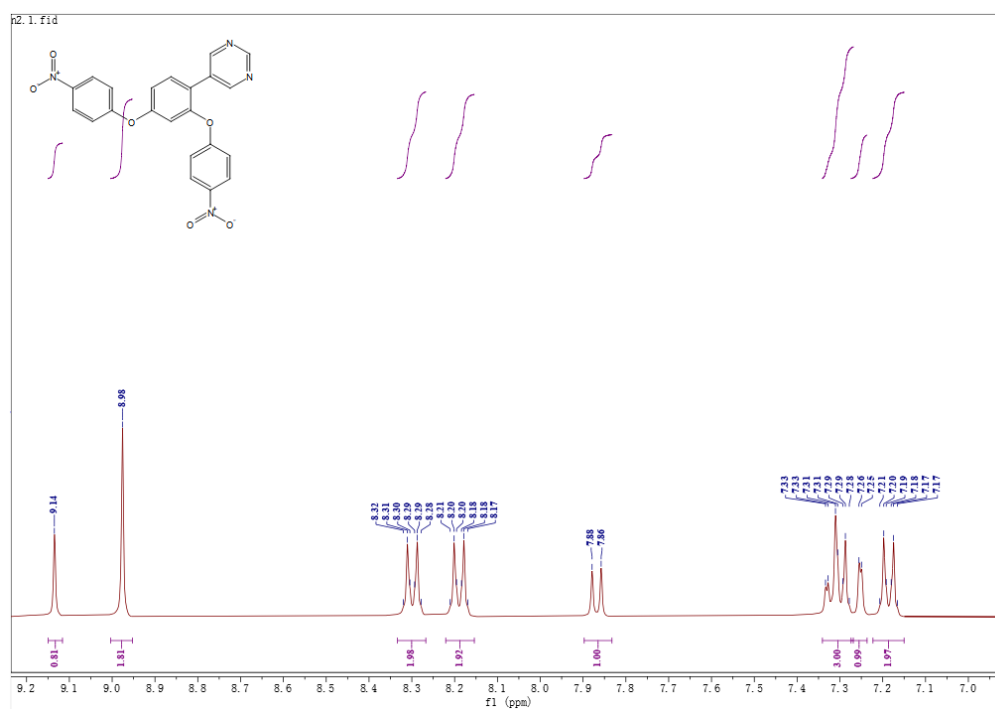


Fig. S4 ¹H NMR spectrum of SPMNO₂ in DMSO-*d*₆.

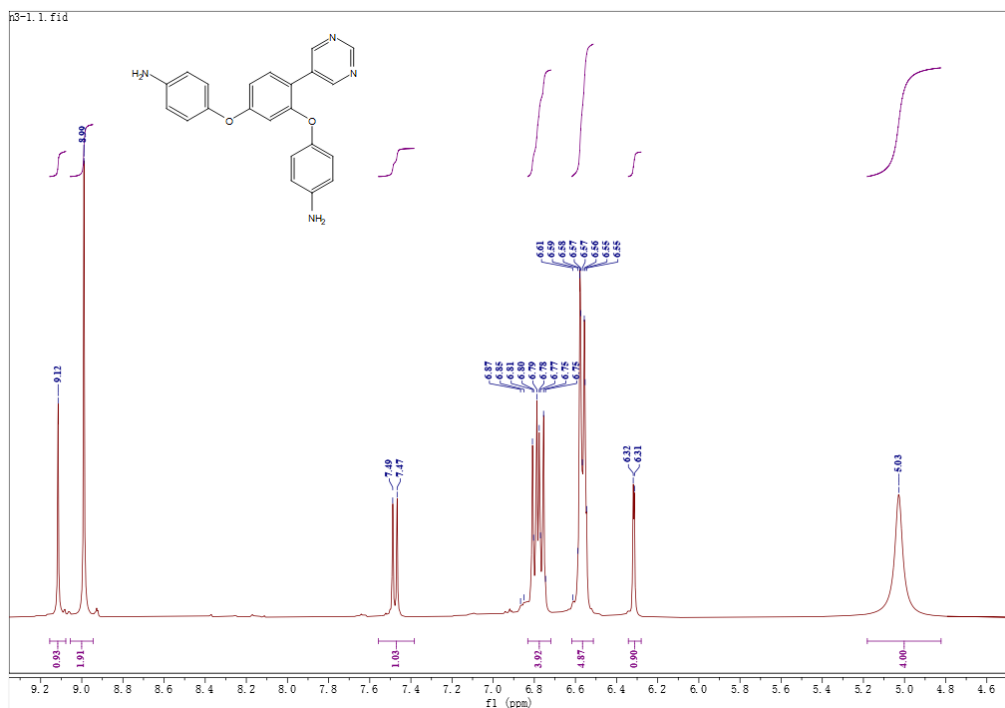


Fig. S5 ¹H NMR spectrum of SPMNH₂ in DMSO-*d*₆.

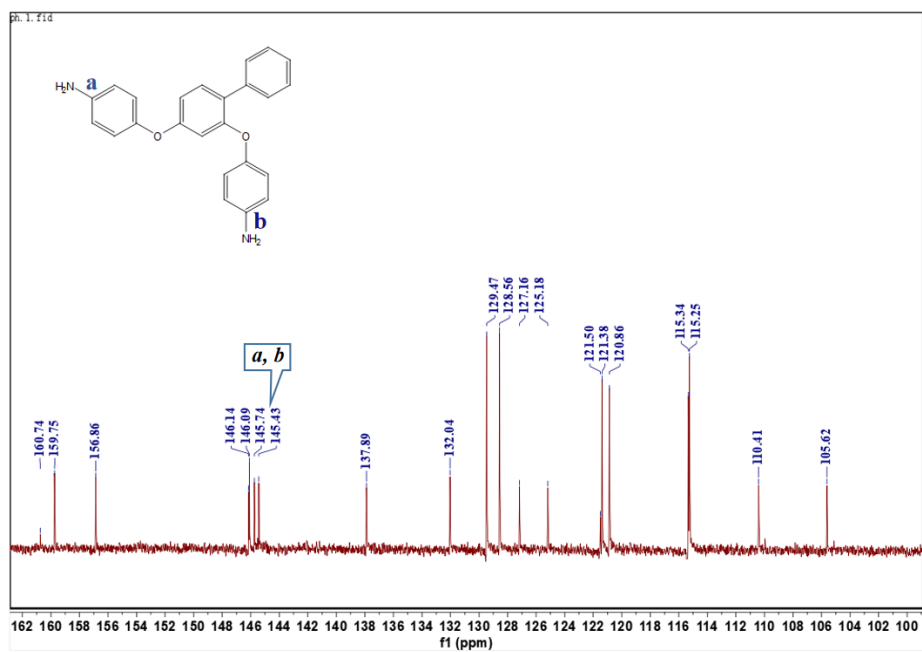


Fig. S6 ¹³C NMR spectrum of PhNH₂ in DMSO-*d*₆.

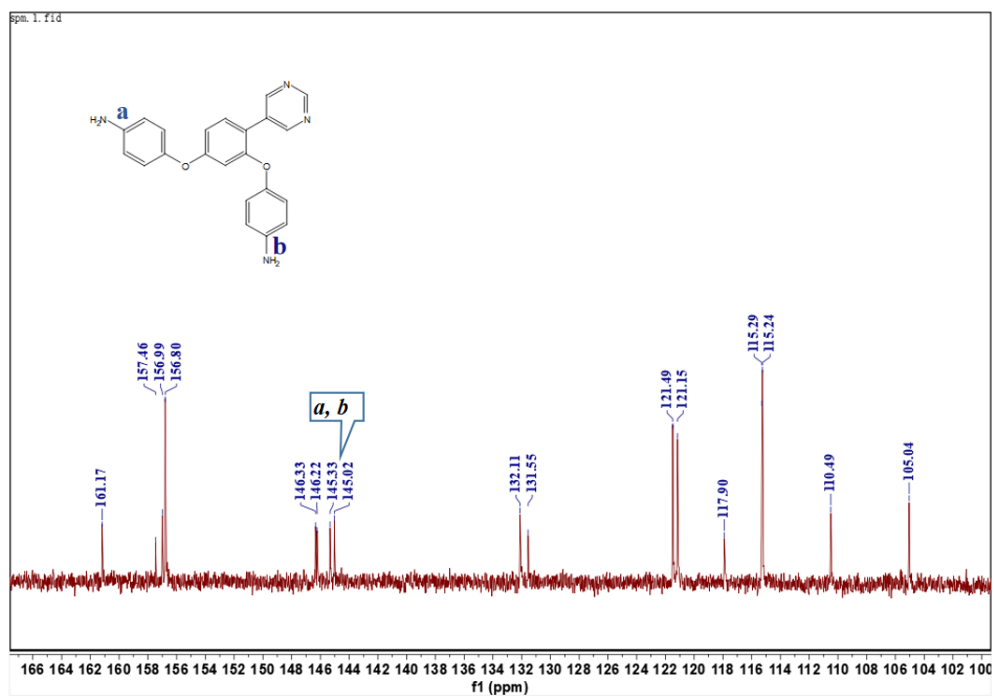


Fig. S7 ¹³C NMR spectrum of SPMNH₂ in DMSO-*d*₆.

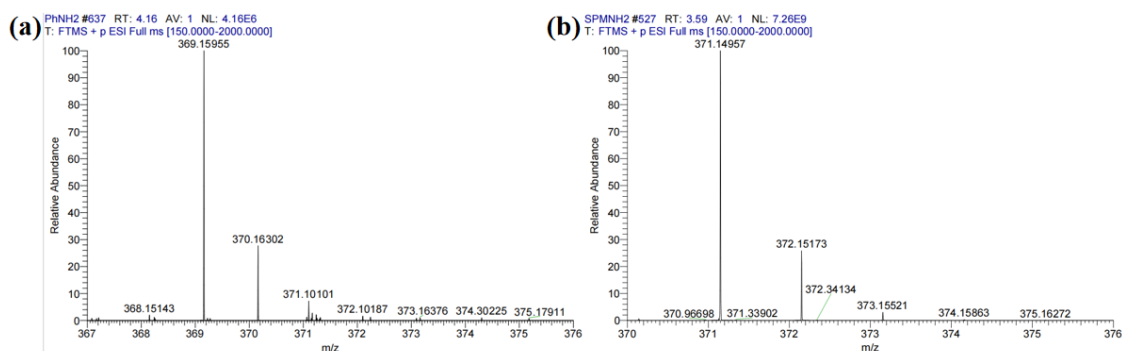


Fig. S8 HRMS spectrum of (a) PhNH₂ and (b) SPMNH₂.

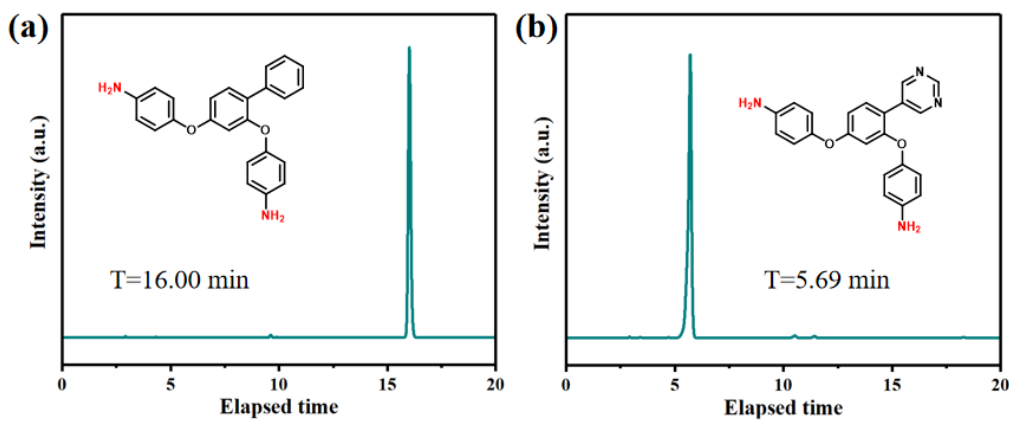


Fig. S9 HPLC spectrum of (a) PhNH₂ and (b) SPMNH₂.

III. Additional FTIR spectra and XRD patterns of PI films.

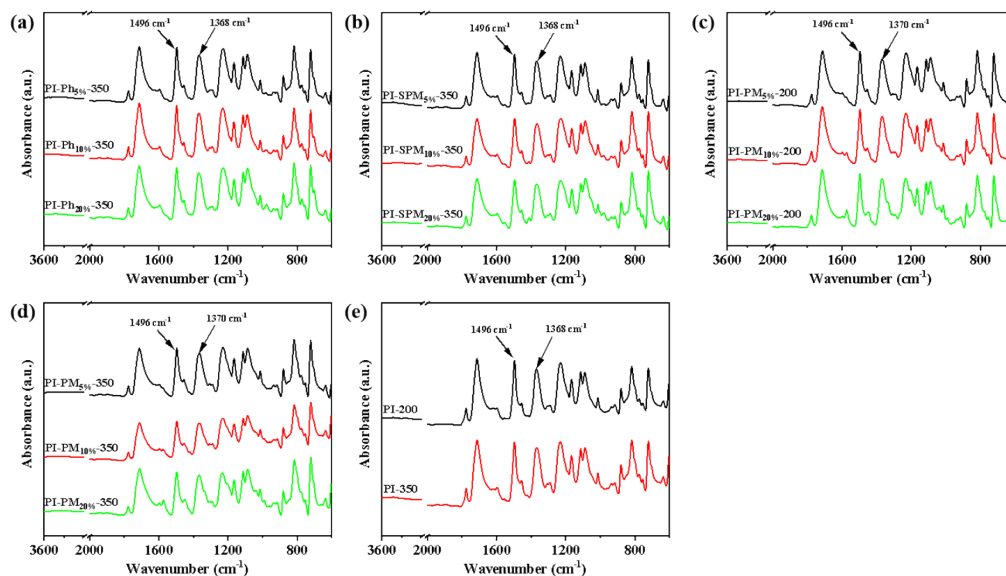


Fig. S10 FTIR spectra of (a) (PhNH₂/ODA)/PMDA co-PI films cured at 350°C, (b) (SPMNH₂/ODA)/PMDA co-PI films cured at 350°C, (c) (PMNH₂/ODA)/PMDA co-PI films cured at 200°C, (d) (PMNH₂/ODA)/PMDA co-PI films cured at 350°C and (e) ODA/PMDA PI films.

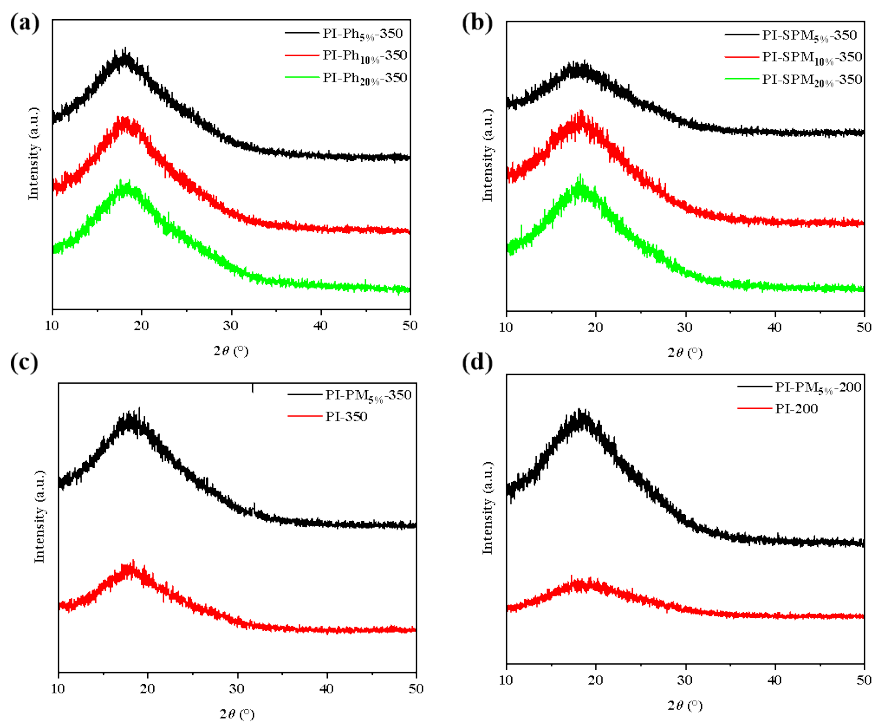


Fig. S11 XRD patterns of (a) (PhNH₂/ODA)/PMDA co-PI films cured at 350°C, (b) (SPMNH₂/ODA)/PMDA co-PI films cured at 350°C, (c) PI-PM_{5%}-350 and PI-350, (d) PI-PM_{5%}-200 and PI-200.

IV. Additional TMA curves and linearly polarized IR spectroscopy of PI films.

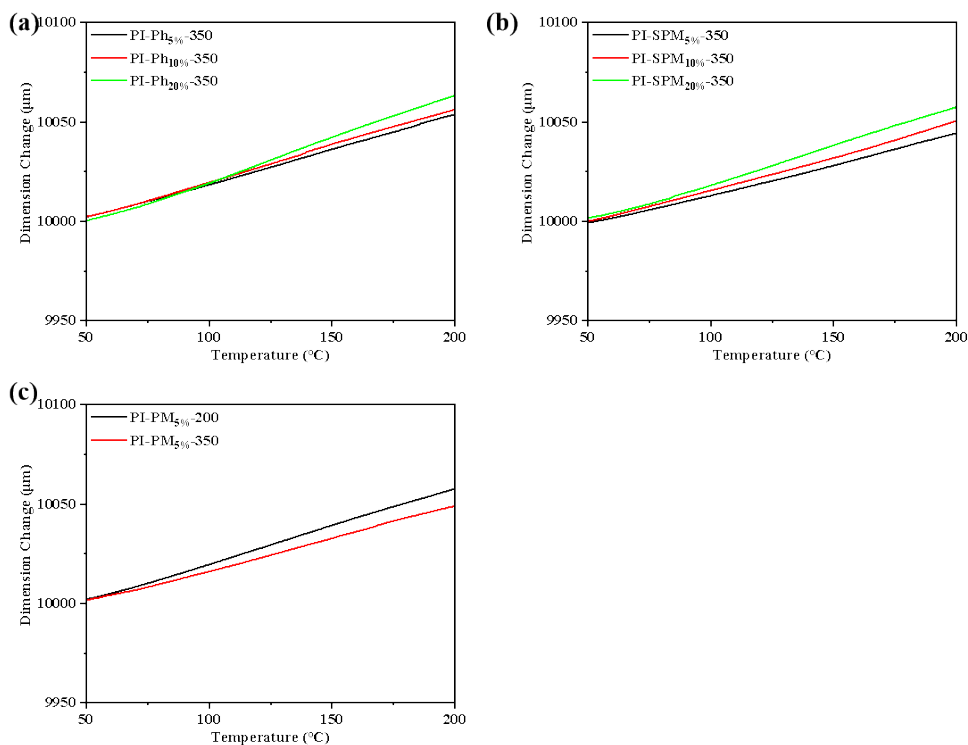


Fig. S12 TMA curves of (a) (PhNH₂/ODA)/PMDA co-PI films cured at 350°C, (b) (SPMNH₂/ODA)/PMDA co-PI films cured at 350°C and (c) PI-PM_{5%}-200 and PI-PM_{5%}-350.

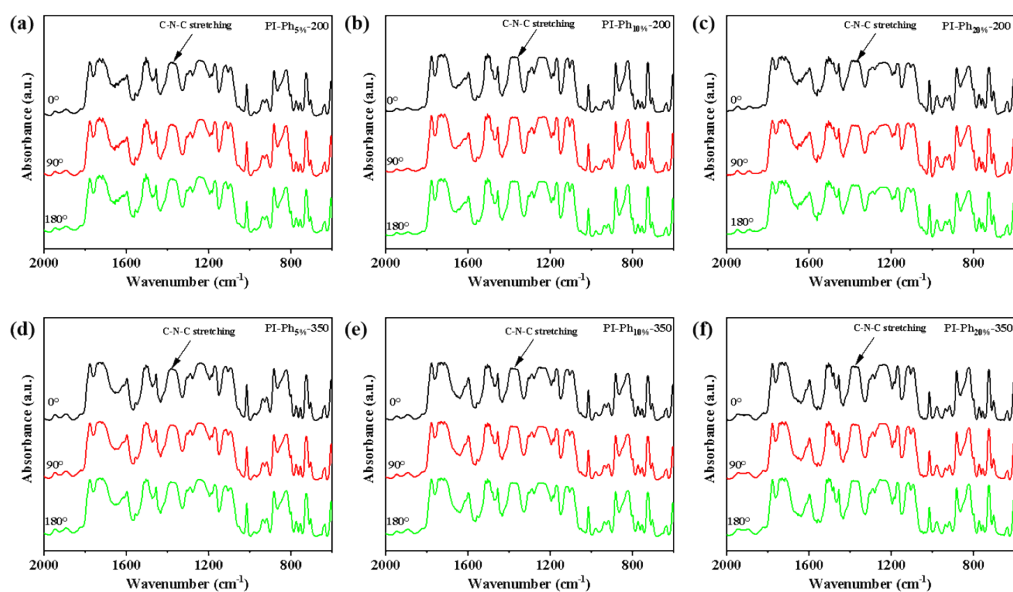


Fig. S13 Linearly polarized IR spectroscopy of (a) PI-Ph_{5%}-200, (b) PI-Ph_{10%}-200, (c) PI-Ph_{20%}-

200, (d) PI-Ph_{5%}-350, (e) PI-Ph_{10%}-350, (f) PI-Ph_{20%}-350.

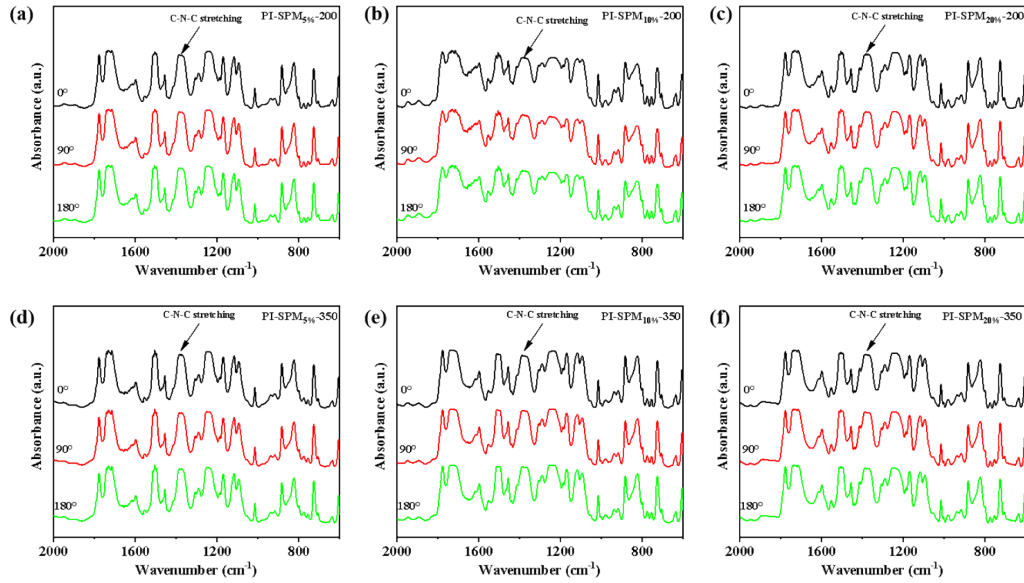


Fig. S14 Linearly polarized IR spectroscopy of (a) PI-SPM_{5%}-200, (b) PI-SPM_{10%}-200, (c) PI-SPM_{20%}-200, (d) PI-SPM_{5%}-350, (e) PI-SPM_{10%}-350, (f) PI-SPM_{20%}-350.

V. Additional TGA curves and stress-strain curves of PI films.

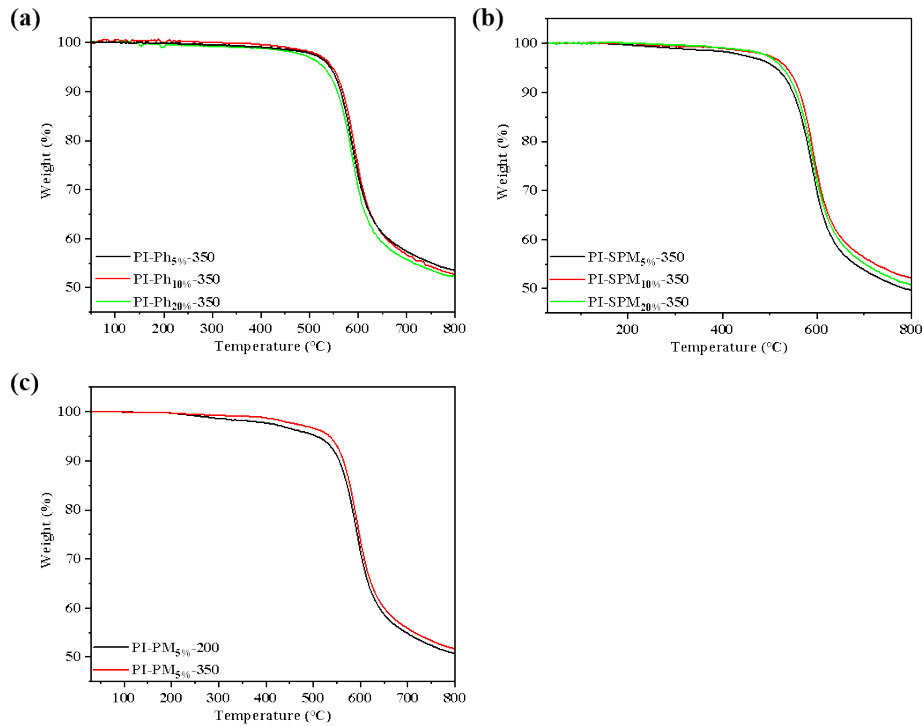


Fig. S15 TGA curves of (a) (PhNH₂/ODA)/PMDA co-PI films cured at 350°C, (b)

(SPMNH₂/ODA)/PMDA co-PI films cured at 350°C and (c) PI-PM_{5%}-200 and PI-PM_{5%}-350.

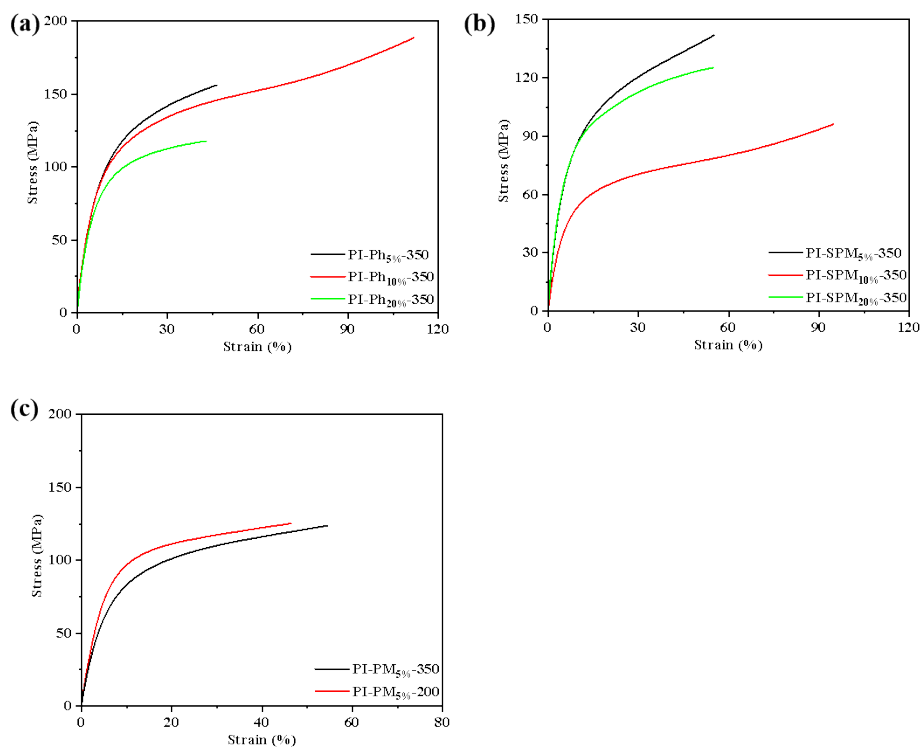


Fig. S16 Typical stress–strain curves of (a) (PhNH₂/ODA)/PMDA co-PI films cured at 350°C, (b) (SPMNH₂/ODA)/PMDA co-PI films cured at 350°C, (c) PI-PM_{5%}-350 and PI-PM_{5%}-200.

VI. Additional detailed data of PI films.

Table S1 Molecular weight of the resulting PAA solutions

Sample Name	<i>M_n</i> (Da)	<i>M_w</i> (Da)	Polydispersity
PAA-0	70673	98942	1.40
PAA-Ph _{5%}	70248	98347	1.40
PAA-Ph _{10%}	69843	99177	1.42
PAA-Ph _{20%}	61082	86736	1.42
PAA-SPM _{5%}	70449	100742	1.43
PAA-SPM _{10%}	68751	97626	1.42
PAA-SPM _{20%}	60993	86610	1.42
PAA-PM _{5%}	70232	94813	1.35
PAA-PM _{10%}	62998	85047	1.35
PAA-PM _{20%}	60674	80090	1.32

Table S2 Detailed data of *d*-spacing, CTE and dichroic ratio of the resulting PI films

Sample Name	ID ₁₃₈₀ (%)	<i>d</i> -Spacing (Å)	CTE (ppm/K)	Dichroic ratio	Diamine Ratio(n)
PI-350	-	4.88	34	2.12	ODA
PI-Ph _{5%} -350	-	4.89	34	2.22	ODA:PhNH ₂ =0.5:9.5
PI-Ph _{10%} -350	-	4.84	36	2.10	ODA:PhNH ₂ =1.0:9.0
PI-Ph _{20%} -350	-	4.79	42	2.11	ODA:PhNH ₂ =2.0:8.0
PI-SPM _{5%} -350	-	4.87	30	2.11	ODA:SPMNH ₂ =0.5:9.5
PI-SPM _{10%} -350	-	4.88	34	2.26	ODA:SPMNH ₂ =1.0:9.0
PI-SPM _{20%} -350	-	4.84	37	2.09	ODA:SPMNH ₂ =2.0:8.0
PI-PM _{5%} -350	-	4.85	42	2.14	ODA:PMNH ₂ =0.5:9.5
PI-PM _{10%} -350	-	4.79	35	2.21	ODA:PMNH ₂ =1.0:9.0
PI-PM _{20%} -350	-	4.65	37	2.16	ODA:PMNH ₂ =2.0:8.0
PI-PM _{5%} -200	94.1	4.81	37	2.14	ODA:PMNH ₂ =0.5:9.5
PI-PM _{10%} -200	92.5	5.06	28	2.21	ODA:PMNH ₂ =1.0:9.0
PI-PM _{20%} -200	92.8	4.85	28	2.24	ODA:PMNH ₂ =2.0:8.0

Table S3 Mechanical and thermal properties of the resulting PI films

Sample Name	<i>T</i> _{d5%} (°C)	<i>T</i> _{d10%} (°C)	<i>T</i> _g (°C)	<i>E</i> (GPa)	σ_{\max} (MPa)	ϵ_b (%)
PI-350	547	561	416	2.56	184	67.2
PI-Ph _{5%} -350	546	569	361	2.58	156	46.5
PI-Ph _{10%} -350	529	557	360	2.78	189	112.0
PI-Ph _{20%} -350	542	564	351	2.37	118	42.9
PI-SPM _{5%} -350	513	549	370	2.45	142	55.1
PI-SPM _{10%} -350	536	563	361	1.47	96	94.8
PI-SPM _{20%} -350	527	556	345	2.76	125	54.9
PI-PM _{5%} -350	534	564	362	2.34	124	54.4
PI-PM _{10%} -350	502	541	393	2.73	154	68.2
PI-PM _{20%} -350	467	528	385	2.88	137	31.1
PI-PM _{5%} -200	507	555	346	2.70	125	46.4
PI-PM _{10%} -200	455	532	373	2.83	130	50.6
PI-PM _{20%} -200	447	511	352	3.06	120	61.6

Table S4 Contact angle and optical properties of the resulting PI films

Sample Name	Dielectric constant (10 GHz)	Dielectric loss factors (10 ⁻²) (10 GHz)	Contact Angle (°)
PI-350	3.36	1.52	67.8
PI-Ph _{5%} -350	3.49	1.94	73.3
PI-Ph _{10%} -350	3.42	1.60	73.3
PI-Ph _{20%} -350	3.49	1.74	78.1
PI-SPM _{5%} -350	3.30	3.38	73.2
PI-SPM _{10%} -350	3.46	2.39	72.1
PI-SPM _{20%} -350	3.33	2.18	76.6
PI-PM _{5%} -350	3.54	2.35	72.3
PI-PM _{10%} -350	3.41	3.31	75.9
PI-PM _{20%} -350	3.51	2.90	79.6
PI-PM _{5%} -200	3.63	2.82	69.7
PI-PM _{10%} -200	3.68	4.07	62.4
PI-PM _{20%} -200	3.49	3.16	69.5

References

- 1 X. Lv, S. Qiu, S. Huang, K. Wang and J. Li, *Polymer*, 2022, **261**, 125418.