

## Supporting Information

### Thermostable birefringent copolyimide films based on azobenzene- containing pyrimidine diamines

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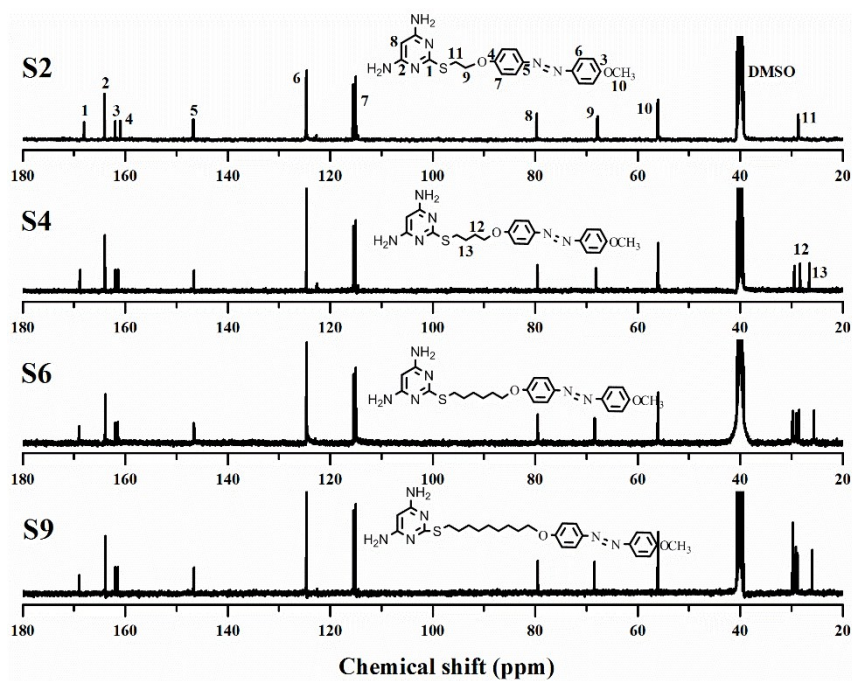
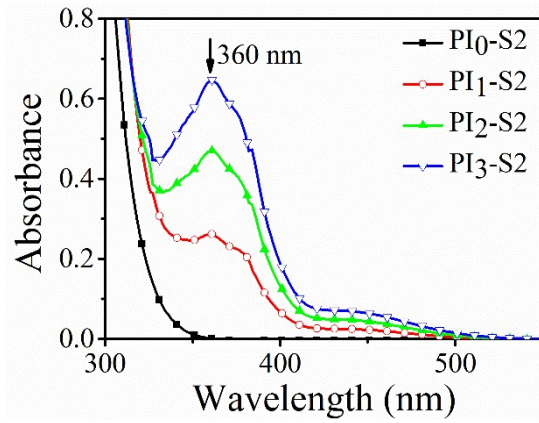
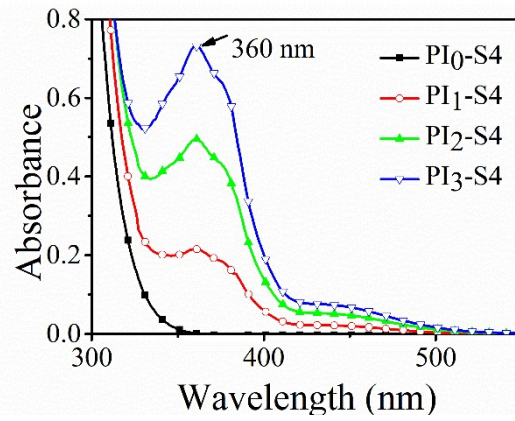


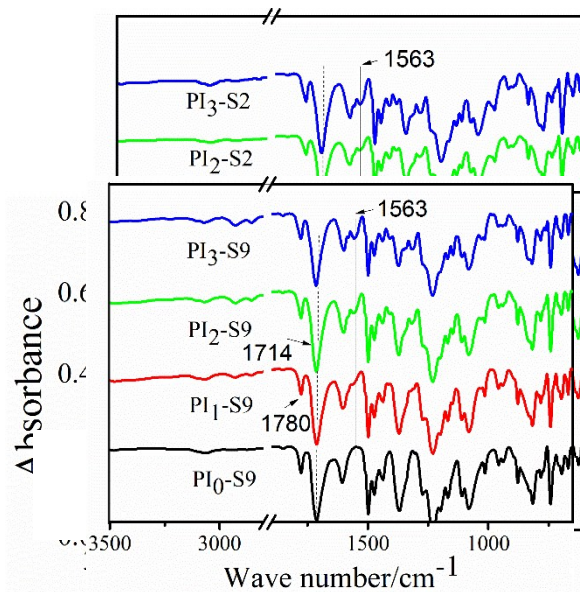
Figure S1.  $^{13}\text{C}$  NMR spectra of diamines in  $[\text{D}_6]$  DMSO.



**Figure S2.** UV-vis absorption spectra of the PAAs of **Plx-S2** in DMAc solution (concentration 0.05 mg/mL).



**Figure S3.** UV-vis absorption spectra of the PAAs of **Plx-S4** in DMAc solution (concentration 0.05 mg/mL).



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**Figure S7.** ATR FTIR spectra of **Plx-S9**.



Figure S8. Optical photographs of **PIx-S2** films.



Figure S9. Optical photographs of **PIx-S4** films.



Figure S10. Optical photographs of **PIx-S9** films.

**Table S1.** Thermal performances of PIs and molecular weights of PAAs.

<b>PIs</b>	<b><math>T_g^b</math> (°C)</b>	<b><math>T_{d5}^c</math> (°C)</b>	<b><math>T_{d10}^c</math> (°C)</b>	<b><math>R_w^d</math> (%)</b>	<b><math>M_n^e</math> (<math>\times 10^{-4}</math>)</b>	<b><math>M_w^e</math> (<math>\times 10^{-4}</math>)</b>	<b><math>M_w/M_n</math></b>
<b>PI<sub>0</sub><sup>a</sup></b>	245	514	552	54.9	12.09	23.15	1.91
<b>PI<sub>1</sub>-S2</b>	229	394	500	57.3	3.71	7.75	2.09
<b>PI<sub>2</sub>-S2</b>	207	376	432	55.2	1.81	4.57	2.52
<b>PI<sub>3</sub>-S2</b>	202	374	407	51.7	1.09	3.19	2.92
<b>PI<sub>1</sub>-S4</b>	235	465	492	56.9	3.59	7.69	2.14
<b>PI<sub>2</sub>-S4</b>	219	431	458	46.5	2.78	5.35	1.93
<b>PI<sub>3</sub>-S4</b>	199	401	435	53.7	1.57	3.02	1.93
<b>PI<sub>1</sub>-S6</b>	224	453	522	56.5	2.67	5.18	1.94
<b>PI<sub>2</sub>-S6</b>	214	424	465	47.3	2.28	4.15	1.82
<b>PI<sub>3</sub>-S6</b>	196	414	444	49.3	1.78	4.29	2.41
<b>PI<sub>1</sub>-S9</b>	226	412	465	51.8	1.60	3.94	2.46
<b>PI<sub>2</sub>-S9</b>	191	400	440	50.1	1.24	3.49	2.81
<b>PI<sub>3</sub>-S9</b>	174	370	408	40.7	1.59	3.69	2.32

<sup>a</sup> PI<sub>0</sub> was prepared by polymerization of ODA and ODPA. <sup>b</sup> From the second DSC heating scan at a heating rate of 20 °C/min in nitrogen. <sup>c</sup> Temperatures corresponding to 5% and 10% weight losses by thermogravimetry at a heating rate of 20 °C/min in nitrogen. <sup>d</sup> Residual weight % at 700 °C. <sup>e</sup> Measured by GPC in DMF; polystyrene was used as a standard.

**Table S2.** Sample IDs, compositions, and mechanical properties of co-polyimide films.

Sample ID	Sn:ODA	Film quality	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
PI <sub>0</sub> <sup>a</sup>	0:1	flexible	126.8	9.6	2.34
PI <sub>1</sub> -S2	1:9	flexible	139.1	7.6	2.75
PI <sub>2</sub> -S2	2:8	flexible	81.9	3.7	1.98
PI <sub>3</sub> -S2	3:7	rigid	--	--	--
PI <sub>1</sub> -S4	1:9	flexible	109.1	6.6	2.10
PI <sub>2</sub> -S4	2:8	flexible	94.3	5.5	1.97
PI <sub>3</sub> -S4	3:7	flexible	64.3	3.1	3.02
PI <sub>1</sub> -S6	1:9	flexible	94.2	5.1	1.94
PI <sub>2</sub> -S6	2:8	flexible	96.7	5.0	2.15
PI <sub>3</sub> -S6	3:7	flexible	83.5	5.3	2.19
PI <sub>1</sub> -S9	1:9	flexible	75.2	3.8	2.16
PI <sub>2</sub> -S9	2:8	flexible	65.6	4.3	2.02
PI <sub>3</sub> -S9	3:7	flexible	73.9	4.8	1.85

<sup>a</sup>PI<sub>0</sub> was prepared by polymerization of ODA and ODPA.

The <sup>1</sup>H NMR of PAAs and elemental analysis of PIs were recorded to confirm the synthesis of azo-PIs as following:

**PAA<sub>0</sub>:** <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 6.99 (ArH, 4H), 7.22 (ArH, 4H), 7.70 (ArH, 4H), 7.98 (ArH, 3H); 10.42 (CONH, 2H), 10.59 (CONH, 2H). **PI<sub>0</sub>:** Anal. Calcd. for C<sub>280</sub>H<sub>140</sub>N<sub>20</sub>O<sub>60</sub> (4740): C, 70.88%; N, 5.91%; H, 3.38%. Found: C, 69.38%; N, 5.86%; H, 3.33%.

**PAA<sub>1</sub>-S2:** <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 3.39 (SCH<sub>2</sub>, 2H), 3.83 (OCH<sub>3</sub>, 3H), 4.22 (OCH<sub>2</sub>, 2H), 5.18 (ArH, 1H), 7.07 (ArH, 4H), 7.24 (ArH, 4H), 7.48 (ArH,4H), 7.65 (ArH, 4H), 7.82 (ArH,4H), 7.95 (ArH, 4H), 10.40 (CONH, 2H), 10.71 (CONH, 2H), 13.23 (COOH, 4H). **PI<sub>1</sub>-S2:** Anal. Calcd. for C<sub>287</sub>H<sub>148</sub>N<sub>24</sub>O<sub>61</sub>S (4936): C, 69.77%; N, 6.81%; H, 2.99%. Found: C, 68.58%; N, 6.80%; H, 3.42%.

**PAA<sub>2</sub>-S2:** <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 3.36 (SCH<sub>2</sub>, 2H), 3.81

(OCH<sub>3</sub>, 3H), 4.24 (OCH<sub>2</sub>, 2H), 5.16 (ArH, 1H), 7.01 (ArH, 4H), 7.25 (ArH, 4H), 7.48 (ArH, 4H), 7.67 (ArH, 4H), 7.83 (ArH, 4H), 7.96 (ArH, 4H), 10.37 (CONH, 2H), 10.61 (CONH, 2H), 13.19 (COOH, 4H). **PI<sub>2</sub>-S2**: Anal. Calcd. for C<sub>294</sub>H<sub>156</sub>N<sub>28</sub>O<sub>62</sub>S<sub>2</sub> (5133): C, 68.73%; N, 7.64%; H, 3.04%. Found: C, 68.47%; N, 7.43%; H, 3.27%.

**PAA<sub>3</sub>-S2**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 3.37 (SCH<sub>2</sub>, 2H), 3.79 (OCH<sub>3</sub>, 3H), 4.27 (OCH<sub>2</sub>, 2H), 5.09 (ArH, 1H), 7.08 (ArH, 4H), 7.23 (ArH, 4H), 7.47 (ArH, 4H), 7.65 (ArH, 4H), 7.81 (ArH, 4H), 7.94 (ArH, 4H), 10.33 (CONH, 2H), 10.51 (CONH, 2H), 13.25 (COOH, 4H). **PI<sub>3</sub>-S2**: Anal. Calcd. for C<sub>301</sub>H<sub>164</sub>N<sub>32</sub>O<sub>63</sub>S<sub>3</sub> (5329): C, 67.78%; N, 8.41%; H, 3.08%. Found: C, 67.39%; N, 8.24%; H, 3.37%.

**PAA<sub>1</sub>-S4**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.80 (SCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.85 (CH<sub>2</sub>CH<sub>2</sub>O, 2H), 3.04 (SCH<sub>2</sub>, 2H), 3.83 (OCH<sub>3</sub>, 3H), 4.08 (OCH<sub>2</sub>, 2H), 5.18 (ArH, 1H), 6.93 (ArH, 4H), 7.11 (ArH, 4H), 7.21 (ArH, 4H), 7.46 (ArH, 4H), 7.64 (ArH, 4H), 7.93 (ArH, 4H), 10.34 (CONH, 2H), 10.42 (CONH, 2H), 13.25 (COOH, 4H). **PI<sub>1</sub>-S4**: Anal. Calcd. for C<sub>289</sub>H<sub>152</sub>N<sub>24</sub>O<sub>61</sub>S (4965): C, 69.85%; N, 6.77%; H, 3.06%. Found: C, 69.27%; N, 6.83%; H, 3.32%.

**PAA<sub>2</sub>-S4**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.77 (SCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.84 (CH<sub>2</sub>CH<sub>2</sub>O, 2H), 3.08 (SCH<sub>2</sub>, 2H), 3.83 (OCH<sub>3</sub>, 3H), 4.08 (OCH<sub>2</sub>, 2H), 5.16 (ArH, 1H), 6.92 (ArH, 4H), 7.08 (ArH, 4H), 7.27 (ArH, 4H), 7.43 (ArH, 4H), 7.72 (ArH, 4H), 7.98 (ArH, 4H), 10.40 (CONH, 2H), 10.64 (CONH, 2H), 13.17 (COOH, 4H). **PI<sub>2</sub>-S4**: Anal. Calcd. for C<sub>298</sub>H<sub>164</sub>N<sub>28</sub>O<sub>62</sub>S<sub>2</sub> (5189): C, 68.92%; N, 7.55%; H, 3.16%. Found: C, 68.26%; N, 7.42%; H, 3.46%.

**PAA<sub>3</sub>-S4**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.75 (SCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.83 (CH<sub>2</sub>CH<sub>2</sub>O, 2H), 3.06 (SCH<sub>2</sub>, 2H), 3.83 (OCH<sub>3</sub>, 3H), 4.08 (OCH<sub>2</sub>, 2H), 5.17 (ArH, 1H), 6.94 (ArH, 4H), 7.10 (ArH, 4H), 7.24 (ArH, 4H), 7.43 (ArH, 4H), 7.70 (ArH, 4H), 7.94 (ArH, 4H), 10.37 (CONH, 2H), 10.41 (CONH, 2H), 13.19 (COOH, 4H). **PI<sub>3</sub>-S4**: Anal. Calcd. for C<sub>307</sub>H<sub>176</sub>N<sub>32</sub>O<sub>63</sub>S<sub>3</sub> (5413): C, 68.06%; N, 8.28%; H, 3.25%. Found: C, 67.92%; N, 8.16%; H, 3.17%.

**PAA<sub>2</sub>-S6**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.41–1.43 (OCH<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>S, 4H), 1.60 (SCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.75 (OCH<sub>2</sub>CH<sub>2</sub>, 2H), 2.98 (SCH<sub>2</sub>, 2H), 3.85 (OCH<sub>3</sub>, 3H), 4.06 (OCH<sub>2</sub>, 2H), 5.14 (ArH, 1H), 7.11 (ArH, 4H), 7.23 (ArH, 4H), 7.52 (ArH, 4H), 7.71 (ArH, 4H), 7.80 (ArH, 4H), 7.93 (ArH, 4H), 10.36 (CONH, 2H), 10.41 (CONH, 2H), 13.13 (COOH, 4H). **PI<sub>2</sub>-S6**: Anal. Calcd. for C<sub>302</sub>H<sub>172</sub>N<sub>28</sub>O<sub>62</sub>S<sub>2</sub> (5245): C, 69.09%; N, 7.47%; H, 3.28%. Found: C, 68.31%; N, 7.26%; H, 3.89%.

**PAA<sub>3</sub>-S6**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.41–1.45 (OCH<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>S, 4H), 1.62 (SCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.75 (OCH<sub>2</sub>CH<sub>2</sub>, 2H), 2.95 (SCH<sub>2</sub>, 2H), 3.83 (OCH<sub>3</sub>, 3H), 4.05 (OCH<sub>2</sub>, 2H), 5.17 (ArH, 1H), 7.10 (ArH, 4H), 7.22 (ArH, 4H), 7.53 (ArH, 4H), 7.67 (ArH, 4H), 7.81 (ArH, 4H), 7.93 (ArH, 4H), 10.34 (CONH, 2H), 10.43 (CONH, 2H), 13.03 (COOH, 4H). **PI<sub>3</sub>-S6**: Anal. Calcd. for C<sub>313</sub>H<sub>188</sub>N<sub>32</sub>O<sub>63</sub>S<sub>3</sub> (5497): C, 68.33%; N, 8.15%; H, 3.42%. Found: C, 67.92%; N, 8.06%; H, 3.63%.

**PAA<sub>1</sub>-S9**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.73–1.35 (OCH<sub>2</sub>C<sub>7</sub>H<sub>14</sub>CH<sub>2</sub>S, 14H), 2.94 (SCH<sub>2</sub>, 2H), 3.77 (OCH<sub>3</sub>, 3H), 3.99 (OCH<sub>2</sub>, 2H), 5.17 (ArH, 1H), 6.92 (ArH, 4H), 7.11 (ArH, 4H), 7.24 (ArH, 4H), 7.45 (ArH, 4H), 7.67

(ArH,4H), 7.97 (ArH, 4H), 10.38 (CONH, 2H), 10.44 (CONH, 2H), 13.18 (COOH, 4H). **PI<sub>1</sub>-S9**: Anal. Calcd. for C<sub>294</sub>H<sub>162</sub>N<sub>24</sub>O<sub>61</sub>S (5035): C, 76.74%; N, 8.89%; H, 4.09%. Found: C, 75.37%; N, 8.73%; H, 4.18%.

**PAA<sub>2</sub>-S9**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.71–1.34 (OCH<sub>2</sub>C<sub>7</sub>H<sub>14</sub>CH<sub>2</sub>S, 14H), 2.93 (SCH<sub>2</sub>, 2H), 3.76 (OCH<sub>3</sub>, 3H), 4.02 (OCH<sub>2</sub>, 2H), 5.16 (ArH, 1H), 6.91 (ArH, 4H), 7.10 (ArH, 4H), 7.26 (ArH,4H), 7.43 (ArH, 4H), 7.66 (ArH,4H), 7.93 (ArH, 4H), 10.37 (CONH, 2H), 10.41 (CONH, 2H), 13.26 (COOH, 4H). **PI<sub>2</sub>-S9**: Anal. Calcd. for C<sub>308</sub>H<sub>184</sub>N<sub>28</sub>O<sub>62</sub>S<sub>2</sub> (5329): C, 69.36%; N, 7.35%; H, 3.45%. Found: C, 69.71%; N, 7.17%; H, 3.39%.

**PAA<sub>3</sub>-S9**: <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>] DMSO, δ(ppm)): 1.73–1.32 (OCH<sub>2</sub>C<sub>7</sub>H<sub>14</sub>CH<sub>2</sub>S, 14H), 2.94 (SCH<sub>2</sub>, 2H), 3.75 (OCH<sub>3</sub>, 3H), 4.05 (OCH<sub>2</sub>, 2H), 5.19 (ArH, 1H), 6.94 (ArH, 4H), 7.12 (ArH, 4H), 7.25 (ArH,4H), 7.40 (ArH, 4H), 7.68 (ArH,4H), 8.02 (ArH, 4H), 10.35 (CONH, 2H), 10.42 (CONH, 2H), 13.11 (COOH, 4H). **PI<sub>3</sub>-S9**: Anal. Calcd. for C<sub>322</sub>H<sub>206</sub>N<sub>32</sub>O<sub>63</sub>S<sub>3</sub> (5623): C, 68.72%; N, 7.97%; H, 3.66%. Found: C, 68.37%; N, 7.87%; H, 3.94%.