Supporting Information

Molecular Engineering of Azobenzene-Functionalized Polyimides to Enhance Both Photomechanical Work and Motion

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[Note: The three-letter prefix to APB for the diamines and associated polymers is used to indicate the di-substitution patterns of the first, second and third phenylene rings of a diamine. The letters are o for ortho (or 1,2 substitution), m for meta (or 1,3 substitution) and p for para (or 1,4 substitution).]

1. Monomer and Polymer Synthesis. Four APB diamine isomers with different geometry were incorporated into polyimide backbones to investigate their position effect on the sub-T_g transitions and photomechanical response. ppp-, mmm- and pmp-APBs are commercially available. The pop-APB was synthesized according to a two-step route (Scheme S1).[1] In the first step, 1,2-bis(4-nitrophenoxy)benzene (**III**) was obtained by a nucleophilic substitution of catechol (**I**) with fluoronitrobenzene (**II**). Dinitro compound III was then reduced to 1,2-bis(4-aminophenoxy)benzene (pop-APB, **2c**) with hydrazine in ethanol. Azobenzene diamine (**4**) and triamine (7) were synthesized as previously described.[2,3]

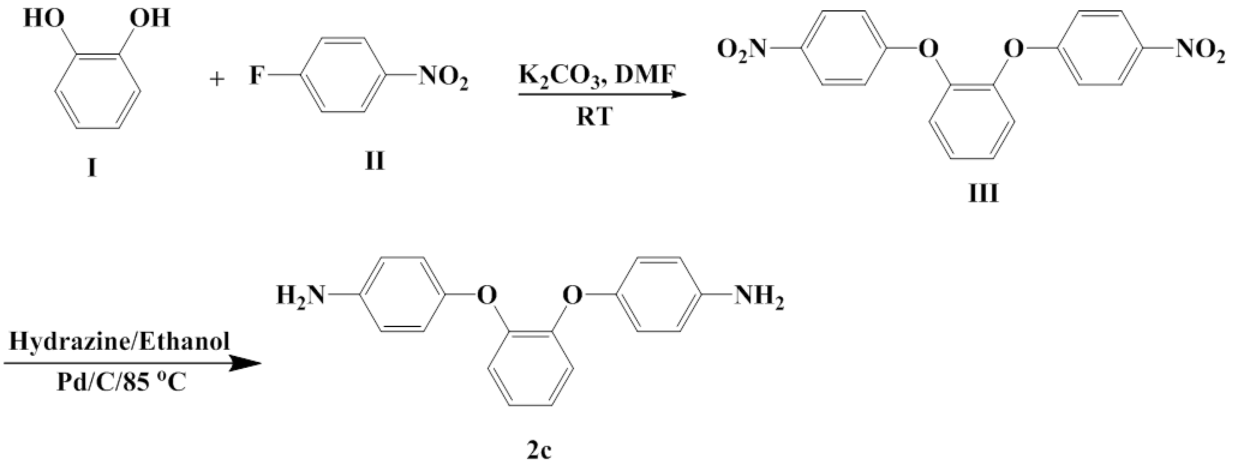
Both linear and crosslinked azobenzene functionalized polyimides (Azo-PIs) were prepared in the same procedure in Ref. 3. Briefly, 6FDA (**1**) and APB (**2**) were dissolved under a nitrogen atmosphere in *N*,*N*-dimethylacetamide (DMAc) at room temperature for 24 h with excess 6FDA to generate poly(amic acid) oligomers (PAA oligomers, **3**) with anhydride end-groups. In order to maintain the same concentrations of azobenzene units in both linear and crosslinked PIs 30 mol% azobenzene diamine (**4,** difunctional monomer, Scheme S2) and 20 mol% of azobenzene triamine (**7,** trifunctional monomer, Scheme S3) were added. After **4** or **7** had completely dissolved, the resulting PAA sol gel precursor was poured onto glass slides and cured in an oven set to 300 °C to imidize the polymer films.

2. EXPERIMENTAL

Materials. 1,3-Bis(3-aminophenoxy)benzene (mmm-APB) (99% min.) was purchased from Chriskev Company, Inc. 1,4-Bis(4-aminophenoxy)benzene (ppp-APB) (98% min.) and 1,3-bis(4-aminophenoxy)benzene (pmp-APB) were purchased from TCI, America. All three APBs were used as received. 1,1,1,3,3,3-Hexafluoro-2,2-bis(4-phthalic anhydride)-propane (6FDA) was purchased from Akron Polymer Systems and sublimed before use. All other reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise noted.

Synthesis of pop-APB (2c)

1,2-Bis(4-nitrophenoxy)benzene (**III**): Into a 500 mL three-necked flask equipped with a magnetic stir bar and nitrogen inlet and outlet were placed catechol (**I**, 15.0 g, 0.135 mol), *p*-fluoronitrobenzene (**II**, 40.2 g, 0.285 mol), anhydrous K_2CO_3 (42.9 g, 0.310 mol) and dry DMF (130 mL) as shown in Scheme S1. The mixture was stirred at room temperature for 24 h. It was poured into a mixture of methanol/water (1:2). After the precipitate was collected by filtration, washed with water and dried, a yellow solid was obtained in a yield of 25.5 g (82.3%). The crude product was recrystallized from acetic acid (200 mL) to afford 22.5 (72.5%) of yellow crystals: m.p. 133.8-135.7 °C (lit. [1]136-138 °C). ^{1}H-NMR (d_6-DMSO, δ in ppm): 6.99-7.02 (d, 4H, Ar-***H***), 7.436-7.440 (d, 4H, Ar-***H***), 8.15-8.18 (d, 4H, Ar-***H***). ^{13}C-NMR (d_6-DMSO, δ in ppm): 116.69, 123.46, 126.07, 127.58, 142.47, 145.37, 162.03.



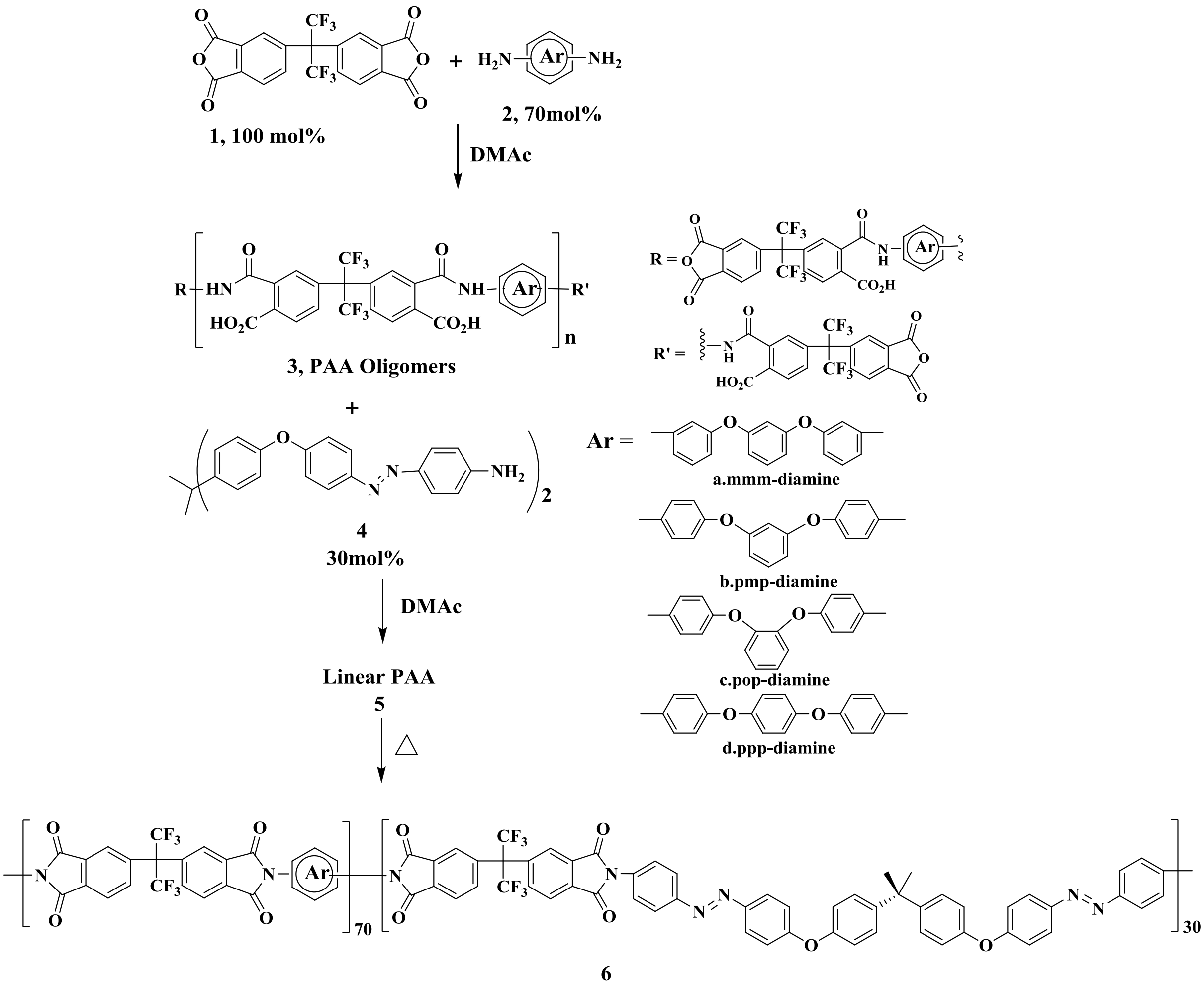
Scheme S1. Synthetic procedure of 1,2-bis(4-aminophenoxy)benzene (**2c**)

1,2-Bis(4-aminophenoxy)benzene (pop-APB, 2c): Into a 500 mL three-necked flask equipped with a magnetic stir bar and nitrogen inlet and outlet were placed 1,2-bis(4-nitrophenoxy)benzene (**III**, 10.5 g, 0.030 mol), 5% Pd-C (0.2 g) and ethanol (150 mL). The mixture was stirred at 85 °C and hydrazine monohydrate (30 mL) was added dropwise within 1 h. After the addition had been completed, the mixture was heated at 85 °C for another 4 h. Then decolorizing carbon (0.5 g) was carefully added and then filtered rapidly after 5 min of stirring. The filtrate was allowed to cool and stored in a refrigerator overnight to afford 7.1 g (81.0%) of colorless needles: m.p. 137-138 °C (lit.[1] 137-138 °C). The filtrate was concentrated under reduced pressure and a suitable amount of water was added to give 1.0 g (11.4%) of white crystals: m.p. 137-138 °C (lit.[1] 137-138 °C). Thus, the total yield was 47 g (82.4%). ^{1}H-NMR (d_6-DMSO, δ in ppm): 4.88 (s, 4H, NH_2), 6.53-6.56 (d, 4H, Ar-***H***), 6.68-6.71 (d, 4H, Ar-***H***), 6.75-6.84 (d, 2H, Ar-***H***), 6.94-6.98 (d, 2H, Ar-***H***). ^{13}C-NMR (d_6-DMSO, δ in ppm): 114.84, 118.88, 119.38, 123.14, 144.79, 146.71, 148.42.

Azobenzene diamine (AzoBPA, 4): The experimental details for the synthesis of the diamine **4** have been previously described in our report.[2]

Tris(azobenzene-amine) crosslinker (7): The experimental details for the synthesis of the crosslinker **7** have been previously described in our report.[3]

Synthesis of Linear Azo-PIs. As shown in Scheme S2, linear azo-PIs were prepared according to the description in ref.2 with some modifications as followed:



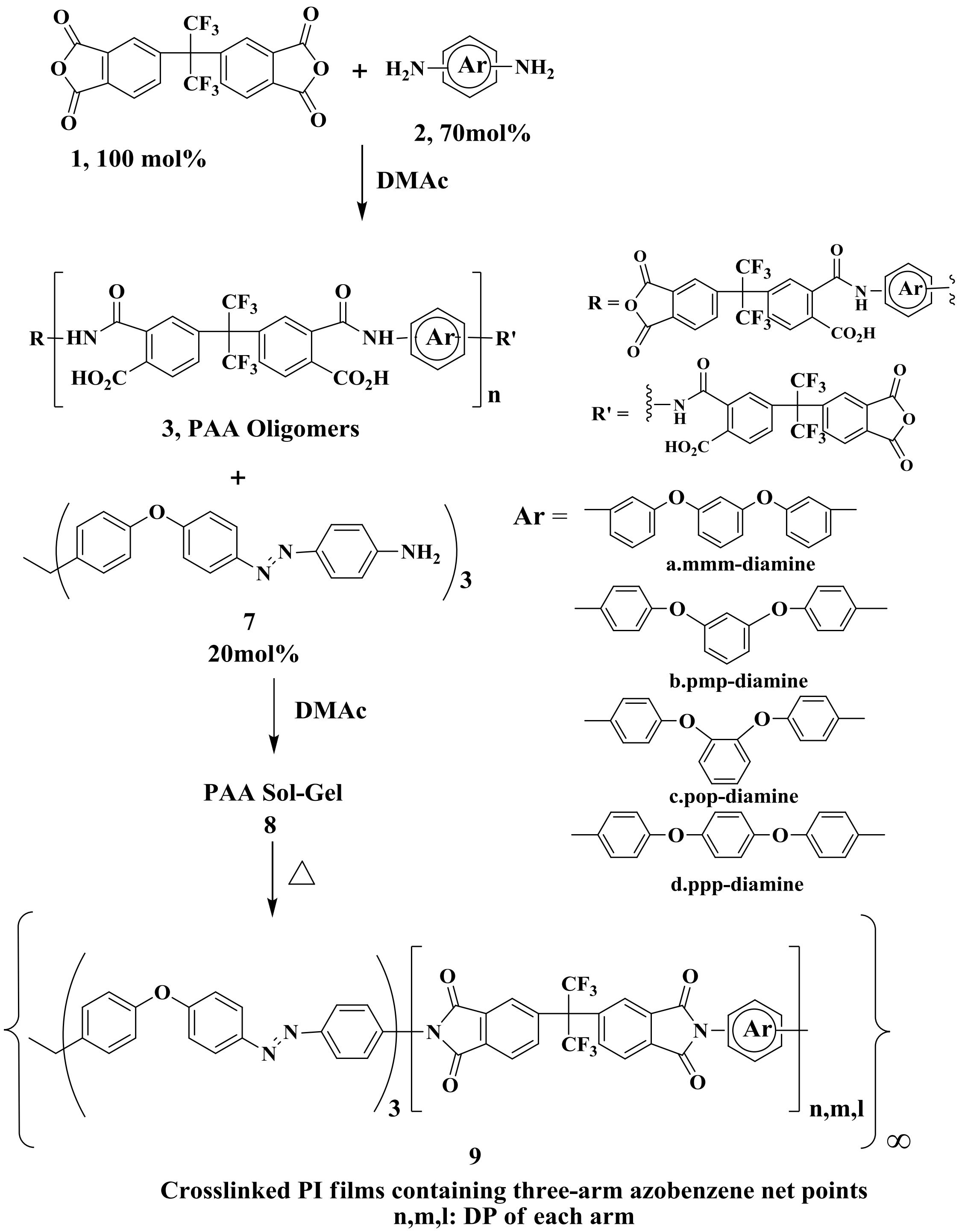
Scheme S2. Synthetic procedure of linear polyimide series

Representative synthetic procedure for linear azobenzene-containing 6FDI polyimides (L-ppp-6FDI, 6d, Scheme S2): 1,4-Bis(4-aminophenoxy)benzene (**2d**, 0.4093 g, 1.40 mmol) and DMAc (8.0 mL) were added to a 50-mL 3-necked flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and stirred under dry nitrogen at room temperature for 30 min. 6FDA (**1**, 0.8885 g, 2.00 mmol) was then introduced to the resulting solution. The light yellow solution was agitated at room temperature for 24 h to afford a poly(amic acid) solution (**3d**). 2,2-bis{4-[4-(4-aminophenyldiazenyl)phenoxy]phenyl}propane (**4;** 0.3712 g, 0.600 mmol) was added and the mixture was agitated for 2 h. The experimental details for the synthesis of the 2,2-Bis{4-[4-(4-

aminophenyldiazenyl)phenoxy]phenyl}propane (AzoBPA, **4**) have been previously described in our report.[1] Then, the mixture poured into a glass petri dish, followed by vacuum evaporation of DMAc at 50 °C, and heat-treated according to following schedule: 100 ^{o}C/2 h, 150 ^{o}C/2 h, 175 ^{o}C/1 h, 200 ^{o}C/2 h, 250 ^{o}C/1 h and 300 ^{o}C/1 h to form polyimide films. The film thickness was approximately 20-100 μm. ATR-IR (film): 1784, 1719, 1590, 1504, 1488, 1365, 1205, 1138, 1081, 982, 961, 828, 719 cm^{-1}. This procedure was followed to prepare other L-xxx-6FDI.

Synthesis of Crosslinked Azo-PIs. As shown in Scheme S3, crosslinked azo-PIs were prepared according to the description in ref.3 with some modifications as followed:

Representative synthetic procedure for crosslinked azobenzene-containing 6FDI polyimides (X-ppp-6FDI, 9d, Scheme S3): 1,4-Bis(4-aminophenoxy)benzene (**2d**, 0.4093 g, 1.40 mmol) and DMAc (8 mL) were added to a 50 mL 3-necked flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and stirred under dry nitrogen at room temperature for 30min. 6FDA



Scheme S3. Synthetic procedure of crosslinked polyimide series.

(**1**, 0.8885 g, 2.000 mmol) was then introduced to the resulting solution. The light yellow solution was agitated at room temperature for 24 h to afford a poly(amic acid) solution (**3**). Then, the tris(azobenzene-amine) cross-linker (**7**, 0.3568 g, 0.400 mmol) was added to this solution. The experimental details for the synthesis of the tris(azobenzene-amine) crosslinker (**7**) have been previously described in our report.[3] After **7** had completely dissolved in DMAc, the mixture poured into a glass petri dish, followed by vacuum evaporation of DMAc at 50 ^{o}C, and heat-treated according to following schedule: 100 ^{o}C/2 h, 150 ^{o}C/2 h, 175 ^{o}C/1 h, 200 ^{o}C/2 h, 250 ^{o}C/1 h and 300 ^{o}C/1 h to form polyimide films. The film thickness was approximately 20 μm. ATR-IR (film, cm-1): 3048, 1784, 1719, 1590, 1489, 1367, 1227, 1207, 1188, 1139, 1086, 982, 962, 828, 719 cm^{-1}. This procedure was followed to prepare the other **X-xxx-6FDI** samples.

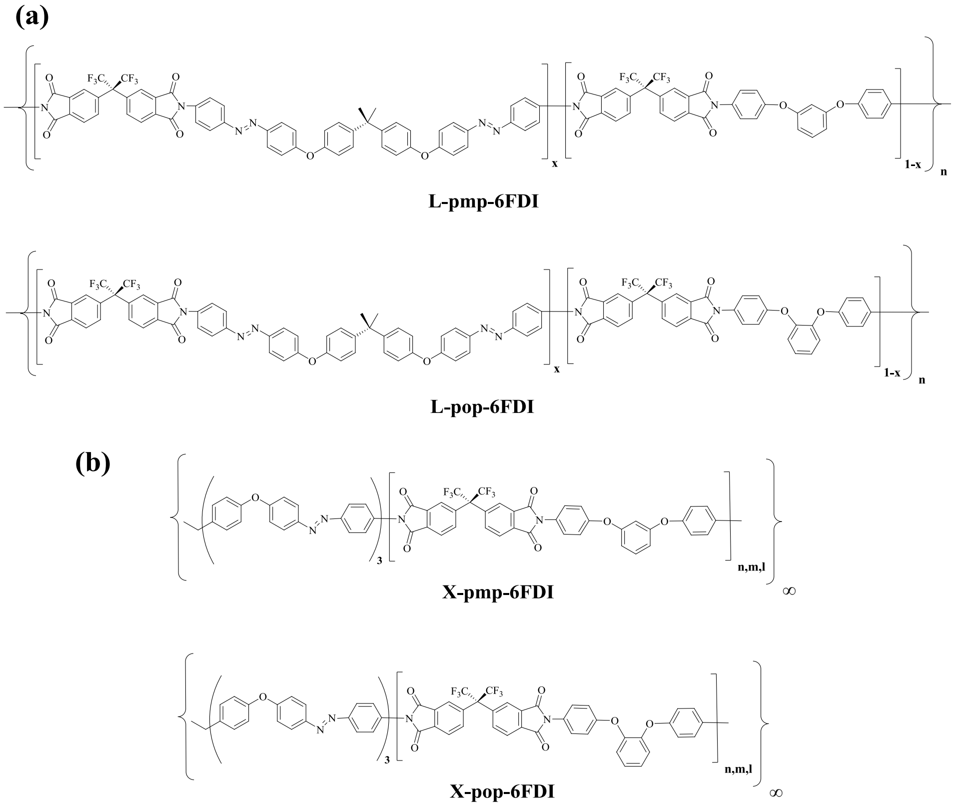


Figure S1. Chemical structures of (a) linear and (b) crosslinked polyimides made with para-meta-para (pmp) or para-ortho-para (pop) 1,4-bis(4-aminophenoxy)benzene isomers.

3. CHARACTERIZATION. Chemical structure of synthesized linear and crosslinked polyimides are shown in Figure 1 and Figure S1. Wide angle X-ray experiments were carried out on a Statton box camera at 53 mm sample to image plate distances in transmission mode using CuK_α generated by a Rigaku Ultrax18 system. As shown in Figure S2, both linear and crosslinked polyimides were all amorphous regardless of structural isomerism.

Thermomechanical properties of polyimides were investigated by a stress controlled DMA (TA Instruments DMA Q800) with a heating rate of 4 °C/min in a nitrogen atmosphere and summarized in Table 1 and Table S1. Modulus was reported from storage modulus value at 25 °C and the glass transition temperature of the polyimides was determined from the maximum loss tan δ (loss modulus/storage modulus). The secondary segmental mobility of polymer chain by β-transition was studied by loss modulus and the results are shown in Figure 2 and Figure S3. Both the pmp and the pop isomers had similar β-transition behaviors.

Time-resolved bending angle measurement for (a) linear and (b) crosslinked polyimides made with pmp (unfilled blue circle) and pop (filled green circle) isomers. All measurements were conducted on films of the same dimensions: 6 mm x 3 mm x 20 μm (length, width and thickness, respectively). The films were subjected to 445 nm light (E//x) at 120 mW/cm^2 intensity for 1 h and subsequently relaxed in dark for 3 days. For both (a) and (b) images are labeled (i)–(ii) denoting 6FDI composed with (i) pmp and (ii) pop isomers. Images marked with (') are taken after 3 days dark relaxation. Both the pmp and the pop isomers had photomechanical responses similar to the para isomers but larger than the meta isomers.

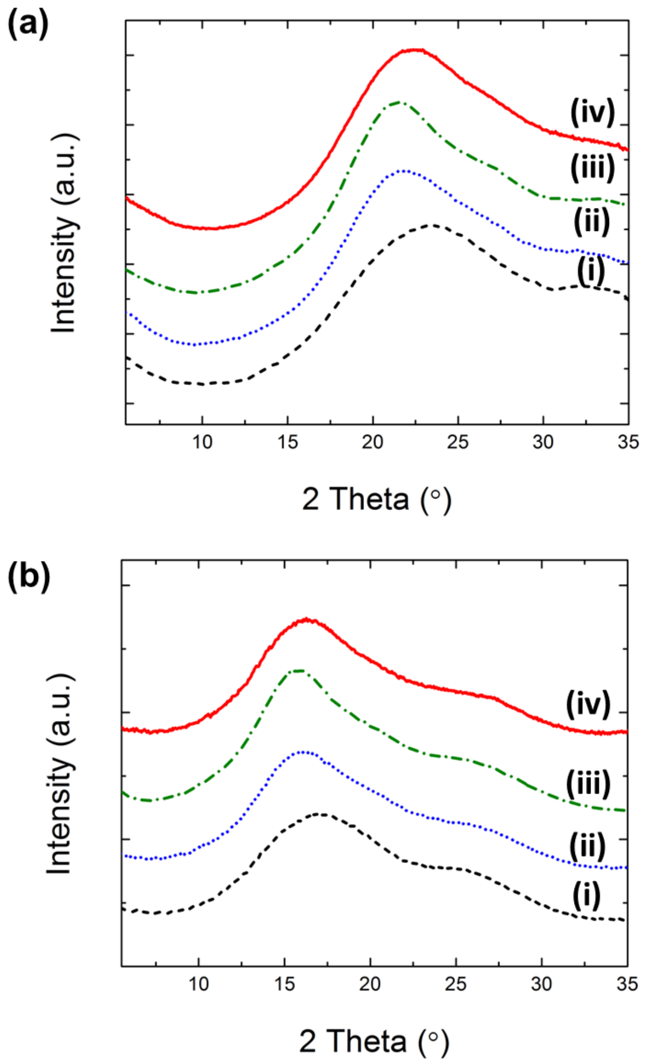


Figure S2. WAXD results for (a) linear and (b) crosslinked polyimides. For both (a) and (b) images are labeled (i)–(iv) denoting 6FDI composed with (i) mmm (ii) pmp (iii) pop and (iv) ppp isomers.

Table S1. Summary of thermomechanical properties of polyimides made with para-meta-para (pmp) or para-ortho-para (pop) 1,4-bis(4-aminophenoxy)benzene isomers.

Sample code	Modulus	T_g (^{o}C)
L-pmp-6FDI	2.64	277
L-pop-6FDI	2.05	277
X-pmp-6FDI	3.13	323
X-pop-6FDI	2.64	321

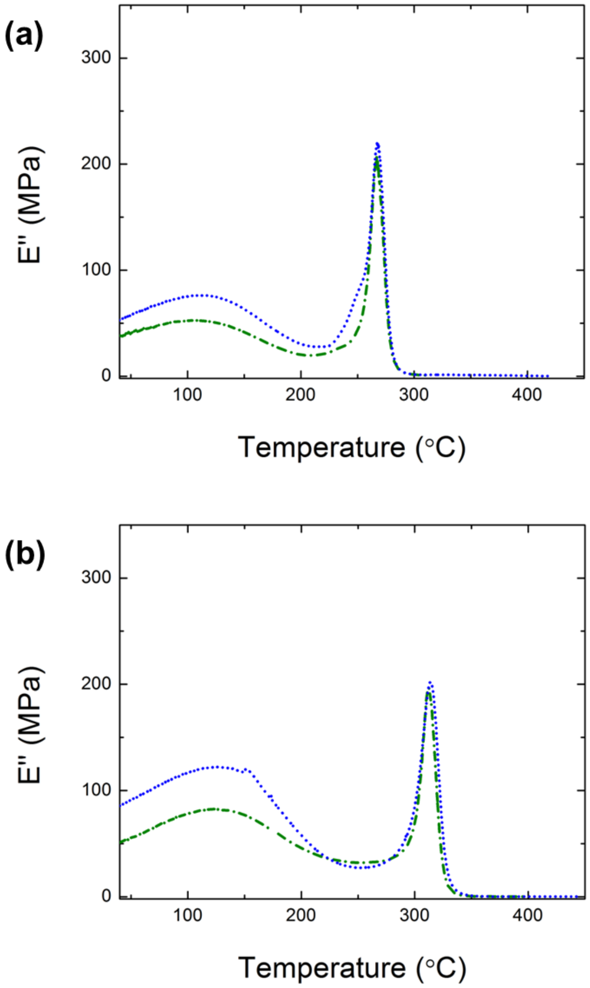


Figure S3. Temperature resolved loss modulus measurements for (a) linear and (b) crosslinked polyimides made with pmp (·····) and pop (—·—) isomers. All measurements were conducted on films of the same dimensions: 6 mm x 3 mm x 20 µm (length, width and thickness, respectively).

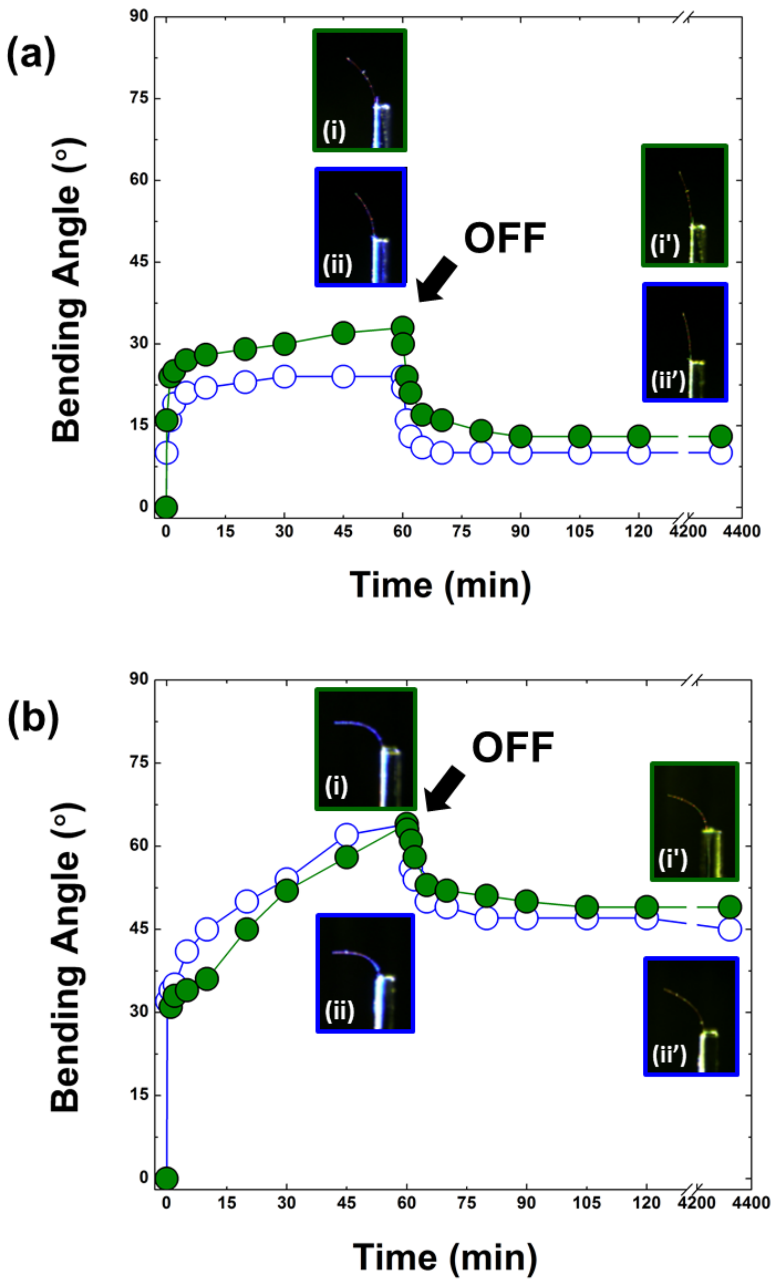


Figure S4. Time-resolved bending angle measurement for (a) linear and (b) crosslinked polyimides made with pmp (unfilled blue circle) and pop (filled green circle) isomers. All measurements were conducted on films of the same dimensions: 6 mm x 3 mm x 20 µm (length, width and thickness, respectively). The films were subjected to 445 nm light (E//x) at 120 mW/cm^2 intensity for 1 h and subsequently relaxed in dark. For both (a) and (b) images are labeled (i)–(ii) denoting 6FDI composed of (i) pmp and (ii) pop isomers. Images marked with (′) are taken after 3 days dark relaxation.

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