<Supplementary Materials>

Enhancement of the mechanical properties of polyimide film by microwave irradiation

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Model Study

*Model study of reaction of phthalic anhydride (**1**) with aniline (**3**)*

A dried 50-mL round-bottom flask was charged with **1** (1.481 g, 0.0100 mol) and **3** (0.9313 g, 0.0100 mol) in NMP (21.1 mL) under nitrogen atmosphere. After **1** was dissolved, **3** was added, and within 1 min the mixture was poured into distilled water, forming a precipitate that was collected by filtration. Washing with water followed by drying in vacuum afforded a white powder (1.734 g, 72% yield). The ^{1}H NMR spectrum of the product (Figure S4d) is practically identical to that of an authentic compound of *N*-phenylphthalamic acid (**4**) (Figure S4e).

*Model study of reaction of phthalic acid (**2**) with **3***

A dried 50-mL round-bottom flask was charged with **2** (1.661 g, 0.0100 mol) and **3** (0.9313 g, 0.0100 mol) in NMP (22.7 mL) under nitrogen atmosphere. ^{1}H NMR spectroscopy was performed using reaction mixture samples after the following three experiments: (1) immediately after **2** and **3** were homogeneously mixed (the reaction time was within 1 min) (Figure 3a), (2) after the mixture solution was stirred at room temperature for 24 h (Figure 3b), and (3) after the mixture solution was drop-cast onto slide glass and then irradiated with MW at 240 W for 2 min (Figure 3c).

*Model study of reaction of N-phenylphthalamic acid (**4**) with **3***

In a dried 20-mL vial, **4** (0.241 g, 0.00100 mol) and **3** (0.0931 g, 0.00100 mol) were dissolved in NMP (2.9 mL). The solution was drop-cast onto slide glass and then irradiated with MW at 240 W for 2 min. The resultant solution was poured into distilled water, forming a precipitate that was collected by filtration. Washing with water followed by drying in vacuum afforded a white powder. The product was analysed by ^{1}H NMR spectroscopy (Figure S5a).

*Preparation of authentic **4***

A dried 50-mL round-bottom flask was charged with **1** (1.481 g, 0.0100 mol) and **3** (0.9313 g, 0.0100 mol) in NMP (21.1 mL) under nitrogen atmosphere. This mixture was stirred for 24 h at room temperature. A white solid was collected by filtration and dried in vacuum at 50 °C. FT-IR ν_{max} (KBr): 1722, 1656, 1549 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz, Figure S4e): δ 13.01 (s, 1H), 10.32 (s, 1H), 7.87–7.89 (d, 1H), 7.65–7.71 (m, 3H), 7.54–7.59 (m, 2H), 7.31–7.35 (m, 2H), 7.05–7.09 ppm (m, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 168.0, 167.8, 140.0, 139.3, 132.2, 130.4, 130.0, 129.9, 129.1, 128.3, 123.8, 119.9 ppm.

*Preparation of authentic N-phenylphthalimide (**5**)*

A 25-mL vial was charged with **1** (0.741 g, 0.0050 mol) and **3** (0.466 g, 0.0050 mol) in NMP (10.5 mL). The mixture was irradiated with MW at 240 W for 10 min. The reaction mixture was poured into distilled water, forming a precipitate that was collected by filtration. Washing with water followed by drying in vacuum afforded a white powder. FT-IR ν_{max} (KBr): 1779, 1709, 1386 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz, Figure S5b): δ 7.92–7.96 (m, 2H), 7.89–7.91 (m, 2H), 7.52–7.55 (m, 2H), 7.43–7.46 ppm (m, 3H). ^{13}C NMR (DMSO- d_6, 100 MHz): δ 167.5, 135.2, 132.4, 132.0, 129.3, 128.6, 127.9, 123.9 ppm.

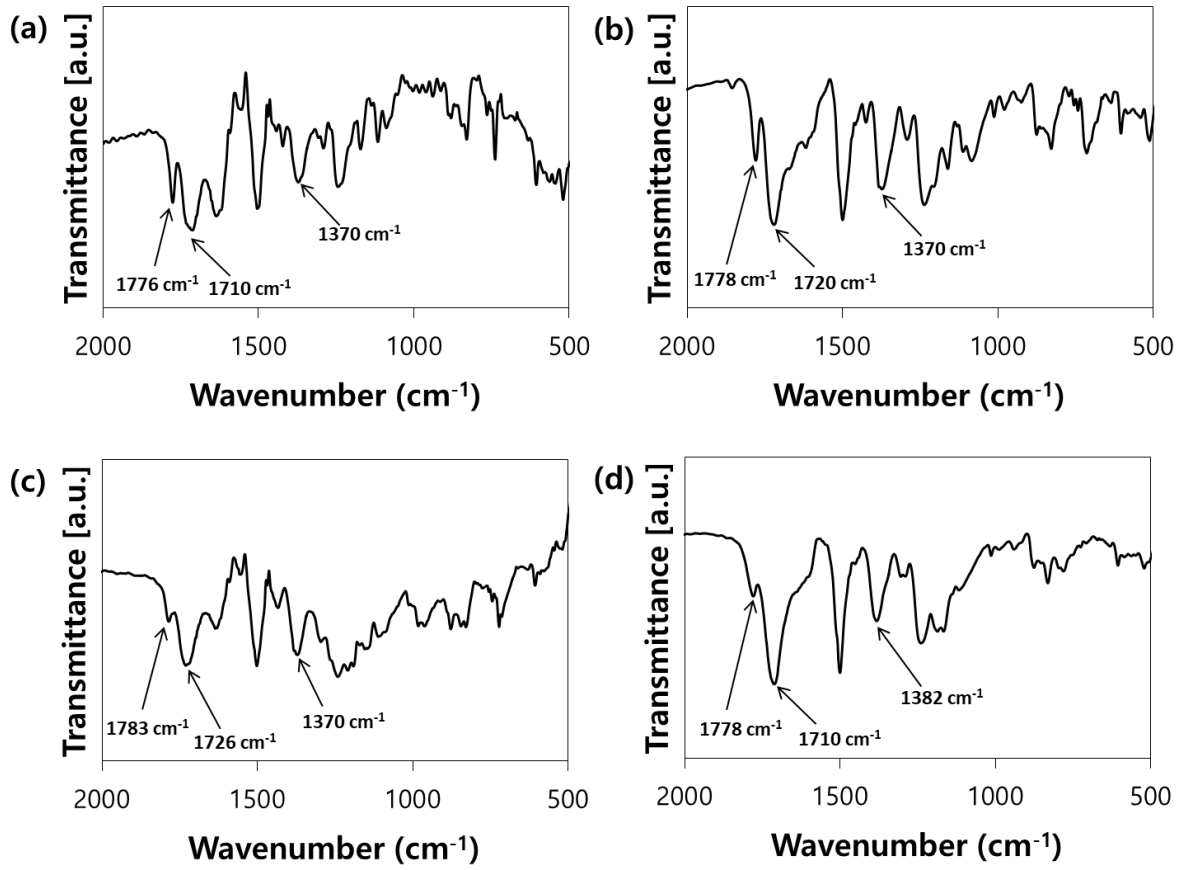


Figure S1. FT-IR-spectra of polyimides: (a) BPO-240-2m, (b) BTO-240-2m, (c) 6FO-240-2m and (d) HPO-240-2m.

FT-IR (KBr, cm^{-1}): (a) 1776 (imide C=O asymmetric stretch), 1710 (imide C=O symmetric stretch), 1370 (imide C–N stretch), (b) 1778 (imide C=O asymmetric stretch), 1720 (imide C=O symmetric stretch), 1370 (imide C–N stretch), (c) 1783 (imide C=O asymmetric stretch), 1726 (imide C=O symmetric stretch), 1370 (imide C–N stretch), (d) 1778 (imide C=O asymmetric stretch), 1710 (imide C=O symmetric stretch), 1382 (imide C–N stretch).

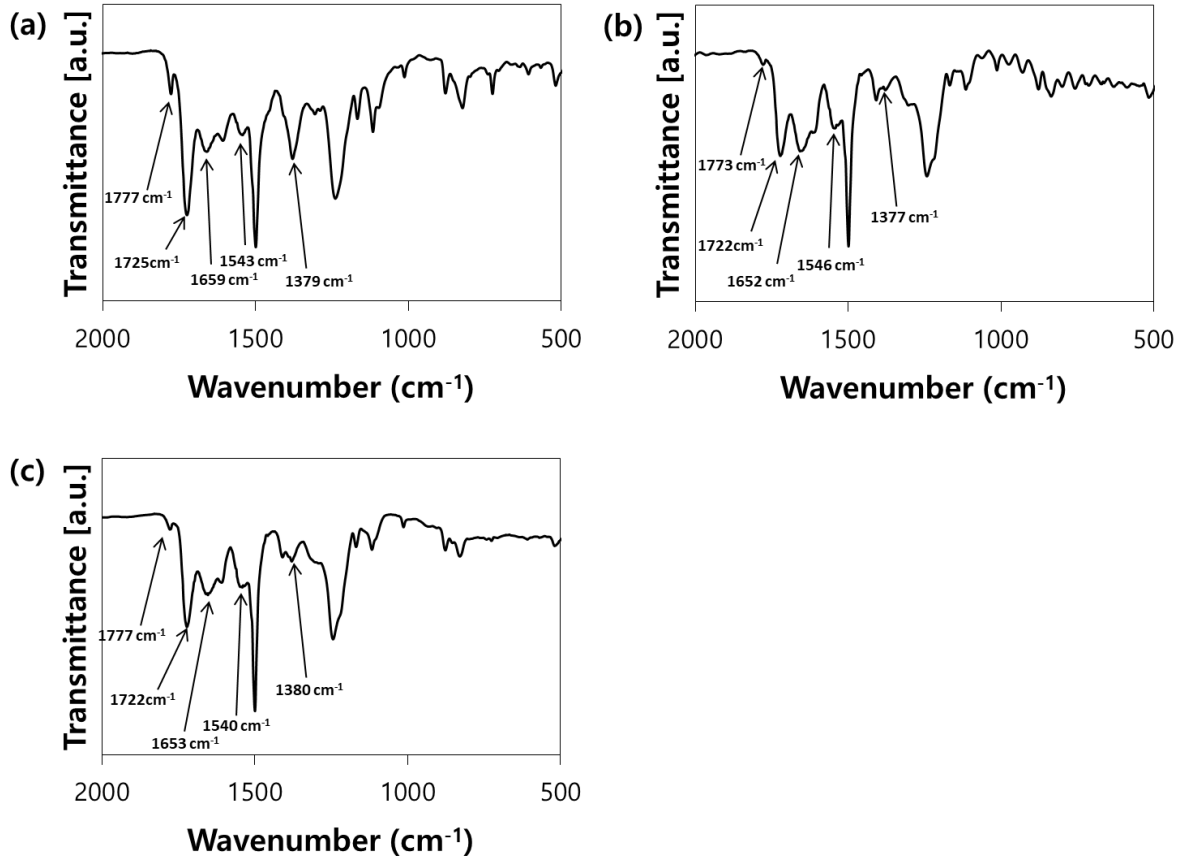


Figure S2. FT-IR-spectra of PAA-POs: (a) PAA-PO-240-3m, (b) PAA-PO-400-2m and (c) PAA-PO-640-1m.

FT-IR (KBr, cm^{-1}): (a) 1777 (imide C=O asymmetric stretch), 1725 (carboxyl C=O stretch), 1659 (amide C=O stretch), 1543 (amide C-N stretch), 1379 (imide C–N stretch), (b) 1773 (imide C=O asymmetric stretch), 1722 (carboxyl C=O stretch), 1652 (amide C=O stretch), 1546 (amide C-N stretch), 1377 (imide C–N stretch), (c) 1777 (imide C=O asymmetric stretch), 1722 (carboxyl C=O stretch), 1653 (amide C=O stretch), 1540 (amide C-N stretch), 1380 (imide C–N stretch).

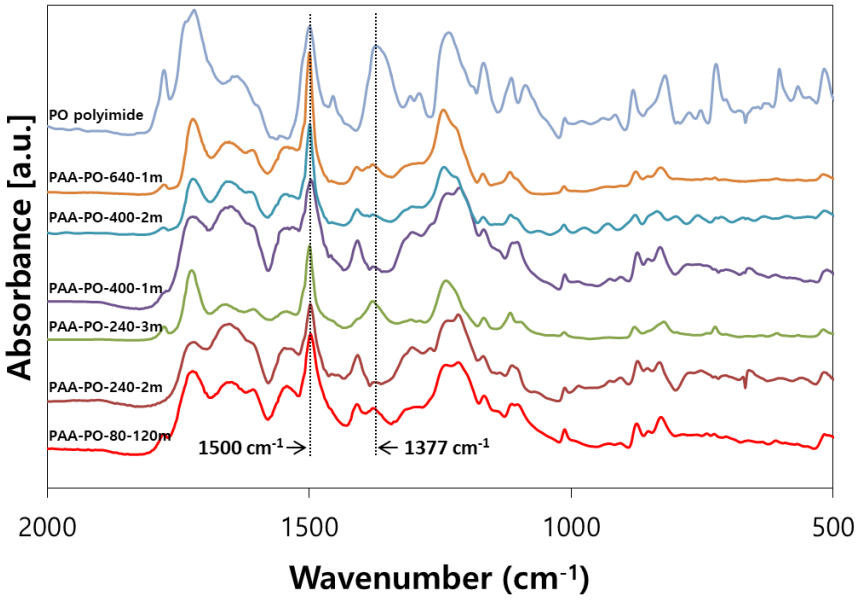


Figure S3. FT-IR spectra of PAA-POs and a reference PO polyimide.

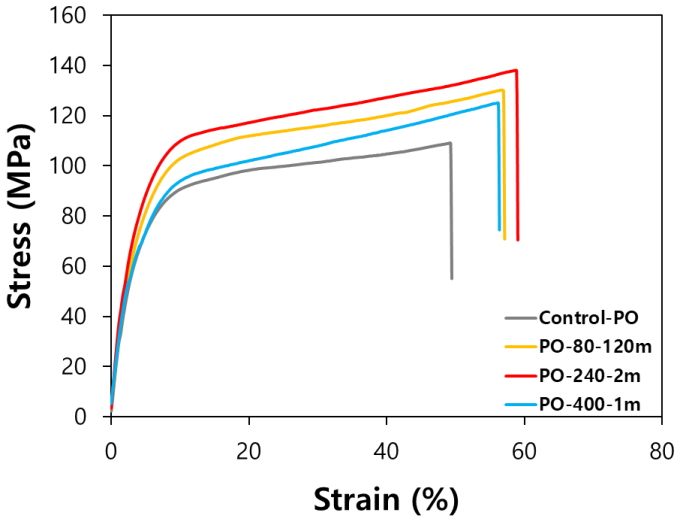


Figure S4. Stress-strain curves of PO films.

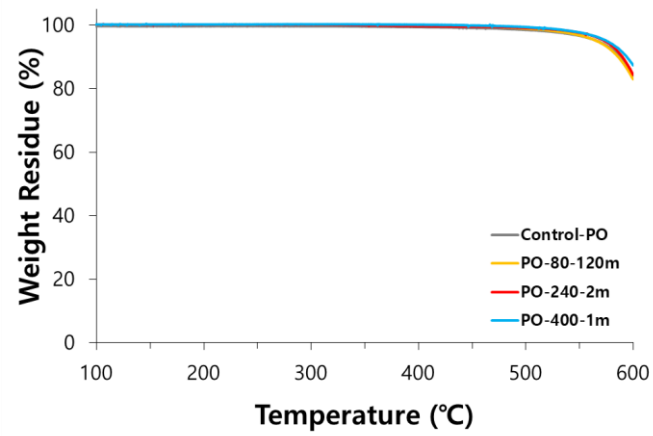


Figure S5. TGA curves of PO polyimides.

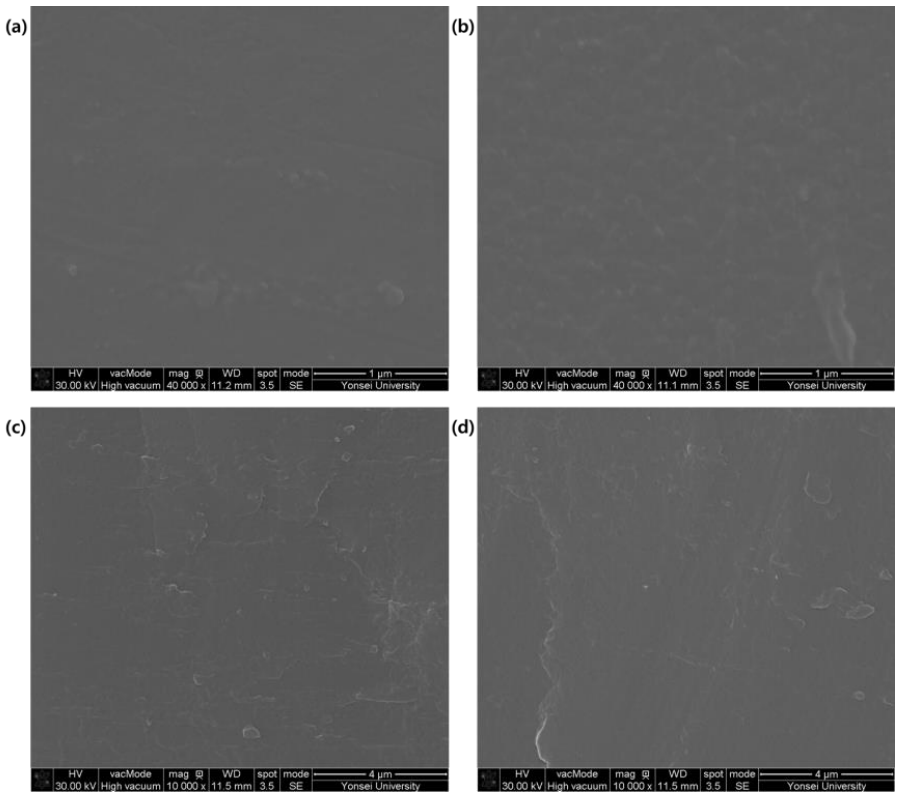


Figure S6. SEM images: surface of (a) Control-PO and (b) PO-240-2m films; cross section of (c) Control-PO and (d) PO-240-2m films.

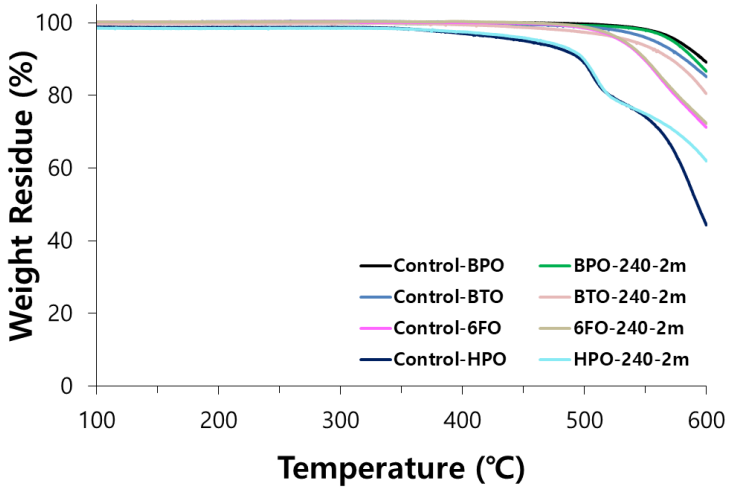


Figure S7. TGA curves of the polyimides.

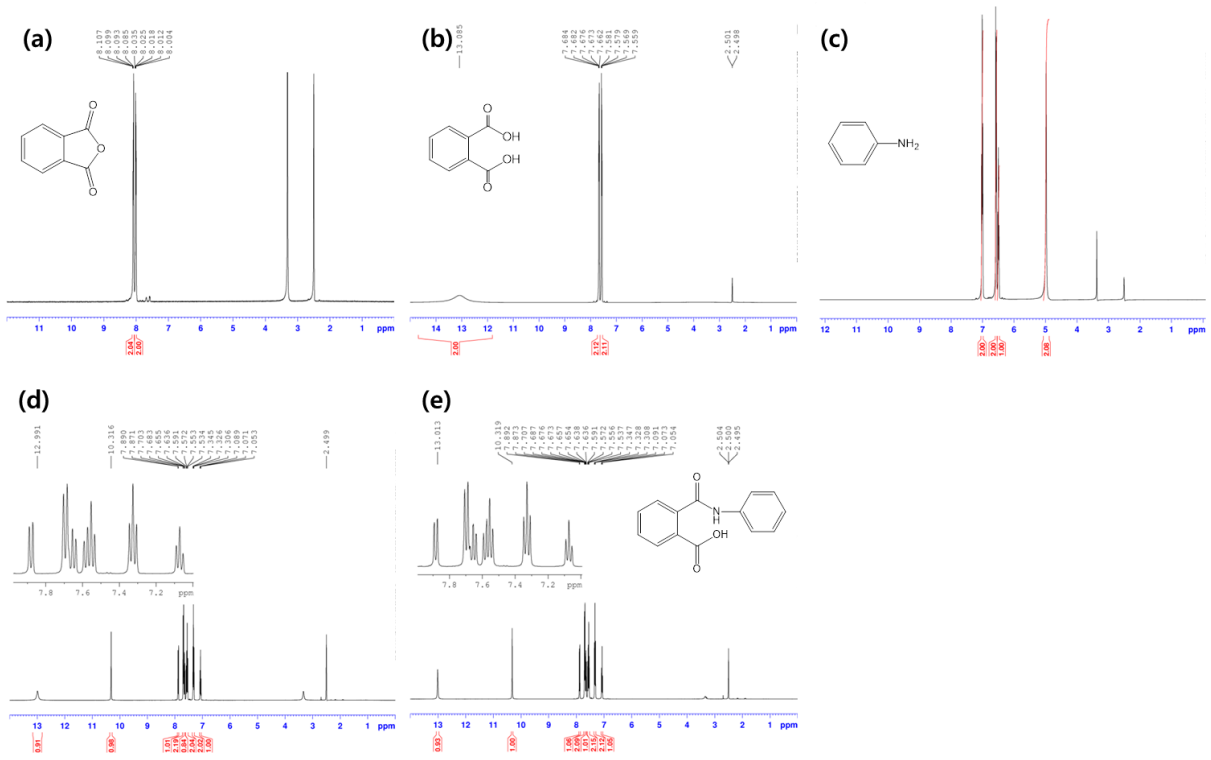


Figure S8. ^{1}H NMR spectra of (a) phthalic anhydride (**1**), (b) phthalic acid (**2**), (c) aniline (**3**), (d) the isolated product from the reaction of **1** with **3** in NMP for less than 1 min and (e) an authentic *N*-phenylphthalamic acid (**4**).

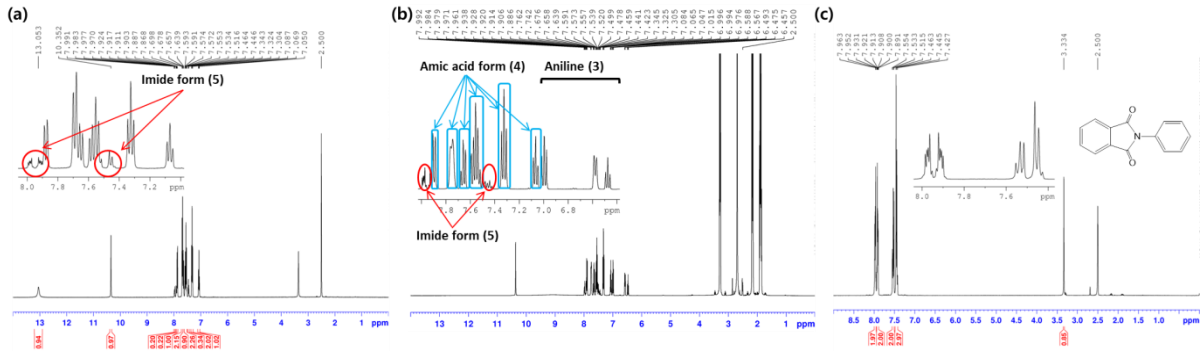
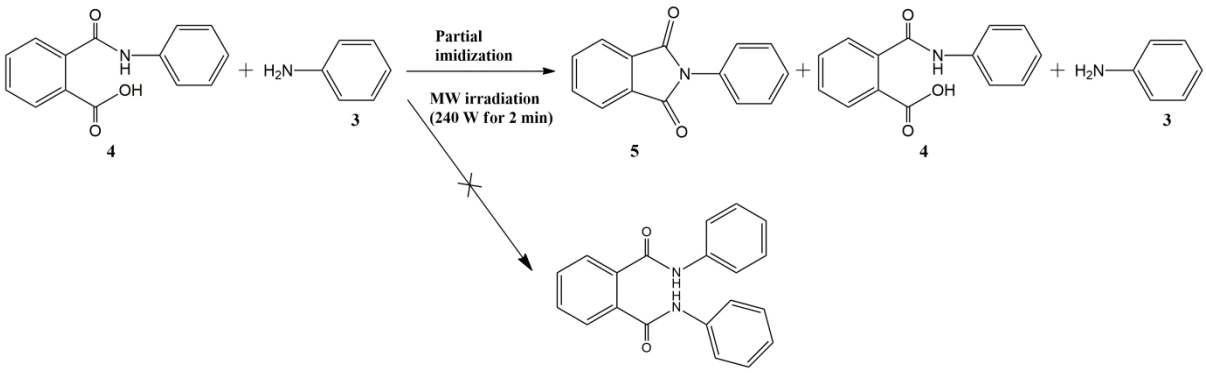


Figure S9. ^{1}H NMR spectra of (a) the isolated product from the reaction of **4** with **3** in NMP by MW irradiation at 240 W for 2 min, (b) the crude product from the reaction of **4** with **3** in NMP by MW irradiation at 240 W for 2 min and (c) an authentic *N*-phenylphthalimide (**5**).



Scheme S1. Model study of the reaction of **4** with **3**.

Table S1. Elemental analysis of the polyimides.

Polyimide[a,b]		Elemental Analysis (%)		
		C	H	N
Control-PO	Calcd.	69.11	2.63	7.33
	Found	67.49	2.63	7.27
PO-240-2m	Calcd.	69.11	2.63	7.33
	Found	67.66	2.74	7.44
Control-BPO	Calcd.	73.36	3.08	6.11
	Found	72.59	3.10	6.18
BPO-240-2m	Calcd.	73.36	3.08	6.11
	Found	72.50	3.12	6.23
Control-BTO	Calcd.	71.61	2.90	5.76
	Found	70.56	2.97	6.52
BTO-240-2m	Calcd.	71.61	2.90	5.76
	Found	70.83	3.02	6.60
Control-6FO	Calcd.	61.19	2.32	4.60
	Found	60.53	2.36	4.68
6FO-240-2m	Calcd.	61.19	2.32	4.60
	Found	60.32	2.47	4.71
Control-HPO	Calcd.	68.04	4.15	7.21
	Found	64.90	4.15	7.25
HPO-240-2m	Calcd.	68.04	4.15	7.21
	Found	64.62	4.22	7.01

[a] PO: PMDA/ODA; BPO: BPDA/ODA; BTO: BTDA/ODA; 6FO: 6FDA/ODA; HPO: HPMDA/ODA. As a representative example, BPO-240-2m is a polyimide film prepared from BPDA and ODA by MW irradiation of a drop-casted PAA-BPO solution at 240 W for 2 min and subsequent thermal imidization. [b] Control polyimides are polyimide films were prepared by the conventional two-step method without MW irradiation.