

Electronic supplementary information (ESI) for

## **Methylsulfone as a leaving group for the synthesis of hyperbranched poly(arylene pyrimidine ether)s by nucleophilic aromatic substitution**

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### Materials

4,6-dichloro-2-(methylsulfonyl)pyrimidine, 4,4'-thiodiphenol, 4-fluorothiophenol and 4,4'-thiobisbenzenethiol were purchased from J&K Chemical Co., Ltd. The other commercially available reagents and solvents were used without further purification.

### Measurements

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER-300 spectrometer at 300 or 75 MHz in deuterated chloroform ( $\text{CDCl}_3$ ). FT-IR spectra were recorded on a Nicolet 6500 spectrometer at a resolution of  $4\text{ cm}^{-1}$  in the range of  $400\text{--}4000\text{ cm}^{-1}$ . Inherent viscosities ( $\eta_{\text{inh}}$ ) of HB-PAE were measured with an Ubbelohde viscometer at  $25\text{ }^\circ\text{C}$  in  $\text{CHCl}_3$  at a concentration of  $0.5\text{ g dL}^{-1}$ . Differential scanning calorimetric (DSC) analysis was carried out on a TA instrument DSC Q100 at a scanning rate of  $10\text{ }^\circ\text{C min}^{-1}$  under nitrogen with  $50\text{ mL min}^{-1}$  gas flow. Thermo gravimetric analysis (TGA) was performed with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under nitrogen atmosphere by the TA 2050. The transmittance and absorption of the polymer was determined by Ultraviolet-visible (UV-vis) spectrometer (Shimadzu UV-Vis 2501). Gel permeation chromatography (GPC) was performed with a Shimadzu apparatus (UV detection) with a PL gel D column (Polymer Laboratories) and DMF as the eluent at  $30\text{ }^\circ\text{C}$  calibrated with polystyrene standards. The out-of-plane ( $n_{\text{TM}}$ ) and in-plane ( $n_{\text{TE}}$ ) refractive indices of PI films were measured with a prism coupler (Metricon, model PC-2000) equipped with a He-Ne laser light source (wavelength:  $632.8\text{ nm}$ ). In plane ( $n_{\text{TE}}$ )/out-of-plane ( $n_{\text{TM}}$ ), birefringence ( $\Delta n$ ) was calculated as a difference between  $n_{\text{TE}}$  and  $n_{\text{TM}}$ . The average refractive index ( $n_{\text{av}}$ ) was calculated according to eq 1:

$$n_{\text{AV}} = \sqrt{(2n_{\text{TE}}^2 + n_{\text{TM}}^2)/3}$$

#### *Synthesis of model compound*

Under nitrogen protection, 4-fluorothiophenol (1.92 g, 15.0 mmol), anhydrous potassium carbonate (2.07 g, 15.0 mmol), 18-crown-6 (1.98 g) and chloroform (36 mL) were charged to a 100-mL three necked flask, equipped with a mechanical stirrer, thermocouple, heating/cooling capacity, nitrogen inlet/outlet and the mixture was stirred at room temperature for 1 h. 4,6-dichloro-2-(methylsulfonyl)pyrimidine (1.14 g, 5.0 mmol) was added to the solution in two portion and then the mixture was stirred for 3h at room temperature. Water (50 mL) was added and stirred for 0.5 h. The mixture was then extracted with chloroform, and the extract was dried over anhydrous sodium sulfate, filtered, and concentrated to give a white product (2.17 g, 95% yield): mp: 153.4 °C( DSC peak); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.36 (p, 6H), 7.02 (d, 6H), 5.77 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 171.8, 155.4, 151.9, 137.3, 123.4, 116.4, 107.9; HRLC-MS (ESI): 459.4 (M+H)<sup>+</sup>, Calcd 458.5 for C<sub>22</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub>.

#### *Synthesis of hyperbranched poly(arylene ether) (HB-PAE-1)*

The hyperbranched polymer was synthesized by using the following procedure. Under nitrogen protection, 4,4'-thiobisbenzenethiol (3.76 g, 15 mol), anhydrous potassium carbonate (4.56 g, 33 mol), 18-crown-6 (1.19g) and chloroform (40.6 g) were charged to a 100-mL three necked flask, equipped with a mechanical stirrer, thermocouple, heating/cooling capacity, nitrogen inlet/outlet and the mixture was stirred at room temperature for 1 h. 4,6-dichloro-2-(methylsulfonyl)pyrimidine (3.41 g, 15 mmol) was added to the solution in two portion and then the mixture was stirred for 12h at room temperature. The mixture was poured into methanol. The precipitate was filtered and dried in vacuum. Then, the precipitate was dissolved in chloroform and poured into methanol. The precipitate was filtered and dried in vacuum. Yield: 5.6 g (95%).

#### *Synthesis of hyperbranched poly(arylene ether) (HB-PAE-2)*

Under nitrogen protection, 4,4'-thiodiphenol (2.18 g, 10 mol), anhydrous potassium carbonate (3.04 g, 22 mol), 18-crown-6 (0.79 g) and chloroform (25 g) were charged to a 50-mL three necked flask, equipped with a mechanical stirrer, thermocouple, heating/cooling capacity, nitrogen inlet/outlet and the mixture was stirred at room temperature for 1 h. 4,6-dichloro-2-(methylsulfonyl)pyrimidine (2.27 g, 10 mmol) was added to the solution in two portion and then the mixture was stirred for 12h at 55 °C. After cooling to room temperature, the mixture was poured into methanol. The precipitate was filtered and dried in vacuum. Then, the precipitate was dissolved in chloroform and poured into methanol. The precipitate was filtered and dried in vacuum. Yield: 3.47 g (95%).

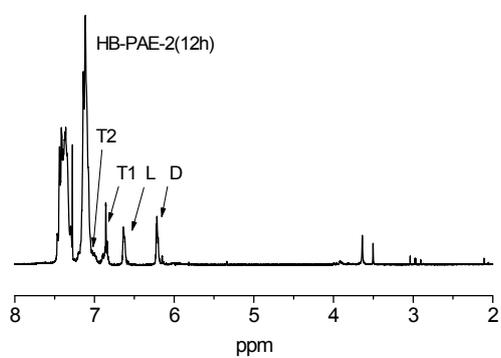
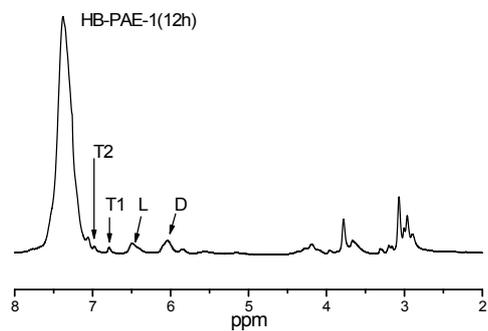


Fig. S1 The  $^1\text{H}$  NMR spectra of HB-PAEs

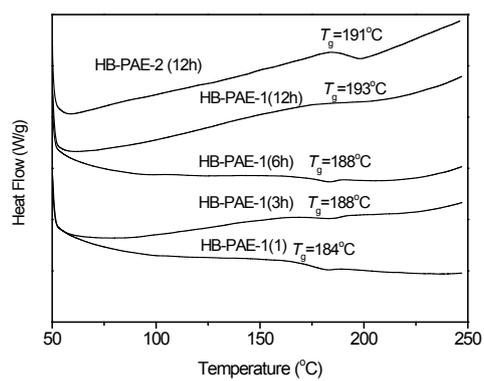


Fig. S2 The DSC curves of HB-PAEs

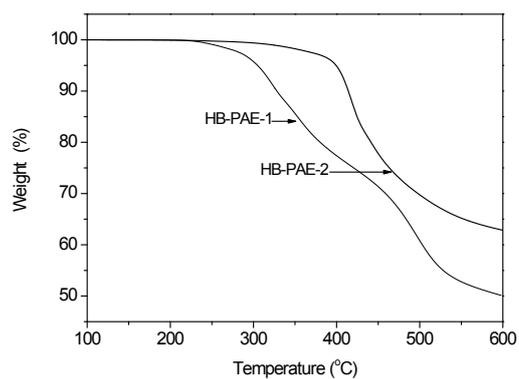


Fig. S3 The TGA curves of HB-PAEs

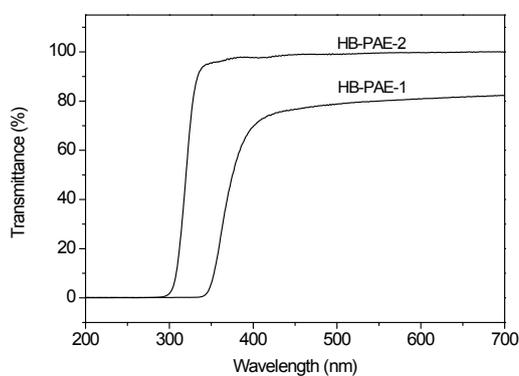


Fig. S4 The UV-vis spectra of HB-PAEs (film thickness:  $\sim 5 \mu\text{m}$ )

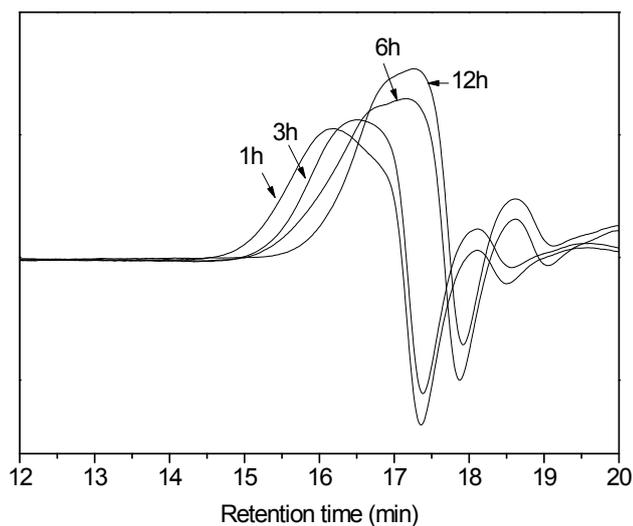


Fig. S5 The GPC curves of HB-PAE-1

Table S1 Characterization data and the thermal property of HB-PAE

Code	Reaction	$\eta_{inh}^a$	$M_w^b (\times 10^4)$	$M_w/M_n^b$	$T_g^c$ (°C)	T5% <sup>d</sup> (°C)
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	time (h)	(dL g <sup>-1</sup> )				
HB-PAE-1	1	0.38	1.88	1.83	184	-
	3	0.46	2.46	1.80	188	-
	6	0.49	2.82	2.02	188	-
	12	0.52	3.06	1.97	193	305
HB-PAE-2	12	0.49	2.89	1.93	191	399

<sup>a</sup> Inherent viscosities ( $\eta_{inh}$ ) of HB-PAE were measured with an Ubbelohde viscometer at 25 °C in CHCl<sub>3</sub> at a concentration of 0.5 g dL<sup>-1</sup>.

<sup>b</sup> Determined by GPC in DMF on the basis of a polystyrene calibration.

<sup>c</sup> Glass transition temperature of polymers detected by the DSC at a heating rate of 10 °C min<sup>-1</sup>.

<sup>d</sup> The 5% weight loss temperature of polymers detected by the TGA under nitrogen at a heating 10 °C min<sup>-1</sup>.

Table S2 Optical properties of HB-PAEs

Code	$d^a$ ( $\mu\text{m}$ )	$T^b$ (%)	Refractive indices and birefringence			
			$n_{TE}^c$	$n_{TM}^d$	$n_{av}^e$	$\Delta n^f$
HB-PAE-1	5	77	1.7307	1.7218	1.7277	0.0089
HB-PAE-2	5	99	-	-	-	-

<sup>a</sup> Film thickness of the polymer.

<sup>b</sup> Transmittance at 450 nm.

<sup>c</sup>  $n_{TE}$ : the in-plan refractive index.

<sup>d</sup>  $n_{TM}$ : out-of-plan refractive index.

<sup>e</sup>  $n_{av}$ : average refractive index.

<sup>f</sup>  $\Delta n$ : birefringence