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## COMMUNICATION

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

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Yue Guan, Chunbo Wang, Daming Wang, Guodong Dang, Chunhai Chen, Hongwei Zhou, Xiaogang Zhao\*

**Using a novel leaving group, methylsulfone activated by pyrimidine, 4,6-dichloro-2-(methylsulfonyl)pyrimidine was used to synthesize two new hyperbranched poly(arylene pyrimidine ether)s with 4,4'-thiobisbenzenethiol and 4,4'-thiodiphenol via a simple nucleophilic substitution polymerization.**

In the past two decades, the macromolecules in three dimensions have been a subject of intensive research focusing on the control of structures and functions due to the unique characteristics of three-dimensional macromolecules and their high application potential in many areas.<sup>1</sup> As important macromolecules, branched polymers, are interesting and versatile materials, and display unique properties, such as low solution and melt viscosities, high solubility and a high degree of functionality, compared to their linear analogs because of their globular structure and spherical shape.<sup>2-3</sup> These features make such highly branched polymers attractive candidates for many material applications in coatings, supports for catalysts, drug and nanotechnology, and surface modification.<sup>4-8</sup>

Nucleophilic aromatic substitution reaction ( $S_NAr$ ) has been known as a very effective way for the formation of aromatic ether groups and utilized in the synthesis of many organic and polymeric compounds.<sup>9</sup> The  $S_NAr$  reaction generally requires a leaving group activated by an electron-withdrawing group such as sulfone, ketone and certain heterocycle.<sup>10</sup> Typical leaving groups are fluorine, bromine, and nitro groups.<sup>11,12,9</sup> Certain aromatic heterocyclic functions similarly, and reports of the use of these nonconventional activating groups in polymer-forming reactions have appeared recently. Poly(arylene ether)s and related polymers comprise a class of materials known as engineering thermoplastics which possess desirable properties including melt and solution processability, high  $T_g$  (glass transition temperature), and good mechanical properties.<sup>13-15</sup> It is of obvious interest to extend this synthesis of hyperbranched poly(arylene ethers) to heterocycle-activated systems.

In this work, we presented a new leaving group ( $-SO_2CH_3$ ) activated by pyrimidine. The reactivity of the monomer, 4,6-dichloro-2-(methylsulfonyl)pyrimidine (DMP), in a nucleophilic aromatic substitution mechanism was estimated using  $^{13}C$  NMR spectroscopy (Fig. 1). The data support the methylsulfone as a leaving group activated by pyrimidine ring for substitution by phenoxide nucleophiles. Moreover, Baiazitov<sup>16</sup> has reported the calculated partial atomic charges on the chlorine- and sulfur-bound carbon atoms in pyrimidine that shows essentially the same activity of methylsulfone and chloride (Fig. 1). According to the results, we presented 4,6-dichloro-2-(methylsulfonyl)pyrimidine as a “BB'2” monomer reacted with 4,4'-thiobisbenzenethiol and 4,4'-thiodiphenol (A2) to synthesize two highly hyperbranched poly(arylene ether)s (HB-PAEs). The structure of synthesized hyperbranched polymers has been characterized by NMR and FTIR, while gel permeation chromatography (GPC), DSC, TGA and UV-Vis were used to investigate the properties.

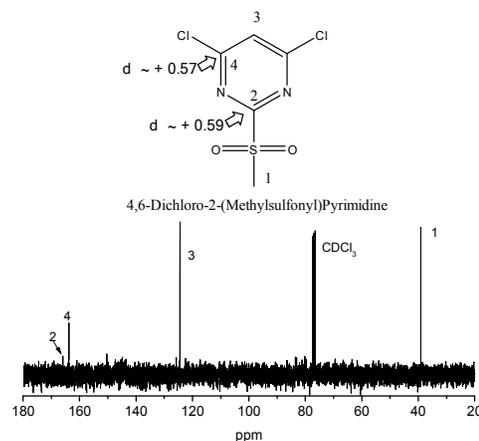
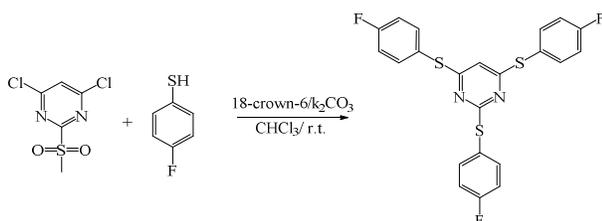


Fig. 1 The  $^{13}\text{C}$  NMR and calculated partial atomic charges of DMPM

The model compound has been synthesized by the reaction of 4,6-dichloro-2-(methylsulfonyl)pyrimidine and 4-fluorothiophenol (Scheme 1). The model compound was synthesized at room temperature to give a high yield (95%) which indicated the methylsulfonyl high reactivity as a leaving group activated by pyrimidine ring for substitution by thiophenoxide nucleophiles. The resulting model compound was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HPLC-MS.  $^1\text{H}$  NMR spectra (Fig. 2) of the model compound illustrates that the proton of the pyrimidine group appears at around  $\delta$  5.77 as a singlet, and the two protons of benzene appear at  $\delta$  7.36 and 7.02, respectively. In  $^{13}\text{C}$  NMR spectra (Fig. 2), the carbon 13 atoms in model compound show 7 signals, which resonate in the regions of 107-171 ppm. All the spectroscopic data obtained agrees with the expected structures. The above model reaction results reveal that the displacement of phenoxide and the methylsulfonyl group of 4,6-dichloro-2-(methylsulfonyl)pyrimidine is feasible at proper reaction conditions.



Scheme 1 Synthesis of the model compound

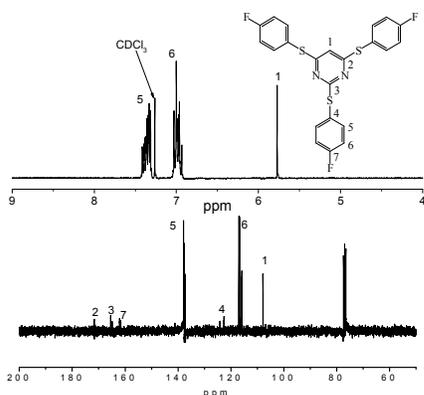
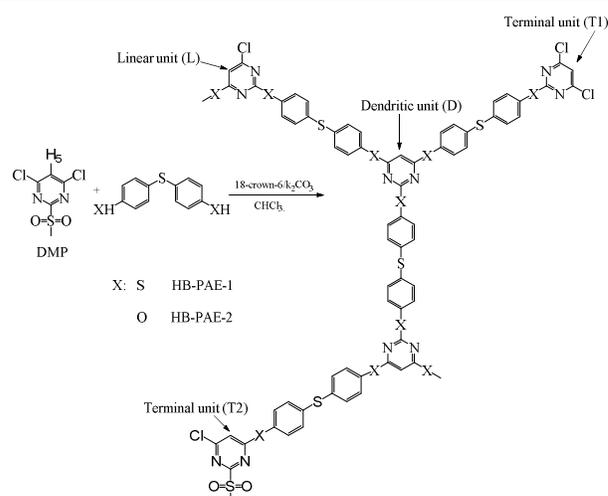


Fig. 2 The NMR spectra of the model compound

On the basis of the results of the model reaction, synthesis of new HB-PAEs containing pyrimidine units was attempted by nucleophilic aromatic substitution of 4,6-dichloro-2-(methylsulfonyl)pyrimidine (DMP) with 4,4'-thiobisbenzenethiol and 4,4'-thiodiphenol, as shown in Scheme 2. The polymerization with DMP and 4,4'-thiobisbenzenethiol was carried out via the one-pot method at room temperature for 12 h to give off-white polymer. Monitoring by GPC (Fig. S5), the weight-average molecular weight of HB-PAE-1 for 1, 3, 6 and 12 h was  $1.88, 2.46, 2.82$  and  $3.06 \times 10^4$ , respectively. The results illustrate that the reaction carried out fast in 3 hours, and after

that the reaction slowed down. Though the real molecular weight of the polymer may be even larger than the value estimated by GPC because dendritic macromolecules generally have smaller size than linear polymers with the same molecular weight and can hardly be expanded in solution.<sup>17</sup> It is feasible that the GPC data with the same polystyrene standards were used to analyse the kinetics of the polymerization.

The polymerization with DMP and 4,4'-thiodiphenol was also carried out via the one-pot method. However, the high molecular weight polymer was not obtained at room temperature ( $\sim 25^\circ\text{C}$ ). The result may be due to the weaker nucleophilic of phenoxide than that of thiophenoxide. After trying different reaction temperature, DMP can react with 4,4'-thiodiphenol at  $55^\circ\text{C}$  to give high molecular weight polymer.



Scheme 2 Synthesis of the HB-PAE

Table 1 Structure parameters of HB-PAE<sup>a</sup>

Code	$^1\text{H}$ chemical shift (ppm)/content(%)				DB <sub>Frechet</sub> <sup>d</sup> (%)
	D <sup>c</sup>	L <sup>c</sup>	T1 <sup>c</sup>	T2 <sup>c</sup>	
HB-PAE-1	6.0/47	6.5/36	6.8/9	7.0/8	64
HB-PAE-2	6.2/32	6.6/29	6.8/33	7.0/6	71

<sup>a</sup> Determined from  $^1\text{H}$  NMR.

<sup>b</sup> T: Terminal unit; L: Linear unit; D: Dendritic unit.

<sup>c</sup>  $\text{DB}_{\text{Frechet}} = (\text{D} + \text{T}) / (\text{D} + \text{T} + \text{L})$ .

The degree of branching (DB) is an important characteristic often used to reveal the structure of hyperbranched polymers. A combination technique of model compound studies and  $^1\text{H}$  NMR spectroscopy (Fig.S1) has been used to quantify the different subunits appearing in the hyperbranched polymer and subsequently determine its DB, and the results were summarized in Table 1.

The structures of the synthesized polymers were confirmed by  $^1\text{H}$  NMR and FTIR. As seen from Fig.3, the FTIR spectra of HB-PAE-1 and HB-PAE-2 showed minor absorption peaks corresponding to methyl at around  $3100\text{ cm}^{-1}$ , and the  $^1\text{H}$  NMR (Fig. S1) spectra of HB-PAE-1 and HB-PAE-2 also showed the

peak, which suggested the methylsulfone did not completed react.

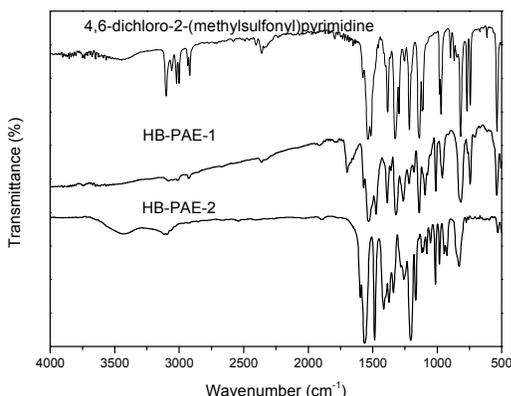


Fig. 3 FTIR spectra of DMPM and HB-PAE

From Table 1, the calculated percentages of the conversion of methylsulfone were 92% and 94% for HB-PAE-1 and HB-PAE-2, respectively.

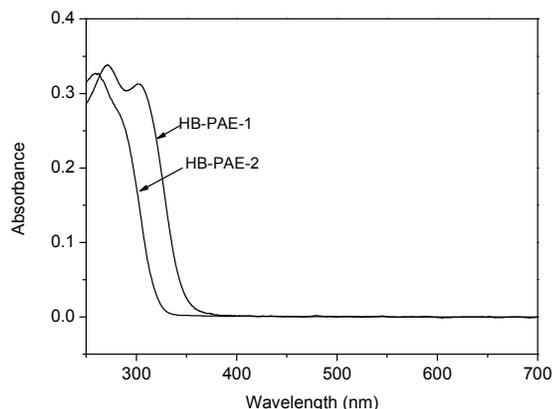


Fig. 4 UV-vis absorption spectrum of HB-PAE.

The characterization data and the thermal property of HB-PAEs are listed in table S1. HB-PAE-1 and HB-PAE-2, with inherent viscosity of 0.52 and 0.49 dL/g, respectively, showed good solubility in common organic solvents, such as acetone, toluene, THF, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub> as well as polar aprotic solvents (DMF, DMAc, and NMP). The glass transition temperature ( $T_g$ ) of HB-PAE-1 and HB-PAE-2 measured by DSC was 193 and 191 °C, respectively. The 5% weight loss temperature of HB-PAE-1 and HB-PAE-2 measured by TGA was 305 and 399 °C under nitrogen.

UV-vis absorption spectra (Fig.4) in CHCl<sub>3</sub> solution at room temperature showed two absorption peaks at 270 and 301 nm of HB-PAE-1 and only one absorption peak at 262 nm of HB-PAE-

2. The  $\lambda_{\text{cut-off}}$  values of HB-PAE-1 and HB-PAE-2 films were 335 and 273 nm, respectively. The transmittance (%) at 450 nm of HB-PAE-1 and HB-PAE-2 films was 77% and 99%, respectively. The in-plane ( $n_{\text{TE}}$ ) and out-of-plane ( $n_{\text{TM}}$ ) refractive indices of the HB-PAE-1 at 633 nm are 1.7307 and 1.7218, respectively. The  $n_{\text{av}}$  value of the polymer at 633 nm is 1.7277. The high refractive index of the polymer is obviously attributed to the introduction of a sulfur atom and pyrimidine unit into the polymer.<sup>18</sup> Moreover, thioether linkages in the molecular chain of the polymer endow with the low  $\Delta n$  of 0.0089.

## Conclusions

Methylsulfone was first employed as a leaving group to prepare hyperbranched poly(arylene ether)s by nucleophilic aromatic substitution. Two novel hyperbranched Poly(arylene pyrimidine ether) was synthesized successfully using 4,4'-thiobisbenzenethiol and 4,4'-thiodiphenol with 4,6-dichloro-2-(methylsulfonyl)pyrimidine under proper conditions utilizing methylsulfone as a new leaving group activated by pyrimidine via a simple nucleophilic substitution polymerization. The synthetic methodology described here provides a novel leaving group for the facile preparation of 3-dimensional macromolecules with a branched aromatic ether backbone containing pyrimidine units in the main chain, which are expected to find numerous applications, especially as an optical material.

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