

# Versatile postmodification of linear poly-*p*-phenylene to prepare microporous polymeric networks using the double aromatic nucleophilic substitution reaction



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## ABSTRACT

Microporous, hypercrosslinked poly-*p*-phenylenes with surface area of up to 1735 m<sup>2</sup> g<sup>-1</sup> have been prepared by combination of super acid catalyzed polymerization and the double aromatic nucleophilic substitution reaction. The surface area and pore size can be controlled by varying the amount of the crosslinking reagents, which tuned the crosslinking degree effectively. The capacity of adsorption of CO<sub>2</sub> of the MPNs largely depends on their specific surface areas.

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## 1. Introduction

Microporous polymeric networks (MPNs) [1–3] have drawn great interests in recent years, because of the intrinsic properties of large specific surface area, high chemical and thermal stability, and low density. They have exhibited potential applications in heterogeneous catalysis [4–7], gas storage and separation [8–11], and supercapacitive energy storage [12], and so on.

Among the wide variety of MPNs, hyper-crosslinked polymers (HCPs) [13–19] are some of the first purely microporous organic materials. As we all know, HCPs are usually developed by a certain crosslinking reaction, that is, crosslinking the precursor material (e.g. linear polymers) which containing reactive groups, thus making crosslinked networks highly rigid and unable to collapse. The crosslinking reactions which have been studied include Lewis acid catalyzed Friedel–Crafts reactions [20–23], *N*-alkylation with diiodomethane or paraformaldehyde [24,25], Ullmann and Buchwald coupling reactions [26], etc. However, the double aromatic nucleophilic substitution reaction, which is highly efficient and mainly used in the synthesis of polymers of intrinsic microporosity (PIMs) [26–31], has not been reported to our knowledge as a crosslinking

reaction to prepare HCPs till now. Recently, super acid such as trifluoromethyl sulfonic acid (TFSA) catalyzed polymerization has been studied systematically by M. G. Zolotukhin and coworkers [32–36]. They found that condensations of carbonyl compounds containing electron-withdrawing substituents, adjacent or relatively close to the carbonyl group, with nonactivated aromatic hydrocarbons, carried out in a TFSA (or in a mixture of TFSA with methylene chloride) medium at room temperature, can afford linear, high-molecular-weight poly-*p*-phenylenes, which are a kind of high performance polymer with high thermal stability. Taking into account the strong electron-withdrawing effect of the fluorine atom, fluorinated aldehydes and ketones, for example, pentafluorobenzaldehyde (PFBA) and trifluoromethylacetophenone (3FK), are all proper candidates for the one-pot synthesis of fluorinated aromatic poly-*p*-phenylenes. The nonactivated aromatic hydrocarbons containing biphenyl, diphenyl ether, *p*-terphenyl, 4,4'-diphenoxybenzophenone, 1,3-bis(4'-phenoxybenzoyl)benzene, and 1,4-bis(4'-phenoxybenzoyl)benzene, and so on. However, HCPs derived from crosslinking of linear poly-*p*-phenylenes have not been studied till now.

In the present work, we for the first time combine the two efficient reactions abovementioned to prepare HCPs, in order to extend beyond polystyrene-based systems which still constitute the majority of examples in the HCPs. The crosslink reagent herein is 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethylspirobisindane (TTSBI). The synthesis of the parent linear poly-*p*-phenylenes, the crosslinking by TTSBI, the characterization of the HCPs' structures, and

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the effect of TTSBI amount on the surface area and pore volume distributions were studied in detail.

## 2. Experimental

### 2.1. Materials

Pentafluorobenzaldehyde (PFBA), biphenyl (BP), *p*-terphenyl (*p*TP), trifluoromethyl sulfonic acid (TFSA), anhydrous potassium carbonate ( $K_2CO_3$ ), and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethylspirobisindane (TTSBI) were all obtained from J&K Scientific Ltd. (Beijing) and used without further purification. *N,N'*-dimethyl acetamide (DMAc) and dichloromethane (DCM) were purchased from Beijing Chemical Reagents Co., China and distilled over CaH<sub>2</sub> and stored over 4 Å molecular sieves prior to use.

### 2.2. Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer 782 Fourier transform spectrophotometer in the form of KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were performed on a Bruker Avance 400 Spectrometer operating at 400 and 100 MHz, using CDCl<sub>3</sub> as the solvents. Solid-state <sup>13</sup>C NMR spectra were performed on a Bruker Avance III Spectrometer operating at a frequency of 100 MHz and using cross-polarization/magic angle spinning (CP/MAS). The magic angle spinning rate was set at 5.0 kHz to minimize spinning sideband overlap. The powder wide-angle X-ray diffraction (PXRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu/Kα-1 radiation, operated at 40 kV and 200 mA. SEM images were obtained with a field emission scanning electron microscope (JSM-5600LV, JEOL, Japan). The powder samples were coated with gold by sputtering prior to observation. TEM images were obtained with A JEM-2010 transmission electron microscopy (TEM), operating at an accelerating voltage of 200 KV. Gel permeation chromatography (GPC) was performed on a Waters GPC (mobile phase, tetrahydrofuran [THF]) using polystyrene standards and a UV detector. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Netzsch thermal analysis system (STA 449C) in nitrogen at a heating rate of 10 °C/min. Nitrogen sorption experiments and micropore analysis were conducted at 77 K using Micromeritics ASAP 2020. Before sorption measurements, the samples were degassed in vacuum overnight at 120 °C. The surface

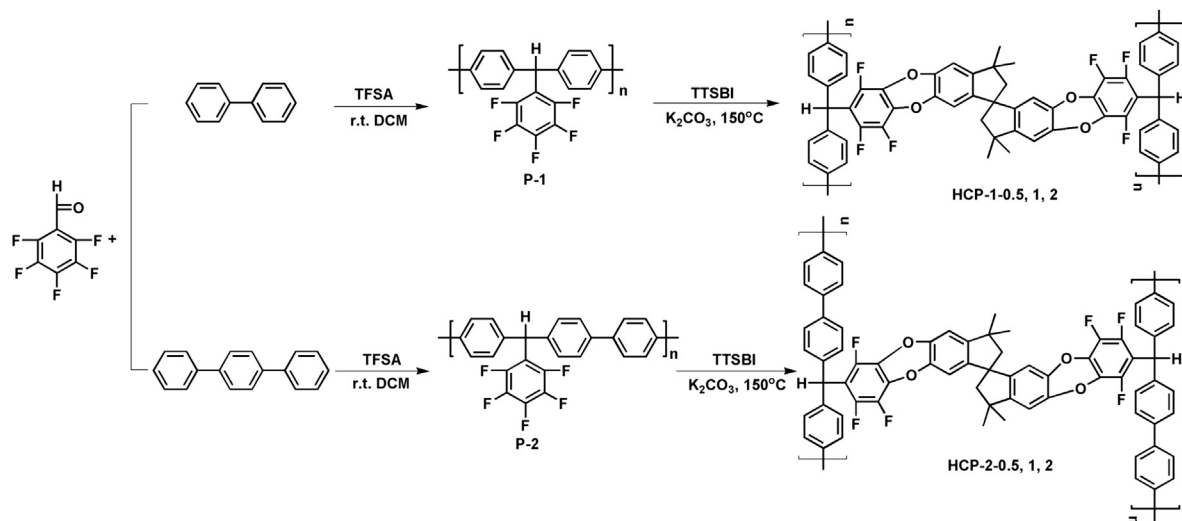
area was calculated from multipoint BET plot, and the pore volume was determined by nonlocal density functional theory (NLDFT). Carbon dioxide sorption isotherms were obtained with a Micromeritics ASAP 2020M + C accelerated surface area and porosimetry analyzer at 273 K; the samples were degassed overnight at 120 °C before test.

### 2.3. Synthesis of the parent linear poly-*p*-phenylene

The polymerization procedure was conducted according to a reported method [32]. Take P-1 for example, into a 100 mL single necked flask equipped with magnetic stirrer, PFBA (1.96 g, 10 mmol), BP (1.54 g, 10 mmol), TFSA (3.0 g, 20 mmol), and DCM (15 mL) were added and the mixture was stirred for about 48 h at room temperature. Then the reaction mixture was dropped into excess amount of methanol. The light color precipitate was collected and washed copiously with water and methanol. The procedure of redissolving in chloroform and precipitating in methanol was performed twice. The final product was dried at 100 °C in vacuum to constant weight. P-2 was synthesized in a similar procedure by changing BP to *p*TP.

### 2.4. Crosslinking by TTSBI

The crosslink reaction was conducted according to the high temperature double aromatic nucleophilic substitution reaction, as studied by M. D. Guiver et al. [28,37]. TTSBI was selected as the crosslinker. The molar ratios of TTSBI to the linear poly-*p*-phenylene (calculated by the  $M_n$  of repeat unit) were 1:2, 1:1, and 2:1, and the final polymer networks' code were set as HCP-1-0.5, HCP-1-1, HCP-1-2, HCP-2-0.5, HCP-2-1, HCP-2-2, respectively, as shown in Scheme 1. HCP-1-0.5 was given as an example. Into a 25 mL, two-necked, round bottom flask equipped with condenser and magnetic stirrer, the linear polymer, P-1 (0.332 g, 1.0 mmol, calculated by repeat unit), TTSBI (0.170 g, 0.5 mmol),  $K_2CO_3$  (0.276 g, 2.0 mmol), and anhydrous DMAc (5 mL) were added. Under nitrogen flow the mixture was heated to 150 °C and remained there for 1 h. On cooling, the mixture was poured into excess amount of distilled water and neutralized with diluted hydrochloric acid. The yellow precipitate was collected and extracted in Soxhlet extractor by CH<sub>3</sub>OH and CHCl<sub>3</sub> for 24 h, respectively. Then the final product was dried at 100 °C in vacuum to constant weight. By altering the amount of TTSBI and the linear polymers (See Table S1 in the



**Scheme 1.** Synthesis of the parent linear poly-*p*-phenylene and the following crosslinking reactions by TTSBI.

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