

Synthesis of Porous Sulfonamide Polymers by Capturing Atmospheric Sulfur Dioxide

Pengfei Zhang,^[a, b] Dong Chen,^[a] Nanqing Chen,^[c] Kuan Huang,^[c] Duanjian Tao,^{*,[c]} Meijun Li,^[c] and Sheng Dai^{*,[b, c]}

The emission of SO₂ from the burning of fossil fuel has resulted in a severe atmospheric pollution. The development of efficient strategies for not only capturing but also utilizing SO₂ is highly welcome. A simple, mild, and versatile method has been developed that exploits atmospheric SO₂ in the synthesis of porous polymers. Inspired by the chemistry of sulfonamides, contorted or bulky monomers with multiple amine groups were cross-linked by SO₂ molecules in the presence of Et₃N and I₂. The sulfonamide polymers have specific surface areas up to 211 m²g⁻¹. In contrast to most porous polymers, the porous sulfonamide polymers (PSPs) are soluble in organic solvents, thus offering a chance to study their structures and molecular weights by liquid-state NMR spectroscopy and gel-permeation chromatography, respectively. Moreover, these PSPs can be easily processed into organic membranes. The current concept should encourage more studies to design porous polymers with SO₂ or CO₂ gases as linkages.

Porous organic polymers (POPs) are an exceptional class of porous materials that have high surface areas, low densities, and great chemical stabilities, and can incorporate various functional groups.^[1] These attractive features make POPs promising candidates for many applications, such as catalysis, separations, gas storage, and energy storage.^[2] Efforts made by chemistry and material scientists in the past decade have made use of a number of organic reactions to build POPs. For example, polymerization/polycondensation through C–X (X = C, O, N) bond formation strategies, such as metal-mediated couplings, cyclotrimerization, imine/amide/imide-based condensation, aromatic nucleophilic substitution, oxidative coupling, hyper-crosslinking processes by Lewis acids, and radical polymerization, are frequently used.^[3] Indeed, these processes have greatly expanded the chemistry of POPs and allowed the

engineering of POPs with specific requirements with regards to surface area, pore size, surface affinity, and target organic group. However, to our knowledge the construction of POPs based on C–S bond formation has not been reported to date, although, given the abundant libraries of sulfur-based precursors, it is of great interest.

As a toxic sulfur-containing molecule, SO₂ has been recognized as a significant source of atmospheric pollution that arises from the burning of fossil fuels. With a view to SO₂ capture, many absorbent systems, such as limestone, ammonia solution, and basic ionic liquids, have been well studied and several are commercially realized in industry already.^[4] Certainly, the chemical transformation of SO₂ is an emerging means of SO₂ remediation. Currently, SO₂ is mostly used as an intermediate in the production of sulfuric acid.^[5] In this regard, the harvesting of SO₂ for high-value materials by organic processes seems more attractive.

Herein, we report the rational and direct utilization of SO₂ in the synthesis of porous sulfonamide polymers (PSPs). The PSPs are bridged by C–S bonds between aromatic amines and SO₂. The current polycondensation is a rapid room-temperature process and makes direct use of atmospheric SO₂. Moderate surface areas up to 211 m²g⁻¹ can be obtained for these PSPs. Interestingly, the products are soluble in organic solvents, which enables processing of the PSPs into membranes.

With a view to the design of sulfonamide polymers with accessible pores, rigid building units with multiple amine groups are required to form a strong cross-linked backbone to withstand the intermolecular packing. The contorted 9,9'-bis(4-aminophenyl)fluorene (ABF) and bulky 1,3,5-tri(4-aminophenyl)benzene (TAB) were selected as amine precursors (Scheme 1). The polycondensation proceeded with Et₃N as SO₂ capturing agent and I₂ as catalyst.^[6] Et₃N is known to form donor–acceptor complexes Et₃N–SO₂ by capturing molecular SO₂.^[7] The addition of I₂ into the system can result in the formation of reactive sulfonyl iodides (SO₂I₂), which are readily attacked by the amine groups on ABF or TAB in nucleophilic substitution reactions.^[8] The polycondensation between amine monomers and SO₂ can thus proceed with formation of sulfonamide (–NH–SO₂–NH–) linkages. A linear polymer with a twisted backbone was obtained from ABF (PSP-1), whereas the coupling of TAB with SO₂ resulted in a cross-linked polymer (PSP-2). Both PSP samples were soluble in *N,N'*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP).

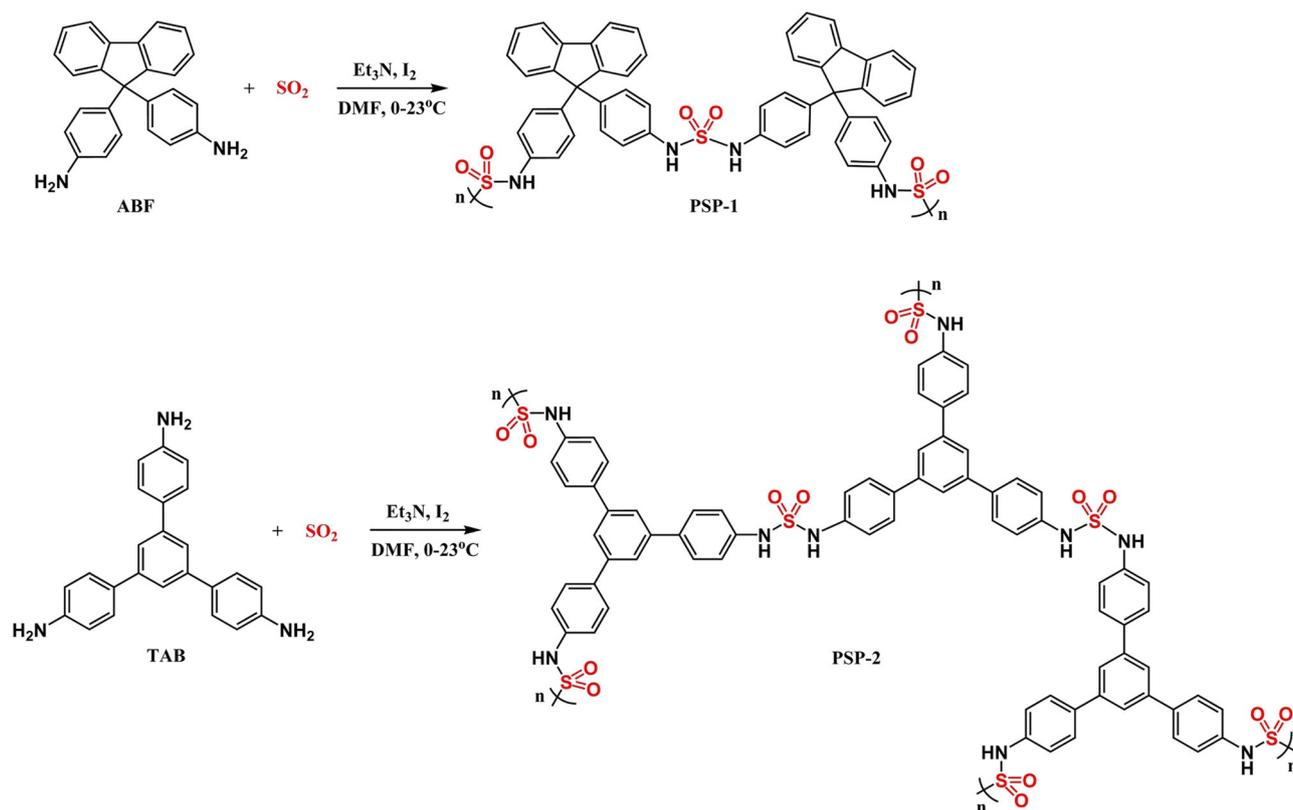
The incorporation of SO₂ into polymers was investigated by Fourier transform infrared spectroscopy (FTIR) spectroscopy of the PSPs before and after polycondensation (Figure 1a,b).

[a] Prof. P. F. Zhang, Dr. D. Chen
School of Chemistry and Chemical Engineering
Shanghai Jiao Tong University, Shanghai 200240 (PR China)

[b] Prof. P. F. Zhang, Prof. S. Dai
Chemical Sciences Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831 (USA)
E-mail: dais@ornl.gov

[c] Dr. N. Q. Chen, Dr. K. Huang, Dr. D. J. Tao, M. Li, Prof. S. Dai
Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996 (USA)
E-mail: djtao@jxnu.edu.cn

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Scheme 1. Preparation of porous sulfonamide polymers from amine precursors and SO_2 (1 bar).

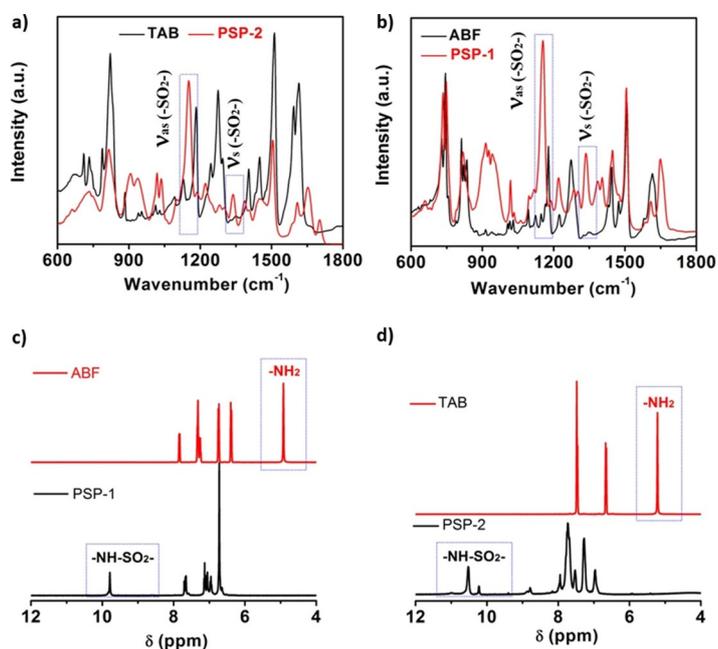


Figure 1. a, b) FTIR spectra of PSPs and amine precursors. c, d) NMR spectra of PSPs and amine precursors.

Compared with the amine precursors, PSPs gave new sorption bands at around 1335 and 1152 cm^{-1} . These bands are characteristic of the sulfonamide group and are attributed to the asymmetric and symmetric stretching vibrations of $\text{O}=\text{S}=\text{O}$, re-

spectively.^[9] The FTIR result gives evidence of the formation of sulfonamide connections. The good solubility of PSPs in DMF offers the chance to study the structure by liquid-state NMR spectroscopy. POPs with highly cross-linked chains—with the exception of polymers of intrinsic microporosity (PIMs)—are generally studied by solid-state NMR spectroscopy with broad peaks, whereas liquid-state NMR spectroscopy can provide more precise information. Indeed, significant shifts were observed in the ^1H NMR spectrum from precursors to PSPs. The signal at 4.92 ppm for aromatic NH_2 within ABF moved to 9.79 ppm for PSP-1, owing to its proximity to the strongly electron-withdrawing sulfone (Figure 1c). A similar shift from 5.21 to 10.52 ppm in the ^1H NMR spectrum took place after the polycondensation of TAB by SO_2 (PSP-2; Figure 1d). Hence, FTIR and NMR spectroscopy both confirm the formation of sulfonamide linkages in PSPs.

The PSP samples were then studied by X-ray diffraction (XRD; Figure 2a). PSP-1 showed several peaks between 10° and 30° , suggesting the crystallinity of this linear sulfonamide product. Meanwhile, PSP-2, with a cross-linked network, is amorphous, as indicated by the broad peaks at 15° and 22° . In addition, the PSP samples both showed good thermal stabilities up to 300°C , in both nitrogen and air atmospheres (Figure 2b).

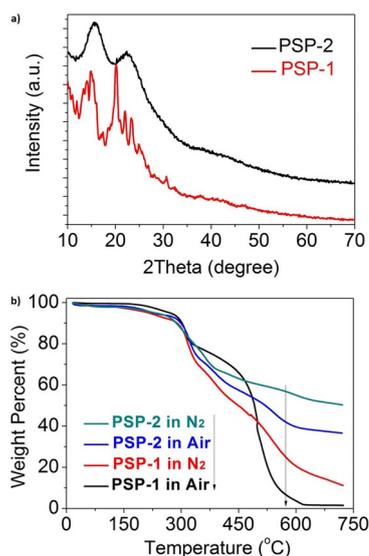


Figure 2. a) XRD patterns of PSP samples. b) TGA curves of PSP samples in air or nitrogen ($10^{\circ}\text{C min}^{-1}$).

The porosities of the PSPs were determined by measuring N_2 adsorption–desorption isotherms at 77 K. The isotherm of PSP-1 showed stable adsorption up to $P/P_0 \approx 0.8$, after which a sharp uptake was observed (Figure 3). This sorption indicates the presence of macropores. The Brunauer–Emmett–Teller (BET) surface area of PSP-1 was $57 \text{ m}^2 \text{ g}^{-1}$. In addition, the adsorption branch of the isotherm for PSP-2 displayed increasing N_2 uptake on increasing the relative pressure, and thus both micro- and mesopores were expected to be present (Figure 3). The BET surface area of PSP-2 was $211 \text{ m}^2 \text{ g}^{-1}$. In comparison to the values for some POPs, which can attain values of $> 1000 \text{ m}^2 \text{ g}^{-1}$,^[1f,g,2a,e] the surface areas of PSPs are moderate.

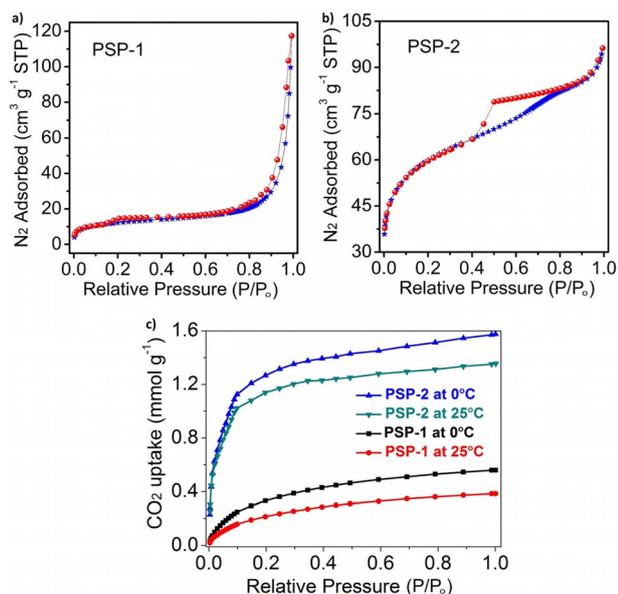


Figure 3. a, b) N_2 -sorption isotherms of PSPs at 77 K. c) CO_2 sorption isotherms at 273 and 298 K.

The exothermicity of SO_2 addition limits the current reaction, which has to be carried out at room temperature or lower. However, the mild temperature cannot provide enough energy for the chain growth of the rigid and twisted backbone at a late stage and the solubility of the macromolecular product at room temperature is somewhat low. Therefore, the polycondensation is terminated prematurely, which in turn endows the PSPs with good solubility in organic solvents. In addition, the CO_2 adsorption capacity of the PSPs is moderate (Figure 3c).

Most POPs (with the exception of PIMs) are insoluble because of their highly cross-linked backbones, whereas the solubility of PSPs offers an opportunity to explore their molecular mass by gel-permeation chromatography (GPC; Table 1). PSP-1

Table 1. Characterization of PSPs by GPC and N_2 sorption measurement. Synthesis of porous sulfonamide polymer.^[a]

Sample	$M_w/10^3$ [g mol^{-1}]	$M_n/10^3$ [g mol^{-1}]	PDI (M_w/M_n)	S_{BET} [$\text{m}^2 \text{ g}^{-1}$]	V_{pore} [$\text{m}^3 \text{ g}^{-1}$]
PSP-1	2.1	1.6	1.31	57	0.08
PSP-2	10.0	9.6	1.05	211	0.14

[a] Molecular mass determined by gel-permeation chromatography based on polystyrene standards. BET surface area determined by N_2 -sorption measurements at 77 K. M_n = number-average molar mass; M_w = weight-average molar mass.

has a low number-average molar mass (M_n) of 1600 and the molecular chain is roughly estimated to be composed of four repeating units ($\text{ABF} + \text{SO}_2$). It is interesting that such a short chain can generate a surface area of $57 \text{ m}^2 \text{ g}^{-1}$. Note that the ABF molecule alone only has a surface area of $2 \text{ m}^2 \text{ g}^{-1}$. We attribute it to the inflexible and contorted structure of PSP-1, which may resist molecular space packing. PSP-2 has a higher molecular mass ($M_n = 9646$ and weight-average molar mass $M_w = 10088$). What is surprising here is the low polydispersity index (PDI; M_w/M_n), which is calculated to be 1.05. The narrow molecular weight distribution may be the result of the low reaction temperature and thus the polycondensation between SO_2I_2 and TAB is assumed to proceed in a mild and controlled manner, which enables uniform growth of the chain.

The morphology of the polymers was studied by scanning electron microscopy (SEM). PSP-1 was composed of nanocubes. The formation of cubic units somewhat agrees with the crystalline structure discerned by XRD (Figure 4a). PSP-2 was made up of sphere-like aggregates, generating a high degree

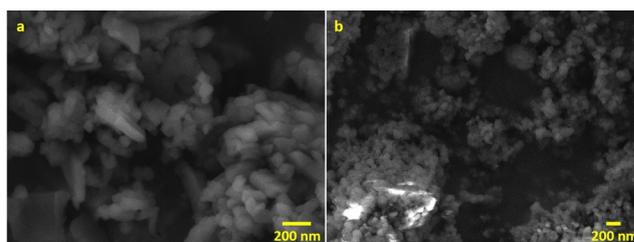


Figure 4. SEM images of PSP-1 (a) and PSP-2 (b).

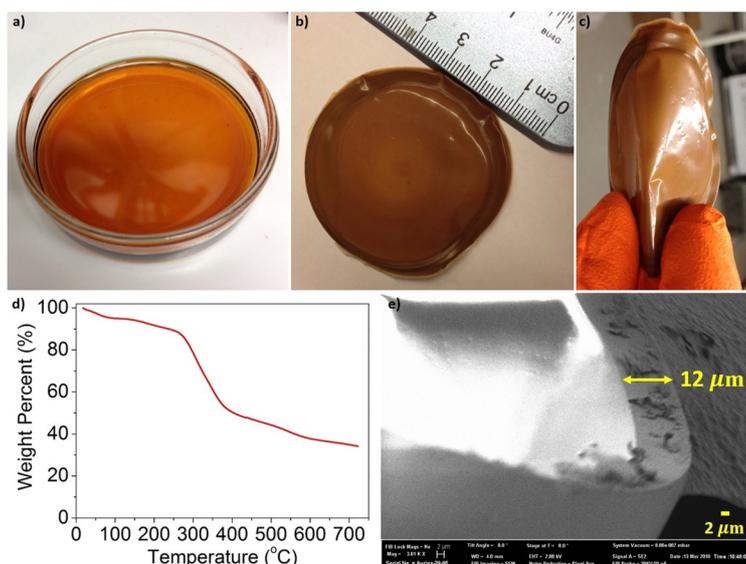


Figure 5. a) Mixture of PSP-2 (100 mg) and polysulfone (50 mg) in DMF (5 mL). b, c) Resulting membrane. d) TGA curve of the membrane in nitrogen (heating rate: $10^{\circ}\text{C min}^{-1}$). e) SEM image of the membrane.

of interstitial porosity (Figure 4b). Inspired by the solubility of the PSPs, we then investigated their processing into organic membranes (Figure 5). A clear solution of PSP-2 and commercial linear polysulfone mixture was present in a dish (Figure 5a). After solvent evaporation, a free-standing membrane with a diameter of approximately 4 cm was obtained (Figure 5b). Interestingly, the membrane is flexible (Figure 5c). In addition, the thermal stability of the membrane is good, as shown by thermogravimetric analysis (TGA; Figure 5d). SEM images show the smooth surface of the membrane and its thickness is around $12\ \mu\text{m}$ (Figure 5e).

In summary, PSPs are a promising class of porous polymers constructed by C–S bond formation, which represent a useful alternative to the reaction library available for POPs. The nucleophilic substitution-mediated polycondensation, which couples amine monomers with SO_2 as a bridge, elegantly offers an effective and facile process to fix atmospheric SO_2 . We believe that a variety of porous polymers based on acid gas linkages (e.g., SO_2 , CO_2) could be prepared after careful selection of monomers.

Experimental Section

General methods and characterization

Both 9,9'-bis(4-aminophenyl)fluorene (ABF) and 1,3,5-tri(4-aminophenyl)benzene (TAB) were purchased from TCI Chemicals America. N_2 adsorption-desorption analysis was performed at 77 K by using a TriStar (Micromeritics Instrument Corp.; Norcross, GA, USA), equipped with automated surface-area and pore-size analyzer. Prior to analysis, samples were degassed at 120°C for 24 h. The specific surface area of the samples was calculated by using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05–0.20. Fourier-transform infrared spectra were collect-

ed by using a PerkinElmer Frontier FTIR spectrometer. Molecular weights and molecular weight distributions were measured by gel-permeation chromatography (GPC) on Ultrastaygel columns with DMF as the eluent at a flow rate of $1\ \text{mL min}^{-1}$. The values obtained were determined by comparison with a series of polystyrene standards.

Synthesis of porous sulfonamide polymers

In a typical procedure, triethylamine (6 mmol) and DMF (10 mL) were stirred in a three-neck 50 mL glass reactor. The reactor was loaded into an ice bath for 10 min. Then, SO_2 gas (1 atm) was bubbled through the amine solution for 10 mins while the reactor was kept in an ice bath. Then, 2 mmol I_2 was added into the mixture, and at the same time SO_2 gas was stopped. The reactor was closed, and the reaction was performed at room temperature for 20 min. Then, 9,9'-bis(4-aminophenyl)fluorene (1 mmol) or 1,3,5-tri(4-aminophenyl)benzene (0.67 mmol) was added into the mixture. The polycondensation reaction was then stirred at room temperature for 20 h. Finally, methanol (35 mL) was added into the mixture and the solid product was collected by centrifugation. The sample was dried at 80°C under vacuum overnight.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–S coupling • porous polymers • pollution remediation • SO_2 capture • sulfonamides

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