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Efficient and simplified strategy to access novel polysulfamate materials: from laboratory research to industrial production†

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The development of materials from laboratory research to industrial production is a complex, challenging, but significant process. Polysulfamates have not been industrially available to date because of the absence of efficient and economical synthetic methods. Herein, a comprehensive process for the development of novel polysulfamate (PSA) materials from laboratory research to industrial manufacture is reported. PSAs were prepared with high molecular weight and narrow polydispersity through nucleophilic polycondensation between aryl bisphenols and disulfamoyl difluorides in the presence of an inorganic base. The polymerization process was stable in moisture and air. The industrial production of PSAs was achieved on 100 kg scale with the assistance of a cooperative factory for the first time. The PSAs displayed excellent solvent tolerance, acid/base resistance, thermal stability, machinability and mechanical properties, which were promising for their application in the area of engineering plastics, as well as high-performance resins.

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Introduction

The sulfur(vi) fluoride exchange (SuFEx) reaction is an efficient and rapid method to synthesize functional molecules containing (poly)sulfates, (poly)sulfonates or sulfamates,^{1,2} which has been widely applied in the fields of organic synthesis, materials science, pharmaceutical chemistry and biochemistry.^{3–5} In materials chemistry, especially, polysulfates and polysulfonates with excellent properties have been successfully synthesized through the SuFEx reaction.⁶ Additionally, this new click reaction has also been instrumental in the formation of S(vi)–N bonds,⁷ resulting in the construction of sulfonamides, sulfamates, and sulfamides.^{8,9} Sulfamides are valuable motifs, which can be found in therapeutic applications^{10,11} and the catalytic synthesis of pyrimidine systems,^{12,13} as well as in polymer synthesis.^{14,15} However, despite their good performance in bioactive compounds, sulfamates are comparatively underexplored because

of the challenges posed by their synthesis. In particular, polysulfamate (PSA) materials have not been available to date because of the absence of an efficient and economical synthetic method. S. Mahapatra *et al.* reported an advanced process to synthesize nitrogenous sulfur(vi) compounds.¹⁶ Compared to traditional synthetic protocols, S(vi) fluorides were activated by calcium triflimide and DABCO for SuFEx with amines (Fig. 1a1). However, the stoichiometric utilization of $\text{Ca}(\text{NTf}_2)_2$ and DABCO sets up a barrier against the large-scale synthesis of PSAs.

With the progress of science and technology, the modification of existing materials or the development of new materials are of great significance.^{17,18} We previously reported a nucleophilic process to construct sulfate bonds through the reaction of aryl phenols and aryl fluorosulfates (Fig. 1a2).¹⁹ Polysulfates are promising engineering polymers due to their excellent mechanical and chemical properties.^{19–21} Thus, we hypothesized that the reaction between aryl phenols and $\text{R}_2\text{N}-\text{SO}_2\text{F}$ in the presence of an inorganic base (IOB) could be applicable to the synthesis of sulfamates. We proposed that polymers bearing a sulfamate bond instead of a sulfate bond may lead to a PSA with the properties of tenacity, machinability and mechanical performance.

Materials science plays an indispensable role in the progress of science, transmission of civilization and the development of human society.^{22–24} The purpose of laboratory research is to provide primary products and technical services for industrial production. Generally, the development of

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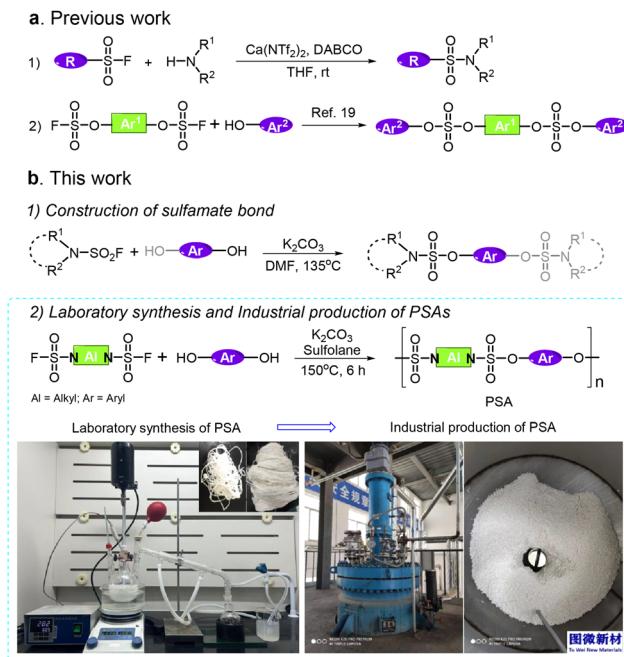


Fig. 1 Reaction of sulfonyl fluorides and nucleophilic reagents.

materials from laboratory research to industrial production and commercial applications is a complex, challenging and protracted process.²⁵ For example, polycarbonates (PCs) were first prepared by Einhorn in 1898, but the widely used PC produced from bisphenol A (BPA) was prepared in 1941.²⁶ The polymerization of vinyl chloride in sealed tubes was reported in 1872, but commercial interest in poly(vinyl chloride) was revealed in 1928.²⁷ Polyethylene (PE) was produced from ethylene in 1936 by Fawcett, but all commercial PE was produced by high-pressure processes until the mid-1950s.²⁸ Therefore, substantial efforts should be made to achieve the scaled-up and industrial production of PSA, which is necessary to support their industrial application.

The goal of our research is to develop an efficient and cost-effective protocol to access polysulfamates with high molecular weight and low polydispersity index (PDI) both in laboratory research and industrial production. Herein, we report a simplified method to access sulfamates (Fig. 1b1) and polysulfamates (Fig. 1b2) efficiently through the reaction between aliphatic sulfonyl fluorides and aryl phenols in the presence of IOBs. We also evaluated the physical and chemical properties of the polysulfamates. This study aims to bridge the gaps between laboratory research, industrial production, and practical applications of PSAs.

Results and discussion

Nucleophilic construction of a sulfamate bond

We began our study by treating pyrrolidine-1-sulfonyl fluoride (**1a**) with 4-(2-phenylpropan-2-yl) phenol (**2a**) in the presence of K_2CO_3 in *N,N*-dimethylformamide (DMF). (For details of the

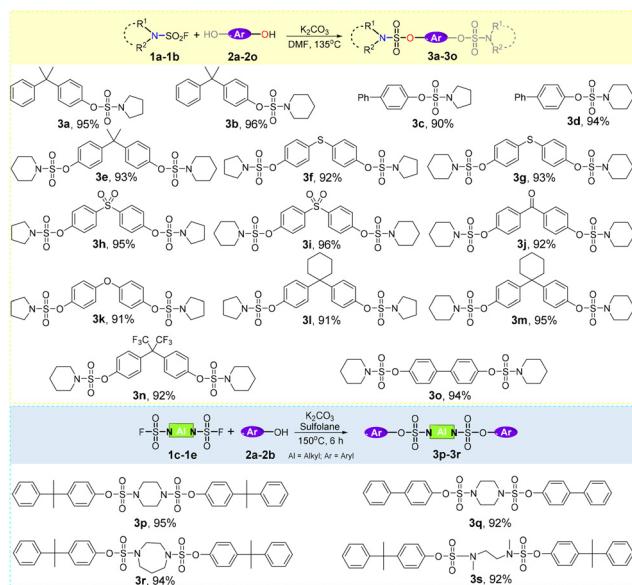


Fig. 2 Substrate scope of the nucleophilic construction of the sulfamate bond.

screening of conditions, see ESI section 2.1.†¹⁹ To our delight, the corresponding sulfamates could be obtained in excellent yields when the reaction was conducted at 135 °C. Fig. 2 shows the substrate scope of this nucleophilic sulfamate bond-construction reaction. Various aliphatic sulfonyl fluorides can react with aryl phenols, affording the desired sulfamates in excellent yields. Among them, piperidine-1-sulfonyl fluoride displayed higher reactivity with aryl phenols than pyrrolidine-1-sulfonyl fluoride under the reaction conditions (Fig. 2). These results inspired us to try polycondensation between disulfamoyl difluorides and aryl diphenols.

Laboratory research into PSAs

Laboratory synthesis of PSAs. In general, the nucleophilic substitution reaction between aryl fluorosulfates and aliphatic amines (see ESI section 3.1† for details)⁷ or the reaction between aryl bisphenols and alkylsulfamoyl fluorides could afford the desired PSAs (Fig. 1). However, our condition screening experiments showed that the reaction between aryl bisphenols and alkylsulfamoyl fluorides was the preferred one to obtain a PSA with a higher M_n and narrow PDI. Screening of the conditions for polycondensation (Table 1) was evaluated on the basis of previous work,¹⁹ using **A1** and **B1** as model monomers. When the polycondensation was conducted at 25 °C in the presence of Na_2CO_3 for 6 h in DMF, no desired polymer was observed (Table 1, entry 1). Then, we increased the reaction temperature to 80 °C and after 6 h, both Na_2CO_3 and K_2CO_3 promoted the polycondensation and gave the poly-sulfamate **P1** with $M_n^{\text{PS}} = 1.26$ kDa (PDI = 1.80) and $M_n^{\text{PS}} = 1.48$ kDa (PDI = 1.93), respectively (Table 1, entries 2 and 3). These results indicated that the polycondensation reaction between **A1** and **B1** could be promoted by K_2CO_3 or Na_2CO_3 . The M_n^{PS} of **P1** was dramatically improved to 61.49 kDa (PDI =

Table 1 Screening of conditions for the synthesis of **P1**^a

| Entry | Base | Solvent | T/°C | M _n ^{PS} /kDa | PDI |
|-------------------|---------------------------------|-----------|------|-----------------------------------|-------------|
| 1 | Na ₂ CO ₃ | DMF | 25 | — | — |
| 2 | Na ₂ CO ₃ | Sulfolane | 80 | 1.26 | 1.80 |
| 3 | K ₂ CO ₃ | Sulfolane | 80 | 1.48 | 1.93 |
| 4 | Na ₂ CO ₃ | DMF | 135 | 61.49 | 1.59 |
| 5 | K ₂ CO ₃ | DMF | 135 | 77.84 | 1.58 |
| 6 ^b | K ₂ CO ₃ | DMF | 135 | 69.52 | 1.69 |
| 7 ^c | K ₂ CO ₃ | DMF | 135 | 64.79 | 1.66 |
| 8 | K ₂ CO ₃ | DMF | 150 | 42.17 | 1.49 |
| 9 ^b | K ₂ CO ₃ | DMF | 150 | 44.57 | 1.52 |
| 10 ^d | K ₂ CO ₃ | DMF | 150 | 61.38 | 1.66 |
| 11 ^{b,d} | K ₂ CO ₃ | DMF | 150 | 60.72 | 1.68 |
| 12 | K ₂ CO ₃ | Sulfolane | 150 | 155.02 | 1.65 |
| 13 | K ₂ CO ₃ | NMP | 150 | 49.73 | 1.53 |
| 14 | K ₃ PO ₄ | Sulfolane | 150 | 76.83 | 1.68 |
| 15 | Na ₃ PO ₄ | Sulfolane | 150 | 65.32 | 1.72 |
| 16 | CaCO ₃ | Sulfolane | 150 | — | — |

^a The reaction was carried out with 2.5 mmol **A1** (1.00 equiv.) and **B1** (1.01 equiv.) in 5 mL of solvent in the presence of 2.2 equiv. of base for 6 h. ^b 10 mL of DMF was used. ^c 1.1 equiv. of base was used. ^d The reaction was carried out for 12 h. *T*, external temperature. M_n^{PS}, number-average molecular weight with polystyrene as standard. PDI, polydispersity index.

1.59) with quantitative yield, by increasing the reaction temperature to 135 °C in the presence of Na₂CO₃ (Table 1, entry 4), while K₂CO₃ exhibited better promotion performance for this reaction (Table 1, entry 5). Reducing the reaction concentration or the amount of base could result in **P1** with lower M_n^{PS} (Table 1, entries 6 and 7). Polycondensation carried out at 150 °C did not show superior results compared with that at 135 °C, producing **P1** with lower M_n^{PS} (42.17–60.72 kDa vs. 77.84 kDa) and relatively unchanged PDI (Table 1, entries 8–11). This might be because of decomposition of the solvent at high temperature. Then we tried sulfolane and NMP, and the results indicated that sulfolane was the best choice when the reaction was carried out at 150 °C, giving **P1** with high molecular weight (M_n^{PS} = 105.10 kDa) and narrow PDI (1.58) in quantitative yield (Table 1, entry 12). When the reaction was conducted in *N*-methylpyrrolidone (NMP), no better result was obtained (Table 1, entry 13). Neither did the employment of K₃PO₄ or Na₃PO₄ show superior results (Table 1, entries 14 and 15). Alkaline-earth metal carbonates, such as MgCO₃, CaCO₃ or BaCO₃, could not promote the reaction (Table 1, entry 16). We did not investigate a higher reaction temperature because attacks by the base on R₂N–SO₂F, decomposition of the solvent and oxidation of aryl phenol at high temperature had negative effects on polycondensation. We have now obtained the optimal conditions (Table 1, entry 12) for this polycondensation reaction to synthesize PSAs.

With the optimal conditions in hand, we then examined monomers with various groups to verify the application scope of our process, and the results are shown in Table 2. Both aliphatic chains or rings of disulfamoyl difluorides could react

Table 2 Synthesis of PSAs from diverse building blocks^{a,b}

| PSA | Mon. | M _n ^{PS} /kDa | PDI | PSA | Mon. | M _n ^{PS} /kDa | PDI | | |
|------------|----------------|-----------------------------------|------|------------------------|---------------------|-----------------------------------|------|--|--|
| P1 | A1 + B1 | 155 | 1.65 | P15 | A3 + B2 | 81 | 1.53 | | |
| P2 | A1 + B2 | 110 | 1.56 | P16 | A3 + B3 | 63 | 1.61 | | |
| P3 | A1 + B3 | 90 | 1.41 | P17 | A3 + B5 | 103 | 1.61 | | |
| P4 | A1 + B4 | 45 | 1.43 | P18 | A3 + B6 | 120 | 1.57 | | |
| P5 | A1 + B5 | 60 | 1.34 | P19 | A3 + B7 | 47 | 1.41 | | |
| P6 | A1 + B6 | 67 | 1.71 | P20 | A3 + B8 | 72 | 1.45 | | |
| P7 | A1 + B7 | 45 | 1.27 | P21 | A4 + B1 | 64 | 1.52 | | |
| P8 | A1 + B8 | 140 | 1.69 | P22 | A4 + B2 | 44 | 1.51 | | |
| P9 | A2 + B1 | 42 | 1.50 | P23 | A4 + B3 | 37 | 1.71 | | |
| P10 | A2 + B2 | 85 | 1.64 | P24 | A4 + B5 | 37 | 1.51 | | |
| P11 | A2 + B3 | 34 | 1.57 | P25 | A4 + B6 | 66 | 1.44 | | |
| P12 | A2 + B7 | 96 | 1.50 | P26 | A4 + B7 | 40 | 1.38 | | |
| P13 | A2 + B8 | 35 | 1.50 | P27 | A4 + B8 | 32 | 1.59 | | |
| P14 | A3 + B1 | 64 | 1.46 | P28^c | A1 + B1 + B7 | 167 | 1.60 | | |

^a The reaction was carried out on 2.5 mmol scale in sulfolane (0.5 M) at 150 °C for 6 h in the presence of K₂CO₃ (2.2 equiv.). ^b For structures of the polymers, see ESI section 3.2.2.† ^c n_{A1} : n_{B1} : n_{B7} = 1 : 0.9 : 0.1; M_n^{PS}, number-average molecular weight with polystyrene as standard; PDI, polydispersity index; Mon., monomers.

with aryl diphenols bearing different groups to produce PSAs with M_n^{PS} ranging from 32 kDa to 167 kDa (for details, see ESI section 4.1†) and narrow PDI (1.34–1.71). Aryl diphenols with large steric hindrance could be applied to this method to afford the target polymers (**P7**, **P8**, **P12**, **P13**, **P19**, **P20**, **P26** and **P27**). We found that the molecular weights of **P13** and **P27** were relatively low, whereas those of **P8** and **P20** were relatively high. The results suggested that steric hindrance is not the sole determining factor, and the polymer may also be influenced by the reactivity of the monomers and the polymerization process. In addition, polymerization involving **B7** as the bisphenol partner may be unsuitable due to the presence of lactone under the conditions of a base and high temperature (**P7**, **P12** and **P26**). Copolymerization of **A1**, **B1** and **B7** could also provide the polymer with high M_n and narrow PDI (**P28**).

Possible mechanism. A nucleophilic polycondensation process was proposed for the formation of PSA (taking the reaction of **A1** and **B1** as an example (Fig. 3b)), according to previous work^{19,29} and the results of control experiments. (When IOBs were absent from the polycondensation reaction, the desired **P1** could not be obtained (Fig. 3a).) First, K₂CO₃ reacted with aryl bisphenol **A** (**B1**) to form potassium 4,4'-(propane-2,2-diyl)diphenolate (BPA-K) at high temperature, with the generation of H₂O and CO₂. Then, the nucleophilic polycondensation reaction between BPA-K and **A1** and chain propagation proceeded with prolonged reaction time, affording the desired polymer with the release of KF: in brief,



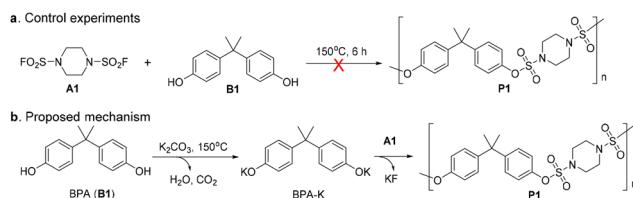


Fig. 3 Mechanistic study.

polycondensation including a “salifying–nucleophilic attack–chain propagation” process. In addition, the by-products (water, CO_2 and KF) of our method are widely used industrial raw materials,³⁰ which lowers the production cost.

Scale-up synthesis of P1. To meet the requirements of industrial manufacture, scaled-up polymerization was investigated (taking the synthesis of **P1** as an example), and the 100 g-scale experiment showed that **P1** with high M_n (148 kDa) and narrow PDI (1.82) was obtained in 97% yield (for details, see ESI section 3.3†). From the results, we found that our protocol was very promising for the industrial production of PSAs. As a next step, we may focus on the industrial production and commercial applications of PSAs.

Characterizations of PSAs. To further investigate their engineering applications, the thermal, mechanical and chemical properties of the PSAs were measured. In line with the T_g values (ranging from 102.2 °C to 234.8 °C) of the PSAs (for details, see ESI section 4.2†), the polymers were amorphous, as we identified no crystalline melting or crystallization peaks (for details, see ESI section 7.3†).³¹ The PSAs exhibited excellent thermal stability, according to TG analysis: a weight loss of 5% occurred at 290–350 °C (Fig. S2†). The T_g and T_d of the polymers with flexible blocks were lower than those of the polymers with rigid blocks (for example: **P2**, **P3** vs. **P1**; **P14** vs. **P1** and **P1** vs. **P7**, **P8**). The stability experiments of **P1** showed that, even when **P1** was soaked in strong acid (conc. HNO_3 and HCl) or NaOH solution (40%) for 7 days, the shape and mechanical properties of the polymer were maintained. These results indicate that PSA materials are promising high-performance acid/alkali-resistant polymers. The polymers also had the property of solvent resistance (for details and other properties of **P1**, see ESI section 4.4†).

Table 3 shows the mechanical properties of the polymers. **P1**, **P9**, and **P21** exhibit high mechanical strength, with tensile strengths of 75 MPa, 77 MPa, and 71 MPa, respectively. The tensile and flexural strengths of PSAs with flexible blocks (**P14**) were lower than those of polymers with rigid blocks (for details of the testing of mechanical properties, see ESI section 4.3†). Compared to polycarbonate,¹⁹ polysulfone,¹⁹ and polyamide 6, the newly synthesized polysulfamates exhibit high strength and modulus, demonstrating their potential applications as engineering materials.

Industrial production and applications of PSAs

Industrial production of P1. Industrial production is the key issue for the commercial application of materials. In our lab

Table 3 Mechanical properties of the polymers^{a,b}

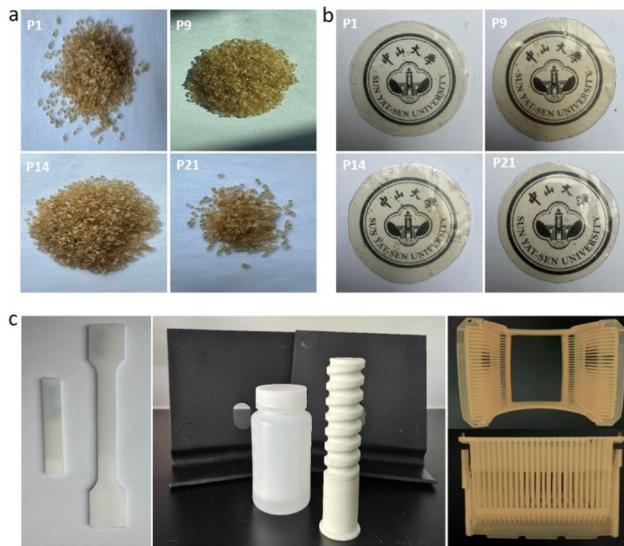
| Polymer | Tensile strength (MPa) | Elastic modulus (MPa) | Flexural strength (MPa) | Flexural modulus (MPa) |
|------------|------------------------|-----------------------|-------------------------|------------------------|
| P1 | 75 | 3500 | 94 | 3531 |
| P9 | 77 | 3600 | 98 | 3560 |
| P14 | 55 | 2300 | 75 | 2500 |
| P21 | 71 | 3500 | 91 | 3500 |
| PC | 60 | 2500 | 79 | 2500 |
| PSU | 68 | 2600 | 88 | 2600 |
| PA 6 | 60 | 2300 | 65 | 2340 |

^a PC (polycarbonate), PSU (polysulfone) and PA 6 (polyamide 6) were applied as contrasting polymers. ^b **P1** with $M_n^{\text{PS}} = 155$ kDa, **P9** with $M_n^{\text{PS}} = 42$ kDa, **P14** with $M_n^{\text{PS}} = 64$ kDa and **P21** with $M_n^{\text{PS}} = 64$ kDa were applied.

research, the 1000-gram-scale synthesis of **P1** was undertaken, which laid the foundation for further large-scale production. With the cooperation of Inner Mongolia Tuwei New Material Technology Co., Ltd, the conditions for the scaled-up production of **P1** were optimized and hundreds of kilograms of **P1** with high M_n (158 kDa) and narrow PDI (1.63) were successfully produced. After postprocessing, including granulating, washing, removal of salts, solvent recovery and drying, the material was used in the next application step without other modification.

We evaluated the mechanical properties of industrial **P1** products ($M_n^{\text{PS}} = 110$ kDa, PDI = 1.61) and found that their mechanical strength was comparable at both the 1000 g and 100 kg production scales. This finding indicates that the mechanical properties of the polymer remain stable during large-scale industrial production (for details, see ESI section 5†).

Processing of PSAs. Machinability is important for engineering materials;³² thus, the machinability of PSAs should be eval-

Fig. 4 Machinability and applications of PSAs. (a) PSA resins, (b) PSA films and (c) processed products using **P1**.

uated for investigation of their further application. Four PSAs with different structures (**P1**, **P9**, **P14**, and **P21**) were selected to assess the processability of PSA. As shown in Fig. 4, PSA polymers can be processed to yield industrial resin raw materials. PSA resin is amber coloured and transparent (Fig. 4a), and the film exhibits good transparency (Fig. 4b). This further indicates that all four polymers possess amorphous structures, in agreement with the DSC results.³³

Applications of PSAs. Due to their excellent mechanical properties, chemical resistance, and thermal stability, PSA materials have broad application potential in various fields, such as automotive plastic parts and acid/alkali-resistant containers.³⁴ Fig. 4c shows application products of **P1**. For example, wafer cassettes are commonly used in acid/base processes within the semiconductor etching industry to carry and transport wafers.³⁵ After being used for 30 days, there were no changes in performance of the wafer cassette prepared using **P1**, which indicated that PSA materials could be applied under acid- and alkali-resistant conditions.

Conclusions

We have developed an efficient method to construct a sulfamate bond. By applying this method, PSA materials were successfully produced both in the laboratory and in a chemical factory. PSAs possess the properties of lower production costs, higher T_g and mechanical strength than PSEs. This research on PSA from laboratory synthesis to industrial production is a successful example of the combination of study, research and production. Our work would make significant contributions to the development of sulfonic materials, as well as materials science. Research into the application of PSAs is underway in our lab and the cooperative enterprises.

Experimental

General procedure for laboratory synthesis of PSA

Aryl phenols (2.50 mmol, 1.0 equiv.) and alkylsulfamoyl fluorides (2.55 mol, 1.02 equiv.) were combined in a 25 mL glass vial equipped with a magnetic stir bar. Sulfolane (5.0 mL) was added, and the vial was placed into a pre-heated 150 °C oil bath with stirring. After 2 min, commercially available anhydrous K_2CO_3 (2.2 equiv.) was added in one portion. The reaction was run for 6 h, during which the reaction mixture turned highly viscous and moisture appeared. At the end of the reaction, it was allowed to cool to 70 °C and the mixture was slowly poured into 50 mL of cold water under vigorous stirring. Polymers precipitated as white fiber or powder once the sulfolane solution touched the water. The polymers were collected *via* filtration and then refluxed in water for 1 h to remove the salts and sulfolane. Finally, the polymers were dried at 40 °C for 12 h *in vacuo*. The molecular weight and polymer distribution were determined on GPC. The thermal properties were determined by DSC and TGA analysis.

Industrial production of **P1**

The 100 kg-scale **P1** was produced in Inner Mongolia Tuwei New Material Technology Co., Ltd. Generally, under N_2 atmosphere, **A1** (70.78 kg) and BPA (64 kg) were dissolved in sulfolane (450 kg) in a 1000 L steel reactor. K_2CO_3 (85.23 kg) was added (within 30 min) to the reaction mixture when the temperature was raised to 170 °C. The moisture was removed by N_2 and collected by condensing. After reaction, the crude product **P1** was post-processed, including granulating, washing, removal of salts, solvent recovery and drying. The obtained **P1** was used without other modification or processing.

Author contributions

Z. W. and J. X. conceived the experiments and led the project. M. X., L. P., C. J., Z. Z., W. X. and Z. Y. performed most experiments. Z. W. and M. X. wrote the manuscript.

Data availability

All relevant data are available from the corresponding author upon reasonable request. The authors declare that all data generated or analyzed during this study are included in this article and its ESI.†

Conflicts of interest

The authors have filed a patent application (CN111072966B), on materials reported in this manuscript and are working to commercialize advanced PSAs.

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