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PAPER
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A mannosylated PEI–CPP hybrid for TRAIL gene targeting delivery for colorectal cancer therapy

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

## Introduction

Sulfur (VI) fluoride exchange (SuFEx) reaction is an efficient and rapid method to synthesize functional molecules containing (poly)sulfates, (poly)sulfonates and sulfamates,[1,2] which has been widely applied in the fields of organic synthesis, materials science, pharmaceutical chemistry and bio-chemistry.[3-5] In material chemistry, especially, polysulfates and polysulfonates with excellent properties have been synthesized successfully through the SuFEx reaction.[6] Besides, 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 catalytic synthesis of pyrimidine systems,[12,13] as well as polymer synthesis.[14,15] However, despite their good performance in bioactive compounds, sulfamates are comparatively underexplored for the challenges existing in the synthesis of sulfamates. Especially, polysulfamate (PSA) materials are not available to date because of the absence of efficient and economical synthetic method. Mahapatra S. et al. reported an advanced process to synthesis of 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. 1, a1). The stoichiometric utilization of $Ca(NTf_2)_2$ and DABCO set up a barrier for the large scale synthesis of PSAs.

With the progress of science and technology, it is of great significance for modification of existing materials or development of new materials.[17,18] We previously reported a nucleophilic process to construct sulphate bonds through the reaction of aryl phenols and aryl fluorosulfates (Fig. 1, a2).[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 R₂N-

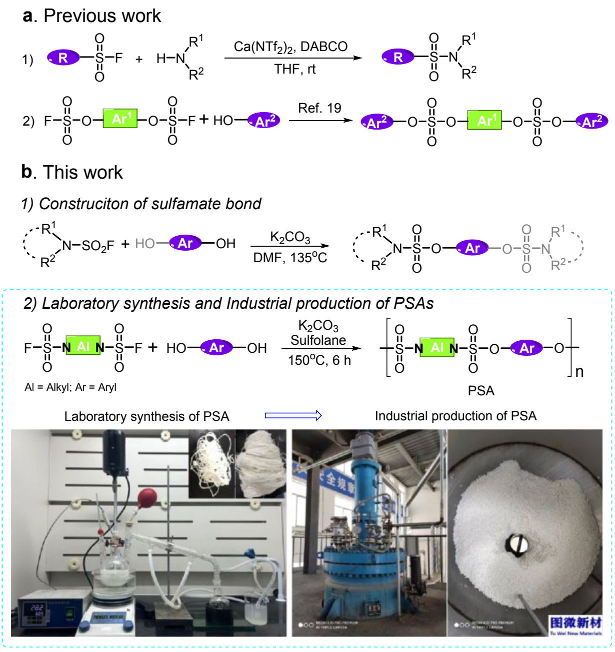

**Fig. 1** Reaction of sulfonyl fluorides and nucleophilic reagents

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$SO_2F$ in the presence of inorganic bases (IOB) could be applicable for synthesis of sulfamates. We proposed that polymers bearing sulfamate bond instead of sulfate bond may lead to PSA with the properties of good tenacity, machinability and mechanical performance.

Materials science plays an indispensable role in the progress of sciences, inheriting civilizations and 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 materials from laboratory research to industrial production and commercial applications is a complex, challenging and protracted process.[25] For example, polycarbonates (PCs) were firstly prepared by Einhorn in 1898 while 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 while the commercial interests in poly(vinyl chloride) was revealed in 1928.[27] Polyethylene (PE) was produced from ethylene in 1936 by Fawcett, and all commercial PE was produced by high-pressure processes until the mid-1950s.[28] Therefore, substantial efforts should be made to achieve the scale-up and industrial production of PSA, which is necessary to support the industrial applications of PSAs.

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. 1, b1) and polysulfamates (Fig. 1, b2) 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 gap between laboratory research, industrial production, and practical applications of PSAs.

## Results and discussion

### Nucleophilic construction of 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) (Conditions screening see Supporting Information section 2.1 for details).[19] To our delight, the corresponding sulfamates could be obtained in excellent yields when the reaction was carried out 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. Wherein, 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.

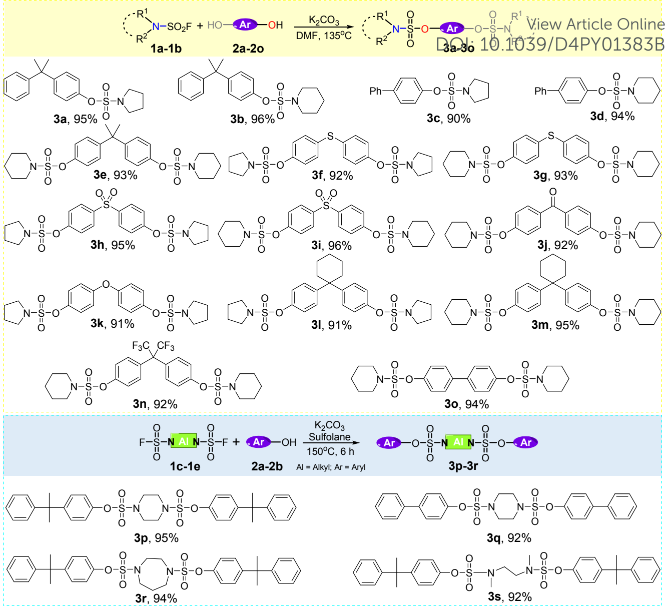
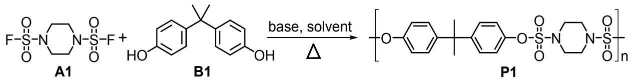


**Fig. 2** Substrates scope of nucleophilic construction of sulfamate bond

### Laboratory research of PSA

**Laboratory synthesis of PSAs.** In general, the nucleophilic substitution reaction between aryl fluorosulfates and aliphatic amines (see Supporting Information section 3.1 for details)[7] or the reaction between aryl bisphenols and alkylsulfamoyl fluorides could afford the desired PSAs (Fig. 1). However, our conditions screening experiments showed that the reaction between aryl bisphenols and alkylsulfamoyl fluorides was the preference to obtain PSA with higher $M_n$ and narrow PDI.

**Table 1** Conditions screening for the synthesis of **P1**[a]



| Entry | Base | Solvent | $T$/°C | $M_n^{PS}$/kDa | PDI |
|---|---|---|---|---|---|
| 1 | $Na_2CO_3$ | DMF | 25 | -- | -- |
| 2 | $Na_2CO_3$ | sulfolane | 80 | 1.26 | 1.80 |
| 3 | $K_2CO_3$ | sulfolane | 80 | 1.48 | 1.93 |
| 4 | $Na_2CO_3$ | DMF | 135 | 61.49 | 1.59 |
| 5 | $K_2CO_3$ | DMF | 135 | 77.84 | 1.58 |
| 6[b] | $K_2CO_3$ | DMF | 135 | 69.52 | 1.69 |
| 7[c] | $K_2CO_3$ | DMF | 135 | 64.79 | 1.66 |
| 8 | $K_2CO_3$ | DMF | 150 | 42.17 | 1.49 |
| 9[b] | $K_2CO_3$ | DMF | 150 | 44.57 | 1.52 |
| 10[d] | $K_2CO_3$ | DMF | 150 | 61.38 | 1.66 |
| 11[b,d] | $K_2CO_3$ | DMF | 150 | 60.72 | 1.68 |
| **12** | **$K_2CO_3$** | **sulfolane** | **150** | **155.02** | **1.65** |
| 13 | $K_2CO_3$ | NMP | 150 | 49.73 | 1.53 |
| 14 | $K_3PO_4$ | sulfolane | 150 | 76.83 | 1.68 |
| 15 | $Na_3PO_4$ | 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 time was carried out for 12 h. $T$, External temperature. $M_n^{PS}$, number-average molecular weight with polystyrene as standard. PDI, poydispersity index.

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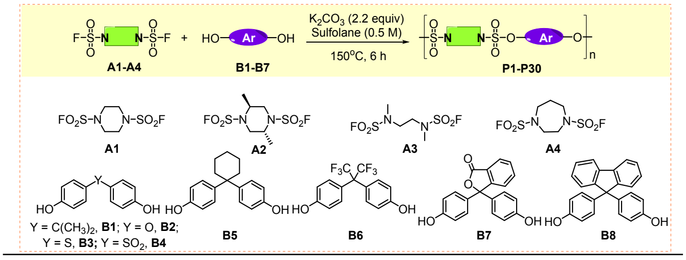
Conditions screening of the polycondensation (Table 1) was evaluated on the basis of previous work[19] by using **A1** and **B1** as the model monomers. When the polycondensation was carried out at 25°C in the presence of $Na_2CO_3$ for 6 h in DMF, no desired polymer was observed (Table 1, entry 1). Then we increased the reaction temperature to 80°C, after 6 h, both $Na_2CO_3$ and $K_2CO_3$ promoted the polycondensation and gave the polysulfamate **P1** with $M_n^{PS}$ = 1.26 kDa (PDI = 1.80) and $M_n^{PS}$ = 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 = 1.59) with quantitative yield by increasing reaction temperature to 135°C in the presence of $Na_2CO_3$ (Table 1, entry 4), while $K_2CO_3$ exhibited better promotion performance for this reaction (Table 1, entry 5). Reducing reaction concentration or the amount of base could result in **P1** with lower $M_n^{PS}$ (Table 1, entries 6 and 7). The polycondensations carried out at 150°C did not show superior results compared with that at 135°C, producing **P1** in lower $M_n^{PS}$ (42.17-60.72 kDa vs 77.84 kDa) with relatively unchanged PDI (Table 1, entries 8-11). This might be because of the decomposition of the solvent under the high temperature. Then we tried sulfolane and NMP, and the results indicated sulfolane is the best choice when the reaction was carried out at 150°C, giving **P1** in high molecular weight ($M_n^{PS}$ = 105.10 kDa) and narrow PDI (1.58) with quantitative yield (Table 1, entry 12). When the reaction was carried out in *N*-methylpyrrolidone (NMP), there was no better result (Table 1, entry 13). The employment of $K_3PO_4$ or $Na_3PO_4$ did not show superior results as well (Table 1, entries 14 and 15). Alkaline-earth metal carbonates such as $MgCO_3$, $CaCO_3$ and $BaCO_3$ could not promote the reaction (Table 1, entry 16). We did not investigate the higher reaction temperature because the attacks of base on $R_2N–SO_2F$, decomposition of the solvent and oxidation of aryl phenol at high temperature had negative effect on the polycondensation. We now got the optimal conditions (Table 1, entry 12) for this polycondensation reaction to synthesize of PSAs.

**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 $K_2CO_3$ (2.2 equiv.); [b]For structures of the polymers, see Supporting Information section 3.2.2 for details; [c]$n_{A1}:n_{B1}:n_{B7}$ = 1:0.9:0.1; $M_n^{PS}$, number-average molecular weight with polystyrenes as standard; PDI, polydispersity index; Mon., monomers.

With the optimal conditions in hand, then we examined monomers with various groups to verify the application scope of our process, and the results are shown in Table 2. As shown in Table 2, both aliphatic chains or rings of disulfamoyl difluorides could react with aryl diphenols bearing different groups to produce PSAs with $M_n^{PS}$ ranging from 32 kDa to 167 kDa (see Supporting Information section 4.1 for details) 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 bisphenols partner may be unsuitable due to the presence of the lactone under the conditions of base and high temperature (**P7**, **P12** and **P26**). Copolymerization of **A1**, **B1** and **B7** could also provide the polymer in high $M_n$ and narrow PDI (**P28**).

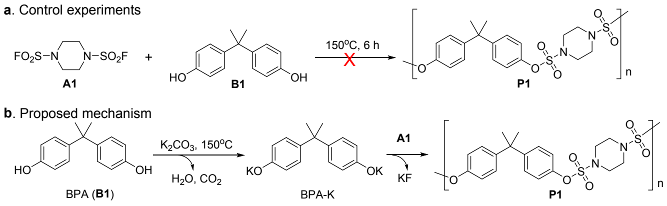


**Fig. 3** Mechanism study.

**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 control experiments results (When IOBs were absent from the polycondensation reaction, the desired **P1** couldn't be obtained, Fig. 3a). At first, $K_2CO_3$ reacted with aryl bisphenol A (**B1**) to form potassium 4,4'-(propane-2,2-diyl)diphenolate (BPA-K) at high temperature with generation of $H_2O$ and $CO_2$, then the nucleophilic polycondensation reaction carried out between BPA-K and **A1** and the chain propagation were proceeded with the reaction time prolonged, affording the desired polymer with releasing of KF. In a word, the polycondensation including a "salifying-nucleophilic attack-chain propagation" process. In addition, the by-products

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(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, scale-up polymerizations were investigated (taking 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 (see Supporting Information section 3.3 for details). From the results, we found that our protocol was very promising for industrial production of PSAs. In next step, we may focus on the industrial production and commercial applications of PSAs.

**Characterizations of PSAs.** To further investigation the engineering applications, the thermal, mechanical and chemical properties of PSAs were measured. In line with the $T_g$ values (ranging from 102.2°C to 234.8°C) of PSAs (see Supporting Information section 4.2 for details), the polymers were amorphous because we found that no crystalline melting or crystallization peaks were identified (see Supporting Information section 7.3 for details).[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 polymers with flexible blocks were lower than those of the polymer with rigid blocks (for examples: **P2**, **P3** vs **P1**; **P14** vs **P1** and **P1** vs **P7**, **P8**). The stability experiments of **P1** displayed that even though **P1** were soaked in strong acid (conc. $HNO_3$ and HCl) or NaOH solution (40%) for 7 days, the shape and mechanical properties of the polymers were maintained. The results indicate that PSA materials are promising high-performance acid-alkali resistant polymers. The polymers also had the property of solvents resistance (for details and other properties of **P1**, see Supporting Information section 4.4).

**Table 3** Mechanical properties of 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 contrasted polymers. [b]**P1** with $M_n^{PS}$ = 155 kDa, **P9** with $M_n^{PS}$ = 42 kDa, **P14** with $M_n^{PS}$ = 64 kDa and **P21** with $M_n^{PS}$ = 64 kDa were applied.

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 mechanical properties testing details, see Supporting Information 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 of commercial applications of materials. In our lab research, 1000 gram-scale synthesis of **P1** was synthesized and this was the foundation for further large-scale production. With the cooperation of Inner Mongolia Tuwei new material Technology Co., LTD., conditions for scale-up production of **P1** were optimized and hundreds kilogram of **P1** with high $M_n$ (158 kDa) and narrow PDI (1.63) were produced successfully. After postprocessing including granulating, washing, removing of salts, solvent recovery and drying, the material was used in next application step without other modifications.

We evaluated the mechanical properties of industrial **P1** products ($M_n^{PS}$ = 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 polymer's mechanical properties remain stable during large-scale industrial production (see Supporting Information section 5 for details).

**Processing of PSAs.** Machinability is important for engineering materials,[32] thus, the machinability of PSAs should be evaluated for investigation of their further applications. 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. The PSA resin is amber 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]

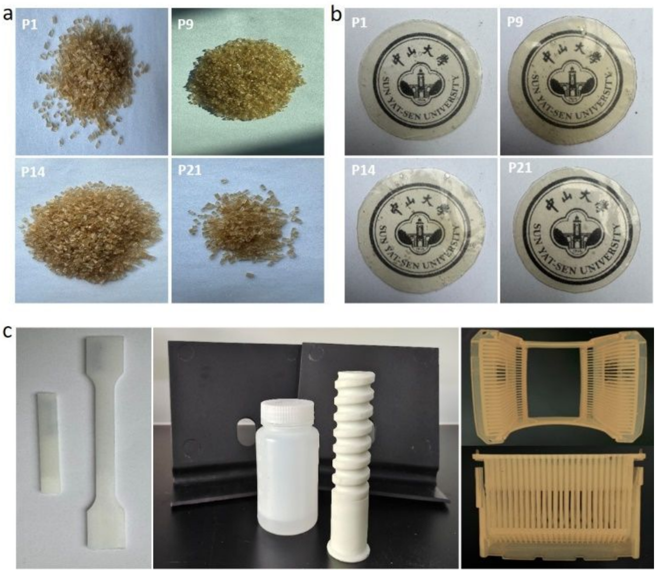

**Fig. 4** Machinability and applications of PSAs. (a) PSA resins, (b) PSA films and (c) processing products using **P1**.

**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

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containers.[34] Fig. 4c shows the 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 PSA materials could be applied in acid and alkali resistant conditions.

## Conclusions

In conclusion, we developed an efficient method to construction of sulfamate bond. Applying this method, PSA materials were produced both in laboratory and chemical factory successfully. PSAs possess the properties of lower production costs, higher $T_g$ and mechanical strength than PSEs. The research of PSA from laboratory synthesis to industrial production is a successful example of the combination of study, research and production. Our work would make significant contributes to the development of sulfonic materials, as well as materials science. The application researches of PSAs are in progress in our lab and the cooperative enterprises.

## Experimental

**General procedure for laboratory synthesis of PSA.** Aryl phenols (2.50 mmol, 1.0 eq) and alkylsulfamoyl fluorides (2.55 mol, 1.02 eq) were combined in a 25 mL glass vial equipped with 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 eq) was added in one portion. The reaction was run for 6 hours, during which course the reaction mixture turned highly viscous while the 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 hours in vacuo. 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 1000 L steel reactor. And $K_2CO_3$ (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, removing of salts, solvent recovery and drying. The obtained **P1** was used without other modifications of 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.

## Conflicts of interest

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

## Acknowledgements

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## References

1 J. Dong, K. B. Sharpless, L. Kwisnek, J. S. Oakdale, V. V. Fokin, *Angew. Chem., Int. Ed. Engl.*, 2014, **53**, 9466–9470.
2 S. Li, P. Wu, J. E. Moses and K. B. Sharpless, *Angew. Chem., Int. Ed. Engl.*, 2017, **56**, 2903-–2908.
3 Z. Liu, G. Meng, T, Guo, J. Dong and P. Wu, *Curr. Protoc. Chem. Biol.*, 2019, **11**, e64.
4 J. Yatvin, K. Brooks and J. Locklin, *Chem. Eur. J.,* 2016, **22**, 16348–16354.
5 D. E. Mortenson, G. J. Brighty, L. Plate, G. Bare, W. Chen, S. Li, H. Wang, B. F. Cravatt, S. Forli, E. T. Powers, K. B. Sharpless, I. A. Wilson and J. W. Kelly, *J. Am. Chem. Soc.,* 2018, **140**, 200–210.
6 B. Gao, L. Zhang, Q. Zheng, F. Zhou, L. M. Klivansky, J. Lu, Y. Liu, J. Dong, P. Wu and K. B. Sharpless, Nat. Chem., 2017, **9**, 1083–1088.
7 J. Dong, L. Krasnova, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2014, **53**, 9430–9448.
8 M. Chrominski, K. Ziemkiewicz, J. Kowalska and J. Jemielity, *Org. Lett.*, 2022, **24**, 4977–4981.
9 Z. Zhan, M. C. Willis, *Chem.*, 2022, **8**, 1137–1146.
10 D. Moi, P. Foster, L. Rimmer, A. Jaffri, A. Deplano, G. Balboni, V. Onnis and B. Potter, *Eur. J. Med. Chem.*, 2019, **182**, 111614.
11 A. Narayanan, L. H. Jones, *Chem. Sci.*, 2015, **6**, 2650–2659.
12 S. A. Sundararaman and A. R. Odom John, *Cell Host Microbe*, 2022, **30**, 1074–1076.
13 K. Debbabi, F. Guittard and S. Geribaldi, *J. Colloid Interf. Sci.*, 2008, **326**, 235–239.
14 C. J. Smedley, M. C. Giel, A. Molino, A. S. Barrow, D. J. D. Wilson and J. E. Moses, *Chem. Commun.*, 2018, **54**, 6020–6023.
15 B. Gao, S. Li, P. Wu, J. E. Moses and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2018, **57**, 1939–1943.
16 S. Mahapatra, C. P. Woroch, T. W. Butler, S. N. Carneiro, S. C. Kwan, S. R. Khasnavis, J. Gu, J. K. Dutra, B. C. Vetelino, J. Bellenger, C. W. am Ende and N. D. Ball, *Org. Lett.*, 2020, **22**, 4389–4394.
17 Y. Gan, *Engineering.*, 2024, **32**, 10–13.
18 M. A. Elkodous, S. O. Olojede, S. Sahoo and R. Kumar, *Chem. Biol. Interact.*, 2023, **379**, 110517.
19 W. Zhu, F. Li, J. Liu, X. Ma and X. Jiang, *React. Chem. Eng.*, 2019, **4**, 2074–2080.
20 T. Guo, G. Meng, X. Zhan, Q. Yang, T. Ma, L. Xu, K. B. Sharpless and J. Dong, *Angew. Chem., Int. Ed.*, 2018, **57**, 2605–2610.

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21 F. Liu, H. Wang, S. Li, G. A. L. Bare, X. Chen, C. Wang, J. E. Moses, P. Wu and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2019,**58**, 8029–8033.
22 S. H. Ali, *Nat. Mater.*, 2018, **17**, 1052–1053.
23 M. Ayman, C. Chen and J. T. Jesper, *Adv. Sci.*, 2024, **11**, 2401401.
24 P. J. J. Alvarez, C. K. Chan, M. Elimelech, N. J. Halas, D. Villagrán, *Nat. Nanotechnol.*, 2018, **13**, 634−641.
25 N. Wang, S. Song, W. Wu, Z. Deng and C. Tang, *Advanced Energy Mater.*, 2024, **14**, e2303451.
26 D. Kyriacos, *Brydson's Plastics Materials*, 2017, **17**, 457–485.
27 M. Gilbert and S. Patrick, *Brydson's Plastics Materials*, 2017, **13**, 329–388.
28 S. Ronca, *Brydson's Plastics Materials*, 2017, **10**, 247–278.
29 W. C. Firth, Jr., *US Pat.*, 3895045, 1973.
30 X. Ru, H. Zhang, Y. Wang, Z. Zhi, Y. Guo, K. Zhang and L. He, *J. Mater. Cycles Waste*, 2024, **26**, 2304–2316.
31 Z. Li, H. Zhang, X. Zhang, J. Wang and Y. Wen, *Polym. Chem.*, 2022, **13**, 1260–1266.
32 G. Cheng, M. Sahli, J. C. Gelin and T. Barriere, *Int. J. Adv. Des. Manuf. Technol.*, 2014, **75**, 225–235.
33 Q. Wei, J. Huang, D. Jia, J. Lei, H. Huang, H. Lin, J. Xu, G. Zhong, and Z. Li, *Macromolecules*, 2024, **57**, 3706–3718.
34 Y. Zhang, G. Ren, G. Nie, S. Hu, D. Li, W. Sun, Z. Li, Z. Cui, D. Lu, X. Shi, L. Li, H. Yu and J. He, *Colloids Surf. A*, 2024, **685**, 133310.
35 S. H. Yu, H. Jeon, H. Ko, J. H. Cha, S. Jeon, M. Jae, G. Nam, K. Kim, Y. Gil, K. Lee and D. S. Chung, *Chem. Eng. J.*, 2023, **470**, 144102.

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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 Supporting Information.

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