4-Vinylbenzenesulfonyl fluoride (VBSF): a highly reactive monomer for RAFT polymerization and exhaustive SuFEx postpolymerization sulfonamidation†

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Abstract

Introduction

Post-polymeriation modification (PPM), a powerful and effective approach to the synthesis of functional polymers, are often complementary to those advanced polymerization methods in polymer chemistry.[1–11] For a long time, most of PPM reactions have been applied to append a limited amount of functional groups into polymer backbone without altering the mechanical properties of polymers.[1–3,8,10,12] On the other hand, the reaction types for “exhaustive (nearly quantitative)” post-polymeriation modifications, which completely modify the original polymers and create the new types of polymers, were relatively limited.[4–7,13–21]

Except for a few classic transformations, the majority of novel “exhaustive” PPMs rely on “click” reactions since Sharpless proposed the concept of "click chemistry" in 2001.[22–23] In 2014, Sharpless reported another highly efficient reaction, namely sulfur(VI) fluoride exchange (SuFEx),[24] which is also known as the "second-generation click chemistry"[25–29] due to the unique reactivities and selectivities of S(VI)–F. Nowadays, SuFEx reactions have emerged as a powerful synthetic tool to create molecular diversity[24,30–34] and have been widely utilized for biomedical science,[35–43] polymer chemistry,[44–65] and material science.[66–71]

Although SuFEx reactions using phenol nucleophiles are well established, the broad-spectrum sulfonamidation of S(VI) – F and amines has not been developed until recently. In 2018, Ball, am Ende, and their coworkers developed an efficient method to synthesize sulfonamides from sulfonyl fluorides and amines using a stoichiometric amount of $Ca(NTf_2)_2$.[72–74] In 2021, our research group developed the first catalytic SuFEx sulfonamidation by using 1-hydroxybenzotriazole (HOBt) as catalyst and tetramethyldisiloxane (TMDS) as fluoride scavenger.[75] Compared to the high cost of $Ca(NTf)_2$, The cost of catalyst and reagent used in our sulfonamidation is much more cost-effective and hence preferable for polymer synthesis.

Although SuFEx chemistry has been applied in polymer synthesis since its emergence,[44] the majority of these studies focus on developing novel SuFEx polymerizations.[44–45,65] In 2015, Locklin and coworkers reported the first PPM reaction of

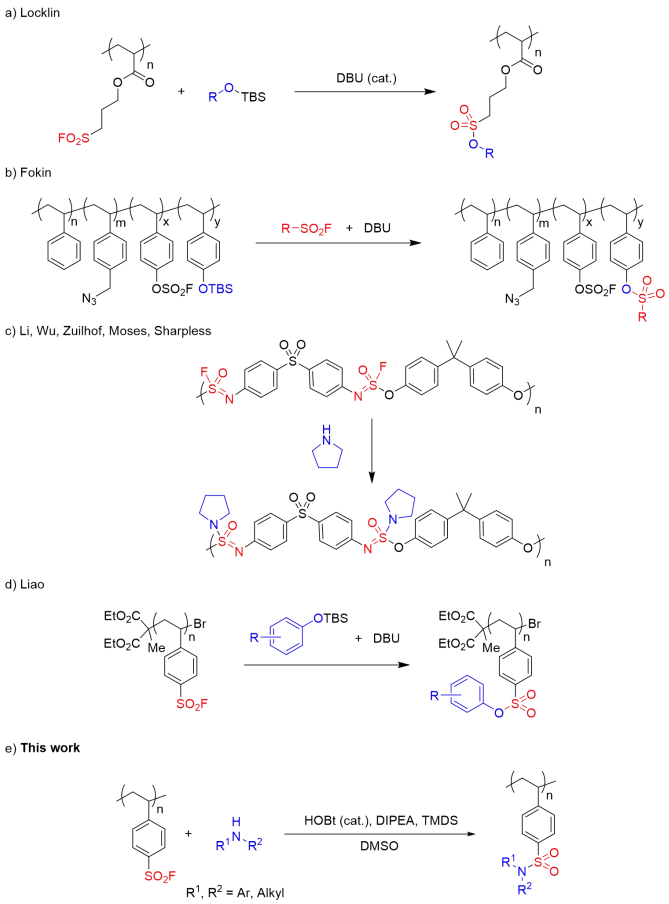

Fig. 1 Postpolymerization SuFEx modification.

sulfonyl fluoride-containing vinyl polymers.[56] Later, they further investigated the kinetics and reactivity of aromatic sulfonyl fluoride, aromatic fluorosulfonate and alkyl sulfonyl fluoride in SuFEx PPM reaction.[60] In 2016, Fokin investigated the PPM reaction of fluorosulfates-containing vinyl polymers.[58] In 2021, Li, Wu, Zuilhof, Moses, Sharpless and their coworkers developed a novel polymerization method of post-modified by aryl silyl ethers.[65] Recently, Liao group studied the atom-transfer radical polymerization (ATRP) of4-vinylbenzenesulfonyl fluoride (VBSF) and the PPM reaction of poly (4-vinylbenzenesulfonyl fluoride) (PVBSF).[64] However, most of these reported SuFEx PPMs on the linkage of *O*-nucleophiles with polymer backbone, studeis on post-sulfonamidation of polymers remain underdeveloped.[74,76] Herein, we demonstrate that VBSF is a suitable monomer for the reversible addition-fragmentation chain transfer (RAFT) polymerization and the exhaustive SuFEx postpolymerization sulfonamidation of PVBSF has been also achieved.

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Results and Discussion

As our long-term interest in developing exhaustive PPMs for the synethesis of novel polymer materials, we started to investigate the efficiency of our catalytic SuFEx sulfonamidation for PPM reactions. Initially, we selected two monomers, 4-vinylbenzenesulfonyl fluoride (VBSF, **1**) and 4-vinylphenyl sulfurofluoridate (VPSF, **2**) for the evaluation.

RAFT polymerization of VBSF and VPSF

RAFT polymerization of VBSF **1** was investigated using two common RAFT agents, CPDT (**CTA-1**) and CPFDB (**CTA-2**) (Table 1). The results (Table 1) showed that the molecular weight and polymer dispersity index (PDI) of **1** and **2** can be well controlled under RAFT polymerization conditions.

Optimization of PPM conditions for PVBSF

The reaction parameters for the PPM sulfonamidation was optimized using the PVBSF prepared from RAFT polymerization and dibenzylamine. Notably, dibenzylamine was chosen due to its relatively low nucleophilicity. Such a choice will facilitate the expansion of the substrate scope for the proposed postpolymerization sulfonamidation. The optimization results were shown in Table 2. When 0.50 equiv of HOBt was used as a promoter, the PPM sulfonamidation proceeded smoothly at 35 ℃ and the conversion of the PVBSF was 65% (Table 2, entry 1). Further studies disclosed the unique role of TMDS. The full conversion of the PVBSF has been achieved using HOBt and TMDS (Table 2, entry 2 and 3). In these cases, all of the sulfonyl fluoride groups have been transformed into sulfonamides. Notably, the conversion was lowered to 83% when 1,1,1,3,3,3-hexamethyldisiloxane (TMS_2O) was used instead of TMDS (Table 2, entry 4). Subsequently, the catalytic amount of HOBt was proved to be sufficient to drive the PPM reaction complete (Table 2, entry 5 and 6). When the amount of HOBt was further reduced to 0.02 equiv, the elevated temperature (50 ℃) was required (Table 2, entry 7 and 8). To obtain the broad substrate scope for the postpolymerization sulfonamidation, we selected the optimal protocol using 0.05 equiv of HOBt, 2.00 equiv of DIPEA, and 2.00 equiv of TMDS in DMSO at 35 ℃ for further evaluation.

The Reactivity Difference between PVBSF 3a and PVPSF 4 in Postpolymerization Sulfonamidation

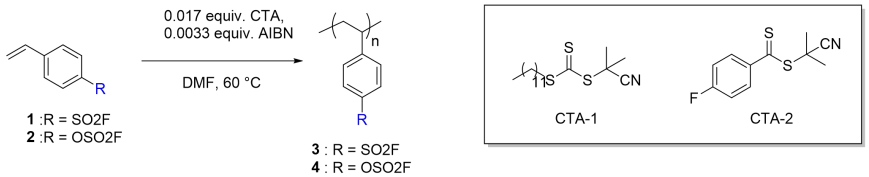
The performance of PVBSF **3a** and PVPSF **4** in PPM sulfonamidation was evaluated using our HOBt/TMDS protocol (Table 3, entry 1 and 2). PVBSF **3a** was quantitatively post-modified while the conversion of PVPSF **4** was low (23%).These results indicated that PVBSF **3a** was much more reactive than PVPSF **4**. As a comparison, the SuFEx protocol using strong organic bases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was also investigated. Unfortunately, low conversions were obtained for the postpolymerization sulfonamidation of both PVBSF **3a** and PVPSF **4** (Table 3, entry 3 and 4), although such a protocol was well suited for SuFEx reactions with phenols.[24−25,27−28,32,44,66,68]

Characterization of the Exhaustive PPM Product 5a

The exhaustive PPM product **5a** was characterized after the PPM conditions were determined. Firstly, As shown in Figure 2, after PPM, the ratio of area integral of the methylenel characteristic peak (e') and the entire aromatic region (c'+d'+f') was 4:14, which indicated that sulfonylated polymer **5a** was successfully prepared by PVBSF **3a**.

Subsequently,**3a** and **5a** were characterized by SEC (DMF as eluent) and the results were shown in Figure 3. The molecular weight of polymers **3a** and **5a** showed little difference on the SEC spectra after sulfonamidation which may due to the polarity and solubility of the two polymers are too different. **3a** is strong polarity polymer and can only be dissolved in a few polar solvents such as DMF and DMSO. However, the polarity of **5a** was weakened after PPM and it began to be soluble in acetonitrile, dichloromethane and other solvents. In this work, sulfonylated polymer **5a** has a relatively strong intermolecular force through π-π packing distinguished to **3a** whose sulfonyl fluoride group forms strong force with DMF, which results in a significantly lower SEC molecular weight of **5a** . To verify this hypothesis, we synthesized PVBSF **3b** with a theoretical molecular weight of 3,000 to 4,000 and its sulfonylated polymer **5b** for MALDI-TOF MS testing.

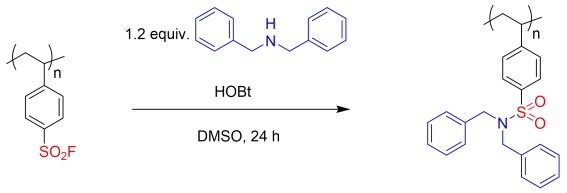
Table 1. RAFT polymerization of VBSF and VPSF[a]



Entry	Monomers	RAFT agents	$M_{n,SEC}$[b] /10^3	PDI[c]
1	**1**	**CTA-1**	9.8	1.08
2	**1**	**CTA-2**	7.9	1.07
3	**2**	**CTA-1**	8.9	1.08

[a]Standard polymerization conditions: under nitrogen protection, monomers (11.9 mmol, 1.0 equiv), RAFT agents (0.2 mmol, 0.017 equiv) and AIBN (0.04 mmol, 0.0033 equiv) were added to DMF (2.0 mL) and stirred at 60 ℃ for 17 h. [b]$M_{n,SEC}$ is the number-average molecular weight determined by size exclusion chromatography in N,N-Dimethylformamide (SEC-DMF) for the polymer, using PEO standards as calibration. [c]PDI is polymer dispersity index.

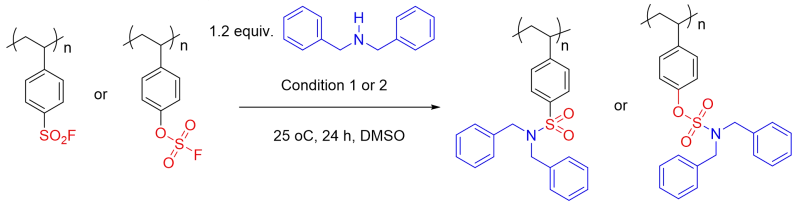
Table 2. Sulfonamidation conditions optimization of PVBSF[a]



Entry	HOBt (equiv)	base	Silicon reagents	Temperature (°C)	Conv. (%)[b]
1	0.50	-	-	35	65
2	0.50	DIPEA	-	35	69
3	0.50	-	TMDS	35	>99
3	0.50	DIPEA	TMDS	35	>99
4	0.50	DIPEA	TMS_2O	35	83
5	0.10	DIPEA	TMDS	35	>99
6	0.05	DIPEA	TMDS	35	>99
7	0.02	DIPEA	TMDS	35	82
8	0.02	DIPEA	TMDS	50	98

[a]Standard experimental conditions: under nitrogen protection, PVBSF **3a** (50.0 mg, including 0.27 mmol repeat unit, 1.00 equiv), dibenzylamine (0.32 mmol, 1.20 equiv), HOBt, DIPEA (95 μL, 0.54 mmol, 2.00 equiv) and silicon reagent (0.54 mmol, 2.00 equiv) were added to DMSO (500 μL) and stirred at a fixed temperature for 24 h. [b]The conversion of reaction was calculated by internal standard method using nuclear magnetic fluorine spectrum, and the internal standard was 1-fluoronaphthalene.

Table 3. Comparison of Sulfonamidation between PVBSF and PVPSF



Entry	Polymer	Condition	Conv. (%)[c]
1	**3a**	**A**[a]	>99.9
2	**4**	**A**[a]	23
3	**3a**	**B**[b]	34
4	**4**	**B**[b]	27

[a]Condition **A**: under nitrogen protection, PVBSF **3a** or PVPSF **4** (0.27 mmol repeat unit, 1.0 equiv), dibenzylamine (0.32 mmol, 1.2 equiv), HOBt, (0.027 mmol, 0.1 equiv), DIPEA (0.54 mmol, 2.0 equiv) and TMDS (0.54 mmol, 2.0 equiv) were added to DMSO (500 μL) and stirred at a room temperature for 24 h. [b]Condition **B**: under nitrogen protection, PVBSF **3a** or PVPSF **4** (0.27 mmol repeat unit, 1.0 equiv), dibenzylamine (0.32 mmol, 1.2 equiv), and TBD (0.054 mmol, 2.0 equiv), were added to DMSO (500 μL) and stirred at a room temperature for 24 h. [c]The conversion of reaction was calculated by internal standard method using nuclear magnetic fluorine spectrum, and the internal standard was 1-fluoronaphthalene.

As shown in Figures 4(a) and 4(b), **3b** and **5b** showed molecular weight distributions similar to normal distribution. The molecular weight intervals were 186.3 and 363.9 respectively (Figures 4(c) and 4(d)), which were consistent with the molecular weight of repeating units of **3b** and **5b** indicating the successful preparation of the polymers. The absolute molecular weight of **3b** and **5b** were 3.4 kDa and 6.5 kDa respectively according to the statistics of the maximum abundance isotope peaks which was quite different from the results of the SEC-DMF (both of which are 4.3 kDa). Therefore, absolute molecular weight tests including MALDI-TOF MS are important when testing the molecular weight of these two polymers.

Thermodynamic properties of **3a** and **5a** were analyzed by DSC and TGA. As shown in Figure 5(a), thermogravimetric loss reached 30% of both **3a** and **5a** after heated to 800 ℃ in nitrogen atmosphere, which was significantly different from the conventional linear polystyrene thermogravimetric loss process (the thermogravimetric loss at 800 ℃ is close to 100%). This attracted our interests of these polymers. The DSC curve in Figure 5(b) showed that after sulfonamidation, the glass transition temperature (Tg) of **5a** was greatly reduced than **3a**. The high Tg of **3a** is not only due to its rigid structure, but also due to the strong intermolecular force caused by the interaction of polar sulfonyl fluoride group and π-π packing. The introduction of two benzyl groups through PPM weakened the polarity of **5a** and also increased the distance between molecular chains of **5a** which caused the decrease of Tg.

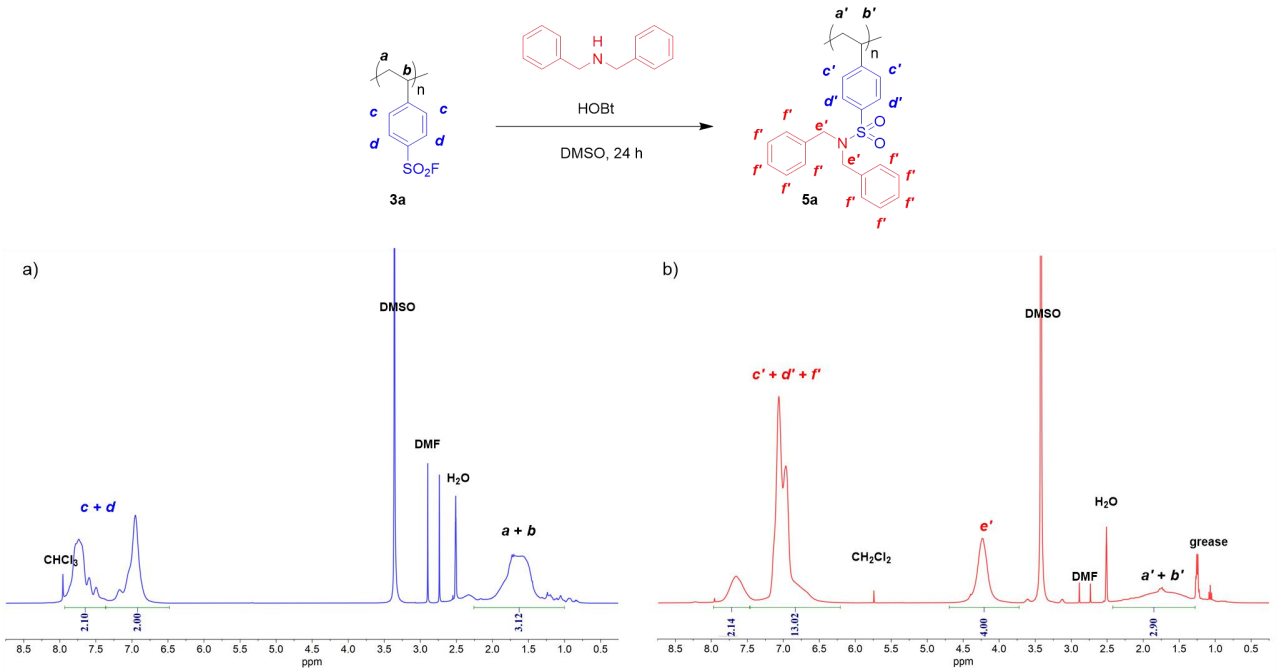


Fig. 2. ^{1}H NMR spectra of **3a** and **5a**: (a) before and (b) after PPM sulfonamidation. The NMR spectra were recorded using $(CD_3)_2SO$ as a solvent.

Other exhaustive sulfonamidation of PVBSF

The conditions for exhaustive sulfonamidation using dibenzylamine as nucleophiles can also apply to other nucleophiles (including arylamines, chiral aliphatic amines, phenols, etc.). We prepared **7a**-**7e** then and SEC, DSC and TGA characterizations were tested on them (Figure 6). The results of SEC showed that the relative molecular weight of **7a**-**7d** were significantly higher than **5a** in DMF. We infer that it is because primary sulfonamide polymers **7a**-**7d** has an acidic hydrogen so its polymer polarity is generally stronger than that of secondary sulfonamide polymer **5a**, thus the solubility of **7a**-**7d** in DMF is stronger than that of **5a** which caused the difference of their relative molecular weight.

It can also be found that in this series of polymers, Tg of **7a** was significantly higher than that of other polymers through DSC, which may relate to that 4-(4-morpholinyl) aniline enhances the polarity and rigidity of the polymer after introducing into the polymer through sulfonamidation.

In addition, such sulfonylated polymers have a high carbonization rate in carbonization procedure. Taking polymer **7d** as an example, it can reach a carbonization rate of 49.7% under nitrogen atmosphere at 800 ℃ which is similar to the carbonization rate of polysulfone (48.0%) and polyimide (49.2%) according to literature reported (Figure 6).[77]

By comparing the thermogravimetric curves (Figure 7) of **7d** in oxygen **7d** (O_2) and polystyrene in nitrogen PS (N_2), it can be found that only 0.6% of the weight of **7d** remained when heated to 800 ℃ in oxygen, which excluded the possibility of inorganic impurities in the sample. The residual weight of polystyrene heated to 800 ℃ under nitrogen was close to 0%, confirming that the introduction of sulfonamide groups can lead to a substantial increase in the carbonization rate.

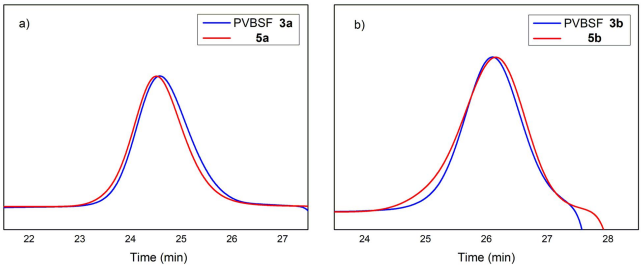


Fig. 3 Comparison of SEC traces (a) before and (b) after exhaustive sulfonamidation of PVBSF **3a** and **3b**.

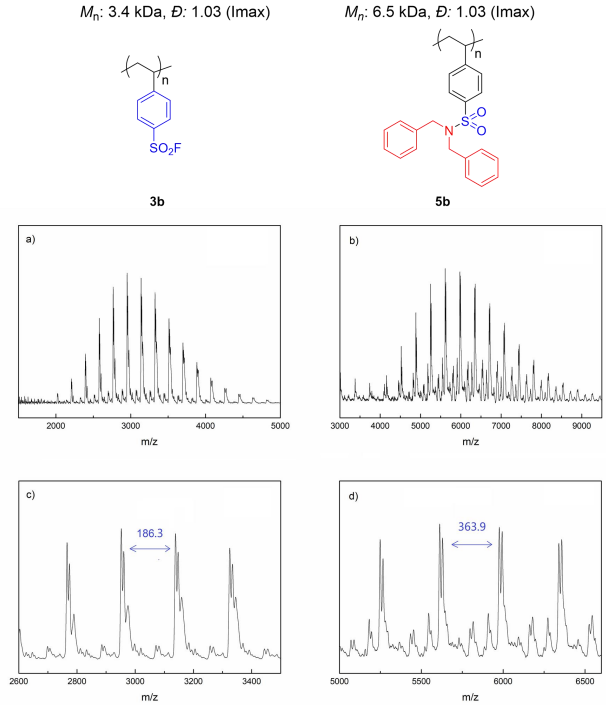


Fig. 4 Comparison of MALDI–TOF MS spectra (a) before and (b) after exhaustive sulfonamidation of PVBSF **3b**.

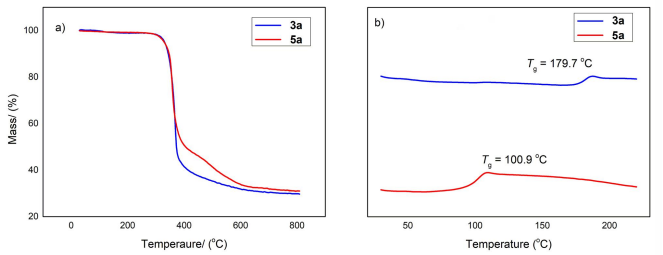


Fig. 5 (a) TGA and (b) DSC tests of **3a** and **5a**.

Exhaustive sulfonamidation of VBSF copolymers

The copolymer **8** with 60/40 repeating unit ratio (VBSF/St) was prepared by free radical polymerization of VBSF and St monomers with 50/50 monomer feeding ratio (Figure 8). The copolymer showed little change in PDI after exhaustive PPM (Figure 9 (a)). The carbonization rate of the modified copolymer **9** was only 9.2% under nitrogen atmosphere at 800 ℃ (Figure 9 (b)) compared with 49.7% of the homopolymer **7d**. We speculate that the main reason is that the structure of **7d** is conducive to condensation into aromatic carbon during combustion. The introduction of styrene group prevents the condensation of phenyl sulfonamide structure in the copolymer **9**, resulting in a significant decrease in the carbonization rate.

Conclusions

In summary, a highly reactive monomer for both RAFT polymerization and exhaustive SuFEx postpolymerization sulfonamidation, 4-Vinylbenzenesulfonyl fluoride (VBSF) was designed and synthesized based on the sulfonyl fluorine catalyzed sulfonylation system developed by our group in the early stage. This monomer has been proven to be well compatible with living/controllable polymerization methods such as RAFT. We optimized conditions of using poly (4-vinylbenzenesulfonyl fluoride, PVBSF) as a substrate for exhaustive sulfonamidation or sulfonation esterification and achieving exhaustive transformation of all sulfonyl fluoride functional groups of PVBSF. In addition, this PPM process showed to be compatible with copolymers. Thermogravimetric analysis had shown that these sulfonamides (or sulfonic esters) polymers exhibited a much lager carbonization rate than ordinary polystyrene. Among them, the polymer obtained by sulfonation of methoxybenzylamine (**7d**) as an amine reagent has a carbonization rate of 49.7% under nitrogen atmosphere at 800 ℃, which is comparable to polysulfone (48%) and similar to polyimide (49.2%). The higher carbonization rate of this polymer may be due to its favorable structure for condensation into aromatic carbon during combustion.

Experimental section

Synthesis of 4-vinylbenzene sulfonyl fluoride and their homopolymers

4-vinylbenzenesulfonyl fluoride (VBSF, **1**) was prepared according to a modification of literature procedure. Under an N_2 atmosphere, sodium 4-vinylbenzene sulfonate (6.34 g, 90 wt%, 30.0 mmol) and phosphorus pentachloride (60.0 mmol, 12.49 g) were added to dichloromethane (120 mL) and cooled to 0 ℃. The reaction mixture was then allowed to warm to room temperature slowly and reacted for 4 h and then washed with half-saturated brine (150 mL). The organic phase was dried with anhydrous sodium sulfate and then filtered, concentrated in vacuo to get the crude product of 4-vinylbenzene sulfonyl chloride. The crude 4-vinylbenzene sulfonyl chloride and potassium hydride fluoride (120.0 mmol) were added to a mixture of acetonitrile (90 ml) and water (12 mL) at room temperature for 18 h. After that most of the acetonitrile in the reaction mixture was removed in vacuo, dichloromethane (150 mL) and distilled water (100 mL) were added for extraction. The organic phase was combined after the water phase was extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with half-saturated brine (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography over

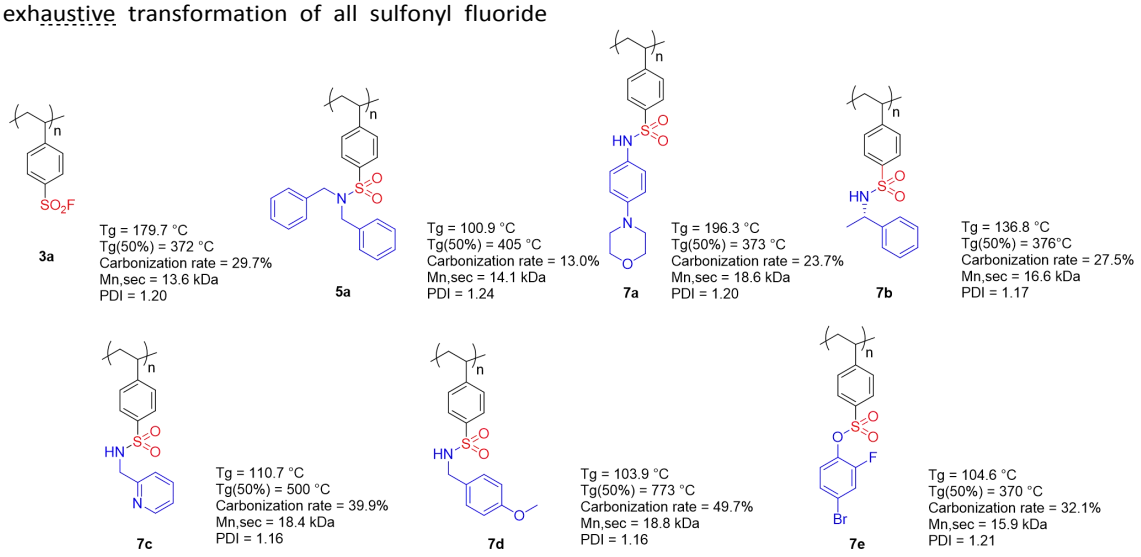


Fig. 6. Exhaustive PPM of PVBSF.

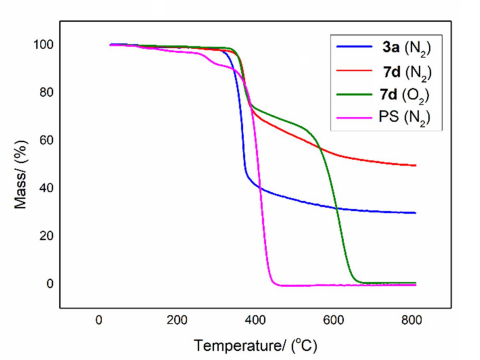


Fig. 7 TGA data comparison of **3a, 7d** and PS in N_2 or O_2 atmosphere**.**

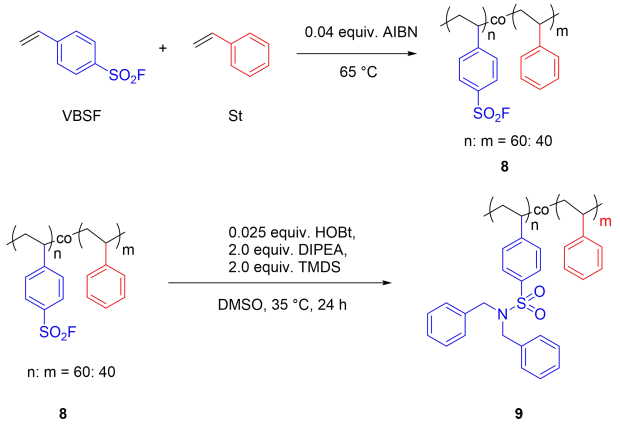


Fig. 8 Preparation and exhaustive sulfonamidation of PVBSF copolymer.

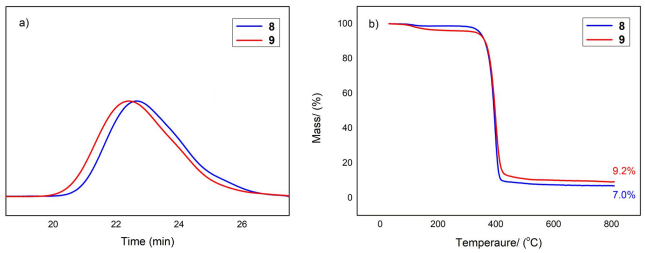


Fig. 9 Comparison of (a) SEC traces and (b) TGA data before and after exhaustive sulfonamidation of PVBSF-co-PS **8.**

silica gel (eluent: petroleum ether/ethyl acetate, 20:1 v/v) to afford the title compound as a white liquid.

Polymer Synthesis

4-vinylbenzene sulfonyl fluoride RAFT polymer: A 10-mL Schlenk flask was charged with compound **1** (2.22 mg, 11.9 mmol), CPDT (68.6 mg, 0.20 mmol), AIBN (6.5 mg, 0.04 mmol) and N, N-dimethylformamide (2.00 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 60 ℃ for 24 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Volatiles were removed in vacuo and the polymer was precipitated in ethanol (3 × 40 mL) three times. The precipitate was collected and dried in a vacuum oven for 12 h at 45 ℃ to afford title polymer as a solid for further characterization.

Preparation of Sulfonamide polymer: The general reaction procedure was: Under nitrogen protection, PVBSF **3a** (150.0 mg, containing 0.81 mmol repeat units), amine (0.96 mmol), HOBt (5.4 mg, 0.04 mmol), N, N-diisopropylethylamine (281 µL, 1.61 mmol), 1,1,3, 3-tetramethyldisiloxane (285 µL, 1.61 mmol) was mixed with anhydrous DMSO (1.50 mL). After stirring at 35 ℃ for 24 h, the mixture was settled in ethanol. After the sedimentation was repeated three times, the solvents were removed in vacuo and the precipitate was dried in a vacuum oven for 45 ℃ for 12 h.

Preparation of PVBSF copolymer: Under nitrogen protection, PVBSF-co-PS **8** (150.0 mg), dibenzylamine (186 µL, 0.96 mmol), HOBt (5.4 mg, 0.04 mmol), N, N-diisopropylethylamine (281 µL, 1.61 mmol), 1,1,3,3-tetramethyldisiloxane (285 µL, 1.61 mmol) was mixed with anhydrous DMSO (1.50 mL). The mixture solution was settled in ethanol after 24 h of stirring at 35 ℃. After sedimentation was repeated three times, the solvents were removed in vacuo and the precipitate was dried in a vacuum oven for 45 ℃ for 12 h, then the solid polymer was obtained.

Exhaustive Sulfonamidation of PVBSF copolymer: Under nitrogen protection, PVBSF-*co*-PS **9** (150.0 mg), dibenzylamine (186 µL, 0.96 mmol), HOBt (5.4 mg, 0.04 mmol), N, N-diisopropylethylamine (281 µL, 1.61 mmol), 1,1,3, 3-tetramethyldisiloxane (285 µL, 1.61 mmol) was mixed with anhydrous DMSO (1.50 mL). The mixture solution was settled in ethanol after 24 h of stirring at 35 ℃. After sedimentation was repeated three times, the solvents were removed in vacuo and the precipitate was dried in a vacuum oven for 45 ℃ for 12 h, then the solid polymer was obtained.

Author Contributions

L.L. conceived the project, L.L. and P.M. designed the experiments, P.M., Y.Z., and B.W. conducted the experimental work, P.M. and Y.Z., analyzed the data and wrote the first draft, L.L. and C.M.P. discussed and revised the manuscript with P.M. and Y.Z..

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 C. M. Plummer, L. Li and Y. Chen, *Polym. Chem.*, 2020, **11**, 6862–6872.

2 J. B. Williamson, S. E. Lewis, R. R. Johnson III, I. M. Manning and F. A. Leibfarth, *Angew. Chem. Int. Ed.*, 2019, **58**, 8654–8668.

3 N. K. Boaen and M. A. Hillmyer, *Chem. Soc. Rev.*, 2005, **34**, 267–275.
4 E. Blasco, M. B. Sims, A. S. Goldmann, B. S. Sumerlin and C. Barner-Kowollik, *Macromolecules*, 2017, **50**, 5215–5252.
5 J. Romulus, J. T. Henssler and M. Weck, *Macromolecules*, 2014, **47**, 5437–5449.
6 K. A. Günay, P. Theato and H.-A. Klok, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 1–28.
7 M. A. Gauthier, M. I. Gibson and H.-A. Klok, *Angew. Chem. Int. Ed.*, 2009, **48**, 48–58.
8 G. M. Rodriguez, M. M. Díaz-Requejo and P. J. Pérez, *Macromolecules*, 2021, **54**, 4971–4985.
9 Y. Li, R. Chang and Y.-X. Chen, *Chem. – Asian J.*, 2022, **17**, e202200318.
10 P. K. Behera, A. Kumar, S. Mohanty and V. K. Gupta, *Ind. Eng. Chem. Res.*, 2022, **61**, 16910−16923.
11 C. J. Smedley, M.-C. Giel, T. Fallon and J. E. Moses, *Angew. Chem. Int. Ed.*, 2023, **62**, e202303916.
12 A. Ashfaq, M.-C. Clochard, X. Coqueret, C. Dispenza, M. S. Driscoll, P. Ulański and M. Al-Sheikhly, *Polymers*, 2020, **12**, 2877.
13 H.-G. Batz, G. Franzmann and H. Ringsdorf, *Angew. Chem. Int. Ed.*, 1972, **11**, 1103–1104.
14 Y. Li, G. Vamvounis, J. Yu and S. Holdcroft, *Macromolecules*, 2001, **34**, 3130–3132.
15 M. Eberhardt, R. Mruk, R. Zentel and P. Théato, *Eur. Polym. J.*, 2005, **41**, 1569–1575.
16 B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 7540–7545.
17 X. Chen, U. C. Tam, J. L. Czlapinski, G. S. Lee, D. Rabuka, A. Zettl and C. R. Bertozzi, *J. Am. Chem. Soc.*, 2006, **128**, 6292–6293.
18 N. V. Tsarevsky, S. A. Bencherif and K. Matyjaszewski, *Macromolecules*, 2007, **40**, 4439–4445.
19 P. Ma, C. M. Plummer, W. Luo, J. Pang, Y. Chen and L. Li, *Chem. Sci.*, 2022, **13**, 11746–11754.
20 A. Soykan, B. Elif, H. Gurkan, T. Umit and D. Hakan, *J. Polym. Sci., Part A: Polym. Chem.*, 2018, **56**, 1181–1198.
21 M. Rimmele, F. Glöcklhofer and M. Heeney, *Mater. Horiz.*, 2022, **9**, 2678–2697.
22 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, **40**, 2004–2021.
23 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, **41**, 2596–2599.
24 J. Dong, L. Krasnova, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2014, **53**, 9430–9448.
25 A. S. Barrow, C. J. Smedley, Q. Zheng, S. Li, J. Dong and J. E. Moses, *Chem. Soc. Rev.*, 2019, **48**, 4731.
26 D. Zeng, W. Deng and X. Jiang, *Chem. Eur. J.*, 2023, **29**, e202300536.
27 T. S.-B. Lou and M. C. Willis, *Nat. Rev. Chem.*, 2022, **6**, 146–162.
28 T. A. Fattah, A. Saeed and F. Albericio, *J. Fluorine. Chem.*, 2018, **213**, 87–112.
29 D. Zeng, W.-P. Deng, and X. Jiang, *Natl. Sci. Rev.,* 2023, **10**, nwad123.
30 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.
31 Q. Chen, P. Mayer and H. Mayr, *Angew. Chem., Int. Ed.*, 2016, **55**, 12664–12667.
32 S. Li, P. Wu, J. E. Moses and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2017, **56**, 2903–2908.
33 J. J. Krutak, R. D. Burpitt,W. H. Moore, J. A. Hyatt, *J. Org. Chem.*, 1979, **44**, 3847−3858.
34 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.
35 K. J. Jang, W. S. Lee, S. Park, J. Han, J. E. Kim, B. M. Kim and J. H. Chung, *Nanomaterials*, 2021, **11**, 318.
36 A. Marra, C. Nativi and A. Dondoni, *New J. Chem.,* 2020, **44**, 4678–4680.
37 N. Wang, B. Yang; C. Fu, H. Zhu, F. Zheng, T. Kobayashi, J. Liu, S. Li, C. Ma, P. G. Wang, Q. Wang and L. Wang, *J. Am. Chem. Soc.*, 2018, **140**, 4995–4999.
38 Z. Liu, J. Li, S. Li, G. Li, K. B. Sharpless and P. Wu, *J. Am. Chem. Soc.*, 2018, **140**, 2919–2925.
39 A. Narayanan and L. H. Jones, *Chem. Sci.*, 2015, **6**, 2650–2659.
40 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.
41 Q. Zheng, J. L. Woehl, S. Kitamura, D. Santos-Martins, C. J. Smedley, G. Li, S. Forli, J. E. Moses, D. W. Wolan and K. B. Sharpless, *Proc Natl Acad Sci USA.*, 2019, **116**, 18808.
42 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.
43 Y. Dong, X. Lu, P. Wang, W. Liu, S. Zhang, Z. Wu and H. Chen, *J. Mater. Chem. B*, 2018, **6**, 4579–4582.
44 J. Dong, K. B. Sharpless, L. Kwisnek, J. S. Oakdale and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2014, **53**, 9466–9470.
45 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.
46 H. Wang, F. Zhou, G. Ren, Q. Zheng, H. Chen, B. Gao, L. Klivansky, Y. Liu, B. Wu, Q. Xu, J. Lu, K. B. Sharpless and P. Wu, *Angew. Chem., Int. Ed.*, 2017, **56**, 11203–11208.
47 C. Yang, J. P. Flynn and J. Niu, *Angew. Chem., Int. Ed.*, 2018, **57**, 16194–16199.
48 X. Xiao, F. Zhou, J. Jiang, H. Chen, L. Wang, D. Chen, Q. Xu and J. Lu, *Polym. Chem.*, 2018, **9**, 1040–1044.
49 W. Zhu, F. Li, J. Liu, X. Ma and X. Jiang, *React. Chem. Eng.*, 2019, **4**, 2074–2080.
50 H. Wan, S. Zhou, P. Gu, F. Zhou, D. Lyu, Q. Xu, A. Wang, H. Shi, Q. Xu and J. Lu, *Polym. Chem.*, 2020, **11**, 1033–1042.
51 Z. Cao, F. Zhou, P.-Y. Gu, D. Chen, J. He, J. R. Cappiello, P. Wu, Q. Xu and J. Lu, *Polym. Chem.*, 2020, **11**, 3120–3124.
52 R. W. Kulow, J. W. Wu, C. Kim and Q. Michaudel, *Chem. Sci.*, 2020, **11**, 7807–7812.
53 H. Kim, J. Zhao, J. Bae, L. M. Klivansky, E. A. Dailing, Y. Liu, J. R. Cappiello, K. B. Sharpless and P. Wu, *ACS Cent. Sci.*, 2021, **7**, 1919–1928.

54 X. Wang, X. Zhang and S. Ding, *Polym. Chem.*, 2021, **12**, 2668–2688.
55 Z. Li, H. Zhang, X. Zhang, J. Wang and Y. Wen, *Polym. Chem.*, 2022, **13**, 1260–1266.
56 J. Yatvin, K. Brooks and J. Locklin, *Angew. Chem., Int. Ed.*, 2015, **54**, 13370–13373.
57 S. Li, L. T. Beringer, S. Chen and S. Averick, *Polymer*, 2015, **78**, 37–41.
58 J. S. Oakdale, L. Kwisnek and V. V. Fokin, *Macromolecules*, 2016, **49**, 4473–4479.
59 J. C. Brendel, L. Martin, J. Zhang and S. Perrier, *Polym. Chem.*, 2017, **8**, 7475–7485.
60 K. Brooks, J. Yatvin, M. Kovaliov, G. H. Crane, J. Horn, S. Averick and J. Locklin, *Macromolecules*, 2018, **51**, 297–305.
61 P. Wang, Y. Dong, X. Lu, Z. Wu and H. Chen, *Macromol. Rapid Commun.*, 2018, **39**, 1700523.
62 M. Colpaert, M. V. Zaton, D. Ladmiral, J. Jones, B. Roziere and B. Ameduri, *Polym. Chem.*, 2019, **10**, 2176–2189.
63 M. Wang, H.-S. Jin, X.-M. Chen, B.-P. Lin and H. Yang, *Polym. Chem.*, 2019, **10**, 3657–3664.
64 M. Li, J.-A. Ma and S. Liao, *Macromolecules*, 2023, **56**, 806–814.
65 S. Li, G. Li, B. Gao, S. P. Pujari, X. Chen, H. Kim, F. Zhou, L. M. Klivansky, Y. Liu, H. Driss, D.-D. Liang, J. Lu, P. Wu, H. Zuilhof, J. E. Moses and K. B. Sharpless, *Nat. Chem.*, 2021, **13**, 858–867.
66 J. Yatvin, K. Brooks and J. Locklin, *Chem. – Eur. J.*, 2016, **22**, 16348–16354.
67 K. Brooks, J. Yatvin, C. D. McNitt, R. A. Reese, C. Jung, V. V. Popik and J. Locklin, *Langmuir*, 2016, **32**, 6600–6605.
68 H. Zhu, D. Chen, N. Li, Q. Xu, H. Li, J. He, H. Wang, P. Wu and J. Lu, *Chem. – Eur. J.*, 2017, **23**, 14712–14717.
69 S. Liu, Y. Cao, Z. Wu and H. Chen, *J. Mater. Chem. B*, 2020, **8**, 5529–5534.
70 W. Liu, Y. Dong, S. Zhang, Z. Wu and H. Chen, *Chem. Commun.*, 2019, **55**, 858–861.
71 D. Gahtory, R. Sen, S. Pujari, S. Li, Q. Zheng, J. E. Moses, K. B. Sharpless and H. Zuilhof, *Chem. Eur. J.*, 2018, **24**, 10550–10556.
72 P. Mukherjee, C. P. Woroch, L. Cleary, M. Rusznak, R. W. Franzese, M. R. Reese, J. W. Tucker, J. M. Humphrey, S. M. Etuk, S. C. Kwan, C. W. am Ende and N. D. Ball, *Org. Lett.*, 2018, **20**, 3943–3947.
73 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.
74 B. Han, S. R. Khasnavis, M. Nwerem, M. Bertagna, N. D. Ball and O. M. Ogba, *Inorg. Chem.*, 2022, **61**, 9746−9755.
75 M. Wei, D. Liang, X. Cao, W. Luo, G. Ma, Z. Liu and L. Li, *Angew. Chem. Int. Ed.*, 2021, **60**, 7397–7404.
76 R. Kakuchi and P.Theato, *Polym.chem.*, 2014, **5**, 2320–2325.
77 A. F. Grand and C. A. Wilkie, *Fire Retardancy of Polymeric Materials*, 2001.

Supporting Information

4-vinylbenzenesulfonyl fluoride (VBSF) : A Highly Reactive Monomer for RAFT Polymerization and Exhaustive SuFEx Postpolymerization Sulfonamidation

*Pengfei Ma, Yongqi Zhang, Christopher M. Plummer,Bin Wu,Yi Zhang and Le Li**

Table of Contents

1. Materials and Methods

Materials.

Characterization Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer at 298 K and referenced to residual protium in the NMR solvent ($CDCl_3$ δ 7.26, CD_2Cl_2 δ 5.30 in ^{1}H NMR) and the carbon resonances of the solvent ($CDCl_3$ δ 77.16, CD_2Cl_2 δ 53.52 in ^{13}C NMR). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. NMR peaks are described as singlet (s), doublet (d), triplet (t), multiplet (m), approximate (app), and broad (br).

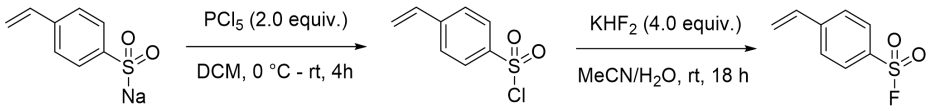
Size exclusion chromatography (SEC) was conducted using an Agilent Technologies 1260 Infinity equipped with a differential refractometer and serially connected PLgel columns (10 *μm* MIXED-BLS, 5 *μm* MIXED-C, and 5 *μm* MIXED-D). The system was equilibrated at 40 °C in DMF as the eluent with a flow rate of 1.0 $mL \cdot min^{-1}$. The weight-average molar mass (M_w) and the number-average molar mass (M_n) of the polymers were determined relative to the linear polystyrene standards and used to estimate the dispersity ($Đ = M_w/M_n$).

Differential scanning calorimetry (DSC) was performed with a NETZSCH DSC 214 Polyma instrument under an atmosphere of nitrogen at a heating rate of 10 $°C \cdot min^{-1}$. The glass transition temperatures (T_g) were obtained from the second heating run.

Thermogravimetric Analysis (TGA) was performed with a NETZSCH STA449F3 Jupiter instrument at a heating rate of 10 $°C \cdot min^{-1}$ from room temperature to 800 °C under an atmosphere of nitrogen.

2. Synthesis of 4-vinylbenzene sulfonyl fluoride monomers and their homopolymers

Synthesis of 4-vinylbenzene sulfonyl fluoride

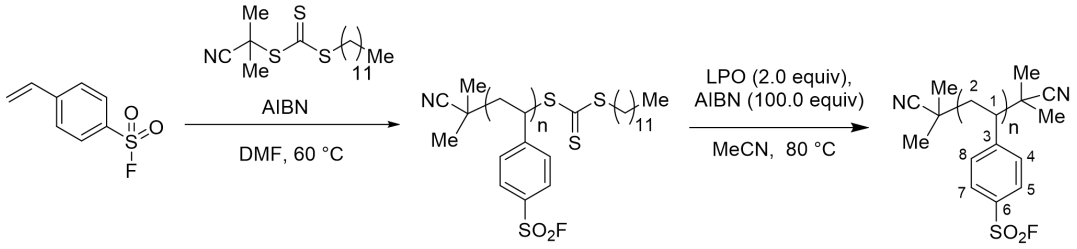


1

The title compound **1** was prepared according to a modification of literature procedure. Under an N_2 atmosphere, sodium 4-vinylbenzene sulfonate (6.34 g, 90 wt%, 30.0 mmol) and phosphorus pentachloride (60.0 mmol, 12.49 g) were added to in dichloromethane (120 mL) and cooled to 0 °C. The reaction mixture was then allowed to warm to room temperature slowly and reacted for 4 hours and then washed with half-saturated brine (150 mL). The organic phase was dried with anhydrous sodium sulfate and then filtered, concentrated *in vacuo* to get the crude product of 4-vinylbenzene sulfonyl chloride. The crude 4-vinylbenzene sulfonyl chloride and potassium hydride fluoride (120.0 mmol) were added to a mixture of acetonitrile (90 ml) and water (12 mL) at room temperature for 18 h. After most of the acetonitrile in the reaction mixture was removed *in vacuo*, dichloromethane (150 mL) and distilled water (100 mL) were added for extraction. The organic phase was combined after the water phase was extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with half-saturated brine (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (eluent: petroleum ether/ethyl acetate, 20:1 v/v) to afford the title compound **1** as a white liquid (3.40 g, 61%). R_f = 0.60 (petroleum ether/ethyl acetate, 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.95 (m, 2H), 7.63–7.61 (m, 2H), 6.81–6.76 (m, 1H), 5.97 (d, J = 17.6 Hz, 1H), 5.54 (d, J = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9, 134.9, 131.7 (d, J = 24.6 Hz), 128.9, 127.3, 119.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ 66.24.

Synthesis of 4-vinylbenzene sulfonyl fluoride copolymer

*PVBSF (**3a**)*



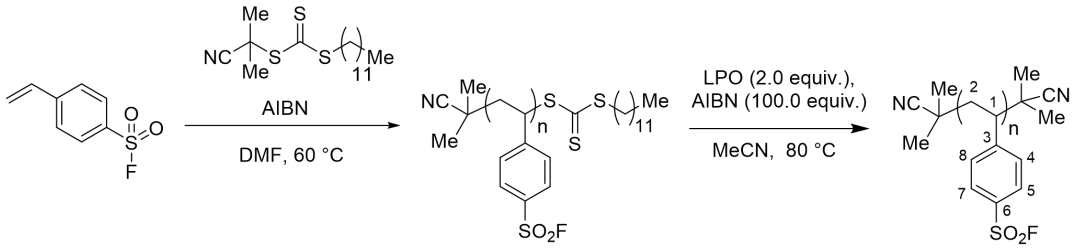
1 **3c** **3a**

A 10-mL Schlenk flask was charged with compound ***1*** (2.22 mg, 11.9 mmol), CPDT (68.6 mg, 0.20 mmol), AIBN (6.5 mg, 0.04 mmol) and *N, N*-dimethylformamide (2.00 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Volatiles were removed *in vacuo* and the polymer was precipitated in ethanol (3 × 40 mL) three times.The precipitate was collected and dried in a vacuum oven for 12 h at 45 °C to afford title polymer ***3c*** as a yellow solid (2.10 g, 95%) for SEC analysis. SEC (DMF, PMMA calibration): M_n: 12.6 kDa, M_w: 15.0 kDa, $Đ$: 1.19.

Trithioester end group of RAFT polymer ***3c*** was removed according to a modification of the literature procedure. A 50-mL Schlenk flask was charged with PVBSF ***3c*** (1.40 g, containing 0.12 mmol RAFT end groups), lauryl peroxide (96.9 mg, 0.24 mmol), AIBN (2.00 g, 12.2 mmol), and acetonitrile (12 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at

80 °C for 6 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Volatiles were removed *in vacuo* and the polymer was precipitated in ethanol (3 × 40 mL).The precipitate was collected and dried in a vacuum oven for 45 °C for 12 hours to obtain a white solid polymer ***3a*** (1.97 g, 94%). ^{1}H NMR (400 MHz, C_2D_6SO): δ 7.94–7.31 (m, $H_{5,7}$), 7.31–6.47 (m, $H_{4,8}$), 2.65–0.80 (m, $H_{1,2}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 153.9 (C_3), 132.0–129.3 ($C_{5,6,7}$), 129.3–127.0 ($C_{4,8}$), 45.6–42.1 (C_2), 42.1–39.2 (C_1). ^{19}F NMR (376 MHz, C_2D_6SO): δ 66.69. SEC (DMF, PMMA calibration): M_n: 13.6 kDa, M_w: 16.3 kDa, $Đ$: 1.20. TGA: 372 °C (50% weight loss). DSC: T_g: 179.7 °C.

*PVBSF (**3b**)*

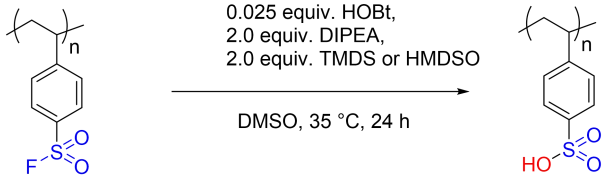


1 **3d** **3b**

A 10-mL Schlenk flask was charged with compound ***1*** (779.0 mg, 4.2 mmol), CPDT (96.5 mg, 0.28 mmol), AIBN(9.2 mg, 0.06 mmol) and *N, N*-dimethylformamide (800 μL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Volatiles were removed *in vacuo* and the polymer was precipitated in ethanol (3 × 40 mL) three times.The precipitate was collected and dried in a vacuum oven for 12 h at 45 °C to afford title polymer **3d** (846.5 mg, 96%) for SEC analysis. SEC (DMF, PMMA calibration): M_n: 3.8 kDa, M_w: 4.4 kDa, $Đ$: 1.15.

Trithioester end group of RAFT polymer ***3d*** was removed according to a modification of the literature procedure. A 50-mL Schlenk flask was charged with PVBSF ***3d*** (700.0 mg, containing 0.22 mmol RAFT end groups), lauryl peroxide (177.8 mg, 0.45 mmol), AIBN (3.66 g, 22.3 mmol), and acetonitrile (10 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 80 °C for 6 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Volatiles were removed *in vacuo* and the polymer was precipitated in ethanol (3 × 40 mL).The precipitate was collected and dried in a vacuum oven for 45 °C for 12 hours to obtain a white solid polymer ***3b*** (626.9 mg, 90%). ^{1}H NMR (400 MHz, C_2D_6SO): δ 7.94–7.31 (m, $H_{5,7}$), 7.31–6.47 (m, $H_{4,8}$), 2.65–0.80 (m, $H_{1,2}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 153.9 (C_3), 132.0–129.3 ($C_{5,6,7}$), 129.3–127.0 ($C_{4,8}$), 45.6–42.1 (C_2), 42.1–39.2 (C_1). ^{19}F NMR (376 MHz, C_2D_6SO): δ 66.69. SEC (DMF, PMMA calibration): M_n: 4.3 kDa, M_w: 5.0 kDa, $Đ$: 1.14.

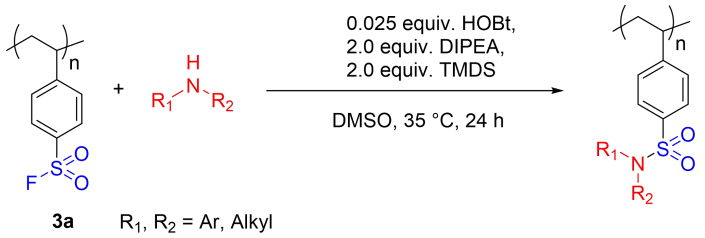
3. Preparation of SuFEx Postpolymerization Sulfonamidation Reaction Optimization



2a

The general reaction procedure was: Under nitrogen protection, PVBSF ***3a*** (50.0 mg, containing 0.27 mmol repeat units), 1-hydroxybenzotriazole (HOBt), *N, N*-diisopropylethylamine (94 μL, 0.54 mmol), 1,1,3, 3-tetramethyldisiloxane (95 μL, 0.54 mmol) or hexamethyldisiloxane (115 μL, 0.54 mmol) mixed with anhydrous DMSO (500 μL). After stirring for 24 hours at a certain temperature, 1-fluoronaphthalene (calibrated by the known mass of PVBSF raw material and 1-fluoronaphthalene) was added as an internal standard for conversion determination by ^{19}F NMR.

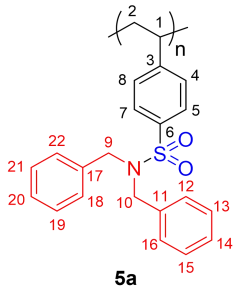
4. Preparation of Sulfonamide polymer



3a R_1, R_2 = Ar, Alkyl

The general reaction procedure was: Under nitrogen protection, PVBSF ***3a*** (150.0 mg, containing 0.81 mmol repeat units), amine (0.96 mmol), HOBt (5.4 mg, 0.04 mmol),*N, N*-diisopropylethylamine (281 µL, 1.61 mmol), 1,1,3, 3-tetramethyldisiloxane (285 µL, 1.61 mmol) was mixed with anhydrous DMSO (1.50 mL). After stirring at 35 °C for 24 hours, the mixture was settled in ethanol. After the sedimentation was repeated three times, the solvents were removed *in vacuo* and the precipitate was dried in a vacuum oven for 45 °C for 12 hours.

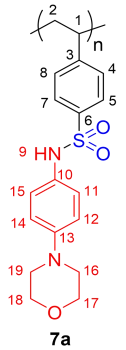
*Poly(N,N-dibenzyl-4-vinylbenzenesulfonamide) (**3a**)*



5a

Target polymer ***5a*** was isolated as a white solid (258.2 mg, 84%) with dibenzylamine (186 µL, 0.96 mmol) as an amine reagent according to the general procedure. ^{1}H NMR (400 MHz, C_2D_6SO): δ 8.30–6.15 (m, $H_{4,5,7,8,12,13,14,15,16,18,19,20,21,22}$), 4.74–3.84 (m, $H_{9,10}$), 2.46–0.77 (m, $H_{1,2}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 150.2 (C_3), 138.6 (C_6), 130.4 ($C_{11,17}$), 130.0–126.2 ($C_{4,5,7,8,12,13,14,15,16,18,19,20,21,22}$), 51.4 ($C_{9,10}$), 44.2–39.0 ($C_{1,2}$). SEC (DMF, PMMA calibration): M_n: 14.1 kDa, M_w: 17.5 kDa, $Đ$: 1.24. TGA: 405 °C (50% weight loss). DSC: T_g: 100.9 °C.

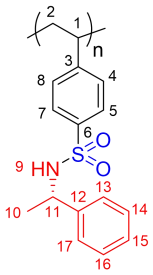
*Poly(N-(4-morpholinophenyl)-4-vinylbenzenesulfonamide) (**7a**)*



7a

Target polymer ***7a*** was isolated as a black solid polymer (163.0 mg, 56%) using 4-(4-morpholinyl) aniline (160 µL, 0.96 mmol) as an amine reagent according to the general procedure. ^{1}H NMR (400 MHz, C_2D_6SO): δ 10.3–9.00 (m, H_9), 8.16–5.61 (m, $H_{4,5,7,8,11,12,14,15}$), 4.09–3.45 (m, $H_{18,17}$), 3.15–2.64 (m, $H_{16,19}$), 2.40–0.51 (m, $H_{1,2}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 148.6 (C_3), 137.8 (C_6), 133.3–114.0 ($C_{4,5,7,8,10,11,12,13,14,15}$), 44.2–39.0 ($C_{1,2}$). SEC (DMF, PMMA calibration): M_n: 18.6 kDa, M_w: 22.3 kDa, $Đ$: 1.20. TGA: 373 °C (50% weight loss). DSC: T_g: 196.3 °C.

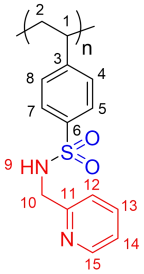
*Poly((S)-N-(1-phenylethyl)-4-vinylbenzenesulfonamide) (**7b**)*



7b

Target polymer ***7b*** was isolated as a white solid polymer (181.7 mg, 73%) using S-1-phenethylamine (125 µL, 0.96 mmol) as an amine reagent according to the general procedure. ^{1}H NMR (400 MHz, C_2D_6SO): δ 8.64–7.77 (m, H_9), 7.76–6.04 (m, $H_{4,5,6,7,13,14,15,16,17}$), 4.74–3.94 (m, H_{11}), 2.35–0.49 (m, $H_{1,2,10}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 151.4–145.8 (C_3), 143.8 (C_{12}), 140.0 (C_6), 129.7–127.6 ($C_{5,7,14,16}$), 127.6–125.5 ($C_{4,8,13,15,17}$), 53.2 (C_{11}), 44.2–39.0 ($C_{1,2}$), 23.7 (C_{10}). SEC (DMF, PMMA calibration): M_n: 18.4 kDa, M_w: 21.4 kDa, $Đ$: 1.16. TGA: 500 °C (50% weight loss). DSC: T_g: 110.7 °C. SEC (DMF, PMMA calibration): M_n: 16.6 kDa, M_w: 19.5 kDa, $Đ$: 1.17. TGA: 376 °C (50% weight loss). DSC: T_g: 136.8 °C.

*Poly(N-(pyridin-2-ylmethyl)-4-vinylbenzenesulfonamide) (**7c**)*

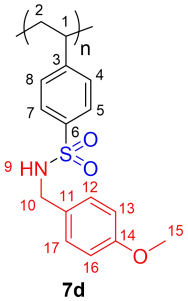


7c

Target polymer ***7c*** was isolated as a white solid polymer(205.8 mg, 87%) using

2-aminomethylpyridine(100 µL, 0.96 mmol) as an amine reagent according to the general procedure. ^{1}H NMR (400 MHz, C_2D_6SO): δ 8.61–8.26 (m, H_{15}), 8.26–7.86 (m, H_9), 7.86–7.42 (m, $H_{4,8,13}$), 7.42–7.23 (m, H_{14}), 7.23–7.04 (m, H_{12}), 7.04–6.19 (m, $H_{5,7}$), 4.54–3.69 (m, H_{10}), 2.46–0.93 (m, $H_{1,2}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 157.5 (C_{11}), 149.6 (C_3), 149.0 (C_{15}), 138.8 (C_6), 137.0 (C_{13}), 128.3 ($C_{5,7}$), 127.1 ($C_{4,8}$), 122.7 (C_{12}), 122.0 (C_{14}), 48.3 (C_{10}), 46.1–41.6 (C_2), 41.4–39.0 (C_1). SEC (DMF, PMMA calibration): M_n: 18.4 kDa, M_w: 21.4 kDa, $Đ$: 1.16. TGA: 500 °C (50% weight loss). DSC: T_g: 110.7 °C.

*Poly(N-(4-methoxybenzyl)-4-vinylbenzenesulfonamide) (**7d**)*



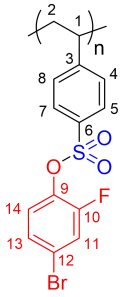
7d

Target polymer ***7d***was isolated as a white solid polymer (218.2 mg, 84%) using

p-methoxybenzylamine (126 µL, 0.96 mmol) as an amine reagent according to the general procedure. ^{1}H NMR (400 MHz, C_2D_6SO): δ 8.38–7.77 (m, H_9), 7.77–7.30 (m, $H_{4,8}$), 7.30–6.99 (m, $H_{5,7}$), 6.99–6.10 (m, $H_{12,13,16,17}$), 4.13–3.73 (m, H_{10}), 3.73–3.53 (m, H_{15}), 2.48–0.70 (m, $H_{1,2}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 158.9 (C_{14}), 149.8 (C_3), 139.3 (C_6), 130.0 (C_{11}), 129.4 ($C_{12,17}$), 128.2 ($C_{5,7}$), 127.0 ($C_{4,8}$), 114.0 ($C_{13,16}$),

55.5 (C_{15}), 46.1 (C_{10}), 44.8–41.4 (C_2), 41.4–38.6 (C_1). SEC (DMF, PMMA calibration): M_n: 18.8 kDa, M_w: 21.9 kDa, $Đ$: 1.16. TGA: 773 °C (50% weight loss). DSC: T_g: 103.9 °C.

*Poly(N-(4-methoxybenzyl)-4-vinylbenzenesulfonamide) (**7e**)*



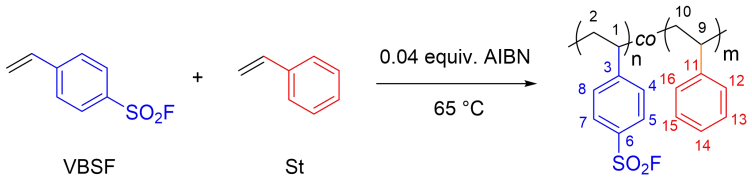
7e

Target polymer ***7e*** was isolated as a white solid polymer (265.7 mg, 87%) using

p-4-bromo-2-fluorophanol (106 µL, 0.96 mmol) as an amine reagent.according to the general procedure. ^{1}H NMR (400 MHz, C_2D_6SO): δ 8.03–7.43 (m, $H_{4,8,11}$), 7.43–7.23 (m, H_{14}), 7.23–6.27 (m, $H_{5,7,13}$), 2.82–0.58 (m, $H_{1,2}$). ^{13}C NMR (101 MHz, C_2D_6SO): δ 155.5 (C_{10}), 153.0 (C_3), 135.7 (C_9), 132.5 (C_6), 130.9–127.4 ($C_{4,8,13}$), 127.4–125.1 ($C_{5,7}$), 121.4–119.8 ($C_{11,12,14}$), 43.4–41.6 (C_2), 41.6–39.3 (C_1). ^{19}F NMR (376 MHz, $CDCl_3$): δ −124. 53. SEC (DMF, PMMA calibration): M_n: 15.9 kDa, M_w: 19.3 kDa, $Đ$: 1.21. TGA: 370 °C (50% weight loss). DSC: T_g: 104.6 °C.

5. Preparation of PVBSF copolymer

*Poly(N,N-dibenzyl-4-vinylbenzenesulfonamide)-co-polystyrene (**8**)*



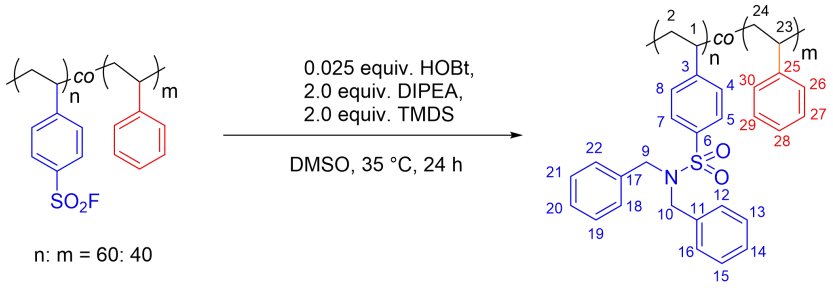
VBSF St

n: m = 60: 40

8

Under nitrogen protection, VBSF (466.5 mg, 2.50 mmol), styrene (287 μL, 2.50 mmol), AIBN (16.4 mg, 0.10 mmol) and DMF (1.00 mL) were added to a 10-mL Schlenk flask. The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 65 °C for 10 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. After the sedimentation operation was repeated three times, the solvents were removed *in vacuo* and the precipitate was dried in a vacuum oven for 45 °C for 12 hours. The white solid polymer ***8*** (589.3 mg, 81%) was obtained. SEC (DMF, PMMA calibration): M_n: 30.7 kDa, M_w: 67.8 kDa, $Đ$: 2.21. TGA: 394 °C (50% weight loss). DSC: T_g: 159.8 °C.

6. Exhaustive Sulfonamidation of PVBSF copolymer



8 **9**

Under nitrogen protection, PVBSF-*co*-PS ***8*** (150.0 mg), dibenzylamine (186μL, 0.96 mmol), HOBt (5.4 mg, 0.04 mmol), *N, N*-diisopropylethylamine (281 μL, 1.61 mmol), 1,1,3, 3-tetramethyldisiloxane (285 μL, 1.61 mmol) was mixed with anhydrous DMSO (1.50 mL). The mixture was stirred at 35 °C for 24 h. After the sedimentation operation was repeated three times, the solvents were removed *in vacuo* and the precipitate was dried in a vacuum oven for 45 °C for 12 hours. The white solid polymer ***9*** (229.6 mg, 82%) was obtained.SEC (DMF, PMMA calibration): M_n: 37.5 kDa, M_w: 87.1 kDa, $Đ$: 2.32. TGA: 397 °C (50% weight loss). DSC: T_g: 86.3 °C.