

# Lawrence Berkeley National Laboratory

LBL Publications

## Title

SuFEx-Based Polysulfonate Formation from Ethenesulfonyl Fluoride—Amine Adducts

## Permalink

<https://escholarship.org/uc/item/7st5t095>

## Journal

Angewandte Chemie International Edition, 56(37)

## ISSN

1433-7851

## Authors

Wang, Hua

Zhou, Feng

Ren, Gerui

et al.

## Publication Date

2017-09-04

## DOI

10.1002/anie.201701160

Peer reviewed

## Click Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201701160  
Internationale Ausgabe: DOI: 10.1002/anie.201701160

## SuFEx-Based Polysulfonate Formation from Ethenesulfonyl Fluoride–Amine Adducts

Hua Wang<sup>+</sup>, Feng Zhou<sup>+</sup>, Gerui Ren, Qinheng Zheng, Hongli Chen, Bing Gao, Liana Klivansky, Yi Liu, Bin Wu, Qingfeng Xu, Jianmei Lu, K. Barry Sharpless, and Peng Wu\*

**Abstract:** The SuFEx-based polycondensation between bisalkylsulfonyl fluorides (AA monomers) and bisphenol bis(*t*-butyldimethylsilyl) ethers (BB monomers) using  $[Ph_3P=N-PPh_3]^+[HF_2]^-$  as the catalyst is described. The AA monomers were prepared via the highly reliable Michael addition of ethenesulfonyl fluoride and amines/anilines while the BB monomers were obtained from silylation of bisphenols by *t*-butyldimethylsilyl chloride. With these reactions, a remarkable diversity of monomeric building blocks was achieved by exploiting readily available amines, anilines, and bisphenols as starting materials. The SuFEx-based polysulfonate formation reaction exhibited excellent efficiency and functional group tolerance, producing polysulfonates with a variety of side chain functionalities in >99% conversion within 10 min to 1 h. When bearing an orthogonal group on the side chain, the polysulfonates can be further functionalized via click-chemistry-based post-polymerization modification.

**P**olycondensation reactions, in which the side-chain functionality is not compromised by main-chain formation, are compelling for synthesizing polymers with desired repeating units.<sup>[1]</sup> Ideally, the side chain groups remain to be further derivatized to gain versatility, complexity, and desired functions.<sup>[2]</sup> Such polymerization reactions usually require a high degree of functional group compatibility, which is a grand challenge in the field of polymer synthesis.<sup>[3]</sup> The develop-

ment of click chemistry provides a timely solution to these obstacles.<sup>[4]</sup>

Click chemistry encompasses any reaction that proceeds with exquisite selectivity, quantitative yield, and near-perfect fidelity in the presence of a wide variety of functional groups.<sup>[3]</sup> The discovery of the Cu<sup>I</sup>-catalyzed azide–alkyne cycloaddition (CuAAC) reaction in 2002<sup>[5]</sup> has provided a versatile and highly efficient method to fabricate functionalized materials with absolute fidelity, high levels of control, and excellent functional group compatibility.<sup>[6]</sup> Several breakthroughs in polymer fabrication have been made possible using this methodology.<sup>[7]</sup> For example, CuAAC enables the facile coupling of two distinct linear polymers to form block copolymers, a notorious synthetic challenge due to the reduced reactivity between polymeric chain ends.<sup>[8]</sup> This reaction also provides a straightforward solution for the construction of templated star polymers and brush-block copolymers.<sup>[9]</sup>

In 2014, we reported a new family of click reactions, which we termed “sulfur(VI) fluoride exchange” (SuFEx),<sup>[10]</sup> to create molecular connections with absolute reliability and unprecedented efficiency through a sulfur(VI) hub. Unlike the S<sup>VI</sup>–Cl bond, which is exceedingly sensitive to reductive environments and yields S<sup>IV</sup> species in such conditions, the S<sup>VI</sup>–F bond allows only the substitution pathway to occur, and therefore it possesses an ideal combination of synthetic accessibility and stability.<sup>[10]</sup> Since then, SuFEx has been successfully applied to surface modification, polymer synthesis, and post-polymerization modification.<sup>[11]</sup> We discovered that 1,8-diazabicycloundec-7-ene (DBU) and 2-*t*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) could initiate the SuFEx-based polycondensation reaction of bisphenol A bis(*t*-butyldimethylsilyl) ethers and bisphenol A bis(fluorosulfate) to form polysulfates with high number-average molecular weight ( $M_n$ ), narrow polydispersity, and near quantitative yields. Compared to bisphenol A-derived polycarbonate, which is a widely used thermoplastic polymer, the bisphenol A-based polysulfates exhibit better thermal and hydrolytic stability, implicating potential applications under harsh environments.

In our exploration of SuFEx-based polycondensation processes, the structurally related polysulfonates –S(O)<sub>2</sub>O– attracted our attention.<sup>[12]</sup> This family of polymers shows considerable potential as moldable high-impact engineering thermoplastics and as useful materials for making films, fibers and coatings. However, most established attempts to synthesize polysulfonates relied on reacting sulfonyl chlorides with phenols under basic condition.<sup>[12,13]</sup> The poor selectivity of sulfonyl chlorides in this process significantly limits the utility

[\*] Dr. H. Wang,<sup>[†]</sup> Prof. P. Wu  
Department of Chemical Physiology, The Scripps Research Institute  
10550 North Torrey Pines Road, La Jolla, CA 92037 (USA)  
E-mail: pengwu@scripps.edu

Dr. H. Wang,<sup>[†]</sup> F. Zhou,<sup>[†]</sup> Dr. G. Ren, Q. Zheng, Dr. H. Chen,  
Dr. B. Gao, Prof. K. B. Sharpless  
Department of Chemistry, The Scripps Research Institute  
10550 North Torrey Pines Road, La Jolla, CA 92037 (USA)

F. Zhou,<sup>[†]</sup> B. Wu, Prof. Q. Xu, Prof. J. Lu  
College of Chemistry, Chemical Engineering and Materials Science,  
Collaborative Innovation Center of Suzhou, Nano Science and  
Technology, Soochow University  
Suzhou 215123 (P.R. China)

Dr. G. Ren  
Department of Applied Chemistry, School of Food Science and  
Biotechnology, Zhejiang Gongshang University  
Hangzhou 310018 (P.R. China)

L. Klivansky, Dr. Y. Liu  
The Molecular Foundry, Lawrence Berkeley National Laboratory  
Berkeley, CA 94720 (USA)

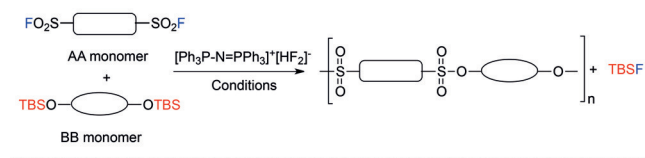
[†] These authors contributed equally to this work.

Supporting information for this article can be found under:  
<https://doi.org/10.1002/anie.201701160>.

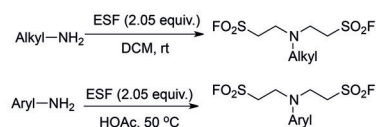
of these methods, and as a consequence, the structures of currently available polysulfonates are quite limited.<sup>[10,11c]</sup>

Herein, we report on the finding that the bifluoride salt  $[\text{Ph}_3\text{P}=\text{N}-\text{PPh}_3]^+[\text{HF}_2]^-$  is an excellent catalyst for the synthesis of polysulfonate polymers via a AA–BB polycondensation process (Figure 1). As low as 1.25 mol% catalyst

#### Polysulfonate formation promoted by bifluoride salts



#### Preparation of ESF-based monomers



**Figure 1.** Bifluoride promoted polysulfonate formation between bisalkylsulfonyl fluorides and bisphenol bis(*t*-butyldimethylsilyl) ethers.

loading is sufficient to produce polysulfonates in 99% conversion in an hour or less. Moreover, we are able to achieve great diversity in the polymeric backbone by harnessing the power of the ethenesulfonyl fluoride (ESF)-based Michael addition reaction for monomer synthesis.<sup>[10,14]</sup> Finally, we demonstrate that polysulfonates formed by this process can be further functionalized by exploiting click-chemistry transformations that are orthogonal to SuFEx.

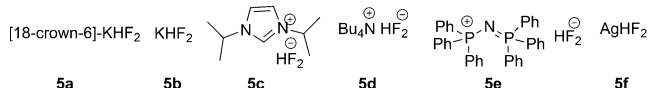
Since its introduction in 1953, ESF has been noted as a dienophile, a 1,3-dipolarophile, and a good Michael acceptor.<sup>[14,15]</sup> In fact, the reactions of ESF with a variety of nucleophiles are excellent approaches to produce alkyl sulfonyl fluorides.<sup>[10,14,15b]</sup> To produce polysulfonates with excellent repeating units variability, we chose ESF-amine/aniline adducts (that is, bis-functionalized alkylsulfonyl fluorides) as AA monomers to react with bisphenol bis(*t*-butyldimethylsilyl) ethers (BB monomers) based on the following considerations: 1) amines, anilines and bisphenols are readily availability from commercial sources; 2) bis-functionalized and multi-functionalized amines and anilines have been wide applied in polymer science.<sup>[16]</sup>

To construct ESF-based AA monomers, we mixed one equivalent of aliphatic amines with 2.05 equivalents of ESF in  $\text{CH}_2\text{Cl}_2$  at room temperature for 2 h to 6 h to give the desired bisalkylsulfonyl fluorides in good to excellent yields without or with only minor purification. In parallel, the aniline-ESF adducts were prepared using acetic acid as the solvent. Reaction at 50 °C overnight afforded the corresponding products in near quantitative yields (Figure 1). It should be noted that by using our recently developed interphase, kilogram-scale ESF synthesis technique,<sup>[15f]</sup> amine/aniline ESF adducts (that is, AA monomers) can be reliably prepared in hundred-gram scale quantities. On the other hand, the synthesis of bisphenol bis(*t*-butyldimethylsilyl) ethers (BB

monomers) is accomplished by reacting *t*-butyldimethylsilyl chloride with bisphenols.<sup>[11c]</sup>

With bisalkylsulfonyl fluorides and bisphenol bis(*t*-butyldimethylsilyl) ethers in hand, we next explored the SuFEx-based polycondensation reaction of these monomers. Exploiting the established catalyst (DBU) developed in the formation of bisphenol A polysulfates, our initial attempt between bis(alkylsulfonyl fluoride) **6a** and bisphenol A bis(*t*-butyldimethylsilyl) ether **7a** in dimethylformamide (DMF) was disappointing (Figure 2, entry 1–3).<sup>[11c,17]</sup> In the presence of

Entry	Cat. (mol%) <sup>a</sup>	Conditions	$M_n^{PS}$ (kDa) <sup>d</sup>	PDI ( $M_w/M_n$ )	isolated polymer <b>8a</b>
1	DBU (0.5)	80 °C, 24 h	No reaction	--	--
2	DBU (2.5)	rt, 2 h	Only oligomer observed <sup>b</sup>	--	--
3	DBU (2.5)	80 °C, 24 h	Only oligomer observed <sup>b</sup>	--	--
4	DBU (5)	80 °C, 24 h	7.5	1.6	455 mg
5	KHF <sub>2</sub> (5)	rt, 12 h	No reaction	--	--
6	AgHF <sub>2</sub> (5)	rt, 12 h	No reaction	--	--
7	<b>5a</b> (5)	rt, 12 h	24	1.7	454 mg
8	<b>5e</b> (5)	80 °C, 3 min	16	1.3	500 mg
9	<b>5e</b> (2.5)	80 °C, 3 min	22	1.5	499 mg
10	<b>5e</b> (1.25)	80 °C, 10 min	23	1.4	501 mg
11	<b>5e</b> (0.5)	80 °C, 12 h	26	1.5	446 mg
12	<b>5c</b> (0.5)	80 °C, 12 h	24	1.4	420 mg
13	<b>5d</b> (0.5)	80 °C, 12 h	24	1.4	398 mg



**Figure 2.** Polysulfonate **8a** formation under different catalytic conditions. a) Workup conditions: After the reaction went to completion, the solution was diluted with same volume of DMF followed by precipitation from methanol). b) No solid precipitation was observed after workup c) Catalyst loading was calculated based on the functional groups. d)  $M_n^{PS}$  values were  $M_n$  in reference to polystyrene standards.

DBU (5 mol%), we obtained polysulfonate **8a** with a relatively low molecular weight ( $M_n^{PS} = 7.5$  kDa) (Figure 2, entry 4). Bis(alkylsulfonyl fluoride) **6a** possesses an acidic proton at the  $\alpha$  position of the sulfonyl fluoride moiety. Chances are that dehydrofluorination takes place under basic condition to yield highly reactive sulfene-type intermediates that may react with trace amounts of impurities, for example, water or dimethyl amine in the polymerization solvent (DMF), thus terminate the chain growth.<sup>[18]</sup>

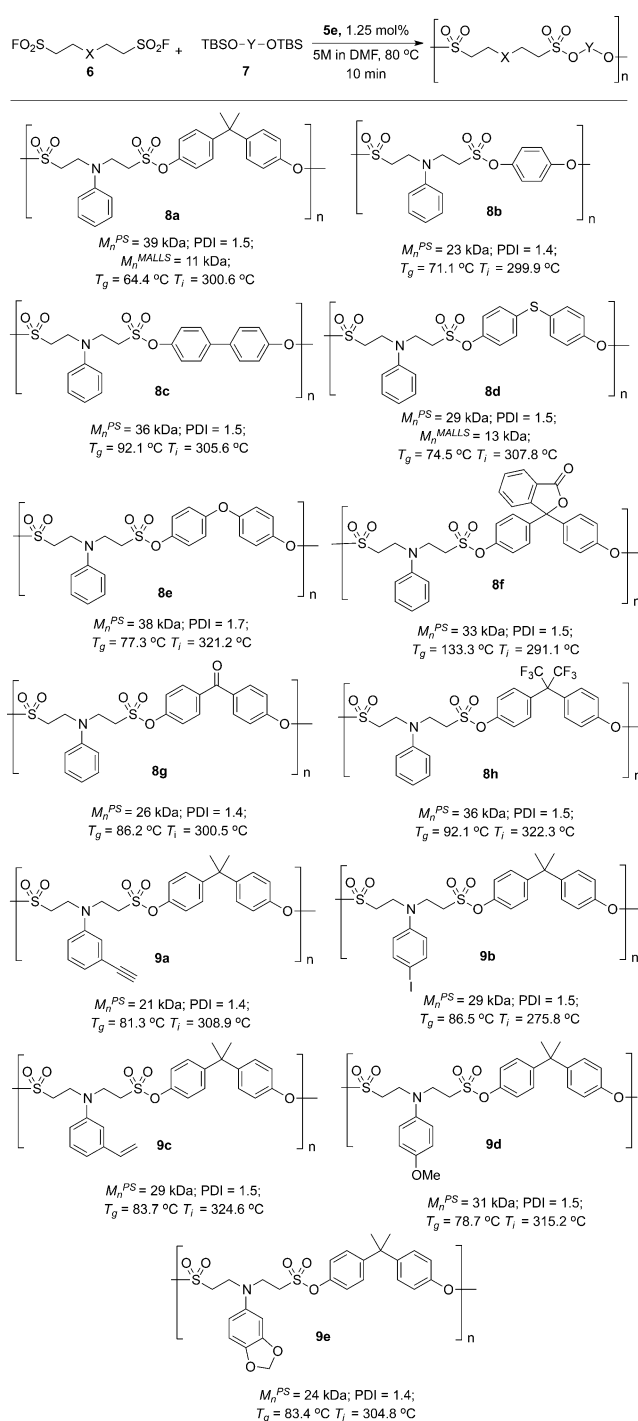
We recently discovered that bifluoride salts serve as excellent catalysts to promote SuFEx-based polymerization between bisphenol A bisfluorosulfate and the bisphenol A bis(*t*-butyldimethyl silyl) ether.<sup>[19]</sup> Compared to DBU, bifluoride salts are superior catalysts in terms of catalyst loading, stability,<sup>[20]</sup> functional group compatibility, as well as cost effectiveness. Most importantly, bifluoride salts are either neutral or slightly acidic<sup>[21]</sup> and are therefore well-suited for activation of base-sensitive alkylsulfonyl fluorides.

Encouraged by these discoveries, we assessed the possibility of using bifluoride salts to catalyze the polycondensation of bis(alkylsulfonyl fluoride) **6a** and bisphenol A bis(*t*-butyldimethylsilyl) ether **7a** (Figure 2, entry 5–13). To eval-

uate the effects of counter ions, six different bifluoride salts, including [18-crown-6]-KHF<sub>2</sub> (**5a**), KHF<sub>2</sub> (**5b**), *N,N'*-diisopropylimidazonium bifluoride (**5c**), tetrabutylammonium bifluoride (**5d**), [Ph<sub>3</sub>P=N-PPh<sub>3</sub>]<sup>+</sup>[HF<sub>2</sub>]<sup>-</sup> (**5e**), and AgHF<sub>2</sub> (**5f**), were selected as catalytic species. As shown in Figure 2, counterions were found to have a profound impact on the catalytic activity of the corresponding bifluoride salts. Neither KHF<sub>2</sub> nor AgHF<sub>2</sub> was able to initiate polysulfonate formation. This might be due to the tightness of the ion pairs in the reaction mixture. With the addition of a cationic chelating agent, [18-crown-6], to KHF<sub>2</sub> (1:1, 0.1M in acetonitrile, 5 mol%), we were able to promote polymerization at room temperature, producing polysulfonate **8a** ( $M_n^{PS} = 24$  kDa, PDI = 1.7) within 12 h (Figure 2, entry 7). By contrast, the organic-ammonium and phosphonium bifluoride salts exhibited excellent catalytic activity. In the presence of only 0.5 mol% of **5e**, the polycondensation reaction was accomplished in 12 h at 80 °C in dimethylformamide (5 M solution of monomers in DMF; condition A) (Figure 2, entry 11). Interestingly, this polycondensation was dramatically accelerated with higher catalyst loading (**5e**, 1.25 mol), producing polysulfonate **8a** ( $M_n = 22$  kDa) in 99% conversion within 10 min (Figure 2, entry 10, condition B). We next carefully monitored the consumption of the sulfonyl fluoride moiety under both conditions described above using <sup>1</sup>H NMR (Supporting Information, Figure S1). Under condition B, the sulfonyl fluoride was consumed much faster; reaching full conversion in only 1 min. By contrast, the consumption of the sulfonyl fluoride moiety under condition A was quite slow, requiring 12 h to complete. Other bifluoride salts, including **5c** and **5d**, also exhibited similar catalytic capability; albeit the weights of the isolated polymer were slightly lower (entry 12, 13).

Notably, we found that bifluoride salt **5e** catalyzed process does not require absolutely anhydrous conditions. However, the addition of 5 vol% water as the co-solvent completely suppressed the polymer formation. This phenomenon was also observed when 5 vol% of water was added as the co-solvent to the **5e** (1.25 mol%) catalyzed SuFEx reaction between alkylsulfonyl fluoride **4** and 4-methylphenol *t*-butyldimethylsilyl ether **3** (Supporting Information, Figure S2). This is not surprising because large amount of water will hydrolyze the reactive intermediates and thereby terminate the polymerization. Furthermore, benzoic acid (1 equiv) also prevented the coupling reaction from taking place, leading to the full recovery of the starting materials. When deuterated 4-Me-phenol was employed as an additive (1 equiv), crossover products were detected by <sup>1</sup>H NMR (Supporting Information, Figure S3), indicating an intermolecular proton transfer between the phenol additive and the bifluoride-activated silyl ether.

After the identification of the optimal polycondensation condition (condition B), we then investigated the substrate scope of this polysulfonate formation process. As shown in Figure 3, when we used **6a** as the coupling partner, bifluoride salt **5e** catalyzed polycondensation was applicable to various substrates, including 1,4-dihydroxybenzene bis(*t*-butyldimethylsilyl) ether (**7b**), 4,4'-biphenol bis(*t*-butyldimethylsilyl) ether (**7c**), 4,4'-thiodiphenol bis(*t*-butyldimethylsilyl) ether

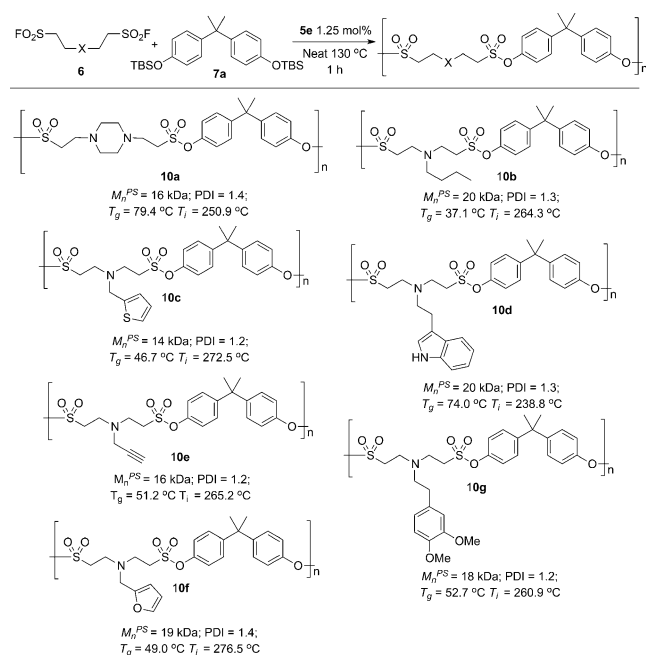


**Figure 3.** Preparation of polysulfonate polymers from aniline ESF adducts **6** and bisphenol A bis(*t*-butyldimethylsilyl) ether **7a**. a) The reactions were conducted with 0.5 mmol of each monomer for 10 min. b) The catalyst loading was calculated based on the functional groups. c) The products were isolated by precipitation from methanol and analyzed by Gel permeation chromatography (GPC). d)  $M_n^{PS}$  values were  $M_n$  in reference to polystyrene standards. e)  $M_n^{MALLS}$  values were determined by multi-angle laser light scattering. f)  $T_i = 5\%$  weight loss temperature.

(**7d**), 4,4'-dihydroxydiphenyl ether bis(*t*-butyldimethylsilyl) ether (**7e**), phenolphthalein bis(*t*-butyldimethylsilyl) ether (**7f**), and 4,4'-dihydroxybenzophenone bis(*t*-butyldimethyl-

silyl) ether (**7g**), affording polysulfonates **8a–h** within 10 min. Other aniline-ESF adducts with functional groups on the phenyl ring (**6b–f**, Supporting Information Sections B, C), which can be exploited for post-polymerization modification, also reacted smoothly with compound **7a** in the presence of 1.25 mol % **5e**, generating polysulfonates **9a–e** (Figure 3) in greater than 99% conversion (Supporting Information, Figure S5). The  $M_n^{PS}$  of these polysulfonates are between 21 kDa to 39 kDa with PDIs ranging from 1.4 to 1.7. The absolute number average molecular weights of polysulfonate **8a** and **8d**, as determined by multi-angle laser light scattering (MALLS), are 11 kDa and 13 kDa, respectively.

Sulfonyl fluorides containing tertiary aliphatic amines that had been derivatized from the Michael addition of aliphatic amines and ESF were also found to be excellent AA monomers for SuFEx-based polymerization (Figure 4). This



**Figure 4.** Preparation of polysulfonates from amine ESF adducts. a) The reactions were conducted with 0.5 mmol of each monomer. The catalyst loading was calculated based on the functional groups. The products were isolated by precipitation from methanol and analyzed by GPC.  $M_n^{PS}$  values were in reference to polystyrene standards. b)  $T_i$  = 5% weight loss temperature.

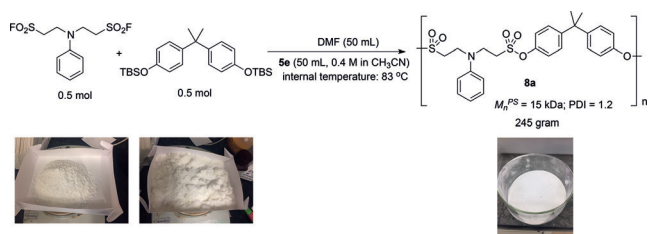
polycondensation reaction takes a longer time and requires higher temperature. We suspect that the protonated tertiary amine in bisulfonyl fluorides may interact with the bifluoride ion, which restricts its free movement, and thus slows down the SuFEx reaction. Nevertheless, the reaction of aliphatic amine-ESF adducts **6g–n** (Supporting Information, section B) and **7a** was performed as a neat mixture under elevated temperature (130 °C) in the presence of 1.25 mol % **5e** for 1 h, and the corresponding polysulfonates were produced with 99% conversion of the sulfonyl fluoride moiety (Supporting Information, Figure S5;  $M_n^{PS}$  from 14 kDa to 20 kDa). The PDIs of the resulting polysulfonates range from 1.2 to 1.4.

We next performed the physical property characterizations of the polysulfonates listed in Figure 3 and 4, including glass-transition temperature ( $T_g$ ) and thermal gravimetric analysis. Depending on the structures of the monomers,  $T_g$ s of the corresponding polysulfonates varied significantly (Figures 3, 4). For example, the  $T_g$  of polysulfonate **10b** is 37 °C, while the  $T_g$  of polysulfonate **8f** is 133 °C.<sup>[22]</sup> Thermal gravimetric analysis indicated that procedural decomposition temperatures ( $T_i$ ) of the polysulfonates are excellent with 5% weight loss occurring from 238 °C to 321 °C.

We discovered that the molecular weight of the polysulfonates formed by this process can be easily controlled by employing non-stoichiometric monomers: the molecular weight decreases along with increasing loading of one monomer. For example, in the preparation of polysulfonate **8a**, by increasing the loading of monomer **6a** from 1 to 1.05 equiv, the  $M_n^{PS}$  of the resulting polysulfonate **8a** decreased from 33 kDa to 26 kDa. When 1.1 equivalent of **6a** was employed, the  $M_n^{PS}$  of the resulting polysulfonate decreased further to 19 kDa (Supporting Information, Figure S6).

<sup>19</sup>F NMR and MALDI-TOF analysis revealed that polysulfonate **8a** possesses linear structure with sulfonyl fluoride as the ending group on both chain ends when excess of **6a** was employed and with phenol as the ending group when excess of **7a** was employed. Under the stoichiometric reaction condition, the linear polysulfonate contains sulfonyl fluoride on one end and a phenol group on the other (Supporting Information, Figures S7 and S8).

To evaluate the feasibility of large scale polysulfonate synthesis, we scaled up the polycondensation of **6a** and **7a** to 0.5 mol (Figure 5; Supporting Information, Figure S9). The



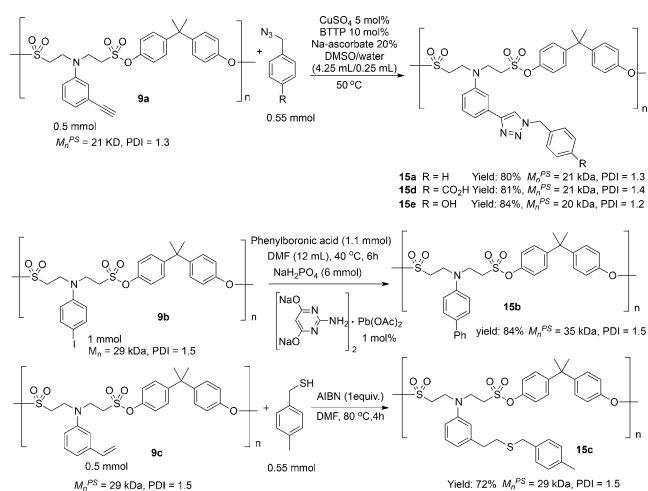
**Figure 5.** Large scale synthesis of polysulfonate **8a**.

reaction was performed in DMF (50 mL) at 83 °C (internal temperature). Catalyst **5e** (50 mL, 0.4 M solution in acetonitrile, 1.00 mol %) was added dropwise. We observed a rapid temperature increase with the addition of the catalyst (from 83 °C to 102 °C), which indicated this polymerization reaction is exothermic. Next, the byproduct *t*-butyldimethylsilyl fluoride and acetonitrile were distilled off, and the residue was diluted with DMF and slowly poured into methanol with vigorous stirring followed by filtration to afford 245 grams of polysulfonate **8a** ( $M_n^{PS}$  = 15 kDa) as a white solid.

The stability of polysulfonate **8a** generated from the large scale synthesis was then evaluated in the presence of sodium carbonate (1M, 1:2 EtOH/H<sub>2</sub>O), sodium hydroxide (1M, 1:2 EtOH/H<sub>2</sub>O), or hydrochloric acid (1M, 1:2 EtOH/H<sub>2</sub>O) at 80 °C, respectively. Polysulfonate **8a** exhibited good hydro-

lytic stability under both acidic and basic conditions as no significant changes in molecular weight were observed within 8 h (Supporting Information, Figure S10).

The orthogonal nature of SuFEx to other types of click reactions enables the incorporation of a diverse array of clickable groups onto the side chains of polysulfonates for post-polymerization modification, which is a facile means to endow parent polymers with new properties.<sup>[23]</sup> As shown in Figure 6, polysulfonate **9b** features a 4-iodophenyl pendant



**Figure 6.** Post-polymerization modification of polysulfonate **9a**, **9b**, and **9c**.

that can be modified via the Suzuki coupling reaction<sup>[24]</sup> to form polysulfonate **15b** in 84% isolated yield. Likewise, reacting polysulfonate **9c** with benzyl thiol via the thiol-ene click reaction<sup>[25]</sup> afforded the corresponding polysulfonate **15c** in 72% isolated yield. In our hands, the ligand-accelerated CuAAC serves as the most efficient approach for post-polymerization modification. Reacting the alkyne containing polysulfonate **9a** with benzyl azide in the presence of CuSO<sub>4</sub> (5 mol%), BTTP (10 mol%),<sup>[26]</sup> and sodium ascorbate (20 mol%) in DMSO–water (95:5) mixture provided polymer **15a** in 80% isolated yield.<sup>[27]</sup> Significantly, CuAAC is also able to introduce functional groups into polysulfonates (for example, acids and phenols) that are otherwise not compatible with the SuFEx-based coupling of sulfonyl fluorides and bisphenol silyl ethers. As shown in Figure 6, 4-azidomethylbenzoic acid and 4-azidomethylphenol were successfully reacted with the alkyne-functionalized polysulfonate **9a** to generate the corresponding 1,2,3-triazole linked derivatives **15d** and **15e** in excellent yields.

In summary, we have developed a [Ph<sub>3</sub>P=N–PPh<sub>3</sub>]<sup>+</sup>[HF<sub>2</sub>]<sup>–</sup> catalyzed AA-BB polycondensation reaction to generate polysulfonates with diverse structures and narrow polydispersity. This process is highly reliable and efficient, requiring only 1.25 mol% catalyst loading. The resulting polysulfonates exhibit excellent thermal and hydrolytic stability. In this process, diversity in the polymeric backbones is introduced by choosing a diverse array of monomers synthesized by the Michael addition of readily available amines or anilines to ESF and the silylation of various bisphenols. Due to the

orthogonal nature of SuFEx to other click-type transformations, clickable functional groups can be incorporated into the side-chains of the resulting polysulfonates to further increase the versatility of the parent polymers. Featuring excellent fidelity, high efficiency, substrate diversity, functional group tolerance, as well as post-polymerization modification compatibility, the process reported herein offers a fast and reliable methodology to fabricate polysulfonates with a variety of side chain functionalities. We expect this polymerization process to have immediate applications to functional macromolecule fabrication. Step growth processes are governed by Carothers kinetics, which describes that polydispersity of polymers formed by polycondensation should approaching 2 with near quantitative conversion. Given that the conversions in this process are greater than 99% and the polydispersity of resulting polysulfonates range from 1.2 to 1.7, we suspect that this polymerization reaction does not follow a conventional step growth mechanism. The mechanistic investigation of this polymerization is currently undergoing in our laboratories.

## Acknowledgements

Financial support for this work was provided by the National Science Foundation (CHE 1610987 to K.B.S.), the National Institutes of Health (R01GM113046 to P.W.), the Chinese National Science Foundation (21336005, 21176164, and 21371128), and the Major Research Project of Jiangsu Province Office of Education (15KJA150008). Part of the work was carried out as a user project at the Molecular Foundry, which was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We thank Dr. Larissa Krasnova for her initial work on this project using DBU as the catalyst.

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** bifluoride salt · click chemistry · ethenesulfonyl fluoride · polysulfonate formation · SuFEx reaction

**How to cite:** *Angew. Chem. Int. Ed.* **2017**, *56*, 11203–11208  
*Angew. Chem.* **2017**, *129*, 11355–11360

- [1] C. K. Ober, S. Z. D. Cheng, P. T. Hammond, M. Muthukumar, E. Reichmanis, K. L. Wooley, T. P. Lodge, *Macromolecules* **2009**, *42*, 465–471.
- [2] a) K. A. Günay, P. Theato, H. A. Klok, *J. Polym. Sci. Part A* **2013**, *51*, 1–28; b) J. Romulus, J. T. Henssler, M. Weck, *Macromolecules* **2014**, *47*, 5437–5449.
- [3] C. J. Hawker, K. L. Wooley, *Science* **2005**, *309*, 1200–1205.
- [4] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; *Angew. Chem.* **2001**, *113*, 2056–2075.
- [5] a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599; *Angew. Chem.*

- 2002, 114, 2708–2711; b) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, 67, 3057–3064.
- [6] J. F. Lutz, *Angew. Chem. Int. Ed.* **2007**, 46, 1018–1025; *Angew. Chem.* **2007**, 119, 1036–1043.
- [7] a) M. Meldal, *Macromol. Rapid Commun.* **2008**, 29, 1016–1051; b) J. Lawrence, S.-H. Lee, A. Abdilla, M. D. Nothling, J. M. Ren, A. S. Knight, C. Fleischmann, Y. Li, A. S. Abrams, B. V. K. J. Schmidt, M. C. Hawker, L. A. Connal, A. J. McGrath, P. G. Clark, W. R. Gutekunst, C. J. Hawker, *J. Am. Chem. Soc.* **2016**, 138, 6306–6310; c) F. Amir, Z. F. Jia, M. J. Monteiro, *J. Am. Chem. Soc.* **2016**, 138, 16600–16603; d) J. C. Barnes, D. J. C. Ehrlich, A. X. Gao, F. A. Leibfarth, Y. Jiang, E. Zhou, T. F. Jamison, J. A. Johnson, *Nat. Chem.* **2015**, 7, 810–815.
- [8] a) J. A. Opsteen, J. C. M. van Hest, *Chem. Commun.* **2005**, 57–59; b) S. F. M. van Dongen, M. Nallani, S. Schoffelen, J. J. L. M. Cornelissen, R. J. M. Nolte, J. C. M. van Hest, *Macromol. Rapid Commun.* **2008**, 29, 321–325.
- [9] a) B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee, K. Matyjaszewski, *Macromolecules* **2005**, 38, 7540–7545; b) W. H. Binder, C. Kluger, *Macromolecules* **2004**, 37, 9321–9330; c) S. Neumann, D. Dohler, D. Strohl, W. H. Binder, *Polym. Chem.* **2016**, 7, 2342–2351.
- [10] J. J. Dong, L. Krasnova, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2014**, 53, 9430–9448; *Angew. Chem.* **2014**, 126, 9584–9603.
- [11] a) J. Yatvin, K. Brooks, J. Locklin, *Angew. Chem. Int. Ed.* **2015**, 54, 13370–13373; *Angew. Chem.* **2015**, 127, 13568–13571; b) K. Brooks, J. Yatvin, C. D. McNitt, R. A. Reese, C. Jung, V. V. Popik, J. Locklin, *Langmuir* **2016**, 32, 6600–6605; c) J. J. Dong, K. B. Sharpless, L. Kwisnek, J. S. Oakdale, V. V. Fokin, *Angew. Chem. Int. Ed.* **2014**, 53, 9466–9470; *Angew. Chem.* **2014**, 126, 9620–9624; d) J. Yatvin, K. Brooks, J. Locklin, *Chem. Eur. J.* **2016**, 22, 16348–16354; e) S. H. Li, L. T. Beringer, S. Y. Chen, S. Averick, *Polymer* **2015**, 78, 37–41.
- [12] a) J. L. Work, J. E. Herweh, *J. Polym. Sci. A1* **1968**, 6, 2022–2030; b) J. E. Forrette, J. E. Burroughs, C. C. Booker, *J. Appl. Polym. Sci.* **1968**, 12, 2039–2045.
- [13] R. V. Vizgert, N. M. Budenkova, N. N. Maksimenko, *Polym. Sci. U.S.S.R.* **1989**, 31, 1508–1511.
- [14] J. J. Krutak, R. D. Burpitt, W. H. Moore, J. A. Hyatt, *J. Org. Chem.* **1979**, 44, 3847–3858.
- [15] a) H. L. Qin, Q. H. Zheng, G. A. L. Bare, P. Wu, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2016**, 55, 14155–14158; *Angew. Chem.* **2016**, 128, 14361–14364; b) R. M. Hedrick, United States Patent 2,653,973, **1953**; c) J. A. Hyatt, A. W. White, *Synthesis* **1984**, 214–217; d) J. Chanetray, R. Vessiere, A. Zeroual, *Heterocycles* **1987**, 26, 101–108; e) P. K. Mykhailiuk, *Chem. Eur. J.* **2014**, 20, 4942–4947; f) Q. Zheng, J. Dong, K. B. Sharpless, *J. Org. Chem.* **2016**, 81, 11360–11362; g) R. Zelli, S. Tommasone, P. Dumy, A. Marra, A. Dondoni, *Eur. J. Org. Chem.* **2016**, 5102–5116; h) Q. Chen, P. Mayer, H. Mayr, *Angew. Chem. Int. Ed.* **2016**, 55, 12664–12667; *Angew. Chem.* **2016**, 128, 12854–12858; i) A. V. Bogolubsky, Y. S. Moroz, P. K. Mykhailiuk, S. E. Pipko, A. I. Konovets, I. V. Sadkova, A. Tolmachev, *ACS Comb. Sci.* **2014**, 16, 192–197.
- [16] a) L. Matejka, *Macromolecules* **2000**, 33, 3611–3619; b) X. L. Wang, J. J. Yin, X. G. Wang, *Macromolecules* **2011**, 44, 6856–6867.
- [17] V. Gembus, F. Marsais, V. Levacher, *Synlett* **2008**, 1463–1466.
- [18] a) J. F. King, *Acc. Chem. Res.* **1975**, 8, 10–17; b) J. F. King, T. Durst, *J. Am. Chem. Soc.* **1964**, 86, 287–288.
- [19] K. B. Sharpless, J. Dong, B. Gao, P. Wu, H. Wang, WO20162099 A1, **2016**.
- [20] H. R. Sun, S. G. DiMagno, *J. Am. Chem. Soc.* **2005**, 127, 2050–2051.
- [21] S. N. Subbarao, Y. H. Yun, R. Kershaw, K. Dwight, A. Wold, *Inorg. Chem.* **1979**, 18, 488–492.
- [22] J. Feng, R. X. Zhuo, X. Z. Zhang, *Prog. Polym. Sci.* **2012**, 37, 211–236.
- [23] a) M. A. Gauthier, M. I. Gibson, H. A. Klok, *Angew. Chem. Int. Ed.* **2009**, 48, 48–58; *Angew. Chem.* **2009**, 121, 50–60; b) N. K. Boanen, M. A. Hillmyer, *Chem. Soc. Rev.* **2005**, 34, 267–275.
- [24] a) J. M. Chalker, C. S. C. Wood, B. G. Davis, *J. Am. Chem. Soc.* **2009**, 131, 16346–16347; b) C. D. Spicer, T. Triemer, B. G. Davis, *J. Am. Chem. Soc.* **2012**, 134, 800–803; c) Z. H. Gao, V. Gouverneur, B. G. Davis, *J. Am. Chem. Soc.* **2013**, 135, 13612–13615.
- [25] a) A. B. Lowe, *Polym. Chem.* **2014**, 5, 4820–4870; b) J. T. Xu, C. Boyer, *Macromolecules* **2015**, 48, 520–529.
- [26] W. Wang, S. L. Hong, A. Tran, H. Jiang, R. Triano, Y. Liu, X. Chen, P. Wu, *Chem. Asian J.* **2011**, 6, 2796–2802.
- [27] P. L. Golas, K. Matyjaszewski, *Chem. Soc. Rev.* **2010**, 39, 1338–1354.

Manuscript received: February 2, 2017

Revised manuscript received: March 31, 2017

Version of record online: May 18, 2017