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Journal:	*Polymer Chemistry*
Manuscript ID	PY-COM-03-2020-000435
Article Type:	Communication
Date Submitted by the Author:	25-Mar-2020
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COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Preparation of Aryl Polysulfonates via a highly efficient SuFEx click reaction, their controllable degradation and functionalized behavior

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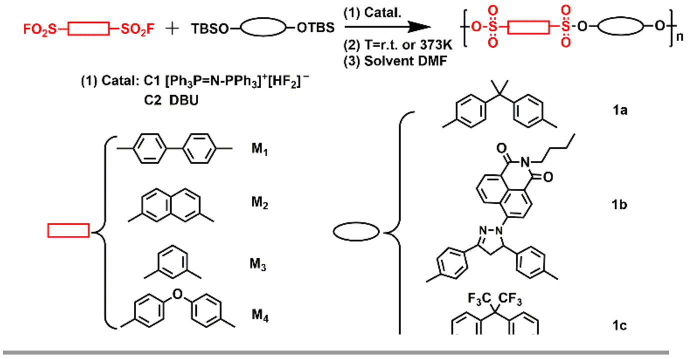
Polysulfonates obtained from SuFEx click reactions can be degraded using DBU as a bifunctional catalyst. A possible mechanism proceeding through the esterification of the R-S(O)-OR' group is proposed. The degradation process was further utilized to prepare functional polymers such as the AIEgen-ended polymer and a ternary polymer with tunable emission.

Recently, sulfonate or sulfate linked condensed polymers, such as polysulfonates (PSFO) and polysulfates (PSFA) have attracted significant interest due to the utility of SuFEx click reactions[1-5]. The polymerization of bis-arylfluorosulfonates (or bis-arylfluorosulfates) and bisphenol silylethers and polysulfonates (or polysulfates) can be processed at room temperature (r.t., 25 °C) and on a large scale indicating the potential application for use in engineering polymers. Previous reports have focused on polymerization methods[6-8], whereas the degradation of polysulfonates (or polysulfates) has not been widely studied, which is of critical importance in the current environment. In this paper, when we prepared a series of polysulfonates (PSFOs) through SuFEx-based polymerization, an unexpected degradation of the PSFOs was observed simultaneously. By using DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as a catalyst, the PSFOs (M_n>73600 gmol^{-1}) gradually decompose into oligomers (M_n<5000 gmol^{-1}), a phenomenon that can be accredited to a reversible sulfonate ester exchange reaction. Moreover, activity of the ends of the oligomer chains are preserved and can be linked covalently with other functional moieties by another SuFEx reaction[8]. This degradation reaction not only provides a new recycling route for PSFOs, but also provides a novel method for the modification of the polymer chains[9-11].

The four bisalkylsulfonyl fluoride monomers (M1-M4, shown in (Scheme 1) were prepared according to a reference procedure[7, 8] and characterized by NMR (see SI). They were then reacted with bis(aryl silyl ether) (1a) in DMF with $[Ph_3P{=}N{-}PPh_3]^+[HF_2]^-$(C1) as the catalyst, resulting in the formation of aromatic polysulfonates with high molecular weights (M_n) and narrow PDIs (Table 1). The copolymer PSFO1 from the monomer M1 (biphenyl sulfonyl fluoride) and monomer 1a showed the highest M_n (73600 g mol^{-1}) and a narrow PDI (about 1.4) at 100 °C. From the perspective of reducing energy consumption, a reduction in reaction temperature means lowering material manufacturing costs. When we further reduced the reaction temperature to r.t., the polymerization still proceeded and the M_n still reached 39800 g mol^{-1}. The other three arylsulfonyl fluoride monomers (M2-M4), possessing different conjugating backbones (phenyl, naphthyl and biphenyl ether), were reacted with 1a to confirm the feasibility of this S-F exchange reaction. All polymers showed a relatively high M_n and narrow PDI (PSFO2, M_n = 31900 g mol^{-1}, PDI = 1.5; PSFO3, M_n = 20700 g mol^{-1}, PDI = 1.3, PSFO4, M_n = 49300 g mol^{-1}, PDI = 1.5). Due to its strong affinity for electrons, the $-SO_2F$ group changes the electron density of the molecule and affects the polymerization activity of the monomers[12]. Thereafter, the benzene group in M3 shows the lowest activity with the smallest M_n, whereas the biphenyl



Scheme 1 Synthetic route to polysulfonates. （M: monomers of bis(alkylsulfonyl fluoride) monomers; 1a ,1b and 1c monomers of bis(aryl silyl ethers)

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† Electronic Supplementary Information (ESI) available: [Synthetic of all realted compounds, procedures, figures, NMR spectra, and GPC chromatograms and other regular data]. See DOI: 10.1039/x0xx00000x

group (M1) has the highest activity with the largest M_n. The polysulfonates exhibit high thermal stability with a decomposition temperature T_d of approximately 350 °C. Furthermore, four analogous sulfonate monomers (O1-O4) were chosen for the polymerization of polysulfates. The GPC results (PSFA1 M_n = 38600 g mol^{-1} PDI = 1.5, PSFA2, M_n = 21900 g mol^{-1}, PDI = 1.3; PSFA3, M_n = 17100g mol^{-1}, PDI = 1.4; PSFA4, M_n = 46300 $gmol^{-1}$, PDI = 1.5) are listed in the SI (Table S1). Under the same reaction conditions, the polysulfates exhibit a lower M_n, indicating that the sulfonyl fluoride group is more reactive than the sulfuryl fluoride group. This can probably be attributed to the electron-rich nature of the sulfur atom, since the reaction of the sulfonyl fluoride is much faster than that of the sulfuryl fluoride[13, 14].

We next investigated another generally used catalyst, DBU, in order to study the effect of the catalyst in this S-F exchange polymerization. An unexpected result occurred when DBU was used as a catalyst. The PSFOs showed an unusually low molecular weight. For example, the M_n of PSFO1 was only 13400 g mol^{-1} at 100 °C after 6 hours, whereas it was 24700 g mol^{-1} at room temperature. Similar results were observed in other PSFOs, while no obvious variation was observed in the PSFAs. We first speculated that DBU was not a good catalyst for the polymerization of PSFOs, which has not been previously mentioned in other reports[6, 7]. We then conducted a kinetic study of PSFO1 using DBU[15]. To our surprise, this study showed that the M_n of PSFO1 reached 33000 g mol^{-1} within the first ten minutes of polymerization. However, after 40 minutes the M_n decreased gradually to lower than 15000 (a drop of 50% in M_n) (Figure S1). While the formation of PSFA1 was different, the M_n of PSFA1 increased from 0 to 33700 following an increase in the reaction time[7].

This illustrates that the polymer PSFO1 was able to degrade in the presence of DBU. Considering the alkalinity of DBU, we selected several bases for studying the influence of basicity on degradation[16]. Firstly, we employed a saturated Na_2CO_3 solution for the polymer degradation (PSFO1, M_n = 73600 g mol^{-1}). The polymer back-bone was retained and no obvious hydrolysis occurred after heating overnight at 80 °C. The GPC result of the base-treated PSFO1 showed that the M_n is 71100 g mol^{-1}, while the polycarbonate decomposes under the same conditions[17]. We used the other organic bases trimethylamine (TMA), pyridine (Py) and 4-dimethylamino pyridine (DMAP) to explore the degradation behavior of PSFO1 (Table S2). Surprisingly, according to the GPC results, almost no degradation occurred after treatment using conditions similar from above (M_n = 72000 g mol^{-1} in TMA, M_n = 61400 g mol^{-1} in Py and M_n = 69800 g mol^{-1} in DMAP). The results also indicated that DBU, while not only acting as a base, plays an important role in the degradation[18]. We also applied three other guanidinium bases including 1,5,7- Triazabicyclo[4.4.0]dec-5-ene (TBD), 7-Methyl-1,5,7-triazabicyc-lo[4.4.0]dec-5-ene (MTBD) and 1,1,3,3-Tetramethylguanidine (TMG) in the polymerization to determine their impact on transesterification reaction rates. The reaction kinetics of these catalysts is compared in Table S3 and Figure S4. As shown in Figure S4, the M_n of PSFO1 reaches the highest molecular weight after five minutes of polymerization with molecular weights of 29700 g mol^{-1}, 51500 g mol^{-1}, 52000 g mol^{-1}, respectively. However, they show different degrees of degradation. Among the three bases, TBD is the most effective catalyst for degradation. By using TBD, the M_n of PSFO1 is reduced to 18100 g mol^{-1}, while the other two catalysts have weaker degradation capabilities. Nonetheless, its degradation ability is still not as good as DBU. Therefore, DBU was chosen as the transesterification catalyst.

Polysulfonate	T	C1		C2		T_d^c
		M_n^a	PDI^b	M_n^a	PDI^b	
PSFO1	RT	39800	1.4	24700	1.4	-
	373K	73600	1.4	13400	1.3	350
PSFO2	373K	31900	1.5	23800	1.5	354
PSFO3	373K	20700	1.3	12800	1.2	357
PSFO4	373K	49300	1.5	17000	1.3	347

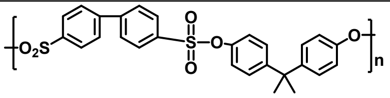
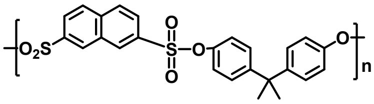
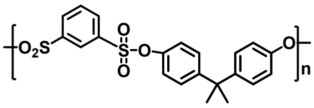
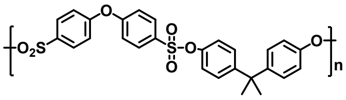
Polysulfonate		T	C1		C2		T_d^c
			M_n^a	PDI^b	M_n^a	PDI^b	
PSFO1		RT	39800	1.4	24700	1.4	-
		373K	73600	1.4	13400	1.3	350
PSFO2		373K	31900	1.5	23800	1.5	354
PSFO3		373K	20700	1.3	12800	1.2	357
PSFO4		373K	49300	1.5	17000	1.3	347

Table 1 The reaction conditions and GPC results of Polysulfonates

^{a}M$_n$(g mol^{-1}) ^{b}PDI(M$_w$/M$_n$) ^{c}T$_d$(°C):Temperature at which 5% weight loss was observed

In addition, we investigated the effect of DBU loadings on the reaction under the same conditions. DBU loadings were varied from 5% to 30%. The results indicated that the amount of DBU has little influence on the molecular weight. The M$_n$s are 11300 g mol^{-1} (5% DBU loadings), 10100 g mol^{-1} (10%), 10800 gmol^{-1} (20%), and 10100 gmol^{-1} (30%) respectively. Accordingly, 5% DBU was sufficient to depolymerize the PFSO1. When the amount of DBU increased to 50% and the reaction time was extended to 24h, the oligomers (M$_n$ = 3000 g mol^{-1}) cannot be further broken down into smaller molecules. As reported by the references, transesterification is prone to an equilibrium reaction[19-22]. It is believed that DBU functions by activating the initiating/propagating hydroxyl group through hydrogen bonding[23]. Therefore, increasing the amount of the catalyst only changes the reaction equilibrium[24].

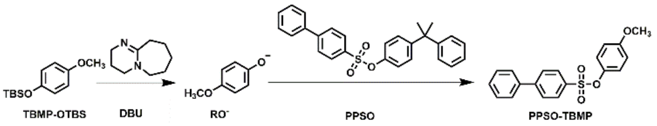


Figure 1 Ester exchange certification and mechanism speculation of the small molecule PPSO

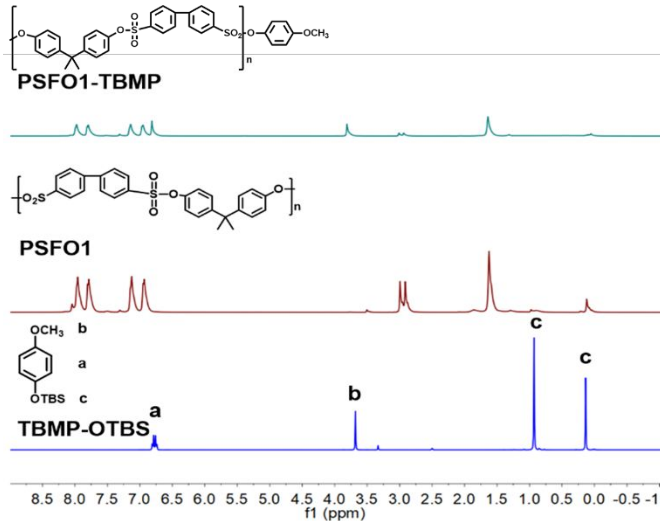


Figure 2 Comparison of 1HNMR spectra before and after PSFO1 capping

Furthermore, a polar solvent can accelerate the degradation. For example, PSFO1 in DMF showed the fastest degradation rate and the smallest M$_n$ compared to degradation in THF and CH_2Cl_2. This indicates that a polar solvent promotes the deprotonation process[25].

We used MALDI-TOF and FTIR to confirm the end groups of degraded oligomers (details in Figure S6-7). After depolymerization by DBU, the degraded polysulfonate mainly possesses sulfonic acid and phenol as end groups, which is similar to some cases of the degraded PC polymers[26-28]. Herein, DBU acts as both an esterification and transesterification catalyst. During the polymerization process, it is an esterification catalyst[29, 30]. However, DBU is an electron-rich compound and an aprotic base. It can break the S-O single bond of the bisphenyl sulfonate with the liberation of phenolic hydroxyl groups[31]. This results in the cleavage of the sulfonate linker in the polymer chain, which is considered to be a transesterification reaction and depolymerization.

In order to investigate the aryl-S-O bond activation mechanism[32, 33], two small molecules, 4-(2-phenylpropan-2-yl) phenyl[1,1'-biphenyl]-4-sulfonate (PPSO) and *tert*-butyl(4-methoxyphenoxy)dimethylsilane (TBMP-OTBS) containing a sulfonate bond and a *t*-butylchlorosilane group were prepared. In a DMF solution, PPSO and TBMP-OTBS were mixed at a ratio of 1:2 and 5 mol% of DBU was added as a catalyst. After one day, an aliquot of the solution was directly taken out for analysis by LC/MS (Figure S2). It was discovered that a new sulfonate compound (PPSO-TBMP) had formed via transesterification[34, 35]. We have also tried other nucleophiles, which include 4-formylbenzonitrile, (1-Bromoethyl) benzene, 4-bis (chloromethyl) benzene to react with the intermediate. However, no new products were generated. A possible mechanism is the alkoxide anion (RO^-) can be generated *in situ* from a silyl ether (TBMP-OTBS) in the presence of DBU. The RO^- attacks the ester bond of the original sulfonate PPSO and produces a new sulfonate PPSO-TBMP. It also indicates that DBU acts as a transesterification catalyst for sulfonate esters (Figure 1).

We further employed the polymer PSFO1 to react with a small molecule, TBMP-OTBS, under similar reaction conditions to those previously mentioned. As the unreacted TBMP- OTBS remains in the methanol solution, the polymer precipitates from methanol at least three times. As a result of the successful sulfonate esterification, the terminus of the degraded oligomers remains reactive and the TBMP moiety is anchored on to the end of the polymer chain, as confirmed by ^1H NMR analysis. For instance, after transesterification the polymer showed signals at δ 3.80 ppm and δ 6.81 ppm. These assignments are characteristic signals of the TBMP moiety. The disappearance of the peaks at δ 0.21 ppm and δ 1.02 ppm in TBMP-OTBS, which belongs to the silyl ethers, indicates the formation of the sulfonate (Figure 2).

We used an AIE ‘star’ molecule[36], TPE-OTBS, as an end-esterification reagent to prepare an AIE-polysulfonate. The synthetic process is similar to the above-mentioned reaction. The proton NMR result confirmed the covalent linkage between the PSFO1 and TPE moiety. As shown in (Figure 3C), the ^1H NMR spectra of TPE-OTBS, a mixture of PSFO2 and TPE-OTBS and only PSFO2-TPE show characteristic TPE signals (δ 6.80 ppm, δ 7.15 ppm). Whereas no corresponding signals can be observed in that of the mixture. Since TPE-OTBS dissolves in methanol, simple mixing does not cause a change in the ^1H NMR spectrum. It is straightforward to compare the FTIR spectra of TPE-OTBS and PSFO2-OTBS, where the primary change is that the peak from the Si-C bond (1251) stretch and Si (CH3)-C bond (835) stretch disappear (Figure S5). A bright blue emission with λ_{max} = 475 nm is observed in the emission spectrum of the polymer, indicating the successful linkage of the emissive TPE moiety and polymer chain. Quantitative characterization of the molar ratio of the end groups to the polymer chain ends can be determined from integration of the ^1H NMR peaks (Figure S3). Integration of the PSFO1 backbone peak (a) was compared with the integration of the protons from the end-cap peak (b). Integration of peak (a) shows an area of 6 which is normalized to protons from six different sites. Whereas integration of peak (b) shows an area of 0.23 which is normalized to protons from two different sites. Thus, the ratio of monomer to end-group is 8.69:1. Such an approach to form an end-functionalized AIE polymer may be useful for the preparation of functional polymers.

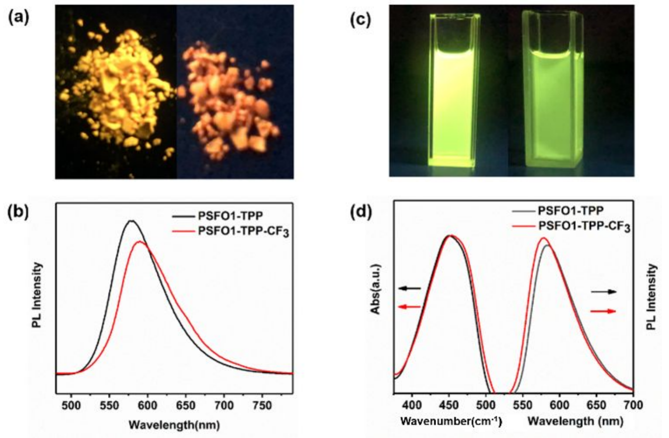


Figure 4 (a) Solid state images of PSFO1-TPP-CF_3 and PSFO1-TPP under UV light at 365 nm (b) images of PSFO1-TPP-CF_3 and PSFO1-TPP in THF solution under UV light at 365 nm (c） Solid fluorescence spectra of PSFO1-TPP-CF_3 and PSFO1-TPP (d) Emission spectra and UV-vis

The described reaction can be further utilized. The monomer M1 can be polymerized with a fluorescent monomer (MTPP-OTBS) bearing pyrazoline and naphthalimide groups. The emissive copolymer PSFO1-TPP is obtained with an M_n = 14200 g mol^{-1} (PDI = 1.3). The maximum emission band (λ_m) of PSFO1-TPP in DMF is 581 nm in the solid state and 578 nm in solution.

A third monomer (CF$_3$-OTBS, 1C) was added to the DMF solution of PSFO1-TPP (polysulfonate), in the presence of DBU (20%). As a result, a new oligomer composed of three units (MTPP-OTBS, S1 and 1C) was obtained. We characterized this oligomer by ^{1}HNMR and GPC (SI), in which the molecular weight of the oligomer is 4260 g mol^{-1} (PDI = 1.3). The emission spectra of the original polymer and degraded ternary oligomer are shown in (Figure 4C). A red emission band shift (9 nm) was observed in the solid state emission spectrum, which can be as-signed to the strong electron-withdrawing trifluoromethyl groups in 1C. A charge-transfer (CT) interaction occurs between the electron donor moieties and the electron acceptor moieties resulting in a red-shift in emission. This also confirmed that the third monomer was present in the former polymer chain. Our method was also effective for the preparation of ternary polymers.

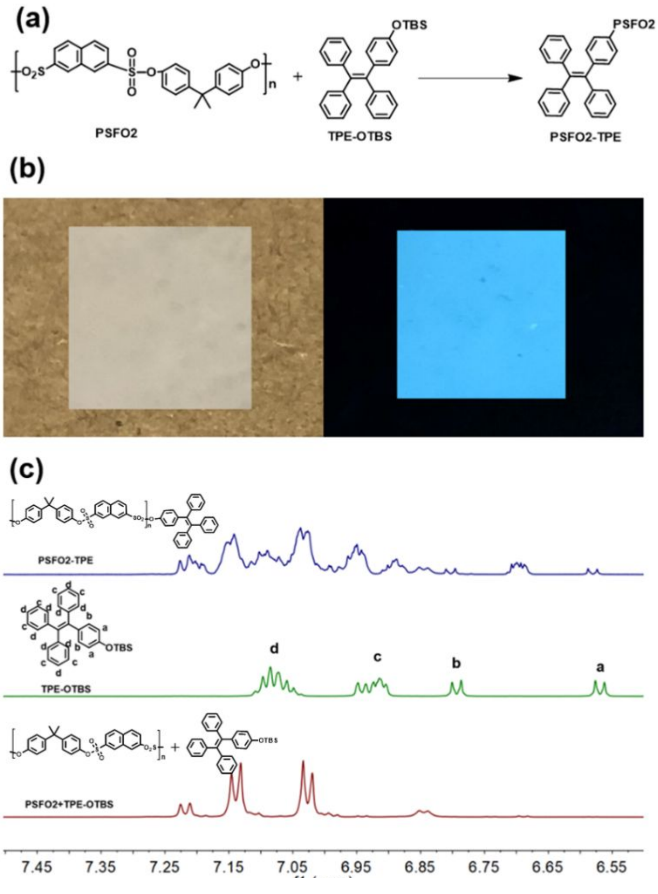


Figure 3 (a) Structure and reaction profile of PSFO2-TPE, (b) Images of PSFO2-TPE/Polysulfone film under room light and UV light at 365 nm; (c) ^{1}HNMR spectra of TPE-OTBS,PSFO2-TPE,mixture of PSFO2 and TPE-OTBS

Conclusions

In conclusion, we have prepared new types of polysulfonates in high yield using a mild SuFEx click polymerization strategy. An unexpected reversible degradation of polymer sulfonates was observed when DBU was employed as a catalyst, providing a reliable method for industrial use and recycling. The degradation process can be further utilized as a new method for polymer functionalization. Several examples in this paper have been reported. We hope this work will attract more attention to the use and application of polysulfonates.

Acknowledgements

We greatly acknowledge financial support from the NSFC (51773144, 21776190, 21938006), Science Foundation of Jiangsu (BE2019659) and PAPD in Jiangsu. John R. Cappiello is partially supported by the NSF (CHE-1610987 to K. Barry Sharpless).

Conflicts of interest

There are no conflicts to declare.

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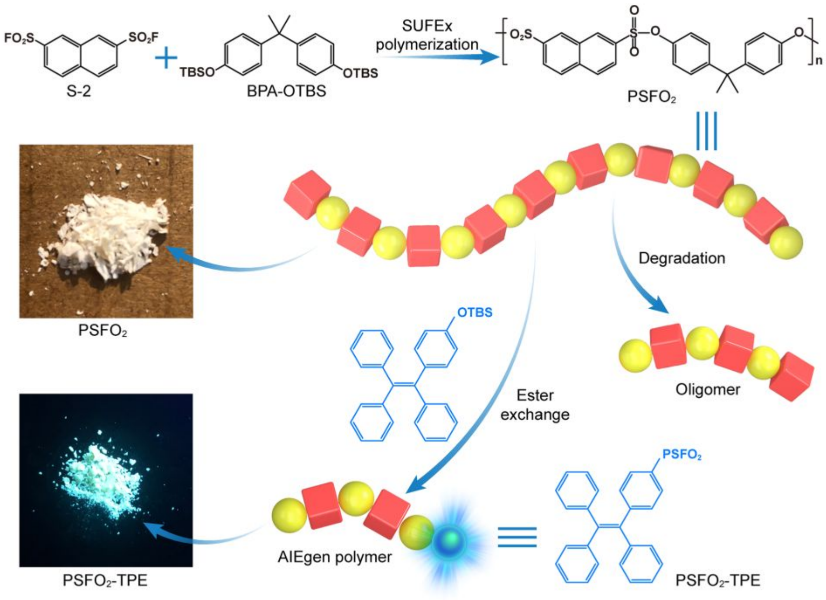

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