Supporting Information for:

Alternating copolymerization of ethylenesulfonyl fluoride and styrene for the synthesis of SuFEx modifiable polymers

Chima Anyaegbu[a], Darsan Haridas[a] and Joel F. Hooper [abc]*

[a] School of Chemistry, Monash University Clayton, Victoria, 3800, Australia

[b] Bioresource Processing Research Institute of Australia (BioPRIA), Monash University, Clayton, Victoria, 3800, Australia

Typical procedure for post modification of PS-ESF copolymer

1. Modification with 4-Bromofluorobenzene:

A flame-dried round-bottom flask was charged with the copolymer PS-ESF (1.00 g, containing approximately 7.5 mmol of -SO_2F groups). 4-Bromofluorobenzene (0.05 mmol) was added as an internal standard, followed by the 4-methoxyphenol (15 mmol, 1.86 g) and K_2CO_3 (30 mmol, 4 g). THF (5 mL) was added, and the reaction mixture was stirred at 50 °C for 1 h. Upon completion, a small aliquot was withdrawn and analyzed by ^{19}F NMR spectroscopy to determine the conversion of the –SO_2F groups. The reaction mixture was then centrifuged to remove inorganic salts, the supernatant was precipitated into cold methanol, repeated twice. The purified polymer was dried under vacuum at 50 °C to constant mass.

2. Crosslinking reaction with $bPEI_{25K}$:

A flame-dried round-bottom flask was charged with the copolymer PS-ESF (1.00 g, containing approximately 7.5 mmol of -SO_2F groups). Branched polyethyleneimine (PEI, $M_n \approx 25$ kDa) (1.00 g) dissolved in DMF (5 mL) was added to the flask, and the reaction mixture was stirred at room temperature for 15 min. Gelation occurred during this time, as confirmed by the flask-inversion test. The resulting gel was transferred and sonicated in DMF (10 mL), followed by two additional washing cycles with THF, to remove unreacted species and residual solvent. The purified gel was then dried in a vacuum oven until constant mass.

Determination of Copolymerization Reactivity Ratios Using the Mayo-Lewis Equation

Here, we examine ESF-styrene copolymerization data through the instantaneous composition framework to estimate reactivity ratios and interpret composition drift with respect to feed composition.

For data analysis, five copolymerization runs at low conversion provided f_1-F_1 data (Table 1).

$$F_1 = [r_1 f_1^2 + f_1(1-f_1)] / [r_1 f_1^2 + 2f_1(1-f_1) + r_2(1-f_1)^2]$$

where ($r_1 = k_{11}/k_{12}$) and ($r_2 = k_{22}/k_{21}$) are the reactivity ratios of ESF and styrene, respectively. f_1 is the ESF feed ratio and F_1 is ESF fraction in polymer.

Copolymerization reactions were carried out in a 10 mL round-bottom flask under a nitrogen atmosphere. In a typical procedure, ESF (0.5 mmol, 1 eq.) and styrene (0.5 mmol, 1 eq.) were dissolved in DMF (1 mL) with fluorobromobenzene (0.1 mmol) as an internal standard. AIBN (0.0625 mmol, 0.125 eq.) was added as the radical initiator. The mixture was degassed by purging with nitrogen for 15 min, sealed, and heated at 75 °C for 0.5 h. Monomer feed ratios (f_1) were determined by ^{1}H NMR before the start of the polymerization reaction, and copolymer composition (F_1) was determined by monomer conversions, measured by ^{1}H NMR (styrene units) and ^{19}F NMR (ESF units) in $CDCl_3$.

Table S1. Copolymerization of ESF-Styrene run data set

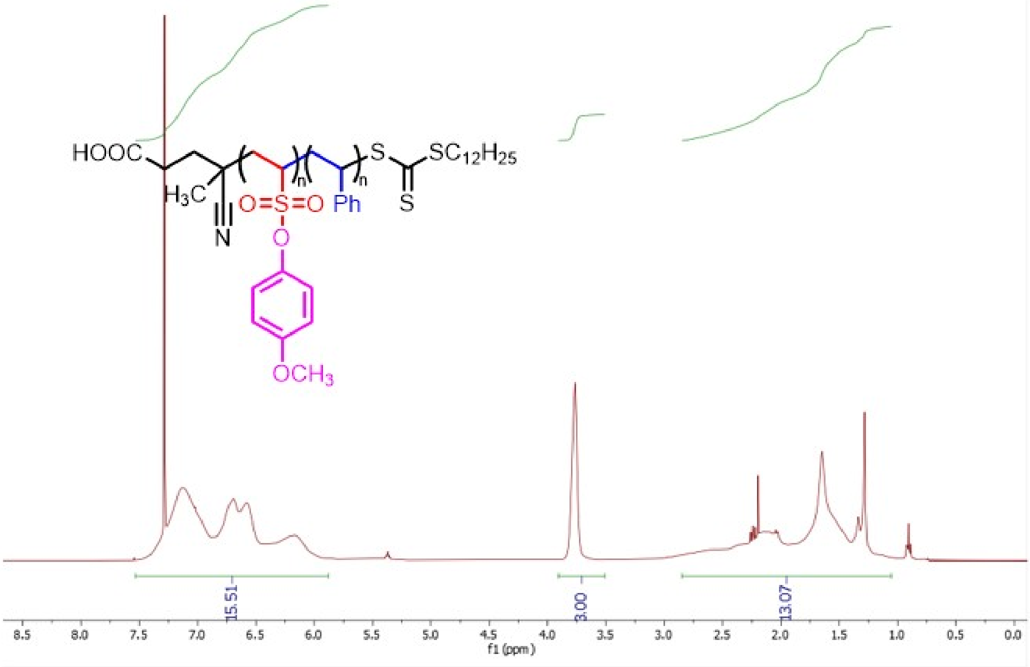
Run	f_1 (feed)	ESF conversion (%)	Styrene conversion (%)	F_1 (copolymer)
1	0.7764	11.3	38.0	0.5087
2	0.6757	2.4	7.1	0.4107
3	0.4792	8.4	13.7	0.3617
4	0.3055	6.9	9.3	0.2460
5	0.0938	16.0	14.2	0.1047

Table S2. Observed vs. fitted ESF mole fraction in copolymer.

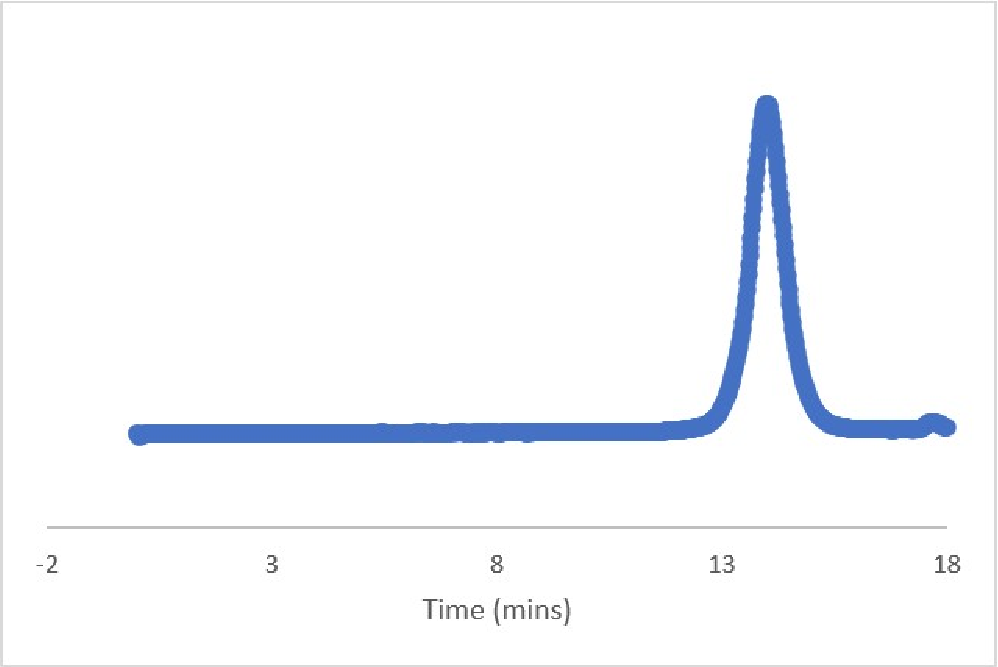
f1	F1 (obs.)	F1 (fit)	Residual
0.7764	0.5087	0.4913	-0.0174
0.6757	0.4107	0.4412	0.0305
0.4792	0.3617	0.3488	-0.0129
0.3055	0.2460	0.2528	0.0068
0.0938	0.1047	0.0944	-0.0103

NMR Spectra and GPC Traces

(a)



(b)



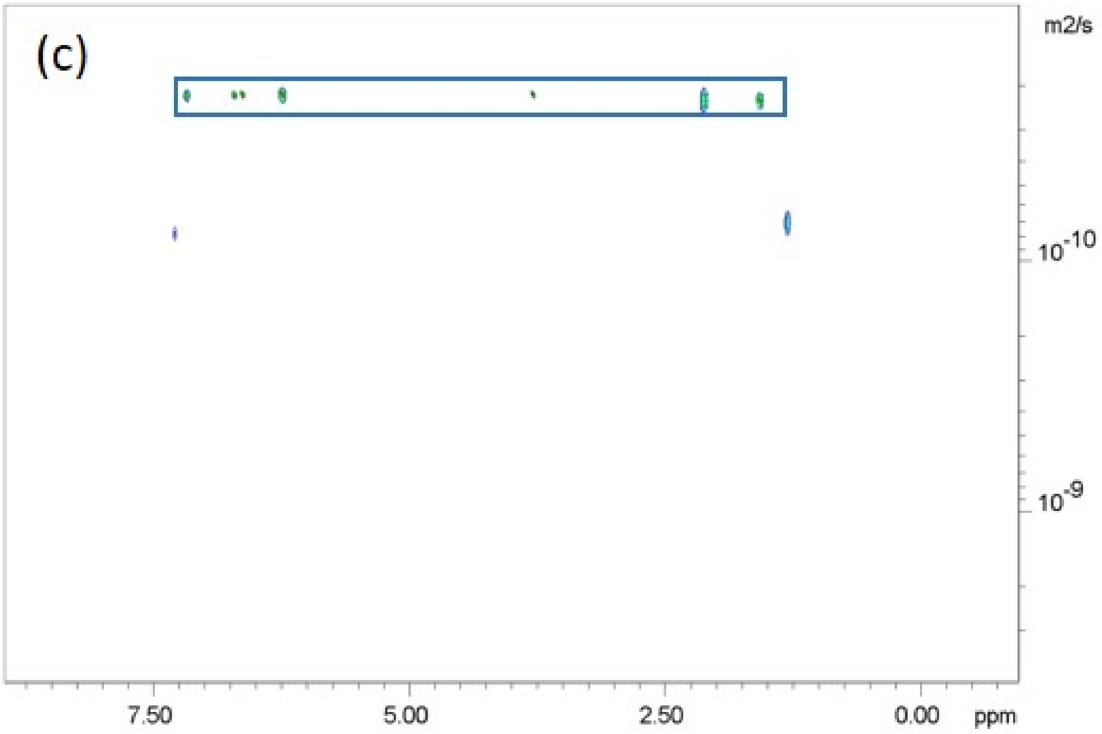


Figure S1. 4-Methoxyphenol modified PS-ESF (a) ^{1}H NMR (400 MHz, $CDCl_3$) (b) GPC trace (c) ^{1}H DOSY NMR

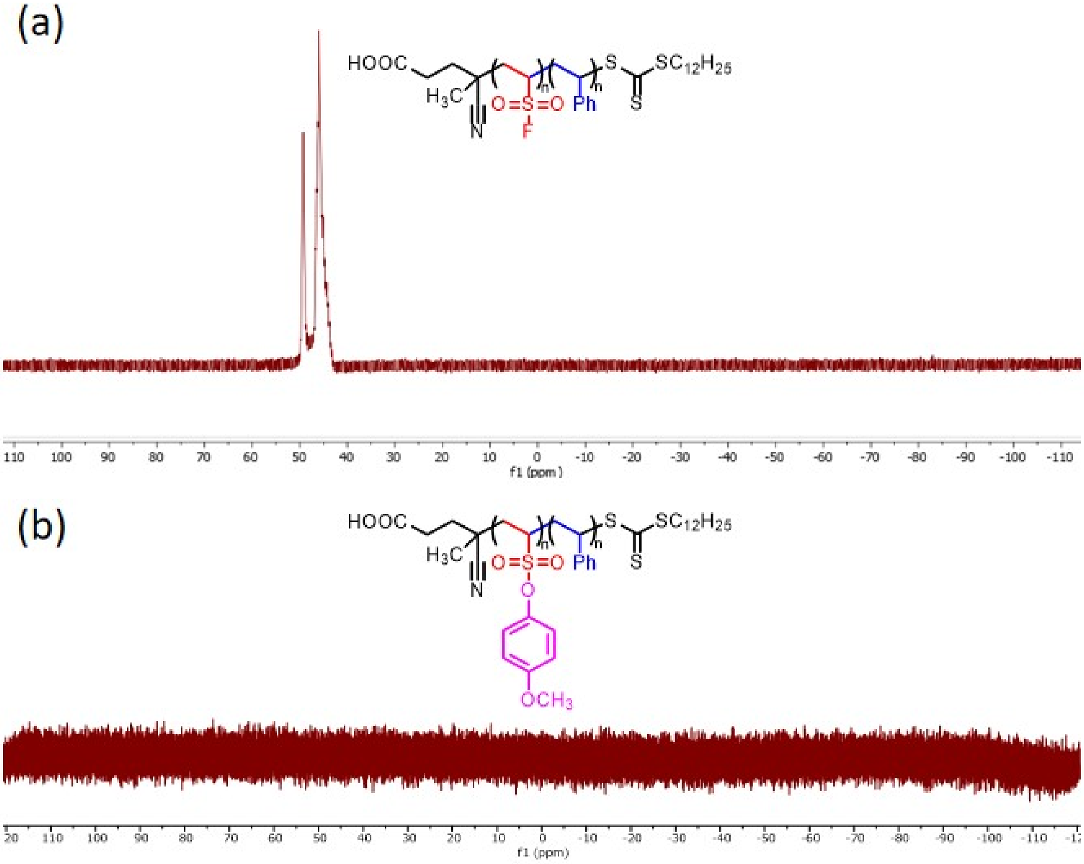
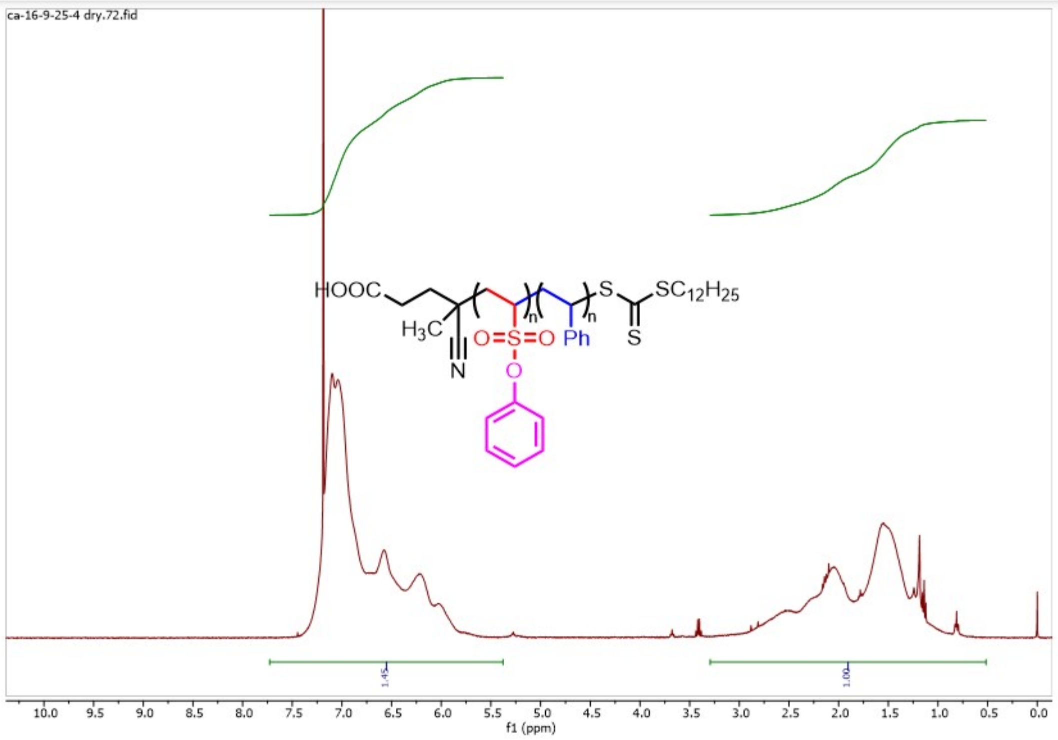
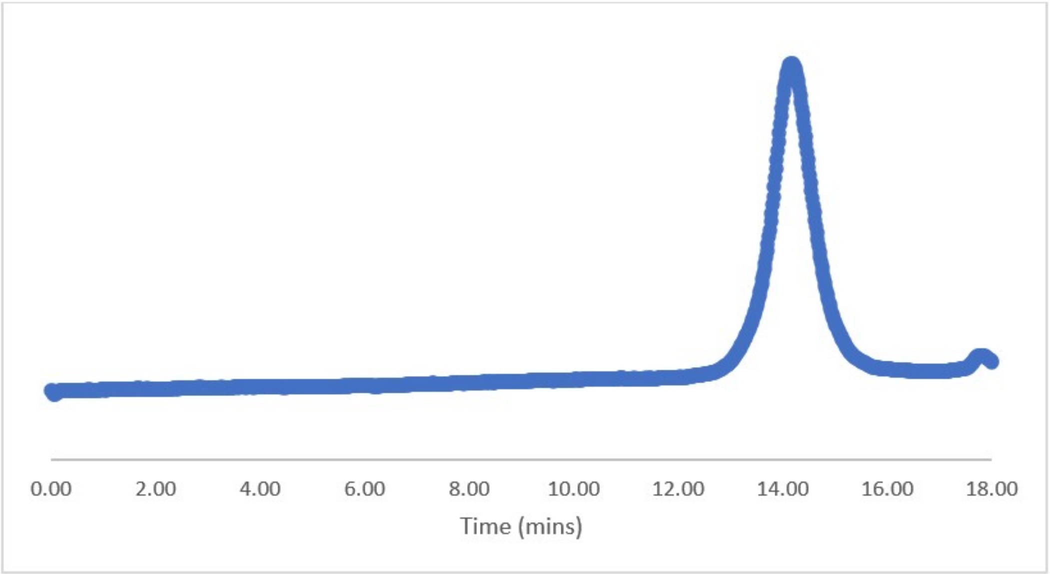


Figure S2. ^{19}F NMR of (a) PS-ESF before modification (b) after modification

(a)


ca-16-9-25-4 dry.72.fid
HOOC
H3C
N
O=S=O
O
Ph
n
n
S
SC12H25
S
1.45
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(b)


0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
Time (mins)

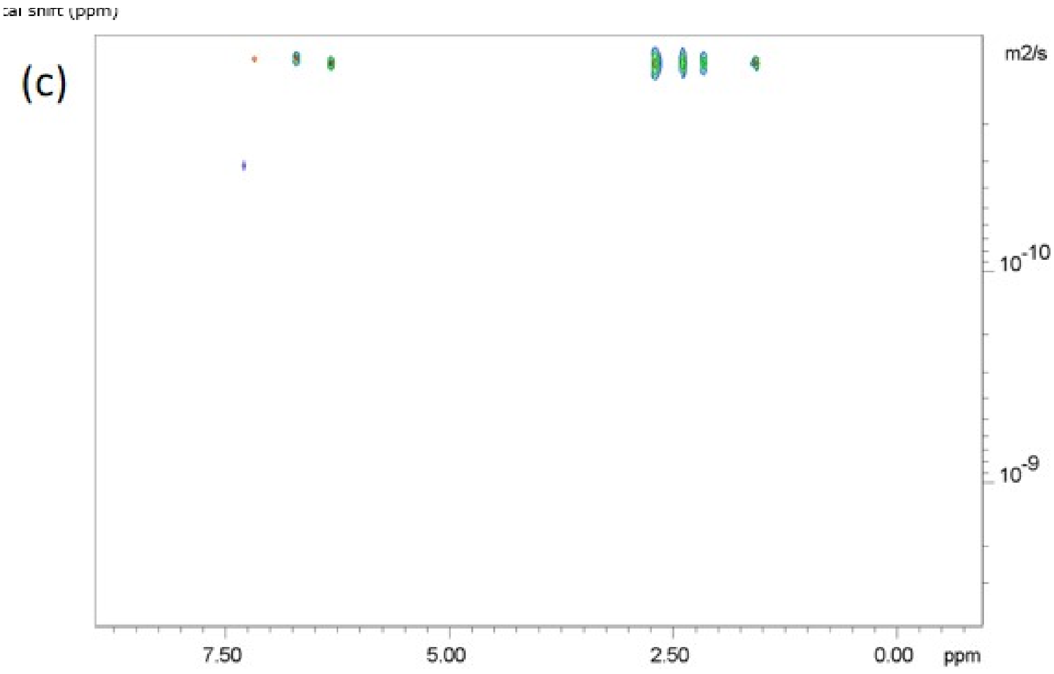
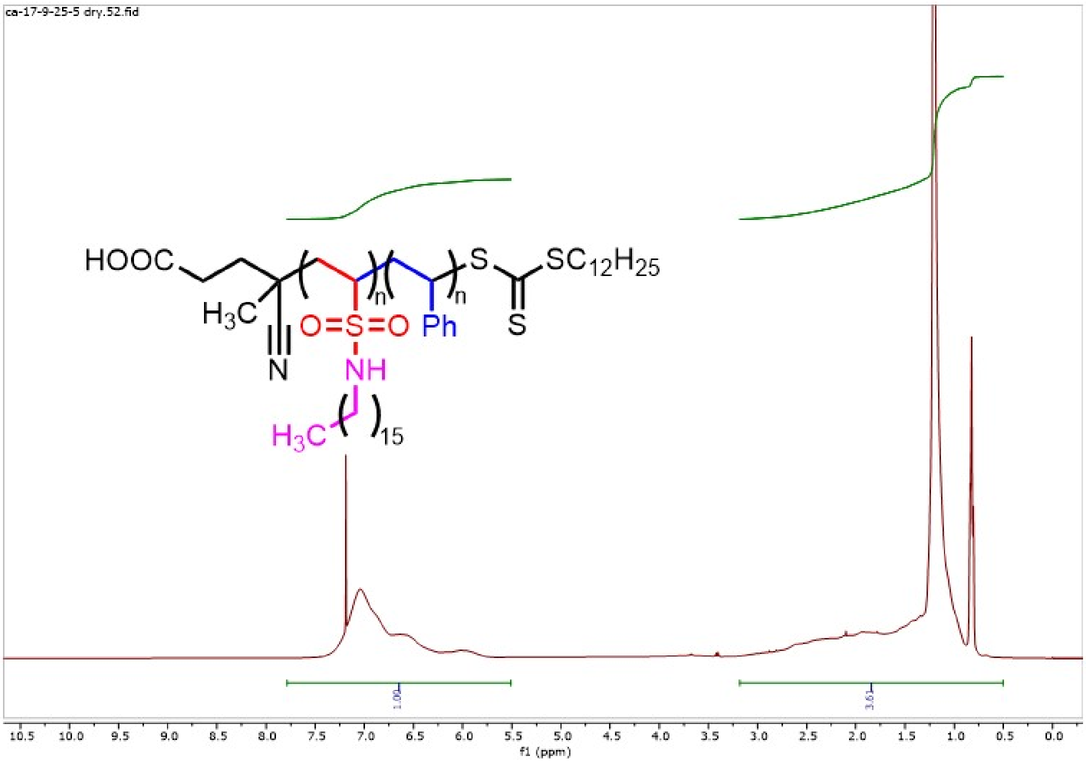
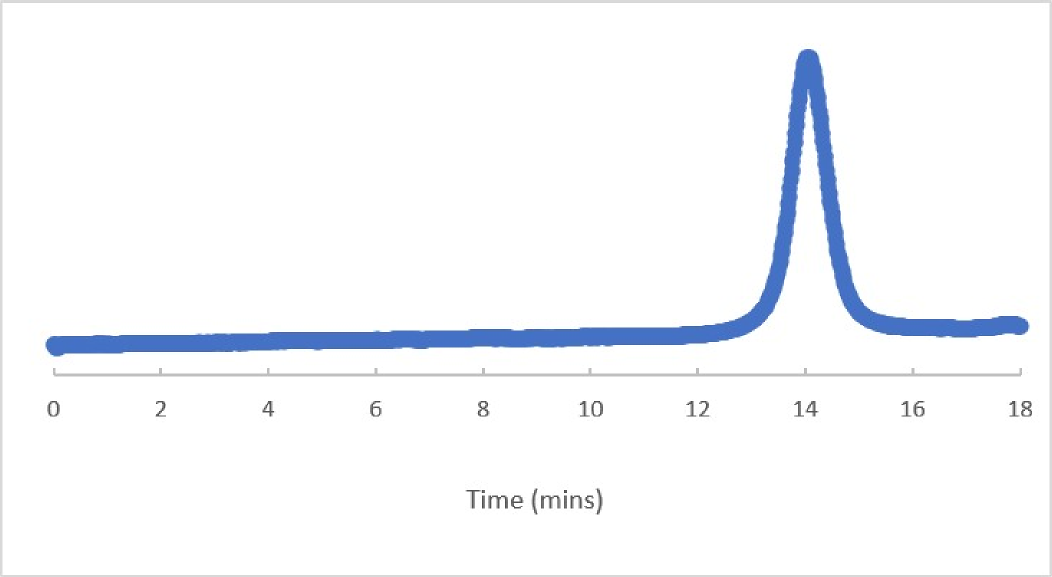


Figure S3. Phenol modified PS-ESF (a) ^{1}H NMR (400 MHz, CDCl$_3$) (b) GPC trace (c) ^{1}H DOSY NMR

(a)


ca-17-9-25-5 dry.52.fid
HOOC
H_3C
N
O=S=O
NH
H_3C
15
n
n
Ph
S
$SC_{12}H_{25}$
S
1.00
3.61
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(b)


0
2
4
6
8
10
12
14
16
18
Time (mins)

(c)

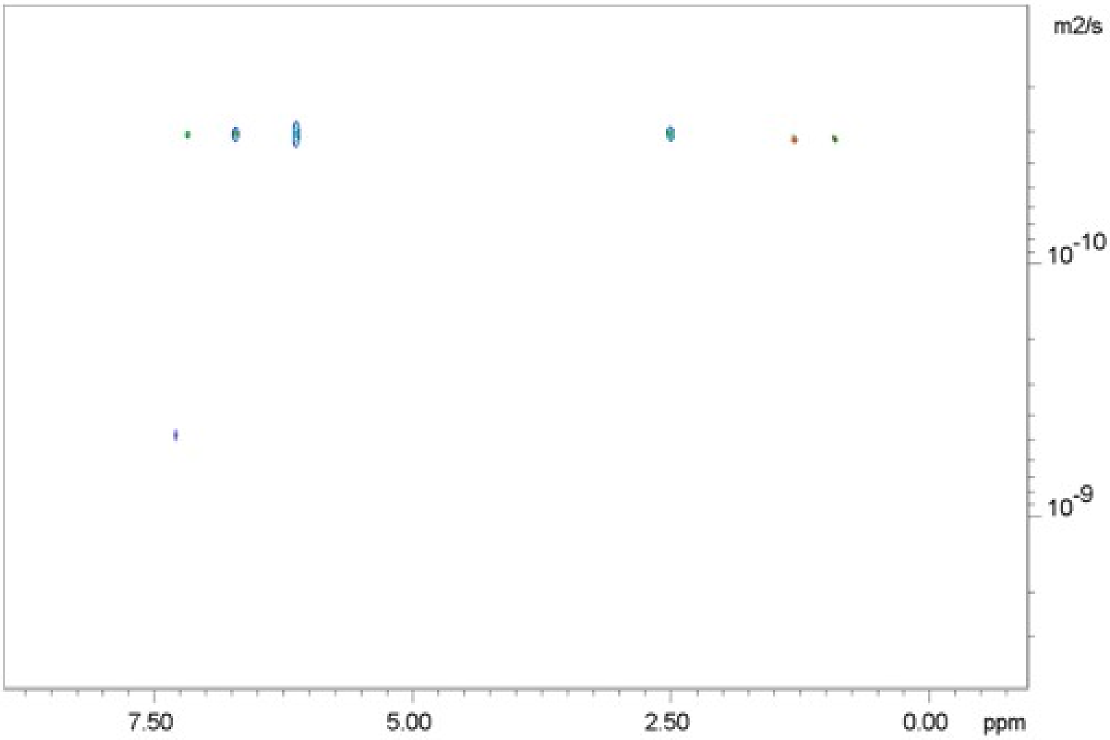


Figure S4. Pentadcyl amine modified PS-ESF (a) ^{1}H NMR (400 MHz, $CDCl_3$) (b) GPC trace

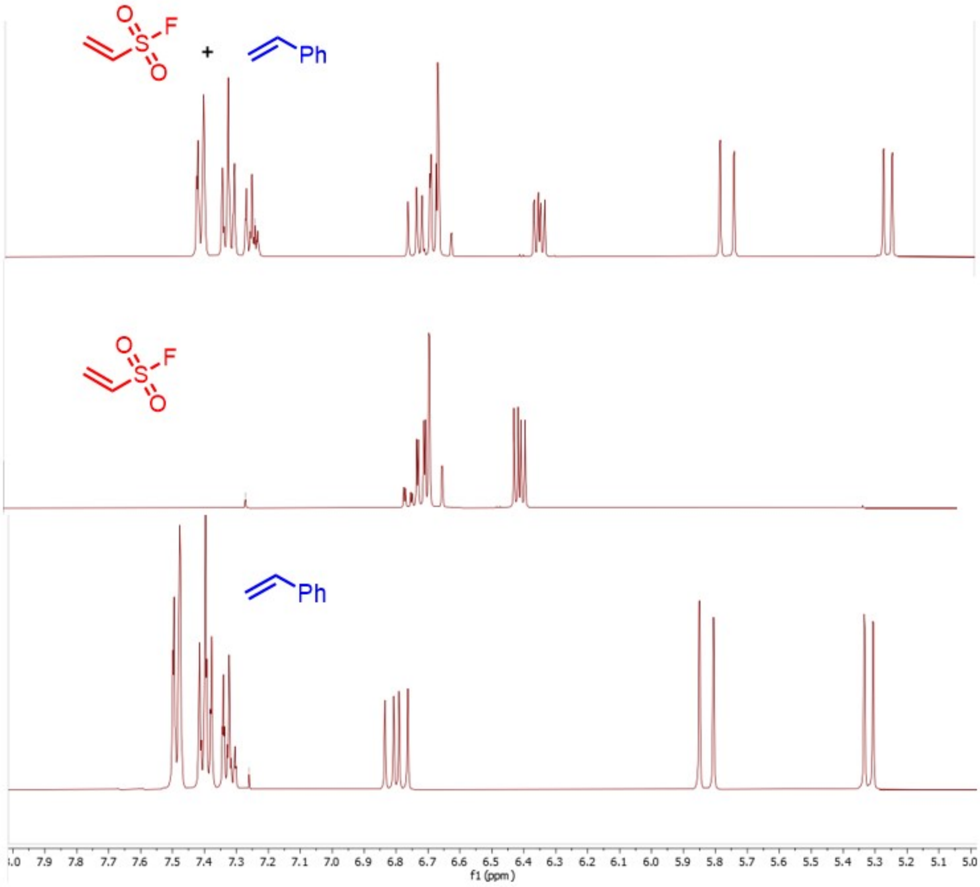


Figure S5. ^{1}HNMR spectra for comparison of monomers and their mixture

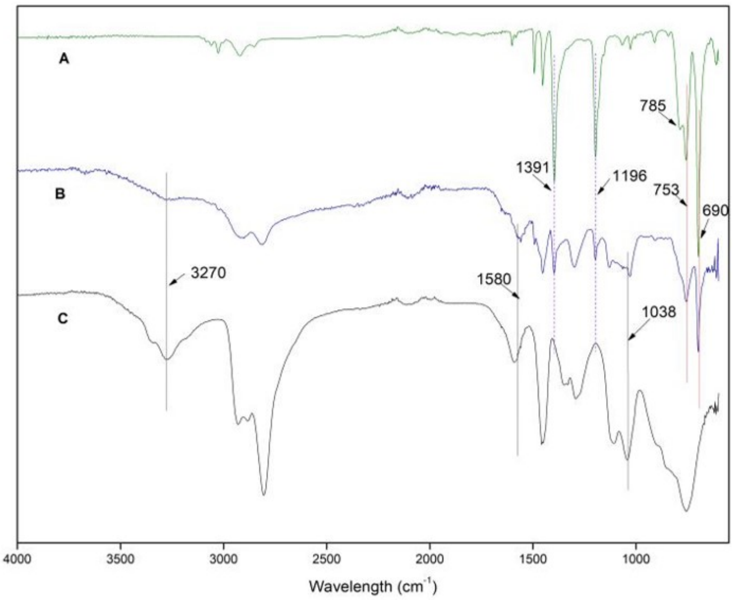


Figure S6. FTIR spectra (a) PS-ESF (b) PS-ESF-bPEI$_{25K}$ gel (c) bPEI$_{25K}$