Supporting Information

SuFEx - A selectively triggered chemistry for fast, efficient and equimolar polymer-polymer coupling reactions

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^{1}H-NMR of 4-(fluorosulfonyl)benzyl butyl trithiocarbonate (FSBBTC)

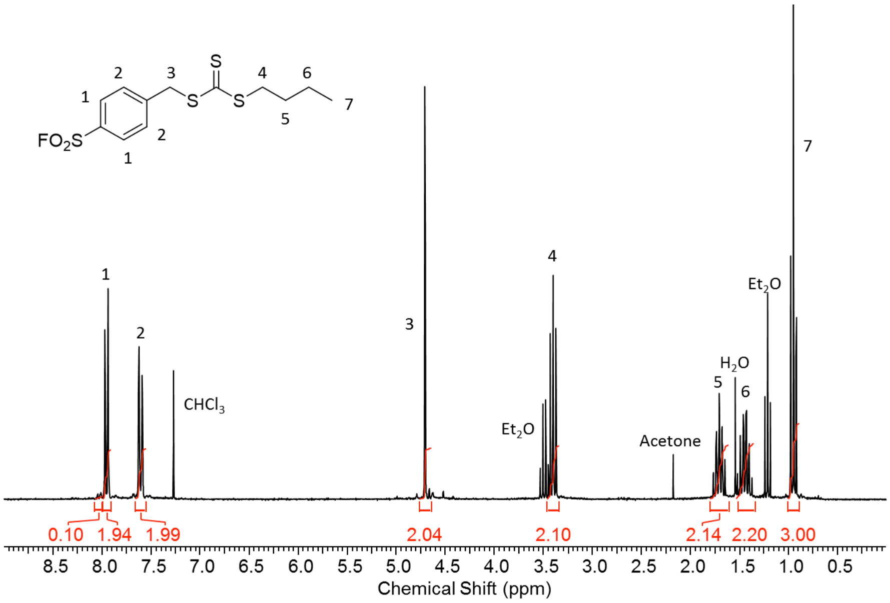

Figure S1. NMR spectrum of the crude 4-(fluorosulfonyl)benzyl butyl trithiocarbonate (FSBBTC) after washing with water.

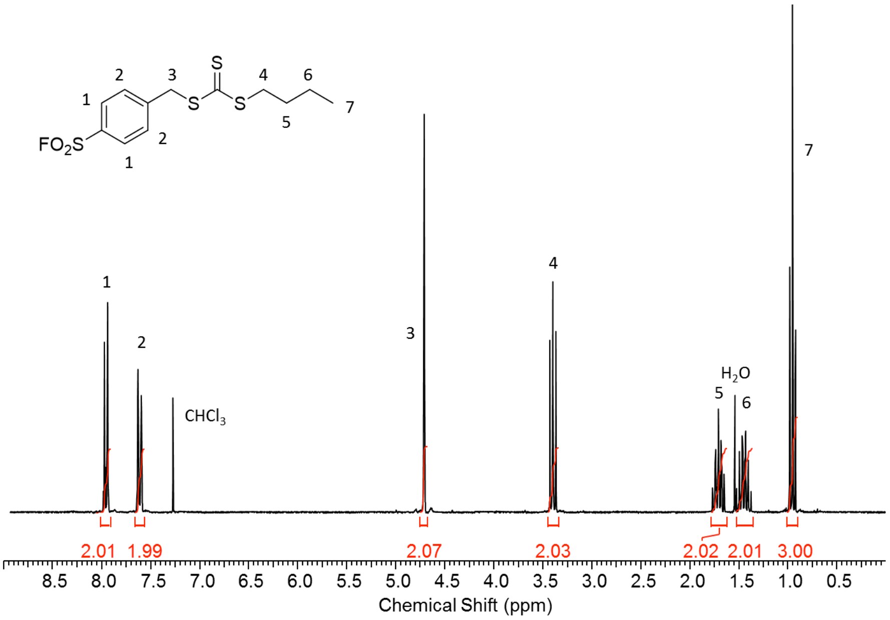

Figure S2. NMR spectrum of the purified 4-(fluorosulfonyl)benzyl butyl trithiocarbonate (FSBBTC).

^{1}H-NMR of both CTAs (FSBBTC and TBDMSPh-PABTC) after being stored at 5°C for more than one year

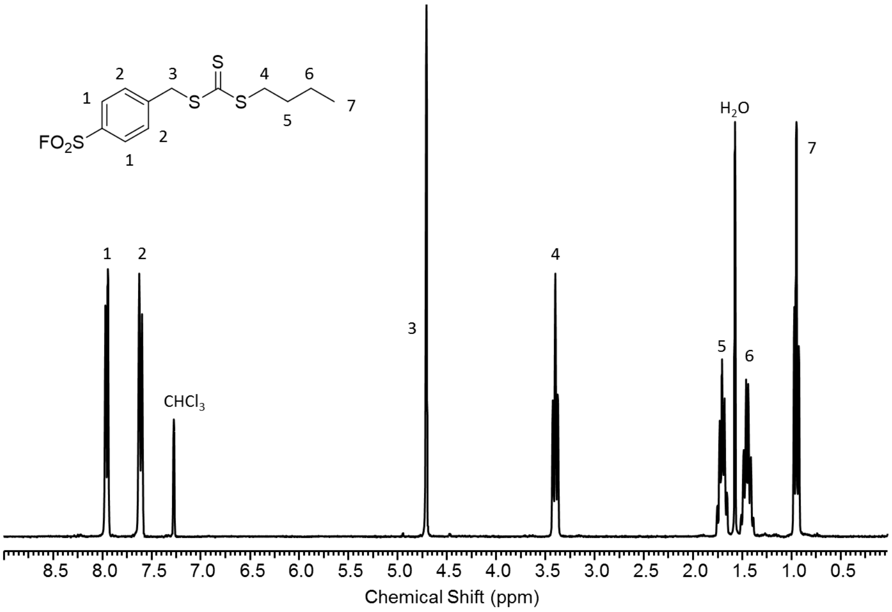

Figure S3. NMR spectrum of 4-(fluorosulfonyl)benzyl butyl trithiocarbonate (FSBBTC).

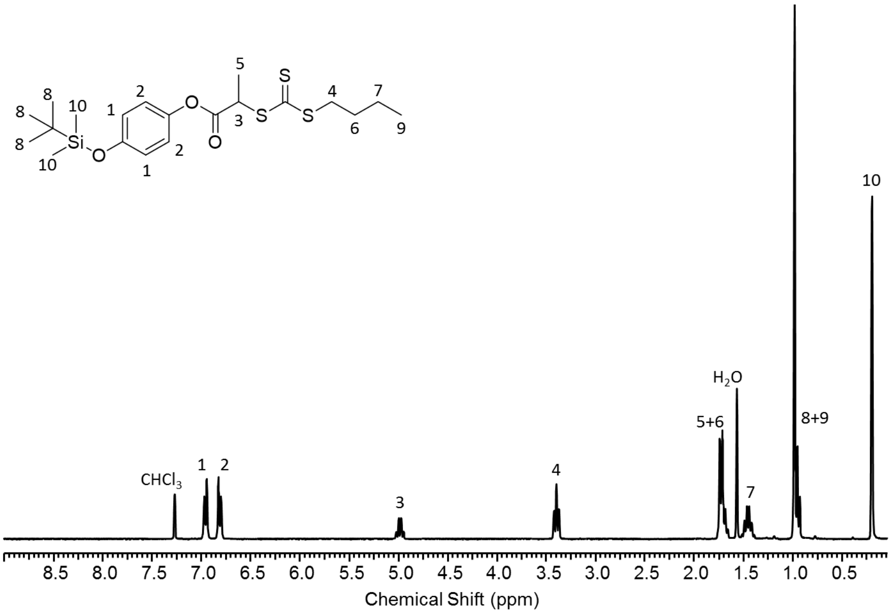

Figure S4. NMR spectrum of 4-((tert-butyldimethylsilyl)oxy)phenyl 2-(((butylthio)carbonothioyl)-thio)-propanoate (TBDMSPh-PABTC).

Deconvolution of the coupling reaction with a bifunctional linker:

Although Poisson distributions are accepted models of molecular weight distributions (number distribution) obtained by living polymerization, they are typically limited to excellently controlled polymerizations resulting in very narrow molar mass distributions ($Đ < 1.05$). For controlled radical polymerization techniques, Gaussian distributions are a good approximation which takes into account the broadening of the molecular weight due to side reaction of irreversible transfer and termination. In order to quantify the efficiency of the coupling reactions, the number distribution obtained by SEC was deconvoluted using Gaussian curves. The position of the initial starting material (single chains) was determined from the number distribution plots of the SEC traces of the polymerization solutions.

The percentage of coupled chains or the efficiency of the coupling was determined using equation 1:

$$\%\ coupled\ polymer\ chains = \frac{\%\ Area\ coupled\ chains * 2}{\%\ Area\ coupled\ chains * 2 + \%\ Area\ single\ chains} \times 100 \qquad (1)$$

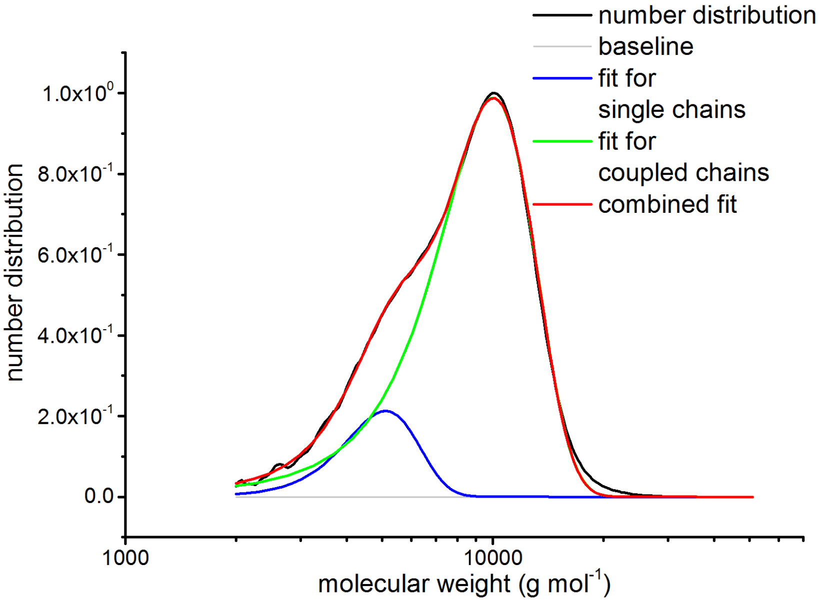

Figure S5. Deconvolution of the SEC number distribution for the homocoupling of pNAM$_{40}$-SO$_2$F using a bifunctional linker (TBDMS Bisphenol A) and DBU as catalyst after 72 h.

Summary of all coupling reactions:

Table S1. Overview on the characteristics of all coupling reactions and the respective precursor polymers.

Coupling reaction using bifunctional linker

Polymer / linker	Catalyst	Solvent	Single chains		Coupled chains		Coupling time	Coupling efficiency [b]
			M_n (10^3 g/mol) [a]	Đ [a]	M_n (10^3 g/mol) [a]	Đ [a]		
pNAM$_{40}$-SO$_2$F / TBDMS Bisphenol A	0.3 eq. DBU	DMF	5.8	1.09	9.9	1.12	72 h	96 %

Coupling reaction on polymers with mixed CTAs

Polymers	Catalyst	Solvent	Single chains		Coupled chains		Coupling time	Coupling efficiency [b]
			M_n (10^3 g/mol) [a]	Đ [a]	M_n (10^3 g/mol) [a]	Đ [a]		
pNAM-SO$_2$F + pNAM-O-TBDMS	0.3 eq. DBU	DMF	5.1	1.11	8.8	1.16	20 h	93 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.3 eq. TBD	DMF	4.9	1.10	5.9	1.26	24 h	60 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.3 eq. MTBD	DMF	4.9	1.10	8.4	1.17	2 h	92 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.3 eq. TBAF	DMF	4.9	1.10	8.5	1.16	2 h	94 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.1 eq. TBAF	DMF	4.9	1.10	8.9	1.17	30 min	94 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.1 eq. BEMP	DMF	4.9	1.10	8.3	1.15	30 min	93 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.3 eq. TBAF	Water	4.4	1.13	5.5	1.21	24 h	44 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.3 eq. DBU	Dioxane	5.8	1.09	5.8	1.09	24 h	0 %
pNAM-SO$_2$F + pNAM-O-TBDMS	0.3 eq. TBAF	Dioxane	5.8	1.09	9.2	1.17	24 h	88 %
pS-SO$_2$F + pS-O-TBDMS	0.3 eq. TBAF	DMF	2.3	1.14	3.8	1.19	30 min	92 %
p(*t*-BA)-SO$_2$F + p(*t*-BA)-O-TBDMS	0.3 eq. TBAF	DMF	5.4	1.07	5.5	1.20	48 h	32 %

Coupling of different polymers

Polymers	Catalyst	Solvent	Single chains		Coupled chains		Coupling time
			M_n (10^3 g/mol) [a]	Đ [a]	M_n (10^3 g/mol) [a]	Đ [a]	
pNAM-SO$_2$F +	0.3 eq. TBAF	DMF	5.1	1.10	6.2	1.21	30 min
pS-O-TBDMS			2.2	1.12			
pNAM-SO$_2$F +	0.3 eq. TBAF	DMF	5.1	1.09	6.3	1.26	48 h
p(*t*-BA)-O-TBDMS			5.6	1.08			

[a] determined by SEC; [b] calculated from deconvolutions of the number distribution plots

NMR after polymerization using FSBBTC and TBDMSPh-PABTC as combined CTAs

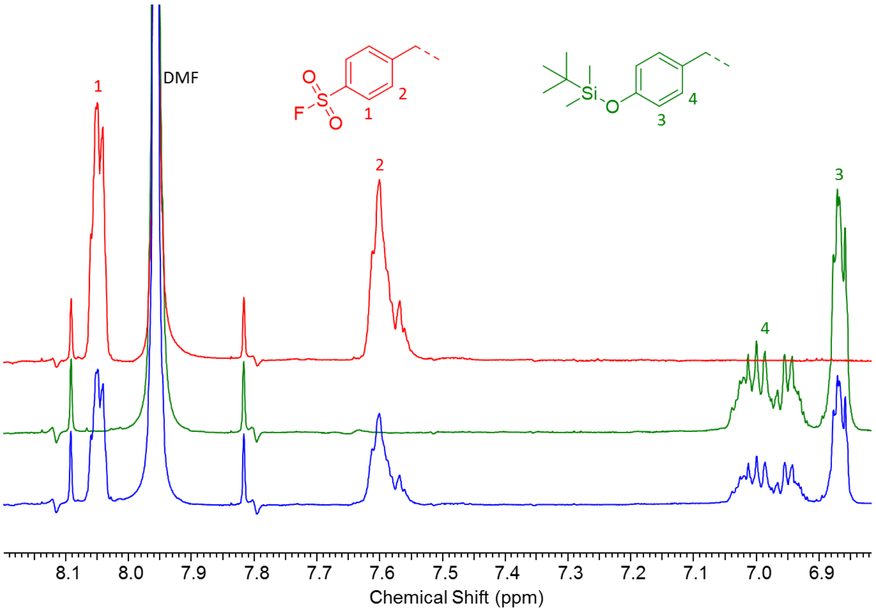

Figure S6. Overlay of the aromatic region in the NMR spectra of the polymers pNAM$_{40}$-SO$_2$F (red), pNAM$_{40}$-O-TBDMS (green) and the equivalent polymers made using a mixture of both CTAs FSBBTC and TBDMSPh-PABTC (blue). The samples were taken directly out of the polymerization solution and dried overnight under vacuum to reduce the amount of residual DMF.

Deconvolution of the coupling reactions between pNAM-SO$_2$F and pNAM-O-TBDMS using different catalysts:

All deconvolutions were done on the final sample taken.

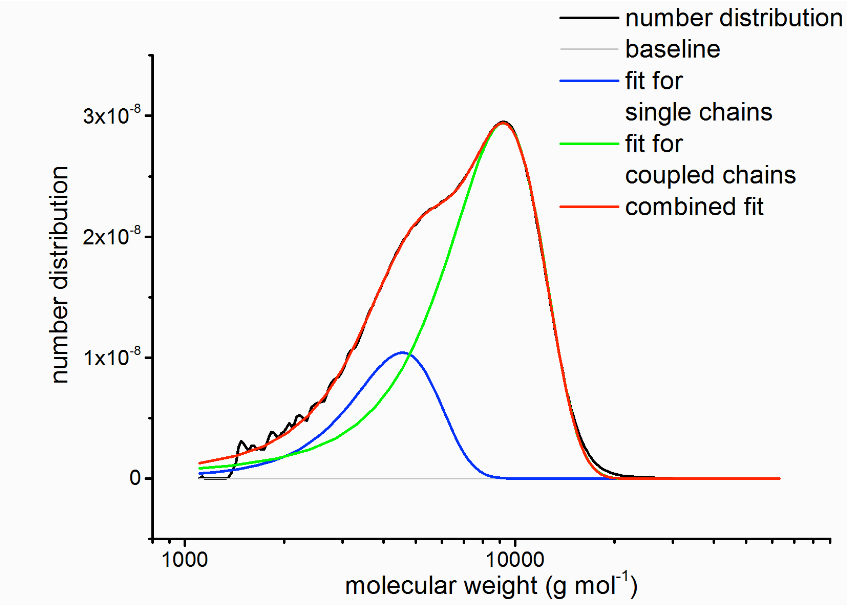

Figure S7. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in DMF using 0.3 eq. of DBU as catalyst. This sample was taken after 20 h.

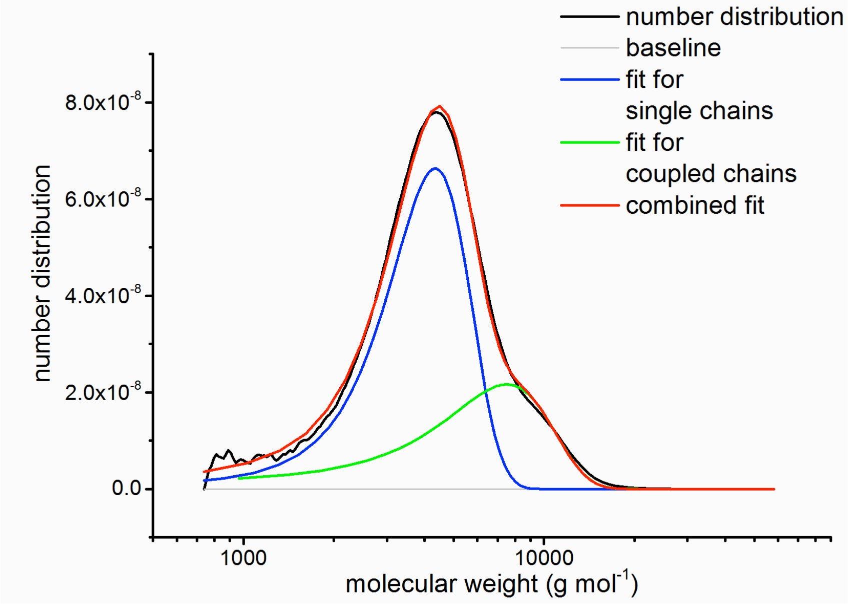

Figure S8. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in DMF using 0.3 eq. of TBD as catalyst. This sample was taken after 24 h.

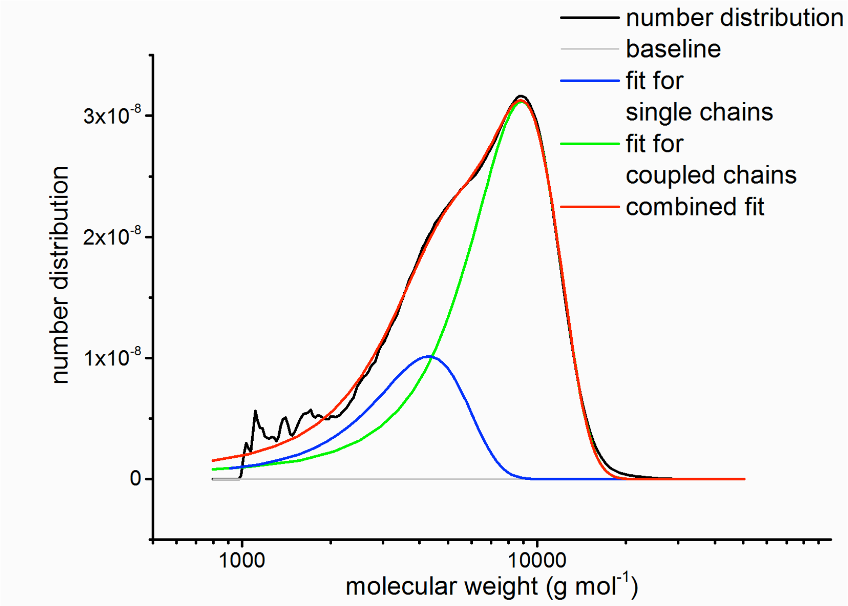

Figure S9. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in DMF using 0.3 eq. of MTBD as catalyst. This sample was taken after 6 h.

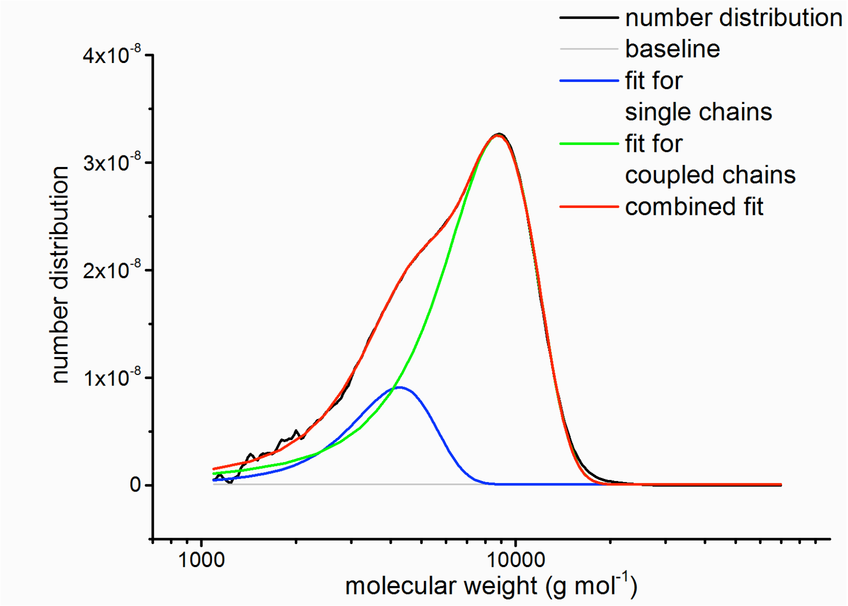

Figure S10. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in DMF using 0.3 eq. of TBAF as catalyst. This sample was taken after 2 h.

SEC traces and the respective deconvolutions for coupling reactions between pNAM-SO2F and pNAM-O-TBDMS using a reduced amount of catalyst:

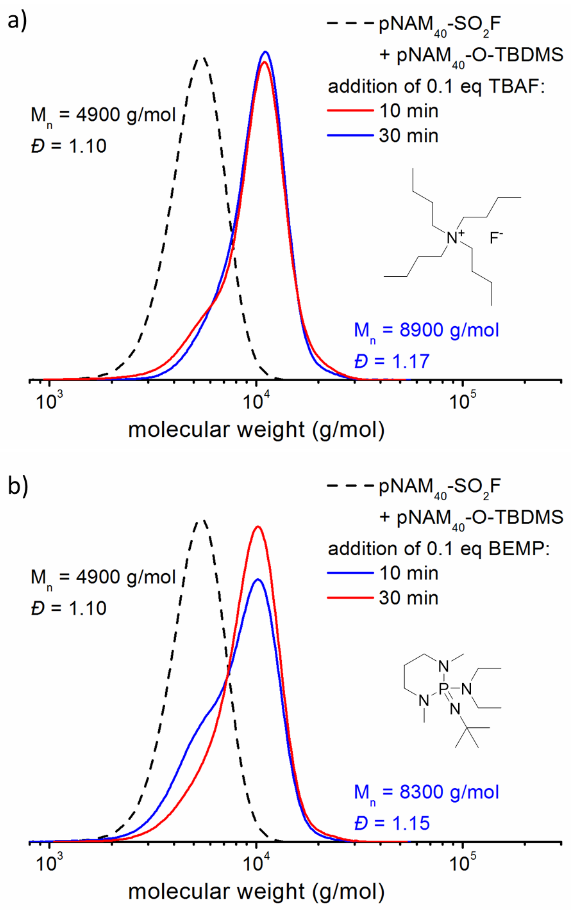

Figure S11. DMF-SEC traces of the precursor mixture (dashed) and the coupling reaction of pNAM-SO2F and pNAM-O-TBDMS catalyzed by 0.1 eq. of TBAF (a) or 0.1 eq. of BEMP (b).

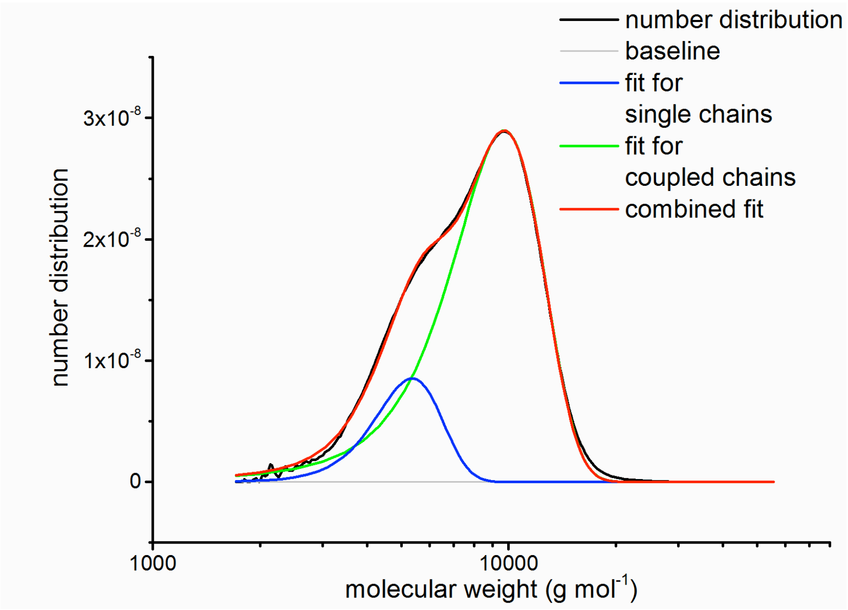

Figure S12. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in DMF using 0.1 eq. of TBAF as catalyst. This sample was taken after 30 min.

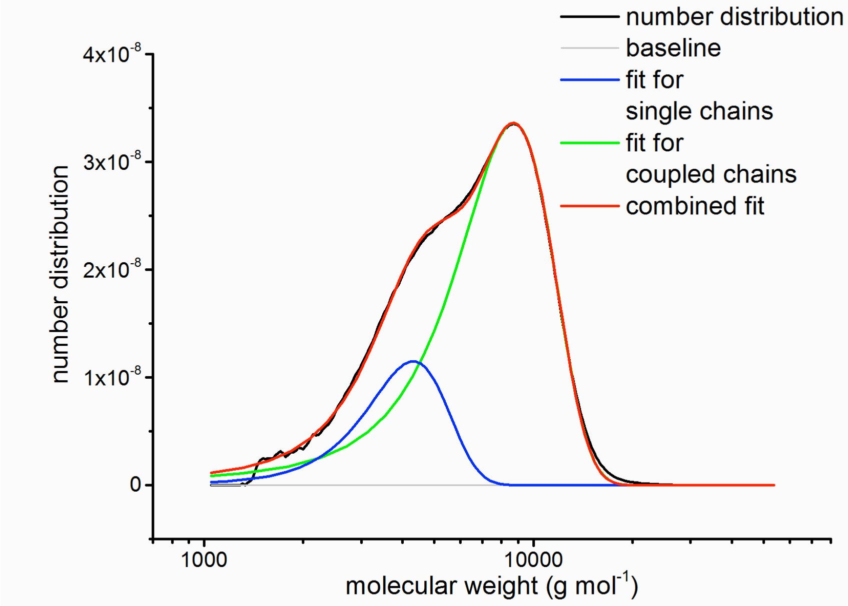

Figure S13. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in DMF using 0.1 eq. of BEMP as catalyst. This sample was taken after 30 min.

Deconvolution of the coupling reactions between pNAM-SO_2F and pNAM-O-TBDMS using different solvents:

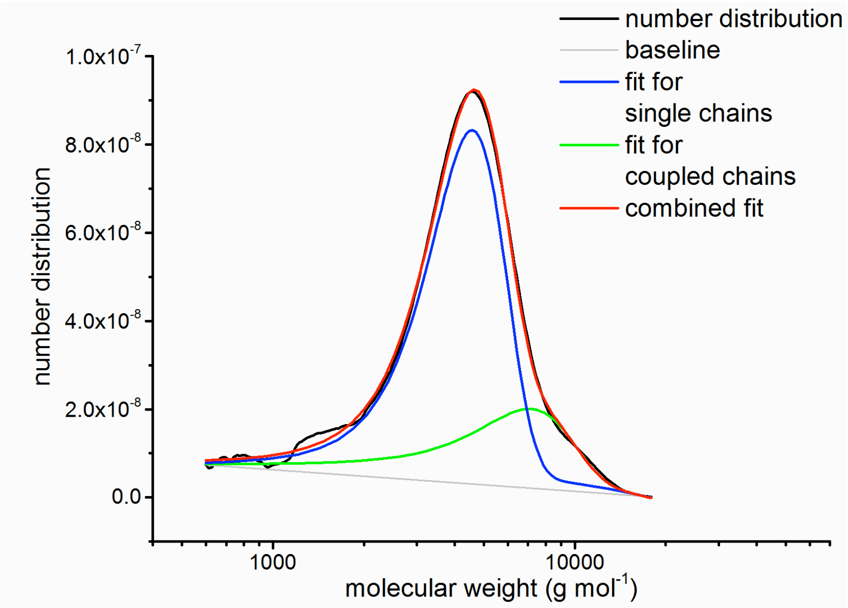

Figure S14. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in water using 0.3 eq. of TBAF as catalyst. This sample was taken after 24 h.

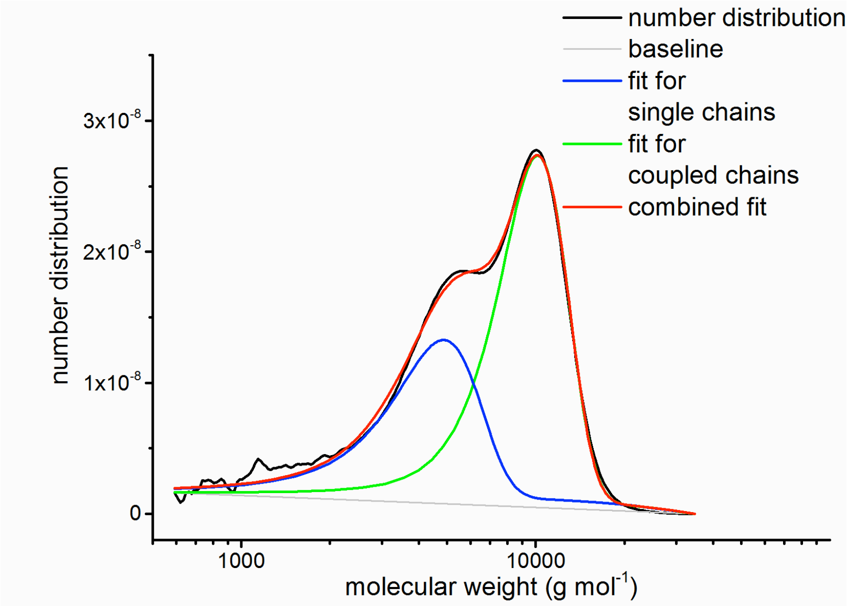

Figure S15. Deconvolution of the SEC number distribution for the coupling of pNAM-SO_2F and pNAM-O-TBDMS in 1,4-Dioxane using 0.3 eq. of TBAF as catalyst. This sample was taken after 24 h.

Deconvolution of the coupling reactions between different polymers:

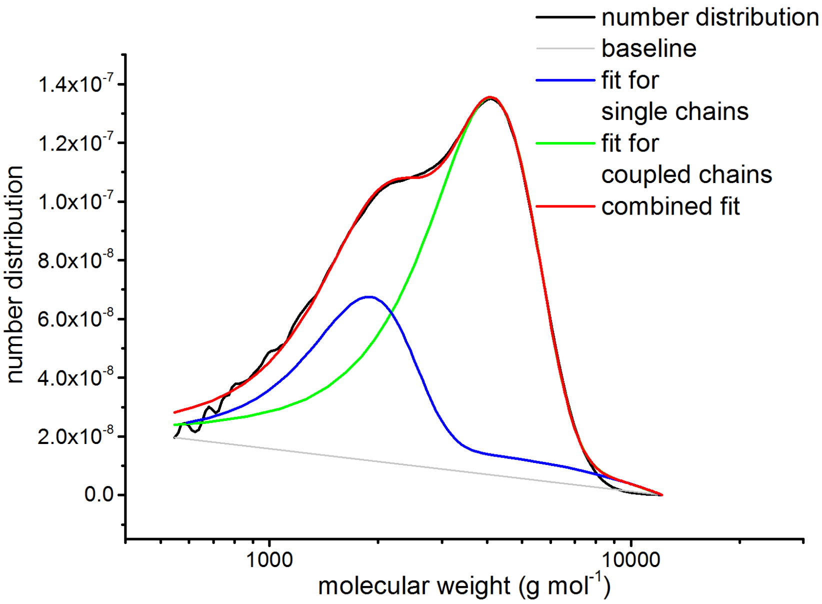

Figure S16. Deconvolution of the SEC number distribution for the coupling of pNAM-SO$_2$F and pS-O-TBDMS in DMF using 0.3 eq. of TBAF as catalyst. This sample was taken after 30 min.

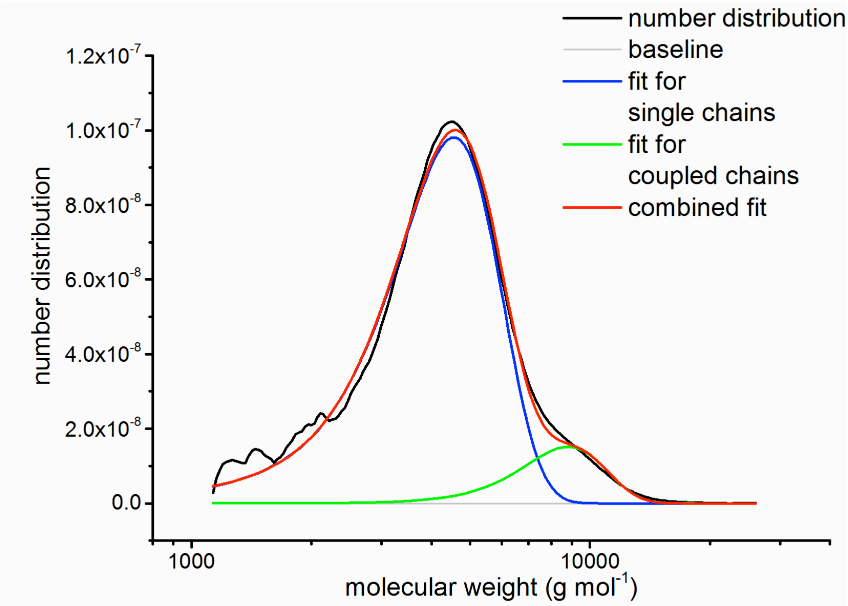

Figure S17. Deconvolution of the SEC number distribution for the coupling of pNAM-SO$_2$F and p(*t*-BA)-O-TBDMS in DMF using 0.3 eq. of TBAF as catalyst. This sample was taken after 48 h.