Tetrakis(dialkylamino)phosphonium Polyelectrolytes Prepared by Reversible Addition-Fragmentation Chain Transfer Polymerization

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Materials and Methods. All reactions and manipulations of compounds were carried out in air unless otherwise specified. Toluene was purchased from Fischer Scientific and was degassed with argon and dried using a JCMeyer solvent system prior to use. All other solvents were purchased from Fischer Scientific and were used as received. $CDCl_3$ was purchased from Cambridge Isotope Laboratories (CIL) and used as received. All reagents were purchased from commercial sources and used as received unless otherwise specified.

NMR Analysis. All NMR spectra were recorded on either a 300 MHz or a 500 MHz Bruker Avance Spectrometer. The $^{31}P\{^{1}H\}$ NMR spectra were referenced to an external standard (85% H_3PO_4). The ^{1}H NMR spectra were reference to residual protio solvents (7.24 for $CHCl_3$ and 2.50 for DMSO-d_5) and ^{13}C NMR were referenced to $CDCl_3$ (77.23 ppm).

High Resolution Electrospray Ionization Mass Spectrometry. High Resolution Electrospray Mass Spectrometry (ESI-MS) was performed in the School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois, Urbana-Champaign.

Gel Permeation Chromatography. GPC measurements were performed on a Waters 2690 separations module apparatus equipped with two SDV columns (Porosity 1000 and 100000 Å; Polymer Standard Services) and a Waters 2414 Refractive Index detector. THF doped with 10 mM $LiNTf_2$ was used as the eluent (flow rate 1 mL/min, 40 °C). A 9-point calibration based on polystyrene standards (Poly(styrene)) ReadyCal Kit, Polymer Standard Services) was applied for determination of molecular weights.

Thermal Gravimetric Analysis. TGA was ran using a Perkin Elmer Pyris under a nitrogen atmosphere starting from 25 °C and ending at 500 °C with a rate of 10 °C/minute.

Differential Scanning Calorimetry. DSC analysis was performed on a Seiko SSC/5200 SII DSC220C Calorimeter using a scan range of 0 – 200 °C at a rate of 10 °C/min under a nitrogen atmosphere for 3 cycles.

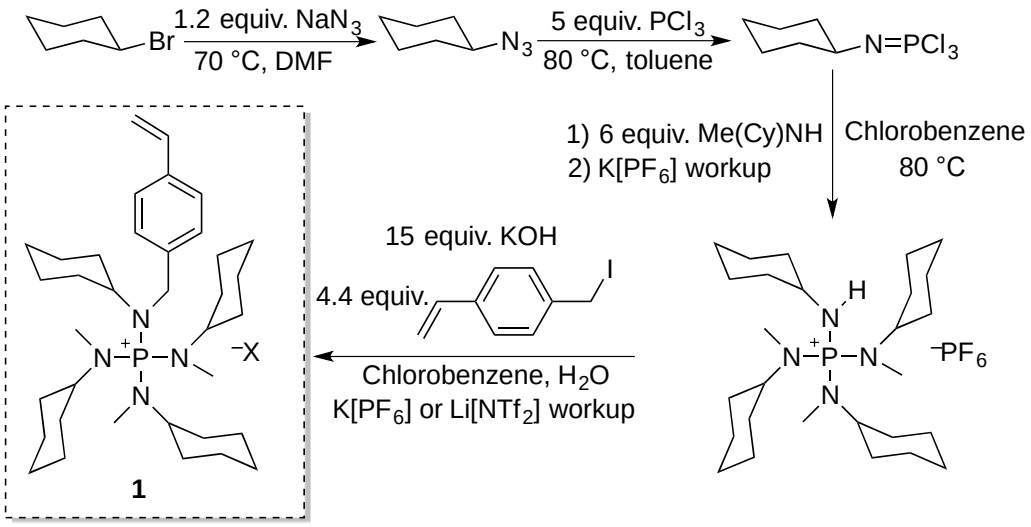
Kinetic Experiments. Conversion was measured by ^{1}H NMR spectroscopy (45 ° tip, delay time = 10 s) and measured as follows. After automatic phase adjustment and baseline correction using a 3rd order Berstein polynomial fit, the area from 3.65 – 4.0 ppm (anisole) was integrated and set to 1. The area from 6.00 – 5.60 ppm was integrated and compared between successive time points. This area corresponds to both vinyl protons for styrene and phosphonium monomer **1**, therefore total monomer conversion was plotted. A plot of $\ln([M]_o/[M])$ versus time was obtained from the calculated conversions.

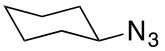
% 1 incorporation in the polymer. The amount of ionic content in the polymer was estimated using ^{1}H NMR spectroscopy and calculated as follows. The area (A_1) from 3.90 – 4.50 ppm was integrated and set to 2 (2 benzylic protons from **1**). The area (A_2) from 6.00 – 7.50 was integrated and the % **1** composition was determined from the equation:

$$\%\,\mathbf{1} = \frac{(\frac{A1}{2})}{(\frac{A1}{2}) + [(A_2 - 4)/5]} x\ 100$$

Experimental Procedures

Scheme S1. **Phosphonium Monomer Synthesis**



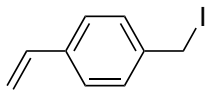
Preparation of azidocyclohexane. This compound was prepared according to a previous report.[1] Bromocyclohexane (36.3 mL, 294 mmol), sodium azide (23.0 g, 
354 mmol) and DMF (300 mL) were combined in a three-necked round bottom flask under a nitrogen atmosphere. The flask was immersed in a 70 °C oil bath and stirred for 16 h (Caution: This experiment has been repeated multiple times and no explosion has occurred but a blast shield was used as a precaution). The reaction mixture was cooled to room temperature and diluted with 300 mL of water and 300 mL of diethyl ether. The mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted twice with diethyl ether (100 mL). The organic extracts were combined and washed five times with water (150 mL). The organic layer was dried over Na_2SO_4, concentrated using rotary evaporation and a light brown oil was obtained (24.9 g, 68% yield). ^{1}H NMR was consistent with the previous report and the product was used without further purification.

Preparation of cyclohexylphosphorimidoyl trichloride. A 500 mL Schlenk bomb was evacuated and backfilled with nitrogen using standard Schlenk techniques. Dry, degassed toluene (75 mL) and cyclohexyl azide (24.0 g, 192 mmol) were added to the reaction vessel and stirred for 10 minutes. Phosphorus trichloride (83.0 mL, 949 mmol) was slowly added to the vessel by syringe and the mixture was stirred for 15 minutes. The flask was then immersed in an 80 °C oil bath and stirred for 30 minutes before sealing the vessel and the mixture was stirred overnight (Caution: This experiment has been repeated multiple times and no explosion has occurred but a blast shield was used as a precaution). The flask was cooled to room temperature, vented, and an aliquot was removed and analyzed using $^{31}P\{^{1}H\}$ NMR spectroscopy. A signal at –74 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum confirmed formation of the desired compound. Excess PCl_3 and toluene were removed *in vacuo* and the resultant red-brown oil was distilled using short path distillation path (59 °C, 400 mtorr). The distilled product was a colorless oil (22.9 g, 51% yield) and was used immediately in subsequent reactions because it tends to dimerize at room temperature. It can be stored for longer periods at –40 °C. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ –62.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50 – 3.34 (m, 1H), 1.90 (dq, *J* = 12.1, 3.8 Hz, 2H), 1.71 (ddt, *J* = 13.4, 6.4, 3.0 Hz, 2H), 1.54 (dt, *J* = 12.6, 4.0 Hz, 1H), 1.44 – 1.33 (m, 2H), 1.32 – 1.11 (m, 3H).

Preparation of tris(cyclohexyl(methyl)amino)(cyclohexylamino)phosphonium hexafluorophosphate(V). A 1000 mL three-necked round bottom flask was evacuated and backfilled with nitrogen using standard Schlenk techniques. Chlorobenzene (70 mL) and cyclohexylphosphorimidoyl trichloride (27.33 g, 117 mmol) were combined in the reaction flask. The flask was cooled to 0 °C using an ice bath and *N*-methylcyclohexylamine (91.6 mL, 702

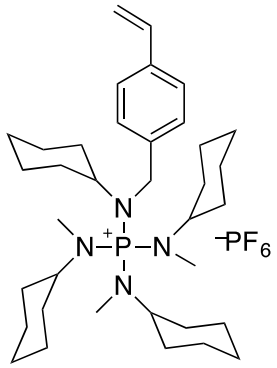
mmol) was slowly added to the reaction mixture and gas evolution was observed. After stirring for 30 minutes at 0 °C, the flask was placed in an oil bath and heated to 80 °C and stirred overnight. An aliquot was removed from the reaction mixture and analyzed using $^{31}P\{^{1}H\}$ NMR spectroscopy and a signal near 38 ppm was observed which corresponded to the desired product. Upon completion, the flask was cooled to room temperature and the reaction mixture was diluted with 100 mL water and 100 mL dichloromethane. The organic layer was separated and the aqueous layer was washed with dichloromethane (3 × 50 mL). The combined organic extracts were washed with water (2 × 100 mL), a saturated aqueous solution of potassium hexafluorophosphate (2 × 100 mL), and again with water (1 × 100 mL). The organic phase was dried over Na_2SO_4, concentrated using rotary evaporation and the resultant oil was precipitated into a large volume of diethyl ether. The precipitate was collected using vacuum filtration and the white solid was dried *in vacuo* (39.38 g, 55% yield). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) δ 38.4 (s, 1P), –144.2 (sep, J_{PF} = 713.9 Hz, 1P). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (dd, J = 12.7, 10.3 Hz, 1H), 3.24 – 3.08 (m, 3H), 2.76 – 2.66 (m, 1H), 2.62 (d, J = 9.9 Hz, 9H), 1.88 – 1.71 (m, 10H), 1.69 – 1.49 (m, 18H), 1.38 – 1.23 (m, 6H), 1.21 – 1.11 (m, 3H), 1.10 – 0.97 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.6 (d, J_{PC} = 5.3 Hz), 52.2, 35.1 (d, J_{PC} = 4.3 Hz), 30.7 (d, J_{PC} = 2.8 Hz), 29.6 (d, J_{PC} = 4.1 Hz), 26.0, 25.4, 24.9. Note: only 8 of the 9 possible signals from the cyclohexyl substituents are visible due to similarities between chemical environments. HRMS (ESI-TOF) (*m*/*z*): $[M]^+$ calculated for $C_{27}H_{54}N_4P^+$: 465.4081; found 465.4077.

Preparation of 1-(iodomethyl)-4-vinylbenzene. 1-(chloromethyl)-4-vinylbenzene was converted into the title compound using a modified literature procedure.[2] Acetone (200 mL), 1-(chloromethyl)-4-vinylbenzene (7.1 mL, 50 mmol), and potassium iodide (25.0 g, 150 mmol) were combined in a 500 mL round-bottom flask. The



flask was covered to minimize light exposure and stirred overnight. The solvent was removed by rotary evaporation and the crude product was combined with water (200 mL) and diethyl ether (200 mL). The organic layer was separated and the aqueous layer was extracted 3 more times with ether (50 mL). The organic extracts were combined and washed with a saturated solution of sodium thiosulfate (3 × 100 mL) and 100 mL water. The organic extracts were dried using Na_2SO_4, concentrated using rotary evaporation, and a yellow oil was obtained (11.24 g, 92% yield). ^{1}H NMR spectrum was consistent with the previous report and the compound was used without further purification.

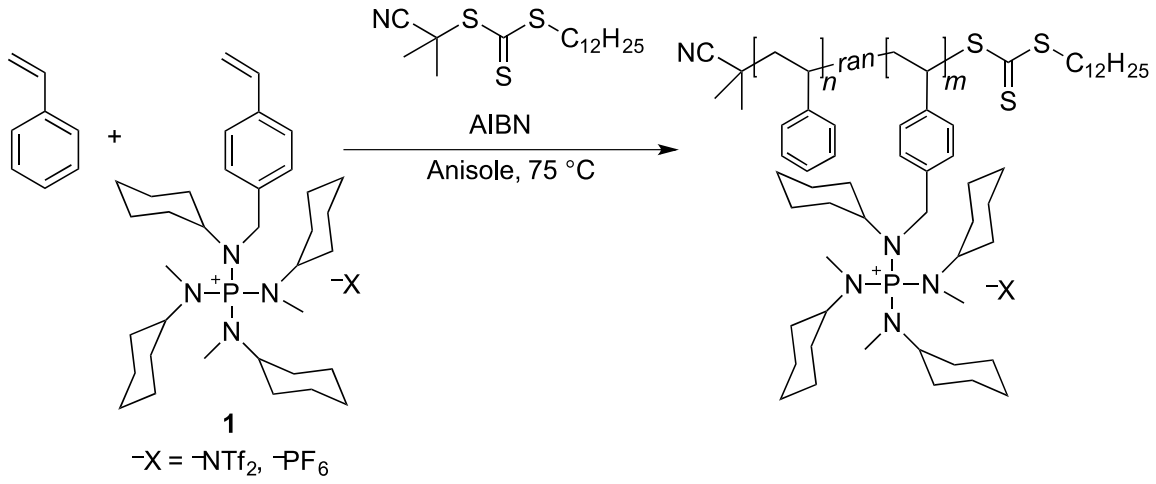
Preparation of (cyclohexyl(4-vinylbenzyl)amino)tris(cyclohexyl(methyl)amino)phosphonium hexafluorophosphate(V) (1[PF_6]). Tris(cyclohexyl(methyl)amino)(cyclohexylamino)phosphonium hexafluorophosphate(V) (4.00 g, 6.5 mmol), chlorobenzene (6 mL), 11.0 g aqueous KOH solution (50/50, w/w) and 1-(iodomethyl)-4-vinylbenzene (7.00 g, 28.6 mmol) were combined in a 50 mL round-bottom flask. The flask was covered to minimize light exposure and stirred at room temperature overnight. Aliquots were removed from the reaction mixture and analyzed using ^{31}P{^{1}H} NMR spectroscopy to monitor the disappearance of the starting material and to confirm formation of the product near 48 ppm. Upon completion, the reaction mixture was diluted with 50 mL water and 50 mL dichloromethane. The mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted once more with dichloromethane and the combined organic extracts were washed twice with a saturated aqueous solution of potassium hexafluorophosphate (50 mL), and once with water (50



mL). The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation. The yellow oil was precipitated into 150 mL diethyl ether. The solid was collected using vacuum filtration and washed with diethyl ether (3 × 50 mL). The compound was redissolved in a minimum amount of dichloromethane and precipitated into diethyl ether twice more. The product was obtained as a white solid (4.1 g, 86% yield). $\delta^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 48.5 (s, 1P), –143.4 (sep, J_{PF} = 712.2, 1P). ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.76 (d, J = 17.7 Hz, 1H), 5.27 (d, J = 11.0 Hz, 1H), 4.32 (d, J = 10.2 Hz, 2H), 3.31 – 3.01 (m, 4H), 2.65 (d, J = 9.9 Hz, 9H), 1.91 (d, J = 11.9 Hz, 6H), 1.85 – 1.50 (m, 20H), 1.50 – 1.00 (m, 13H), 0.99 – 0.81 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 137.3 (d, J_{PC} = 5.4 Hz), 136.2, 127.8, 126.7, 114.7, 59.5 (d, J_{PC} = 3.8 Hz), 56.3 (d, J_{PC} = 4.4 Hz), 48.2 (d, J_{PC} = 4.6 Hz), 33.2 (d, J_{PC} = 3.1 Hz), 30.7 (d, J_{PC} = 2.7 Hz), 30.4 (d, J_{PC} = 3.8 Hz), 26.9, 26.1, 25.2, 25.1. HRMS (ESI-TOF) (m/z): $[M]^+$ for $C_{36}H_{62}N_4P^+$: calculated 581.4707; found 581.4705.

Anion metathesis for phosphonium monomer. 5.0 g of **1[PF$_6$]** was dissolved in 150 mL of dichloromethane. The mixture was washed with a saturated solution of $Li[NTf_2]$ (3 × 50 mL). Anion exchange could be monitored using ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy (Final spectra shown in Figures S9 and S10). After full conversion to the $^-[NTf_2]$ counterion, the organic layer was washed with water, dried over Na_2SO_4 and concentrated using rotary evaporation.

Scheme S2. **RAFT Copolymerization of Styrene and 1**



General RAFT Polymerization of Polyelectrolyte copolymers. Phosphonium monomer **1**, styrene, the RAFT agent (2-cyano-2-propyl dodecyl trithiocarbonate) and anisole were added to a 10 mL Schlenk flask (monomer and solvent amounts are included in Table S1). Reactions were typically conducted at total monomer concentrations of 5 M. The flask was degassed by three freeze-pump-thaw cycles. While the contents of the flask were frozen, AIBN was added and the flask was evacuated and backfilled with nitrogen three more times. The flask was then submerged in a 75 °C oil bath. Samples were taken periodically via syringe and analyzed by ^{1}H NMR to measure percent conversion. Exposing the contents of the flask to air stopped the polymerizations. The polymers were precipitated into methanol and filtered to yield off-white powders.

Preparation of Polyisoprene-*block*-(Poly(1[PF_6])-*ran*-Poly(styrene)). Polyisoprene macro-RAFT agent was prepared according to a modified literature report using 2-cyano-2-propyl dodecyl trithiocarbonate as the chain transfer agent.[3] In a 10 mL Schlenk flask, styrene (0.91 mL), **1[PF_6]** (0.80 g), and the macro-RAFT agent (0.22 g, M_n = 10 100, $Đ$ = 1.23) were added to 2.2 mL anisole. The contents were subjected to three consecutive freeze-pump-thaw cycles.

While the contents of the flask were frozen, AIBN (2 mg) was added and the flask was evacuated and backfilled with nitrogen three more times. The flask was then submerged in a 75 °C oil bath. Exposing the contents of the flask to air stopped the polymerization. The polymer was precipitated into ethanol and filtered to yield a white powder (M_n = 26 000, $Đ$ = 1.27).

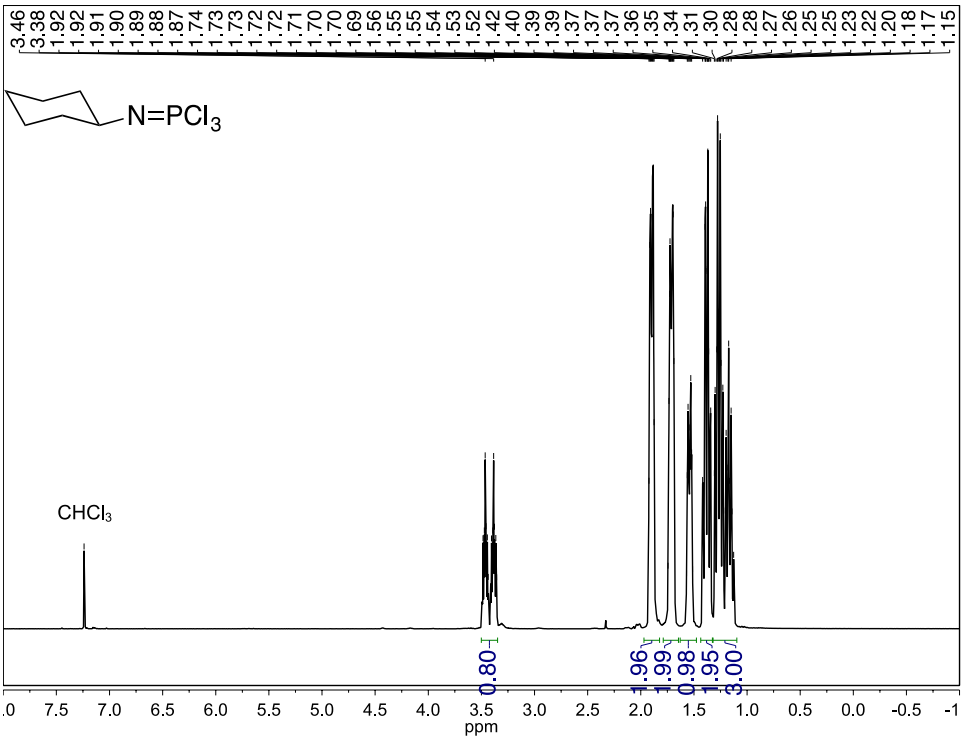


Figure S1. ^{1}H NMR spectrum in $CDCl_3$, 500 MHz.

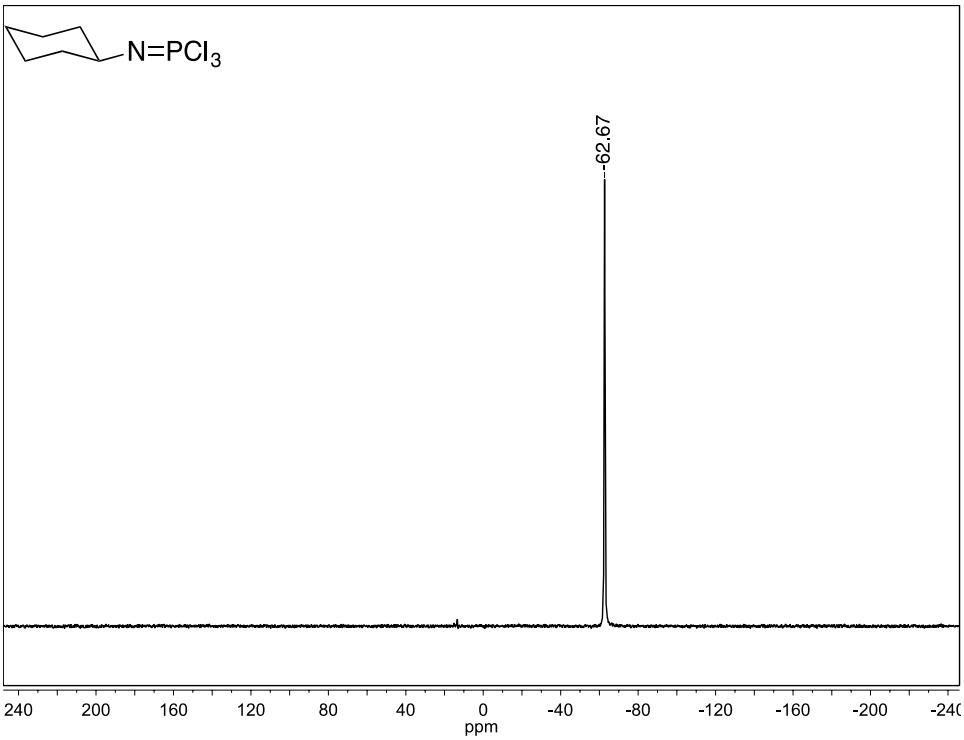


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum in $CDCl_3$, 202 MHz.

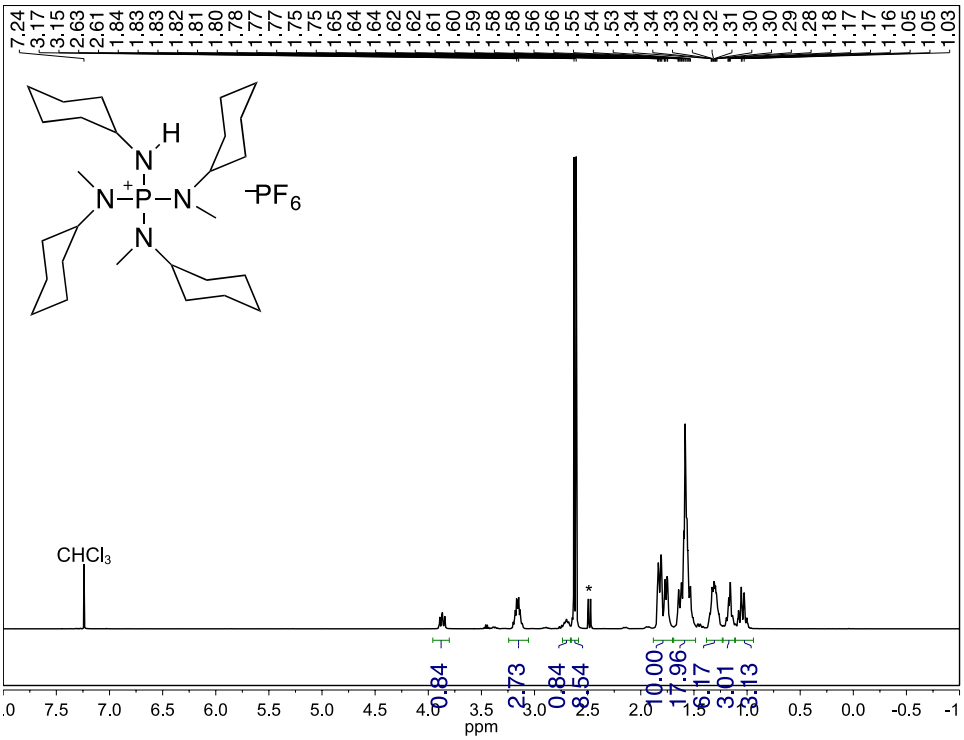


Figure S3. ^{1}H NMR spectrum in $CDCl_3$, 500 MHz.

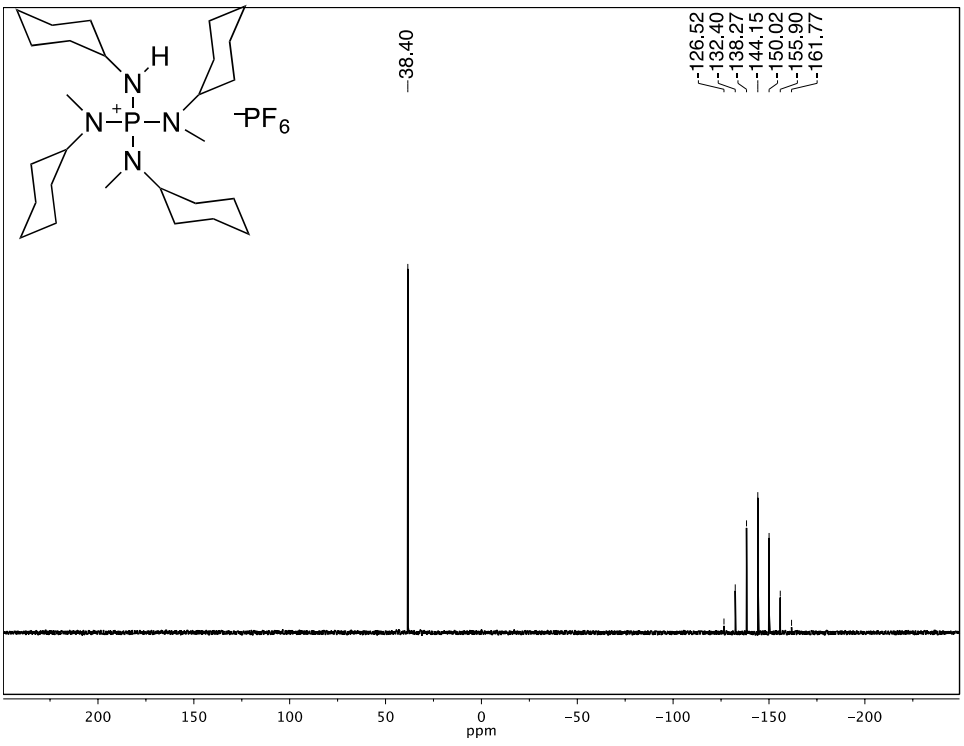


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum in $CDCl_3$, 121 MHz.

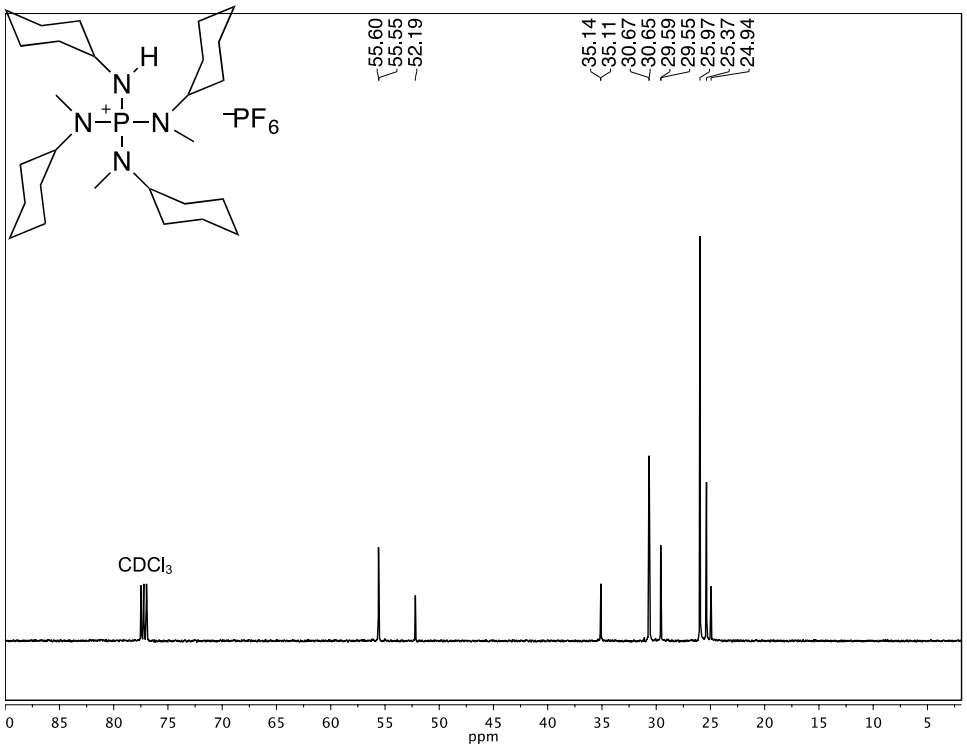


Figure S5. ^{13}C NMR spectrum in $CDCl_3$, 126 MHz.

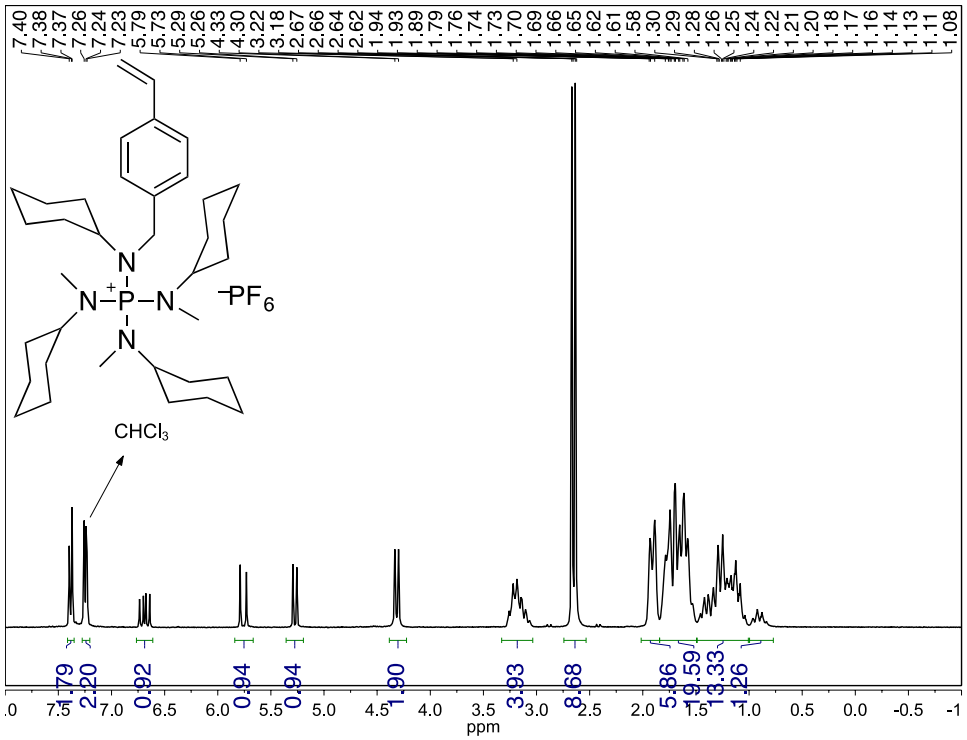


Figure S6. ^{1}H NMR spectrum in $CDCl_3$, 300 MHz.

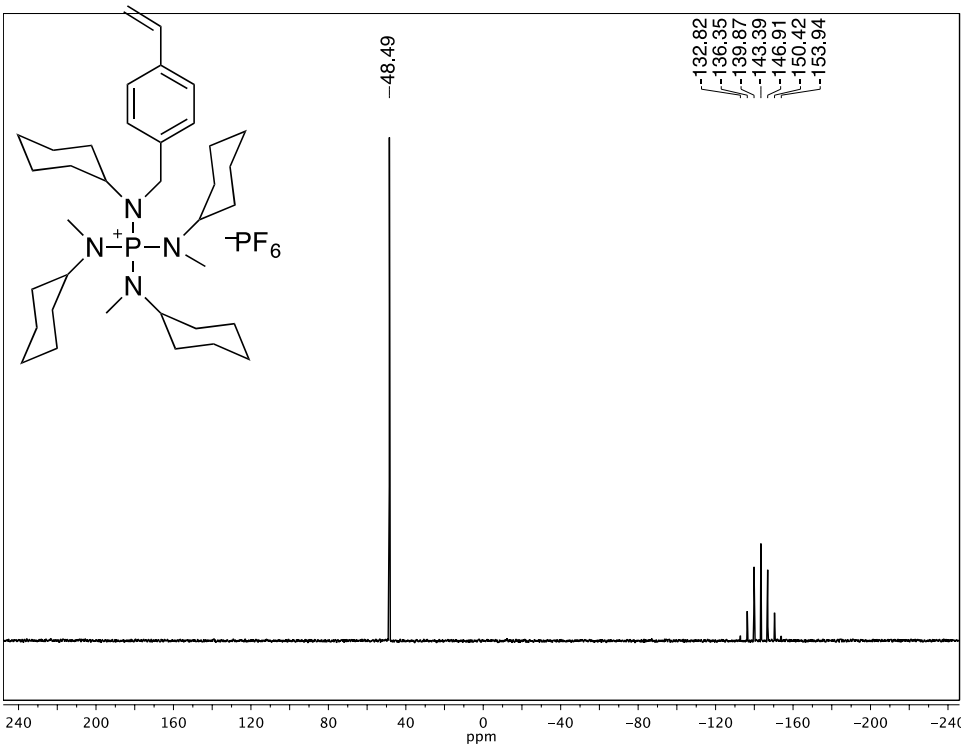


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum in $CDCl_3$, 202 MHz.

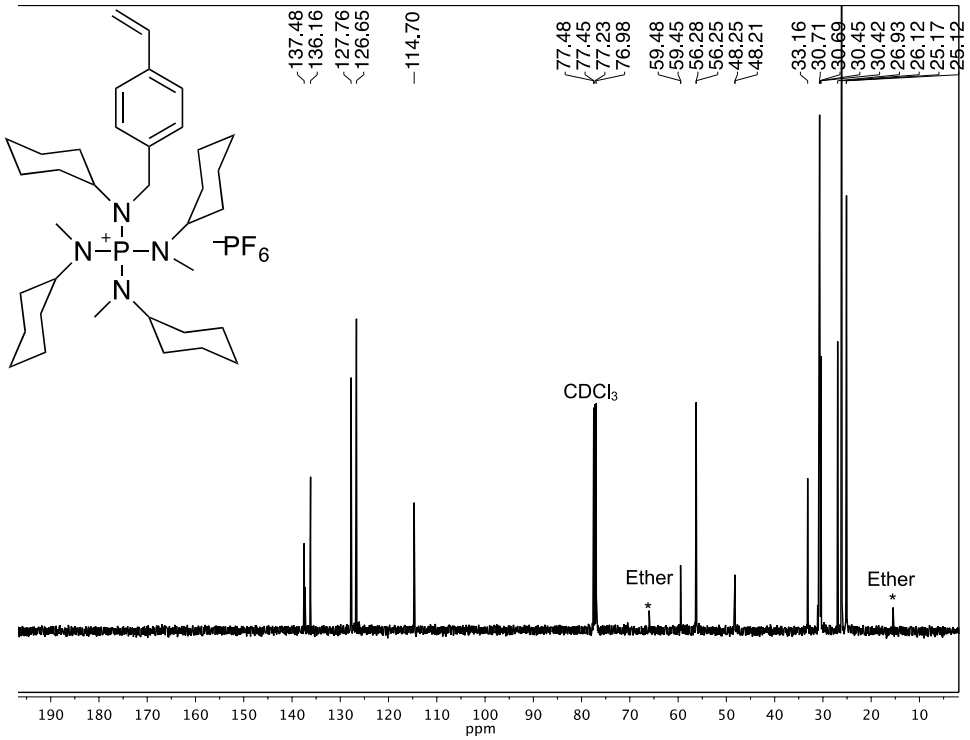


Figure S8. ^{13}C NMR spectrum in $CDCl_3$, 126 MHz.

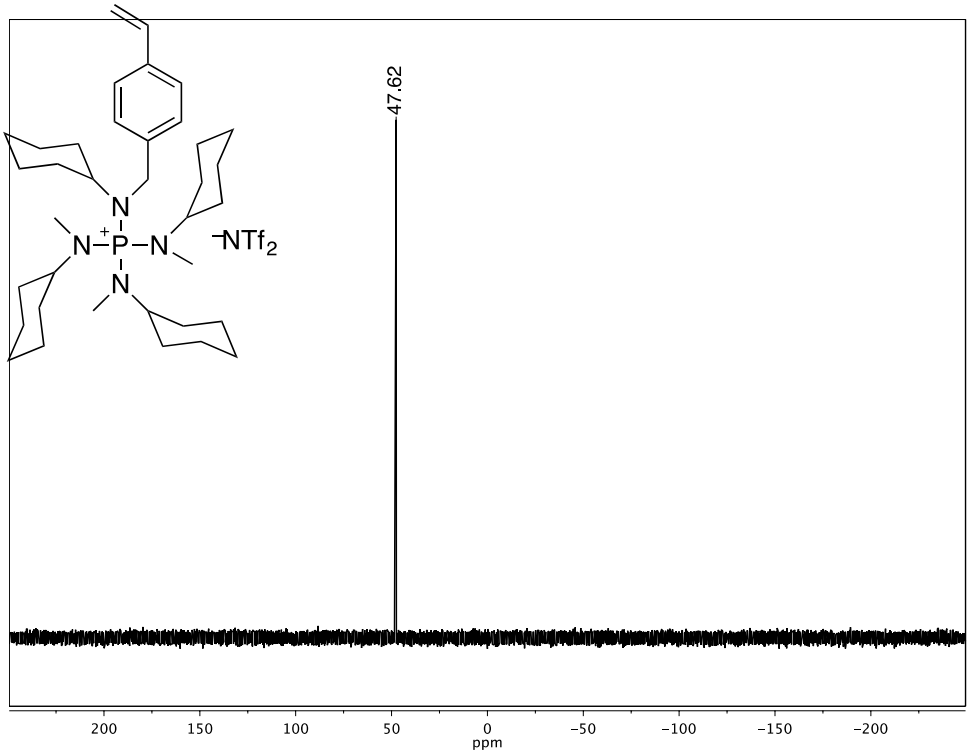


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum in $CDCl_3$ (anion exchange), 121 MHz.

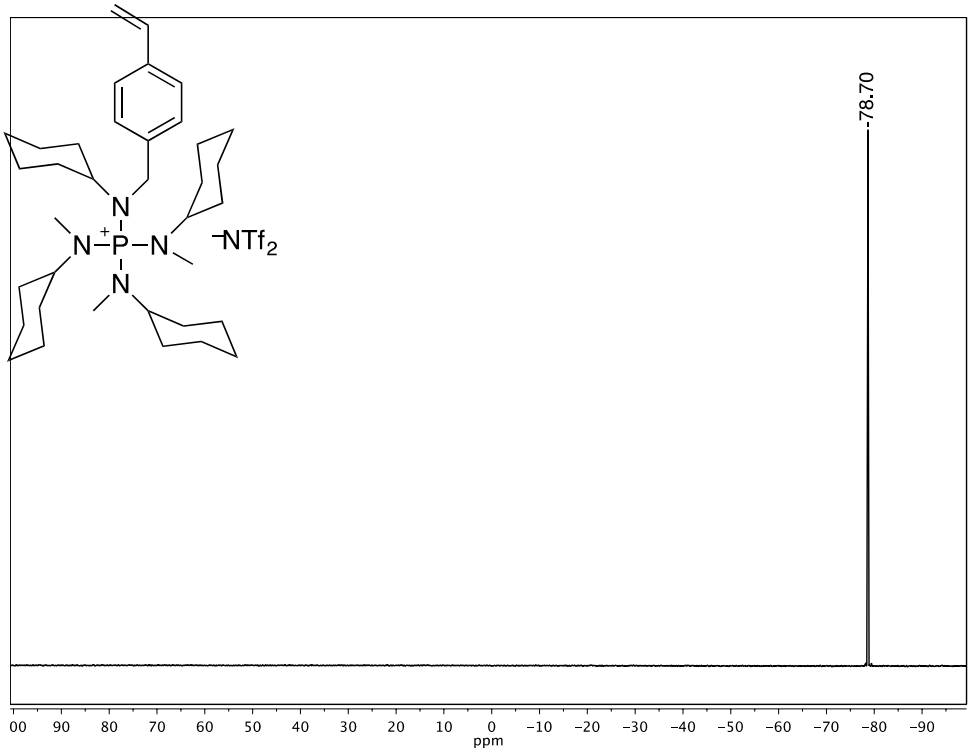


Figure S10. ^{19}F NMR spectrum in $CDCl_3$ (anion exchange), 282 MHz.

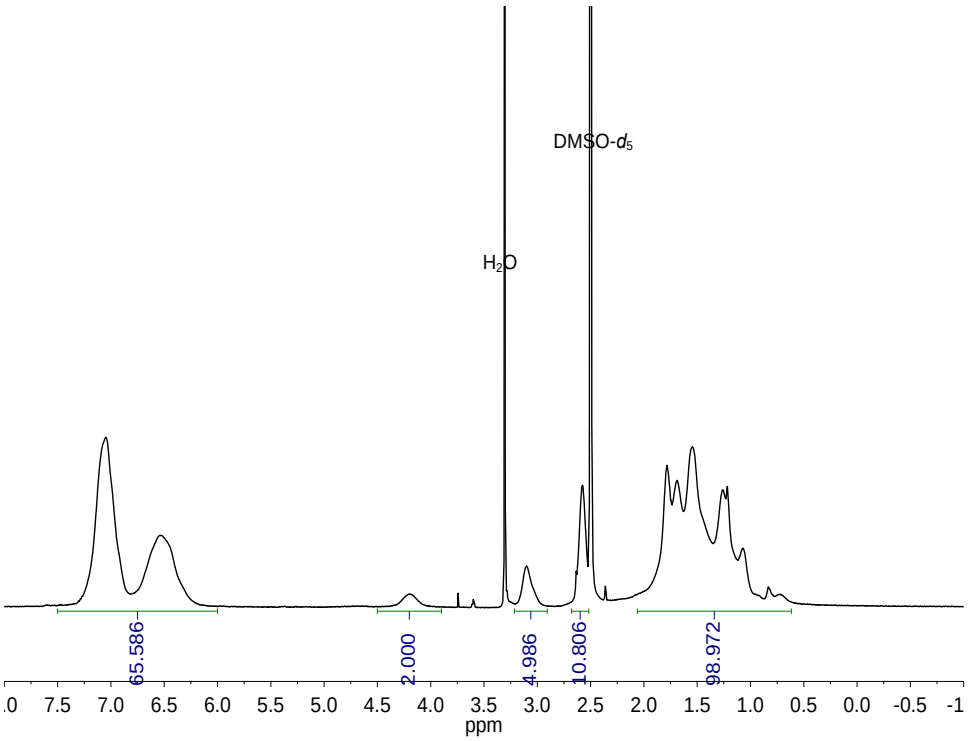


Figure S11. ^{1}H NMR spectrum in DMSO-d_6 of copolymer (Table S1, entry b), 500 MHz.

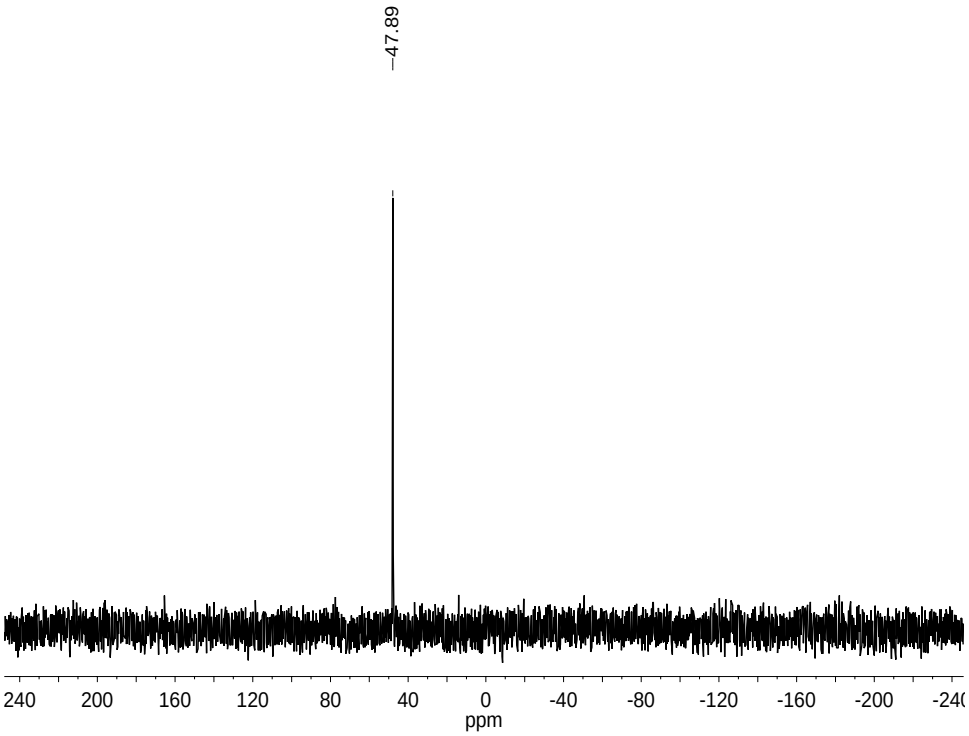


Figure S12. ^{31}P{^{1}H} NMR spectrum in DMSO-d_6 of copolymer (Table S1 entry b), 202 MHz.

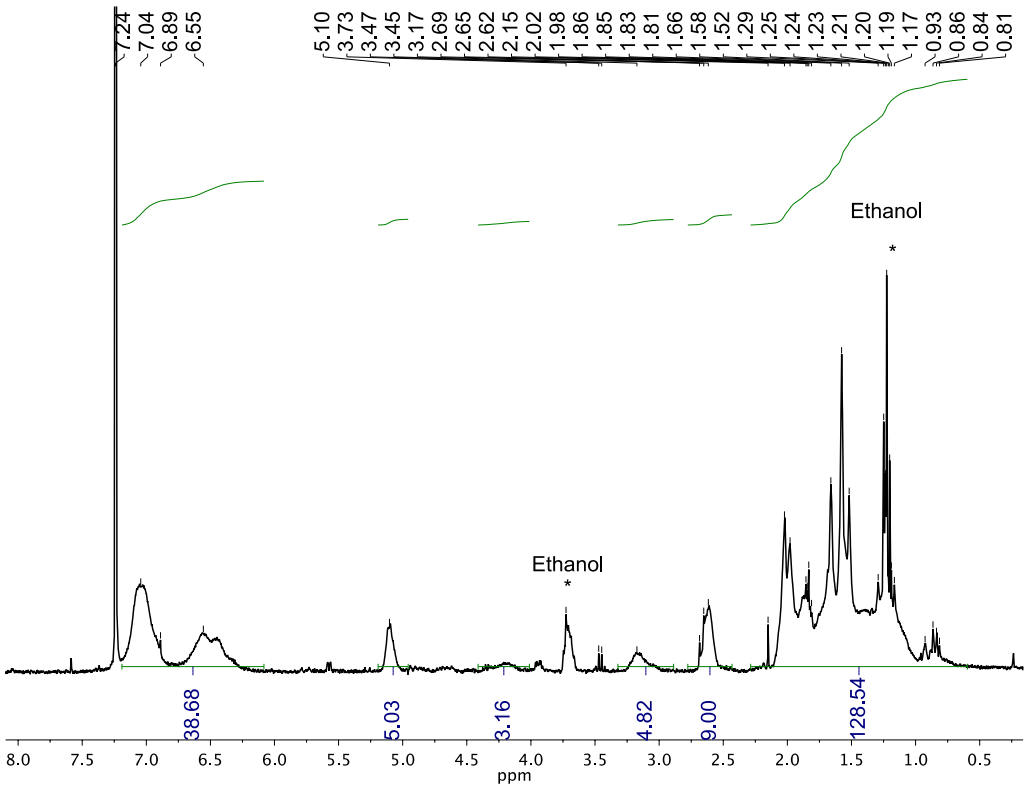


Figure S13. ^{1}H NMR spectrum of polyisoprene-*block*-(Poly(**1**[PF_6]-*ran*-Poly(styrene)) in $CDCl_3$, 300 MHz. The different configurations of polyisoprene from radical polymerization afforded a relatively complicated ^{1}H NMR spectrum, particularly with the incorporation of monomer **1**. The presence of some residual ethanol from precipitation affected the integration of the alkyl region.

Kinetic Data

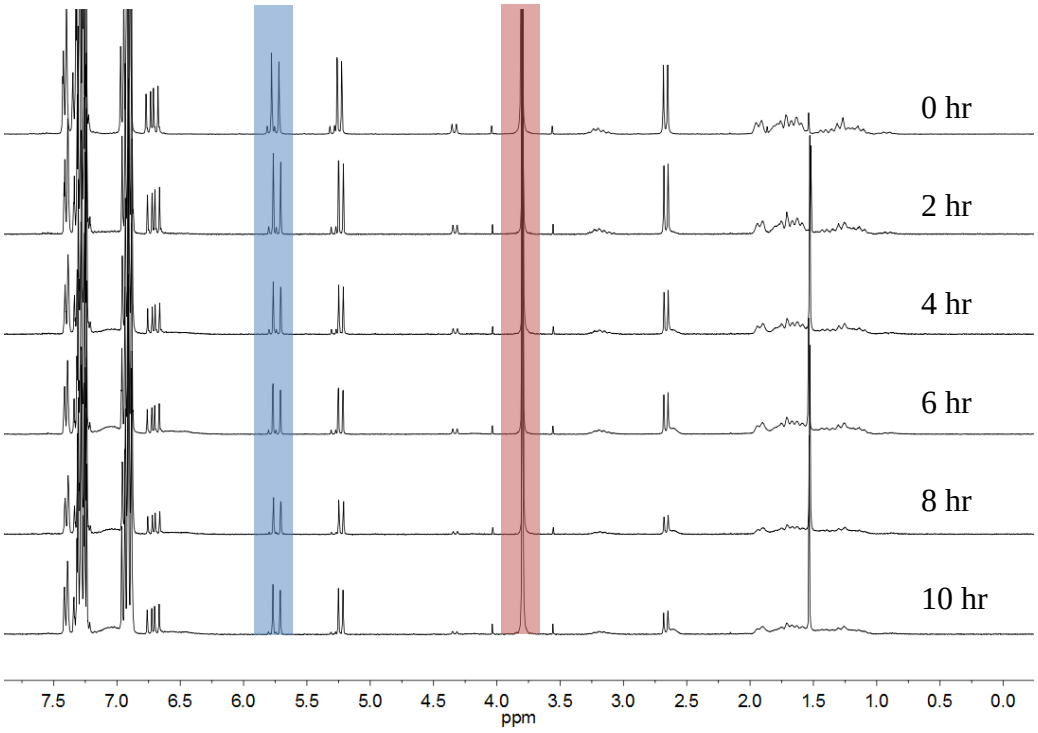


Figure S14. Representative Stacked ^{1}H NMR spectra of 0, 2, 4, 6, 8, 10 h for copolymerization with 90:10 styrene:**1[NTf$_2$]** and starting with 0.5 mol % RAFT agent (Table S1, entry b). 300 MHz.

Table S1. RAFT polymerization conditions of **1** with styrene.

Entry	Mol % styrene/**1**/CPDTTC/AIBN	counterion	solvent	Styrene (mL)	Phosphonium (g)	Anisole (mL)
a	95/5/0.5/0.25	$^{-}$NTf$_2$	anisole	0.63	0.25	1.15
b	90/10/0.5/0.25	$^{-}$NTf$_2$	anisole	1.18	1.01	2.30
c	85/15/0.5/0.25	$^{-}$NTf$_2$	anisole	0.75	1.02	1.54
d	80/20/0.5/0.25	$^{-}$NTf$_2$	anisole	0.26	0.50	0.58
e	90/10/0.5/0.25	$^{-}$PF$_6$	anisole	0.71	0.50	1.37
f	85/15/0.5/0.25	$^{-}$PF$_6$	anisole	0.45	0.50	0.92
g	90/10/0.2/0.1	$^{-}$NTf$_2$	anisole	0.59	0.50	1.15
h	90/10/0.1/0.05	$^{-}$NTf$_2$	anisole	0.59	0.50	1.15

Polymerizations were conducted at 75 °C with a total monomer concentration $[M]_{total}$ = 5 M.

Table S2. Kinetic data for 95:5 styrene: **1[NTf_2]** with 0.5 mol % RAFT agent in anisole (Table S1, entry a)

Time	$[M]_o$	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.175	0.000	5.00	0.000
120		0.147	0.160	4.20	0.174
240		0.124	0.291	3.54	0.345
360		0.110	0.371	3.14	0.464
480		0.100	0.429	2.86	0.560
600		0.093	0.469	2.66	0.632

Table S3. Kinetic data for 90:10 styrene: **1[NTf_2]** with 0.5 mol % RAFT agent in anisole (Table S1, entry b)

Time	$[M]_o$	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.172	0.000	5.00	0.000
120		0.146	0.151	4.24	0.164
240		0.121	0.297	3.52	0.352
360		0.105	0.390	3.05	0.494
480		0.084	0.512	2.44	0.717
600		0.074	0.570	2.15	0.843

Table S4. Kinetic data for 85:15 styrene: **1[NTf_2]** with 0.5 mol % RAFT agent in anisole (Table S1, entry c)

Time	$[M]_o$	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.174	0.000	5.00	0.000
120		0.146	0.161	4.20	0.175
240		0.116	0.333	3.33	0.405
360		0.096	0.448	2.76	0.595
480		0.082	0.529	2.36	0.752
600		0.074	0.575	2.13	0.855

Table S5. Kinetic data for 80:20 styrene: **1[NTf_2]** with 0.5 mol % RAFT agent in anisole (Table S1, entry d)

Time	[M]o	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.173	0.000	5.00	0.000
120		0.163	0.058	4.71	0.060
240		0.127	0.266	3.67	0.309
360		0.103	0.405	2.98	0.519
480		0.081	0.532	2.34	0.759
600		0.072	0.584	2.08	0.877

Table S6. Kinetic data for 90:10 styrene: **1[PF_6]** with 0.5 mol % RAFT agent in anisole (Table S1, entry e)

Time	$[M]_o$	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.174	0.000	5.00	0.000
120		0.149	0.144	4.28	0.155
240		0.128	0.264	3.68	0.307
360		0.102	0.414	2.93	0.534
480		0.089	0.489	2.56	0.670

Table S7. Kinetic data for 85:15 styrene: **1[PF_6]** with 0.5 mol % RAFT agent in anisole (Table S1, entry f)

Time	$[M]_o$	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.172	0.000	5.00	0.000
120		0.142	0.174	4.13	0.192
240		0.106	0.384	3.08	0.484
360		0.089	0.483	2.59	0.659
480		0.075	0.564	2.18	0.830

Table S8. Kinetic data for 90:10 styrene: **1[NTf_2]** with 0.2 mol % RAFT agent in anisole (Table S1, entry g)

Time	$[M]_o$	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.173	0.000	5.00	0.000
120		0.169	0.023	4.88	0.023
240		0.152	0.121	4.39	0.129
360		0.137	0.208	3.96	0.233
480		0.119	0.312	3.44	0.374
600		0.117	0.324	3.38	0.391

Table S9. Kinetic data for 90:10 styrene: **1[NTf_2]** with 0.1 mol % RAFT agent in anisole (Table S1, entry h)

Time	$[M]_o$	NMR integral	conversion	[M]	ln ($[M]_o$/[M])
0	5.00	0.172	0.000	5.00	0.000
120		0.165	0.041	4.80	0.042
240		0.148	0.140	4.30	0.150
360		0.134	0.221	3.90	0.250
480		0.12	0.302	3.49	0.360
600		0.116	0.326	3.37	0.394

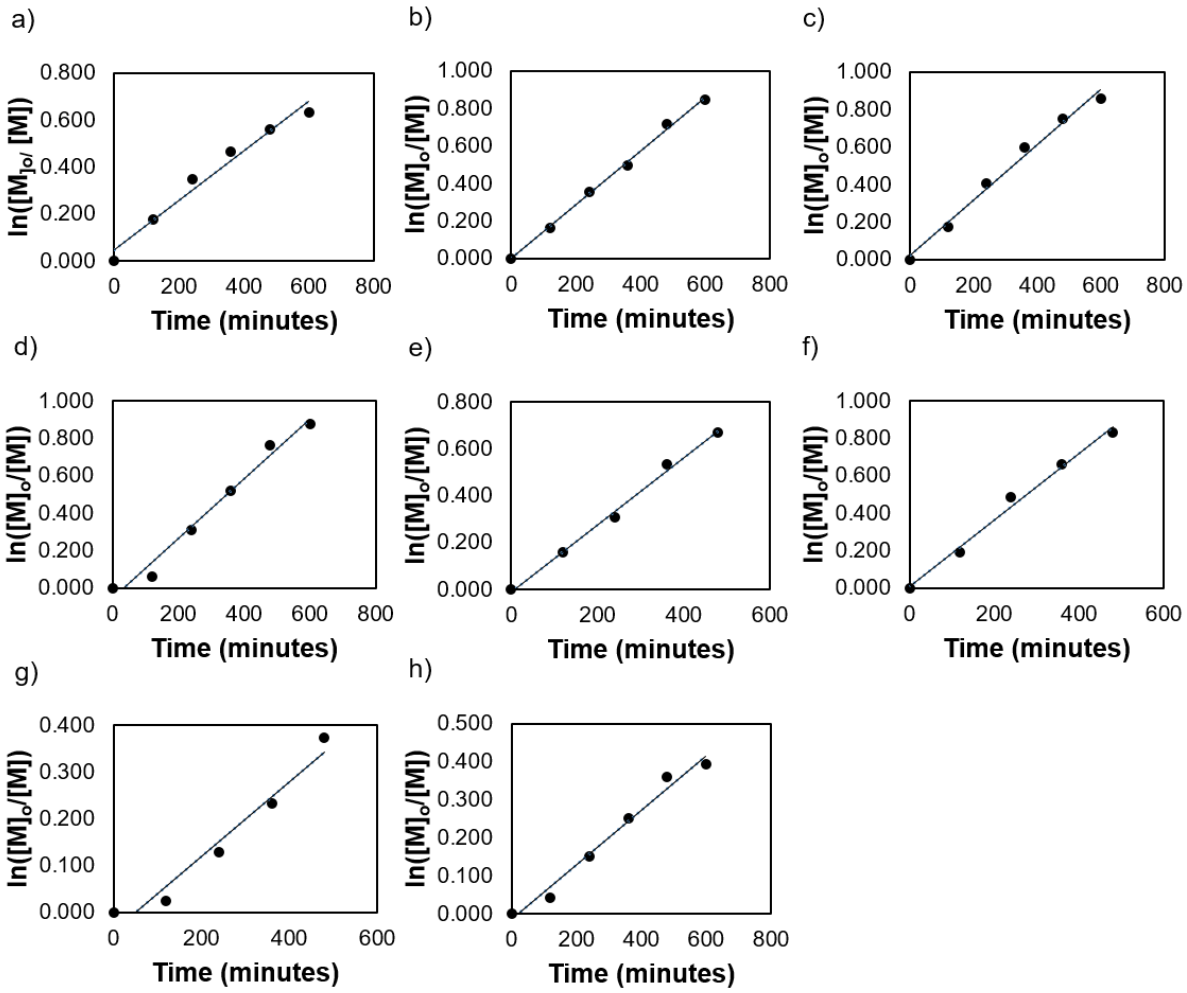


Figure S15. Kinetic plots of ln([M]$_o$/[M]) vs time. Entries a-h correspond to entries in Table S1.

Gel Permeation Chromatography Traces.

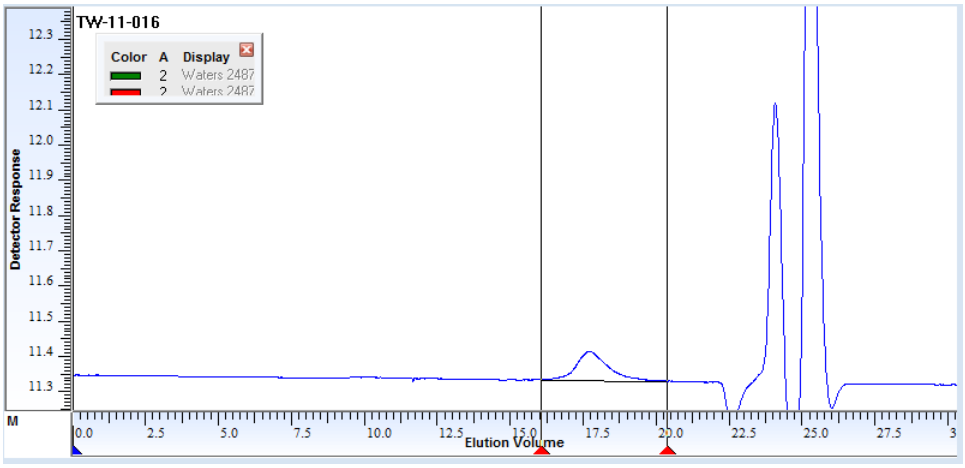


Figure S16. GPC trace of Table S1, entry a.

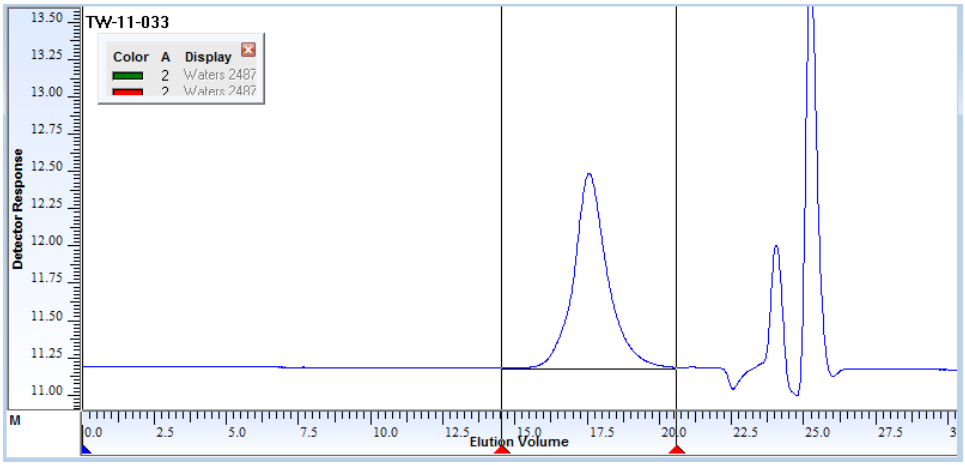


Figure S17. GPC trace of Table S1, entry b.

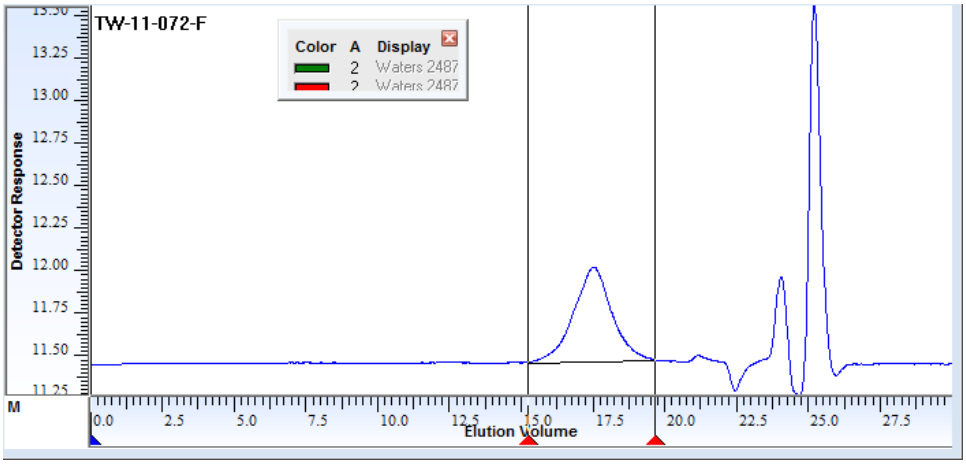


Figure S18. GPC trace of Table S1, entry c.

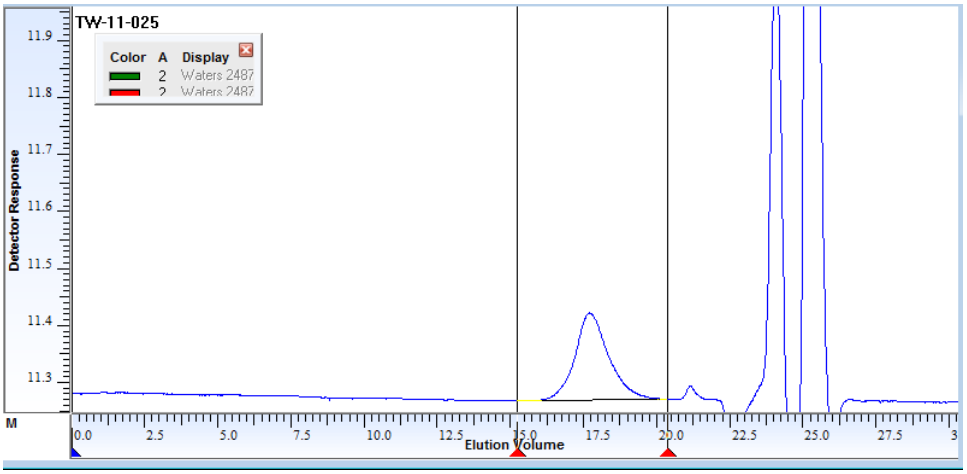


Figure S19. GPC trace of Table S1, entry d.

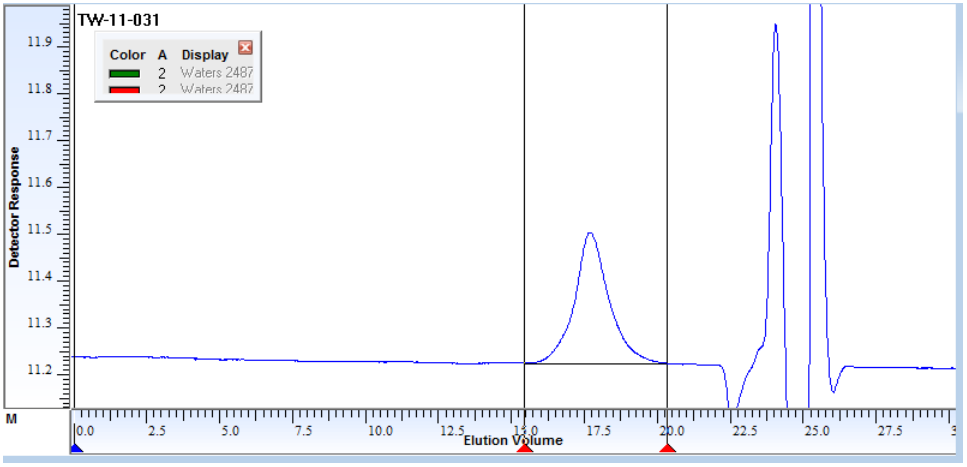


Figure S20. GPC trace of Table S1, entry e.

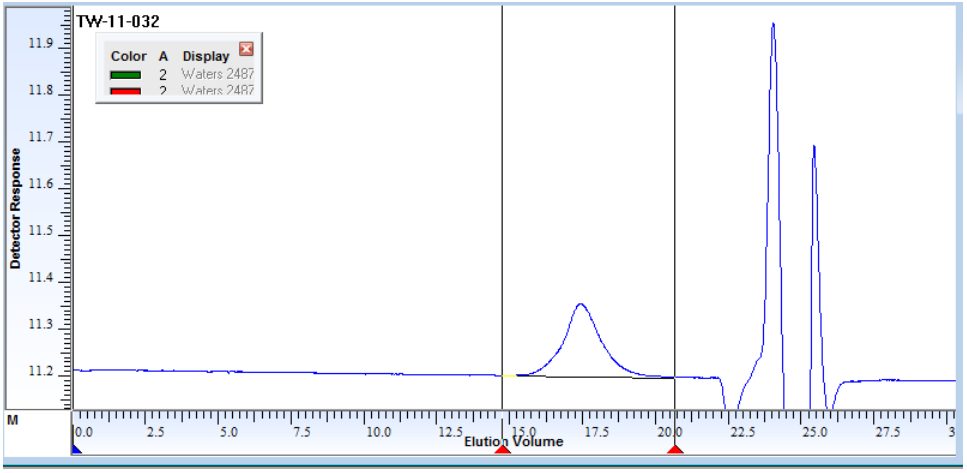


Figure S21. GPC trace of Table S1, entry f.

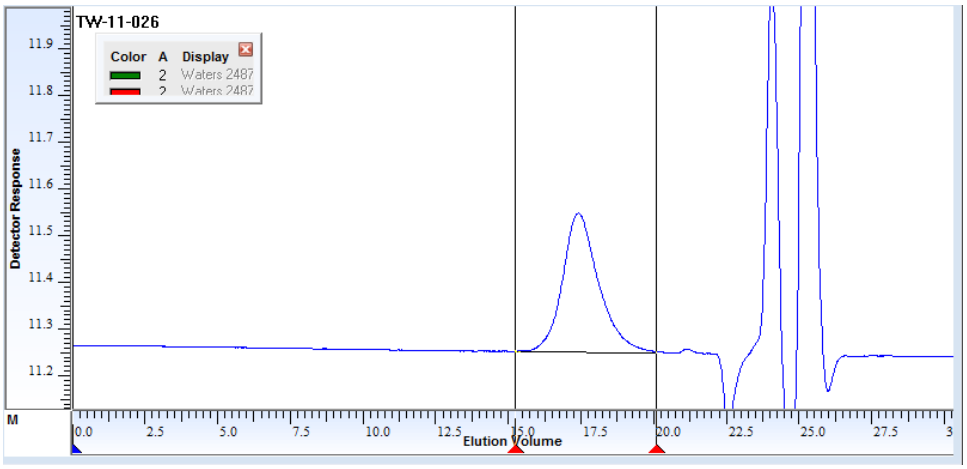


Figure S22. GPC trace of Table S1, entry g.

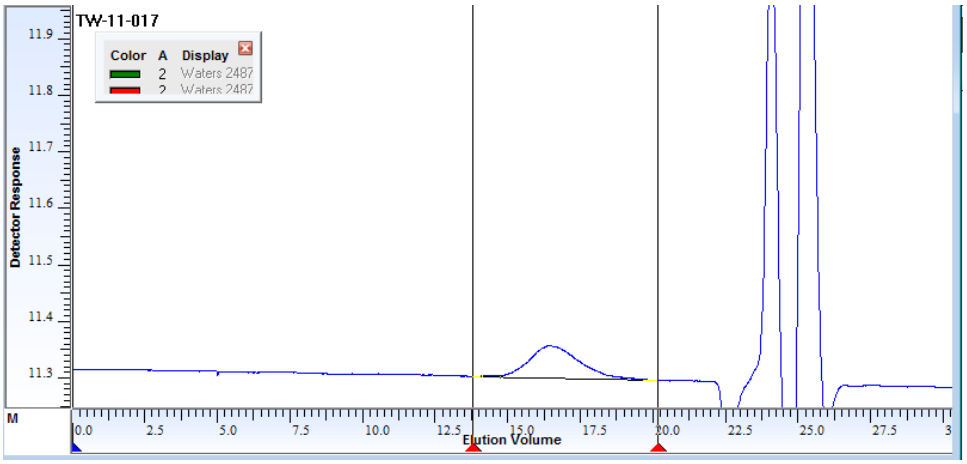


Figure S23. GPC trace of Table S1, entry h.

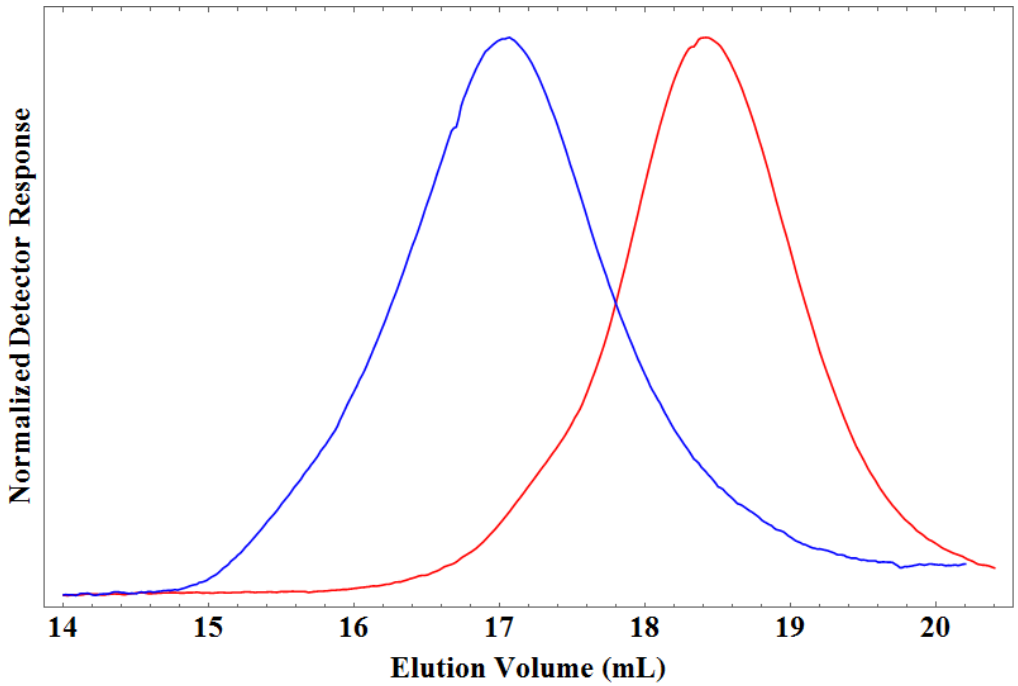


Figure S24. GPC traces for the Polyisoprene macro-RAFT Agent (red, M_n = 10 100, $Đ$ = 1.23) and chain extended block copolymer (blue, M_n = 26 000 , $Đ$ = 1.27). GPC traces were collected using THF doped with 10 mM Li[NTf_2] as the eluent.

Thermal Gravimetric Analysis Curves

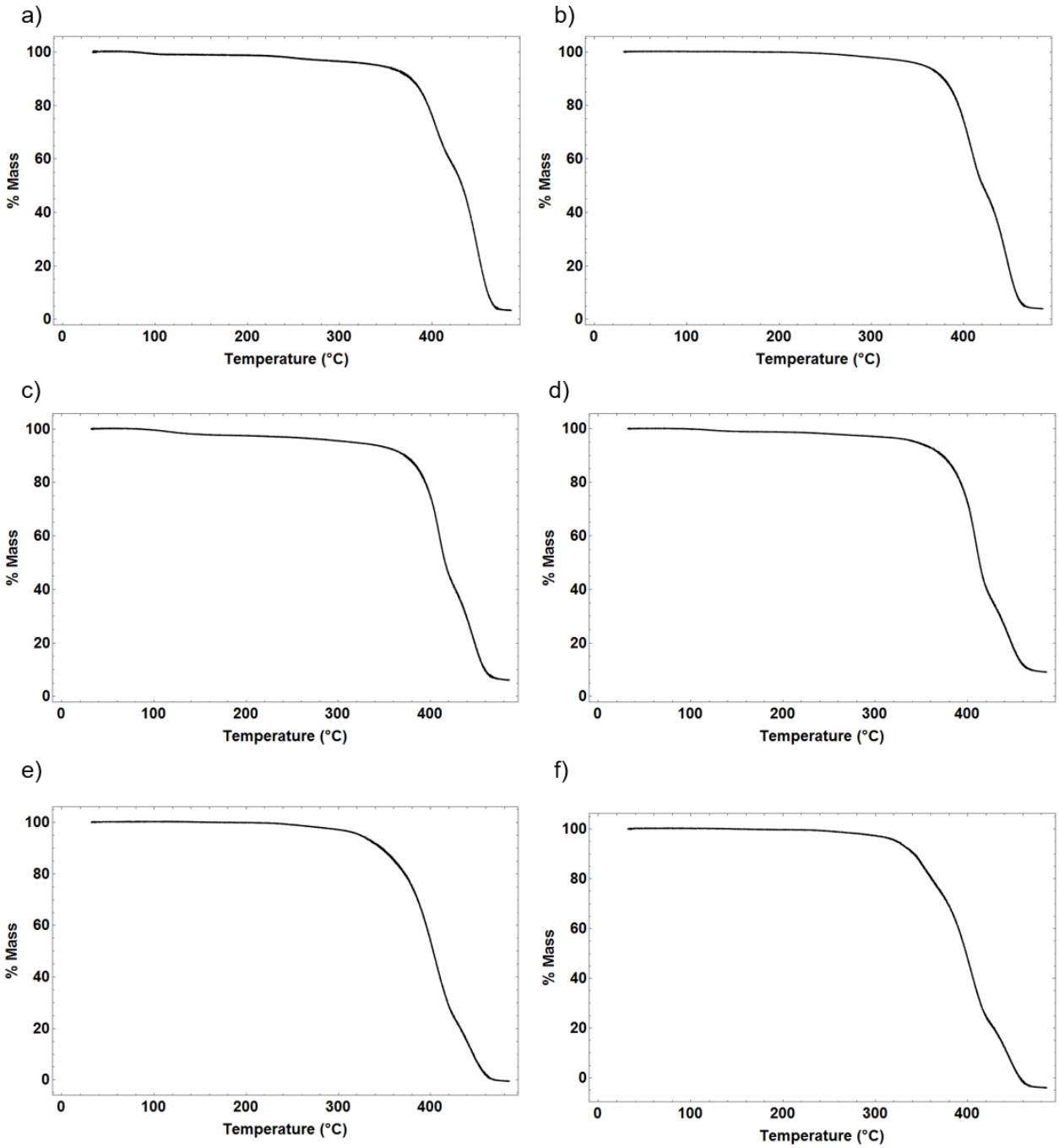


Figure S25. TGA curves of entries a-f (Table S1).

4. Differential Scanning Calorimetry Data

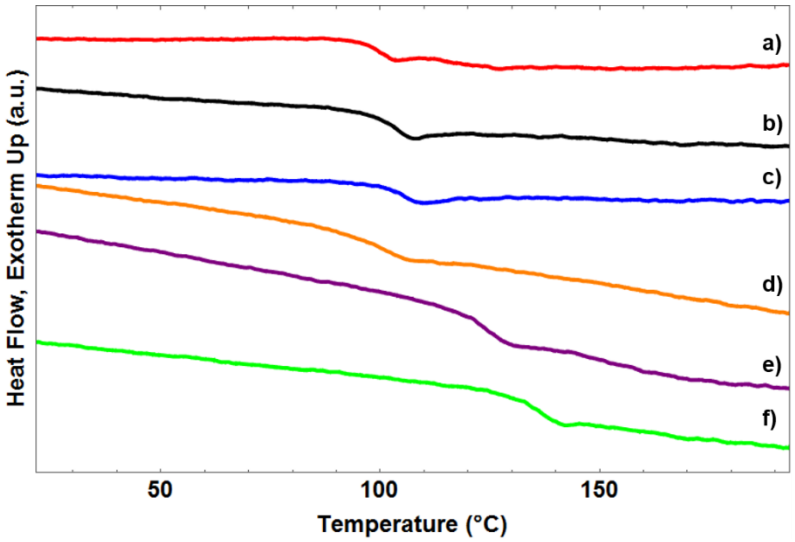


Figure S26. DSC curves of entries a-f from Table S1.

References

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(2) Dudek, S. P.; Sikes, H. D.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2001**, *123*, 8033-8038.
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