Gradient Copolymer Prepared from Alternating Ring-Opening Metathesis of Three Monomers

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Table S1. Molar feed ratios used to monitor kinetics of **1a**-*alt*-**2** and **1b**-*alt*-**2** gradient copolymerization.

Entry	Feed ratio **1a** /**1b**	**1a** mmol/ mg/ volume (µL)	**1b** mmol/mg/volume (µL)	**2** mmol/ µL	**G3** mmol/ µL
1	0.9/ 0.1	0.185/ 35.8 / 138	0.0206/ 5.5/ 12.1	0.206 / 20	0.0103/ 36.3
2	0.8/ 0.2	0.165 / 31.9 / 123	0.0412 / 11.0 / 24.2	0.206 / 20	"
3	0.7/ 0.3	0.144 / 27.8 / 107	0.0618 / 16.5 / 36.4	0.206 / 20	"
4	0.6/ 0.4	0.124 / 23.9 / 92	0.0824 / 22.0 / 48.5	0.206 / 20	"
5	0.5/ 0.5	0.103 / 19.9 / 77	0.103 / 27.5 / 60.6	0.206/ 20	"
6	0.4/ 0.6	0.0824 / 15.9 / 61	0.124 / 33.0 / 72.8	0.206 / 20	"
7	0.3/ 0.7	0.0618 / 11.9 / 46	0.144 / 38.5 / 85	0.206 / 20	"
8	0.2/ 0.8	0.0412 / 7.96 / 31	0.165 / 44.1 / 97	0.206 / 20	"
9	0.1/ 0.9	0.0206 / 3.98 / 15.3	0.185 / 49.4 / 109	0.206 / 20	"

Table S2. Parameters determined for **1a**-*alt*-**2** and **1b**-*alt*-**2** in gradient copolymerization of **1a**, **1b**, and **2**.

entry	F_{1a}[a]	F_{1a-2}[b]	F_{1b-2}[b]	Z_{1a}[c]	Z_{1b}[c]	Z[d]	F[e]	G[f]	H[g]	η[h]	ξ[i]
1	0.9	0.961	0.039	0.766	0.392	2.918	24.64	8.099	2.892	2.642	0.944
2	0.8	0.919	0.081	0.658	0.387	2.192	11.34	4.719	2.360	1.863	0.932
3	0.7	0.894	0.106	0.585	0.332	2.179	8.433	3.410	1.775	1.751	0.911
4	0.6	0.842	0.158	0.5	0.271	2.192	5.329	1.974	1.108	1.541	0.865
5	0.5	0.744	0.256	0.753	0.518	1.916	2.906	0.995	0.792	1.031	0.821
6	0.4	0.656	0.344	0.532	0.342	1.814	1.906	0.500	0.579	0.664	0.770
7	0.3	0.412	0.588	0.791	0.399	3.074	0.701	-0.100	0.074	-0.394	0.300
8	0.2	0.258	0.742	0.813	0.458	2.737	0.348	-0.238	0.046	-1.086	0.211
9	0.1	0.055	0.945	0.816	0.51	2.373	0.058	-0.397	0.010	-2.165	0.056

[a] Molar feed ratio of **1a**. [b]Molar fraction of **1a-2** in copolymer determined by ^{1}H NMR spectroscopy. [c]Monomer conversion determined by ^{1}H NMR spectroscopy, [d]$Z = \log(1–\zeta_{1a})/\log(1–\zeta_{1b})$, [e]$F = F_{1a}/F_{1b}$, [f]$G' = (F-1)/Z$ where, [g]$H' = F/Z^2$, [h]$\eta = G'/(H'+\alpha)$ where $\alpha = (H'_{max} H'_{min})^{0.5}$, [i]$\xi = H'/(H'+\alpha)$.

Table S3. mean sequence length (μ) of each monomer and probability of finding *x* sequence $N_{1a-2}(x)$ and $N_{1b-2}(x)$

entry	**f_{1a}**	**f_{1b}**	**Mean sequence length μ_{1a-2}**	**Mean sequence length μ_{1b-2}**	**$N_{1a-2}(1)$: $N_{1b-2}(1)$**	**N_{1a-2} (2): N_{1b-2} (2)**	**N_{1a-2} (3): N_{1b-2} (3)**
1	0.9	0.1	20.5	1.04	nd[a]	nd	nd
2	0.8	0.2	9.68	1.09	nd	nd	nd
3	0.7	0.3	6.06	1.15	nd	nd	nd
4	0.6	0.4	4.26	1.25	nd	nd	nd
5	0.5	0.5	3.17	1.37	.32 / .74	.21 / .20	.15 / .05
6	0.4	0.6	2.45	1.56	nd	nd	nd
7	0.3	0.7	1.93	1.86	.52 / .54	.25 / .25	.12 / .11
8	0.2	0.8	1.54	2.48	nd	nd	nd
9	0.1	0.9	1.24	4.33	nd	nd	nd

[a] ”nd” stands for not determined.

$$\mu_{\mathbf{1a\text{-}2}} = 1 + r_{\mathbf{1a\text{-}2}}\,(f_{\mathbf{1a}} / f_{\mathbf{1b}}),\ \mu_{\mathbf{1b\text{-}2}} = 1 + r_{\mathbf{1b\text{-}2}}\,(f_{\mathbf{1a}} / f_{\mathbf{1b}})$$

$$N_{\mathbf{1a\text{-}2}}(x) = P_{11}^{(x-1)} .\ (1 - P_{11});\ N_{\mathbf{1b\text{-}2}}(x) = P_{22}^{(x-1)} .\ (1 - P_{22})$$

$$P_{11} = r_{\mathbf{1a\text{-}2}} / (r_{\mathbf{1a\text{-}2}} + (f_{\mathbf{1b}} / f_{\mathbf{1a}});\ P_{22} = r_{\mathbf{1b\text{-}2}} / (r_{\mathbf{1b\text{-}2}} + (f_{\mathbf{1a}} / f_{\mathbf{1b}}),$$

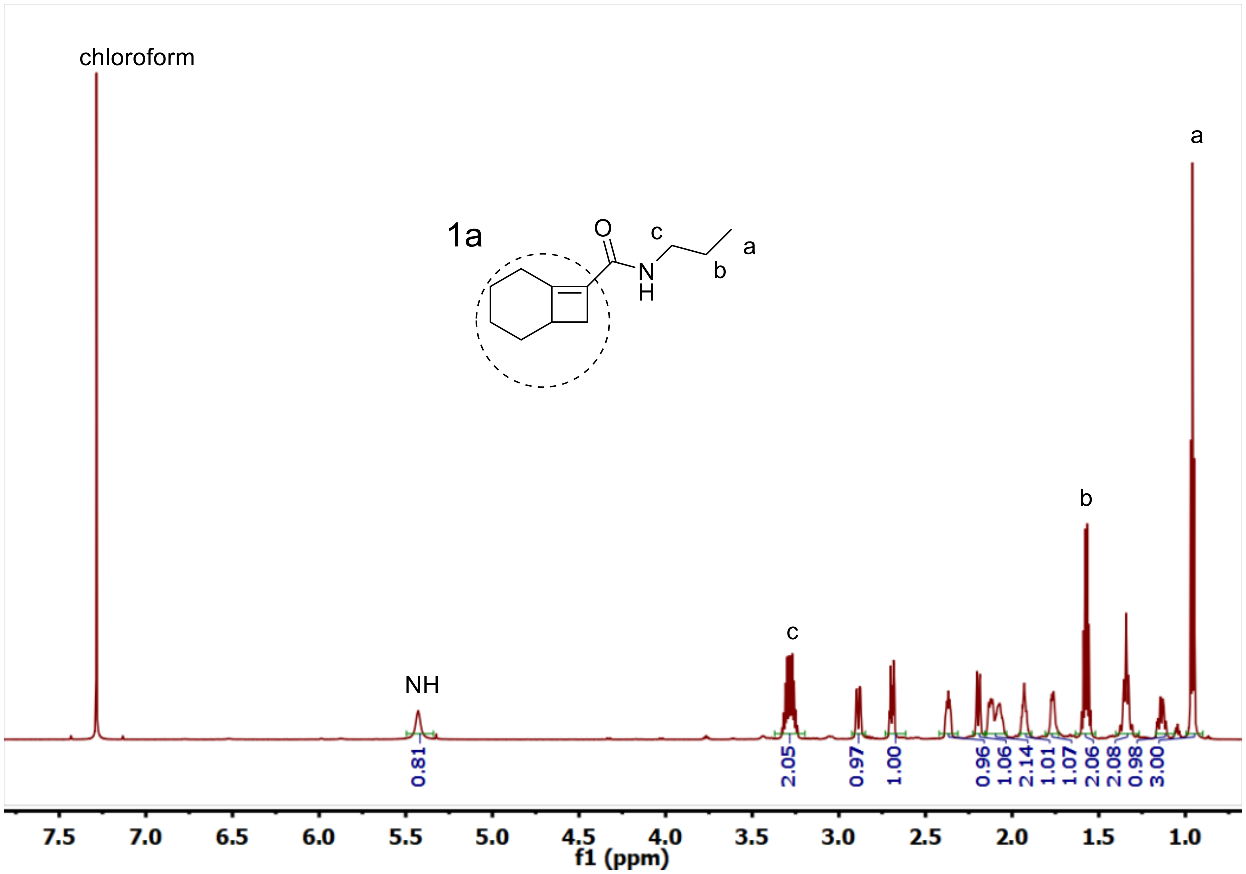


Fig. S1 ^{1}H NMR ($CDCl_3$) spectrum of monomer **1a** with side chain protons assigned.

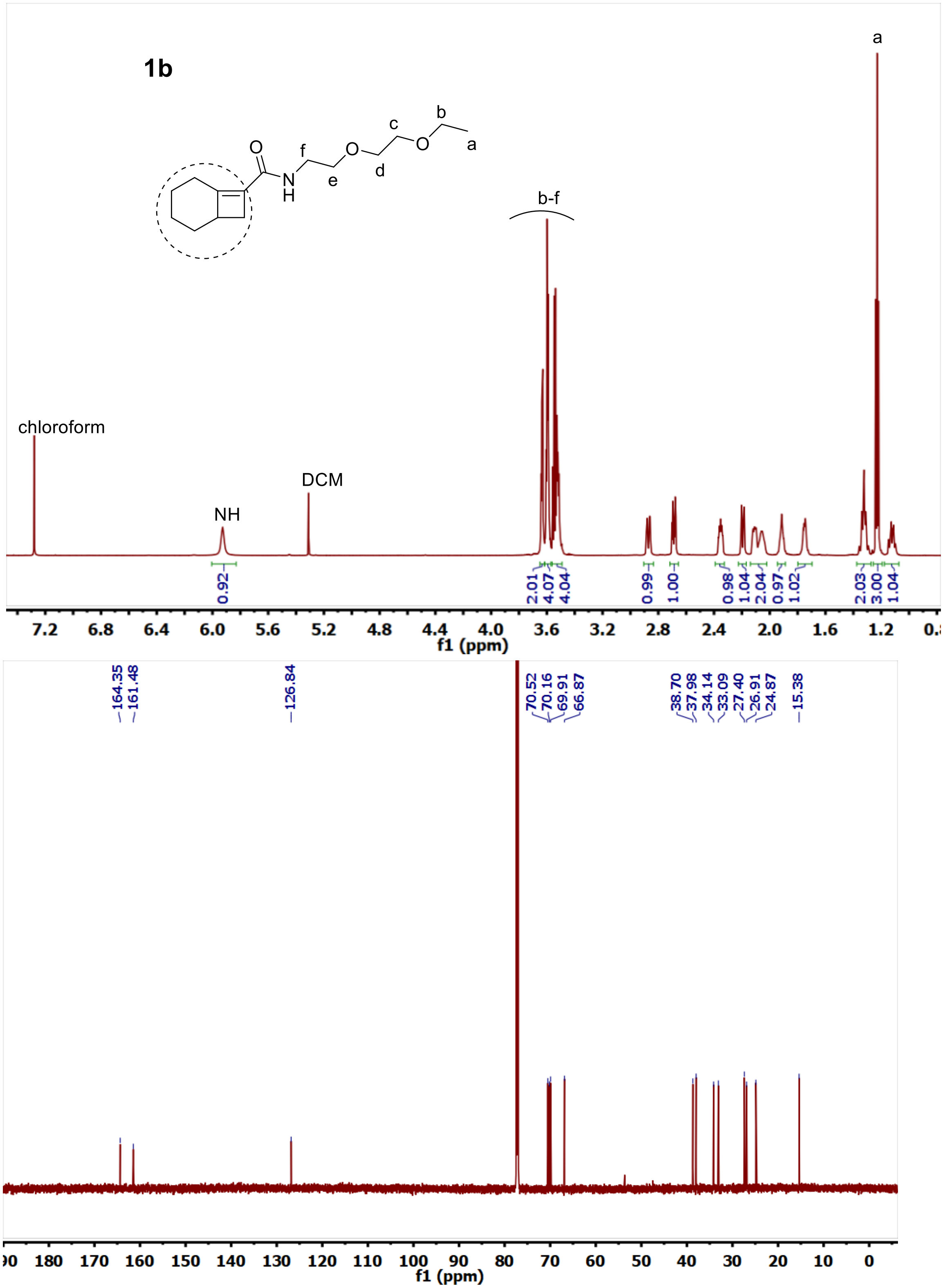


Fig. S2 ^{1}H NMR spectrum (top) with side chain protons assigned and ^{13}C NMR spectrum (bottom) of monomer **1b**.

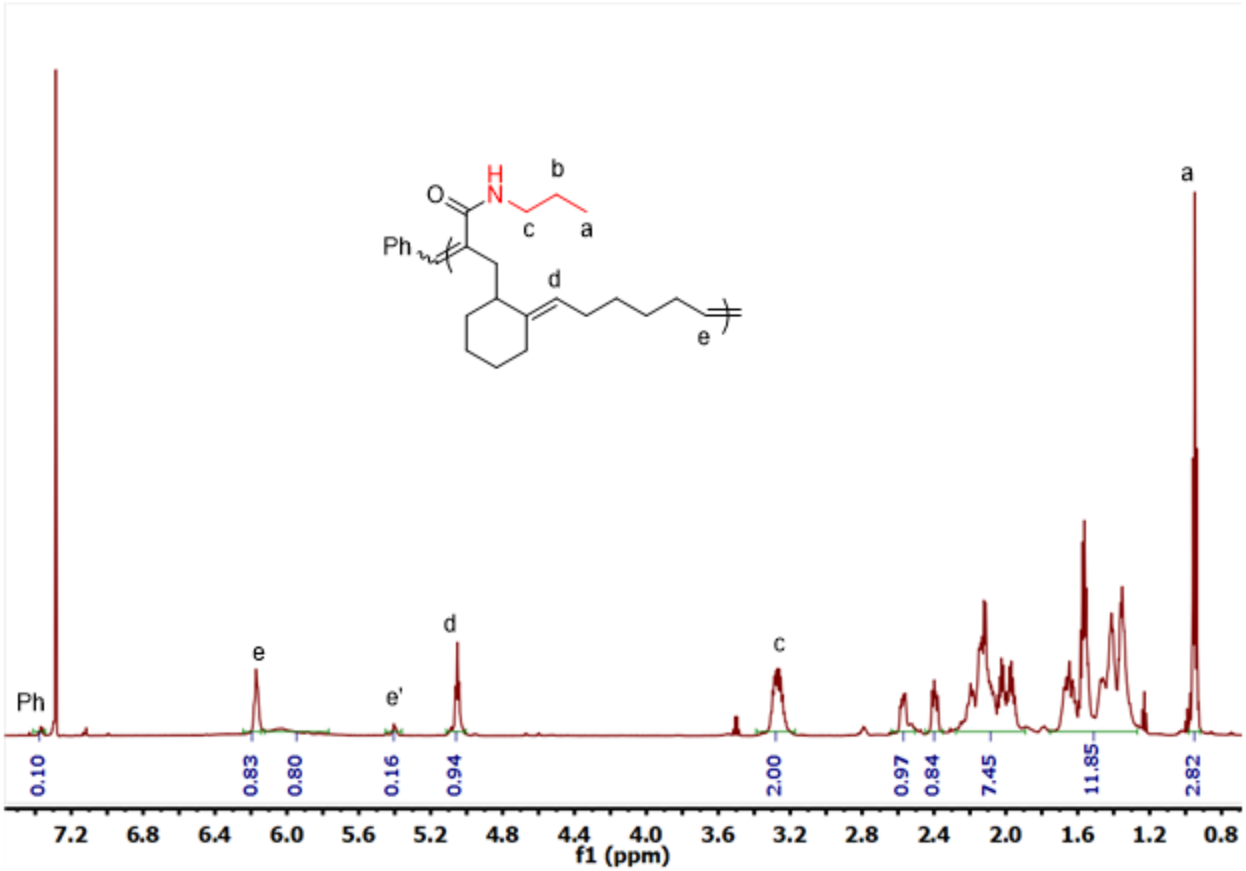


Fig. S3 ^{1}H NMR ($CDCl_3$) spectrum of precipitated poly(**1a**-*alt*-**2**)$_{20}$, **P1.**

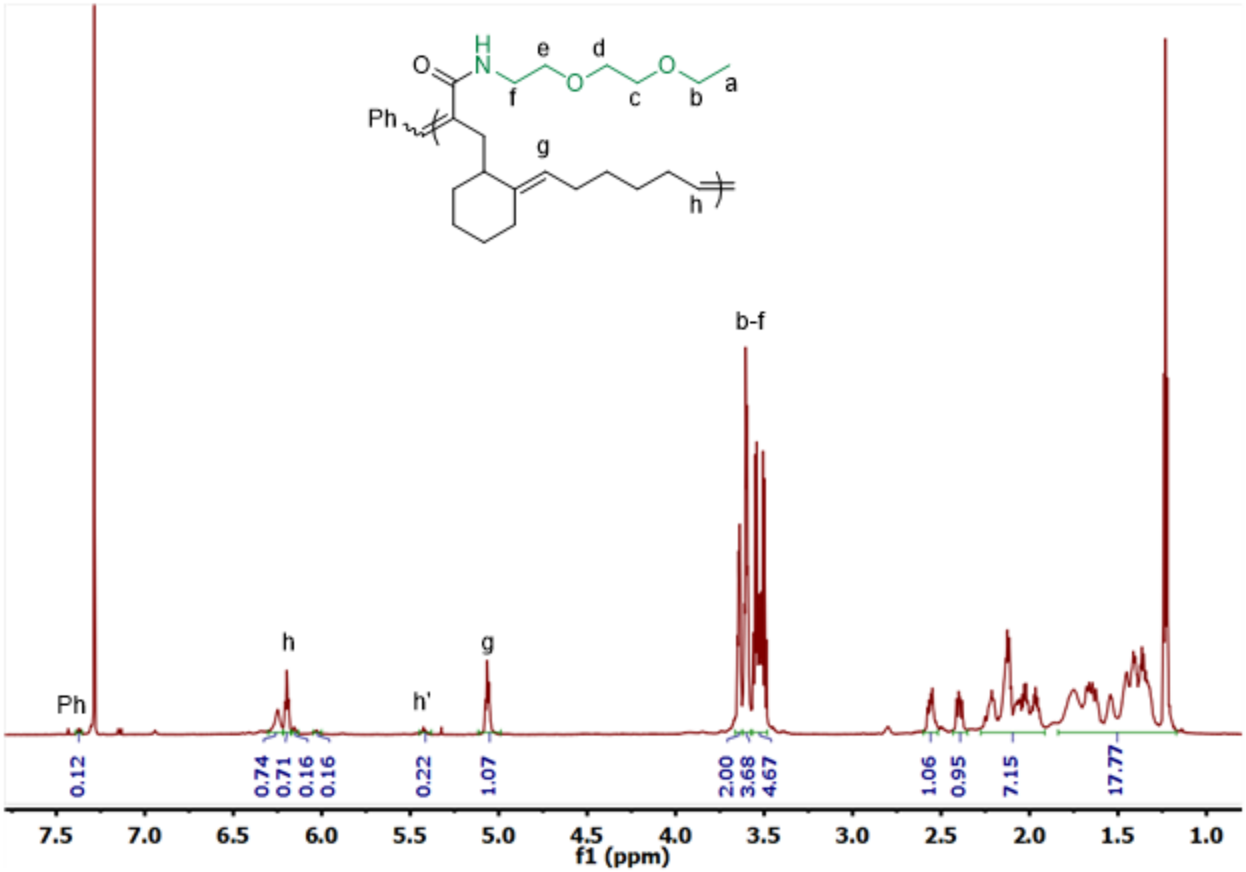


Fig. S4 ^{1}H NMR ($CDCl_3$) spectrum of precipitated poly(**1b**-*alt*-**2**)$_{20}$, **P2**.

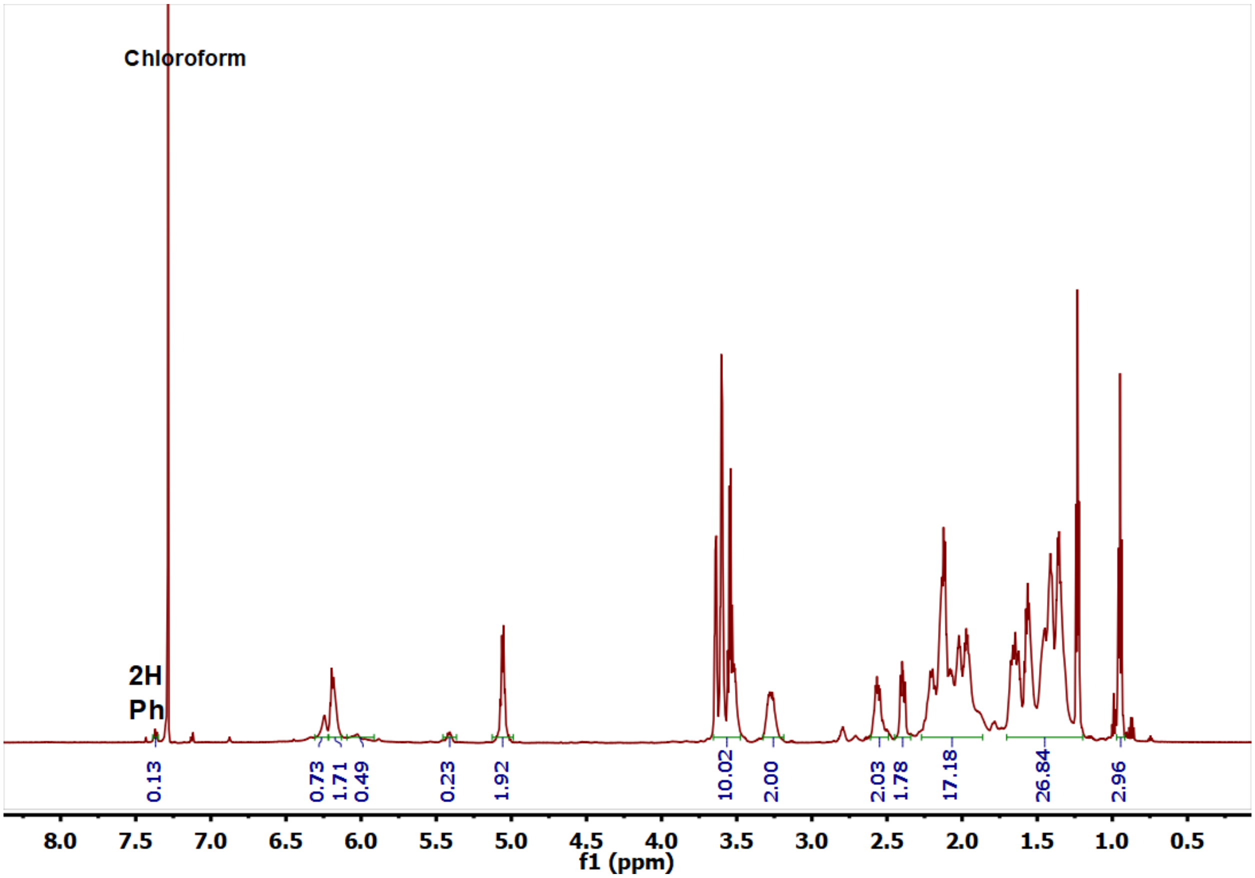


Fig. S5 ^{1}H NMR ($CDCl_3$) spectrum of precipitated diblock copolymer, **P3.**

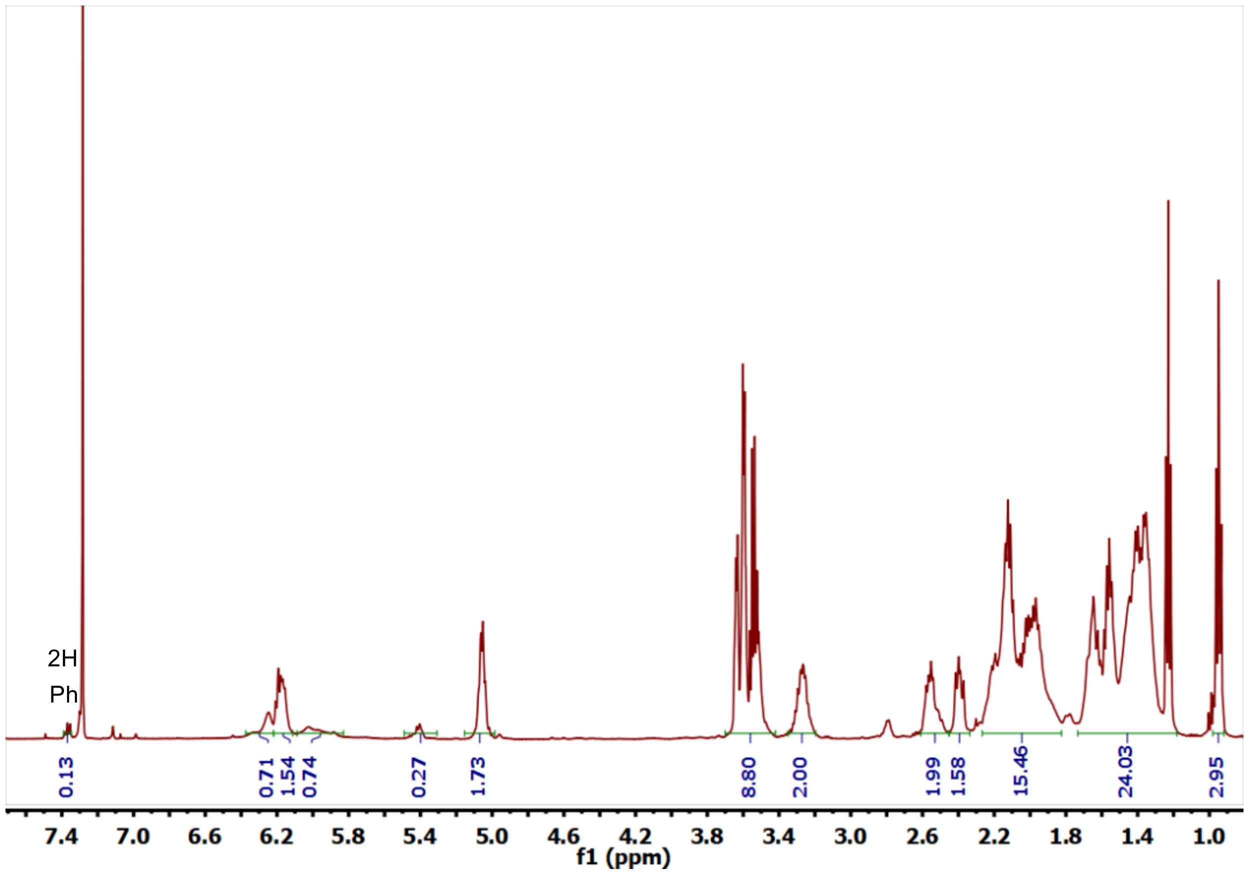


Fig. S6 ^{1}H NMR ($CDCl_3$) spectrum of precipitated hexablock copolymer, **P4.**

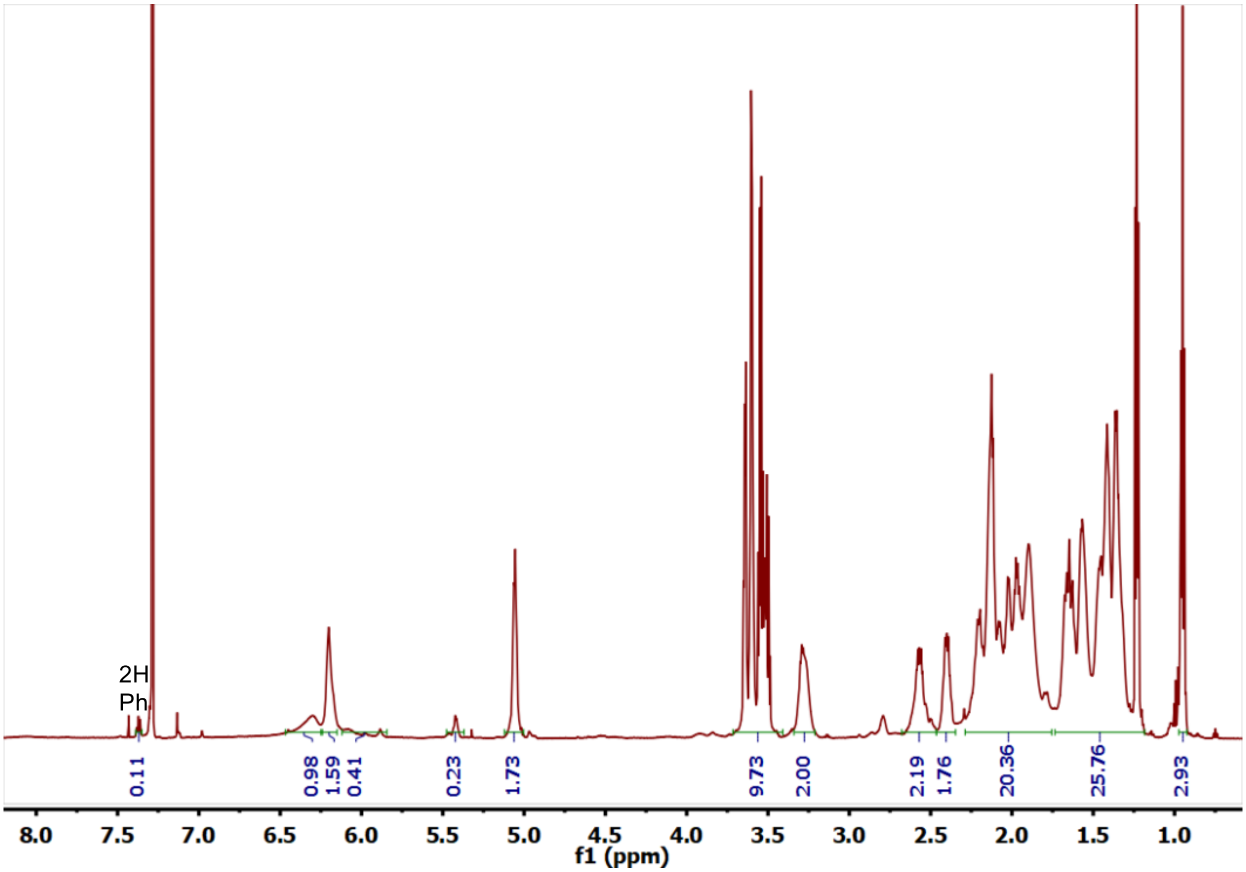


Fig. S7 ^{1}H NMR ($CDCl_3$) spectrum of precipitated gradient copolymer, **P5.**

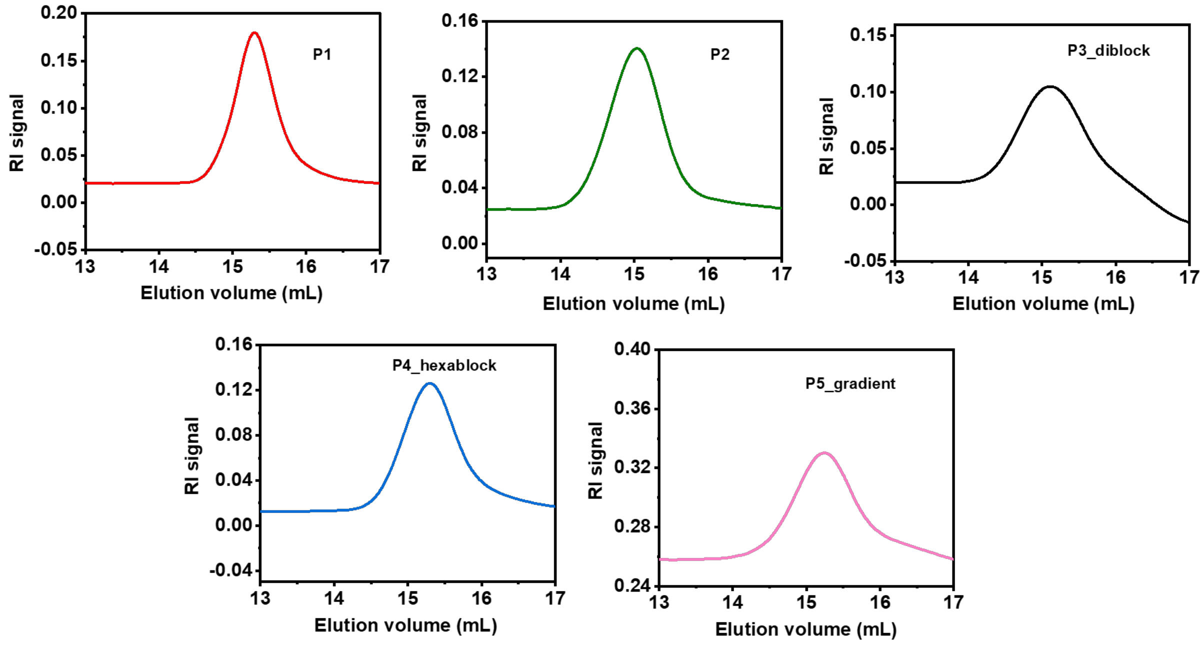


Fig. S8 GPC chromatograms of copolymers P1-P5.

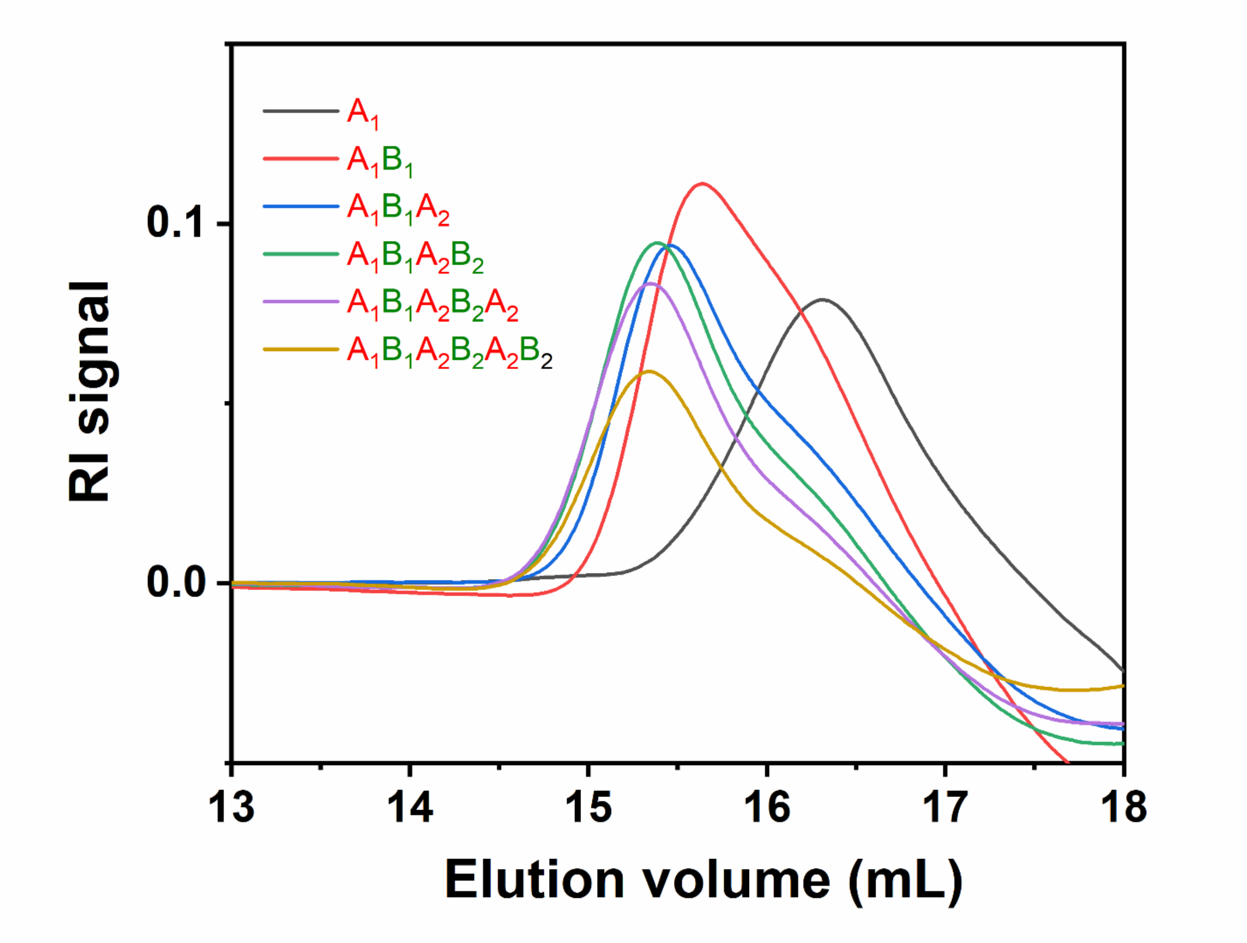
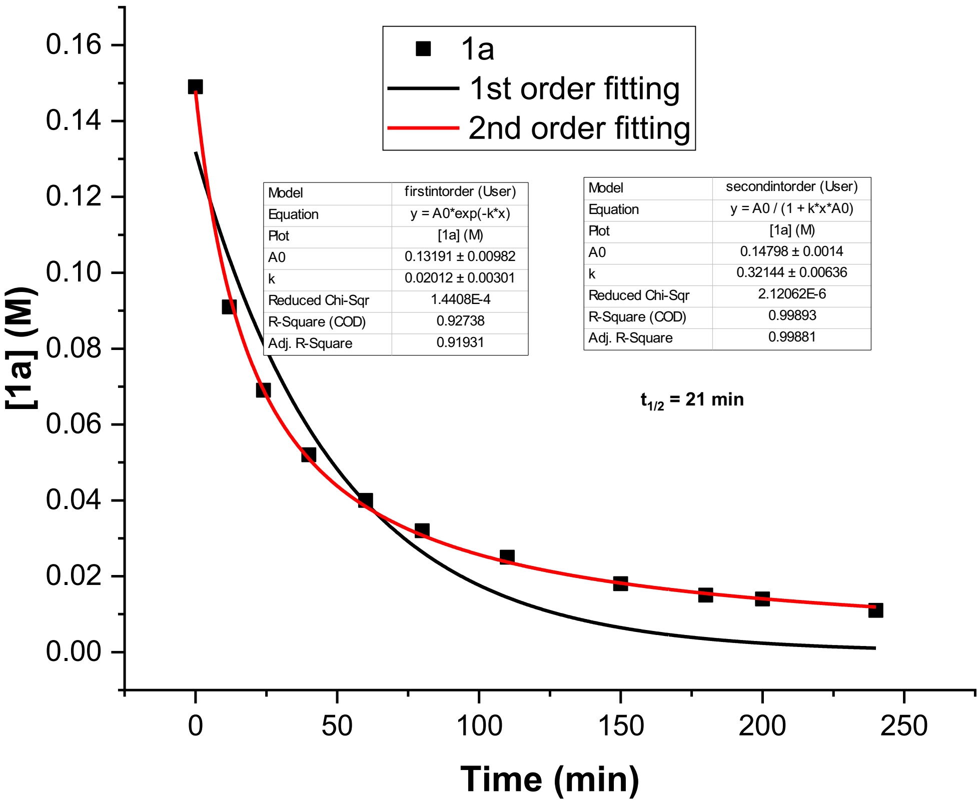


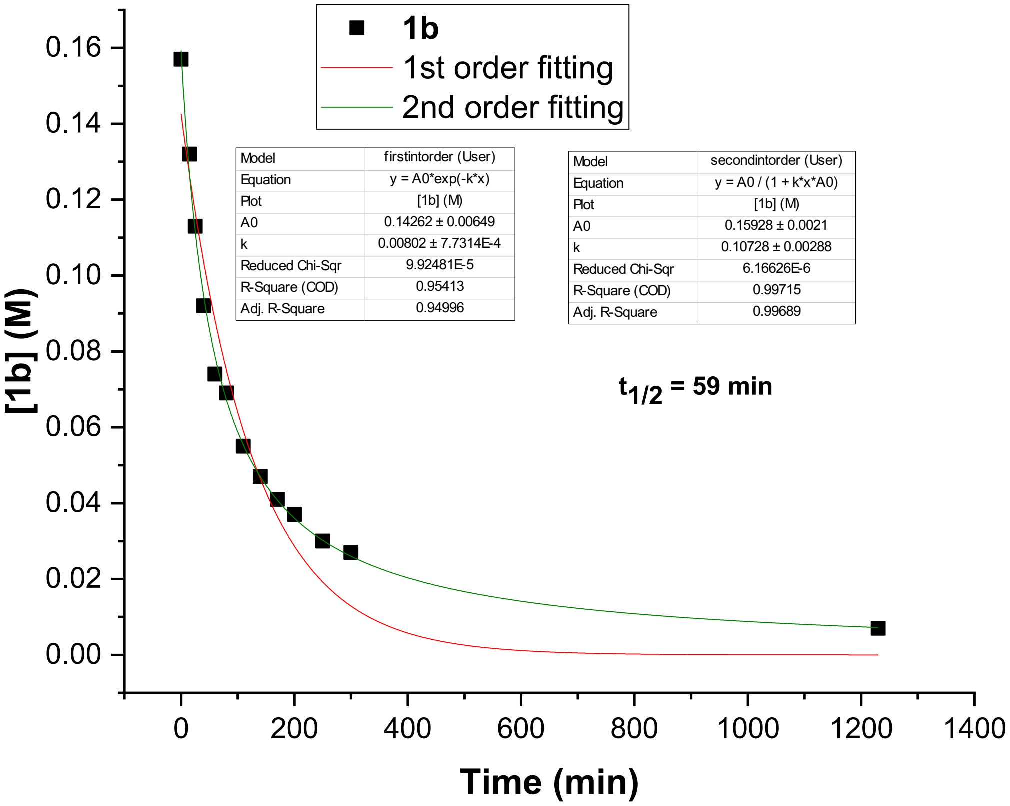
Fig. S9 Multi-step synthesis of hexablock copolymer **P4** prepared by sequential addition. A_1 and B_1 refer to (**1a**-*alt*-**2**)$_4$ and (**1b**-*alt*-**2**)$_4$ respectively. A_2 and B_2 refer to (**1a**-*alt*-**2**)$_3$ and (**1b**-*alt*-**2**)$_3$ respectively.



Model	firstintorder (User)
Equation	y = A0*exp(-k*x)
Plot	[1a] (M)
A0	0.13191 ± 0.00982
k	0.02012 ± 0.00301
Reduced Chi-Sqr	1.4408E-4
R-Square (COD)	0.92738
Adj. R-Square	0.91931

Model	secondintorder (User)
Equation	y = A0 / (1 + k*x*A0)
Plot	[1a] (M)
A0	0.14798 ± 0.0014
k	0.32144 ± 0.00636
Reduced Chi-Sqr	2.12062E-6
R-Square (COD)	0.99893
Adj. R-Square	0.99881

Fig. S10 ROM of **1a** shows second-order kinetics with half-life of 21 min.



Model	firstintorder (User)
Equation	y = A0*exp(-k*x)
Plot	[1b] (M)
A0	0.14262 ± 0.00649
k	0.00802 ± 7.7314E-4
Reduced Chi-Sqr	9.92481E-5
R-Square (COD)	0.95413
Adj. R-Square	0.94996

Model	secondintorder (User)
Equation	y = A0 / (1 + k*x*A0)
Plot	[1b] (M)
A0	0.15928 ± 0.0021
k	0.10728 ± 0.00288
Reduced Chi-Sqr	6.16626E-6
R-Square (COD)	0.99715
Adj. R-Square	0.99689

Fig. S11 ROM of **1b** shows second-order kinetics with half-life of 59 min.

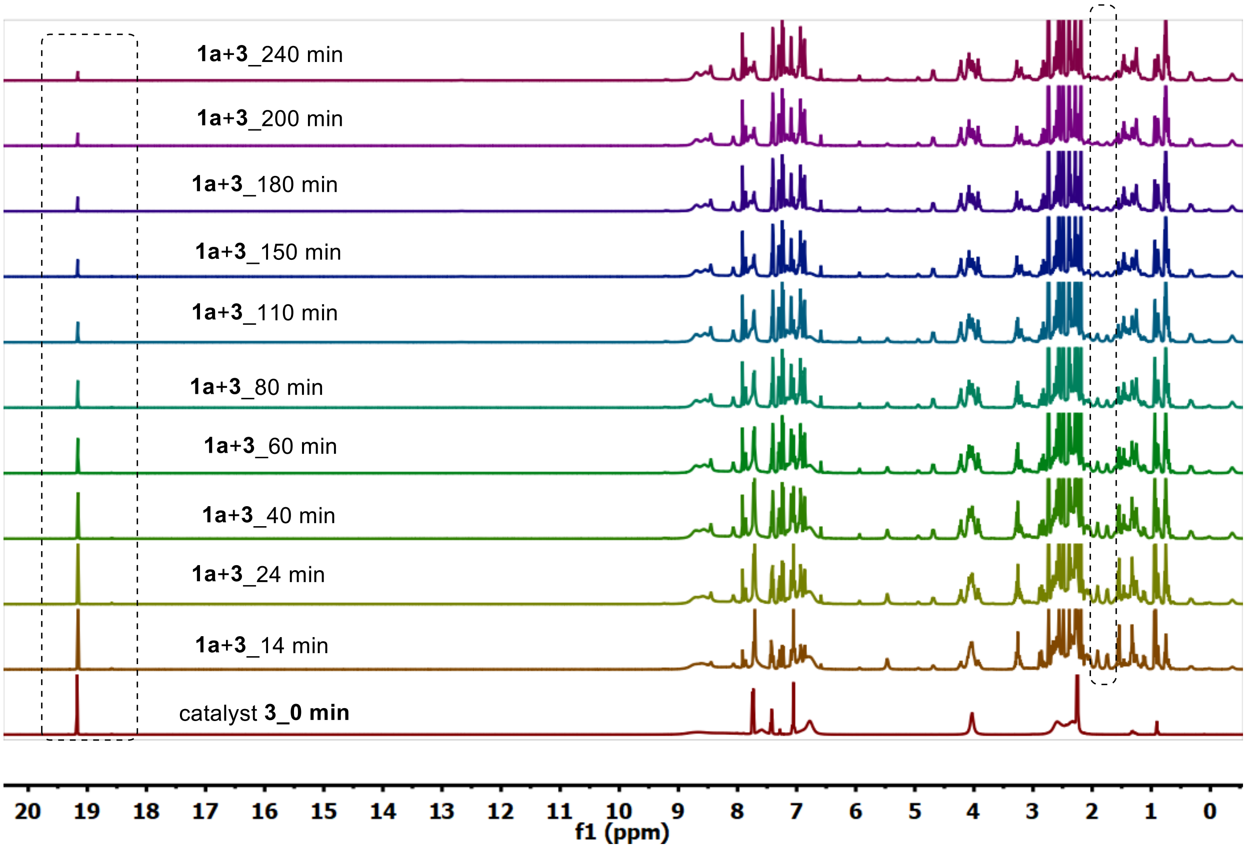


Fig. S12 ^{1}H NMR showing the kinetics of ROM reactivity of **1a** with **3**

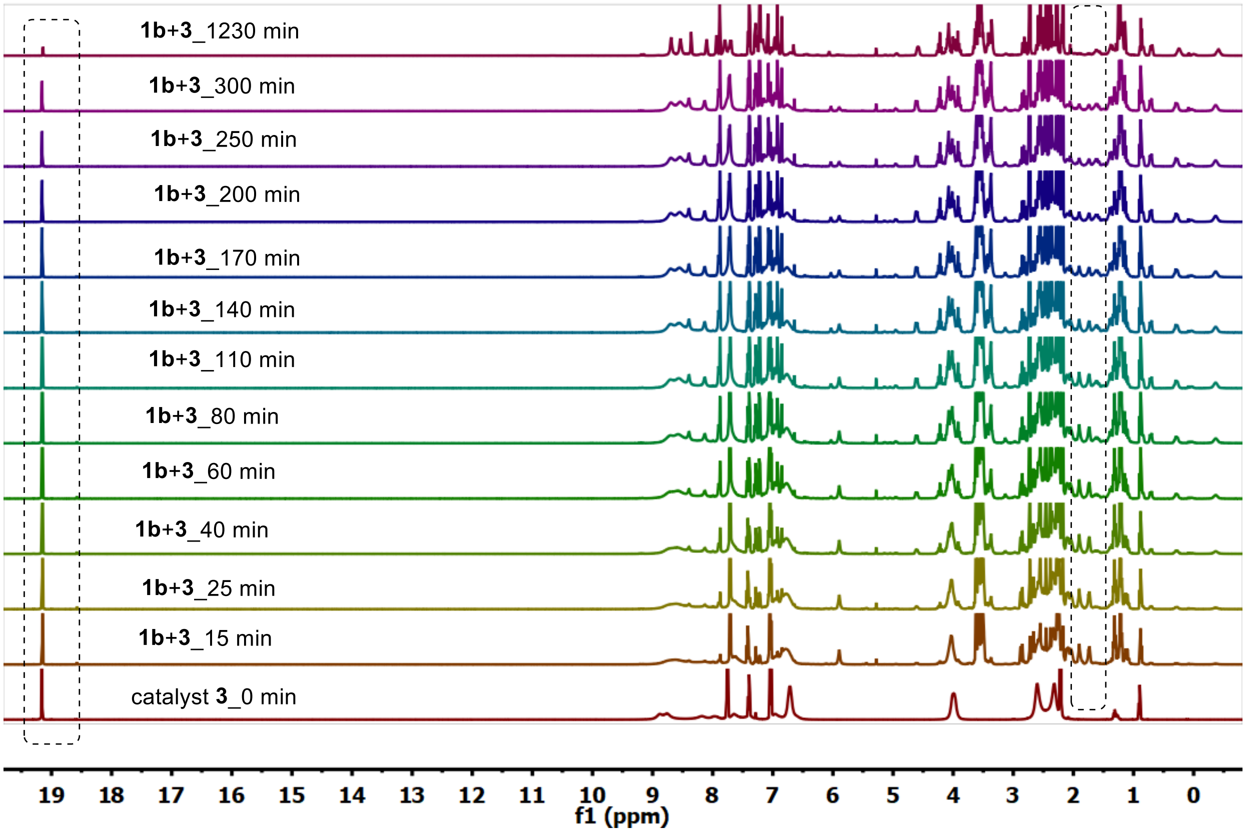


Fig. S13 ^{1}H NMR showing the kinetics of ROM reactivity of **1b** with **3**

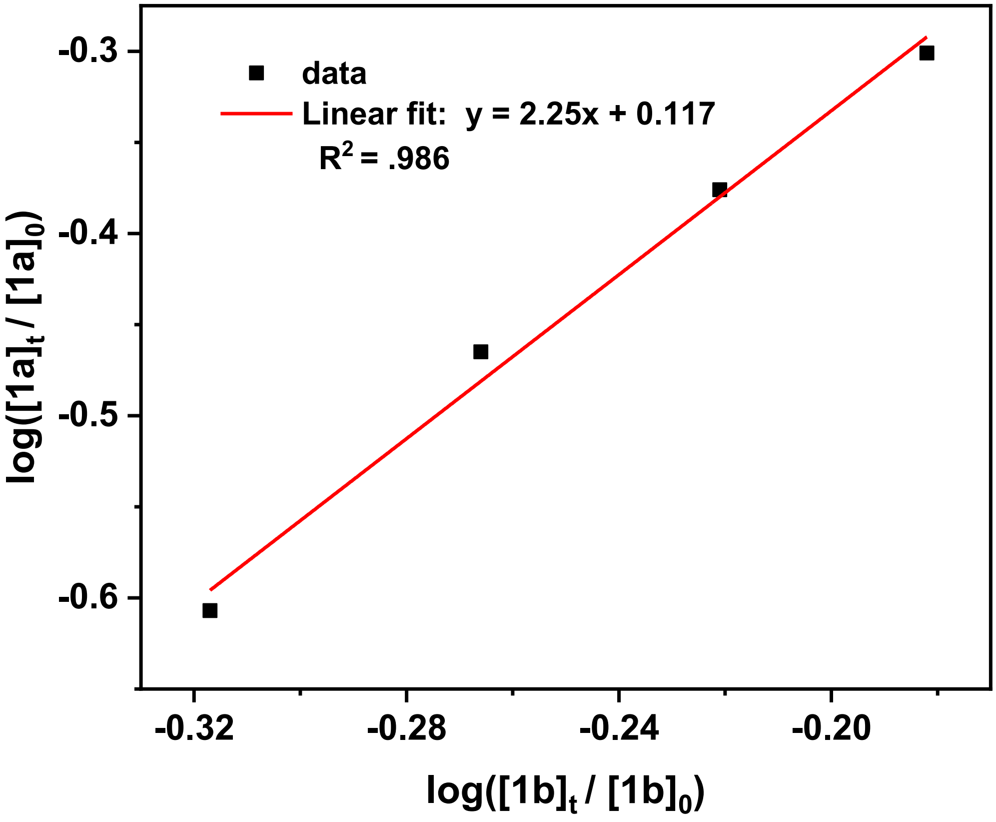


Fig. S14 Data from Table S2 fit to the Jaacks model (ref. 3). Reactivity ratios are $r_{1a\&2} = 2.25$, $r_{1b\&2} = 0.44$

With Jaacks model, reactivity ratios are estimated based on the assumption of ideal copolymerization, thus $r_1 \times r_2 = 1$

$d[M_1] / d[M_2] = r_1 ([M_1] / [M_2]$

$[M_1] / [M_{1,0}] = ([M_2] / [M_{2,0}])^{r1}$

$\text{Log} ([M_1] / [M_{1,0}]) = r_1 \log([M_2] / [M_{2,0}])$

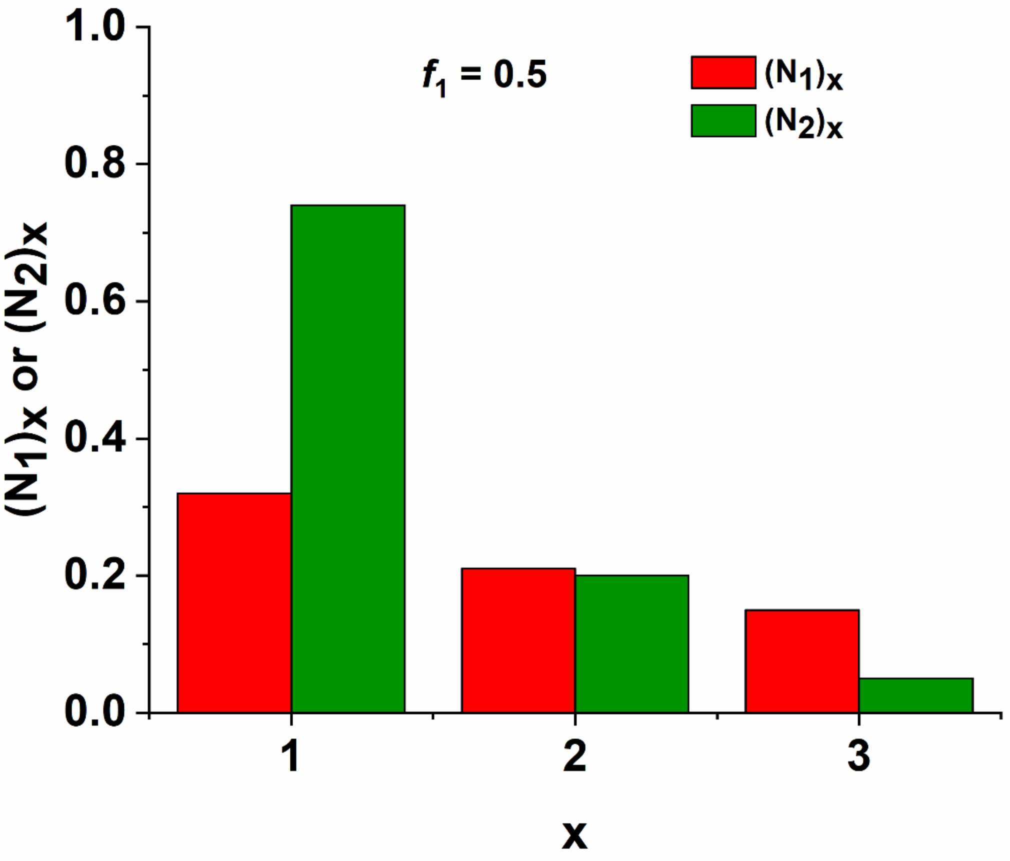


Fig. S15 Sequence-length distributions of the **1a**-*alt*-**2**/**1b**-*alt*-**2** copolymer, f_1 =0.5. x is the number of sequence-length of **1a**-*alt*-**2**/**1b**-*alt*-**2** unit. $(N_1)_x$ and $(N_2)_x$ is the probability of **1a**-*alt*-**2** and **1b**-*alt*-**2** unit in **1a**-*alt*-**2**/**1b**-*alt*-**2** copolymer, respectively.

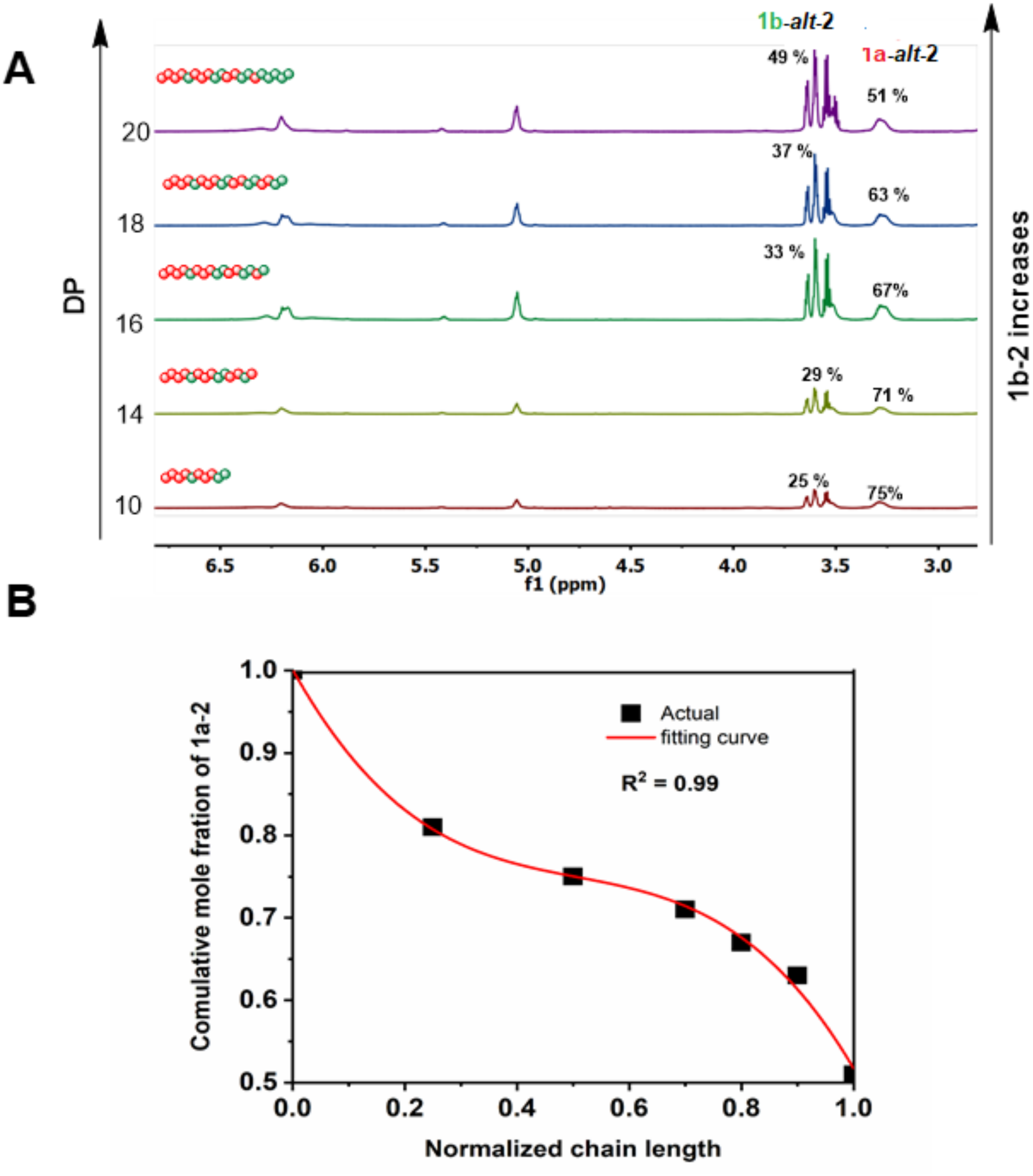


Fig. S16 Gradient microstructure of copolymer **P5** shown by ^{1}H-NMR (A) and the distribution plot (B).

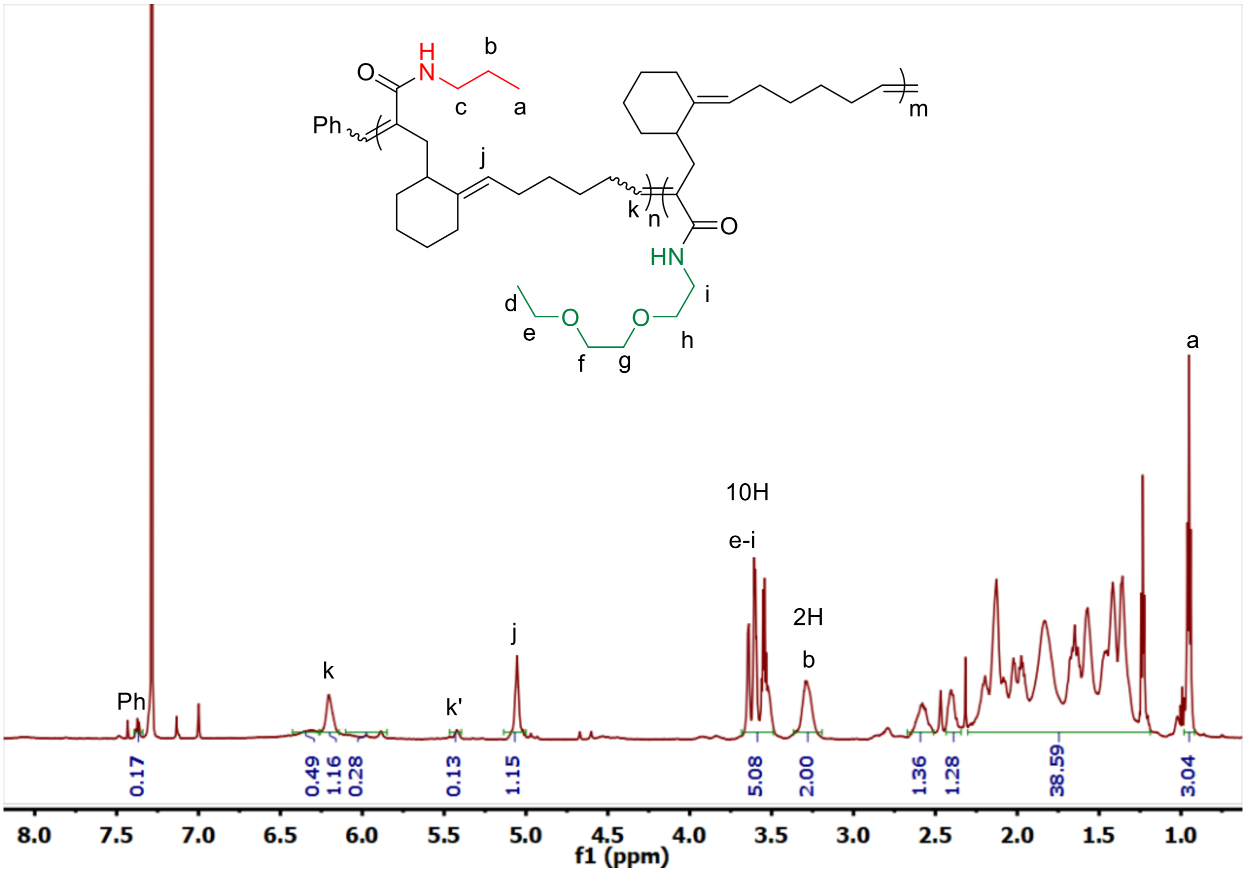


Fig. S17 ^{1}H NMR (CDCl$_3$) spectrum of poly(**1a**-*alt*-**2**)$_{10}$-grad-(**1b**-*alt*-**2**)$_{10}$ precipitated at 20 min during reaction (thus DP = 10). **10H and 2H are the expected number of protons.**

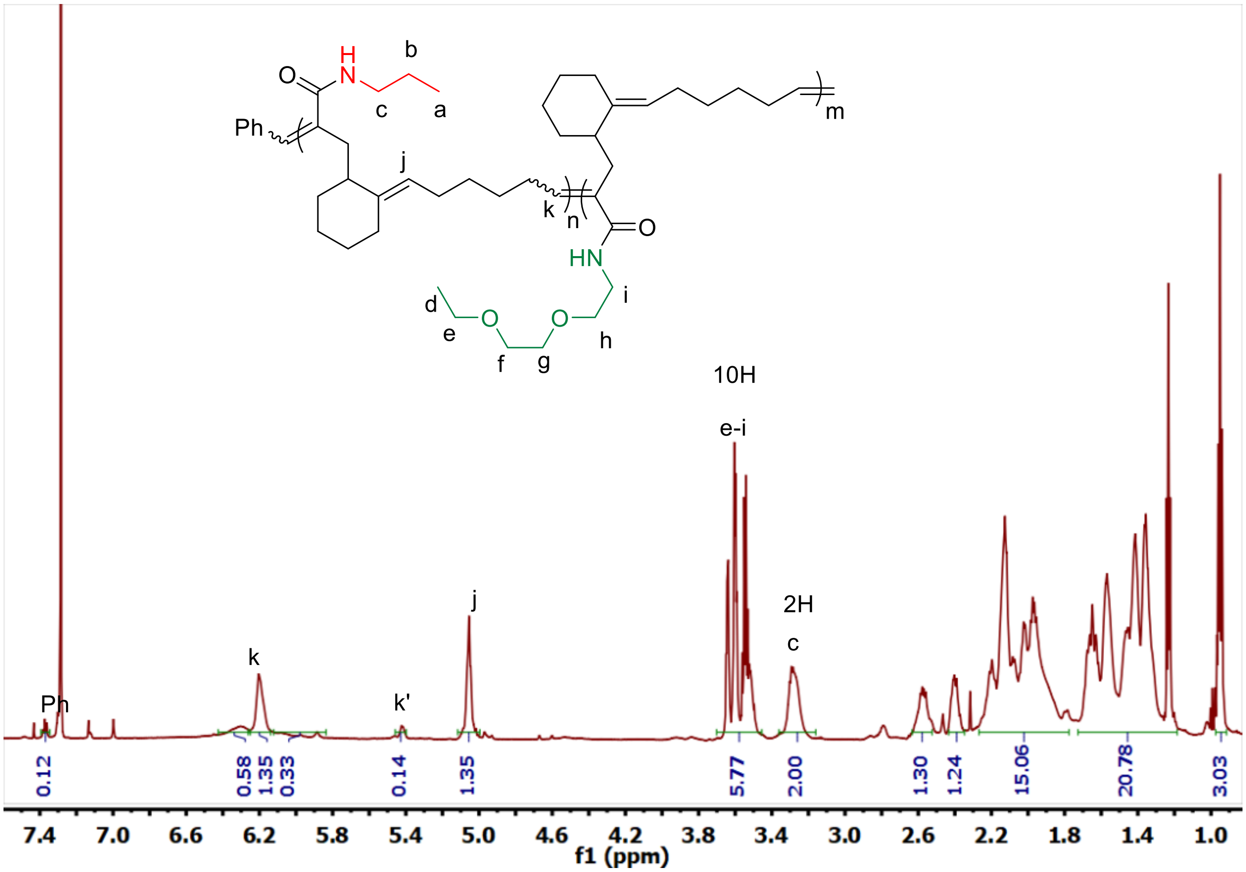


Fig. S18 ^{1}H NMR ($CDCl_3$) spectrum of poly(**1a**-*alt*-**2**)$_{10}$-grad-(**1b**-*alt*-**2**)$_{10}$ precipitated at 50 min during reaction (thus DP = 14). **10H and 2H are the expected number of protons.**

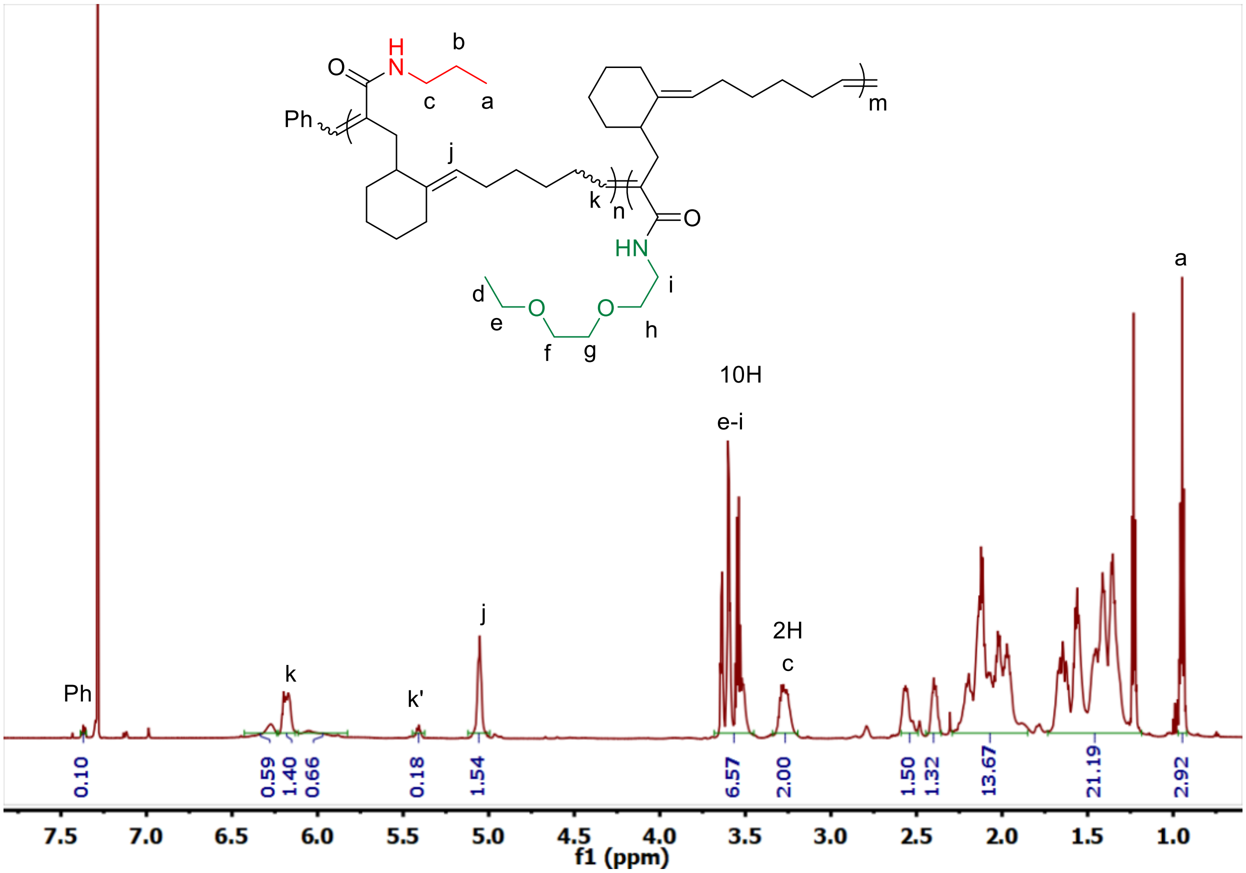


Fig. S19. ^{1}H NMR ($CDCl_3$) spectrum of poly(**1a**-*alt*-**2**)$_{10}$-grad-(**1b**-*alt*-**2**)$_{10}$ precipitated at 90 min during reaction (thus DP = 16). **10H and 2H are the expected number of protons.**

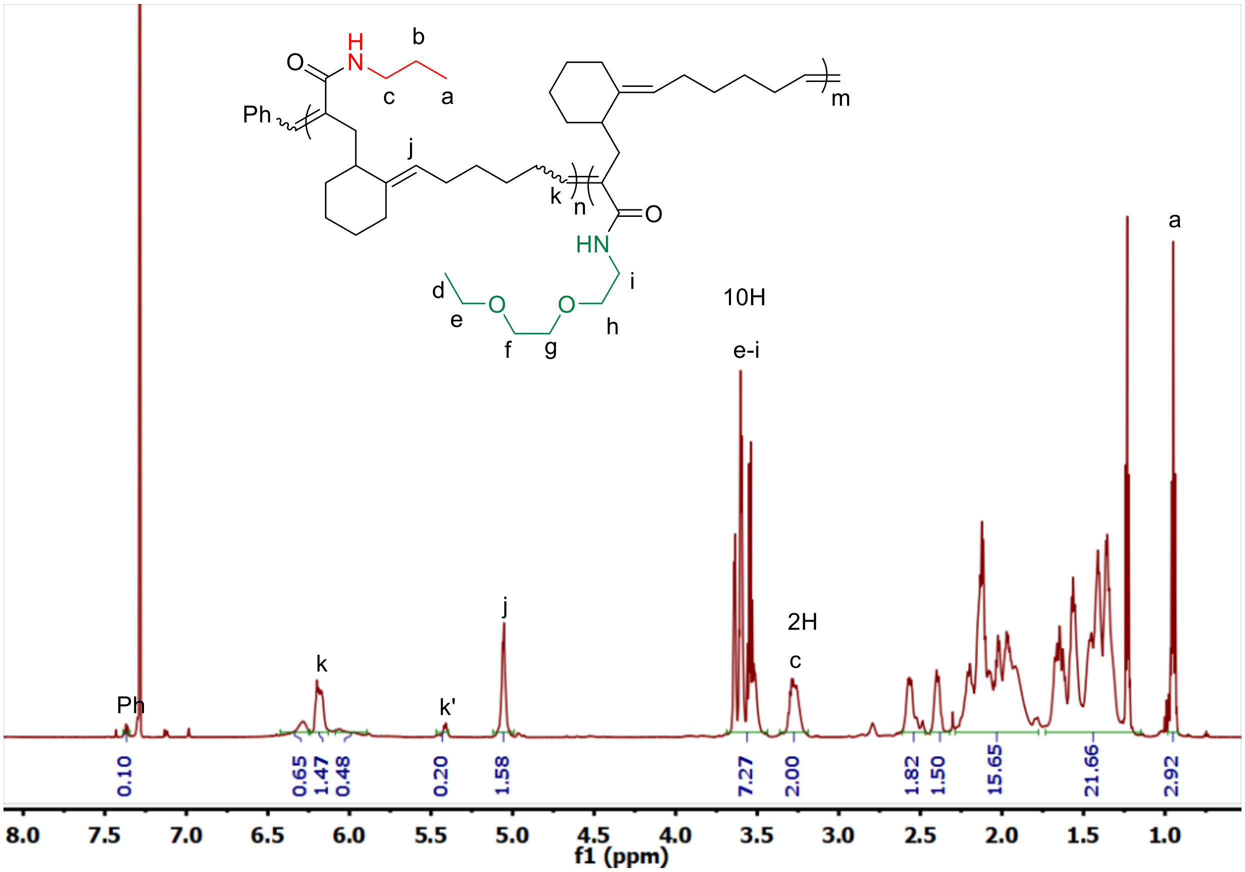


Fig. S20. ^{1}H NMR (CDCl$_3$) spectrum of poly(**1a**-*alt*-**2**)$_{10}$-grad-(**1b**-*alt*-**2**)$_{10}$ precipitated at 120 min during reaction (thus DP = 18). **10H and 2H are the expected number of protons.**

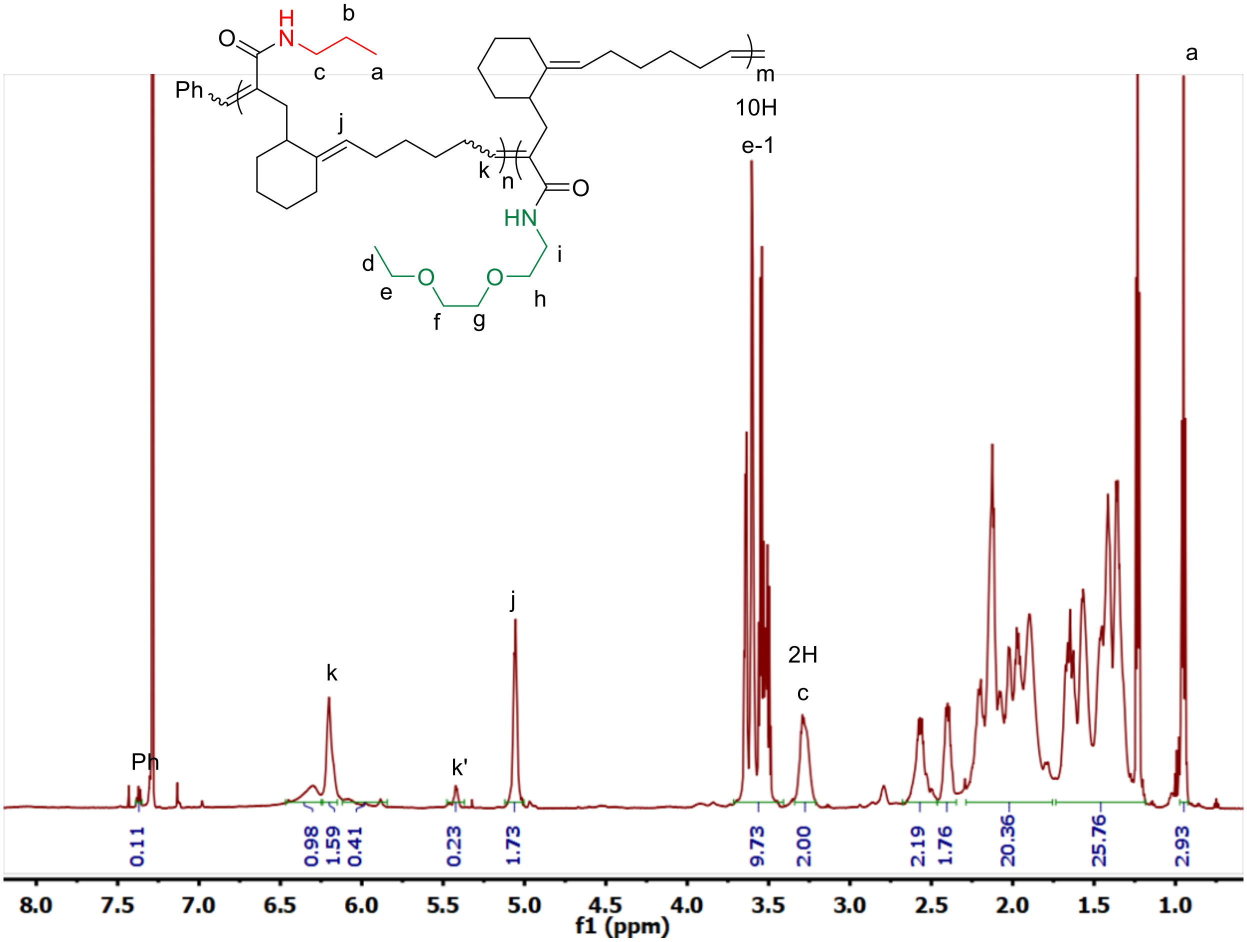


Fig. S21. ^{1}H NMR (CDCl$_3$) spectrum of poly(**1a**-*alt*-**2**)$_{10}$-grad-(**1b**-*alt*-**2**)$_{10}$ precipitated at 180 min during reaction (thus DP = 20). **10H and 2H are the expected number of protons.**

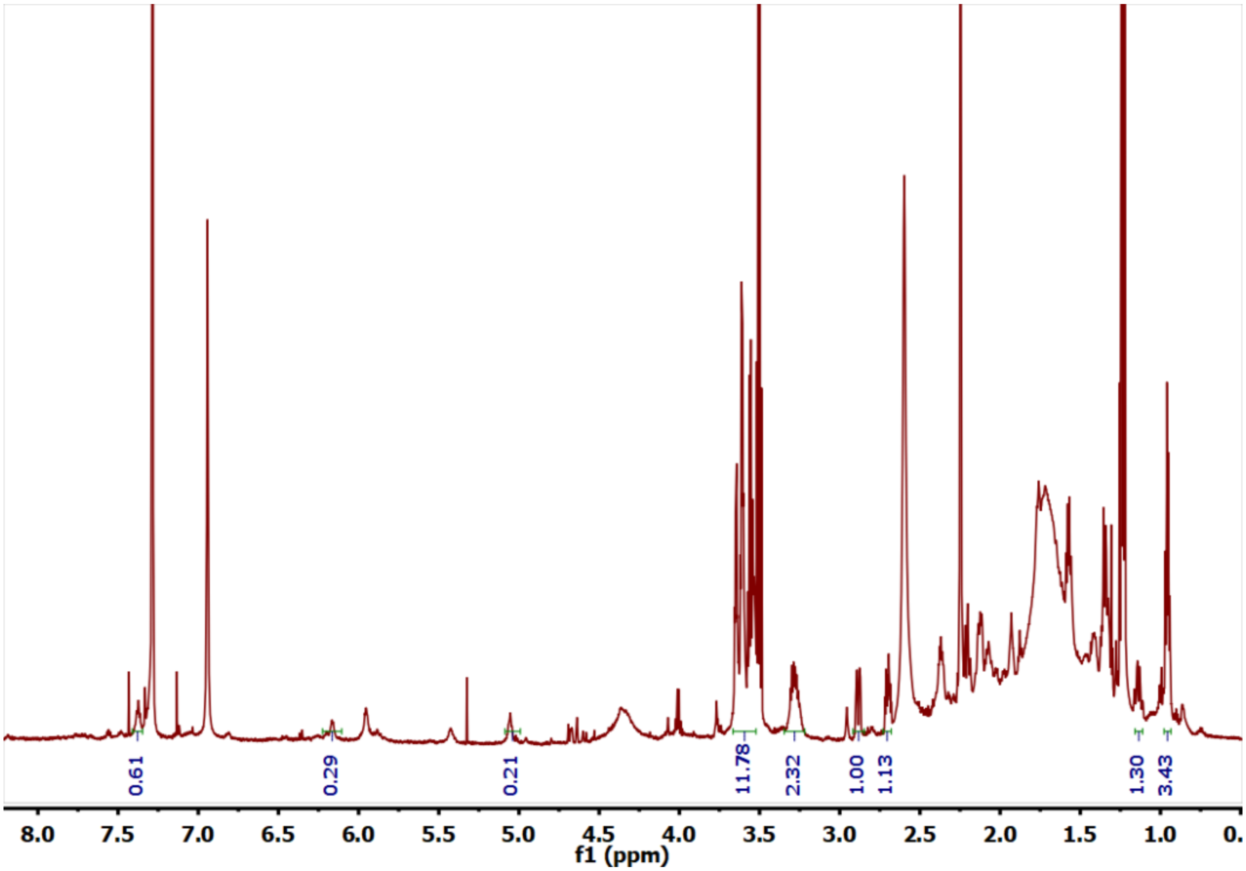


Fig. S22. ^{1}H NMR ($CDCl_3$) spectrum of poly(**1a**-*alt*-**2**)$_{10}$-grad-(**1b**-*alt*-**2**)$_{10}$ at 10 min during reaction (thus DP = 5). 10H and 2H are the expected number of protons.

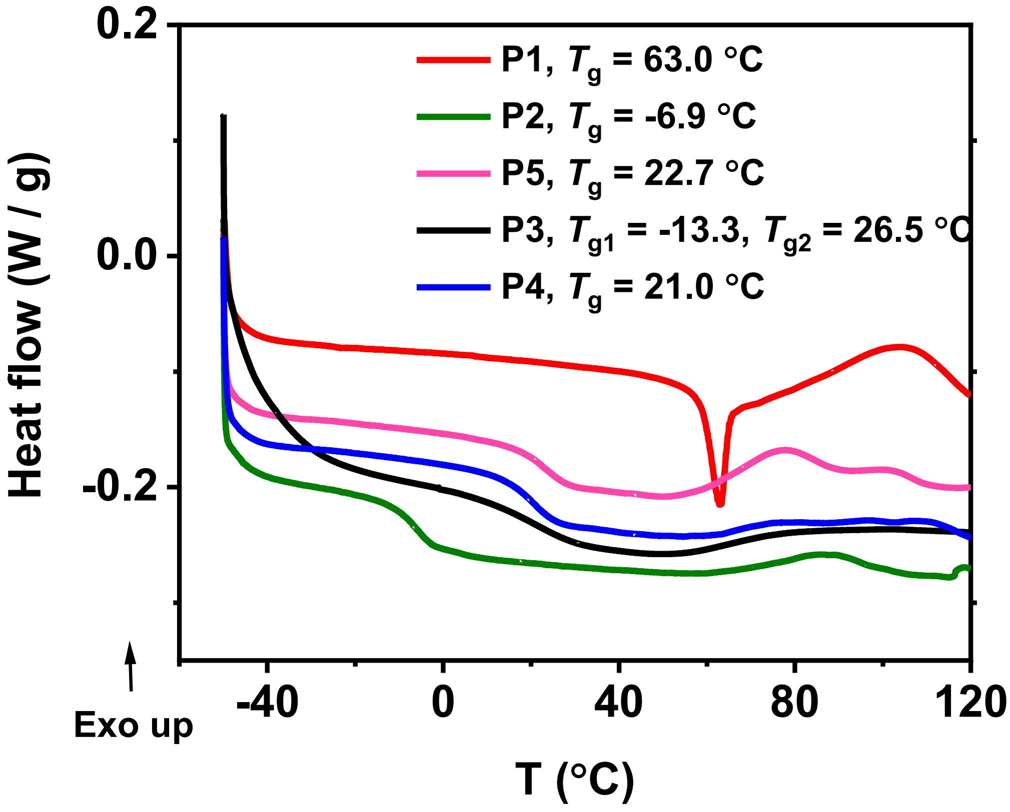


Fig. S23. Differential scanning calorimetry of polymers **P1**-**P5**.

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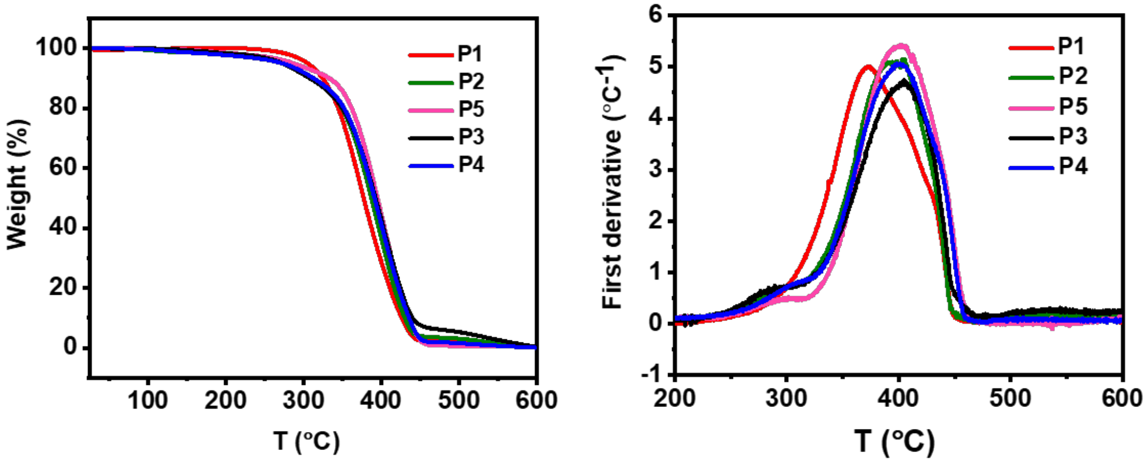

Fig. S24. Thermogravimetric (TGA, left) and derivative thermogravimetry (DTG, right) analysis of polymers **P1**-**P5**.

Fig. S25. Representative water contact angle images for polymers **P1**-**P5** and control (thus silicon wafer without polymer).

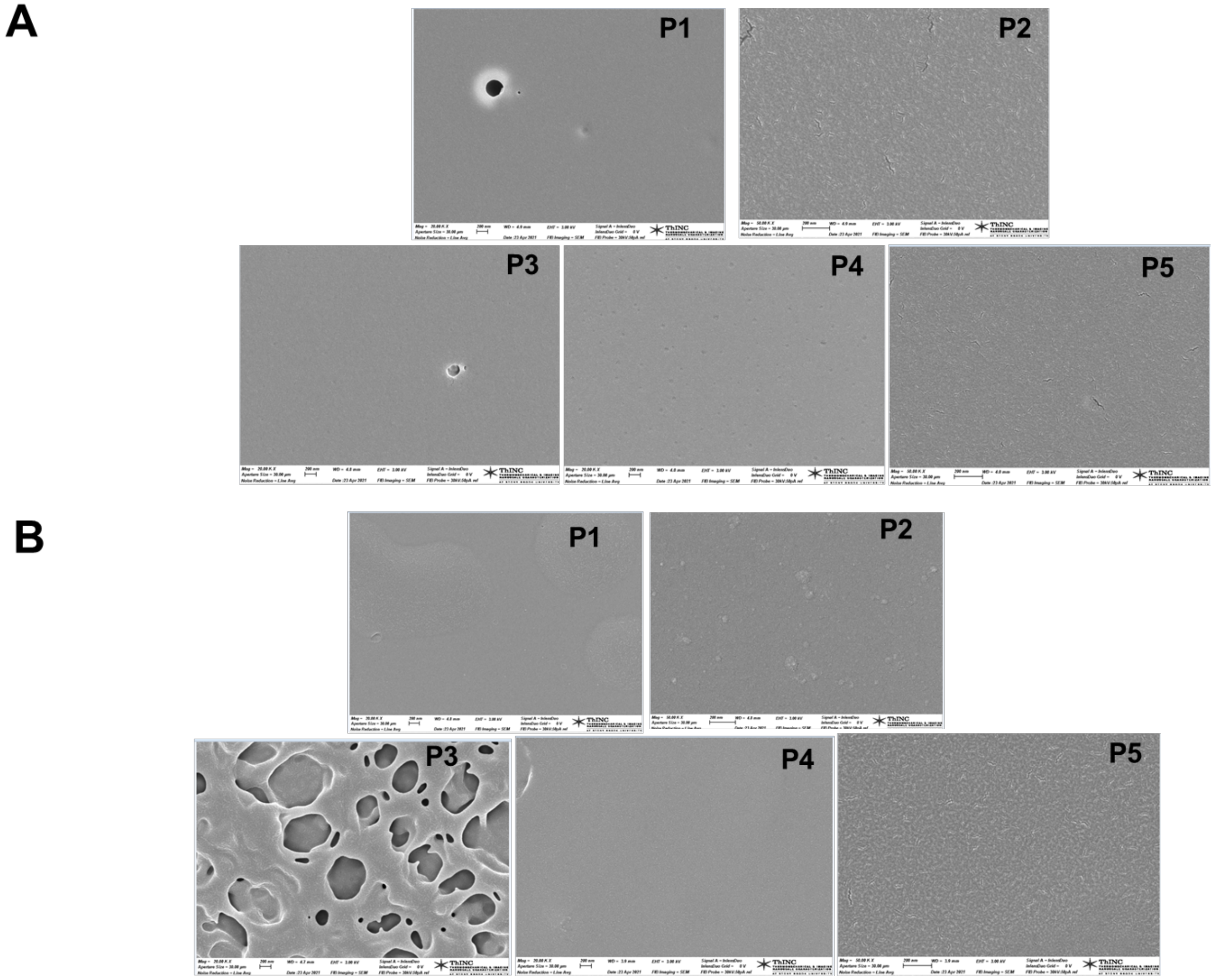

Fig. S26. Representative SEM images of polymer films prepared from (A) chloroform, (B) 2-propanol.

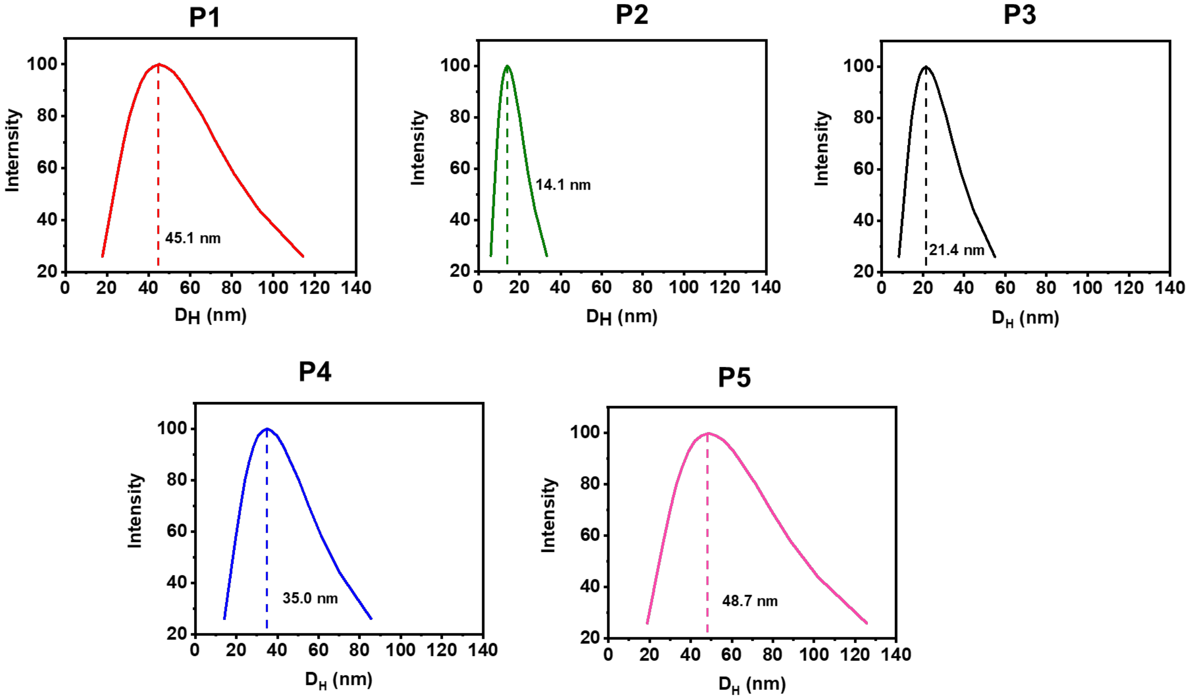

Fig. S27. Intensity distribution dynamic light scattering profiles of polymers **P1-P5** in chloroform.

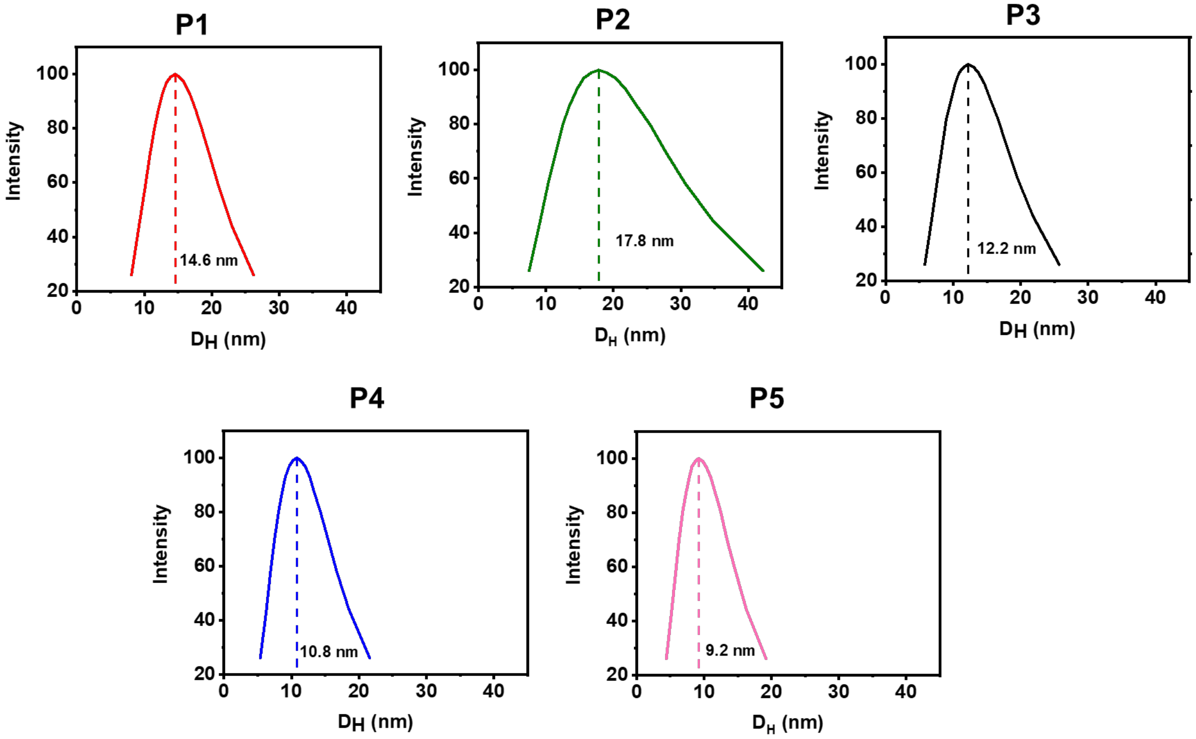

Fig. S28. Intensity distribution dynamic light scattering profiles of polymers **P1-P5** in 2-propanol.

References

1. Tüdos, F.; Kelen, T.; Földes-berezsnich, T.; Turcsányi, B., Analysis of Linear Methods for Determining Copolymerization Reactivity Ratios. Iii. Linear Graphic Method for Evaluating Data Obtained at High Conversion Levels. *J. Macromol. Sci. A* **1976,** *10* (8), 1513-1540.
2. Brar, A. S.; Sunita; Satyanarayana, C. V. V., Microstructure Determination of Styrene-Butyl Acrylate Copolymers by Nmr Spectroscopy. *Polym. J.* **1992,** *24* (9), 879-887.
3. Gleede, T.; Markwart, C. J.; Huber, N.; Rieger, E.; Wurm, R. F., Competitive Copolymerization: Access to Aziridine Copolymers with Adjustable Gradient Strengths. *Macromolecules* **2019**, 52, 9703-9714.