Supporting Information
Application of ^{1}H DOSY for Facile Measurement of Polymer Molecular Weights.

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Figures and Tables

General information

Benzene-d_6 was kept with 4 Å molecular sieves under argon. 1, 5- cyclooctadiene, cyclooctene, Cu(I)Br (99.999%), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), methyl 2-bromoisobutyrate, 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) azobisisobutyronitrile (AIBN) and styrene were obtained from Aldrich Chemical Co., and used as received. Polystyrene commercial standards were purchased from Polysciences Inc. (9000 g/mol, 60000 g/mol, and 80000 g/mol), Pressure Chemical Co. (30000 g/mol and 200000 g/mol), and Shodex Denko America (156000 g/mol).

ATRP experiments

In a Schlenk flask, CuBr (50 mg), PMDETA (60.4 mg) and methyl 2-bromoisobutyrate (63 mg) were placed. The solid reagents containing Schlenk flask was repeatedly vacuumed and backfilled with dry argon for three times. Degased styrene (7.3 g) and Anisole (8 ml) were added to the solid reagent containing Schlenk flask. The first aliquot was taken prior to placing the reaction mixture in 90 ˚C oil bath. Kinetic aliquots (0.3 ml) were taken at designated times for DOSY and GPC characterization. For each aliquot, the polymerization was stopped by removing heat followed by exposure the reaction solution in the air. The polymer solution was filtered through neutral alumina packed column to remove copper complex.

RAFT experiments

All solid reagents, DDMAT (100 mg), AIBN (9 mg) were placed in Schlenk flask and the Schlenk flask was repeatedly vacuumed and backfilled with dry argon for three

times. Degased styrene (5.7 g) and anisole (6.3 ml) were added to the Schlenk flask and then the reaction mixture was degased by argon bubbling. The reaction mixture was heated at 70 ˚C with stirring. Aliquots (0.3 ml) were taken at designated times for DOSY and GPC characterization.

ROMP experiments

The kinetic experiments of COD ROMP. In a flame-dried and argon-charged 50 mL flask was added 1.696 mg (0.002 mmol) The 2nd generation "Sheng Ding" catalyst **8** and 20 mL dry dichloromethane at room temperature. Timing was started as soon as 1.230 mL (10 mmol) 1, 5- cyclooctadiene was injected into the solution. 1 mL aliquots were extracted via syringe from the reaction mixture at designated times into a scintillation vial with two drops of ethyl vinyl ether. 40 μL of the quenched reaction mixture were transferred to an NMR tube and diluted with 1 mL of benzene-d_6 for NMR experiments.

The kinetic experiments of COE ROMP. In a flame-dried and argon-charged 50 mL flask was added 1.696 mg (0.002 mmol) the 2nd generation "Sheng Ding" catalyst **8** or 1.450 mg (0.002 mmol) the 3rd generation "bispyridine" catalyst **9** and 20 mL dry dichloromethane at room temperature. Timing was started as soon as 1.303 mL (10 mmol) cyclooctene was injected into the solution. 1 mL aliquots were extracted via syringe from the reaction mixture at designated times into a scintillation vial with two drops of ethyl vinyl ether. 40 μL of the quenched reaction mixture were transferred to an NMR tube and diluted with 1 mL of benzene-d_6 for NMR experiments.

Synthesis of polyCOE samples by ROMP. In a nitrogen-filled glovebox, a scintillation vial with a PTFE-coated stirbar was charged with *cis*-cyclooctene (COE, 2.6 ml, 20 mmol), *trans*-stilbene (chain-transfer agent, given below) and THF (10 ml).

A solution of the initiator (17 mg, 0.02 mmol, [COE]/[initiator]=1000) in THF (1 ml) was added to the monomer solution in one portion. The scintillation vial was sealed with a PTFE-line cap, removed from the glovebox and heated at 40 °C for 2 hours. At the end of the polymerization, the solution was cooled to room temperature and the initiator was quenched with ethyl vinyl ether (1 ml) for 15 minutes. The viscous polymer solution was precipitated into MeOH (200 ml). The PCOE isolated by filtration followed by removal the residual solvent *in vacuo* to give a white powder.

NMR experiments

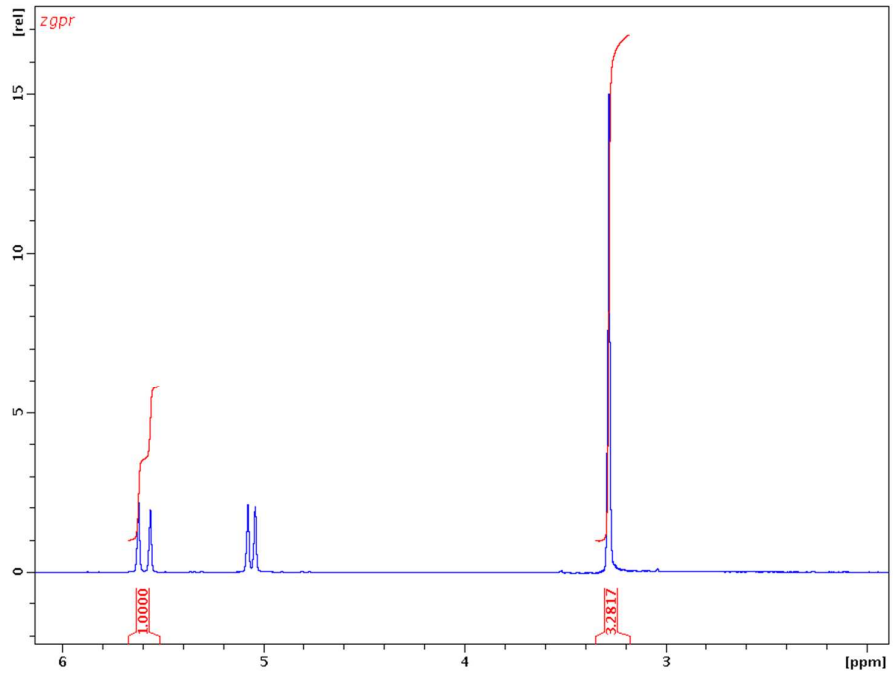
All NMR tubes were flame dried and evacuated *in vacuo* in advance. NMR experiments were performed at 25 ^{o}C. All NMR samples were stabilized at 25 °C for 5 min before data collection. For polystyrene standard samples, each NMR tube contained 0.5 mg polystyrene and 1 mL benzene-d_6. For ATRP, RAFT, and ROMP samples, each NMR tube contained 40 μL reaction mixture and 1 mL benzene-d_6. DOSY experiments were performed on a Bruker DRX 300 spectrometer equipped with an Accustar *z*-axis gradient amplifier and an ATMA BBO probe with a z-axis gradient coil. All experiments were run without spinning to avoid convection. Maximum gradient strength was 0.214 T/m. The standard Bruker pulse program, stegp1s, employing a stimulated echo sequence and 1 spoil gradient was utilized. Bipolar rectangular gradients were used with a total duration of 0.5-10 ms (7 ms for polystyrene measurement). Gradient recovery delays were 0.5-1 μs. Diffusion times were between 100-2000 ms (200 ms for polystyrene measurement). The number of gradient steps was set to be 32. Individual rows of the quasi-2-D diffusion databases were phased and baseline corrected. DOSY spectra were processed by Topspin 1.3 software. Diffusion dimension was generated using inverse Laplace Transform driven by maximum entropy method.[1] Diffusion coefficients of a chosen narrow chemical shift range were extracted from T1/T2 analysis module of Topspin 1.3 calculated

from the maximum entropy (GIFA) module developed by Delsuc *et al*.[2] Unless otherwise mentioned, the DOSY spectrum was processed without additional processing parameter modifications.

GPC characterization

GPC analysis of polymer was performed by two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector (Wyatt Technology), an Optilab DSP differential refractometer (Wyatt Technology), and a ViscoStar viscometer (Wyatt Technology) in THF eluent. The analysis was performed with a flow rate of 1 ml/min at room temperature. Absolute molecular weights and PDI were calculated from dn/dc values that were obtained by assuming 100% mass elution from the GPC columns.

^{1}H NMR spectra of ATRP reaction mixtures for integration



Figuire S1. ^{1}H NMR spectrum of the ATRP reaction mixture at 0 min in benzene-d_6 at room temperature.

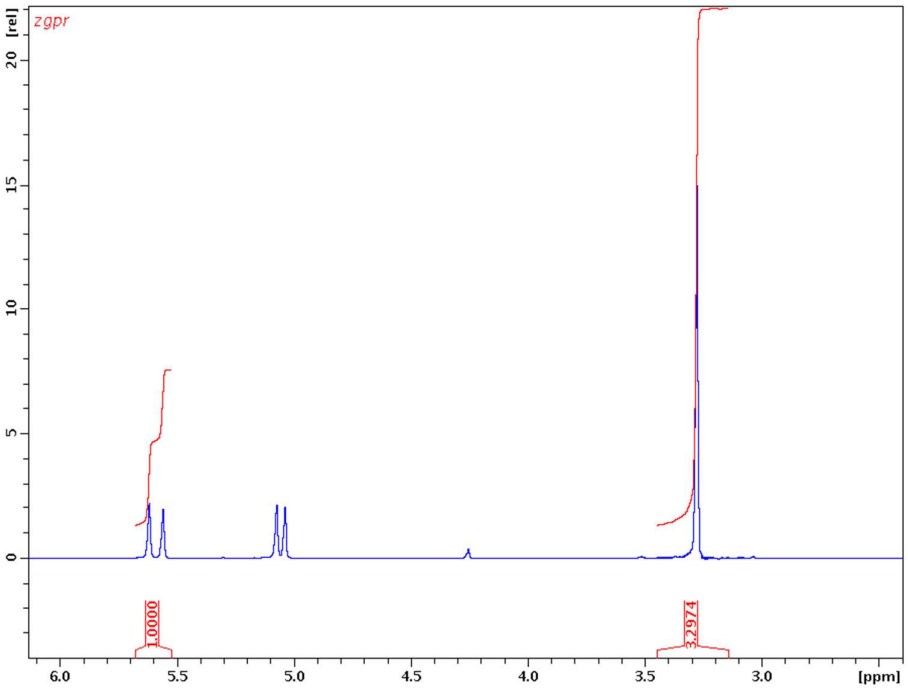


Figure S1. ^{1}H NMR spectrum of the ATRP reaction mixture at 5 min in benzene-d_6 at room temperature.

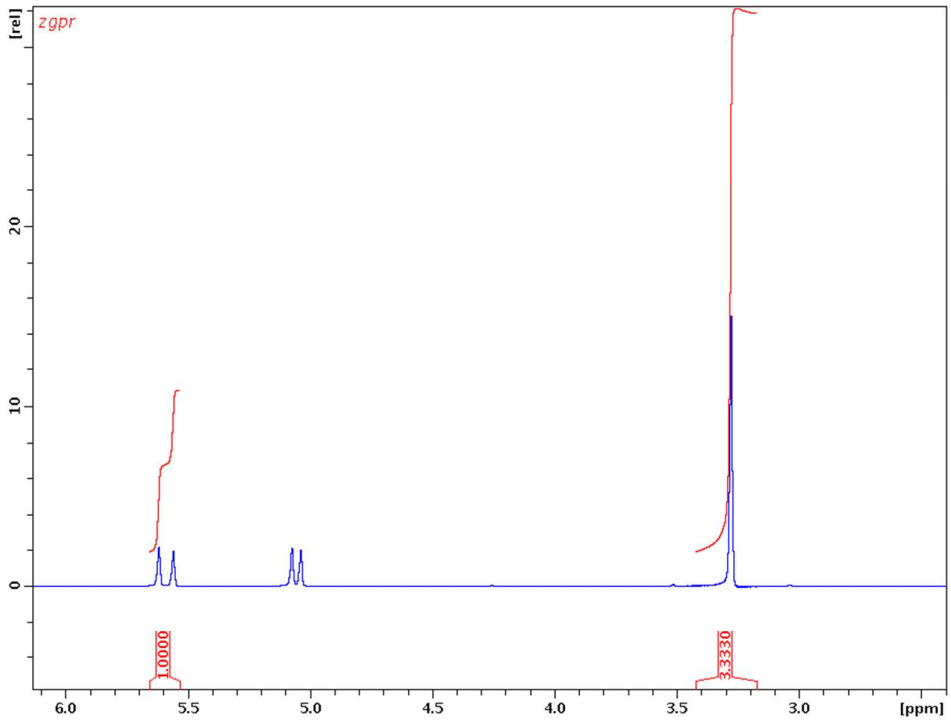


Figure S2. ^{1}H NMR spectrum of the ATRP reaction mixture at 20 min in benzene-d_6 at room temperature.

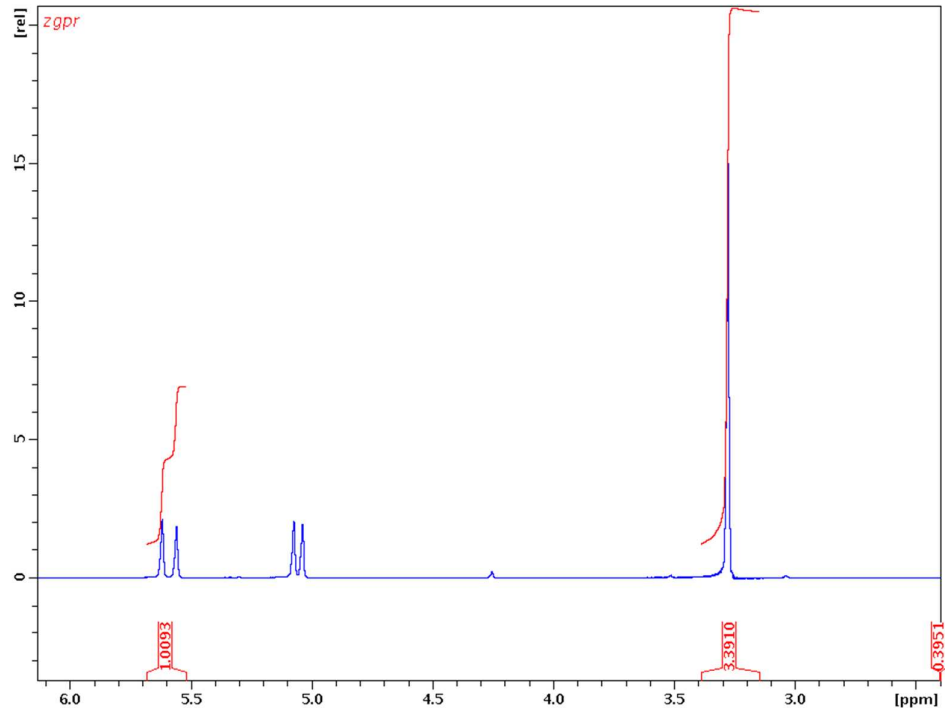


Figure S3. ^{1}H NMR spectrum of the ATRP reaction mixture at 50 min in benzene-d_6 at room temperature.

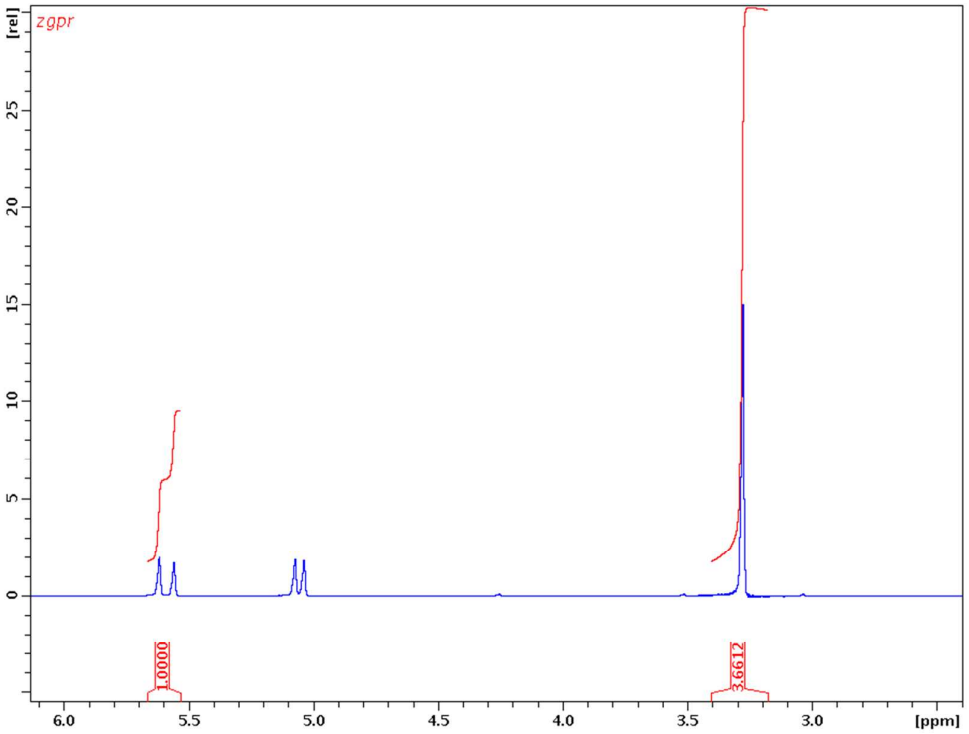


Figure S4. ^{1}H NMR spectrum of the ATRP reaction mixture at 2 hours in benzene-d_6 at room temperature.

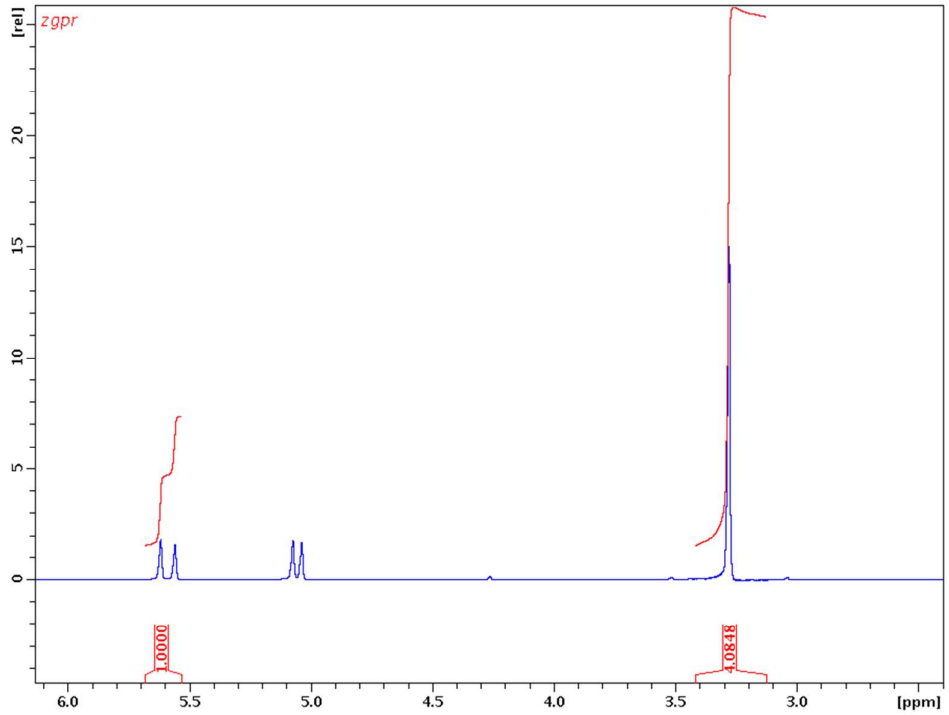


Figure S5. ^{1}H NMR spectrum of the ATRP reaction mixture at 4 hours in benzene-d_6 at room temperature.

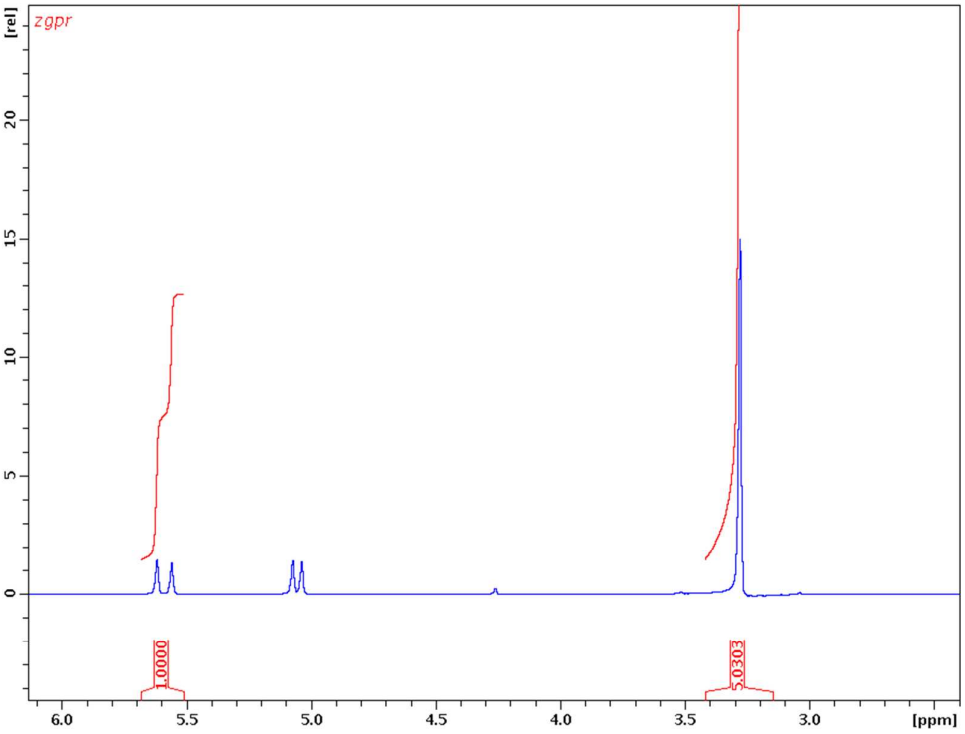


Figure S6. ^{1}H NMR spectrum of the ATRP reaction mixture at 8 hours in benzene-d_6 at room temperature.

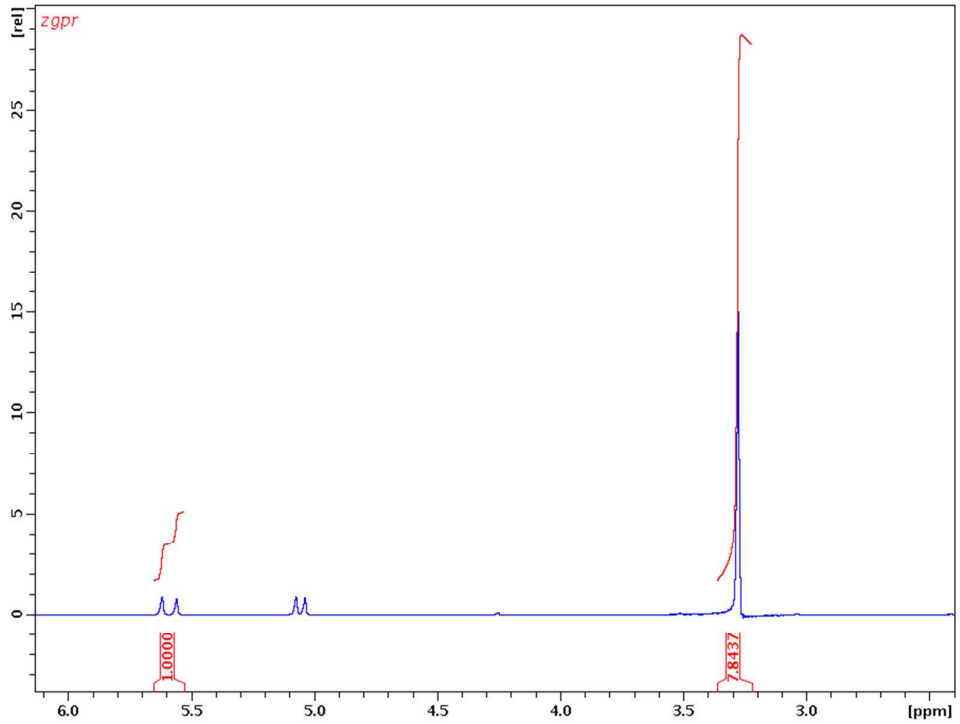


Figure S7. ^{1}H NMR spectrum of the ATRP reaction mixture at 20 hours in benzene-d_6 at room temperature.

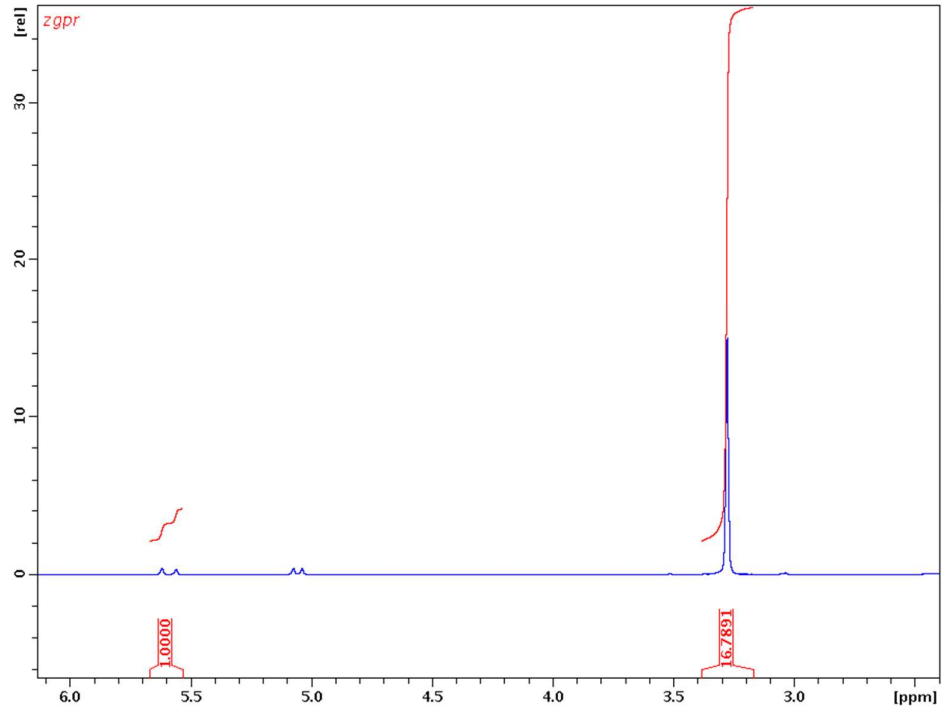


Figure S8. ^{1}H NMR spectrum of the ATRP reaction mixture at 45 hours in benzene-d_6 at room temperature.

^{1}H NMR spectra of RAFT reaction mixtures for integration

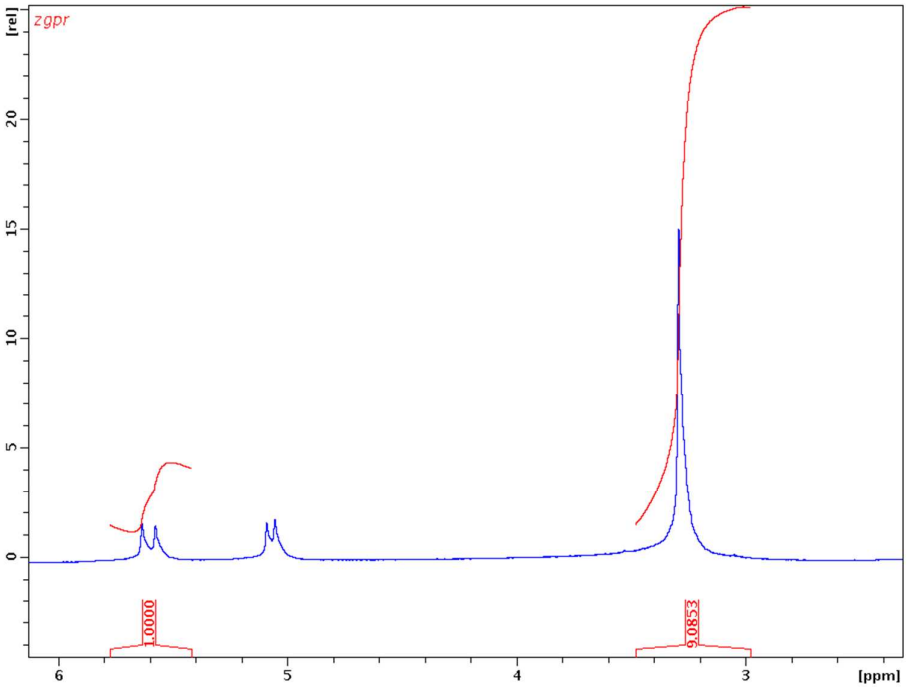


Figure S9. ^{1}H NMR spectrum of the RAFT reaction mixture at 9h50m in benzene-d_6 at room temperature.

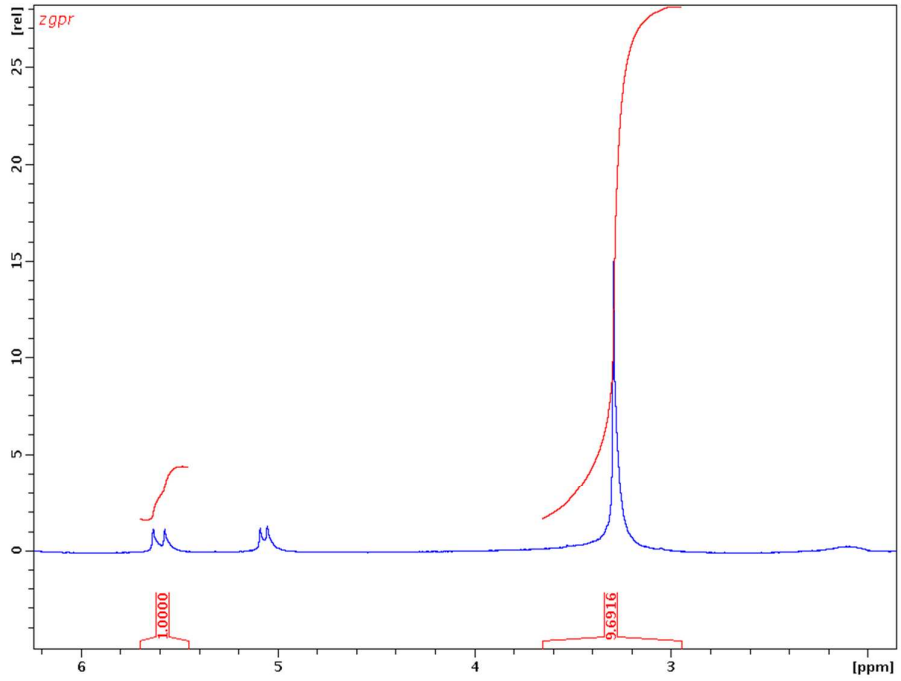


Figure S10. ^{1}H NMR spectrum of the RAFT reaction mixture at 22h25m in benzene-d_6 at room temperature.

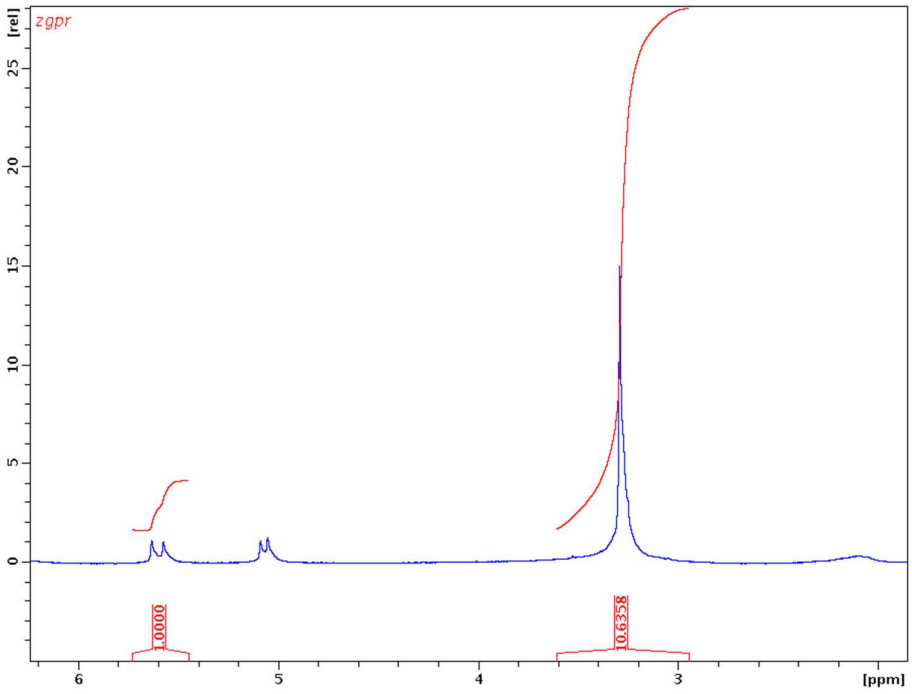


Figure S11. ^{1}H NMR spectrum of the RAFT reaction mixture at 29h20m in benzene-d_6 at room temperature.

^{1}H NMR spectra of ROMP of COD reaction mixtures for integration

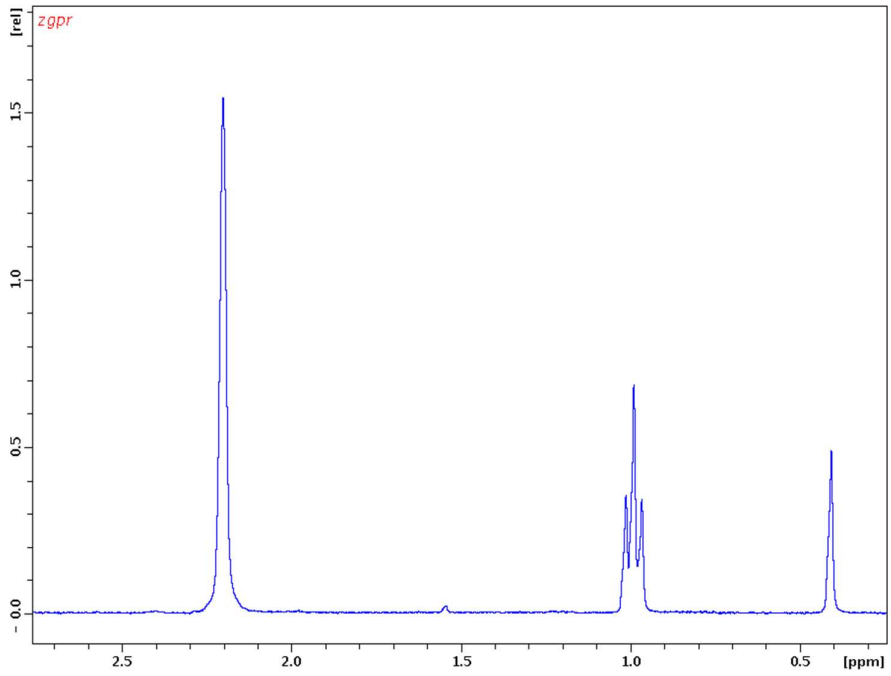


Figure S12. ^{1}H NMR spectra of the COD ROMP mixture at 1 min in benzene-d_6 at room temperature.

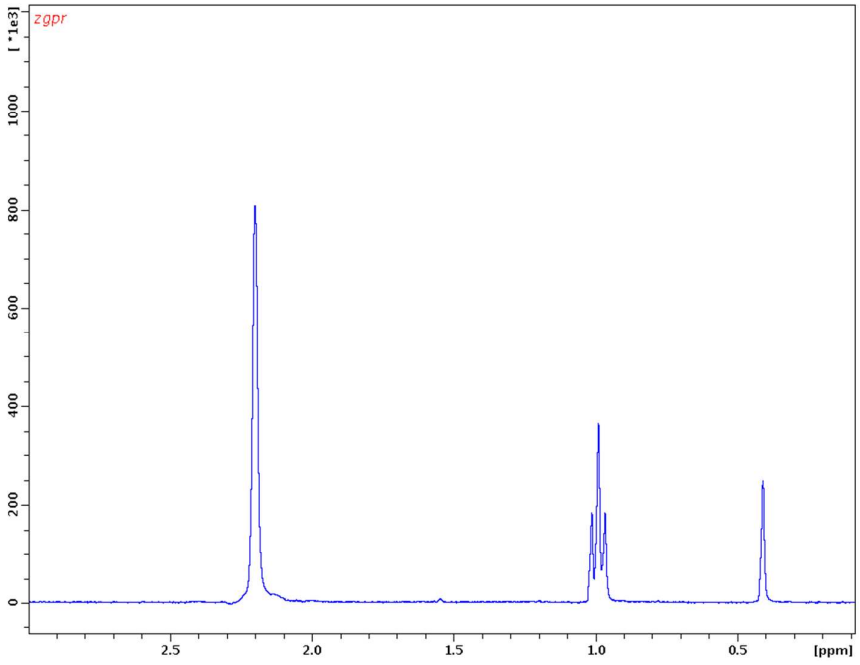


Figure S13. ^{1}H NMR spectra of the COD ROMP mixture at 5 min in benzene-d_6 at room temperature.

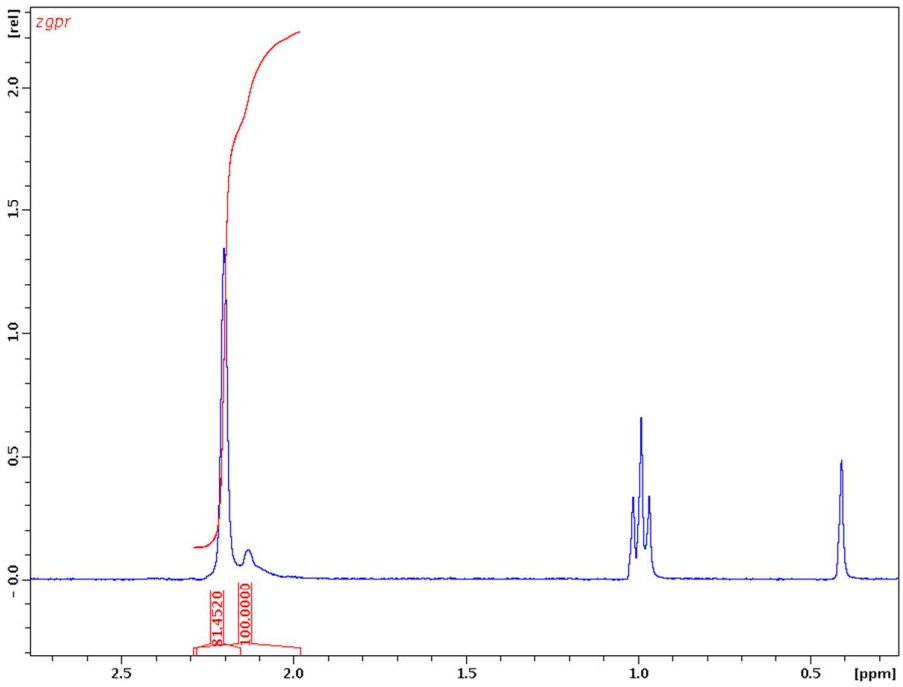


Figure S14. ^{1}H NMR spectra of the COD ROMP mixture at 10 min in benzene-d_6 at room temperature.

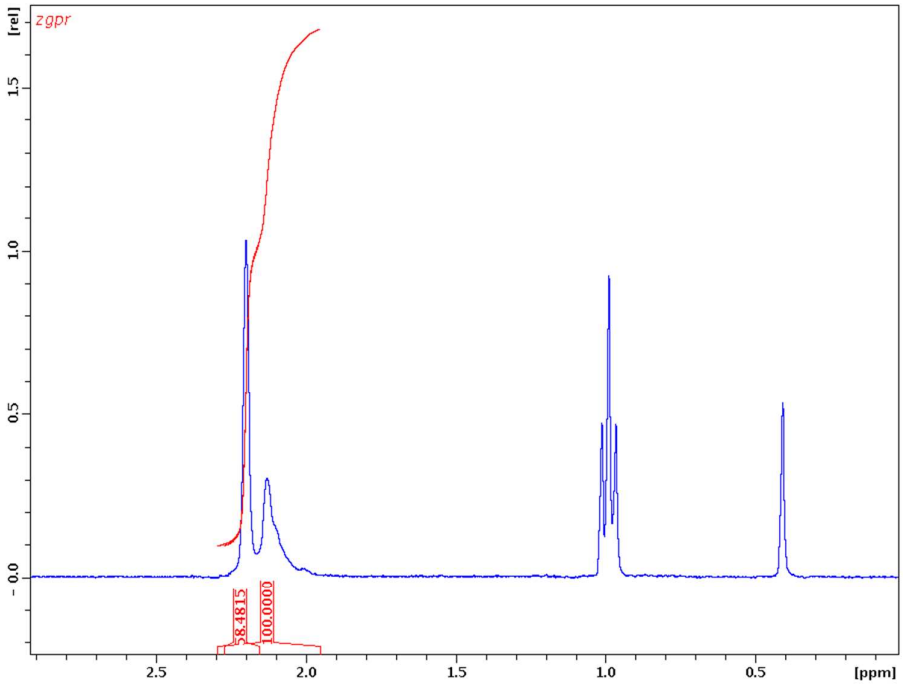


Figure S15. ^{1}H NMR spectra of the COD ROMP mixture at 15 min in benzene-d_6 at room temperature.

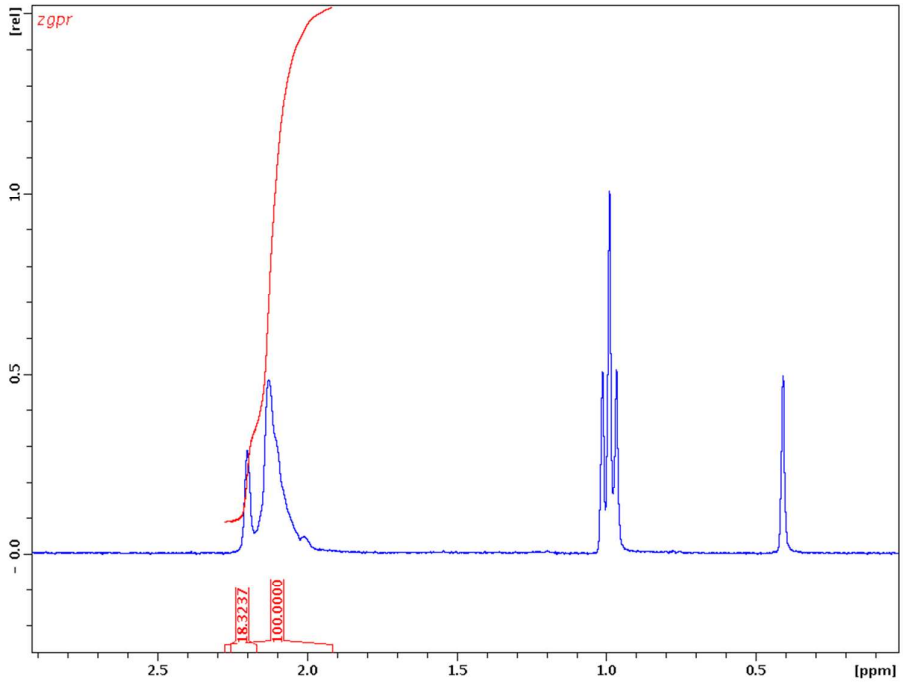


Figure S16. ^{1}H NMR spectra of the COD ROMP mixture at 25 min in benzene-d_6 at room temperature.

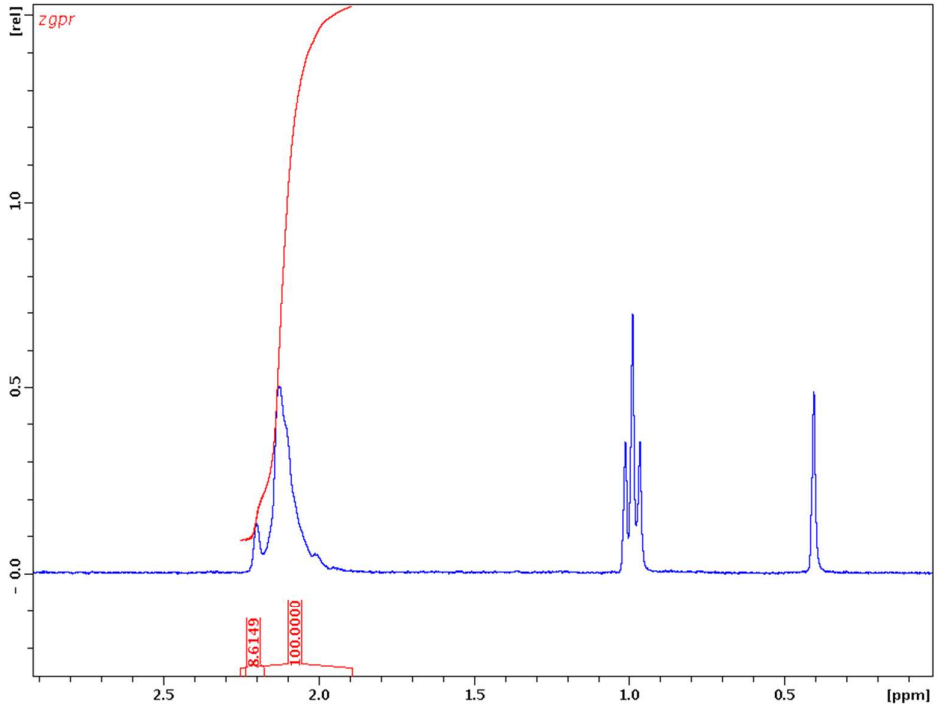


Figure S17. ^{1}H NMR spectra of the COD ROMP mixture at 30 min in benzene-d_6 at room temperature.

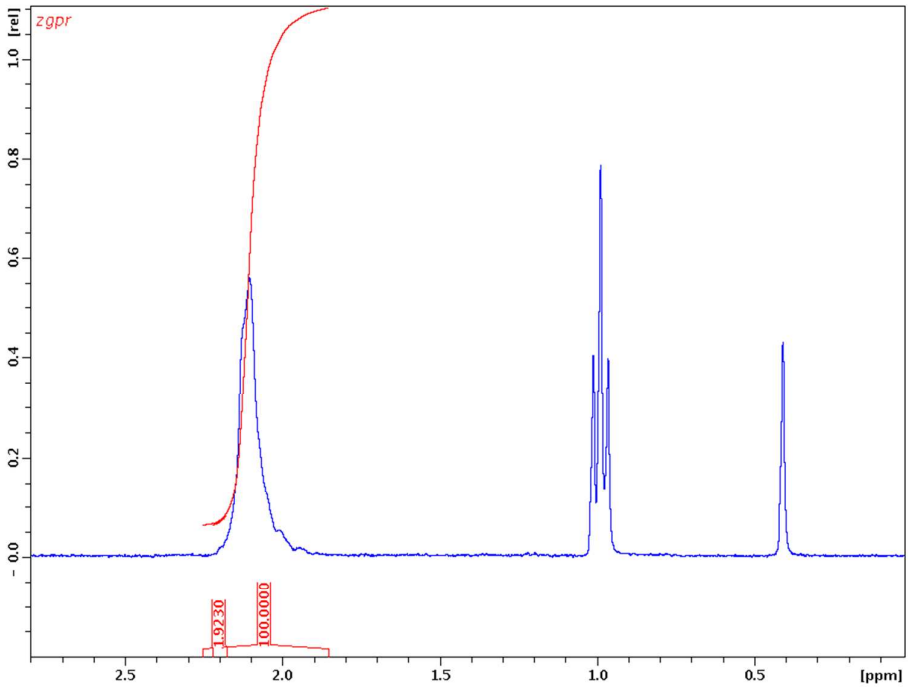


Figure S18. ^{1}H NMR spectra of the COD ROMP mixture at 45 min in benzene-d_6 at room temperature.

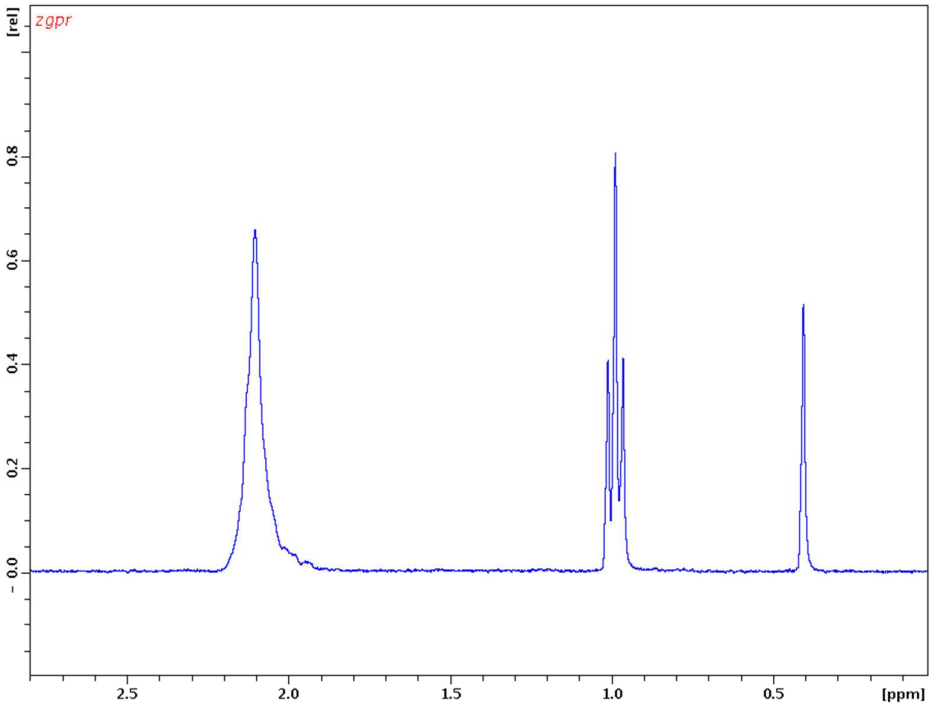


Figure S19. ^{1}H NMR spectra of the COD ROMP mixture at 60 min in benzene-d_6 at room temperature.

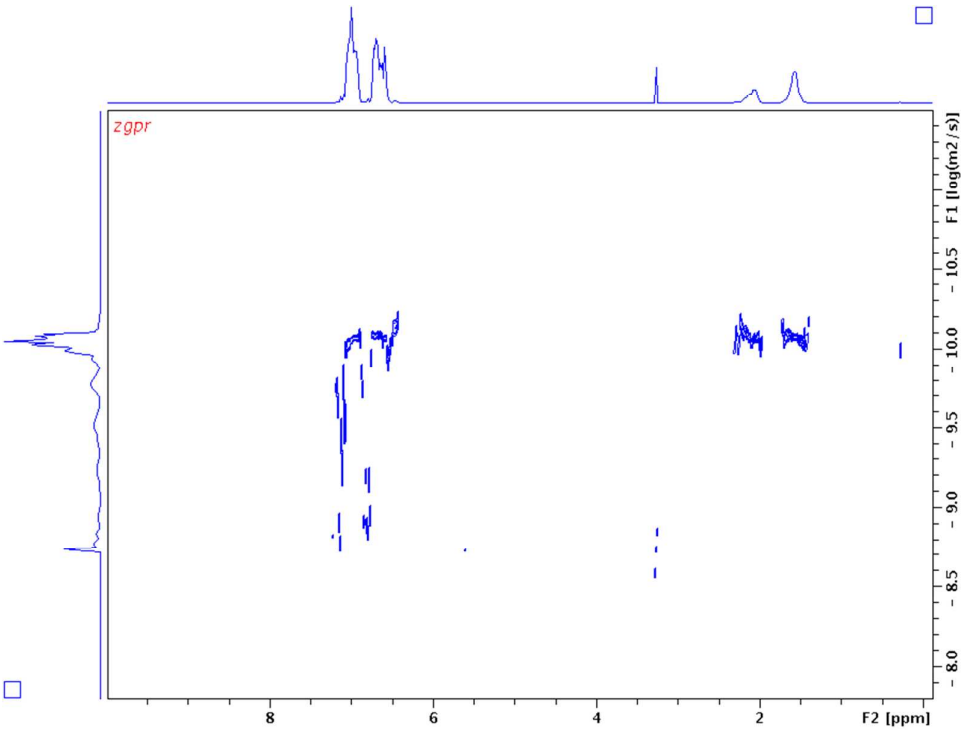


Figure S20. Representative ^{1}H DOSY of ATRP reaction crude after 45h in benzene-d6 at rt.

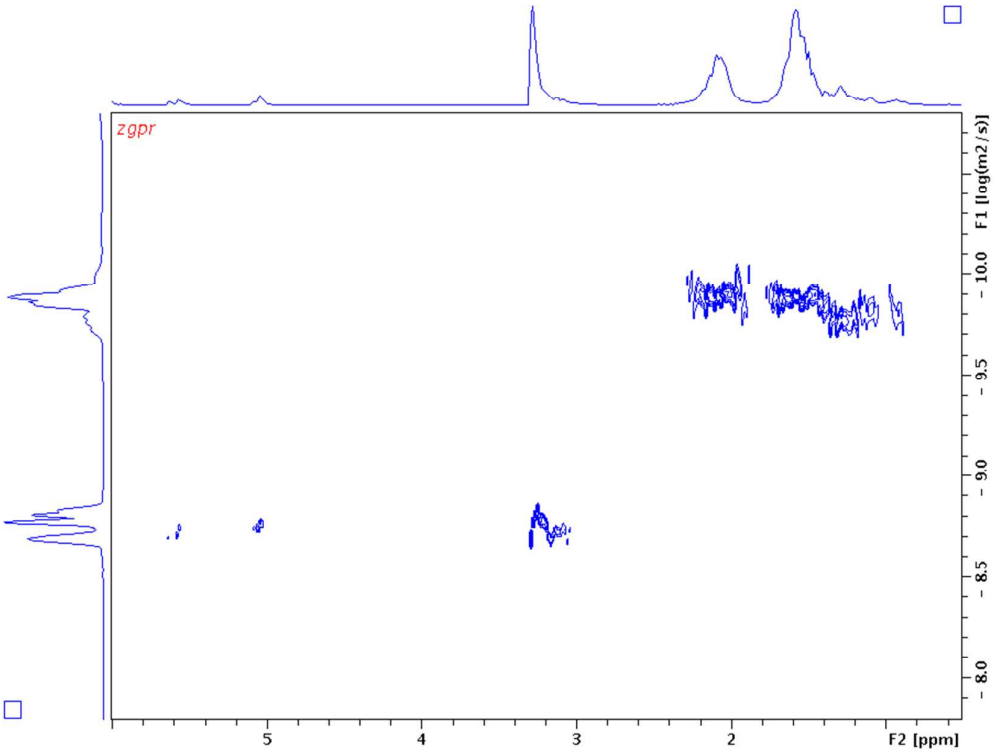


Figure S21. Representative ^{1}H DOSY of RAFT reaction crude after 29h20m in benzene-d6 at rt.

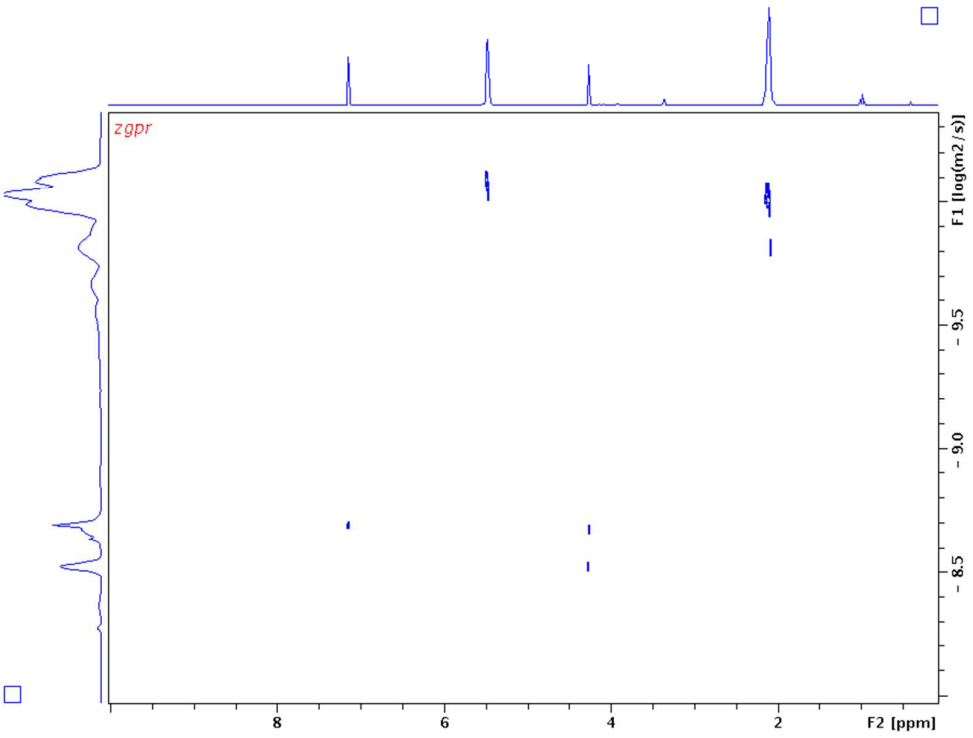


Figure S22. Representative ^{1}H DOSY of ROMP of COD reaction crude after 45m in benzene-d6 at rt.

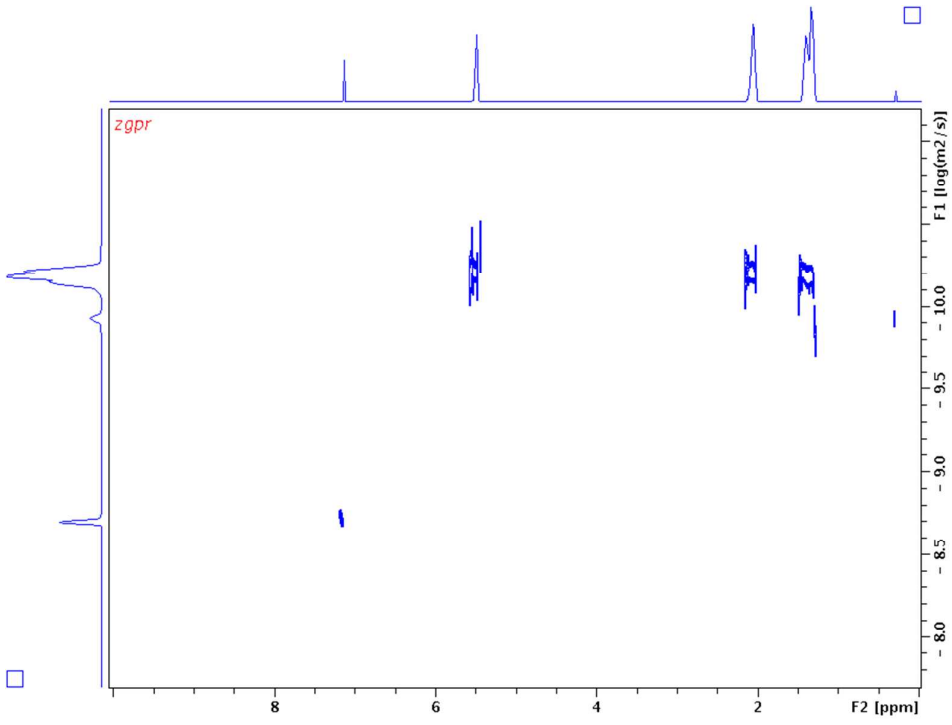


Figure S23. Representative ^{1}H DOSY of ROMP of COE reaction crude after 45m in benzene-d6 at rt.

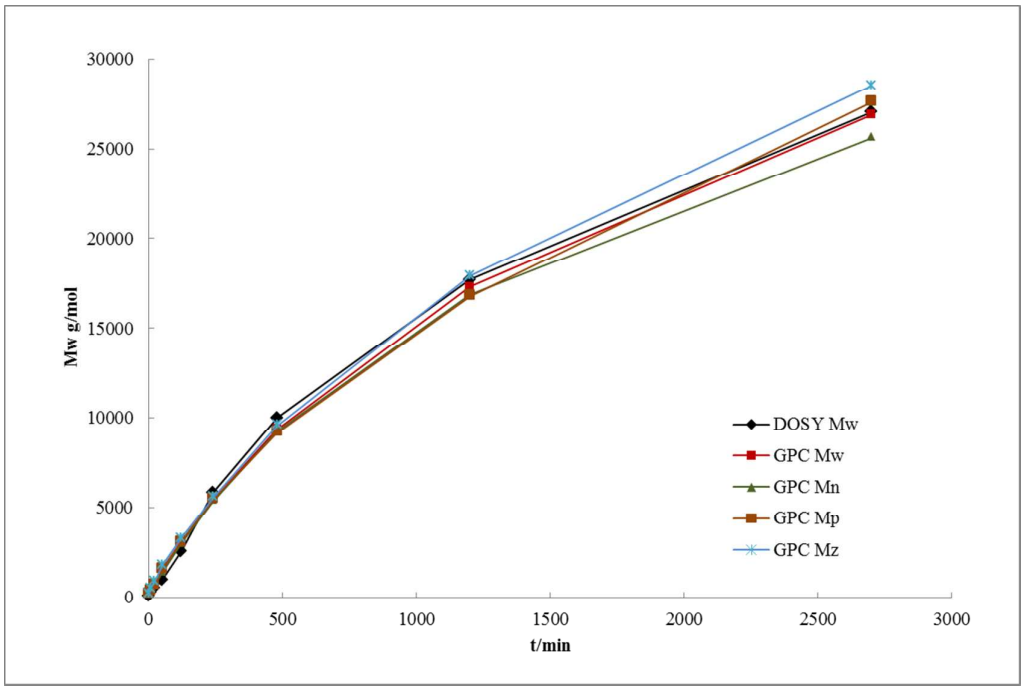


Figure S24. Mw-t plot of polymerization of styrene by ATRP. Black ball: results given by DOSY, red square: results given by GPC.

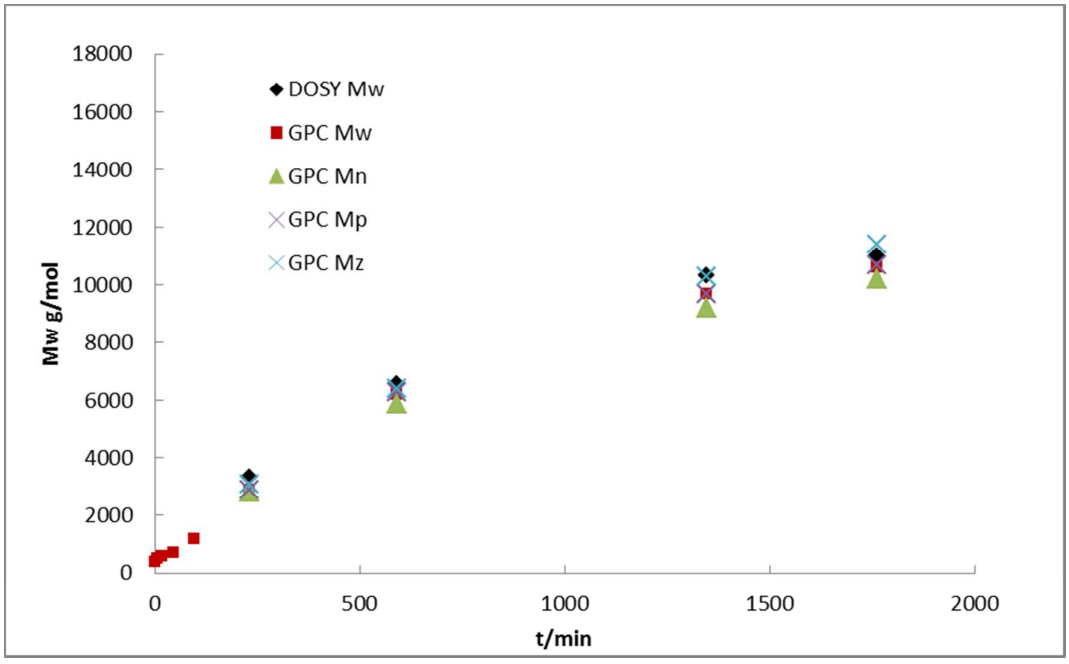


Figure S25. Mw-t plot of polymerization of styrene by RAFT. Black ball: results given by DOSY, red square: results given by GPC.

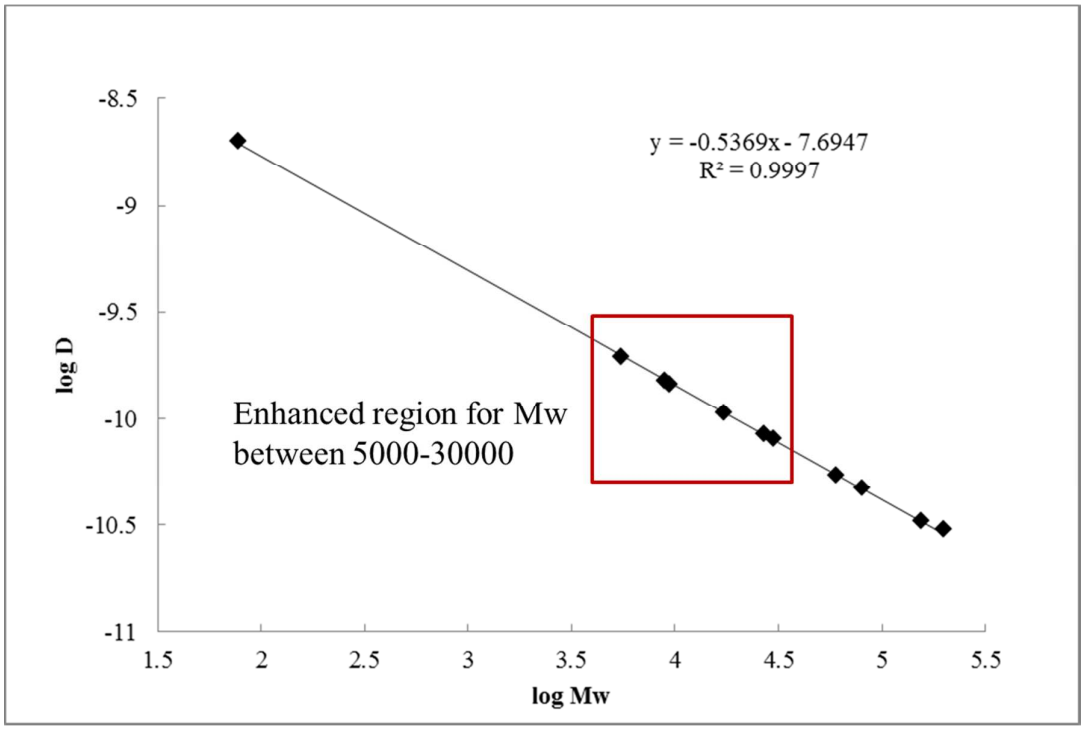


Figure S26. Enhanced PS calibration curve in benzene-d_6 for Mw prediction between 5000-30000 g/mol.

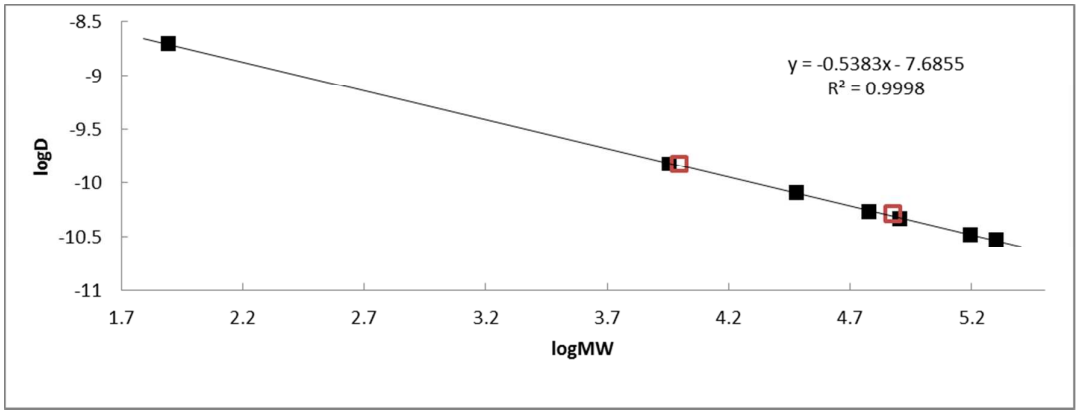


Figure S27. PS calibration curve in benzene-d_6 for Mw prediction. Black square: PS standards and benzene, red hollow square: polycyclooctene samples.

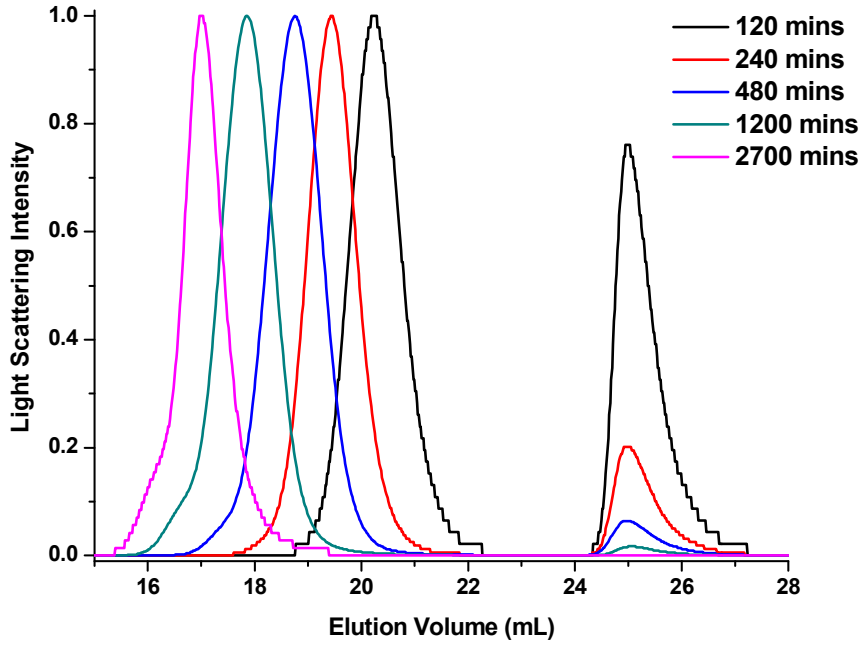


Figure S28. GPC traces of polystyrene which synthesized by ATRP

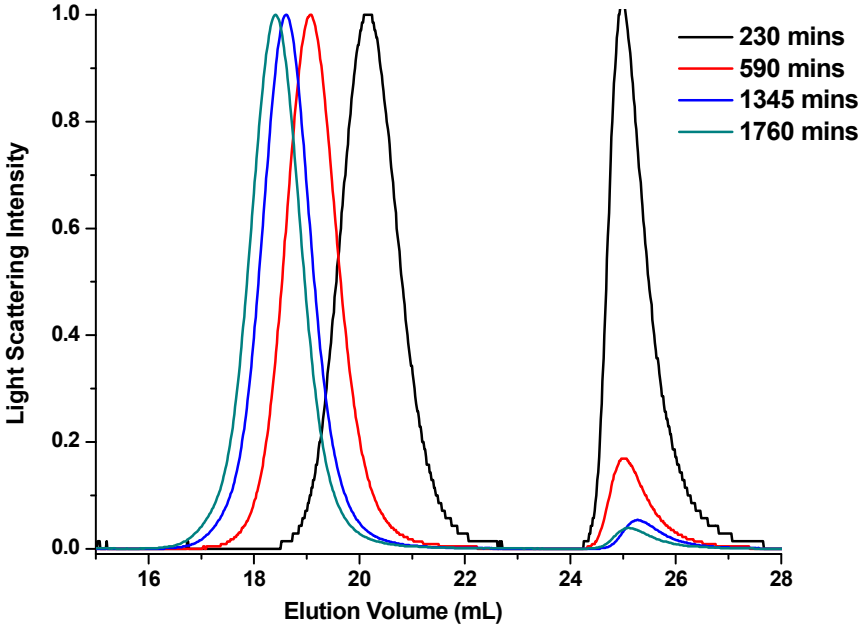


Figure S29. GPC traces of polystyrene which synthesized by RAFT

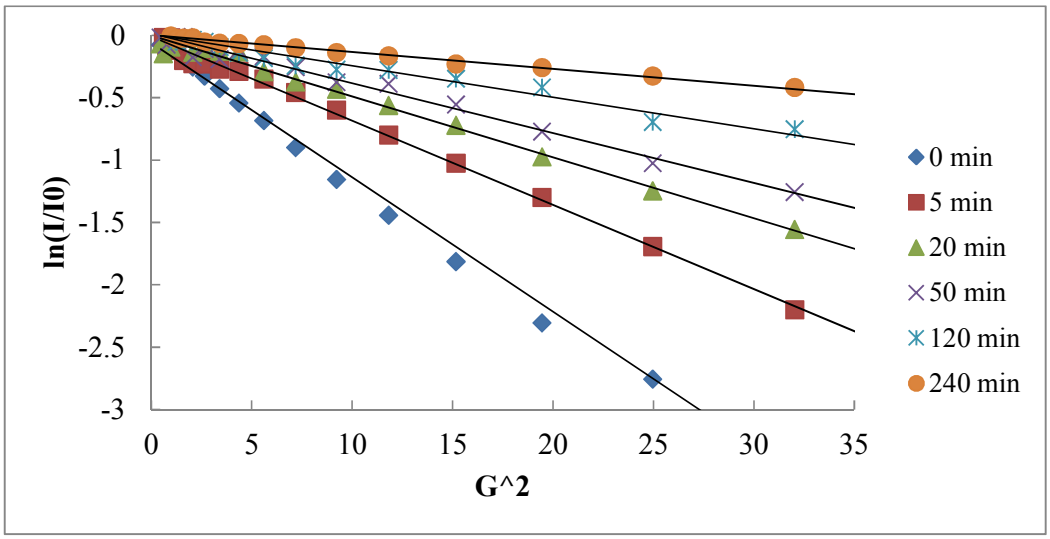


Figure S30. Stejskal – Tanner Plot of diffusion results from ATRP.

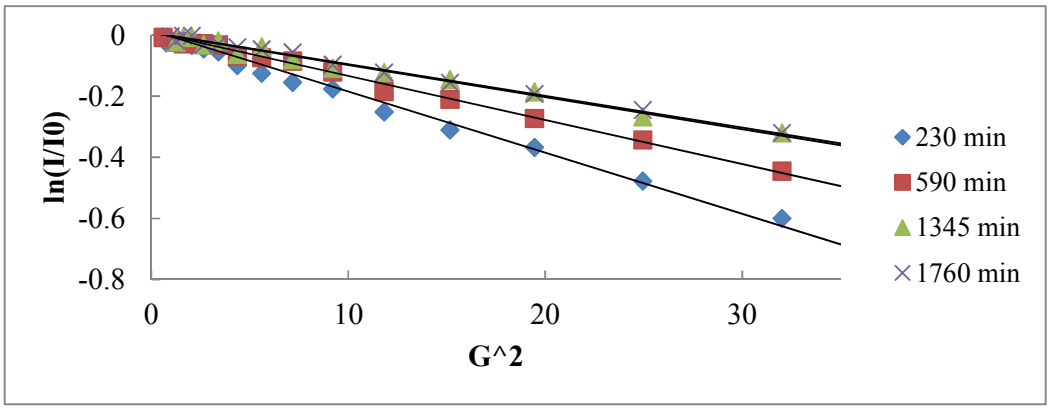


Figure S31. Stejskal – Tanner Plot of diffusion results from RAFT.

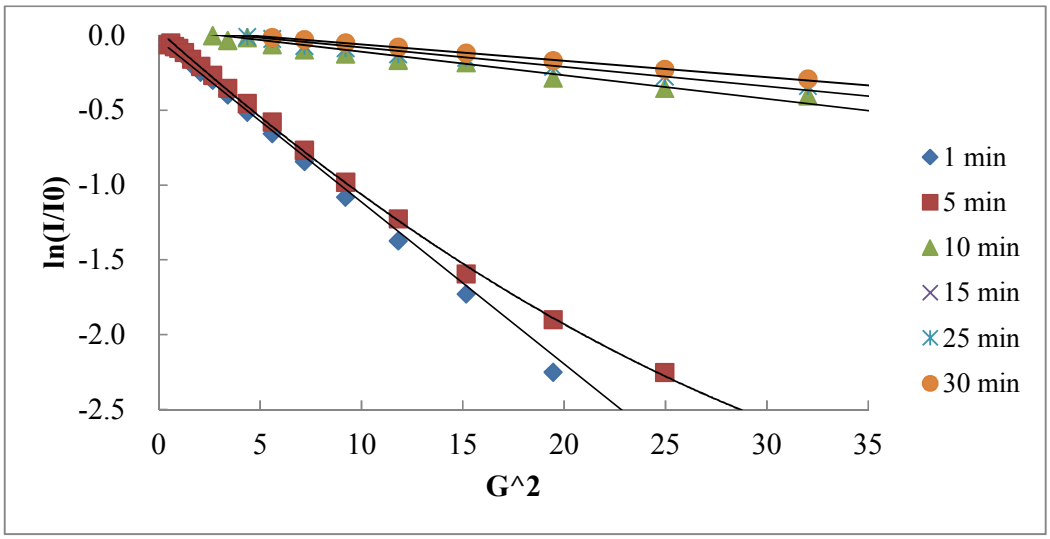


Figure S32. Stejskal – Tanner Plot of diffusion results from ROMP.

Table S1. D-Fw results of PS calibration curve and predictions.

Samples	Mw (GPC) g/mol	ave.D (10^{-11})	D (δ 1.95) (10^{-11})	D (δ 1.48) (10^{-11})	STDEV	% error
PS	9000	15.02	15.00	15.05	0.03	0.2
PS	30000	8.08	8.078	8.087	0.006	0.08
PS	60000	5.40	5.38	5.41	0.02	0.4
PS	80000	4.69	4.67	4.70	0.02	0.5
PS	156000	3.31	3.28	3.33	0.03	1.0
PS	200000	3.00	2.97	3.02	0.03	1.0

Samples	Mw (δ 1.95) g/mol	Mw (δ 1.48) g/mol	STDEV	% error
PS	9145	9094	36	0.4
PS	28964	28905	42	0.1
PS	61733	61055	479	0.8

PS	80317	79271	740	0.9
PS	154958	150993	2803	1.8
PS	185817	181033	3383	1.8

Table S2. ATRP results from GPC and externally referenced DOSY.

t/min	Mw GPC g/mol	ave.D (10^{-10})	D (δ 1.95) (10^{-10})	D (δ 1.48) (10^{-10})	STDEV	% error
0	-	17.6	17.3	18.0	0.5	3
5	-	9.17	9.16	9.19	0.02	0.3
20	-	7.00	6.96	7.10	0.09	1.4
50	-	4.97	4.94	4.99	0.03	0.6
120	3100	3.00	2.99	3.02	0.02	0.7
240	5500	1.93	1.92	1.95	0.03	1.4
480	9400	1.45	1.43	1.47	0.03	2.1
1200	17300	1.07	1.05	1.09	0.03	2.7
2700	26900	0.849	0.847-	0.850	0.002	0.3

t/min	Mw (δ 1.95) g/mol	Mw (δ 1.48) g/mol	STDEV	% error
0	100	93	5	5.0
5	326	324	2	0.5
20	542	523	14	2.6
50	1024	1007	12	1.2
120	2603	2559	32	1.2
240	5964	5756	147	2.5

480	10301	9760	382	3.8
1200	18343	17108	873	4.9
2700	27147	26946	142	0.5

time/min	Mn g/mol	Mp g/mol	Mz g/mol	Mw g/mol	PDI g/mol
120	3000	3100	3300	3100	1.03
240	5400	5500	5600	5500	1.02
480	9300	9200	9600	9400	1.01
1200	16900	16800	17900	17300	1.02
2700	25600	27600	28500	26900	1.03

Table S3. RAFT results from GPC and externally referenced DOSY.

t/min	Mw GPC g/mol	ave.D (10^{-10})	D (δ 1.95) (10^{-10})	D (δ 1.48) (10^{-10})	STDEV	% error
230	2900	2.60	2.57	2.65	0.06	2.2
590	6200	1.80	1.83	1.81	0.04	1.9
1345	9700	1.41	1.40	1.43	0.02	1.5
1760	10600	1.36	1.35	1.38	0.03	1.9

t/min	Mw (δ 1.95) g/mol	Mw (δ 1.48) g/mol	STDEV	% error
230	3390	3201	133	4.0
590	6697	6361	238	3.6
1345	10451	10048	285	2.8

1760	11321	10763	395	3.6

t/min	Mn g/mol	Mp g/mol	Mz g/mol	Mw g/mol	PDI
230.00	2800.00	2900.00	3100.00	2900.00	1.04
590.00	5900.00	6300.00	6400.00	6200.00	1.04
1345.00	9200.00	9700.00	10300.00	9700.00	1.06
1760.00	10200.00	10700.00	11400.00	10600.00	1.06

Table S4. D-Fw results of PS calibration curve and predictions with enhanced PS calibration for Mw prediction between 9000-30000 g/mol.

Samples	Mw (GPC) g/mol	ave. D (10^{-10})	ave. Mw (DOSY) g/mol	Diff %
PS	9000	15.02	9100	-1.3
PS	30000	8.082	28900	3.6
PS	60000	5.397	61300	-2.3
PS	80000	4.688	80000	0.2
PS	156000	3.305	153000	1.9
PS	200000	2.998	183000	8.2
BEN	78	200.0	73	5.9
PS ATRP	5500	1.934	5700	-4.6
PS ATRP	9400	1.447	9800	-5.1
PS ATRP	17300	1.066	17400	-0.9
PS ATRP	26900	0.8489	26700	0.8

Table S5. D-Fw results of PS calibration curve for Mw prediction of polycyclooctene samples.

Samples	Mw (GPC) g/mol	ave. D (10^{-10})	ave. Mw (DOSY) g/mol	Diff %
PS	9000	15.02	9400	-4.1
PS	30000	8.082	29600	1.3
PS	60000	5.397	62700	-4.5
PS	80000	4.688	81500	-1.8
PS	156000	3.305	15600	0.02
PS	200000	2.998	187000	6.5
BEN	78	200.0	76	2.1
PolyCOE	71800	5.130	68900	3.9
PolyCOE	9800	14.47	9700	1.2

Table S6. D-Fw results of PS calibration curve with incorporated polycyclooctene samples for ROMP measurements.

Samples	Mw (GPC) g/mol	ave. D (10^{-10})	ave. Mw (DOSY) g/mol	Diff %
PS	9000	15.02	9700	-7.8
PS	30000	8.082	30800	-2.5
PS	60000	5.397	65300	-8.7
PS	80000	4.688	84800	-6.0
PS	156000	3.305	163000	-4.2
PS	200000	2.998	195000	2.4
BEN	78	200.0	78	-0.2
PolyCOE	71800	5.130	69500	3.1
PolyCOE	9800	14.47	9800	0.4

Table S7. D-Fw results of 1,5-Cyclooctadiene ROMP reaction mixtures in DCM.

t/min	ave.D (10^{-10})	D (δ 1.48) (10^{-10})	D (δ 1.95) (10^{-10})	STDEV	% error
1	16.8	16.7	16.9	0.2	1.0
5	14.8	14.5	15.0	0.02	2.1
10	1.29	1.27	1.29	0.09	1.3
15	1.07	1.05	1.09	0.03	2.2
25	0.880	0.876	0.883	0.02	0.6
30	0.843	0.840	0.844	0.03	0.3
45	0.819	0.816	0.823	0.03	0.6
60	0.815	0.807	0.821	0.03	1.2

t/min	Mw (δ 1.48) g/mol	Mw (δ 1.95) g/mol	STDEV	% error
1	109	106	2	1.8
5	140	133	5	3.9
10	13029	12583	315	2.5
15	18365	17313	743	4.2
25	25968	25586	270	1.0
30	28026	27798	161	0.6
45	29583	29117	329	1.1
60	30220	29269	672	2.3

Table S8. D-Fw results of cyclooctene ROMP reaction mixtures with 2nd generation Grubbs catalyst in DCM.

t/min	ave. D (10^{-10})	ave. Mw (DOSY) g/mol
1	15.50	124
5	13.40	162
10	9.70	297
15	6.05	714
20	3.42	2065
25	0.916	23884
30	0.565	58582
45	0.522	67887
60	0.463	84939

Table S9. D-Fw results of cyclooctene ROMP reaction mixtures with 3rd generation Grubbs catalys in DCM.

t/min	ave. D (10^{-10})	ave. Mw (DOSY) g/mol
1	1.800	6804
5	0.8297	28701
10	0.6290	48021
15	0.6150	50073
20	0.5980	52751
25	0.5894	54190
30	0.5844	55055
45	0.5753	56685
60	0.5751	56721

Table S10. D-Fw results of cyclooctene ROMP reaction mixtures with 2nd generation Grubbs catalyst in THF

t/min	ave. D (10^{-10})	ave. Mw (DOSY) g/mol
1	7.816	440
5	6.225	673
10	4.805	1088
15	3.969	1552
20	3.544	1916
25	2.424	3880
30	2.187	4697
45	2.045	5322
60	1.013	19628

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