Supporting Information for:

Degradable Polyolefins Prepared by Integration of Disulfides into Metathesis Polymerizations with 3,6-Dihydro-1,2-Dithiine

Hong-Gyu Seong,[1] *Thomas P. Russell*,[1,2] *and Todd Emrick*[1]*

[1]*Polymer Science & Engineering Department, Conte Center for Polymer Research, University of Massachusetts, 120 Governors Drive, Amherst, Massachusetts 01003, United States*

[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States*

*Corresponding author E-mail: tsemrick@mail.pse.umass.edu

Materials

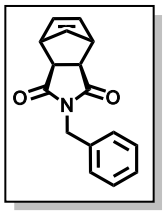
Diallyl disulfide (≥98%, HPLC, LDS), Grubbs Catalyst® M204, pyridine anhydrous (99.8%), Hoveyda-Grubbs Catalyst® M720 (Umicore, 97%), *cis*-cyclooctene (contains 100-200 ppm Irganox 1076 FD as antioxidant, 95%), benzylamine (purified by redistillation, ≥99.5%), ethanolamine (≥98%), *N*-boc-ethylenediamine (≥98%, NT), *β*-alanine *t*-butyl ester hydrochloride (≥98% (TLC)), ethyl *α*-bromoisobutyrate (98%, EBiB), styrene (ReagentPlus®, contains 4-*tert*-butylcatechol as stabilizer, ≥99%), sodium azide (ReagentPlus®, ≥99.5%, NaN_3), ethyl vinyl ether (≥99%, EVE), propagylamine (98%), *N,N*-dimethylformamide (anhydrous, 99.8%, DMF), copper (I) bromide (98%, Cu^IBr), *N,N,N',N'',N''*-pentamethyldiethyltriamine (99%, PMDETA), triethylamine (≥99%) 1-decanethiol (96%), tri-*n*-butylphosphine (99%, n-TBP), and pentane (reagent grade, 98%) were purchased from Sigma Aldrich. *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (98%) was purchased from Oakwood Chemical. Hexane (certified ACS, ≥98.5 %), ethyl acetate (certified ACS, ≥99.5 %, EtOAc), toluene (certified ACS, ≥99.5 %), dichloromethane (ACS, 99.5%, DCM), tetrahydrofuran (certified, THF), diethyl ether (BHT stabilized/certified ACS, ≥99 %), methanol (MeOH), sodium sulfate (Na_2SO_4) and sodium bicarbonate ($NaHCO_3$) were purchased from Fisher Scientific. Deuterated chloroform ($CDCl_3$) for NMR spectroscopy was purchased from Cambridge Isotope Laboratories. DCM was purified by distillation over calcium hydride and THF was purified by distillation over sodium-benzophenone ketyl.

Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-500 spectrometer operating at 500 and 126 MHz respectively, and chemical shifts reported in ppm were calibrated to residual solvent signals. Size-exclusion chromatography (SEC) in THF was performed at 40 ^oC at a flow rate of 1.0 mL min^{-1} on an Agilent 1260 infinity system with a G1362A refractive index detector and G1310B isocratic pump, equipped with a PLgel 5 μm mixed-c (7.5 x 300 mm), a PLgel 5 μm mixed-d (7.5 x 300 mm), and a 5 μm guard column (7.5 x 50 mm) calibrated against poly(styrene) (PS) standards.

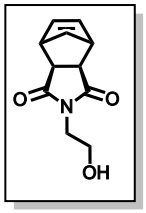
Synthesis

N-(benzyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide (1)



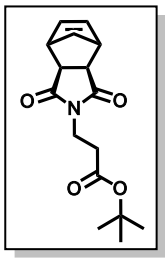
Compound **1** was synthesized according to a published procedure with slight modifications.[1] *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (10.0 g, 60.9 mmol), benzylamine (7.3 mL, 67.0 mmol), TEA (9.4 mL, 67.1 mmol) and toluene (300 mL) were combined in a 1 L one-neck round bottom flask equipped with a magnetic stirring bar, a Dean-Stark apparatus, and a reflux condenser. The mixture was stirred at 120 °C for 24 hours, after which the solution was allowed to cool to room temperature. The solvent was removed under reduced pressure and the crude product was redissolved in EtOAc (150 mL). The crude mixture was washed with 1 M $HCl_{(aq)}$ (3 x 100 mL), water (3 x 100 mL), and brine (3 x 100 mL). The washed organic phase was dried over $Na_2SO_{4(s)}$, filtered, then the solvent was removed under reduced pressure to yield a white solid (14.3 g, 92.5 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.30 (m, 5H), 6.27 (t, J = 2.0 Hz, 2H), 4.62 (s, 2H), 3.25 (t, J = 2.0 Hz, 2H), 2.68 (d, J = 1.5 Hz, 1H), 1.40 and 1.07 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 177.84, 138.08, 136.04, 129.03, 128.79, 128.06, 47.95, 45.44, 42.78, 42.51.

N-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide (2)



Compound **2** was synthesized according to our previously published procedure[1] to yield a white powder (26.1 g, 68.8 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.28 (t, J = 1.5 Hz, 2H), 3.76-3.78 (m, 2H), 3.68-3.70 (m, 2H), 3.26-3.31 (m, 2H), 2.69-2.73 (m, 2H), 2.3 (s, 1H), 1.48-1.54 (m, 1H), 1.32-1.37 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 178.90, 137.98, 60.72, 48.05, 45.44, 42.93, 41.51.

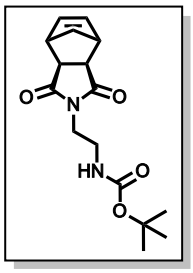
N-(*t*-butyl ester)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide (3)



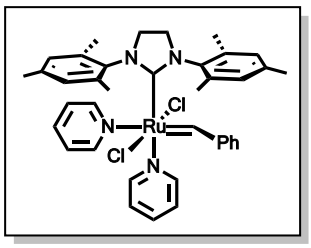
t-Butyl ester **3** was synthesized according to a published procedure with slight modifications.[1] *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (2.0 g, 12.2 mmol), *β*-alanine *t*-butyl ester hydrochloride (2.65 g, 14.6 mmol), TEA (2.2 mL, 15.9 mmol) and toluene (60 mL) were combined in a 500 mL one neck round bottom flask equipped with a magnetic stirring bar, a Dean-Stark apparatus, and a

reflux condenser. The mixture was stirred at 120 °C for 24 hours and the solution was cooled to room temperature. The crude solution was concentrated under reduced pressure, redissolved in DCM (100 mL), and washed with 1 M $HCl_{(aq)}$ (3 x 150 mL) and brine (1 x 150 mL). The solution was dried over $Na_2SO_{4(s)}$, filtered, and concentrated under reduced pressure to yield a yellow a white solid (2.83 g, 79.7 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.26 (t, *J* = 2.5 Hz, 2H), 3.72 (t, *J* = 9.0 Hz, 2H), 3.25 (t, *J* = 2.0 Hz, 2H), 2.66 (d, *J* = 1.5 Hz, 2H), 2.51 (t, *J* = 9.0 Hz, 1H), 1.49 and 1.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 177.76, 169.97, 137.95, 81.22, 47.90, 45.30, 42.86, 34.69, 33.45, 28.08.

_N_-(_t_-boc aminoethyl)-_cis_-5-norbornene-_exo_-2,3-dicarboxyimide (4)



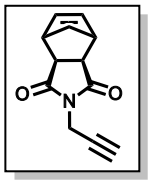
t-Boc aminoethyl **4** was synthesized according to a published procedure with slight modifications.[1] *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (3.8 g, 23.0 mmol), *N*-boc-ethylenediamine (4.0 mL, 25.3 mmol) and toluene (150 mL) were combined in a 500 mL one neck round bottom flask equipped with a magnetic stirring bar, a Dean-Stark apparatus, and a reflux condenser. The mixture was stirred at 120 °C for 24 hours and the solution was cooled to room temperature. The crude solution was concentrated under reduced pressure, redissolved in DCM (100 mL), and washed with 1 M $HCl_{(aq)}$ (3 x 150 mL) and saturated $NaHCO_{3(aq)}$ (3 x 150 mL). The solution was dried over $Na_2SO_{4(s)}$, filtered, and concentrated under reduced pressure to yield a yellow a white solid (5.61 g, 79.7 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.28 (t, *J* = 2.0 Hz, 2H), 4.77 (s, 1H), 3.62 (t, *J* = 6.0 Hz, 2H), 3.34 (d, *J* = 5.0 Hz, 2H), 3.27 (t, *J* = 1.5 Hz, 2H), 2.69 (d, J = 1.0 Hz, 2H), 1,64 and 1.26 (m, 2H), 1.40 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 178.35, 156.01, 137.97, 48.04, 45.30, 43.00, 39.28, 38.58, 28.47.



***Grubbs 3rd generation catalyst (G3**, ligand substitution)*

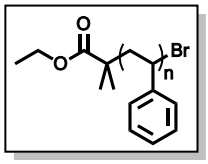
The **G3** catalyst was synthesized according to the previously published procedure[2] to yield the compound as a green powder (376 mg, 87 % yield).

***N*-(propargyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide**



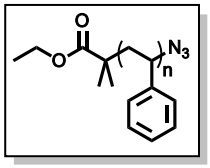
The alkynyl product was synthesized according to our previously published procedure[3] to yield a pale-yellow crystalline solid (26.5 g, 90.7 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.28 (s, 2H), 4.21 (m, 2H), 3.26 (m, 2H), 2.70 (s, 2H), 2.17 (m, 1H), 1.51 (d, J = 11 Hz, 1H), 1,27 (d, J = 11 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 176.73, 138.10, 76.64, 71.49, 47.94, 45.65, 42.88, 27.69.

PS-Br *(via atom-transfer radical polymerization)*



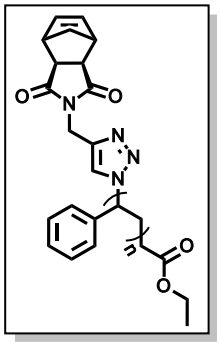
PS-Br was synthesized according to our previously published procedure[4] to yield a white powder (36.6 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.23-7.24 (br, 130H), 4.43 (br, 1H), 3.64 (br, 2H). $M_{n,NMR}$ = 2.9 kDa, $M_{n,SEC}$ = 2.3 kDa, PDI = 1.09.

PS-N₃ *(via azidation)*



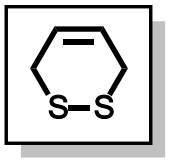
PS-N_3 was synthesized according to our previously published procedure[4] to yield a white powder (15.9 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.23-7.24 (br, 127H), 3.96 (br, 1H), 3.65 (br, 2H).

NB-PS *(copper-catalyzed azide-alkyne cycloaddition product)*



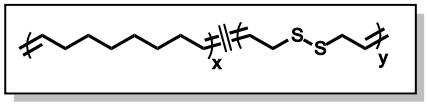
NB-PS was synthesized according to our previously published procedure[4] to yield a white powder (10.9 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.30-7.23 (br, 126H), 6.25 (s, 2H), 5.01 (br, 1H), 4.60 (m, 2H), 3.63 (br, 2H+impurity), 3.23 (s, 2H), 2.64 (m, 2H), $M_{n,NMR}$ = 2.9 kDa, $M_{n,SEC}$ = 2.6 kDa, PDI = 1.07.

(Z)-3,6-dihydro-1,2-dithiocine (CDS)



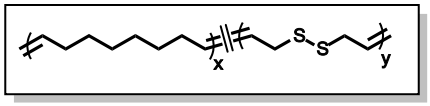
LDS (0.50 mL, 3.5 mmol) and anhydrous THF (340 mL) were charged in a flame-dried, 2-neck round bottom flask (500 mL) equipped with a condenser and a magnetic stir bar. G3 (8.6 mL from a G3 stock solution in anhydrous THF with 0.02 M) was added and the flask was immersed in an oil bath pre-heated to 70 °C, and the mixture stirred under $N_{2(g)}$ atmosphere for 5 hours. After cooling to room temperature, the solution was exposed to air and stirred for 30 additional minutes. The crude product was concentrated under reduced pressure and the remaining product was redissolved in hexane (50 mL, a good solvent for diallyl disulfide but bad solvent for G3) and passed through a basic alumina. The collected organic solution was concentrated under reduced pressure to yield a colorless, transparent oil (0.26 g, 63.7 %). When the product was stored at -20 °C, it became a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 5.99 (m, 2H), 3.74 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm):125.87, 28.42.

Example ring-opening metathesis copolymerization of CDS with COE: Entry 2 in Table 2



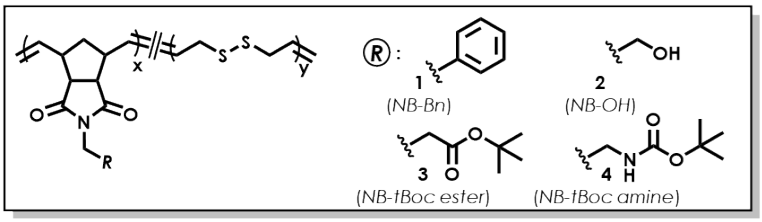
COE (65.7 μL, 0.50 mmol) and **CDS** (14.7 mg, 0.12 mmol) were added to a flame-dried 7 mL scintillation vial with a magnetic stir bar. The vial was purged with $N_{2(g)}$ and anhydrous THF (total [MM] = 0.5 M) (previously purged with $N_{2(g)}$ for 15 min) was added. A stock solution of G3 (0.01 M) was prepared under $N_{2(g)}$ atmosphere in a flame-dried 7 mL scintillation vial. Polymerization was initiated by adding the G3 solution to the COE + **CDS** mixture in stoichiometric amounts intended to yield half of the desired N_{BB} ([M]/[Cat.]). The solution was stirred at room temperature for 2 hours under $N_{2(g)}$. EVE (0.1 mL) was added to quench the polymerization. After removing the solvent, monomer conversion, M_n, and PDI were assessed by ^{1}H NMR and SEC, for the latter eluting with THF.

Kinetic study of ring-opening metathesis copolymerization of CDS with COE (P-20-k)



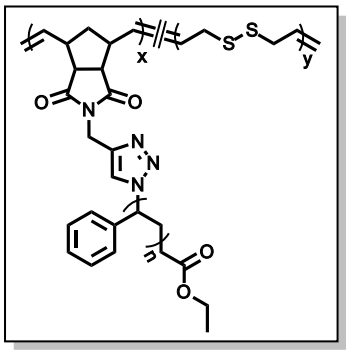
COE (131.0 μL, 0.99 mmol) and **CDS** (29.4 mg, 0.25 mmol) were added to a flame-dried 7 mL scintillation vial with a magnetic stir bar. The vial was purged with $N_{2(g)}$ and anhydrous THF (310 μL, intended to yield total [MM] = 2.0 M, previously purged with $N_{2(g)}$ for 15 min) was added to the vial. A stock solution of Grubbs initiator (G3, 0.01 M) was prepared under $N_{2(g)}$ atmosphere in a flame-dried 7 mL scintillation vial. The polymerization was initiated by adding the G3 solution (310 μL) to the reaction mixture intended to yield N_{BB} ([M]/[Cat.]) = 400. The solution was stirred at room temperature under $N_{2(g)}$. Aliquots (~50 μL) were removed at 1, 3, 5, 10, 20, and 180 min, and directly added into a 7 mL scintillation vial with EVE (~0.5 mL) to quench the reaction. After removing the solvent of the quenched samples under reduced pressure, M_n and PDI of the crude aliquots were checked by SEC eluting with THF (ROMP after 180 min: $M_{n,\,SEC}$ = 29.1 kDa, PDI = 1.50 with PS standard).

Example ring-opening metathesis copolymerization of CDS with 1-4: Entry 3 in Table 3 as an example



CDS (14.7 mg, 0.12 mmol) and **1** (125.9 mg, 0.50 mmol) were added to a flame-dried 7 mL scintillation vial with a magnetic stirring bar. The vial was purged with $N_{2(g)}$ and anhydrous THF (total [MM] = 0.05 M) (previously purged with $N_{2(g)}$ for 15 min) was added to the vial. A stock solution of G3 (0.01 M) was prepared under $N_{2(g)}$ atmosphere in a flame-dried 7 mL scintillation vial. The polymerization was initiated by adding the G3 solution to the **CDS**+**1** mixture in stoichiometric amounts intended to yield a half of desired N_{BB} ([M]/[Cat.]). The solution was stirred at room temperature for 2 hours under $N_{2(g)}$. EVE (0.1 mL) was added to quench the polymerization. After removing the solvent, the conversion of ROMP and M_n and PDI were checked by ^{1}H NMR and SEC eluting with THF.

Ring-opening metathesis copolymerization of CDS with NB-PS, BP-10



NB-PS (117 mg, 0.045 mmol) was added to a flame-dried 7 mL scintillation vial with a magnetic stirring bar. The vial was purged with $N_{2(g)}$ and anhydrous THF (total [MM] = 0.05 M) (previously purged with $N_{2(g)}$ for 15 min) was added to the vial. Each stock solution of **CDS** (0.1 M) and Grubbs initiator (G3, 0.01 M) were prepared under $N_{2(g)}$ atmosphere in the flame-dried 7 mL scintillation vials. Upon injection of stock solution of **CDS** (0.6 mg, 0.005 mmol), the polymerization was initiated by adding the Grubbs initiator solution to the **CDS**+**NB-PS** mixture in stoichiometric amounts intended to yield a half of desired N_{BB} ([M]/[Cat.]). The solution was stirred at room temperature for 2 hours under $N_{2(g)}$. EVE (0.1 mL) was added to quench the polymerization. After removing the solvent, the conversion of ROMP and M_n & PDI were checked by ^{1}H NMR and SEC eluting with THF characterizations. The crude product was used for the disulfide reduction experiment without further purification ($M_{n,\,SEC}$ = 76.2 kDa, PDI = 1.28 with PS standard).

Example terpolymerization of COE, LDS, and CDS (COE:LDS:CDS = 8:1:1)

COE (65.7 μL, 0.50 mmol), LDS (9.0 mg, 0.06 mmol), and **CDS** (7.3 mg, 0.06 mmol) were added to a flame-dried 7 mL scintillation vial with a magnetic stirring bar. The vial was then purged with $N_{2(g)}$. A stock solution of G3 (0.01 M) was prepared under $N_{2(g)}$ atmosphere in a flame-dried 7 mL scintillation vial. The polymerization was initiated by adding the Grubbs initiator solution to the COE + LDS + **CDS** mixture in stoichiometric amounts intended to yield half of desired N_{BB} ([M]/[Cat.]). Upon injection of the initiator solution, the overall solution concentration was ~2.0 M. The solution was stirred at room temperature for 2 hours under $N_{2(g)}$. EVE (0.1 mL) was then added to quench the polymerization. After removing solvent, the conversion of ROMP and M_n and PDI were assessed by ^{1}H NMR spectroscopy and SEC eluting with THF characterizations.

Degradation kinetics study of polyolefins via disulfide reduction

(a) Linear polymer example

P-20-*k*, synthesized for the ROMP kinetic study ($M_{n,\ SEC}$ = 29.1 kDa and PDI = 1.50), was selected as a model PCOE for this experiment. **P-20-*k*** (30 mg, 0.001 mmol, ~0.08 mmol of disulfide) and DCM (1 mL) were added in a 7 mL scintillation vial with a magnetic stir bar. n-TBP (100 μL, 0.4 mmol) was then added and the resultant solution was stirred at room temperature. Aliquots (0.1 mL) were removed at 5, 20, and 60 min, each added directly into a 7 mL scintillation vial, and dried under vacuum. After removing solvent from the quenched samples under reduced pressure, the resultant, degraded linear polymer was analyzed by SEC, eluting with THF (Degradation after 60 min: $M_{n,\ SEC}$ = 2.8 kDa, PDI = 2.17).

(b) Bottlebrush polymer case

BP-10 (10.0 mg, 0.0004 mmol of disulfide) and DCM (0.2 mL) were combined in a 2 mL scintillation vial with a magnetic stir bar. n-TBP (1 μL, 0.004 mmol) was added and the resultant solution was stirred at room temperature for 60 min. The crude product was dried under vacuum. The degraded bottlebrush polymer product was analyzed by SEC, eluting with THF (degradation after 60 min: $M_{n,\ SEC}$ = 31.3 kDa, PDI = 1.43 with PS standard).

Degradation of polyolefin via thiol-disulfide exchange

P-20-*k*, synthesized for ROMP kinetics experiments ($M_{n,\ SEC}$ = 29.1 kDa and PDI = 1.50), was selected as a model PCOE for this experiment. **P-20-*k*** (6.0 mg, 0.0002 mmol, 0.016 mmol of disulfide) and DCM (0.3 mL) were added to a 2 mL scintillation vial with a magnetic stir bar. 1-Decanethiol (case 1: 1 equiv., 4 μL, 0.016 mmol; case 2: 5 equiv., 19 μL, 0.08 mmol) was added in the solution, followed by stirring at room temperature for 60 min. The crude products were dried under vacuum. The degraded bottlebrush polymer was analyzed by SEC, eluting with THF (case 1: $M_{n,\ SEC}$ = 17.8 kDa, PDI = 1.71 / case 2: $M_{n,\ SEC}$ = 9.1 kDa, PDI = 1.76 with PS standard).

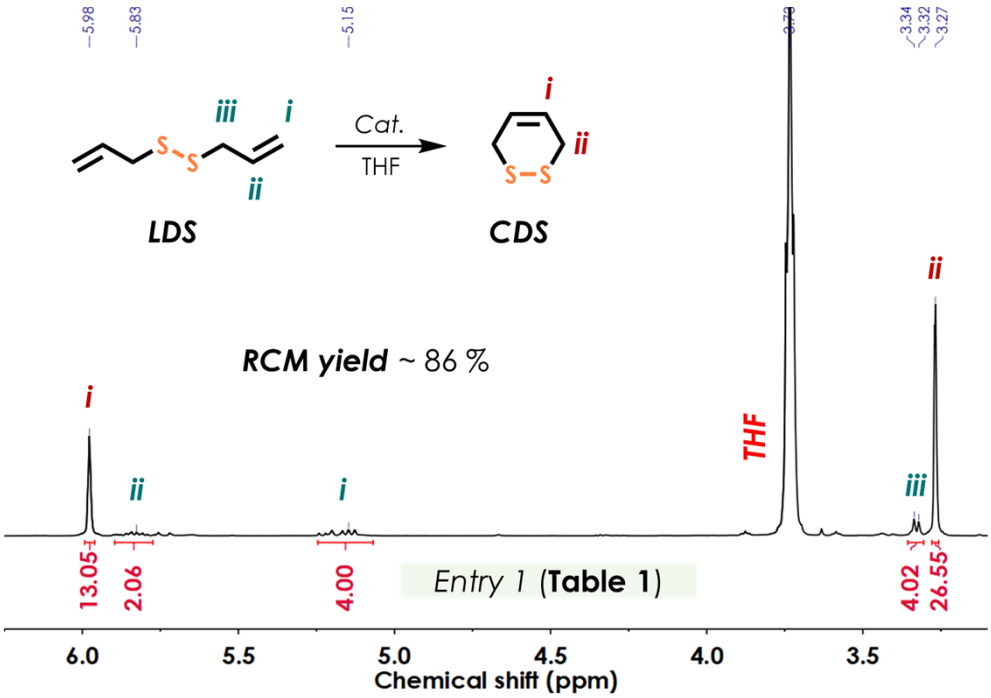


Figure S1. ^{1}H NMR spectrum of **CDS** (Entry 1, Table 1) recorded in $CDCl_3$.

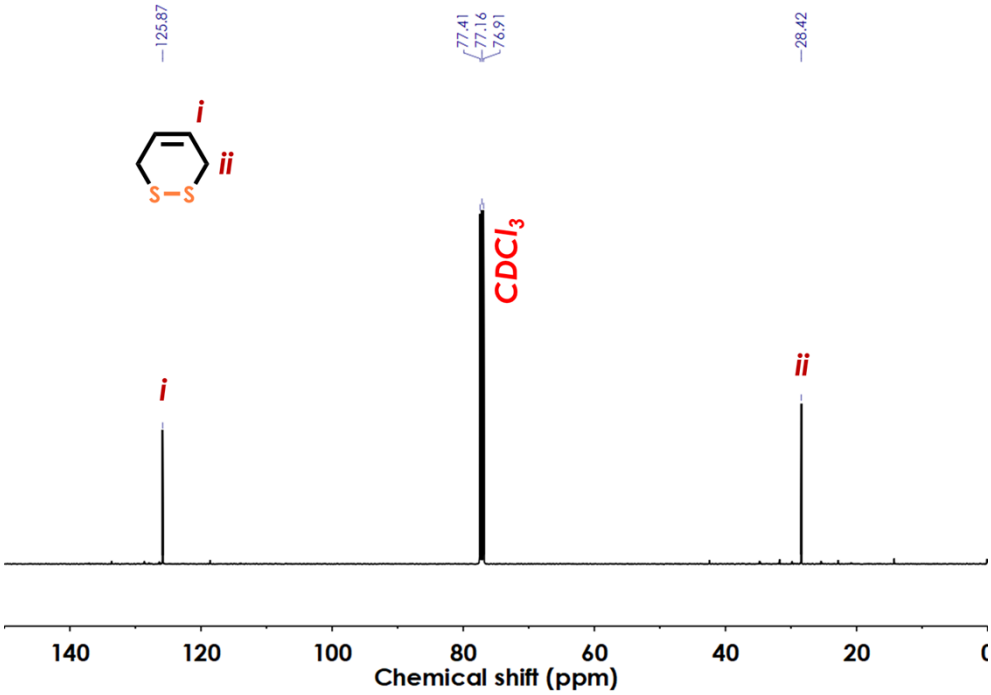


Figure S2. ^{13}C NMR spectrum of **CDS** recorded in $CDCl_3$.

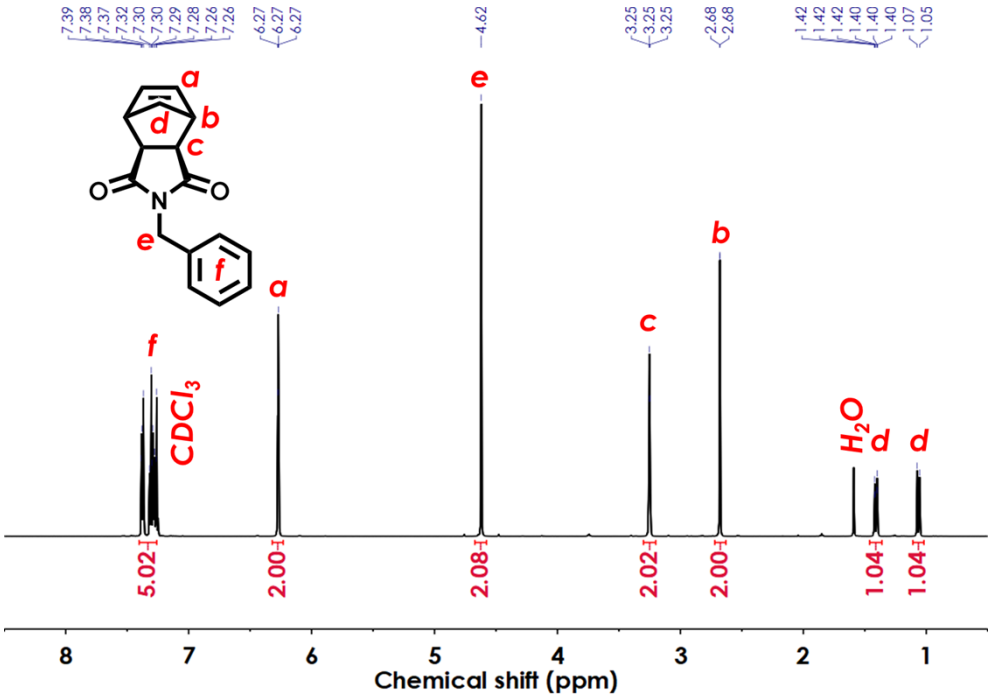


Figure S3. ^{1}H NMR spectrum of *N*-(benzyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide recorded in $CDCl_3$.

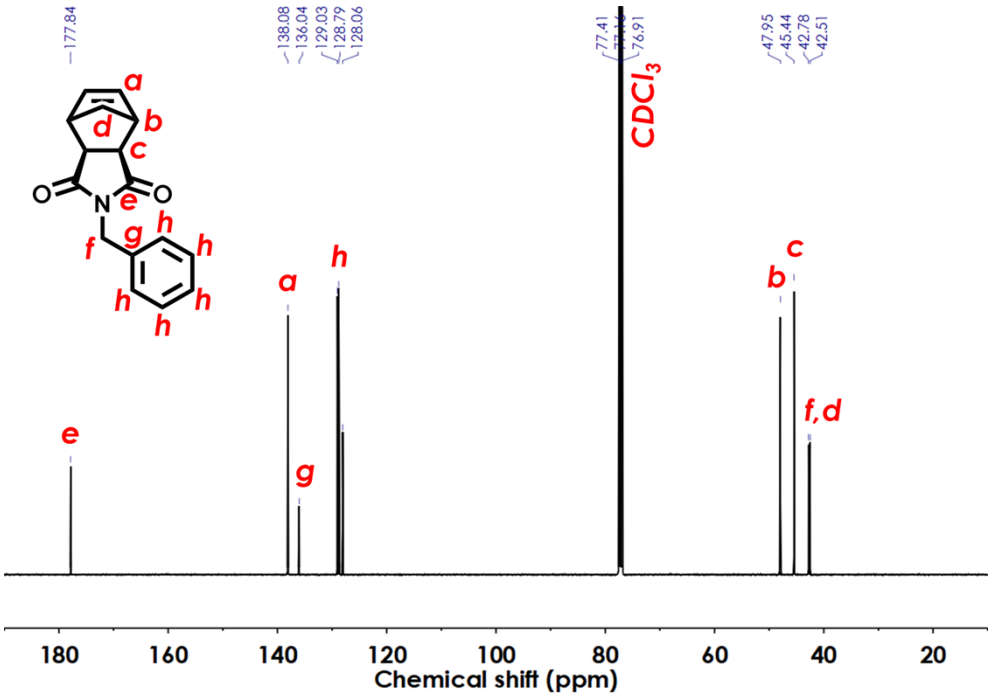


Figure S4. ^{13}C NMR spectrum of *N*-(benzyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide recorded in $CDCl_3$.

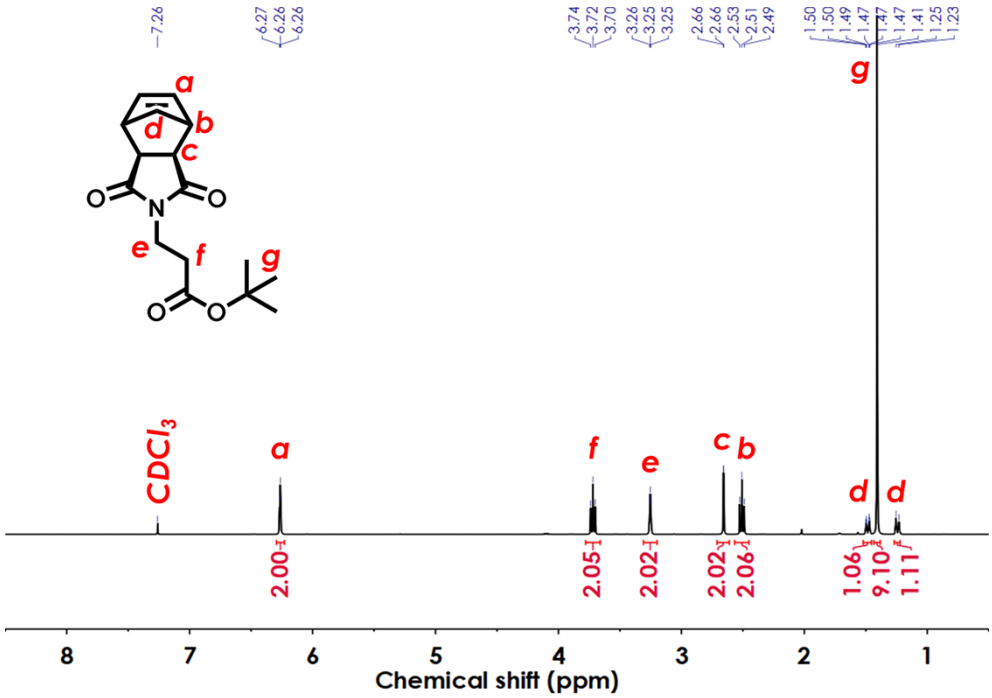


Figure S5. ^{1}H NMR spectrum of *N*-(*t*-butyl ester)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide recorded in $CDCl_3$.

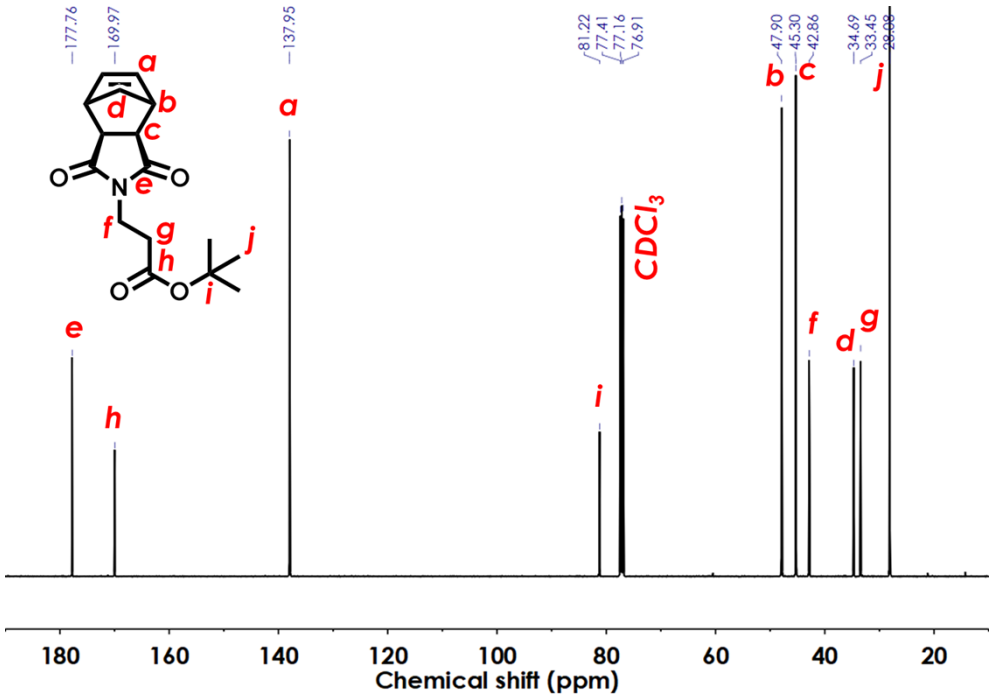


Figure S6. ^{13}C NMR spectrum of *N*-(*t*-butyl ester)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide recorded in $CDCl_3$.

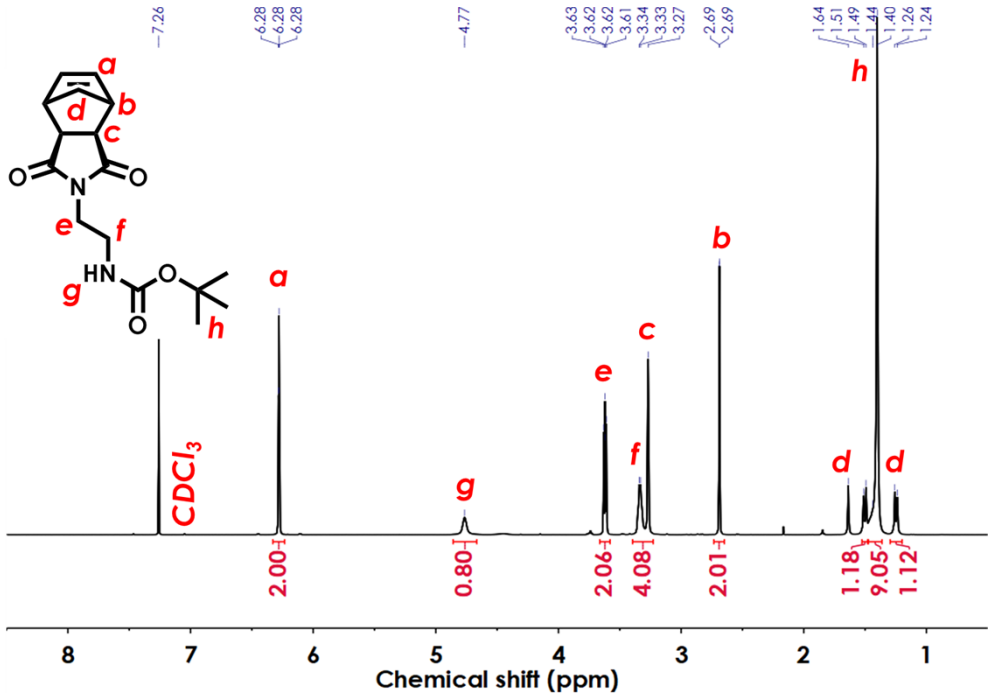


Figure S7. ^{1}H NMR spectrum of *N*-(*t*-boc aminoethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide recorded in $CDCl_3$.

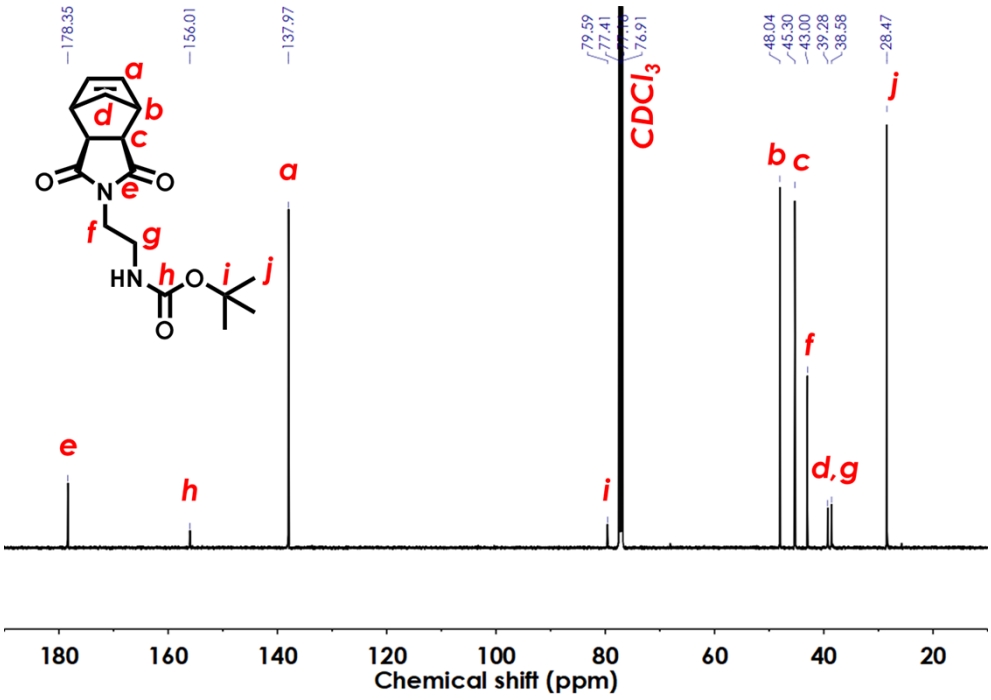


Figure S8. ^{13}C NMR spectrum of *N*-(*t*-boc aminoethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboxyimide recorded in $CDCl_3$.

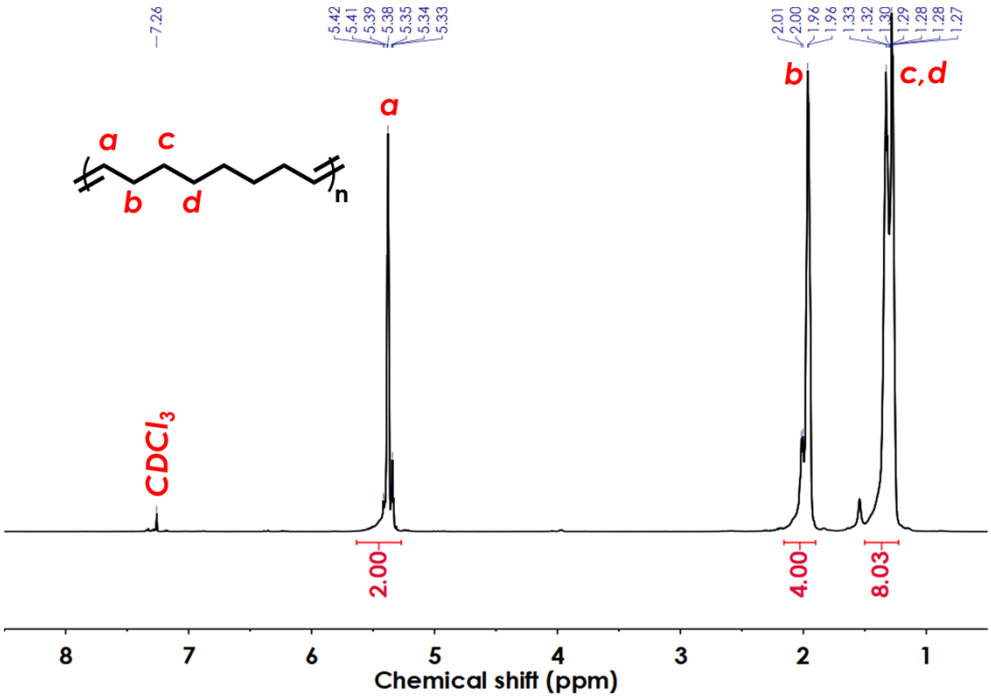


Figure S9. ^{1}H NMR spectrum of PCOE homopolymer recorded in $CDCl_3$.

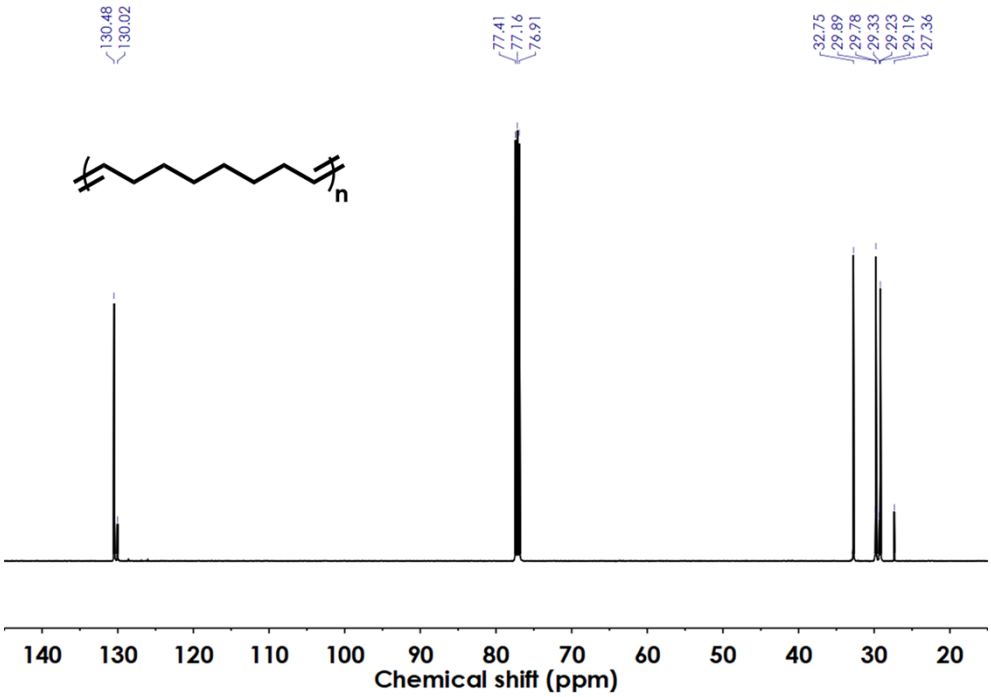


Figure S10. ^{13}C NMR spectrum of PCOE homopolymer recorded in $CDCl_3$.

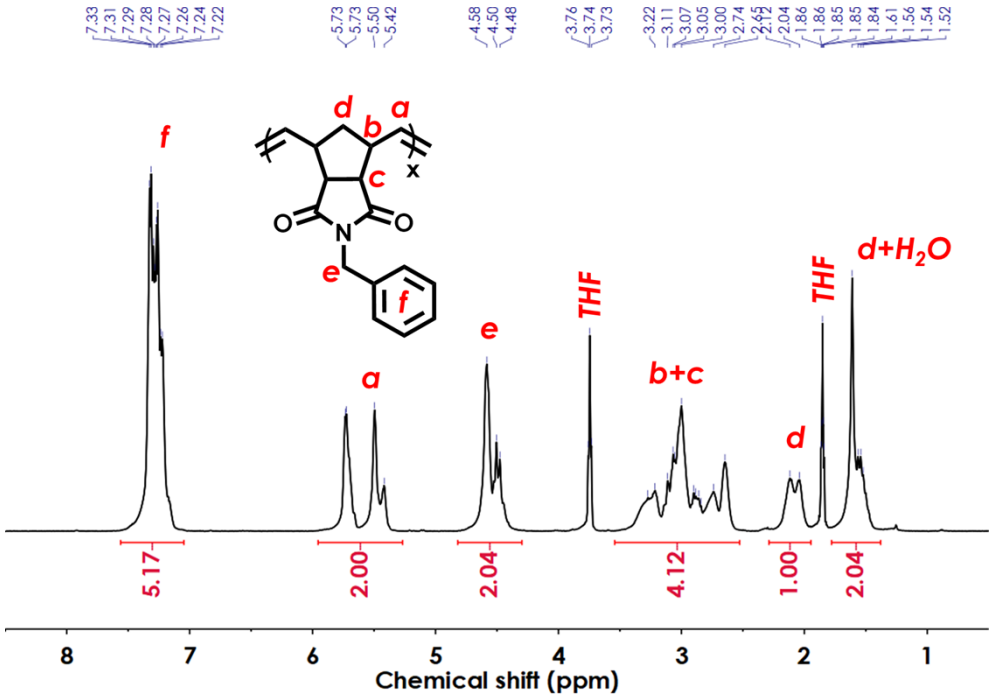


Figure S11. ^{1}H NMR spectrum of PNB-Bn homopolymer recorded in $CDCl_3$.

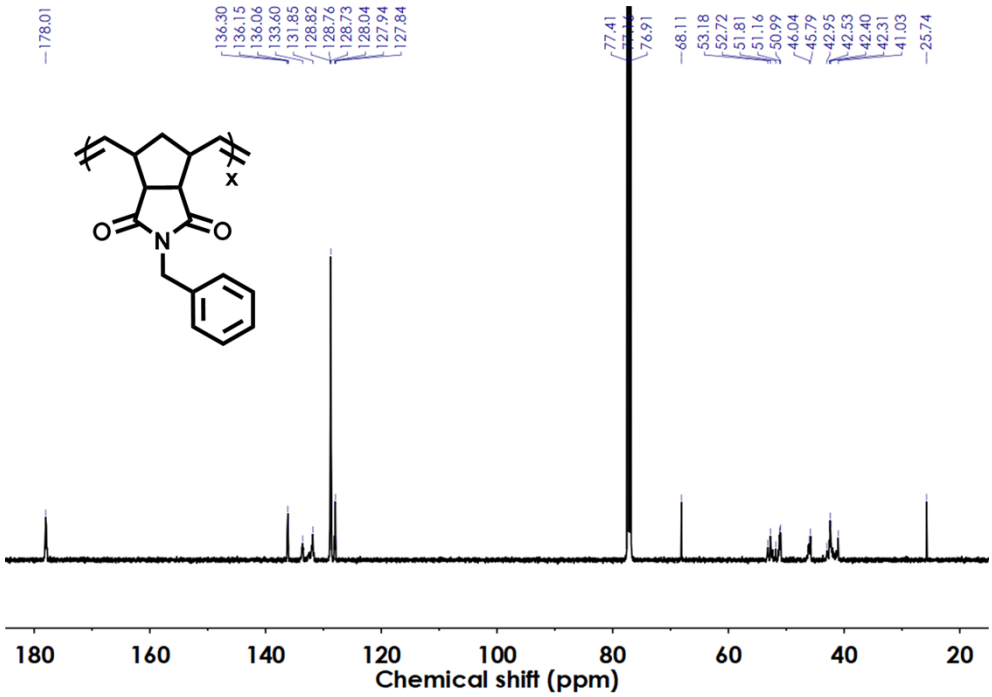


Figure S12. ^{13}C NMR spectrum of PNB-Bn homopolymer recorded in $CDCl_3$.

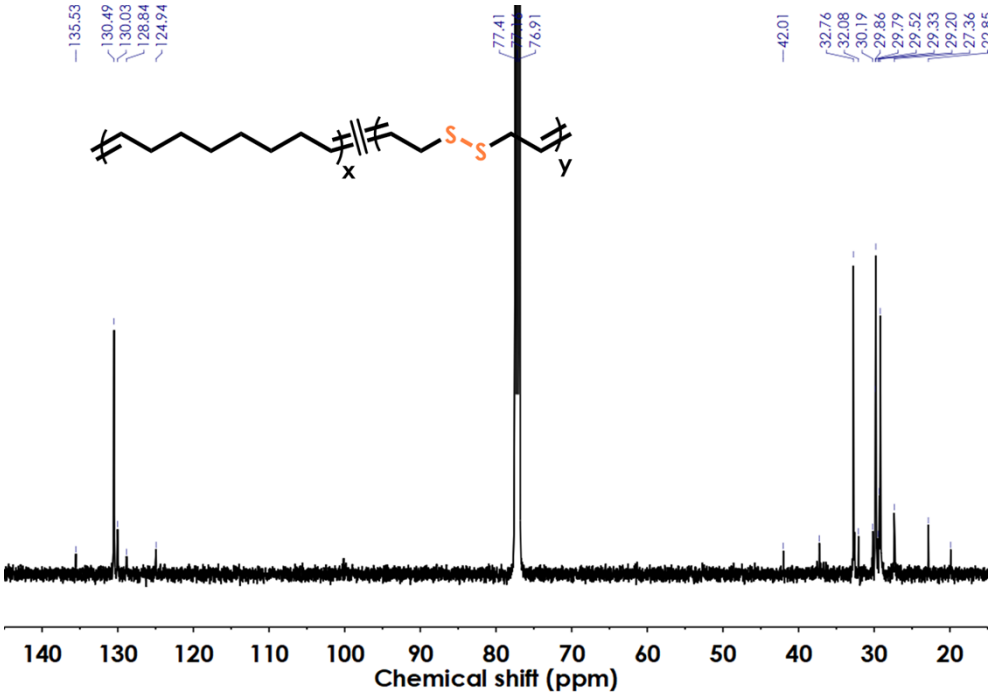


Figure S13. ^{13}C NMR spectrum of P-20 recorded in $CDCl_3$.

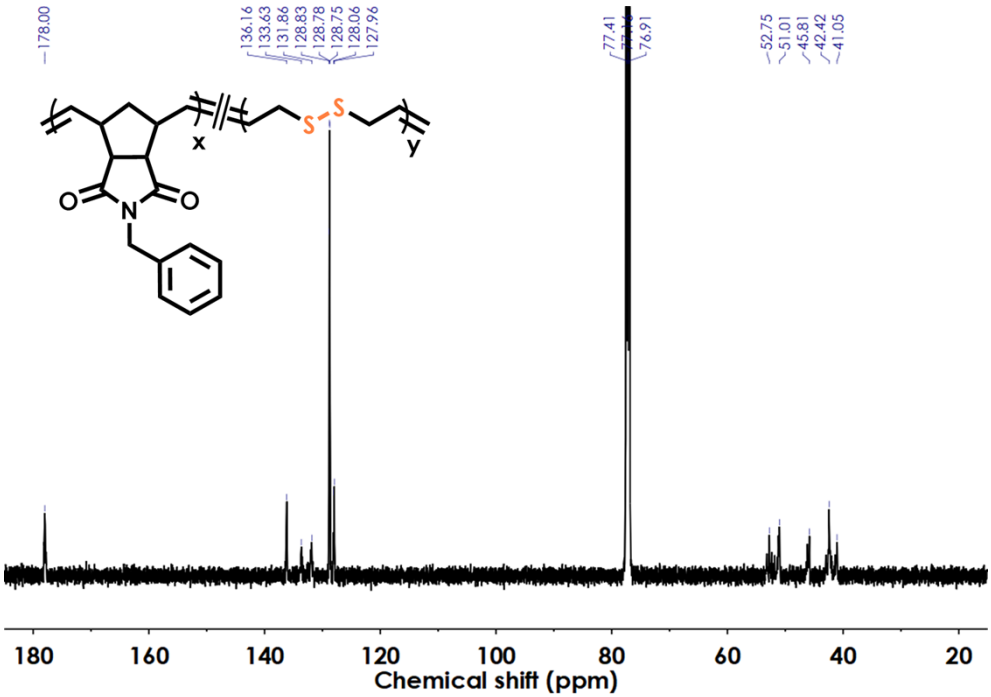


Figure S14. ^{13}C NMR spectrum of P1-20 recorded in $CDCl_3$.

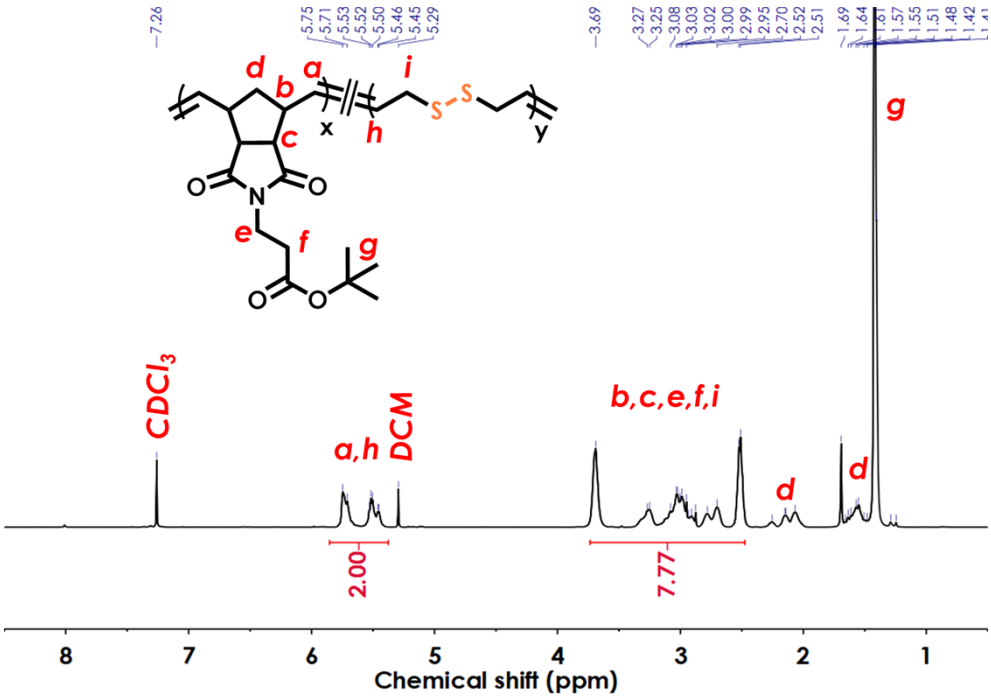


Figure S15. ^{1}H NMR spectrum of P3-20 recorded in $CDCl_3$.

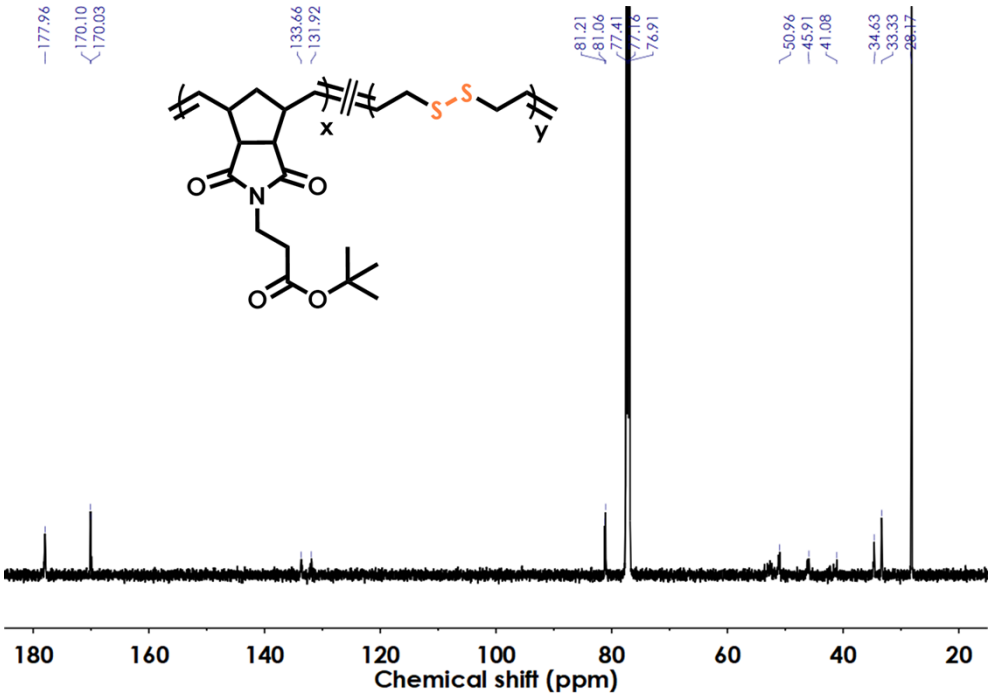


Figure S16. ^{13}C NMR spectrum of P3-20 recorded in $CDCl_3$.

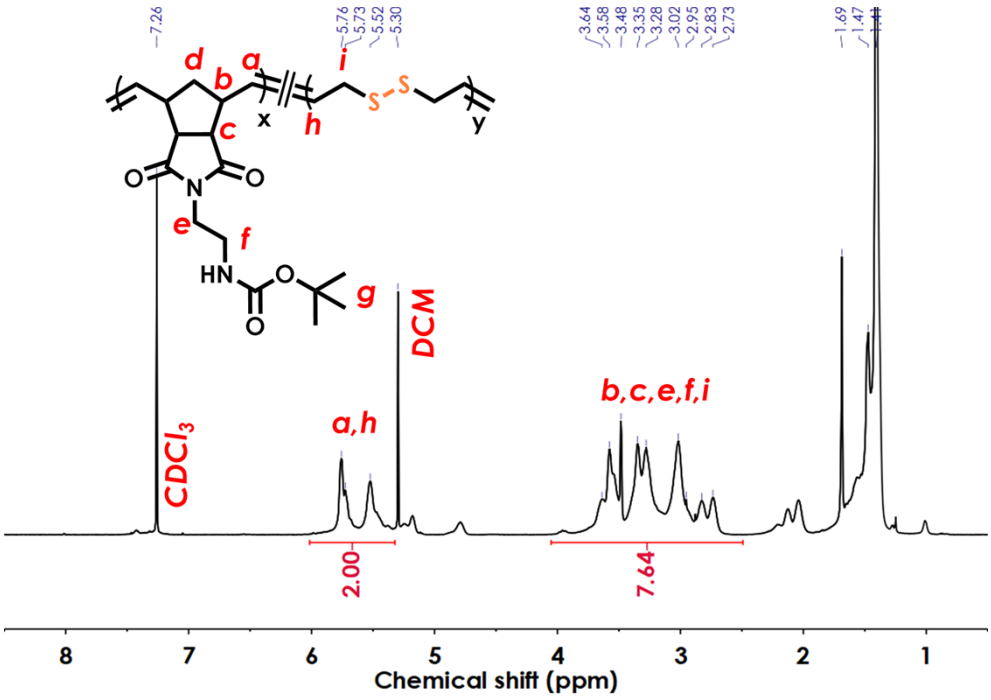


Figure S17. ^{1}H NMR spectrum of P4-20 recorded in $CDCl_3$.

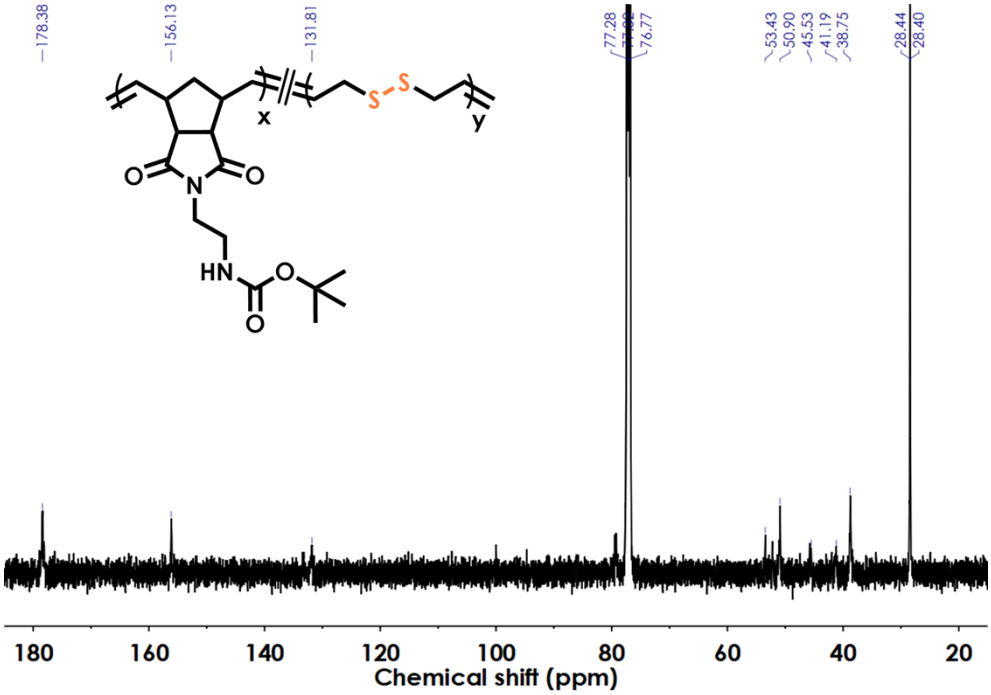


Figure S18. ^{13}C NMR spectrum of P4-20 recorded in $CDCl_3$.

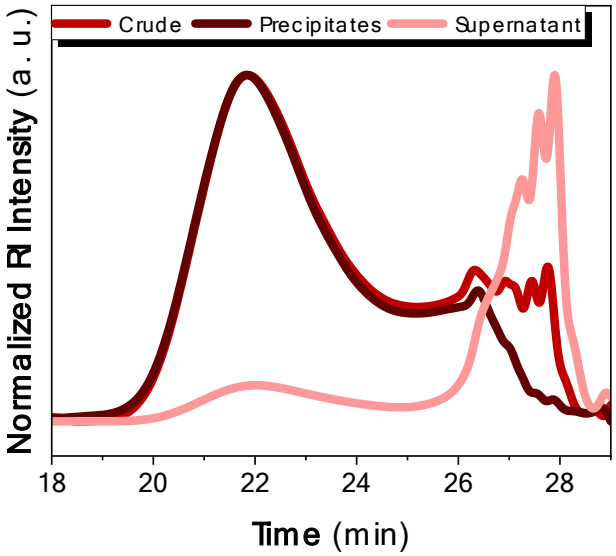


Figure S19. Chromatograms (SEC eluting with THF) of Entry 2 in Table 2, before and after precipitation.

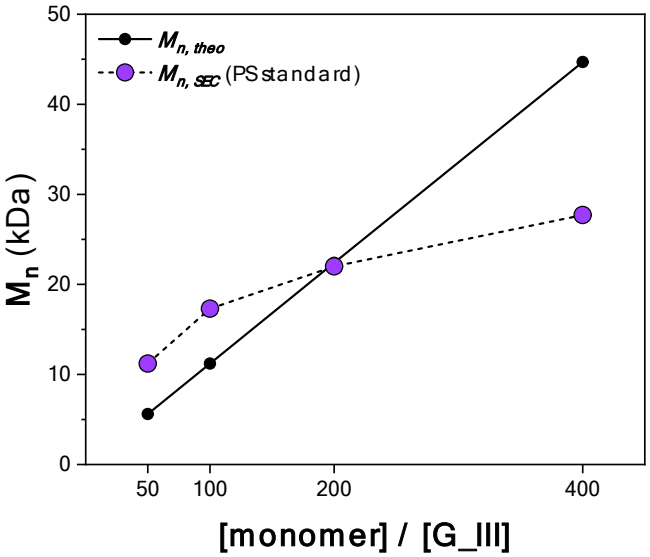


Figure S20. $M_{n,SEC}$ *vs.* target DP of ROMP copolymerizations: COE and **CDS**.

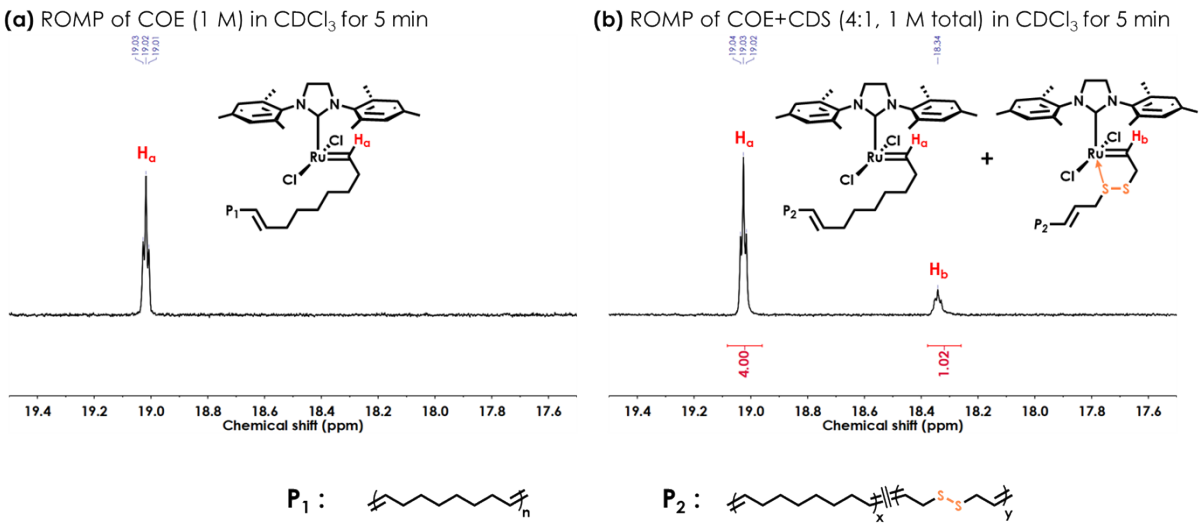


Figure S21. ^{1}H NMR spectrum of ruthenium alkylidene of (a) COE and (b) COE+**CDS** (4:1 molar ratio) during ROMP in $CDCl_3$ with total monomer concentration of 1 M. Proposed disulfide-ruthenium interactions shown in (b).

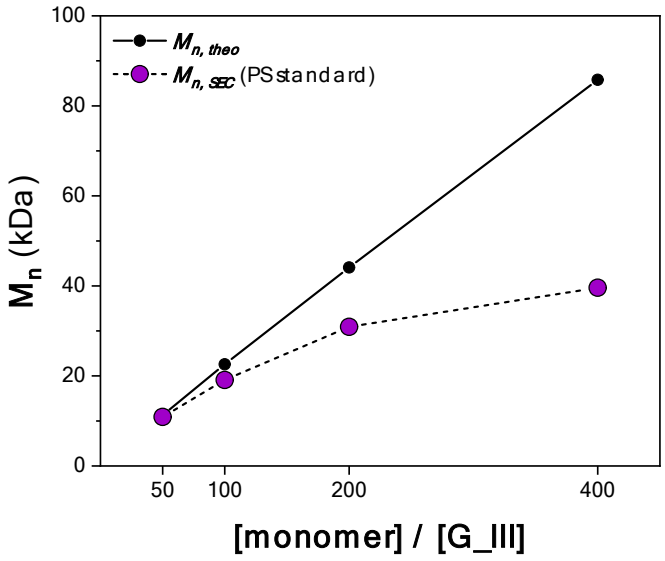


Figure S22. $M_{n,SEC}$ *vs.* target DP of ROMP copolymerizations: NB-Bn and **CDS**.

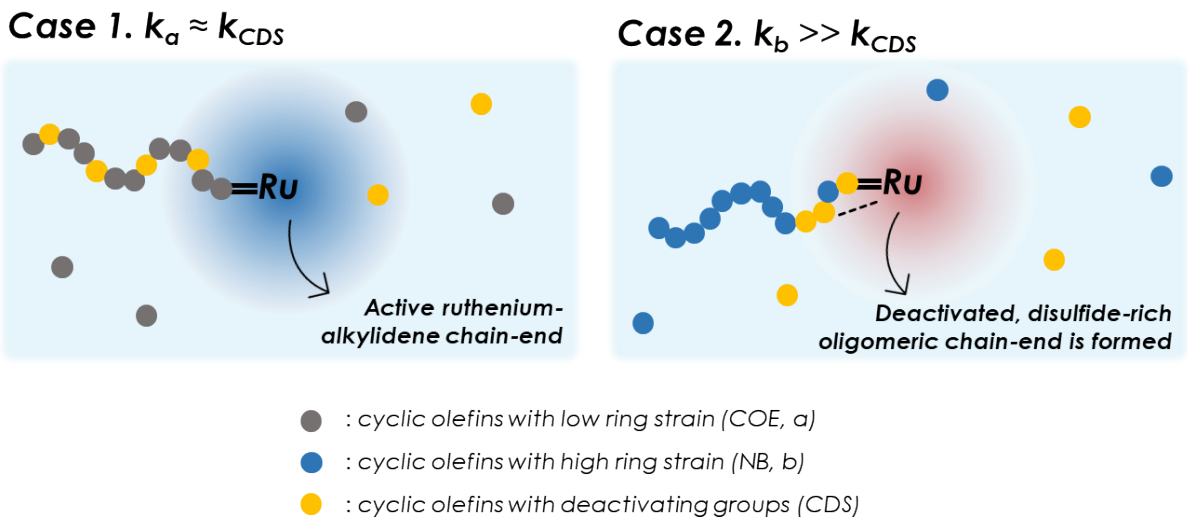


Figure S23. Hypothetical illustration of ROMP copolymerizations, showing ***Case 1*** with COE and **CDS** where randomly distributed CDS units along the chain minimize disulfide chelation to the ruthenium catalyst, and ***Case 2*** with NB-derivatives and **CDS** where consecutive CDS units exacerbate disulfide chelation to the ruthenium catalyst.

References

1. H. -G. Seong, Z. Chen, T. Emrick and T. P. Russell, Reconfiguration and Reorganization of Bottlebrush Polymer Surfactants, *Angew. Chem. Int. Ed.*, 2022, **61**, e202200530.
2. J. A. Love, J. P. Morgan, T. M. Trnka and R. H. Grubbs, A practical and highly active ruthenium-based catalyst that effects the cross metathesis of acrylonitrile, *Angew. Chem. Int. Ed.*, 2002, **41**, 4035-4037.
3. H. -G. Seong, Z. Fink, Z. Chen, T. Emrick and T. P. Russell, Bottlebrush Polymers at Liquid Interfaces: Assembly Dynamics, Mechanical Properties, and All-Liquid Printed Constructs, *ACS Nano*, 2023, **17**, 14731-14741.
4. Z. Chen, H. -G. Seong, M. Hu, X. Gan, A. E. Ribbe, J. Ju, H. Wang, M. Doucet, T. Emrick and T. P. Russell, Janus Bottlebrush Compatibilizers, *Soft Matter*, 2024, **20**, 1554-1564.