Appendix A

Appendix to Chapter 2: Control over the Graft Polymer Architecture via Ring-Opening Metathesis Polymerization

1. Lin, T.-P.; Chang, A. B.; Chen, H.-Y.; Liberman-Martin, A. L.; Bates, C. M.; Voegtle, M. J.; Bauer, C. A.; Grubbs, R. H. Control of Grafting Density and Distribution in Graft Polymers by Living Ring-Opening Metathesis Copolymerization. *J. Am. Chem. Soc.* **2017**, *139*, 3896–3903.

2. Chang, A. B.;[+] Lin, T.-P.;[+] Thompson, N. B.; Luo, S.-X.; Liberman-Martin, A. L.; Chen, H.-Y.; Grubbs, R. H. Design, Synthesis, and Self-Assembly of Polymers with Tailored Graft Distributions. *J. Am. Chem. Soc.* **2017**, *139*, 17683–17693. ([+]*Equal contributions.*)

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A-1 Instrumentation

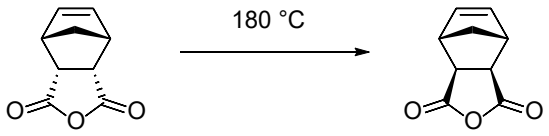
Ambient-temperature NMR spectra were recorded on a Varian 400 MHz or 500 MHz NMR spectrometer. Chemical shifts (δ) were given in ppm and referenced against residual solvent signals (^{1}H, ^{13}C). SEC data were collected using two Agilent PLgel MIXED-B 300 × 7.5 mm columns with 10 μm beads, connected to an Agilent 1260 Series pump, a Wyatt 18-angle DAWN HELEOS light scattering detector, and Optilab rEX differential refractive index detector. Online determination of d*n*/d*c* assumed 100% mass elution under the peak of interest. The mobile phase was THF. Thermal profiles of polymer samples were obtained using a Hitachi DSC7020 calorimeter with an aluminum reference pan. Following an initial run to erase thermal history (by heating from 25 °C to 130 °C at a rate of 10 °C/min), sample temperature was maintained at 120 °C in an external oven while the furnace cooled for approximately 20 minutes. Samples were then removed from the oven, cooled for 45 seconds on a thermally conductive surface, then rerun through an identical calorimeter cycle (25–130 °C, 10 °C/min). The reported data were collected on the second heating ramp.

A-2 Macromonomer Synthesis

The work presented in this thesis employs macromonomers featuring poly(D,L-lactide) (**PLA**), polystyrene (**PS**), poly(dimethyl siloxane) (**PDMS**), and poly(ethylene oxide) (**PEO**) side chains. This section describes the synthesis of all macromonomers.

*A-2.1 Synthesis of Poly(D,L-lactide) Macromonomer (**PLA**)*[1]

Scheme A.1: Synthesis of *cis*-5-norbornene-*exo*-dicarboxylic anhydride (**A.1**).

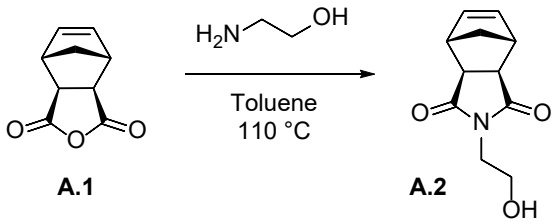


A.1

A 500 mL round bottom flask was half filled with commercially available *cis*-5-norbornene-*endo*-dicarboxylic anhydride (carbic anhydride), fitted with a reflux

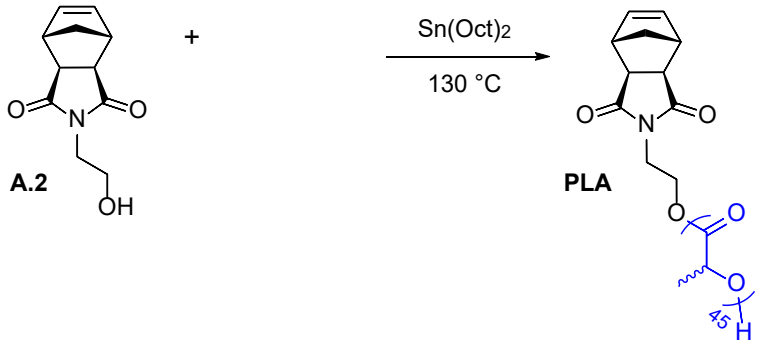
condenser, and heated neat at 180 °C for 16 hours. The resulting molten yellow solid was slowly cooled to 75 °C and benzene was added before the entire volume crystallized to facilitate dissolution. The resulting mixture was heated to reflux and crystallized at room temperature. The recrystallization in benzene was repeated three additional times to yield a white or slightly off-white crystalline solid (**A.1**, ca. 30 g isolated mass). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.31 (2H, t), 3.43 (2H, s), 2.99 (2H, s), 1.65 (1H, m), 1.42 (1H, m).

Scheme A.2: Synthesis of *N*-hydroxyethyl-*cis*-5-norbornene-*exo*-dicarboximide initiator (**A.2)**.



Cis-5-norbornene-*exo*-dicarboxylic anhydride (**A.1**) (1.0 eq., 2.07 g, 12.6 mmol), 2-aminoethanol (1.05 eq., 0.80 mL, 13.2 mmol), triethylamine (0.1 eq., 0.18 mL, 1.3 mmol) and toluene (15 mL) were mixed in a round bottom flask equipped with a Dean-Stark trap. The mixture was heated to reflux for 15 hours. The resulting orange solution was cooled to room temperature, and the toluene was removed *in vacuo*. The crude solid was recrystallized in ethanol to yield **A.2** as a white solid (2.4 g). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.29 (2H, t), 3.78 (2H, m), 3.70 (2H, m) (2H, d), 3.28 (2H, t), 2.71 (2H, d), 1.50 (1H, dt), 1.34 (1H, d).

Scheme A.3: Synthesis of ω-norbornenyl poly($_{D,L}$-lactide) (**PLA)** macromonomer.



For this representative example, ^{1}H NMR end group analysis indicates M_n = 3450 g/mol. A flame-dried Schlenk flask was charged with a stir bar, initiator **A.2** (2.00 g, 9.65 mmol, 1.00 equiv), and racemic 3,6-dimethyl-1,4-dioxane-2,5-dione (29.2 g, 203 mmol, 21.0 equiv). The flask was subjected to three pump-purge cycles using argon, then transferred to an oil bath heated to 130 °C. Once the contents of the flask had fully melted (approx. 0.5 hr), one drop of the catalyst, tin (II) 2-ethylhexanoate (≈ 5 mg), was added using a 21G needle. The reaction was allowed to stir at 130 °C for 4 hr, then quenched by rapidly cooling in a dry ice bath. The solid was dissolved in dichloromethane, and then the solution was filtered through basic alumina to remove the tin catalyst. The solution was concentrated by rotary evaporation until slightly viscous, then precipitated dropwise to stirring cold (−78 °C) methanol. The solid was isolated by centrifugation and dried under high vacuum to yield the PLA macromonomer as a white crystalline solid. The ^{1}H NMR spectrum in $CDCl_3$ is provided in Figure A.1.

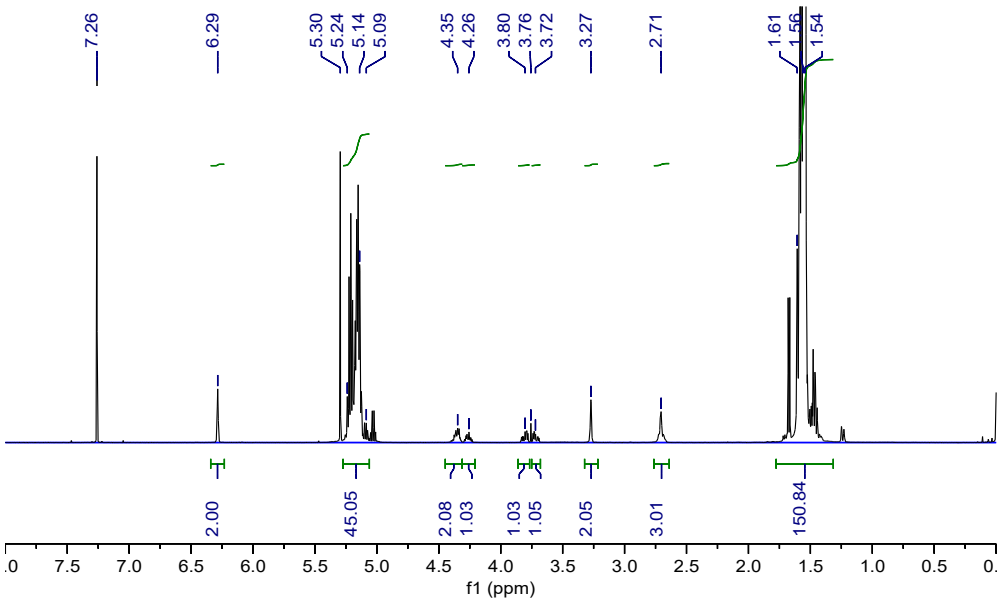
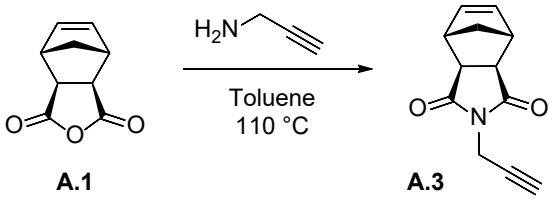


Figure A.1: ^{1}H NMR spectrum of **PLA** macromonomer in $CDCl_3$.

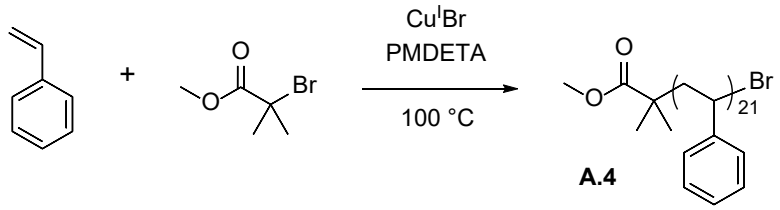
*A-2.2 Synthesis of Polystyrene Macromonomer (**PS**)*[2]

Scheme A.4: Synthesis of *N*-propargyl-*cis*-5-norbornene-*exo*-dicarboximide (**A.3**).



Cis-5-norbornene-*exo*-dicarboxylic anhydride (**A.1**) (1.0 eq., 62.59 g, 381.2 mmol), propargylamine (1.0 eq., 21 g, 381.2 mmol), triethylamine (0.1 eq., 3.86 g, 38.1 mmol) and toluene (300 mL) were mixed in a round bottom flask equipped with a Dean-Stark trap. The mixture was heated to reflux for 15 hours. The resulting orange solution was cooled to room temperature, and the toluene was removed *in vacuo*. The crude solid was recrystallized in ethanol to yield **A.3** as light brown, plate-like crystals (56.25 g). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.28 (2H, m), 4.20 (2H, d), 3.30 (2H, m), 2.70 (2H, d), 2.17 (1H, t), 1.50 (1H, d), 1.25 (1H, d).

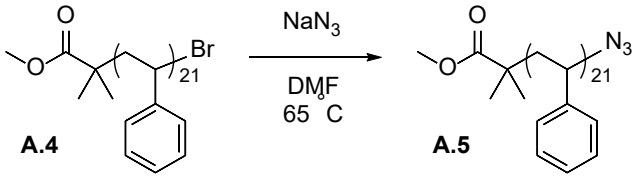
Scheme A.5: Synthesis of PS-Br (**A.4**) by atom-transfer radical polymerization (ATRP).



For this representative example, ^{1}H NMR end group analysis indicates M_n = 2390 g/mol. Styrene monomer (500 mL) was stirred with basic alumina for 30 min and filtered to yield a clear liquid. Styrene (50.0 eq., 350 mL, 3.054 mol) was added to a 500 mL Schlenk flask equipped with a stir bar and septum. The flask was charged with ligand *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (0.3 eq., 3.83 mL, 0.018 mol) and subsequently freeze-pump-thawed three times to remove oxygen. The flask was frozen in liquid nitrogen, placed under an active flow of argon (while still frozen), and Cu^IBr (0.3 eq., 2.63 g, 0.018 mol) was quickly added upon removal of the septum. The septum was re-attached, the argon flow stopped, and the flask was evacuated. (Caution: argon condenses at liquid nitrogen

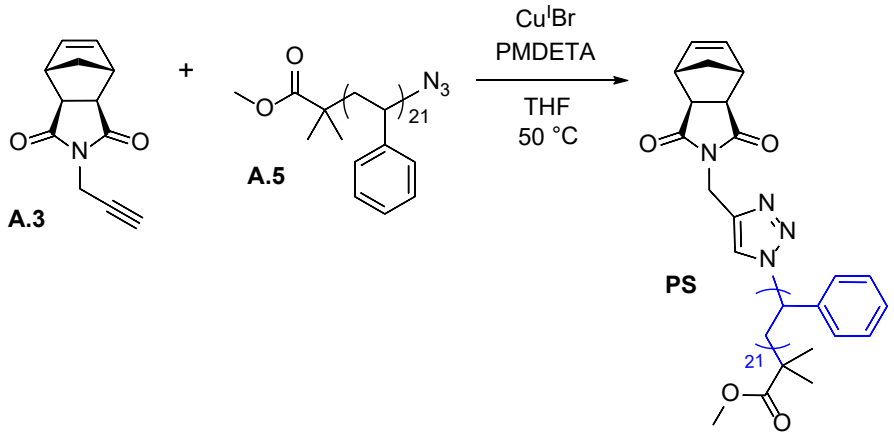
temperatures and can cause an explosion upon expansion when thawed.) Three additional pump/purge (argon/vacuum) cycles were performed and the flask was left under dynamic vacuum for at least 5 min. The flask was thawed in warm water and placed under argon. Most, but not all, of the copper dissolved to yield a green solution. (A blue color indicates oxygen contamination; a yellow color indicates insufficient copper dissolution – both result in a failed polymerization.) In a separate flask, methyl α-bromoisobutyrate was freeze-pump-thawed three times. Methyl α-bromoisobutyrate (1.0 eq., 7.90 mL, 0.061 mol) was injected into the Schlenk flask containing styrene and the mixture was heated in an oil bath pre-set to 100 °C. Aliquots were collected every ca. 30 min under a dynamic flow of argon. Conversion was monitored by ^{1}H NMR. The polymerization was quenched in liquid nitrogen after 2 hr 35 min at approximately 38% conversion. The viscous solution was warmed to room temperature, diluted with tetrahydrofuran (100 mL), filtered through basic alumina to remove copper, and precipitated into methanol at -78 °C. The polymer was redissolved in THF, precipitated five more times into methanol at −78 °C, and dried *in vacuo* to yield **A.4** as a white powder.

Scheme A.6: End group conversion: PS-Br to PS-N_3 (**A.5**)



Bromo-terminated polystyrene (**A.4**) (1.0 eq., 73 g, 37.0 mmol), sodium azide (3.0 eq., 7.12 g, 109.5 mmol), and dimethylformamide (350 mL) were mixed in a round bottom flask equipped with a stir bar and reflux condenser. The mixture was heated at 65 °C for 16 hr and then cooled to room temperature. The product was precipitated into methanol at −78 °C then redissolved in THF five times in total. Quantitative conversion of the end group was observed by ^{1}H NMR ($CDCl_3$) δ (ppm): PS-Br 4.6–5.0 ppm, PS-N_3 3.75–4.25.

Scheme A.7: Synthesis of ω-norbornenyl polystyrene macromonomer (**PS**).



Azide-terminated polystyrene (**A.5**) (1.0 eq., 64.30 g, 30.6 mmol), *N*-propargyl-*cis*-5-norbornene-*exo*-dicarboximide (**A.3**) (1.5 eq., 9.24 g, 45.9 mmol), and $Cu^{I}Br$ (0.4 eq., 1.76 g, 12.3 mmol) were added to a 500 mL three-neck round bottom flask equipped with a stir bar, reflux condenser, and two septa. The flask was pump/purged with argon three times and placed under argon. Dry tetrahydrofuran (180 mL) was added via syringe, followed by *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (0.4 eq., 2.56 mL, 12.3 mmol), upon which the solution turned light green and clear. The flask was heated at 50 °C for 16 hr and cooled to room temperature. The solution was diluted with tetrahydrofuran (100 mL), filtered through basic alumina to remove the copper, and precipitated into methanol at −78 °C. The precipitation was repeated five additional times to yield a white powder. Quantitative conversion of the end group was observed by ^{1}H NMR ($CDCl_3$) δ (ppm): PS-N_3 3.75–4.25, PS-norbornene 4.89–5.05 (Figure A.2).

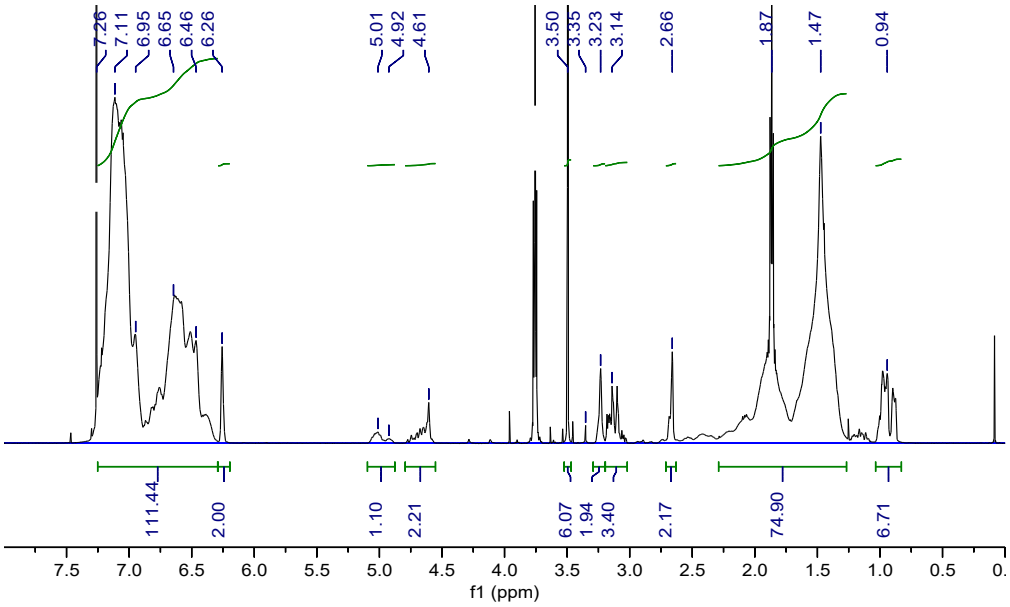
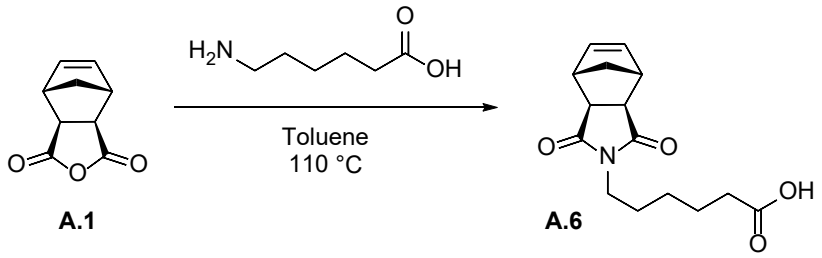


Figure A.2: ^{1}H NMR spectrum of **PS** macromonomer in $CDCl_3$.

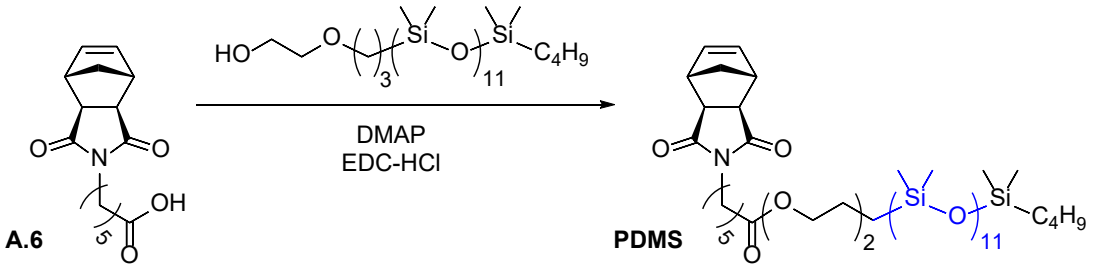
*A-2.3 Synthesis of Poly(dimethyl siloxane) Macromonomer (**PDMS**)*[3]

Scheme A.8: Synthesis of *N*-(hexanoic acid)-*cis*-5-norbornene-*exo*-dicarboximide (**A.6**).



Cis-5-norbornene-*exo*-dicarboxylic anhydride (**A.1**) (1.0 eq., 8.00 g, 48.7 mmol), 6-aminohexanoic acid (1.0 eq., 6.39 g, 48.7 mmol), triethylamine (0.1 eq., 0.679 mL, 4.87 mmol), and toluene (51 mL) were added to a round bottom flask equipped with a stir bar and reflux condenser. The mixture was heated at 110 °C for 19 hr, cooled to room temperature, and the solvent was removed *in vacuo*. The remaining solid was redissolved in dichloromethane, washed with water (x3) then brine (x3), and dried with magnesium sulfate. The solvent was removed *in vacuo* to yield **A.6** as a white solid. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.28 (2H, m), 3.46 (2H, t), 3.27 (2H, m), 2.35 (2H, t), 1.72–1.18 (10H, m).

Scheme A.9: Synthesis of ω-norbornenyl poly(dimethyl siloxane) macromonomer (**PDMS**).



N-(hexanoic acid)-*cis*-5-norbornene-*exo*-dicarboximide (**A.6**) (1.2 eq., 6.00 g, 21.6 mmol), alcohol-terminated PDMS (1.0 eq., 18.1 g, 18.1 mmol, M_n = 1000 g/mol from Gelest), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (1.6 eq., 5.52 g, 28.8 mmol), 4-dimethylaminopyridine (0.1 eq., 0.22 g, 1.80 mmol), and dichloromethane (250 mL) were mixed in a 500 mL round bottom flask equipped with a stir bar. The reaction was stirred for 20 hr under air at room temperature. The mixture was washed with 1 M HCl (x3), brine (x3), and deionized water (x3). The organic solution was stirred over anhydrous $MgSO_4$ then filtered, and dichloromethane was removed *in vacuo*. The product was filtered through a plug of silica with dichloromethane (2 L) then dried *in vacuo* to yield **PDMS** as a colorless oil (18.6 g, 82%).

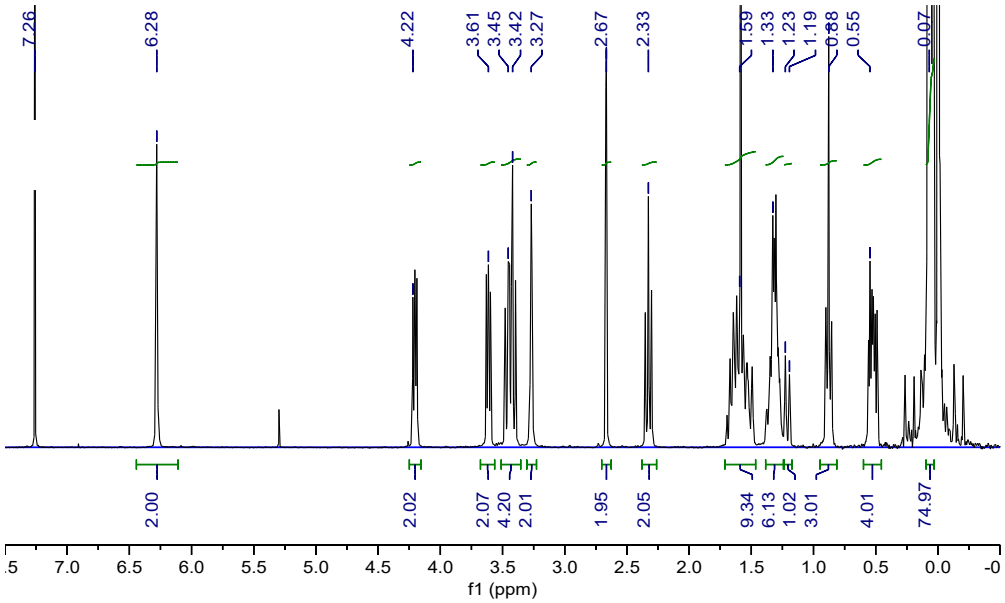
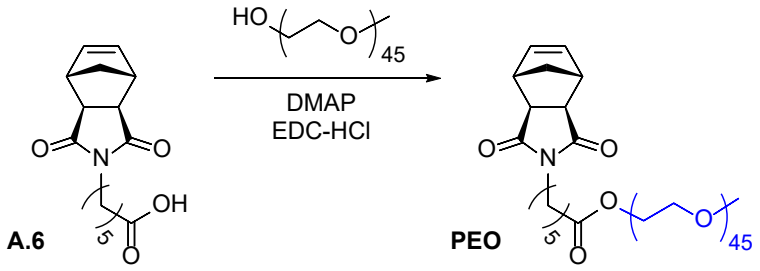


Figure A.3: ^{1}H NMR spectrum of **PDMS** macromonomer in $CDCl_3$.

*A-2.4 Synthesis of Poly(ethylene oxide) Macromonomer (**PEO**)*[2]

Scheme A.10: Synthesis of *ω*-norbornenyl poly(ethylene oxide) macromonomer (**PEO**).



N-(hexanoic acid)-*cis*-5-norbornene-*exo*-dicarboximide (**A.6**) (1.2 eq., 19.74 g, 71.2 mmol), poly(ethylene glycol) methyl ether (1.0 eq., 118.64 g, 59.3 mmol, M_n = 2000 g/mol, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (1.6 eq., 18.24 g, 117.5 mmol), 4-dimethylaminopyridine (0.1 eq., 0.73 g, 5.9 mmol), and dichloromethane (790 mL) were mixed in a 1 L round bottom flask equipped with a stir bar. The reaction was stirred for 24 hr, then half of the dichloromethane was removed *in vacuo*. The mixture was washed with 1 M HCl (x3), brine (x1), and dried with sodium sulfate. Most of the solvent was removed *in vacuo* and the remaining solution was precipitated into diethyl ether at −78 °C. The off-white solid was filtered and dried *in vacuo* to yield 123.3 g (93%) of isolated material.

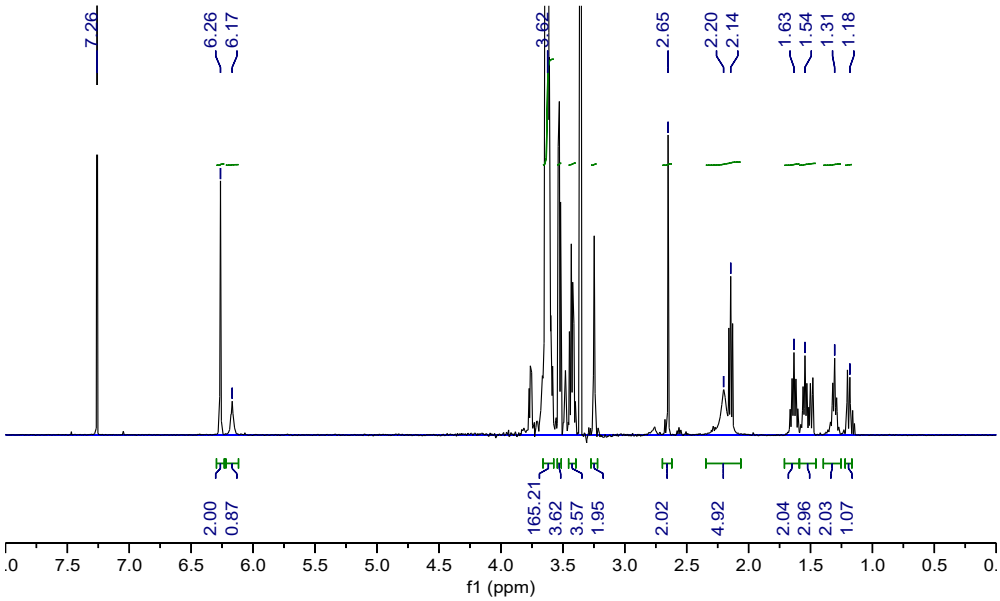
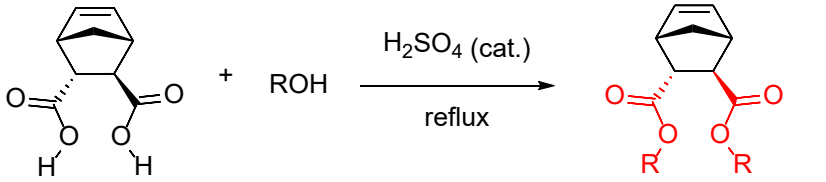


Figure A.4: ^{1}H NMR spectrum of **PEO** macromonomer in $CDCl_3$.

A-3 Diluent Synthesis

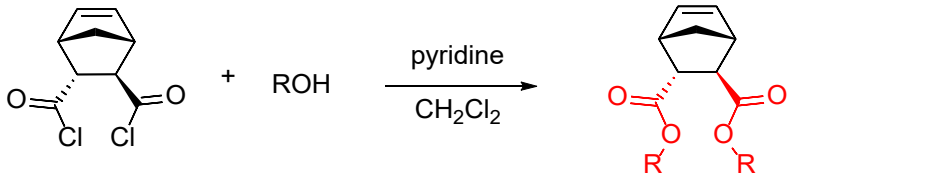
Norbornene diluents were prepared according to reported procedures. General synthetic schemes are provided in Schemes A.11−A.16. Diluents are identified as reported in Chapter 2 (**1a**, **1b**, etc.).

Scheme A.11: Synthesis of *endo*,*exo*-norbornenyl diester diluents (**1a**–**1d**).



Cis-5-norbornene-*endo,exo*-2,3-dicarboxylic acid (5 g, 27.5 mmol) was added to 50 mL of the corresponding anhydrous alcohol. To this mixture was added ~50 mg of conc. H_2SO_4. After stirring at 50 °C for 12 h, an excess of solid $KHCO_3$ was added to quench the reaction. The alcohol was removed under reduced pressure, and 30 mL CH_2Cl_2 was added. The organic solution was washed with brine (20 mL × 3), dried with $MgSO_4$, and filtered to afford a colorless oil. The product was purified by either vacuum distillation or recrystallization from cold *n*-pentane.

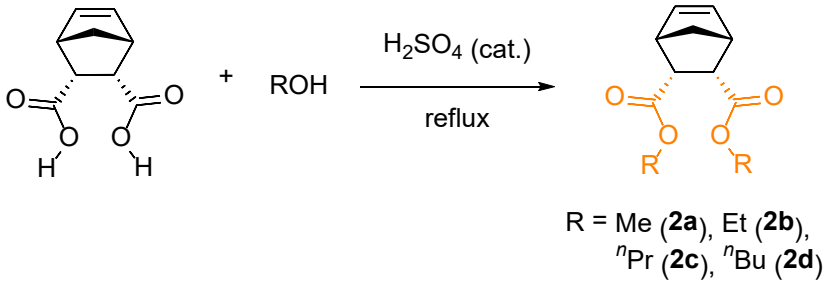
Scheme A.12: Synthesis of *endo*,*exo*-norbornenyl diester diluents (**1e**–**1j**).



Cis-5-norbornene-*endo,exo*-2,3-diacyl chloride (3 mL, 18.5 mmol) was dissolved in CH_2Cl_2 (25 mL) and pyridine (4.91 mL, 61.0 mmol). A CH_2Cl_2 solution (5 mL) of the corresponding anhydrous alcohol (42.5 mmol) was slowly added at –78 °C. The mixture

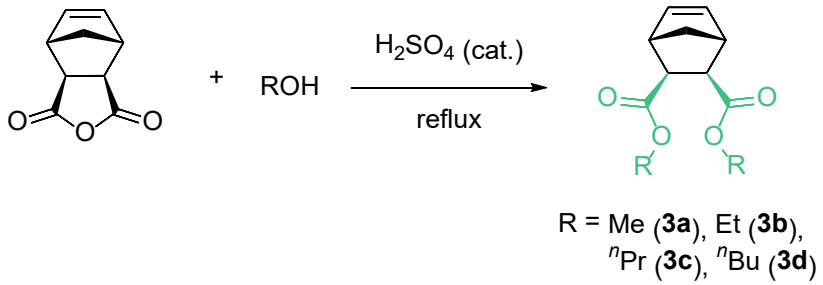
was allowed to slowly warm to room temperature over 1 hour and was allowed to stir for 12 h. The pyridinium salt was removed by filtration. The organic solution was washed with brine (20 mL × 3), dried with $MgSO_4$, and filtered to afford a colorless oil. The product was purified by either vacuum distillation or recrystallization from cold *n*-pentane.

Scheme A.13: Synthesis of *endo*,*endo*-norbornenyl diester diluents (**2a**–**2d**).



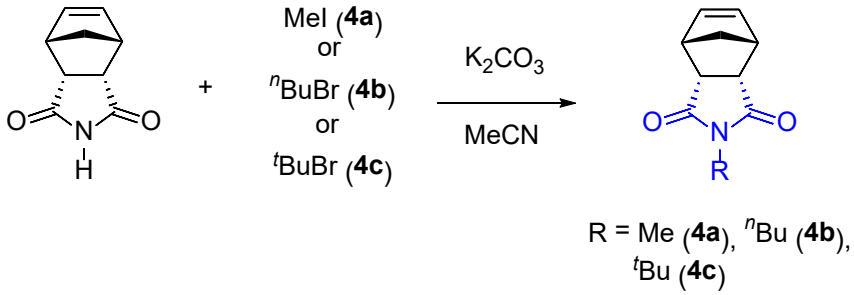
A suspension of *cis*-5-norbornene-*endo,endo*-2,3-dicarboxylic acid (2.0 g, 11 mmol), 4 drops of concentrated sulfuric acid, and 20 mL of the corresponding anhydrous alcohol was stirred under air at 75 °C. After 36 hours, the solution was cooled to room temperature and was concentrated under reduced pressure. The resulting oil was redissolved in 50 mL CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (1 × 30 mL). The organic solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford an oil. The oil was filtered through a plug of basic alumina, precipitated from cold (–78 °C) hexanes, and dried *in vacuo* to obtain the product as a white crystalline solid (**2a**), pink oil (**2b–2c**) or colorless oil (**2d**).

Scheme A.14: Synthesis of *exo*,*exo*-norbornenyl diester diluents (**3a**–**3d**).



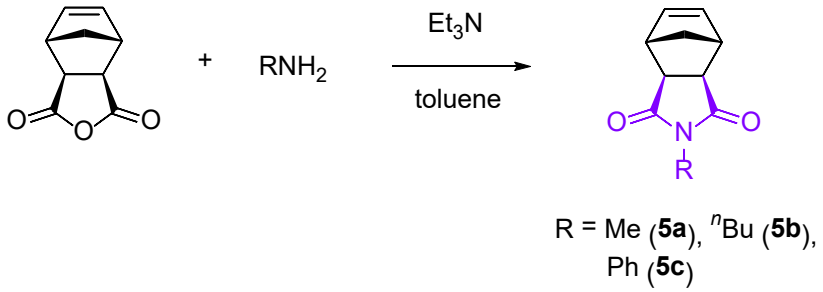
A suspension of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (2.00 g, 12.2 mmol), 4 drops of concentrated sulfuric acid, and 20 mL of the corresponding anhydrous alcohol was stirred under air at 75 °C. After 20 hours, the colorless solution was cooled to room temperature and was concentrated under reduced pressure. The resulting pale yellow oil was redissolved in 50 mL CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (1 × 30 mL). The organic solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford a colorless oil. Precipitation from cold (–78 °C) hexanes produced the product as a white crystalline solid (**3a**) or colorless oil (**3b**–**3d**) that was dried *in vacuo.*

Scheme A.15: Synthesis of *endo*-norbornenyl imide diluents (**4a**–**4c**).



To a 10 mL MeCN solution of *cis*-5-norbornene-*endo*-2,3-diimide (1 g, 6.13 mmol) was added the corresponding alkyl halide (12.3 mmol) and K_2CO_3 (1.69 g, 12.3 mmol). The resulting mixture was allowed to stir at room temperature for 24 h (**4a**) or at 65 °C for 54 h (**4b** and **4c**). The product was purified using column chromatography.

Scheme A.16: Synthesis of e*xo*-norbornenyl imide diluents (**5a**–**5c**).



To a 20 mL toluene solution of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (1 g, 6.09 mmol) was added the corresponding alkyl amine (6.70 mmol) and Et_3N (0.85 mL, 0.609 mmol). The resulting mixture was allowed to stir at 110 °C for 15 h. The product was purified using column chromatography.

A-4 Standard Procedures for Homo- and Copolymerization Kinetics

A-4.1 *Standard Procedure for the Determination of Homopolymerization Rate Constants*

A 4 mL vial was charged with a flea stir bar and a norbornene monomer (0.025 mmol) in CH_2Cl_2 at 298 K. While stirring vigously, the polymerization was initiated by adding a CH_2Cl_2 solution of **G3** (0.0125 M, 20 μL, 0.25 μmol) to achieve initial conditions of $[\text{norbornene}]_0$ (0.05 M) and $[\mathbf{G3}]_0$ (0.5 mM). During the course of the reaction, aliquots (~20 μL) were extracted at different time points and immediately quenched into a seperate vial containing a large excess of ethyl vinyl ether (~0.2 mL) and silica-bound metal scavenger (SiliaMetS, dimercaptotriazine [DMT]) in THF. The quenched reaction mixtures were subsequentially subjected to SEC and ^{1}H NMR analysis, allowing the determination of $[\text{norbornene}]_t$. For each homopolymerization experiment, the self-propagation rate constant k_{homo} was determined according to Eq. 2-1.

A-4.2 *Standard Procedure for the Determination of Copolymerization Reactivity Ratios*

A 4 mL vial was charged with a flea stir bar and a CH_2Cl_2 solution of two norbornene monomers (M_1, M_2, each 0.025 mmol) at 298 K. While stirring vigously, the copolymerization was initiated by adding a CH_2Cl_2 solution of **G3** (0.0125 M, 20 μL, 0.25 μmol) to achieve initial conditions of $[M_1]_0$ (0.05 M), $[M_2]_0$ (0.05 M), and $[\mathbf{G3}]_0$ (0.5 mM).

During the course of the reaction, aliquots (~20 μL) were extracted at different time points and immediately quenched in a seperate vial containing a large excess of ethyl vinyl ether (~0.2 mL) and silica-bound metal scavenger (SiliaMetS, dimercaptotriazine [DMT]) in THF. The quenched reaction mixtures were subsequentially subjected to SEC and ^{1}H NMR analysis, allowing the determination of $[M_1]_t$ and $[M_2]_t$. Values of k_{12} and k_{21} were obtained by fitting the experimentally determined kinetic data to the numerical solutions for Eq. 2-2 to 2-5 using a MATLAB non-linear least-square solver (*lsqcurvefit*) in conjunction with non-stiff differential equation solver (*ode45*).[3]

A-5 Characterization of (PLA^z-*ran*-DME^{1-z})$_n$ Graft Polymers

Table A.1: SEC characterization of (**PLA**^{z}-*ran*-**DME**$^{1-z}$)$_n$ with variable grafting densities z and backbone degrees of polymerization n.

z	n	Expected M_n (kg mol^{-1})	Measured M_n[a] (kg mol^{-1})	Difference in M_n	$Đ$[a]
1.00	167	539	548	1.7%	1.03
	133	431	432	0.1%	1.01
	100	323	335	3.7%	1.01
	67	216	227	5.3%	1.01
	33	108	109	1.0%	1.02
0.75	167	413	404	-2.2%	1.03
	133	330	337	1.9%	1.03
	100	248	250	0.8%	1.03
	67	165	169	2.2%	1.02
	33	82.6	81.1	-1.8%	1.02
0.50	167	287	296	3.3%	1.03
	133	230	234	1.7%	1.02
	100	172	179	3.9%	1.01
	67	115	119	3.4%	1.01
	33	57.4	60.1	4.7%	1.02
0.25	167	161	161	0.2%	1.01
	133	129	126	-2.6%	1.01
	100	96.6	97.4	0.8%	1.01
	67	64.4	66.1	2.6%	1.01
	33	32.2	32.3	0.2%	1.02

[a] Determined by SEC of quenched aliquots of the copolymerization mixtures without further workup.

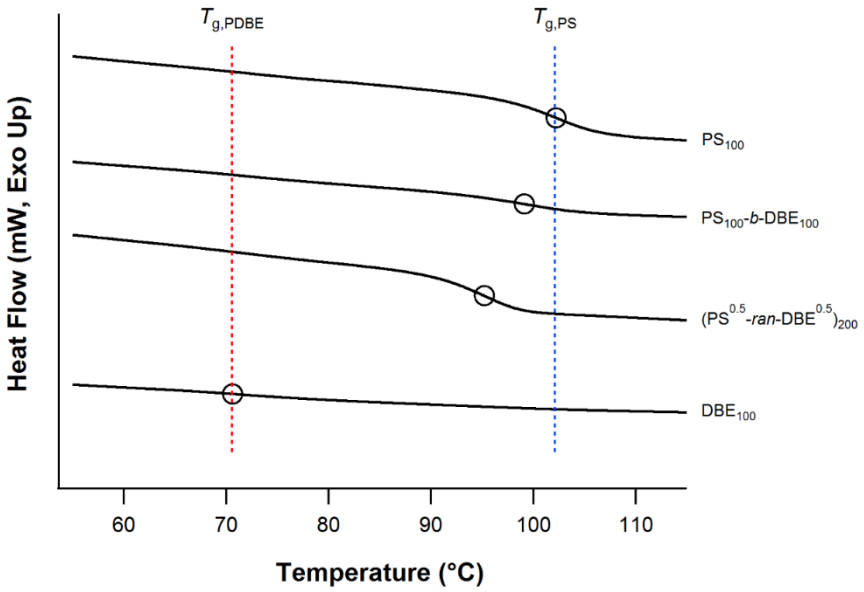
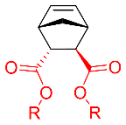
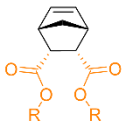
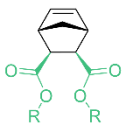
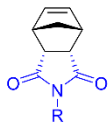
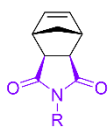


Figure A.5: Differential scanning calorimetry (DSC) data for $\mathbf{PS}_{100}$, $\mathbf{DBE}_{100}$, and two copolymers thereof: ($\mathbf{PS}_{100}$-*b*-$\mathbf{DBE}_{100}$), a block polymer with one fully grafted block and one ungrafted block, synthesized by sequential addition of **PS** and **DBE**; and $(\mathbf{PS}^{0.5}$-*ran*-$\mathbf{DBE}^{0.5})_{200}$, a random bottlebrush copolymer with 50% grafting density, synthesized by copolymerizing **PS** and **DBE** in a 1:1 feed ratio. The data were collected on the second heating cycle using a 10 °C/min ramp rate, and glass transition temperatures (T_g, open circles) were identified from the corresponding derivative curves. Both copolymers exhibit a single T_g between the T_gs of the pure components, indicating successful incorporation of both **PS** and **DBE**. The T_g of $\mathbf{PS}_{100}$-*b*-$\mathbf{DBE}_{100}$ (which has a guaranteed blocky sequence) differs from the T_g of $(\mathbf{PS}^{0.5}$-*ran*-$\mathbf{DBE}^{0.5})_{200}$ in terms of both position and shape, suggesting that $(\mathbf{PS}^{0.5}$-*ran*-$\mathbf{DBE}^{0.5})_{200}$ is at least not blocky and instead likely random as expected.

A-6 Expanding Monomer Scope: Homopolymerization Rate Constants

Table A.2: Structures and homopolymerization rate constants (k_{homo}) for all monomers synthesized and studied herein.

Anchor Group		ID	R	k_{homo} (M^{-1} s^{-1})
endo,exo-diester (*dx*-DE)		**1a**	Me	18.7
		1b	Et	14.6
		1c	^{n}Pr	10.4
		1d	^{n}Bu	6.90
		1e	^{i}Pr	6.14
		1f	^{t}Bu	5.32
		1g	CH_2CF_3	10.5
		1h	Ph	8.36
		1i	*p*-CF_3Ph	5.14
		1j	*p*-MeOPh	7.76
endo,endo-diester (*dd*-DE)		**2a**	Me	2.24
		2b	Et	0.934
		2c	^{n}Pr	0.518
		2d	^{n}Bu	0.362
exo,exo-diester (*xx*-DE)		**3a**	Me	30.8
		3b	Et	16.4
		3c	^{n}Pr	11.2
		3d	^{n}Bu	10.4
endo-imide (*d*-I)		**4a**	Me	0.814
		4b	^{n}Bu	0.930
		4c	^{t}Bu	0.782
exo-imide (*x*-I)		**5a**	Me	82.4
		5b	^{n}Bu	63.2
		5c	Ph	34.8
		PDMS	PDMS (1k)	21.6
		PLA	PLA (3k)	17.2
		PS	PS (4k)	4.18

A-7 Mechanistic Studies

A-7.1 *Pyridine Binding*

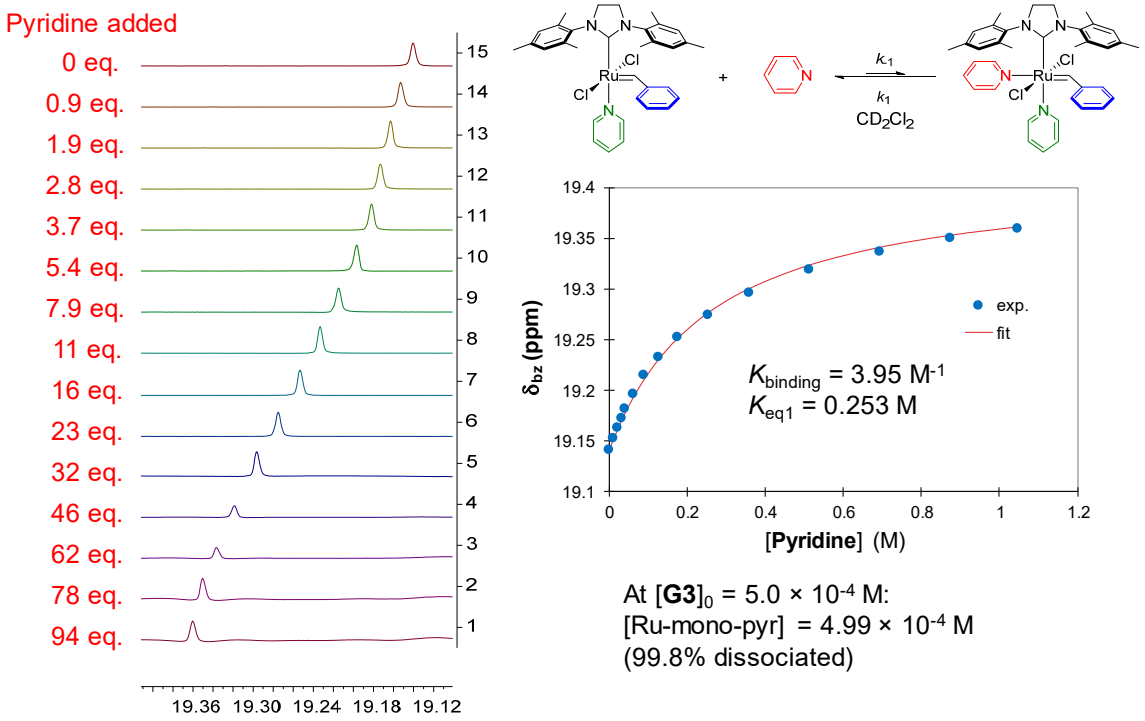
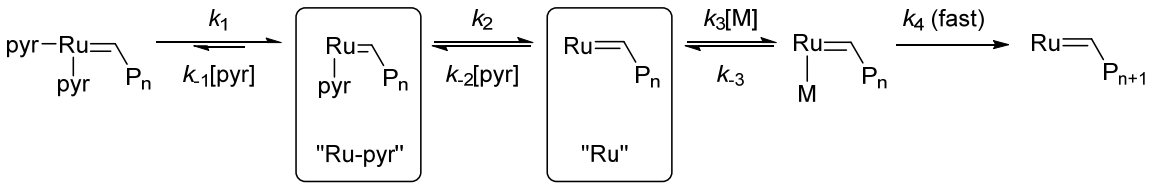


Figure A.6: Stacked ^{1}H NMR spectra obtained during the pyridine titration experiments. To an NMR tube containing a CD_2Cl_2 solution of the monopyridine complex (11.2 mM) was titrated with a CD_2Cl_2 solution containing both pyridine (1.47 M) and the monopyridine complex (11.2 mM). The concentration of the monopyridine complex remained constant during the titrations. The chemical shifts of the benzylidene ^{1}H resonance was monitored at 298 K and could be employed to fit the pyridine binding constant ($K_{binding}$ = $1/K_{eq,1}$).

A-7.2 Derivation of Rate Expression (Eq. 2-8)

We derived a simplified rate expression corresponding to the proposed dissociative ROMP mechanism in which olefin coordination is the rate-limiting step:



The large value estimated for $K_{eq,1} = k_1/k_{-1}$ indicates that >99.8% of the precatalyst **G3** exists as the monopyridine adduct in solution under the conditions employed in our homo- and copolymerization studies. The initial concentration of **G3** equals the sum of the concentrations of the monopyridine adduct ("Ru-pyr") and the 14-electron vacant species ("Ru"):

$$[\mathbf{G3}]_0 = [\mathrm{Ru-pyr}] + [\mathrm{Ru}] \qquad \text{Eq. A-1}$$

A steady-state approximation can be made for the 14-electron vacant species:

$$-\frac{\mathrm{d[Ru]}}{\mathrm{dt}} = k_2[\mathrm{Ru-pyr}] - k_{-2}[\mathrm{Ru}][\mathrm{pyr}] - k_3[\mathrm{Ru}][\mathrm{M}] = 0 \qquad \text{Eq. A-2}$$

Substituting A-1 in A-2 obtains the following:

$$-\frac{\mathrm{d[Ru]}}{\mathrm{dt}} = k_2[\mathbf{G3}]_0 - k_2[\mathrm{Ru}] - k_{-2}[\mathrm{Ru}][\mathrm{pyr}] - k_3[\mathrm{Ru}][\mathrm{M}] = 0 \qquad \text{Eq. A-3}$$

$$[\mathrm{Ru}] = \frac{k_2[\mathbf{G3}]_0}{k_2 + k_{-2}[\mathrm{pyr}] + k_3[\mathrm{M}]} \qquad \text{Eq. A-4}$$

$$[\mathrm{Ru}] \times \frac{1/k_{-2}}{1/k_{-2}} = \frac{K_{\mathrm{eq},2}[\mathbf{G3}]_0}{K_{\mathrm{eq},2} + [\mathrm{pyr}] + \frac{k_3}{k_{-2}}[\mathrm{M}]} \approx \frac{K_{\mathrm{eq},2}[\mathbf{G3}]_0}{K_{\mathrm{eq},2} + [\mathrm{pyr}]} \qquad \text{Eq. A-5}$$

In Eq. A-5, since $k_3 << k_{-2}$, the third term in the denominator is close to 0. The time-dependent consumption of the monomer ("M") is provided by Eq. A-6 (Eq. 2-8 in Chapter 2):

$$-\frac{d[M]}{dt} = k_3[Ru][M] = \frac{K_{eq,2}k_3}{K_{eq,2}+[pyr]}[\mathbf{G3}]_0[M] \qquad \text{Eq. A-6}$$

A-7.3 Rate Dependence on Catalyst Concentration

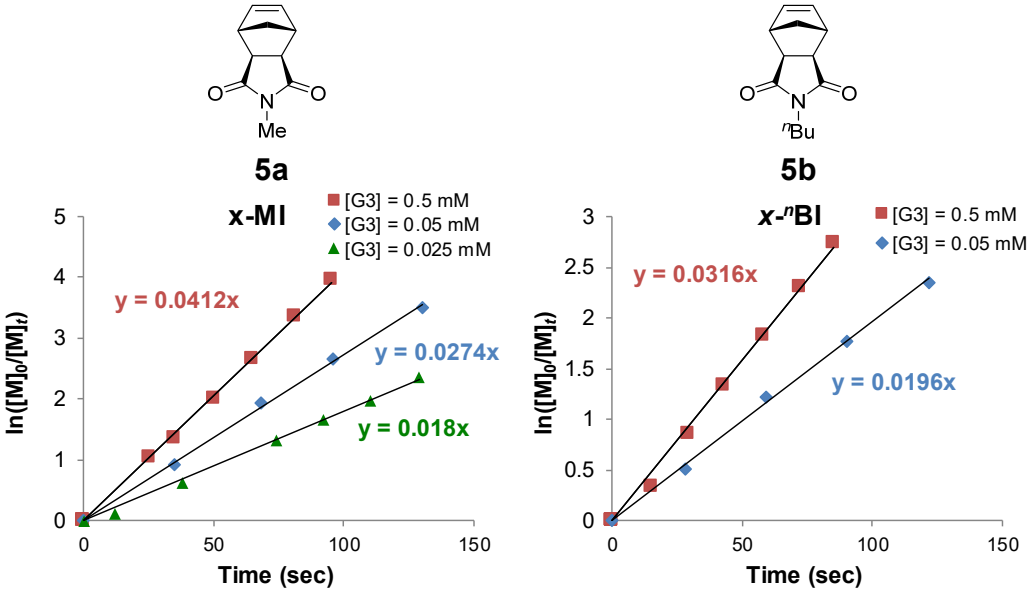


Figure A.7: ROMP of **5a** (left) and **5b** (right) in CH_2Cl_2 at 298 K showing the rate dependence on $[\mathbf{G3}]_0$ (maroon: $[\mathbf{G3}]_0$ = 0.5 mM, blue: $[\mathbf{G3}]_0$ = 0.05 mM, green: $[\mathbf{G3}]_0$ = 0.025 mM). The slope corresponds to the k_{obs} (s^{-1}). These polymerization reactions have the same $[\mathbf{5a}]_0/[\mathbf{G3}]_0$ and $[\mathbf{5b}]_0/[\mathbf{G3}]_0$ ratio of 100. Time-lapse kinetic traces were obtained using our standard homopolymerization procedure.

A-8 Copolymerization Kinetics Data

Table A.3: Compiled SEC data for **PLA** + diluent copolymerizations at full conversion.

ID	Diluent	M_n (kDa)[a]	$Đ$
2d	*dd*-D^{n}BuE	95.4	1.07
4c	*d*-^{t}BuI	89.9	1.10
4a	*d*-MeI	90.5	1.04
4b	*d*-^{n}BuI	103	1.04
2a	*dd*-DMeE	94.5	1.05
1d	*dx*-D^{n}BuE	101	1.04
3d	*xx*-D^{n}BuE	—[b]	—[b]
3c	*xx*-D^{n}PrE	101	1.08
3b	*xx*-DEtE	99.5	1.06
1a	*dx*-DMeE	108	1.05
3a	*xx*-DMeE	95.4	1.04
5b	*x*-^{n}BuI	95.9	1.02
5a	*x*-MeI	86.4	1.02

[a] Reported relative to polystyrene in THF (dn/dc = 0.185 mL g^{-1}).
[b] Data is not available for **PLA** + **3d**.

Table A.4: Kinetic data for the copolymerization of **PLA** (M_1, M_n = 3230 g mol^{-1}) with selected diluents (M_2). The self-propagation rate constants k_{22} and k_{11} were determined from homopolymerization experiments, and the cross-propagation rate constants k_{12} and k_{21} were determined by fitting copolymerization data using non-linear least squares regression. The reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are also provided.

ID	Diluent	k_{22} (M^{-1} s^{-1})	k_{11} (M^{-1} s^{-1})	k_{12} (M^{-1} s^{-1})	k_{21} (M^{-1} s^{-1})	r_1	r_2	r_1r_2	r_1/r_2
2d	*dd*-D^{n}BuE	0.362	17.2	8.03	0.860	2.14	0.421	0.902	5.09
4c	*d*-^{t}BuI	0.782	17.2	11.0	1.72	1.56	0.455	0.708	3.43
4a	*d*-MeI	0.814	17.2	4.55	1.24	3.78	0.656	2.48	5.76
4b	*d*-^{n}BuI	0.930	17.2	8.14	1.08	2.11	0.861	1.82	2.45
2a	*dd*-DMeE	2.24	17.2	8.05	2.71	2.14	0.827	1.77	2.58
1d	*dx*-D^{n}BuE	6.90	17.2	16.4	7.35	1.05	0.939	0.983	1.12
3d	*xx*-D^{n}BuE	10.4	17.2	46.0	8.94	0.374	1.17	0.436	0.320
3c	*xx*-D^{n}PrE	11.2	17.2	47.2	9.38	0.364	1.20	0.436	0.304
3b	*xx*-DEtE	16.4	17.2	48.6	10.1	0.354	1.63	0.577	0.217
1a	*dx*-DMeE	18.7	17.2	18.0	15.7	0.953	1.19	1.13	0.801
3a	*xx*-DMeE	30.8	17.2	49.2	18.3	0.350	1.68	0.588	0.208
5b	*x*-^{n}BuI	63.2	17.2	27.2	21.4	0.633	2.95	1.87	0.214
5a	*x*-MeI	82.4	17.2	28.4	27.1	0.606	3.05	1.85	0.199

Table A.5: Kinetic data for the copolymerization of **PDMS** (M_1, M_n = 1280 mol^{-1}) with selected diluents (M_2). The self-propagation rate constants k_{22} and k_{11} were determined from homopolymerization experiments, and the cross-propagation rate constants k_{12} and k_{21} were determined by fitting copolymerization data using non-linear least squares regression. The reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are also provided.

ID	Diluent	k_{22} (M^{-1} s^{-1})	k_{11} (M^{-1} s^{-1})	k_{12} (M^{-1} s^{-1})	k_{21} (M^{-1} s^{-1})	r_1	r_2	r_1r_2	r_1/r_2
4a	*d*-MeI	0.814	21.6	3.34	2.44	6.47	0.334	2.16	19.4
4b	*d*-^{n}BuI	0.930	21.6	6.85	2.00	3.15	0.465	1.47	6.78
1d	*dx*-D^{n}BuE	6.90	21.6	19.5	15.9	1.11	0.434	0.481	2.55
3d	*xx*-D^{n}BuE	10.4	21.6	48.2	10.3	0.448	1.02	0.455	0.441
1a	*dx*-DMeE	18.7	21.6	19.9	19.9	1.09	0.940	1.02	1.16
3a	*xx*-DMeE	30.8	21.6	50.4	26.3	0.429	1.17	0.502	0.367

Table A.6: Kinetic data for the copolymerization of **PS** (M_1, M_n = 3990 mol^{-1}) with selected diluents (M_2). The self-propagation rate constants k_{22} and k_{11} were determined from homopolymerization experiments, and the cross-propagation rate constants k_{12} and k_{21} were determined by fitting copolymerization data using non-linear least squares regression. The reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are also provided.

ID	Diluent	k_{22} (M^{-1} s^{-1})	k_{11} (M^{-1} s^{-1})	k_{12} (M^{-1} s^{-1})	k_{21} (M^{-1} s^{-1})	r_1	r_2	r_1r_2	r_1/r_2
1d	*dx*-D^{n}BuE	6.90	4.18	5.23	5.66	0.799	1.22	0.974	0.656
3d	*xx*-D^{n}BuE	10.4	4.18	29.9	7.58	0.140	1.38	0.193	0.102
1b	*dx*-DEtE	14.6	4.18	7.77	8.75	0.538	1.67	0.897	0.322
1a	*dx*-DMeE	18.7	4.18	7.74	13.2	0.540	1.42	0.765	0.381
3a	*xx*-DMeE	30.8	4.18	30.8	23.3	0.136	1.32	0.180	0.103
5b	*x*-^{n}BuI	63.2	4.18	30.8	38.9	0.136	1.63	0.221	0.0836
5a	*x*-MeI	82.4	4.18	31.9	63.2	0.131	1.30	0.171	0.100

Table A.7: Compiled SEC data for **PDMS** + diluent copolymerizations at full conversion.

ID	Diluent	M_n (kDa)[a]	$Đ$
4a	*d*-MeI	39.3	1.04
4b	*d*-^{n}BuI	42.7	1.05
1d	*dx*-D^{n}BuE	32.5	1.06
3d	*xx*-D^{n}BuE	39.9	1.09
1a	*dx*-DMeE	32.2	1.04
3a	*xx*-DMeE	37.9	1.03

[a] Reported relative to polystyrene in THF (dn/dc = 0.185 mL g^{-1}).

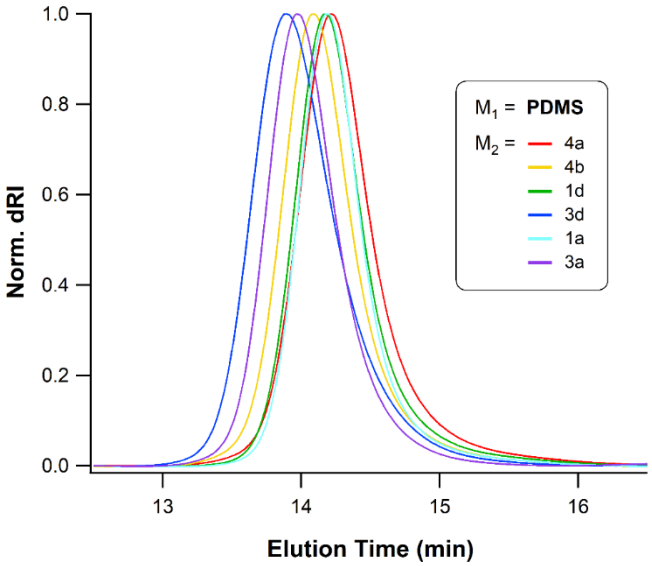


Figure A.8: SEC traces for **PDMS** + diluent copolymerizations at full conversion.

Table A.8: Compiled SEC data for **PS** + diluent copolymerizations at full conversion.

ID	Diluent	M_n (kDa)	$Đ$
1d	*dx*-D^{n}BuE	362	1.09
3d	*xx*-D^{n}BuE	379	1.09
1b	*dx*-DEtE	398	1.10
1a	*dx*-DMeE	375	1.04
3a	*xx*-DMeE	376	1.05
5b	*x*-^{n}BuI	386	1.04
5a	*x*-MeI	364	1.06

[a] Reported relative to polystyrene in THF (d*n*/d*c* = 0.185 mL g^{-1}).

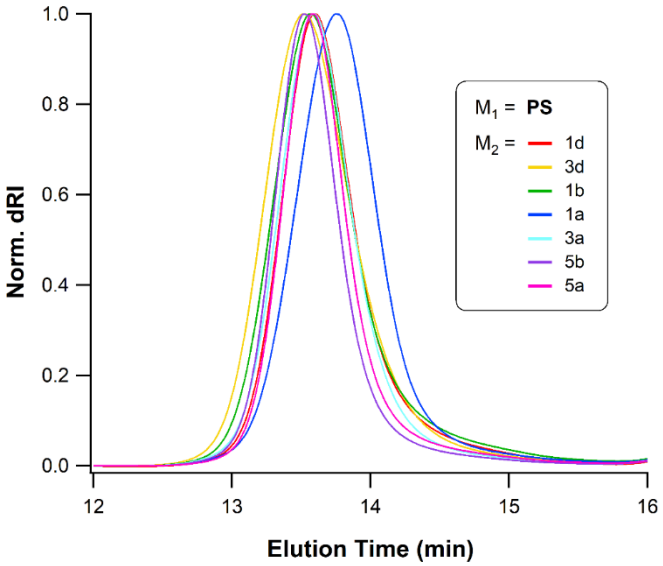


Figure A.9: SEC traces for **PS** + diluent copolymerizations at full conversion.

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(2) Bates, C. M.; Chang, A. B.; Momčilović, N.; Jones, S. C.; Grubbs, R. H. *Macromolecules* **2015**, *48*, 4967–4973.

(3) Lin, T.-P.; Chang, A. B.; Chen, H.-Y.; Liberman-Martin, A. L.; Bates, C. M.; Voegtle, M. J.; Bauer, C. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2017**, *139*, 3896–3903.