Electronic Supporting Information to:

One-pot synthesis of poly(norbornene)-block-poly(lactic acid) copolymers using a bifunctional initiator

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Materials

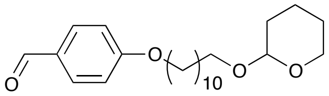
All chemicals were purchased either from Acros Organics, Alfa Aesar, Cambridge Isotope Labs, or Sigma-Aldrich and used without further purification unless otherwise noted. The dichloromethane used in polymerization was distilled twice from calcium hydride and degassed by the freeze-pump-thaw method. L-lactide was recrystallized three times from toluene. Compound **1**[1] and *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid **6**[2] were synthesized according to literature reports.

Characterization methods

^{1}H- and ^{13}C-NMR spectroscopy measurements were performed on a Bruker Avance-600 (^{1}H: 600 MHz; ^{13}C: 150 MHz), Avance-500 (^{1}H: 500 MHz; ^{13}C: 125 MHz) and Avance-400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) NMR Spectrometer. Chemical shifts are reported in ppm and referenced to the corresponding residual protons in deuterated solvents. ^{31}P NMR spectroscopy measurements were performed on a Bruker Avance-600 (^{31}P: 242 MHz) and Avance-500 (^{31}P: 203 MHz) spectrometer. Size Exclusion Chromatography (SEC) analyses were carried out using a Shimadzu pump and Shimadzu UV and RI detectors, with tetrahydrofuran (THF) as the eluent, and a set of Polymer Standards columns (AM GPC gel, 10 μm, precolumn, 300 Å and linear mixed bed). Commercially available PS standards were used. The flow rate used for all measurements was 1 mL/min. M_n^{app} and PDI^{app} represent the apparent number-average molecular weight, and apparent polydispersity index, respectively. The ESI mass spectra were obtained using an Agilent 1100 series Capillary LCMSD Trap SCT Spectrometer using methanol solutions of the products. Elemental Analysis (EA) (CHN) experiments were performed by Atlantic Microlab, Inc. (Norcross, GA, USA).

Synthesis bifunctional initiator

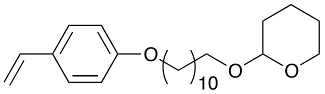
4-((11-((tetrahydro-2*H*-pyran-2-yl)oxy)undecyl)oxy)benzaldehyde (2)



To a solution of compound **1** (6.12 g, 18.24 mmol) in DMF (30 mL), 4-hydroxybenzaldehyde (2.90 g, 23.71 mmol) and K_2CO_3 (7.56 g, 54.71 mmol) were added. The mixture was stirred for 12 h at 90°C. The DMF was removed *in vacuo*, the residue was dissolved in dichloromethane and washed with water (2 x 30 mL). The organic layer was dried ($MgSO_4$) and concentrated. Purification was carried out by column chromatography (hexanes / ethyl acetate = 4 : 1) to afford **2** (6.48 g, 94%).

^{1}H-NMR (600 MHz; $CDCl_3$): δ 9.86 (s, 1H, *H*COAr), 7.81 (d, *J* = 8.9 Hz, 2H, Ar*H*), 6.97 (d, *J* = 8.7 Hz, 2H, Ar*H*), 4.57 (dd, *J* = 4.5, 3.0 Hz, 1H, CH_2OCH), 4.02 (t, *J* = 6.6 Hz, 2H, $ArOCH_2$), 3.86 (ddd, *J* = 11.2, 7.8, 3.3 Hz, 1H, OCH_2 of tetrahydropyran), 3.72 (dt, *J* = 9.6, 6.9 Hz, 1H, OCH_2 of tetrahydropyran), 3.49 (dt, *J* = 11.1, 5.5 Hz, 1H, CH_2-O-tetrahydropyran), 3.37 (dt, *J* = 9.6, 6.7 Hz, 1H, CH_2-O-tetrahydropyran), 1.85-1.77 (m, 3H), 1.73-1.68 (m, 1H), 1.61-1.30 (m, 20H). ^{13}C NMR (151 MHz; $CDCl_3$): δ 190.8, 164.3, 132.2, 132.0, 129.8, 114.8, 68.5, 67.7, 62.4, 30.9, 29.8, 29.61, 29.57, 29.53, 29.4, 29.1, 26.3, 26.0, 25.6, 19.8. MS-ESI $(M+Na)^+$ m/z calcd for $C_{23}H_{36}O_4Na$: 399.25, found 399.2. Elemental anal calcd for $C_{23}H_{36}O_4$: C 73.37, H 9.64; found C 73.23, H 9.67.

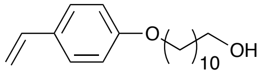
2-((11-(4-vinylphenoxy)undecyl)oxy)tetrahydro-2*H*-pyran (3)



Methyltriphenylphosphonium bromide (6.61 g, 18.49 mmol) and potassium *tert*-butoxide (2.08 g, 18.49 mmol) were dissolved in THF (30 mL). The reaction was stirred at 25 °C for 30 min. To this solution, compound **2** (6.33 g, 16.81 mmol) was added as a solution in THF (5 mL). After the mixture was stirred at 25 °C for 1 h, water (150 mL) was added and the THF was evaporated. The mixture was extracted with dichloromethane, and the combined organic layers were dried ($MgSO_4$) and concentrated. Compound **3** was purified by column chromatography (hexanes / ethyl acetate = 19 : 1) to yield 5.35 g (85% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.85 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H, CH_2=C*H*), 5.60 (d, *J* = 18.6 Hz, 1H, CH_2=CH), 5.11 (d, *J* = 11.8 Hz, 1H, CH_2=CH), 4.58 (dd, *J* = 4.5, 2.9 Hz, 1H, CH_2OC*H*), 3.95 (t, *J* = 6.6 Hz, 2H, ArOCH_2), 3.87 (ddd, *J* = 11.2, 7.8, 3.4 Hz, 1H, OCH_2 of tetrahydropyran), 3.73 (dt, *J* = 9.6, 6.9 Hz, 1H, OCH_2 of tetrahydropyran), 3.52-3.48 (m, 1H, CH_2-O-tetrahydropyran), 3.38 (dt, *J* = 9.6, 6.7 Hz, 1H, CH_2-O-tetrahydropyran), 1.86-1.69 (m, 4H), 1.62-1.29 (m, 20H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.1, 136.4, 130.4, 127.5, 114.6, 111.5, 99.0, 68.2, 67.9, 62.5, 31.0, 29.91, 29.72, 29.70, 29.68, 29.63, 29.54, 29.41, 26.4, 26.2, 25.7, 19.9. MS-ESI $(M+Na)^+$ m/z calcd for $C_{24}H_{38}O_3Na$: 397.27, found 397.3. Elemental anal calcd for $C_{15}H_{16}O_2$: C 76.96, H 10.23; found C 76.68, H 10.14.

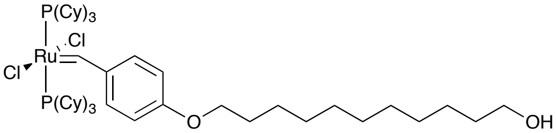
11-(4-vinylphenoxy)undecan-1-ol (**4**)



Compound **3** (5.35 g, 14.28 mmol) and *p*-toluenesulfonic acid monohydrate (271 mg, 1.43 mmol) were dissolved in methanol (60 mL) and stirred at 25 °C for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes / ethyl acetate = 4 : 1) (2.62 g, 63%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.85 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H, CH_2=C*H*), 5.60 (d, *J* = 17.6 Hz, 1H, CH_2=CH), 5.11 (d, *J* = 11.8 Hz, 1H, CH_2=CH), 3.95 (t, *J* = 6.6 Hz, 2H, ArOCH_2), 3.64 (t, *J* = 6.6 Hz, 2H, CH_2OH), 1.80-1.75 (m, 2H, OCH_2CH_2), 1.59-1.54 (m, 2H), 1.47-1.29 (m, 14H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.0, 136.4, 130.3, 127.4, 114.6, 111.5, 68.1, 63.1, 32.9, 29.70, 29.65, 29.62, 29.54, 29.49, 29.37, 26.1, 25.9. MS-ESI $(M+Na)^+$ m/z calcd for $C_{19}H_{30}O_2Na$: 313.21, found 313.1. Elemental anal calcd for $C_{19}H_{30}O_2$: C 78.57, H 10.41; found C 76.48, H 10.41.

Bifunctional initiator (5)

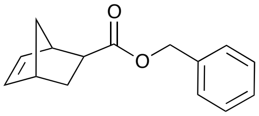


11-(4-vinylphenoxy)undecan-1-ol **4** (0.3 g, 1.03 mmol) and Grubbs' first-generation initiator (1.28 g, 1.55 mmol) were dissolved in anhydrous, degassed CH_2Cl_2 (15 mL) under an argon atmosphere and stirred at 25 °C for 30 min. The product was purified by column chromatography (hexanes / ethyl acetate = 4 : 1) to yield 651 mg of purple solid (62 % yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 19.42 (s, 1H, Ru=CH), 8.39 (br s, 2H, *o*-H of Ar), 6.79 (d, *J* = 9.1 Hz, 2H, *m*-H of Ar), 3.98 (t, *J* = 6.6 Hz, 2H, ArOC*H*$_2$), 3.63 (dt, *J* = 9.2, 5.9 Hz, 2H, C*H*$_2$OH), 2.59 (m, 6H), 1.79-1.15 (m, 78H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 147.8, 134.1, 114.4, 68.4, 63.3, 33.0, 32.4, 29.90, 29.80, 29.74, 29.73, 29.64, 29.59, 29.3, 28.1, 26.8, 26.2, 26.0. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.8 (*P*Cy$_3$). Elemental anal calcd for $C_{54}H_{94}O_2Cl_2P_2Ru$: C 64.26, H 9.39; found C 64.65, H 9.52.

Monomer synthesis

5-Norbornene-2-carboxylic acid benzyl ester (7)



Exo-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1.0 g, 7.24 mmol), benzyl alcohol (939 mg, 8.69 mmol), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (2.08 g, 10.86 mmol) and 4-dimethylaminopyridine (catalytic amount) were dissolved in dichloromethane (10 mL). After the mixture was stirred at 25 °C for 12 h, water (30 mL) was added and the mixture was extracted with dichloromethane (3 x 30 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow oil that was further purified by column chromatography on silica gel in hexanes/EtOAc (9 : 1) to yield 1.53 g of **7** as a clear oil (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.39-7.31 (m, 5H, CH_2Ar*H*), 6.11 (dq, *J* = 22.7 Hz, 3.0 Hz, 2H, C*H*=C*H*), 5.14 (d, 1H, *J* = 1.0 Hz, CH_2ArH), 3.07 (s, 1H, CH=CHC*H*CH), 2.93 (s, 1H, CH=CHC*H*CH2), 2.30-2.27 (m, 1H, CHCH_2CHCH), 1.95 (dt, J = 11.9 Hz, 4.0 Hz, 1H, CHCH_2CHCOO), 1.57-1.53, (m, 1H, CHCH_2CHCOO), 1.41-1.36 (m, 2H, CH=CHCHCH_2). ^{13}C NMR (151 MHz, CDCl3): δ175.93, 138.08, 138.00, 136.26, 135.73, 135.60, 128.49, 128.46, 127.99, 66.26, 46.64, 46.55, 46.34, 43.13, 43.10, 41.68, 41.57, 30.36, 30.33. MS-ESI $(M+Na)^+$ m/z calcd for $C_{15}H_{16}O_2Na$: 251.10, found 250.9. Elemental anal calcd for $C_{15}H_{16}O_2$: C 78.92, H 7.06; found C 78.89, H 7.12.

Polymer synthesis

General homopolymerization procedure of norbornene (8)

The desired amount of norbornene monomer **7** was dissolved in anhydrous, degassed CH_2Cl_2. A solution of bifunctional initiator **5** in CH_2Cl_2 was added. The monomer concentration after addition of bifunctional initiator **5** was 0.1 M. The solution was stirred at 25 °C for 30 min. Upon complete polymerization, ethyl vinyl ether was added to quench the polymerization. The residue was purified by repeated precipitation into MeOH.

General homopolymerization procedure of L-lactide (9)

In a glove box, the desired amount of L-lactide and bifunctional initiator **5** were dissolved in anhydrous, degassed CH_2Cl_2. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was added as a solution in CH_2Cl_2. The monomer concentration after addition of TBD was 1 M. The reaction was allowed to stir at 25 °C for 12 hours. After the reaction was complete, excess benzoic acid was added to quench the polymerization. The polymer was isolated and purified by repeated precipitations into MeOH.

General copolymerization of L-lactide and norbornene (10)

In a glove box, norbornene monomer **7** was dissolved in anhydrous, degassed CH_2Cl_2 in a screw-top vial. A solution of bifunctional initiator **5** in CH_2Cl_2 was added and the reaction was allowed to stir at room temperature for 1 hour. A solution of L-lactide monomer in CH_2Cl_2 and a solution of TBD in CH_2Cl_2 were added to the PNB solution. The monomer (L-lactide) concentration after addition of all components was 0.1 M. The reaction was allowed to stir at room temperature for 12 hours. Ethyl vinyl ether and benzoic acid were added to quench the polymerization. The residue was purified by repeated precipitation into MeOH.

Initiator characterization

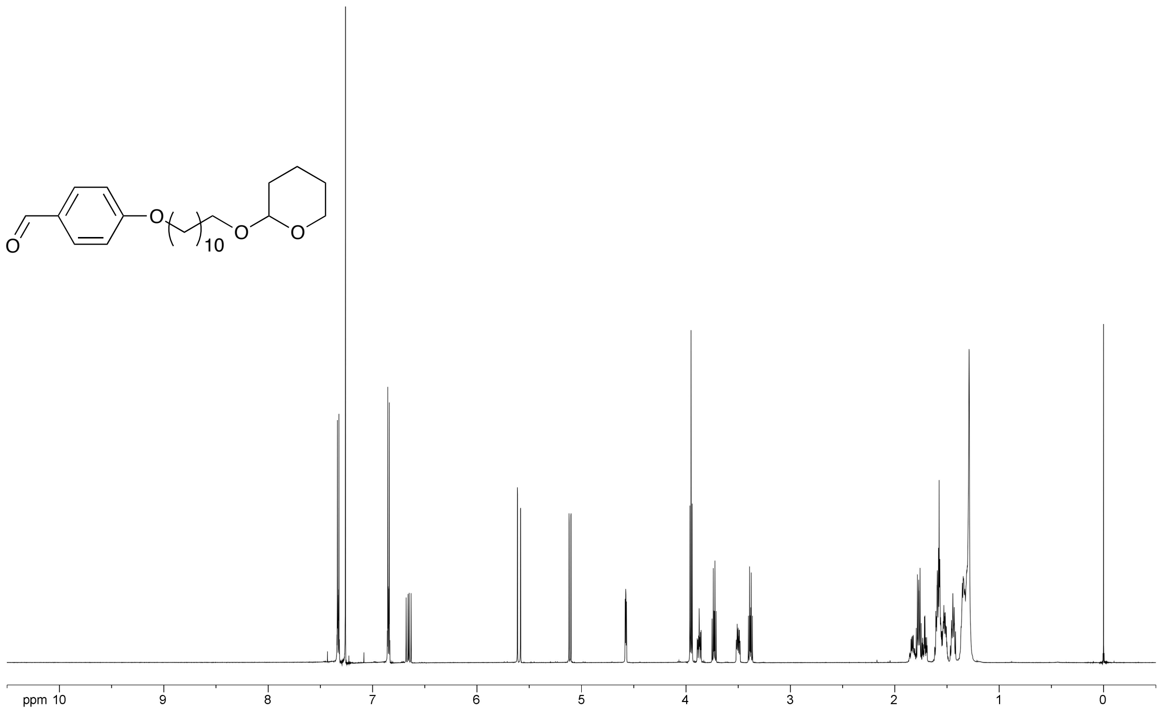


Figure SI 1. ^1H NMR spectrum ($CDCl_3$, 400 MHz) of 4-((11-((tetrahydro-2*H*-pyran-2-yl)oxy)undecyl)oxy)benzaldehyde (**2**).

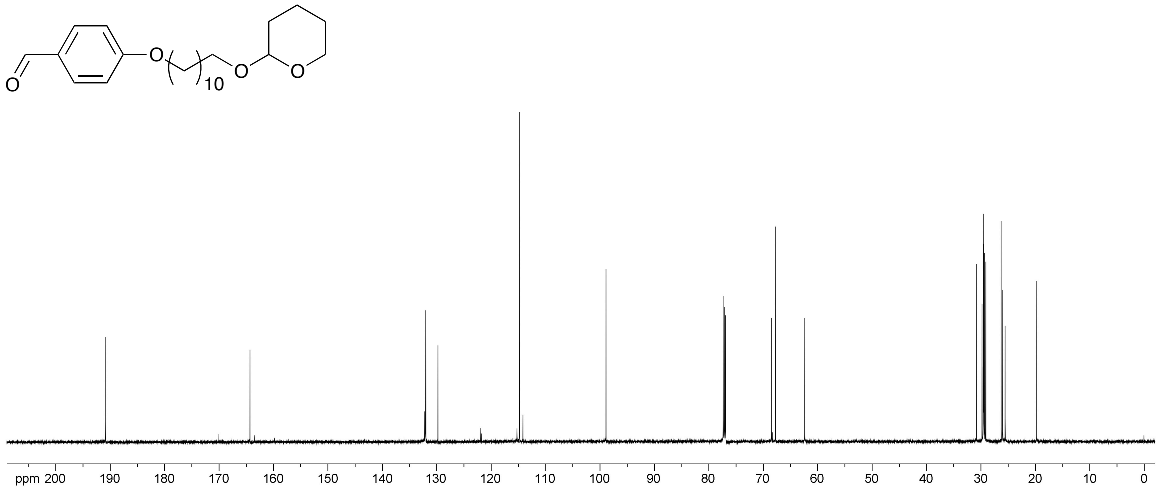


Figure SI 2. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 4-((11-((tetrahydro-2*H*-pyran-2-yl)oxy)undecyl)oxy)benzaldehyde (**2**).

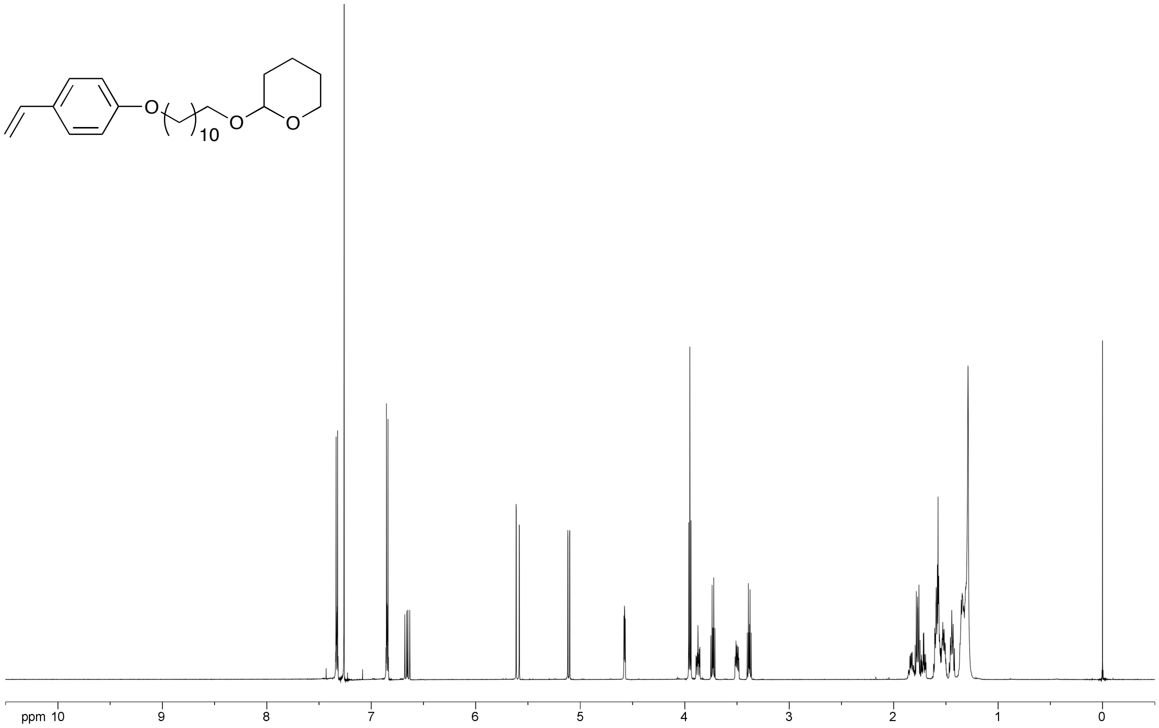


Figure SI 3. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of 2-((11-(4-vinylphenoxy)undecyl)oxy)tetrahydro-2*H*-pyran (**3**).

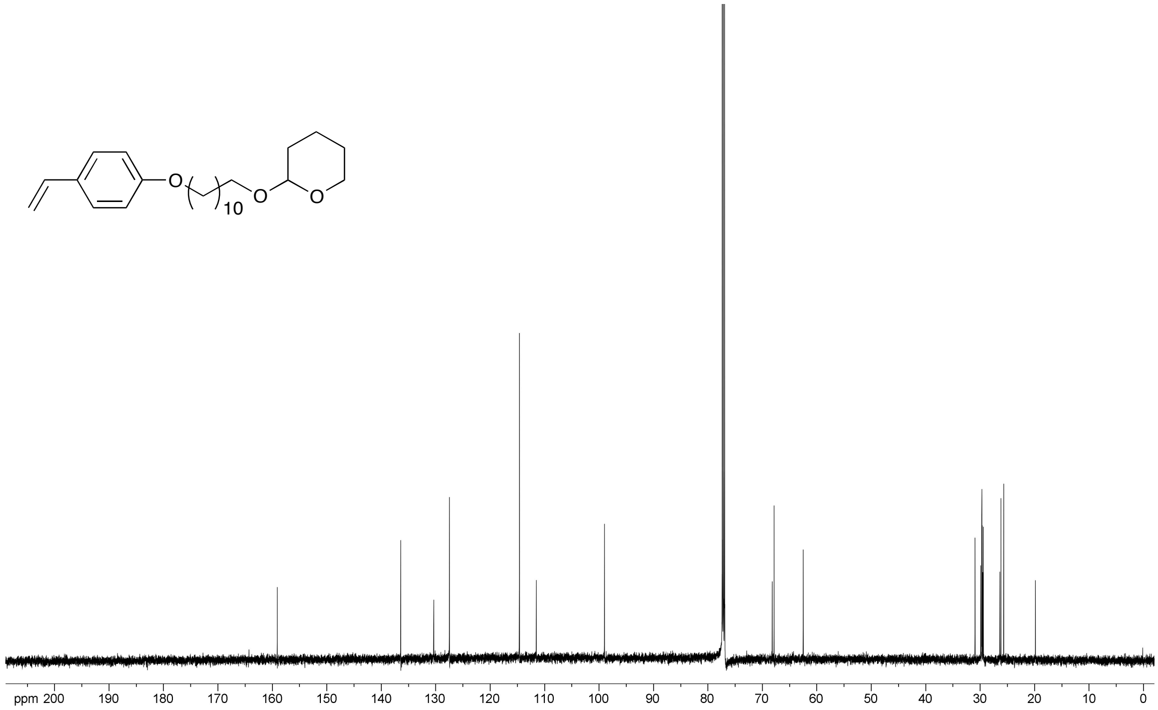


Figure SI 4. ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) of 2-((11-(4-vinylphenoxy)undecyl)oxy)tetrahydro-2*H*-pyran (**3**).

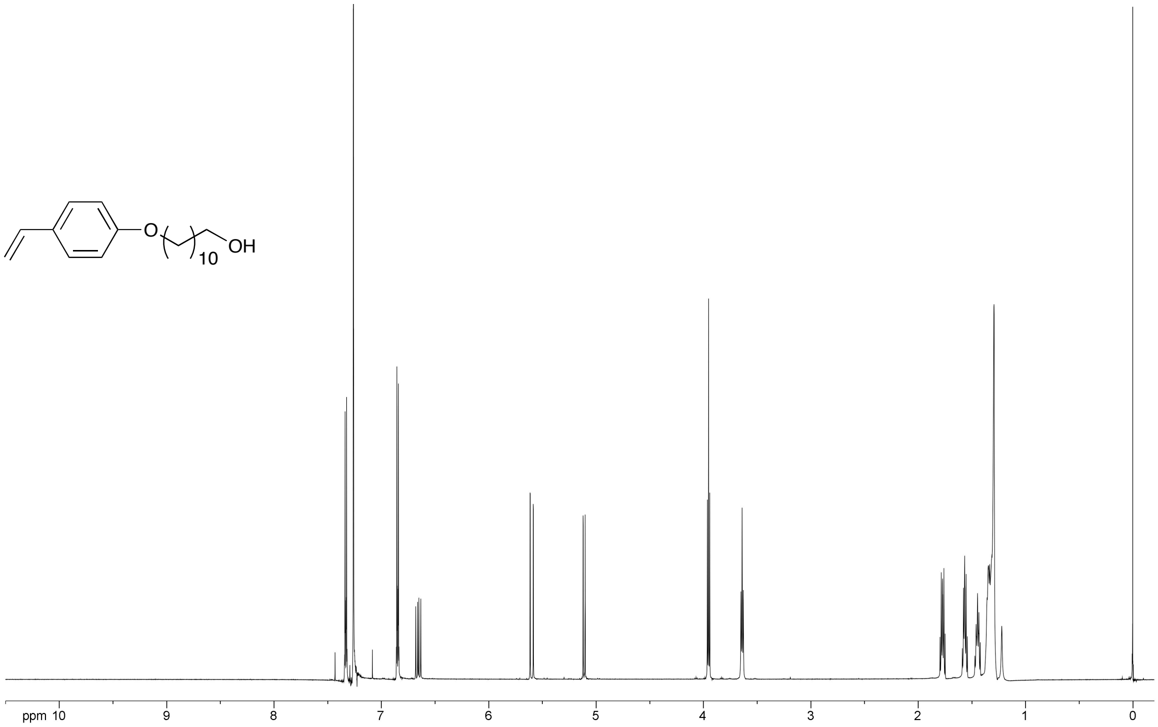


Figure SI 5 ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of 11-(4-vinylphenoxy)undecan-1-ol (**4**).

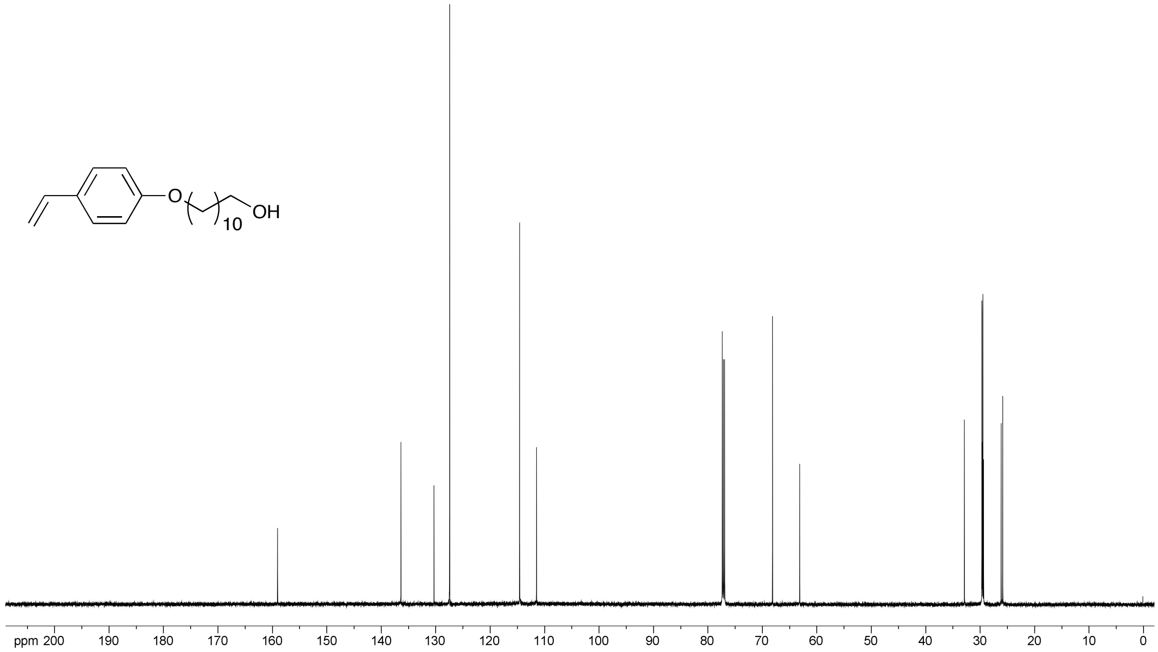


Figure SI 6. ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) of 11-(4-vinylphenoxy)undecan-1-ol (**4**).

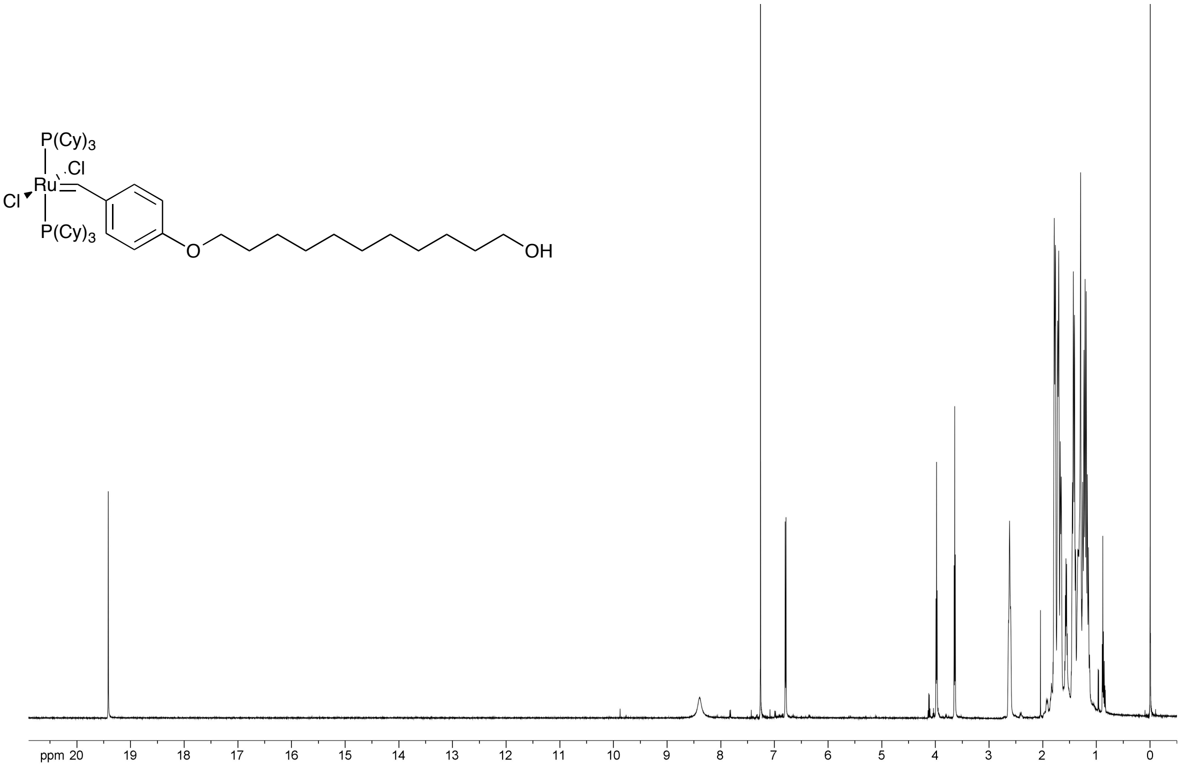


Figure SI 7. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of bifunctional initiator **5**.

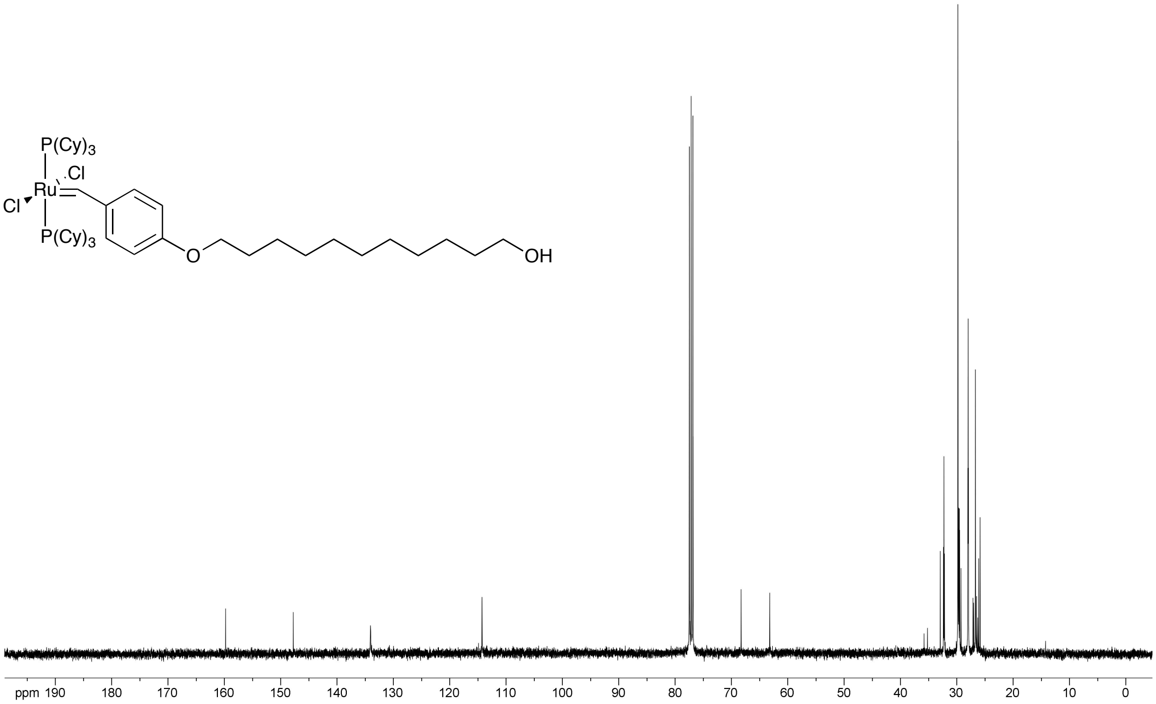


Figure SI 8. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of bifunctional initiator **5**.

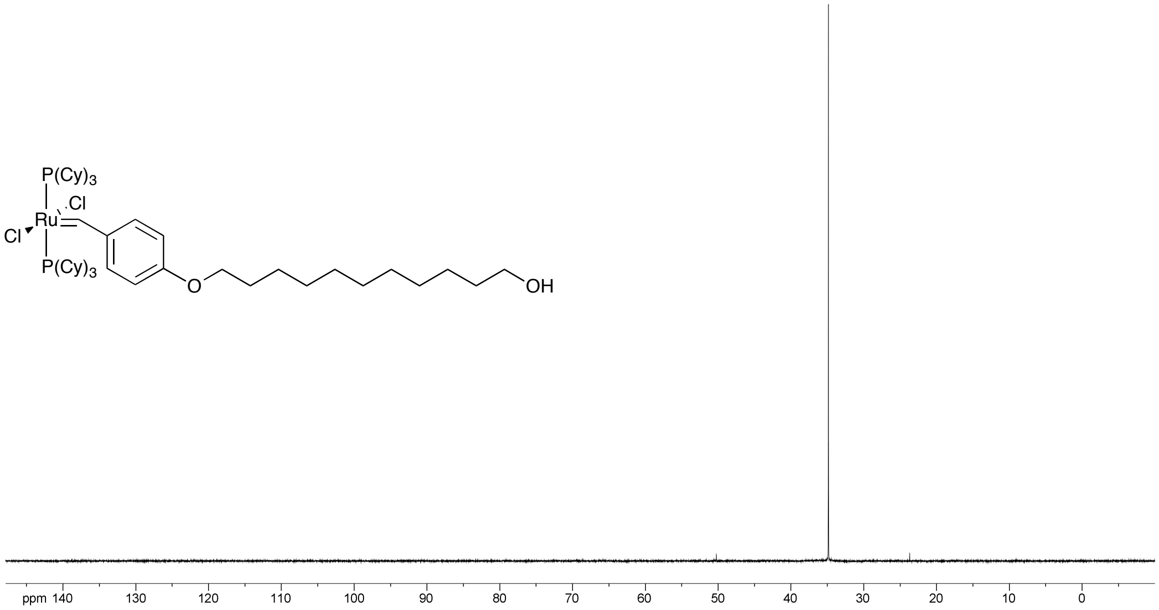


Figure SI 9. ^{31}P NMR spectrum ($CDCl_3$, 243 MHz) of bifunctional initiator **5**.

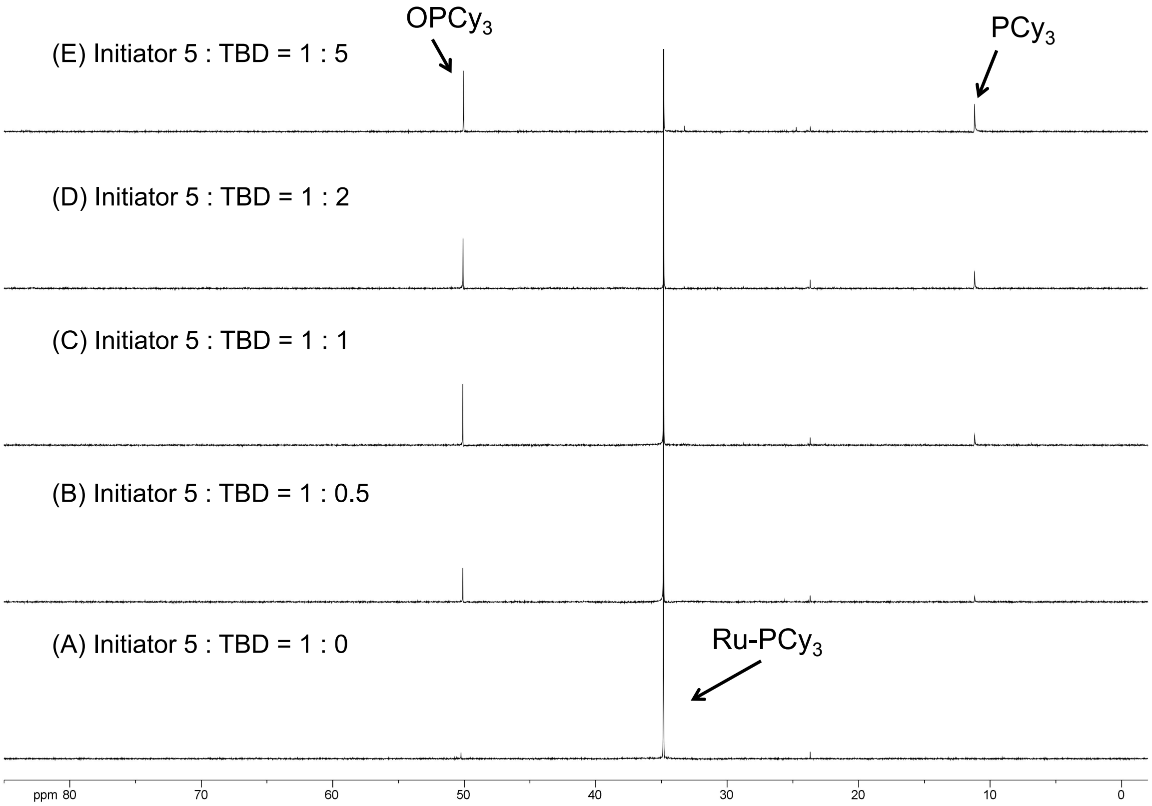


Figure SI 10. ^{31}P NMR spectrum of bifunctional initiator **5** in the presence of A: 0, B: 0.5, C: 1, D: 2 and E: 5 eq. of TBD.

Monomer characterization

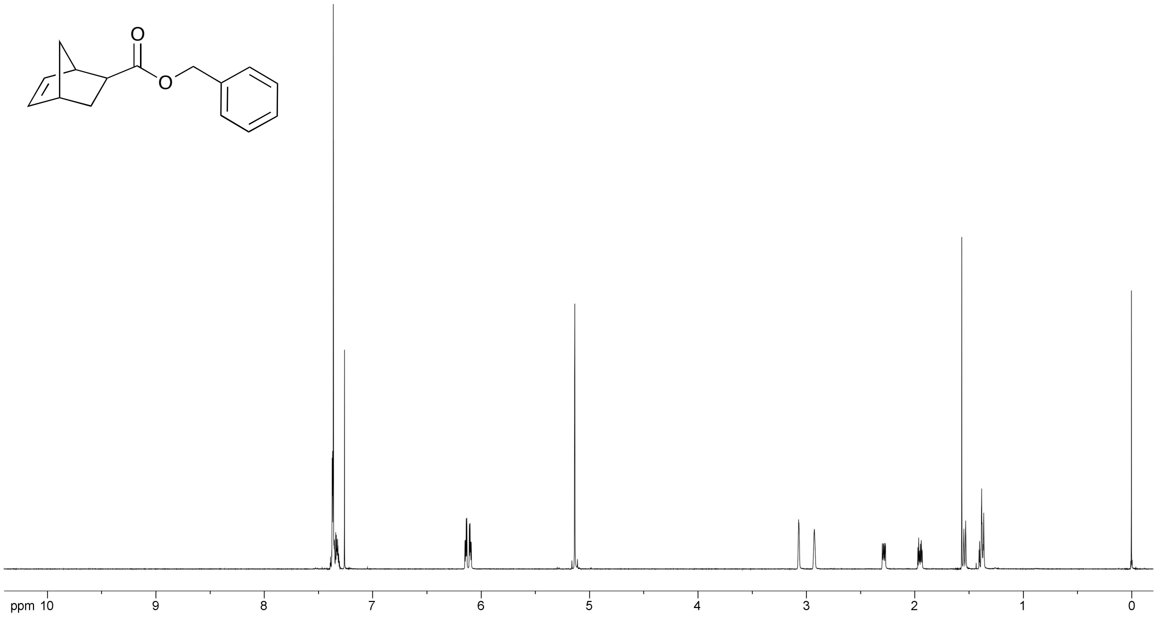


Figure SI 11. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **7**.

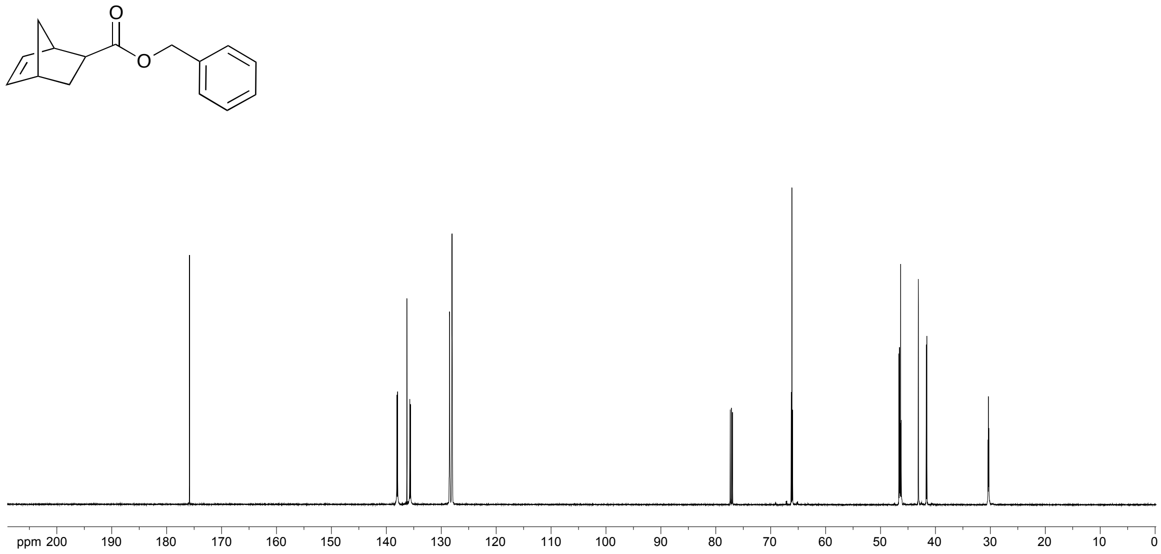


Figure SI 12. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of monomer **7**.

Polymer characterization

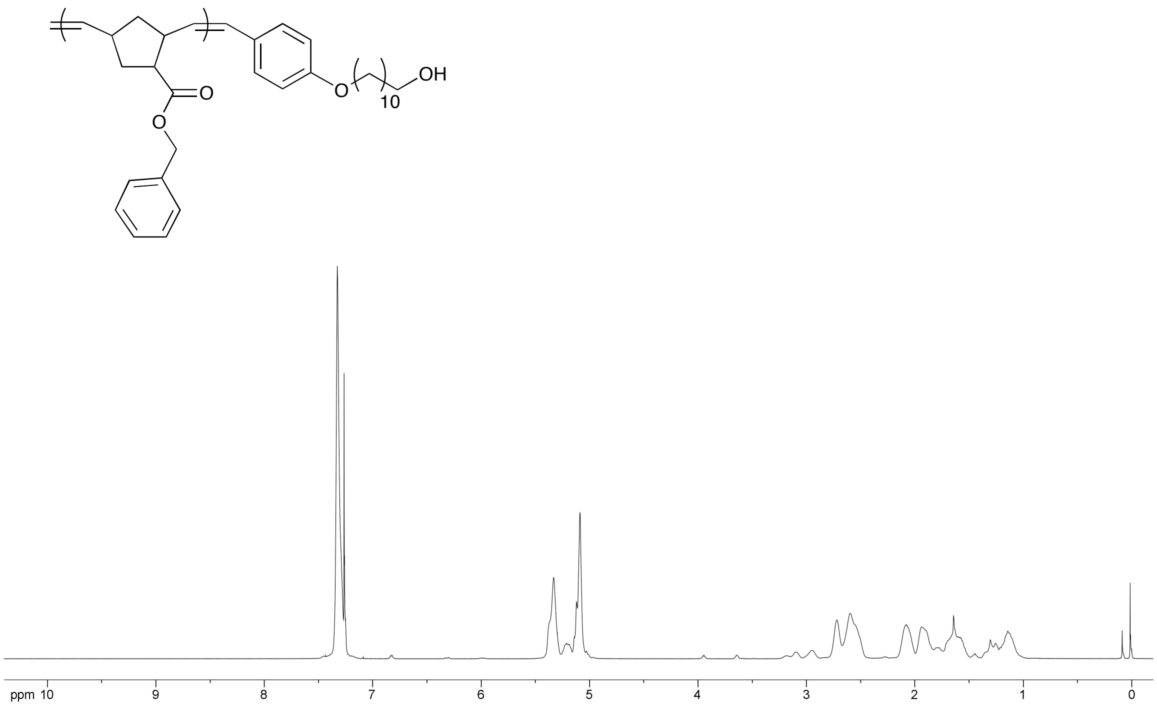


Figure SI 15. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of PNB homopolymer **8**.

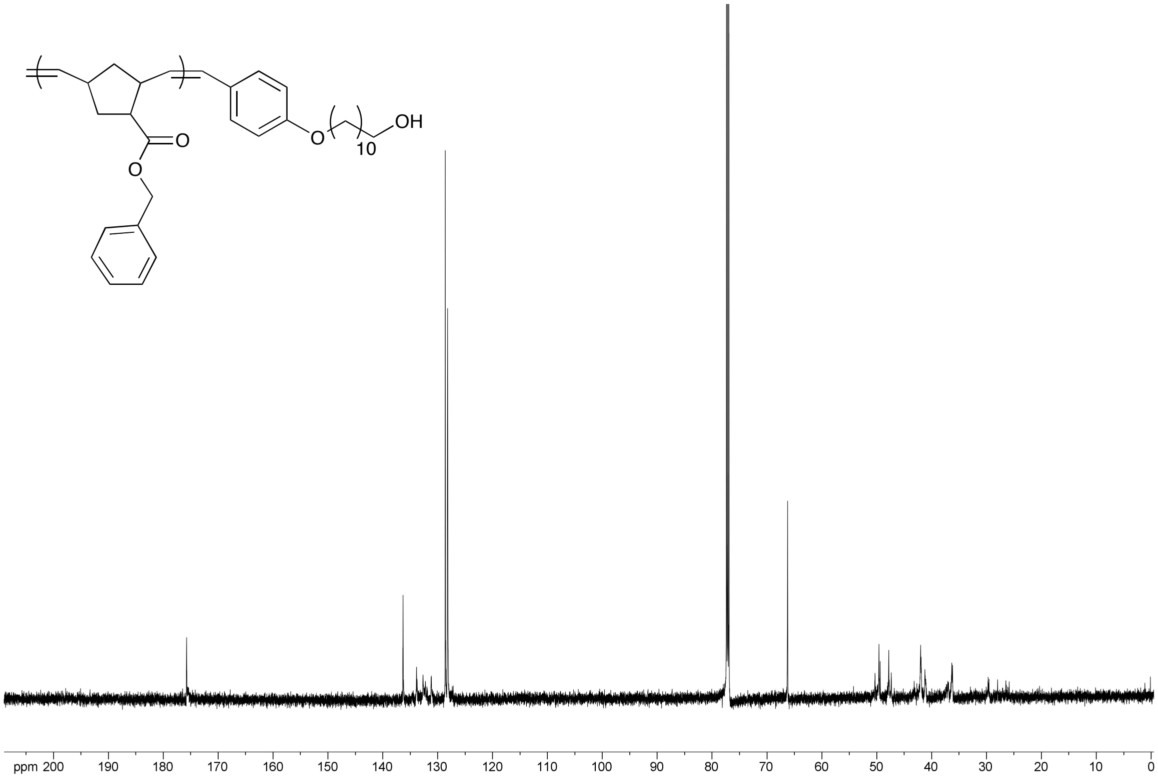


Figure SI 16. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of PNB homopolymer **8**.

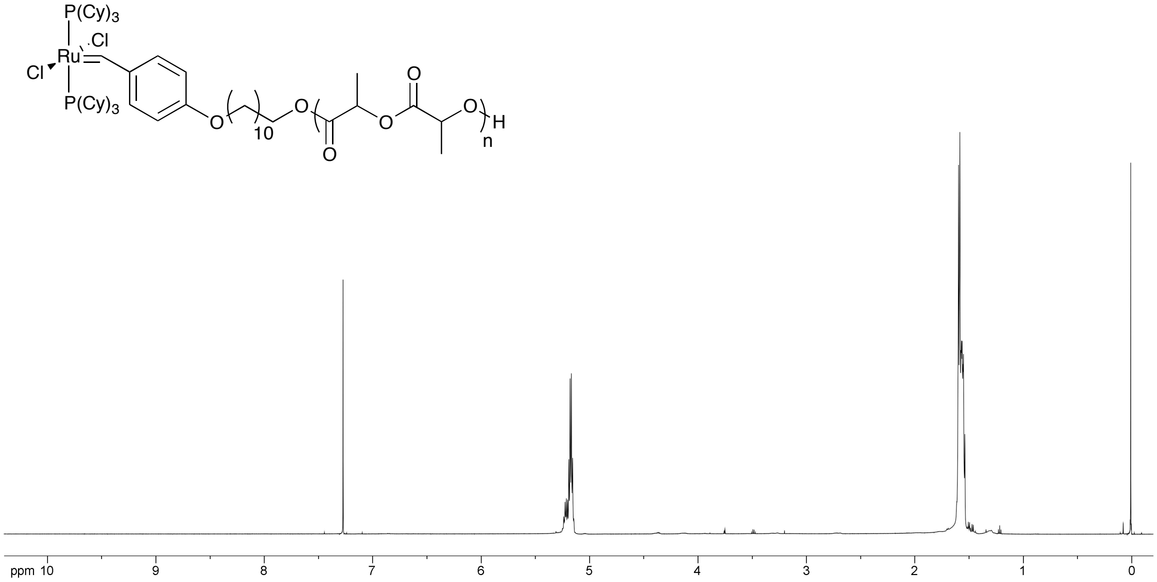


Figure SI 13. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of PLA homopolymer **9**.

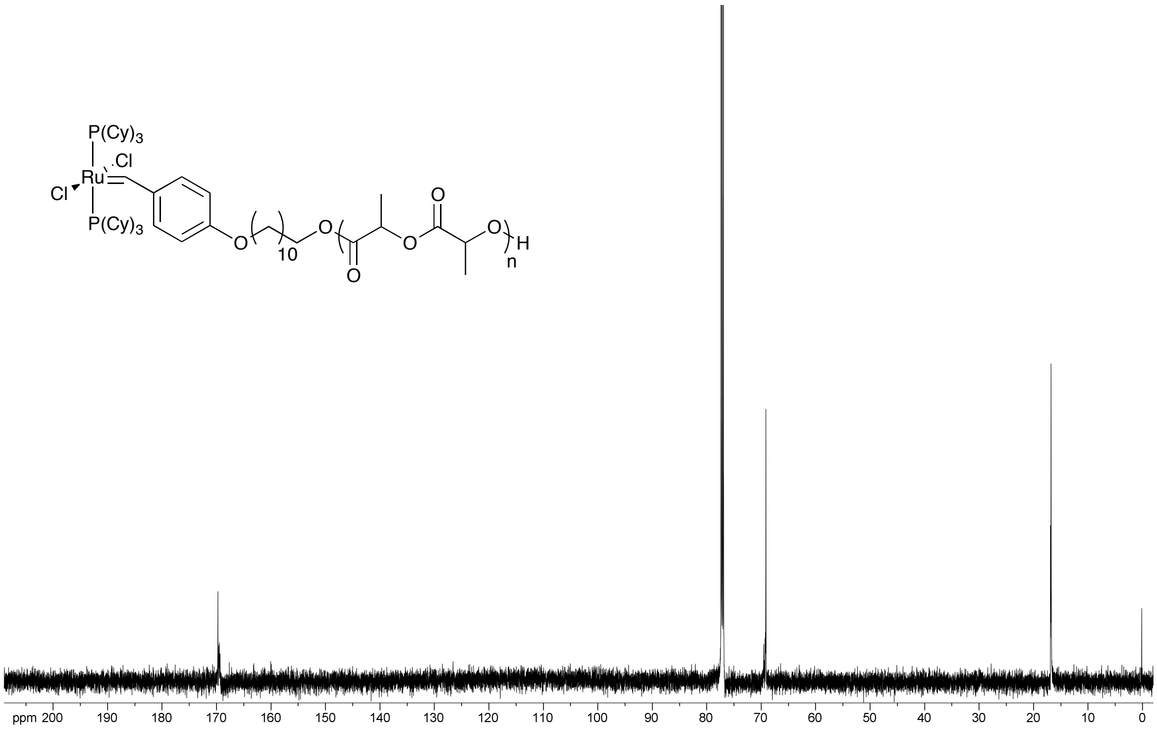


Figure SI 14. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of PLA homopolymer **9**.

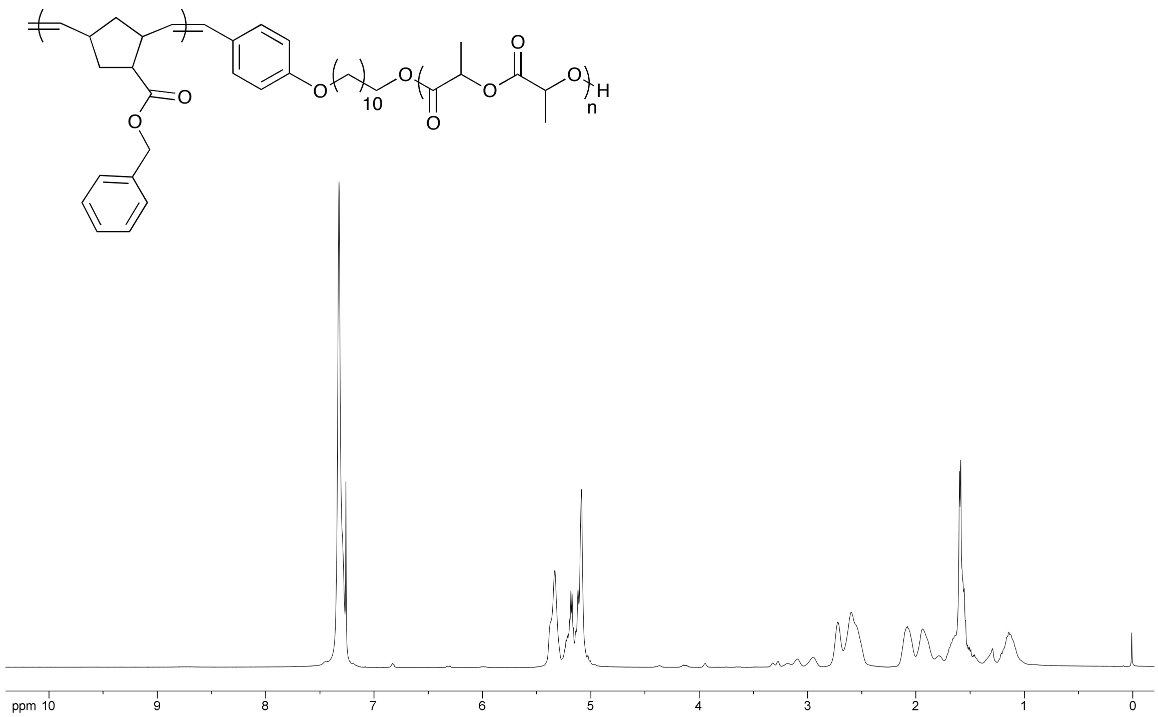


Figure SI 17. ^{1}H NMR spectrum (CDCl$_3$, 600 MHz) of PNB-*b*-PLA block copolymer **10**.

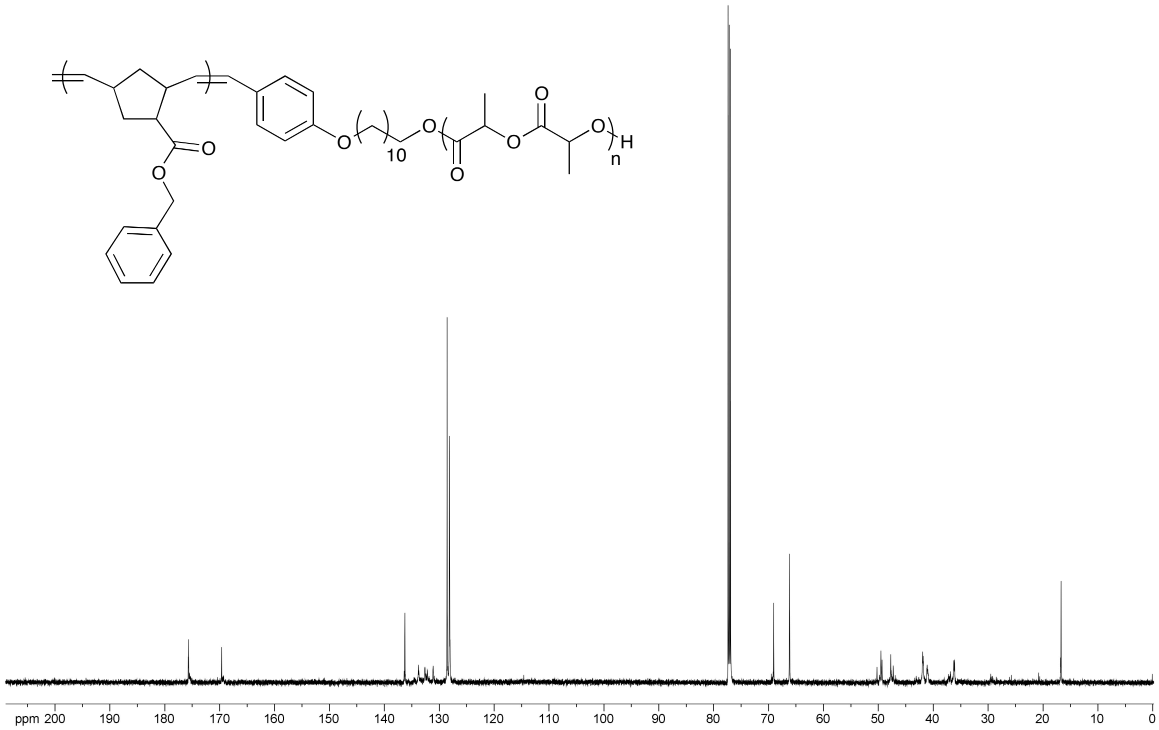


Figure SI 18. ^{13}C NMR spectrum (CDCl$_3$, 150 MHz) of PNB PNB-*b*-PLA block copolymer **10**.

Table SI 1. Characterization data of PLA (SEC, THF, PS standard, RI detection) for **9a**-**9e**.

Polymer	$[M]_{LA}$	[I]	Conversion	conv•[M] / [I]	M_n^{app}•10^3g/mol	PDI^{app}
9a	50	1	97%	49	3.6	2.37
9b	100	1	77%	77	5.7	3.34
9c	150	1	70%	105	7.2	2.08
9d	200	1	50%	100	6.6	2.36
9e	250	1	41%	103	7.1	2.01

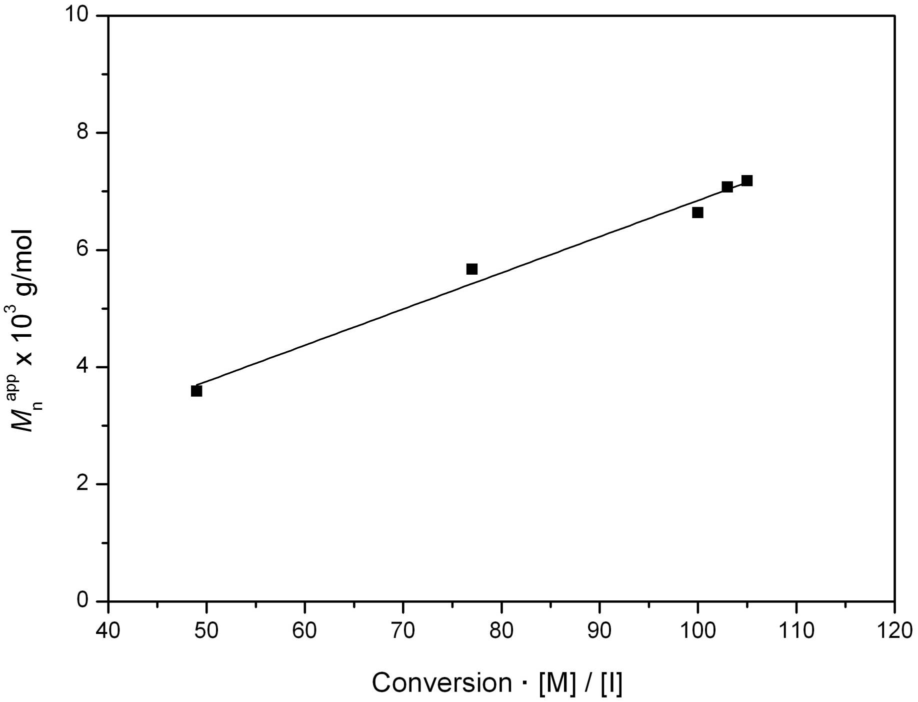


Figure SI 19. M_n^{app}s of PLA homopolymers as determined by SEC (THF, RI detection) as a function of the conversion and [M]/[I].

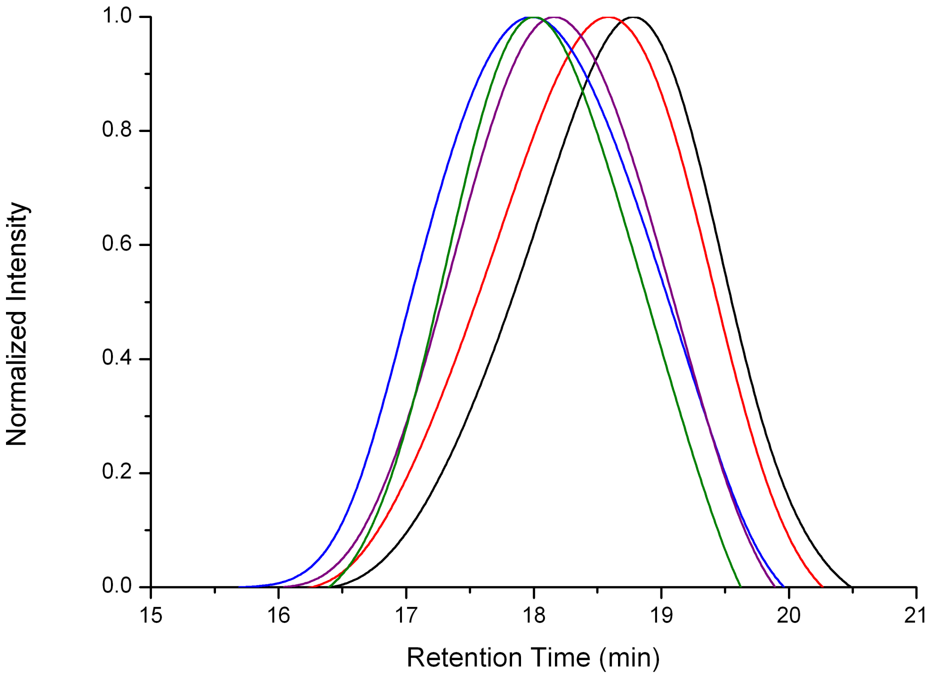


Figure SI 20. SEC chromatograms (THF, RI detection) of PLA homopolymers **9a** (black), **9b** (red), **9c** (blue), **9d** (purple), and **9e** (green).

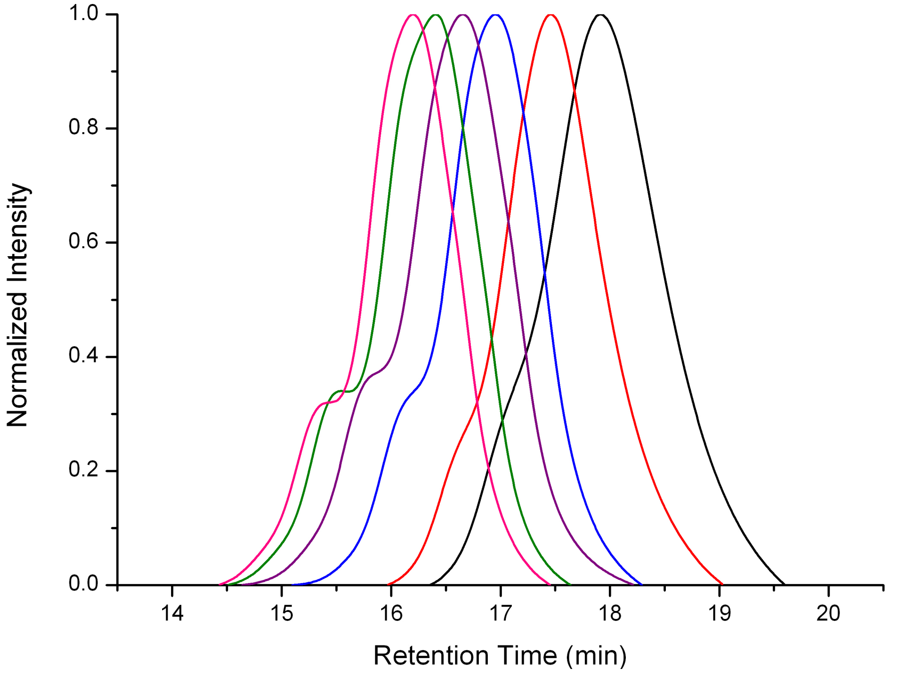


Figure SI 21. SEC chromatograms (THF, RI detection) of PNB homopolymers **8**. Monomer to initiator ratios are: 25 (black), 50 (red), 100 (blue), 150 (purple), 200 (green), and 250 (pink).

[1] A. Pulsipher, N. P. Westcott, W. Luo, M. N. Yousaf, *J. Am. Chem. Soc*. 2009, **131**, 7626.

[2] D. D. Manning, L. E. Strong, X. Hu, P. J. Beck, L. L. Kiessling, *Tetrahedron*, 1997, **53**, 11937.