ROMP−ATRP Block Copolymers Prepared from Monotelechelic Poly(oxa)norbornenes Using a Difunctional Terminating Agent

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ABSTRACT: Novel block copolymers were prepared by combining ROMP and ATRP. Using the fast initiating ruthenium metathesis catalyst $(H_2IMes)(Cl)_2(pyr)_2RuCHPh$ and (*Z*)-but-2-ene-1,4-diyl bis(2-bromopropanoate) as a terminating agent, three different monotelechelic poly(oxa)norbornenes were synthesized. Complete end-functionalization was shown by carrying out the ATRP of styrene and *tert*-butyl acrylate from the poly(oxa)norbornenes using a CuBr/PMDETA catalyst system. GPC showed no remaining homopolymer, and all block copolymers were found to have matching theoretical and observed molecular weights and low polydispersities.

Introduction

Combination of multiple distinct types of living polymerization methods has been the subject of intense study in recent years.[1–5] This research is driven by the fact that while the number of cheap, accessible monomers is relatively low, the different types of materials that can be produced from these monomers is much higher due to copolymerization and manipulation of microstructure. Still, many monomer combinations cannot be copolymerized using a single method due to the diverse conditions, requirements, and monomer types of the various living polymerization methods,[6] such as living anionic polymerization, controlled/living radical polymerization (CRP), and living ring-opening metathesis polymerization (ROMP). This problem is typically overcome by the development of multifunctional initiators, monomers, and chain-transfer agents that allow for multiple polymerization techniques to be used in the preparation of a single polymer.

ROMP polymers provide unique materials because unlike radical, anionic, and cationic polymerizations, no unsaturation in the monomer is lost.[7] These types of unsaturated-backbone polymers, such as poly(oxa)norbornenes, polycyclooctenes, and polycyclobutenes, are either unattainable or have imperfect microstructure when made using radical and ionic polymerization techniques. While great efforts have been made at merging various types of CRP polymerization methods in a single polymer synthesis,[6] only a few reports exist that show the combination of living ROMP with any other polymerization method.[8–15] Reliable techniques for joining living ROMP with other living polymerization methods will provide synthetic routes to new materials inaccessible by any other means. We chose to investigate combining living ROMP with ATRP because of the ability of both methods to easily produce highly functional polymers under mild conditions.

Most of the reports that describe the combination of ROMP and living radical polymerization techniques use functionalized ROMP monomers capable of initiating ATRP, also known as inimers.[10–16] Both grafting-from and grafting-through approaches have been used to synthesize polymers with a backbone made by ROMP and side chains made by ATRP. While useful in making brush polymers, inimers have limited utility because they cannot be used to reliably make other polymer structures.

Linear polymers have been made by combining ROMP and ATRP by using a difunctional chain-transfer agent (CTA).[17,18] The resulting telechelic ROMP polymers were used to initiate ATRP, producing ABA triblock copolymers. This strategy suffers from the drawback that the middle B block is not made in a living fashion, so a polydisperse product is obtained. Additionally, only monomers that can undergo secondary metathesis (backbiting) can be used in these reactions, leaving out substituted norbornene monomers from these types of materials.

A synthetic method for the preparation of monotelechelic ROMP polymers could allow for incorporation of an ATRP initiator on the chain end. This would facilitate the synthesis of low-polydispersity linear ROMP−ATRP block copolymers, which could be further end-functionalized in a variety of ways, expanding the scope of ROMP−ATRP hybrid materials to more complex graft copolymers, star polymers, multiblock copolymers, and others. Monotelechelic ROMP polymers have been made through either the custom initiator method or the end-capping method. The custom initiator method is typically carried out by exchanging the benzylidene on the metathesis catalyst for an alkylidene with the desired functionality.[19,20] This strategy, while effective, suffers from the necessity of synthesizing a new catalyst for each new desired end-functional group. The end-capping method involves the addition of a small molecule that is added onto the end of the polymer chain by reaction with the living chain end. End-capping chains with aldehydes is a reliable technique for end-functionalization of ROMP polymers made using early transition metal catalysts,[9,21] but until recently no reliable techniques existed for this type of transformation using the more air, moisture, and functional group tolerant ruthenium metathesis catalysts.

Hilf et al. described the sacrificial monomer method of producing hydroxyl-terminated ROMP polymers.[22] This technique involves the synthesis of a diblock copolymer with one block composed of the desired monomer, followed by a second short block composed of a dioxepine monomer. Subsequent cleavage of the poly(dioxepine) yields the hydroxyl-functionalized monotelechelic polymer. These types of monotelechelic polymers have been used to make all-ROMP graft copolymers[23] as well as poly(norbornene)-*b*-poly(ethylene glycol) copolymers by further end-functionalization of the ROMP polymer.[24] While the sacrificial monomer strategy could be used to create many types of polymer architectures, the alcohol-functionalized polymer must always be further derivatized to enable further reactivity. This process requires long reaction times and often does not reach completion. A technique that could directly incorporate the desired functional group onto the polymer by reaction with the living chain end would allow for the

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incorporation of diverse chain end functionality without the need to perform difficult postpolymerization transformations.

We are aware of one report that utilizes this type of transformation. Li et al. used the ruthenium initiator $(PCy_3)_2(Cl)_2RuCHPh$ to prepare liquid crystalline block copolymers using a symmetrical olefin to place an α-bromoester on one end of the ROMP polymer.[8] They were then able to initiate the ATRP of *n*-butyl acrylate from the functionalized chain end. However, recent reports have shown that the ruthenium metathesis catalyst $(H_2IMes)(Cl)_2(pyr)_2RuCHPh$ (**1**) and related structures afford living polymers of extremely low polydispersity much faster than with previous catalysts.[25,26] Polymerizations with catalyst **1** are often complete in only a few minutes, and facile synthesis of block copolymers can be achieved.[27] These qualities, as well as its air and moisture tolerance and its long benchtop stability, make catalyst **1** an ideal initiator for the synthesis of end-functionalized ROMP polymers. We sought to extend the approach of Li et al. to this highly active ruthenium metathesis catalyst and to examine the scope of this type of transformation.

Experimental Section

Materials. CH_2Cl_2 and THF were purified by passage through solvent purification columns.[34] $(H_2IMes)(pyr)_2(Cl)_2RuCHPh$ (**1**) was prepared from $(H_2IMes)(PCy_3)(Cl)_2RuCHPh$ according to a literature procedure.[35] *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride was purchased from Acros Organics, and *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride was prepared as described previously.[27] 6-Methoxyhex-5-en-1-ol (**2**) was prepared according to a literature procedure and isolated as 76% *trans* product.[29] Styrene and tBA were passed through a column of basic alumina immediately before use. *cis*-2-Butene-1,4-diol was distilled from CaH_2. All other materials were obtained from Aldrich Chemical Co. and used as received unless otherwise noted.

General Methods. NMR spectra were measured in $CDCl_3$ or DMSO-d_6 on Varian Mercury 300 MHz spectrometers unless otherwise noted. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to $CDCl_3$ ($\delta = 7.27$). Flash column chromatography of organic compounds was performed using silica gel 60 (230−400 mesh). High-resolution mass spectra (EI and FAB) were provided by California Institute of Technology Mass Spectrometry Facility. Infrared spectra were recorded using a Perkin-Elmer Spectrum BXII spectrometer. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/d*c* values were obtained for each injection by assuming 100% mass elution from the columns.

6-Methoxyhex-5-enyl 2-Bromopropanoate (3). An oven-dried, two-necked, round-bottom flask under argon was charged with 6-methoxyhex-5-en-1-ol (**2**) (82 mg, 1 equiv) in 1 mL of THF. NEt_3 (0.22 mL, 2.5 equiv) was added, and the flask was cooled to 0 °C. 2-Bromopropionyl bromide (0.13 mL, 2.0 equiv) was added dropwise to the reaction mixture, and a white precipitate developed. After stirring at room temperature for 6 h, the reaction mixture was diluted with CH_2Cl_2 and water. The organic layer was removed, and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined and washed with brine and dried over $MgSO_4$. The crude product was purified by silica gel chromatography (5% EtOAc in hexanes) to give **6** as a clear oil in 88% yield (77% *trans* product). ^1H NMR: δ 1.45 (m, 2H), 1.66 (m, 2H), 1.81−1.90 (m, 5H), 1.93−2.11 (m, 3H), 3.51−3.58 (m, 4H), 4.07−4.40 (m, 3.2H), 4.70 (m, 0.8H), 5.88 (d, $J = 3.3$ Hz, 0.2H), 6.28 (d, $J = 12.3$ Hz, 0.8H). ^{13}C NMR: δ 170.51, 170.42, 147.64, 146.75, 102.49, 66.21, 66.12, 65.12, 56.12, 44.15, 40.43, 40.20, 33.17, 29.27, 28.08, 27.89, 27.42, 27.27, 27.04, 26.03, 23.48, 21.88. HRMS: calculated 265.0440; found 265.0439.

(*Z*)-But-2-ene-1,4-diyl Bis(2-bromopropanoate) (6). An oven-dried, three-necked, round-bottom flask under argon was charged with *cis*-2-butene-1,4-diol (2.0 mL, 1 equiv) in 40 mL of THF. NEt_3 (9.0 mL, 2.5 equiv) was added, and the flask was cooled to 0 °C. 2-Bromopropionyl bromide (7.7 mL, 3.0 equiv) was added dropwise to the reaction mixture, and a white precipitate developed. After stirring at room temperature for 6 h, the reaction mixture was diluted with CH_2Cl_2 and water. The organic layer was removed, and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined and washed with brine and dried over $MgSO_4$. The crude product was purified by silica gel chromatography (10% EtOAc in hexanes) to give **6** as a clear oil in 63% yield. Further purification was accomplished by Kugelrohr distillation. ^1H NMR: δ 1.83 (d, $J = 6.9$ Hz, 6H), 4.38 (q, $J = 6.9$, 2H), 4.80 (d, $J = 4.8$, 4H), 5.81 (m, 2H). ^{13}C NMR: δ 170.12, 128.11, 61.50, 39.95, 21.78. HRMS: calculated 358.9317; found 358.9309.

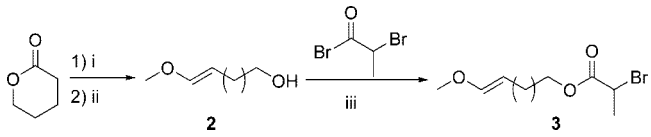
***tert*-Butyl Ester Norbornene Imide (tBENI) (7).** A 100 mL round-bottom flask was charged with glycine−*tert*-butyl ester (3.88 g, 1.1 equiv) in 45 mL of C_6H_6. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (4.25 g, 1 equiv) and NEt_3 (0.375 mL, 0.1 equiv) were added, and the reaction mixture quickly solidified. The flask was immersed in an oil bath and heated at reflux with a Dean−Stark trap. The solids slowly dissolved, leaving a clear solution. After 2 h the heat was removed and the solvent was removed in vacuo. The residue was taken up in CH_2Cl_2 and washed with 0.1 N HCl, H_2O, and brine and then dried over $MgSO_4$. A pale yellow oil was recovered, which solidified after 10 h under high vacuum. The solid was purified by sublimation, yielding a white powder in 50% yield. ^1H NMR: δ 1.43 (s, 9H), 1.51 (dt, $J = 9.9$, 1.5 Hz, 1H), 1.71 (d, $J = 9.9$ Hz, 1H), 2.71 (d, $J = 1.2$ Hz, 2H), 3.29 (t, $J = 1.5$ Hz, 2H), 4.10 (s, 2H), 6.28 (t, $J = 1.8$ Hz, 2H). ^{13}C NMR: δ 177.37, 165.91, 138.12, 83.00, 48.14, 45.51, 43.13, 40.37, 28.16. HRMS: 278.1392; found 278.1389.

***N*-Butyl Norbornene Imide (NBNI) (8).** A 100 mL round-bottom flask was charged with cis-5-norbornene-*exo*-2,3-dicarboxylic anhydride (1.0 g, 1 equiv) and 25 mL of glacial acetic acid. Once homogeneous, *n*-butylamine (0.66 mL, 1.1 equiv) was added slowly to the flask. A condenser and a drying tube were attached, and the flask was immersed in an oil bath at 120 °C. After 2 h, the heat was removed, and once cool, the contents of the flask were added to 50 mL of chilled H_2O. The cloudy solution was extracted with toluene three times. The combined organic layers were washed with H_2O and brine and dried over $MgSO_4$ to yield a pale yellow oil. The oil was purified by elution in CH_2Cl_2 through a column of neutral alumina. ^1H NMR: δ 0.93 (t, $J = 7.2$ Hz, 3H), 1.21−1.36 (m, 3H), 1.48−1.62 (m, 3H), 2.67 (d, $J = 1.2$ Hz, 2H), 3.27 (m, 2H), 3.46 (t, $J = 7.5$ Hz, 2H), 6.28 (t, $J = 1.8$ Hz, 2H). ^{13}C NMR: δ 178.33, 138.04, 48.00, 45.37, 42.92, 38.72, 30.04, 20.43, 13.84. HRMS: calculated 220.1338; found 220.1344.

***N*-Methyl Oxanorbornene Imide (NMON) (9).** A Schlenk tube was charged with *N*-methylmaleimide (4.11 g, 1 equiv), followed by Et_2O (25 mL) and furan (5.2 mL, 1.9 equiv). Three freeze−pump−thaw cycles were performed, and the tube was sealed under argon. The tube was immersed in an oil bath at 90 °C, and the solids slowly dissolved. After 4 h the heat was removed and the tube was allowed to cool. The white precipitate was collected by filtration and purified by recrystallization from EtOAc in 48% yield. ^1H NMR: δ 2.86 (s, 2H), 2.98 (s, 3H), 5.28 (s, 2H), 6.52 (s, 2H). ^{13}C NMR: δ 176.42, 136.64, 80.95, 47.63, 25.04. HRMS: calculated 180.0661; found 180.0657.

General Polymerization Procedure for Monotelechelic Poly(oxa)norbornenes (4, 10−12). A 2 dram vial with a septum cap was charged with the desired amount of monomer and a stirbar under argon flow. CH_2Cl_2 (0.1 M) was added to the vial. The desired amount of catalyst **1** as a stock solution in CH_2Cl_2 was quickly added to the vigorously stirring monomer solution. After stirring at room temperature for 3 min under argon flow, vinyl ether **3** or TA **6** was added as a solution in CH_2Cl_2. The reaction mixture was allowed to stir for 3−24 h. The reaction mixture was precipitated into a large volume of diethyl ether/hexanes (1:1), and

Scheme 1. Synthesis of Vinyl Ether[a]



[a] Reaction conditions: (i) DIBAL, THF, −40 °C; (ii) $ClPh_3PCH_2OCH_3$, *sec*-BuLi, THF, 0 °C; (iii) THF, NEt_3, 0 °C.

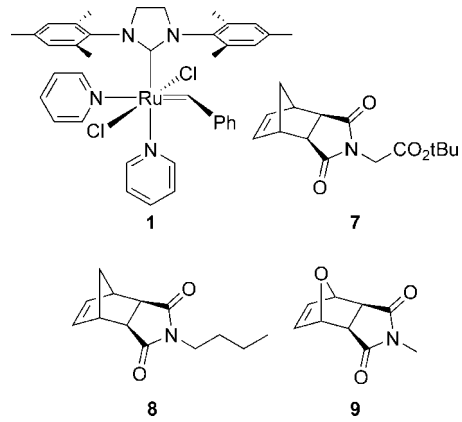


Figure 1. Monomers and metathesis catalyst used in ROMP reactions.

the product was recovered by filtration and multiple washings with ether followed by drying under vacuum.

Poly(tBENI) (10). The product was recovered as a tan powder in 93% yield. GPC: M_n = 8520, M_w/M_n = 1.03. IR: 2979, 2931, 1779, 1742, 1710, 1415, 1394, 1369, 1324, 1235, 1160, 919, 846, 750. ^{1}H NMR: δ 1.20−1.80 (m, 9n H), 1.82 (d, 3H) 2.00−2.30 (m, n H), 2.70−3.40 (m, 4n H), 4.05 (s, 2n H), 4.38 (q, 1H), 4.65 (d, 2H), 5.40−5.80 (d, 2n H).

Poly(NBNI) (11). The product was recovered as a tan powder in 93% yield. GPC: M_n = 7190, M_w/M_n = 1.02. IR: 2956, 2872, 1771, 1698, 1436, 1397, 1368, 1341, 1265, 1190, 1135, 1046, 970, 922, 763. ^{1}H NMR: δ 0.80−1.00 (m, 3n H), 1.20−1.40 (m, 2n H), 1.40−1.80 (m, 4n H), 1.82 (d, 3H), 1.95−2.40 (m, n H), 2.60−3.60 (m, 5n H), 4.38 (q, 1H), 4.65 (d, 2H), 5.40−5.80 (d, 2n H).

Poly(NMONI) (12). The product was recovered as a tan powder in 76% yield. GPC: M_n = 4840, M_w/M_n = 1.06. IR: 3604, 3464, 3059, 2952, 2890, 1778, 1713, 1436, 1383, 1328, 1283, 1131, 1031, 971, 920, 807, 734, 700, 632. ^{1}H NMR: δ 1.82 (d, 3H), 2.85−3.00 (s, 3n H), 3.20−3.45 (s, 2n H), 4.30−4.60 (m, nH + 1H), 4.70−5.00 (m, n H), 5.70−6.10 (m, 2n H).

ATRP of S and tBA from Monotelechelic Poly(oxa)norbornenes (5, 13−18). A dry vial with a septum cap was charged with the desired macroinitiator (**4**, **10**, **11**, or **12**) (0.050 mmol) and a stirbar. Neat monomer (0.25 mL) was added, followed by DMF (0.2 mL) and PMDETA (1.0 μL, 0.050 mmol). Three freeze−pump−thaw cycles were performed on this solution. The vial was backfilled with argon, and CuBr (0.7 mg, 0.050 mmol) was added. Two more freeze−pump−thaw cycles were performed, and then the vial was sealed under argon and placed in an oil bath at 90 °C (**5**, **13**−**15**) or 70 °C (**16**−**18**). Monomer conversion was measured by ^{1}H NMR, and reactions were quenched at the desired conversion by removal of heat, exposure to air, and dilution with THF. The copper catalyst was removed by passing the reaction mixture through a column of alumina, eluting with THF. The polymer solution was concentrated and precipited into a large volume of methanol (**5**, **13**−**15**) or methanol/H_2O (70:30) (**16**−**18**). The product was recovered by filtration (**5**, **13**−**15**) or by decanting off the supernatant (**16**−**18**). All products were dried under vacuum for several hours.

Poly(tBENI-*b*-S) (13). The product was recovered as a white, fluffy powder in 34% yield. GPC: M_n = 19 100, M_w/M_n = 1.07. IR: 3026, 2924, 2853, 1779, 1743, 1710, 1601, 1493, 1453, 1415, 1394, 1369, 1324, 1236, 1168, 1071, 1029, 970, 846, 750, 698. ^{1}H NMR: δ 1.20−2.40 (m, 10n + 2m H), 2.70−3.40 (m, 4n H), 4.05 (s, 2n H), 5.40−5.80 (d, 2n H), 6.30−7.25 (m, 5m H).

Poly(NBNI-*b*-S) (14). The product was recovered as a white, fluffy powder in 50% yield. GPC: M_n = 25 800, M_w/M_n = 1.13. IR: 3060, 3026, 2926, 2853, 1944, 1771, 1700, 1602, 1493, 1453, 1397, 1368, 1343, 1266, 1190, 1136, 1029, 968, 908, 758, 698. ^{1}H NMR: δ 0.80−1.00 (m, 3n H), 1.20−2.40 (m, 7n + 2m H), 2.60−3.60 (m, 5n H), 5.40−5.80 (d, 2n H) 6.30−7.25 (m, 5m H).

Poly(NMONI-*b*-S) (15). The product was recovered as a white, fluffy powder in 20% yield. GPC: M_n = 28 600, M_w/M_n = 1.21. IR: 3618, 3060, 3026, 2925, 2850, 1944, 1870, 1778, 1704, 1602, 1493, 1452, 1382, 1283, 1130, 1029, 968, 909, 758, 698. ^{1}H NMR: δ 1.20−2.30 (m. 2m H) 2.85−3.00 (s, 3n H), 3.20−3.45 (s, 2n H), 4.30−4.60 (m, nH), 4.70−5.00 (m, n H), 5.70−6.10 (m, 2n H) 6.30−7.25 (m, 5m H).

Poly(tBENI-*b*-tBA) (16). The product was recovered as a hard, white solid in 38% yield. GPC: M_n = 25 300, M_w/M_n = 1.10. IR: 2978, 2931, 1980, 1731, 1456, 1417, 1393, 1368, 1326, 1257, 1153, 846, 737, 701. ^{1}H NMR: δ 1.20−1.80 (m, 9n + 10.5m H), 1.80−2.00 (m, 0.5m H), 2.00−2.30 (m, n H + m H), 2.70−3.40 (m, 4n H), 4.05 (s, 2n H), 5.40−5.80 (d, 2n H).

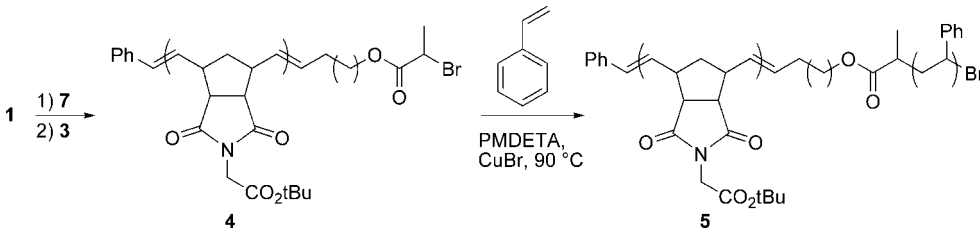
Poly(NBNI-*b*-tBA) (17). The product was recovered as a hard, white solid in 60% yield. GPC: M_n = 26 800, M_w/M_n = 1.07. IR: 2978, 2944, 2873, 1771, 1728, 1700, 1480, 1448, 1394, 1367, 1258, 1150, 1038, 846, 751. ^{1}H NMR: δ 0.80−1.00 (m, 3n H), 1.20−2.00 (m, 6n + 11m H), 1.95−2.40 (m, n H + m H), 2.60−3.60 (m, 5n H), 5.40−5.80 (d, 2n H).

Poly(NMONI-*b*-tBA) (18). The product was recovered as a hard, white solid in 43% yield. GPC: M_n = 28 000, M_w/M_n = 1.06. IR: 2978, 2932, 1728, 1447, 1393, 1368, 1257, 1149, 1034, 846, 752. ^{1}H NMR: δ 1.20−2.00 (m, 11m H), 2.10−2.40 (m, m H) 2.85−3.00 (s, 3n H), 3.20−3.45 (s, 2n H), 4.30−4.60 (m, nH), 4.70−5.00 (m, n H), 5.70−6.10 (m, 2n H).

Results and Discussion

Functionalized vinyl ethers were used to end-cap poly(norbornenes) in an example by Owen et al. using $(PCy_3)_2(Cl)_2RuCHPh$ as the metathesis catalyst.[28] Although their capping efficiencies were not 100%, we chose to reexamine this route using catalyst **1** in hopes that the more active catalyst would enable complete end-capping. To test this hypothesis, we prepared α-bromoester end-functionalized polymers using vinyl ether **3** to terminate the reaction. Vinyl ether **3** was synthesized by reduction of δ-valerolactone with DIBAL,

Scheme 2. ROMP and Chain Termination Using Vinyl Ether Followed by ATRP of Styrene



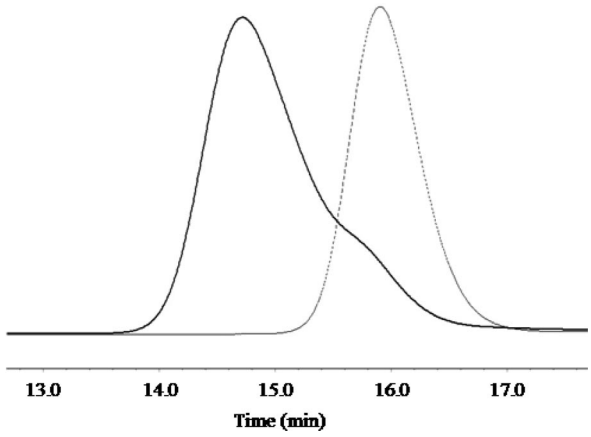
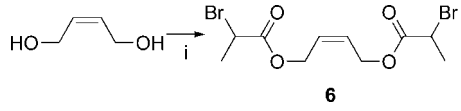


Figure 2. GPC traces of P(tBENI) homopolymer **4** (dashed line) and P(tBENI-*b*-S) block copolymer **5** (solid line).

Scheme 3. Preparation of Terminating Agent[a]



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[a] Reaction conditions: (i) 2-bromopropionyl bromide, THF, NEt_3, 0 °C.

followed by transformation of the aldehyde to vinyl ether **2** by a Wittig reaction with a phosphonium ylide as previously reported.[29] Addition of 2-bromopropionyl bromide afforded vinyl ether **3** (Scheme 1).

ROMP was carried out by reacting ruthenium initiator **1** with *tert*-butyl ester norbornene imide monomer (tBENI) **7** (Figure 1) in CH_2Cl_2 until complete (3 min), followed by addition of 10 equiv of vinyl ether **3** (Scheme 2). The reaction mixture was stirred for an additional 24 h, and then the product, **4**, was precipitated and recovered by filtration. GPC analysis showed a monomodal peak with M_n as measured by GPC very close to the theoretical value and PDI = 1.02.

Table 1. Polymer Characterization Data for Monotelechelic Poly(oxa)norbornenes and ROMP−ATRP Block Copolymers

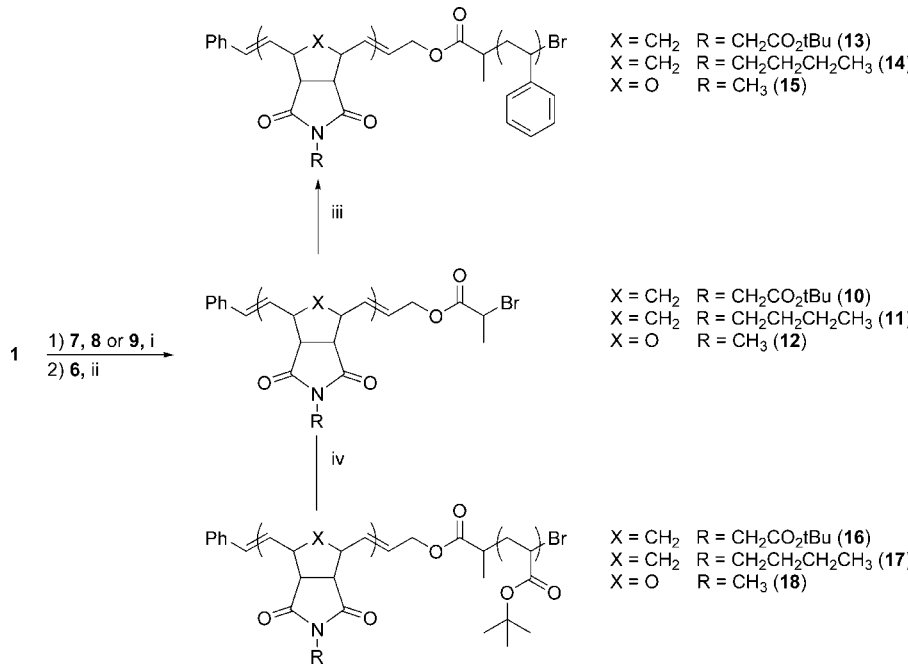
polymer	structure	M_n(theo)[a]	M_n(NMR)	M_n(GPC)[b]	PDI
10	P(tBENI)	7 460	10 200	8 520	1.03
11	P(NBNI)	6 820	5 230	7 190	1.01
12	P(NMONI)	4 790	4 490	4 840	1.06
13	P(tBENI-*b*-S)	19 800	18 800	19 100	1.07
14	P(NBNI-*b*-S)	29 100	27 000	25 800	1.13
15	P(NMONI-*b*-S)	28 400	40 300	28 600	1.21
16	P(tBENI-*b*-tBA)	27 500	24 900	25 300	1.10
17	P(NBNI-*b*-tBA)	27 500	24 300	26 800	1.07
18	P(NMONI-*b*-tBA)	28 800	32 100	28 000	1.06

[a] Determined by monomer catalyst ratio (**11**−**13**) or percent monomer conversion as determined by NMR (**14**−**19**). [b] Measured in THF eluent using RI and MALLS detectors.

To determine the extent of end-capping, this product was used to initiate the ATRP of styrene using a CuBr/PMDETA catalyst system, yielding block copolymer product **5**. As seen in the low molecular weight shoulder in the GPC trace in Figure 2, a significant amount of unreacted homopolymer remains, further corroborating the results found by Owen et al.[28] We attribute the incomplete end-capping to an initial undesirable cross-metathesis reaction between the living polymer chain end and **3** that puts the vinyl ether instead of the α-bromoester onto to polymer chain. Further cross-metathesis between the vinyl ether-functionalized polymer and the α-bromoester-functionalized ruthenium complex is expected to be slow, limiting the ability of this strategy to afford the desired product before catalyst death occurs. With this knowledge in hand, we decided to abandon the functionalized vinyl ether route and pursue a new strategy.

When a cyclic olefin is sterically unencumbered enough to undergo secondary metathesis, internal *cis*-olefins are widely used as CTAs to afford telechelic polymers.[5,17,30,31] In polymers with repeat units that are too bulky to undergo secondary metathesis, a *cis*-olefin can act instead as a terminating agent

Scheme 4. Synthesis of Monotelechelic Poly(oxa)norbornenes and ROMP−ATRP Block Copolymers[a]



[a] Reaction conditions: (i) 0.3 M in CH_2Cl_2, 3 min; (ii) 8 equiv in CH_2Cl_2, 3 h; (iii) styrene, CuBr, PMDETA, 90 °C; (iv) tBA, DMF, CuBr, PMDETA, 70 °C.

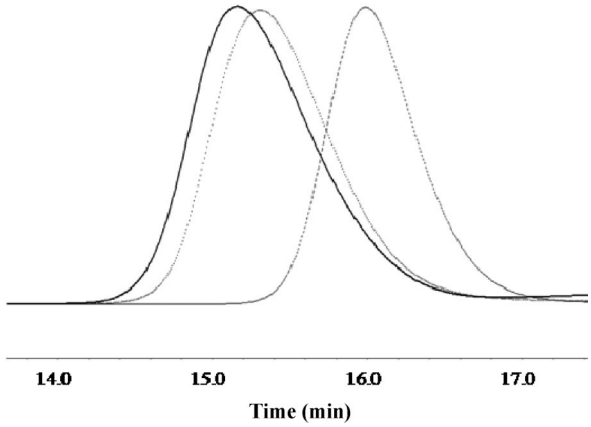


Figure 3. GPC traces of P(tBENI) homopolymer **10** (dashed line), P(tBENI-*b*-S) block copolymer **13** (dotted line), and P(tBENI-*b*-tBA) block copolymer **16** (solid line).

(TA).[8] In this case, reaction with only the living polymer chain end affords the monotelechelic polymer and the free ruthenium alkylidene in a ring-opening cross-metathesis reaction. Any further reaction between the functionalized chain end and the ruthenium alkylidene is redundant due to the symmetrical nature of the TA. The other chain end containing the phenyl group derived from the initiator is expected to be too deactivated to participate in further metathesis reactions.

We prepared TA *cis*-2-butene-1,4-diyl bis(2-bromopropanoate) (**6**) in one step by addition of 2 equiv of 2-bromopropionyl bromide to commercially available *cis*-2-butene-1,4-diol (Scheme 3). Poly(oxa)norbornenes were prepared from tBENI, *N*-butyl norborneneimide (NBNI), and *N*-methyl oxanorborneneimide (NMONI) (**7**−**9**) using the same reaction conditions described above (Scheme 4). 8 equiv of TA **6** was added to the reaction mixture after 3 min, and the reaction was quenched by precipitation after 3 h. These polymers (**10**−**12**) were found to be narrowly dispersed, and molecular weights were in agreement with theoretical values (Table 1).

Next, a PS block was added to each of polymers **7**−**9** using a CuBr/PMDETA catalyst system in neat styrene at 90 °C to produce polymers **13**−**15**. Figure 3 shows the GPC traces of homopolymer **10** and block copolymer **13**. Unlike block copolymer **5**, a monomodal peak was observed. This proves that complete end-functionalization of the polymer has been achieved and that full initiation of the α-bromoester has occurred. Complete disappearance of the homopolymer peak was observed for polymers **14** and **15** as well. Polymer polydispersities remained low, and the molecular weights were close to theoretical values based on monomer conversion. This confirms that only the living chain end has reacted, leaving the phenyl group derived from initiator **1** untouched. Interestingly, when THF was used as the solvent for the ROMP reaction, P(tBENI-*b*-S) block copolymers showed a low molecular weight shoulder with the same peak retention time as the homopolymer, indicating that P(tBENI) end-functionalization was incomplete. This observation is in agreement with previous reports demonstrating that the rate of secondary metathesis during ROMP using ruthenium catalysts is slower in THF than in CH_2Cl_2.[32,33]

To explore the utility of this reaction with other α-olefins, *tert*-butyl acrylate (tBA) was added to each of the poly(oxa)norbornenes homopolymers using the same CuBr/PMDETA catalyst system in DMF at 70 °C to produce polymers **16**−**18**. GPC analysis of these polymers also showed monomodal peaks, and molecular weights measured by NMR and GPC matched the theoretical values. These polymers demonstrate the generality of this approach, and it is expected that many other acrylates and styrenes can be used to make multiblock copolymers using this method.

Conclusions

In summary, we have demonstrated a method for making monotelechelic poly(oxa)norbornenes containing α-bromoesters as ATRP initiators using a symmetrical *cis*-olefin TA. Both PS and PtBA blocks were grown from the chain ends, and a complete shift in the GPC peak was observed. This proves that complete end-functionalization and initiation of ATRP from the poly(oxa)norbornenes occurred. Many more types of multiblock copolymers using this strategy can be envisioned, including diblocks and triblocks of both the ROMP and ATRP portions. Additionally, any strained cyclic olefin that can undergo living ROMP could be used, so the possible types of multiblock copolymers are not limited to poly(oxa)norbornenes. We also expect this method to be general for the preparation of monotelechelic living ROMP polymers, allowing for the incorporation of virtually any functionality to be placed onto the polymer chain end, as long as it is compatible with the ruthenium catalyst and an appropriate TA can be synthesized. Future work includes the synthesis of novel tri- and tetrablock copolymers and end-functionalized polymers to be used in biological applications.

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