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Investigation of Organoboronates in Metathesis Polymerization

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ABSTRACT: Molybdenum and ruthenium catalysis has been used to synthesize main-chain boronate ADMET polymers under bulk conditions; however, the long-term stability and solution characterization of these polymers are dramatically influenced by ligand-exchange reactions within the boronate moiety. Placing the boronate pendent to the main chain obviates this phenomenon as demonstrated in the ROMP polymerization of norbornene monomers with boronates both in *exo* and *endo* positions. The stereochemistry of the monomer influences both the rate of polymerization and the microstructure of the resulting polymer; these effects are more pronounced in the case of ruthenium catalysis. The thermal stability of these polymers also is dependent upon monomer stereochemistry.

Introduction

Organoboronates have commonly been used as protecting groups in organic synthesis[1] and as coupling reagents in Suzuki coupling reactions,[2] but their use in olefin metathesis polymerization has not been pursued to a large extent. The majority of boronate-containing polymers reported in the literature involve either boronate or boronic acid derivatives positioned as a pendent group along the polymer backbone. These macromolecules exhibit such properties as controlled release[3] and T-cell stimulation in mice.[4] The interesting macromolecular properties available due to these functionalities, as well as the paucity of data concerning their syntheses, has prompted our investigation of the use of the boronate moiety in metathesis polymerization.

To date, only two investigations of molecules containing the boron atom in olefin metathesis have been performed. Chung and co-workers synthesized telechelomers using difunctional trialkylborane chain-transfer reagents in the ring-opening polymerization of 1,7-cyclooctadiene.[5] The resulting α,ω-bis(trialkylborane)polybutadiene telechelic oligomers were then transformed under relatively mild reaction conditions into hydroxy- or iodo-terminated polybutadiene. Chung extended this interesting methodology to ring-opening metathesis polymerization by producing 9-BBN-substituted polynorbornenes with both well-defined and classical catalytic systems,[6,7] showing the versatility that boranes provide in macromolecular substitution reactions. More recently, Renaud and Ouellet investigated the use of alkenylboronates in ring-closing metathesis to produce cyclic boronate intermediates.[8] Both of these research groups undeniably demonstrated the compatibility of boranes with metathesis catalysts.

The successful application of boron-containing functionalities in metathesis polymerization and ring closure has led us to investigate the possibility of producing organoboronate functionalized macromolecules via similar routes. A series of symmetrical α,ω-dienes, containing both methyl- and phenyl-substituted boronate functionalities, were synthesized and examined in acyclic diene metathesis (ADMET) polymerization as an extension of our previous work.[9] Boronate chemistry has been investigated further by the preparation of several norbornene monomers containing methyl- and phenyl-substituted boronates and the synthesis of unsaturated polymers via ring-opening metathesis polymerization (ROMP). In both cases, the well-defined alkylidene catalysts $RuCl_2(CHPh)(PCy_3)_2$ (**1**) and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OC(CF_3)_2CH_3)_2$ (**2**) were employed; the reaction schemes are shown in Figure 1.

Experimental Section

Materials and Instrumentation. $RuCl_2(CHPh)(PCy_3)_2$ (**1**),[10] $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OC(CF_3)_2CH_3)_2$ (**2**),[11] *cis-exo*-5-norbornene-2,3-diol (**5**),[12] and *cis-endo*-5-norbornene-2,3-diol (**8**)[13] were synthesized according to the published procedures. All alkenols and boronic acids used were purchased from either Aldrich Chemical Co. or Acros Organics and used as received. All solvents were distilled from sodium

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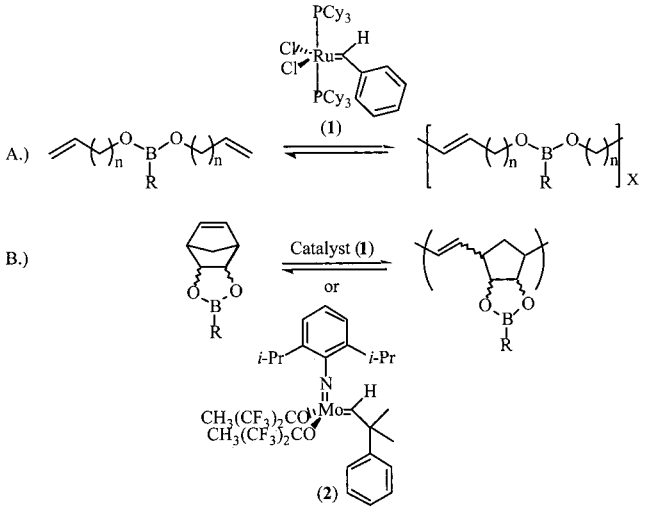

Figure 1. Proposed syntheses of polymers containing the boronate functionality: (A) acyclic diene metathesis (ADMET) polymerization; (B) ring-opening metathesis polymerization (ROMP).

benzophenone ketal or CaH_2, degassed, and stored over 4 Å molecular sieves under an atmosphere of argon before use.

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were performed on either a Varian VXR 300 MHz or a Gemini 300 MHz instrument in $CDCl_3$ containing 0.05% TMS as an internal standard unless stated otherwise. ^{11}B NMR (96 MHz) was performed on a Varian VXR 300 MHz instrument using BF_3:OEt_2 in $CDCl_3$ (50% v/v) as an external standard. Elemental analysis was performed by Atlantic Microlabs, Inc., Norcross, GA. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were not corrected. Low-resolution GC/MS was performed on a Finnigan MAT 95Q instrument.

Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with a Perkin-Elmer LC-25 refractive index detector and an ABI Spectroflow 757 UV detector. Measurements were taken using THF as the eluent at a flow rate of 1.0 mL/min through three Phenomenex Phenogel columns connected in series (50 000, 5000, and 500 Å). The instrument was calibrated with polystyrene standards (M_p = 580, 1900, 7700, 12 000, 30 000, 48 900, 59 000, 79 000, 139 400, and 650 000 g/mol). Vapor pressure osmometry was performed in toluene at 50 °C on a Wescan Instruments model 233A molecular weight apparatus. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 thermal analysis system interfaced to a TAC 7/DX thermal analysis controller. Measurements were taken from 30 to 800 °C under an inert atmosphere of nitrogen and repeated with a fresh sample in air.

Monomer Synthesis and Polymerizations. *Synthesis of Bis(4-pentenyl)phenylboronate,* ***3a***. A 500 mL round-bottom flask containing a magnetic stir bar and 230 mL of benzene was charged with 14.16 g (0.116 mol) of phenylboronic acid and 20.00 g (0.232 mol) of 4-penten-1-ol. A Dean−Stark trap filled with benzene was attached followed by a reflux condenser and a drying tube filled with Dri-Rite. The reaction mixture was refluxed for 15 h before slowly removing the benzene by simple distillation, ensuring the removal of the remaining benzene/water azeotrope. The remaining liquid was dried over CaH_2 for 48 h under vacuum before being fractionally distilled and collection of the fraction boiling at 130−131 °C (5 mmHg). Yield = 25.74 g (86%). ^{1}H NMR: δ (ppm) = 7.2−7.6 (m, 5H); 5.8 (m, 2H); 5.0 (m, 4H); 4.0 (t, 4H); 2.1 (q, 4H); 1.7 (m, 8H). ^{13}C NMR: δ (ppm) = 138.0, 133.3, 129.5, 127.6, 114.7, 63.8, 30.9, 30.0. ^{11}B NMR: δ = 28.6. Elemental analysis calculated for $C_{16}H_{23}BO_2$. Calculated: H (8.91%); C (74.42%). Found: H (8.99%); C (74.36%). GC/MS: m/e = 259 ($M^+ + 1$).

Synthesis of Bis(4-pentenyl)methylboronate, ***3b***. Synthesized as for **3a** from 7.11 g (8.27×10^{-2} mol) of 4-penten-1-ol and 2.48 g (4.13×10^{-2} mol) of methaneboronic acid yielding 7.24 g (89%) of **3b**. Bp = 59−61 °C. ^{1}H NMR: δ (ppm) = 5.8 (m, 2H); 5.0 (m, 4H); 3.8 (t, 4H); 2.1 (q, 4H); 2.6 (m, 4H); 0.2 (s, 3H). ^{13}C NMR: δ = 138.0, 114.5, 62.9, 30.7, 29.9. ^{11}B NMR: δ (ppm) = 31.4 ppm. Elemental analysis calculated for $C_{11}H_{21}BO_2$. Calculated: H (10.77%), C (67.69%). Found: H (10.77%), C (67.73%). GC/MS: m/e = 197 ($M^+ + 1$).

Synthesis of Bis(5-hexenyl)phenylboronate, ***4a***. Synthesized as for **3a** from 9.14 g (0.075 mol) of phenylboronic acid and 14.99 g (0.15 mol) of 5-hexen-1-ol, yielding 15.85 g (74%) of **4a** boiling at 144−145 °C (2 mmHg). ^{1}H NMR: δ (ppm) = 7.2−7.6 (m, 5H); 5.8 (m, 2H); 4.9 (m, 4H); 4.0 (t, 4H); 2.1 (q, 4H); 1.4−1.6 (m, 8H). ^{13}C NMR: δ (ppm) = 138.6, 133.2, 129.4, 127.6, 114.4, 64.3, 33.4, 31.1, 25.1. ^{11}B NMR: δ (ppm) = 28.4. Elemental analysis calculated for $C_{18}H_{27}BO_2$. Calculated: H (9.51%); C (75.54%). Found: H (9.56%); C (75.62%). GC/MS: m/e = 287 ($M^+ + 1$).

Synthesis of Bis(5-hexenyl)methylboronate, ***4b***. Synthesized as for **3a** from 2.51 g (4.18×10^{-2} mol) of methaneboronic acid and 8.37 g (8.37×10^{-2} mol) of 5-hexen-1-ol yielding 8.69 g (93%) of **4b** boiling at 53−55°C. ^{1}H NMR: δ = 5.80 (m, 2H); 4.92−5.03 (m, 4H); 3.80 (t, 4H); 2.07 (m, 4H); 1.6−1.4 (m, 8H); 0.23 (s, 3H). ^{13}C NMR: δ = 138.6, 114.4, 63.5, 33.4, 31.0, 25.2. ^{11}B NMR: δ (ppm) = 31.4. Elemental analysis calculated for $C_{13}H_{25}BO_2$. Calculated: H (11.24%); C (69.66%). Found: H (11.00%); C (68.99%). GC/MS: m/e = 225 ($M^+ + 1$).

ADMET Polymerization of Bis(4-pentenyl)phenylboronate, ***3a****, Using Catalyst* ***1***. A 50 mL round-bottom flask equipped with a magnetic stir bar and a Kontes high-vacuum valve was charged with 996 mg (3.9×10^{-3} mol, 325 equiv) of bis(4-pentenyl)phenylboronate (**3a**) and 10 mg (1.2×10^{-5} mol, 1 equiv) of catalyst **1** in an argon-purged drybox. The flask was sealed, removed from the drybox, and placed on a high-vacuum Schlenk line where it was allowed to stir under full vacuum. The reaction mixture was stirred at room temperature for 16 h and then heated to 40 °C for 7 days. ^{1}H NMR: δ (ppm) = 8.1−7.6 (multiplet, C_6H_5−B=); 5.74 (s, br, −C*H*=C*H*−); 4.34 (multiplet); 4.08 (multiplet, −CH_2−O−); 2.6−2.26 (multiplet); 2.1−1.6 (multiplet). ^{13}C NMR: δ (ppm) = 138.4; 138.2; 134.8; 134.5; 134.1; 133.3; 130 (multiplet); 127.8; 127.6; 127.5; 114.9; 114.7; 114.5; 63.1 (multiplet); 32.4; 31.0 (multiplet); 30.1; 28.8; 23.5. ^{11}B NMR: δ (ppm) = 28.3. M_n (VPO) = 174 g/mol.

ADMET Polymerization of Bis(4-pentenyl)methylboronate, ***3b****, Using Catalyst* ***1.*** Polymerized as for **3a** from 999 mg (5.1×10^{-3} mol, 300 equiv) of **3b** and 14 mg (1.7×10^{-5}, 1 equiv) of catalyst **1**. ^{1}H NMR: δ (ppm) = 5.4 (s, br, −C*H*=C*H*−); 4.3 (multiplet); 3.8 (multiplet, −CH_2−O−); 3.6 (s, br); 2.2 (multiplet); 2.0 (s, br, −CH_2−CH=CH−); 1.6 (m, −CH_2−CH_2−O−); 1.4 (multiplet); 0.23 (s, br, CH_3−B=); 0.2 (s, br, CH_3−B=). ^{13}C NMR: δ (ppm) = 132.4; 130.0 (multiplet); 126.4; 63.2 (multiplet); 36.0; 35.0; 32.4; 31.4 (multiplet); 28.8; 25.6; 23.4. ^{11}B NMR: δ (ppm) = 31.8.

ADMET Polymerization of Bis(5-hexenyl)phenylboronate, ***4a****, Using Catalyst* ***1.*** Polymerized as for **3a** from 510 mg (1.8×10^{-3} mol, 300 equiv) of **4a** and 5 mg (6×10^{-6} mol, 1 equiv) of catalyst **1**. ^{1}H NMR: δ (ppm) = 7.8 (doublet); 7.7 (doublet); 7.6 (multiplet);. 7.3 (multiplet); 5.4 (s, br, −C*H*=C*H*−); 4.0 (multiplet, −CH_2−O−); 3.8 (multiplet); 3.5 (s, br); 2.0 (s, br); 1.61 (multiplet); 1.4 (multiplet). ^{13}C NMR: δ (ppm) = 134.3−127.4 (multiplet); 64.2−62.4 (multiplet); 32.3−30.6 (multiplet); 28.6; 26.7; 25.6. ^{11}B NMR: δ (ppm) = 28.2.

ADMET Polymerization of Bis(5-hexenyl)methylboronate, ***4b****, Using Catalyst* ***1***. Polymerized as for **3a** from 500 mg (2.23×10^{-3} mol, 301 equiv) of **4b** and 6 mg (7.4×10^{-6} mol, 1 equiv) of catalyst (**1**). ^{1}H NMR: δ (ppm) = 5.3 (s, br, −C*H*=C*H*−); 3.7 (s, br, −CH_2−O−); 3.5 (s, br); 1.9 (s, br); 1.4 (s, br); 1.3 (s, br); 0.1 (s, br, CH_3−B=). ^{13}C NMR: δ (ppm) = 130.0 (−C*H*=C*H*−, *trans*); 129.5 (−C*H*=C*H*−, *cis*); 63.3 (−CH_2−O−); 62.0; 32.0; 30.8; 26.7; 25.7; 25.6. ^{11}B NMR: δ (ppm) = 32.1.

Synthesis of cis-exo-5-Norbornene-2,3-(phenyl)boronate, ***6***. Monomer synthesis required a two-step preparation. The synthesis of the precursor *cis-exo*-5-norbornene-2,3-diol (**5**) was performed using a reported procedure, obtaining a yield of 15% (Figure 7).[12] Recrystallization from hexane, as reported, yields impure product which can be avoided by using cyclohexane

as an alternative. *cis-exo*-5-Norbornene-2,3-diol (**5**) (1.02 g, 4.81 × 10^{-3} mol), phenylboronic acid (973 mg, 7.98 × 10^{-3} mol), and 50 mL of benzene were charged to a 100 mL round-bottom flask equipped with a magnetic stir bar. A Dean−Stark trap filled with benzene was attached followed by a reflux condenser and a drying tube filled with Dri-Rite. The reaction mixture was refluxed for 3 h. After cooling to ambient temperature, the remaining solvent was slowly distilled away, leaving a solid which was recrystallized from hexanes at −30 °C and further purified by a slow sublimation yielding 1.96 g (96%) of product. Mp = 42−44 °C. Elemental analysis calculated for $C_{13}H_{13}BO_2$. Calculated: H (6.18%); C (73.63%). Found: H (6.25%); C (73.64%). ^{11}B NMR: δ (ppm) = 37.7 ppm. ^{1}H NMR: δ (ppm) = 7.3−7.7 (m, 5H); 6.0 (d (fine splitting), 2H); 4.5 (d (fine splitting), 2H); 2.9 (s, 2H); 1.7 (m, 2H). ^{13}C NMR: δ (ppm) = 136.4, 134.8, 131.4, 127.7, 80.6, 46.4, 41.4. GC/MS (M^+): *m/e* = 212.

Synthesis of cis-exo-5-Norbornene-2,3-(methyl)boronate, ***7***. Synthesized as for **6** from methaneboronic acid (1.00 g, 7.9 mmol) and *cis-exo*-5-norbornene-2,3-diol (**5**) (474 mg, 7.9 mmol) yielding 820 mg (69%) of **7** boiling at 46−47 °C (24 mmHg). Elemental analysis calculated for $C_8H_{11}BO_2$. Calculated: H (7.39%), C (64.07%). Found: H (7.30%), C (63.83%). ^{1}H NMR: δ (ppm) = 5.9 (t (fine splitting), 2H); 4.2 (s, 2H); 2.8 (t (fine splitting), 2H); 1.6 (t (fine splitting), 2H); 0.2 (s, 3H). ^{13}C NMR: δ (ppm) = 136, 80.7, 46.0, 41.1. ^{11}B NMR: δ (ppm) = 40.1 ppm. GC/MS ($M^+ + 1$): *m/e* = 151.

Synthesis of cis-endo-5-Norbornene-2,3-(phenyl)boronate, ***9***. The synthesis of the precursor *cis-endo*-5-norbornene-2,3-diol (**8**) was accomplished using a combination of two published procedures, shown in Figure 7.[13] Heating freshly cracked dicyclopentadiene, vinylene carbonate, and toluene at 220 °C in a sealed tube for 6 h provides the *endo* Diels−Alder adduct in a moderate 65% yield. Sublimation of the crude product followed by saponification with 5% NaOH(aq) solution for 3 h yields *cis-endo*-5-norbornene-2,3-diol (**8**). Recrystallization from cyclohexane gives long, fibrous needles of pure product in 77% yield. The boronate **9** was synthesized as for **6** from 1.02 g (8.1 mmol) of *cis-endo*-5-norbornene-2,3-diol (**8**) and 988 mg (8.1 mmol) of phenylboronic acid yielding 1.35 g (78%) of **9** melting at 67−69 °C after recrystallization from pentane (−30 °C). ^{1}H NMR: δ (ppm) = 7.7−7.3 (m, 5H); 6.1 (m, 2H); 4.9 (m, 2H); 3.2 (s, 2H); 1.6 (m, 1H); 1.2 (m, 1H). ^{13}C NMR: δ (ppm) = 134.5, 131.2, 127.7, 81.4, 46.4, 42.8. ^{11}B NMR: δ (ppm) = 36.0. Elemental analysis calculated for $C_8H_{11}BO_2$: Calculated: H (6.18%); C (73.63%). Found: H (6.16%); C (73.40%). GC/MS (M^+): *m/e* = 212.

ROMP Polymerization of cis-exo-5-Norbornene-2,3-(methyl)-boronate, ***7****, Using Catalyst* ***1***. In an argon-purged drybox, 1.02 g (6.8 × 10^{-3} mol, 310 equiv) of *cis-exo*-5-norbornene-2,3-(methyl)boronate (**7**) was weighed into a 40 mL glass vial containing a magnetic stir bar and diluted with 19 mL of toluene. In a separate glass vial was weighed 18 mg (2.19 × 10^{-5} mol, 1 equiv) of catalyst **1** and dissolved in 1 mL of toluene. The catalyst solution was added to the agitated monomer solution rapidly in one portion. An exothermic reaction ensued, and the reaction was stirred vigorously for 30 min. After this period, the reaction mixture was diluted with an additional 10 mL of toluene containing 0.1 mL of ethyl vinyl ether and a crystal of 2,6-*tert*-butylcatechol. The polymer was precipitated by pouring into 250 mL of cold pentane, filtered, and dried in vacuo, yielding 981 mg (96%) of product **10**. ^{1}H NMR: δ (ppm) = 5.6 (−C*H*═C*H*−, *trans*); 5.4 (−C*H*═C*H*−, *cis*); 4.4 (−C*H*-O−); 2.8 (−C*H*−CH= , allylic *cis*); 2.5 (−C*H*−CH= , allylic *trans*); 1.9 (═CH−CH−C*H*−CH−CH= , *endo*); 1.2 (═CH−CH−C*H*−CH−CH= , *exo*); 0.3 (B−CH_3). ^{13}C NMR: δ (ppm) = 132.1; 131.3; 131.1; 86.4; 85.8; 50.1; 46.0; 36.2; 35.4. ^{11}B NMR: δ (ppm) = 35.6. Elemental analysis. Calculated: H (7.39%); C (64.07%). Found: H (7.44%); C (63.98%). M_n (GPC) = 115 000 g/mol. M_w/M_n (GPC) = 1.8. TGA (onset) = 406 °C (air).

(ROMP) Polymerization of cis-exo-5-Norbornene-2,3-(methyl)boronate, ***7****, Using Catalyst* ***2***. In an argon-purged drybox, 517 mg (3.45 × 10^{-3} mol, 246 equiv) of *cis-exo*-5-norbornene-2,3-(methyl)boronate (**7**) was placed into a 40 mL glass vial containing a magnetic stir bar and diluted with 9 mL of toluene. In a separate glass vial was weighed 11 mg (1.4 × 10^{-5} mol, 1 equiv) of catalyst (**2**) and dissolved in 1 mL of toluene. The catalyst solution was charged in one portion to the vigorously stirring monomer solution, and heat was evolved. The reaction was terminated after 10 min by precipitating the polymer solution directly into 200 mL of cold pentane, yielding 485 mg (94%) of polymer **10**. ^{1}H NMR: δ (ppm) = 5.6 (−C*H*═C*H*−, *trans*); 5.4 (−C*H*═C*H*−, *cis*); 4.4 (−C*H*−O−); 2.9 (−C*H*−CH= , allylic *cis*); 2.5 (−C*H*−CH= , allylic *trans*); 1.9 (═CH−CH−C*H*−CH−CH= , *endo*); 1.2 (═CH−CH−C*H*−CH−CH= , *exo*); 0.3 (B−CH_3). ^{13}C NMR: δ (ppm) = 132.4; 131.1; 87.1; 85.8; 50.3; 46.2; 37.1; 36.2; 35.8. ^{11}B NMR: δ (ppm) = 35.6. Elemental analysis. Calculated: H (7.39%); C (64.07%). Found: H (7.49%); C (63.45%). M_n (GPC) = 181 000 g/mol. M_w/M_n (GPC) = 3.6. TGA (onset) = 396 °C (air).

ROMP Polymerization of cis-exo-5-Norbornene-2,3-(phenyl)-boronate, ***6****, Using Catalyst* ***1*****.** In an argon-purged drybox, 505 mg (2.38 × 10^{-3} mol, 300 equiv) of *cis-exo*-5-norbornene-2,3-(phenyl)boronate (**6**) was placed into a 40 mL glass vial containing a magnetic stir bar and diluted with 9 mL of toluene. In a separate glass vial was weighed 7 mg (7.94 × 10^{-6} mol, 1 equiv) of catalyst **1** and dissolved in 1 mL of toluene. The reaction was allowed to stir for 30 min and then diluted with 10 mL of toluene containing 0.1 mL of ethyl vinyl ether and a crystal of 2,6-*tert*-butylcatechol. Polymer **11** was then isolated in 95% yield (480 mg) after precipitation from cold pentane and drying to constant weight in a vacuum oven. ^{1}H NMR: δ (ppm) = 7.9−7.2 (B−C$_6H_5$); 5.8 (−C*H*═C*H*−, *trans*); 5.6 (−C*H*═C*H*−, *cis*); 4.6 (−C*H*−O−); 3.1 (−C*H*−CH−, allylic *cis*); 2.7 (−C*H*−CH= , allylic *trans*); 2.0 (═CH−CH−C*H*−CH−CH= , *endo*); 1.4 (═CH−CH−C*H*−CH−CH= *exo*). ^{13}C NMR: δ (ppm) = 134.9; 132.5; 131.4; 127.8; 87.4; 86.5; 50.2; 46.2; 36.2; 35.4. Elemental analysis. Calculated: H (6.18%); C (73.63%). Found: H (6.22%); C (73.43%). M_n (GPC) = 137 000 g/mol. M_w/M_n (GPC) = 1.5. TGA (onset) = 279 °C (air).

ROMP Polymerization of cis-exo-5-Norbornene-2,3-(phenyl)-boronate, ***6****, Using Catalyst* ***2*****.** In an argon-purged drybox, 512 mg (2.41 × 10^{-3} mol, 307 equiv) of *cis-exo*-5-norbornene-2,3-(phenyl)boronate (**6**) was added into a 40 mL glass vial containing a magnetic stir bar. The monomer was diluted with 19 mL of toluene and was placed on a stir plate to stir. A 6 mg (7.84 × 10^{-6} mol, 1 equiv) sample of catalyst **2** was placed into a separate glass vial, and 1 mL of toluene was added. After catalyst addition, heat was evolved immediately, and the reaction was allowed to stir for 10 min. The solution was removed from the drybox and precipitated directly into 150 mL of pentane yielding 462 mg (90%) of polymer **11**. ^{1}H NMR: δ (ppm) = 7.8−7.0 (B−C$_6H_5$); 5.7 (−C*H*═C*H*−, *trans*); 5.5 (−C*H*═C*H*−, *cis*); 4.7 (−C*H*-O−); 3.0 (−C*H*-CH= , allylic *cis*); 2.6 (−C*H*−CH= , allylic *trans*); 1.9 (═CH−CH−C*H*−CH−CH= , *endo*); 1.2 (═CH−CH−C*H*−CH−CH= , *exo*) ^{13}C NMR: δ (ppm) = 134.9; 132.5; 131.1; 127.6; 87.8; 86.5; 50.3; 46.2; 36.9. Elemental analysis. Calculated: H (6.18%); C (73.63%). Found: H (6.13%); C (73.05%). M_n (GPC) = 150 000 g/mol. M_w/M_n (GPC) = 2.4. TGA (onset) = 292 °C (air).

ROMP Polymerization of cis-endo-5-Norbornene-2,3-(phenyl)boronate, ***9****, Using Catalyst* ***1*****.** In an argon-purged drybox, 510 mg (2.4 × 10^{-3} mol, 329 equiv) of *cis-endo*-5-norbornene-2,3-(phenyl)boronate (**9**) was weighed into a 40 mL glass vial containing a magnetic stir bar and then diluted with 19 mL of toluene. A 6 mg (7.30 × 10^{-6} mol, 1 equiv) sample of catalyst **1** was weighed into a separate vial and dissolved in 1 mL of toluene. After catalyst addition and stirring for 24 h, a viscous solution resulted, and the solution was diluted further with 10 mL of toluene containing 0.1 mL of ethyl vinyl ether and a crystal of 2,6-*tert*-butylcatechol. The polymer was then precipitated from the toluene solution into 300 mL of vigorously stirring pentane yielding 215 mg (42%) of polymer **12**. ^{1}H NMR: δ (ppm) = 7.8−7.1 (B−C$_6H_5$); 5.8 (−C*H*═C*H*−, *trans*); 4.9 (−C*H*−O−); 2.8 (−C*H*−CH= , allylic *trans*); 2.6 (═CH−CH−C*H*−CH−CH= , *endo*); 2.3 (s, unknown); 1.6 (═CH−CH−C*H*−CH−CH= , *exo*) ^{13}C NMR: δ (ppm) = 137.8; 134.9; 131.3;

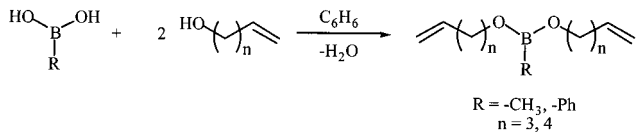

Figure 2. Synthesis of bis(alkenyl)boronates.

129.4; 129.0; 128.2; 127.7; 125.2; 84.7; 48.3; 43.3; 34.6; 21.4. Elemental analysis calculated for $C_{13}H_{13}BO_2$. Calculated: H (6.18%); C (73.63%). Found: H (5.75%); C (67.24%). M_n (GPC) = 51 000 g/mol. M_w/M_n (GPC) = 3.8. TGA (10% weight loss) = 276 °C (air).

*ROMP Polymerization of cis-endo-5-Norbornene-2,3-(phenyl)boronate, **9**, Using Catalyst **2***. In an argon-purged drybox, 296 mg (1.40×10^{-3} mol, 268 equiv) of *cis-endo*-5-norbornene-2,3-(phenyl)boronate (**9**) was weighed into a 40 mL glass vial containing a magnetic stir bar and diluted with 9 mL of toluene. In a separated vial was weighed 4 mg (5.23×10^{-6} mol, 1 equiv) of catalyst **2**, which was then dissolved in 1 mL of toluene. After catalyst addition, evolution of heat occurred, and the reaction mixture was stirred for 10 min. The vial was taken from the drybox and precipitated directly into 150 mL of stirring pentane, yielding 280 mg (95%) of polymer **12**. ^{1}H NMR: δ (ppm) = 7.8−7.4 (B−C_6H_5); 5.8 (−C*H*=C*H*−, *trans*); 4.9 (−C*H*−O−); 2.8 (−C*H*−CH= , allylic *trans*); 2.6 (=CH−CH−C*H*−CH−CH= , *endo*); 1.6 (=CH−CH−C*H*−CH−CH= , *exo*) ^{13}C NMR: δ (ppm) = 135.0 131.4; 129.4; 128.7; 127.8; 84.6; 48.2; 43.5; 35.2. Elemental analysis calculated for $C_{13}H_{13}BO_2$. Calculated: H (6.18%); C (73.63%). Found: H (6.23%); C (73.64%). M_n (GPC) = 115 000 g/mol. M_w/M_n (GPC) = 2.0. TGA (onset) = 300 °C (air). Note: in the cases of the ROMP polymerization of monomer **9**, insufficient solubility of the polymer prevented an adequate ^{11}B NMR determination to be made.

Results and Discussion

Acyclic Diene Metathesis of Dienes Containing the Boronate Moiety. The synthesis of boronate-containing ADMET monomers is relatively trivial, where a route analogous to the synthesis of boronate protected diols gives good yields of four pure bis-(alkenyl)boronate diene monomers, **3a**, **3b**, **4a**, and **4b**. The syntheses were accomplished by azeotropically distilling a stoichiometric amount of alkenol with either benzeneboronic acid or methaneboronic acid (Figure 2). Elemental analyses and a single resonance peak in the ^{11}B NMR spectra of the products indicate high monomer purity after only one distillation.

Previously, it has been shown that symmetrical dienes containing oxygen heteroatoms such as ethers,[14] ketones,[15] esters,[16] and carbonates,[17] are compatible with well-defined metathesis catalysts in ADMET polymerization. Furthermore, the successful ADMET polymerization of symmetrical dienylacetal[18] derivatives of benzaldehyde lends some precedence to the polymerization of boronates. The presence of two oxygen atoms, as in the case with acetals, within the boronate functionality does not interfere significantly with the ADMET polymerization mechanism. In fact, the Lewis acidic boron atom withdraws electron density away from its oxygen neighbors via $\pi-\pi$ O−B back-bonding, and this should, in effect, decrease the tendency of the oxygen atoms to coordinate to the metal center, a well-known deactivating mechanism of metathesis catalysts.

The evolution of ethylene ensues immediately upon exposure of boronate diene monomers **3a, 3b, 4a**, and **4b** to Grubbs' ruthenium catalyst **1** under high vacuum, and significant viscosity increases are apparent over a 24 h period. These experimental observations are normal for ADMET conversions of monomer to high polymer; for example, in the case of monomer **4b** the ^{13}C NMR spectra of monomer and subsequent polymer (Figure 3) illustrate that clean metathesis has occurred. Signals for both *trans* and *cis* internal olefins appear at 130 and 129.5 ppm, respectively, where the integration of the internal olefin signals displays a 70:30 ratio of *trans:cis* olefin linkages within the product's structure, also typical for ADMET polymerization.

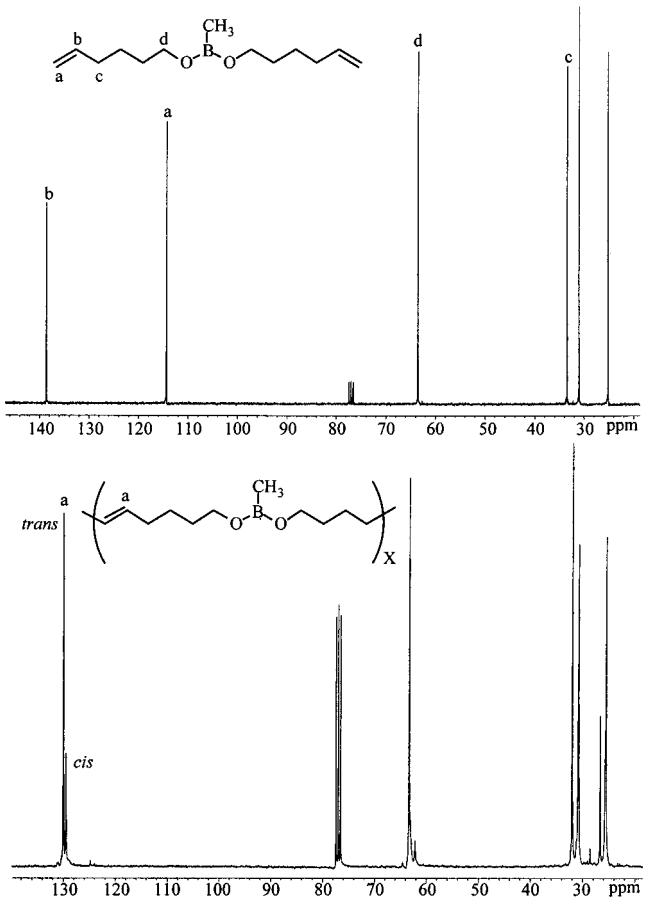

Figure 3. Quantitative ^{13}C NMR spectra of monomer (**4b**) and the product of the reaction with catalyst (**1**).

While there is no question that all four ADMET monomers are metathesis active, ligand-exchange reactions among the boronate functional groups can preclude isolation of these polymers. Bulk polymerization conditions favor polymer formation, whereas solution polymerization conditions—particularly in the case of the boronate functionality—favor ring formation and ligand exchange, and this phenomenon makes it difficult to characterize these polymers. For example, the ^{13}C NMR solution spectrum (Figure 4) for the product obtained from the reaction of monomer **3b** shows additional resonances beyond typical metathesis product spectra, suggesting that other chemistry may be involved. Changing the substituent on boron from methyl to a phenyl—monomers **3a** or **4a**—does not alter this situation, since the ^{11}B NMR spectra of the products illustrate that the boron environment does not significantly change. Any differences in product microstructure must be due to a rearrangement of the carbon skeleton.

While the solution spectra of several of the ADMET boronate polymerization products are similar to ADMET products generated using classical catalytic systems,[19] it appears that solution-induced depolymerization is

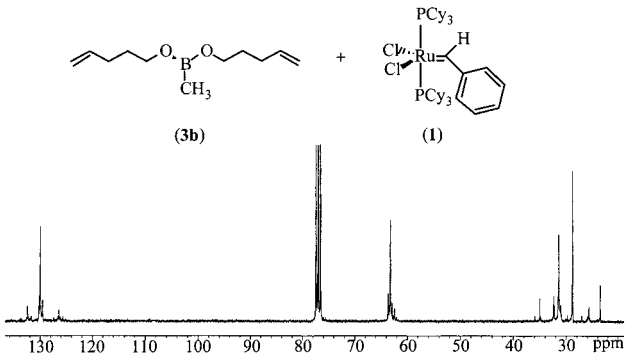

Figure 4. Quantitative ^{13}C NMR of the product obtained from the reaction of monomer (**3b**) with the ruthenium catalyst (**1**).

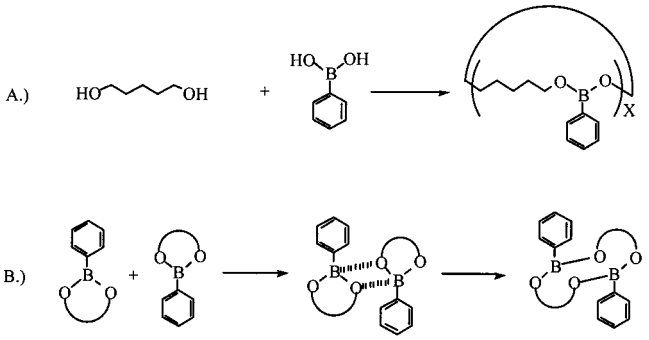

Figure 5. (A) Gerwarth's attempted step-condensation polymerization of 1,5-pentanediol with phenylboronic acid. (B) Intermolecular cyclization reactions between boronate functionalities.

responsible for the characterization anomalies observed.

In any event, the materials resulting immediately from bulk ADMET polymerization range from glassy hard plastics to highly viscous oils, observations which unequivocally indicate that oligomers and/or polymers can be formed. Standard workup conditions lead to depolymerization, most likely via ring formation, a result which is supported by the work of Gerwarth.[20] His research group attempted to polymerize phenylboronic acid with a series of long-chain diols (Figure 5A) via a conventional step-condensation polymerization. No high molecular weight polymers could be obtained; instead, an equilibrium mixture of cyclic materials was formed due to intermolecular and intramolecular ligand exchange reactions occurring between boronate moieties (Figure 5B). The same reaction—ligand exchange—appears to be happening in our case over time during ADMET bulk polymerization and upon solution workup of the polymerization products.

Since high-viscosity materials initially can be obtained after the ADMET polymerization of all four bis(alkenyl)boronate monomers, it is safe to assume that the ADMET metathesis reaction is substantially faster than ligand exchange (Figure 6); i.e., polymer can be formed at first. Eventually depolymerization via ligand exchange of the boronate moiety occurs, since these materials significantly decrease in viscosity over time. Further, simple dilution of these boronate polymers in a solvent accelerates the depolymerization mechanism—a result noted by Gerwarth as well.

ROMP of Boronate Derivatives of 5-Norbornene-2,3-diol. While slow ligand exchange of the boronate moiety in the main chain influences the viability of maintaining high molecular weight polymers, this should not be a problem when placing the boronate pendent to

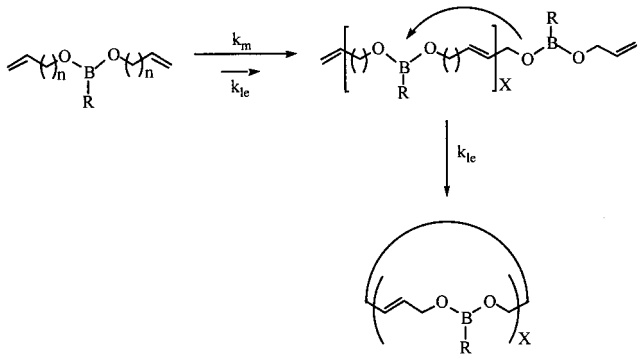

Figure 6. General representation of the competition between metathesis polymerization, designated k_m, and ligand exchange, k_{le}.

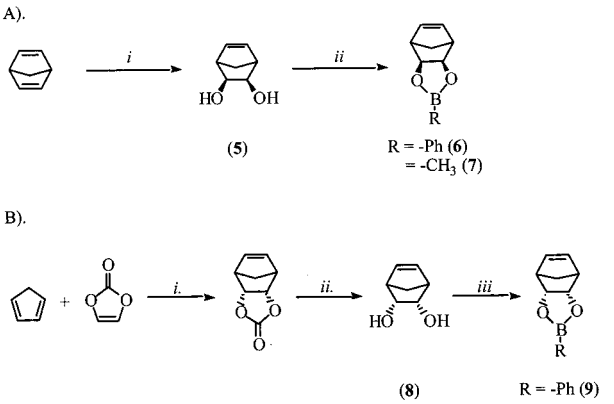

Figure 7. (A) Synthesis of *cis-exo*-5-norbornene-2,3-(phenyl)-boronate (**6**) and *cis-exo*-5-norbornene-2,3-(methyl)boronate (**7**): (i) $KMnO_4$, acetone, −78 °C; (ii) $C_6H_5B(OH)_2$ or $CH_3B(OH)_2$, benzene, reflux. (B) Synthesis of *cis-endo*-5-norbornene-2,3-(phenyl)boronate (**9**): (i) toluene, 220 °C, 6 h; (ii) 5% NaOH(aq), 3 h; (iii) $C_6H_5(OH)_2$, benzene, reflux.

Table 1. Yields of ROMP Polymers 10−12

polymer	catalyst	R	M_n[a] (g/mol)	PDI[a]	% *cis*[b]	yield[c] (%)	TGA (onset) °C
10	**1**	−CH_3	115 000	1.8	12	96	407
10	**2**	−CH_3	181 000	3.6	73.5	94	396
11	**1**	−Ph	137 000	1.5	18	95	279
11	**2**	−Ph	150 000	2.4	72	90	292
12	**1**	−Ph	51 000	3.8	0	42	276[d]
12	**2**	−Ph	115 000	2.0	0	95	300

[a] Determined by GPC using THF as eluent. [b] Determined by ^1H NMR. [c] Isolated yields. [d] Measurement taken at 10% weight loss.

the main chain. To test this hypothesis, three ROMP monomers (Figure 7) possessing pendent boronate groups were synthesized. It was necessary to examine each of the enantiomerically pure *endo*- and *exo*-norbornene derivatives in order to observe differences, if any, in polymerization behavior for each isomer. If one isomer is not tolerated by the catalyst, isolation from its enantiomer prevents an unsuccessful polymerization being attributed solely to the presence of the functional group within the molecule. To reach this goal, and as illustrated in Figure 7, each of the norbornenes was transformed into its isomeric boronate derivative by performing the analogous chemistry used to synthesize the boronate-containing α,ω-dienes.

Indeed, placing the boronate moiety pendent to the polymer main chain results in the formation of high molecular weight materials, even during solution polymerization conditions using either Mo or Ru catalysis

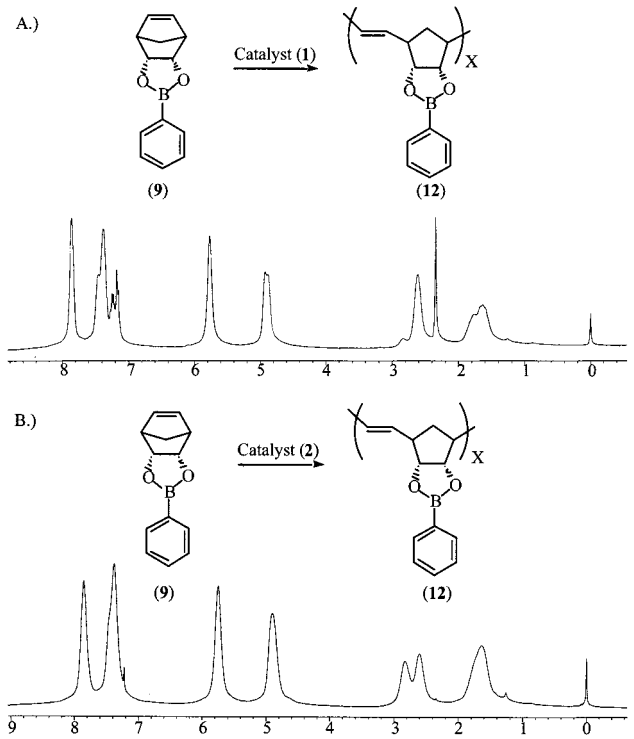

Figure 8. Ring-opening polymerization of monomer (**9**): (A) polymer **12** produced using the ruthenium catalyst **1**; (B) polymer **12** produced using the molybdenum catalyst **2**. NMR performed on precipitated polymer in $CDCl_3$.

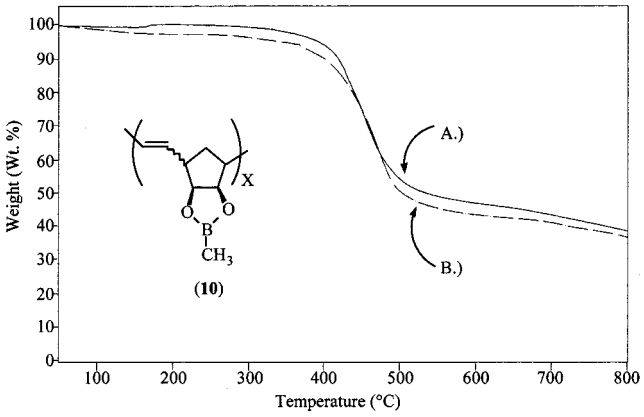

Figure 9. TGA thermogram of polymer (**10**) produced from (A) catalyst **1** and (B) catalyst **2**. The experiment was performed in air.

(Table 1). Molecular weights are higher than calculated, but dividing the molecular weights in half as suggested by Katz[21] adjusts the experimental values to agree closely with the theoretically determined weights. Polydispersities (PDI) are higher than expected for typical ring-opening metathesis polymerization. The ruthenium catalyst **1** produces polymers with polydispersity indices in the range 1.5−2.0, typical for this catalyst system due to its propensity to perform intramolecular backbiting reactions and intermolecular chain transfer.[12] Molybdenum alkylidene **2** catalysis also produces abnormally broad dispersities, possibly due to nonsimultaneous chain initiation by each catalyst molecule.

While high molecular weight polymers were obtained in all ROMP reactions, both catalysts are sensitive to the isomeric form of the norbornene monomer. The molybdenum alkylidene **2** produces a completely *trans* polymer **12** from the *endo* monomer **9** whereas this

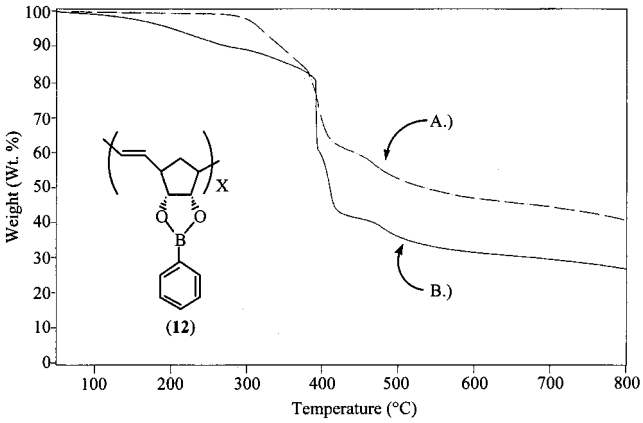

Figure 10. TGA thermogram of polymer **12** produced from (A) catalyst **2** and (B) catalyst **1**. The experiment was performed in air.

catalyst generates the *cis* polymer using the *exo* monomer. While less obvious regiochemical effects are observed using ruthenium catalysis, reaction rates are considerably slower.

Figure 8 illustrates the NMR spectra for two different versions of polymer **12** resulting from the polymerization of the *endo* monomer **9**, demonstrating that catalyst choice—Ru or Mo—results in significant differences in microstructure. Both spectra should be identical, with the exception of *cis*/*trans* ratios, if olefin metathesis is the only mechanism operating regardless of catalyst choice; obviously this is not the case.

It appears that close proximity of the *endo* monomer oxygen atoms in the metallacycle reaction intermediate affects ruthenium catalysis more so than molybdenum catalysis. Once these oxygens coordinate to the ruthenium catalyst in the metallacycle, polymerization kinetics apparently are slowed to a point that other competing reaction mechanisms are energetically favored. Consequently, ruthenium catalysis results in a change in the outcome of the polymerization, producing a more complex microstructure.

Atmospheric thermogravimetric analysis (TGA) illustrates that polymer **10** containing the methyl-substituted boronate exhibits significantly greater thermal stability than does the phenyl-substituted analogue, polymer **11**. This enhanced thermal stability most likely is a direct reflection of the increased stability of the boron−carbon bond in an alkylboronate compared to an aryl carbon−boron bond. Catalyst choice makes no difference for polymer **10**, as illustrated in Figure 9.

The situation is different for polymer **12** (generated from the *endo* monomer), with significant differences in thermal stability being observed depending upon catalyst choice (Figure 10). Molybdenum catalysis produces a polymer thermally stable up to 300 °C, after which multiple thermal decomposition onsets are observed; ruthenium catalysis, however, results in immediate thermal decomposition while displaying multiple onsets (Figure 10). These differences in thermal stability support the hypothesis that significant differences in microstructure exist in the molybdenum and ruthenium versions of polymer **12**.

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