Preparation of Alternating Copolymers from the Ring-Opening Metathesis Polymerization of 3-Methylcyclobutene and 3,3-Dimethylcyclobutene†

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ABSTRACT: Monomers 3-methylcyclobutene (**1**) and 3,3-dimethylcyclobutene (**2**) can be polymerized by well-defined alkylidene complexes of the type $M(CHC(CH_3)_3)(NAr)(OC(CH_3)_n(CF_3)_{3-n})_2$ (where Ar = 2,6-diisopropylphenyl; M = Mo or W; n = 2 or 3) to give polymers, which upon hydrogenation are equivalent to alternating copolymers of poly(ethylene-*alt*-propylene) and poly(ethylene-*alt*-isobutylene), respectively. Monomer **2** can be polymerized in a highly regioselective fashion to give polymers with exclusively *trans* and head-to-tail configuration. The high regioselectivity of the polymerization is attributed to the steric directing effect of the bulky substituent on the 3-position of the cyclobutene as the monomer approaches the propagating alkylidenes. In the presence of $PPhMe_2$ narrowly dispersed poly(3-methylcyclobutene) can be obtained.

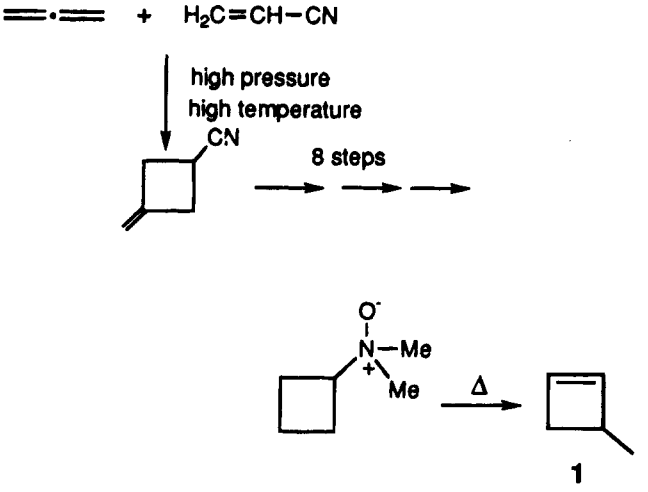
Introduction

Ring-opening metathesis polymerization (ROMP) of strained cyclic olefins is an extremely useful technique for the synthesis of new materials,[1-3] especially since the recent development of living ROMP methods have allowed the preparation of several novel block copolymers.[4] Copolymers, such as poly(ethylene–propylene) and poly(ethylene–styrene), represent important classes of copolymers, which can be synthesized by Ziegler–Natta polymerization of a mixture of the two monomers.[5] Although some successful examples of synthesizing perfectly alternating CO and styrene copolymers were reported recently,[6] it heretofore has not been possible to insert two similar monomers in an alternating fashion to yield polymers with high regioselectivities (i.e., high head-to-tail regularity). In general, the synthesis of perfectly alternating copolymers remains a synthetic challenge.

ROMP of substituted cyclobutenes followed by hydrogenation provides one solution to this problem and offers the advantage of producing polymers with low polydispersities, well-defined structures in comparison to other types of polymerizations,[7] and allows the incorporation of a wide range of functionalities into the polymer.[2] In order to establish the factors controlling the ROMP of functionalized cyclobutenes, the polymerizations of 3-methylcyclobutene (**1**)[8] and 3,3-dimethylcyclobutene (**2**)[9] using high-oxidation-state molybdenum and tungsten alkylidene complexes were studied.[7] The structures of poly-**1** and poly-**2** after hydrogenation are equivalent to alternating copolymers of ethylene/propylene and ethylene/isobutylene, respectively. The relief of ring strain in the monomer should drive these living polymerizations to proceed essentially irreversibly, which offers the possibility of preparing near-monodispersed polymers with controlled molecular weights.[1,10]

Since the microstructures of ring-opened polymers of cyclobutene derivatives are still unknown,[11] this investigation should allow a better understanding of the effects of the substituents on the regioselectivity and stability of the propagating species during the ROMP of strained cyclic olefins.

Scheme 1. Literature Synthesis of Monomer 1



Results and Discussion

Monomer Synthesis. In the literature, **1** was synthesized in 10 steps as shown in Scheme 1, starting from allene and acrylonitrile.[12] We encountered difficulties in scaling up the reactions and in purifying the final product, since **1** decomposes above 135 °C, which is near the reaction temperature required for the final step. In addition, the first step requires very high pressures and temperatures.

Therefore, a modified procedure, as shown in Scheme 2, was developed. The four-membered ring was easily constructed by a [1+3] nucleophilic addition reaction. Diethyl malonate was first reacted with 1-bromo-2-methyl-3-chloropropane to form diethyl 3-methylcyclobutane-1,1-dicarboxylate (**3**) in 55.4% yield. Compound **3** was readily hydrolyzed to its diacid analog **4** in 97% yield. Compound **4** lost one carboxyl group upon

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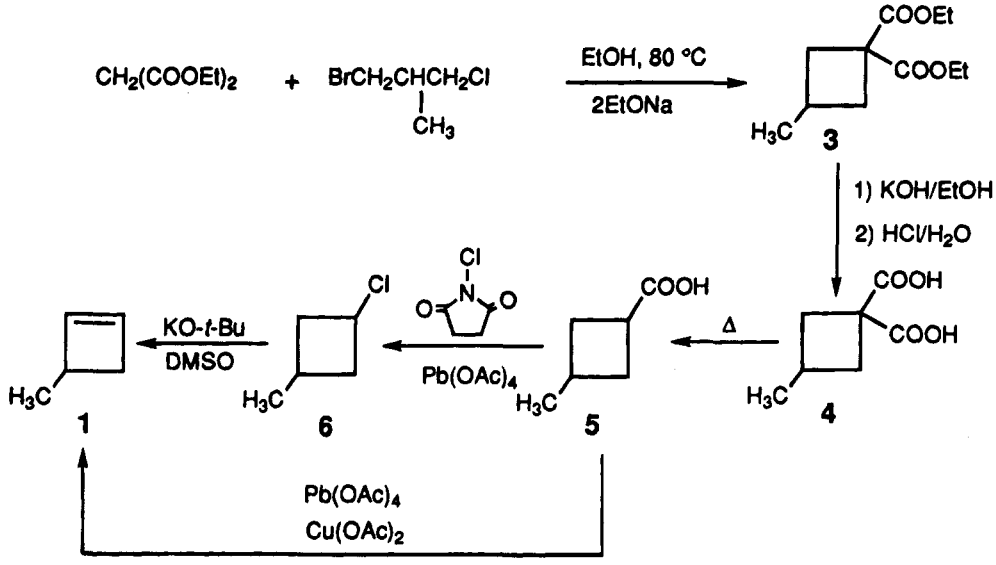
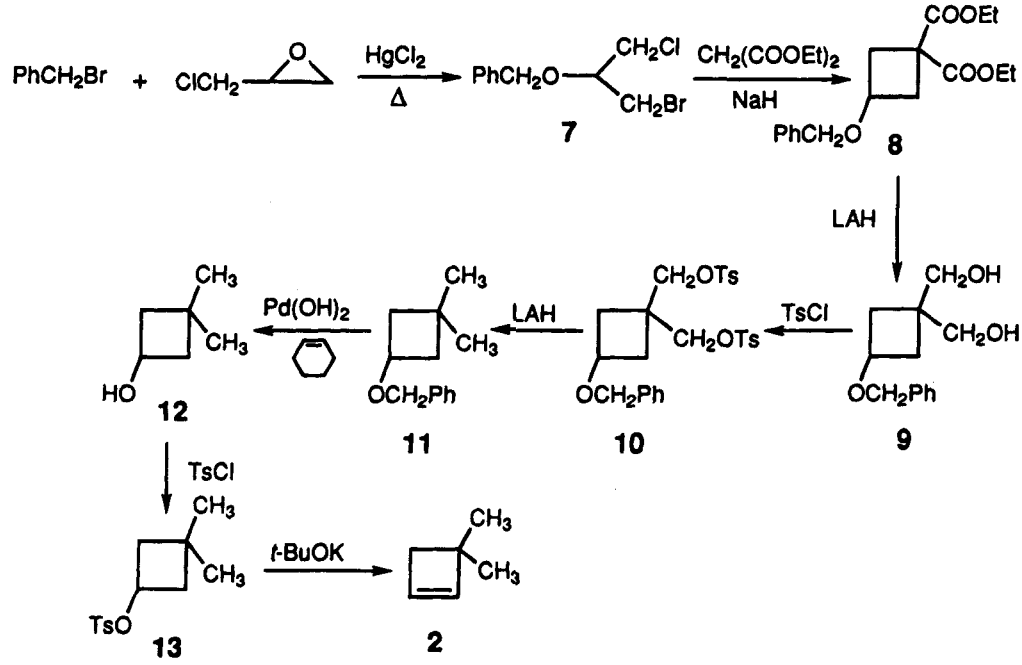
Scheme 2. New Route to Monomer 1



Scheme 3. Synthesis of Monomer 2



heating to give **5** in 96% yield.[13] Although **5** could be directly decarboxylated in the presence of $Pb(OAc)_4$ and $Cu(OAc)_2$ to give **1**, a very low yield of **1** resulted.[14] As an alternative route, **5** was first converted to 1-chloro-3-methylcyclobutane (**6**) followed by decarboxylation.[15] Compound **6** readily underwent elimination on treatment with *t*-BuOK to form the desired product **1** in good yield.[16]

The synthesis of 3,3-dimethylcyclobutene (**2**) used here (Scheme 3) is based on a modified literature procedure.[17] 1-Bromo-2-(benzyloxy)-3-chloropropane (**7**) was synthesized in 73% yield. Diethyl 3-(benzyloxy)-cyclobutane-1,1-dicarboxylate (**8**) was obtained in 43% yield by reacting **7** with diethyl malonate/NaH in dioxane for several days. Compound **8** was readily reduced to 1,1-bis(hydroxymethylene)-3-(benzyloxy)cyclobutane (**9**) in 87% yield using LAH in THF. Compound **9** was further converted to the ditosylate **10** in high yield by reaction with tosyl chloride. Compound **10** was reduced by LAH in THF to yield 3,3-dimethyl-1-(benzyloxy)cyclobutane (**11**) in 83.3% yield. Attempts to cleave the benzyl protecting group in **11** via hydrogenation using Pd/C as catalyst were not successful,[17] perhaps because of poisoning by trace amounts of sulfur in **11**. However, the deprotection of **11** to produce **12** in 63% yield was accomplished by hydrogen transfer from cyclohexene employing the more tolerant $Pd(OH)_2$ as catalyst.[18] Reaction of **12** with tosyl chloride gave **13** in high yield, which readily eliminated tosylate in the presence of *t*-BuOK to yield **2**.

Polymerization. As shown in eq 1, 3-methylcyclobutene (**1**) can be rapidly polymerized by well-defined molybdenum and tungsten alkylidene complexes at room temperature. Low-temperature NMR studies revealed that the polymerization initiated at −60 °C in toluene, which was similar to the onset polymerization temperature of cyclobutene.[10b] This observation suggests that the methyl substituent on the 3-position of cyclobutene does not decrease the ability of the monomer to undergo the ring-opening polymerization with **14** or **15** as catalysts. When 10 equiv of **1** was added to a toluene solution containing 0.011 M of catalyst Mo-

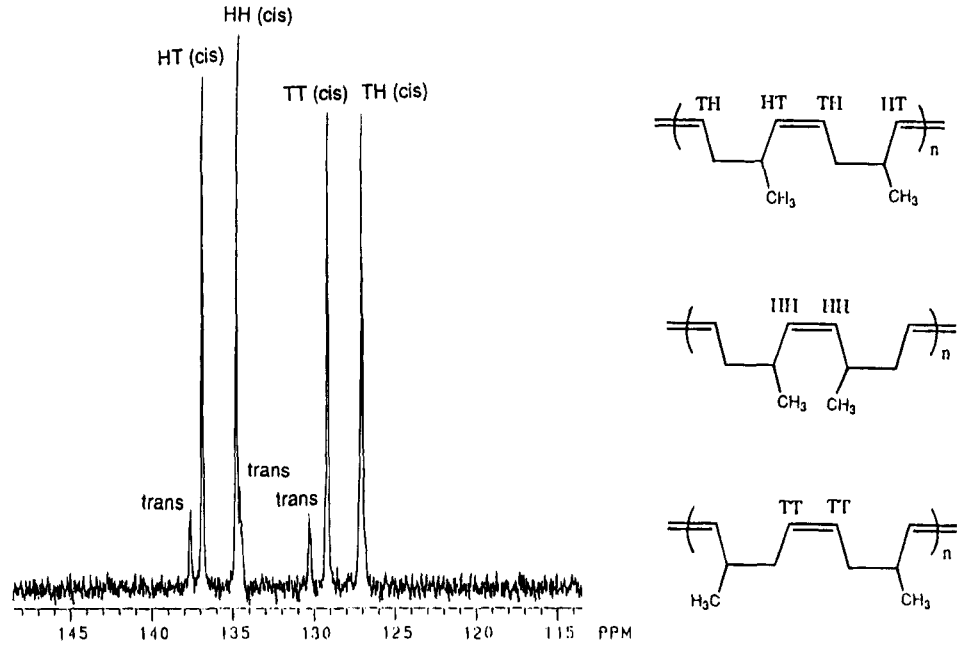


Figure 1. Olefinic region of the ^{13}C NMR spectrum of poly-**1** (n = 130) and the corresponding diad structures of the polymer backbone.[23]

$(CHC(CH_3)_3)(NAr)(OC(CH_3)_3)_2$ (Ar = 2,6-diisopropylphenyl) (**14**) at room temperature, two doublets at 11.95 ppm (J_{H-H} = 6.6 Hz) and 11.50 ppm (J_{H-H} = 9.5 Hz) were observed by ^1H NMR spectroscopy. These resonances are attributed to the two rotamers (anti and syn) of the propagating alkylidenes, where anti and syn refer to whether the polymer chain attached to the metal–alkylidene double bond points away from (anti) or toward (syn) the imido group.[19] The methyl substituent of the cyclobutene is on the β-carbon of the propagating species of the ring-opened polymers and apparently stabilizes the propagating alkylidene to a certain degree.[20]

On a preparative scale, 207 equiv of **1** was polymerized by **14** and the polymer obtained had a PDI of 2.46 and 84% cis double bond configuration in the polymer backbone.[21] The polymerization of 212 equiv of **1** catalyzed by **15** yielded a polymer having a PDI of 1.38 and 79% cis double bond configuration in the backbone.[21] Analysis of ^{13}C NMR data of both poly-**1** and its hydrogenated analog revealed that the polymer was atactic and had no head-to-tail (HT) bias. For example, in the olefinic region of poly-**1**, four cis olefinic resonances at δ (ppm) 136.8, 134.7, 129.1, and 127.0 were observed corresponding to four different structures in poly-**1** (Figure 1) and the peaks with lower intensities corresponded to the trans olefinic resonances.[22,23] Figure 2 shows four types of configurations in the backbone of the hydrogenated poly-**1**. The head–head and tail–tail configurations are assigned in the hydrogenated

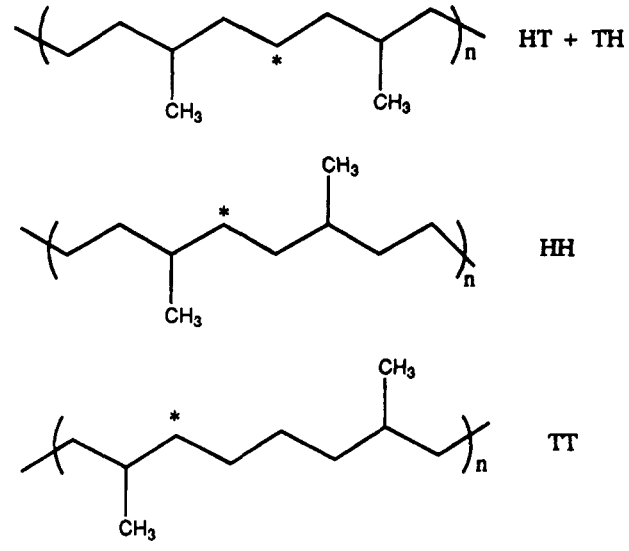
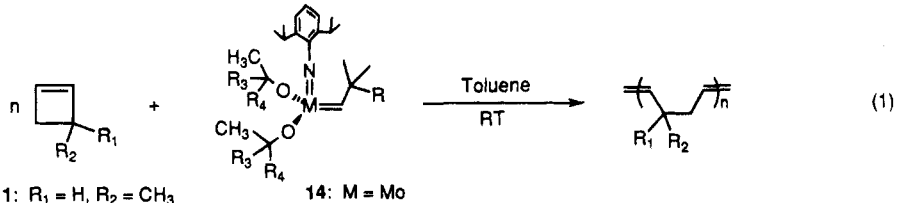


Figure 2. Backbone configurations of hydrogenated poly-**1** (n = 130). Asterisks represent the resonances that were used for calculating the ratio of HT versus HH and TT.

polymer. For example, the peaks at δ (ppm) 37.5 (TT), 34.9 (HH), and 27.99 (TT) in the ^{13}C NMR spectrum of the hydrogenated polymer correspond to the resonances of CH_2 carbons in the irregular head–head (HH) and tail–tail (TT) structures by comparison of the literature data of EP rubber[24] and that of the completely head-to-tail hydrogenated poly(1-methylcyclobutene).[25]



1: R_1 = H, R_2 = CH_3
2: R_1 = R_2 = CH_3

14: M = Mo
R_3 = R_4 = CH_3, R = CH_3
15: M = W
R_3 = R_4 = CH_3, R = CH_3
16: M = Mo
R_3 = CH_3, R_4 = CF_3, R = Ph

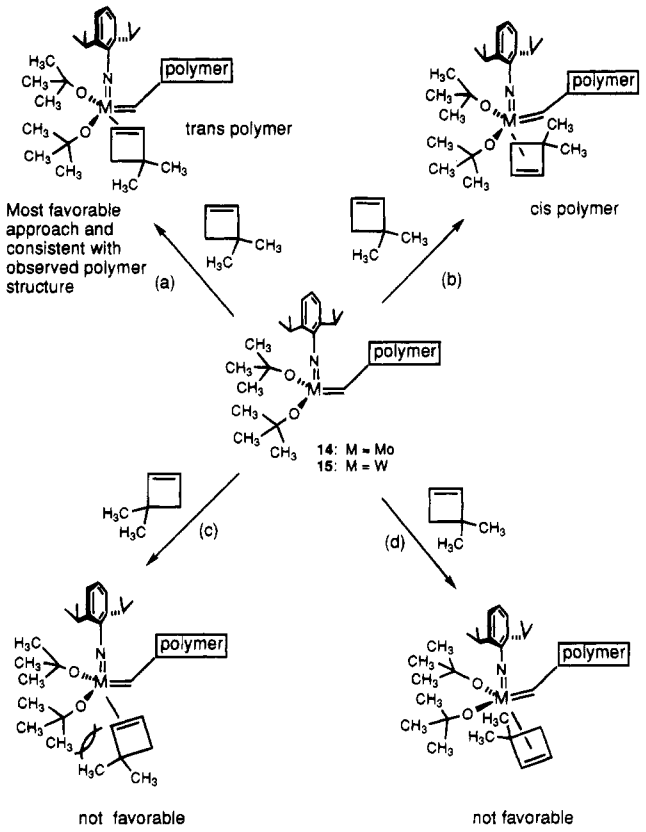


Figure 3. Possible modes of interaction of **2** with the metal center during the polymerization by attacking the C/N/O face of **14** or **15**.[26]

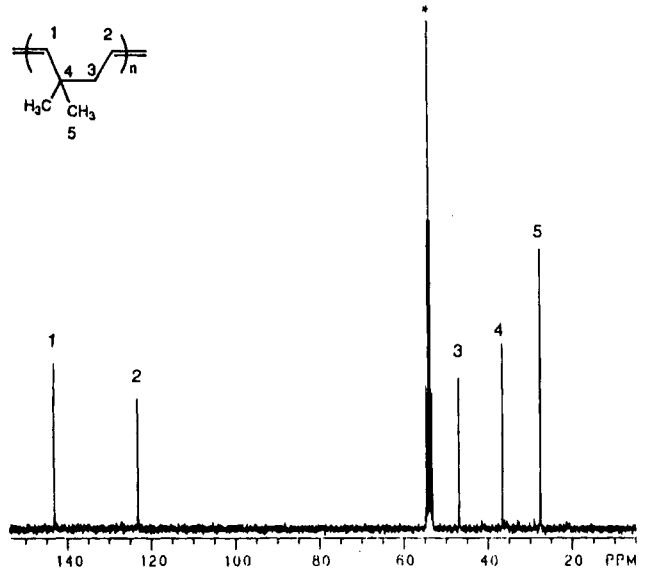


Figure 4. ^{13}C NMR spectrum of poly-**2**. The asterisk marks the resonance of the solvent (CD_2Cl_2).

The ratio of the regular structures (HT + TH) versus the irregular structures (HH + TT) is calculated to be 1:1 from the area under the corresponding peaks of the CH_2 carbons in the ^{13}C NMR spectrum. The random regiochemistry indicates that the methyl group is not sufficiently bulky to interact with the bulky alkoxide and imido ligand and to favor the formation of only one type of metallacyclobutane intermediate during the reaction.[25] We interpret this result to indicate that the metal complexes to the double bond on the side away from the methyl group.

To increase the interaction of the substituent with the metal center during reaction and to control the micro-

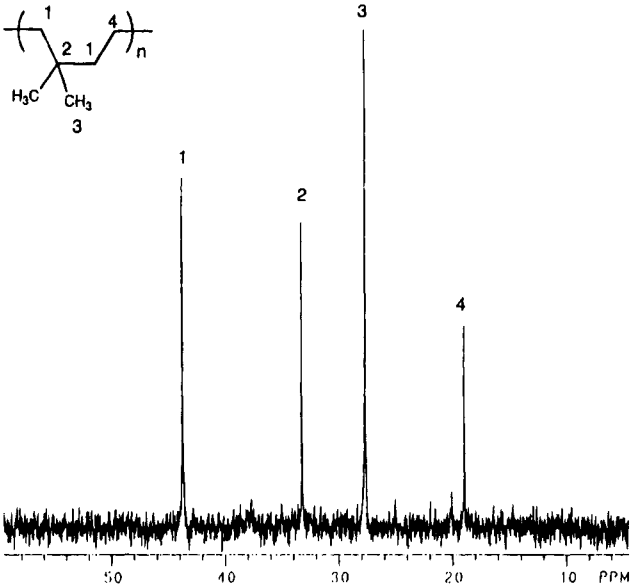


Figure 5. ^{13}C NMR spectrum of hydrogenated poly-**2**.

structure of the resulting polymer, the polymerization of **2** (eq 1) was examined. Monomer **2** is rapidly polymerized at room temperature by **14** and **15**. When 14 equiv of **2** was added to a 0.013 M toluene solution of **14**, a triplet resonance was observed at 11.80 ppm (J_{H-H} = 6.4 Hz) corresponding to the H_a of the propagating alkylidenes. Similarly, when **15** was used, a triplet resonance (H_a) was observed at 8.53 ppm (J_{H-H} = 5.9 Hz). These observations suggest that the monomer approaches the metal center in a regioselective fashion, with the bulky dimethyl groups away from the metal center as shown in Figure 3.

As a consequence, the polymers obtained by ROMP of **2** using **14** and **15** as catalysts are high trans (>99%) and regioregular (HT > 98%).[27] For example, in the ^{13}C NMR spectrum of the polymer obtained, only five peaks are observed at δ (ppm) 142.9 (CH), 122.95 (CH), 46.8 (CH_2), 36.40 (C), and 27.40 (CH_3) (Figure 4). The structure of the polymer upon hydrogenation is consistent with the assigned stereochemistry. The ^1H NMR spectrum of the hydrogenated polymer shows only three resonances at δ (ppm) 1.32 (CH_2), 1.31 (CH_2), and 0.99 (CH_3). In the ^{13}C NMR spectrum of the hydrogenated polymer (Figure 5), only four resonances are observed at δ (ppm) 43.7 (CH_2), 33.1 (C), 27.6 (CH_3), and 18.9 (CH_2), which confirms a highly regioselective polymer.[28] A totally random hydrogenated poly-**2** will be expected to have at least nine resonances at the dyad level.[29] The high trans content of the polymer is a result of the steric interactions of dimethyl substituents with the alkylidene ligands and the growing polymer chain as depicted in Figure 3, and it is expected that metallacycle formation with this highly strained monomer would be irreversible. As a specific example, when 102 equiv of **2** is polymerized by **14**, the polymer obtained has a molecular weight of 11 700 and a PDI of 1.6.[21] When 200 equiv of **2** is polymerized by **15**, the polymer obtained has a molecular weight of 27 600 and a PDI of 1.5.[21]

Polymerization of 3-Methylcyclobutene in the Presence of Dimethylphenylphosphine. Since 3-methylcyclobutene has ROMP reactivity that is similar to that of cyclobutene as shown by the low-temperature NMR studies (vide supra), phosphines, as shown in previous studies,[10b] should be able to regulate the rate of the polymerization and to allow the formation of a

narrowly dispersed polymer. Indeed, we found that $PPhMe_2$ binds reversibly to $[Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)_2CF_3)_2$ (Ar = 2,6-diisopropylphenyl)] (**16**) in toluene and the phosphine-bound alkylidenes were observed at 13.30 ppm (J_{H-P} = 7.8 Hz). When 12 equiv of **1** were added to a 0.015 M toluene solution of **16** in the presence of 2 equiv of $PPhMe_2$, two broad resonances with a ratio of 2:3 were observed at 12.76 and 12.96 ppm, respectively, corresponding to the H_α of the propagating species. The polymer obtained by reacting 62 equiv of **1** with **16** in the presence of 50 equiv of $PPhMe_2$ showed two narrow GPC traces with a ratio of areas equal to 2:3. Analysis of the ^{13}C NMR data indicated that the polymer had 88% cis double bond configuration and no HT bias. Interestingly, there is no high molecular weight trace observed by GPC. These observations suggest a new role of added ligands in the control of polymer structure in ROMP of strained olefins.

Conclusion

These investigations demonstrate for the first time that a perfectly alternating isobutylene–ethylene copolymer and narrow dispersed ethylene–propylene (EP) copolymer can be synthesized by ROMP. The ROMP of 3-methylcyclobutene catalyzed by **14** or **15** gives polymers that have no HT bias. The successful preparation of a perfectly alternating copolymer of ethylene–isobutylene has provided a good example for studying the stereocontrol in ROMP and for synthesizing polymers with novel properties. These studies also reveal that the steric bulk on both of the 3-positions of the cyclobutene ring is crucial in regulating the regioselectivity of the polymerization of substituted cyclobutenes catalyzed by molybdenum or tungsten alkylidene complexes. Future studies will involve the ROMP of cyclobutene derivatives with other bulkier substituents on the 3-position and the stereoselective synthesis of polymers with novel properties.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or an N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4-Å molecular sieves. ^1H NMR spectra were recorded on a JEOL GX-400 MHz (399.65 MHz ^1H; 100.5 MHz ^{13}C) or on a QE Plus-300 MHz (300.1 MHz ^1H; 75.49 MHz ^{13}C) spectrometer. Gel permeation chromatography (GPC) utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on a 0.5% w/v solution of polymer in dichloromethane. An injection volume of 0.1 mL and a flow rate of 1.0 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polysciences) ranging from M_n = 3550 to 600 000. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Gas chromatography was performed using a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with a 30-mm SE-30 (OV-1) capillary column and an HP 3396 Series II integrator.

Materials. Catalysts **14**–**16** were synthesized according to published procedures.[30-32] $Pb(OAc)_4$ and *N*-chlorosuccinimide were crystallized from acetic acid before use. $HgCl_2$ was purified by sublimation under high vacuum at 150 °C. Tosyl chloride was purified by recrystallization from pentane. CH_2Cl_2, DMSO, and DMF were distilled from CaH_2. Dioxane and pyridine were dried over 3-Å molecular sieves. Common solvents used were distilled from sodium benzophenone ketyl. All the other materials were either dried, distilled, or degassed before use. Deuterated compounds were purchased from Cambridge Isotope Laboratories. The commercially available compounds were purchased from Aldrich or Lancaster chemical companies.

Synthesis of Diethyl 3-Methylcyclobutane-1,1-dicarboxylate (3). Inside a nitrogen-filled drybox, NaOEt (204 g, 3.00 mol) was weighted into a 2-L round-bottom flask, and the solid was dissolved into 1200 mL of absolute ethanol outside of the drybox. The solution was then transferred into a dropping funnel. In another 3-L three-necked round-bottom flask, diethyl malonate (228 mL, 1.50 mol) and 1-bromo-3-chloro-2-methylpropane (175 mL, 1.50 mol) were mixed together and heated to 80 °C. At this temperature, the NaOEt solution was added dropwise over a period of 3 h. The mixture was refluxed overnight and cooled to room temperature. The solution was concentrated and then neutralized by the addition of dilute HCl. The organic layer was separated, and the aqueous phase was extracted with ether. The ether layer was washed with H_2O saturated Na_2CO_3 and dried with Na_2SO_4. Evaporation of the ether yielded a reddish viscous solution, which was distilled (78–82 °C/2 Torr) to afford a colorless liquid (181 g, 55.4%). ^1H NMR (300 MHz, $CDCl_3$): δ 4.17 (quartet, 4H, CH_2), 2.64 (m, 2H, CH_2), 2.42 (m, 1H, CH), 2.1 (m, 2H, CH_2), 1.08 (d, 3H, CH_3), 1.03 (t, 6H, CH_3).

Synthesis of 3-Methylcyclobutane-1,1-dicarboxylic Acid (4). KOH (185 g, 3.30 mol) was dissolved in 500 mL of ethanol in a 2-L round-bottom flask. The solution was cooled to room temperature, and a mechanical stirrer was assembled. Compound **3** (181 g, 0.830 mol) was added dropwise to the potassium hydroxide solution. After the addition was complete, the mixture was refluxed for 6 h and then filtered. The salt collected was dissolved in hot water, and a calculated amount of 37% HCl was added to neutralize the solution. The organic layer was separated, and the solid was filtered off and washed with ether. The aqueous solution was extracted several times with ether. All the organics were combined and concentrated to yield an off-white powder (130 g, 97%).

Synthesis of 3-Methylcyclobutanecarboxylic Acid (5). Diacid **4** (129 g) was added to a 300-mL round-bottom flask equipped with a reflux condenser, and the flask was heated to 200 °C in an oil bath under Ar. Evolution of gas was complete after heating was continued at 175 °C for 1.5 h. The resulting brown solution was distilled at 75–85 °C/6 Torr to yield a colorless liquid (89 g, 96%) with a distinct odor. ^1H NMR (300 MHz, $CDCl_3$): δ 12.07 (s, 1H, COOH), 4.11 (quartet, 1H), 1.8–3.2 (m, 5H), 1.11 (d, 1.5H, CH_3), 1.04 (d, 1.5H, CH_3).

Synthesis of 1-Chloro-3-methylcyclobutane (6). Inside the drybox, *N*-chlorosuccinimide (547 g, 4.09 mol) was weighted into a 3-L three-necked round-bottom flask and dissolved in 340 mL of DMF. The flask was brought out of the drybox and was mixed with **5** (81.4 g, 0.714 mol) and 67.8 mL of acetic acid. $Pb(OAc)_4$ (333 g, 0.714 mol) was then added to the flask, and an exothermic reaction started. After the bubbling ceased, the solid was filtered and washed with pentane. The filtrate was washed with H_2O, diluted $HClO_4$, and a saturated Na_2CO_3 solution. The pentane solution was dried over Na_2SO_4 and distilled through a helices-packed column to yield a yellow residue, which was vacuum-transferred to give a colorless liquid (26 g, 35%). ^1H NMR (300 MHz, $CDCl_3$): δ 4.1–4.6 (m, 1H), 1.2–2.8 (m, 5H), 1.13 (d, 3H).

Synthesis of 3-Methylcyclobutene (1). Inside the drybox, *t*-BuOK (65.4 g, 0.584 mol) was weighed into a three-necked round-bottom flask and dissolved in 250 mL of dry DMSO after the flask was removed from the drybox. Compound **6** (23 g, 0.22 mol) was dissolved in 30 mL of DMSO and transferred into an Ar-filled 125-mL dropping funnel. The condenser and dropping funnel were connected to the flask under Ar, and two cold traps were connected via a manifold from the top of the condenser. An Ar inlet was connected to the top of the dropping funnel. The flask was heated to 80 °C, and at this temperature, **6** was added dropwise over a 0.5-h period. After the addition was complete, the temperature was increased to 95 °C and the mixture was stirred for 3 h. The liquid collected in the traps was vacuum-transferred into a thick-walled flask containing NaH and capped with a Teflon valve. The contents of the flask were vacuum-transferred again to yield a pure liquid (7.0 g, 50%) by NMR. ^1H NMR (300 MHz, $CDCl_3$): δ 5.86 (d, 1H, J_{H-H} = 2.68 Hz, CH), 5.8 (d,

1H, J_{H-H} = 2.23 Hz, CH), 2.70 (m, 1H, CH), 2.49 (dd, 1H, J_{H-H} = 3.96 and 4.13 Hz, CH_2), 1.80 (d, J_{H-H} = 13.41 Hz, CH_2), 0.94 (d, 3H, J_{H-H} = 7.0 Hz, CH_3).

Preparation of 1-Bromo-2-(benzyloxy)-3-chloropropane (7). Benzyl bromide (500 g, 2.92 mol), epichlorohydrin (228.6 mL, 2.920 mol), and $HgCl_2$ (0.5 g, 1.8 mmol) were added to a 2-L three-necked round-bottom flask. The mixture was slowly heated to 160 °C over a period of 2 h. As the temperature increased, the solution became viscous and more (10 mL) epichlorohydrin was added. The heating was maintained at 160 °C for 6 h. The resulting brown solution was distilled under high vacuum (120 °C/0.03–0.06 Torr) to yield **7** (556 g, 73.0%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (m, 5H), 4.7 (s, 2H), 3.5–3.9 (m, 4H). GC/MS: M^+ = 264.

Synthesis of Diethyl 3-(benzyloxy)cyclobutane-1,1-dicarboxylate (8). In the drybox, NaH (41 g, 1.7 mol) was weighed into a three-necked round-bottom flask, and 500 mL of dioxane was added to make a suspension. The flask was brought out of the drybox, assembled with a mechanical stirrer and a reflux condenser, and then cooled to 0 °C. To the above solution, diethyl malonate (250 mL, 1.65 mol) was added dropwise over 1-h period. As the addition continued, the solution became viscous and difficult to stir. After the addition, **7** (308 mL, 1.65 mol) was added to the flask over a 20-min period and the mixture was refluxed for 2 days. More NaH (51 g) in 500 mL of dioxane was added, and the mixture was refluxed for 8 days more. The solvent was removed under vacuum, and H_2O was added to quench the reaction. The aqueous phase was extracted with ether several times, and the ether solution was dried over $MgSO_4$ and evaporated. The residue was fractionally distilled to yield a colorless oil. The first fraction from the distillation was repurified by flash chromatography on silica gel (10% ethyl acetate–petroleum ether). Combination of all the product gave **8** (218 g, 43.0%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 5H), 4.43 (s, 2H), 4.17 (quartet, 4H, CH_2), 4.13 (m, 1H), 2.8 (m, 2H), 2.56 (m, 2H), 1.27 (t, 3H, CH_3).

Synthesis of 1,1-Bis(hydroxymethylene)-3-(benzyloxy)cyclobutane (9). In the drybox, LAH (54.0 g, 1.35 mol) was weighed into a 2-L three-necked round-bottom flask. The flask was brought out of the drybox, and freshly distilled THF (400–500 mL) was added. To the above flask, diester **8** (218 g, 0.712 mol) dissolved in 200 mL of THF was added dropwise over a period of 2 h at 0 °C. The mixture was refluxed at 60 °C for 48 h. The flask was cooled to 0 °C, and saturated Na_2SO_4 solution was added to quench the reaction. The solid was filtered, and the filtrate was concentrated and redissolved in dilute HCl. The aqueous phase was extracted with $CHCl_3$ several times. The organic phase was washed with H_2O and a saturated NaCl solution and dried by Na_2SO_4. Evaporation of the solvent yielded an off-white solid **9** (138 g, 87.0%) pure by NMR. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (m, 5H, Ph), 4.42 (s, 2H, CH_2), 4.08 (m, 1H, CH), 3.71 (m, 4H), 2.89 (d, 2H, J_{H-H} = 6 Hz), 1.6–2.4 (m, 4H).

Synthesis of 1,1-Bis[(tosyloxy)methylene]-3-(benzyloxy)cyclobutane (10). A 1-L round-bottom flask containing **9** (137 g, 0.617 mol) and 500 mL of pyridine was cooled to 0 °C. TsCl (237 g, 1.24 mol) was added to the flask in small portions over an hour. After the addition was complete, the mixture was warmed to room temperature and stirred overnight. The contents of the flask was then poured into 3 L of ice water containing 500 mL of concentrated HCl. The organic layer was separated, and the aqueous phase was extracted with ether. The ether layer was washed with HCl, saturated Na_2CO_3, and H_2O and dried by $MgSO_4$. Evaporation of the solvent and recrystallization in ether yielded a white solid **10** (286 g, 87.4%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.2–7.8 (m, 8 H, Ph), 4.30 (s, 2H, CH_2), 4.0 (m, 1H), 3.95 (s, 2H, CH_2), 3.92 (s, 2H, CH_2), 2.45 (d, 6H, J_{H-H} = 6.8 Hz), 1.7–2.2 (m, 4H, CH_2).

Synthesis of 3,3-Dimethyl-1-(benzyloxy)cyclobutane (11). Inside the drybox, LAH (44 g, 1.1 mol) was weighed into a 3-L round-bottom flask and dissolved in 500 mL of THF. Outside the drybox, a 1000-mL THF solution of **10** (286 g, 0.54 mol) was added dropwise at 0 °C over a 1-h period to the LAH solution. After the addition was complete, the mixture was heated to 60 °C and refluxed overnight. The reaction was quenched with a 15% NaOH solution, and the solid was redissolved in dilute HCl. The aqueous phase was extracted with ether, and the ether layer was washed with saturated Na_2CO_3 and H_2O and dried by $MgSO_4$. An orange solution was obtained after evaporation of the solvent. Fractional distillation (75 °C/1.5 Torr) gave 82.5 g of a colorless liquid. The residue and the first fraction from the distillation were repurified by flash chromatography on silica gel (5% Et_2O–hexanes) to yield another 3.2 g of product. Combination of all the fractions gave **11** in 83.3% total yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (m, 5H, Ph), 4.38 (s, 2H, CH_2), 4.05 (quintet, 1H, CH), 1.7–2.2 (m, 4H, CH_2), 1.15 (s, 3H, CH_3), 1.11 (s, 3H, CH_3).

Synthesis of 3,3-Dimethylcyclobutanol (12). To a 3-L round-bottom flask was added 1200 mL of EtOH, **11** (30 g, 0.16 mol), cyclohexene (600 mL, 5.92 mol), and 7.5 g of 20% $Pd(OH)_2$ on carbon. The mixture was refluxed for 2 days and then filtered through a fine-frit funnel. The solvent was distilled at atmospheric pressure, and the residue was distilled at 55 °C/15 Torr to give a colorless liquid **12** (10 g, 63%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.23 (quintet, 1H, J_{H-H} = 7.3 Hz), 1.6–2.2 (m, 4H, CH_2), 1.11 (s, 3H, CH_3), 1.07 (s, 3H, CH_3).

Synthesis of 3,3-Dimethylcyclobutyl Tosylate (13). In a 100-mL round-bottom flask, **12** (9.3 g, 0.093 mol) was dissolved in 50 mL of dry pyridine and cooled to 0 °C. TsCl (20.0 g, 0.105 mol) was added in small portions to the flask, and the rate of the addition was controlled so that the temperature did not rise above 5 °C. After the addition, the reaction mixture was allowed to stir at room temperature overnight. The contents were poured into a large beaker containing ice/H_2O and dilute HCl. The aqueous phase was extracted several times with ether, and the ether solution was washed with saturated Na_2CO_3 and H_2O and dried with $MgSO_4$. The solvent was evaporated, and the residue was recrystallized from pentane at −50 °C to give **13** (22 g, 93%) as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.76 (d, 2H, J_{H-H} = 8.3 Hz), 7.37 (d, 2H, J_{H-H} = 8.1 Hz), 4.80 (quintet, 1H, J_{H-H} = 7.36 Hz), 2.45 (s, 3H, CH_3), 1.8–2.2 (m, 4H, CH_2), 1.10 (s, 3H, CH_3), 1.05 (s, 3H, CH_3).

Synthesis of 3,3-Dimethylcyclobutene (2). In the drybox, *t*-BuOK (31 g, 0.276 mol) was weighed into a 500-mL three-necked round-bottom flask. The flask was brought out of the drybox and charged with 100 mL of dry DMSO and heated to 90 °C in an oil bath. Tosylate **13** (22.0 g, 0.0866 mol) dissolved in 30 mL of DMSO was added dropwise to the flask at this temperature over a 20-min period, and the mixture was stirred at 85 °C for 2 h. The volatile products generated were collected in two consecutive cold traps at −78 °C and were then vacuum-transferred to a flask capped with a Teflon valve to yield **2** (4.0 g, 57%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.03 (d, 1H, J_{H-H} = 2.81 Hz, CH), 5.96 (d, 1H, J_{H-H} = 2.84 Hz, CH), 2.21 (s, 2H, CH_2), 1.15 (s, 3H, CH_3).

General NMR Tube Reactions. Inside the drybox, 3–5 mg of catalysts was weighed into an NMR tube and dissolved in toluene-d_8. Calculated amounts of monomer were added with a gas-tight syringe. The tube was capped with a septum and brought out of the drybox and shaken vigorously. NMR spectra were recorded at selected intervals.

General Procedure for Polymerizations. In the drybox, the catalyst was weighed and dissolved into a flask equipped with a Teflon valve. The flask was capped, brought out of the drybox, and put into a −78 °C dry ice/acetone bath. Calculated amounts of the monomer were added either by using a gas-tight syringe at −78 °C while the solution was rapidly stirring or by vacuum-transfer from another tared flask while the catalyst solution was kept at −196 °C. The flask was then warmed up to room temperature and stirred for 0.5–1.0 h. Several drops of degassed methanol or benzaldehyde were added to terminate the reaction, and the contents of the flask was added dropwise to rapidly stirred methanol. Polymers were collected by filtration and dried at room temperature under full vacuum. The isolated yield was greater than 80%.

General Procedures for Hydrogenation of the Polymers. In a small Schlenk flask, unsaturated polymer was dissolved in a calculated amount of *p*-xylene to make a solution

of 0.3–0.4 M (concentration of the repeating units), and a small amount of BHT was added. A total of 6 equiv (relative to the repeat units) of tosylhydrazide was added to the flask, and the mixture was degassed twice using a freeze–pump–thaw cycle. While the solution was maintained under Ar, a reflux condenser was attached and the mixture was heated to 120 °C for 3 h until the generation of gas bubbles ceased. The flask was cooled to room temperature, and its contents were added to rapidly stirred methanol. The polymer was purified by reprecipitation into methanol. The material was dried under vacuum, and the isolated yields in all runs were greater than 60%.

Polymerization of 1 in the Presence of $PPhMe_2$. In the drybox, **16** (14.6 mg, 0.0222 mmol) and $PPhMe_2$ (150 μL, 50 equiv) were weighed into a small flask equipped with a Teflon valve. Toluene (2 mL) was added to the flask before it was capped and brought out of the drybox. 3-Methylcyclobutene (**1**; 0.114 g, 1.38 mmol) was vacuum-transferred into the flask cooled to 77 K, and the mixture was thawed at −78 °C and then stirred at room temperature for an hour. Several drops of methanol were added to quench the reaction, and the solution was added to rapidly stirred methanol. The polymer (yield = 62%) obtained was dried under high vacuum. M_n = 9800, PDI = 1.08; M_n = 4500, PDI = 1.06.

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(20) For example, in the polymerization of cyclobutene by **14** and **15**, where the propagating alkylidene is a linear chain without substituents, no propagating alkylidene was observed, in part, as a result of the decomposition of the propagating species. In fact, there is literature precedence that the increase of steric bulk of the β-carbon on the propagating species can stabilize the propagating alkylidene. For example, in the polymerization of norbornene, well-defined propagating alkylidene species were observed, see: Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169. No γ-substituted propagating alkylidene observed during the polymerization of **1** can be partially attributed to the instability of this species.

(21) All the molecular weight data were obtained from GPC using polystyrene standards.

(22) In the aliphatic region of the ^{13}C NMR spectrum of poly-**1**, the resonances at δ 40.82 (CH_2, t), 37.28 (CH, t), 35.63 (CH_2, c), 35.49 (CH_2, c) 35.35 (CH_2, c), 32.56 (CH, c), 32.96 (CH, c), 21.29 (CH_3, c), 20.91 (CH_3, c), 20.48 (CH_3, t), and 20.45 (CH_3, t) were assigned using DEPT experiments and the Ivin rule (Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983; p 201) where *c* and *t* are abbreviations for *cis* and *trans* isomerism.

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