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Communications to the Editor

Circumventing Pericyclic Reactions To Realize Insertion Polymerization of Cyclobutene Derivatives

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Internal double bonds are notoriously difficult to polymerize in an insertion mode unless they are incorporated as cis bonds in strained rings. While insertion polymerization examples of 3-membered rings, 5-membered rings, and strained bicyclics (norbornene derivatives) are common, noticeably absent are examples of four-membered rings. Although cyclobutene has sufficient ring strain, 31 kcal/mol,[1] very few examples of vinylic polymerization of cyclobutene are known. This is due to the fact that simple cyclobutenes will undergo rapid pericyclic ring opening reactions to form butadiene or alternatively undergo ROMP. Attempts to polymerize cyclobutene results in a polymer that contain both the cyclobutene repeats and 1,4-butadiene repeat units. These butadiene repeats decrease the thermal stability of the polymer.[2]

In 1960s, Dall'asta and co-workers reported several studies of the polymerization of cyclobutene; however, their polymer contains butadiene units and ring-opening polymerization units. Also, the molecular weight information is obscure.[2−4] They also tried to polymerize a fused ring system, but the resulting polymer has quite low molecular weights and contains ring opened units up to 10 mol %.[5] To the best of our knowledge, no reports of high molecular weight, genuine vinylic polymers of any cyclobutene derivatives have been published.

In recent years, a number of new high performance engineering materials have been prepared through the insertion polymerization of norbornene. These polymers can have outstanding properties, such as low moisture absorption, low dielectric constants, chemical resistance, low birefringence, high breakdown voltages and high glass transition temperatures. A number of those polynorbornene materials are now commercially available and include Appear optical polymer material for flat panel display and waveguides, Aprima adhesives and covercoat, Avatrel low-κ materials, Duvcor 193 and 157 nm photoresists (Promerus), as well as copolymers of olefins and norbornenes, Topas (Topas Advanced Polymers) and Apel (Mitsui Chemical).

As stated earlier, the insertion polymerization of the four-membered ring, although highly strained, has been less successful. The unwanted pericyclic ring-opening of cyclobutene to the more stable butadiene has limited advancement in this field. Our approach to eliminating the pericyclic ring opening reaction has been to tie the 3,4-carbons of the butadiene together through an additional fused ring. This "cis" fused ring prevents the facile pericyclic ring opening from occurring because it forces a trans double bond into the cyclic structure. Bicyclo[4.2.0]oct-7-ene (**1**) and bicyclo[3.2.0]hept-6-ene (**2**) are two examples of these fused systems. The synthesis of monomers **1** and **2** is summarized in Scheme 1. All the steps are quite straightforward and proceed in reasonable yields.

Since monomers **1** and **2** have fused ring systems similar to norbornene, it was assumed that β-hydride elimination would not be a significant process during polymerization because of Bredt's rule. Late transition metal catalysts are prone to β-hydride elimination unless bulky ligands are used, such as those in the Brookhart type nickel or palladium catalysts. For monomers like norbornene that do not have the intrinsic ability to β-hydride eliminate, simple nickel or palladium complexes can be very active catalyst systems.[6] Among the late transition metal catalyst systems, nickel(acetylacetonate) or its derivative with tris(pentafluorophenyl)borane system is simple yet shows high activity toward norbornene polymerization.[7−9] Another simple nickel catalyst system active for norbornene polymerization is [1,2-bis(diphenylphosphino)ethane]dichloronickel with methylaluminoxane (MAO). This catalyst system was first reported for ethylene polymerization in 1993,[8] and Janiak and co-workers recently reported that this system shows good polymerization activity toward norbornene.[10] While these simple

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Scheme 1. Synthesis of Monomers 1 and 2 from 1,5-Cyclooctadiene and 1,3-Cycloheptadiene, Respectively

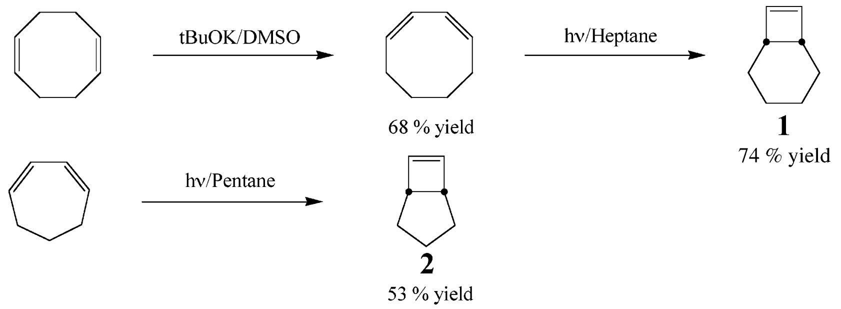
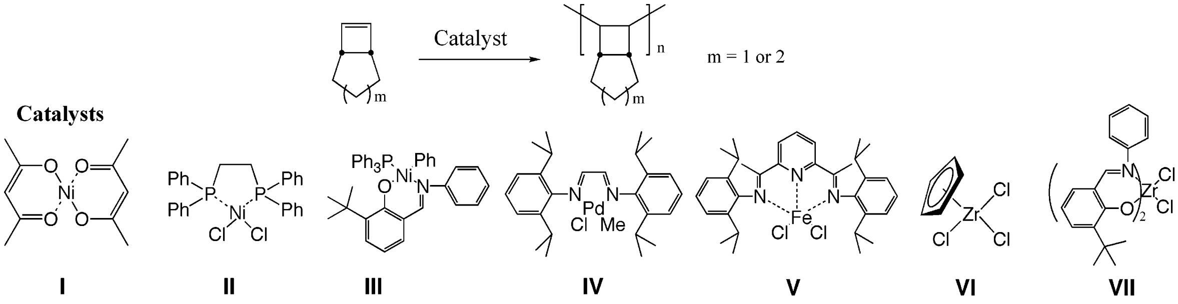


Chart 1. Catalyst Precursors Studied for the Polymerization of 1 and 2



nickel complexes work very well toward the polymerization of norbornene, nickel or palladium complexes with well-designed bulky ligand such as Grubbs type, salicylaldiminate neutral nickel catalyst system,[11] or Brookhart type, α-diimine palladium cationic catalyst system, are also reported to be active toward norbornene/functionalized norbornene and ethylene copolymerization.[12,13]

In contrast, early transition metal catalysts based on titanium or zirconium are known to have less of a tendency to β-hydride eliminate. However, titanium complexes, based on bis(cyclopentadienyl)titanium for instance, are known to catalyze ring opening metathesis polymerization of norbornene as well.[14,15] In contrast, activated bis(cyclopentadienyl)zirconium complexes exclusively catalyze addition polymerization of norbornene.[14,16] Because of steric repulsion, bis(cyclopentadienyl)zirconium species do not show high catalytic activity toward norbornene and a more open form of zirconocene would be better suited for a strained cyclic olefin such as norbornene. The catalysts used for this study are shown in Chart 1.

Surprisingly, none of the late transition metal catalyst systems that were tried and are active toward norbornene showed activity toward monomer **1**. Only $CpZrCl_3$/MAO, **VI**, showed activity, offering a 50% yield of the polymeric product. Since the polymeric product from polymerization of **1** catalyzed by **VI** is soluble in 1,2-dichlorobenzene and partially soluble in toluene and chloroform, we studied its structure by NMR and found signals for olefinic protons. Gel permeation chromatography showed a trimodal polymer distribution of relatively low molecular weight.

A polymerization attempt with monomer **1** in toluene with zirconium complex **VII** activated by 3400 equiv of MAO afforded a low molecular weight polymeric product (M_w = 3300) with a moderate yield of 64%. Monomer **2** was also polymerized under same conditions and gave 74% yield. Poly-**2** was found to be insoluble in all solvents even at high temperature. The ^{1}H NMR spectra of the poly-**1** obtained using **VI** and **VII** are shown in Figure 1. A diminished olefin peak is clearly seen in the material obtained using catalyst **VII**.

Bulky monomers do not always compete well with ethylene, but it was also discovered that monomer **1** will copolymerize with ethylene. The copolymerization of monomer **1** with ethylene was successful using catalyst **VII**. Poly(**1**-*co*-E) is not soluble at room temperature, so we performed high temperature ^{13}C NMR of the homopolymer and copolymer. The differences between the two spectra clearly indicate formation of a random copolymer, and does not indicate a mixture of two homopolymers or block copolymers. Monomer incorporation ratio is calculated ethylene/**1** = 5/1 based on quantitative ^{13}C NMR. GPC analysis again showed relatively low molecular weight material (M_w = 8200) and no T_g could be detected between −35 and +380 °C.

We investigated the source of the olefin peak in the NMR samples and have concluded that olefin formation occurs through β-hydride elimination. Control experiments show that 1,3-cyclooctadiene, which would result from pericyclic ring-opening does not polymerize with **VII**, and the ROMP polymer (made using Grubbs' ruthenium catalyst with **1**) displays a very different NMR spectrum. Although β-hydride elimination from a poly-**1** chain is unlikely because of the formation of a bridgehead olefin (Bredt's rule), in this case the bridgehead olefin, bicyclo[4.2.0]oct-8-ene, is known, and can be isolated.[17] To help confirm the bridgehead olefin structure at the terminal repeat unit, we employed 2D-NMR experiments. ^{1}H−^{13}C short range (one bond correlation) and long range (two bonds correlation) 2D-NMR spectra of polymeric sample from monomer **1** polymerization using **VI** clearly show the correlations between the olefinic proton and corresponding carbons, which appear at 132 and 44 ppm, respectively. These two carbon peaks are well matched with predicted values of the 7- and 8-positions of the bicyclo[4.2.0]oct-8-ene unit.

On the basis of ring strain analysis of bridgehead olefin,[18] monomer **2** might have more potential to polymerize when catalyzed by late transition metals than monomer **1**, because of its moderately high strain energy. We attempted the polymerization of monomer **2** with **I**, but surprisingly, the reaction did not proceed. Since **2** cannot form a bridgehead olefin (and hence, β-eliminate) we investigated the interaction of this olefin with the well-defined nickel complex **III**. In toluene-d_8, monomer **2** was allowed to react with a stoichiometric amount of Grubbs' nickel complex **III**, activated by bis(cyclooctadiene) nickel.

Table 1. Results of Activator Modification To Polymerize Monomer 1[a]

run	cocatalyst	yield (g)	M_w	M_n	M_w/M_n
1	MAO 3,400 equiv	0.64	3300	1100	3.0
2	MAO 500 equiv	0.97	219 000	141 000	1.6
3	"dried" MAO 500 equiv	0.83	164 000	99 000	1.7
4	MAO 500 equiv, H_2O 100 equiv, C_6F_5OH 100 equiv	0.90	7400	2100	3.5
5	iso-Bu_3Al 40 equiv, $Ph_3C(C_6F_5)_4$ 2 equiv	0.14	2400	700	3.4
6	Oct_3Al 20 equiv, $B(C_6F_5)_3$ 10 equiv	trace			
7	iso-Bu_3Al 150 equiv, MAO 350 equiv, H_2O 150 equiv	0.86	245 000	155 000	1.6

[a] 1.0 g (0.94 mol) of monomer **1** was used. Room temperature. 10.0 μmol of complex **VII** was used. Molecular weight is relative to polystyrene. See Supporting Information for detailed conditions.

Because there are no geminal hydrogens in **2**, it is impossible to confirm the existence of a β-agostic complex by observing coupling of the proton signals. Hence, we conducted 2D-NMR, $^1H-^{13}C$ correlation, with our sample. The reaction was slow, and after 7 h, an upfield peak was observed at −2.2 ppm, which has no correlation with other hydrogens and has correlation with carbon at 30 ppm. This chemical shift is reasonable for an agnostic interaction in a neutral nickel species.[19−21] We believe this is an evidence for the formation of an inert nickel insertion product of **2** stabilized by β-agostic interactions that prevent further insertions.

MAO, its purity, and its concentration are known to influence many factors including molecular weight by chain transfer to aluminum. A number of solutions to this have been put forward and include trimethylaluminum free ("dried") MAO, modified MAOs, produced or reported by Akzo Nobel and Sumitomo Chemical, and the use of borane or other additives.[22−24]

Taking all these possible solutions under consideration, we conducted activator modification experiments in attempt to produce high molecular weight poly-**1**, Table 1. All **VII** and activator combinations produced polymers and all the materials obtained were not soluble in 1,2-dichlorobenzene at room temperature, so high temperature GPC was performed. These results clearly show that reducing the amount of MAO down to 500 equiv produced high molecular weight poly-**1** with excellent productivity. Polydispersities lower than 2.0 indicate single active species. Water and pentafluorophenyl modified MAO showed a little improvement on yield, but not in molecular weight. "Dried" MAO also produced much higher molecular weight poly-**1** with good productivity. Finally, the modified MAO also showed high productivity.

Thermogravimetric analysis revealed that both poly-**1** and poly-**2** have thermal stabilities close to 400 °C even with very low molecular weights. Differential scanning calorimetric analysis of samples with both low and high molecular weights (poly-**1**, the molecular weights of poly-**2** samples are unknown due to insolubility**)** showed both polymers have almost the same glass transition temperature near 80 °C regardless of molecular weight. Since we expected our polymers to possess similar thermal behavior as polynorbornenes do, this was quite a surprising result to us.

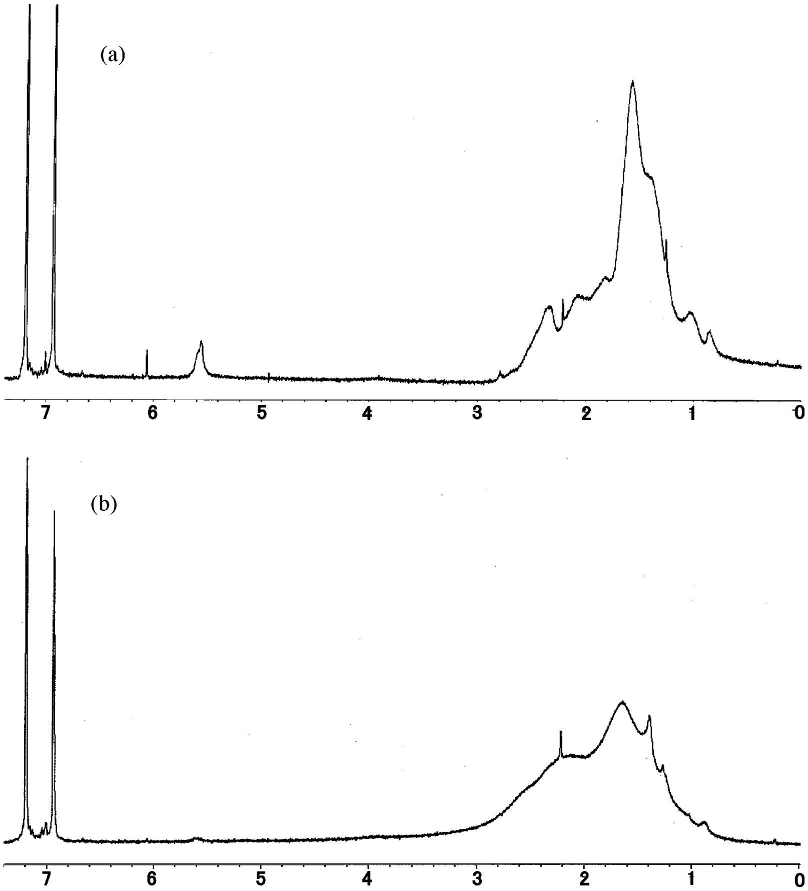


Figure 1. ^1H NMR spectra of polymeric product from monomer **1** (a) catalyzed by **VI** and (b) catalyzed by **VII**, in o-DCB-d_4 at room temperature.

Glass transition temperature depends on the microstructure of polymer, the rigidity of polymer main chain, steric bulk of side chain, and stereoregularity. High glass transition temperatures of polynorbornene, >340 °C, is understood to arise from its tightly connected bulky repeat unit and relatively regular microstructure, which results in tightly packed polymer chains (low free volume). The low glass transition temperature of poly-**1** could be due in part to a less tightly packed structure of polymer (higher free volume). These studies on glass transition temperature and their copolymers with other monomers are still in progress.

In conclusion, we have presented the first high molecular weight polymer of cyclobutene derivatives. The fused ring hydrocarbons, 4−6 and 4−5 ring systems, were successfully polymerized through exclusively addition polymerization to afford high molecular weight materials. Glass transition temperatures of those polymers were found to be lower than that of addition polymer of norbornene. However, this new class of saturated hydrocarbon polymer opens the door to provide and create new engineering plastics. Copolymerization with other monomers and alternative catalysts are currently being investigated.

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Supporting Information Available: Figures showing the ^{13}C NMR spectra of homopolymer (poly-**1)** and copolymer (poly(**1**-*co*-E)) and text giving the detailed conditions for monomer synthesis and polymerization listed in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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