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Acyclic Diene Metathesis (ADMET) Polymerization

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ABSTRACT: The synthesis of the first high molecular weight polymers by acyclic diene metathesis (ADMET) polymerization is reported, using a catalyst free of Lewis acids. Previous attempts, most recently in our laboratory and in several other laboratories over the past 20 years, had proven to be unsuccessful. 1,9-Decadiene has been converted to poly(octenylene), and 1,5-hexadiene has been converted to exclusively 1,4-polybutadiene by this procedure. The metathesis polymerization reaction is quantitative at or near room temperature and yields only polymer and ethylene as a byproduct. No other products are observed. Poly(octenylene) exhibits a minimum weight-average molecular weight of 108 000 and is more than 90% trans in its stereochemistry. Exclusively 1,4-polybutadiene is of a minimum weight-average molecular weight of 28 000 and is more than 70% trans in its stereochemistry. The stereochemistry appears to be controlled thermodynamically due to the equilibrium nature of the polymerization, and this stereochemical feature distinguishes ADMET polymerization from ring-opening metathesis polymerization (ROMP).

Introduction

Since its discovery about 30 years ago,[1-3] the olefin metathesis reaction illustrated in Figure 1 has intrigued chemists from both mechanistic and practical points of view. Few reactions in organic chemistry exhibit such a dramatic change between reactants and products (the cleavage and formation of two pairs of C–C double bonds). The mechanism of the metathesis reaction has aroused intense interest over the past 30 years,[4,5] since control of the reaction could result in a useful synthesis of olefins.

The potential of olefin metathesis was first extended to polymer synthesis by applying the reaction to cyclic olefins (Figure 2). Ring-opening metathesis polymerization (ROMP) is driven by the release of ring strain in the starting olefin substrate and was first reported in 1957 by Eleuterio.[1] This discovery led to an enormous research effort directed toward the synthesis of new polymeric materials. There have been commercial successes, and the field remains large and quite active today.[2-7]

Though acyclic diene metathesis (ADMET) polymerization (illustrated in Figure 3) represents another opportunity to use the olefin metathesis reaction to create polymers, relatively little effort has been focused on exploring this polymerization scheme. During the early 1970s Dall'Asta attempted the polymerization of 1,4-pentadiene,[8] and other studies were made by Doyle and Zuech without polymer being observed,[9,10] probably due to the presence of competing side reactions. Only oligomers were created by this approach, and the work was essentially stopped in the mid-1970s. Feast also reported the attempted acyclic diene metathesis polymerization of divinylbenzene to poly(phenylenevinylene) with no apparent success.[11]

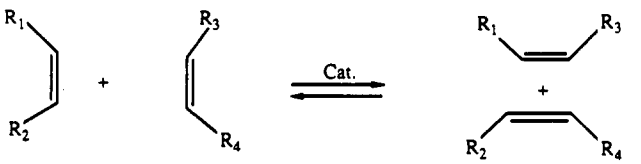

Figure 1. The metathesis reaction.

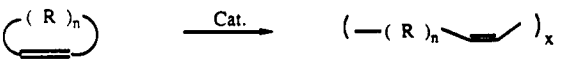

Figure 2. Ring-opening metathesis polymerization (ROMP).

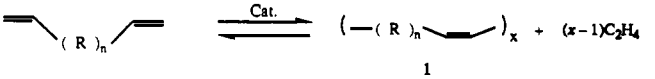

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Figure 3. Acyclic diene metathesis (ADMET) polymerization.

This paper reports the metathesis of acyclic dienes as a viable new method of polymer synthesis. Recent mechanistic studies of the olefin metathesis reaction have made it possible to design specific metal complexes as catalysts for the reaction. Acyclic diene metathesis (ADMET) polymerization now complements ring-opening metathesis polymerization, thereby broadening the scope of metathesis polymerization in general beyond monomers possessing ring strain. The success of ADMET requires the elimination of all competing side reactions,[12] thereby permitting acyclic diene metathesis to be the only reaction that occurs.

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Experimental Section

General Information. A Varian XL Series NMR superconducting spectrometer system was used to obtain 200-MHz ^1H NMR and 50-MHz ^{13}C NMR spectra. Chemical shifts are reported in parts per million downfield from the internal reference tetramethylsilane. Infrared spectral analysis was performed on a Perkin-Elmer 281 infrared spectrophotometer as KBr pellets. Ultraviolet spectroscopy was done with a Perkin-Elmer Lambda-9 UV/vis/NIR spectrometer with THF as solvent. Elemental analyses were done by Atlantic Microlab, Inc. (Norcross, GA). Mass spectroscopic data were obtained from a Finnigan 4600 gas chromatographic mass spectrometer. Differential scanning calorimetry data were obtained with the Perkin-Elmer 7 Series thermal analysis system. The instrument was calibrated by a two-point method using cyclohexane and indium. Dry argon was used as purge gas, and a scan rate of 10 °C/min was used.

Size-exclusion chromatograph data were obtained by a Waters Associates liquid chromatograph apparatus equipped with an RI detector. Tetrahydrofuran or toluene were used as solvent, and μ-Styragel columns covering the region of interest were employed. A constant flow rate of 1.04 mL/min was maintained and the instrument calibrated by using polybutadiene or polystyrene standards (Polysciences, Inc.) that covered the region of interest. Intrinsic viscosities were determined by an Oswald dilution viscometer at 25 °C with toluene as the solvent. A Wescan vapor pressure osmometer Model 233 was used for osmometry. Toluene was the solvent of choice at an operating temperature of 51 °C.

Purification of Monomers, Reagents, and Solvents. All chemicals were of high-grade purity (>98%). Due to the reactive nature of catalyst, all monomers, reagents, and solvents used in conjunction with these catalysts were of greater than 99% purity. In order to ensure absolute dryness and an oxygen-free atmosphere, all chemicals used were distilled, dried over calcium hydride for 24 h, degassed several times by freeze–pump–thawing cycles, and then vacuum transferred into a potassium-mirrored flask. The reagents were stirred over the mirror for 0.5 h and then vacuum transferred into break-seal ampules filled with the desired amounts of reagent frozen in liquid nitrogen and sealed under a 10^{-6} mmHg vacuum.

In cases where a reagent had impurities not removed by distillation or drying techniques, the reagent was allowed to react with a single aliquot (20 mg) of catalyst for 15 min, and then the purified reagent was vacuum transferred into a new break-seal and sealed under high vacuum. Allowing any impurities to react with catalyst (in effect destroying the catalyst) and then removing the remainder of the pure reagent from the reaction vessel proved effective for removing impurities that would otherwise poison the catalyst and prevent metathesis. *Without exception*, reagents purified by exposure to catalyst metathesized and produced only the expected products in high yields.

General Polymerization Procedure. Several acyclic diene metathesis (ADMET) polymerization reactions were explored on a vacuum line using a Lewis acid free catalyst and 1,9-decadiene or 1,5-hexadiene as the monomer. The catalyst, W(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)[OCMe$(CF_3)_2]_2$ (4; Figure 6) was prepared according to published procedures.[13] Aliquots of 20 mg of catalyst 4 were dissolved in 2 mL of pentane and transferred into a break-seal ampule in a drybox containing a nitrogen atmosphere and subsequently sealed under vacuum.

Break-seal ampules containing aliquots of the catalyst solution and the purified monomer were connected to the apparatus, which was designed specifically to perform these polymerizations (see Figure 4). Prior to all polymerizations, the entire apparatus was flame dried under high vacuum to remove all traces of oxygen and moisture.

All polymerizations were conducted by first transferring the catalyst solution from a break-seal ampule to the reaction vessel and then removing the solvent under reduced pressure. The monomer was introduced from its break-seal ampule directly into the reaction vessel containing the catalyst. Upon addition of the monomer, a gas was released, which was determined to be pure ethylene by GC mass spectrometry. Ethylene was continuously removed from the vessel and collected in a liquid-nitrogen trap that was built into the reaction vessel. The monomer also

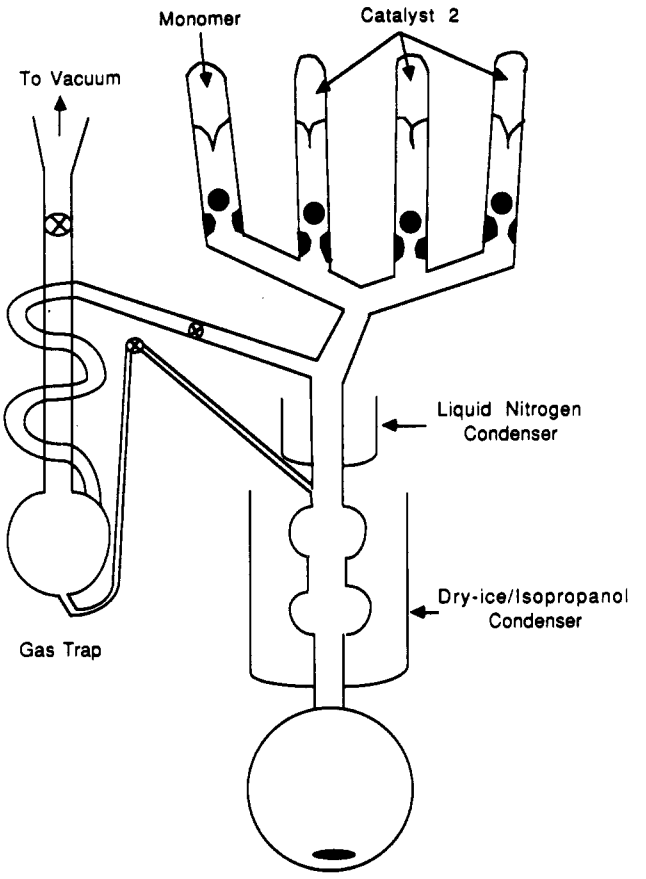


Figure 4. ADMET polymerization apparatus.

distilled in the process but was allowed to reflux with a partial condenser and returned to the reaction vessel.

All polymerizations were performed either by using carefully dried toluene as the solvent or under bulk conditions. The temperature of the reaction was varied between 20 and 65 °C. All polymerizations were terminated by exposure to the atmosphere.

The polymers were purified by dissolution in benzene and precipitation with methanol, giving white solids for the high molecular weight samples and soft elastomers for the oligomers.

Reaction Conditions for 1,9-Decadiene Polymerization. To optimize the reaction conditions for the acyclic diene metathesis polymerization of 1,9-decadiene, several different reactions were performed with the goal of obtaining high molecular weight polymer samples in the shortest possible reaction times. The optimal procedure involves starting the reaction with bulk monomer as solvent, allowing the polymerization to proceed until magnetic stirring is not possible, warming to 50 °C, and then adding enough solvent to dissolve the polymer. A typical procedure is described below.

The reaction vessel was fitted with a magnetic stir bar and evacuated on a high-vacuum line. A solution of catalyst (20 mg, 0.029 mmol) in ca. 2 mL of pentane was added to the reaction vessel via break-seal ampule, and pentane was removed under vacuum, leaving a solid catalyst residue. The monomer, 1,9-decadiene (2.0 mL, 1 mmol), was added to the reaction vessel via a second break-seal ampule. There was vigorous evolution of a gas (ethylene) when the monomer dissolved the catalyst, and the reaction was continued until stirring was no longer possible due to the viscosity of the reaction mixture. The temperature then was raised to 50 °C, and when the polymer solidified, 10 mL of toluene was added along with another aliquot of catalyst (20 mg, 0.025 mg) at 25 °C. The reaction temperature was raised to 50 °C over a period of 6 h, and a third aliquot of catalyst was added. The reaction was allowed to continue for an additional 24 h at 50 °C. The reaction vessel was then opened to the air and the polymer precipitated by the addition of methanol. Anal. Calcd for $(C_8H_{14})_x$: C, 87.27; H, 12.73. Found: C, 87.11; H, 12.68. Molecular weight: $\bar{M}_n$, 57 000 (SEC); $\bar{M}_w$, 108 000 (SEC).

Further Polymerization of an Existing Polymer. A sample of poly(octenylene) (1 g, $\bar{M}_n$ = 11 000; IV = 0.26 dL/g) was

dissolved in 20 mL of toluene, syringed into the reaction vessel, and degassed by using four freeze–thaw–vacuum cycles. The reaction vessel was evacuated, and a solution of catalyst (20 mg, 0.025 mmol in 2 mL of pentane) was added from a break-seal ampule. The mixture was heated slowly to 65 °C. The ethylene that was evolved was collected as described above, and after 36 h the reaction was terminated by exposure to air. The product was precipitated by addition of methanol. Anal. Calcd for $(C_8H_{14})_x$: C, 87.27; H, 12.73. Found: C, 87.18; H, 12.69. Molecular weight: $\bar{M}_v$ = 83 000; IV = 0.76 dL/g.

Reaction Conditions for 1,5-Hexadiene Polymerization. A solution of the catalyst (20 mg, 2.5×10^{-5} mol) in 2 mL of hexane was transferred into an evacuated flask from a break-seal ampule, and then the hexane was removed under reduced pressure, leaving a residue of solid catalyst. The monomer (1,5-hexadiene, 5 mL, 6.0×10^{-2} mol) was introduced into the flask from a separate break-seal ampule, which resulted in an instantaneous, reaction producing ethylene as the only observable gaseous product. High vacuum was applied to the reaction mixture periodically to remove the ethylene.

After the polymerization proceeded to the extent that the reaction medium became too viscous to be stirred in the bulk state, 50 mL of dry toluene was added to the reaction vessel. The reaction was stirred continuously, and high vacuum was applied periodically. A second addition of catalyst (20 mg) was made, and the reaction allowed to continue at ambient temperature for several hours; the reaction was terminated by opening it to the atmosphere. The product was precipitated from solution by the addition of methanol. Anal. Calcd for $(C_4H_6)_x$: C, 88.8; H, 11.2. Found: C, 88.6; H, 11.2. Molecular weight: $\bar{M}_n$, 8300 (SEC); $\bar{M}_w$, 16 400 (SEC).

A second set of polymerizations was conducted under similar initial conditions with only one addition of catalyst. Bulk polymerization conditions were maintained by heating the reaction mixture to 52 °C. A continuous high vacuum was applied until the reaction mixture became too viscous to stir (ca. 5 h). The reaction was terminated by exposure to the atmosphere, and the resultant polymer was dissolved in benzene and precipitated by the addition of methanol. Anal. Calcd for $(C_4H_6)_x$: C, 88.8; H, 11.2. Found: C, 88.5; H, 11.2. Molecular weight: $\bar{M}_n$, 14 000 (SEC); $\bar{M}_w$, 28 000 (SEC).

Results and Discussion

Mechanism of Polymerization. Acyclic diene metathesis (ADMET) polymerization is an inherently more complicated process than the ring-opening metathesis (ROMP) reaction. An example of an acyclic diene metathesis polymerization mechanism as catalyzed by a metal alkylidene complex is shown in Figure 5, in which the reaction sequence shown is the simplest set of steps leading to a productive metathesis polymerization of 1,9-decadiene to give poly(octenylene). Some of the salient features of this mechanism include the following:

1. Ethylene is produced.
2. Two metallacyclobutane intermediates are present in each propagation step, rather than one as in ROMP.
3. The newly formed oligomer must dissociate from a metallacyclobutane intermediate, giving a methylene complex as an intermediate.
4. The association of the oligomer via a terminal olefin generates a second metallacycle from which ethylene can dissociate, giving an alkylidene attached to the growing polymer chain as an intermediate.

Because all of the steps in the above reaction are equilibria and because ethylene is a product of the reaction, the overall polymerization can be driven by the removal of ethylene from the system, and thus, by definition, this is a step propagation condensation type polymerization, which should produce a molecular weight distribution of 2.0. The success reported herein in metathesizing 1,9-decadiene and 1,5-hexadiene to high polymer by performing the reaction under high vacuum demonstrates

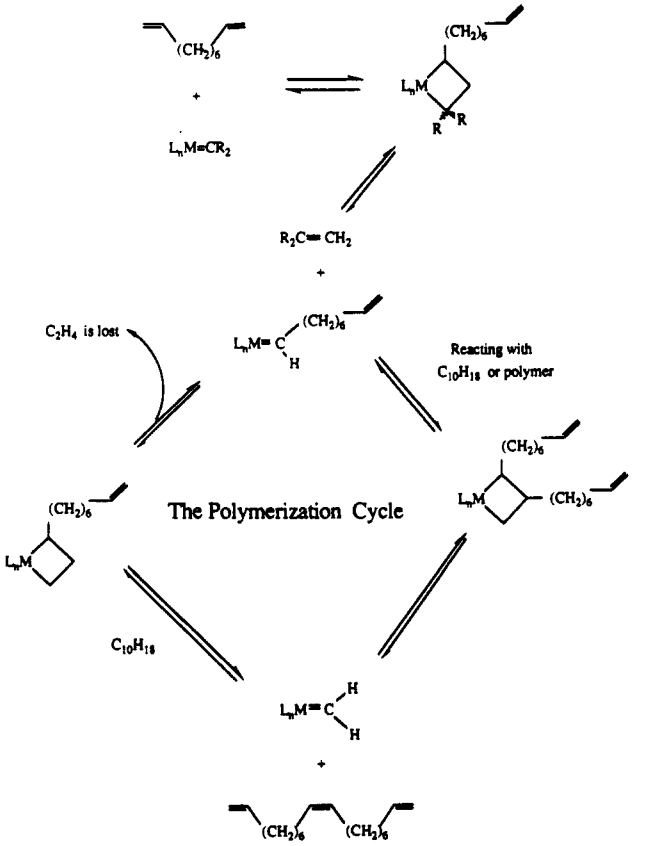


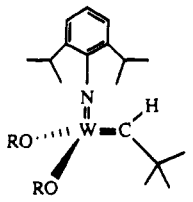
Figure 5. Acyclic diene metathesis chemistry illustrated with 1,9-decadiene.

the viability of this approach to polymer synthesis. Ethylene is produced during the entire course of the reaction, and high molecular weight polymers are not found immediately, which is consistent with a step rather than a chain polymerization mechanism. Further, the molecular weight distribution for all polymers found in this research is in the range of 1.9–2.1. Thus, polymerization by first forming rings is unlikely.

This mechanism, like all step polymerization mechanisms, requires essentially complete conversion of reactants for high molecular weight products to form. All other reaction possibilities must be excluded, which in fact can be realized by choosing a Lewis acid free catalyst. The key point appears to be obviation of cation formation.[12] The polymerizations described below demonstrate that the polymerization cycle shown in the mechanism can be repeated on average up to 500 times without interruption.

Rationale behind Catalyst Selection. The significance of successful acyclic diene metathesis polymerization is noteworthy, since the demands in any equilibrium step propagation condensation type polymerization are stringent, and while literally hundreds of reactions have been considered during the past 50 years as potential polycondensation reactions, very few have successfully satisfied the criteria for polycondensation chemistry.[14] It now appears that acyclic diene metathesis polymerization is one of them.

The preparation of poly(octenylene) via the polycondensation of 1,9-decadiene was selected as a model polymerization, since the polymer is already known.[15–24] Consequently, it has been possible to examine the details relevant to successful ADMET polymerization rather than having to characterize an unknown polymer. Also, poly(octenylene) is a commercial polymer, and alternate routes to its synthesis are of interest. Initial attempts at the synthesis of poly(octenylene) or 1,4-polybutadiene via AD-



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R = t-Bu; CMe_2CF_3; $CMe(CF_3)_2$; $C(CF_3)_2CF_2CF_2CF_3$

Figure 6. Lewis acid free catalyst structure for ADMET polymerization.

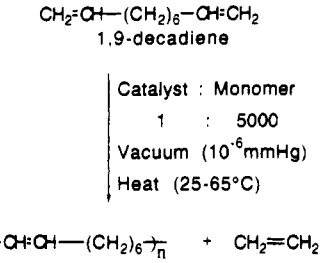

Figure 7. ADMET polymerization of 1,9-decadiene.

MET of 1,9-decadiene or 1,5-hexadiene using the "classical" $WCl_6/EtAlCl_2$ catalyst, though encouraging, ultimately failed due to catalyst deficiencies. It was apparent that $WCl_6/EtAlCl_2$ catalyzed vinyl addition cross-linking reactions as well as the desired metathesis reaction.[25] Furthermore, the actual catalytically active species were (and remain) unknown. The stringent requirements for a successful polycondensation reaction led to a search for well-defined catalysts that do not contain strong Lewis acids (to decrease the probability of vinyl addition) and whose well-defined structure would limit the formation of multiple catalytic sites.

The family of tungsten alkylidene complexes 1 in Figure 3 is a likely candidate as potential catalysts for this reaction since they have been shown to be active metathesis catalysts by Schrock.[13] Complex 4 (Figure 6) has been used by both the Schrock and Grubbs research groups to catalyze the living ring-opening metathesis polymerization of cyclic olefins, yielding uniformities approaching 1.0.[26-28] These results strongly suggest that only one type of catalyst site is present during the reaction. Since the compounds 4 do not contain strong Lewis acid centers, it was believed that they would not catalyze competing vinyl addition reactions.

Studies using styrene as a model substrate proved that 4 was effective in metathesizing a substrate that is readily disposed to undergo vinyl addition chemistry. These same studies confirmed that 4 is the most active catalyst of the series and, because only metathesis chemistry was observed,[12] indicated that 4 was the catalyst of choice for ADMET polymerization chemistry. Thus, 4 has been used exclusively in the synthesis of the polymers reported herein.

Poly(octenylene) Synthesis. The synthesis of poly(octenylene) was accomplished in a straightforward manner using vacuum-line techniques, with the reaction conditions as illustrated in Figure 7. The polymerization was accomplished under bulk conditions at room temperature until a change of state (from liquid to solid) was observed. The temperature of the reaction was subsequently increased to maintain the liquid state up to a temperature of approximately 50 °C. At this point, a small quantity of solvent was added in order to maintain the liquid state, and the polymerization was continued under these conditions. An apparent increase in viscosity was observed over a period of 12 h, and the polymerization was terminated after no further increase in viscosity was observed. The gas that evolved was collected in a liquid-nitrogen-cooled flask, and its composition was determined by GC mass spectrometry. Only ethylene was found.

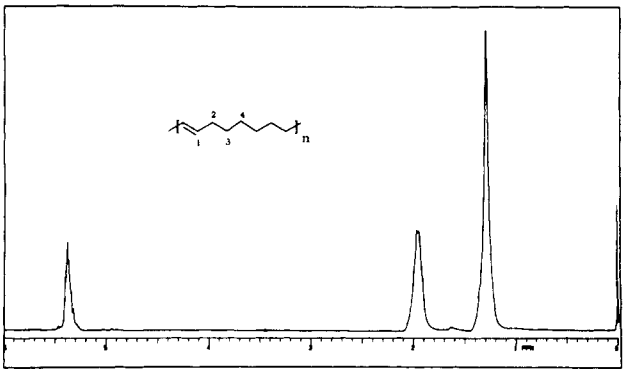

Figure 8. 200-MHz ^1H NMR of linear poly(octenylene) produced by ADMET polymerization of 1,9-decadiene.

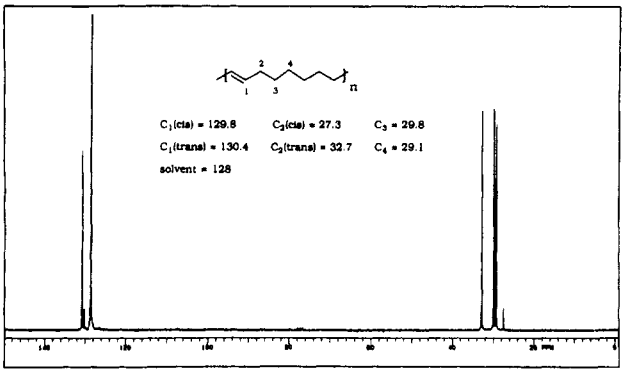

Figure 9. 50-MHz ^{13}C NMR of linear poly(octenylene) produced by ADMET polymerization of 1,9-decadiene.

Structure determination of the polymer was done by NMR spectroscopy (Figures 8 and 9) in comparison with the known spectra for poly(octenylene).[18] The 200-MHz proton NMR spectrum illustrates the purity of the polymer and exhibits the correct integration for the sp^2 and sp^3 protons present in the repeat structure. The carbon NMR spectrum provides proof of structure in that all resonances can be unequivocally assigned. It is particularly important to note that no evidence of vinyl addition chemistry is apparent in these NMR spectra. Since vinyl addition reactions have been shown to be the principle competing reaction in previous attempts to employ ADMET polymerization chemistry,[25] these NMR results confirm the hypothesis that proper catalyst selection is necessary for the success of this reaction.

It is also important to note that the poly(octenylene) formed by ADMET polymerization appears to be more than 90% trans based on NMR assignments.[18] It is possible to distinguish between both the cis and trans internal sp^2 carbons from the ^{13}C NMR, as well as for the allylic carbon adjacent to the internal vinyl position. The internal cis olefinic carbon appears at 129.8 ppm, and the trans internal olefinic carbon appears at 130.4 ppm. Katz[18,29] has shown that the carbon atom adjacent to the internal olefinic carbon also has two different resonances, i.e., the cis carbon at 27.3 ppm and the trans carbon at 32.7 ppm. A direct correlation between the peak intensities of these allylic carbon resonances and those of the internal vinyl carbons corroborates the assignments of the percentage trans stereochemistry for specific polymer samples. Infrared spectroscopy was also used to assign the percent trans stereochemistry present, and Figure 10 illustrates

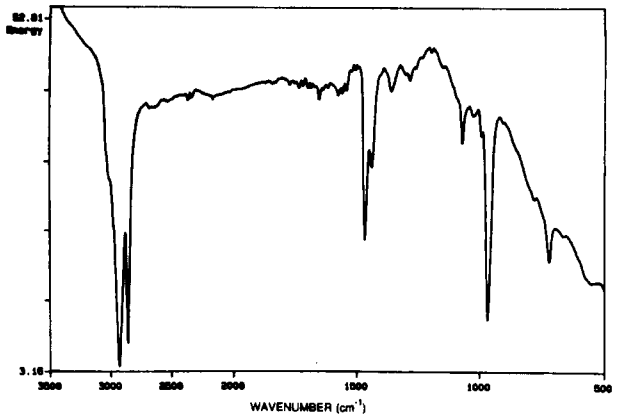

Figure 10. Infrared spectrum of linear poly(octenylene) produced by ADMET polymerization of 1,9-decadiene.

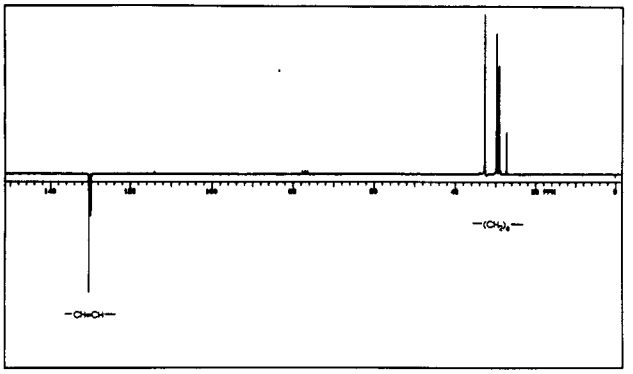

Figure 11. 50-MHz ^{13}C NMR (attached proton test) of low molecular weight poly(octenylene) produced by ADMET polymerization of 1,9-decadiene.

the FTIR spectrum of the polymer produced by ADMET polymerizations. The typical poly(octenylene) sample has two absorption bands of 1404 and 970 cm^{-1}, arising respectively, from the in-plane bending of the cis olefin unit and the out-of-plane deformation of the trans olefin unit.

It is particularly important to note how selective the metathesis chemistry is in the conversion of 1,9-decadiene to poly(octenylene). In addition to the NMR spectra that have been shown, mass spectrometry data suggest that no ring formation is apparent once the polymerization is complete, and, thus, the reaction produces only high molecular weight poly(octenylene) and ethylene as a byproduct. An attached proton test carbon NMR spectrum (Figure 11) of an oligomer shows that resonances are present that are identical with those for the high molecular weight polymer shown previously, in addition to two other sp^2 resonances, which can be assigned to the vinyl end groups present in the polymer. This spectrum shows that the end groups of the polymer are well-defined, an observation that can be corroborated by molecular weight determination using quantitative ^{13}C NMR as an end-group analysis technique.[30] A number-average molecular weight of 11 000 is observed for this oligomer, which is in good agreement with the value (12 000) determined by vapor pressure osmometry ($\bar{M}_n$ = 12 000). ADMET polymerization produces very clean polymers with well-defined end groups.

These poly(octenylene) oligomers can be converted to high polymer ($\bar{M}_n$ = 57 000; $\bar{M}_w$ = 108 000; $\bar{M}_w/\bar{M}_n$ = 2.1) by further condensation under vacuum, or monomer can be taken directly to high polymer under high vacuum. Continued polymerization can be observed in the solid state as well so long as a high vacuum is maintained.

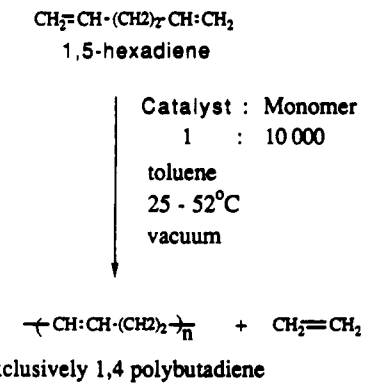

Figure 12. Hexadiene polymerization.

1,4-Polybutadiene Synthesis. With the procedures described above, it is also possible to polymerize 1,5-hexadiene to exclusively 1,4-polybutadiene. This approach is distinctly different from conventional chain polymerization methods for polybutadiene synthesis.[31] Normally, the monomer used in these chain polymerizations is 1,3-butadiene, a conjugated diene capable of undergoing both 1,2- and 1,4-addition reactions,[32] leading to cis- and trans-1,4-addition repeat units plus (*R*)- and (*S*)-1,2-addition repeat units.

While the relative amount of each repeat unit present is dependent on the reaction conditions and polymerization techniques used, the mechanism of any conjugated vinyl addition chain polymerization suggests that all three possible repeat units could be present, at least to some degree. It is debatable whether perfectly linear, perfectly 1,4-polybutadiene has ever been produced by chain techniques, though researchers have reported that samples without the presence of 1,2-vinyl linkages have been made.[33-36] The physical properties of any given polybutadiene sample depend upon the ratio and distribution of these repeat units, and, consequently, the polymerization of 1,5-hexadiene was conducted in order to control the number and types of repeat units present and ultimately to produce stereochemically pure polymers.

Generally, organoalkali initiation in hydrocarbon solvents yields polybutadiene containing 35–50% *trans*-1,4-olefin, 6–35% *cis*-1,4-olefin, and 13–60% 1,2-vinyl repeat units.[37] If THF is used as a solvent, the polymer that is produced contains 87% 1,2-vinyl units.[38] Numerous other initiators and solvent systems exist, and the percentage of 1,2-vinyl units can be minimized.[38] In contrast to this situation, acyclic diene metathesis (ADMET) polymerization proceeds through a polymerization mechanism that completely eliminates the possibility of forming 1,2-vinyl repeat units, and, thus, 1,5-hexadiene should produce perfectly linear polybutadiene without the presence of any 1,2-linkages.

It is well-known that the ring-opening polymerization of 1,5-cyclooctadiene[4,39-41] or cyclobutadiene[18,29,42,43] produces perfectly linear 1,4-polybutadiene. The polymers produced via ROMP reactions have variable stereochemistry depending upon the catalyst system used, whereas polymer synthesized using ADMET chemistry as reported below has a high trans content. The observation that 1,5-hexadiene can be polymerized by ADMET techniques provides further evidence for the viability of metathesis polycondensation (ADMET) chemistry.

The reaction conditions that were used for the ADMET polymerization of 1,5-hexadiene are summarized in Figure 12. When the compound W(CH-*t*-Bu)(N-2,6-*i*-PrC_6H_3)-[$OCCH_3(CF_3)_2$]$_2$ was used to catalyze the ADMET polymerization of 1,5-hexadiene, only two products were

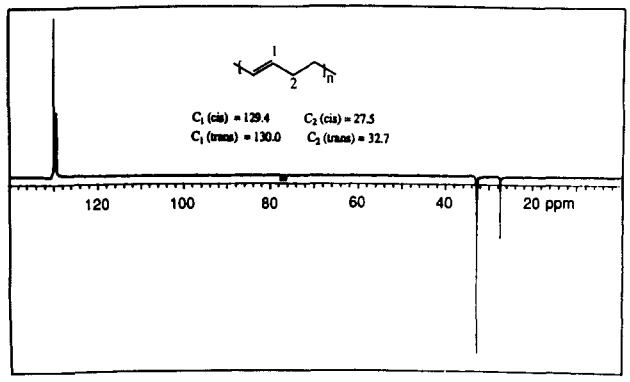

Figure 13. Polybutadiene ^{13}C NMR.

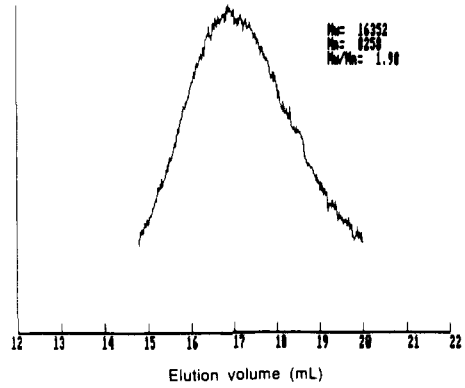

Figure 14. SEC curve for exclusively 1,4-polybutadiene.

formed, poly(1,4-butadiene) and ethylene. This polymerization is reproducible and leads to polymers as characterized below.

Polymerizations were done initially in bulk at room temperature, followed by the addition of the minimum amount of solvent, toluene, to maintain the liquid state; otherwise, the reaction mixture forms the solid state, which considerably decreases the reaction rate. Further, all hexadiene polymerizations were taken to the highest molecular weight possible, where molecular weights were limited not by reaction chemistry but instead by practical constraints. Agitation was provided by a magnetic stirring bar, which in fact became motionless on a significant increase in the viscosity of the reaction medium. There is little question that higher molecular weights could be achieved. The polymer produced from this monomer is completely soluble in aromatic or chlorinated hydrocarbon solvents, quite unlike the material obtained from the polymerization of 1,5-hexadiene with the $WCl_6/EtAlCl_2$ catalyst system.[25]

Figure 13 shows the ^{13}C NMR spectrum (run in APT mode) of exclusively 1,4-polybutadiene produced using the reaction conditions specified above. The spectrum has resonances only attributable to *cis*- and *trans*-poly(1,4-butadiene), where the trans and cis internal olefins appear at 130.0 and 129.4 ppm while the methylene groups adjacent to the cis and trans olefin groups appear at 27.5 and 32.7 ppm, respectively. Most importantly, there is no evidence for poly(1,2-butadiene) (resonances at 144, 114, 39.1, 35.0, 30.9 ppm) or cross-linked products (which give rise to positive peaks in the aliphatic carbon region of the spectrum). A trans content of ca. 75% is present as determined by quantitative ^{13}C NMR spectroscopy, a value close to the thermodynamically expected value for poly(1,4-butadiene),[44] a situation similar to the thermodynamically dictated results obtained from the studies of poly(octenylene) synthesized using ADMET chemistry (poly(octenylene) is 92% trans when in thermodynamic equilibrium). The cis/trans ratio also is evidence that the reaction proceeds via an equilibrium process since the catalyst should isomerize the double bonds in the polymer chain as well as cause the growth of the polymer chain via metathesis chemistry.

A typical SEC curve for exclusively 1,4-polybutadiene is shown in Figure 14. A polydispersity of approximately 2 exists (actual value is 1.98) as is expected for an equilibrium step propagation, condensation polymerization, and this polydispersity is in marked contrast to that for ring-opening metathesis polymerizations (ROMP), which has been shown to be living, with polydispersities approaching 1.0.

Complete Determination of the Molecular Weights of the Poly(octenylene) Samples Produced by Acyclic Diene Metathesis Polymerization. Several mathematical relationships exist that correlate the physical properties of a polymer sample with its influence on the molecular weight of a sample.[45] The viscosity molecular weight (eq 1) is one such relationship that corrects for the

$$\ln [\eta] = \ln K + a \ln [\bar{M}_v] \quad (1)$$

changes in physical properties by using the Mark–Houwink–Sakurada constants, "K" and "a". Without these constants, only relative molecular weight comparisons can be made between different samples of the same type of polymer. Consequently, it is important to know the Mark–Houwink–Sakurada constants for any polymer. These constants, which were unknown for poly(octenylene), have been determined in the course of this work. Several methods exist for the determination of the molecular weight of a polymer sample. By employment of different molecular weight determination techniques, values for the K and a were calculated for poly(octenylene) samples having molecular weights in the range 10^3–10^5.

Since the Mark–Houwink–Sakurada constants of poly(octenylene) at 25 °C using toluene as solvent were unknown, the measured intrinsic viscosities could not be converted to molecular weights by using eq 1. Estimated Mark–Houwink–Sakurada constants were calculated from the molecular weights determined by NMR end-group and/or vapor pressure osmometry analysis for polymers produced in two separate experiments. The molecular weights needed for these calculations were determined as described below.

As mentioned previously, it is possible to detect the vinyl end groups of low molecular weight poly(octenylene) samples produced by acyclic diene metathesis polymerization by ^{13}C NMR spectroscopy, and consequently number-average molecular weights ranging from 1700 to 11 000 were determined by ^{13}C NMR end-group analysis for ADMET poly(octenylene). This opportunity does not always exist in ring-opening metathesis polymerization since ROMP polymers often possess an unknown chain-capping group on the termination end and the alkylidene ligand, initially present on the catalyst, on the initiated end.

In order to verify these number-average molecular weights obtained by end-group analysis, the molecular weights of poly(octenylene) samples produced in two separate experiments were also determined by vapor pressure osmometry. Sucrose octaacetate (MW = 678.6) was used to calibrate the vapor pressure osmometer at 51 °C by using toluene as solvent, and a calibration factor K of 6705 was obtained, which is in good correlation with the value of 6510 reported by the manufacture of the instrument. A number-average molecular weight of 12 000 was obtained for one sample, which was in excellent agreement

with the value of 11 000 found by NMR end-group analysis. A second polymer sample produced a VPO value of 25 000.

The most widely used method of determining the Mark–Houwink–Sakurada constants employs very narrow molecular weight fractionated polymer samples,[46] where molecular weight is determined by using absolute methods such as light scattering or osmometry. Fractionation is done to ensure very narrow molecular weight uniformity ($\bar{M}_w/\bar{M}_n = 1$, for which $\bar{M}_w = \bar{M}_n = \bar{M}_v$ provides a good approximation). The light-scattering molecular weight ($\bar{M}_w$) or osmometry molecular weight ($\bar{M}_n$) can be used to solve the viscosity molecular weight (eq 1) since these molecular weights are virtually equivalent when the polydispersity ratio approaches unity.

One important class of polymers that constitutes an exception to the restriction of narrow molecular weight distribution consists of linear polyamides and polyesters polymerized under equilibrium conditions. For equilibrium condition samples the molecular weight uniformities are always random and eq 2 can be applied.[46] For this

$$[\eta] = K\bar{M}_n^a \tag{2}$$

group (in which $\bar{M}_w = 2\bar{M}_n$), whole polymer samples can be used in calculations.

Acyclic diene metathesis polymerization is an example of an equilibrium polymerization and thus should lead to a molecular weight distribution of 2.0; the poly(octenylene) samples produced by acyclic diene metathesis polymerization fall into the category of equilibrium polymers, and thus eq 2 can be applied. Mark–Houwink–Sakurada constants are not strictly independent of the molecular weight range over which they are determined. Oligomers (less than about 100 repeating units in most vinyl polymers) often conform to eq 3, where K and the exponent a are

$$[\eta] = K\bar{M}_v^{0.5} \tag{3}$$

independent of the solvent.[46] Since solvent independence is assumed, i.e., a Θ solvent, the a value for the ideal statistical coil is 0.5 and applies to these oligomers.

Absolute molecular weights of poly(octenylene) samples produced in two acyclic diene metathesis polymerizations were determined. The intrinsic viscosities of both polymer samples and Mark–Houwink–Sakurada constants for poly(octenylene) were calculated by using eq 1. A K value of 1.46×10^{-3} and an exponent a of 0.552 were obtained from these calculations. Both polymers fall in the 10^3–10^5 molecular weight range, which is above the lower limit of calibration (100 repeating units). A value of close to 0.5 but slightly higher is expected since approximately ideal chain behavior is realistic for this molecular weight range in a good solvent.

Reduced viscosities of the poly(octenylene) samples of higher molecular weight were determined by viscometry. Size-exclusion chromatography was also done to determine molecular weight and the uniformity of ADMET polymer samples. A three-point calibration curve was constructed by using polystyrene standards dissolved in toluene at room temperature. The polymer that formed when a minimal amount of solvent was used was determined to have a $\bar{M}_w$ = 239 000 and $\bar{M}_n$ = 127 000 according to polystyrene calibration. These are not poly(octenylene) molecular weights and had to be converted. The universal calibration curve (eq 4) proposed by J. V. Dawkins[47,48]

$$\log M_p = \log M_{ps} + \log A_{ps}/A_p \tag{4}$$

was used to convert the above molecular weight values to actual poly(octenylene) molecular weights. These "polystyrene" molecular weights can be converted to poly(octenylene) molecular weights by multiplying by 0.45,[49] which represents the estimated ratio of the unperturbed dimensions ($A = \langle L_0^2 \rangle / M$) for polystyrene divided by that of poly(octenylene). Thus, the actual molecular weights of this poly(octenylene) sample are $\bar{M}_w$ = 108 000 and $\bar{M}_n$ = 57 000. Molecular weights of this order of magnitude confirm that high molecular weight poly(octenylene) can be produced by acyclic diene metathesis polymerization. The polyuniformity of the sample is 1.89, indicating that the sample was produced by a step propagation type polymerization.

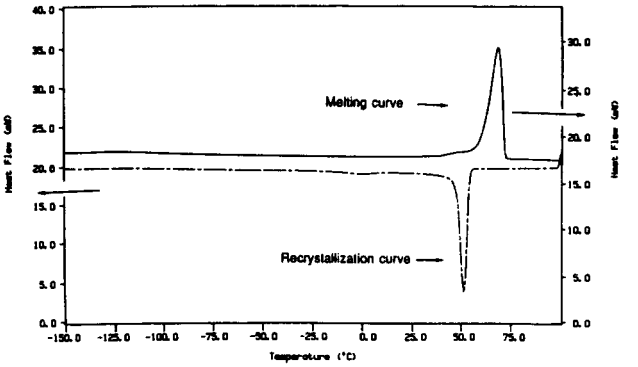

Figure 15. Differential scanning calorimetry data of linear poly(octenylene) produced by ADMET polymerization of 1,9-decadiene.

Thermal Behavior of Poly(octenylene) Produced by ADMET Polymerization. Poly(octenylene) produced by ring-opening metathesis polymerization is an elastomer with a trans content of between 60 and 80% and with crystals that melt between 50 and 55 °C. With this information as a point of reference, the thermal behavior of the poly(octenylene)s generated by ADMET polymerization was examined by differential scanning calorimetry. Figure 15 displays the DSC scan for an ADMET poly(octenylene) possessing more than 90% trans stereochemistry. First, the sample exhibits crystalline behavior, melting close to 70 °C and recrystallizing at ca. 50 °C. This melt/recrystallization behavior is reversible, and because of the high crystalline content of these polymers, they are not elastomers but instead would be regarded as plastics. The high trans content in ADMET poly(octenylene)s appears to be a function of contact time of the polymer with the catalyst, and it is possible to generate a series of polymers with different trans contents as a function of reaction time.

Calderon was the first to recognize the linear relationship between melting point and percent trans olefinic units present in poly(octenylene)s.[50] He predicted that 100% trans poly(octenylene) would exhibit a melting point of 73 ± 2 °C via eq 5. Flory[51] illustrated that this equation

$$1/T_m - (1/T_m^\circ) = -(R/\Delta H_u) \ln N_T \tag{5}$$

applies to the melting points of copolymers having randomly placed repeat units of the type T, which crystallize, and type C, which do not crystallize, where N_T is the mole fraction of the repeat units of type T, T_m° is the melting point where $N_T = 1$; T_m is the melting point for any given value of N_T; H_u is the heat of fusion per mole of repeat unit of type T, and R is the universal gas constant. In this case, a random distribution of crystallizable trans olefinic units and noncrystalline cis olefinic units for the poly(octenylene)s is assumed.

Table I
Melting and Crystallization Temperatues of Poly(octenylene) Samples Prepared by Means of Acyclic Diene Metathesis Polymerization, Listed with the Percent Trans Stereochemistry of Every Sample

reaction	% trans	mp, °C	crystallizn point, °C
1	77	52.0	31.6
2	80	55.7	36.8
6	85	57.1	41.7
5	88	63.5	44.2
8	90	66.3	52.3
7	91	67.6	54.1
4	93	69.2	56.8

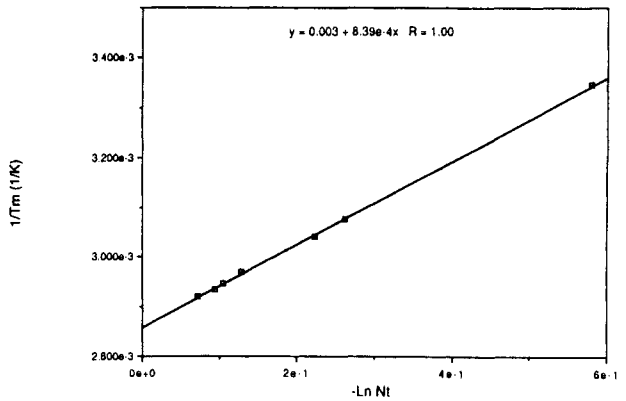

Figure 16. Linear relationship between $1/T_m$ and $-\ln N_T$ for elucidation of the melting point of 100% trans poly(octenylene).

ADMET poly(octenylene) also exhibits a linear relationship between melting point and percent trans olefinic units. Data obtained for seven different polymerizations is presented in Table I. Using eq 5 after plotting $1/T_m$ vs $-\ln N_T$, we obtain a $T_m°$ of 77 ± 1 °C calculated from the intercept of the line shown in Figure 16, which is 4 °C higher than what was predicted by Calderon. This difference can be attributed to limitations in the accuracy of the infrared and proton NMR methods and most probably does not reflect a difference in polymer properties. Integration of quantitative ^{13}C NMR signals separated by 5 ppm (this work), as opposed to infrared extinction coefficients of peaks masked by strongly absorbing adjacent peaks or ^1H NMR decoupled spectra in which no base-line separation between integrated peaks occurs (prior work), should be more accurate in assigning the percentage trans stereochemistry present in these polymers.

The recrystallization temperature of poly(octenylene) can also be related to the percent trans stereochemistry of the polymer, an observation not made before. Recrystallization temperatures of poly(octenylene) produced by acyclic diene metathesis are independent of their thermal histories, and thus it is possible to predict recrystallization temperatures relative to the percentage trans stereochemistry of the sample. This is in contrast with the recrystallization temperatures of ring-opening metathesis polymerization poly(octenylene), which exhibit dependence on previous thermal history[50] due to low percent trans stereochemistry. The variations in recrystallization temperatures previously made it impossible to predict recrystallization points relative to percentage trans stereochemistry for ROMP poly(octenylene) samples.[50]

By differential scanning calorimetry, it was possible to accurately determine the recrystallization temperatures of samples produced by acyclic diene metathesis polymerization. Using eq 1 and plotting $1/T_{rc}$ vs $-\ln N_T$, we established a linear relationship between the two variables. From the intercept of the linear relationship (Figure 17)

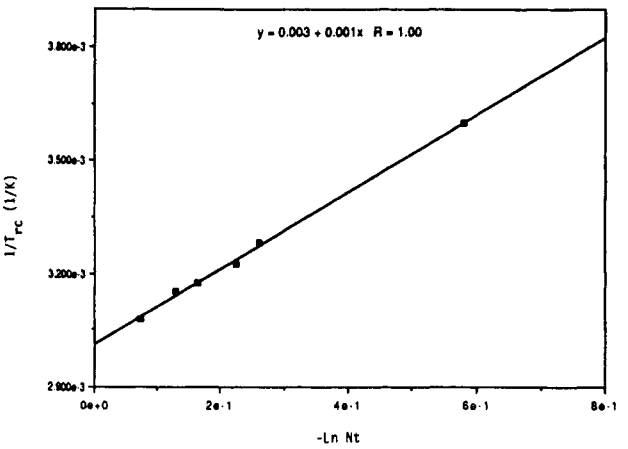

Figure 17. Linear relationship between recrystallization temperature and trans content $1/T_{rc}$ and $-\ln N_T$ for elucidation of the recrystallization point of 100% trans poly(octenylene).

a recrystallization temperature of 58 ± 2 °C for trans poly(octenylene) can be predicted.

Conclusions

Acyclic diene metathesis (ADMET) polymerization is a reality and can produce high molecular weight polymers at room temperature. The opportunities for broadening this synthetic procedure are enormous, possibly leading to polymers with chiral centers, a high electrical conductivity, a high degree of rigidity, or a high flexibility. Limitations appear to be catalyst oriented in nature, since the catalyst is influenced by the presence of polar groups, as is the case for Ziegler–Natta chemistry.

We plan to investigate alternative catalyst structures in terms of their ruggedness, to explore the kinetics involved in this reaction, to show unequivocally that the reaction is equilibrium step polymerization chemistry, and to broaden the synthetic technique as much as possible.

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Registry No. 4 (R = $CMe(CF_3)_2$), 101249-40-5; $CH_2{=}CH(CH_2)_6CH{=}CH_2$, 1647-16-1; $CH_2{=}CH(CH_2)_6CH{=}CH_2$ (homopolymer), 108793-14-2; $CH_2{=}CH(CH_2)_6CH{=}CH_2$ (SRU), 28702-45-6; $CH_2{=}CH_2$, 74-85-1; $CH_2{=}CH(CH_2)_2CH{=}CH_2$, 592-42-7; $CH_2{=}CH(CH_2)_2CH{=}CH_2$ (homopolymer), 25067-96-3; $CH_2{=}CH(CH_2)_2CH{=}CH_2$ (SRU), 25038-44-2.