

Synthesis and Catalyst Issues Associated with ADMET Polymerization

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Abstract: Acyclic diene metathesis (ADMET) is a flexible approach for the production of diverse polymeric materials. The advent of well-defined catalysts and the simplification of laboratory techniques has made the ADMET reaction useful for many applications, such as polyolefin model studies and the synthesis of organic/inorganic hybrid polymers, telechelics, copolymers, conjugated polymers, liquid crystalline polymers, and amino acid-based chiral polymers. Many of the polymer architectures that have been produced using ADMET cannot be made by other means.

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1 Introduction

The phenomenon of olefin metathesis has been known for half of a century, but it was not until recently, concurrent with the discovery of well-defined catalysts, that the acyclic diene metathesis (ADMET) reaction could be utilized to make high molecular weight polymers. The term “olefin metathesis” was coined by Calderon in 1967,^[1–7] and refers to a reaction in which the carbon atoms between a pair of double bonds are interchanged.^[8] The chemistry, however, dates back to the discovery of transition metal catalysts for olefin polymerization by Ziegler and Natta in the late 1940's.^[9,10]

In the mid-1950's, olefin metathesis reactions were observed by several research groups using Ziegler–Natta-type catalysts,^[11–13] but most of these early metathesis catalysts involved multi-component systems that were ill-defined, so the identity of the active catalyst and the reaction mechanism were unknown. Proof that the alkene double bond is broken and reassembled by the active catalyst did not exist until Dall'Asta reported detailed labeling studies in the early 1960's.^[14–16] Due to

the nebulous nature of the active catalyst, the mechanism of the reaction remained unknown until 1970, when Chauvin proposed that the key step in the reaction involves the formation of a metallocyclobutane ring intermediate from a metal carbene and an alkene.^[5,17–21] Although not universally accepted at first, this mechanism eventually led to the rational design of more well-defined catalyst complexes and a better understanding of structure-activity relationships, without which the ADMET reaction could not have been extensively developed. It is instructive to summarize the advancements in metathesis catalyst design that led to the discovery of ADMET polymerization, before we discuss the chemistry and utility of the ADMET reaction itself.

1.1 History of Metathesis Catalysts

Today, olefin metathesis has a variety of diverse applications, which stem from the mechanistically related reactions shown in Figure 1. These reactions include: ring-opening metathesis (ROM), ring-closing metathesis (RCM), ring-opening metathesis polymer-

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Cameron Church received her B. S. degree from the College of Charleston in South Carolina in 1996. She completed her graduate studies in polymer chemistry at the University of Florida in 2001, and presently is teaching chemistry at Lander University in Greenwood, SC. Her research interests lie in organosilicon chemistry, particularly related to metathesis routes to carbosilane polymers.



John Schwendeman received his B. S. degree in chemistry from Penn State University, the Behrend College in 1997, then joined the Wagener Research Group at the University of Florida. He will be completing his Ph. D. in polymer chemistry in 2002. His research interests revolve about creating well-defined polymer structures using metathesis chemistry in order to better understand crystallization behavior.

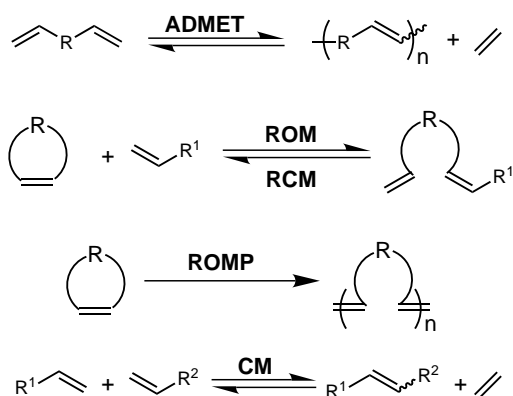


Figure 1. Various metathesis reactions.

ization (ROMP), cross-metathesis (CM), and ADMET polymerization. The development of these diverse reactions and their applications closely parallels the advancements in metathesis catalyst design. Until the early 1980's, the use of olefin metathesis was limited by the ill-defined, multi-component catalysts that were available. In general, these "classical" catalyst systems were composed of an early transition metal halide, such as WCl_6 , and an alkylating agent, such as Bu_4Sn or EtAlCl_2 , or a solid support. Revolutionary in their day, such catalysts were successful under certain conditions, such as high temperatures (100 °C). Since they are cheap and easy to prepare, they still have important commercial applications, such as the Shell Higher Olefin Process (SHOP) used in the production of large, functionalized olefins from simple alkenes.^[8,10] The inherent disadvantages of the "classical" catalysts are that the identity and concentration of the active catalytic species could not be known or controlled, and the harsh conditions and Lewis acid activators made the metathesis of functionalized alkenes difficult.

The discoveries of organometallic carbene complexes in 1964^[10] and the mechanism of olefin metathesis by Chauvin in 1970 eventually led to the rational design of progressively more advanced, well-defined catalyst systems. A significant breakthrough occurred in 1990 with Schrock's discovery of the well-defined, single-site tungsten and molybdenum (**1**) alkylidene catalysts (Figure 2).^[22–27] The unprecedented activity of these catalysts greatly expanded the utility of the olefin metathesis reaction, allowing Wagener and coworkers to successfully polymerize 1,9-decadiene via the ADMET reaction in that same year.^[28,29] However, these early transition metal-based complexes are highly oxophilic, making them susceptible to air and moisture poisoning if they are not employed under rigorously dry, oxygen-free conditions. They are also relatively intolerant of many functional groups, such as alcohols, aldehydes, and carboxylic acids. These factors have limited the use of early transition metal-based catalyst, like **1**, for the metathesis of certain functionalized olefins.

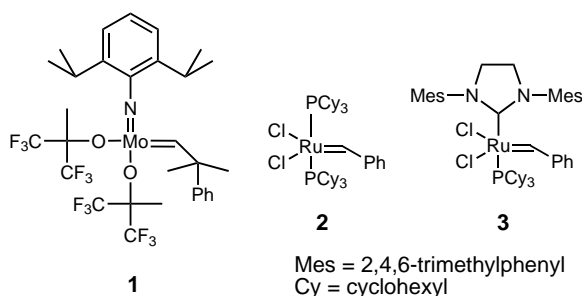


Figure 2. Three well-defined metathesis catalysts: Schrock's molybdenum alkylidene (**1**) and Grubbs' "first generation" (**2**) and "second generation" (**3**) benzylidene catalysts.

The development of well-defined ruthenium-based catalysts by Grubbs in the early 1990's,^[30–36] overcame many of the limitations of the Schrock-type catalysts. As a later transition metal, ruthenium tends to react preferentially with olefins in the presence of most other functional groups.^[32] In as early as the 1960's, it had been observed that $\text{RuCl}_3(\text{hydrate})$ could be used to obtain modest polymer yields in the ROMP of norbornene derivatives, even in the presence of ethanol and water.^[32,37,38] Developments in the 1980's led researchers in the Grubbs group to examine the use of well-defined ruthenium alkylidene complexes as catalysts for olefin metathesis reactions. The most versatile and active of this "first generation" of Grubbs' carbene catalysts, ruthenium benzylidene **2** shown in Figure 2, is stable in air and is much more tolerant of water and most functional groups than catalysts based on early transition metal complexes, like **1**. However, catalyst **2** could not match the high activity of catalyst **1**. The discovery that *N*-heterocyclic carbene ligands could be used to improve the activity of the Grubbs-type ruthenium complex by Herrmann in 1999^[39–42] prompted others to explore their use to bridge this gap in activity. The Grubbs group found that, by replacing only one of the phosphine ligands in **2** with an *N*-heterocyclic carbene ligand, high activity (similar to that of **1**) could be achieved without sacrificing the catalyst's functional group tolerance.^[32,43–47] The most active of this "second generation" of Grubbs' catalysts (**3**) is shown in Figure 2.

Far from complete, the story of metathesis catalyst development is still unfolding. Challenges remaining include: the formation of tetrasubstituted alkenes by CM, the ROMP of barrelenes, the tolerance of basic functional groups like nitriles and amines, and the stereoselective control of certain metathesis reactions.^[32] Several research groups are working in each of these areas, and we anticipate future developments and the opportunities they will present for olefin metathesis.

1.2 The ADMET Reaction

The ADMET reaction has been the primary focus of research in the Wagener group since our successful polymerization of 1,9-decadiene with Schrock's tungsten alkylidene catalyst in 1990.^[28,29] Previous research conducted by Wagener and coworkers in the late 1980's led to the demonstration that ADMET of α,ω -dienes meets the stringent requirements of step polymerization.^[48] Subsequent studies sought to define the requirements for the reaction, including steric and electronic factors, functional groups tolerated by available catalysts, catalyst selection, and the necessary length and structural characteristics of the diene monomer.^[28,49–63]

The mechanism of the ADMET reaction, first described by Wagener, Boncella, and Nel in 1991,^[57] is shown in Figure 3. Essentially, ADMET is a step-growth polycondensation reaction that is driven by the removal of a small molecule, or condensate. Several features of this mechanism differentiate ADMET from its chain polymerization relative, ROMP. Every step in the reaction cycle is reversible and in equilibrium, so it is the removal of the small olefinic by-product (typically ethylene since terminal dienes are most often employed) that irreversibly shifts the equilibrium from monomer to polymer. This is usually accomplished by using reduced pressure ($< 10^{-2}$ Torr), or in some cases an argon or nitrogen flow, to remove the condensate as it forms. ROMP, by contrast, is driven by the release of ring strain and no small molecule is produced during the reaction. Further, the ADMET cycle contains two metallocyclobutane intermediates (**3d** and **3f**), while the ROMP cycle has one. The first of these (**3d**) is formed when the monomer, or oligomer, associates with the alkylidene that bears another monomer or the growing polymer chain (**3c**). The second is **3f**, which is formed when the terminal olefin from an oligomer, or monomer, associates with the methyldiene (**3e**). Upon collapse of **3f**, ethylene is removed and an alkylidene (**3c**) is formed that bears the growing polymer chain. The "true" catalyst in the reaction is the methyldiene complex (**3e**), which is thought to be the most susceptible to decomposition of the alkylidene species present in the mechanism. Repetition of the cycle shown in Figure 3 leads to high molecular weight polymers at high conversion.

Similar to other polycondensation reactions, such as those used to produce polyesters and polyamides,^[64] internal interchange reactions may occur during the ADMET reaction. This happens when an alkylidene on a polymer chain end (**3c**) reacts with an internal double bond in another polymer chain. While this results in two new polymer chains, there is no corresponding change in the overall molecular weight distribution. Typically, the observed molecular weight distribution is the Flory, or most probable, distribution, in which the polydispersity index (M_w/M_n) approaches 2.0 at high conversion.^[65]

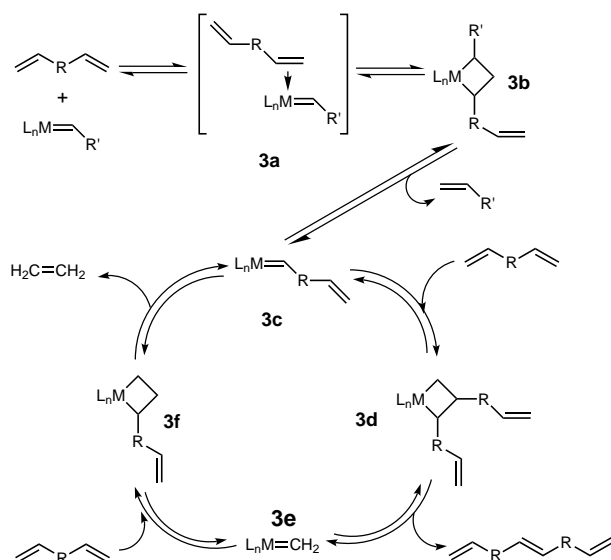


Figure 3. The mechanism of ADMET polymerization.

The molecular weights of ADMET polymers are typical for step-growth polymers, like the polyesters and polyamides mentioned above. Currently, the number average molecular weight (M_n) can range from 1,000 to 100,000 grams per mole in ADMET polymers, but it usually lies between 20,000 and 70,000 grams per mole. The molecular weight attainable depends on many factors, such as the efficiency of stirring and condensate removal, purity of reagents, catalyst efficiency and lifetime, monomer-catalyst compatibility, and the physical properties of the monomer and/or polymer. Many of these factors will be discussed in the sections that follow.

The general conditions for ADMET are like most other polycondensation reactions. The reaction is usually carried out in bulk monomer, where the monomer acts as both reactant and solvent. This maximizes the monomer concentration and shifts the equilibrium towards polymer formation. It also reduces the occurrence of intramolecular cyclization of the monomer by RCM, which becomes more kinetically favorable at lower diene concentrations. Cyclization is a common phenomenon in polycondensation chemistry,^[64] but it can be substantially avoided in ADMET reactions by using α,ω -dienes with a chain length of ten atoms or more. If the dienes are any shorter, they may form thermodynamically stable five-, six-, and seven-membered rings in preference to polymer. Ultimately, thermodynamics rather than kinetics determine whether cyclics or polymers are preferred for a given monomer, because ADMET polymerizations are carried out under equilibrium conditions over extended periods of time.

Another general reaction condition for ADMET polymerizations is the use of reduced pressure to remove the condensate. As mentioned above, this shifts the equilibrium irreversibly towards polymer formation,

but it also serves to accelerate monomer conversion and increase the molecular weight of the polymer. These and other reaction conditions are discussed in more detail under the heading of Section 2 “Experimental Considerations”, below.

1.3 Applications of ADMET

In the past decade, ADMET has moved smoothly from its development phase towards a broad realm of applications. With the advent of highly active, robust metathesis catalysts, such as **1**, **2**, and **3**, the challenge in ADMET chemistry has essentially been reduced to the synthesis and cost of the diene monomer. In other words, with few exceptions, if the diene monomer can be made, then a polymer can be produced by ADMET. This chemistry provides access to a variety of polymers and polymer architectures that are not available using other polymerization methods. Figure 4 shows a variety of polymers produced recently in the Wagener group.^[56–63,66] In addition to these, we have produced several alkyl branched and functionalized polymers with unprecedented regioselectivity for the modeling of commercial ethylene copolymers, perfectly spaced graft (or comb) copolymers, reactive carbosilane polymers for use as solvent-resistant elastomers with tunable properties, telechelic polymers for use in polymer modification or incorporation into block copolymers, and numerous other types of useful polymers.

Following a discussion of the general synthetic techniques used to create many of the polymers shown in Figure 4, Section 3 provides a more detailed description of these ADMET polymers and their unique properties. Several examples from other research groups are mentioned, but the focus is on recent research conducted in the Wagener laboratories.

2 Experimental Considerations

In this section, several issues that are critical to the successful experimental implementation of the ADMET reaction are discussed. Among these issues are the selection of the catalyst, the preparation of monomers and solvents, and the choice of the reaction apparatus to be used. After addressing these issues below, a description of a general ADMET polymerization procedure is provided to illustrate many of the factors that affect the success of the reaction.

2.1 Catalyst Selection Issues

The recent progress in ADMET polymerization is closely tied to developments in catalyst design. Representatives from three types of catalysts, “classical”

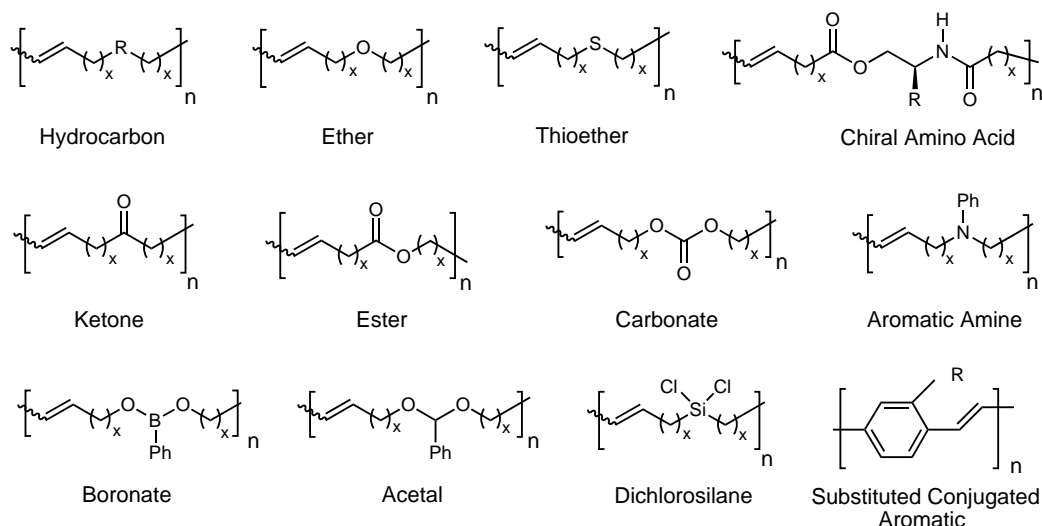


Figure 4. A variety of polymers made by ADMET.

catalysts, Schrock-type alkylidenes, and Grubbs-type carbenes, can be used in ADMET polymerizations. Each type has strengths and weaknesses, so the choice of catalyst for a given reaction is based on the particular diene to be polymerized and the physical properties of the polymer that will be formed, as well as other practical considerations.

By far the most widely used catalysts for ADMET are Schrock's molybdenum alkylidene (**1**) and Grubbs' ruthenium benzylidene (**2**), shown in Figure 2, because they are reliable and their chemistry is now well-established. Also shown in Figure 2 is the "second generation" Grubbs' catalyst (**3**), which has gained attention recently because it combines the high activity of **1** with the functional group tolerance of **2**. The multi-component "classical" catalysts are rarely employed in ADMET reactions, because their ill-defined nature can lead to unpredictable reactivity and undesired side reactions. However, their low cost and ease of preparation make "classical" catalysts useful for some applications.

So, which catalyst is right for a particular ADMET reaction? While some generalities can be made, the choice is complicated by subtleties in the mechanism and reactivity of each catalyst. For instance, kinetic studies comparing the reactivity of **1** with **2**, using 1,5-hexadiene as the monomer, showed that different products were formed for each catalyst under identical reaction conditions.^[55] Linear polymer was the major product when catalyst **1** was used, while cyclics, such as 1,5-cyclooctadiene, were the major products when catalyst **2** was used. This result is attributed to mechanistic differences between these two catalysts. The same study showed that both catalysts produced primarily linear polymer when 1,9-decadiene was used as the monomer, but catalyst **1** accomplished the transformation an order of magnitude faster than **2**. In another

recent study, a comparison of the kinetic behavior of the Grubbs' catalysts, **2** and **3** showed that **3** is the more active catalyst by about an order of magnitude, but only at higher temperatures.^[67] At 45, 60, and 75 °C catalyst **3** becomes progressively more active than **2** for the polymerization of 1,9-decadiene, but at 30 °C catalyst **2** is almost twice as fast as **3**. Also, an induction period was observed for catalyst **3** at all temperatures studied, which made it slower than **2** at the initial stage of the reaction. We attribute this to the slower rate of phosphine dissociation (a necessary step in the initiation of catalytic activity) for catalyst **3** than for **2**, which has been reported by Grubbs.^[68,69]

We conclude that, generally, catalysts **1** and **3** are faster than **2**, but the reaction temperature is an important variable, particularly for catalyst **3**. Catalyst **3** is also more stable at higher temperatures than **1** or **2**. This is important in bulk ADMET polymerizations, where the viscosity of the growing polymer can impede stirring and the diffusion of the condensate, limiting the ultimate molecular weight of the polymer. By increasing the reaction temperature, the viscosity can usually be lowered and higher molecular weights may be obtainable.

The choice of catalyst becomes even more complicated when monomers with functional groups are used. In general, catalysts **2** and **3** are more tolerant of air, water, and a wide range of functional groups, such as alcohols, esters, and ketones, than is catalyst **1**. However, catalyst **1** is more tolerant than **2** of functionalities based on sulfur.^[22–27] Additionally, the oxophilicity of molybdenum makes catalyst **1** highly susceptible to air and moisture poisoning. As a result, all solvents and monomers must be rigorously dried and degassed, and air-free, Schlenk-line techniques must be employed when catalyst **1** is used. The use of catalysts **2** and **3** is not hindered by these inconveniences. However, care

should still be taken to keep reagents dry and air-free no matter which catalyst is used, as ADMET reaction times are often on the order of days, so catalyst decomposition can become an issue, particularly when solvents and elevated temperatures are used.

Ultimately, optimal catalyst selection is based partly on generalizations of catalyst reactivity and partly on experience. In some cases, experimentation with several catalysts may be required to find the best one for a particular reaction.

2.2 Monomer and Solvent Preparation

The monomers and solvents used in ADMET reactions should be of high purity to avoid possible side reactions and premature catalyst decomposition. A variety of methods exist for the purification of monomers, and the choice, or combination of choices, depends on the physical properties of both the monomer and any impurities present. Among the methods most often employed are distillation (simple, fractional, or spinning band), recrystallization, column chromatography, and high-performance liquid chromatography (HPLC).^[70–72] Particular care must be taken when using catalyst **1** to ensure that monomers and solvents are devoid of water or dissolved oxygen. Drying is usually accomplished by vacuum distillation of a liquid monomer (or solvent) from an appropriate drying agent, or by heating a solid monomer under vacuum in the presence of a desiccant using an Abderhalden-type drying apparatus. Liquid monomers and solvents are then degassed by three freeze-pump-thaw cycles, as a final preparation, before they are exposed to catalyst **1**. While purity is important, monomers and solvents need not be rigorously dry or air-free when the ruthenium-based catalysts **2** and **3** are used.

2.3 ADMET Reaction Apparatus

The glassware used in ADMET reactions has evolved from complex apparatuses to increasingly more simple ones. The elaborate break-seal glassware that was initially used to understand many monomer structure-reactivity relationships,^[57] has given way to simple Schlenk tubes or round-bottomed flasks. Today, a typical setup is merely a reaction flask, equipped with a magnetic stir bar and a Teflon valve (or glass stopcock) that allows for easy vacuum control when attached to a high vacuum line. An illustration of this simple apparatus is shown in Figure 5a.

Depending on the nature of the monomer or the polymer that is to be formed, several minor modifications to the apparatus can be made in order to maximize the molecular weight and/or polymer yield. For example, if the monomer is very volatile, or if a volatile

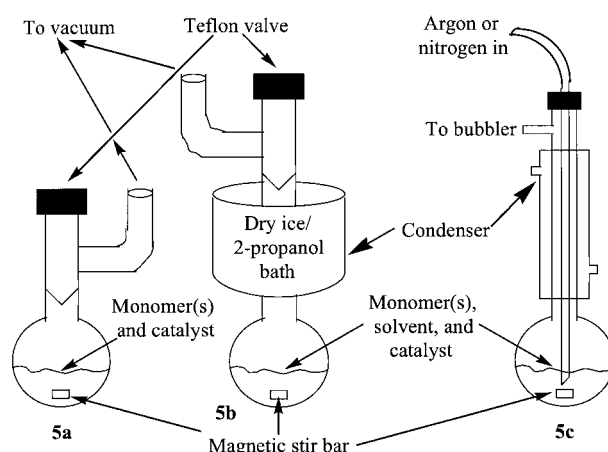


Figure 5. Apparatuses used in ADMET reactions.

solvent is used to dissolve a solid monomer (or polymer), then a dry ice/2-propanol filled, Dewar-type condenser is attached to the reaction flask to prevent the loss of volatiles (Figure 5b). An alternative is the use of an argon or nitrogen flow to drive off the ethylene condensate. The apparatus is shown in Figure 5c, and it involves bubbling the gas through a needle directly into the reaction mixture and out through an oil-filled bubbler. However, this method is not as efficient at removing ethylene, so its use is usually restricted to cases where high vacuum is undesirable due to the volatility of certain reaction components.

The flexibility and simplicity of the apparatuses used in the ADMET polymerization have helped to make it a useful method for the preparation of a variety of macromolecules with diverse properties. The experimental method and apparatus can be critical to the ultimate efficiency and success of an ADMET reaction, so they should always be carefully considered and planned before beginning the reaction.

2.4 General ADMET Polymerization Procedure

Most often, ADMET reactions are conducted in the bulk state (where the catalyst is dissolved in pure monomer) and under reduced pressure (high vacuum), to drive the equilibrium towards polymer by maximizing the monomer concentration and removing the ethylene condensate. A typical procedure involves taking the purified, dried, and degassed monomer (see Section 2.2 above) and an oven-dried reaction flask, with stir bar and Teflon valve, into an argon (or nitrogen) atmosphere glovebox, where the monomer is then weighed into the reaction flask. The appropriate catalyst (see Section 2.1) is weighed out to the desired monomer to catalyst ratio; usually 500 – 1000:1 for catalyst **1**, 100 – 500:1 for catalyst **2**, or 100 – 1000:1 for catalyst **3**. The catalyst is then added to the reaction flask, where it

usually rapidly dissolves in the monomer with stirring, and the immediate evolution of ethylene is observed as it bubbles out of the solution. As quickly as possible, the reaction flask is closed, taken from the glovebox, and attached to a high vacuum line. Catalysts **2** and **3** can actually be handled in air, but the above precautions are often taken to ensure the longevity of the active catalyst and to maximize the molecular weight of the polymer.

Once the reaction flask is on the vacuum line, it is briefly (about 1 second) opened to vacuum at periodic intervals until the vigorous bubbling subsides and the viscosity (molecular weight) is such that stirring becomes more difficult. At this point, the flask is opened to full vacuum ($< 10^{-2}$ Torr) and the reaction temperature is gradually increased from the initial temperature, which is catalyst- and monomer-dependent. Usually, the reaction is started at room temperature for more volatile monomers, while initial temperatures of 30–40 °C may be used for most higher boiling monomers. Due to its high activity, reactions using catalyst **1** are started at lower temperatures (20–30 °C) to avoid excessive bubbling that could cause the monomer to splatter on the sides of the reaction flask and lower the polymer yield. Since the rate of decomposition becomes accelerated at different temperatures for each of the catalysts, the maximum effective operating temperature under ADMET reaction conditions is different for each one. Catalyst **1** is used up to 50–55 °C, catalyst **2** is used up to 60–70 °C, and catalyst **3** can be used as high as 70–90 °C. Of course, these values depend on other variables, such as the presence of air, moisture, solvent, and monomer functional groups.

The reaction is considered complete when the evolution of ethylene (bubbling) is no longer observed and/or the mixture can no longer be stirred. The importance of a good magnetic stir bar and a powerful magnetic stirrer cannot be overstressed. As the viscosity (molecular weight) of the polymer increases, the percent conversion becomes increasingly limited by the diffusion of reactive end-groups. If the stir bar can no longer move through the thickening mixture, then the diffusion of end-groups may be sufficiently retarded to effectively halt the further increase of molecular weight. Once the reaction has reached this stage, it is cooled to room temperature and the catalyst is quenched by adding a terminating agent, such as ethyl vinyl ether or benzaldehyde, or by exposure to air. The polymer may then be isolated by precipitation and filtration, or by column chromatography. Additionally, Grubbs' catalyst (**2**) can be efficiently removed with the aid of water-soluble chelating phosphines.^[57,73] Any residual solvent is then removed from the polymer by heating it under vacuum. The resulting ADMET polymer typically has a number average molecular weight in the range of 20,000 to 70,000 grams per mole and a polydispersity index of 2. The polymer can be characterized using various analytical techniques, such as nuclear magnetic resonance

spectroscopy (NMR), infrared spectroscopy (IR), elemental analysis, gel-permeation chromatography (GPC), vapor pressure osmometry (VPO), membrane osmometry (MO), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC).

3 Diverse Materials via ADMET

The versatility of the ADMET reaction for producing polymer structures and morphologies that are difficult or impossible to obtain by other methods is remarkable. ADMET has allowed the synthesis of perfectly linear polyethylene and a variety of alkyl branched and functionalized polyethylenes that have precisely placed pendant groups along the hydrocarbon backbone. Such polymers make excellent models for the study of structure-property relationships in commercial polymers and copolymers. Several hybrid organic/inorganic ADMET polymers, containing silicon, tin, germanium, and phosphazene as their inorganic components, have been recently produced. A variety of end-functional (telechelic) polymers has been made, both directly and by the ADMET depolymerization of unsaturated polymers, and some of these were used to make segmented and ABA-type block copolymers. Graft copolymers with "perfect comb" structures are also accessible using ADMET polymerization. It has even been possible to make certain conjugated polymers and both main-chain and side-chain liquid crystalline polymers via ADMET. Recently, biopolymers that contain chiral, amino acid moieties were added to the growing list of polymeric materials made *via* ADMET. Many representative examples of these diverse materials are briefly surveyed below.

3.1 Perfectly Linear, Alkyl Branched, and Functionalized Polyethylenes

In recent years, the Wagener group has focused considerable attention towards the modeling of polymers and copolymers made from ethylene. We have been studying the effect that precise placement of alkyl branches and functional groups along the polyethylene backbone has on the properties of this commercially important class of polymers. This work began with the production of perfectly linear polyethylene by the exhaustive hydrogenation of polyoctenamer made by ADMET of 1,9-decadiene (**6a** in Figure 6).^[74,75] The linear ADMET polyethylene has a melting point (131–134 °C) that is comparable to industrially produced high-density polyethylene (133–138 °C) and approaches the theoretical value for infinitely long, perfectly linear polyethylene (141.5–146.5 °C) determined by Hoffman.^[76,77]

In subsequent studies, we found that precise placement of branches along the polyethylene backbone has

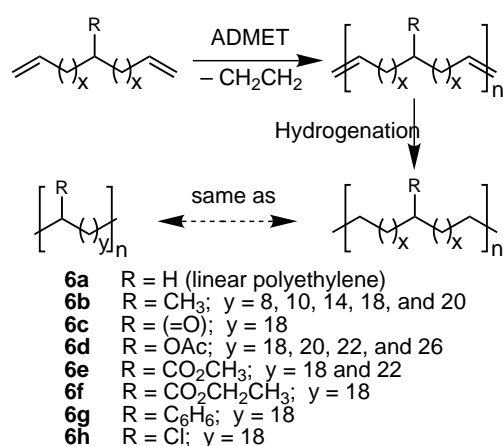


Figure 6. Perfectly linear, methyl branched, and functionalized ADMET polyethylenes with precisely placed pendant groups (R).

dramatic effects on the polymer's crystallization and melting behavior, which had not been observed previously. One such study involved the synthesis of a series of methyl branched polyethylenes, where the methyl groups were placed precisely on every 9th, 11th, 15th, 19th, and 21st carbon atom of the backbone, respectively (**6b**).^[78] These precise structures are made possible by the clean condensation chemistry of ADMET using well-defined catalysts and symmetric methyl branched α,ω -diene monomers. As expected, we found that increasing the frequency of the methyl branches decreases the melting temperature (T_m) of the polymer. The melting temperatures, determined by DSC, ranged from 62 °C for the methyl branch on every 21st carbon to –14 °C for the methyl branch on every 9th carbon of the backbone. In contrast to their ethylene/propylene copolymer counterparts, made by chain-growth polymerization techniques, these ADMET polymers all exhibited very sharp melting endotherms in their DSC traces. They also had substantially lower T_m ranges than the chain-made polymers with similar mole fractions of methyl branches. These observations are most likely due to the effect of precise, regular placement of the methyl branches on the polyethylene backbone for the ADMET models, which creates a type of semi-crystalline order that has not been found in chain-made, branched polyethylenes.

In other studies, the effects of precisely placed functional groups on the polyethylene backbone were examined, using the same methodology. Model copolymers of ethylene with carbon monoxide (**6c**), vinyl acetate (**6d**), acrylates (**6e**, **f**), styrene (**6g**), and vinyl chloride (**6h**) were made via ADMET polymerization of symmetric α,ω -dienes followed by hydrogenation of the unsaturated polymer.^[79–82] Many of these reactions were performed using a tandem ADMET polymerization/heterogeneous hydrogenation method developed in our

laboratories.^[81] This process involves the addition of chromatographic grade silica gel to the Grubbs' ruthenium benzylidene (**2**)-catalyzed reaction after the polymerization is complete, which results in a silica-supported ruthenium species that catalyzes rapid and quantitative hydrogenation of olefins. The method uses mild conditions (moderate pressures, room temperature) and has the added benefit of facilitating catalyst removal from the product.

The commercially relevant model ethylene copolymers, **6c** – **h**, were compared to their chain-made counterparts, and to each other, to determine the effects that precise placement of the functional groups along the backbone and variation of the type of functional group have on their properties. ADMET produced functionalized polyethylene is different from a perfect ethylene/functional monomer model copolymer, in that the pendant functionality is separated by an even number of carbon atoms in the ADMET polymers instead of an odd number. However, we believe that this minor difference can be ignored for the comparison of our model copolymers to random copolymers with similar mole fractions of functional groups, due to the fairly large spacing of the pendant functional groups. Consistent with our methyl branch studies mentioned above, we found that our ADMET model copolymers exhibited sharper, more defined melting endotherms and their melting temperatures were lower than their chain-made counterparts.

The melting points of an analogous series of functionalized ADMET polyethylenes with perfectly spaced pendant groups on every 19th carbon atom of the backbone are shown in Table 1. The analogous methyl branched polyethylene and perfectly linear ADMET polyethylene are included for comparison. Significantly, the width of the melting point range spans nearly 150 °C within the series, and the melting points decrease with increasing steric bulk in the pendant groups. For the largest functional group studied, the phenyl group (entry **6g** in Table 1), crystallization is virtually nonexistent in the absence of annealing. However, a comparison of the model copolymers containing chloro and methyl groups (entries **6h** and **6b** in Table 1), which

Table 1. Melting transitions (T_m) of the ADMET model polyethylenes **6a** – **6g**, listed in order of increasing steric bulk of the pendant group (R).

Polymer	Functional Group (R)	T_m [°C]
6a	H	134
6c	= O	134
6h	Cl	77
6b	CH ₃	56
6d	OAc	23
6e	CO ₂ CH ₃	14
6f	CO ₂ CH ₂ CH ₃	13
6g	C ₆ H ₅	–12

have similar steric requirements but differ in melting point by more than 20 °C, suggests that the size of the substituent is not the only factor that determines the melting point in ethylene copolymers. Future efforts will concentrate on expanding the number of precise models, and will include more detailed crystallographic and morphological studies in order to better understand the crystallization and melting behavior of functionalized polyethylene copolymers.

3.2 Organic/Inorganic Hybrid Polymers

Organic/inorganic hybrid polymers are macromolecules that contain linkages between inorganic groups, such as transition or main group metal atoms, and organic (carbon-containing) groups. Such polymers are desirable, because they combine the properties of inorganic polymers, such as heat resistance and ionic conductivity, with the processibility, flexibility and lower cost of organic polymers. They are also useful as processible precursors for ceramic materials. A variety of organic/inorganic hybrid polymers, containing silane, siloxane, germanium, tin, and phosphazene inorganic components, has been made recently using ADMET.

The Wagener group has been involved in the synthesis of silicon-containing polymers by ADMET for many years. We have produced several polycarbosi-lanes^[56,63,66,83–86] and siloxanes,^[87] as well as telechelic and copolymer versions of these polymers.^[63,84–86,88] Linear polycarbosi-lanes are an important class of silicon-containing polymers due to their thermal, electronic, and optical properties, while polycarbosi-lanes are interesting due to their hydrophobicity, low-temperature flexibility, and thermal stability.^[89–92] Polycarbosi-lanes are also ceramic precursors to silicon carbide after pyrolysis. Several examples of polycarbosi-lanes and siloxanes made by ADMET are shown in Figure 7.

The first type of silicon-containing polymer synthesized using ADMET was a poly[carbo(dimethyl)silane].^[56] Initial attempts to polymerize the divinyl-dimethylsilane monomer were unsuccessful due to steric interactions between the methyl groups on the silicon

atom adjacent to the double bond and the transition metal catalyst. However, it was found that dimethylsilane-based monomers with additional methylene spacer units between the double bond and silyl group were readily polymerized in the presence of Schrock's tungsten alkylidene catalyst. Consequently, diallyldimethylsilane, bis(allyldimethylsilyl)ethane, and bis(allyldimethylsilyl)benzene were successfully condensed to yield polymers **7a–c**.

The polycarbosi-lanes **7d–f** were prepared using Schrock's molybdenum catalyst (**1**), demonstrating the compatibility of this catalyst with the siloxane functionality.^[87] However, attempts to polymerize siloxane monomers **8a** and **8b**, shown in Figure 8, failed. Monomer **8a** is metathesis inactive due to an unfavorable steric interaction with the catalyst, similar to the divinyl-dimethylsilane monomer mentioned above, while monomer **8b** only forms the cyclic RCM product due to the Thorpe–Ingold effect.^[93–95] Cyclization can be avoided by extending the siloxane linkage or by increasing the number of methylene spacers between the siloxane and the double bond. Both methods were used to produce polymers **7d–f**.

Other silicon-containing ADMET polymers synthesized in our laboratories include the poly(chlorocarbo-silane) **7g**,^[66,83] which is readily cross-linked through the hydrolysis of the Si–Cl bonds to form a network polymer, and the copolymers shown in Figure 9. The first of the copolymers (**9c**) is produced by reacting the telechelic polycarbosi-lane (**9a**) with the biphenyl diene mono-

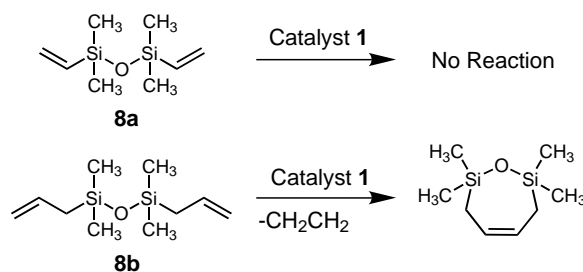


Figure 8. Two carbosi-lane monomers that did not polymerize.

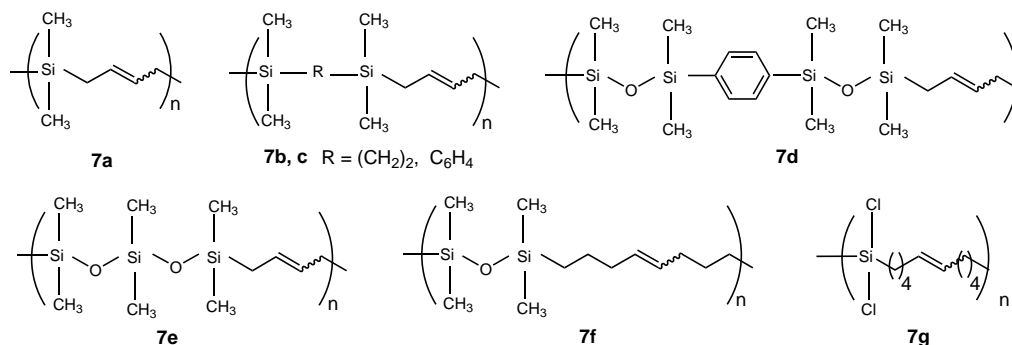


Figure 7. A sample of polycarbosi-lanes and siloxanes made by ADMET.

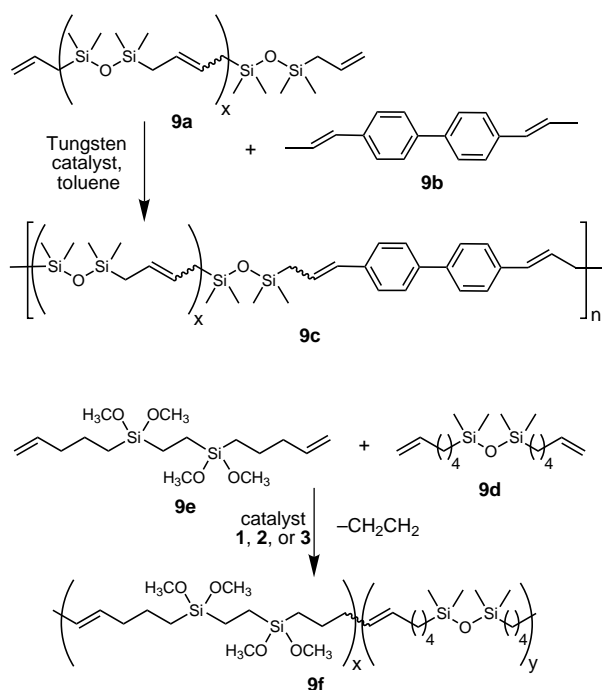


Figure 9. Two silicon-containing copolymers made by ADMET.

mer (**9b**) in the presence of Schrock's tungsten alkylidene catalyst.^[88] The telechelic oligomer (**9a**) is produced before copolymerization to prevent extensive self-metathesis of **9b**, which would result in the formation of a low molecular weight, insoluble solid. The copolymerization of **9b** with **9a** is advantageous, because it allows for a higher molecular weight material to be obtained, and it imparts excellent solubility and improved physical properties to the resultant copolymer. The copolymer (**9c**) contains about 13 mole percent of the biphenylene subunit in the polymer backbone.

The other copolymer (**9f**) shown in Figure 9 is a latent-reactive polymer, because slow cross-linking occurs after polymerization through the hydrolysis of the Si-OCH₃ bonds.^[63,84–86] It is made by the ADMET copolymerization of monomers **9d** and **9e** with the use of either Schrock's (**1**) or Grubbs' (**2** and **3**) catalysts. Each monomer imparts its distinct properties to the copolymer. The "soft" siloxane unit imparts flexibility, whereas the "hard" carbosilane unit possesses four reactive Si-OCH₃ moieties, which provide strength to the material through cross-linking. The resulting copolymer has high thermal stability, yet a low glass transition temperature.

The germanium- and tin-containing polymers shown in Figure 10 are other examples of organic/inorganic hybrid polymers made using ADMET. Main group metal-containing materials of this type are useful due to their thermal and optical behavior. For instance, germanium-based polymers have potential applications in microlithography and in the preparation of ceramic materials.^[96] The polygermanes **10a** – **c**, made via

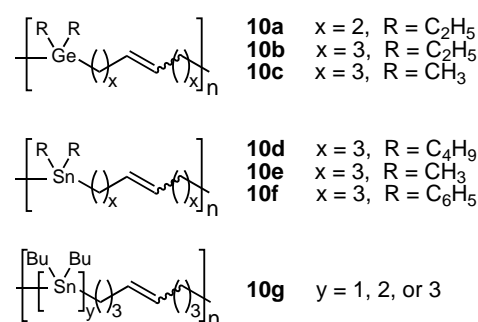


Figure 10. Germanium- and tin-containing ADMET polymers.

ADMET using catalyst **1**, are viscous liquids at room temperature and are amorphous materials with low glass transition temperatures ($T_g = -89$ to -98 °C).^[96] Their pyrolysis behavior demonstrates that germanium-containing volatile species are formed during decomposition, since the ceramic yield does not correlate with the theoretical amount of germanium in the polymer.

The polycarbostannanes (**10d** – **f**) were made using catalyst **1**, or with the use of classical catalyst systems based on phenoxide derivatives of tungsten halides, where the organostannane diene acts as both monomer and catalyst activator.^[97,98] As was seen in production of silicon-containing polymers above, we found that the success of the ADMET polymerization of the organostannane monomer depends on the number of methylene spacers between the tin moiety and the double bond, with three being the minimum number in this case. Like the polycarbogermanes, polymers **10d** – **f** were viscous liquids at room temperature and exhibited low glass transition temperatures. However, unlike their germanium-containing counterparts, the ceramic yields of **10d** and **10f**, upon pyrolysis, were nearly quantitative with respect to tin content.

This study also demonstrated that polymers with polymetallane segments could be made using ADMET.^[99] Polymer **10g** contains mono-, di-, and tristanane functionalities along its backbone, and exhibits properties similar to those of polycarbostannanes **10d** – **f**.

The phosphazene-containing polymers shown in Figure 11 are the latest organic/inorganic hybrid polymers to be made via ADMET. By incorporating a small amount of appropriately designed phosphazene into an organic polymer, its fire retardance, ionic conductivity, biological compatibility, or other properties can be improved.^[100] Researchers in the Allcock group prepared a series of substituted cyclic phosphazene-containing polymers, with various pendant substituents on the phosphorus atoms, from the corresponding diene monomers using Grubbs' catalysts **2** and **3**.^[100,101] These polymers (**P11a** – **c**) had typical molecular weights (M_n) in the range of 10,000 – 40,000. The effects of varying the

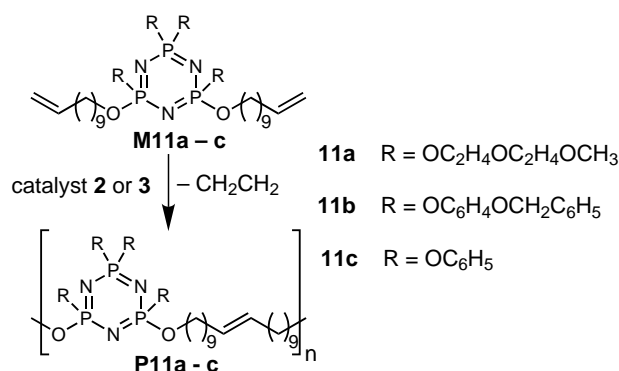


Figure 11. Phosphazene-containing polymers made by ADMET.

substituents on the phosphazene ring and the number of methylene spacers between the ring and double bonds were examined, with the findings that four methylene spacers were required for meaningful polymerization to occur and both steric and electronic effects surrounding the substituents can impede productive metathesis.^[101] The glass transition temperatures of these polymers varied widely (from -75 to $+28$ °C), and two of the polymers (**P11a** and **P11b**) were semi-crystalline, with melting transitions at -55 °C and 47 °C, respectively. Copolymers of monomer **M11c** and 1,9-decadiene were also produced in this study, and it was found that the melting temperatures of both the unsaturated and hydrogenated copolymers decreased with increasing phosphazene content.

3.3 Telechelic Oligomers, and Block and Graft Copolymers

Telechelic, or chain end-functional, polymers are useful because their reactive end-groups permit further modification and the production of phase-separated materials, such as ABA and segmented block copolymers. ADMET polymerization and depolymerization methods have been used in the synthesis of telechelic oligomers. Additionally, ADMET has been used to make block copolymers from telechelic dienes. Using macromonomer dienes, this polymerization route has also been employed to make “perfect comb” graft copolymers, where the grafts are perfectly spaced along the polymer backbone. Schematic representations of these different types of copolymers, as well as one of a telechelic polymer, are shown in Figure 12.

The ADMET depolymerization of unsaturated polymers, such as 1,4-polybutadiene, has been used extensively in the Wagener group to synthesize telechelic oligomers. The metathesis depolymerization of 1,4-polybutadiene is accomplished, with or without the use of a monofunctional diene, by adding a well-defined catalyst (**1**, **2**, or **3**) and a small amount of solvent to the

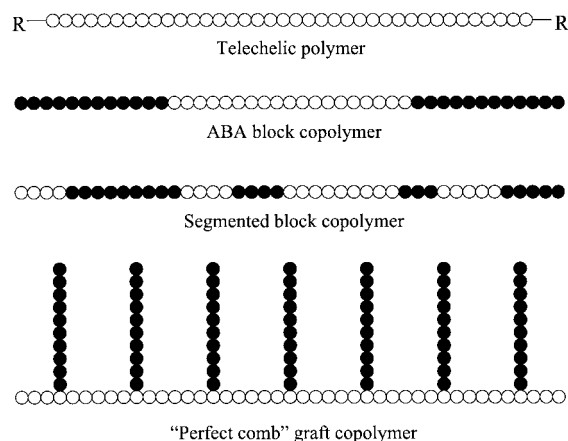


Figure 12. Schematic representations of a telechelic polymer and three types of copolymers made by ADMET.

unsaturated polymer. When a monofunctional diene is used, such as ethylene or an end-functionalized monoene, telechelic oligomers with terminal alkene or other functional groups may be prepared.^[102,103] Several examples, including ester, silyl ether, and imide terminated polymers, are shown in Figure 13. Macrocylic intermediates are formed during the depolymerization reaction, followed by ring-opening metathesis with the monoene to give the telechelic oligomer. The depolymerization of 1,4-polybutadiene has even been accomplished in the absence of added solvent, and this reaction has possible applications in the recycling of commercial elastomers to chemical feedstocks.^[59,104,105] Other telechelics, with end-functionalities that are not well-tolerated by current catalysts, such as alcohols and acyclic amines, can be synthesized using protecting group strategies. Telechelics with both of these types of end-groups have recently been synthesized using the direct ADMET polymerization of α,ω -dienes in the presence of a functional group-protected α -olefin.^[106,107]

Chlorodimethylsilane-terminated telechelics, made via the direct ADMET method, have been used to make ABA triblock copolymers through coupling

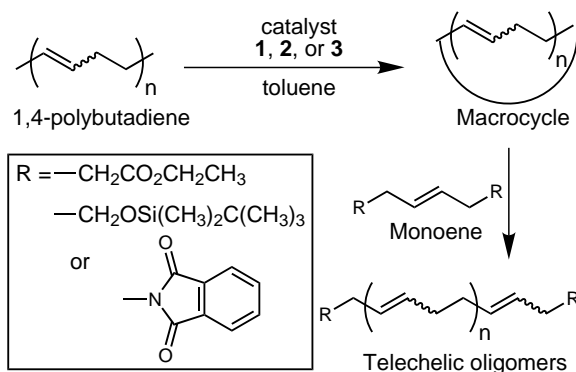


Figure 13. Telechelic oligomers made by the ADMET depolymerization of 1,4-butadiene.

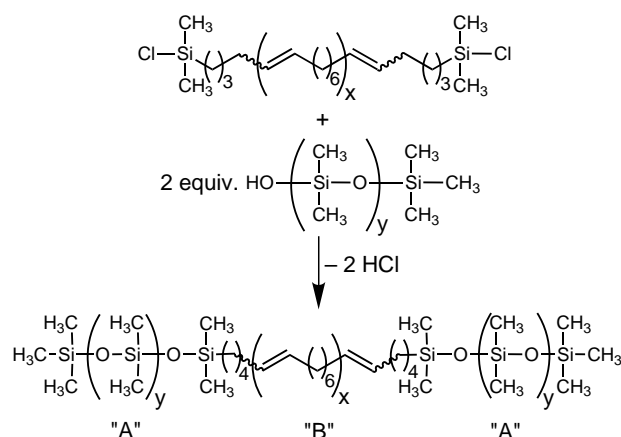


Figure 14. A silicon-containing ABA block copolymer made with an ADMET-produced chlorodimethylsilane-terminated telechelic polymer.

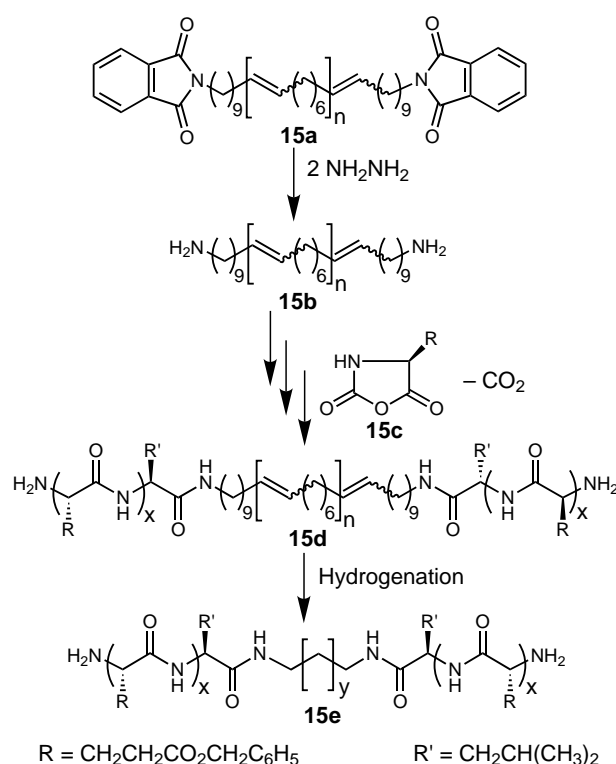


Figure 15. A polypeptide/hydrocarbon ABA block copolymer made with an ADMET-produced amine-terminated telechelic polymer.

reactions with hydroxy-terminated poly(dimethylsiloxane) (Figure 14).^[108] The biologically and structurally interesting polypeptide/hydrocarbon ABA triblock copolymer shown in Figure 15 has also been prepared, using an amine-terminated telechelic oligomer made via ADMET.^[106] The difunctional telechelic (**15b**) was used for the living polymerization of **15c**, followed by hydrogenation of the olefins to give ABA triblock copolymer **15e**.

Segmented block copolymers, where alternating sections of “hard” and “soft” units are linked in the polymer chain, can also be prepared by ADMET chemistry. One example, mentioned in Section 3.2 and shown in Figure 9 above, involves the copolymerization of telechelic diene oligomer **9a** with the biphenyl diene monomer **9b**, to produce the segmented block copolymer **9c**.^[88] Another example, shown in Figure 16, involves the ADMET copolymerization of a poly(tetrahydrofuran) telechelic diene (**16a**) with 1,9-decadiene to produce the well phase-separated segmented copolymer (**16b**).^[65] Such copolymers are useful materials due to the strength imparted by physical cross-linking within the hard segments combined with the toughness or elasticity provided by the phase-separated soft segment.

A third type of copolymer, graft copolymers, has recently been made using α,ω -diene macromonomers and the ADMET polymerization method.^[109] Unlike other graft copolymers synthesized previously, these exhibit a “perfect comb” architecture. The nearly monodisperse side-chains are placed along the hydrocarbon backbone in a perfectly regular manner that is analogous to the model copolymers discussed in Section 3.1. Shown in Figure 17 are both short (**17b**) and long (**17c**) side-chain graft copolymers. The long side-chain grafts are made by the anionic ring opening polymerization of ethylene oxide from the alcohol substituted α,ω -diene (**17a**), while the short side-chain grafts are made by a nucleophilic substitution reaction. These materials may be of use in biomedical applications and as compatibilizers in polymer blending.

3.4 Conjugated Polymers

During the past 20 years, conjugated polymers (CPs) have been the subject of an enormous amount of experimental and theoretical work devoted to their synthesis and the understanding of their properties. They are of interest for a variety of applications, such as antistatic coatings, EMI shieldings or energy storage, electroluminescent diodes (LEDs), and a variety of other highly sophisticated electronic, photonic, and

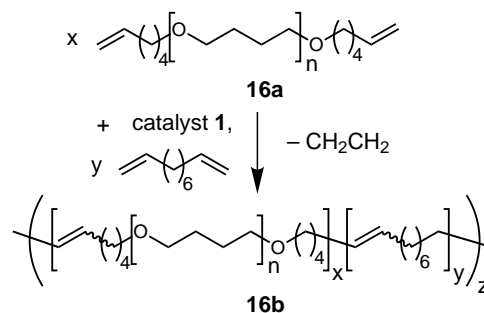


Figure 16. A poly(tetrahydrofuran)/hydrocarbon segmented block copolymer made by ADMET.

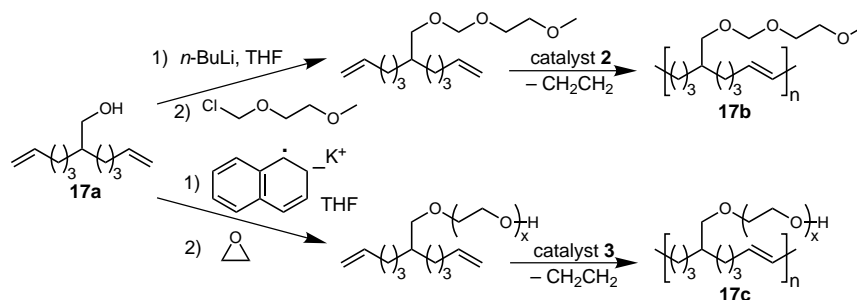


Figure 17. "Perfect comb" graft copolymers.

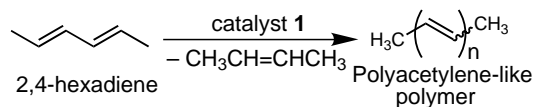


Figure 18. A conjugated polyacetylene-like polymer made by ADMET.

bioelectronic devices.^[110] ADMET polymerization techniques have been used to make several conjugated polymer systems in recent years.

In 1994, we reported the synthesis of conjugated polyacetylene-like polymers by ADMET polymerization of conjugated dienes with catalyst **1**.^[111] The polymers, shown in Figure 18, contained only about 6–10 repeat units on average, but the method may be useful for the synthesis of carotenoid-like products and telechelic polyacetylene oligomers, which could be used in the synthesis of multiphase copolymers.

Collaboration between the Wagener and Reynolds groups in the late 1990's led to the synthesis of the thienylene vinylene-derived conjugated polymer shown in Figure 19.^[112] Schrock's molybdenum catalyst (**1**) was used in the ADMET polymerization to produce polymers with average numbers of repeat units of 10 or more. Upon oxidative doping with SbCl_5 , the deeply red colored solution of the neutral polymer was converted to a pale green.

Recently, Schlick and coworkers have prepared a number of conjugated phenylenevinylene copolymers by ADMET using catalyst **1**.^[113] Several of these polymers are shown in Figure 20. Comonomers, such as *exo,exo*-2,3-norbornylene diacetate or alkoxy-substituted phenylenes, were introduced to improve the solubility of the polymers. However, differing degrees of

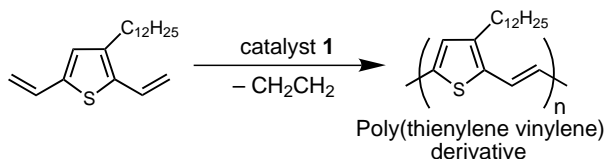


Figure 19. A poly(thienylene vinylene) conjugated polymer made by ADMET.

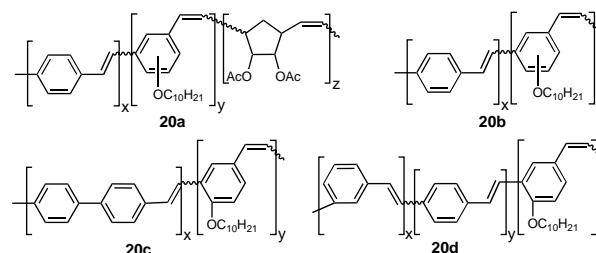


Figure 20. A sample of conjugated phenylenevinylene copolymers made by ADMET.

reactivity of the comonomers led to multimodal molecular weight distributions. The photoluminescent efficiencies of these polymers reached as high as 52%, making them interesting materials for LED applications.

3.5 Liquid Crystalline Polymers

Liquid crystalline (LC) polymers can be used to combine the second-order nonlinear optical properties of small molecule ferroelectric LC's, which are liquids with a thermodynamically stable polar supermolecular structure, with the excellent processibility of polymeric materials. Two types of LC polymers, main-chain and side-chain LC polymers, have been prepared using ADMET polymerization techniques. Researchers in the Grubbs group synthesized a series of main-chain LC polymers, where the mesogenic unit is incorporated into the polymer backbone.^[114] These polymers, shown in Figure 21, were made using a well-defined Grubbs' alkylidene catalyst, and consisted primarily of oligomers

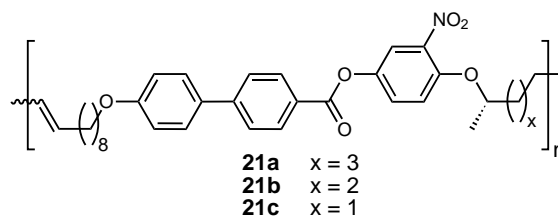


Figure 21. Grubbs' main-chain LC polymers.

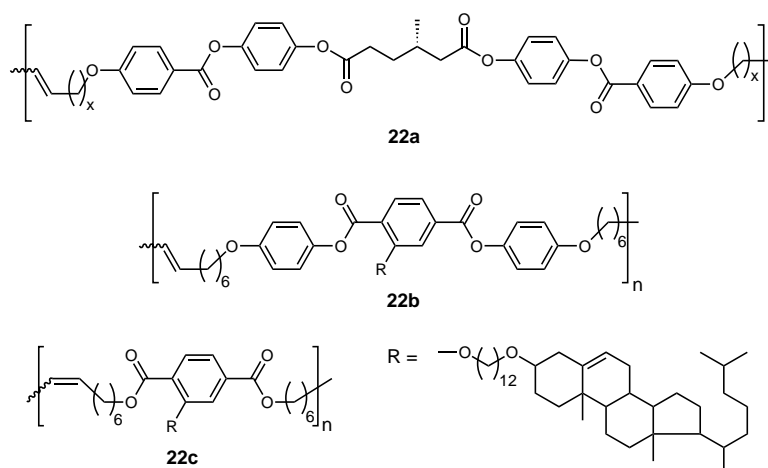


Figure 22. Jin's main-chain and side-chain LC polymers.

of about 10 repeat units. The smectic C* tilt angle was measured for polymer **21a**, and it was found to be a well-behaved ferroelectric LC with a high polar excess (about 40%).

Both main-chain LC polymers and side-chain LC polymers, in which the mesogenic unit is pendant to the polymer chain, have been synthesized recently by Jin and coworkers.^[115] The three LC polymers shown in Figure 22 were made using catalyst **2**. Their molecular weights (M_n) ranged from 3500 to 53000 grams per mole, corresponding to an average number of 5 to 134 repeat units. Preliminary results indicate nematic and smectic LC behavior in these polymers.

3.6 Amino Acid-Based Chiral Polymers

Polymers that contain amino acid-based moieties are interesting for a variety of applications, due to their inherent biological compatibility and degradability. Such properties make these polymers ideal for use in drug delivery systems, biomimetic systems, biodegradable materials, biomaterials, and chiral purification media.^[116–118] We have recently synthesized three types of chiral polymers bearing amino acid groups via ADMET, using the “second generation” Grubbs’ catalyst (**3**).^[119] Shown in Figure 23, they include the linear amino alcohol polymers **23a – e**, the ester-terminated amino acid branched polymers **23f** and **23g**, and the amide-terminated amino acid branched polymer **23h**. Typical molecular weights for these polymers are in the range of 20,000 to 30,000 grams per mole. The branched polymers (**23f – h**) are strong film-forming materials at room temperature, and polymers **23f** and **23g** have high melting transitions (114 and 135 °C, respectively). Additionally, peptide sequences can be attached to the amino-acid pendant groups on polymer **23h** after deprotection of the amine. Future work will involve

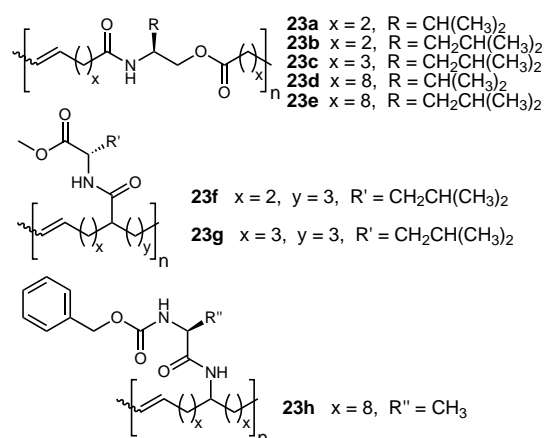


Figure 23. Amino acid-based chiral polymers made by ADMET.

circular dichroism and tensile strength studies, and the exhaustive hydrogenation of these polymers.

The examples outlined in Sections 3.1 – 3.6, above, represent a fraction of the polymer materials and architectures available through the use of ADMET polymerization. The flexibility and versatility of this method is apparent from the number of diverse materials illustrated in these examples. This is due, in no small part, to the advent of well-defined metathesis catalysts and the creativity of the minds that define the possibilities.

4 Conclusion and Outlook

We have recounted the historical context for the discovery of the ADMET reaction, discussed many of the experimental preparations necessary for the successful implementation of the ADMET polymerization method, and demonstrated the applicability of this

versatile reaction. As evidenced in Section 3, ADMET is an extremely flexible approach to the synthesis of a wide range of polymeric materials. With the well-defined metathesis catalysts that are available today, almost any functional group that can be incorporated into an α,ω -diene monomer can also be incorporated into a polymer. However, exceptions still exist, and there is room for improvement in catalyst design to permit the metathesis of basic functional groups, such as amines, as well as in experimental methods to allow higher molecular weights to be obtained when solid monomers are used. Aggressive efforts are being made in both of these areas, and we are confident that the utility of the ADMET reaction will continue to be demonstrated with, or without, these improvements.

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