REVIEW ARTICLE

Acyclic diene metathesis polymerization and precision polymers

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Abstract The history of and major advances in the acyclic diene metathesis (ADMET) reaction are described. Because precise branch identity and frequency can be achieved by ADMET polymerizations of symmetrical α,ω-dienes, polyethylenes with precisely spaced alkyl branches of specified length have been prepared. Investigations of their morphologies and thermal properties have provided valuable insight into the behavior of polyethylene. ADMET preparation of ethylene copolymers and telechelic oligomers, as well as the properties of these materials, is also discussed.

Keywords ADMET polymerization · Olefin metathesis · Precision polymers · Polyethylene

Introduction

The development of olefin metathesis has led to remarkable achievements in organic and polymer chemistry. From allowing facile synthesis of complex natural products to producing intricate polymer architectures, olefin metathesis has had an undeniable impact on organic and polymer synthesis. There are two distinct modes of metathesis polymerization: ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization [1, 2] (Fig. 1). The development of the ADMET reaction is the subject of this review.

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Historical background

The development of well-defined, efficient olefin metathesis catalysts (Fig. 2) was paramount to the development of the ADMET reaction. Although classical olefin metathesis catalysts were effective in some cases, the exact nature of the catalytically active species was not known. Early work by Grubbs [3–7] and Schrock [8–12] produced some of the first spectroscopically identifiable olefin metathesis catalysts.

The introduction of Schrock's catalysts (e.g., **[Mo]1**) enabled significant progress in olefin metathesis and its use in organic and polymer synthesis. However, these catalysts are sensitive to air, water, and some polar functional groups, and this sensitivity has limited their application in some cases. To address this issue, late transition metal catalysts were developed both by Schrock [13] and Grubbs [14]. Of these, the Grubbs ruthenium-based catalysts have been particularly successful. The first generation of these ruthenium complexes was reported in 1992 and 1993 [15–18]. Although first-generation ruthenium catalysts such as **[Ru]1** have less activity than the Mo-based Schrock catalysts, the Grubbs' complexes are more tolerant to moisture, oxygen, and polar functional groups. A second-generation of ruthenium catalysts, principally **[Ru]2**, resulted from the replacement of a phosphine with an *N*-heterocyclic carbene (NHC) ligand. These catalysts are very reactive in olefin metathesis reactions and possess greater functional group tolerance than the first-generation ruthenium catalysts [19–21]. The activity of some second-generation ruthenium catalysts is comparable to the activity of **[Mo]1** [22]. In 1999, a new class of olefin metathesis catalysts with an isopropoxy group on the benzylidene moiety, **[Ru]3**, was reported by Hoveyda and coworkers [23]. Soon thereafter, the second-generation Hoveyda–Grubbs catalysts were
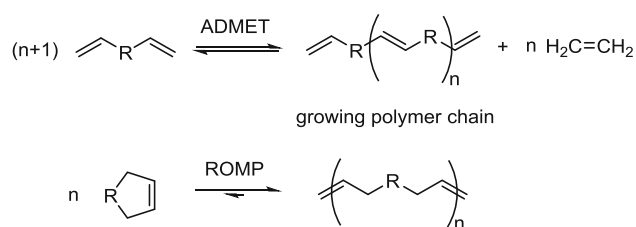
Fig. 1 The ADMET reaction

reported, all incorporating an NHC ligand ([**Ru**]4 is one example). These catalysts are very effective for many different olefin metathesis reactions [22, 24].

These and other catalyst developments [25] allowed ADMET to be a useful and feasible reaction. The Wagener group began investigating unconjugated α,ω-diene polycondensation, later known as ADMET polymerization, using the WCl_6/$EtAlCl_2$ catalyst system in the late 1980s [26]. These reactions resulted in a combination of soluble oils and intractable solids. It was determined that the oil was a low molecular weight polymer—the result of olefin metathesis. It was believed that the insoluble product resulted from a vinyl addition reaction, which, in competition with metathesis, would result in a crosslinked polymer, but the solid product was not rigorously characterized. In order to test this hypothesis, Wagener and coworkers reacted WCl_6/$EtAlCl_2$ with styrene. The predicted product of olefin metathesis for this reaction would be stilbene; however, the reaction also yielded polystyrene. This result demonstrated that vinyl addition and olefin metathesis are competing reactions when these catalyst systems are used. To achieve high polymer, the competing vinyl addition reaction must be eliminated. Serendipitously, this work coincided with the report of catalyst [**Mo**]1. The concurrence of these advances enabled ADMET to be applied as a means of synthesizing high molecule weight polymer.

The ADMET reaction

Acyclic diene metathesis polymerization is an equilibrium step-growth condensation of α,ω-dienes promoted by a suitable metathesis catalyst. The reaction produces a growing unsaturated polymer chain that retains the symmetry and functionality of the monomer.

Over the years, monomer design and the development of suitable catalysts have opened the way to a variety of well-defined polymer structures which are not readily achievable by other common techniques. The ADMET polymerization proceeds via a metal-carbene mechanism, in which the metal methylidene is the true catalyst formed during the polymerization cycle (Fig. 3). This is the same metal-carbene mechanism operating in cross-metathesis [27]. Coordination of the metallic center of the catalyst with a terminal olefin from either the monomer or polymer is followed by a reversible 2 + 2 cycloaddition to produce a metallocyclobutane intermediate. This undergoes further reversion leading to either a productive or a non-productive pathway. Chain growth is promoted by the productive metathesis pathway resulting from cycloreversion, which will not restore the coordinating olefin and free catalyst. This pathway is characterized by production of ethylene, which should be removed from the reaction mixture in order to drive the equilibrium towards chain growth. AD-MET polymerization affords PDIs around 2, which are typical for step-growth polymerization. Also, molecular weights up to 50,000 g/mol can be achieved, depending primarily on catalyst life time, monomer purity, and reaction conditions. It is fair to say that catalyst compatibility and monomer design/purification are the main challenges to be overcome in order to achieve high polymer with well-defined primary structure.

ADMET polymerization usually requires relatively long reaction times in order to guarantee high conversion and consequently high molecular weight polymers. Because some reactions require days to be completed, catalyst lifetime can be a limiting parameter. Catalyst lifetime depends primarily on the rate of deactivation by catalyst poisoning and can be a major problem if a compatible metathesis catalyst is not available. Grubbs' ruthenium-based and Schrock's molybdenum-based catalysts [28] are among the most used catalysts for ADMET. Grubbs' first-generation catalyst is very common due to its high tolerance towards moisture, oxygen and coordinating functional groups, even though its reactivity is not as high as Schrock's catalyst [29]. The highly reactive Schrock's catalyst

Fig. 2 Five examples of well-defined olefin metathesis catalysts

Cy=cyclohexyl
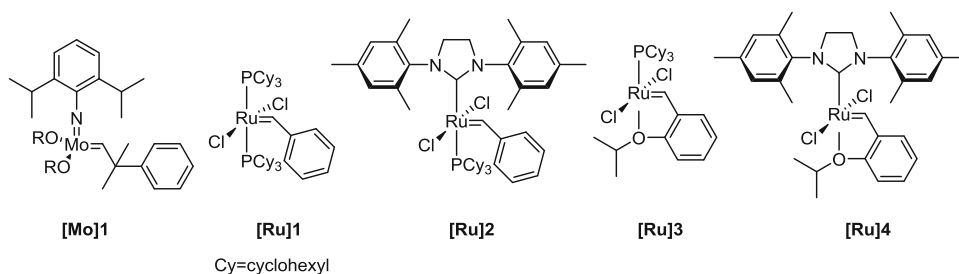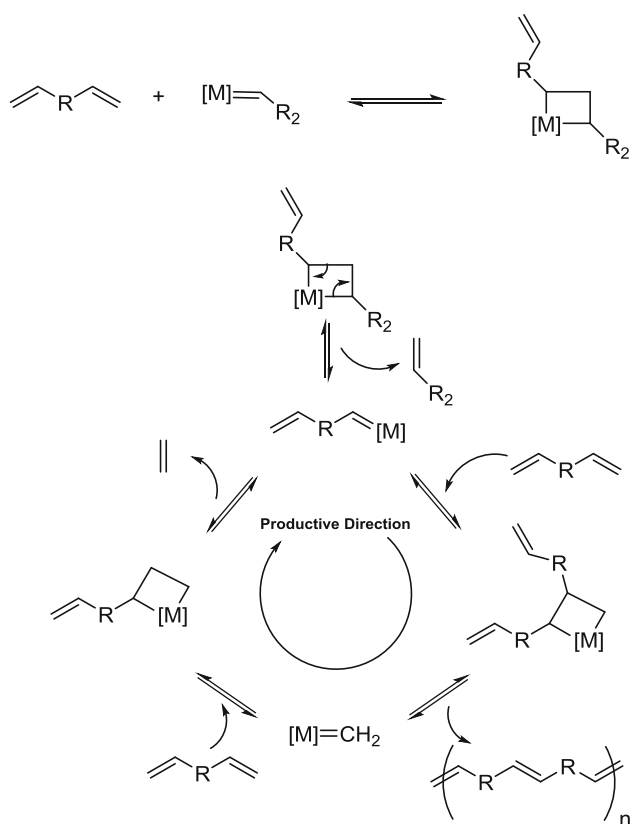
Fig. 3 The ADMET mechanism

is much more sensitive and requires careful handling and extremely dry and pure monomers. The high oxidation state of the molybdenum metal center makes the catalyst highly vulnerable to polar functional groups, water and oxygen. Traces of impurities can deactivate the catalyst rendering very poor conversion/molecular weights.

Even though there are a large number of metathesis catalysts available, many are known to promote isomerization, which ultimately results in loss of control over the polymer primary structure. Grubbs' first generation and Schrock's catalysts are known to promote minimal isomerization under regular ADMET reaction conditions, while studies on Grubbs' second generation, as well as other ruthenium-based metathesis catalysts, shows significant isomerization under similar conditions [30, 31]. Isomerization is a drawback, especially when the choice of a catalyst is limited by monomer functionality. Fortunately, several methods are available to minimize isomerization, usually by use of special additives such as benzoquinones [32, 33] or boron-containing Lewis acids [34].

Virtually any α,ω-diene can be polymerized via ADMET if a suitable catalyst is available that tolerates the desired monomer functionality. The mechanism governing metathesis ensures control over primary structure based on retention of monomer symmetry/asymmetry in the final

polymer. Saturation of the internal olefins of the unsaturated ADMET polymer eliminates the *cis/trans* distribution, allowing for polymers with well-defined primary structures. Tacticity in ADMET polymers is not yet fully controlled and is being currently addressed by the Wagener group.

ADMET polymerization is ideally carried out in the bulk with monomer-to-catalyst ratios typically in the range of 100–500:1 under high vacuum. The increased viscosity during polymerization is overcome by performing the reaction at temperatures ranging from 40 to 75 °C under constant stirring. Where solubility is not an issue, solvents can be used to maintain low viscosity levels, as long as the catalyst is not deactivated in solution. Plenio and coworkers showed that high-boiling solvents such as 1,2-dichlorobenzene can be used in ADMET polymerization when a slight vacuum is desirable [35]. More recently, Simocko et al. [36] demonstrated that ionic liquids are excellent media to perform ADMET polymerizations. Grubbs' catalyst is usually employed when solvents need to be used, given its higher tolerance towards contaminants and polar functional groups. During the polymerization, removal of ethylene condensate can be achieved by applying high vacuum, or by purging the reaction vessel with an inert gas, in order to drive the reaction to completion. This can be achieved by applying high vacuum or by purging the reaction vessel with an inert gas in order to push the reaction to completion. Reaction progress can be easily followed by comparing the relative ^{1}H NMR signal intensities of the terminal olefin on the monomer and internal olefin of the resulting unsaturated polymer.

Modeling polyethylene

Polyethylene (**PE**) is the most produced polymer and still dominates the polymer market because of its low cost, versatility, and ease of manufacture [37]. Conventional industrial methods inherently afford polyethylenes with random branches of various lengths along the polymer chain, and this branching greatly affects **PE** properties [38]. Over the years, considerable effort has been devoted to controlling branching and ideally to producing linear polyethylene. In addition, copolymerization of ethylene with polar vinyl monomers often leads to a higher branching content in conjunction with the low incorporation of the polar entity in the polymer backbone. This eventually produces a gradient polymer rather than a statistical polymer.

ADMET polymerization of symmetrical diene monomers is a remarkable tool to afford flawless and impeccably regular polyolefins. Subsequent hydrogenation produces polyethylene copolymers possessing a functionality (either within the polymer backbone or side branching) at

Fig. 4 Monomer synthesis
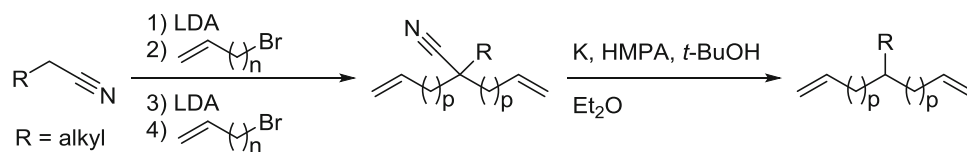
**Fig. 5** Synthesis of precision alkyl-branched polyethylene
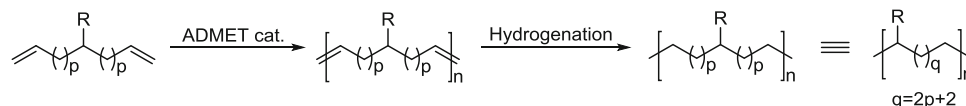
perfectly unvarying intervals (i.e., separated by a constant number of methylene spacers). Depending on the catalyst, molecular weights (M_n) of ADMET polyethylene copolymers usually range from 5,000 to 50,000 g/mol. These M_ns are sufficient to be accepted as polyethylene models, given that the entanglement molecular weight of linear polyethylene is about 1,000 g/mol [39].

ADMET polymerization offers a unique way to model branched polyethylene, as well as any copolymers of ethylene and α-alkenes (C_nH_{2n}). A two-step route involving a dialkylation of a nitrile intermediate followed a reductive decyanation [40] has been used to prepare a collection of symmetrical alkyl-branched α,ω-dienes (Fig. 4).
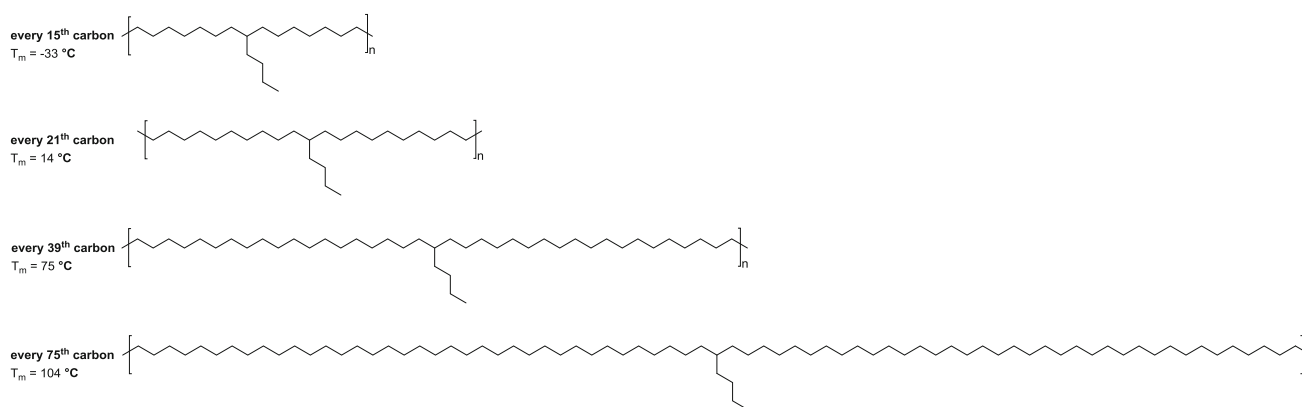
Subjecting these monomers to ADMET polymerization and subsequent exhaustive hydrogenation afforded polyethylenes with precise placement (every nth carbon) of alkyl branches on their backbones (Fig. 5).

Conversely, statistical placement of alkyl branches can be obtained by copolymerization of the aforementioned symmetrical monomer with a linear α,ω-diene (typically 1,9-decadiene) [41]. Precision alkyl-branched polyethylenes were found to possess enhanced thermal properties due to higher crystallinity, leading to sharper melting transitions at lower temperatures and greater heats of fusion. In precision polymers, two factors determine the thermal properties and morphologic parameters of these materials: the branch identity and the branch frequency. The crystalline structures have been studied using wide and small angle X-ray scattering (WAXS and SAXS), transmission electron microscopy (TEM) and infrared (IR) spectroscopy. Morphology is greatly influenced by the alkyl branch size and spacing.

Regularity in primary structure predictably translates to uniformity in the form of narrow lamellar thickness distributions in polyethylene containing precisely spaced alkyl branches [42]. The lamellar thickness corresponds to the distance between branch sites in these materials, which suggests that the chains are folding at the branch sites, with the branches residing at the interface of the lamellae [43]. As a consequence of the narrow lamellar thickness distribution, ADMET polymers have a narrower melt temperature range compared to other polyethylenes.
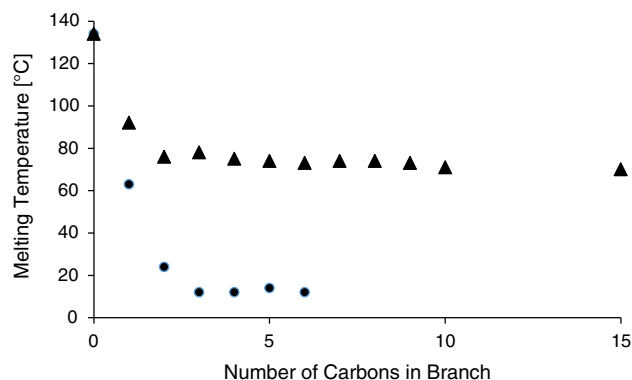
Fig. 6 The effect of alkyl branch size on T_m can be seen for ADMET polyethylenes with branches on every 21st (*filled circle*) and 39th (*filled triangle*) carbon along the polymer backbone

Multifarious branch sizes, ranging from methyl to pentadecyl, have been incorporated in a precise fashion on the polyethylene backbone. It was discovered that the resulting fusion temperatures were highly dependent on the nature of the branching (Fig. 6). As a general rule, the melting temperature dwindles with longer alkyl branches. The effect of alkyl branch size on the melting temperature can be seen for ADMET polyethylenes with branches on every 21st [44] and 39th [45] carbon. Polymers with branches excluded from the lamellae exhibit similar fusion temperatures. This expulsion of alkyl chains from the lamellae is affected by defect size, as ADMET polymers bearing smaller alkyl groups (e.g., methyl) crystallize with a greater degree of branch inclusion. This is true of precision polymers of varying branch spacing, and the maximum included branch size decreases with increasing branch interval. Indeed, when the branch is placed on every 21st carbon, methyl and ethyl branches are included in the unit cell and afford polymers displaying melting transitions at 63 and 24 °C, respectively. Conversely, polymers with branches larger than the maximum included branch size exhibit similar melting temperatures. In other words, the transition becomes independent of the branch identity with T_ms of approximately 12 °C. Similarly, when an alkyl defect is placed every 39th carbon, only a methyl branch can be included in the unit cell, and as a consequence,

every 15th carbon
T_m = -33 °C

every 21th carbon
T_m = 14 °C

every 39th carbon
T_m = 75 °C

every 75th carbon
T_m = 104 °C

Fig. 7 Branch frequency: alkyl branch every nth carbon

similar melting temperatures are found for the polymers bearing longer branches.

Various branch frequencies have been investigated with the goal of diminishing the frequency (increasing the spacing) as much as possible. The general observation is that for a given branch identity, thermal transitions occur at higher temperatures with diminished frequencies. The Wagener group has synthesized butyl-branched polyethylenes in which the branch appears every 9th, 21st, 39th, and 75th [46] carbon (Fig. 7).

This has led to the discovery of a linear relationship between the branch frequency and fusion temperature of the aforementioned polymers. It also suggested a melting temperature of 136 °C for an infinitely low frequency which is quite close to that of linear ADMET polyethylene (134 °C).

The distance between alkyl branches also has an effect on the crystalline lattice, as less frequent branching leads to more ordered structure. The extreme case, with no branching, leads to orthorhombic structure. The introduction of branches leads to less-ordered crystalline structures, of which there are several examples in the literature [47, 48]. When precisely spaced alkyl groups are placed every 7th carbon or closer, the resulting polymers are amorphous.

The morphological effects described in the preceding paragraphs can be further understood by considering the crystallization behavior of representative polymers. As is the case in polyethylenes synthesized by other means, ADMET polyethylenes crystallize through the formation of a hexagonal mesophase, which expands as the chains slide past one another in the all *trans* conformation until the equilibrium lamellar thickness is reached [49]. While crystallization of longer methylene sequences occurs before shorter sequences in metallocene PE, forcing shorter methylene sequences into the amorphous phase, all methylene sequences are of the same length in ADMET polyethylene, allowing crystallites of equilibrium lamellar thickness to form from the transient hexagonal mesophase [50].

By varying the size and interval of alkyl branches on polyethylene, the resulting morphological effects are delineated. Uniform ethylene sequences allow a metastable mesophase to form, at which point the chains can reposition themselves into an energetically stable morphology, resulting in a material with narrow lamellar thickness distribution. Depending on defect size, the branches may be contained within the lamellar stem in the case of smaller branches, or excluded to the surface of the crystallite in the case of longer branches. The lamellar thickness and crystalline lattice type depend on the distance between defects, with longer intervals leading to more ordered polymorphisms.

Beyond the thermal and morphologic elucidation of precision alkyl-branched polyethylene, molecular dynamics were probed utilizing deuterium quadrupolar echo NMR in the solid state. The ^{2}H-NMR spectra of precision CD_3-branched polyethylene were acquired for a wide range of temperatures [51, 52]. A T_1-fitting methodology was applied to deconvolute the spectral contributions of the amorphous and crystalline phases, allowing isolation of two distinctive dynamic behaviors. This is the consequence of a bi-exponential behavior of the spin–lattice relaxation in the CD_3 branches. The amorphous phase exhibited a similar behavior to that of linear polyethylene [53]. Conversely, the crystalline domains displayed a harmonic liberational axial rotation reorientation model with a mean jump angle up to 40° when approaching the melting transition. Various other deuterated precision polymers are being analyzed by deuterium quadrupolar echo methods with the intention of elucidating the dynamics of precision polymers.

Ethylene copolymers

The advent of ADMET polymerization not only promoted modeling of polyethylene, but also stimulated the understanding of numerous classes of polymers. Various

Fig. 8 Synthesis of precision poly(ethylene-*co*-acrylic acid)
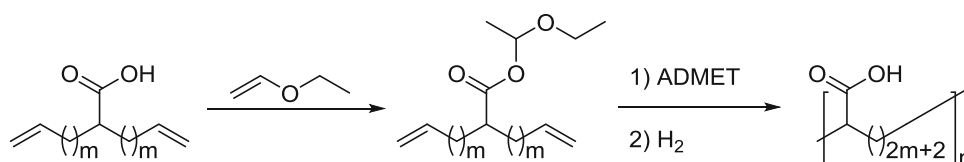
copolymers of ethylene and polar vinyl intermediates were scrutinized and compared to commercial samples. All syntheses relied on the ADMET polymerization of symmetrical α,ω-diene monomers followed by exhaustive hydrogenation to afford the desired polyethylene precision copolymers. Relevant examples are briefly described in this section.

Ethylene–vinyl acetate copolymers (EVA) are widespread materials, with hot-melt adhesives and plastic wraps being common applications [54]. Although free-radical copolymerizations usually produce gradient or block polymers, perfectly random copolymers are obtained from the polymerization of ethylene and vinyl acetate due to similar reactivities [55]. However, undesired and random branching is inherently promoted via a back-biting process, significantly altering the characteristics and performance of the copolymers. However, perfectly linear ethylene–vinyl acetate copolymers can be prepared by means of ADMET polymerization [56]. A number of monomers with various methylene run lengths ranging from 8 to 12 were subjected to polymerization and subsequent hydrogenation, furnishing copolymers with different vinyl acetate contents (acetate branches separated by 18–26 carbons). Commercial samples with similar vinyl acetate ratios were compared with the ADMET copolymers. Similar to the commercial copolymers, the precision polymers displayed a linear relationship between the melting temperature and vinyl acetate content, but with dissimilar slopes. A larger slope, underlining the precision factor, evidenced the greater order in precision polymers. With a similar approach, copolymers of ethylene and vinyl alcohol were made without difficulty.

While metathesis catalysts such as **[Ru]1** can tolerate a variety of functional groups, functionalities such as primary or secondary amines, sulfides, or carboxylic acids deactivate the catalyst, thereby precluding preparation of high molecular weight materials (oligomers to about 3,000 g/mol were produced). In the case of carboxylic acids, this problem can be circumvented by protecting the acid functionality. Various agents can be employed, but ethyl vinyl ether was found to be extremely convenient [57]. The resulting 1-ethoxyethyl ester, inert to ruthenium catalysts, is quantitatively cleaved during the hydrogenation of the resulting polyolefin (Fig. 8).

The ethylene–acrylic acid copolymers were found to be amorphous when only 8 or 14 methylene units separated two consecutive branching sites. Conversely, increasing the

spacing to 20 methylenes resulted in a semicrystalline material displaying dimerized acid moieties in an orthorhombic lattice. Simple treatment of the copolymer with zinc reagents, produced a zinc-neutralized material containing 22 % free acid and 66 % zinc dicarboxylates. The zinc dicarboxylate components aggregated into a self-assembled structures adopting a cubic crystalline lattice, an unprecedented observation for ionomers having a purely hydrocarbon backbone [58].

Precision ethylene–vinyl halide copolymers have also been examined [59]. Contrary to many other systems, it was discovered that regardless of the halide identity (except iodide) and appearance frequency on the polymer backbone, the halogen atoms were included in the unit cell. This yielded an orthorhombic system in the case of fluorine, and triclinic systems in the case of the larger chlorine and bromine substituents.

Motivated by the recent advances in fuel cell membranes, precision polymers incorporating sulfonic [60] and phosphonic [61, 62] acids have been investigated for potential uses as proton carriers. As with carboxylic acids, the aforementioned functionalities must be protected prior to polymerization to prevent poisoning of the metathesis catalyst. While ethyl phosphonates could straightforwardly be deprotected post-hydrogenation, the sulfonate analogues have not led to comparable results. The significant insolubility of the poly(ethylene-*co*-vinylsulfonic acid)s promotes premature precipitation of the material and prevents complete deprotection. This problem is currently being addressed by the Wagener group. With sufficient spacing (20 methylene spacers or greater), the ethylene–vinylphosphonic acid copolymers show a semicrystalline behavior. Amorphous materials are promoted by shorter methylene segments.

Finally, among others, ADMET polymerization has been utilized to produce precision materials containing ether [63], silicon [64], or amine [65] moieties.

Telechelic oligomers via ADMET

Many telechelic oligomers (oligomers with functionalized end groups) have been synthesized by ADMET. These materials are often macromonomers used to synthesize larger polymers, and they have many other uses as well. Telechelic oligomers of polybutadiene (Fig. 9) have been prepared via the reaction of 1,5-hexadiene and a mono- or

Fig. 9 Synthesis of telechelics via ADMET
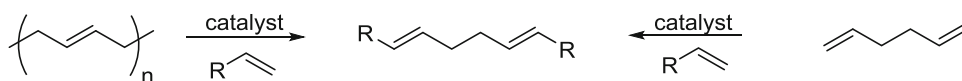
R= silane, ester, alkyl

di-functional olefin [66, 67]. ADMET polybutadiene may alternatively be achieved by the polymerization of 1,5-hexadiene. This polymer can then be used to prepare telechelic oligomers by reacting with a suitable olefin. Sometimes the reaction is incomplete, producing telechelic oligomers. Additionally, polybutadiene produced by cationic polymerization can undergo ADMET depolymerization with acrylates to yield ester-terminated telechelics [68]. This approach was also used to produce a polyamide by depolymerizing polybutadiene with acryloyl chloride and subsequently reacting with 1,6-diaminohexane. Ester-end-capped polyethylene oligomers have been made by ADMET by reacting 1,9-decadiene and 9-decenyl acetate and subsequently hydrogenating the unsaturated units. Telechelic polyacetylenes have been synthesized by ADMET polymerization of 2,4-hexadiene with 1,2-disubstituted olefins [69]. Polyacetylene oligomers terminated with a variety of end groups, including silanes, alkyl groups, and esters were prepared with this method.

Hydrophobic, amorphous telechelic diols have also been synthesized by ADMET [70]. These materials could potentially be used in UV- and hydrolysis-resistant polyurethanes. The hydrocarbon backbone was produced by ADMET polymerization followed by hydrogenation of a gem-dimethyl substituted α,ω-diene, and this material was then endcapped with alcohol-containing monoenes with varied numbers of methylenes between the alcohol group and olefin. Some molecular weight control was achieved in the resulting telechelics, which had 2.0 functionality.

In another report, 1,9-decadiene was polymerized using **[Ru]1** with epoxy-containing monoenes [71].The resulting telechelic polymer was then reacted with toluene diisocyanate resulting in a copolymer containing oxazolidone linkages. ADMET has been used to synthesize ester-terminated telechelics with a similar approach [72].

Conclusion

Over the last two decades, ADMET polymerization has been extensively studied as a unique and valuable means to access and synthesize precision polymers. These materials have provided better understanding of structure–property relationships in various systems, as they serve as models for their ill-defined commercial counterparts. While significant advances have resulted from precision polymers, many more systems have yet to be explored [73].

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