

Recent Advances in ADMET Polymerization

Travis W. Baughman · Kenneth B. Wagener (✉)

George and Josephine Butler Polymer Laboratory, Department of Chemistry,
University of Florida, Gainesville, FL32605, USA
wagener@chem.ufl.edu

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Abstract Acyclic diene metathesis (ADMET) polymerization techniques and methodologies developed over the past five years are reviewed. Through constant catalyst development and further understanding of catalytic activity and side reactions, metathesis has solved a

number of synthetic problems through the mild carbon-carbon bond-forming reaction. Polymerization of functionalized α,ω -dienes has afforded strictly linear copolymers of ethylene and various polar monomers that are unattainable through chain polymerization methodology. Telechelic preparation via ADMET allows the synthesis of reactive polymers as starting points for block and segmented copolymers. Application of ADMET to materials synthesis has yielded novel amino acid and peptide polymers as well as silicon-based materials.

Keywords ADMET · Metathesis · Polymerization · Polyethylene · Copolymers

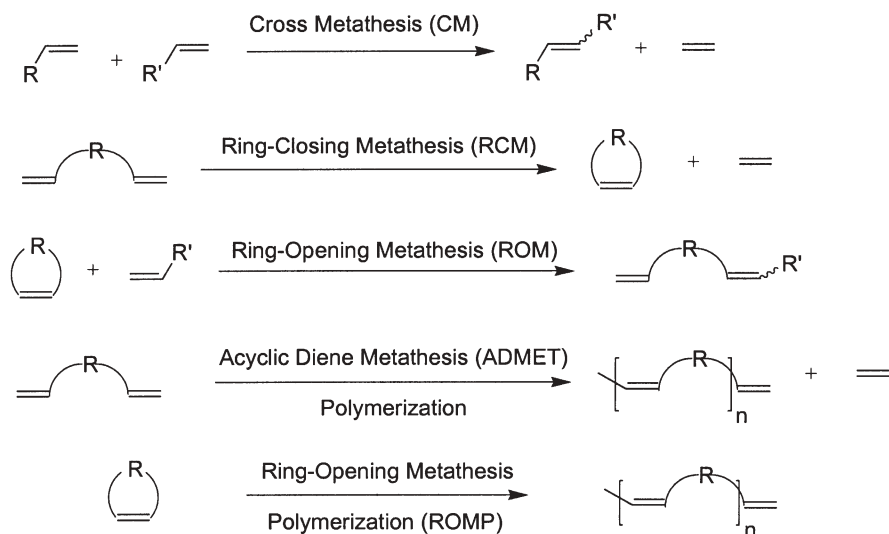
List of Abbreviations

ADMET	Acyclic diene metathesis
ATRP	Atom transfer radical polymerization
CPE	Chlorinated polyethylene
DSC	Differential scanning calorimetry
EEA	Ethylene-ethylacrylate
EMA	Ethylene-methylacrylate
EVA	Ethylene-vinyl acetate
ES	Ethylene-styrene
GPC	Gel permeation chromatography
LALLS	Low-angle laser light scattering
MALDI-TOF	Matrix assisted laser desorption ionization-time of flight
MEM	methoxyethoxymethyl
OLED	Organic light emitting diode
PDMS	Poly(dimethylsiloxane)
PEG	Poly(ethylene glycol)
PPV	Poly(<i>p</i> -phenylene vinylene)
PS	Poly(styrene)
RCM	Ring-closing metathesis
ROMP	Ring-opening metathesis polymerization
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
VPO	Vapor pressure osmometry

1

Introduction

Olefin metathesis has quickly become one of the most widely used methods for mild carbon-carbon bond formation in organic synthesis [1, 2]. With the development of highly active, functional group-tolerant catalysts, like Grubbs' second generation catalyst ($[\text{Ru}]^*$), metathesis has been successfully applied across many areas of research, and some reviews already exist that deal with metathesis catalysis and applications [1–5]. This review focuses on recent developments in acyclic diene metathesis (ADMET) polymerization chemistry and methodology that have been published over the past five years, starting with a short discussion on the history of olefin metathesis and ADMET polymerization.



Scheme 1 Olefin metathesis

A metathesis reaction is defined as a chemical transformation in which atoms from different functional groups interchange with one another, resulting in the redistribution of functionality yielding similar bonding patterns for both molecules [6].

For olefin metathesis, two carbon-carbon double bonds are reacted to form two new olefins (Scheme 1). This transformation was initially reported in the 1950s, but it was not until 1967 that Calderon coined the term “olefin metathesis” [7–11]. Since then, olefin metathesis has been applied to polymer and small molecule synthesis. Pharmaceutical chemists rely on olefin metathesis to create complex cyclic systems, and previously difficult medium and large ring closures can now be achieved rather easily using ring-closing metathesis (RCM) [1, 2, 12, 13]. While RCM is performed at low concentrations to inhibit dimerization, reactions in the presence of high olefin concentrations yield polymers. Macromolecular chemists have embraced olefin metathesis, as it allows the preparation of functionalized hydrocarbon polymers through ring-opening metathesis polymerization (ROMP) [6, 14, 15] and acyclic diene metathesis (ADMET) [16–20].

1.1

History of Olefin Metathesis

Olefin metathesis began as an industrial process involving ill-defined heterogeneous catalysts comprising high oxidation state metal salts and various activating metal oxides [3]. Due to low concentrations of the active species, no spectroscopic evidence could be obtained and little mechanistic data was avail-

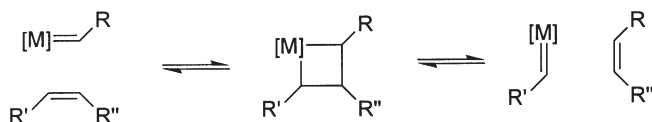


Fig. 1 Chauvin mechanism

able. Debates over the metathesis mechanism continued until the introduction of the now widely accepted Chauvin mechanism in 1971 (Fig. 1) [21, 22].

His proposal involved a metal carbene and a metallocyclobutane intermediate and was the first proposed mechanism consistent with all experimental observations to date. Later, Grubbs and coworkers performed spectroscopic studies on reaction intermediates and confirmed the presence of the proposed metal carbene. These results, along with the isolation of various metal alkylidene complexes from reaction mixtures eventually led to the development of well-defined metal carbene-containing catalysts of tungsten and molybdenum [23–25] (Fig. 2). After decades of research on olefin metathesis polymerization, polymer chemists started to use these well-defined catalysts to create novel polymer structures, while the application of metathesis in small molecule chemistry was just beginning. These advances in the understanding of metathesis continued, but low catalyst stability greatly hindered extensive use of the reaction.

In particular, Schrock-type catalysts suffered from extreme moisture and air sensitivity because of the high oxidation state of the metal center, molybdenum. Due to the oxophilicity of the central atom, polar or protic functional groups coordinate to the metal center, poisoning the catalyst and rendering it inactive for metathesis. Since late transition metal complexes are typically more stable in the presence of a wide range of functionalities, research was focused on the creation of late transition metal carbene complexes for use as metathesis catalysts.

Grubbs' first well-defined ruthenium carbene catalyst ([Ru]) was introduced in the early 1990s as the first air stable metathesis catalyst allowing for manip-

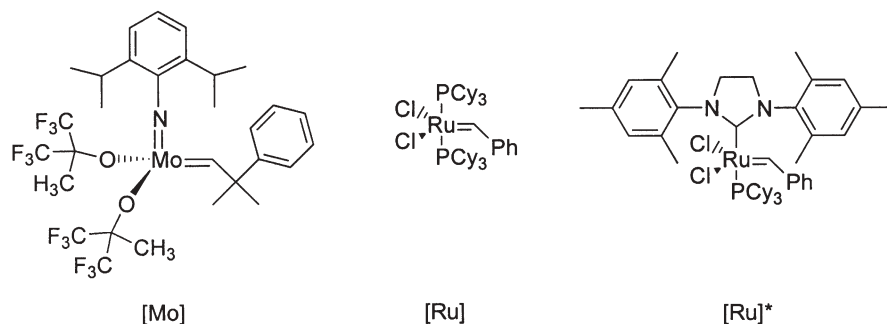


Fig. 2 Metathesis catalysts

ulation of this species outside of inert atmospheres (Fig. 3) [26]. Although catalyst stability was significantly improved, the metathesis activity was reduced substantially relative to Schrock-type catalysts, and the first-generation complexes exhibited slower, lower-yielding reactions. Metathesis activity and functional group tolerance were substantially increased for $[\text{Ru}]^*$ with the introduction of the *N*-heterocyclic carbene ligand as a replacement for one of the trialkyl phosphine ligands [27–36]. These catalysts exhibited activity close to that of $[\text{Mo}]$, and this development brought olefin metathesis to the forefront of modern chemistry. However, one major disadvantage was later discovered; the second-generation complex simultaneously catalyzed metathesis and olefin isomerization. Since then, cross metathesis studies have revealed isomerization occurring at the same time as metathesis, leading to a myriad of olefin products [37, 38]. While this creates synthetic issues for the design of exact chemical structures through RCM or ADMET, polymer chemists who only desire the incorporation of functionality into polymer systems through ROMP or ADMET are still able to take advantage of the improved stability and reactivity of the $[\text{Ru}]^*$ complex.

1.2

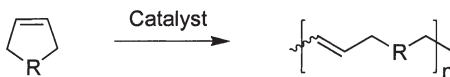
History of ADMET

ADMET polymerization is performed on α,ω -dienes to produce strictly linear polymers with unsaturated polyethylene backbones, as shown in Scheme 2. This step-growth polymerization is a thermally neutral process driven by the release of a small molecule condensate, ethylene [16–20]. Ring-opening metathesis polymerization (ROMP) is widely used to polymerize cyclic olefins and is performed with the same catalysts as in ADMET polymerizations.

Acyclic Diene METathesis (ADMET)



Ring-Opening Metathesis Polymerization (ROMP)



Scheme 2 Metathesis polymerization

The equilibrium of the ADMET polymerization is forced towards high polymer by running bulk polymerizations under vacuum to remove ethylene. Working under bulk conditions or in solution, ADMET polymer products have been isolated up to 80 kg mol^{-1} using $[\text{Mo}]$ on hydrocarbon monomers and up to 70 kg mol^{-1} using $[\text{Ru}]^*$ on peptide functionalized monomers [39, 40].

Near-quantitative conversion of monomer to polymer is standard in these polymerizations, as few side reactions occur other than a small amount of cyclic formation common in all polycondensation chemistry [41]. ADMET depolymerization also occurs when unsaturated olefins are exposed to pressures of ethylene gas [42, 43]. In this case, the equilibrium nature of metathesis is shifted towards low molecular weight products under saturation with ethylene. Due to the high catalytic activity of $[\text{Ru}]^*$ and the ability of $[\text{Mo}]$ and $[\text{Ru}]$ to create exact structures, ADMET has proven a valuable tool for production of novel polymer structures for material applications as well as model copolymer systems to help elucidate fundamental structure property relationships [5].

2

Functionalized Polyethylene via ADMET: Model Copolymers of Ethylene and Vinyl Monomers

Polyethylene is the polymer produced in the greatest amounts (by weight) around the world, and is sought after for various applications due to its cost-effectiveness, ease of production and range of available polymer properties. For decades, researchers have been trying to produce functionalized polyethylenes in an attempt to enhance overall properties of the material through incorporation of polar groups along the polymer backbone. Addition of polar functional groups within the hydrophobic material has been shown to improve polymer adhesion, barrier properties, and chemical resistance [44].

Post-polymerization functionalization has been used to this end, but most research has been directed toward the copolymerization of ethylene with polar monomers. In this manner, inexpensive monomers can be used to create novel polymeric materials with a wide range of applications. The major drawback to this methodology is the inherent difference in reactivity between ethylene and other vinyl monomers during chain polymerization. This phenomenon is known to yield copolymers with low polar monomer incorporation and increased branch content arising from chain transfer events caused by side reactions with polar and/or protic functionalities [45].

Historically, high-pressure free radical copolymerization has been used to produce highly branched, ill-defined copolymers of ethylene and various polar monomers. Although these materials are in production and extensively used throughout the world, the controlled incorporation of polar functionality coupled with linear polymer structure is still desired to improve material properties. Recent focus in this area has led to the development of new transition metal catalysts for ethylene copolymerization; however, due to the electrophilicity of the metal centers in these catalysts, polar functional groups often coordinate with the metal center, effectively poisoning the catalyst. There has been some success, but comonomer incorporation is hard to control, leading to end-functionalized, branched polyethylenes [44, 46]. These results are undesirable due to low incorporation of polar monomer into the polymer as well

as the inability to control branching, that leads to decreased material properties relative to the linear systems. Linear systems afford better materials due to their regular polymer structures, allowing for greater overall crystallinity. Since the goal of this research is to enhance polymer properties, incorporation of polar groups into a linear polyethylene backbone would be ideal, as material properties tend to increase with polymer crystallinity.

ADMET offers a synthetic route to strictly linear, functionalized polyethylenes through the polymerization of α,ω -dienes followed by exhaustive hydrogenation. Researchers have been able to use metathesis catalysts in conjunction with the functionalized monomers to produce statistical or sequenced copolymers of ethylene with various polar monomers. With the improved tolerance and reactivity of $[\text{Ru}]^*$, the broadening of ADMET methodology will allow the syntheses of numerous functionalized systems [4]. However, due to the well known olefin isomerization that occurs during the metathesis polymerization with $[\text{Ru}]^*$, monomer sequence control is lost and the methylene run length between functional groups varies widely.

While ROMP provides a facile synthetic route to functionalized polyethylene through polymerization and hydrogenation, the products lack monomer sequence control and usually fall within a short range of comonomer compositions relative to ethylene copolymers. This can be overcome by copolymerization, but as with any chain addition chemistry, the reactivity ratios of the two monomers – in this case olefins – must be essentially identical to obtain a truly random copolymer. Otherwise, a gradient polymer is obtained. ADMET does allow sequence control through the use of symmetrical α,ω -dienes affording vinyl monomer analog polymers, and due to the step-growth nature of the reaction, ADMET copolymerizations are truly random. These benefits of ADMET can be used to create ethylene copolymer analogs for materials testing and fundamental studies of polymer structure-property relationships. As illustrated in ethylene-propylene ADMET copolymer research, sequence control of comonomers in functionalized ethylenes results in higher degrees of crystallinity, leading to enhanced polymer properties [39, 47].

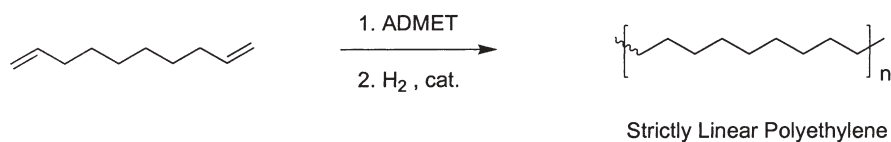
2.1

Ethylene-Propylene Copolymers

Controlling branching in polyethylene has been of significant synthetic interest for over 60 years, and numerous studies have been conducted on polyethylenes with different branch contents and structures [48–56]. Ethylene-propylene (EP) copolymers are methyl branched polyethylenes and can be used to study fundamental branching effects on polymer properties. Due to the large range of material properties available from branched polyethylenes, various architectures have been synthesized using free-radical, Ziegler-Natta, homogeneous metallocene, and, more recently, late transition metal catalysts [57–64]. However, side reactions such as chain transfer and chain walking persist in these polymerizations, causing unwanted branching and broad molecular

weight distributions [65–67]. These structural defects, although exploited to create novel polyethylene materials, become unfavorable when trying to understand specific interactions and how they affect the microstructure in copolymers of ethylene and α -olefins. After decades of research focused on chain polymerization synthesis of strictly linear polyethylenes, Wagener et al. proposed a new synthetic approach to these polymers through step-growth metathesis polymerization, better known as ADMET.

Polyethylene modeling using ADMET step-polymerization began with the production of strictly linear polyethylene by polymerization of 1,9-decadiene followed by exhaustive hydrogenation (Scheme 3) [68, 69].

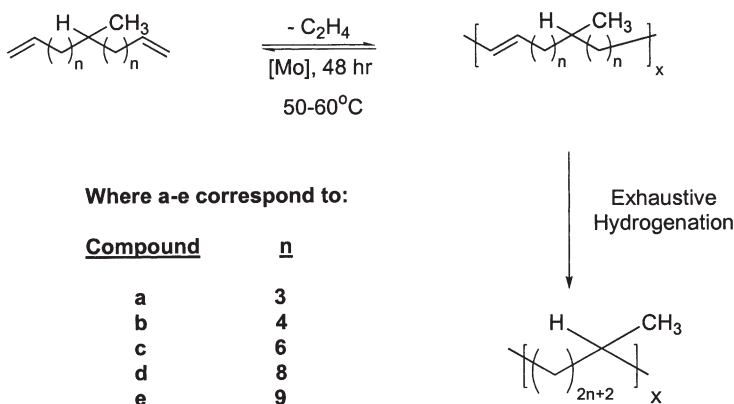


Scheme 3 Linear polyethylene via ADMET polymerization

This metathesis polymerization successfully creates defect-free macromolecules due to the mild nature of metathesis and its lack of side reactions. Although the molecular weights of ADMET polymers are less than that of industrial polyethylene, the entanglement molecular weight for linear polyethylene is 1.0 kg mol^{-1} . Since the molecular weights of ADMET polymers are far above this value, polymers produced via ADMET make good model polymers. We now have the ability to fully control branching in linear polyethylene, allowing isolation of fundamental structure-property interactions.

Synthesis of precisely methyl-branched polyethylene began with the preparation of symmetrical methyl-branched α,ω -dienes to serve as ADMET monomers [71]. A family of monomers was designed not only to determine the effects of regular branching, but also to probe the effect of comonomer incorporation, in this case by adding propylene into an ethylene backbone. These molecules can be polymerized using [Ru] and later hydrogenated, affording the unsaturated, methyl-branched polyethylenes with number average molecular weights ranging from $8.5\text{--}17.5 \text{ kg mol}^{-1}$ and PDIs approaching 2.0, typical of step-growth polymerization [73]. A family of polymers with multiple branch contents was obtained by varying the methylene run length between olefins in the monomer, leading to different spacings of the methyl branches along the polymer (Scheme 4).

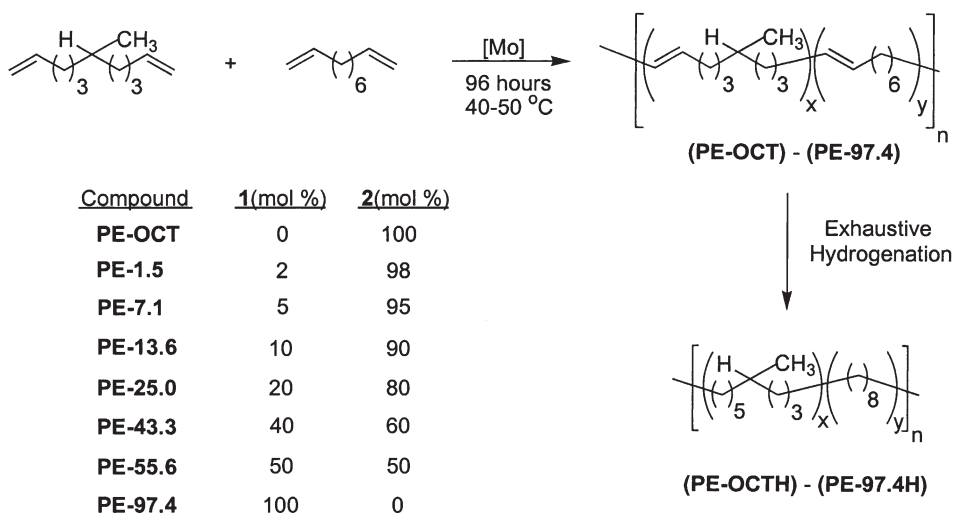
For catalyst comparison, the same monomer was polymerized with [Mo] and [Ru], affording polymers of equal branch content and M_n values of 72.0 and 17.4 kg mol^{-1} , respectively. Upon thermal analysis of these two polymers, both produced sharp melt transitions at $57 \text{ }^\circ\text{C}$, indicating no difference in polymer morphology across this range of molecular weights. In-depth discussions on structural and thermal characterization are included in this report [71]. These synthetic studies proved that ADMET step-growth chemistry was a viable



Scheme 4 Precise methyl branching in polyethylene (from [73])

alternative to chain addition polymerization for creating model polyethylenes. Control over molecular weight, and most importantly over branching and polydispersity, allow the kind of precise control over the polymer microstructure that has been sought for over 60 years.

Upon realizing that ADMET could be successfully used in a polymer modeling motif, expansion of ADMET methodology allowed for the modeling of random methyl branches by copolymerizing previously-used monomers with different weight percentages of 1,9-decadiene using [Mo] as the catalyst (Scheme 5). These experiments produced a family of randomly branched, linear polyethylenes containing 1.5–97.4 methyl branches per 1000 carbons in



Scheme 5 Random methyl branching in polyethylene (from [72])

the polymer backbone. Molecular weights between 14 and 31 kg mol⁻¹ were determined by low angle laser light scattering (LALLS) and were in close agreement with those measured by gel permeation chromatography (GPC) when compared to ethylene-propylene standards. Stringent structural characterization was performed using FT-IR, ¹H and ¹³C NMR to check the random structures of these ADMET copolymerizations [72].

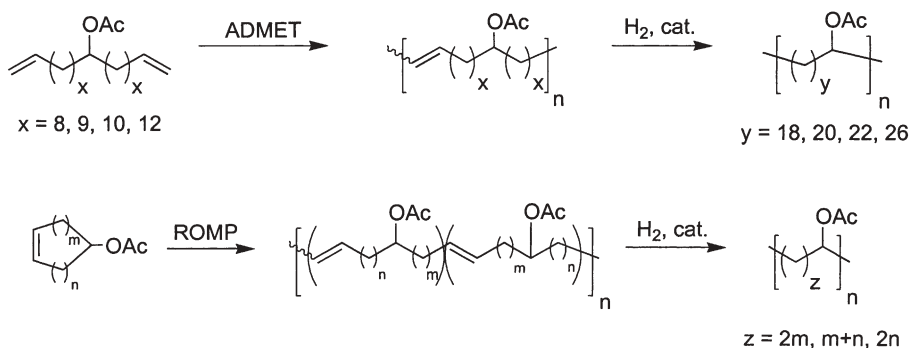
Thermal characterization was performed by differential scanning calorimetry (DSC) on all unsaturated and saturated ADMET copolymers. As expected, the percent crystallinity and heats of fusion for all copolymers containing up to 25 branches per 1000 carbons increased substantially as the polymer backbone of the copolymers became more saturated. Also, as branch content increased, melt transitions shifted to lower temperatures and heats of fusion decreased, indicating a reduction of overall crystallinity. As the structural order of the polymer chain is increased by hydrogenating the remaining olefins and reducing the branch content, the material is able to crystallize more easily, yielding higher melt transitions and improved material properties relative to industrial polymers. For highly branched systems with 43 branches per 1000 carbons or higher, broad endotherms were observed, similar to the broad melts seen with commercial polyethylenes. Even though ADMET copolymers represent a good model for ethylene-propylene copolymers over a wide range of branch contents, their lack of both extensive long chain branching and improved structural order is evident through characterization. Due to the growing interest in ADMET polymer modeling, current work includes the incorporation of longer branches into precisely and randomly branched systems to perfect the modeling and further understand industrial polyethylene materials.

2.2

Ethylene-Vinyl Acetate Copolymers

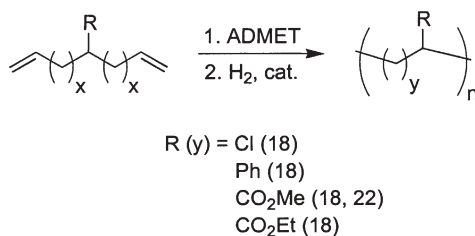
Historically, ethylene-vinyl acetate (EVA) copolymers have been produced through high-pressure free-radical copolymerization, and have been used in hot melt adhesives, packaging films, and toys [74]. Although free-radical chemistry has failed to produce many ethylene copolymers, ethylene and vinyl acetate represent an ideal, or Bernoullian chain copolymerization. In this particular case, the reactivity ratio product $r_1 r_2 \cong 1.0$, and $r_1 \cong r_2 \cong 1.0$, resulting in a truly random incorporation of monomers into the polymer chain. Also, the copolymer composition is identical to the monomer feed ratio [75]. Due to the facile synthesis of EVA copolymers with varying degrees of vinyl acetate content, many studies on structure-property relationships have been performed, gathering fundamental data for polymer behavior [76–78]. Even though the availability of many EVA copolymers has created a large database, free-radical polymerization stills suffer from unwanted chain transfer, leading to extensive branching. Metathesis step polymerization offers a route to strictly linear EVA copolymers with a wide range of comonomer incorporation.

ADMET and ROMP followed by hydrogenation have been used to create novel, linear EVA copolymers (Scheme 6) [79, 80]. ROMP polymers were obtained by polymerizing a functionalized cyclooctene followed by hydrogenation using [Ru] residue under hydrogen pressure. Although these polymers were the first examples of linear EVA copolymers, ADMET methodology could expand our understanding of EVA copolymers, yielding sequenced copolymers that allow insight into fundamental polymer interactions.



Scheme 6 EVA polymer modeling via metathesis polymerization

Starting with various acetate-functionalized dienes, ADMET polymerization was used to model sequenced EVA copolymers. These polymers were produced by bulk polymerization of the acetate-functionalized diene with [Ru] followed by hydrogenation (see Scheme 7). The hydrogenation procedure, reported as the saturation method for ROMP EVA copolymers, involves addition of silica to the reaction mixture after polymerization followed by addition of toluene. This heterogeneous catalyst mixture was then subjected to hydrogen pressures until the polymers were fully saturated. After filtration and solvent removal, colorless semicrystalline polymers of molecular weights ranging from 31–66 kg mol⁻¹ were obtained. Due to the sequence control and lack of branching, narrow melting temperatures were found relative to the commercially-available Elvax series of EVA copolymers, usually exhibiting a broad melt transition typical of industrial copolymers. Experimental observations and characterization of ADMET model polymers illustrates the idea that synthesis of regular



Scheme 7 Functionalized polyethylenes via ADMET

polymer structure allows access to novel polymer properties unattainable in current industrial processes.

2.3

Other Ethylene Copolymers

More industrial polyethylene copolymers were modeled using the same method of ADMET polymerization followed by hydrogenation using catalyst residue. Copolymers of ethylene-styrene, ethylene-vinyl chloride, and ethylene-acrylate were prepared to examine the effect of incorporation of available vinyl monomer feed stocks into polyethylene [81]. Previously prepared ADMET model copolymers include ethylene-*co*-carbon monoxide, ethylene-*co*-carbon dioxide, and ethylene-*co*-vinyl alcohol [82, 83]. In most cases, these copolymers are unattainable by traditional chain polymerization chemistry, but a recent report has revealed a highly active Ni catalyst that can successfully copolymerize ethylene with some functionalized monomers [84]. Although catalyst advances are proving more and more useful in novel polymer synthesis, poor structure control and reactivity ratio considerations are still problematic in chain polymerization chemistry.

2.3.1

Ethylene-Styrene Copolymers

Ethylene-styrene copolymers have been difficult to produce in the past due to reactivity differences between these monomers in chain polymerization chemistry. Although incorporation of styrene into a polyethylene backbone has been successfully achieved with Ziegler-Natta and metallocene catalysts, the styrene content is low and is usually included at the chain ends [85–88]. ADMET polymerization followed by hydrogenation has produced copolymers of this nature with exactly one phenyl substitution on every 19th carbon of polyethylene. Characterization by GPC yielded a molecular weight of 18 kg mol^{-1} when compared to polystyrene standards, while the presence of speculated low molecular weight oligomers and cyclics were detected at longer retention times. Thermal analysis of the styrene branched polyethylene using DSC showed two broad melt transitions at $-22.5 \text{ }^\circ\text{C}$ and $-1.5 \text{ }^\circ\text{C}$. After annealing the sample between the two endotherms, a single melt transition at $-6 \text{ }^\circ\text{C}$ is obtained with second order transitions detected as an unstable baseline between $5\text{--}20 \text{ }^\circ\text{C}$. These interesting thermal characteristics are left as assumptions with future morphological and crystallographic work to be performed.

2.3.2

Ethylene-Acrylate Copolymers

Acrylate-ethylene copolymers have also been synthesized using the same tandem polymerization/hydrogenation methodology. Commercially, ethylene-

methyl acrylate (EMA) and ethylene-ethyl acrylate (EEA) copolymers are available with about 20 wt% acrylate via high-pressure free radical polymerization. EMA and EEA copolymers suffer from extensive branching defects and large polydispersities; differences in the reactivity ratios of the two monomers make the synthesis of copolymers with varying comonomer contents difficult [89].

ADMET polymerization of methoxy- and ethoxycarbonyl-containing dienes followed by hydrogenation has been used to prepare suitable models of methyl acrylate and ethyl acrylate copolymers [83]. Both acrylate copolymers were synthesized with ester functionality on every 19th carbon. One methacrylate copolymer was synthesized with an ester on every 23rd carbon for direct comparison with similar EVA model copolymers already discussed in this review [79]. Molecular weights of 4.8 kg mol^{-1} and 6.4 kg mol^{-1} were obtained by GPC analysis for the methyl and ethyl acrylate polymers, respectively. Melting temperatures of $14.4 \text{ }^\circ\text{C}$ and $37 \text{ }^\circ\text{C}$ were found by DSC for the methyl acrylate polymers, again illustrating that an increase in functional group size on the polymer backbone leads to a greater decrease in polymer crystallinity. The ethyl acrylate polymer exhibited two melt transitions at $9.8 \text{ }^\circ\text{C}$ and $15.1 \text{ }^\circ\text{C}$, similar to the phenyl-substituted polymer. Although the appearance of two endothermic events is not explained, the increased size of the pendant group is responsible for such a low melting point and possibly for second order transitions involving side group conformation similar to those seen in commercial EVAs and EMAs. The ethylene-methyl acrylate copolymer and the previously synthesized ethylene-vinyl acetate copolymer were compared in extensive discussions that also focused on NMR spectroscopy and thermal behavior [81]. This comparison is interesting, as EMA and EVA pendant groups exist as structural isomers.

2.3.3

Ethylene-Vinyl Chloride Copolymers

The final copolymer synthesized in this report on functionalized polyethylenes was an ethylene-vinyl chloride copolymer. Also referred to as chlorinated polyethylene (CPE), this copolymer is of significant interest to the polymer community for morphological and crystallinity studies [90–93]. Wegner et al. performed X-ray and DSC studies on CPEs developed from post-functionalization of polyethylene, which indicated that the relatively small chlorine atom can be incorporated into the polyethylene crystalline structure as a defect [92]. This means that CPEs could lead to materials with improved properties by adding polar functionality without sacrificing crystallinity. Wegner's studies proved that crystallinity control was dependent on functional group placement along the polymer chain. This is in agreement with all results obtained for the ADMET functionalized polyethylenes.

The synthesis of ADMET CPE started with the isolation of the symmetrical chlorine functionalized α,ω -diene. Upon polymerization with [Ru] followed

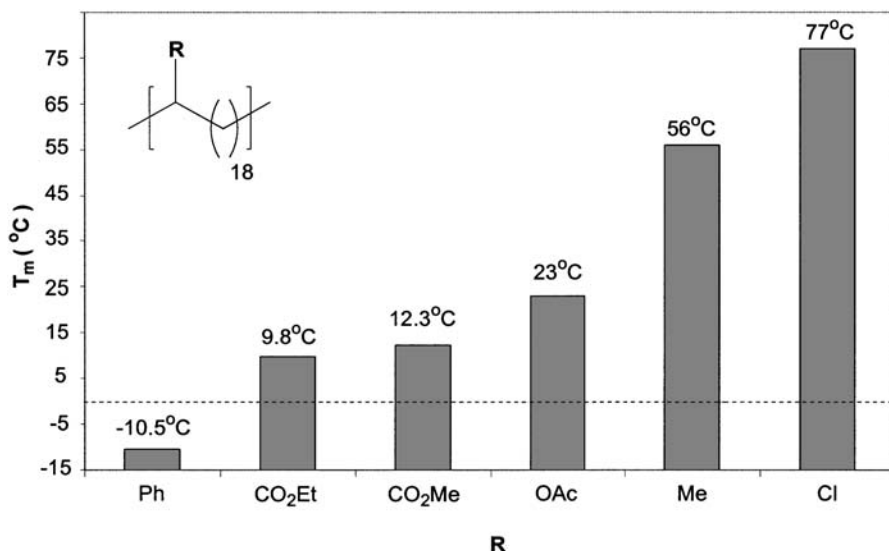


Fig. 3 Bar graph of melt transitions versus functional group on every 19th carbon (from [81])

by hydrogenation and precipitation in acidic methanol, a colorless crystalline polymer was obtained in good yield. Thermal analysis via DSC revealed an expectedly high melting point of 77 °C due to chlorine incorporation into the polyethylene crystal lattice. The melting point is sharp and well-defined, similar to melting points of precisely methyl-branched polyethylenes [71]. When comparing free radical ethylene-vinyl chloride and ethylene-propylene copolymers, a linear relationship is observed between melting points of the copolymers and the comonomer content [90]. For ADMET model copolymers, the situation is reversed, and the methyl and chloro polymers melt at 20 and 57 °C, respectively. In addition, the high degree of crystallinity and lack of branching accounts for the low solubilities of the model CPEs in various organic solvents.

A family of ADMET model copolymers were synthesized and used to study the effects of regular microstructure on polymer properties, in particular functionalized polyethylenes. The structure-property relationships of various ethylene copolymers can be clarified using these model systems. This is illustrated in Fig. 3 by the relationship of T_m to functional group size. Future studies on these and similar systems should lead to fundamental discoveries concerning the class of materials known as polyethylenes and their physical properties.

3 Block and Graft Copolymers via ADMET

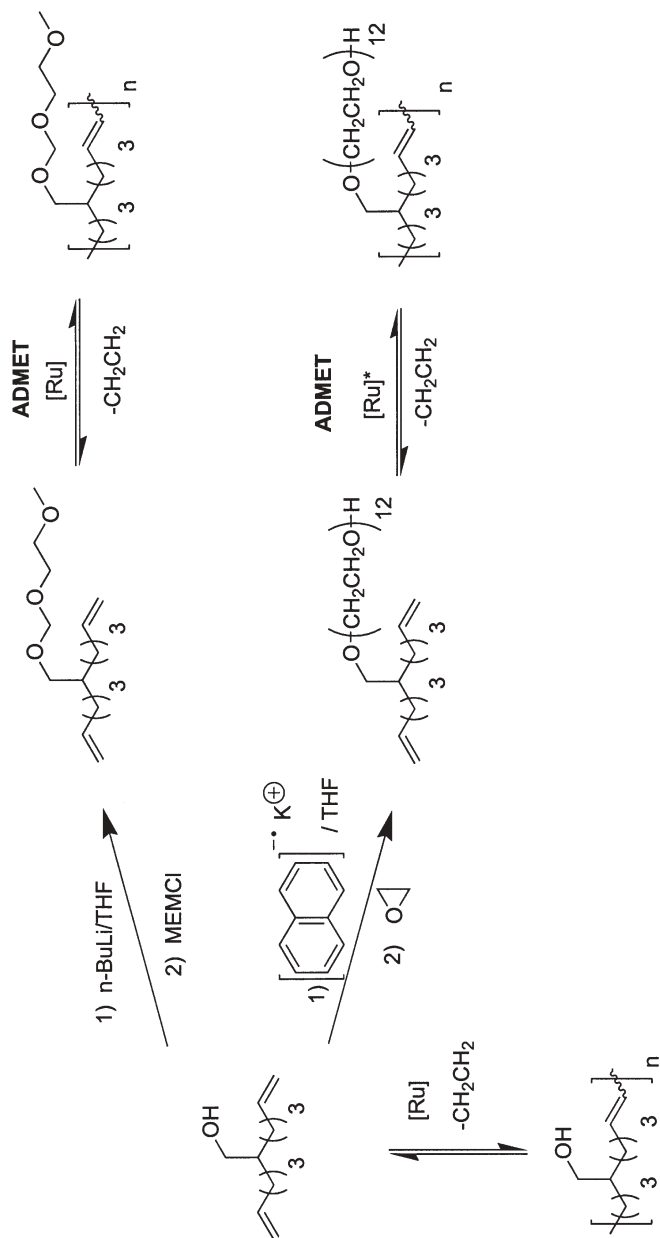
3.1 Grafted Polyethylenes

ADMET has been used to create well-defined architectures of various functionalized polyethylenes that have been discussed throughout this review. Combinations of ADMET with atom transfer radical polymerization (ATRP) and ring-opening polymerization have both proven successful in synthesizing well-defined graft copolymers. Careful polymerization techniques are extremely important in grafted polymer synthesis as the graft density, graft length, and chemical nature of the graft must all be controlled to attain the desired polymer structure. Properties of grafted systems render them desirable for many purposes, including impact-resistant materials and polymeric emulsifiers, while poly(ethylene glycol) (PEG) grafted polymers have shown some success in biomedical applications due to the biocompatibility of this polymer [94–99]. Applying macromonomer and macroinitiator polymerization techniques, ADMET polymerization in conjunction with other common polymerization techniques has afforded PEG and polystyrene (PS) grafted unsaturated polyethylenes [100, 101].

3.2 Polyethylene-*g*-Poly(Ethylene Glycol)

For this study, two polyether graft copolymers were synthesized, one containing a short polyether graft and another with an extended graft architecture (Scheme 8) [102]. The short graft was prepared by reacting an alcohol functionalized diene with methoxyethoxymethyl chloride (MEMCl) to afford the MEM functionalized alcohol. This monomer was polymerized with [Ru] affording the precisely spaced short graft copolymer. Although molecular weight determination by NMR endgroup analysis was impossible, GPC analysis by comparison to PS standards determined a molecular weight of 15 kg mol^{-1} for the MEM grafted copolymer.

For the longer polyether graft, the same alcohol functionalized diene was used to initiate a ring-opening polymerization of ethylene oxide. This reaction afforded a graft length of twelve repeat units of PEG on the diene macromonomer, which was verified via MALDI-TOF analysis, confirming the monodispersity of the graft length prior to polymerization. Upon isolation of the PEG grafted diene, polymerizations were conducted using [Ru], and a polymer of 5.5 kg mol^{-1} was obtained. Catalyst complexation with the PEG graft may be responsible for low conversions during the ADMET reaction. Macromonomer polymerization was also performed using [Ru]^{*}, affording a 12.0 kg mol^{-1} polymer as analyzed by GPC. Although this report refers to these structures as “perfect comb” graft copolymers, it is now well known that [Ru]^{*} isomerizes



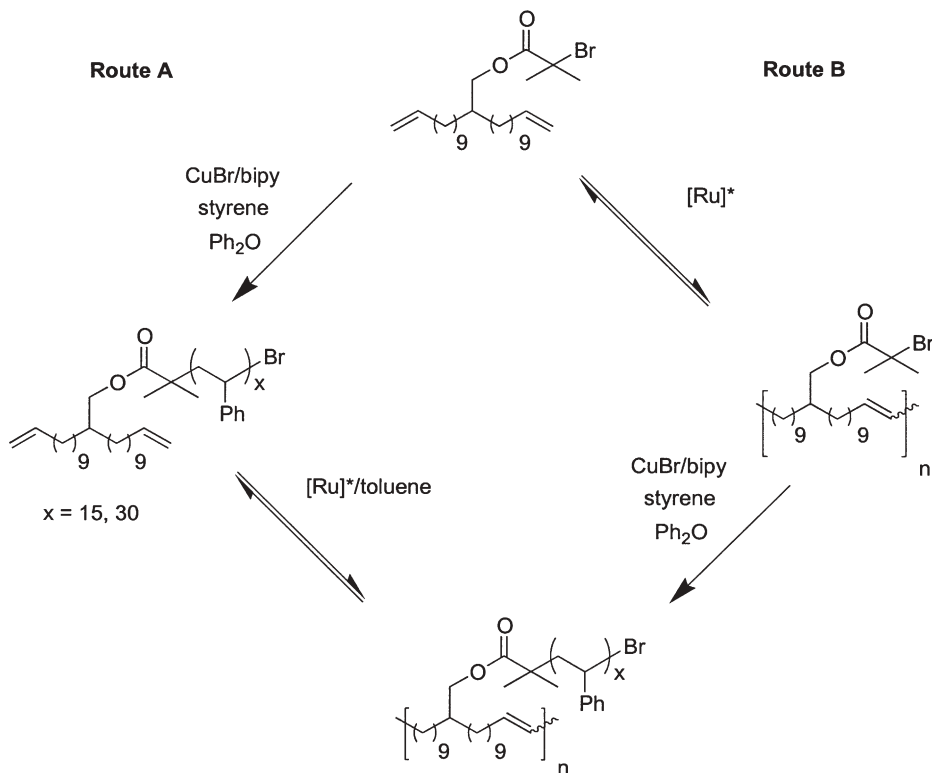
Scheme 8 Polyether grafted ADMET polymers (from [102])

olefins prior to and during polymerization, yielding polymers with irregular methylene run lengths between grafts. Despite imperfect polymer structure, a novel PEG grafted unsaturated polyethylene was successfully prepared. This copolymer demonstrated interesting thermal behavior when analyzed by DSC, and extensive discussion concerning thermal and spectroscopic characterization is included within the article [102].

3.3

Polyethylene-*g*-Polystyrene

Polyethylene-*g*-polystyrene has also been prepared using similar macromonomer and macroinitiator techniques [103]. In these experiments, ATRP was performed with an α,ω -diene macromonomer or a previously synthesized polymer was used as a multiple point macroinitiator (Scheme 9). For the ADMET macromonomer synthesis, PS grafts were prepared by exposing the diene initiator to ATRP conditions in the presence of styrene. Following removal of the initiator by passing the crude polymerization mixture through silica, two macromonomers with graft lengths of 15 and 30 repeat units were isolated by precipitation in cold methanol.



Scheme 9 Polystyrene grafted ADMET polymers (from [103])

All graft lengths were verified by MALDI-TOF analysis, and the molecular weights of two macromonomers were determined at $2\text{--}3\text{ kg mol}^{-1}$ by GPC. Since these macromonomers existed as solids, ADMET polymerization could not be performed in the bulk, so polymerizations were performed in solution. Dissolution of the macromonomer in dried, degassed toluene followed by addition of $[\text{Ru}]^*$ afforded only dimerization for the large PS-grafted macromonomer and a degree of polymerization of 5 for the shorter PS-grafted macromonomer. Steric hinderance was speculated as the cause for these low conversions as the large PS grafts reside close to the metathesis reactive site on the macromonomer. The PS-grafted diene was copolymerized with 1,9-decadiene, but similar conversions were obtained and the polymers exhibited number average molecular weights between 7.4 and 13.8 kg mol^{-1} . Again, macromonomer sterics were to blame for the low olefin conversion. Once macromonomer techniques were exhausted, the ATRP initiator functionalized diene was polymerized yielding the highest molecular weight polymer in this study at 17 kg mol^{-1} . Application of this polymer as a macroinitiator was attempted under ATRP conditions in the presence of styrene; however, only short graft lengths were obtained.

The thermal characterization of these novel grafted systems revealed unique behavior not associated with either of the two homopolymers or random copolymers of styrene and ethylene. These results are discussed in the original article along with NMR and GPC characterization. This is not the first example of the use of metathesis coupled with ATRP to create novel copolymers, as ROMP followed by ATRP has successfully produced novel ABA triblock copolymers [104, 105]. In this study, Grubbs and colleagues performed ROMP on cyclooctene with a small amount of ATRP initiator functionalized monoolefin. The telechelic obtained allowed for the ATRP of styrene or methylmethacrylate from the chain ends. Telechelic monomers have produced copolymers up to 40 kg mol^{-1} , well above the molecular weights obtained with the ADMET studies. This is most likely due to the placement of the ATRP initiator at the chain ends rather than throughout the polymer backbone, creating a less hindered environment for subsequent radical polymerization. Further application of telechelics as metathesis products will be discussed in the next section.

Combination of ADMET with other well-known polymerization techniques has yielded new materials with interesting thermal behaviors. Further use of tandem techniques in this type of materials synthesis can be useful for creating hybrid materials unattainable through conventional methods.

3.4

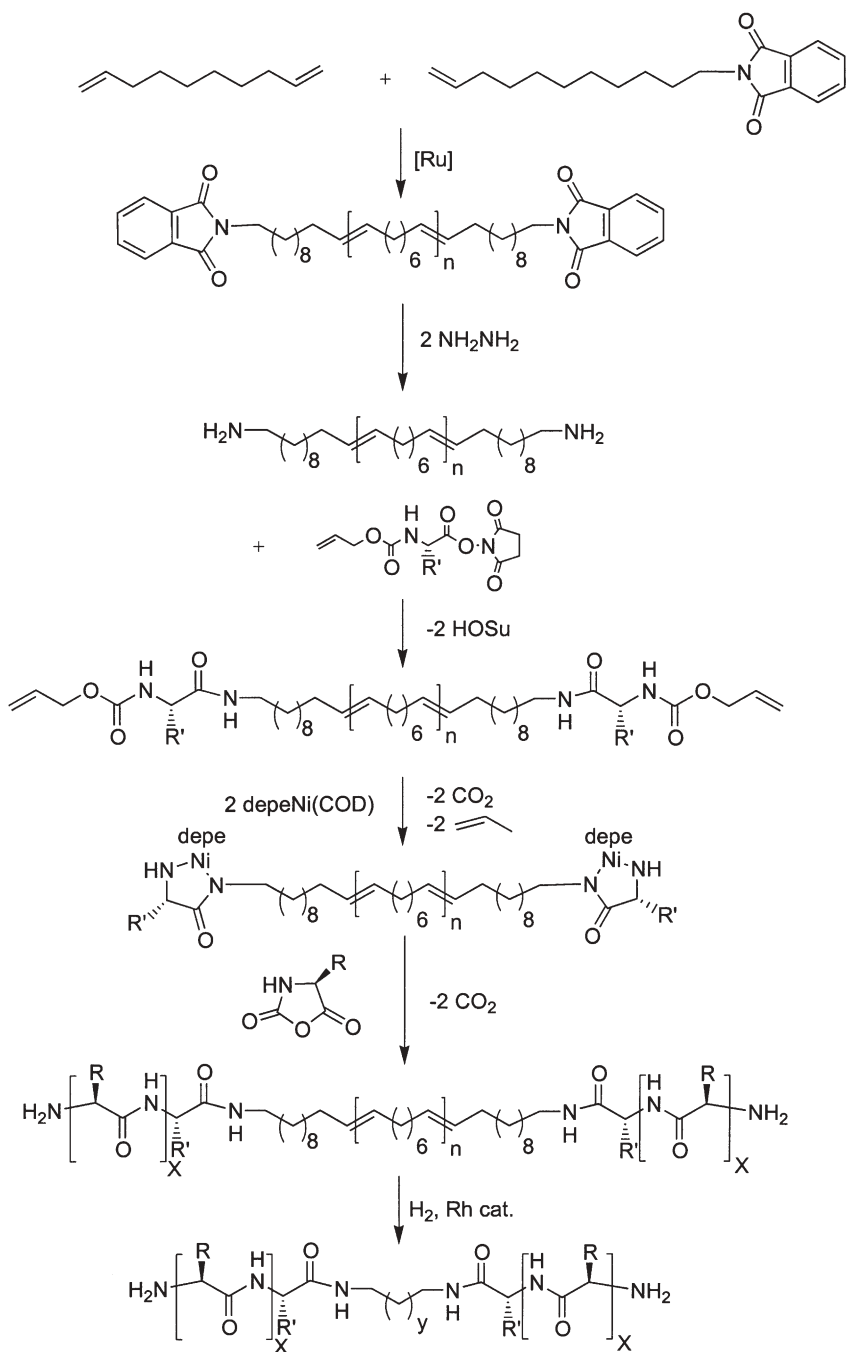
Block Copolymers via ADMET Polyoctenamer Telechelics

Telechelic polymers are defined as macromolecules with reactive sites on the polymer chain, usually as endgroups on linear polymers [106]. This macromolecular architecture has successfully produced a wide variety of block copolymers using macroinitiated polymerizations. Living anionic polymeriza-

tions have been used to create well-defined block copolymers for various applications. In this case, the anionic chain ends act as initiators in the sequential polymerization of vinyl monomers. This method allows for the preparation of highly monodisperse block copolymers that exhibit a range of widely varying physical properties. Upon termination of the anionic chain ends with electrophilic reagents such as anhydrides, carbon dioxide, or ethylene oxide, selective placement of the desired end groups can be achieved for future functionalization or polymerization. Initiators containing protected functionality have also been used to this end when, upon deprotection, reactive groups reside on chain ends. Diblock copolymers are synthesized through this methodology using the macroinitiator approach to polymerize a different monomer from the reactive chain end. For metathesis polymerization, monofunctional olefins are added to the polymerization mixture not only to control overall molecular weight, but also to attach desired functionality to the chain ends.

A variety of telechelic polymers have been synthesized through tandem ADMET and cross metathesis experiments [107–109]. Although the vinyl end groups created from ADMET polymerization are reactive and able to be used in subsequent polymerization, chemical differentiation of these olefins from the internal olefins in the polymer chain is difficult in most reactions and impossible in metathesis chemistry. Copolymerization of an α,ω -diene monomer with a previously synthesized ADMET polymer yielded a copolymer randomized through *trans*-metathesis along the polymer backbone [110, 111]. The inability to differentiate olefins leads to a randomization of olefins within the metathesis regime, and end groups can be incorporated into the polymer using a functionalized monoolefin that can undergo cross metathesis with any double bonds in the polymer creating chain ends *in situ*. As long as the functionality within the endcapping unit does not affect metathesis, telechelic polymers of desired mass and low polydispersities can be prepared. Recently, triblock copolymers and segmented copolymers have been synthesized using this methodology. Subsequent polymerization from the chain ends and use of the telechelic as a reactive monomer in a second polymerization has been performed, yielding novel block copolymer architectures.

Brzeznska and Deming have synthesized novel poly(γ -benzyl-L-glutamate)-*b*-polyoctenamer-*b*-(γ -benzyl-L-glutamate) triblock copolymers (Scheme 10) [112]. These copolymers are of interest as the incorporation of biopolymers into a block system may offer morphological control through tunable conformations of biological materials. Specifically, the production of synthetic protein-lipid bilayers for membrane development has been targeted [113]. Previous work has shown that influences of alpha and beta conformations of biological systems can alter the morphologies and thermal properties of common homopolymers [109, 114]. The recent development of low glass transition telechelic polymers has become of interest in regard to the development of novel polymeric networks. As the methodology of incorporating chemically different polymers into covalent networks becomes available, access to previously unattainable morphologies and polymer properties will also become available.

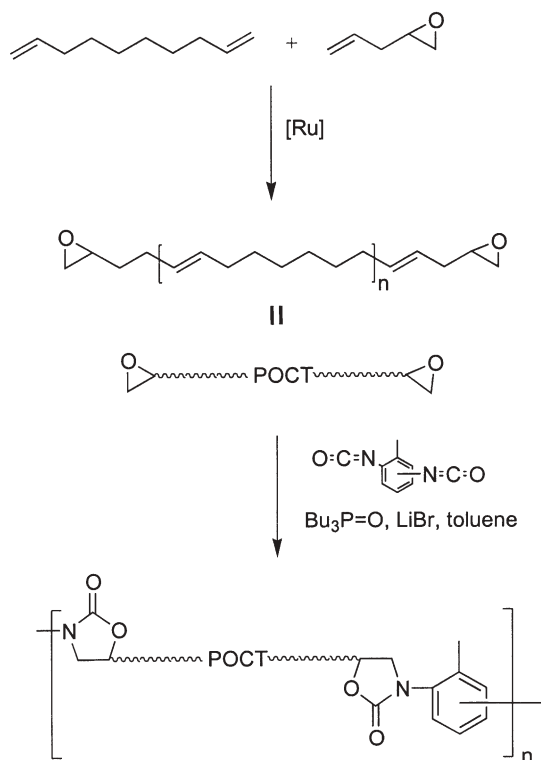


Scheme 10 Block copolymers via ADMET telechelics (adapted from [112])

Synthesis of poly(γ -benzyl-L-glutamate)-*b*-polyoctenamer-*b*-(γ -benzyl-L-glutamate) triblock copolymers began with the preparation of a telechelic polyoctenamer via ADMET polymerization [112]. 1,9-decadiene was polymerized in the presence of 11-phthalimido-1-undecene with [Ru], affording a telechelic polymer endcapped with phthalimido groups. Incorporation of the phthalimido groups undoubtedly begins with the polymerization, but trans metathesis incorporates units of 1,9-decadiene while retaining chain end functionality. In this case, telechelics were synthesized at desired molecular weights of 2.1–12.5 kg mol⁻¹ by careful control of catalyst to monomer ratio. Molecular weight data were obtained by endgroup analysis in ¹H NMR and by GPC. Upon full characterization of the telechelic, the phthalimido endgroups were converted to amino end groups by reaction with hydrazine. This deprotected telechelic was then utilized as a macroinitiator in the living polymerization of glutamic acid-*N*-carboxyanhydride [115, 116, 117]. Thermal characterization by DSC isolated melt transitions arising from the polyoctenamer block at 48.6 °C. Selective polyoctenamer degradation studies using osmium tetroxide allowed isolation of homo poly(glutamic acid) and confirmed the identity and structure of different blocks within this copolymer [119]. Upon isolation of the unsaturated triblock copolymer, hydrogenation was performed with Wilkinson's Rh catalyst to attain a linear polyethylene middle block, in the hope of raising the melt transition of this block, affording desirable material properties. Creation of homopolypeptide contaminants was avoided through the use of macroinitiator methodology that only allowed initiation from the polyoctenamer chain ends. This work has proven beneficial, illustrating the flexibility of ADMET chemistry in syntheses of novel materials with possible biological activity.

Tamura and colleagues have synthesized novel triblock copolymers through a starting middle block of epoxy functionalized polyoctenamer (Scheme 11) [119]. A telechelic polyoctenamer was synthesized via metathesis condensation of 1,9-decadiene with an epoxy functionalized monoolefin at 90 °C for 96 hours. A relationship between molecular weight and temperature dependence was determined and allowed synthesis of the ideal telechelics for these experiments. Ethylene removal was accomplished through intermittent vacuum cycles every three hours. Following precipitation of the reaction mixture from chloroform into acetone to remove catalyst residue, NMR and GPC analysis confirmed the synthesis of the epoxy telechelic of M_n 4700. Yields of the telechelic synthesis were around 25%, but high conversion of the olefin was noted in crude NMR experiments. The authors attributed these results to the loss of low molecular weight oligomers during post polymerization precipitation.

Copolymerization of the telechelic polyoctenamer diepoxide was performed by exposure to toluene diisocyanate, tributyl phosphate, and lithium bromide in toluene. Upon reaction of the isocyanate and epoxide, an oxazolidone moiety is placed in-between each segment of polyoctenamer. IR, NMR, and GPC analysis support these claims, but molecular weight data could not be obtained. GPC data alluded to the presence of two polymeric species in the



Scheme 11 Segmented copolymer via ADMET telechelic

product and current work is underway to separate and analyze the reaction products. Evaluation of small molecule test reactions of epoxy olefin dimerization and small molecule oxazolidone synthesis was performed and is also discussed within the article.

Numerous block copolymer architectures can be devised using functionalized polyoctenamer telechelics via ADMET polycondensation. Using protecting group chemistry or metathesis friendly functionalized monoolefins, almost any reactive group can be placed on the terminus of polyoctenamer through the previously reported procedures. One other example of silane-terminated telechelics was recently published, and discussion of this is included in the later section concerning silicon-containing polymers.

3.5 Alternating Copolymers

Alternating copolymers have been previously synthesized via metathesis polymerization by Grubbs et al. using ring-opening insertion metathesis polymerization (ROIMP) [120, 121]. Here, a fast ROMP polymerization of a cyclic olefin

is followed by incorporation of a linear electron deficient diolefin into the polymer chain via in situ CM. While this method offers a synthetic route to AB copolymers, monomer selection is limited by ROIMP methodology. Recently, ADMET has been applied to this synthetic problem of affording novel AB alternating copolymers of widely varying structures.

Insertion metathesis polycondensation based on ADMET has been developed as a method of alternating copolymer production. Alternating diene metathesis polycondensation (ALTMET) was performed by reacting electron-poor dienes with terminal alkyl diolefins [122]. This polymerization successfully creates perfectly AB alternating structures due to the use of olefins with widely varying reactivity. Production of the electron-poor diene cross-product is suppressed due to the lower activity of the acrylate relative to the alkyl-substituted olefin and the inherent inactivity of the acrylate-functionalized catalyst intermediate towards other electron poor olefins. This selectivity allows for the polymerization of the alkyl diolefin followed by CM of the electron-poor olefin into the polymer backbone. A library of alternating copolymers was produced by copolymerization of monomers from families of alkyl diolefins and electron-poor diacrylates [122]. Since no electron-poor diolefin can be placed next to a similar monomer in the polymer, acrylates are incorporated into the polymer between two dissimilar monomers, creating the alternating AB copolymer. A wide range of unsaturated polyesters were produced, illustrating the flexibility of ALTMET relative to ROIMP for the synthesis of alternating copolymers.

4

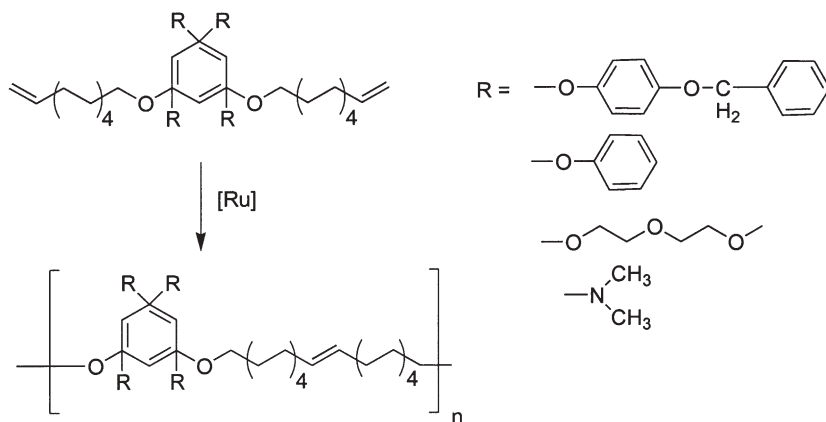
Polymeric Materials via ADMET

4.1

Phosphazene Polymers

Phosphazenes are an interesting class of hybrid materials that have been used to create polymers with widely varying mechanical properties, and they have been recently incorporated into polyimides, polyamides, polyesters, polyurethanes, and polyketones [123–131]. Offering synthetic flexibility due to the labile P–Cl bond, parent cyclic phosphazene trimers are easily accessible starting materials that allow substitution of almost any nucleophile to the phosphazene prior to polymerization. Linear phosphazene polymers have been produced in this manner with a wide range of substituents, allowing tunability of polymer properties [132]. Many of these polymers are suitable for use in fuel cell membranes, ion transport, elastomers, and biodegradable polymers. To date, literally hundreds of phosphazene polymers have been produced, ranging from water soluble, biodegradable polymers to hydrophobic elastomers [123, 124, 132]. Using metathesis to incorporate cyclic phosphazene units into commodity polymers like polyethylene has been of interest for morphology control as well as preparation of combustion-resistant materials.

Allcock and colleagues have used ROMP and ADMET to create novel polymeric systems containing cyclic phosphazene trimer units in the polymer. Using ROMP, phosphazene units are incorporated as pendant groups throughout the main chain of an unsaturated polymer by polymerization of a functionalized norbornene [133]. For ADMET polymerization, a cyclic phosphazene was disubstituted with a terminal diene yielding the target monomer. Upon bulk polymerization, the cyclic phosphazene was included in the main chain of the polymer, creating a cycloliner macromolecule [134–136]. As seen in Scheme 12, many cycloliner polymers were prepared, containing various substituents.



Scheme 12 Phosphazene-containing ADMET polymers

Allcock and colleagues isolated the off-white polymers by reprecipitation from THF into hexanes. Subsequent hydrogenation was performed, and as expected, the hydrogenated products exhibited higher melt transitions relative to the unsaturated polymers. An overall decrease in polymer melting point relative to polyethylene was observed due to the disruption of polymer crystallinity by incorporation of the cyclic moieties into the system. While the crystallinity decrease was expected, more robust materials were desired. To achieve this end, polymers containing more sterically encumbered groups and lower incorporations of the cyclic phosphazene were prepared and exhibited higher glass transition temperatures. Although material properties were significantly improved, preparation of polymers with even lower phosphazene contents were desired. Copolymerization of the phosphazene monomer with 1,9-decadiene afforded a copolymer of higher crystallinity and low phosphazene incorporation. Combustion resistance experiments are ongoing.

4.2

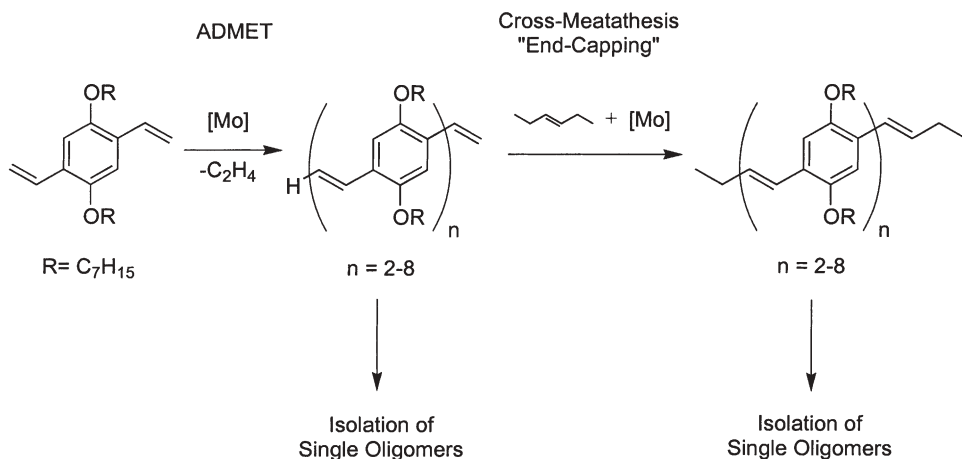
Poly(*p*-phenylene vinylene) Oligomers

Poly(*p*-phenylene vinylene) and various substituted derivatives belong to the family of conducting polymers [137]. This family of polymers can conduct electrons along the polymer chain through an uninterrupted arrangement of π orbitals. These polymers exhibit many unique properties due to this conductivity, and much research is underway to incorporate these flexible conductors into numerous applications. Due to low densities relative to metallic conductors and the chemical resistance of these systems, lightweight electronic devices can be fabricated and put into use where old technology fails. Electroluminescence, nonlinear optical response, photoconductivity, and photoluminescence are just a few properties of these polymers that make them attractive for use in many novel applications or devices [138–143]. Production of viable organic light emitting diodes is of interest, as applications of these polymers in flat panel displays become a reality.

Although much is known about these polymers, they continue to be studied throughout the world to delineate structure-property relationships, especially relating to conjugation length and electronic properties. Polymer modification via substitution has proven useful in determining systemic effects on bulk polymer systems, but additional research is directed toward conjugated oligomers to determine precisely what happens as you add repeat units into the system one at a time. These studies should yield a fundamental understanding of how conjugation length affects material properties. Once these relationships are well understood, novel conjugated polymers of desired conjugation lengths may be constructed, affording enhanced electronic properties for use in various devices.

Recently, a family of diheptyloxy-substituted PPV oligomers has been synthesized using ADMET methodology [144]. Upon polymerization of 2,5-deheptyloxy-1,4-divinylbenzene with [Mo], vinyl-endcapped PPV oligomers were obtained (Scheme 13). Although the vinyl-endcapped PPVs lack thermal stability and cannot be used directly for any applications, the vinyl groups allow unique possibilities for further functionalization through cross metathesis of the oligomers. In this case, *trans*-3-hexene was added to the polymerization mixture to endcap the oligomers with 1-butenyl groups rather than the vinyl substituents. Column chromatography with basic alumina was used to separate the vinyl and butenyl oligomers into crude mixtures, followed by subsequent rounds of chromatography on the crude mixtures to isolate the single oligomers of each type.

Characterization of the oligomers was performed using DSC, MALDI-TOF, FT-IR and NMR. DSC analysis on the monomer and all endcapped oligomers revealed an expected trend of increasing melting point with increasing oligomer molecular weight. MALDI-TOF was used to verify the monodispersity of each oligomeric sample, ensuring that chemical separation was suitable for isolating single oligomers. Extensive characterization by FT-IR and NMR



Scheme 13 PPV oligomers (adapted from [144])

was performed and is included within the text, focusing on the relation of oligomer size to spectral properties [144].

Upon isolation and characterization of single oligomers containing 2–8 PPV repeat units, research was focused on preparation of easily separable, higher order oligomers through metathesis telomerization; the polymerization of low oligomers [145]. Using [Mo], selective telomerization was performed on monodisperse low oligomers to obtain only CM products with terminal double bonds and no reaction with internal vinylene units. Since only the terminal double bonds of monodisperse oligomers react, product mixtures will contain oligomers of integer multiplicity relative to the starting material. This creates oligomeric mixtures differing by the number of repeat units in the original low oligomer material. Easily separable reaction mixtures of all *trans* configured PPV oligomers can be isolated and purified on a large scale using standard chromatographic techniques. Application of previously described methods fails in this motif if higher degrees of polymerization or larger quantities of monodisperse oligomers are needed. NMR analysis of products and time-dependent MALDI-TOF characterization of telomerization reactions are discussed in detail. While [Ru]^{*} seems the catalyst of choice for dimerization of low oligomers, [Mo] is the catalyst of choice for telomerization due to higher conversions, no “side reactions” with internal vinylene units, and the kinetic control displayed during telomerization. Selective dimerization of lower oligomers has been shown to be a valuable method of monodisperse *trans*-PPV oligomer synthesis.

The PPV oligomers synthesized here represent a novel class of oligomers that prove valuable as model compounds for furthering the understanding of conjugated systems. Optical characterization along with detailed microstructure analysis of the oligomers correlated to the chain length should yield valuable data concerning conjugation length and optical properties of conjugated polymers.

5

Chiral Polymers via ADMET

Chiral polymers have been applied in many areas of research, including chiral separation of organic molecules, asymmetric induction in organic synthesis, and wave guiding in non-linear optics [146, 147]. Two distinct classes of polymers represent these optically active materials: those with induced chirality based on the catalyst and polymerization mechanism and those produced from chiral monomers. Achiral monomers like propylene have been polymerized stereoselectively using chiral initiators or catalysts yielding isotactic, helical polymers [148–150]. On the other hand, polymerization of chiral monomers such as diepoxides, dimethacrylates, diisocyanides, and vinyl ethers yields chiral polymers by incorporation of chirality into the main chain of the polymer or as a pedant side group [151–155]. A number of chiral metathesis catalysts have been made, and they have proven useful in asymmetric RCM as well as in stereospecific polymerization of norbornene and norbornadiene [156–159]. This section of the review will focus on the ADMET polymerization of chiral monomers as a method of chiral polymer synthesis.

5.1

Amino Acid-Containing Polymers

Amino acid-containing polymers are target molecules of great interest due to their possible application as biocompatible materials. Incorporation of glutamic acid functionality into a triblock copolymer has already been discussed in a previous section of this review [116]. Incorporation of these moieties into commodity polymers resulting in chiral materials is now feasible due to recent advances in amino acid isolation and purification [160]. Polymer chemists are interested in amino acids due to the hydrogen bonding nature of these units and their ability to take on a higher degree of order through α -helix or β -sheet formation. These ordered structures may lead to enhanced polymer behavior or advanced applications, as found in drug-delivery agents, chiral recognition stationary phases, or metal-ion absorbents [160].

Synthetic methods targeting amino acid incorporation into functional materials vary widely. Free-radical polymerization of various amino acid substituted acrylates has produced many hydrocarbon-amino acid materials [161, 162]. In separate efforts, Morcellet and Endo have synthesized and meticulously characterized a library of polymers using this chain addition chemistry [163–166]. Grubbs has shown ROMP to be successful in this motif, polymerizing amino acid substituted norbornenes [167–168]. To remain within the scope of this review, the next section will focus only on ADMET polymerization as a method of amino acid and peptide incorporation into polyethylene-based polymers.

Wagener and colleagues first reported the use of ADMET as a method of amino acid incorporation into polymers in 2001, and have since expanded their research to focus on the production of novel polymeric materials targeted

Table 1 Properties of amino acid-containing ADMET polymers I (from [169])

Monomer	Polymer	$[\alpha]_m$ (deg)	$[\alpha]_p$ (deg)	M_n (g/mol) ^a	PDI ^b	T_m (°C) ^c	T_m (°C) ^d
4	12	-32	-32	4700	1.73	^e	^e
5	13	-34	-20	27000	1.77	29	38
6	14			33000	1.64	^e	39
7	15	-13	-64	31000	2.02	114	114
8	16	-13	-7	26000	2.10	135	135
9	17			21000	1.70	^e	46

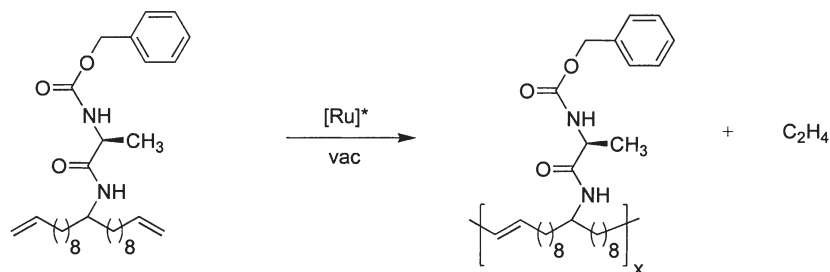
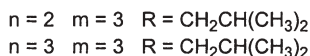
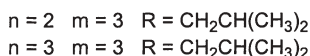
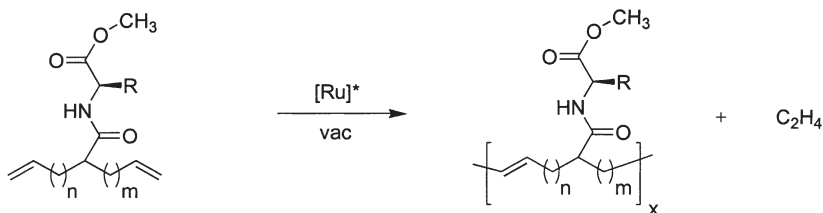
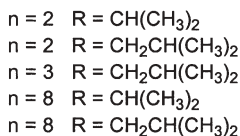
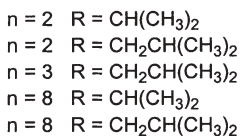
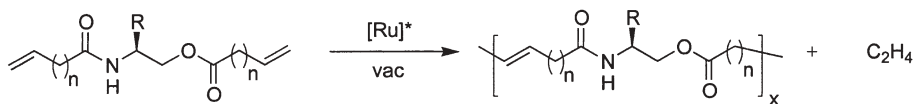
^a M_n values were calculated by GPC vs polystyrene standards. Specific rotations were measured in CH_2Cl_2 at 25 °C, where $[\alpha]_m$ is the specific rotation of the monomer and $[\alpha]_p$ is the specific rotation of the polymer; ^b the polydispersity was determined by GPC analysis; ^c determined by DSC. Reported T_m is due to melt crystallization; ^d Determined by DSC. Reported T_m is due to solution crystallization; ^e No T_m was detected.

at biological applications [169, 170]. The first report revealed a novel approach for synthesis of amino acid moieties within the main chain and as pendant groups in an unsaturated polyethylene backbone (Table 1, Schemes 14 and 15). Due to reaction mixture solidification after only a few couplings, standard bulk polymerization procedures were inappropriate, and solution polymerization procedures were developed to counteract this phenomenon. Polymers synthesized with amino acids within the main chain were hydrolytically unstable, as degradation of the amino acid lead to polymer degradation. These

Table 2 Properties of amino acid and peptide ADMET polymers (from [170])

Polymer	M_w (g/mol) ^a	PDI ^a	T_m (°C) ^b	T_g (°C) ^b
19	26,000	1.54	^e	28
20	36,000	1.45	^e	18
21	73,000	1.55	132	^d
22	63,000	1.67	^e	7
23	21,000	1.62	38 ^c	-21
24	25,000	1.91	^e	5
25	42,000	1.85	^e	-10
26	29,000	1.59	^e	3
27	44,000	1.80	79	^d
28	26,000	1.40	^e	69
29	73,000	1.50	106	5
30	21,000	1.40	71 ^c	^d
31	38,000	1.64	74	^d

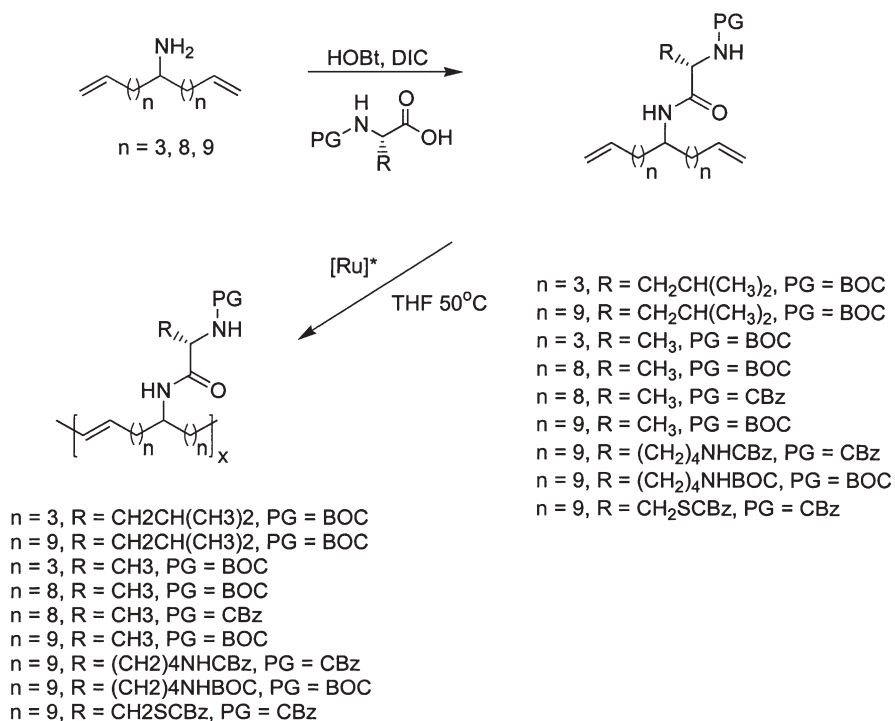
^a M_w and PDI values were calculated by GPC using LALLS; ^b data obtained using a Perkin-Elmer DSC 7 at 10 °C/min; ^c the T_m reported is that of the solvent crystallized sample and no T_m was observed from the melt crystallized sample; ^d no T_g was observed over the scanned range of -80 to +180 °C; ^e No T_m was observed over the scanned range of -80 to +180 °C.



Scheme 14 Amino acid-containing ADMET polymers I (from [169])

polymers were synthesized in the hope that they could be used as biodegradable materials.

Pendant amino acid and peptide polymers synthesized via ADMET have been studied in greater detail than their linear analogs; to date more than twenty pendant functionalized unsaturated polyethylenes have been prepared and characterized (Table 2, Scheme 16) [170]. Synthesis of these polymers began with the synthesis of an amino acid functionalized diene for polymerization with $[\text{Ru}]^*$ in THF at 50 °C. Extra catalyst and solvent was added when necessary. Initial thermal characterization of unsaturated polymers revealed significant differences in morphologies, with some polymers being fully amorphous while others were crystalline. Wide-angle X-ray studies have revealed crystalline domains unlike any ever seen in polyethylene materials. Optical studies and material characterizations are underway to determine solution and bulk morphological properties of this family of polymers. If biomaterials can be



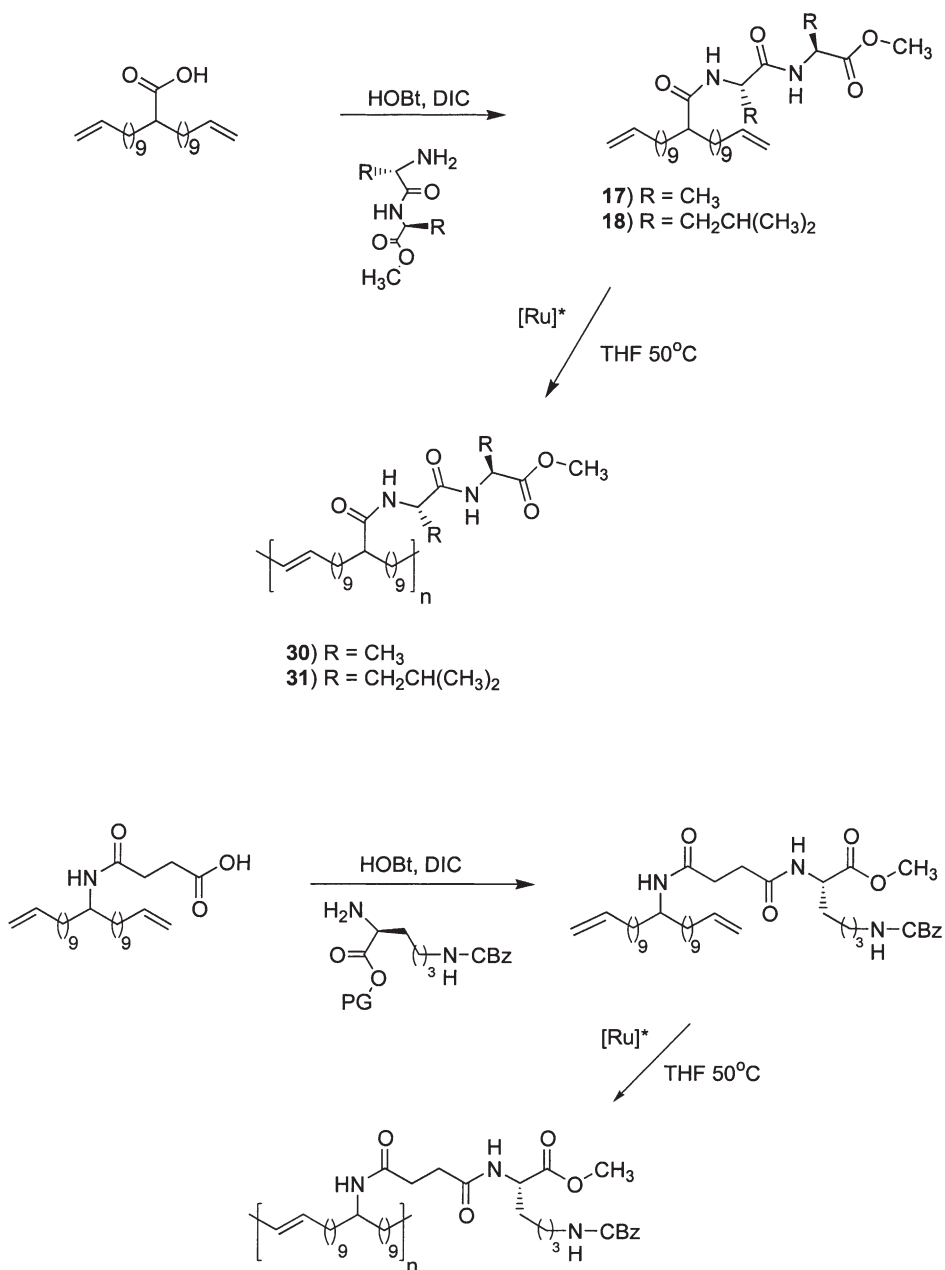
Scheme 15 Amino acid-containing ADMET polymers II (from [170])

produced with selective surface aggregation of amino acid functionality, bio-activity of the bulk polymer could be used in various applications.

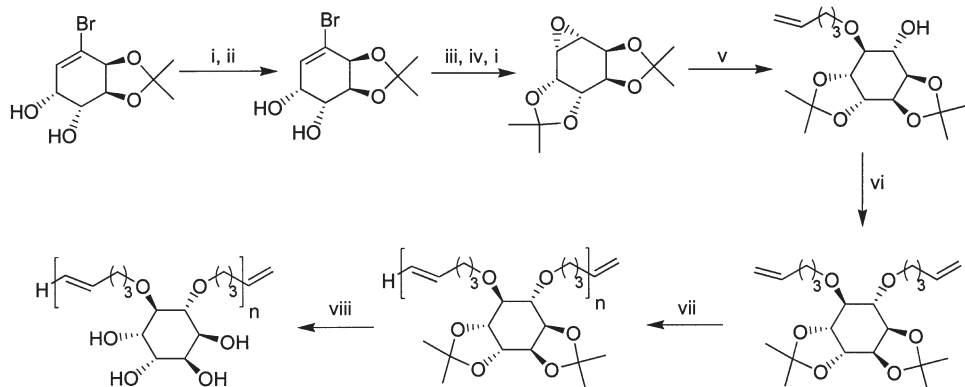
5.2

D-chiro-Inositol-Based ADMET Polymers

ADMET polymers containing D-chiro-inositol have been prepared by polymerizing the acetonide-protected inositol diene followed by deprotection to the D-chiro-inositol containing polymer [171]. Synthesis of the monomer precursor was performed using whole-cell fermentation of bromobenzene with *E. coli* JM109.pDTG601A, a recombinant organism expressing toluene dioxygenase [172]. This diol precursor was easily converted to the acetonide protected inositol and then exposed to [Ru] to obtain the protected polymer (Scheme 17). The 18 kg mol⁻¹D-chiro-inositol polymer was isolated in good yield upon quantitative deprotection with trifluoroacetic acid, and applications of this polymer in chiral separation and/or catalyst development are being investigated.



Scheme 16 Peptide-containing ADMET polymers (from [170])



Scheme 17 D-chiro-Inositol ADMET polymer synthesis: (i) DMP, pTsOH; (ii) acetone, H₂O, NMO, OsO₄; (iii) Bu₃SnH, AIBN, PhH; (iv) mCPBA, CH₂Cl₂; (v) BF₃Et₂O, CH₂Cl₂, 4-penten-1-ol; (vi) DMF, NaH, 5-bromopentene; (vii) [Ru]; (viii) THF-TFA-H₂O 4:1:1 (adapted from [171])

6 Silicon-Containing Polymers

Silicon-containing polymers have been of great interest in the polymer community. Such polymers have found use in biomedical, electronic, ceramic, and agricultural applications, since they offer properties unattainable with organic polymers [173]. Siloxane-based polymers retain flexibility and impact resistance far below operating temperatures of conventional elastomeric materials [174]. Desirable features, such as low glass transition, water repellency, oxidation resistance, and chemical stability, have led to applications as elastomers, sealants, lubricants, and laminates across many areas of industrial and domestic use. Carbosilane polymers exhibit enhanced thermal stability, yielding materials applicable in high-temperature applications. Hybrid inorganic-organic materials have been the goal of many synthetic chemists in recent years, as incorporation of these desirable properties into existing organic materials should lead to improved performance. Relatively few synthetic routes exist to produce materials containing silicon and organic polymers, and with the recently expanded graft and block copolymer methodologies of ADMET polymerization, synthesis of hybrid copolymers in this manner is now feasible.

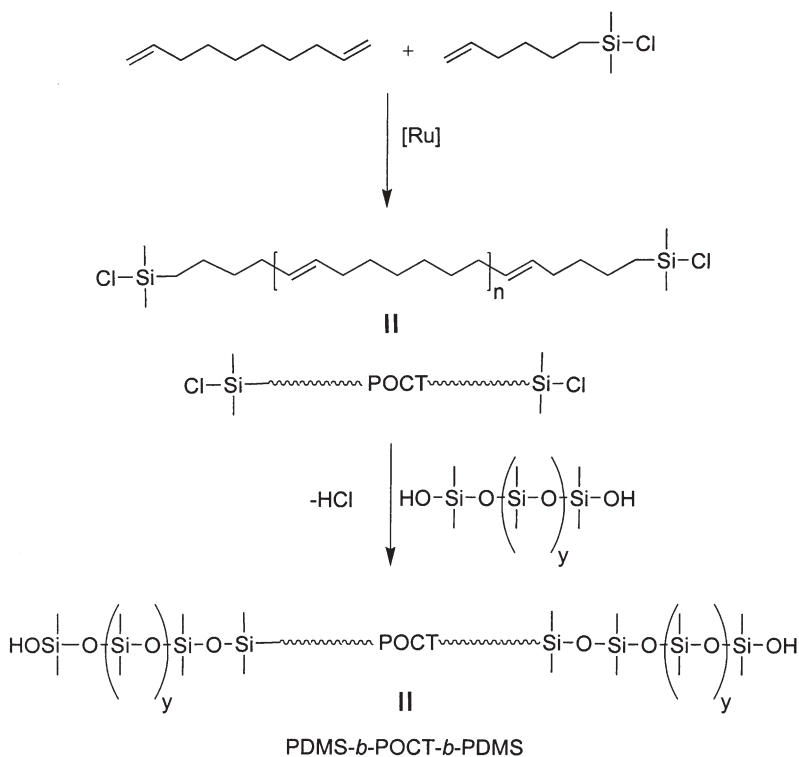
ADMET polymerization has been used to integrate silicon into linear and network hydrocarbon polymers in an attempt to produce novel materials with enhanced thermal and mechanical stability. While ADMET has been used to produce copolymeric architectures unattainable through conventional methods, application of this polymerization to synthesis is feasible only if the silicon-based functionality does not inhibit metathesis. This research, initiated in the early 1990s by Wagener and colleagues, has shown that the silane and siloxane

functionalities can be tolerated by [Mo], and even by the most highly reactive tungsten-based metathesis catalysts, to produce hybrid polymers [175–178].

6.1

PDMS-*b*-Polyoctenamer-*b*-PDMS

ADMET telechelic synthesis has been employed to produce novel block copolymers of polyoxygenamer and poly(dimethylsiloxane) (PDMS) [108]. In this synthesis, 4-pentenylchlorodimethylsilane was prepared as a chain terminating endgroup for the telechelic. This endcapping unit was polymerized with 1,9-decadiene using either [Mo] or [Ru] to afford the telechelic oligomers (Scheme 18); NMR, GPC, and vapor pressure osmometry (VPO) confirmed the synthesis of telechelics with M_n values between 1–10 kg mol⁻¹. These highly reactive silane-terminated polyoxygenamers were then converted to block copolymers by exposure to hydroxy-terminated PDMS polymer. The single hydroxyl group present at one chain end of the PDMS chain quickly reacted with the disilane telechelics forming two Si–O bonds, releasing HCl, and yielding a novel block copolymer represented as PDMS-*b*-polyoxygenamer-*b*-PDMS. Again, NMR, GPC, and VPO were used to confirm the block copolymer struc-



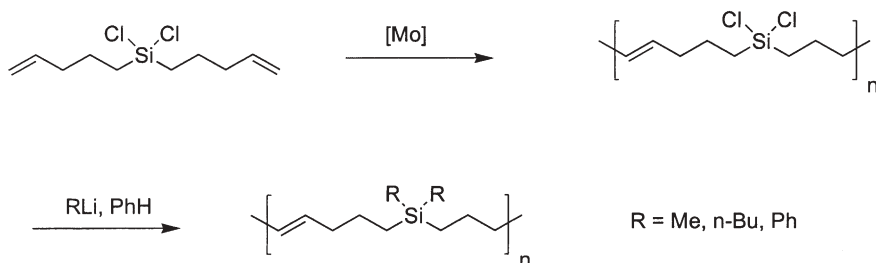
Scheme 18 PDMS-*b*-POCT-*b*-PDMS synthesis

ture; number average molecular weights of around 11.5 kg mol^{-1} were obtained for the block copolymers.

6.2

Carbosilane Polymers via ADMET

Upon synthesis of the telechelic oligomers and further modification of the reactive Si–Cl bond, Wagener and colleagues devised a macromolecular substitution route to polycarbosilanes (Scheme 19) [179]. These experiments involved synthesis of a reactive polymer followed by substitution chemistry throughout the polymer chain. Although many chemical transformations have been attempted on macromolecular systems, few have proven quantitative due to the increased sterics associated with main chain functionality, leading to decreased reactivity and low conversions. However, quantitative substitutions using highly reactive chlorosilanes have been achieved. As an example, West and coworkers demonstrated quantitative substitutions when synthesizing functionalized polycarbosilanes through macromolecular substitution chemistry [180, 181].



Scheme 19 Carbosilane ADMET polymers

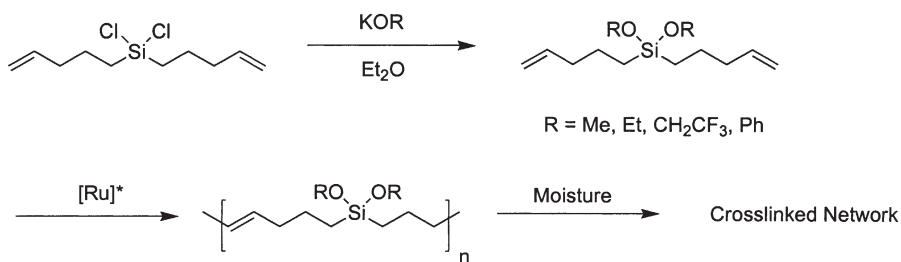
With this past success in mind, ADMET experiments began with the synthesis of di(4-pentenyl)dichlorosilane via Grignard addition of 4-pentenyl bromide to tetrachlorosilane. This monomer was polymerized under stringently dry conditions, yielding linear, unsaturated homopolymers with highly reactive Si–Cl bonds dispersed along the polymer backbone. Quantitative substitution of methyl and *n*-butyl groups onto the polymer was then accomplished by exposure of the polymer to the appropriate alkyl lithium salt. Only partial substitution with phenyl lithium was accomplished; addition of methyl lithium allowed the preparation of an air stable polymer. Upon substitution and conversion of the Si–Cl bonds to Si–C bonds, the polymer was no longer hydrolytically unstable. NMR analysis of all three polymers indicated quantitative substitution of the Si–Cl bond, which was also evident by the solubilities of the polymers, as they had not crosslinked upon exposure to atmospheric moisture. It had been previously shown that only 1% of unreacted Si–Cl bonds would yield an insoluble network upon exposure to moisture [182]. GPC ana-

lyses of the modified parent polymer and all substituted polymers were performed, that indicated number average molecular weights near 20 kg mol^{-1} and polydispersities around 2.0. Production of amorphous hybrid materials via ADMET methodology has proven successful, and this method enables the synthesis of novel functionalized systems through well-known silane substitution chemistry.

6.3

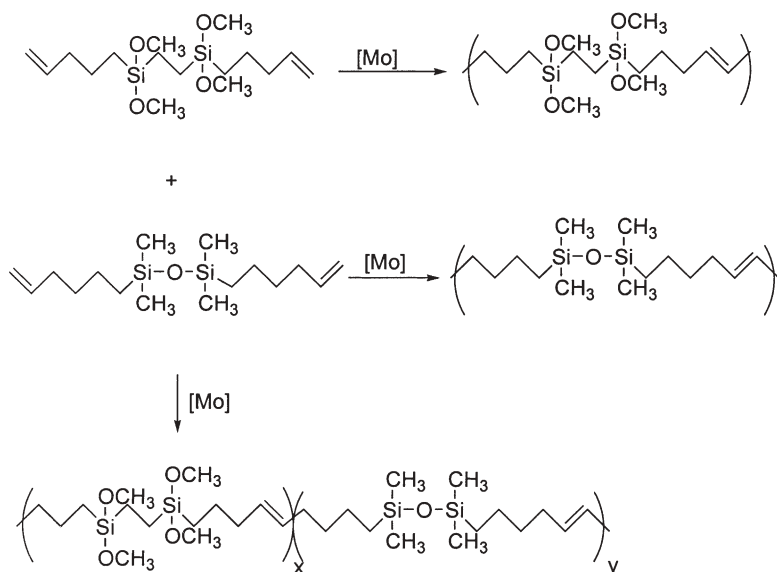
Latent Reactive Carbosilane Polymers

The ADMET monomer di(4-pentenyl)dichlorosilane was also used in the synthesis of carbosilane-based latent reactive polymers [183]. Here, the parent silane was used as a starting point to synthesize a library of silane monomers. Phenoxy, methoxy, ethoxy, and trifluoroethoxy bis chloro silanes were synthesized using standard small substitution techniques, and polymerization was conducted using $[\text{Ru}]^*$ with a monomer/catalyst ratio of 200:1 (Scheme 20). Only the phenoxy substituted polymer could be characterized via GPC analysis due to the inherent air instabilities of the other alkoxy silane polymers. NMR end group analysis revealed number average molecular weights of 11–15 kg mol^{-1} for the air sensitive polymers, while the phenyl silyl ether polymer was measured at 18 kg mol^{-1} and had a polydispersity of 1.8 via GPC. These polymers illustrate the apparent inactivity of the silicon-oxygen bond during metathesis polymerization.



Scheme 20 Latent reactive carbosilane polymers

Homopolymers and copolymers containing carbosiloxane and carbosilane units have been produced that bear latent reactive sites along the chain [184]. Reactive carbosiloxane and unreactive carbosilane homopolymers were first prepared in order to ensure catalyst monomer compatibility and to set end points for copolymer properties. Carbosiloxane homo- and copolymers were synthesized with latent reactivity dispersed throughout the polymer chain in the form of methyl silyl ethers (Scheme 21). It is well known that Si–OMe bonds, although inert during metathesis, can react with atmospheric moisture creating stable Si–O–Si bonds and methanol [185].



Scheme 21 ADMET carbosilane and carbosiloxane homopolymer and copolymers (from [173])

This type of network synthesis allows for the preparation of a wide variety of copolymers and ultimately networks, offering widely varying chemical and physical properties depending on the comonomer ratio and the density of latent reactive groups along the polymer chain. Linear homo- and copolymers were obtained by ADMET with [Mo] in a glovebox. NMR analysis of the product polymers illustrated the appearance of an internal olefin peak indicative of metathesis polycondensation, as well as the unchanged silyl ether signal indicating the presence of the latent reactive site.

Latent reactive silyl ethers have been used in the sealant industry to cure siloxane caulks and adhesives [185]. A silanol (Si-OH) group is produced upon exposure of the silyl ether to atmospheric moisture, which can undergo further reaction with another silyl ether to create a thermodynamically stable Si-O-Si bond between polymer chains. Varying the molar ratio of the latent reactive carbosilane to the unreactive carbosiloxane allows us to control the crosslink density and material properties of the resultant polymer network. Previous work from this research group has shown the ability of other latent reactive sites to be used to prepare novel hybrid polymers, but the rate of reaction of the Si-Cl bond is much faster than that of the silyl ether, making the latent reactivity hard to control and too fast to allow proper molding of the linear polymer prior to crosslinking [179]. Metathesis polymerization of latent reactive carbosiloxanes into various homo- and copolymeric systems has shown that ADMET is a useful method for synthesizing functional materials. Currently, a family of novel latent reactive monomers is being prepared by copolymer-

ization of carbosilane and carbosiloxane monomers in order to prepare novel hybrid segmented networks for various low temperature applications [186].

7

Conclusion

Recent developments in ADMET polymerization and its use in materials preparation have been presented. Due to the mild nature of the polymerization and the ease of monomer synthesis, ADMET polymers have been incorporated into various materials and functionalized hydrocarbon polymers. Modeling industrial polymers has proven successful, and continues to be applied in order to study polyethylene structure-property relationships. Ethylene copolymers have also been modeled with a wide range of comonomer contents and absolutely no branching. Increased metathesis catalyst activity and functional group tolerance has allowed polymer chemists to incorporate amino acids, peptides, and various chiral materials into metathesis polymers. Silicon incorporation into hydrocarbon-based polymers has been achieved, and work continues toward the application of latent reactive ADMET polymers in low-temperature resistant coatings.

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