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Synthesis of Telechelic Polyolefins

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Abstract:

Telechelic polymers, polymers with two reactive end-groups, are sought after for their role in synthesizing macromolecules with complex structures such as multiblock copolymers and graft-polymers. Many strategies for the synthesis of telechelic polymers of vinyl monomers using controlled radical polymerizations, anionic polymerizations exist. However, polyolefins—which account for the major fraction of polymer production—are not easily synthesized with two reactive end-groups. This difficulty is related to the sensitivity of olefin polymerization catalysts and their propensity for intramolecular chain transfer reactions. As the result, the most common strategies to access telechelic polyethylene and polypropylene (the two major polyolefins) do not rely on the insertion polymerization of ethylene nor propylene but rather on the polymerization of dienes or cyclic olefins. Nonetheless, recent advances in insertion polymerization and post-polymerization functionalization have resulted in the emergence of novel synthetic methods to access telechelic polyolefins. In this review, we present a comprehensive review of all of these strategies to synthesize telechelic polyolefins.

Introduction

Telechelic polymers are polymers with two reactive end-groups.[1] The reactivity of these end-groups has been used to access, for example, block copolymers, or polymers with complex architectures through post-polymerization reactions.[2] Today, telechelic polymers are most commonly synthesized via controlled radical polymerization, living anionic polymerization and living ring-opening metathesis polymerization.[2–5] While very successful, these polymerization methods are not compatible with the polymerization of ethylene and propylene, and thus, telechelic polyolefins remain difficult to access, despite the usefulness of these telechelic polyolefins,[6] and the critical importance of polyethylene (PE) and polypropylene (PP) for our society.[7–9] The failure of effectively producing telechelic polyolefins through insertion polymerization encumbers the synthesis of for example (multi)block copolymers containing polyolefin. This challenge represents a significant limitation in materials science in view of the promises held by combining the mechanical and chemical properties of polyolefins to the unique attributes of block polymers.[10–12] To address this limitation, different methodologies have been developed over the years to synthesize telechelic polyolefins. In this review, we provide a comprehensive description of all these procedures (**Figure 1**). Note that semi-telechelic polyolefins are intentionally not discussed. This is in part motivated by the fact that in absence of a chain transfer agent, any non-living insertion polymerization of olefin results in polyolefin chains containing a terminal unsaturation (semi-telechelic polymer). The use of these semi-telechelic polymers to yield block copolymers has been recently reviewed.[13–15]

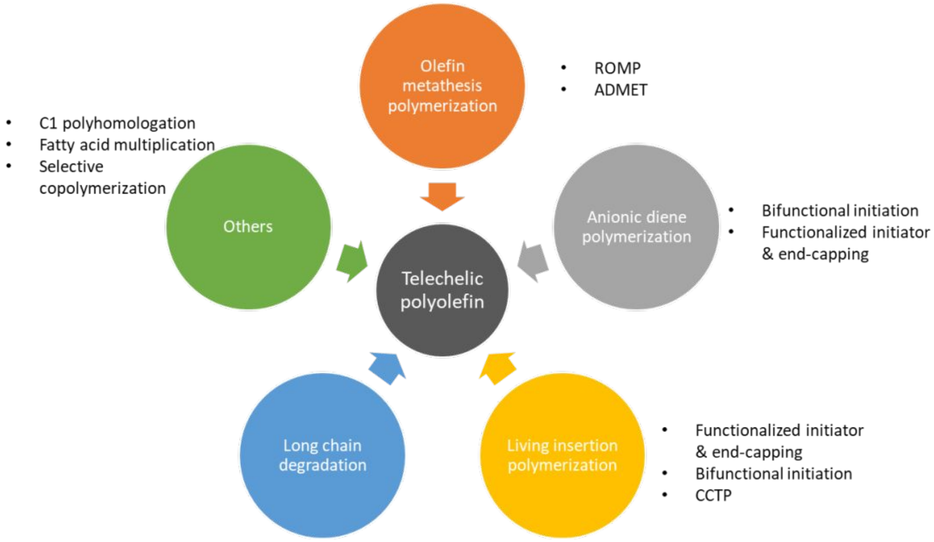

Figure 1. Synthetic strategies for telechelic polyolefins

Olefin metathesis polymerization

With the development of robust ring-opening metathesis polymerization (ROMP) catalysts, ROMP has become one of the most common methodologies to synthesize well-defined telechelic polyolefins.[16–18] 8-Membered cyclic olefins, like cyclooctene and 1,5-cyclooctadiene, are commonly polymerized in presence of difunctional acyclic olefins that serve as chain transfer agents (CTAs) to yield polyene with functional end-groups.[16,19,20] The unsaturation in the polyene is subsequently hydrogenated to yield the targeted telechelic polyolefins. The tunability of this method is reflected in the control of the degree of polymerization through variation in the CTA loading, the variety of end-functionalities from CTA, and the different alkyl branches introduced from modified cyclic olefin monomers.[21,22] The ROMP of cyclic olefins has given access to telechelic PE with unique composition and architecture (**Figure 2**), based on which crosslinked and photocurable elastomers were constructed.[21,23] However, an intrinsic limitation of ROMP is that it cannot produce PP. This represents a non-trivial limitation since isotactic PP is the largest thermoplastic produced worldwide.[24]

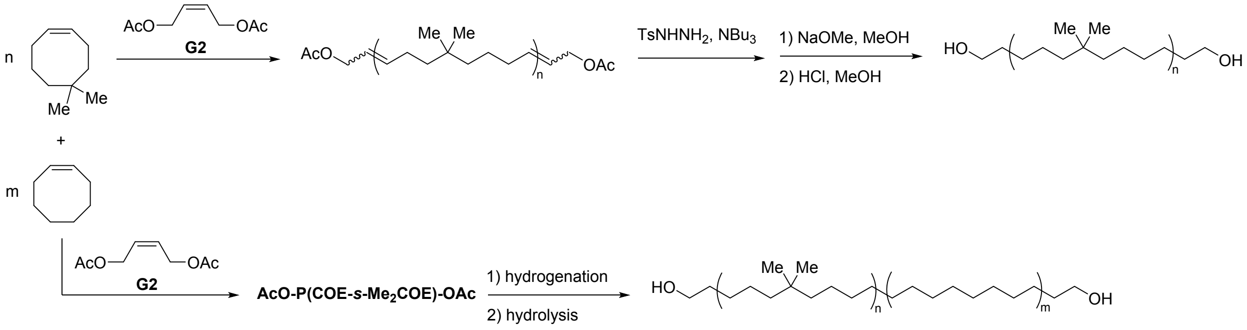

Figure 2. Hydroxy-telechelic poly(ethylene-*co*-isobutylene) through ROMP. Adapted with permission from ref.22. Copyright RSC 2015.

Acyclic diene metathesis polymerization (ADMET) of α,ω-diene monomers represents another strategy to access telechelic polyolefin via an olefin metathesis reaction.[25–27] This step-growth polymerization—that consists of a cascade of cross-metathesis reaction between α,ω-diene terminated chains (and the release of ethylene)—provides a reliable strategy to access high purity telechelic polyolefins. Functional olefins have been added to simultaneously control the degree of polymerization and introduce more reactive end-groups.[28–30] Modifying the α,ω-diene monomers with branches leads to "precision-branched PE".[31] As with any step-growth polymerization, the challenge of ADMET is related to the need for high purity monomer to reach high molecular weight polymers. Here again, the synthesis of PP via ADMET is not trivial and has yet to be reported.

Anionic diene polymerization

Living anionic diene polymerization, followed by post-polymerization hydrogenation is the other most common approach to access telechelic polyolefins. The styrene-*b*-ethylene-butylene-*b*-styrene (SEBS) thermoplastic elastomer is one of the few commercially available polyolefin-containing block copolymers made using living anionic diene polymerization.[32,33] High degree of control on the polymer molecular weight distribution and high end-group fidelity of functional groups make it an appealing strategy for the synthesis of end-functionalized polyoelfins and block copolymers.[2,34–37] Hydroxyl-terminated telechelic polyolefins are easily accessed from anionic polymerization of diene monomers.[37] Binuclear diinitiators like alkali metal naphthalenides are used to initiate the polymerization, and ethylene oxide is subsequently used to convert both metal alkyl end-groups into hydroxyl groups. [38] The high polarity of the diinitiators requires the use of polar solvents like THF that favor the 1,2-addition of the diene and impede the synthesis of strictly linear PE. [39] Although diinitiators soluble in non-polar solvents were later developed, the low ionic dissociation still required polar additives as electron donor, preserving the side impact of 1,2-addition.[39,40] The resulting polyene contains upwards of 80% 1,2-addition structure. The subsequent hydrogenation with Pd/C yields the saturated polyolefin backbone.

Functional alkali-initiators have also been used for diene polymerization to yield hetero-telechelic polymers. The polymerization of isoprene initiated by 3-(tert-butyldimethylsilyloxy)-1-propyllithium, quenched by ethylene oxide and a subsequent hydrogenation has been reported to yield a hydroxylated end-group and a silyl ether end-group (Mn = 16 kg/mol and Đ = 1.18,

Figure 3).[41] The hetero-telechelic poly(ethylene-*alt*-propylene) was then used to construct star-shaped polymers.

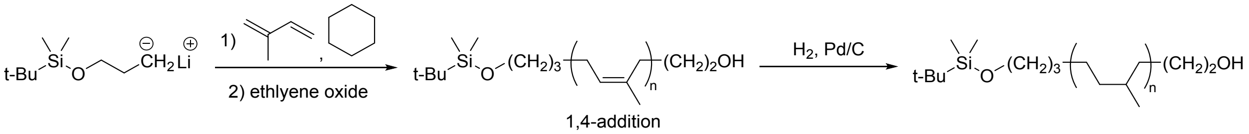

Figure 3. Using functionalized initiator and end-capping to access hetero-telechelic poly(ethylene-*alt*-propylene). Adapted with permission from ref.41. Copyright ACS 2006.

The living anionic diene polymerization, however, only works with a limited number of monomers—narrowing the range of available polymer blocks—and does not offer any stereocontrol. Therefore, the synthesis of stereoregular PP from anionic diene polymerization remains unachieved. Furthermore, the 1,2-addition of butadiene during the anionic polymerization introduces butyl branches into the polymer chain which ultimately limit the crystallinity of the polyethylene. Despite the commercial success and precision of this synthesis method, the anionic polymerization of dienes does not allow many compositional variants in the polyolefin. It is worth noting that polymerization of isoprene yields (after hydrogenation) a perfect ethylene-*alt*-propylene copolymer that could not be synthesized through an ethylene/propylene copolymerization.[33]

Living insertion polymerization

Functionalized initiators and end-capping reagents. Performing a living insertion polymerization with a functionalized initiator and quenching it with an end-capping reagent represents the most straightforward approach to synthesize (hetero)-telechelic polymers. In the insertion polymerization of olefins, the functionalization of the initiating species, however, is not trivial as it requires the organometallic catalyst to be compatible with functional groups. The lower oxophilicity of late transition metal-based catalysts over their early transition metal counterparts makes them more amenable to this approach.[42] An example of the functional group tolerance of late transition metal-based catalysts is that palladium diimine catalysts were the first late transition metal catalysts reported to yield high molecular weight ethylene and polar monomer/olefin copolymers.[43,44] The propensities of this family of catalysts to insert acrylates and chain walk result in a facile synthesis of a stable and chemically tunable 6-member palladium chelate. Under very specific reaction conditions, this functionalized palladium complex was reported to perform the living polymerization of ethylene.[45–48] Using this chelate to initate the living polymerization of ethylene and after the desire molecular weight PE is achieved, the unreacted ethylene is relieved and excess functional vinyl polar monomer was added to yield an hetero-telechelic branched polyethylene (only one polar monomer is inserted). Alternatively, the insertion of 5-hexenyl-1-ol (followed by chain-walking and elimination) has been employed to introduce a reactive aldehyde end-group in the polymer (**Figure 4**).[49] The same concept and catalyst have been applied to the polymerization of propylene, however, the unfavored coordination of propylene over the chelating ester group results in extremely slow initiation and overall low catalyst activity.[48]

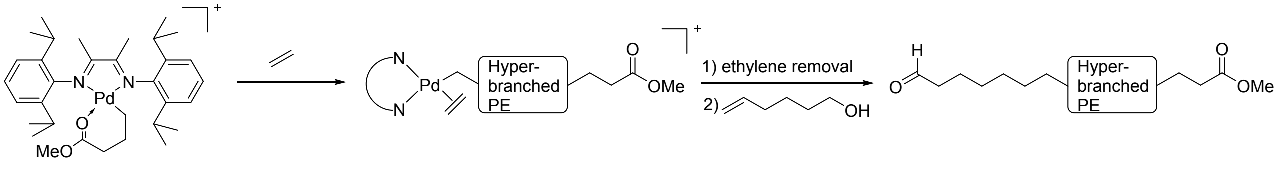

Figure 4. Living ethylene polymerization end-capped by 5-hexenyl-1-ol. Adapted with permission from ref.49. Copyright ACS 2020.

Functionalized early transition metal catalysts combined with an end-capping reaction have been implemented to access (hetero-)telechelic polyolefins through the formation of an in-situ functionalized initiator.[50] A bis(phenoxy imine) titanium precatalyst was reacted with stoichiometric amount of trimethyl(undec-10-en-1-yloxy)silane to form a cationic titanium alkyl complex bearing a protected alcohol group. This *in-situ* formed titanium alkyl complex was then used to initiate the living stereocontrolled polymerization of propylene (syndiotactic polymer). After a given reaction time, the propylene was released and trimethyl(undec-10-en-1-yloxy)silane was added to cap the polymer chain end (**Figure 5**). The very slow consecutive insertions of the end-capping monomer ensured the introduction of a single functionality at the end of the polymer chain. Hydrolysis of the alkoxysilane group yielded a hydroxy-telechelic syndiotactic PP with the molecular weight of 9.6 kg/mol and a dispersity of 1.08. The stereoregularity of the polymer was illustrated by the high melting temperature of the polymer (T_m = 143 ^oC). The same strategy was also implemented for the synthesis of telechelic PE. However, the low solubility of the PE caused its precipitation during the polymerization which significantly hindered the insertion of the end-capping monomer and thus the polymerization yielded primarily semi-telechelic PE. This result illustrates the challenge associated with the functionalization of polymers with low solubilities. This problem is particularly preponderant with PE as it presents mediocre solubility below its melting temperature (~120 ^oC) and most living polymerizations of ethylene are performed (far) below this temperature.[47]

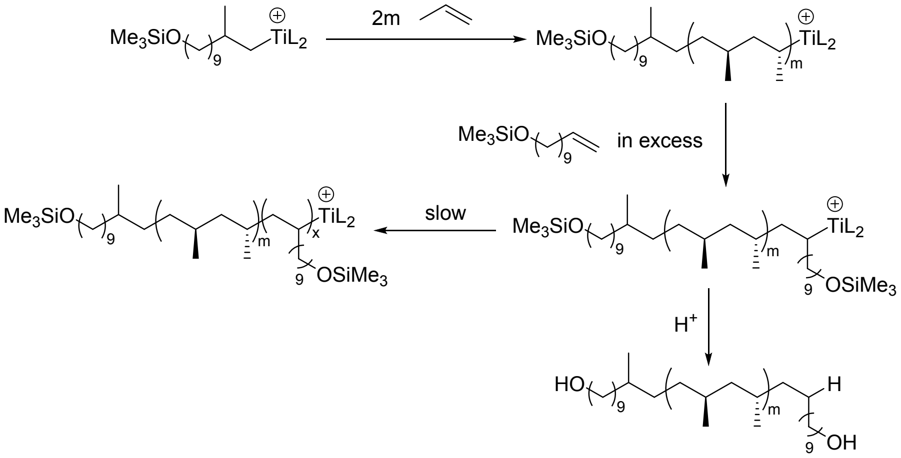

Figure 5. Syndiotactic hydroxy-telechelic PP synthesized from functionalized initiators and end-capping reagents. Adapted with permission from ref.50. Copyright Wiley VCH 2007.

Binuclear initiators/bifunctional initiators. Inspired by the anionic polymerization of dienes strategy, binuclear insertion polymerization catalysts have been used to synthesize telechelic polyolefin without suffering from the low functional group tolerance of the catalyst. Through an electron transfer reaction with ethylene, divalent samarium complexes form binuclear samarocene derivatives.[51] The living polymerization of ethylene initiated by binuclear samarocene derivatives was used to access telechelic PE (and subsequent triblock polymer, **Figure 6**).[52] The absence of chain transfer and chain termination reactions during the ethylene polymerization resulted in PE consisting of a samarocene alkyl complex on both ends. These PE-samarium complexes were then used to initiate the living polymerizations of methyl methacrylate, ε-caprolactone or 2,2-dimethyltrimethylene carbonate and yielded the corresponding triblock copolymers. The molecular weight of the PE block reached up to 130 kg/mol, but presented a broad dispersity (Đ = 1.7~4), caused by the significant mass transport limitation due to the precipitation of the growing polymer chains (note that the broad dispersity does not imply that a large fraction of PE homopolymer was formed).[53] The PE content in the triblock copolymer ranged from 65% to 97%, under the described reaction conditions.

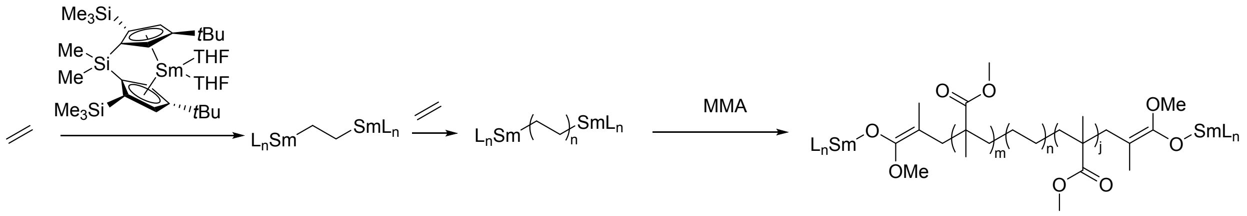

Figure 6. PE-containing triblock copolymer from binuclear samarocene-initiated polymerization. Adapted with permission from ref. 52. Copyright Wiley VCH 2000.

The same concept of using a binuclear initiator was also implemented for the synthesis of a telechelic PP.[54] A binuclear vanadium complex was synthesized in-situ using α,ω-dienes, vanadium(III) acetylacetonate and $AlEt_2Cl$. Living propylene polymerization initiated by this in-situ binuclear complex and followed by end-capping with CO yielded an aldehyde-terminated telechelic PP (**Figure 7**), with the molecular weight of 30 kg/mol and bimodal molecular weight distribution. The targeted telechelic polymers were obtained through purification via a circulating chromatographic method, the synthesis overall yielded a significant fraction of undesired semi-telechelic PP. To address the heterogeneity of their product, the authors studied the interaction of α,ω-dienes with the vanadium complex and proposed several possible reaction pathways for the presence of semi-telechelic PP: 1) The vanadium species attached to the diene may not be fully activated. 2) The unconjugated diene can undergo cyclization-oligomerization. 3) Active species on one end may be quickly deactivated. The rapid deactivation of the catalyst and its propensity for chain transfer reactions illustrate the challenges of performing a living insertion polymerization to yield a telechelic polymer.

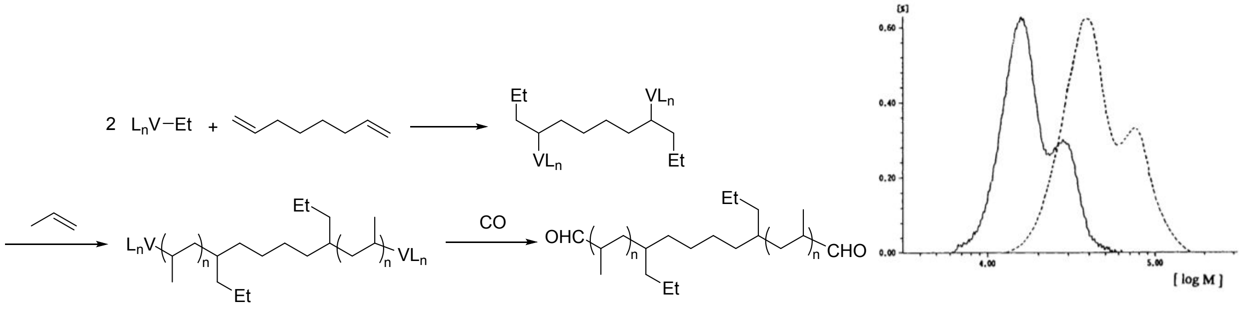

Figure 7. Reaction scheme (left) and molecular weight distribution (right). Solid line: propylene polymerization at -78 °C. Dashed line: propylene polymerization at -65 °C followed by CO quenching. Adapted with permission from ref.54. Copyright Wiley VCH 1998.

Binuclear late transition metal catalysts were also developed for the synthesis of telechelic polyolefins. A series of binuclear nickel complexes linked by a bis(benzyl) fragment were implemented to synthesize telechelic PE containing a nickel alkyl complex at each end of the polymer.[55] The tolerance of the nickel catalyst towards polar functional groups was utilized to copolymerize a functionalized norbornene with ethylene and yield the corresponding triblock polymer. Subsequent pressurization of the reaction mixture with ethylene led to the formation of a penta-block copolymer (PE-*b*-P(NB-*ran*-E)-*b*-PE-*b*-P(NB-*ran*-E)-*b*-PE, **Figure 8**), with a molecular weight greater than 100 kg/mol and a dispersity ranging around 1.4. The architecture of the polymer was further modified through the addition of poly(butyl acrylate) side chains via a "grafting-from" synthesis using the functionalized norbornene units as initiator for atom transfer radical polymerization. The evidence for the success of the synthesis of this pentablock polymer relied primarily on the linear increase of the polymer's molecular weight as a function of time throughout the polymerization.

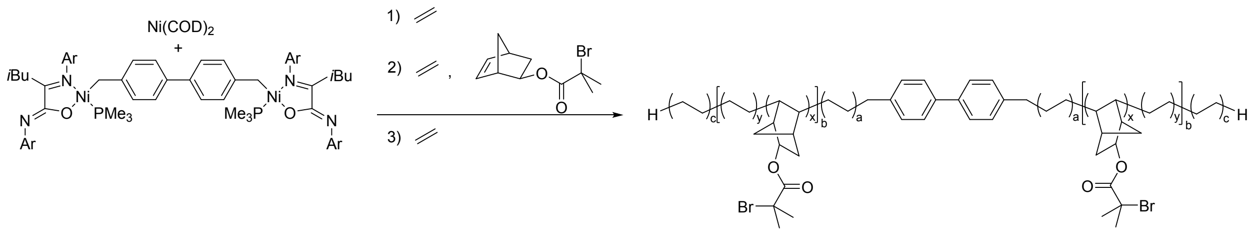

Figure 8. Living sequential polymerization starting from binuclear nickel complex. Adapted with permission from ref.55. Copyright ACS 2010.

Recently a binuclear palladium diimine complex linked by fluorinated diacrylate was used for the synthesis of a PE-containing triblock copolymer.[56] The molecular weight of the resulting PE block reached 100 kg/mol, with a dispersity as low as 1.05. After the ethylene polymerization, methyl acrylate was added to the reaction mixture to form a 6-member palladium chelate and stop the insertion polymerization. Photolysis of the Pd-C bond generated a PE macroradical and irreversibly switched the polymerization pathway to radical polymerization of acrylate, resulting in a triblock copolymer with the molecular weight of over 300 kg/mol and a dispersity of 1.6.

Coordinative chain transfer polymerization. An intrinsic limitation of living polymerizations is that each initiator yields only one polymer chain, this ultimately results in polymerization with low productivity.[47] Coordinative chain transfer polymerization (CCTP) was developed to enable the growth of several polymer chains per catalyst.[57] The reactivity of the chain transfer agents used in CCTP was readily used to introduce chain-end functional groups. Telechelic polyolefins were obtained from either chain transfer agents that already carry a functionality, or multinuclear chain transfer agents.[57–59]

Telechelic PE was synthesized using functionalized magnesium chain transfer agents and neodymium catalyst.[58,60–64] After the CCTP, vinyl and protected amine groups were incorporated at one end of the PE chain from the functionalized CTA, while the other end remained attached to the magnesium center for the subsequent functionalization. The inability of the neodymium catalyst to insert linear olefin prevented the insertion of the pending olefinic chain end.[62] Hetero-telechelic PE with a relatively low molecular weight of 2 kg/mol and a narrow dispersity (Đ = 1.2) were synthesized. Various methods were employed to convert the chain-end magnesium into dithiocarbamate, iodine, vinyl, and silane functionalities. The di-vinyl telechelic PE was further derived with a thiol-ene click reaction to yield a large variety of telechelic PE (**Figure 9**), and was later used to construct polymers with complex architectures.[63,64]

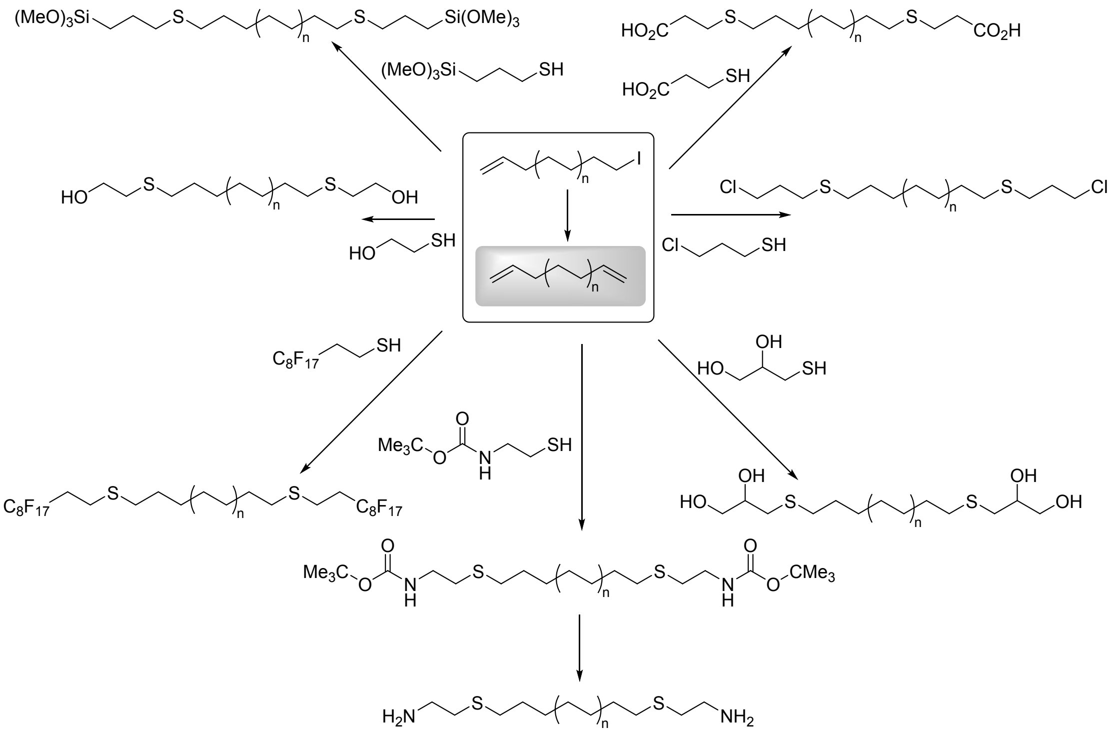

Figure 9. Telechelic PE obtained from thiol-ene reaction of various functional thiols with divinyl telechelic PE. Adapted with permission from ref.61. Copyright Wiley VCH 2015.

Linear multinuclear α,ω-alkylene zinc compounds were recently developed for use as chain transfer agents.[59,65] Two or more zinc atoms connected by hexylene or decylene units were used as a CTA. The polymeric zinc molecule enables the telechelic polymers to grow from the α,ω-alkylenes via CCTP, using typical early transition metal catalysts for olefin polymerization, e.g., zirconocene, pyridylaminohafnium, and bis(phenoxy-imine) titanium complexes. The molecular weight of the telechelic polyolefins synthesized from the CCTP of ethylene or mixture of ethylene and α-olefins reached up to 49 kg/mol, with dispersities ranging from 1.6 to 3.2. After

CCTP, the resulting α,ω-di-zinc polyolefins were oxidized to give hydroxy-telechelic polyolefins. The α,ω-di-zinc polyolefin itself also acted as a macroinitiator in the anionic polymerization of styrene, providing an alternative way to produce PS-*b*-EP-*b*-PS.[66–68]

Although telechelic PE and the copolymer of ethylene and propylene were accessed, telechelic stereoregular PP via CCTP has not yet been achieved. This omission is mostly due to the reversible chain transfer reaction that results in stereoerror formation.[57,69] Instead, the stereoregular PP-containing, multiblock ethylene/α-olefin copolymers are synthesized via a chain shuttling polymerization mechanism.[70,71]

Long-chain degradation

All the strategies to construct telechelic polyolefin described above follow a "bottom-up" strategy: the functionalization happens during or right after polymerization, and only occurs at the ends of the entire chains. A "top-down" approach consisting of cleaving long polymer chains into telechelic polymer has also been implemented.

Thermal degradation of isotactic PP to prepare telechelic isotactic propylene oligomers (M_n = 3.3 – 6.5 kg/mol) with terminal vinylidene double bonds (iPP-TVD) has been reported to access telechelic stereoregular PP.[72–74] The chain scission occurs through bond dissociation and a radical mechanism (inter-and intramolecular transfer and β-scission). The various mechanisms of end-group formation did not guarantee complete functionalized chain ends. In-depth NMR characterization of the cleaved PP showed that 80% of the oligomer products have an α,ω-diene structure and the functionalized end-group is exclusively isopropenyl group. This end-group was further reacted through an ene reaction with maleic anhydride—or hydroboration/oxidation then esterification—and multiblock copolymers were constructed from the modified telechelic isotactic PP.[75,76] This radical degradation pathway is, however, even less selective for PE.

Oxidative degradation is another common degradation method. The oxidative degradation of *cis*-polybutadiene rubber was developed to yield carboxyl-terminated PE.[77] The repeating double bonds in *cis*-polybutadiene rubber were randomly epoxidized by *m*CPBA and subsequently cleaved by periodic acid in one pot to form aldehyde-terminated polybutadiene. The molecular weight of the product was tuned by changing the reaction temperature and time, ranging from 0.8 to 6 kg/mol. The aldehyde groups were further oxidized to carboxylic acids, and the backbone unsaturation was hydrogenated to give the desired telechelic PE.

Oxidative degradation was also applied to PP.[78] Carboxyl-terminated PP was accessed by stirring isotactic PP in hot concentrated nitric acid. The PP end groups obtained from oxidative degradation were exclusively carboxylic acids. Further derivations of these carboxylic acids were performed to yield alkyl, hydroxyl and alkene end-groups The molecular weight of the polymer was controlled by tuning the temperature and reaction time, ranging from 1.4 to 20 kg/mol. However, the harsh reaction conditions also caused side reactions. Nitro groups were distributed along the polymer chain. Epimerization also frequently took place on the low molecular weight fraction, leading to a loss of stereoregularity in the telechelic polymer.

Olefin metathesis was also developed as an effective method to cleave polyolefin chains containing olefinic groups. A random copolymer of ethylene, 1-octene and butadiene with 2.8% butadiene was treated with ethylene and ruthenium indenylidene complexes.[79] Under optimized reaction conditions, the ethenolysis exhausted all of the internal double bonds (1,4-insertion of butadiene) and yielded a fully depolymerized α,ω-vinyl polymer of 1.1 kg/mol. This copolymerization-olefin metathesis method was also implemented to get telechelic PP. A small amount of butadiene was copolymerized with propylene using isospecific zirconocene catalysts, which resulted in isotactic PP with several 1,2- and 1,4-inserted butadiene units along the backbone. Then ethenolysis cleaved the PP chains into α,ω-vinyl polymers.[80] The cleaved products carried approximately two newly formed vinyl groups from ethenolysis. The molecular weight of the cleaved products decreased by a factor of two to six compared to the original copolymer, ranging from 12 to 57 kg/mol. In this example, the low number of chain scission events per macromolecule did not equate to a high fraction of semi-telechelic polymer. Indeed the authors demonstrated that the majority of the original macromolecules are terminated by butadiene insertion.

Another method derived from olefin metathesis to obtain telechelic polyolefins consists of introducing functional groups within the polymer that are subsequently cleaved. This method is referred to as sacrificial synthesis.[18,81,82] A functionalized cyclic monomer is copolymerized with cyclic olefin monomers to introduce the cleavable groups along the polymer backbone (**Figure 10**). Telechelic polyolefins functionalized with hydroxyl-, carboxyl-, thiol-, and amine groups have thus been successfully synthesized using this method.[16–18] The molecular weight of the resulting telechelic polyolefin is controllable through variation of the ratio between the functional comonomer and the main monomer forming the polyolefin segment. An intrinsic limitation of this process is, however, the inverse relationship between the molecular weight of the telechelic polymer and the precision of the synthesis. Indeed, to synthesize a telechelic polymer with a high molecular weight, it is necessary to incorporate only a small amount of functional monomer (resulting in few chain scission events per original macromolecule). However, if the original macromolecule chain is only "cut" once, the resulting two polymers obtained may be long but only semi-telechelic. If the polymer is "cut" twice the polymer is shorter and the product is composed of 1/3 telechelic polymer and 2/3 semi-telechelic polymer.

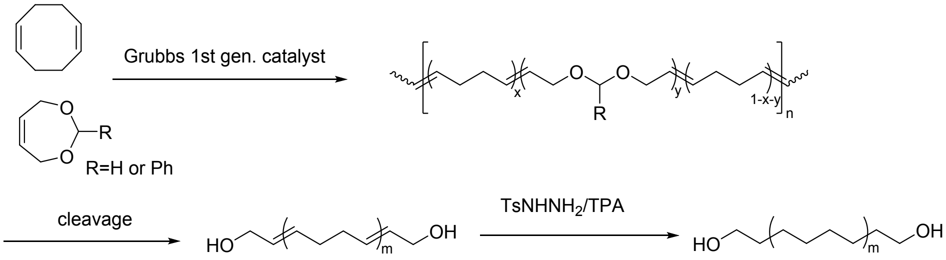

Figure 10. Hydroxy-telechelic PE synthesized from ROMP with cyclic acetal comonomer.

Adapted with permission from ref.81. Copyright ACS 1995.

Other synthetic methods

Boron-catalyzed living polymerization of dimethylsulfoxonium methylide was reported to prepare telechelic polymethylene.[83] Functionalized trialkyl borane initiators were readily obtained from functional olefins and borane. The living polymerization (**Figure 11**), through an intramolecular 1,2-migration, was well-controlled with a narrow dispersity of less than 1.1 and molecular weights up to 20 kg/mol.[83] The reaction is tolerant of many chemical functionalities and thus the initiator is used to introduce the first reactive end-group. After polyhomologation, the star-shaped borane is treated to release the functionalized polymethylene. Several possible functional groups such as hydroxyl, iodine, or dithiocarbamate have been incorporated to yield hetero-telechelic PE.[84] Difunctional borane initiator derived from 9-BBN was also used to construct telechelic polymethylene.[85]

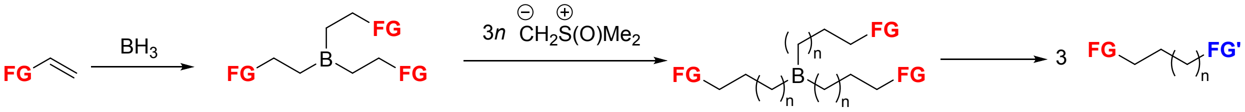

Figure 11. Polyhomologation to access hetero-telechelic polymethylene. Adapted with permission from ref.83. Copyright ACS 2002.

Short telechelic PEs with discrete molecular weights were synthesized through chain multiplication (**Figure 12**).[86] Mono-unsaturated fatty acids were self-metathesized with Grubbs catalyst and esterified to form α,ω-diesters with a central double bond. Then the "chain multiplication" refers to a selective shift of the double bond to one end (driven by crystallization) using palladium isomerization catalyst, and a subsequent olefin metathesis with a ruthenium catalyst resulting in a virtual doubling of the chain length, while the both ends were functionalized with ester groups. Eventually, the hydrogenation and reduction of the ester gave a a crystalline linear PE-diol with a uniform chain length, up to 700 g/mol. Polyesters with high melting point were accessed from the monodispersed linear PE-diol and diester, as a recyclable PE-like material.[87] The self-assembly behavior of these monodispersed telechelic PE was also studied.[88]

Inspired by this combination of olefin metathesis and isomerization,[15] we developed a post-polymerization functionalization strategy to convert polyethylene into difunctional polymers.[89] The synthetic methodology consists of performing four consecutive post-polymerization reactions on polyethylene obtained from any insertion polymerizations performed in absence of chain transfer agent (to ensure the presence of an olefinic group per chain). First, the olefinic end-group of the polyethylene is converted into an α,β-unsaturated ester via a cross-metatheis reaction.[90,91] Second, the double bond is isomerized to a random position along the PE backbone. Third, the double bond is converted into an aldehyde group via a hydroformylation reaction.[92] Finally, the aldehyde- and ester-functionalities are simultaneously reduced to yield two terminal hydroxyl groups. This methodology was performed on a polyethylene with a molecular weight of

M_n = 13 kg mol^{-1}. The corresponding di-hydroxyl functionized PE were used as macroinitiator for the ring opening polymerization of cyclic esters and epoxides monomers.

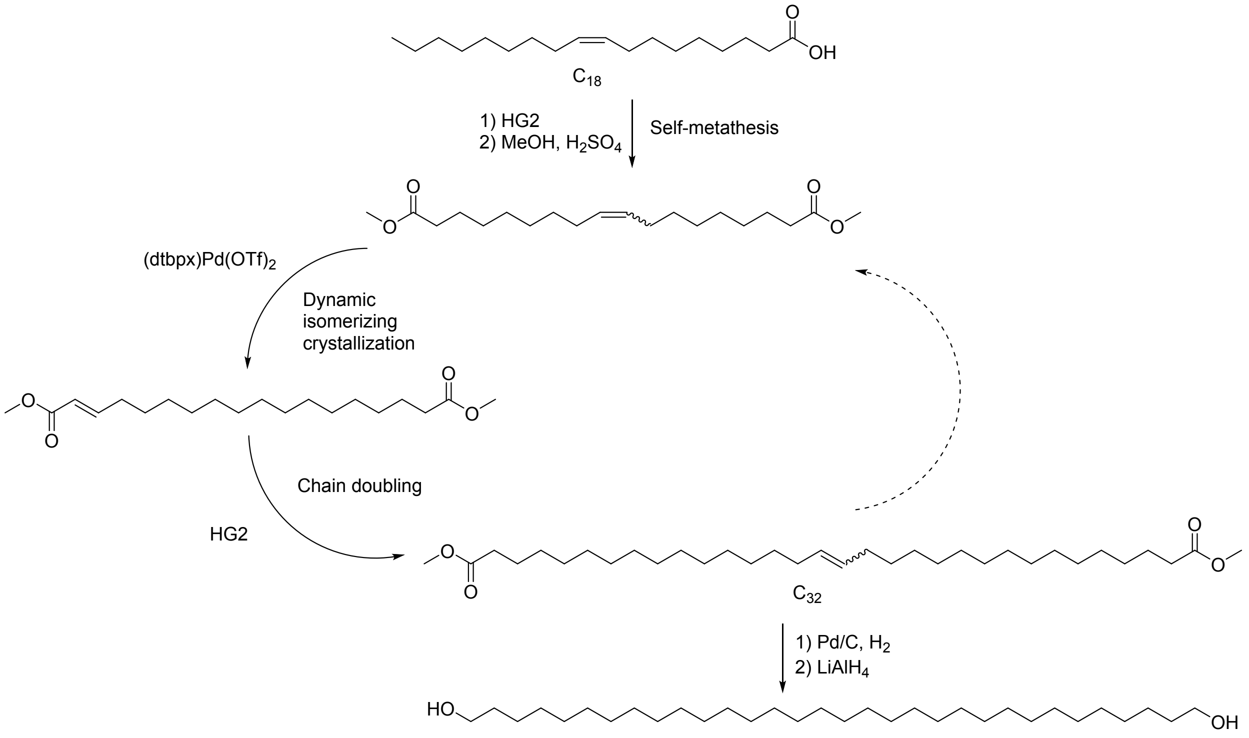

Figure 12. The "Chain multiplication" strategy for the preparation of ultra-long-chain diester and diol. Adapted with permission from ref.86. Copyright Wiley VCH 2017.

Selective copolymerization of ethylene with 2-vinylfuran (2-VF) using Drent type catalyst was reported to yield PE with furan rings at both ends (molecular weight of 1.9 kg/mol and dispersity of 2).[93] In this system the comonomer was preferentially incorporated at the beginning of the polymer (insertion into Pd-H) instead of ethylene. This initiation step was then followed by the consecutive insertion of multiple ethylene units. When a 2-VF was inserted into the palladium alkyl bond, a chain transfer reaction occurred and yielded α,ω-difuran telechelic PE and a palladium hydride to initiate another chain. Our group also implemented a selective copolymerization technique to synthesize telechelic isotactic PP using an isospecific zirconocene catalyst and a difunctional comonomer 1,3-diisopropenylbenzene (DIB).[94] DIB is a unique monomer as it is reactive toward the zirconium hydride (initiation) while it is not reactive toward the zirconium alkyl bond (no copolymerization). By increasing the DIB concentration, the initiation of the polymer chain occured exclusively through DIB insertion (introduction of the first olefinic end-group), propagation proceeded through propylene insertion and chain termination occured via chain transfer reactions (introduction of the second olefinic end-group). The molecular weight of the isotactic PP reached 10 kg/mol. The α,ω-unsaturated PP was further converted to the hydroxy-telechelic form, and water-soluble amphiphilic triblock copolymers were accessed using the telechelic isotactic PP.

Conclusion

The importance of the polyolefins to our society combined with the versatility of structures obtainable from telechelic polymers has motivated the development of a series of distinct synthetic methods to access telechelic polyolefins. An example of such potential is the use of multiblock polymers as compatibilizing agent that decrease the burden on separation for plastics mechanical separation.[70,71,95–97] We here reviewed all these synthetic methods. The major obstacle for telechelic polyolefins to be more widely implemented remain the difficulty to simultaneously achieve functional group fidelity, scalability, control over molecular weight control and stereoregularity. Nonetheless, linear and branched telechelic PE as well as stereoregular telechelic PP have been synthesized through both bottom-up (monomer to polymer) and top-down approaches (polymer chain scission). The tremendous progress made in telechelic polyolefin synthesis has also illustrated the challenges related to the precise characterization of its structure. Indeed the quantitative characterization of the end-groups of a high molecular weight polymer is not trivial and the use of GPC to illustrate the possibility of extending the telechelic polymers suffers from low sensitivity.[98,99] Future advances in telechelic polyolefin synthesis will benefit from more quantitative structure characterization. Finally, in view of the sustainable benefit of performing polyolefin depolymerization and/or polyolefin upcycling, we believe that the top-down conversion of polyolefins to telechelic polyolefins is poised for a vibrant future.

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