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Review

Design and synthesis of structurally well-defined functional polyolefins via transition metal-mediated olefin polymerization chemistry

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Contents

Abstract

The functionalization of polyolefins has long been an industrially important yet scientifically challenging research subject ever since the commercialization of polyethylene (PE) and polypropylene (PP) in the 1950s. However, only until recently has considerable progress been made thanks to the enormous development of transition metal olefin polymerization catalysis (Ziegler-Natta, metallocene and post-metallocene). This review covers recent achievements in the functionalization of polyolefins, with special attention being paid to the chemistries using transition metal-catalyzed process to synthesize structurally well-defined functional polyolefins, including side group-functionalized polyolefins, chain end-functionalized polyolefins and functional polyolefins with graft and block structures.

Keywords: Polyolefins; Functionalization; Well-defined molecular structure; Design and synthesis; Progress; Transition metal-mediated olefin polymerization chemistry

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1. Introduction

Polyolefins – including polyethylene (PE), polypropylene (PP), poly(1-butene), poly(1-octene), poly(4-methyl-1-pentene), ethylene–propylene elastomer (EPR) and ethylene–propylene–diene rubber (EPDM) – are the most important commercial polymers. Due to their excellent combination of good chemical and physical properties with low cost, superior processibility and good recyclability, polyolefins find widespread applications in modern human life. However, the major drawback of polyolefins is the lack of functional groups, which poses serious problems when polyolefins are used in areas where adhesion, dyeability, printability or compatibility with other polymers is paramount. As the current development of polyolefins is being centred on the enhancement of their overall performances in order to expand their application areas, the lack of chemical functionality has become the major stumbling block.

In fact, ever since the commercialization of PE and PP in the 1950s, the functionalization of polyolefins has been a very interesting research subject attracting attention from both academic and industrial communities [1–5]. The so-called polyolefin functionalization is explained as introducing polar functional groups into polyolefins. With the precondition of maintaining the desired properties of polyolefins, polyolefin functionalization confers reactivity to polyolefins, improving adhesion and compatibility between polyolefins and other materials, such as pigments, paints, glass fibers, metals, carbon black and most polymers. The application of polyolefins after functionalization can be extended to such areas that even involve catalyst supporting, medication, photoelectron material, biomaterial, photo material and environmental protection, which have never been previously accessed by polyolefins [6].

As for the chemistry required to achieve polyolefin functionalization, the most traditional one is the chemical modification of the preformed polyolefins (the post-polymerization approach, the product is named functionalized polyolefins) [7–11]. However, due to the inert nature of the polyolefins, this approach has to resort to high-energy sources (such as molecular radical, irradiation and plasma) to break the stable C–H bonds in polyolefins to form polymeric radicals. The polymeric radicals will then react with polar chemical reagents present in the modification system via either addition or coupling reaction to combine functional groups with polyolefins [9–13]. In general, because there is no obvious reaction site in polyolefins, the functionalization efficiency using the post-polymerization approach is quite low. The functionalized polyolefins so obtained, usually possess complex molecular structure coupled with a non-uniform distribution of functional groups (functional groups are mainly contained by low molecular weight polymers). In addition, the polymeric radicals in polyolefins are ready to undergo β-scission reaction or coupling reaction between each other, causing polymer degradation or cross-linking that will severely deteriorate the superior mechanical and processing properties of polyolefins [11–13].

It is essential to retain the superior properties of polyolefins while achieving polyolefin functionalization. This requires the functionalization process to proceed in a controlled manner, that is, the functionalization of polyolefins should be carried out in such a way that renders the structure of the obtained functional polyolefins well-definable, with all structural and compositional parameters including concentration of functional groups and their distributions as well as polymer molecular weight, molecular weight distribution and stereoregularity being highly controllable [14]. To meet such a requirement, molecular design is the best tool to be employed.

In the history of polymer chemistry, the past half-century has witnessed a rapid development of transition metal-mediated olefin coordination polymerization. To date, both the transition metal catalysts and the knowledge of their olefin polymerization mechanism have proliferated. The development of chemistry stimulates the evolvement of polymer. In particular, the newly developed single site catalysts (including metallocene and post-metallocene catalysts), with a great combination of high activity and the possibility to tailor polymer properties such as molecular weight and molecular weight distribution, co-monomer incorporation and distribution and stereoregularity by simply tuning catalyst structure, have proven themselves attractive and promising catalysts for olefin polymerization in the new century. There exist abundant evidence to show the molecular design of functional polyolefins is executable with the assistance of the transition metal-mediated olefin coordination polymerization chemistry.

In this review, we summarize the recent progress in the functionalization of polyolefins using molecular design approach to access structurally well-defined functional polyolefins via transition metal-mediated olefin polymerization chemistry. Research activity on this subject carried out in industrial and academic laboratories has not only generated a large number of academic journal publications but also been embodied in an even larger number of technical patents. However, as we focus our attention in this review on chemistry, we intend to make a collection of arts of polyolefin functionalization with proved validity. For such a reason, in this review, we gather information mainly from the open literature with only limited comment on the patent literature.

2. Classification of functional polyolefins by structure

Functional polyolefins can be classified into four categories, in terms of their structural characteristics, as illustrated in Fig. 1. They include (a) side group-functionalized polyolefins, which can be further explained as polyolefins containing functional groups each either directly substituting from polyolefin backbone or being separated from the backbone by an alkyl spacer, (b) functional polyolefin graft

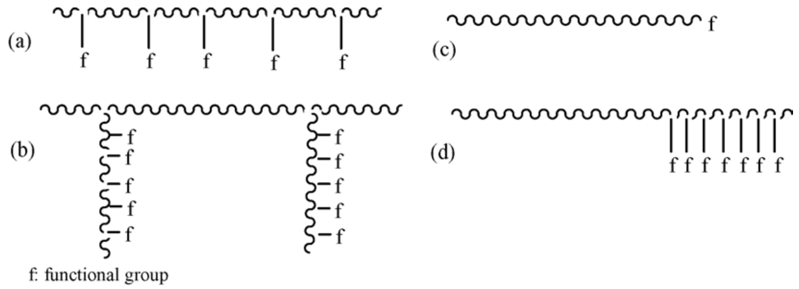

Fig. 1. Structural classification of functional polyolefins.

copolymers, which are structurally similar to side group-functionalized polyolefins except that the functional substituent is not a group but rather a polymer chain composed of many functional repeating units, (c) chain end-functionalized polyolefins, which contain only a functional group at the polymer chain end and (d) functional polyolefin block copolymers, which, being also functionalized at the chain end, consist of a polyolefin block and a functional polymer block [15].

3. Design and synthesis of side group-functionalized polyolefins

Theoretically, the direct, random copolymerization of α-olefins with functional monomers is the most straightforward way to access side group-functionalized polyolefins. This approach has the advantages of ensuring a random distribution of the incorporated functional groups along the polyolefin chain and that the functional groups being quantitatively controllable simply by tuning the insertion efficiency of the functional monomers during copolymerization [16]. Unfortunately, due to a strong complexation between the Lewis acid components (Ti, Zr, Hf, V and Al) of the transition metal catalysts and the non-bonded electron pairs on N, O and X (halides) of the functional monomers, which is in preference to that between the catalysts and the π-electrons of the double bonds, the direct α-olefin/functional monomer copolymerization usually suffers from catalyst deactivation. The development of metallocene and other single-site olefin polymerization catalysts including the less oxophilic late transition metal catalysts based on Fe, Ni, Co and Pd, has provided new opportunities for the direct copolymerization of α-olefins with functional monomers. Recently, successful copolymerizations of α-olefins with various functional monomers were maneuvered by either exerting steric and electronic protection on the functional groups [17–19], or enhancing the steric hindrance of the catalyst active sites, or employing the heteroatom-resistant late transition metal catalysts [20–22]. In addition, in order to avoid catalyst deactivation caused by the direct copolymerization with functional monomers, an alternative approach (the reactive polyolefin intermediate approach) was developed [23].

3.1. Direct copolymerization of α-olefins with functional monomers

With the concern of catalyst deactivation by functional group, the successful direct copolymerizations of α-olefins with functional monomers reported in the literature mostly involve two methods: (i) protecting the functional group to inhibit the complexation between the heteroatom of the functional group and the catalyst active site, (ii) using less oxophilic late transition metal catalyst [15], as illustrated in Fig. 2.

3.1.1. Functional group protection method

Most of the commercial polyolefins (including high density polyethylene (HDPE), isotactic polypropylene (i-PP) and syndiotactic polystyrene (s-PS)) are prepared by early transition metal-based Ziegler-Natta and metallocene catalysts. Thus, it is of great significance to develop the functional group protection method to facilitate the direct copolymerization of α-olefins with functional monomers in order to obtain commercial polyolefins containing side group functionality.

As illustrated in Fig. 2, the synthesis of side group-functionalized polyolefins employing the functional group protection method involves not only the copolymerization of α-olefins with functional monomers, but also the functional group protection and deprotection reactions. In this context, a selection of protection agent is very crucial. A good protection agent should not only effectively prevent

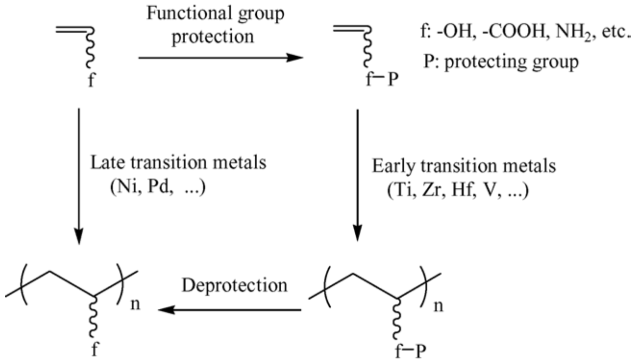

Fig. 2. Direct copolymerization of α-olefins with functional monomers involving either functional group protection or late transition metal catalyst [15].

the catalyst active site from being poisoned by the functional group but also render facile protection and deprotection processes. The most frequently accessed functional groups (including alcohol, ester, amine and halides) are usually protected by –$CH(CH_3)_2$, –AlR_nCl_{2-n}, $Al(CH_3)_3$, methylaluminoxane (MAO) and –$Si(CH_3)_3$, where –$CH(CH_3)_2$ is a steric shielding agent while –AlR_nCl_{2-n}, $Al(CH_3)_3$, MAO and –$Si(CH_3)_3$ provide both steric shielding and electronic neutralization of the Lewis basic functional groups. Besides protecting the functional group, it is also viable to exert protection on the catalyst active site by designing the structure of catalyst as well as cocatalyst. The recent research indicates that a combined usage of both functional group and catalyst active site protections effects better result than using functional group protection alone [24]. In addition, an adequate separation of functional group from C=C double bond of a functional monomer is also shown necessary to warrant a successful α-olefin/functional monomer copolymerization [25–28].

From early on, Giannini et al. systematically studied the polymerization of a series of tertiary amine-substituted α-olefins using the $TiCl_3$.AA/Al(R′)$_2$Cl catalyst system [29]. They found that the catalyst was completely deactivated because of insufficient shielding of the functional group when the nitrogen atom in the functional monomer is separated from the vinyl double bond by only one or two methylene units, or the other two substituents of the tertiary amine group are less bulky methyl or ethyl groups. On the other hand, when the substituents of the nitrogen atom are bulky isopropyl groups and there are at least three methylene units in between the nitrogen atom and the vinyl double bond, the polymerization proceeded smoothly and high molecular weight polymers could be obtained. They also found that when the spacer between the nitrogen atom and the vinyl double bond is a methylene chain of more than three units in length and the nitrogen atom is substituted only by methyl groups, polymerization could still occur if the functional monomer was treated with $AlEt_2Cl$ prior to polymerization.

Mulhaupt and co-workers synthesized *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene and copolymerized it with ethylene by a metallocene/MAO catalyst system, obtaining polyethylene containing alkylamine side groups after hydrolysis to remove the –$Si(CH_3)_3$ protection group [30]. Waymouth and co-workers further replaced MAO with $B(C_6F_5)_3$ and $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ to form a cationic catalyst with a methylated metallocene. This catalyst performed better than MAO-activated one for the copolymerization of α-olefins with protected amine-containing functional monomers [17,31,32].

Recently, Xu and Chung also adopted the functional group protection method to prepare s-PS polymers containing amine side groups by homopolymerization of primary amino group-containing styrenes. They used half-sandwiched titanocene catalysts in combination with perfluoroborane cocatalysts [33].

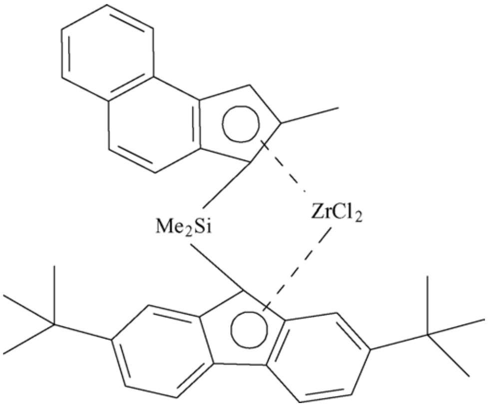

Fig. 3. The structure of the Kashiwa-type metallocene catalyst.

By employing the functional group protection method, oxygen-containing (including alcohol, carboxylic acid and ester groups) functional monomers were also copolymerized with α-olefins by Ziegler-Natta and metallocene catalysts [34–37]. A representative example is reported by Fink and co-workers who used MAO to in situ protect 1-hydroxy-10-undecene and then directly synthesized PE and PP polymers containing hydroxyl side groups using $Et(Ind)_2ZrCl_2$ and $Me_2Si(Ind)_2ZrCl_2$ with MAO [18,25]. Kashiwa and co-workers further synthesized a special ansa-zirconocene catalyst (Fig. 3) structurally featured by a large steric hindrance, which allows a good protection of the catalyst active sites [24]. They used this catalyst to copolymerize ethylene and 1-hydroxy-10-undecene pre-treated with trimethyl aluminum to synthesize polyethylene functionalized with hydroxyl side groups.

3.1.2. Late transition metal catalyst method

Due to the weak oxophilicity of late transition metal catalysts, they are not as sensitive as Ziegler-Natta and metallocene catalysts to functional groups and thus applicable to catalyze the direct copolymerization of α-olefins with functional monomers.

In 1996, Brookhart and co-workers first reported the direct copolymerization of ethylene and propylene with acrylate monomers by MAO-activated α-diimine-Pd(II) catalysts (Fig. 4), which introduced acrylate groups to the terminal of the side chains, resulting in highly branched polyethylene functionalized with ester groups [21,38]. Later, Marques and Chien et al. studied the copolymerization of ethylene and

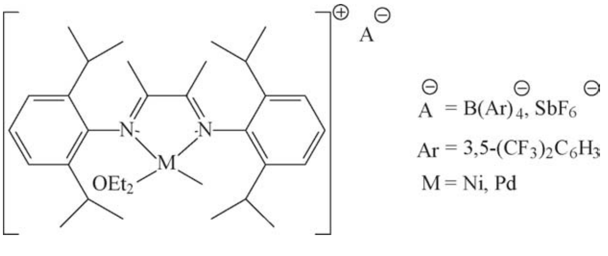

Fig. 4. The structure of the Brookhart-type late transition metal catalysts.

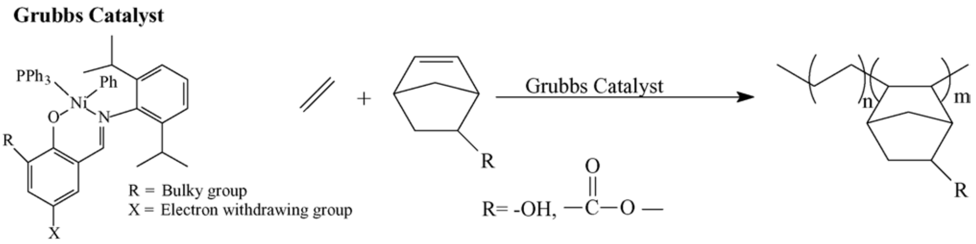

Fig. 5. The structure of the Grubbs catalysts and their copolymerization of ethylene with functionalized norbornene monomers.

terpolymerization of ethylene and propylene with a variety of functional monomers using an α-diimine-Ni(II) catalyst ([bis(*N*,*N*′-dimesitylimino)-acenaphthene]dibromonickel) and MAO. The functional monomers include tetrahydrofuran, caprolatone, acrylonitrile, vinyl acetate, methyl methacrylate and methyl vinyl ketone [39–42]. The results indicate that the use of alkylaluminums as functional group protection agent is crucial for a successful copolymerization. In general, no polymers could be obtained without the use of a protection agent. Trimethylaluminum was found to be a good protection agent for tetrahydrofuran, and triisobutylaluminum was preferred for acrylontrile, caprolactone, methyl methacrylate, etc. However, despite the many claims of successful copolymerization of ethylene with functional monomers by the Brookhart-type late transition metal catalysts, there exist controversies. Recently, Jordan and co-workers studied the reactions of acrylonitrile with representative L_2-$PdMe^+$ olefin dimerization and polymerization catalysts that contain bidentate N-donor ligands with an aim to probe the possibility of acrylonitrile polymerization by insertion polymerization [43]. Their results, however, indicate that acrylonitrile may not be able to undergo insertion polymerization and copolymerization with α-olefins.

In 2000, Grubbs and co-workers reported a series of single-component highly active neutral salicylaldimine nickel complexes (Fig. 5). They found that the catalytic performance of these catalysts was unaffected by polar reagents such as ester, either, ketone, amine and even water [44–46]. In the copolymerization of ethylene with functionalized norbornene monomer (5-norbornen-2-yl acetate or 5-norbornen-2-ol) using these catalysts (Fig. 5), the functional monomer incorporation can reach 22 mol%.

In late transition metal-mediated copolymerization of α-olefins with functional monomers, there exist two complex species in the beginning of the copolymerization reaction, one is the π-complex formed by the C=C double bond of the functional monomers and the transition metal, the other is the σ-complex formed by the heteroatom (O or N) and the transition metal. During the polymer chain propagation process, these two types of complexation compete each other. A mechanistic study of the direct copolymerization of α-olefins with functional monomers by late transition metal catalysts using DFT indicates that, for Brookhart-type catalysts, the π-complex of Pd is more stable than its σ-complex whereas the σ-complex of Ni is more stable than its π-complex, however, for Grubbs-type catalysts, the π-complexes of Pd and Ni are both more stable than their σ-complexes [47,48]. Thus, it is believed that the Grubbs-type neutral salicylaldimine-late transition metal catalysts are more suitable for direct copolymerization of α-olefins with functional monomers than the Brookhart-type catalysts.

Despite the limited success achieved for the direct copolymerization of α-olefins with functional monomers using the functional group protection and the late transition metal catalyst methods, one must be aware that both methods are still very immature and far from commercially applicable to produce side group-functionalized polyolefins. Both steric shielding and electronic neutralization of functional group cannot completely prohibit the deactivating effect of the heteroatoms on the catalyst active site. With the increment of the functional monomer concentration, both the steric and electronic protections become weaker, and the catalyst tends to be rapidly deactivated. Although the sensitivity of the late transition metal catalysts to functional groups is relatively lower than their early transition metal counterparts, the facile chain transfer reactions occurring during polymerization result in polymers with low molecular weight. In addition, it is very difficult to prepare stereoregular polyolefins, such as i-PP and s-PS, using late transition metal catalysts.

3.2. *“Reactive polyolefin intermediate” approach*

Besides direct α-olefin/functional monomer copolymerization, the “reactive polyolefin intermediate” approach provides another effective way to access side group-functionalized polyolefins. The rise of the “reactive polyolefin intermediate” approach was originally aimed at circumventing the many difficulties encountered in the direct functional copolymerization with Ziegler-Natta and metallocene catalysts to prepare stereoregular functional polyolefins such as i-PP and s-PS. Differing from the direct copolymerization approach, the “reactive polyolefin intermediate” approach does not allow α-olefins to directly copolymerize with functional monomers (so as to avoid catalyst poisoning). Instead, a substituted α-olefin monomer containing a reactive group, which is free of any catalyst-deactivating heteroatoms, is used in Ziegler-Natta or metallocene-catalyzed α-olefin copolymerization to prepare polyolefins having pen-

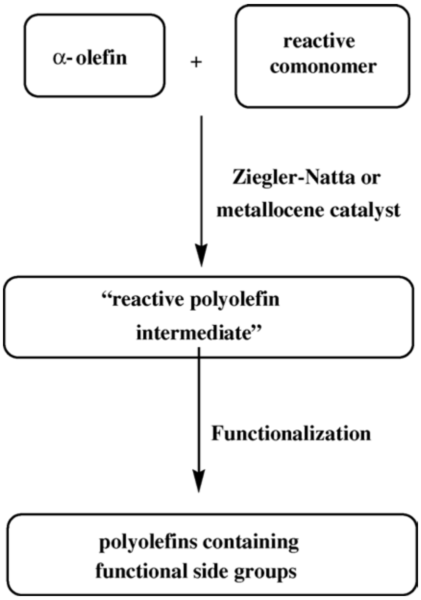

Fig. 6. An illustration of the "reactive polyolefin intermediate" approach for the synthesis of polyolefins containing functional side groups.

dant reactive groups. With these reactive polyolefin intermediates on hand, upon chemical transforming the reactive groups to polar functional groups, polyolefins containing functional side groups can be obtained, as illustrated in Fig. 6.

Obviously, the key step in the "reactive polyolefin intermediate" approach is the design of the substituted α-olefin monomer containing a reactive group (the reactive comonomer). A successful candidate should simultaneously fulfill the following requirements: (i) it is stable to Ziegler-Natta and metallocene catalysts and soluble in hydrocarbon polymerization media, (ii) it has comparable reactivity with α-olefins and (iii) the reactive group is facile in the subsequent interconversion reaction to form polar functional groups under mild reaction conditions.

In fact, the "reactive polyolefin intermediate" approach greatly benefits from the metallocene catalysts. On one hand, the superior copolymerization capability of metallocene catalysts allows a broad range of selections of reactive comonomers, which on a fundamental basis vitalize the practicability of the "reactive polyolefin intermediate" approach. On the other hand, the metallocene-catalyzed copolymerization results in copolymers with narrow molecular weight and composition distributions, which is essential to a uniform distribution of reactive groups in the reactive polyolefin intermediates obtained.

The reactive polyolefin intermediates having been reported in literature include polyolefins containing borane side groups [49–54], polyolefins containing benzyl side groups [55–57], and polyolefins containing unsaturated side groups [54,58–61]. Their corresponding reactive comonomers are B-5-hexenyl-9-BBN, *para*-methylstyrene (*p*-MS) and dienes (including divinylbenzene, 1,4-hexadiene, 5-vinyl-2-norbornene, 2,5-norborn-diene, etc.).

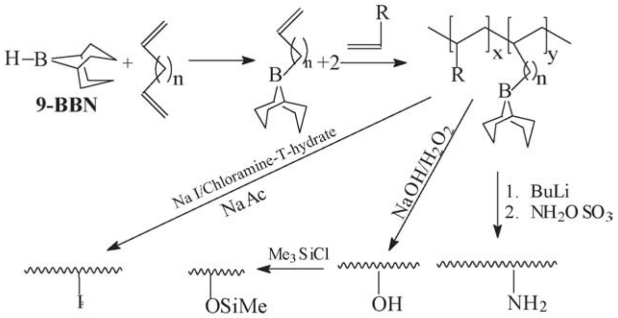

Fig. 7. An illustration of the synthesis of side group-functionalized polyolefins via the borane-containing reactive polyolefin intermediate.

Borane-containing polyolefins might be the first generation of reactive polyolefin intermediates used to synthesize side group-functionalized polyolefins. Chung and Rhubright found that borane groups do not interfere with Ziegler-Natta and metallocene-catalyzed α-olefin polymerization and are chemically stable against Ziegler-Natta and metallocene catalysts as well as their cocatalysts [50]. They then designed a series of borane-containing substituted α-olefin monomers (including B-5-hexenyl-9-BBN, B-7-octenyl-9-BBN, B-4-(4-vinylphenyl)-butyl-9-BBN, etc.) by mono-hydroboration of symmetric aliphatic dienes and asymmetric aromatic dienes such as 1,5-hexadiene, 1,7-octadiene and 4-(butenyl)styrene. Employing these substituted α-olefin monomers as reactive comonomer in Ziegler-Natta and metallocene-catalyzed α-olefin (ethylene, propylene and 1-octene) and syndiotactic styrene copolymerizations resulted in reactive polyolefin and s-PS intermediates containing borane groups. By taking advantage of the reactivity of borane groups in many chemical transformation reactions, Chung and co-workers synthesized various side group-functionalized polyolefins and s-PS [62]. Fig. 7 illustrates the synthesis of side group-functionalized polyolefins via the borane-containing reactive polyolefin intermediates.

Fig. 8 schemes the synthesis of side group-functionalized polyolefins via the benzyl-containing reactive polyolefin intermediate [55–57]. Metallocene catalysts, especially the constrained geometry one $[(C_5Me_4)SiMe_2N(t\text{-Bu})]TiCl_2$ with a superior copolymerization capability, show good incorporations even for sterically bulky monomers. Both the binary copolymerization between ethylene and *p*-MS and the tertiary copolymerization between ethylene, propylene (or 1-octene) and *p*-MS with $[(C_5Me_4)SiMe_2N(t\text{-Bu})]TiCl_2$/MAO catalyst are quite effective in terms of catalyst activity, polymer molecular weight and *p*-MS incorporation. The incorporation of *p*-MS can be higher than 40 mol%, and the incorporated *p*-MS units are uniformly distributed along the copolymer chains. Both the copolymer composition and molecular weight distributions are narrow. The benzylic proton in the *p*-MS units is very reactive and can undergo halogenation, metalation and oxidation reactions under mild conditions to form various polar functional groups at the benzyl position. All the functional transformation reactions

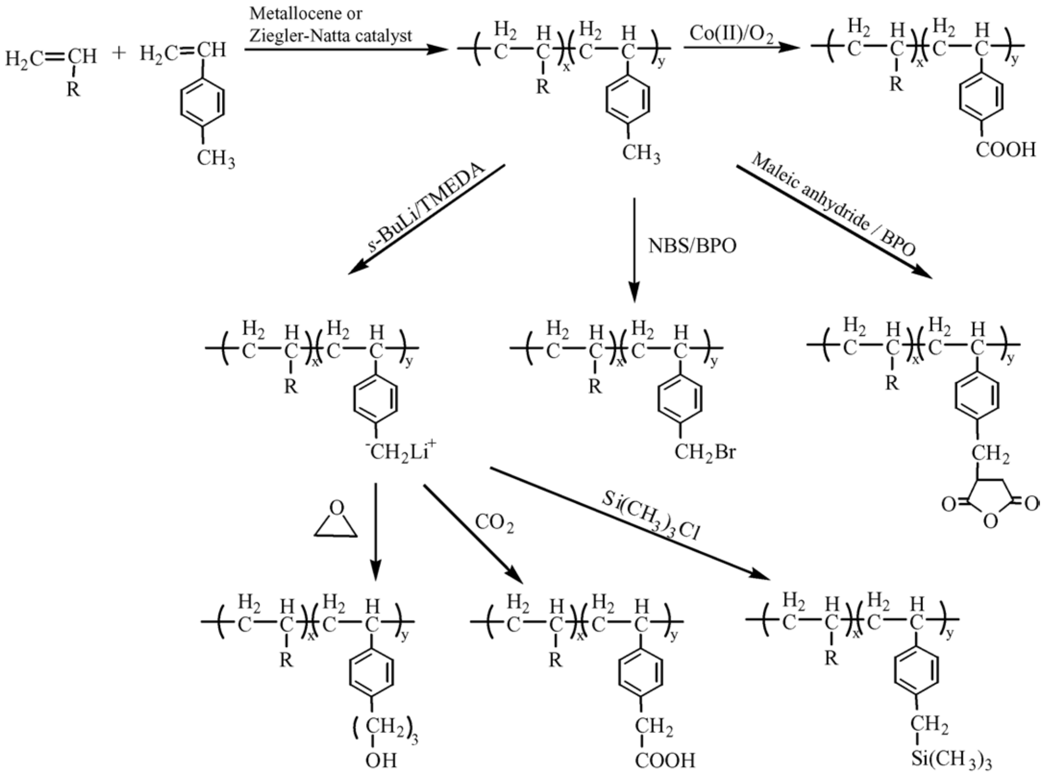

Fig. 8. The synthesis of side group-functionalized polyolefins via the benzyl-containing reactive polyolefin intermediate.

are proposed to selectively occur at the primary benzylic methyl group, as illustrated in Fig. 8.

As for the functionalization of polyolefins with the unsaturated group-containing reactive polyolefin intermediate, the chemical reactivity of the unsaturated group is directly related to functionalization efficiency. As far as the unsaturated polyolefin intermediates are concerned, polyolefins containing pendant vinylbenzene groups are the most reactive. The vinylbenzene group, resembling styrene monomer, can effectively engage in many organic functionalization reactions to synthesize various side group-functionalized polyolefins [59]. Unfortunately, because vinylbenzene group can also insert into the catalyst active site during metallocene or Ziegler-Natta catalyzed α-olefin copolymerization, it is usually very difficult to synthesize vinylbenzene-containing reactive polyolefin intermediates. Recently, Chung and Dong successfully performed the binary copolymerization between ethylene and divinylbenzene and the tertiary copolymerization between ethylene, propylene (or 1-octene) and divinylbenzene using metallocene catalysts [58]. In these copolymerization reactions, divinylbenzene is incorporated into polyolefin chains in a selective mode with only one of its double bonds being involved in copolymerization while the other is left un-attacked (Fig. 9). The copolymerization reactions result in reactive polyolefin intermediates containing pendant vinylbenzene groups with controlled reactive group concentration and narrow composition and molecular weight distributions.

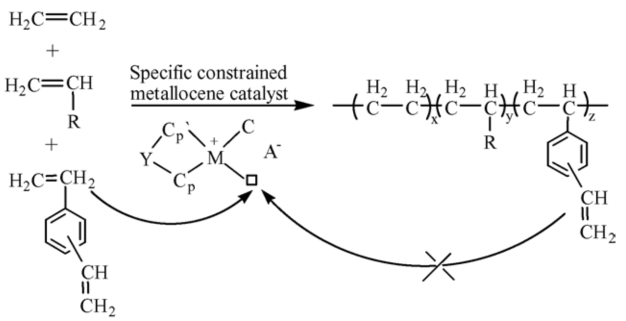

Fig. 9. The synthesis of reactive polyolefin intermediate containing pendant vinylbenzene groups via metallocene-catalyzed α-olefin copolymerization [58].

Radhakrishnan and Sivaram synthesized ethylene-co-2,5-norborn-diene copolymers by metallocene catalysts, which were also used as reactive polyolefin intermediate to prepare side group-functionalized polyolefins [63]. Polyolefins containing –OH and –COOH groups were obtained by oxidation of the pendant cyclic olefin double bonds with $KMnO_4$.

4. Design and synthesis of functional polyolefins with graft structure

Although side group-functionalized polyolefins present the most conceivable structure of functional polyolefins, they have limitation in functional group concentration. The higher the concentration of the functional side groups, the more the loss of the desired properties (such as melting point and crystallinity) of polyolefins. To simultaneously achieve high functional group concentration and yet retain the polyolefin properties, it is necessary to synthesize functional polyolefins with graft structure.

For functional polyolefin graft copolymers, the major structural parameters are graft density and graft length. In terms of the linking mode of polyolefin and functional polymer, the currently available chemistries for the synthesis of functional polyolefin graft copolymers can be classified into two categories: (i) the graft copolymerization approach and (ii) the macro-monomer approach. In the graft copolymerization approach, in order to facilitate the control of graft density and graft length, evident grafting sites are needed to generate in polyolefin chains prior to graft reaction, and the graft reaction is required to follow a living polymerization mechanism. The macro-monomer approach for the synthesis of functional polyolefin graft copolymers follows the general procedure of a graft copolymer synthesis via macro-monomers, that is, the grafting chain is first designed to be a macro-monomer and then the copolymerization of the macro-monomer results in the graft copolymers. In fact, there are two routes to apply the macro-monomer chemistry to the synthesis of functional polyolefin graft copolymer: (i) the functional polymers are designed to be the polymer chain-substituted α-olefin macro-monomers, followed by copolymerization with α-olefins via coordination polymerization (the obtained graft copolymer has a polyolefin backbone and functional polymer side chain) and (ii) polyolefins are designed to be macro-monomer and used in the copolymerization with functional monomers mostly via radical polymerization (the obtained graft copolymer has a functional polymer backbone and polyolefin side chain). Despite the absence of the latter structure in the structural categories of functional polyolefins listed in Section 2 of this review, graft copolymers of this type of structure are still very important functional polyolefins. The structural parameters of polyolefin graft copolymers synthesized by the macro-monomer approach are well controllable, the graft length being determined by the molecular weight of the macro-monomer while the graft density is controlled by the incorporation of the macro-monomer during copolymerization.

4.1. Graft copolymerization approach

The graft copolymerization approach is widely used to synthesize functional polyolefin graft copolymers. Its general procedure is as follows. First, grafting sites are generated in polyolefins. The grafting site can be an initiator (or its precursor) moiety for living anionic or controlled/“living” radical polymerizations (including atom transfer radical polymerization (ATRP), nitroxide-mediated stable radical polymerization (NMP) and peroxyborane-initiated stable radical polymerization) or a chain transfer agent moiety for reversible addition-fragmentation chain transfer polymerization (RAFT). Secondly, graft polymerization of functional monomer either from (in the case of the grafting site being an initiator moiety) or onto (in the case of the grafting site being a chain transfer agent moiety) the grafting sites to obtain functional polyolefin graft copolymers.

Chung et al. combined the reactive polyolefin intermediate containing benzyl or vinylbenzene groups with butyllithium via a lithiation reaction to transform the pendant benzyl or vinylbenzene group to an initiator moiety of benzyllithium [64], as illustrated in Fig. 10. The benzyllithium moieties in polyolefins initiated living anionic polymerization of styrene, methyl methacrylate (MMA) and acrylonitrile (AN) to obtain polyolefins grafted by PS, poly(methyl methacrylate) (PMMA) and polyacrylonitrile (PAN), respectively.

Anionic ring-opening polymerization was also used to synthesize functional polyolefin graft copolymers. Chung

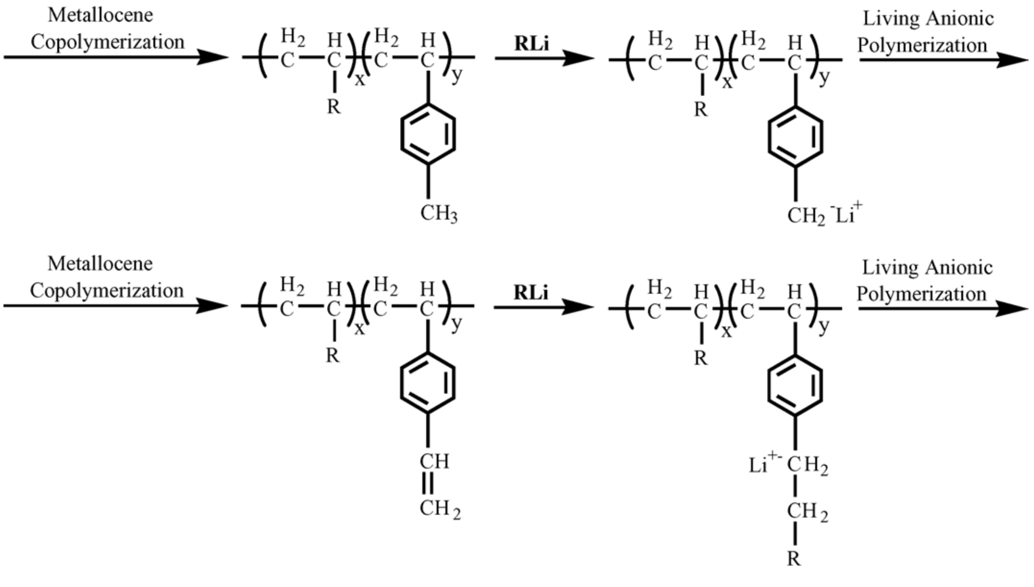

Fig. 10. The synthesis of functional polyolefin graft copolymers by living anionic graft-from polymerization.

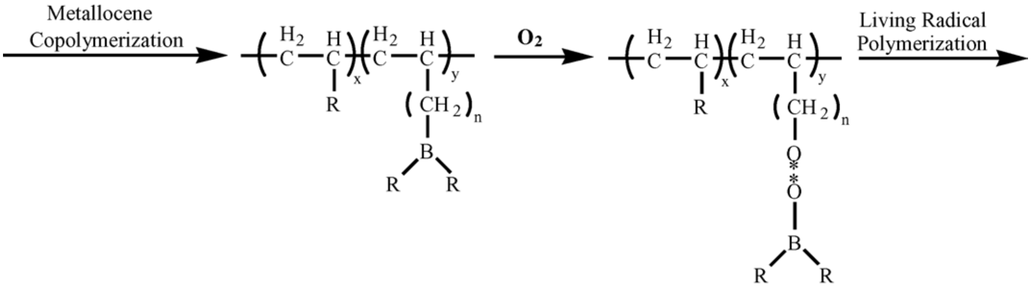

Fig. 11. The synthesis of functional polyolefin graft copolymers by peroxyborane-initiated living radical polymerization.

and Rhubright synthesized PP containing pendant aluminum alkoxide groups starting from OH-containing PP. The aluminum alkoxide moieties initiated living anionic ring-opening polymerization of ε-caprolactone (CL) and PP-g-poly(ε-caprolactone) (PP-g-PCL) graft copolymers were obtained [65]. Hu and co-workers synthesized sodium alkoxide-containing polyethylenes from ethylene-*p*-MS random copolymers. They then prepared PE-g-poly(ethylene oxide) (PE-g-PEO) graft copolymers by living anionic ring-opening polymerization of ethylene oxide [66]. Both graft copolymers possess well-tuneable structure and composition parameters in broad ranges.

Controlled/“living” radical polymerizations are even more frequently used to synthesize functional polyolefin graft copolymers due to their excellent adaptability for many polar monomers. Chung et al. ever prepared polyolefins containing alkyl-9-BBN side groups by copolymerization of α-olefins with B-5-hexenyl-9-BBN over Ziegler-Natta and metallocene catalysts [67–69]. In the presence of O_2, the pendant alkyl-9-BBN groups in polyolefins were selectively oxidized at the aliphatic C–B groups, forming peroxyborane (B-O-O-C) that initiated living radical polymerizations of various polar monomers including methacrylate and vinyl acetate (Fig. 11). Recently, the same chemistry was extended to synthesize functional graft copolymers possessing s-PS backbone [62].

The relatively new methods of controlled/“living” radical polymerization, including ATRP, NMP and RAFT, were also used to synthesize functional polyolefin graft copolymers. In 1998, Stehling et al. reported copolymerization of α-olefins (propylene or 4-methyl-1-pentene) with an alkoxyamine-substitutedα-olefin by a cationic metallocene catalyst $[\text{rac-Et}(H_4Ind)_2ZrMe]^+[B(C_6F_5)_4]^-$. This copolymerization incorporates functional alkoxyamine, a unimolecular initiator of NMP, into polyolefins, allowing the synthesis of polyolefin-g-PS graft copolymers via NMP (Fig. 12) [70]. Subsequently, Mulhaupt and co-workers employed Pd-based late transition metal catalysts to copolymerize ethylene and alkoxyamine-substituted α-olefins. They synthesized graft copolymers of highly branched PE grafted by PS and styrene–acrylonitrile random copolymers, respectively [71].

TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)-mediated stable radical polymerization was employed by Shimada and co-workers to prepare PP-g-PS graft copolymers from PP containing peroxide species generated by irradiation [72]. The obtained PP-g-PS graft copolymers possess PS grafts with well-controlled molecular weight and narrow molecular weight distribution (Fig. 13).

Liu and Sen carried out selective bromination of an ethylene–styrene random copolymer prepared with a metallocene catalyst, introducing bromine at the benzylidene position of the styrene unit [73]. The ethylene–styrene random copolymer containing benzyl bromine groups functions as a multifunctional initiator of ATRP and initiates, in the presence of CuBr and PMDETA, homopolymerizations of MMA

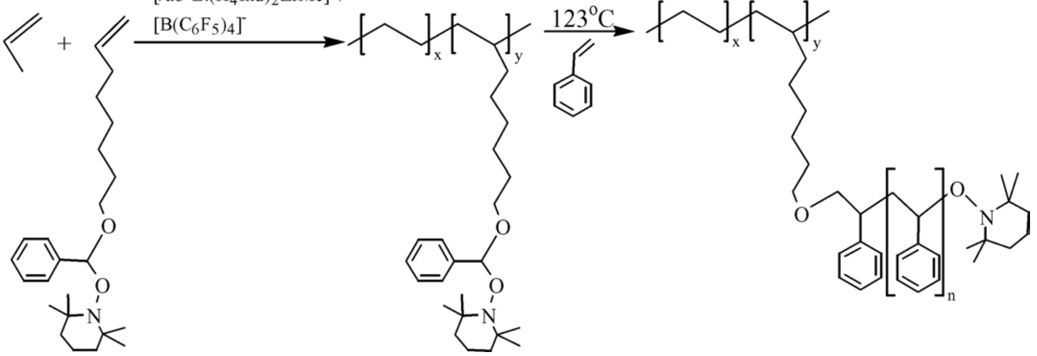

Fig. 12. The synthesis of polyolefin graft copolymers by nitroxide-mediated stable radical polymerization [70].

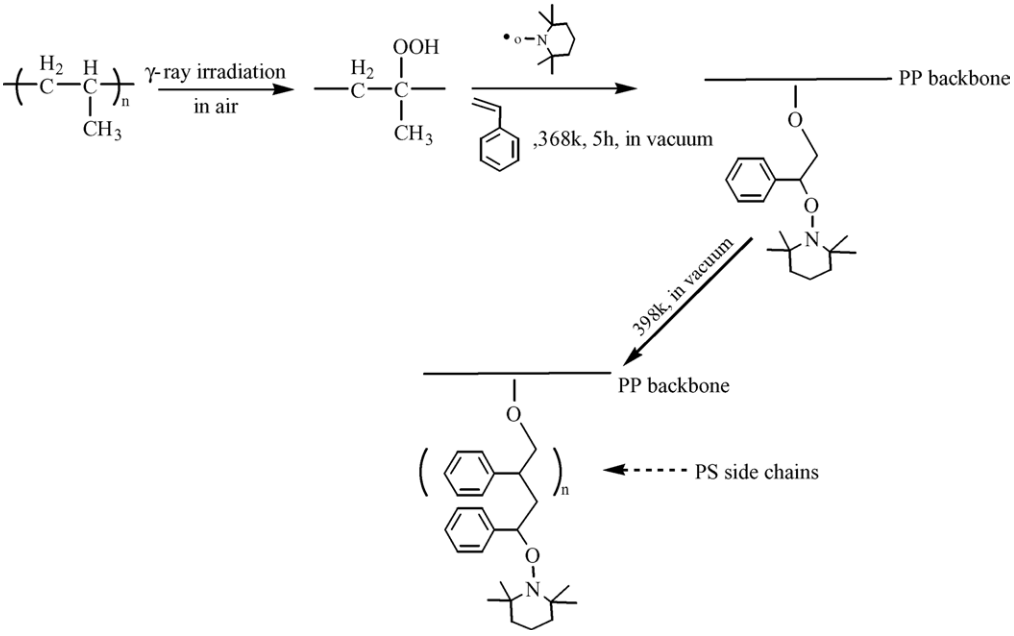

Fig. 13. The synthesis of PP-g-PS graft copolymers via TEMPO-mediated stable radical polymerization [72].

and styrene and block copolymerization of MMA/styrene and MMA/methacrylate (MA), respectively. Polyethylene graft copolymers with various functional polymer grafts were synthesized (Fig. 14). Analogously, s-PS-backboned graft copolymers were also obtained [74].

Shimada and co-workers created peroxide groups in PE via γ-ray irradiation. The reversed ATRP of MMA initiated by the PE chain-pending peroxide with $FeCl_3/PPH_3$ as a catalyst resulted in PE-g-PMMA graft copolymers with well-controlled graft structure [75].

ATRP was also used to combine with commercial functional polyolefins to synthesize polyolefin graft copolymers. Matyjaszewski et al. reported the transformation of ethylene-co-glycidyl methacrylate copolymer to a polymeric initiator of ATRP by reaction with several chemical reagents including chloroactic acid and 2-bromoisobutyl acid [76]. Graft copolymers of PE-g-PS and PE-g-PMMA were prepared by subsequent ATRP process. Analyses of the molecular weight and molecular weight distribution of the PS grafts cleaved from the graft copolymers proved that the PS graft grew at

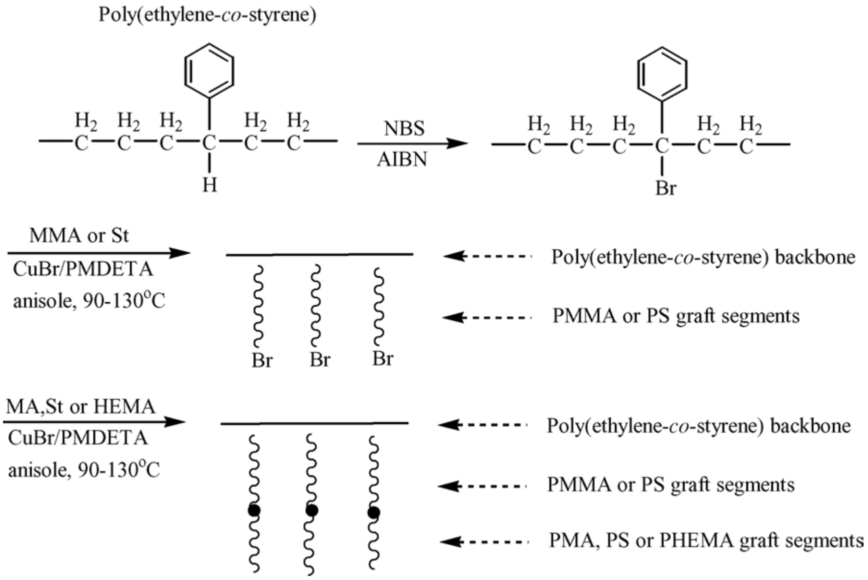

Fig. 14. The synthesis of polyethylene graft copolymers from ethylene–styrene random copolymer via ATRP process [73].

the side chains of PE in a controlled manner. Soares and co-workers started from commercial ethylene-co-vinyl acetate copolymer containing chloropropionate groups to prepare graft copolymers of ethylene-co-vinyl acetate copolymer grafted by PMMA via ATRP with CuCl/ppy catalyst [77].

ATRP of MMA was also carried out on the surface of PE films that was pretreated by 2,2,2-tribromoethanol and benzophenone [78]. PE films containing surface functional polymer grafts were obtained.

Recently, Davis and co-workers reported the grafting of PS onto PP via RAFT process [79]. With cumyl phenyldithioacetate as a chain transfer agent, they initiated the living radical polymerization of styrene onto PP by γ-ray irradiation and obtained PP-g-PS graft copolymers. The molecular weight of the PS graft is highly controllable.

4.2. Macro-monomer approach

Usually, a macro-monomer is synthesized by termination of a living polymerization reaction with a terminating agent containing a polymerizable group. This process produces a macro-monomer with controlled and uniform molecular weight.

Henschke et al. synthesized a PS macro-monomer containing a terminal vinyl group by terminating BuLi-initiated living anionic polymerization of styrene with allyl bromide [80]. The preparation of PP-g-PS graft copolymers was realized by copolymerization of propylene with such a macro-monomer over a metallocene catalyst.

Matyjaszewski and co-workers took advantage of Pd-based late transition metal-catalyzed living ethylene polymerization to introduce a methyl acrylate group at PE chain end [81]. The ATRP copolymerization of *n*-butyl acrylate with the macro-monomer resulted in poly(*n*-butyl acrylate) grafted by PE. This is the first example of the successful combination of living olefin coordination polymerization with controlled/“living” radical polymerization for the synthesis of polyolefin graft copolymers.

Recently, Kashiwa et al. synthesized PCL-g-PE graft copolymers with PE being the polymer graft by condensation polymerization of ε-caprolactone with OH-terminated PE using trimethyl aluminum as a catalyst [82]. It is worthy to note that, although the OH-terminated PE polymers were synthesized via chain transfer reaction in metallocene-catalyzed olefin polymerization instead of living polymerization process, their molecular weights still kept narrow distribution characteristic because of the well-defined and controlled chain transfer reaction.

Besides graft copolymerization and macro-monomer methods, functional polyolefin graft copolymers with well-defined structure can also be obtained via coupling reaction between polyolefins containing functional side groups and functional polymers containing a reactive terminal group. Recently, Hu and co-workers reported that PE-g-PEO graft copolymers could also be prepared by coupling maleic anhydride-modified polyethylene with PEO via esterification reaction [83].

5. Design and synthesis of chain end-functionalized polyolefins

Compared to the synthesis of side group-functionalized polyolefins, it is even more difficult to selectively introduce only one polar functional group to polyolefin chain terminal to synthesize chain end-functionalized polyolefins. In general, three approaches are available in the literature to achieve chain end-functionalization of polyolefins: (i) chemical modification of chain end-unsaturated polyolefins, (ii) living olefin coordination polymerization and (iii) in situ chain transfer reaction by chain transfer agent containing a polar functional group or its precursor during metallocene or Ziegler-Natta catalyzed olefin polymerization.

5.1. Chemical modification of chain end-unsaturated polyolefins

β-Hydride and β-methyl elimination reactions occurring during polymer chain propagation in olefin coordination polymerization result in unsaturated polyolefin chain ends. By tuning catalyst structure as well as polymerization conditions, it is possible to have β-hydride and β-methyl elimination reactions dominate the chain termination process and render a majority of termination chain ends being composed of unsaturated groups. The functional modification of unsaturated chain ends will lead to chain end-functionalization of polyolefins.

Shiono et al. synthesized a series of chain end-functionalized PP, including PP containing magnesium bromide, primary amine and secondary amine end groups, by appropriate chemical modifications of vinylidene-terminated PP resulting from metallocene and Ziegler-Natta-catalyzed propylene polymerization [84–87].

Thus far, the most successful example of a synthesis of chain end-functionalized polyolefins from terminally unsaturated ones was reported by Chung and Lu who employed a combination of hydroboration and oxidation reactions to synthesize PP containing terminal maleic anhydride, hydroxyl and amine functionalities [88–90]. In their experiments, propylene was first polymerized by rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst at a relatively high temperature (>60 °C) to obtain predominantly vinylidene-terminated PP. The terminal vinylidene group was then quantitatively hydroborated to introduce a borane group at the polymer chain end. The terminal borane group underwent effective functional transformation reactions including hydroxylation and oxidation followed by maleation and amination to obtain versatile chain end-functionalized polyolefins.

5.2. Living olefin polymerization approach

Living polymerization provides a classical way to position a polar functional group at the polymer chain end. However, in the case of polyolefins, it is usually very difficult to apply the living coordination polymerization chemistry to synthesize chain end-functionalized polyolefins due to a very high demand of catalyst as well as polymerization conditions. In addition, the inherent nature of living polymerization allows each active site to generate only one polymer chain, resulting in very low synthetic efficiency and thus limited practical value.

Doi et al. achieved living polymerization of propylene with $V(acac)_3/Al(C_2H_5)_2Cl$ catalyst at a very low temperature ($<-65\,^{\circ}C$) and obtained iodine-terminated PP by adding I_2 into the polymerization system at the end of polymerization [91–94]. Later, in the 1990s, some new transition metal complexes (Sm, Co, Ni) were found to exhibit living olefin polymerization characteristics at some higher temperatures (even room temperature) [95–99]. These catalysts were also attempted in the chain end functionalization of polyolefins. Recently, Brookhart et al. employed a Co(III) complex containing para-substituted phenyl group to initiate living polymerization of ethylene, resulting in polyethylene containing an initiation terminal of substituted phenyl group [100]. A series of end-functionalized polyethylenes were then obtained by changing the substituent of the phenyl group in the catalyst.

5.3. Chain transfer approach

Chain transfer approach is so far the most efficient and also widely applied chemistry for the synthesis of chain end-functionalized polyolefins. In the process of olefin polymerization, a chain transfer reaction initiated by chain transfer agent containing a functional group allows the functional group to be introduced at the terminating chain end of the resultant polyolefin. Because the occurrence of chain transfer reaction simultaneously generates new catalyst sites, which are still active for olefin polymerization, the overall polymerization efficiency is usually not significantly affected.

Soga and co-workers added $Zn(C_2H_5)_2$ into propylene polymerization system catalyzed by $TiCl_3/AlEt_3$ and obtained zinc-terminated PP [101–103]. The terminal alkylzinc group was transformed to other functional groups including hydroxyl, carboxylic acid and halide.

Marks and co-workers synthesized silane-terminated polyolefins by using alkylsilanes containing a Si–H bond as chain transfer agent in olefin polymerization catalyzed by various catalysts, including $Me_2Si(Me_4C_5)_2LnCH(SiMe_3)_2$, $[(Me_4C_5)_2LnH]_2$ Ln = Sm, Lu, Y, La and $[Me_2SiC_5Me_4{}^tBuN]TiMe^+B(C_6F_5)_4^-$ (Fig. 15) [104–107]. The general formula of the alkylsilane chain transfer agents is $RSiH_3$ (R = *n*-Bu, $C_6H_5CH_2$, Ph). Further reactions on the silane terminal led to chain end-functionalized polyolefins containing various functional groups. For example, Jayaraman et al. synthesized elastic polyolefins terminally functionalized by two hydroxyl groups on the basis of silane-terminated polyolefins [108].

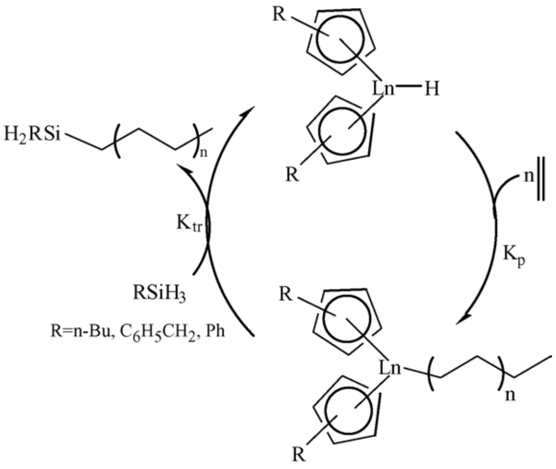

Fig. 15. The synthesis of terminally silane-functionalized polyethylene by using alkylsilane chain transfer agents [107].

Chung and co-workers introduced alkylborane group at polyolefin chain end by employing alkylboranes containing B–H bond as chain transfer agent in metallocene-catalyzed olefin polymerization (Fig. 16) [109–111]. The reaction involves a ligand exchange between B and H in the chain transfer agent and the metal-alkyl in the catalyst active site. The terminal alkylborane group is available for many functional transformation reactions. PE, ethylene-co-α-olefin copolymer, ethylene-co-styrene copolymer and s-PS were all terminally functionalized using this approach.

Hessen and co-workers used thiophene as a chain transfer agent in metallocene-catalyzed ethylene polymerization [112]. The mechanism of this chain transfer reaction involves facile *ortho* C–H bond activation by $[Cp^*LaH]_2$ catalyst due to the strong Lewis basic of the sulfur in thiophene. A thiophene-terminated polyethylene was then obtained by ethylene polymerization with $[Cp^*LaH]_2$ catalyst (Fig. 17).

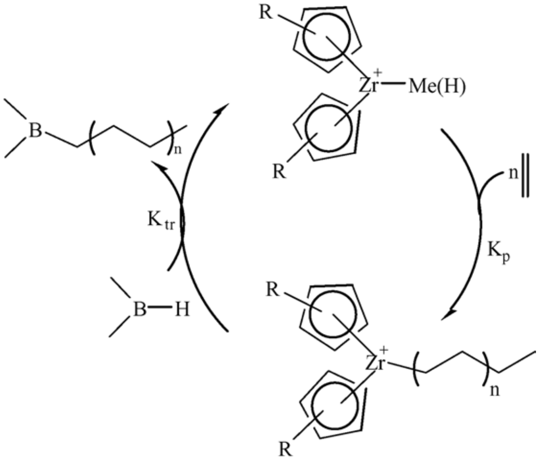

Fig. 16. The synthesis of terminally borane-functionalized polyethylene by using alkylborane chain transfer agents [109].

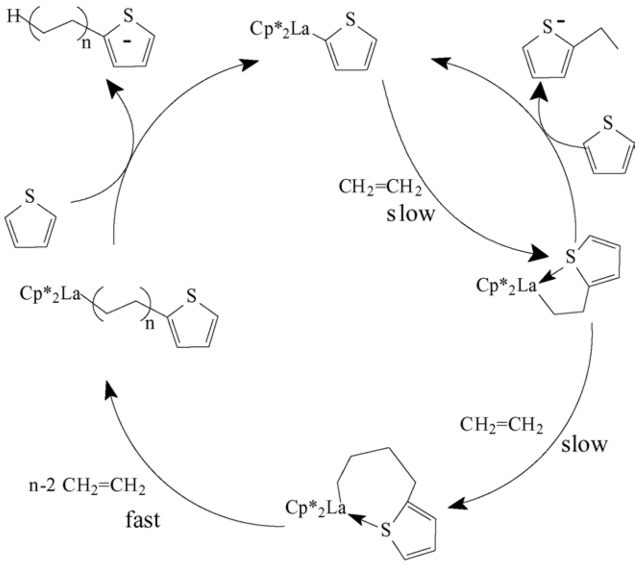

Fig. 17. The synthesis of thienyl-terminated polyethylene with thiophene as chain transfer agent in $[Cp^{*}LaH]_2$ catalyzed ethylene polymerization [112].

Kim and co-workers found that, in the homo- and copolymerization of ethylene, the increment of steric hindrance of catalyst ligand led to the effective restraint of β-hydride elimination reaction [113,114]. Under certain conditions, chain transfer to MAO becomes the predominant chain termination reaction in metallocene-catalyzed polymerization, resulting in aluminum-terminated polyolefins. Terminally hydroxylated polyolefins were then obtained by reacting the aluminum-terminated polyolefins with H_2O_2/NaOH (Fig. 18).

Dong et al. synthesized several styrene derivatives containing polar functional groups (such as 4-(*tert*-butyldimethylsilyloxy)styrene, 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene and 4-chlorostyrene) and used them as chain transfer agent in rac-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO-catalyzed propylene polymerization with the assistance of hydrogen (Fig. 19) [115]. *i*-PPs containing terminal halide, phenol and primary amine groups were then synthesized by propylene polymerization in the presence of the respective chain transfer agents followed by an un-masking step at the end of polymerization using HCl.

6. Design and synthesis of functional polyolefins with block structure

Although the synthesis of functional polyolefins with block structure is known to be difficult, several approaches were still successfully explored and are now available for their syntheses [116,117]. Among them, the most studied ones include (i) living olefin coordination polymerization, (ii) transformation from olefin coordination to living anionic polymerization and (iii) transformation from olefin coordination to controlled/"living" radical polymerization. The latter two approaches are particularly interesting in that they offer simple reaction processes and produce functional polyolefin di-block copolymers with a broad range of copolymer composition and well-designed structure. In fact, these two approaches greatly benefit from the single site metallocene catalysts that provide effective and well-controlled chain transfer reactions for olefin polymerization. By designing suitable chain transfer agents containing the desired initiator moiety or its precursor for living anionic or free radical polymerization, olefin coordination polymerization mediated by metallocene catalyst in the presence of chain transfer agent will result in polyolefin-based macromolecular initiator that is ready for chain extension reaction to synthesize functional polyolefin block copolymers. In addition, as the polyolefin segment in the block copolymer is prepared by metallocene-catalyzed polymerization via a controlled chain transfer reaction, and the functional polymer segment is obtained by a living polymerization, a controlled synthesis of di-block copolymers is expected.

6.1. Living olefin polymerization approach

In fact, it is very rare to apply transition metal-mediated living coordination polymerization with sequential monomer addition to synthesize functional polyolefin di-block copolymers due to the enormous encumbrance for the simultaneous fulfillment of the requirements of living coordination polymerization and of catalyst compatibility with functional monomers. Only a few experimental results have indicated catalyst systems capable of carrying out living coordination polymerization as well as other polymerization mechanisms upon changing the reaction conditions.

Doi et al. achieved syndio-specific living polymerization of propylene with $V(acac)_3/Al(C_2H_5)_2Cl$ catalyst system at −78 °C [93,94]. By raising temperature to 25 °C, they then transformed the active polymer chain end C–V bond to a free radical C* and initiated MMA polymerization to afford syndio-PP-b-PMMA di-block copolymers.

Yasuda et al. reported an organolanthanide complex ($LnRCp^{*}_2$) (Ln = Sm, Yb, Lu; R = H, CH_3) in the early 1990s, which is capable of serving the dual functions of polymerizing both ethylene and polar functional monomers (MMA, CL, etc.) in living manners (Fig. 20) [95]. The mechanisms of the polymerization of the functional monomers are either ring-opening polymerization or group transfer polymerization.

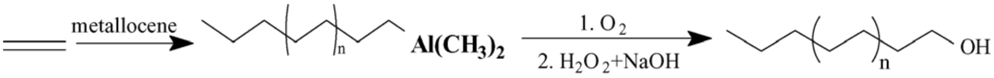

Fig. 18. The synthesis of OH-terminated polyethylene via chain transfer to MAO [114].

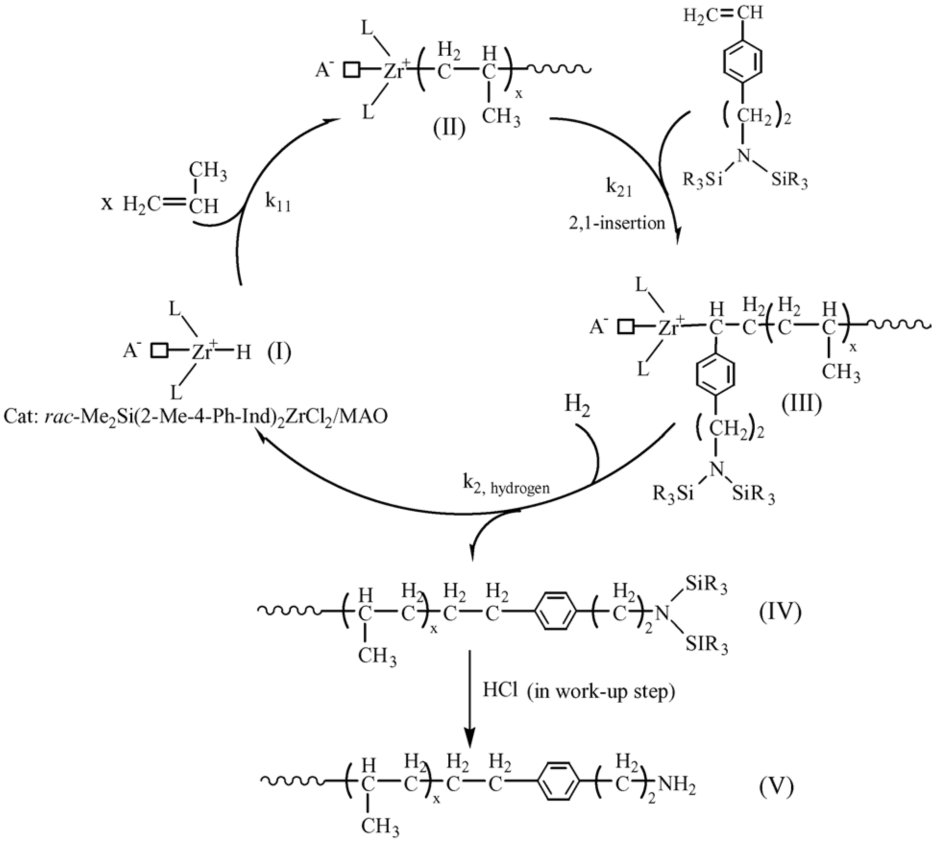

Fig. 19. The synthesis of i-PP containing a terminal primary amine group via chain transfer reaction with 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene as chain transfer agent [115].

In general, the living coordination approach for the synthesis of functional polyolefin di-block copolymers is a very special but limited chemistry. So far, examples of successful synthesis of di-block copolymers consisting of a functional polymer and a stereoregular polyolefin such as i-PP and s-PS have not yet been reported.

6.2. Transformation from olefin coordination to living anionic polymerization

The preparation of functional polyolefin di-block copolymers via transformation from olefin coordination to living anionic polymerization is mostly achieved by converting the terminal functional or reactive group of a polyolefin to an initiating group of living anionic polymerization followed by chain extension polymerization of a functional monomer.

Soga and co-workers started from metallocene-catalyzed terminally unsaturated PP containing a vinylidene end group to prepare magnesium bromide-terminated PP by reacting with a borane–dimethylsulfide complex and pentane-1,5-diyldi-(magnesium bromide) [118]. In the presence of MMA, the magnesium bromide moiety at PP chain end initiated living anionic polymerization of MMA to obtain PP-b-PMMA di-block copolymers.

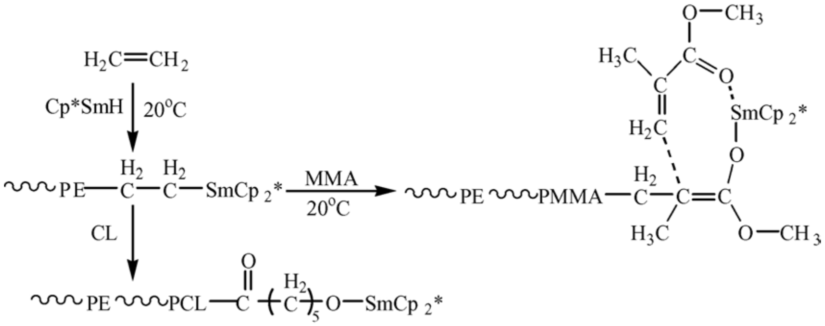

Fig. 20. The synthesis of PE-b-PMMA and PE-b-PCL di-block copolymers via living polymerization with an organolanthanide complex [95].

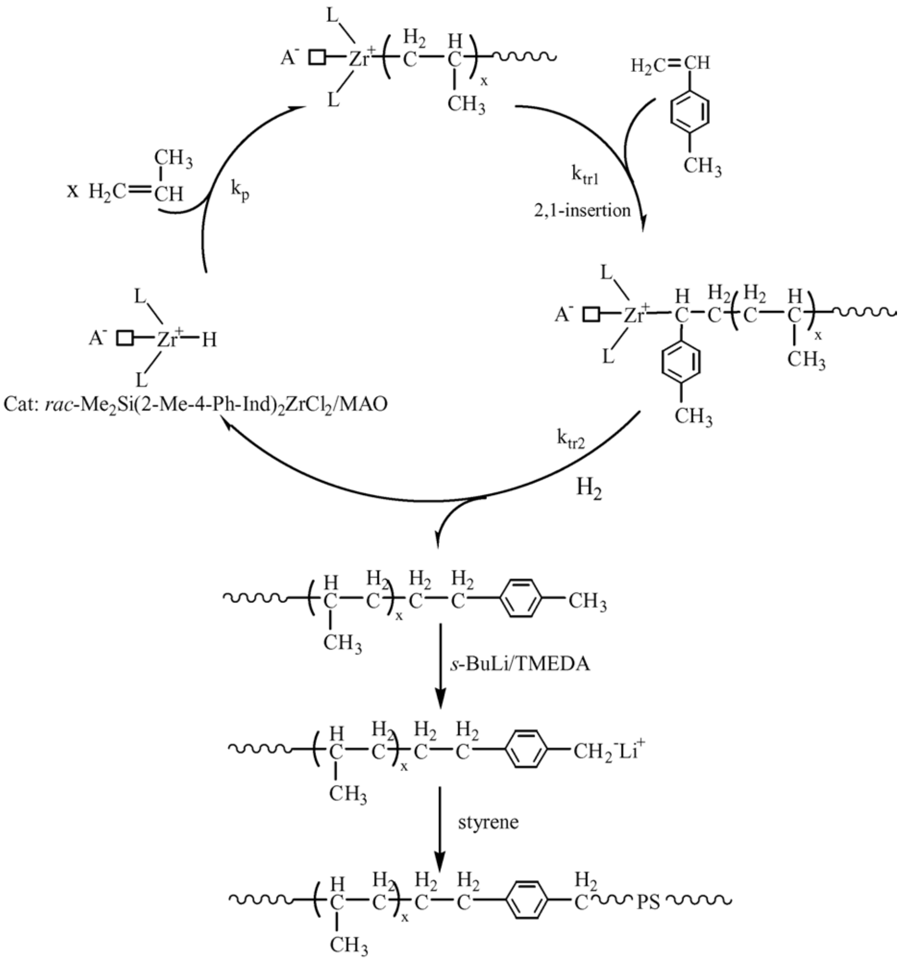

Fig. 21. The synthesis of PP-b-PS di-block copolymers via transformation from olefin coordination to living anionic polymerization [119].

Chung and Dong used *p*-MS as chain transfer agent in metallocene-catalyzed propylene polymerization and obtained *p*-MS-terminated PP in high yield [119]. The terminal benzyl group underwent effective lithiation reaction with sec-butyllithium to implant alkyllithium at PP chain end (Fig. 21). In the presence of styrene, PP-b-PS di-block copolymers with a broad range of composition and well-defined structure were prepared by the PP-substituted

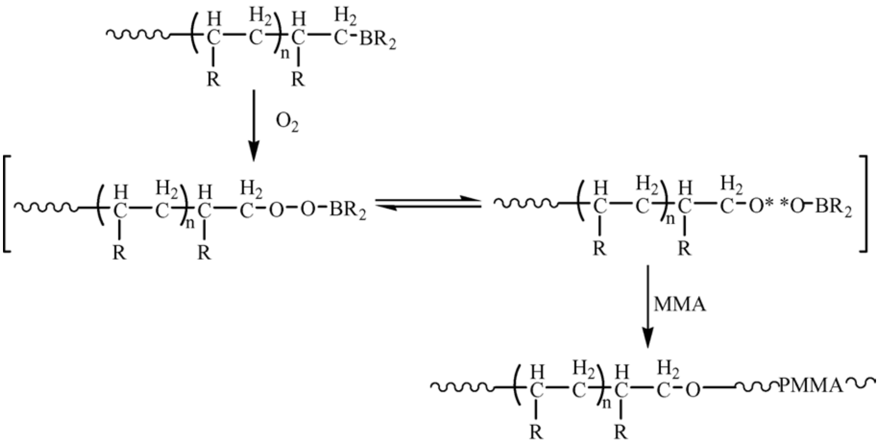

Fig. 22. The synthesis of polyolefin-b-PMMA di-block copolymers by the transformation from olefin coordiantion to peroxyborane-initiated living radical polymerization of MMA [111].

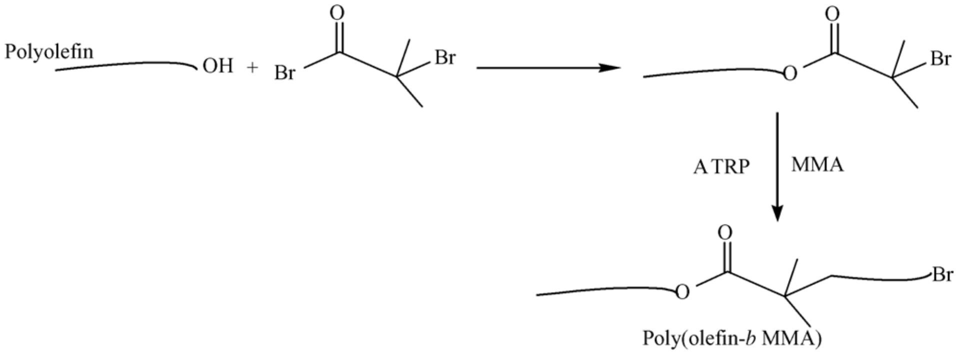

Fig. 23. The synthesis of polyolefin-b-PMMA di-block copolymers by means of ATRP from polyolefins containing a terminal hydroxyl group [121,122].

alkyllithium-initiated living anionic polymerization of styrene.

Lu et al. synthesized polyolefins containing a terminal sodium alkoxide group from hydroxyl-terminated PE and ethylene-α-olefin copolymers [120]. The terminal sodium alkoxide initiated living anionic ring-opening polymerization of ethylene oxide. A series of polyolefin-b-PEO di-block copolymers were obtained.

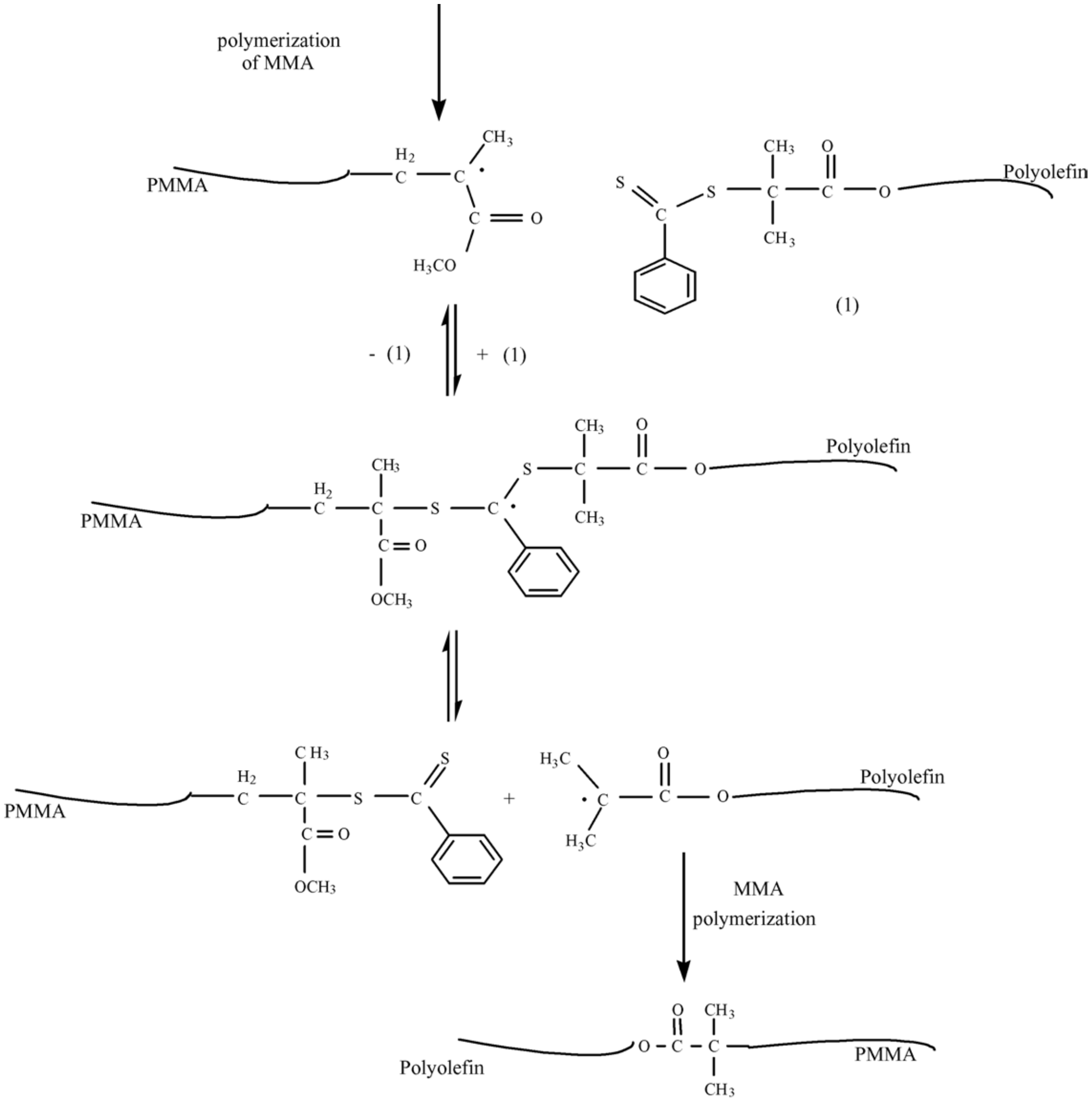

Fig. 24. The synthesis of polyolefin-b-PMMA di-block copolymers by RAFT [124].

Kim and co-workers employed hydroxyl-terminated PE resulting from controlled chain transfer by aluminum during metallocene-catalyzed ethylene polymerization to be a macromolecular initiator for living anionic ring-opening polymerization of ε-caprolactone [114]. With stannous octoate as a catalyst, they obtained PE-b-PCL di-block copolymers.

6.3. Transformation from olefin coordination to controlled/"living" radical polymerization

The transformation from olefin coordination to controlled/"living" radical polymerization is the most widely used method for the synthesis of functional polyolefin di-block copolymers. Chung and co-workers first applied the in situ chain transfer approach using alkylboranes containing B–H bond as chain transfer agent in metallocene-catalyzed olefin polymerization and introduced an alkylborane group at polyolefin (PE, s-PS, etc.) chain end (Fig. 22) [89,109–111]. In the presence of oxygen, the terminal alkylborane underwent an autooxidation process to form a peroxyborane (B-O-O-C) at the aliphatic C–B bond, which initiated living polymerization of MMA to prepare polyolefin-b-PMMA di-block copolymers.

Schellekens and Klumperman proposed that functional polyolefin di-block copolymers could be synthesized by means of ATRP from polyolefins containing a terminal hydroxyl group [121], as schemed in Fig. 23.

There are various routes to access hydroxyl-capped polyolefins via olefin coordination polymerization. The reaction between the terminal hydroxyl group and 2-bromo isobutyrylbromide results in a polyolefin containing a terminal ATRP initiator moiety. This will then initiate ATRP polymerization of a variety of polar and non-polar monomers including MMA, acrylate and styrene to prepare functional polyolefin di-block copolymers.

Matyjaszewski et al. took advantage of the terminal vinyl double bond of metallocene-catalyzed low molecular weight PP ($M_n = 3100$ g/mol) to attach an ATRP initiator moiety at PP chain end via hydrosilation reaction with 1-(2-bromoisobutyryloxy)propyl-tetramethyldisiloxane [123]. ATRP polymerization of polar monomers such as MMA and *n*-butyl acrylate initiated by the macro-initiator afforded functional polyolefin di-block copolymers based on low molecular weight PP.

Due to the great adaptability of RAFT for a broad range of polar functional monomers, RAFT has a vast potential in the preparation of functional polyolefin block copolymers via transformation from olefin coordination to radical polymerization. Monteiro and co-workers implanted a dithioester group at the chain end of ethylene–butylene copolymer via esterification reaction between the hydroxyl terminal group in the polyolefin copolymer and an acid-functionalized dithioester (4-yano-4-[(thiobenzoyl)sulfanyl]pentanoic acid) [124]. The polyolefin copolymer containing the terminal dithioester group was then used as a macromolecular RAFT agent in 2,2′-azobisisobutyronitrile (AIBN)-initiated RAFT polymerization of MMA and alternating copolymerization of styrene and maleic anhydride to prepare polyolefin-b-PMMA and polyolefin-b-poly(styrene-alt-maleic anhydride) di-block copolymers (Fig. 24).

Besides the aforementioned three methods, coupling reaction between a polyolefin containing a terminal functional or reactive group and a reactive group-terminated functional polymer also produces functional polyolefin di-block copolymers. However, the major drawback of this approach is that the coupling reaction products generally contain un-reacted homopolymers due to the low reaction efficiency of two high polymers.

7. Outlook

We have summarized recent achievements in the functionalization of polyolefins, with special attention being paid to chemistry using transition metal-catalyzed process to synthesize structurally well-defined functional polyolefins, including side group-functionalized polyolefins, chain end-functionalized polyolefins and functional polyolefins with graft and block structures. Despite the varied structures, the aforementioned functional polyolefins are all new polyolefin materials of high added value. Through fine adjustment of structure in order to realize effective control over properties in broad ranges, new functional polyolefin polymers fulfilling different application demands are accessible. In fact, design and synthesis of structurally well-defined functional polyolefins has become the major research direction in the field of polyolefin functionalization.

However, from a practical viewpoint, many of the so far available approaches to structurally well-defined functional polyolefins exhibit the disadvantage being multi-step, which greatly reduces their practical application value. Future research on polyolefin functionalization must, on the basis of ensuring a high degree of structure controllability, focus on the simplification of the synthetic procedures.

Acknowledgements

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