Post-polymerization functionalization of polyolefins

Nicole K. Boaen and Marc A. Hillmyer*

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Polyolefins are macromolecular alkanes and include the most familiar and most commercially produced plastic, polyethylene. The low cost of these materials combined with their diverse and desirable property profiles drive such large-scale production. One property that renders polyolefins so attractive is their resistance to harsh chemical environments. However, this attribute becomes a severe limitation when attempting to chemically convert these plastics into value-added materials. Functionalization of polymers is a useful methodology for the generation of new materials with wide ranging applications, and this *tutorial review* describes both new and established methods for the post-polymerization modification of polyolefins.

Introduction

The polymerization of olefins such as ethylene and propylene generates a class of materials known as polyolefins. Despite their name, these macromolecular alkanes contain only sp^3-hybridized carbons. For example, polyethylene, the most widely recognized in the class, consists of long chains of entrained ethylene (–CH_2–CH_2–) subunits. Polyolefins comprise the least expensive, most widely used, and most commercially produced polymers available. In fact, tens of billions of pounds of polyethylene are produced in the United States annually. Hailed for their excellent attributes including outstanding chemical resistance and broad-ranging mechanical properties, polyolefins are found in applications as diverse as food packing, rubbish disposal bags, ultra-high strength fibers, and automobile bumpers. Of course, one-size does not fit all, and there are many applications for which these materials are poorly suited.[1] For example, the poor compatibility of polyolefins with oxygen- and nitrogen-containing polymers, polar pigments, and additives has limited the use of these polymers in applications that require, for example, good coating/adhesion characteristics. These practical limitations can often be traced back to the lack of polar functional groups along the polymer backbone. The introduction of even low concentrations of functional groups into polyolefins can be sufficient to alter the properties of these plastics for speciality applications without compromising the desired features characteristic of the parent materials (*e.g.*, processability, chemical robustness, and mechanical strength).[1] Furthermore, controlling the level of functional group incorporation allows for precise property tailoring. There is no question that systematic control over the type and concentration of polar functional groups along a polyolefin backbone would render these ubiquitous materials even more versatile. The incorporation of functional groups along the backbone of polyolefins such as polyethylene and polypropylene in a selective, controlled, and mild manner is one of the most important challenges facing synthetic polymer chemists today.

There are at least four contemporary methodologies employed to meet this goal, and all have both advantages and shortcomings. These methods are shown schematically in Fig. 1. Maybe the most direct method, shown in Fig. 1(a), is copolymerization of common olefins (*e.g.*, ethylene and propylene) with olefins (typically mono-substituted α-olefins)

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*hillmyer@chem.umn.edu

Nicole K. Boaen

Nicole Boaen received her BA in chemistry from Austin College in Sherman, Texas in 1995. She is currently pursuing her PhD in the Department of Chemistry at the University of Minnesota and is advised by Professor Marc A. Hillmyer.

Marc A. Hillmyer

Marc Hillmyer received his BS in chemistry from the University of Florida in 1989, and his PhD in chemistry under the guidance of Professor Robert H. Grubbs from the California Institute of Technology in 1994. After a postdoctoral appointment with Professor Frank S. Bates in the Department of Chemical Engineering and Materials Science at the University of Minnesota, he joined the chemistry department at the same institution where he is currently an Associate Professor of Chemistry.

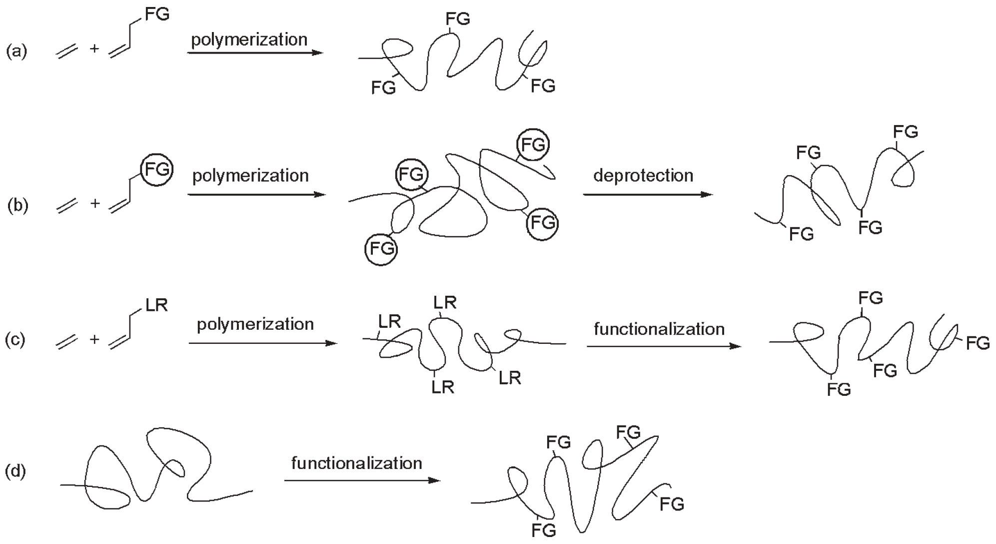

Fig. 1 Synthetic strategies for the preparation of functionalized polyolefins. (a) Direct copolymerization with olefins bearing the desired functional group (FG). (b) Direct copolymerization with olefins containing a protected functional group followed by deprotection to generate the desired chemical moiety. (c) Direct copolymerization with a monomer bearing substituents with latent reactivity (LR) and then subsequent functionalization. (d) Direct post-polymerization functionalization of a polyolefin.

containing the desired functional group. For example, the high-pressure free radical copolymerization of ethylene and methacrylic acid is practiced commercially and leads to the "cut-resistant" material found in golf ball covers. Unfortunately, the extension of this methodology to the more controlled transition-metal-catalyzed olefin polymerizations is fraught with difficulties. The high reactivity of general metal complexes used in these polymerizations typically renders them readily deactivated by polar functionality in the comonomer. This problem can be side-stepped through protection of the comonomer functional group pre-polymerization (Fig. 1(b)). Hiding (or shielding) the functional group, using an appropriately selected protecting group, from the metal during polymerization requires deprotection post-polymerization, resulting in a multi-step approach. These two strategies have been reviewed,[2] and recent progress in the direct copolymerization of functionalized olefins has resulted from the development of new catalysts that tolerate polar functionality in comonomer candidates.[3]

Fig. 1(c) shows a related scheme that utilizes copolymerization, but in this case the comonomer is compatible with most transition metal catalysts and contains a moiety with latent reactivity. That is to say, the product copolymer can be functionalized directly by reaction of the "functional group precursor" on the comonomer. This "reactive copolymer approach" was pioneered by the author of a recent book on the subject of polyolefin functionalization.[4] This scheme relies on the development of monomers that do not negatively impact the catalytic production of polymer, but carry functional group precursors that are readily converted into a variety of pendant groups. For example, *p*-methylstyrene can be incorporated into polyethylene and polypropylene using traditional transition metal catalysts, and the aryl methyl group can be converted into halogen, hydroxyl, carboxyl, and silicon-containing functional groups. This approach is very attractive in that the appropriate choice of comonomer can lead to the preparation of various functionalized polymers from one parent material.

The schemes shown in Figs. 1(a), 1(b) and 1(c) all require the copolymerization of an olefin and a "functional" or "pre-functional" comonomer. As in all copolymerizations, both the level of comonomer incorporation and sequence distribution are dictated by the relative reactivity of the monomers with the propagating centers (parameterized through the reactivity ratios) and concentration of comonomer in the feed through the well-known copolymerization equation. This means that for each comonomer, polymerization conditions need to be carefully tuned to dictate the desired outcome in terms of the copolymer composition. Under certain circumstances the inherent reactivity of the comonomer can severely limit the range of possible products. Furthermore, in the case of transition-metal-catalyzed polymerization, the stereoregularity of the polyolefins (*e.g.*, the isotacticty of polypropylene) can be compromised using catalysts that have been optimized for functional group tolerance.[2] Also, catalyst activities are often remarkably lower for copolymerization of olefins with polar comonomers than for homopolymerization of ethylene or other alkyl α-olefins, rendering the copolymerization inefficient.[2] In sum, the incorporation of comonomers *via* a polymerization process carries with it complications that can render these three approaches undesirable. An alternative scheme to functionalized polyolefins is given in Fig. 1(d). The *direct* functionalization of polyolefins is a method that avoids the above complications and is the central topic of this *tutorial review*.

The direct post-polymerization functionalization of polyolefins has many desirable attributes. Firstly, one can use garden-variety polyolefins as starting materials; thus no new copolymerization technology is necessary. Secondly, the level of functional group incorporation can be tuned through simple stoichiometric considerations. Thirdly, random incorporation of functional groups is far more likely than in the copolymerization approaches. Finally, any functionalization chemistry that can be accomplished on small-molecule analogs of the polymer can, in principle, be carried out on the polymer. Herein lies the problem, the functionalization of alkanes is a difficult chemical transformation. (Karl Reichenbach coined the name paraffins, the common name for alkanes, from the Latin *parum* meaning "too little" and *affinitas* meaning "affinity" due to their innate low reactivity.) This "inertness" leads to the desired robust nature of polyolefins as mentioned above. Nonetheless, chemists have been tackling the general problem of alkane functionalization for well over 100 years. Success with both low-molecular-weight and polymeric alkanes has been achieved, and there are direct polyolefin functionalizations commercially practiced. However, there are many obstacles that need to be overcome to bring polyolefin functionalization to the level of practicality enjoyed in the (metal-catalyzed) functionalization of other more reactive polymers such as polydienes[5] and polystyrenes.[6]

In the post-polymerization functionalization of polymers, there are several side reactions that must be minimized such that the desirable properties of the parent material are retained in the functionalized product. Basically, this comes down to the idea that any transformation one does on these materials should not break or couple (*i.e.*, crosslink) chains, should not significantly compromise the mechanical/physical properties (*e.g.*, level of crystallinity) of the parent material, and should only incorporate the desired functional group. In addition, chemical reactions on polymers can be challenging due to solubility limitations, restrictive chain conformations, and difficulty in product purification. These potential difficulties notwithstanding, there are many efforts aimed at the direct functionalization of polyolefins to convert cheap commodity plastics into products with new, desirable, and tunable properties.

This *tutorial review* is subdivided into four sections. The first section describes recent advances in the most widely practiced direct polyolefin functionalization method, free radical reactions. The second section describes the reaction of carbenes and nitrenes with polyolefins, a methodology with certain practical advantages. After that we illustrate two very recent examples that exploit C–H bond activation chemistry in a section on the catalytic modification of polyolefins. In those three sections we will describe the chemistry employed to obtain the functionalized polyolefins and, in some cases, the utility of the product materials. We do not cover the industrially important surface modification of polyolefins (*e.g.*, by corona, plasma, or flame treatment), and we refer the reader to ref. 4 for a brief overview of this topic. We end this *tutorial review* with a look to the future of polyolefin modification. Here, emphasis will be on new catalytic methodologies that could be implemented in the mild, selective, and direct functionalization of polyolefins.

Free radical methodologies

In commercially practiced polyolefin functionalization, highly reactive free radical species are utilized. Free radicals can be generated during mechanical processes, photo-oxidation, or peroxide initiation (most common). These species can react with labile C–H bonds on the polyolefin backbone through abstraction of a hydrogen atom to create radical sites on the main chain. In the most commonly practiced functionalization, maleic anhydride adds to the polymeric radical thus generating a new maleic anhydride based radical. Subsequent addition of another maleic anhydride is not kinetically favorable, and that radical ideally abstracts a hydrogen atom from another polymer backbone and the process is repeated in a chain reaction fashion. The anhydride-functionalized polymers are reactive toward nucleophilic reagents such as amines and can be used to compatibilize blends containing, for example, amine-terminated polyamides.[7]

For practical and economic considerations, these functionalizations are preferably carried out in the melt at high temperatures (*e.g.*, >200 °C).[8] At this high temperature there are problems, particularly uncontrolled processes that result in side reactions. In the case of polypropylene (PP), chain scission (termed β-scission) competes with functionalization, and in polyethylene (PE) crosslinking of polymer chains complicates the reaction leading to a mixture of linear and branched chains. These two deleterious reactions can often compromise the ultimate properties of the products. There has been recent progress in combating these problems; for example, the degradation of PP was shown to be greatly reduced by performing reactions at temperatures less than 150 °C in the presence of monomer, leading to branched PP products with enhanced mechanical properties.[9]

Even with the difficulties associated with maleic anhydride grafting, and despite its corrosive nature, volatility, and toxicity, this process is used extensively in industry to fulfil the many commercial applications of these functionalized materials. For example, typical polyolefins do not have good oxygen barrier properties, an essential component in food packaging applications; however, melt blends containing 65% poly(ethylene-propylene) (EP) and 30% polyketones, "compatibilized" with maleic anhydride grafted PP (5 wt%) resulted in a 70% decrease in the oxygen permeability relative to the starting EP polymer due to the excellent oxygen barrier properties of polyketones.[10] Scanning electron microscopy (SEM) analysis of cryofractured samples prepared by compression molding revealed that the surface layers were distinct from the matrix. IR analysis of the surface layer *versus* the middle of the sample revealed that the surface was polyketone-enriched relative to the interior. The authors suggest the morphology resulted from the low viscosity of the polyketone, which migrated to the surface, and the interfacial adhesion is improved due to hydrogen-bonding of carboxylic acid residues of hydrolyzed maleic-anhydride grafted PP with carbonyl functional groups of polyketones. In addition, the impact properties of these blends could be improved by not only the addition of the functionalized PP but also a low-molecular-weight diamine, which coupled anhydride functionalized chains.

Although maleic anhydride-grafted polyolefins are commercially important, alternative functionalizations have been actively pursued. In recent work aimed at addressing the deficiencies of maleic anhydride, one class of functionalizing agents that has received attention is long-chain oxazoline-containing maleates.[8] Grafting of these molecules onto polyolefins leads to pendant oxazoline functional groups that are versatile electrophiles (Fig. 2). Long chain oxazolines exhibit greatly reduced volatility and toxicity as compared to maleic anhydride. Furthermore, the oxazoline functional group reacts well with amine and carboxylic acid (and other) nucleophiles, thus increasing the breadth of possible reactions that can occur at the polymer backbone. The free radical functionalization of commodity polyolefins with ricinoloxazoline maleinate was carried out on a variety of polyolefins in a twin-screw extruder with no solvent using a peroxide initiator at high temperatures (between 170 and 260 °C). The degree of functionalization increased with higher monomer concentrations (*ca.* 2 wt%), and grafting yields of ricinoloxazoline maleinate were usually near 30% for both EP rubbers and polystyrene–poly(ethylene-butylene)–polystyrene (SEBS) triblock copolymers *versus* approximately 23% for PE. Using an appropriate initiator, the successful grafting of PE without substantial crosslinking was accomplished.

Application of ricinoloxazoline maleinate-grafted polyolefins (*e.g.*, PE-*g*-OXA) as modifiers in blends of polyolefins and engineering plastics, such as polyesters and polyamides (PA), revealed that the addition of oxazoline-functionalized polyolefins to these binary blends produced significantly toughened materials.[11] Vocke and coworkers reported the mechanical properties of a series of blends containing 60 wt% polyolefin (PE or PP), 30 wt% engineering plastic (PA or SEBS), and 10 wt% ricinoloxazoline maleinate-grafted polymer *versus* the binary blend (70/30) and the ternary blend with an un-grafted polymer as a control (60/30/10). In one example a four-fold increase in impact strength (as measured by a standard "Charpy Impact" test) was observed in the ternary blend of PE/PA/PE-*g*-OXA compared to the unfunctionalized PE/PA/non-functionalized PE and PE/PA blends. SEM images of the cryofractured surfaces for each of the ternary blends with and without the grafted oxazoline moiety sharply contrasted with the image of the blend containing functionalized PE showing smaller, more evenly dispersed PE domains. The authors attributed the toughening observed in the PE/PA/PE-*g*-OXA ternary blends to the morphology of the composite material. They proposed that the good dispersion of the particles and their small size was stabilized by both the miscibility of the polyolefin domain of PE-*g*-OXA and by more extensive grafting between PE-*g*-OXA and PA *via in situ* reaction of the oxazoline functional group and terminal amino groups of PA during melt blending.

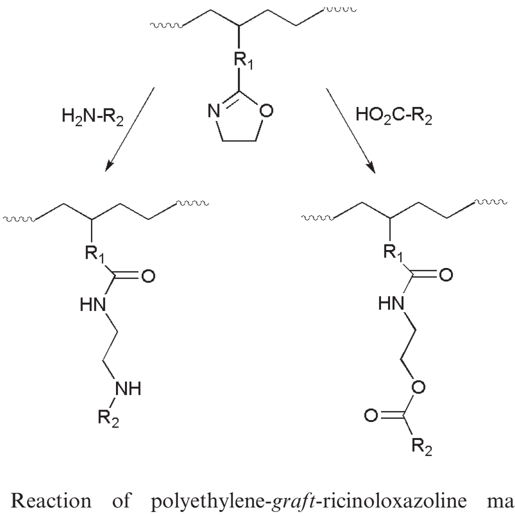

Fig. 2 Reaction of polyethylene-*graft*-ricinoloxazoline maleinate (PE-*g*-OXA) with carboxylic acids and amines. Reprinted with permission from ref. 11, Copyright (1998) John Wiley and Sons, Inc.

In another example, vinyltriethoxysilane was grafted onto PP with good efficiency to produce PP functionalized with silane coupling agents, a potentially useful compatibilizer in inorganic particulate-filled PP composites.[12] The highest levels of functionalization (*ca.* 5 and 7 wt%) were reported at *ca.* 0.5 wt% dicumylperoxide when 5 and 10% silane were employed, respectively. However, large decreases in molecular weight from 36 to 22 kg mol^{-1} were observed. Degradation of pure PP in the absence of peroxide was also observed and attributed to radicals generated with mechanical shear at mixing temperature, consistent with the observed silane functionalization of PP without peroxide initiator.

In the above approaches, a free radical initiator (typically a peroxide) was used to initiate the chain functionalization reaction with some suitable reagent (*e.g.*, maleic anhydride, maleated oxazoline, or vinyltriethoxysilane). An interesting approach that is related but could prove to be more efficient is the direct functionalization with organic peroxides alone. Ideal routes to functionalize polyolefins using only a peroxide compound would, upon homolytic cleavage of the O–O bond, provide a primary radical for hydrogen abstraction, and a suitable radical for recombination with the radical generated on the polyolefin backbone to achieve the desired functionalized product. Recently, the functionalization of PE by peroxyketals[13] and peroxyesters[14] was shown to yield ester-functionalized materials in good yields with low levels of crosslinking (Fig. 3). These reactions have been studied from a mechanistic viewpoint and high levels of functionalization have been reported with very low levels of PE crosslinking, a common deleterious reaction in other free radical reactions. However, in the case of PP functionalization the efficiency was much lower, even though the degree of functionalization of PP was expected to be higher relative to PE based on lower C–H bond dissociation energies for methine hydrogens relative to methylene or methyl hydrogens.[15] Saule *et al.* concluded that the methyl groups present in PP must hinder hydrogen abstraction by, in this case, 1,1-dimethylethoxy radicals.

Carbene and nitrene methodologies

In 1969 Osteraas and Olsen at the Ashland Chemical Company showed that carbenes and nitrenes (electron deficient carbon and nitrogen species, respectively) could be used to modify the surface of PE through the putative insertion of the reactive species (*e.g.*, the carbene :$CHCO_2Et$) into a backbone C–H bond.[16] These coworkers extended their work to other polymers (and fibers) including PP modification using difluorocarbene (:CF_2).[17] While their work was limited to surface modification, the idea of using these reactive species to modify polyolefins is intriguing. However, not much work in the open literature followed these initial reports.

In 1989 Aglietto *et al.* reported on the structure of carbene-modified bulk PE by comparison to discrete model

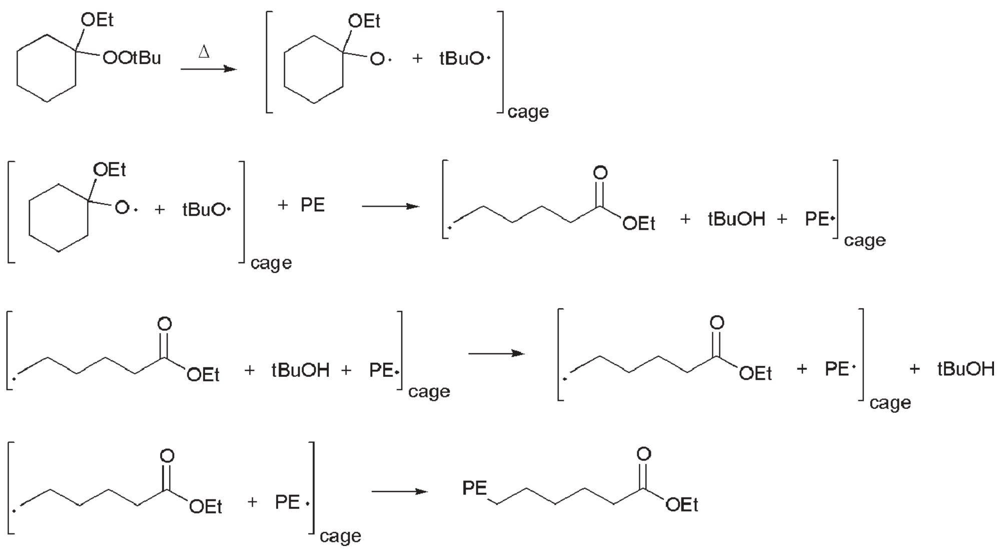

Fig. 3 Proposed mechanism for the chemical modification of polyethylene with a peroxyketal. Reprinted from ref. 13, Copyright (2001), with permission from Elsevier.

compounds.[18] In this work, the authors make the clear point that "clean" chemical modification of PE (in the melt) using functionalized carbene species is possible. In a follow-up publication, this group reported on the details of carbene insertion into polyolefins and the influence of the degree of polar functional group incorporation on the molecular interactions with low-molecular-weight polar additives.[19] The authors conclude that under the functionalization conditions using ethyldiazoacetate, the carbene produced (:$CHCO_2Et$) reacts in the singlet state and thus any free radical behavior is significantly suppressed. The :$CHCO_2Et$ simply inserts into backbone C–H bonds (Fig. 4). This results in minimization of unwanted side reactions such as polymer crosslinking. In fact, no crosslinking reactions are reported in this work. Upon three successive functionalization reactions, 5 wt% functional groups were incorporated into an EP substrate.

Metal-catalyzed examples of carbene insertion into aliphatic C–H bonds have also been reported. For example, Demonceau *et al.* reported the room temperature rhodium-catalyzed decomposition of diazoesters to carbenes that functionalized linear alkanes, small-molecule models of PE in the 1980s.[20] This mild, metal-catalyzed approach should also be useful in the functionalization of polyolefins, circumventing possible degradative side reactions from the more typical high temperature reaction conditions. In a related metal-catalyzed system, Davies and coworkers have shown that diazo compounds can be used to functionalize alkanes in a catalytic manner involving the formation of the high-energy metal-carbenoid intermediate, driven by loss of nitrogen from the starting diazo compound (Fig. 5).[21] The most active metal catalysts have included dirhodium tetracarboxylates and dirhodium tetraprolinate complexes. The use of carbenoid precursors with both electron-withdrawing and electron-donating substituents resulted in improved chemoselectivity in intermolecular C–H insertion reactions. Furthermore, using electron-donating substituents on the carbenes (*e.g.*, aryl rings) helped to stabilize the carbenoid, which in turn limited carbene dimerization, and led to improved selectivity of the reaction. For example, functionalization of cyclohexane using a rhodium catalyst and ethyl diazoacetate or methyl phenyldiazoacetate under the same conditions resulted in 10 and 94% yields of the insertion products. This approach of metal-carbenoid-induced C–H bond activation seems to be very promising as a potential functionalization methodology for polyolefins and is complementary to the analogous non-catalyzed work.

Nitrenes are another class of functionalizing agents with potential and demonstrated utility in the modification of polyolefins.[22] Nitrenes will insert into alkane C–H bonds and can do so selectively provided the nitrene reacts in the singlet

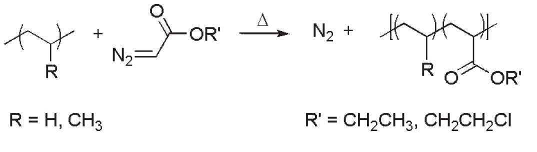

Fig. 4 Polyolefin functionalization with carbenes generated by the thermal decomposition of diazoesters. Reprinted from ref. 19, Copyright (1989), with permission from Elsevier.

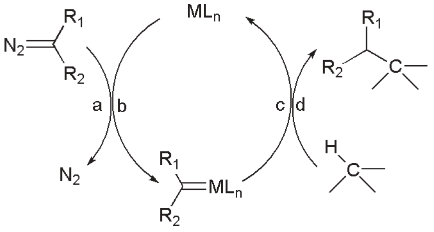

Fig. 5 Catalytic alkane functionalization with diazo compounds using rhodium catalysts. (a) Rhodium-catalyzed decomposition of a diazo compound. (b) Formation of the rhodium-carbenoid intermediate. (c) Regeneration of catalytic species. (d) C–H insertion by rhodium carbenoid intermediate. Reprinted from ref. 21, Copyright (2002), with permission from Elsevier.

state and not in the triplet state where H atom abstraction occurs (*i.e.*, analogous to free radical reactions). Thermolysis of sulfonyl azides generates singlet nitrenes that could be used for this purpose. In one specific example, nitrenes generated *in situ* by thermal decomposition of sulfonyl azides, underwent C–H insertion with PE.[23] Use of these singlet nitrenes provided functionalized polyethylenes with pendant sulfonamide groups (Fig. 6). These materials proved to be effective in the compatibilization of blends containing Nylon as compared to non-functionalized polyethylene. Intermolecular interactions between the pendant sulfonamide groups and the Nylon backbone were suggested to improve the interfacial adhesion between the dispersed and matrix phases. In work reported in the patent literature, poly(sulfonyl azide)s have been used to modify the rheology of polyolefins in the melt state through presumably a related mechanism.[24] Functionalized and "rheology-modified" thermoplastic polyolefins obtained from the modification were both melt processable and showed improved melt strength, a property important for optimized polymer processing. This novel polyolefin functionalization has proven to have commercial utility.

Transition metal C–H bond activation methodologies

C–H bond activation of low-molecular-weight alkanes and subsequent functionalization (*i.e.*, the "insertion" of functional groups into this rather unreactive bond) with transition metals is an important synthetic transformation of these poorly reactive substrates that has garnered much academic and industrial interest. The ability to produce industrially significant products containing primary alcohol, amine, or olefin functional groups from relatively inert alkane feedstocks would be very valuable. For example, the conversion of methane to methanol is one such reaction that is being explored that would transform a widely available gas to an economical liquid fuel.[25] While there are currently many systems under development for the activation of C–H bonds in alkanes, virtually all of the organometallic complexes that effect C–H activation have some drawbacks (*e.g.*, low turnover number, low alkane conversions), and there is work to be done in this area. In an excellent recent review by Crabtree that highlights the progress in C–H activation over the last century, he states "development of an economically viable C–H activation system for alkanes remains a major unsolved problem for the new millennium."[25] Conspicuously absent from that review is any work on the modification of polyolefins (*i.e.*, macromolecular alkanes) using C–H activation chemistry. By now it should be clear that the development of a simple, catalytic, selective, mild, and efficient process for the introduction of functional groups along the backbone of PE is highly desirable. We certainly agree with Mülhaupt's statement in a 2003 review on catalytic polymerization technology that "the emerging new catalyst technology for C–H activation is expected to have a major impact on catalytic polymer modifications of hydrocarbon polymers."[26] In this section we will briefly describe salient features of C–H activation chemistry and some available systems, and then give two specific examples of catalytic C–H activation/functionalization on polyolefins from our recent work in this area.

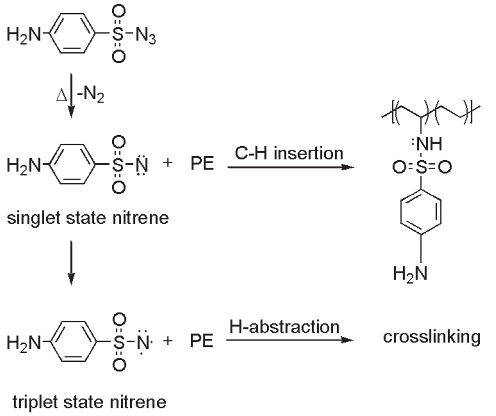

Fig. 6 Functionalization of polyethylene by C–H insertion of a nitrene generated from the thermal degradation of a sulfonyl azide. Reprinted with permission from ref. 23, Copyright (2002) John Wiley and Sons, Inc.

Thermodynamically, for any C–H activation process to be practical, the overall transformation should be energetically favorable. Hydroxylation is a common product desired from C–H activation, and in most cases the insertion of an electronegative element into a C–H bond (*i.e.*, C–H to C–X–H) is exothermic. Also, in most alkane substrates there is more than one type of C–H bond, and regioselectivity is an important concern. Typically, although not exclusively, tertiary C–H bonds are the most reactive (*i.e.*, lowest bond strength) and primary C–H bonds are the least reactive. Of course the selectivity depends strongly on the actual catalytic process employed. For example, using organometallic approaches, it is often true that oxidative addition of C–H bonds to metal complexes (*i.e.*, $L_nM + R_3C\text{–}H \rightarrow L_nM(CR_3)(H)$, where L represents some ligand or ligands and M is a transition metal) sterically favors linear M–C bond formation, and thus good selectivity for the functionalized linear product in an appropriate catalytic cycle. Unlike the organometallic approach, the so-called "coordination chemistry approach" has been developed to mirror natural processes effected by enzymes. In these systems, the common pathway is activation of some metal fragment to give a highly reactive (often oxygen-containing) species that "attacks" the alkane substrate to give the functionalized products. Biomimetic systems based on enzymes are typically coordination complexes containing biologically significant metals, such as Fe, Co, Cu, or Mn. In the following, we describe efforts toward C–H functionalization of polyolefins using firstly the coordination chemistry approach and secondly the organometallic approach. Importantly, in all of these metal-catalyzed processes, minimization of the metal content in the final polymer product will be imperative due to potential undesirable oxidative degradation processes catalyzed by these residues.[27]

Attempts to model the cytochrome P-450 monooxygenase enzymes, which catalyze the derivatization of inert compounds in the body for excretion, have resulted in model biomimetic systems employing metalloporphyrins, which catalyze the epoxidation of alkenes and the hydroxylation of alkanes by oxygen atom transfer.[25] In one particular system the oxidation of alkanes was performed at room temperature in the presence of a nitrogen base, a buffered aqueous solution of potassium hydrogenpersulfate ($KHSO_5$, an inorganic peroxide species), a phase transfer catalyst, and the sterically-hindered manganese porphyrin complex manganese tetra-2,6-dichlorophenylporphyrin chloride (Mn(TDCPP)Cl).[28] The authors hypothesize that the reaction proceeds by hydrogen abstraction of the alkane by a high-valent metal-oxo complex and reaction of the alkyl radical with the resultant hydroxyl group on the metal complex based on the high retention of configuration during the alkane hydroxylation (Fig. 7). Due to the similar kinetic isotope values for the metalloporphyrin-mediated oxidation of alkanes and carbene insertion into a C–H bond, the authors suggest that the transition state of the active species contains an oxene moiety. Furthermore, reactivity profiles of adamantane, cyclohexane, and hexamethylethane, were consistent with the stability of carbon-based free radicals: 3° > 2° > 1°. The bottom line for these and related systems is that alkanes can be catalytically converted into alcohols (and ketones) under relatively mild conditions. It was this general behavior and the wealth of information on these systems that turned our attention to this class of alkane functionalization systems for polyolefin modification.

In 2003, we reported that application of the Mn(TDCPP)–$KHSO_5$ oxidation system to a model polyolefin, polyethylene-*alt*-propylene (PEP), provided hydroxylated PEP, exclusively at the tertiary position without degradation of the polymer molecular weight (Fig. 8).[29] Functionalization of squalane, a model small molecule alkane structurally similar to PEP, was also performed to provide products for definitive identification. IR and NMR spectroscopy were consistent with the introduction of alcohol and ketone functional groups, while DEPT ^{13}C NMR spectroscopy allowed for the identification of the alcohol moieties as tertiary hydroxyl groups. For the functionalization of squalane, mass spectrometry and elemental analysis identified both mono- and dihydroxylated products. Acetylation of the hydroxyl groups in PEP demonstrated that the functional groups are accessible for further derivatization and allowed for the degree of functionalization to be determined by ^1H NMR analysis. Higher levels of functionalization were observed as the concentration of $KHSO_5$ was increased. Functionalization of a high-molecular-weight (50 kg mol^{-1}) PEP was also successful, resulting in an average degree of functionalization of twelve hydroxyls per chain with only minimal coupling as a side reaction. The mild reaction conditions allowed for the direct oxyfunctionalization of a model polyolefin without disrupting the molecular parameters of the parent material. We also showed that the glass transition temperatures of the product polyolefins could be modulated by controlling the number of hydroxyl groups per polymer chain. While this system is not without drawbacks (multi-phase reactions, relatively slow reaction times, and the use of complicated oxidants), this study establishes the use of systems typically relegated to low-molecular-weight alkane functionalization reactions for polymeric substrates.

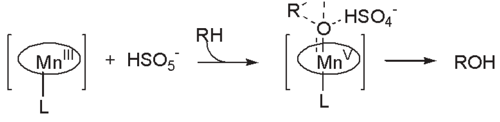

Fig. 7 Proposed active species in the manganese porphyrin-catalyzed hydroxylation of alkanes with $KHSO_5$. Reprinted with permission from reference 28. Copyright (1988) CNRS-Gauthier-Villars.

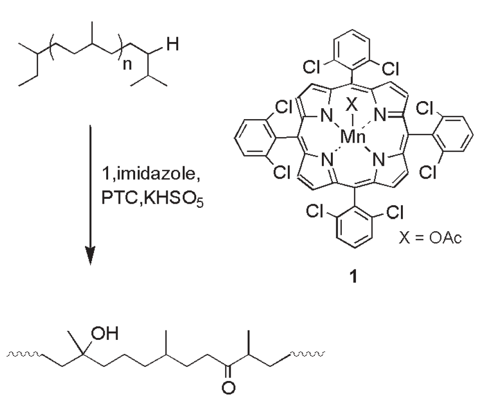

Fig. 8 Selective oxyfunctionalization of polyethylene-*alt*-ethylene (PEP) using a manganese porphyrin catalyst. (a) Manganese *meso*-tetra-2,6-dichlorophenylporphyrin acetate **1** (Mn(TDCPP)OAc) and (b) oxyfunctionalization reaction scheme. PTC = phase transfer catalyst. Reprinted with permission from ref. 29. Copyright (2003) American Chemical Society.

We also recently explored a new organometallic approach to the functionalization of polyolefins. In 2000, the catalytic, regiospecific functionalization of linear alkanes was reported by Hartwig's group.[30] In this report, the rhodium-catalyzed ($Cp^*Rh(\eta^4\text{-}C_6(CH_3)_6)$) coupling of borane reagents with alkanes provided exclusive borylation of primary carbons in *n*-octane, 2-methylheptane, and methylcyclohexane in good yields. Furthermore, the alkylboronate esters produced are amenable to various organic transformations yielding a range of useful products. The regioselectivity of the reaction is attributed to the formation of a linear metal–alkyl complex in the oxidative addition of alkane substrate to the rhodium center, giving the least sterically hindered linear metal–alkyl complex. The attractive regiospecificity, versatility, and robust nature (*i.e.*, high temperature stability) of this system motivated the application of this functionalization to polyolefins.

In a collaboration with the Hartwig group we reported the functionalization of a model polyolefin, polyethylethylene (PEE), using the rhodium-catalyzed system described above (Fig. 9) in 2002.[31a] Unlike the manganese porphyrin system, the borylation reactions were carried out without solvent in the neat polymer melt. The model polymer we used had a very narrow molecular weight distribution, and thus any side reactions that led to either chain cleavage or chain coupling could be readily identified by size exclusion chromatography (SEC). In this work, model PEEs with controlled molecular weights (1.2 and 37 kg mol^{-1}) were prepared by anionic polymerization of butadiene, followed by subsequent complete hydrogenation of the pendant double bonds. The borylation reaction was catalyzed with 5 mol% of a related rhodium reagent ($[Cp^*RhCl_2]_2$) in the melt of PEE between 150 and 200 °C. The product polymers were treated with basic

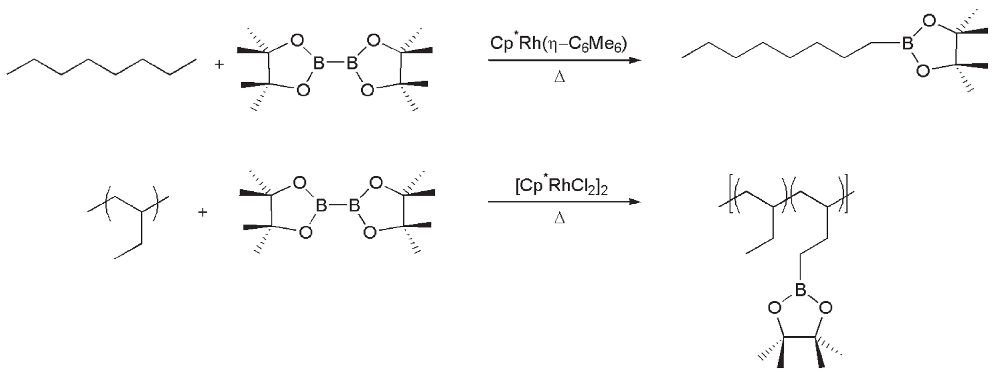

Fig. 9 Catalytic borylation of (a) octane and (b) a representative polyolefin. (a) Reprinted with permission from ref. 30. Copyright (2000) American Association for the Advancement of Science. (b) Reprinted with permission from ref. 31. Copyright (2002) American Chemical Society.

hydrogen peroxide to generate the corresponding alcohol functional groups. This strategy resulted in the regiospecific hydroxylation of the methyl carbons along the polymer backbone. By increasing the concentration of the borane reagent relative to the methyl sites on the polymer chain, the average degree of functionalization was 2.6 hydroxyls per chain, as confirmed by ^{1}H NMR analysis and mass spectrometry. The functionalization of a higher-molecular-weight PEE (37 kg mol^{-1}) provided similar results, except at higher levels of functionalization, coupling reactions were apparent during the oxidation of the boronate esters. Like the functionalized PEP in the manganese system, the glass transition temperatures of the hydroxylated PEE products increased with increasing level of functionalization. These results have provided incentive to study the functionalization of commercially relevant polyolefins, and to subsequently explore the utility of these novel materials in graft copolymer synthesis, polymer blend compatibilization, and polymer adhesion applications.[31b]

Future prospects in polyolefin modification

Utilizing commodity materials to synthesize speciality polymers has an obvious economic advantage, and the motivation for the development of new materials from polyolefins has been demonstrated. The introduction of polar functional groups into polyolefin materials improves, for example, the surface properties for printing and bonding and can influence the compatibility of polyolefins with other polar additives. Historically, conventional methods of functionalization of polyolefins utilize highly reactive free radical processes that promote functionalization but can also lead to deleterious side reactions such as chain coupling and chain cleavage. New radical- and carbene-based methodologies have been developed that can address the shortcomings of the classic maleic anhydride approach, and these certainly merit further attention. Having stated that, we feel that future emphasis should be placed on the catalytic modification of polyolefins using newly developed transition-metal-catalyzed (*i.e.*, C–H bond activation/functionalization) protocols. Significant advances in alkane functionalization have been made in the past decade. While emphasis has been largely on the conversion of low-molecular-weight alkanes to their heteroatom functionalized analogs, the opportunities in polyolefin modification should be given appropriate attention. Below we describe a few relevant systems that could be applied to polyolefin functionalization and the relevant benefits.

An interesting variation on an alkane functionalization reaction was observed in a cobalt(II) porphyrin complex.[32] Depending on ligand choice, these cobalt catalysts were effective in either the chlorination or sulfochlorination of alkane substrates in good yields. The reaction is simply performed by combining the alkane, sulfuryl chloride and the catalyst and heating to 85 °C. Chlorine incorporation into polyethylene could certainly impact the barrier properties and polarity of the material and sulfochlorination would lead to polymers with reactive sulfonyl chlorides that could be used for reactive compatibilization and/or polymer grafting reactions. Given the availability of the catalysts and the straightforward protocol, this system may prove useful in a polyolefin functionalization.

Porphyrin systems are quite versatile, and in a recent report by Yu *et al.* the amidation of saturated C–H bonds was carried out using a Ru or Mn porphyrin complex,[33] wherein the porphyrin ligand contained perfluorinated phenyl groups. The amidation reagent used was the nitrene precursor PhI=N(tosylate) or in some cases, simple combinations of $PhI(OAc)_2$ and H_2NR. For example, using the Mn version of the catalyst, $PhI(OAc)_2$ and H_2N(tosylate), the authors showed that ethyl benzene could be converted into the amidated product resulting from insertion of the –NH-(tosylate) fragment into a benzylic C–H bond. In the case of polyolefin functionalization, this type of reaction could be used to attach pendant amines (upon hydrolysis of the amides) along the backbone of PE. The polarity, basicity, and nucleophilicity of amines renders materials such as this quite useful for reactive compatibilization methodologies.[31c]

Systems that could prove quite ideal for polyolefin functionalization are based on early transition-metal oxo anion clusters, commonly referred to as polyoxometalates (and robust inorganic analogs of metalloporphyrins). In 1995, Neumann *et al.* reported the hydroxylation of alkanes with molecular oxygen catalyzed by a ruthenium-substituted polyoxometalate.[34] Using dioxygen as the oxidation reagent has obvious advantages. The use of dioxygen and the robust nature of the metal complexes employed in these systems make these attractive candidates for polyolefin functionalization, although the turnover numbers are somewhat low (about 2 turnovers per hour).

Formally an oxidation reaction, the dehydrogenation of alkanes is a potentially attractive route to polyolefin functionalization since the derivatization of polymers containing backbone and side chain unsaturation is versatile and well established.[35] One recent development in this area was reported by Liu *et al.* in 1999.[36] In that work, so called iridium ''pincer'' complexes were shown to be very effective for the dehydrogenation of octane to give predominantly 1-octene. This terminal olefin can isomerize under the reaction conditions to yield the corresponding internal olefins. The mechanism is thought to proceed by direct C–H activation of the substrate, β-hydride elimination to give the corresponding dihydrogen complex, and subsequent hydrogenation of the sacrificial alkene (to render the overall reaction thermodynamically favorable). This work is particularly interesting because the reactions are performed in pure alkane at high temperatures (*e.g.*, 150 °C) in the presence of a hydrogen acceptor (*e.g.*, norbornene) using very low concentrations of catalyst (*e.g.*, 1.0 mM). One can readily envision an analogous reaction using a melt of polyethylene to give a polymeric product containing unsaturated sites poised for further functionalization.

The above examples only scratch the surface of the work currently being done on alkane oxidation and we refer the reader to both the Crabtree review[25] and a recent review on the homogeneous oxidation of alkanes by late transition metal catalysts.[37] There are certainly catalytic C–H activation/functionalization systems available that could be applied to the functionalization of polyolefins, and we suspect that this technology will keep advancing at a rapid pace. Just as the transition-metal-catalyzed polymerization of olefins discovered by Ziegler and Natta revolutionized the field of olefin polymerization, we believe that the application of appropriate transition-metal-catalyzed alkane functionalization chemistry in polymer modification reactions will significantly impact the post-polymerization modification of polyolefins.

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Nicole K. Boaen and Marc A. Hillmyer*
Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431, USA.
E-mail: hillmyer@chem.umn.edu; Fax: +1 612 624 7029;
Tel: +1 612 625 7834

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