

Metal-Catalyzed Postpolymerization Strategies for Polar Group Incorporation into Polyolefins Containing C–C, C=C, and Aromatic Rings

Gabriel Menendez Rodriguez, M. Mar Díaz-Requejo,* and Pedro J. Pérez*

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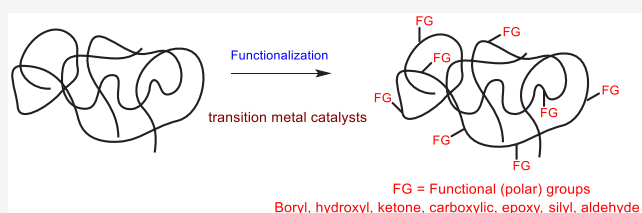
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ABSTRACT: Polymeric materials bearing polar groups constitute a class of macromolecules with interest in a number of uses. Because the direct synthesis employing polymerization strategies from polar monomers is very often precluded by catalyst poisoning or uncontrolled side reactions, the alternative postpolymerization route consisting in modifying a previously prepared polymer is continuously progressing. However, such *a posteriori* modification depends on the existence of potential reaction sites in the polymer. Because of this, polyolefins are the most challenging substrates to work with and, among them, the saturated ones. In this contribution, the current state of the art of the metal-catalyzed modification of polyolefins and subsequent polar group incorporation is provided.



1. INTRODUCTION

Polyolefins are a class of materials obtained at multiton worldwide scale, which nowadays represent an integral part of daily life. The popularity of such synthetic polymers stems from their low price and synthesis from abundant starting materials.^{1,2} This has resulted in a large number of applications for which these materials are suited such as packaging, food containers, and household products as well as in sophisticated ones in the fields of medicine, automotive, and electronics. However, the lack of polar groups in the backbone of these macromolecules makes these materials unsuitable for applications that require good surface adhesion properties, toughness, solvent resistance, or miscibility with other polymers, among others.³ Thus, the introduction of polar functionalities into nonpolar polymers is highly desirable since it would increase the number of potential applications and render these materials even more versatile.

Different strategies have been developed toward that end. One approach involves the direct copolymerization with functionalized (polar) monomers (Scheme 1A).^{4–7} This strategy is very attractive since the desired material can be obtained with precisely defined molecular weight, composition, and architecture. However, limitations of this approach are (i) the extra synthetic steps required to prepare some not readily available monomers, (ii) each copolymerization reaction needs a new optimization process to obtain the desired polymer composition, and (iii) only limited possibilities of polar monomers can be introduced in the case of metal-catalyzed polymerizations reactions. The presence of heteroatoms in the monomer may either prevent the controlled polymerization or completely deactivate the metal catalyst. To avoid the latter

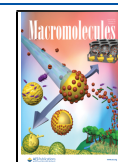
problem, copolymerization with appropriately protected monomers has been employed. However, this methodology requires an additional deprotection step that may also compromise the integrity of the polymer chain.

An alternative approach for the synthesis of functionalized polymers that overcomes the above limitations is the so-called postpolymerization modification (Scheme 1B).^{10–13} This methodology shows several advantages over the direct polymerization of polar monomers. First, any polymer can be targeted for postpolymerization modification; thus, the development of new polymerization processes is not a requirement. Second, polymers with different properties can be obtained from the same starting material by using different reagents for modification or by tuning the degree of functionalization. And finally, it allows the incorporation of functionalities that are incompatible with the polymerization process. This strategy also suffers from some limitations, as the need of working in polymer solutions which may be a challenge in some cases due to the low solubility of the macromolecules, thus requiring high temperatures or providing low concentration solutions. Alternative tactics are based on surface postpolymerization reaction where the polymer is not solubilized but forming dispersions.¹⁴ Current noncatalytically commercial applications of postpoly-

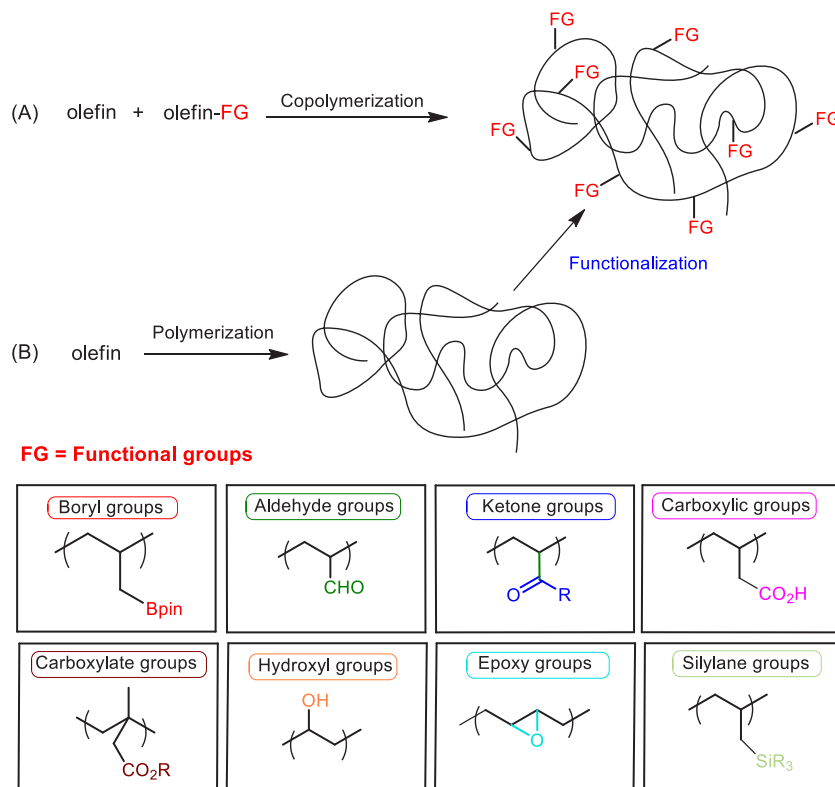
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Scheme 1. Functionalized Polyolefins: Alternative Routes



merization processes are radical reactions or ozone surface treatments, which show high efficiency.^{8,15,16} However, those reactions rely on nonselective reagents and very harsh conditions that result in scission or cross-linking of the polymer chain. Importantly, even small amounts of those side reactions can alter the molecular weight distribution of the functionalized material and erode its mechanical properties.¹⁷ When retaining the properties of the parent material (molecular weight distribution, polydispersities) is a requirement, the incorporation of the polar functionality should occur, avoiding any deleterious side reactions such as C–C bond cleavage or cross-linking events.

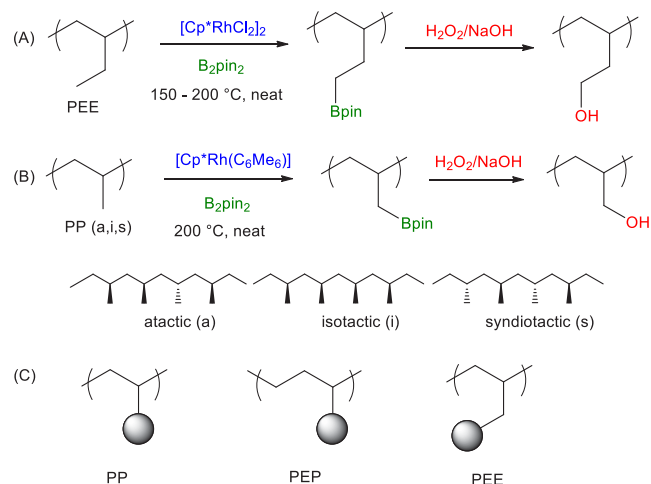
This postpolymerization functionalization strategy relies on the existence of potential reaction sites in the polymer chains. It seems clear that the presence of heteroatoms originates more reactive environments, either at those sites or at the polarized vicinal C–H bonds. Therefore, there are very many examples of postpolymerization reactions with polymers already containing polar groups.¹⁸ On the other hand, polyolefins generated from direct olefin polymerization containing C–C, C=C, and aromatic groups display a more limited reactivity compared to those containing heteroatoms. This Perspective focuses on the progress achieved in postpolymerization functionalization strategies via metal-mediated processes with those apolar polyolefins, showing the progress of catalytic reactions that have been implemented for both saturated and unsaturated polyolefins. The organization is based on the functional group incorporated to the polymer chains.

2. METAL-CATALYZED POSTPOLYMERIZATION PROCESSES

Boryl Group Incorporation. In 2002, Hillmyer, Hartwig, and co-workers achieved the regioselective functionalization of

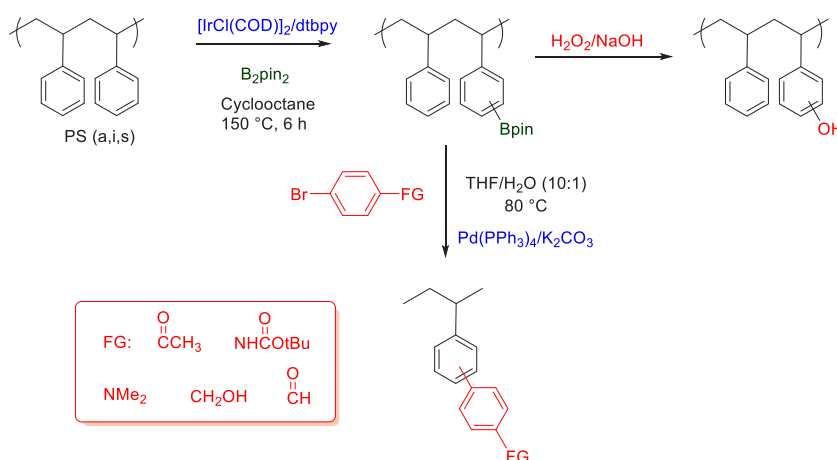
polyethylene (PEE) through rhodium-catalyzed borylation using bis(pinacolato)diboron (B_2pin_2) followed by oxidation of the alkylboronate ester.¹⁹ The reactions were performed in the neat polymer substrate at temperatures between 150 and 200 °C, with 5 mol % of $[Cp^*RhCl_2]_2$ as catalyst and various B_2pin_2 :polymer ratios (Scheme 2A). Oxidation of the borylated

Scheme 2. Borylation of Saturated Polymers with Rhodium Catalysts



polymer by H_2O_2 in THF/ H_2O basic media afforded the corresponding alcohols. In line with previous observations in the rhodium-catalyzed borylation of alkanes, this approach resulted in the regioselective hydroxylation of the methyl groups of the side chains. The degree of functionalization increased with increasing ratios of B_2pin_2 :polymer, although the catalytic

Scheme 3. Polymer Borylation with Iridium-Based Catalysts and Subsequent Derivatization Reactions



efficiency dramatically decreased at elevated loadings of B_2pin_2 . The altered properties of the hydroxylated polymer were stated by the change in the glass transition temperatures (T_g) with respect to the parent material. In fact, the T_g increased nearly 55 °C in the polymer with the higher degree of functionalization (4.4 wt %).

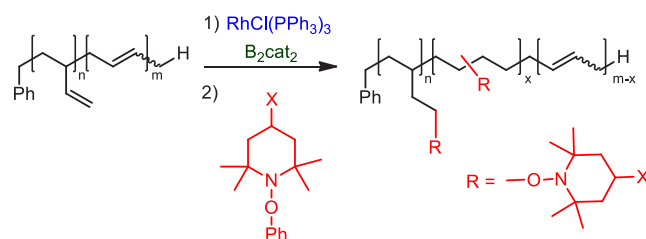
This methodology was also applied to a series of both model and commercial polypropylenes (PP) with different molecular weights and tacticities (Scheme 2B).²⁰ The catalytic efficiency depended strongly on the steric properties of the methyl groups. Upon comparison of polymers with different steric pressures onto the targeted methyl groups, a trend was observed, the less hindered sites being more prone to functionalization. As shown in Scheme 2C, such pressure decreases from polypropylene to poly(ethylene-*alt*-propylene) (PEP) and poly(ethylene) *alt* propylene (PEE). The efficiency of the borylation process was also affected by the molecular weight of the polymer, although this effect was less significant compared to the steric effect. In fact, the yield of borylation of isotactic-PPs decreased from 26% to 5.4% with the increase of the molecular weight from 17.6 to 66.8 kg/mol. A more pronounced decrease from 66% to 26% was observed when moving from ethyl (PEE) to methyl (PP) as the pending groups. The relative orientation of these side chains of PPs did not affect the degree of functionalization. Importantly, with this methodology the functionalized polymers exhibited similar molecular weight distributions to the precursor polymer. Furthermore, the versatility of this rhodium-based catalytic system was demonstrated by using the functionalized polymers for the synthesis of graft copolymers and as an intermediate for the incorporation of other functionalities.^{21–23}

Lee, Noh, Bae, and co-workers developed the borylation of aromatic C–H bonds of polystyrenes (PSs) with different tacticities using a commercially available iridium catalyst (Scheme 3).²⁴ Catalytic borylation reactions were performed with B_2pin_2 in cyclooctane at 150 °C. Among all the catalysts tested, the system $[IrCl(COD)]_2/dtbpy$ gave the best results compared with other iridium-based catalysts as well as with the rhodium complex $[Cp^*Rh(\eta^4-C_6Me_6)]$. The efficiency of this approach was remarkable since it allowed the introduction of a boronate ester group into the aromatic ring of the styrene repeating unit up to 42 mol %, without affecting the tacticity and the molecular weight distributions of the initial polymer. Furthermore, neither the tacticity nor the molecular weight of the polystyrene chain seemed to affect the degree of functionalization. Notably, an atactic-PS with $M_n = 247$ kg/

mol was successfully functionalized in 85% yield by using a B_2pin_2 -to-monomer ratio of 0.1. However, the use of higher B_2pin_2 :monomer ratios results in a decrease in the yield of the borylation reaction. 1H NMR studies on the borylated polymer indicated the presence of a mixture of meta- and para-substituted isomers. Interestingly, the ratio of meta- and para-substituted polymers was found to be 4:3, which is substantially different from that observed for cumene as a low-molecular-weight pendant under the same identical conditions (7:3). The higher percentage of the para isomer is probably due to the difficulty of the iridium catalyst to reach the more hindered meta C–H bonds. The aromatic borate groups introduced by this methodology were used as intermediates for further conversion to other functionalities. Classical oxidation afforded hydroxylated polymers whereas a variety of new functional groups were obtained through palladium-catalyzed Suzuki–Miyaura cross-coupling (Scheme 3).^{25–30} All these processes proceeded efficiently without observation of deleterious side reactions as polymer chain degradation or cross-linking reactions.

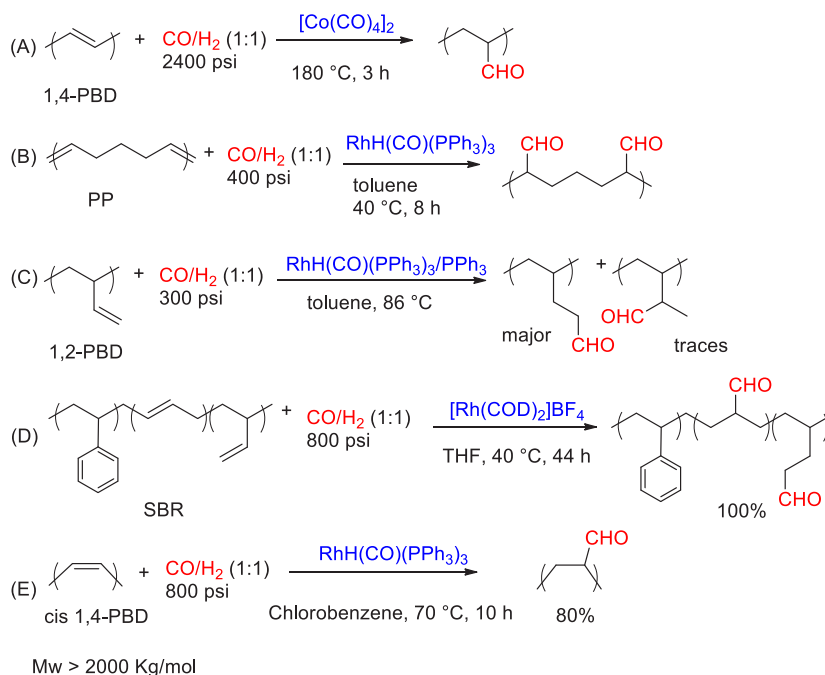
Another strategy to introduce boryl groups into polymer chains consists in the hydroboration of materials containing C=C bonds. Thus, Studer and co-worker achieved the introduction of alkoxyamines functionalities into a low-molecular-weight polybutadiene (PBD) via hydroboration with catecholborane (B_2cat_2) followed by nitroxide oxidation (Scheme 4).³¹ The

Scheme 4. Unsaturated Polymer Borylation and Subsequent Oxyfunctionalization



reaction was conducted at 0 °C in CH_2Cl_2 by using $RhCl(PPh_3)_3$ as catalyst. The intermediate hydroboration product was *in situ* oxidized with different TEMPO derivatives to afford the corresponding alkoxyamines. 1H NMR studies showed that hydroboration occurred preferentially at terminal olefins, and the percentage of unreacted C=C moieties was ~50%. No data on PDI values were provided. In a later report,

Scheme 5. Catalytic Hydroformylation of Diene-Based Polymers with Cobalt (A) and Rhodium (B–E) Complexes



the authors used the alkoxyamine-functionalized PBDs as macroinitiator for nitroxide-mediated polymerization of styrene and butyl acrylate.³²

Aldehyde and Ketone Functionalities. The hydroformylation of alkenes using syngas (carbon monoxide and hydrogen) is a well-known transformation that has been used for a long time in many industrial processes. The first application of this methodology for the introduction of formyl groups into olefinic polymers was reported in 1966.³³ The hydroformylation of different diene-based polymers was performed with the dicobalt octacarbonyl complex as catalyst, requiring harsh conditions. Complete conversions were achieved at 180 °C for 3 h, with an initial H_2 :CO pressure of 2400 psi (Scheme 5A). However, cross-linking reactions, mainly due to aldehyde polymerization and main-chain degradation, occurred during the reaction. Milder reaction conditions could be employed when using rhodium-based catalysts developed by the group of Wilkinson.^{34,35} The first rhodium-catalyzed hydroformylation of olefinic polymers was reported in 1974.³⁶ Hydroformylation of a polypentenamer ($M_n = 172 \text{ kg/mol}$) containing 99% of backbone double bonds and only 1% of vinyl side groups was reported with the Wilkinson's complex $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ as catalyst (Scheme 5B). Incorporation of up to 20 mol % of formyl groups took place at 40 °C under a total pressure of H_2 :CO of 400 psi, without significantly altering the molecular weight distribution of the starting material.

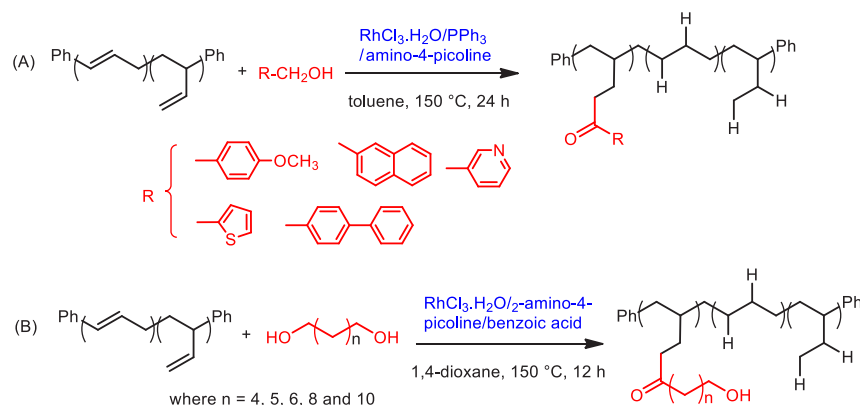
After that initial report, many studies on the hydroformylation of different polybutadiene (PBD) systems and styrene–butadiene block copolymers (SBR) were reported using rhodium catalysts under similar conditions.³⁷ As an example, Mills and co-workers studied^{38,39} the hydroformylation of low-molecular-weight 1,2-PBD and 1,4-PBD in the presence of that Wilkinson's catalyst and an excess of triphenylphosphine. They showed that hydroformylation of 1,2-syndiotactic polybutadiene resulted in the selective formation of terminal-branched aldehydes as the major product with a trace amount of the iso(secondary)-branched product (Scheme 5C). Furthermore,

the initial rate of hydroformylation of 1,2-syndiotactic polybutadiene was found to be ~ 6 times higher than that observed for the hydroformylation of 1,4-*cis*-polybutadiene, a difference attributed to the different accessibility of the carbon–carbon double bonds. However, GPC analyses revealed that the hydroformylated products had undergone cross-linking either during the reaction or during the polymer product recovery step. They speculated that the altered molecular weight properties of the hydroformylated polymers might be due to the high excess of triphenylphosphine used in those experiments (PPh_3 :Rh = 163:1) which increased the basicity of the solution, thus promoting the self-aldolization reaction to form condensation products.

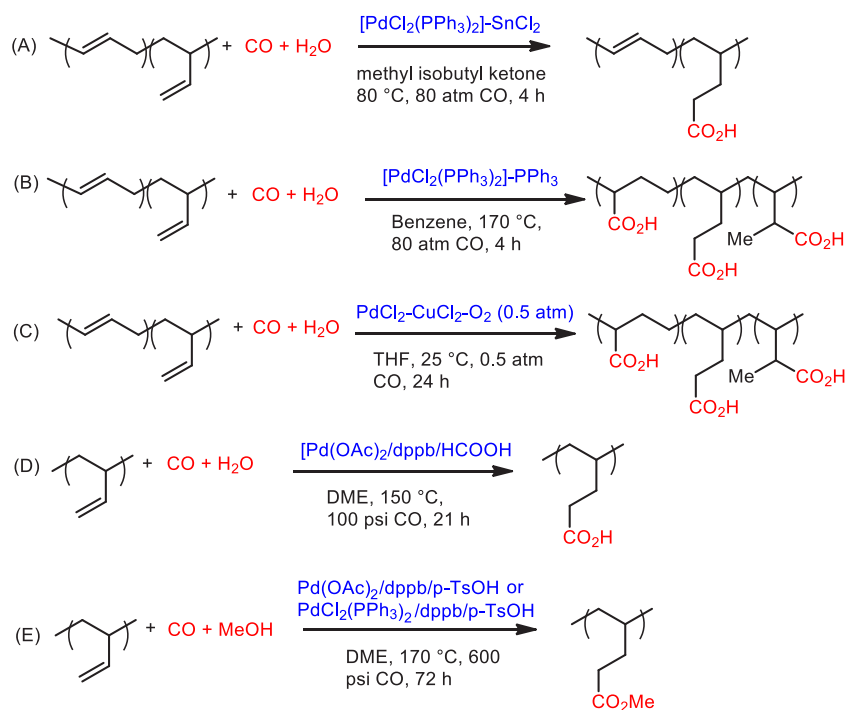
High conversions without side reactions products were obtained by Alper and co-workers.⁴⁰ They reported the hydroformylation of high-molecular-weight styrene–butadiene copolymers ($M_w = 200 \text{ kg/mol}$) in the presence of various rhodium catalysts. Remarkably, under a total pressure of 800 psi of H_2 and CO (at 40 °C), full conversion of carbon–carbon double bonds could be achieved by using $[\text{Rh}(\text{COD})_2]\text{BF}_4$ or $[\text{Rh}(\text{COD})\text{Cl}]_2$ as the hydroformylation catalyst, although long reaction times were required (44 h, Scheme 5D). The functionalized polymers were not cross-linked during the hydroformylation process; however, it was noted that gel formation occurred after their exposure to air, probably due to polyacetal formation which occurs in the presence of O_2 . Under similar reaction conditions (800 psi of H_2 /CO at 70 °C), Rempel and co-workers achieved the hydroformylation of ultrahigh-molecular-weight *cis*-1,4-polybutadiene ($M_w > 2000 \text{ kg/mol}$).^{41–43} A final conversion of nearly 80% of the C=C bonds was obtained after 10 h by using the Wilkinson's catalyst (Scheme 5E). However, no data were provided regarding the molecular weight distribution of the functionalized polymer.

Transition-metal-catalyzed C–C bond coupling by hydroacylation of alkenes constitutes a method to convert an unsaturated moiety into a ketone functionality. The first examples of this reaction appeared in the 1980s, but it was not

Scheme 6. Simultaneous Hydroacylation and Hydrogenation of Phenyl-Terminated PBD



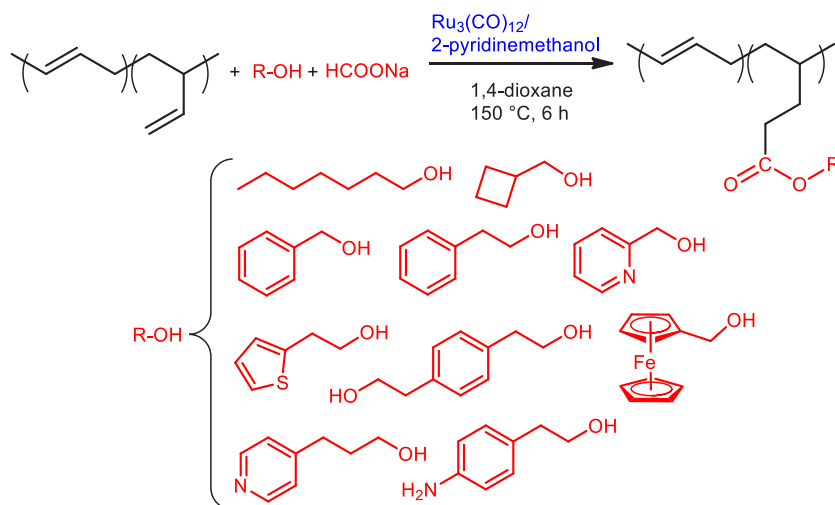
Scheme 7. Palladium-Catalyzed Hydrocarboxylation (A–D) and Hydroesterification (E) of PBDs



until 1998 that such strategy to the functionalization of diene-based polymers appeared.⁴⁴ Jun and co-workers achieved the incorporation of ketone groups into the vinyl groups of phenyl-terminated polybutadienes using a rhodium catalyst along with 2-aminopyridine derivatives (Scheme 6A). This approach involved one-pot oxidation of a primary alcohol to aldehyde by transition-metal-mediated hydrogen transfer and hydroacylation of the aldehyde to produce the ketone functionality with the aid of the same catalyst.⁴⁵ Because the alkene acts both as hydrogen acceptor and as hydroacylation substrate, the incorporation of ketone functionalities is accompanied by the simultaneous hydrogenation of the C=C bonds. Hydroacylation of mixed PBDs resulted in the selective formation of terminal-branched ketone functionalities, whereas hydrogenation occurred at both the internal olefins and the vinyl groups. A maximum of 23% of the total C=C bonds were hydroacylated by using benzylic alcohol derivatives at 150 °C for 24 h in the presence of a mixture of RhCl₃·H₂O, PPh₃, and 2-amino-4-picoline. In a later report, the substrate scope was expanded with the use of aliphatic alcohols and α,ω -diols. Under similar

reaction conditions, 7–26% of the total alkene functionalities were hydroacylated.⁴⁶ The best results were obtained with α,ω -diols with longer alkyl linkers (6–11 –CH₂–), whereas no reaction was observed for α,ω -diols bearing shorter linkers, such as 1,4-butanediol or 1,5-pentanediol (Scheme 6B). The reason for this lack of reactivity could be attributed to catalyst deactivation due to the chelation of the diols containing short alkyl linkers.⁴⁶

Carboxylic and Carboxylate Functionalities. A common method to prepare carboxylated polymers consists in the catalytic reaction of unsaturated polyolefins with carbon monoxide and either water (hydrocarboxylation) or an alcohol (hydroesterification). Thus, the palladium-catalyzed hydrocarboxylation of different low-molecular-weight polybutadienes (M_n up to 4.5 kg/mol) was reported in 1991 by Cole-Hamilton and co-workers.⁴⁷ The use of [PdCl₂(PPh₃)₂]-SnCl₂ in methyl isobutyl ketone at 80 °C in the presence of 1200 psi of CO led to selective functionalization on the terminal carbon atom of the vinyl groups (Scheme 7A). When the reaction was performed with [PdCl₂(PPh₃)₂]-PPh₃ in benzene (1200 psi of CO, 170

Scheme 8. Polymer Hydroesterification Using $\text{Ru}_3(\text{CO})_{12}$ /2-Pyridinemethanol as Catalyst

$^{\circ}\text{C}$, Scheme 7B) or with $\text{PdCl}_2\text{-CuCl}_2\text{-O}_2$ (70 psi, room temperature, Scheme 7C), functionalization took place at terminal and internal carbon atoms of pendant double bonds together with backbone double bonds. Although high functionalization of $\text{C}=\text{C}$ bonds (up to 90%) could be obtained with these systems, the work did not include the molecular weight distributions of the carboxylated product. This piece of information was later furnished by the groups of Alper and Gong.^{48,49} They found that the $\text{PdCl}_2\text{-CuCl}_2\text{-O}_2$ catalytic system always resulted in highly unstable products, which underwent chain cross-linking during the reaction or the isolation of the polymers. On the other hand, hydrocarboxylation of high-molecular-weight PBD ($M_w = 1000\text{--}2000$ kg/mol) was achieved without significant chain scission or cross-linking reactions with $[\text{PdCl}_2(\text{PPh}_3)_2]\text{-SnCl}_2$ as the catalytic system. However, contrary to the previous findings by Cole-Hamilton and co-workers, only a low extent of hydrocarboxylation could be reached (up to 10 mol %) even under more severe reaction conditions, such as a higher temperatures or pressures. Such behavior was explained as derived from the distinct reactivities of the PBDs depending on their molecular weights. Furthermore, with such elevated temperatures (145 $^{\circ}\text{C}$) and pressures (1900 psi of CO), hydrocarboxylation also occurred at the backbone double bonds, thus causing the loss of the previously observed selective functionalization of the pendant double bonds.

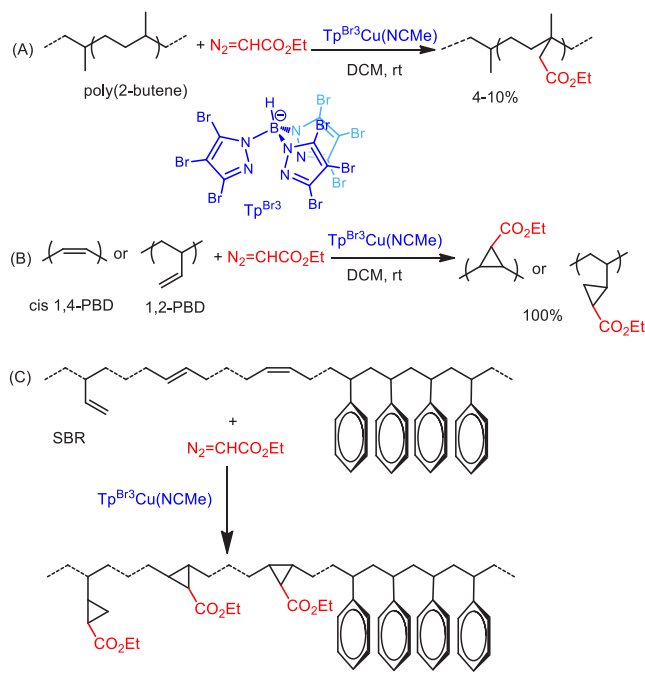
Alper and co-workers also described a novel method for the hydrocarboxylation of low-molecular-weight PBD ($M_w = 2.4$ kg/mol) based on formic acid that operates under low pressures of carbon monoxide.⁴⁰ They achieved the synthesis of carboxylated PBD using catalytic amounts of $\text{Pd}(\text{OAc})_2/1,4\text{-bis}(\text{diphenylphosphino})\text{butane}$ (dppb), formic acid (2 equiv relative to the number of vinyl groups) and 100 psi of CO in 1,2-dimethoxyethane (DME) at 150 $^{\circ}\text{C}$ (Scheme 7D). Under these conditions, all the vinyl groups were hydrocarboxylated selectively at the terminal carbon atom of the pendant double bonds without cross-linking or chain scission. Hydroesterification with MeOH was also attempted by using different Pd/dppb catalytic systems in the presence of *p*-TsOH and 600 psi of CO. Full conversion of the vinyl pendant groups into terminal methoxycarbonyl groups was observed by using $\text{Pd}(\text{OAc})_2$ or $\text{PdCl}_2(\text{PPh}_3)_2$ (Scheme 7E). Although high temperatures (170

$^{\circ}\text{C}$) and long reaction times (72 h) were required, no side reactions occurred under these conditions.

More recently, Jun and co-workers developed a new hydroesterification methodology for the functionalization of PBD.⁵⁰ The modified PBDs were prepared by employing primary alcohols and sodium formate in the presence of $\text{Ru}_3(\text{CO})_{12}$ and 2-pyridine-methanol in 1,4-dioxane at 150 $^{\circ}\text{C}$ (Scheme 8). Using this protocol, they converted up to 62% of the vinyl groups of phenyl-terminated polybutadiene ($M_n = 1.8$ kg/mol) into the corresponding ester groups; the remaining vinyl groups were mostly reduced or isomerized. Furthermore, they showed that polybutadienes containing more than one ester group can also be prepared, and the ratio between the different ester groups can be controlled by regulating the relative amount of the alcohol substrates.

An alternative, completely different approach to introduce ester groups into polyolefins is based on the incorporation of carbene units containing COOR fragments from diazo compounds, either thermally induced or metal mediated. Integration of CHCO_2Et units into polyethylene and polypropylene by thermal decomposition of ethyl diazoacetate (EDA) was reported by Aglietto and co-workers in 1989.^{51,52} However, the main drawback of this methodology was the high reaction temperature ($T > 180$ $^{\circ}\text{C}$) required, which might cause cross-linking of chain scission reactions. On the other hand, Pérez, Brookhart, Mecking, and co-workers described the catalytic counterpart performed under very mild conditions (i.e., room temperature), employing the copper-based catalyst $\text{Tp}^{\text{Br}3}\text{Cu}(\text{NCMe})$ ($\text{Tp}^{\text{Br}3} = \text{hydrotris}(3,4,5\text{-tribromopyrazolyl})\text{-borate}$).⁵³ The strategy was further expanded to PBDs⁵⁴ and SBR rubbers,⁵⁵ with no undesired side reactions. In the case of poly(2-butene), carbene insertion exclusively took place into tertiary C-H bonds, whereas in the case of a random poly(ethylene-1-octene) polymer, secondary C-H bonds were preferentially activated, although tertiary C-H bond functionalization occurred as well. The observed regioselectivity was attributed to the greater number of methylene sites in comparison with the tertiary C-H bonds along with the fact that methylene units suffer from a lower steric hindrance. Degrees of functionalization were within the 4–10% of the tertiary sites (Scheme 9A) and could be finely tuned by controlling the EDA:polyolefin ratio. When diene-based polymer substrates are used (Scheme 9B), addition of the

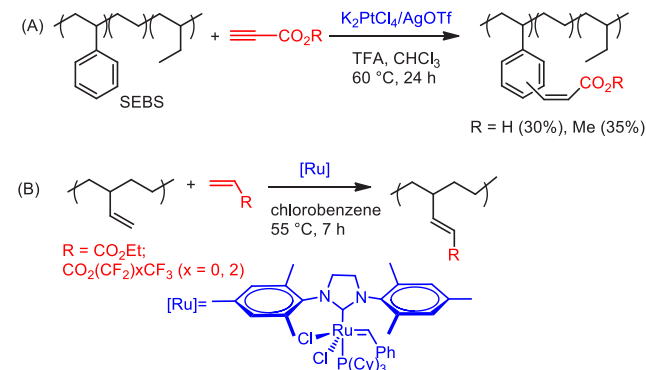
Scheme 9. Copper-Catalyzed Carbene Insertion (A) and Addition to PDBs (B) or SBRs (C)



carbene to the unsaturated moieties was preferred over C–H bond activation due to the significantly higher reactivity of the C=C double bonds toward the electrophilic metalcarbene intermediates. Consequently, even PBDs with degrees of functionalization up to 100% could be obtained depending on the EDA to polymer double bond ratio used. Unsaturated styrene–butadiene rubbers were also functionalized by this strategy, with the modified polymer containing cyclopropane rings along the chain, in the pendant or internal positions (Scheme 9C). It was later noted that although the catalytic process proceeds without cross-linking or C–C bond scission, the exposure of the functionalized materials to air slowly led to degradation during the storage, a fact explained as the result of traces of the copper catalyst present in the isolated polymers.⁵⁵

Other examples of polymer modification with carboxylated functionalities were reported by Kitamura and Coates.^{56,57} The former reported the introduction of an acrylate moiety into styrene-based polymers by hydroarylation of propiolic acid or its methyl ester.⁵⁶ The reaction of polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) with propiolic acid or methyl propiolate in the presence of K_2PtCl_4 and AgOTf in trifluoroacetic acid/ $CHCl_3$ at 60 °C led to the alkenylation of 30 and 35% of the total styrene units, respectively (Scheme 10A). Under the same identical reaction conditions, a lower degree of functionalization (5–7%) was observed for the hydroarylation of polystyrene (PS), probably due to the low solubility of PS in the trifluoroacetic acid/ $CHCl_3$ mixture. The authors speculated that a mixture of *ortho*- and *para*-functionalized polystyrenes is obtained by using this protocol. However, they did not provide the molecular weight values for the functionalized product. Coates and co-workers reported the synthesis of carboxylated polyolefins by a cross-metathesis strategy.⁵⁷ The reaction of vinyl-containing polyolefins ($M_n \approx 200$ kg/mol) with acrylates, in the presence of Grubbs catalyst at 55 °C, allowed the conversion of 45–91% of the total vinyl groups (Scheme 10B). A ratio of 10:1 of alkene-to-vinyl group was employed, leading to

Scheme 10. Hydroarylation of SEBS via Pt Catalysis (A) or Ruthenium-Catalyzed Metathesis (B)

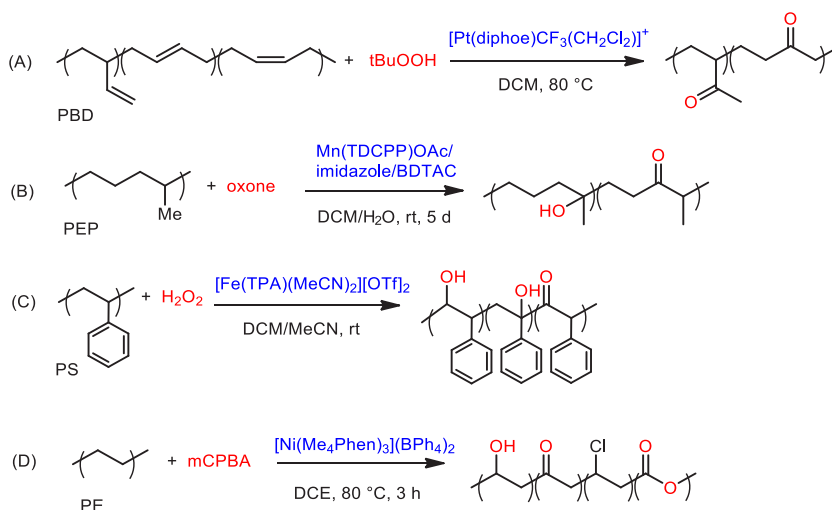


high conversions. Furthermore, the conversion was found to be dependent on the boiling point of the alkene; the higher the boiling point, the higher the conversions since it favors working at temperatures at which removal of ethylene is more efficient. In addition to acrylate moieties, this cross-metathesis strategy tolerated the introduction of other functional groups such as hydroxyl groups or fluorinated moieties without significantly altering the molecular weight properties of the starting material. However, the main drawback of this approach is that it is limited to polymers containing only pendant alkene groups since the presence of main-chain C=C bonds would result in the cleavage of the polymer backbone.

Hydroxyl and Ketone Groups. Several methods have been also developed to add hydroxyl or carbonyl groups into polymers. Oxidation of different polybutadienes to polyketones was reported by Cole-Hamilton and co-workers in 1991.⁵⁸ Reactions were performed with $tBuOOH$ in CH_2Cl_2 in the presence of $[Pt(diphoe)CF_3(CH_2Cl_2)]^+$ (diphoe = $Ph_2PCH=CHPh_2$) at 80 °C. Analysis of the resulting polymers indicated that the overall conversion of C=C double bonds was within the 12–57% range, depending on the polymer structure (Scheme 11A). Because the vinyl double bonds showed a slightly higher reactivity than that of the backbone ones (the reactivity ratio of terminal/internal double bonds was ca. 4:3), conversion increased as the proportion of the vinyl groups increased. Furthermore, the *trans* double bonds were found to be more reactive than those having the *cis* configuration. Hillmyer and co-workers reported the direct oxidation of PEP (poly(ethylene-*alt*-propylene)) in the presence of the manganese complex $Mn(TDCPP)OAc$ (*meso*-tetra-2,6-dichlorophenylporphyrin), imidazole, BDTAC (benzyltrimethyltetradecylammonium chloride) as phase transfer agent BDTAC), and oxone under ambient conditions (Scheme 11B).⁵⁹ Using this two-phase oxidation system, they were able to incorporate oxygen functionalities into both low-molecular-weight ($M_n = 8.9$ kg/mol) and high-molecular-weight ($M_n = 62.0$ kg/mol) PEP polymers without alteration of the molecular weight distribution of the starting material. This methodology led to the selective incorporation of 0.4–1.1 tertiary hydroxyl groups per 100 backbone carbons although long reaction times were required (2–5 days). However, incorporation of ketone products occurred as well, probably due to further oxidation of previously formed secondary alcohols.

Oxyfunctionalization of PS with hydrogen peroxide mediated by iron-based catalysts was reported by Baird and co-worker.⁶⁰ They found that the use of $[Fe(TPA)(MeCN)_2][OTf]_2$ (TPA =

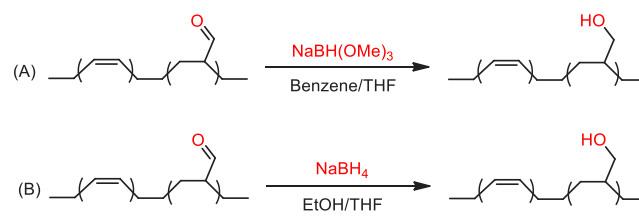
Scheme 11. Homogeneous Metal-Catalyzed Oxyfunctionalization of Polymers



tris(2-pyridylmethyl)amine) or $[\text{Fe}(\text{BPMEN})][\text{OTf}]_2$ (BPMEN = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine) catalytic systems to functionalize high-molecular-weight polystyrene ($M_n = 120$ kg/mol) with hydrogen peroxide (Scheme 11C) resulted in the formation of insoluble materials, suggesting cross-linking events. The utilization of a lower molecular weight PS ($M_n = 1.0$ kg/mol) combined with iterative addition of $[\text{Fe}(\text{TPA})(\text{MeCN})_2][\text{OTf}]_2$ and H_2O_2 resulted in functionalized products with very similar molecular weights properties to that of the starting material. Characterization of such oxyfunctionalized polymer showed the incorporation of 10–20 keto and hydroxyl groups per 100 repeat units. This high degree of functionalization was further supported by a higher glass transition temperature of the functionalized product ($T_g = 82\text{--}100$ °C) relative to the starting material ($T_g = 60$ °C). More recently, Ni-catalyzed C–H oxidation of polyethylenes with different molecular weights and microstructures was reported by Hartwig and co-workers.⁶¹ The use of the nickel complex $[\text{Ni}(\text{Me}_4\text{Phen})_3](\text{BPh}_4)_2$ and *m*-chloroperoxybenzoic acid (*m*CPBA) as the oxidant in DCE at 80–90 °C led to introduction of 2.0–5.5 functional groups per 100 monomers, maintaining the initial molecular weight parameters (Scheme 11D). By use of this method, a mixture of hydroxy, ketone, chloride, and ester groups was incorporated into the polymer backbone with the alcohol representing 60%–88% of the total functionality introduced.

Hydroformylation and subsequent hydrogenation of formylated polymer also constitute an effective, albeit indirect method to introduce pendent hydroxyl groups onto the polymer chain. However, under the catalytic conditions in which aldehyde C=O bonds are reduced to hydroxyl groups, reduction of remaining double bonds in the polymer backbone constitutes a drawback. Azuma and co-workers⁶² used different reducing agents in a stoichiometric manner to synthesize polydienes having pendant hydroxymethyl groups. In all cases selective reduction of the carbonyl groups was accomplished; sodium trimethoxyborohydride was found to be the most effective reducing agent in terms of solubility of the reduced polymers and the reduction rate of the formyl group (Scheme 12A). In fact, kinetic experiments using sodium trimethoxyborohydride as the reducing agent showed that complete reduction of carbonyl groups takes only 30 min without any cross-linking reaction among the formyl groups. The use of NaBH_4 in combination with a proton source

Scheme 12. Reduction of Polyaldehydes by Stoichiometric Reductants



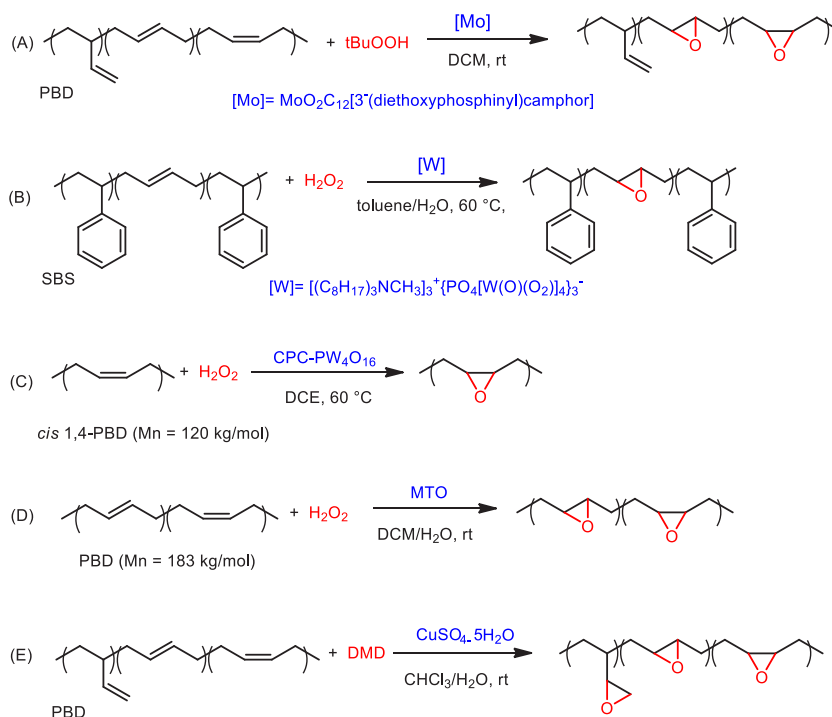
is another an effective method to selectively transform C=O bonds into C–OH bonds, as reported by McGrath and co-workers⁶³ (Scheme 12B). The presence of ethanol as proton source in the reaction mixture has a dual role: it helps to complete the reduction process and prevents cross-linking reactions.

Another indirect method to introduce hydroxyl groups into the polymer chains involves the oxidation of borylated polymers by basic H_2O_2 in THF/ H_2O . This methodology was applied to different polymer substrates (see Schemes 2 and 3)^{17–20} and in all cases proceeded efficiently without causing deleterious side reactions. Furthermore, the altered properties of the hydroxylated polymer were testified by the change in the glass transition temperatures (T_g) with respect to the parent material.

Epoxy Groups. Epoxidation of diene-based polymers is an important process in polymer chemistry since epoxides are key starting materials for a wide variety of products.^{64,65} Oxirane-ring-containing polymers can be prepared by the reaction of diene-based polymers with stoichiometric amounts of oxidants. Although some of those noncatalytic methods provide good conversions under mild conditions and without side reactions, the use of metal catalysts allows controlling the selectivity and/or precluding side reactions.

Catalytic epoxidation of unsaturated polymers was reported by Cole-Hamilton and co-workers in 1989.⁶⁶ Epoxidation of polybutadiene containing *cis*-1,4-, *trans*-1,4-, and 1,2-polymerized units was performed with $t\text{BuOOH}$ in CH_2Cl_2 in the presence of $\text{MoO}_2\text{C}_1_2[3\text{-(diethoxyphosphinyl)camphor}]$ as catalyst at room temperature. Under these conditions, high conversions of the backbone double bonds could be achieved, whereas the vinyl double bonds remained almost unreacted (Scheme 13A). The order of reactivity of double bonds found was *cis*-1,4 > *trans*-

Scheme 13. Epoxidation of Diene-Based Polymers with Transition-Metal Catalysts

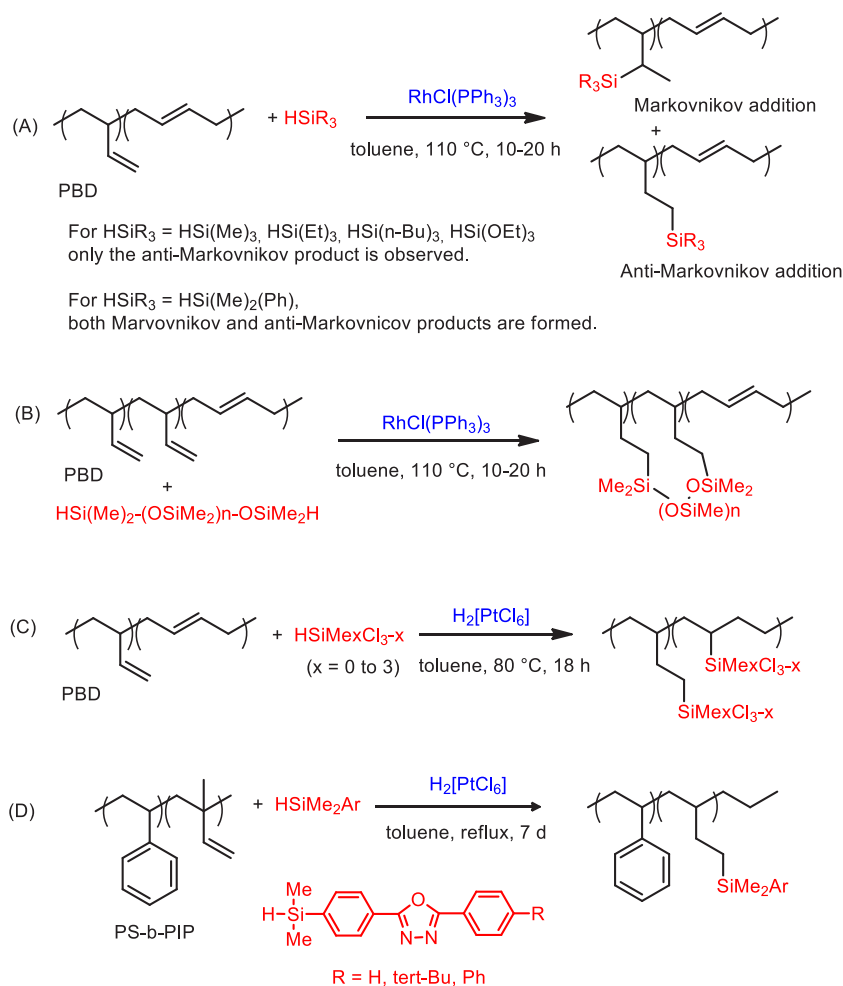


1,4 \gg 1,2. Kinetic experiments showed that the rate of epoxidation dramatically decreases after a very rapid initial phase, thus suggesting that catalyst transformation into a lesser active species occurred during the reaction. The reason for this degradation process was ascribed to the presence of water in the reaction mixture that causes epoxide ring-opening leading to the formation of diols. The so-formed diol group then displaces the diethoxyphosphorylcamphor from the molybdenum complex to give a less active catalyst. To overcome this problem, epoxidation reactions were performed in the presence of molecular sieves 4 Å.⁶⁷ A marked decrease in the amount of diol was observed together with higher conversions (>95%) and reaction rates. Furthermore, conversion of the pendant double bonds was further reduced by the presence of molecular sieves, thus increasing the selectivity of the catalytic system.

Epoxidation under biphasic conditions was also found to be an effective method to avoid undesired side reactions. Hay and co-worker⁶⁸ reported the epoxidation of styrene–butadiene–styrene linear block copolymer (SBS, $M_w = 92$ kg/mol) using hydrogen peroxide as the oxidant and methyltriocylammonium tetrakis(diperoxotungsto)phosphate $[(C_8H_{17})_3NCH_3]_3^+ \{PO_4[W(O)(O_2)]_4\}^{3-}$ as the catalyst in toluene/water at 60–80 °C. This epoxidation system allowed the conversion of up to 70% of the double bonds with the functionalization of 1,4-unsaturation preferred over the epoxidation of the 1,2-unsaturation (Scheme 13B). More recently, Li and co-workers reported a similar catalytic system for the epoxidation of high-molecular-weight PBD (*cis*-1,4 = 96.7%; $M_n = 120$ kg/mol).⁶⁹ By use of H_2O_2 as the oxidant and the phase transfer catalyst $[\pi-C_3H_5NC_{16}H_{33}]_3[PO_4(WO_3)_4]$ (CPC-PW₄O₁₆) in DCE, epoxy ratios up to 20 mol % could be obtained with quantitative consumption of H_2O_2 (Scheme 13C). Hydrogen peroxide was also used as oxidant for the epoxidation of 1,4-PBD ($M_n = 183$ kg/mol) in combination with methyltrioxorhenium (MTO) as the catalyst precursor.⁷⁰ The reactions were performed in a CH_2Cl_2/H_2O biphasic system at

room temperature. Degrees of functionalization ranging from 12 to 48% could be achieved with 100% selectivity in epoxide formation (Scheme 13D). However, GPC analysis of the epoxidized polydienes showed an increase of the weight-average molecular weight which was attributed to chain ramification or cross-linking reactions. The same catalytic system was later applied to the epoxidation of other polydienes, such as polyisoprene (PI), random styrene–butadiene rubber (SBR), and low-molecular-weight liquid hydroxylated polybutadiene (LHPB), leading to comparable activities and selectivities.⁷¹ Nijke and co-workers investigated the epoxidation of different diene-based polymers by using *in-situ*-generated dimethyldioxirane (DMD) as the oxygen source under mild conditions. Dimethyldioxirane is an oxidizing agent formed by the reaction of acetone and ozone and was used either as stoichiometric reagent^{72–74} or in combination with transition-metal catalysts (Ti, V, Cd, Ni, Zn, Mn, and Cu).⁷⁵ Among all them, $CuSO_4 \cdot 5H_2O$ gave the best results with the highest yields and without epoxy group ring-opening and hydroxyl group interconversion reactions (Scheme 13E). Similar results were also obtained by using the Cu(II)–ABTZ (2,2',-diamino-4,4'-bithiazole) catalytic system.⁷⁶

In 2003, Rowan and co-workers⁷⁷ described a novel epoxidation system that mimics the ability of some enzymes to attach the biopolymer substrate and catalyze multiple rounds of reaction before dissociating. In this system, the polymer chains of PBD are threaded to a macrocycle capped with a manganese(III) porphyrin catalyst. The cavity of the macrocycle moves along the polymer chain while catalyzing the conversion of the double bonds into the corresponding epoxide functions. In the presence of a bulky axial ligand such *tert*-butylpyridine (tbp) (which forces catalysis to occur inside the cavity) and PhIO as the oxidant, a maximum of 56% of the C=C bonds of PBD ($M_w = 300$ kg/mol, 98% *cis*) were converted to epoxide functionalities. Moreover, analysis of the functionalized polymer showed the formation of 80% *trans*- and 20% *cis*-epoxide rings.

Scheme 14. Hydrosilylation of Vinyl Units of Unsaturated Polymers Using $\text{RhCl}(\text{PPh}_3)_3$ (A, B) and $\text{H}_2[\text{PtCl}_6]$ (C, D) as Catalysts

This stereoselectivity strongly differed from that obtained with the related unlinked manganese catalyst (78% *cis*- and 22% *trans*-epoxide rings), which suggest that catalysis occurs in the sterically demanding cavity of the macrocycle.

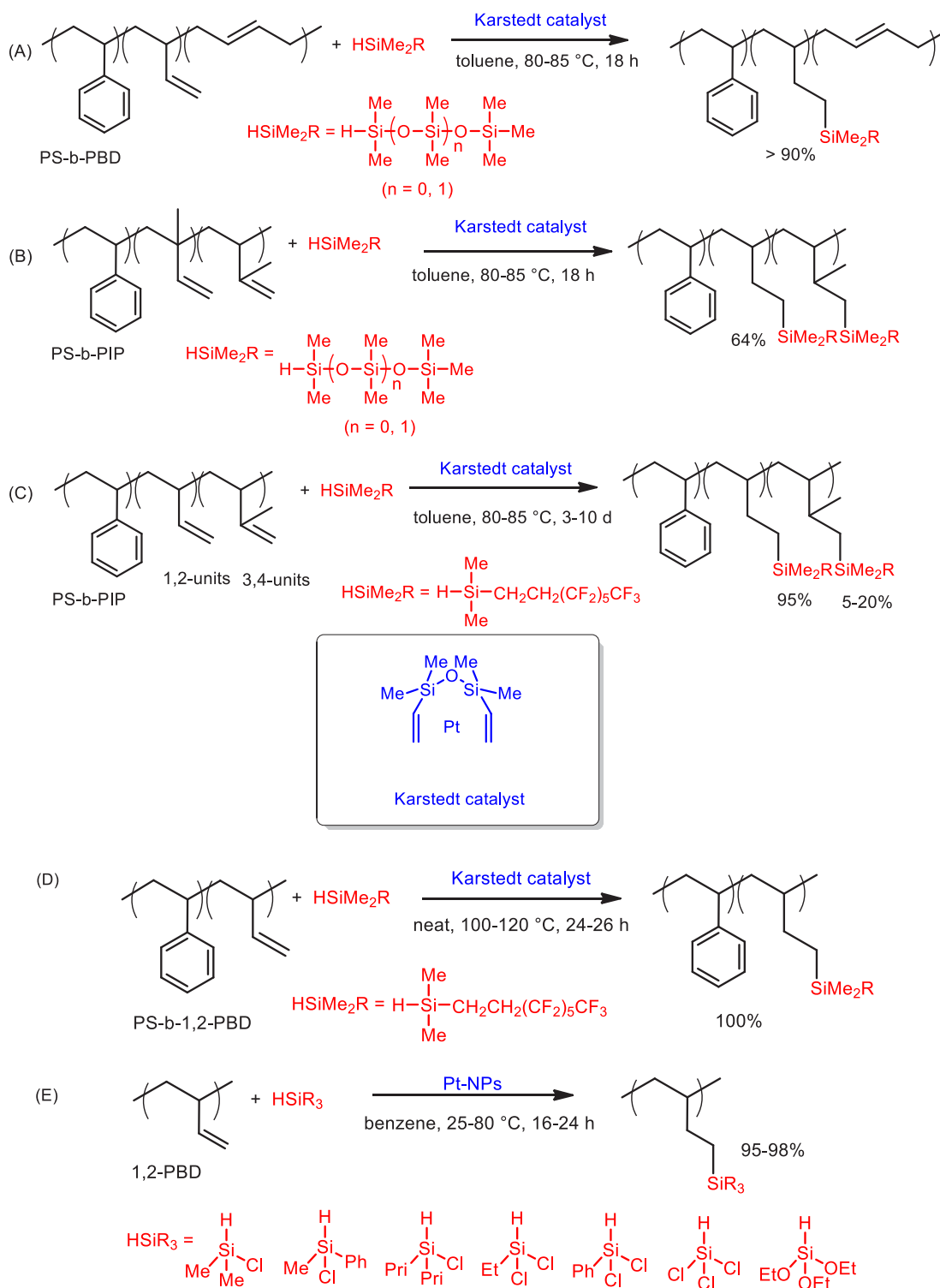
Silylane Functionalities. The chemical modification of unsaturated polymers via catalytic hydrosilylation offers an efficient synthetic route to prepare materials with special properties. Polymers containing silane functional groups may find potential applications as adhesives, rubber materials, and drug delivery agents. Rempel and co-workers investigated the hydrosilylation reactions of unsaturated polymers in the presence of the Wilkinson $\text{RhCl}(\text{PPh}_3)_3$ catalyst in toluene at 110°C .^{78,79} The addition of silane groups to PBDs with different microstructures ($M_n = 4.5\text{--}30$ kg/mol) resulted in the quantitative hydrosilylation of the vinyl $\text{C}=\text{C}$ bonds of the polymers and occurred regioselectively via an anti-Markovnikov addition with the silicon atom being attached at the terminal position of the 1,2-PBD unit. Neither the steric effect of the alkyl groups nor the molecular weight of the polymer induces a significant effect on the regioselectivity of the hydrosilylation reaction. However, the nature of the substituents in the silanes influences the hydrosilylation mechanism since the use dimethylphenylsilane resulted in both the Markovnikov and anti-Markovnikov products (Scheme 14A). GPC analysis of the hydrosilylated polymer showed similar molecular weight distribution to the parent material, suggesting that no side reactions occurred during the hydrosilylation reactions.

Hydrosilylation of PBD with hydride-terminated poly(dimethylsiloxane) using the same catalytic system afforded novel polymer architectures depending on the hydride-to-vinyl ratio.⁸⁰ For a low hydride-to-vinyl ratio, formation of side loops takes place from the hydrosilylation of adjacent vinyl groups (Scheme 14B). At higher ratios, hydrosilylation of distant vinyl groups may result in a compact, dendrimer-like molecule.

Besides the Rh-catalyzed hydrosilylation reaction, platinum catalysts were also extensively used to prepare silyl-functionalized materials. Cole-Hamilton and co-workers investigated the hydrosilylation of PBDs having a variety of microstructures using $\text{H}_2[\text{PtCl}_6]$ (Speier's catalyst).⁸¹ The addition of $\text{HSiMe}_x\text{Cl}_{3-x}$ ($x = 0\text{--}2$) to PBDs in toluene at 80°C resulted in complete functionalization of the pendant double bonds via an anti-Markovnikov addition mechanism. However, unlike the Rh catalytic system, with this Pt catalyst functionalization occurred also on the internal double bonds of the polymer (Scheme 14C). This backbone hydrosilylation decreases as the number of chlorine atoms on the silicon atom increases, and it is accompanied by double-bond migration along the polymer backbone to give conjugated diene units within the polymer backbone.

The same catalytic system was also used to functionalize a series of polystyrene-*block*-polyisoprene (PS-*b*-PIP) with aromatic oxadiazoles.⁸² The addition of various aryldimethylsilanes to the block copolymers yielded approximately 4–17% of silyl incorporation (Scheme 14D).

Scheme 15. Hydrosilylation of Vinyl Units of Unsaturated Polymers with the Karstedt Catalyst (A–D) and with Platinum Nanoparticles (E)



Karstedt's catalyst [1,3-divinyltetramethyldisiloxane–platinum(0)] is frequently used for catalytic hydrosilylation.^{83–86} Ober and co-workers investigated the hydrosilylation of polystyrene block copolymers with hydroxysiloxanes in toluene at 80–85 °C. The silyl groups were selectively attached to the side-chain double bonds of the diene polymers. They found that when attaching the hydroxysiloxanes to the 1,2-butadiene units of the styrene–butadiene copolymers, the conversion was >90%

(Scheme 15A). However, the incorporation of the hydroxysiloxane into the 1,2- and 3,4-isoprene units of the styrene–isoprene copolymer did not exceed 64% even upon addition of fresh catalyst and/or hydroxysiloxane and with longer reaction times (Scheme 15B). They suggested that the decreased conversion of the 1,2-isoprene units compared to 1,2-butadiene units was probably due to steric effects. Karstedt's catalyst was also employed to modify styrene block copolymers with

perfluoro-based silanes. The conversion of the 1,2 and 3,4 units of the styrene–isoprene copolymer in toluene at 80 °C took several days (3–10 days) and reached 95% and 5–20%, respectively (Scheme 15C). The quantitative hydrosilylation of the pendant double bonds of the styrene–butadiene copolymer was achieved in 24–26 h in the absence of any solvent (Scheme 15D). GPC analysis of the functionalized material showed unchanged molecular weight distributions suggesting that no side reactions occurred.

In addition to molecular complexes, also metal nanoparticles can operate as hydrosilylation catalysts as reported by Chauhan and co-workers.⁸⁷ They described the hydrosilylation of PBD using readily synthesized and recyclable Pt nanoclusters. A variety of silane structures were screened including chloro-, alkyl-, and alkoxy-silanes (Scheme 15E). Almost complete conversion (95–98%) of the pendant vinyl groups of the PBD was achieved regardless of the nature of the silane. As in the case of molecular catalysts, the hydrosilylation reaction catalyzed by these Pt nanoclusters occurred selectively via an anti-Markovnikov addition. Furthermore, the activity and selectivity were retained up to five cycles without chain scission or cross-linking reactions.

3. OUTLOOK AND CHALLENGES

The existing methods for the incorporation of polar groups to polyolefins (generated from nonpolar group containing olefins) employing transition-metal-based catalysts have been presented. This so-called postpolymerization functionalization strategy becomes crucial when the direct polymerization of a given monomer is not feasible due to either catalyst poisoning or monomer unavailability. It seems clear that the number of examples is yet limited and that some transformations which are extensively developed at the molecular level are yet unknown for polyolefins. As an example, the formation of C–N bonds at polyolefins remains unreported, in contrast with the intense research developed with discrete molecules. Another goal that can be also challenged in this field corresponds to the development of catalysts that can exert the incorporation of two different polar groups in the polyolefin. In this manner, controlling the amount of each group, a given polyolefin may end in an array of modified materials with varied properties. Overall, this is a field that is yet underdeveloped and that may boost the use of readily and inexpensive polyolefins to generate value-added materials.

AUTHOR INFORMATION

Corresponding Authors

Pedro J. Pérez – *Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los Materiales, Unidad Asociada al CSIC, Centro de Investigación en Química Sostenible (CIQSO), Campus de El Carmen s/n, Universidad de Huelva, 21007 Huelva, Spain; orcid.org/0000-0002-6899-4641; Email: perez@dqcm.uhu.es*

M. Mar Díaz-Requejo – *Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los Materiales, Unidad Asociada al CSIC, Centro de Investigación en Química Sostenible (CIQSO), Campus de El Carmen s/n, Universidad de Huelva, 21007 Huelva, Spain; orcid.org/0000-0001-8295-4059; Email: mmdiaz@dqcm.uhu.es*

Author

Gabriel Menendez Rodriguez – *Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los*

Materiales, Unidad Asociada al CSIC, Centro de Investigación en Química Sostenible (CIQSO), Campus de El Carmen s/n, Universidad de Huelva, 21007 Huelva, Spain; orcid.org/0000-0003-2793-7760

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

Biographies



Dr. Gabriel Menendez Rodriguez is a postdoctoral researcher in Prof. Pedro J. Pérez's group at Universidad de Huelva. He completed his Ph. D. at Università degli Studi di Perugia in 2019 under the supervision of Prof. Alceo Macchioni. His current research focuses on the development of catalytic systems for the functionalization of polyolefins.



M. Mar Díaz-Requejo is Professor of Inorganic Chemistry at the Universidad de Huelva, Spain. She obtained her Ph. D. at Universidad de Huelva (2000, Pedro J. Pérez, Advisor), and she moved to the University of North Carolina, Chapel Hill, in 2001 as a postdoctoral fellow under the supervision of Prof. Maurice Brookhart. In 2003 she was enrolled as a researcher in the "Ramón y Cajal" Program in Spain and returned to the Universidad de Huelva, where she continues her scientific career. She has received the Young Researcher Award from the Royal Society of Chemistry of Spain (2005) and the Lilly Research Award (2008). Her research interests focus on the development of coinage-metal catalysts for carbene, nitrene, and oxo transfer to

saturated or unsaturated substrates to form new C–C and C–heteroatom bonds.



Pedro J. Pérez (FRSC, CE Fellow) is Professor of Inorganic Chemistry at Universidad de Huelva, Spain. He graduated at Universidad de Sevilla (1991, Ernesto Carmona, Advisor) before a postdoctoral Fulbright fellowship at the University of North Carolina, Chapel Hill (1991–1993, Maurice Brookhart, supervisor). His work is mainly devoted to the development of late-transition-metal complexes as catalysts for transformations involving saturated and unsaturated hydrocarbons. He is the founder of the Center for Research in Sustainable Chemistry (CIQSO) at Universidad de Huelva, where he is the Leader of the Homogeneous Catalysis Laboratory. He has been recognized by the Royal Society of Chemistry of Spain with the Research Prize and Gold Medal (2016) and the Inorganic Chemistry Award (2007). The Royal Society of Chemistry awarded him with the 2015 Homogeneous Catalysis Award. He is member of the Academia Europaea (2018) and the Royal Academy of Sciences of Spain (2014).

REFERENCES

- (1) Alt, H. G.; Köppl, A. Effect of the Nature of Metallocene Complexes of Group IV Metals on Their Performance in Catalytic Ethylene and Propylene Polymerization. *Chem. Rev.* **2000**, *100*, 1205–1222.
- (2) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-metal catalysts for ethylene homo- and copolymerization. *Chem. Rev.* **2000**, *100*, 1169–1204.
- (3) Boffa, L. S.; Novak, B. M. Copolymerization of Polar Monomers with Olefins Using Transition-Metal Complexes. *Chem. Rev.* **2000**, *100*, 1479–1494.
- (4) Nakamura, A.; Ito, S.; Nozaki, K. Coordination–Insertion Copolymerization of Fundamental Polar Monomers. *Chem. Rev.* **2009**, *109*, 5215–5244.
- (5) Franssen, N. M. G.; Reek, J. N. H.; de Bruin, B. Synthesis of functional ‘polyolefins’: state of the art and remaining challenges. *Chem. Soc. Rev.* **2013**, *42*, 5809–5832.
- (6) Carrow, B. P.; Nozaki, K. Transition-Metal-Catalyzed Functional Polyolefin Synthesis: Effecting Control through Chelating Ancillary Ligand Design and Mechanistic Insights. *Macromolecules* **2014**, *47*, 2541–2555.
- (7) Tan, C.; Chen, C. Emerging Palladium and Nickel Catalysts for Copolymerization of Olefins with Polar Monomers. *Angew. Chem., Int. Ed.* **2019**, *58*, 7192–7200.
- (8) Chen, Z.; Brookhart, M. Exploring Ethylene/Polar Vinyl Monomer Copolymerizations Using Ni and Pd α -Diimine Catalysts. *Acc. Chem. Res.* **2018**, *51*, 1831–1839.
- (9) Chen, C. Designing catalysts for olefin polymerization and copolymerization: beyond electronic and steric tuning. *Nat. Rev. Chem.* **2018**, *2*, 6–14.
- (10) Boen, N. K.; Hillmyer, M. A. Post-polymerization functionalization of polyolefins. *Chem. Soc. Rev.* **2005**, *34*, 267–275.
- (11) Mohanty, A. D.; Bae, C. Transition Metal-Catalyzed Functionalization of Polyolefins Containing C–C, C=C, and C–H Bonds. *Adv. Organomet. Chem.* **2015**, *64*, 1–39.
- (12) Williamson, J. B.; Lewis, S. E.; Johnson, R. R.; Manning, I. M.; Leibfarth, F. A. C–H Functionalization of Commodity Polymers. *Angew. Chem., Int. Ed.* **2019**, *58*, 8654–8668.
- (13) Plummer, C. M.; Li, L.; Chen, Y. The post-modification of polyolefins with emerging synthetic methods. *Polym. Chem.* **2020**, *11*, 6862–6872.
- (14) Korthals, B.; Morant-Miñana, M. C.; Hohberger, C.; Mecking, S. Conveniently Accessible Polymer Nanoparticles of Adjustable Polarity. *Langmuir* **2009**, *25*, 10554–10557.
- (15) Passaglia, E.; Coiai, S.; Cicogna, F.; Ciardelli, F. Some recent advances in polyolefin functionalization. *Polym. Int.* **2014**, *63*, 12–21.
- (16) Walsh, D. J.; Hyatt, M. G.; Miller, S. A.; Guironnet, D. Recent Trends in Catalytic Polymerizations. *ACS Catal.* **2019**, *9*, 11153–11188.
- (17) Coiai, S.; Passaglia, E.; Aglietto, M.; Ciardelli, F. Control of degradation reactions during radical functionalization of polypropylene in the melt. *Macromolecules* **2004**, *37*, 8414–8423.
- (18) Günay, K. A.; Theato, P.; Klok, H.-A. Standing on the shoulders of Hermann Staudinger: Post-polymerization modification from past to present. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 1–28.
- (19) Kondo, Y.; García-Cuadrado, D.; Hartwig, J. F.; Boen, N. K.; Wagner, N. L.; Hillmyer, M. A. Rhodium-Catalyzed, Regiospecific Functionalization of Polyolefins in the Melt. *J. Am. Chem. Soc.* **2002**, *124*, 1164–1165.
- (20) Bae, C.; Hartwig, J. F.; Boen Harris, N. K.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A. Catalytic Hydroxylation of Polypropylenes. *J. Am. Chem. Soc.* **2005**, *127*, 767–776.
- (21) Bae, C.; Hartwig, J. F.; Chung, H.; Harris, N. K.; Switek, K. A.; Hillmyer, M. A. Regiospecific Side-Chain Functionalization of Linear Low-Density Polyethylene with Polar Groups. *Angew. Chem., Int. Ed.* **2005**, *44*, 6410–6413.
- (22) Shin, J.; Chang, A. Y.; Brownell, L. V.; Racoma, I. O.; Ozawa, C. H.; Chung, H.; Peng, S.; Bae, C. Hydrophilic Graft Modification of a Commercial Crystalline Polyolefin. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3533–3545.
- (23) Jo, T. S.; Yang, M.; Brownell, L. V.; Bae, C. J. Synthesis of Quaternary Ammonium Ion-Grafted Polyolefins via Activation of Inert C–H Bonds and Nitroxide Mediated Radical Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4519–4531.
- (24) Shin, J.; Jensen, S. M.; Ju, J.; Lee, S.; Xue, Z.; Noh, S. K.; Bae, C. Controlled Functionalization of Crystalline Polystyrenes via Activation of Aromatic C–H Bonds. *Macromolecules* **2007**, *40*, 8600–8608.
- (25) Jo, T. S.; Kim, S. H.; Shin, J.; Bae, C. Highly Efficient Incorporation of Functional Groups into Aromatic Main-Chain Polymer Using Iridium-Catalyzed C–H Activation and Suzuki–Miyaura Reaction. *J. Am. Chem. Soc.* **2009**, *131*, 1656–1657.
- (26) Brownell, L. V.; Shin, J.; Bae, C. Synthesis of Polar Block Grafted Syndiotactic Polystyrenes via a Combination of Iridium-Catalyzed Activation of Aromatic C–H Bonds and Atom Transfer Radical Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6655–6667.
- (27) Chang, Y.; Brunello, G. F.; Fuller, J.; Disabb-Miller, M. L.; Hawley, M. E.; Kim, Y. S.; Hickner, M. A.; Jang, S. S.; Bae, C. Polymer electrolyte membranes based on poly(arylene ether sulfone) with pendant perfluorosulfonic acid. *Polym. Chem.* **2013**, *4*, 272–281.
- (28) Chang, Y.; Lee, H. H.; Kim, S. H.; Jo, T. S.; Bae, C. Scope and Regioselectivity of Iridium-Catalyzed C–H Borylation of Aromatic Main-Chain Polymers. *Macromolecules* **2013**, *46*, 1754–1764.
- (29) Mohanty, A. D.; Lee, Y. B.; Zhu, L.; Hickner, M. A.; Bae, C. Anion Exchange Fuel Cell Membranes Prepared from C–H Borylation and Suzuki Coupling Reactions. *Macromolecules* **2014**, *47*, 1973–1980.
- (30) Mohanty, A. D.; Ryu, C. Y.; Kim, Y. S.; Bae, C. Stable Elastomeric Anion Exchange Membranes Based on Quaternary Ammonium-Tethered Polystyrene-*b*-poly(ethylene-co-butylene)-*b*-polystyrene Triblock Copolymers. *Macromolecules* **2015**, *48*, 7085–7095.

- (31) Wagner, C. B.; Studer, A. Oxidation of Alkylcatecholboranes with Functionalized Nitroxides for Chemical Modification of Cyclohexene, Perallylated Polyglycerol and of Poly(butadiene). *Eur. J. Org. Chem.* **2010**, *2010*, 5782–5786.
- (32) Wagner, C. B.; Studer, A. Synthesis of Macro(alkoxyamines) via Hydroboration of Polyolefins with Subsequent Nitroxide Oxidation for Controlled NMP. *Macromol. Chem. Phys.* **2010**, *211*, 2510–2516.
- (33) Ramp, F. L.; Dewitt, E. J.; Trapasso, L. E. Hydroformylation of High Polymers. *J. Polym. Sci., Part A-1: Polym. Chem.* **1966**, *4*, 2267–2279.
- (34) Brown, C. K.; Wilkinson, G. Homogeneous Hydroformylation of Alkenes with Hydridocarbonyltris(triphenylphosphine)rhodium(I) as Catalyst. *J. Chem. Soc. A* **1970**, 2753–2764.
- (35) Evans, D.; Osborn, J. A.; Wilkinson, G. Hydroformylation of Alkenes by Use of Rhodium Complex Catalysts. *J. Chem. Soc. A* **1968**, 3133–3142.
- (36) Sanui, K.; MacKnight, W. J.; Lenz, R. W. Hydroformylation of a Polypentenamer and Preparation of Derivatives Therefrom. *Macromolecules* **1974**, *7*, 952–954.
- (37) Azuma, C.; Mitsuboshi, T.; Sanui, K.; Ogata, N. Synthesis and Properties of Polydiene and Polypentenamer Having Formyl or Hydroxymethyl Groups and Their Photosensitive Derivatives. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 781–797.
- (38) Tremont, S. J.; Remsen, E. E.; Mills, P. L. Hydroformylation of 1,2- and 1,4-Polybutadiene and Their Mixtures with Hydridocarbonyltris(triphenylphosphine)rhodium(I) Catalyst and Excess Triphenylphosphine. *Macromolecules* **1990**, *23*, 1984–1993.
- (39) Mills, P. L.; Tremont, S. J.; Remsen, E. E. Synthesis, Characterization, and Kinetics of Functionalized Polybutadiene Using a Homogeneous Rhodium Hydroformylation Catalyst. *Ind. Eng. Chem. Res.* **1990**, *29*, 1443–1454.
- (40) Chen, J.; Ajjou, A. N.; Chanthateyanonth, R.; Alper, H. Catalytic Hydroformylation of Styrene-Butadiene Copolymers. *Macromolecules* **1997**, *30*, 2897–2901.
- (41) Sibtain, F.; Rempel, G. L. Chemical Modification of Polymers: Catalytic Hydroformylation and Hydroxymethylation of Styrene-Butadiene Copolymers. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 629–635.
- (42) Scott, P. J.; Rempel, G. L. Homogeneous Catalytic Hydroformylation of Styrene-Butadiene Copolymers in the Presence of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. *Macromolecules* **1992**, *25*, 2811–2819.
- (43) Im-Erbsin, S.; Prasassarakich, P.; Rempel, G. L. Hydroformylation of High-Molecular-Weight *cis*-1,4-Polybutadiene Catalyzed by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. *J. Appl. Polym. Sci.* **2004**, *93*, 854–869.
- (44) Jun, C. H.; Hwang, D. C. Simultaneous Hydrogenation and Hydroacylation of Vinyl Groups in Polybutadiene by use of a Rhodium Catalyst. *Polymer* **1998**, *39*, 7143–7147.
- (45) Jun, C. H.; Huh, C. W.; Na, S. J. Direct Synthesis of Ketones from Primary Alcohols and 1-Alkenes. *Angew. Chem., Int. Ed.* **1998**, *37*, 145–147.
- (46) Lee, J. H.; Jo, E. A.; Jun, C. H. Modification of Polybutadiene: Chelation-Assisted Hydroacylation of α,ω -Diol with a Rhodium(I) Catalyst. *Synlett* **2009**, *2009* (16), 2647–2650.
- (47) Narayanan, P.; Clubley, B. G.; Cole-Hamilton, D. J. Polycarboxylic Acids via Catalytic Hydrocarboxylation of Polybutadienes. *J. Chem. Soc., Chem. Commun.* **1991**, *12*, 1628–1630.
- (48) Ajjou, A. N.; Alper, H. Catalytic Hydrocarboxylation and Hydroesterification Reactions of 1,2-Polybutadiene. *Macromolecules* **1996**, *29*, 1784–1788.
- (49) Gong, L.; Wool, R. P.; Friend, A. D.; Goranov, K. Synthesis and Characterization of High Molecular Weight Carboxylated Polybutadiene. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3129–3138.
- (50) Park, W. J.; Lee, C. H.; Kim, D. S.; Jun, C. H. A Catalytic Hydroesterification Process Using HCO_2Na , $\text{Ru}_3(\text{CO})_{12}$ and Alcohols for the Preparation of Ester Modified Polybutadienes. *Chem. Commun.* **2015**, *51*, 14667.
- (51) Skell, P. S.; Aglietto, M.; Ruggeri, G.; Speranza, S.; Ciardelli, F. Italian patent IT48950A/85, 1985.
- (52) Aglietto, M.; Bertani, R.; Ruggeri, G.; Fiordiponti, P.; Segre, A. L. Functionalization of Polyolefins. Structure of Functional Groups in Polyethylene Reacted with Ethyl Diazoacetate. *Macromolecules* **1989**, *22*, 1492–1493.
- (53) Díaz-Requejo, M. M.; Wehrmann, P.; Leatherman, M. D.; Trofimenko, S.; Mecking, S.; Brookhart, M.; Pérez, P. J. Controlled, Copper-Catalyzed Functionalization of Polyolefins. *Macromolecules* **2005**, *38*, 4966–4969.
- (54) Urbano, J.; Korthals, B.; Díaz-Requejo, M. M.; Pérez, P. J.; Mecking, S. Catalytic Cyclopropanation of Polybutadienes. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 4439–4444.
- (55) Beltrán, Á.; Gómez-Emeterio, B. P.; Marco, C.; Ellis, G.; Parellada, M. D.; Díaz-Requejo, M. M.; Corona-Galván, S.; Pérez, P. J. Mild Catalytic Functionalization of Styrene-Butadiene Rubbers. *Macromolecules* **2012**, *45*, 9267–9274.
- (56) Hashimoto, T.; Iguchi, N.; Oyamada, J.; Kitamura, T. Direct Functionalization of Polystyrenes by Platinum(II)-catalyzed Hydroarylation. A New Methodology for Utilization of Polymers. *Chem. Lett.* **2008**, *37*, 910–911.
- (57) Mathers, R. T.; Coates, G. W. Cross metathesis functionalization of polyolefins. *Chem. Commun.* **2004**, *10*, 422–423.
- (58) Iraqi, A.; Cole-Hamilton, D. J. Polyketones via Oxidation of Polybutadienes Catalysed by Complexes of Platinum(II). *Polyhedron* **1991**, *10*, 993–995.
- (59) Boalen, N. K.; Hillmyer, M. A. Selective and Mild Oxyfunctionalization of Model Polyolefins. *Macromolecules* **2003**, *36*, 7027–7034.
- (60) McArthur, S.; Baird, M. C. Oxyfunctionalization of Polystyrene by Hydrogen Peroxide Using Non-Heme Iron Catalysts. *Eur. Polym. J.* **2014**, *55*, 170–178.
- (61) Bunescu, A.; Lee, S.; Li, Q.; Hartwig, J. F. Catalytic Hydroxylation of Polyethylenes. *ACS Cent. Sci.* **2017**, *3*, 895–903.
- (62) Azuma, C.; Mitsuboshi, T.; Sanui, K.; Ogata, N. Synthesis and Properties of Polydiene and Polypentenamer Having Formyl or Hydroxymethyl Groups and Their Photosensitive Derivatives. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 781–797.
- (63) McGrath, M. P.; Sall, E. D.; Forster, D.; Tremont, S. J.; Sendjarevic, A.; Sendjarevic, V.; Primer, D.; Jiang, J.; Iyer, K.; Klempner, D.; Frisch, K. C. Novel Polymeric Alcohols by Controlled Catalytic Polymer Functionalization. *J. Appl. Polym. Sci.* **1995**, *56*, 533–543.
- (64) Rajabi, F. H.; Nikje, M. M. A.; Taslimipour, T. Epoxidation of Styrene-Butadiene Rubber (SBR) Using In Situ Generated Dimethyldioxirane (DMD): Characterization and Kinetic Study. *Des. Monomers Polym.* **2010**, *13*, 535–546.
- (65) Nikje, M. M. A.; Rafiee, A.; Haghshenas, M. Epoxidation of polybutadiene using in situ generated dimethyl dioxirane (DMD) in the presence of tetra-*n*-butyl ammonium bromide. *Des. Monomers Polym.* **2006**, *9*, 293–303.
- (66) Gahagan, M.; Iraqi, A.; Cupertino, D. C.; Mackie, R. K.; Cole-Hamilton, D. J. A High Activity Molybdenum containing Epoxidation Catalyst and its Use in Regioselective Epoxidation of Polybutadiene. *J. Chem. Soc., Chem. Commun.* **1989**, *21*, 1688–1690.
- (67) Nicol, M.; Cole-Hamilton, D. J. The Synthesis of Polyepoxides from Unsaturated Polymers and their Attempted Isomerisation to Polyketones. *J. Mater. Chem.* **1998**, *8*, 1511–1515.
- (68) Jian, X.; Hay, A. S. Catalytic Epoxidation of Styrene-Butadiene Triblock Copolymer with Hydrogen Peroxide. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1183–1189.
- (69) Xu, L.; Li, B. G.; Jie, S.; Li, Z.; Bu, Z. 110th Anniversary: The Epoxidation of Polybutadiene via Reaction Controlled Phase-Transfer Catalysis. *Ind. Eng. Chem. Res.* **2019**, *58*, 13085–13092.
- (70) Gregório, J. R.; Gerbase, A. E.; Martinelli, M.; Jacobi, M. A. M.; De Luca Freitas, L.; Von Holleben, M. L. A.; Marcico, P. D. Very Efficient Epoxidation of 1,4-polybutadiene with the Biphasic System Methyltrioxorhenium (MTO)- $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}_2$. *Macromol. Rapid Commun.* **2000**, *21*, 401–403.
- (71) Gregório, J. R.; Gerbase, A. E.; Mendes, A. N. F.; Marcico, P. D.; Rigo, A. Pre-determination of the Epoxidation Degree of Polydienes

Using Methyltrioxorhenium-CH₂Cl₂/H₂O₂ Biphasic Catalytic System. *React. Funct. Polym.* **2005**, *64*, 83–91.

(72) Rajabi, F. H.; Alavi Nikje, M. M.; Taslimipour, T. Epoxidation of Styrene-Butadiene Rubber (SBR) Using *In Situ* Generated Dimethyldioxirane (DMD): Characterization and Kinetic Study. *Des. Monomers Polym.* **2010**, *13*, 535–546.

(73) Alavi Nikje, M. M.; Mozaffari, Z. Chemoselective Epoxidation of Hydroxyl-terminated Polybutadiene (HTPB) Using *In Situ* Generated Dimethyldioxirane (DMD). *Des. Monomers Polym.* **2007**, *10*, 67–77.

(74) Alavi Nikje, M. M.; Rafiee, A.; Haghshenas, M. Epoxidation of Polybutadiene Using *In Situ* Generated Dimethyldioxirane (DMD) in the Presence of Tetra-*n*-butyl Ammonium Bromide. *Des. Monomers Polym.* **2006**, *9*, 293–303.

(75) Alavi Nikje, M. M.; Mozaffari, Z. Polybutadiene and Hydroxyl-Terminated Polybutadiene Epoxidation Using *In Situ* Generated Dimethyl Dioxirane (DMD)/Transition Metal Salts Complex. *Des. Monomers Polym.* **2008**, *11*, 271–281.

(76) Alavi Nikje, M. M.; Soleimani, M.; Mozaffari, Z. *In situ* Generated Dimethyl Dioxirane (DMD)/Copper(II) (2,20-diamino-4,4'-bithiazole) Complex as a New Oxidant for Polybutadiene and Hydroxyl Terminated Polybutadiene (HTPB) Epoxidation. *J. Elastomers Plast.* **2009**, *41*, 41–64.

(77) Thordarson, P.; Bijsterveld, E. J. A.; Rowan, A. E.; Nolte, R. J. M. Epoxidation of Polybutadiene by a Topologically Linked Catalyst. *Nature* **2003**, *424*, 915–918.

(78) Guo, X.; Rempel, G. L. Catalytic Hydrosilylation of Diene-Based Polymers. 2. Hydrosilylation of Styrene-Butadiene Copolymer and Nitrile-Butadiene Copolymer. *Macromolecules* **1992**, *25*, 883–886.

(79) Guo, X.; Farwaha, R.; Rempel, G. L. Catalytic Hydrosilylation of Diene-Based Polymers. 1. Hydrosilylation of Polybutadiene. *Macromolecules* **1990**, *23*, 5047–5054.

(80) Baum, K.; Baum, J. C.; Ho, T. Side-Loop Polymers Based on the Hydrosilylation of Polybutadiene. *J. Am. Chem. Soc.* **1998**, *120*, 2993–2996.

(81) Iraqi, A.; Seth, S.; Vincent, C. A.; Cole-Hamilton, D. J.; Watkinson, M. D.; Graham, I. M.; Jeffrey, D. Catalytic Hydrosilylation of Polybutadienes as a Route to Functional Polymers. *J. Mater. Chem.* **1992**, *2*, 1057–1064.

(82) Hou, S.; Gong, X.; Chan, W. K. Synthesis and Characterization of Polystyrene-*block*-polyisoprene Functionalized with Aromatic 1,3,4-oxadiazoles by Metal Catalyzed Reaction. *Macromol. Chem. Phys.* **1999**, *200*, 100–105.

(83) Gabor, A. H.; Lehner, E. A.; Mao, G.; Schneggenburger, L. A.; Ober, C. K. Synthesis and Lithographic Characterization of Block Copolymer Resists Consisting of Both Poly(styrene) Blocks and Hydrosiloxane-Modified Poly(diene) Blocks. *Chem. Mater.* **1994**, *6*, 927–934.

(84) Hwang, S. S.; Ober, C. K.; Perutz, S.; Iyengar, D. R.; Schneggenburger, L. A.; Kramer, E. J. Block Copolymers with Low Surface Energy Segments: Siloxane- and Perfluoroalkane-Modified Blocks. *Polymer* **1995**, *36*, 1321–1325.

(85) Samuel, J. D. J. S.; Dhamodharan, R.; Ober, C. K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1179–1183.

(86) Naga, N.; Ishinoda, S.; Ishiguro, H.; Ishikawa, G.; Noguchi, K. Modification and Thermal Properties of Syndiotactic-1,2-polybutadiene. *Polym. Bull.* **2019**, *76*, 241–257.

(87) Chauhan, B. P. S.; Balagam, B. Silyl Functionalization of Polyolefins. *Macromolecules* **2006**, *39*, 2010–2012.