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Towards Sustainable Polymer Chemistry with Homogeneous Metal-Based Catalysts

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Abstract

In the last two decades, numerous catalytic methods have become woven into the fabric of green and sustainable chemistry. In order to qualitatively evaluate and construct a tangible meaning for sustainable processes in polymer chemistry, this perspective outlines ten desirable attributes of homogeneous metal-based catalysts to prepare monomers and polymers within the context of sustainability. Catalysts were evaluated with respect to their activity, composition, and potential environmental impact. In many cases, the most pertinent catalysts tolerate a wide range of functional groups and eliminate purification or synthetic steps. Desirable catalysts also exhibit low toxicity, diminish chemical waste, and allow replacement of toxic chemicals with benign alternatives. Ideally, catalysts operate with extended lifetimes and only require minimal catalyst loadings.

Introduction

The concept of green chemistry, which represents one aspect of the broader notion of sustainability, was introduced in the early 1990's to promote awareness about the impact of chemical processes on natural environments.[1,2] Green chemistry has been defined as preferentially utilizing renewable raw materials while eliminating waste and avoiding the use of toxic elements or hazardous reagents and solvents.[3] Metal-based catalysis has become an integral part of more environmentally friendly chemical processes since metal catalysts can facilitate chemical transformations while eliminating waste by-products.[4] Thus, catalysis represents an essential facet of sustainability and its importance continues to increase with the global emphasis on pollution reduction. Decades of research on metal-based catalysts[5,6] combined with the conceptual framework of green chemistry[7,8] have laid the foundation for developing an understanding of how to best address issues related to sustainable polymer chemistry.

The following perspective outlines some helpful criteria for optimizing homogeneous metal-catalyzed processes in the context of sustainable polymer chemistry. These criteria bear similarity to the green chemistry principles which have been specifically addressed by Anastas and Warner[3] and broadly defined by Collins.[9,10] The criteria have also been influenced by the concept of atom economy,[11,12] the broader picture of sustainability,[1,10,13] the ongoing discussion of sustainability ethics,[14,15] and dialogues regarding future global challenges.[16-18] Additionally, green chemistry metrics, such as Sheldon's E factor (environmental factor)[19] and effective mass yield (EMY),[20] have been a contributing factor in the development of the criteria.

This perspective is not intended to be comprehensive, but rather to identify current trends and help evaluate catalytic processes in relation to the synthesis of monomers and polymeric materials. The interested reader is referred to other excellent sources for further background information on green chemistry.[4,21,22]

Desirable Attributes of Catalysts

The concept of a sustainable polymerization rests on a continuum that depends on many attributes. Since metal-based catalysis can serve as a vehicle to achieve sustainability in polymer chemistry, this perspective addresses two questions:

First, *what attributes will enable a catalytic monomer synthesis or polymerization process to maximize the degree of sustainability?* Accordingly, the first seven attributes listed below describe the benefits of selectivity, efficiency, functional group tolerance, and sustainable reaction conditions. The last three criteria describe potential methods for the synthesis of catalysts in an effort to achieve a completely benign chemical process as mentioned in criteria 1-7. These ten criteria are envisioned to reflect the momentum that continues to build toward sustainable polymer chemistry.

Second, *how do we evaluate whether a metal-mediated catalytic process is sustainable?* Sustainability metrics[23,24] and indicators[25] are often used to help assess an individual chemical process. The criteria listed below offer a more qualitative approach to evaluate sustainability in polymer chemistry. Each criterion is followed by selected examples of metal-mediated catalysis for either monomer or polymer synthesis.

An integral evaluation of all the criteria outlined in this perspective is discussed in the final section. In many cases, the catalytic examples in this brief perspective focus on the 7th principle of green chemistry (use of renewable resources) as well as potentially useful organic reactions for the synthesis of monomers. The desirable attributes for green and sustainable catalytic processes are listed below:

1) Maximizing selectivity – towards regioselective and stereoselective reactions.
2) Choosing catalysts which provide maximum atom economy – avoiding by-products and replacing undesirable reagents.

3) Decreasing catalyst loading – from high catalyst loadings to ppm loadings.
4) Catalyst recovery and recycling – immobilization and smart systems for recovery of catalyst components.
5) Extending the lifetime of catalytic systems – from catalysts which are sensitive to impurities towards robust ones.
6) Selecting catalysts tolerant to different functional groups – from a limited to a broader substrate scope.
7) Sustainable reaction conditions – operating in alternative reaction media and mild conditions.
8) Synthesizing ligands and catalyst complexes in one or two steps from commercial sources – from tedious to facile catalyst preparation.
9) Selecting the most suitable elements – from expensive rare elements to inexpensive abundant ones.
10) Selecting catalyst components with low toxicity – from toxic elements to non-toxic ones.

1) Maximizing selectivity

Obtaining high degrees of chemo-, regio- and/or stereo-control has been a long sought after goal for metal-based catalytic processes. Historically, an important achievement in polymer chemistry was Ziegler's discovery of ethylene polymerization using $TiCl_4$ with triethylaluminum as a cocatalyst.[26] The ability to obtain high molecular weight linear polyethylene at low pressures (<1 MPa) and temperatures (60-110 °C) provided an invaluable alternative to the branched polyethylene obtained from radical polymerizations at high pressure (~300 MPa) and temperatures (~300 °C).[27,28] Natta's application of these systems to propylene and other α-olefins led to development of a stereoregular polymerization catalyst that produced isotactic polymers.[29,30] For these remarkable discoveries, Ziegler and Natta were awarded the Nobel Prize in 1963.

The findings of Ziegler and Natta combined with the synthesis of titanocene dichloride (Cp_2TiCl_2) by Wilkinson and Birmingham[31] in 1954 began to inspire decades of work on homogeneous, single-site catalysts for olefin polymerization. The field was further invigorated by the discovery of methylaluminoxane (MAO) by Sinn and Kaminsky[32] and the synthesis of chiral *ansa* metallocene derivatives by Brintzinger.[33,34] The ansa metallocenes paved the way for the isotactic polypropylene work of Ewen[35] at Exxon Chemical Company and Kaminsky's[36] group in Hamburg. Subsequently, many great advances in catalyst design unfolded to provide stereo- and regio-control,[37-39] alternating copolymers,[40] living single–site polymerization,[41,42] functional group incorporation,[43-45] and polar vinyl monomer incorporation.[46-49] Other homogeneous metal-based catalysts, such as those which allow atom transfer radical polymerization (ATRP), have also emerged as powerful tools to control macromolecular architectures in terms of composition, function and topology.

Given the rich history of homogeneous catalysts in the last 50 years, the stage has been set for selective metal-based catalysts to contribute to the goal of sustainability. Already, a range of small molecule reactions have been reported that indicate the potential of homogeneous catalysts in the area of monomer synthesis. For example, catalytic oxidation of glycerol to dihydroxyacetone,[50] isomerizing alkoxycarbonylation of methyl oleate,[51] and oligomerization of ethylene[52] all proceed with high yields and selectivity. These types of selective reactions are more efficient and produce less undesired products. Consequently, selectivity can be viewed as a way to address Principle 1 (Prevent Waste) of the 12 Principles of green chemistry. Additionally, if a highly selective reaction can avoid the need for additional purification steps, such as distillation, then principle 6 (Design for Energy Efficiency) can also be addressed. For polymerization systems, stereoselectivity has been reported for the polymerization of renewable methylene butyrolactones,[53] lactides,[54] and β-butyrolactone.[55]

2) Choosing catalysts which provide maximum atom economy

Catalysts which are well suited for sustainable polymer chemistry should maximize atom economy. This section will highlight two approaches for improving atom economy in the design of synthetic experiments through elimination or replacement of components, such as reagents and solvents. This discussion of atom economy, which is Principle 2 of the 12 Principles of green chemistry, overlaps with Principle 1 (Prevent Waste) and Principle 3 (Less Hazardous Chemical Syntheses).

Quantifying atom economy has been aptly achieved with the E factor.[4] In contrast to the E factor [total waste (kg) / product (kg)], Hudlicky has proposed "effective mass yield" (EMY) as a metric for quantifying aqueous systems or those involving "reagents or solvents that have no known environmental risk associated with them."[20] The EMY value represents a percentage that is calculated by considering the product mass relative to the mass of materials that are not benign. In other words, water, saline, and ethanol would not be part of the EMY calculation.

A *first method* for maximizing atom economy reduces the E factor by eliminating workup procedures, extra synthetic steps, and waste by-products. For instance, a one-pot multicatalytic strategy involving carbonylation of propylene oxide and subsequent polymerization of the resulting lactone with a Zn-BDI catalyst has been used to eliminate workup and exposure to a toxic β-butyrolactone monomer.[56] Catalytic chain-growth polymerizations with anhydrides and epoxides provide an alternative to step-growth polymerizations with diesters and diols.[57,58]

Since solvents and inorganic salts from oxidations and reductions comprise a substantial fraction of the waste generated during chemical reactions used in the synthesis of monomers,[19] a *second strategy* for improving atom economy involves replacing reagents with better alternatives.[20,59] For example, catalytic oxidations with hydrogen peroxide and oxygen offer advantages over less desirable stoichiometric reagents for a number of heterogeneous[60,61] and homogeneous[62-64] catalyst systems.

Table 1 gives a selection of applied oxidants with their actual oxygen content. The wt % oxygen in Table 1 emphasizes that hydrogen peroxide and molecular oxygen provide the best choices from the standpoint of Principle 2 (Atom Economy), Principle 3 (Less Hazardous Chemical Syntheses), and Principle 4 (Design Benign Chemicals) of green chemistry. Since oxidation reactions are commonly used for synthesis of a variety of monomers, Table 1 has wide ranging implications.

Table 1. Selection of commonly used oxidants in organic and industrial chemistry.[65]

Entry	Oxidant	Active oxygen content [wt %]	Waste product
1	O_2	100	-
2	H_2O_2	47	H_2O
3	NaOCl	21.6	NaCl
4	*t*-BuOOH	17.8	*t*-BuOH
5	*m*-CPBA	9.3	*m*-CBA

The homogeneous synthesis of 1,4-cyclohexadiene (1,4-CHD) from the polyunsaturated fraction of plant oils replaces undesirable reagents by providing an alternative to the Birch reduction of benzene.[66] In Figure 1, isomerization of 1,4-CHD to 1,3-CHD also avoids the need for dehydrohalogenation reactions which produce halogenated waste.[67]

Polymerization of the resulting 1,3-CHD with Ni(acac)$_2$ in the presence of methylaluminoxane (MAO) resulted in highly crystalline polycyclohexadiene (polyCHD).

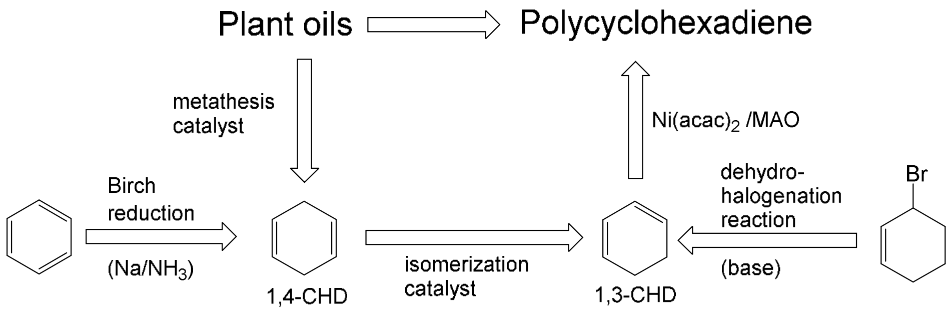

Figure 1. Green alternatives to the synthesis and polymerization of cyclohexadiene isomers which provide options for Birch reduction of benzene and dehydrohalogenation reactions.

3) Decreasing catalyst loading

Low catalyst loadings combined with high turnover numbers (TON) and large polymerization activities have always been desirable from industrial and academic standpoints. Many Ziegler-Natta polymerization catalytic systems composed of $MgCl_2/TiCl_4$ demonstrate extremely high catalyst activities that translate into ppm levels (or less) of catalyst in the final polyolefin. For instance, fifth-generation diether-based Ziegler-Natta systems will catalyze polymerization of propylene with activities > 100 kg polypropylene/g catalyst which equates to < 10 ppm.[68]

Although high catalyst loadings are often necessary to demonstrate proof of concept, the influence of green chemistry and the desire for sustainability in polymer chemistry has resulted in the development of catalytic systems which operate below 100 ppm (0.01 mol %). Certain metal-amide complexes, such as the well-known [BDI-^{i}Pr]ZnN(SiMe$_3$)$_2$ catalyst (BDI = β-diimine), have been reported to polymerize up to 20000 equivalents (50 ppm Zn) of lactide for the preparation of polylactide-*block*-polystyrene diblock copolymers[69] and up to 50000 equivalents (20 ppm Zn) of TMC.[70]

Microreactors have the potential to reduce the catalyst loading that is typically required for heterogeneous[71,72] and homogeneous [73] reactions. Although the term microreactor denotes chemistry done in small channels (10-1000 μm), the continuous flow conditions can result in faster output than batch reactions without heat transfer problems. Additionally, microreactors often offer improved selectivity, higher yields, and lower waste.[74,75] For example, integrating metathesis catalysts with microfluidic systems improves the ethenolysis of methyl oleate (Figure 2) by increasing the ethylene diffusion and results in conversions at low catalyst loadings of 50 ppm.[76] The terminal alkene in methyl 10-undecenoate provides a variety of options for subsequent conversion to polyesters and polyurethanes.[77,78]

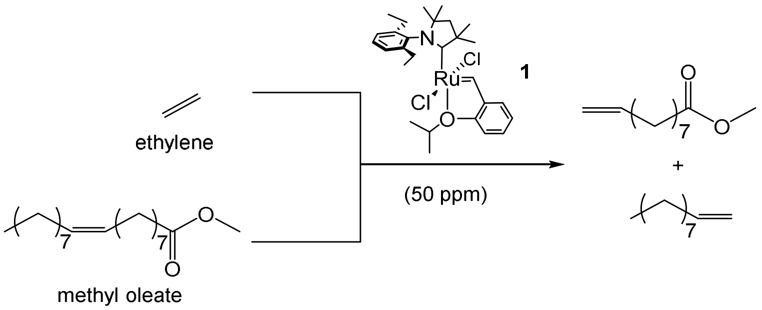

Figure 2. Ethenolysis of methyl oleate to methyl 10-undecenoate with dual-phase microchemical reactor system.

Certain copper-based catalyst systems for atom transfer radical polymerization (ATRP) have improved greatly during the last decade.[79-81] These systems can operate with substantial reduction in catalyst loadings for the polymerization of vinyl monomers, such as styrenes, acrylates, and methacrylates.[42,82] Current methods, such as activators regenerated by electron transfer (ARGET) ATRP,[83] and initiators continuously activated by reduction (ICAR) ATRP,[84] have reduced Cu loading from ~1 mol % for normal ATRP to only 1-50 ppm. The conversion of oxidatively stable CuX_2 to CuX (X = Cl, Br) can be accomplished with reducing agents, such as ascorbic acid or AIBN (Figure 3). Since Cu^{II}/Ligand complexes act as deactivators, the resulting reduction of Cu^{II}/Ligand to Cu^{I}/Ligand allows polymerization to continue.

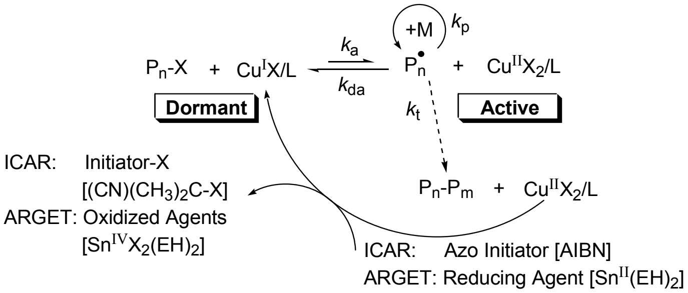

Figure 3. Novel methods of atom transfer radical polymerization (ATRP) with ppm amounts of Cu-based catalysts which utilize reducing agents or free-radical sources to regenerate Cu^{I}.

4) Catalyst recovery and recycling

Catalyst recovery, recycling, and regeneration represent an important facet of sustainability.[85-87] The following section focuses on immobilized systems, smart systems, and physical methods of recycling homogeneous systems. Immobilizing catalysts on heterogeneous supports is a common method for catalyst recovery. Generally, the desire to recover catalyst components increases as the abundance of the components decreases and the toxicity increases. Even before the field of green chemistry was developed in the early 1990s, many industrial polymerization processes had a long history of addressing the issue of catalyst recovery using inert supports composed of silica, alumina, calcium carbonate, magnesium chloride, and carbon.[88]

Currently, many types of supported catalysts are an important part of polymer chemistry as well as organic chemistry and petroleum processing.[88,89] Advances in nanoparticles, magnetic particles, and polymer supports offer many benefits and options for recovery of catalysts.[85,87,90-96] Renewable sources of carbon are also well suited as supports for heterogeneous catalysts.[97] Such supports can make it easier to recover components for the purpose of recycling, but do not guarantee that an active species will be recovered or that the catalyst will not leach off the support.[98] Ideally, a catalyst should be able to maintain activity and demonstrate acceptable TON values for multiple cycles.[99]

A number of solution-phase methods have been reported for the recovery and recycling of catalysts.[100] These include membrane separation methods[101] as well as solid/liquid[87] and liquid/liquid[102] methods for recovery of catalysts. Additionally, photo-activated conversion of homogeneous reactions to solid-phase systems has been reported for organic synthesis[103] and polymer chemistry.[104,105] For industrial hydroformylation reactions, aqueous biphasic catalysis with a sulfonated triphenylphosphine ligand **2** (Figure 4) makes the rhodium catalyst water soluble while the product is solubilized in an organic layer.[106] Non-polar α-olefins, which are often used as comonomers in ethylene polymerization are prepared using the Shell Higher Olefin Process (SHOP). This example of biphasic recycling for nickel catalysts[100] allows separation of the non-polar α-olefins from a 1,4-butanediol layer containing the catalyst.

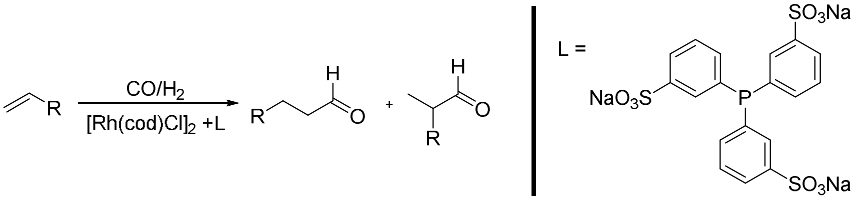

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Figure 4. Hydroformylation of alkenes with a recyclable rhodium catalyst system.

5) Extending the lifetime of catalytic systems

All catalysts eventually experience deactivation, leaching, oxidation, or decomposition which limits the activity.[86] Problems with catalyst lifetime may result from sensitivity to water, oxygen, salts, or other impurities that may be present in petroleum-based chemicals or biomass. An important aspect of green chemistry is to extend lifetime of catalysts and catalyst precursors through regeneration.[107] Historically, such practices were commonly employed for optimizing Ziegler-Natta catalysts over the course of several decades which preceded the field of green chemistry.[88]

Iterative ligand design strategies are widely used across the fields of polymer chemistry and green chemistry for the synthesis of robust catalyst systems. For iron-based tetra-amido macrocyclic ligands (TAML), such strategies have led to new generations of more robust TAML catalysts.[108] Complexes which hydroxylate tertiary CH bonds using hydrogen peroxide have also greatly benefited from an iterative ligand design by applying the concept of steric isolation of the metal site.[109,110]

Electron transfer offers interesting possibilities for activating catalyst precursors and extending the lifetime of the active catalytic species through subsequent regeneration. Although electron transfer does not necessarily qualify a catalytic process as green or sustainable, such benign activation has potential to control chemical processes.[111] For example, electrochemical activation provides the ability to turn transition metal catalysts on and off during ATRP.[112] The resulting electrochemical polymerization with copper-based ATRP catalysts allows precise control of polymerization rate. In other cases, zero valent metals, such as Zn^0, Mg^0, and Fe^0, allow the heterogeneous reactivation of homogeneous catalysts during ATRP of methyl acrylate with $CuBr_2$/Me_6TREN.[113-117]

6) Selecting catalysts tolerant of different functional groups

In order to realize Principle 7 (Use of Renewable Feedstocks) in the context of catalysis (Principle 9), a high level of functional group tolerance is necessary. For example, it is not uncommon to find renewable-based molecules with alcohols (sucrose, glucose), esters (triglycerides, lactide), amides (chitin), ketones (levulinic acid), aldehydes (furfural), ethers (cellulose, lignin), phenols (lignin, eugenol), carboxylic acids (citric acid, succinic acid), and alkenes (terpenes).[118] Additionally, many of the 30 most potentially useful bio-based molecules, which have been identified by the US Department of Energy, contain carboxylic acids.[119] These include three-carbon (lactic acid), four-carbon (succinic acid, malic acid), five-carbon (levulinic acid), and six-carbon (citric acid, 2,5-furan dicarboxylic acid) molecules.

Since renewable resources span a wide range of functional groups, they often require a sequential combination of catalytic methods that extends beyond homogeneous catalysis and usually includes biotechnology and heterogeneous catalysis.[22,120,121] In Figure 5, these challenges have been addressed for a variety of monomers. For homogeneous polymerizations, catalysts which tolerate the functional groups in renewable lactones,[53,122] lactides,[123,124] glycolides,[125] cyclic carbonates,[126,127] have substantially advanced the field.

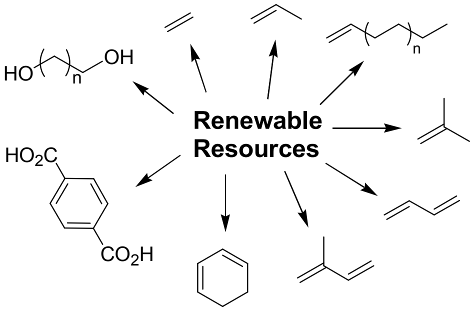

Figure 5. Synthesis of industrially relevant monomers from biomass.[121]

7) Sustainable reaction conditions

The concept of sustainable reaction conditions stems from the 12 principles of green chemistry and the desire to minimize the E factor. As a result, this section provides examples which emulate principle 5 (Benign Solvents and Auxiliaries), principle 6 (Design for Energy Efficiency), and principle 12 (Inherently Benign Chemistry for Accident Prevention).

Designing catalysts which operate in benign solvents,[128] unconventional media,[129] or under solvent free conditions[130] is advantageous in many aspects especially to minimize waste. Example of alternative media include ionic liquids,[131,132] supercritical water,[133] supercritical CO_2,[134-136] lignin derivatives,[137] and glycerol.[138] Monoterpenes such as *D*-limonene and *β*-pinene, will solvate a variety of transition metal catalysts[139] while controlling molecular weight,[140] polymer architecture,[141] and modulus[142] through chain transfer. Other strategies have used styrene as a solvent for lactide polymerization prior to the polymerization of polylactide-*block*-polystyrene diblock copolymers.[69]

Traditionally, many ionic type reactions involving electrophilic or nucleophilic addition require inert atmospheres, anhydrous solvents, certain temperatures ranges, or other special conditions.[143,144] For example, the cationic polymerization of isobutylene has traditionally been conducted at low temperatures (-90 to -30 °C) in halogenated solvents such as chloromethane.[145] Recent advances allow cationic polymerizations of β-pinene,[146] isobutylene,[147,148] and isoprene[149] under more mild conditions. In Figure 6, perfluoroarylated aluminum and gallium complexes produce polyisobutylene at a relatively high temperatures (-20 to 26 °C) without the need for chlorinated solvents. Other Lewis acids, such as gallium triflate,[150] have also been shown to be water stable and useful for the synthesis of ε-caprolactam via the Beckmann rearrangement. These examples underscore the need to consider alternative approaches when designing sustainable chemical reactions.

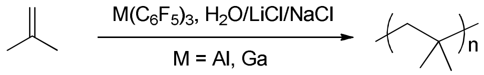

Figure 6. Polymerization of isobutylene with aluminum and gallium-based Lewis acids at ambient temperature.[148]

Mild reaction conditions reflect the 12 principles of green chemistry[7] by reducing energy consumption and hazardous reaction conditions. Ambient temperature,[151] atmospheric pressure,[152] and decreased sensitivity to impurities[107] are all valid parameters for evaluating whether reaction conditions are mild. Bimetallic cobalt[127,153] and iron[154] catalysts successfully copolymerize CO_2 and epoxides at 1 atm of CO_2. Alternate strategies involving microwave irradiation[155,156] and photochemical transformations[157,158] are also an integral part of ongoing research efforts. Although the pursuit of mild reaction conditions is highly desirable, challenging problems related to catalyst solubility, low reaction yields, reduced activity at ambient temperatures, poisoning of active sites, and side reactions often result. For Heck, Suzuki-Miyaura, Sonogashira, and Negishi-like C-C couplings, incorporation of designer surfactants (Figure 7) helps overcome solubility limitations and facilitates improved reactivity in water at room temperature.[159]

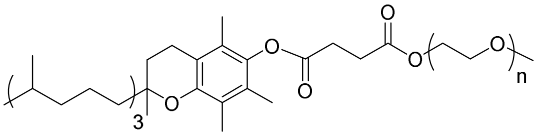

Figure 7. Example of an environmentally benign surfactant (n ~16) for metal-based catalysts.

Formation of lactones,[160] lactams,[160] nitriles,[161] carbamates,[162] and oxazolines[163] under mild conditions has wide ranging implications for monomers. In the case of heterocycle carbonylation with homogeneous catalysts, many of these catalyst systems combine cationic Lewis acids with a nucleophilic anion to facilitate ring-opening of the heterocycle before insertion of CO and subsequent ring-closing.[160] Generally, many of these catalysts often require high pressures of CO (~45 to 60 atm) to suppress ketone formation as a side product. In Figure 8, carbonylation of epoxides with a $[(\text{salph})\text{Cr}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$ catalyst [salph = *N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine] at 1 atm and ambient temperature resulted in high conversions (> 98%) and minimal ketone formation after 24 h.[164]

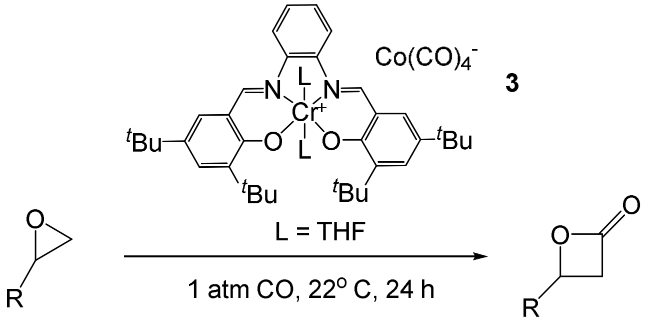

Figure 8. Carbonylation of epoxides with a $[(salph)Cr(THF)_2]^+[Co(CO)_4]^-$ catalyst [salph = *N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine].

8) Synthesizing ligands, complexes, and catalysts in one or two steps from commercial sources

Ideally, the synthesis of ligands and homogeneous catalysts could be synthesized in one- or two-steps. Although many procedures to synthesize catalysts often require multiple steps to achieve high catalyst activity, the need for benign, efficient protocols for synthesizing and immobilizing catalysts reflects Principle 2 (Atom Economy) and Principle 8 (Reduce Derivatives) of green chemistry. Furthermore, it has been suggested that the perfect scenario for such a synthesis procedure would involve “readily available and inexpensive” reagents without the need for solvents, heating, cooling, or inert atmospheres.[107] The desire for one-step procedures to simplify the synthesis of catalysts mirrors the use of one-pot procedures in organic chemistry to create small molecules.[61]

Mannich condensation reactions, such as shown in Figure 9, allow the one-step synthesis of phenolic ligands using inexpensive reagents for the preparation of alumatrane complexes **1**.[165] Other ligand procedures utilizing Mannich reactions have been reported with amine-bis(phenolate) iron(III) complexes for ATRP.[166]

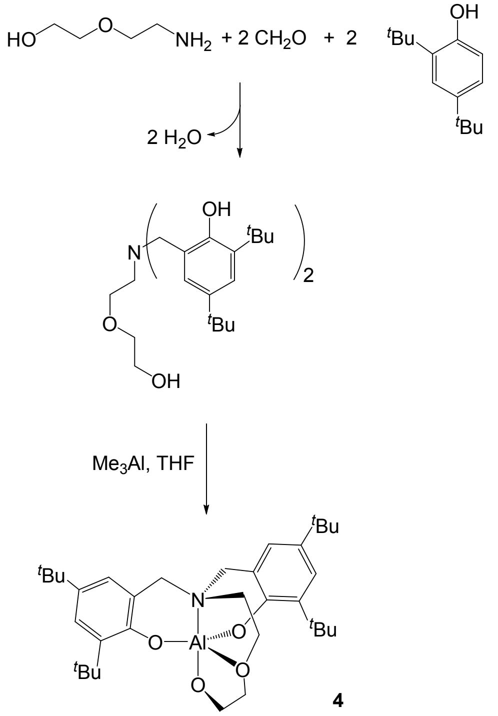

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Figure 9. One-step synthesis of a phenolic-amino-alcohol ligand via Mannich condensation followed by metalation with trimethylaluminum to yield an alumatrane complex **1**.[165]

9) Selecting the most suitable elements

Choosing the most appropriate elements for catalyst systems is an integral part of green chemistry and sustainability. One criterion for element selection is the natural abundance in the earth's crust. Abundance can be roughly categorized into extremely abundant (> 30,000 ppm; e.g. O, Si, Al, Fe, Ca), highly abundant (15,000-30,000 ppm; e.g. Mg, Na, K), moderately abundant (300-15,000 ppm, e.g. Ti, H, P, Mn, F, C, S), low abundance (10-300 ppm; e.g Zr, V, Cl, Cr, Ni, Zn, Cu, Ce, Nd, La, Co), scarce elements (1-10 ppm; e.g. B, Br, I,) and those only present in trace quantities (< 1 ppm; e.g. Pd, Pt, Ir, Ru, Rh).[167,168] Selecting abundant elements can alleviate economic concerns (Figure 10) as there will typically be multiple mining sources. Often, obtaining trace elements (Pd, Pt, Ir, Ru, Rh) is difficult as they are only mined in limited areas of the world.[169,170] Some elements, such as iridium, ruthenium, and osmium are both geographically limited and present in extremely small quantities.[169] The selection of abundant elements is of high priority but in some cases, these metals will not produce the desired chemical outcome and consequently, they cannot always be used. A second consideration in element selection for monomer and polymer synthesis is biocompatibility.[171,172] Polymers which are being targeted for biological or environmental applications will ideally, be prepared from "biochemically common elements."[10]

Most often, catalyst choice is driven by economics (Figure 10), function and selectivity. However, to utilize only these criteria may not be viable in the broader picture of sustainability. A recent life cycle assessment of metals has suggested that many efforts to recycle common metals are inefficient (Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) or practically

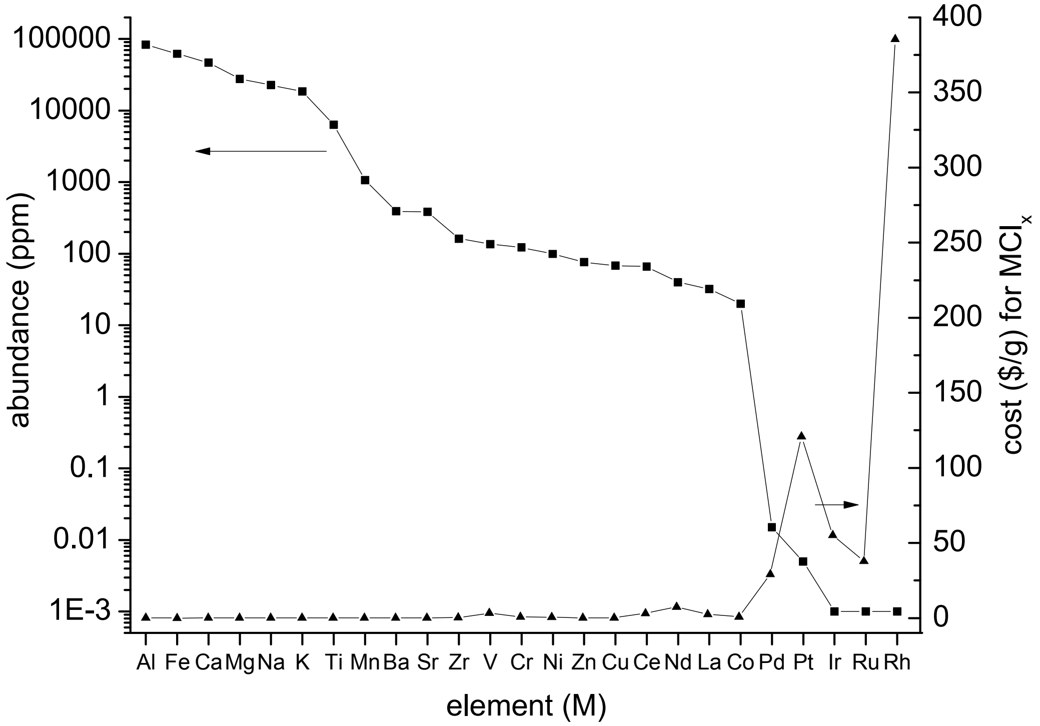


Figure 10. Abundance[167] and cost[173] for the twenty most abundant metals compared to five examples of metals (Pd, Pt, Ir, Ru, Rh) with trace abundance.

nonexistent (<1%) for rare earths and specialty metals (Li, Sc, V, Ga, Sr, Y, Zr, In, Ba, Hf, Ta, Os).[174] Consequently, to reduce toxic metal waste within the natural environment, catalysis with abundant metals and "biochemically common elements" has emerged. The following examples highlight aluminum, some first-row transition metals, as well as a few alkali and alkaline earth metals in monomer and polymer synthesis.

Aluminum often plays a wide variety of roles in catalysis. For example, methylaluminoxane (MAO) is commonly used as a cocatalyst during the polymerization of olefins.[88] Aluminum complexes have also been shown to ring-open lactides[165,175] to form poly(lactic acid) (PLA)[176] and also catalyze the formation and polymerization of cyclic carbonates.[177] Especially in heterogeneous catalysis, alumina is widely employed and frequently found as a support for selective oxidation, reduction and polymerization (Figure 11).[178]

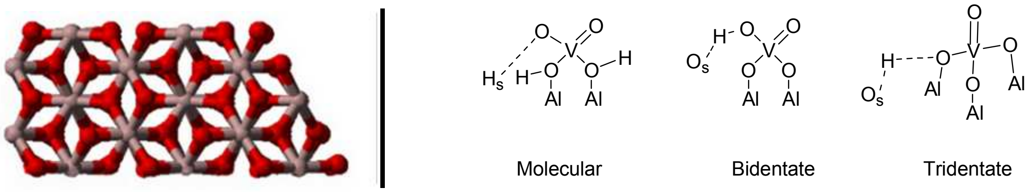


Figure 11. Aluminum oxide support and molecular view of several monomeric VO_x structures on dehydrated alumina surface(s) predominately present at low V loadings.[179]

First row transition metals, such as manganese, iron, cobalt, nickel, and copper, which are non-precious metals may provide economical alternatives to less abundant metals.[180] In this regard, great advances in homogeneous iron catalysts have been made during the last decade in the areas of oxidation,[181] reduction,[182] cross-coupling,[183] and vinyl monomer polymerization.[184-187] Epoxidation of alkenes (Figure 12) with hydrogen peroxide utilizing iron salts represents a convenient process for new monomer preparation.[62,188] Epoxidized monomers are prevalent in polymer chemistry and allow access to polyesters,[189] polycarbonates,[190] and polyurethanes.[191,192]

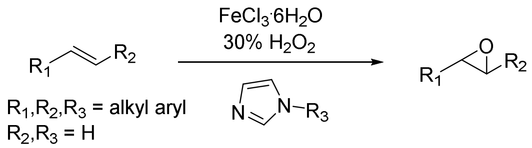
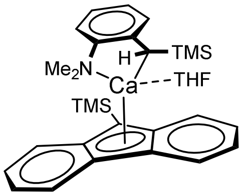


Figure 12. Epoxidation of olefins with homogeneous iron-based catalysts.

Due to their natural abundance, a number of complexes based on alkaline earth metals, such as calcium and magnesium, have also been reported.[193] Recently, dimagnesium complexes were reported for the copolymerization of CO_2 and cyclohexene oxide to produce polycarbonates.[194] Since calcium is the most abundant element of the alkaline earth metals, numerous homogeneous catalysts exist. For example, a wide variety of calcium catalysts facilitate the ring-opening polymerization of lactide,[195,196] ε-caprolactone,[197] tetrahydrofuran,[198] and trimethylene carbonate (TMC).[172,199] In addition, certain catalysts, such as those depicted in Figure 13, polymerize styrene.[200-202]


5

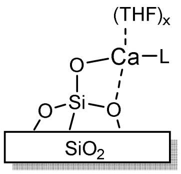

6

Figure 13. Calcium-based catalysts for polymerization of styrene [TMS = $SiMe_3$; L = $N(SiMe_3)_2$].

Due to the natural abundance of sodium in the earth's crust, the oceans, and the human body, sodium is also ideally suited for sustainability. In Figure 14, well-defined sodium complexes with commercially available 2,2’-ethylidene-bis(4,6-di-*tert*-butylphenol) (**4**) will polymerize *L*-lactide in toluene under ambient temperature and pressure.[203]

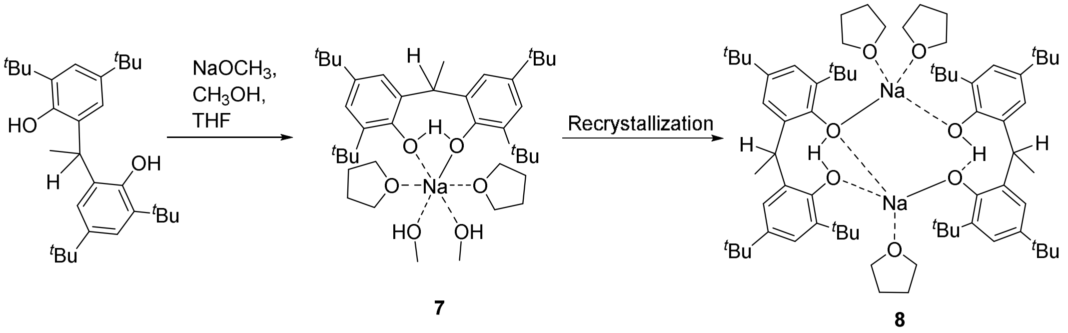


Figure 14. Synthesis of sodium catalyst for ring-opening polymerization of lactide.[203]

10) Selecting catalyst components with low toxicology

Many chemical products which are commonly found in society in the form of biomaterials, electronic materials, and thermosets depend heavily on catalysis and often contain catalyst residues. Consequently, using components (*i.e.* metals, activators, ligands) which exhibit low toxicity is advantageous and adheres to Principle 3 (Less Hazardous Chemical Syntheses) and Principle 4 (Design Benign Chemicals) of green chemistry. For homogeneous catalysts, it is worthwhile to examine potential effects of a metal-ligand complex as well as demetalation scenarios which produce ligand and metal ion.

To consider the effect of metal ions, which may result from demetalation of homogeneous catalysts, an atomistic perspective is useful. Generally, a trend in toxicity parallels the natural abundance of atoms and is known as the “abundance principle.”[204] As a result, the use of first-row transition metals has been growing across the field of green chemistry.[4,6,180] For polymer chemistry, catalytic strategies for monomer synthesis[205] and polymerization[193,206] often employ first-row transition metals.

Although the permitted daily exposure (PDE) for metals does not guarantee the absence of hazards that might arise from exposure below the limit, this atomistic approach does give a relative guide that is somewhat related to the “abundance principle.” For instance, the PDE for a 50 kg adult during an 8 h day is 100 μg/day for Pt, 250 μg/day for V, 2500 μg/day for Cu, and 13000 μg/day for Zn.[207] With this approach in mind, metals can be categorized as those with minimal safety concern (Fe, Zn), low safety concern (Cu, Mn) and significant safety concern (Pt, Pd > Ir, Rh, Ru, Os > Mo, Ni, Cr, V).[207] Figure 15 gives selected examples of the many homogeneous polymerization catalysts based on desirable metals, such as iron,[185,186,208] zinc,[209,210] and copper.[80,211]

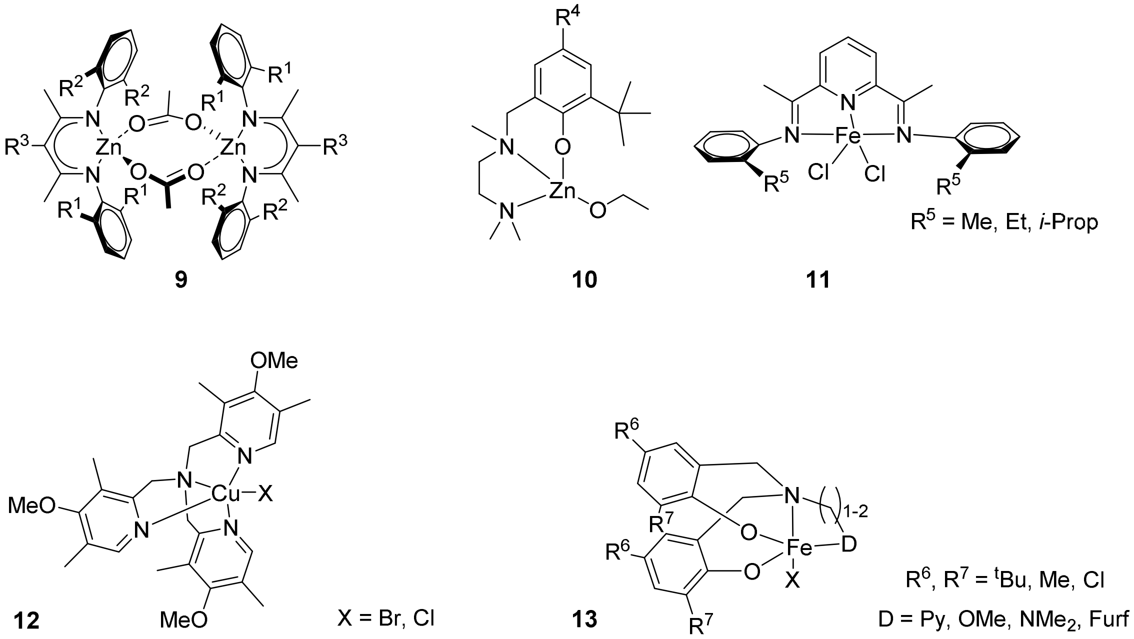


Figure 15. Examples of homogeneous metal-based catalysts using iron, zinc, and copper.

From a molecular standpoint, studies which correlate physical and chemical properties of organic molecules, such as molecular size, shape (globularity), flexibility, electronic properties, and solubility, with toxicity are particularly insightful for potential ligands or additives.[212,213] Although the toxicology of organic molecules receives considerable attention from the pharmaceutical and pesticide industries as well as regulatory agencies,[214,215] recent advances in the understanding of endocrine disrupting chemicals suggest that low doses of certain organic molecules can have adverse effects even at ppb and ppt levels.[216] Perhaps the most thorough approach for assessing risks of organic molecules is the Tiered Protocol for Endocrine Disruption (TiPED).[217] This five-tier strategy progresses from simple assessments via computational methods (Tier 1) and high-throughput screening with cells (Tier 2) to complex methodologies involving biological systems (Tiers 3-5).

Exposing developing biological systems to a homogeneous metal-ligand complex is a very informative method to examine potential hazards. For instance, a recent cellular study determined the optimum conditions and ligand environment for eliminating the toxicity of Cu(I) complexes used in azide-alkyne cycloaddition reactions.[218] Other notable models include embryonic/larval zebrafish which are permeable to chemicals up to 5 days post-fertilization.[219] Due to the wide variety of developing physiological systems in these zebrafish, the embryos offer a convenient method for screening ruthenium-*N*-heterocyclic carbene complexes[220] and octahedral iridium (III) complexes.[221] These important studies with metal-based catalysts could be highly beneficial in the future design and evaluation of catalysts for biomaterial applications.

Evaluating strategies for a homogeneous "green" polymerization processes

Zinc-based catalysts with β-diimine (BDI) ligands, such as $[(BDI)ZnO^{i}Pr]_2$ and $[BDI-^{i}Pr]ZnN(SiMe_3)_2$, have been chosen to evaluate the suggested criteria for achieving a sustainable system in polymer chemistry. As examined below, these homogeneous catalysts address many of the attributes that make a catalyst suitable for sustainable chemistry.

1) Maximizing selectivity: The $[(BDI)ZnO^{i}Pr]_2$ catalysts will polymerize *(S,S)*-lactide to isotactic PLA and *rac*-lactide to heterotactic PLA.[222]

2) Choosing catalysts which provide maximum atom economy: Zn-BDI catalysts will polymerize CO_2 and epoxides in an alternating fashion with excellent atom economy.[223] Additionally, they proceed without the need for high CO_2 pressures.

3) Decreasing catalyst loading: Since the $[BDI\text{-}^{i}Pr]ZnN(SiMe_3)_2$ catalysts operate at [monomer]/[catalyst] ratios up to 50000, they meet the requirement for minimal catalyst loading. [70]

4) Catalyst recovery and recycling: Zn-BDI type catalysts are not typically recovered after a polymerization. This is a potential future direction for these polymerization reactions.

5) Extending the lifetime of catalytic systems: These catalysts are fairly robust and allow sequential monomer addition up to a hexablock copolymers.[224] Copper catalysts have also been reported in the synthesis of decablock copolymers.[225]

6) Selecting catalysts tolerant of different functional groups. Generally, the polymerization of CO_2 with various aliphatic epoxides has been reported without functional groups tethered to the epoxide. One exception is the polymerization of vinylcyclohexene oxide and CO_2 using $[(BDI)ZnOAc]_2$.[226]

7) Sustainable reaction conditions: Zn catalysts have been reported to operate in neat monomer, such as styrene,[69] but often use petroleum based solvents such as toluene or THF. For polymerization of CO_2 and epoxides, certain zinc catalysts are capable of operating under mild reaction conditions at fairly low pressures of CO_2 gas.

8) Synthesizing ligands and catalysts in one or two steps from commercial sources. The pre-ligands are readily prepared by stirring commercial anilines with either 2,4- pentanedione or malonaldehyde bis(dimethyl acetal).[223] Deprotonation of the ligand followed by treatment with diethylzinc affords the desired zinc-dimiinate catalysts. Thus the desired criterion of a 1-2 step ligand synthesis is fulfilled.

Moreover, the availability of various anilines offers facile methods to modulate the steric and electronic environment of the ligand framework.

9) Selecting the most suitable elements: This class of catalysts meets the first requirement for a green catalyst since the elements (Zn, N, and C) are moderately abundant.
10) Selecting catalyst components with low toxicity: The Zn based catalysts employ components which probably demonstrate low toxicity, but have not been experimentally verified.

Conclusion and Outlook

This perspective has attempted to provide qualitative insight into the question of how to maximize sustainability in polymer chemistry with homogeneous metal-based catalysts. Since the degree of sustainability rests on a continuum, the best systems exhibit multiple attributes, such as low catalyst loading, high TON values, abundant elements, low toxicity, and the ability to operate under mild conditions with options for extending the catalyst lifetime or recycling the catalyst. Strategies which improve the atom economy and reduce the number of synthetic steps are also highly desirable. Catalysts which selectively transform or incorporate renewable resources into existing polymerization processes or convert renewable materials into polymers will continue to be a challenging endeavor.

Many of the suggested attributes for sustainable polymerization catalysts are interrelated. For example, the subject of toxicology has a direct link to the abundance of atoms, catalyst loading, and ability to recycle or recover catalyst components. In order to minimize toxicity, choosing abundant elements and ppm concentrations of catalyst represents a starting point for metal-based homogeneous catalysis. However, in some cases, low catalyst activities may require much higher catalyst loadings or components with low natural abundance. In this case, immobilization of the catalyst system or devising recycling strategies could be very beneficial.

In the future context of polymer chemistry, many opportunities exist for homogeneous catalysis if the system can be designed to maximize the degree of sustainability. Although the brevity of this perspective only allowed a limited number of examples to be discussed, many other unmentioned catalytic processes will continue to play a critical role in conversion of petroleum and biomass-based starting materials into monomers and polymers.

Acknowledgement

RTM thanks the Alcoa Foundation for continued support of green chemistry and sustainability at Penn State. The authors acknowledge Prof. Terry Collins (CMU) for many helpful suggestions. The authors appreciate the comments and helpful suggestions of the anonymous reviewers. K.S. acknowledges the Deutsche Forschungsgemeinschaft (DFG) for her post-doctoral scholarship (SCHR 1314).

References

(1) Grassian, V. H.; Meyer, G.; Abruna, H.; Coates, G. W.; Achenie, L. E.; Allison, T.; Brunschwig, B.; Ferry, J.; Garcia-Garibay, M.; Gardea-Torresday, J.; Grey, C. P.; Hutchison, J.; Li, C.-J.; Liotta, C.; Ragauskas, A.; Minteer, S.; Mueller, K.; Roberts, J.; Sadik, O.; Schmehl, R.; Schneider, W.; Selloni, A.; Stair, P.; Stewart, J.; Thorn, D.; Tyson, J.; Voelker, B.; White, J. M.; Wood-Black, F. *Environ. Sci. Technol.* **2007**, *41*, 4840.
(2) Beach, E. S.; Cui, Z.; Anastas, P. T. *Energy Environ. Sci.* **2009**, *2*, 1038.
(3) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.
(4) Sheldon, R. A.; Arends, I.; Hanefeld, U. *Green Chemistry and Catalysis*; Wiley-VCH: Weinheim, Germany, 2007.
(5) Hagen, J. *Industrial Catalysis: A Practical Approach*; 2nd ed.; Wiley-VCH: Weinheim, Germany, 2006.
(6) Beller, M.; Renken, A.; Van Santen, R. A. *Catalysis: From Principles to Applications*; John Wiley & Sons, 2012.
(7) Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2010**, *39*, 301.
(8) Anastas, P. T.; Kirchhoff, M. M.; Williamson, T. C. *Appl. Catal., A* **2001**, *221*, 3.
(9) Collins, T. J. In *Macmillan Encyclopedia of Chemistry*; Simon and Schuster Macmillan: New York, 1997; Vol. 2, p 691.
(10) Collins, T. J. *Science* **2001**, *291*, 48.

(11) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695.
(12) Trost, B. M. *Science* **1991**, *254*, 1471.
(13) Mecking, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1078.
(14) Collins, T. *Green Chem.* **2003**, G51.
(15) Frank, H.; Campanella, L.; Dondi, F.; Mehlich, J.; Leitner, E.; Rossi, G.; Ioset, K. N.; Bringmann, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 8482.
(16) Miller, S. A. *ACS Macro Letters* **2013**, *2*, 550.
(17) Whitesides, G. M.; Deutch, J. *Nature* **2011**, *469*, 21.
(18) Panda, A. K.; Singh, R. K.; Mishra, D. K. *Renew. Sust. En. Rev.* **2010**, *14*, 233.
(19) Sheldon, R. A. *Chem. Commun.* **2008**, 3352.
(20) Hudlicky, T.; Frey, D. A.; Koroniak, L.; Claeboe, C. D.; Brammer Jr., L. E. *Green Chem.* **1999**, *1*, 57.
(21) *Handbook of Green Chemistry*; Crabtree, R. H., Ed.; Wiley-VCH: Weinheim, 2009; Vol. 1-3.
(22) Thomas, J. M. *Design And Applications Of Single-Site Heterogeneous Catalysts: Contributions to Green Chemistry, Clean Technology and Sustainability*; World Scientific Publishing Co.: London, 2012.
(23) Selva, M.; Perosa, A. *Green Chem.* **2008**, *10*, 457.
(24) Calvo-Flores, F. G. *ChemSusChem* **2009**, *2*, 905.
(25) Ruiz-Mercado, G. J.; Smith, R. L.; Gonzalez, M. A. *Ind. Engin. Chem. Res.* **2012**, *51*, 2309.
(26) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 541.
(27) Ziegler, K.; Martin, H. *Makromolekulare Chemie* **1956**, *18/19*, 186.
(28) Wu, L.; Wanke, S. E. In *Handbook of Transition Metal Polymerization Catalysts*; Hoff, R., Mathers, R. T., Eds.; John Wiley & Sons: Hoboken, NJ, 2010, p 231.
(29) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E. *J. Am. Chem. Soc.* **1955**, *77*, 1708.
(30) Natta, G. *J. Polym. Sci.* **1955**, *16*, 143.
(31) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281.
(32) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.
(33) Schnutenhaus, H.; Brintzinger, H. H. *Angew. Chem. Int. Ed.* **1979**, *18*, 777.
(34) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.
(35) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
(36) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem. Int. Ed.* **1985**, *24*, 507.
(37) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.
(38) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.
(39) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.
(40) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, *46*, 1438.
(41) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 2236.
(42) Ouchi, M.; Terashima, T.; Sawamoto, M. *Chem. Rev.* **2009**, *109*, 4963.
(43) Nomura, K.; Kitiyanan, B. *Current Org. Synth.* **2008**, *5*, 217.
(44) Younkin, T. R.; Connor, E. F.; Jason, I. H.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.
(45) Franssen, N. M. G.; Reek, J. N. H.; de Bruin, B. *Chem. Soc. Rev.* **2013**, *42*, 5809.
(46) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.
(47) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215.

(48) Chen, E. Y. X. *Chem. Rev.* **2009**, *109*, 5157.

(49) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(50) Painter, R. M.; Pearson, D. M.; Waymouth, R. M. *Angew. Chem. Int. Ed.* **2010**, *49*, 9456.

(51) Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 17696.

(52) Son, K.; Waymouth, R. M. *Organometallics* **2010**, *29*, 3515.

(53) Chen, X.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X. *J. Am. Chem. Soc.* **2012**, *134*, 7278.

(54) Sauer, A.; Kapelski, A.; Fliedel, C.; Dagorne, S.; Kol, M.; Okuda, J. *Dalton Trans.* **2013**, *42*, 9007.

(55) Fang, J.; Tschan, M. J. L.; Roisnel, T.; Trivelli, X.; Gauvin, R. M. *Polym. Chem.* **2013**, *4*, 360.

(56) Dunn, E. W.; Coates, G. W. *J. Am. Chem. Soc.* **2010**, *132*, 11412.

(57) Robert, C.; de Montigny, F.; Thomas, C. M. *Nat. Commun.* **2011**, *2*, 586.

(58) Jeske, R. C.; DiCiccio, A. M.; Coates, G. W. *J. Am. Chem. Soc.* **2007**, *129*, 11330.

(59) Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**, *45*, 851.

(60) Thomas, J. M.; Raja, R. *Chem. Commun.* **2001**, 675.

(61) Climent, M. J.; Corma, A.; Iborra, S. *Chem. Rev.* **2011**, *111*, 1072.

(62) Schröder, K.; Enthaler, S.; Bitterlich, B.; Schulz, T.; Spannenberg, A.; Tse, M. K.; Junge, K.; Beller, M. *Chem. Eur. J.* **2009**, *15*, 5471.

(63) Costas, M. *ChemCatChem* **2012**, *4*, 175.

(64) Schröder, K.; Join, B.; Amali, A. J.; Junge, K.; Ribas, X.; Costas, M.; Beller, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 1425.

(65) Adolfsson, H. In *Modern Oxidation Methods*; Bäckvall, J.-E., Ed.; WILEY-VCH: Weinheim, 2004, p 22.

(66) Mathers, R. T.; Shreve, M. J.; Meyler, E.; Damodaran, K.; Iwig, D. F.; Kelley, D. J. *Macromol. Rapid Commun.* **2011**, *32*, 1338.

(67) Mao, J. X.; Mathers, R. T.; Damodaran, K. *J. Organomet. Chem.* **2013**, *741–742*, 15.

(68) Severn, J.; Jones, R. L. In *Handbook of Transition Metal Polymerization Catalysts*; Hoff, R., Mathers, R. T., Eds.; Wiley: New York, 2010.

(69) Poirier, V.; Duc, M.; Carpentier, J.-F.; Sarazin, Y. *ChemSusChem* **2010**, *3*, 579.

(70) Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Adv. Syn. Catal.* **2009**, *351*, 1312.

(71) Frost, C. G.; Mutton, L. *Green Chem.* **2010**, *12*, 1687.

(72) Irfan, M.; Glasnov, T. N.; Kappe, C. O. *ChemSusChem* **2011**, *4*, 300.

(73) Chinnusamy, T.; Yudha, S. S.; Hager, M.; Kreitmeier, P.; Reiser, O. *ChemSusChem* **2012**, *5*, 247.

(74) Mason, B. P.; Price, K. E.; Steinbacher, J. L.; Bogdan, A. R.; McQuade, D. T. *Chem. Rev.* **2007**, *107*, 2300.

(75) Longstreet, A. R.; McQuade, D. T. *Acc. Chem. Res.* **2013**, *46*, 327.

(76) Park, C. P.; Van Wingerden, M. M.; Hans, S.-Y.; Kim, D.-P.; Grubbs, R. H. *Org. Lett.* **2011**, *13*, 2398.

(77) More, A. S.; Maisonneuve, L.; Lebarbe, T.; Gadenne, B.; Alfos, C. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 61.

(78) Ronda, J. C.; Lligadas, G.; Galià, M.; Cádiz, V. *React. Funct. Polym.* **2013**, *73*, 381.

(79) Pintauer, T.; Matyjaszewski, K. *Chem. Soc. Rev.* **2008**, *37*, 1087.

(80) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev. (Washington, DC, United States)* **2007**, *107*, 2270.

(81) Matyjaszewski, K.; Tsarevsky, N. V. *Nat. Chem.* **2009**, *1*, 276.

(82) Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015.

(83) Jakubowski, W.; Matyjaszewski, K. *Angew. Chem. Int. Ed.* **2006**, *118*, 4594.

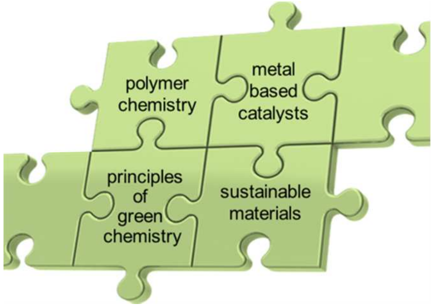
(84) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A.; Tsarevsky, N. V. *Proc. Nat. Acad. Sci.* **2006**, *103*, 15309.
(85) Madhavan, N.; Jones, C. W.; Weck, M. *Acc. Chem. Res.* **2008**, *41*, 1153.
(86) Gladysz, J. A. In *Recoverable and Recyclable Catalysts*; Benaglia, M., Ed.; John Wiley & Sons: New York, 2009.
(87) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev. (Washington, DC, United States)* **2009**, *109*, 530.
(88) *Handbook of Transition Metal Polymerization Catalysts*; Hoff, R.; Mathers, R. T., Eds.; Wiley: New York, 2010.
(89) Wittcoff, H. A.; Reuben, B. G.; Plotkin, J. S. *Industrial Organic Chemicals*; 2nd ed.; Wiley: Hoboken, NJ, 2004.
(90) Hong, S. C.; Lutz, J.-F.; Inoue, Y.; Strissel, C.; Nuyken, O.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 1075.
(91) Hong, S. C.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 7592.
(92) Hong, S. C.; Paik, H.-J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 5099.
(93) Ding, S.; Xing, Y.; Radosz, M.; Shen, Y. *Macromolecules* **2006**, *39*, 6399.
(94) Polshettiwar, V.; Varma, R. S. *Green Chem.* **2010**, *12*, 743.
(95) Clercq, B. D.; Lefebvre, F.; Verpoort, F. *Appl. Catal. A: Gen.* **2003**, *247*, 345.
(96) Liu, Y.; Rawlston, J.; Swann, A. T.; Takatani, T.; Sherrill, C. D.; Ludovice, P. J.; Weck, M. *Chem. Sci.* **2011**, *2*, 429.
(97) Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. *Nature* **2005**, *438*, 178.
(98) De Vos, D.; Vankelecom, I. F. J.; Jacobs, P. A. *Chiral Catalyst Immobilization and Recycling*; WILEY-VCH: Weinheim, 2000.
(99) *Recoverable and Recyclable Catalysts*; Benaglia, M., Ed.; Wiley: New York, 2009.
(100) Muldoon, M. J. *Dalton Trans.* **2010**, *39*, 337.
(101) Janssen, M.; Muller, C.; Vogt, D. *Green Chem.* **2011**, *13*, 2247.
(102) Bergbreiter, D. E.; Sung, S. D. *Adv. Synth. Catal.* **2006**, *348*, 1352.
(103) Bosanac, T.; Yang, J.; Wilcox, C. S. *Angew. Chem.* **2001**, *113*, 1927.
(104) Honigfort, M. E.; Brittain, W. J.; Bosanac, T.; Wilcox, C. S. *Macromolecules* **2002**, *35*, 4849.
(105) Honigfort, M. E.; Liou, S.; Rademacher, J.; Malaba, D.; Bosanac, T.; Wilcox, C. S.; Brittain, W. J. *ACS Symposium Series* **2003**, *854*, 250.
(106) Cornils, B.; Herrmann, W. A. *J. Catal.* **2003**, *216*, 23.
(107) Gladysz, J. A. *Pure Appl. Chem.* **2001**, *73*, 1319.
(108) Collins, T. J. *Acc. Chem. Res.* **2002**, *35*, 782.
(109) Chen, M. S.; White, M. C. *Science* **2007**, *318*, 783.
(110) Gómez, L.; Garcia-Bosch, I.; Company, A.; Benet-Buchholz, J.; Polo, A.; Sala, X.; Ribas, X.; Costas, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 5720.
(111) Hudlicky, T.; Claeboe, C. D.; Brammer, L. E. J.; Koroniak, L.; Butora, G.; Ghiviriga, I. *J. Org. Chem.* **1999**, *64*, 4909.
(112) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81.
(113) Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *J. Am. Chem. Soc.* **2006**, *128*, 14156.
(114) Wang, Y.; Zhong, M.; Zhu, W.; Peng, C.-H.; Zhang, Y.; Konkolewicz, D.; Bortolamei, N.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 3793.
(115) Zhong, M.; Wang, Y.; Krys, P.; Konkolewicz, D.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 3816.

(116) Peng, C.-H.; Zhong, M.; Wang, Y.; Kwak, Y.; Zhang, Y.; Zhu, W.; Tonge, M.; Buback, J.; Park, S.; Krys, P.; Konkolewicz, D.; Gennaro, A.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 3803.
(117) Konkolewicz, D.; Wang, Y.; Zhong, M.; Krys, P.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. *Macromolecules* **2013**.
(118) Gandini, A. *Green Chem.* **2011**, *13*, 1061.
(119) Werpy, T.; Petersen, G.; Aden, A.; Bozell, J.; Holladay, J.; White, J.; Manheim, A. *Top Value Added Chemicals from Biomass: Volume 1 - Results of Screening for Potential Candidates from Sugars and Synthesis Gas*, Pacific Northwest National Laboratory (PNNL) and National Renewable Energy Laboratory (NREL), 2004.
(120) *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N.; Gandini, A., Eds.; New York: Elsevier, 2008.
(121) Mathers, R. T. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1.
(122) Lowe, J. R.; Martello, M. T.; Tolman, W. B.; Hillmyer, M. A. *Polym. Chem.* **2011**, *2*, 702.
(123) Thomas, C. M. *Chemical Society Reviews* **2010**, *39*, 165.
(124) Dijkstra, P. J.; Du, H.; Feijen, J. *Polymer Chemistry* **2011**, *2*, 520.
(125) Dutta, S.; Hung, W.-C.; Huang, B.-H.; Lin, C.-C. *Adv. Polym. Sci.* **2011**, 219.
(126) Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Transactions* **2010**, *39*, 8363.
(127) Lu, X.-B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462.
(128) Kerton, F. M. *Alternative solvents for green chemistry*; RSC Publishing: Cambridge, 2009.
(129) Gu, Y. *Green Chem.* **2012**, *14*, 2091.
(130) Mathers, R. T.; LeBlond, C.; Damodaran, K.; Kushner, D. I.; Schram, V. A. *Macromolecules* **2008**, *41*, 524.
(131) Zhang, Q.; Zhang, S.; Deng, Y. *Green Chem.* **2011**, *13*, 2619.
(132) Stahlberg, T.; Fu, W. J.; Woodley, J. M.; Riisager, A. *ChemSusChem* **2011**, *4*, 451.
(133) Das, S.; Wendt, B.; Möller, K.; Junge, K.; Beller, M. *Angew. Chem. Intern. Ed.* **2012**, *51*, 1662.
(134) Grignard, B.; Jerome, C.; Calberg, C.; Jerome, R.; Wang, W. X.; Howdle, S. M.; Detrembleur, C. *Macromolecules* **2008**, *41*, 8575.
(135) Álvarez de Cienfuegos, L.; Robles, R.; Miguel, D.; Justicia, J.; Cuerva, J. M. *ChemSusChem* **2011**, *4*, 1035.
(136) Wood, C. D.; Cooper, A. I.; DeSimone, J. M. *Curr. Opin. Solid State Mat. Sci.* **2004**, *8*, 325.
(137) Azadi, P.; Carrasquillo-Flores, R.; Pagan-Torres, Y. J.; Gurbuz, E. I.; Farnood, R.; Dumesic, J. A. *Green Chem.* **2012**, *14*, 1573.
(138) Gu, Y. L.; Jerome, F. *Green Chem.* **2010**, *12*, 1127.
(139) Mathers, R. T.; Damodaran, K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3150.
(140) Mathers, R. T.; McMahon, K. C.; Damodaran, K.; Retarides, C. J.; Kelley, D. J. *Macromolecules* **2006**, *39*, 8982.
(141) Mathers, R. T.; Damodaran, K.; Rendos, M. G.; Lavrich, M. S. *Macromolecules* **2009**, *42*, 1512.
(142) Delancey, J. M.; Cavazza, M. D.; Rendos, M. G.; Ulisse, C. J.; Palumbo, S. G.; Mathers, R. T. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 3719.
(143) Quirk, R. P.; Hsieh, H. L. *Anionic polymerization: Principles and practical applications*; Marcel Dekker: New York, 1996.
(144) *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996.

(145) Lewis, S. P.; Mathers, R. T. In *Renewable Polymers, Synthesis, Technology and Processing*; Vikas, M., Ed.; Wiley-VCH: New York, 2011, p 69.
(146) Kukhta, N. A.; Vasilenko, I. V.; Kostjuk, S. V. *Green Chem.* **2011**, *13*, 2362.
(147) Kostjuk, S. V.; Yeong, H. Y.; Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 471.
(148) Mathers, R. T.; Lewis, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1325.
(149) Kostjuk, S. V.; Ouardad, S.; Peruch, F.; Deffieux, A.; Absalon, C. *Macromolecules* **2011**, *44*, 1372.
(150) Prakash, G. K. S.; Mathew, T.; Olah, G. A. *Acc. Chem. Res.* **2012**, *45*, 565.
(151) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740.
(152) Abad, A.; Concepcion, P.; Corma, A.; Garcia, H. *Angew. Chem. Int. Ed.* **2005**, *44*, 4066.
(153) Kember, M. R.; Jutz, F.; Buchard, A.; White, A. J. P.; Williams, C. K. *Chem. Sci.* **2012**, *3*, 1245.
(154) Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. *Chem. Comm.* **2011**, *47*, 212.
(155) Singh, V.; Kumar, P.; Sanghi, R. *Prog. Polym. Sci.* **2012**, *37*, 340.
(156) Senra, J. D.; Aguiar, L. C. S.; Simas, A. B. C. *Curr. Org. Synth.* **2011**, *8*, 53.
(157) Hoffmann, N. *ChemSusChem* **2012**, *5*, 352.
(158) Kaneko, T.; Thi, T. H.; Shi, D. J.; Akashi, M. *Nature Mat.* **2006**, *5*, 966.
(159) Lipshutz, B. H.; Ghorai, S.; Abela, A. R.; Moser, R.; Nishikata, T.; Duplais, C.; Krasovskiy, A.; Gaston, R. D.; Gadwood, R. C. *J. Org. Chem.* **2011**, *76*, 4379.
(160) Church, T. L.; Getzler, Y. D. Y. L.; Byrne, C. M.; Coates, G. W. *Chem. Commun.* **2007**, 657.
(161) Kim, J.; Stahl, S. S. *ACS Catalysis* **2013**, *3*, 1652.
(162) Kreye, O.; Mutlu, H.; Meier, M. A. R. *Green Chem.* **2013**, *15*, 1431.
(163) Li, B.; Devaraj, K.; Darcel, C.; Dixneuf, P. H. *Green Chem.* **2012**, *14*, 2706.
(164) Kramer, J. W.; Lobkovsky, E. B.; Coates, G. W. *Org. Lett.* **2006**, *8*, 3709.
(165) Weil, J.; Mathers, R. T.; Getzler, Y. D. Y. L. *Macromolecules* **2012**, *45*, 1118.
(166) Allan, L. E. N.; MacDonald, J. P.; Reckling, A. M.; Kozak, C. M.; Shaver, M. P. *Macromol. Rapid Commun.* **2012**, *33*, 414.
(167) Earnshaw, A.; Greenwood, N. *Chemistry of the elements*; 2nd ed.; Butterworth-Heinemann: Oxford, 1997.
(168) Emsley, J. *The Elements*; 3rd ed.; Clarendon Press: Oxford, 1998.
(169) Kettler, P. B. *Org. Proc. Res. Devel.* **2003**, *7*, 342.
(170) Nakamura, E.; Sato, K. *Nature Mat.* **2011**, *10*, 158.
(171) Darensbourg, D. J.; Choi, W.; Richers, C. P. *Macromolecules* **2007**, *40*, 3521.
(172) Darensbourg, D. J.; Choi, W.; Karroonnirun, O.; Bhuvanesh, N. *Macromolecules* **2008**, *41*, 3493.
(173) www.strem.com.
(174) Reck, B. K.; Graedel, T. E. *Science* **2012**, *337*, 690.
(175) Dijkstra, P. J.; Du, H.; Feijen, J. *Polym. Chem.* **2011**, *2*, 520.
(176) Stanford, M. J.; Dove, A. P. *Chem. Soc. Rev.* **2010**, *39*, 486.
(177) North, M.; Young, C. *ChemSusChem* **2011**, *4*, 1685.
(178) Wegener, S. L.; Marks, T. J.; Stair, P. C. *Acc. Chem. Res.* **2012**, *45*, 206.
(179) Kim, H.-S.; Zygmunt, S. A.; Stair, P. C.; Zapol, P.; Curtiss, L. A. *J. Phys. Chem. C.* **2009**, *113*, 8836.
(180) *Catalysis without precious metals*; Bullock, R. M., Ed.; Wiley-VCH: Weinheim, 2010.
(181) Popescu, D. L.; Chanda, A.; Stadler, M.; de Oliveira, F. T.; Ryabov, A. D.; Munck, E.; Bominaar, E. L.; Collins, T. J. *Coord. Chem. Rev.* **2008**, *252*, 2050.
(182) Junge, K.; Schröder, K.; Beller, M. *Chem. Commun.* **2011**, *47*, 4849.

(183) *Iron Catalysis in Organic Chemistry: Reactions and Applications*; Plietker, B., Ed.; Wiley-VCH: Weinheim, 2008.
(184) Zhang, W.; Sun, W.-H.; Redshaw, C. *Dalton Trans.* **2013**, *42*, 8988.
(185) O'Reilly, R. K.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 8450.
(186) Wang, Y.; Zhang, Y.; Parker, B.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 4022.
(187) Wang, Y.; Kwak, Y.; Matyjaszewski, K. *Macromolecules* **2012**, *45*, 5911.
(188) Hasan, K.; Brown, N.; Kozak, C. M. *Green Chem.* **2011**, *13*, 1230.
(189) Nejad, E. H.; Paoniasari, A.; van Melis, C. G. W.; Koning, C. E.; Duchateau, R. *Macromolecules* **2013**, *46*, 631.
(190) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404.
(191) Del Rio, E.; Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5009.
(192) Lligadas, G.; Ronda, J. C.; Galia, M.; Biermann, U.; Metzger, J. O. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 634.
(193) *Green Polymerization Methods: Renewable Starting Materials, Catalysis and Waste Reduction*; Mathers, R. T.; Meier, M. A. R., Eds.; Wiley-VCH: Weinheim, 2011.
(194) Kember, M. R.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, *134*, 15676.
(195) Chisholm, M. H. *Inorg. Chim. Acta* **2009**, *362*, 4284.
(196) Liu, B.; Roisnel, T.; Guégan, J.-P.; Carpentier, J.-F.; Sarazin, Y. *Chem. Eur. J.* **2012**, *18*, 6289.
(197) Huang, T.-L.; Chen, C.-T. *Dalton Trans.* **2013**, *42*, 9255.
(198) Huang, M.; Chu, W.; Liao, X.; Dai, X. *Catal. Lett.* **2011**, *141*, 1670.
(199) Harder, S. *Chem. Rev. (Washington, DC, United States)* **2010**, *110*, 3852.
(200) Harder, S.; Feil, F.; Knoll, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 4261.
(201) Piesik, D. F. J.; Haebe, K.; Harder, S. *Eur. J. Inorg. Chem.* **2007**, *2007*, 5652.
(202) Gauvin, R. M.; Buch, F.; Delevoye, L.; Harder, S. *Chem. Eur. J.* **2009**, *15*, 4382.
(203) Chen, H.-Y.; Zhang, J.; Lin, C.-C.; Reibenspies, J. H.; Miller, S. A. *Green Chem.* **2007**, *9*, 1038.
(204) Wolterbeek, H. T. V., T. G. *Sci. Total Environ.* **2001**, *279*, 87.
(205) Yao, K.; Tang, C. *Macromolecules* **2013**, *46*, 1689.
(206) Tschan, M. J. L.; Brule, E.; Haquette, P.; Thomas, C. M. *Polym. Chem.* **2012**, *3*, 836.
(207) *Guideline on the Specification Limits for Residues of Metal Catalysts or Metal Reagents*, Guideline on the Specification Limits for Residues of Metal Catalysts or Metal Reagents, Committee for Medicinal Products for Human Use, European Medicines Agency, 2008.
(208) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143.
(209) Coates, G. W.; Moore, D. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6618.
(210) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G. *J. Am. Chem. Soc.* **2003**, *125*, 11350.
(211) Schröder, K.; Mathers, R. T.; Buback, J.; Konkolewicz, D.; Magenau, A. J. D.; Matyjaszewski, K. *ACS Macro Lett.* **2012**, *1*, 1037.
(212) Voutchkova, A. M.; Ferris, L. A.; Zimmerman, J. B.; Anastas, P. T. *Tetrahedron* **2010**, *66*, 1031.
(213) Voutchkova, A. M.; Kostal, J.; Steinfeld, J. B.; Emerson, J. W.; Brooks, B. W.; Anastas, P.; Zimmerman, J. B. *Green Chem.* **2011**, *13*, 2373.
(214) Fabre, N.; Anglade, I.; Vericat, J. A. *Toxicology Lett.* **2009**, *186*, 13.
(215) *Designing Safer Chemicals*; Boethling, R.; Voutchkova, A. M.; Anastas, P., Eds.; Wiley-VCH: Weinheim, 2011.

(216) Vandenberg, L. N.; Colborn, T.; Hayes, T. B.; Heindel, J. J.; Jacobs, D. R.; Lee, D.-H.; Shioda, T.; Soto, A. M.; vom Saal, F. S.; Welshons, W. V.; Zoeller, R. T.; Peterson Myers, J. *Endocrine Rev.* **2012**, *33*.
(217) Schug, T. T.; Abagyan, R.; Blumberg, B.; Collins, T. J.; Crews, D.; DeFur, P. L.; Dickerson, S. M.; Edwards, T. M.; Gore, A. C.; Guillette, L. J.; Hayes, T.; Heindel, J. J.; Moores, A.; Patisaul, H. B.; Tal, T. L.; Thayer, K. A.; Vandenberg, L. N.; Warner, J. C.; Watson, C. S.; vom Saal, F. S.; Zoeller, R. T.; O'Brien, K. P.; Myers, J. P. *Green Chem.* **2013**, *15*, 181.
(218) Kennedy, D. C.; McKay, C. S.; Legault, M. C. B.; Danielson, D. C.; Blake, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 17993.
(219) Helenius, I. T.; Yeh, J. R. J. *J. Cell. Biochem.* **2012**, *113*, 2208.
(220) Alfaro, J. M.; Prades, A.; del Carmen Ramos, M.; Peris, E.; Ripoll-Gomez, J. *Zebrafish* **2010**, *7*, 13.
(221) Wilbuer, A.; Vlecken, D. H.; Schmitz, D. J.; Kraeling, K.; Harms, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 3839.
(222) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2001**, *123*, 3229.
(223) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738.
(224) Kim, J. G.; Cowman, C. D.; LaPointe, A. M.; Wiesner, U.; Coates, G. W. *Macromolecules* **2011**, *44*, 1110.
(225) Boyer, C.; Soeriyadi, A. H.; Zetterlund, P. B.; Whittaker, M. R. *Macromolecules* **2011**, 8028.
(226) Cherian, A. E.; Sun, F. C.; Sheiko, S. S.; Coates, G. W. *J. Am. Chem. Soc.* **2007**, *129*, 11350.



A qualitative approach to maximizing sustainability in polymer chemistry.