Main-chain organometallic polymers: synthetic strategies, applications, and perspectives

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Main-chain organometallic polymers utilize transition metal-organic ligand complexes as primary components of their backbones. These hybrid materials effectively integrate the physical and electronic properties of organic polymers with the physical, electronic, optical, and catalytic properties of organometallic complexes. Combined with the rich and continuously growing array of ligands for transition metals, these materials have outstanding potential for use in a broad range of applications. This *tutorial review* discusses the major classes of main-chain organometallic polymers, including coordination polymers, poly(metal acetylide)s, and poly(metallocene)s. Emphasis is placed on their synthesis, characterization, physical properties, and applications, as well as ongoing challenges and limitations. These discussions are supplemented with highlights from the recent literature. The review concludes with perspectives on the current status of the field, as well as opportunities that lie just beyond its frontier.

1 Introduction

The genesis of organometallic polymers took place over 50 years ago with the successful free radical polymerization of vinyl ferrocene.[1] Since that initial discovery there have been tremendous efforts to diversify and apply this exciting area of macromolecular chemistry. Today, organometallic polymers take on a multitude of design concepts and their breadth of applications is as varied as their structures.[2–5] Existing at an interface of inorganic, materials, and traditional polymer chemistry, the field of organometallic polymers offers the ability to prepare functional macromolecules that combine the physical and electronic properties of organic polymers with the physical, electronic, optical, and catalytic properties inherent to organometallic complexes.

Irrespective of the application, the utility and performance of metal-containing polymers can, in varying degrees, be ascribed to the ability of the transition metal centers to change oxidation states and/or facilitate electron flow in ways that organic materials simply cannot. For example, many contemporary carbon–carbon or carbon–heteroatom bond-forming reactions are catalyzed by transition metals that are able to undergo oxidative insertions and reductive eliminations. Likewise, changes in oxidation states are essential to facilitate the high rates of charge transfer through metallic wires. Currently, there are no known "all organic" compounds that have these capabilities.

While there are various strategies for incorporating transition metals into polymeric scaffolds, main-chain organometallic polymers (MCOPs) are a special subclass that involves transition metals as integral components of the polymer backbone.[6] This distinctive trait inherently brings about unique considerations with regard to polymer synthesis, characterization, physical properties, and applications. When

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engineering a desired property into a MCOP, focus is often initially placed on the transition metal. However, the design of the organic moieties linking metal centers along the polymer backbone must also be considered. These bridging groups are primary components of the polymer backbone and strongly influence the physical and mechanical characteristics of the resulting material. Furthermore, they are also ligands and therefore influence the electronic, optical, catalytic and physical properties of the embedded transition metals. A caveat of these intimate relationships is that any modification of one characteristic of the polymeric material often ends up impacting others. Ultimately, when designing a new MCOP, it is important to consider both the transition metal and the linker equally. Specific examples from the literature that describe such metal–ligand relationships in MCOPs are included in the discussions that follow this section.

The remarkable potential of these organic–inorganic hybrid materials will drive the development of metal-containing macromolecules and continue to intrigue chemists. As such, the presence of MCOPs at the forefront of many areas of science will undoubtedly continue to increase. The aim of this *tutorial review* is to introduce and discuss fundamental structural and synthetic aspects of designing MCOPs, as well as their characterization, chemical attributes, physical characteristics, and applications. We will begin with a discussion concerning what constitutes a MCOP and how it is distinguished amongst other types of organometallic polymers. This will be followed by a summary of the various metal–ligand interactions used to incorporate transition metals into MCOPs. In particular, three general, synthetic strategies will be presented followed by examples and descriptions organized by the polymer's primary metal–ligand interaction. Ensuing discussions of MCOP characterization and applications will be highlighted by examples from the recent literature. Our *tutorial review* will conclude with a brief summary and outlook of the field.

Christopher W. Bielawski

Christopher W. Bielawski's interest in chemical research began when he was an undergraduate working in the laboratories of Professor Jeffrey S. Moore at the University of Illinois, Urbana-Champaign. After receiving his BS degree in chemistry in 1997, he moved to the California Institute of Technology (Pasadena, CA) where he studied designer Ru-based polymerization catalysts under the direction of Professor Robert H. Grubbs. Soon after finishing his PhD in chemistry in 2003, he moved back east (slightly) and began a postdoctoral appointment in the laboratories of Professor David A. Tirrell (also at Caltech). In 2004, he accepted a position at The University of Texas at Austin where he is currently an assistant professor of chemistry. His research interests are centered around the synthesis and application of multitopic N-heterocyclic carbenes.

1.1 Generalized structural designs for organometallic polymers

In a broad sense, an organometallic polymer is any macromolecule that contains both organic and metallic (*i.e.*, transition-metal containing) moieties. Synthetic and structural characteristics can be accurately generalized by dividing organometallic polymers into two subclasses designated by the position of the metal atom relative to the primary polymer backbone. As shown in Fig. 1, we designate these two classes as: (1) side-group and (2) main-chain organometallic polymers.

Side-group organometallic polymers (SGOPs) are identified by an "all-organic" polymer backbone. Perhaps the most important implication of the side-group arrangement is that polymeric structure exists regardless of the presence of metal atoms. Metal incorporation in SGOPs is achieved by installing a metal binding site pendant to an organic-based polymer chain, and the characteristics of the metal center as well as the polymer backbone can generally be independently adjusted. In situations where metal binding is quantitative, SGOPs offer a convenient method for using "traditional" polymerization reactions to prepare hybrid materials. For example, organic monomers containing a pendant ligand can be polymerized using standard addition (*e.g.*, ionic or radical), ring-opening, or various types of condensation polymerization reactions.[7] Once the organic polymer is prepared, subsequent addition of a transition metal precursor binds to the tethered ligand and completes the synthesis of the SGOP. Alternatively, a monomer containing a pendant metal-complex can often be polymerized directly. While this synthetic convenience is certainly advantageous, the structural independence of the organic and inorganic components in SGOPs can complicate accurate determinations of metal content in these materials.

In contrast, MCOPs rely on the presence of metal–ligand bonds in order to exist. Therefore, as noted above, focus must be equally applied toward both the transition metal and the organic ligand. The ligand must simultaneously enable the embedded transition metal to exhibit a desired property (*e.g.*, low oxidation/reduction potentials) and facilitate polymer formation while maintaining control over physical attributes of the overall material (*e.g.*, solubility). To give an example of how these interrelated properties may impact one another, consider a material desired for electrical conductivity. A rigid, conjugated organic linker is often ideal for such purpose because of its ability to maximize electronic communication. The extensive delocalization and rigid structure, however, generally impedes solubility. Installation of solubilizing alkyl groups on the periphery of the linker may remedy solubility

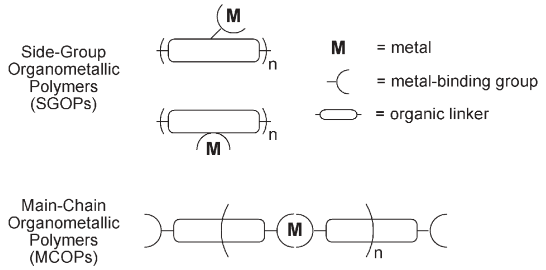

Fig. 1 Depiction of side-group (top) and main-chain (bottom) organometallic polymer motifs.

issues, but if this results in congestion about the metal center then the polymer may suffer reduced stability (due to lowered metal–ligand affinity) or may exhibit an undesired oxidation/reduction potential. These conflicting issues are often balanced through empirical experimentation until an optimal result is achieved.

Another important structural consideration when designing MCOPs is the coordination number of the transition metal and the organic linker. To facilitate the formation of linear polymer *via* bidirectional chain elongation, two opposing points of contact are required at the metal atom, and the ligand must be capable of binding two metals. Since transition metals can (theoretically) bind up to eight ligands to varying degrees, an ability to control this diversity is often the defining point when designing new MCOPs. As will be discussed in more detail below, ligands that show high affinities toward transition metals must be employed in order to have sufficient thermodynamic driving force to facilitate polymerization and afford polymeric materials with high molecular weights. The following section discusses specifics of how the metal-binding motif (*i.e.*, ligand denticity, strength of ligation, and coordination number) can synergistically dictate the resulting properties of the MCOPs.

2 Overview of metal-binding motifs in main-chain organometallic polymers

The bidirectional, ditopic organic ligands commonly used in MCOPs exhibit broad diversity in their capacities to bind transition metals. The most widely used systems employ coordination (or dative) bonding, ionic metal–carbon or metal–heteroatom bonding, or metal–arene complexation. Generalized examples of each of these interactions are depicted in Fig. 2.

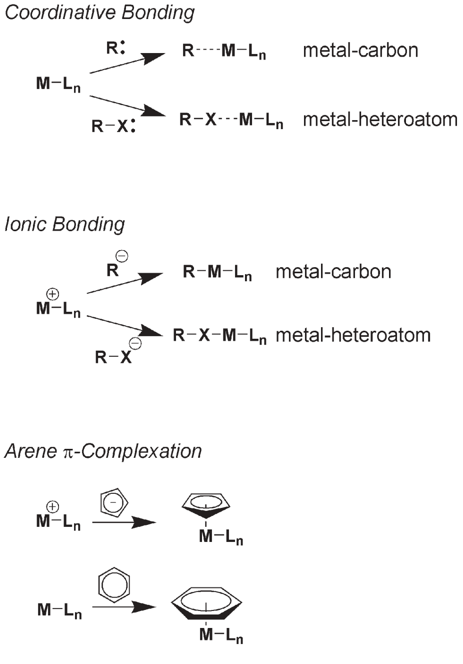

Fig. 2 Generalized examples of different types of metal–ligand interactions.

2.1 Metal-binding motifs used in coordination polymers

Organometallic polymers that employ dative-type interactions between the metal atoms and the bridging ligands are sometimes called coordination polymers. Coordination occurs between transition metals and neutral donor moieties such as phosphines, carbenes, amines, ethers, ketones, imines, nitriles, and thio compounds. These interactions can be utilized to form mono-, bi-, or tridentate systems. Examples of such types of coordination, within the context of pyridine-based ligands, are shown in Fig. 3 and will be discussed in more detail below. For an in-depth analysis of the coordination polymer literature, we recommend the excellent review by Dobrawa and Würthner.[4]

Coordination polymers encompass perhaps the broadest spectrum of metal–ligand stability spanning from systems that readily depolymerize in solution to those that retain their structure even under intense external stimuli (*e.g.*, heat, light, ultra-sound, *etc.*). Precisely tuning the metal–ligand affinities is sometimes nontrivial, however, due to the fact that many factors influence this stability. Increasing the strength of the metal–ligand interaction is usually done in two ways: (1) using donor ligands of exceptionally high metal affinity, and/or (2) increasing the number of donor atoms bonding to the metal (multidentate binding). As will be discussed below, combinations of these two strategies enables exceptional control over the physical properties of coordination polymers. Examples utilizing mono- and multidentate binding motifs are depicted in Fig. 4.

In general, there are few examples of highly stable coordination polymers that utilize a single monodentate donor at each terminus of the ditopic bridging ligand. Key examples include the use of strong donors such as phosphines (*e.g.*, polymers **1**) which have been shown to retain their structural integrity even in highly coordinating solvents (such as acetonitrile).[8,9] In comparison with other neutral two-electron donors, N-heterocyclic carbenes (NHCs) typically display some of the highest metal affinities and are compatible with nearly every transition metal. Accordingly, polymers such as **2**

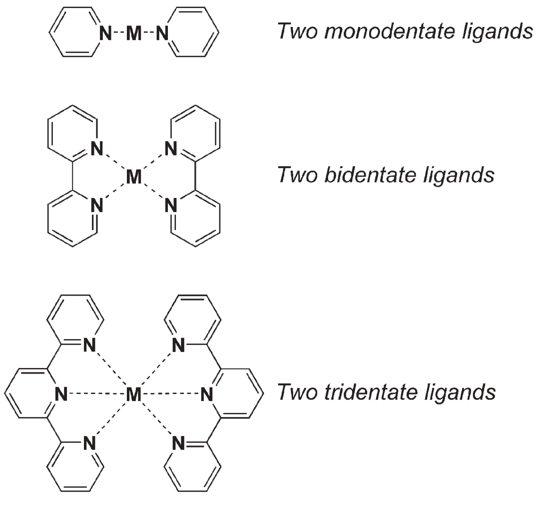

Fig. 3 Representative examples of coordination with mono-, bi-, and tridentate pyridine-based ligands.

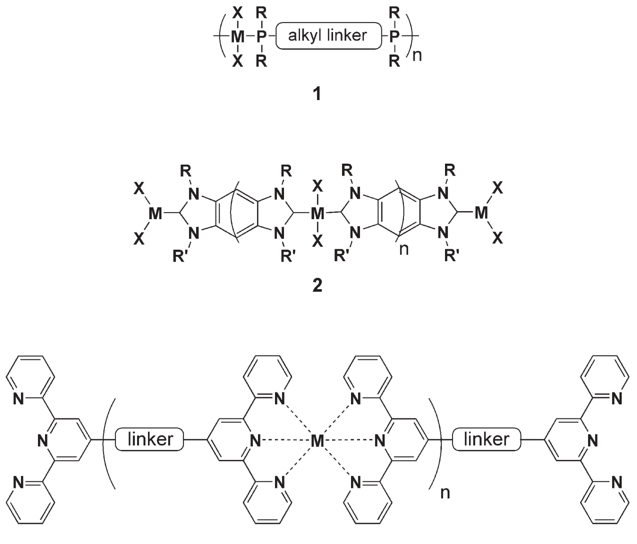

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Fig. 4 Examples of mono- and multidentate binding motifs in coordination polymers.

have been synthesized and shown to have excellent thermal and chemical stabilities.[10,11] When less donating moieties (*e.g.*, amines) are used, polymer strength decreases, as expected from the weaker metal–ligand interaction. To counter this effect, multidentate binding arrays are often employed.[4] For example, incorporation of pyridines into a multidentate array (*e.g.*, polymer **3** which utilizes terpyridines in conjunction with cationic metal(II) species: Ru, Os, Zn, Fe),[12] provided access to relatively stable coordination polymers.

Since dative bonds are often weak and under thermodynamic control, the potential for coordination polymers to depolymerize (even to minor extents) can introduce additional challenges with regard to longevity or storage of the polymers. For example, the metal–ligand lability observed in the "weakest" of coordination polymers is partly ascribed to the fact that these systems involve coordination from neutral donor atoms. When the ligand dissociates from the metal atom, the free ligands are often prone to oxidation or other destructive pathways. More details regarding the effects of coordination number and donor strength are discussed below, within the context of polymer synthesis.

2.2 Metal-binding motifs employing ionic metal–ligand bonds

A well studied class of MCOPs that utilizes ionic metal–carbon bonds is poly(metal acetylide)s of the general structure **4** (Fig. 5).[13] Related polymers have also been reported that utilize biphenylene bridges in combination with Ni(II) metal centers, as depicted by structure **5**.[14] In poly(metal acetylide)s, bis(acetylides) are used formally as dianions which form ionic bonds to cationic metal atoms. In general, metal acetylide polymers show good air and moisture stability which permits handling of the polymers in the solid state for extended periods of time, although lifetimes may be shorter in aerated solutions.

Fig. 6 illustrates an interesting structural constraint regarding the geometries about the metal centers in poly(metal acetylide)s. Attachment of two carbanions to a transition metal can lead to reductive elimination of the metal atom. When this happens, a carbon–carbon bond is formed between two of the organic ligands, and the metal is extruded from the backbone in a reduced state. This can be avoided by judicious choice of the ancillary ligands (L_n) so that they maintain a trans geometry about the metal center, or through the use of late transition metals, such as Hg,[15] which are less likely to facilitate this elimination reaction.

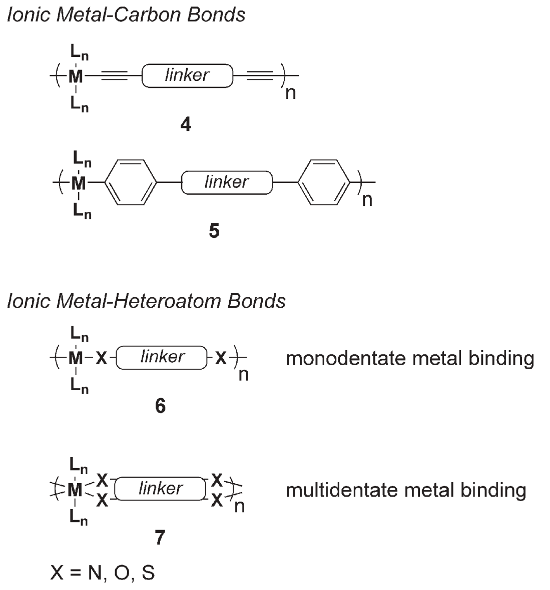

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Fig. 5 Generalized examples of MCOPs that utilize metal–carbon or metal–heteroatom ionic σ-bonds.

In addition to carbon (*i.e.*, acetylides), MCOPs also utilize ionic interactions based on heteroatoms such as nitrogen, oxygen, and sulfur. And, as depicted in the generalized structures **6** and **7** shown in Fig. 5, both mono- and multidentate binding arrangements are found in these polymers. The particular combination of the transition metal and heteroatom can influence both polymer stability and its physical properties (*e.g.*, conductivity). In accordance with hard–soft acid–base (HSAB) theory, early transition metals[16] (*e.g.*, group IV) generally show greater oxo- and azophilicities

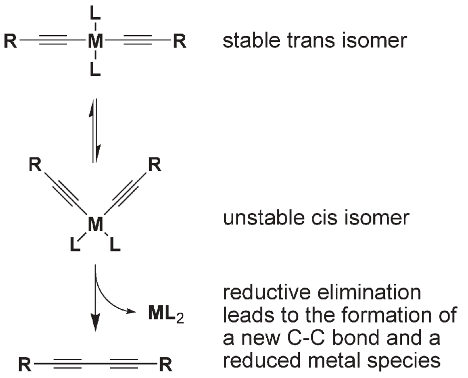
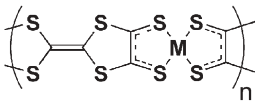


Fig. 6 General depiction of a stable *trans* isomer, and reductive elimination from an unstable *cis* isomer of a metal bis(acetylide). Use of large L groups pushes the equilibrium toward the stable *trans* isomer.



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M	σ (S/cm)
Fe	10^{-5}
Pd	10^{-3}
Pt	10^{-2}
Cu	10^{-1}
Ni	30

Fig. 7 Metal-dependent conductivities of a poly(thiolate).

whereas late transition metals (*e.g.*, group X metals) exhibit particularly high thiophilicities.[2] With proper matching of the metal and heteroatoms, polymers with tunable properties can be prepared. One excellent example of this is the electrically-conductive poly(thiolate)-based system of the general structure **8** (Fig. 7). Due to the broad metal compatibility inherent to sulfur, the conductivities of these materials could be varied from 10^{-5} to 30 S cm^{-1} by simply changing the incorporated transition metal.[17]

2.3 Metal-binding motifs based on metal–arene complexation

One of the most widely-studied types of organometallic polymers are the poly(metallocene)s. Fig. 8 depicts some general structures for poly(metallocene)s prepared from various arene sandwich complexes and linking moieties. A broad range of transition metals (both early and late) have been incorporated into poly(metallocene)s and, in some cases, more than one metal can be used to yield bimetallic materials (*e.g.*, **13** and **14**). One notable property that is almost universally shared by these materials is their very high thermal stabilities. For example, polymer **10** (R = H) retained 90% of its initial mass when heated to 600 °C.[2]

The structure of the arene linker is usually modular (*i.e.*, contains interchangeable features) and a wide range of mono- and polycyclic aromatics (*e.g.* benzene, naphthalene and helicene) have been used to form polymers. The arene is generally susceptible to functionalization, and therefore usually the point at which connections between monomers are made (*e.g.* **9–11**, **13**, **14**). A notable exception to this general connectivity is depicted by polymer **12** which uses ionic metal–ligand linkages. In this polymer, metal–oxo bonds are used in the main-chain of the metallocene-containing macromolecule. Although additional details on this class of MCOPs will be discussed below, we encourage the reader to consult the excellent review by Manners and coworkers for a comprehensive overview of the poly(metallocene) literature.[2]

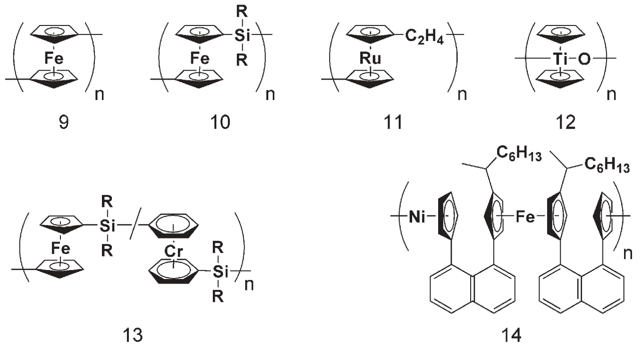

Fig. 8 Representative examples of poly(metallocene)s.

3 Synthetic strategies for accessing main-chain organometallic polymers

In contrast to SGOPs, the synthetic strategies used to prepare MCOPs require that the metal complex be either: (1) constructed during the polymerization event, or (2) already present in an organometallic monomer. Fig. 9 depicts three general types of polymerization reactions used to form MCOPs. An obvious requirement with each strategy is that the metal centers present in the resulting polymers must be stable to the reaction conditions used for polymerization.

In the polymerization reaction shown in Path A, polymer is created in a step-growth fashion as the ditopic ligands form bonds to metal atoms. Path A is unique from Paths B and C (both discussed below) in that polymerizations are conducted using two discrete comonomer reactants (the bridging ligand and the metal species). The experimental protocol to form polymers using Path A can be as simple as combining the organic linker with an appropriate metal precursor in a compatible solvent. The resulting, and often spontaneous, coordination events lead to polymer formation. This practical method often makes Path A an attractive choice for preparing coordination polymers.

Path B involves polymerization of a monomer that already contains a ligated transition metal (*i.e.*, a preformed organometallic complex). The nature of the polymerization event is unique from Path A in that the bonds formed during polymerization occur between organic ligands. That is, the ligands generally possess polymerizable functional groups and reactions common to synthesizing ''all-organic'' polymers (*e.g.*, electropolymerization, C–C cross-coupling, olefin metathesis, *etc.*) may be used. In other words, bonds to the metal center are neither made nor broken during the polymerization reaction which clearly distinguishes this approach from Path A. However, the polymerization described in Path B does share one similarity to that of Path A: they are both step-growth polymerizations. Accordingly,

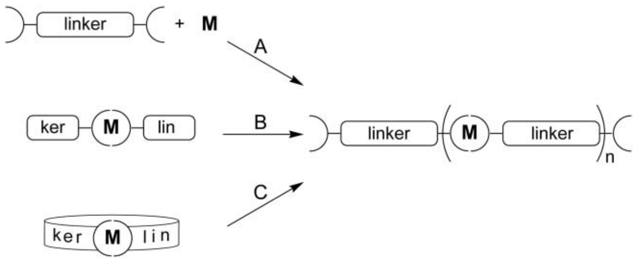

Fig. 9 General synthetic routes for preparing MCOPs. Path A: Polymerization of a ditopic organic linker with a transition-metal precursor. Path B: Polymerization of the organic component of a ditopic organometallic complex. Path C: Ring-opening polymerization of a cyclic organometallic monomer.

precise stoichiometry is usually required to obtain high molecular weight materials.

The polymerization reaction described in Path C also does not involve any changes to the bonding arrangement at the metal center as polymer is formed. Instead, the reaction involves the opening of a cyclic monomer. A primary advantage of such ring-opening polymerizations (ROPs) is that it proceeds *via* a chain-growth mechanism. This means that molecular weight can often be controlled by simply altering the initial monomer to catalyst ratio and precise stoichiometric control is usually not necessary to form high molecular weight polymer. This polymerization strategy has been widely used in the synthesis of poly(metallocene)s and further discussion will be provided in later sections.

With the considerations of Paths A, B and C in mind, basic monomer designs can be categorized according to the polymerization strategy to be employed. Path A requires a ditopic (and usually symmetric) ligand system that can undergo metal complexation during polymerization. Path B necessitates a ditopic organometallic monomer bearing appropriate organic functional groups that are susceptible to polymerization. Path C also involves an organometallic monomer, but one that is cyclic (and often strained). Interestingly, as will be shown below, different polymerization methods can sometimes be used to achieve the same polymeric product.

3.1 Coordination polymers

As noted above for polymerizations that conform to Path A, the simplest route to access MCOPs is the coordination of ditopic ligands to the metal atom. The polymerization process involves the formation of bonds between a ditopic organic linker and a transition metal, which often results in the displacement of neutral spectator species bound to the metal. Generally these spectator ligands (*e.g.*, triphenylphosphine, cycloocta-1,5-diene, acetonitrile, *etc.*) are present on readily-available precursors to enhance the solubility or stability of the metal-containing reagent. That is, the presence of the spectator ligands is often not necessary, rather it is coincidental.

Since the thermodynamic driving force for polymer formation is dictated largely by metal–ligand affinity, ligands with very high affinities for transition metals are required to obtain high molecular weight polymer. Likewise, it is important that the ligands to be displaced exhibit lower metal affinity than the ditopic linker used for polymerization. External factors such as concentration, temperature, and solvent are also important for obtaining high molecular weight polymer. Strongly coordinating solvents can reduce molecular weight by competing for vacant coordination sites on the metal, which ultimately facilitates depolymerization. Capitalizing on this latter phenomenon, Rehahn synthesized a series of ditopic bridging ligands based on multidentate pyridine-containing binding motifs (*e.g.* terpyridine[18] and phenanthroline[19]) as well as their respective polymeric materials with various transition metals such as Ru, Cu and Ag (*e.g.*, see polymer **3** shown in Fig. 4). By excluding competing ligands or solvents, such as acetonitrile, kinetically unstable macromolecules were formed in solution. Under optimized conditions, these polymers maintained their structural integrity solely by coordinative bonds and exhibited molecular weights on the order of 10^4 Da, corresponding to a degree of polymerization (DP) of about 30–43. Interestingly, addition of acetonitrile to these polymers resulted in depolymerization as confirmed by NMR spectroscopy as well as by changes in material viscosity.[20]

Complementary to Rehahn's work,[19] Chen and MacDonnell demonstrated that optically active coordination-type polymers can be obtained by copolymerizing enantiomerically pure Ru complexes (Fig. 10).[21] Specifically, two common monomers, one functionalized with diones (**15**) and another with diamines (**16**) were reacted in a polycondensation-type reaction to produce an optically active coordination polymer **17**. Collectively, the study demonstrated the ability to control the local stereochemistry of the metal centers as well as the global stereochemistry of the polymer chain to produce ribbon-like polymers that coil. This level of stereochemical control may ultimately provide materials with potential applications in asymmetric catalysis or sensory materials.

Constable, Forster and co-workers demonstrated electrochemical polymerization as yet another synthetic method to obtain polymers of similar structure to those of Rehahn and MacDonnell (Fig. 11).[22] In this approach, terpyridines featuring thiophene, bithiophene, and terthiophene moieties (*i.e.*, m = 1, 2 and 3, respectively) were prepared and complexed to Ru(II) and Os(II) species to obtain electropolymerizable organometallic monomers (**18**). The process produced polymers **19** directly as films deposited onto an electrode (or microelectrode array) which were further studied in the solid state. The deposited films were found to have conductivities on the order of 10^{-3} S cm^{-1}, depending on the nature of the bridging groups. Subsequently, the thiophene moieties were overoxidized, effectively minimizing electronic communication between metal centers in the polymer chain. These "non-conjugated" analogues showed reduced conductivity (*i.e.*, two orders of magnitude less) in comparison with the fully conjugated variants.

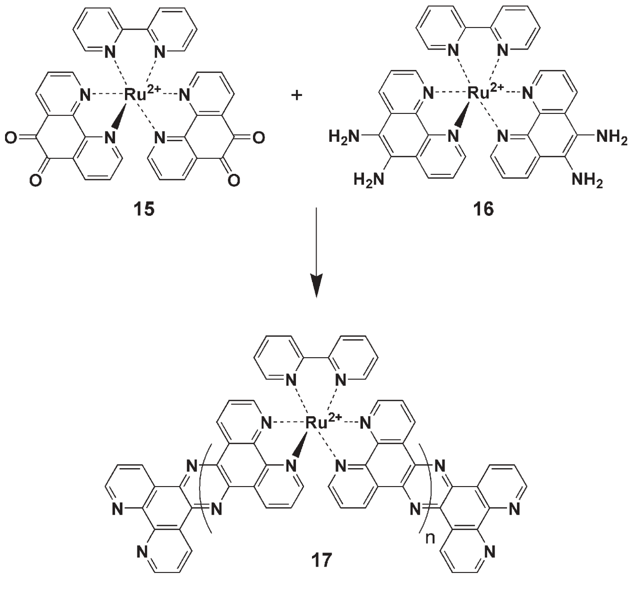

Fig. 10 Synthesis of optically active coordination polymers from enantiomerically pure organometallic complexes.

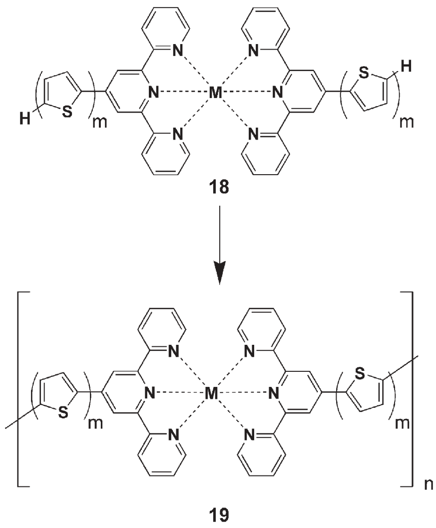

Fig. 11 Dehydrogenative electropolymerization of thiophene-functionalized terpyridine complexes (**18**).

Monodentate amine-based linkers have also been utilized and, as expected from the reduced number of coordinating amines, these polymers are generally labile with structures that are highly dependent on external conditions. Craig recently reported a series of experiments that elegantly demonstrated how such lability can be used to control the molecular weight of MCOPs.[23] As shown in Fig. 12, polymer **22** was synthesized by reacting a ditopic Pd-pincer complex (**20**) with a bis(pyridine) moiety (**21**) in DMSO at room temperature. Notably, the viscosities (and therefore molecular weights) of these materials could be controlled by simply modulating the steric bulk of the NR_2 groups (*e.g.*, R = Me *vs.* Et) about the Pd center in **20**. Additional details regarding this unique dynamic behavior will be discussed later.

Compared to amines, phosphines are generally regarded as stronger donors. Therefore it is often possible to obtain coordination-type polymers of relatively high stability with the latter. For example, Sijbesma and co-workers synthesized a series of palladium and platinum polymers (*e.g.*, see polymer **1** shown in Fig. 4) by combining substoichiometric amounts of metal(II) chlorides with ditopic phosphines in dichloromethane at room temperature for several days.[8] After removal of unreacted metal salts *via* filtration and evaporation of the solvent, the resulting polymers were found to display sufficient stabilities to draw fibers. Ligand structure and purity, as well as the solubility of the metal species were optimized to drive reactivity away from competing cyclic oligomerization to polymers with molecular weights greater than 70,000 Da (reported as their polystyrene equivalent). These molecular weights were determined using gel permeation chromatography (GPC), which was an impressive achievement because many coordination polymers cannot retain macromolecular form under the high dilution and coordinating solvent conditions common to GPC analysis.

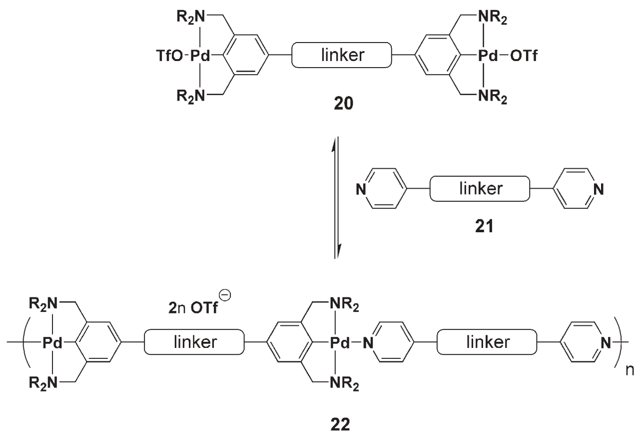

Fig. 12 Examples of reversible coordination polymers that exhibit concentration- and structure-dependent binding affinities.

Similarly, Ding and co-workers have used ditopic phosphine linkers (**23**) in the construction of Rh-containing polymers **24** (Fig. 13). The synthesis of polymers **24** was accomplished by combining the reactive bridging ligands with $Rh(COD)_2BF_4$ (COD = cycloocta-1,5-diene), a readily available Rh precursor. These polymers proved effective as recyclable hydrogenation catalysts.[9] For example, for the hydrogenation depicted in Fig. 13, the seventh run using the same recycled catalyst provided >99% yield and 89.5% enantiomeric excess (ee).[24]

Although the chemistry of NHC-metal complexes has been developed over several decades, their appearance in macromolecular chemistry has only recently been introduced.[11] This was primarily due to a lack of appropriately structured multitopic NHC-based building blocks. Specifically, while chelating (or pincer) NHCs have been known for over two decades,[25] rigid facially-opposed bis(NHC)s poised for polymer formation have received considerably less attention.[26] Recently, several new methods of synthesizing annulated bis(carbene)s,[27] and their precursor bis(azolium) salts,[10,28,29] have been reported. Access to these monomers has made possible the synthesis of a series of NHC-based MCOPs[10,29] as well as discrete bimetallic model systems.[27]

From a synthetic standpoint, two methods lend themselves to the formation of NHC-based MCOPs. First, metal ligation using ditopic bis(NHC)s offers a clean polymerization reminiscent of the phosphine- and amine-based coordination

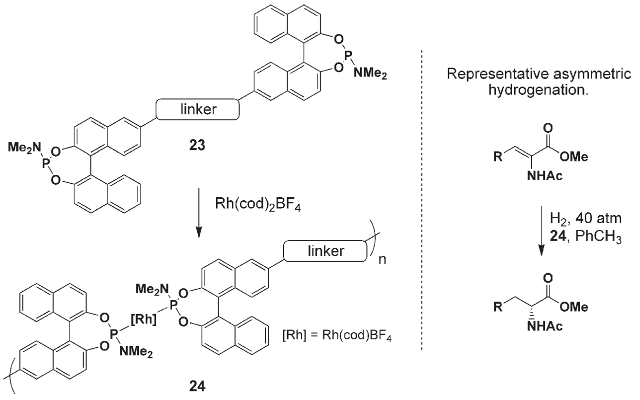

Fig. 13 Left: Recyclable hydrogenation catalysts synthesized by coordination of ditopic phosphines with $Rh(cod)_2BF_4$ (cod = cycloocta-1,5-diene). Right: Representative asymmetric hydrogenation catalyzed by Rh-based MCOP **24**.

polymers discussed previously. It is one of the few methods that form metal–carbon bonds (without the generation of any byproducts or loss of ancillary ligands) during the polymerization reaction. As shown in Fig. 14, generation of the free bis(NHC)s produced an equilibrium mixture of free carbenes (**25**) and poly(enetetraamine)s (poly(**25**), a product of carbene dimerization).[30] Introduction of $PdCl_2$ resulted in metal incorporation and formation of the Pd-containing polymers **26** with mixtures of *cis* and *trans* isomers about the metal centers. The polymers were found to be remarkably air and moisture stable, and exhibited molecular weights on the order of 10^4 Da as determined by GPC relative to polystyrene standards.

One current limitation of MCOPs prepared using bis(NHC)s is the need for inert atmosphere conditions to avoid oxidation of the enetetraamine moieties[27] or protonation of the relatively basic free carbenes.[31] In contrast, stable bis(azolium) salts are not only stable to air and moisture, but also serve as excellent bis(NHC) precursors. These salts can be copolymerized with various metal species to obtain bis(NHC)-based MCOPs.[10] Coupled with the robust nature of the resulting MCOPs, the use of bis(azolium) salts allows the polymerization to be performed under ambient atmosphere with wet solvents, which collectively is advantageous to the aforementioned method of generating free carbenes *in situ*. As shown in Fig. 15, the polymerization of bis(azolium) salts (**27**) directly with Pd(II) or Pt(II) salts provided polymers **28** with molecular weights up to 1.8×10^6 Da and good thermal stabilities (decomposition temperatures up to 300 °C under an atmosphere of nitrogen as determined by thermogravimetric analysis).

Despite the high affinities of NHCs for various transition metals, direct incorporation of metals other than Pd and Pt were plagued by hydrolytic instability when linear architectures were targeted. To further enhance the binding affinity of the bis(NHC) ligands, a new bis(azolium) system was designed to feature pendant phenol moieties. As shown in Fig. 15, this NHC-phenol bidentate motif was found to bind to incorporated transition metals in a chelating-type fashion and facilitated the first synthesis of Ni-containing bis(NHC)-based macromolecules (**29**). The structural adjustment also increased thermal stabilities by 50–60 °C, when compared to their Pd and Pt non-chelating analogues.[32]

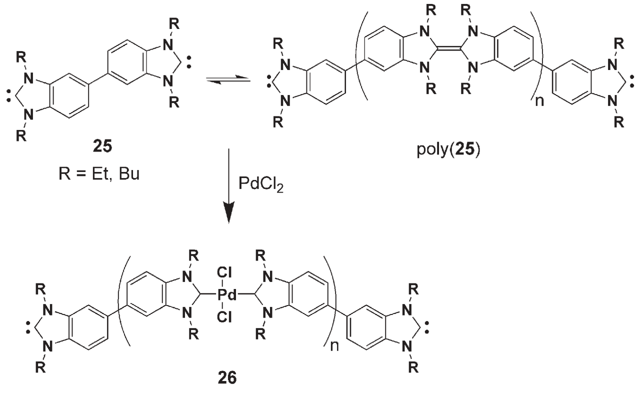

Fig. 14 Pd-based MCOPs synthesized by combining ditopic free bis(NHC)s with $PdCl_2$.

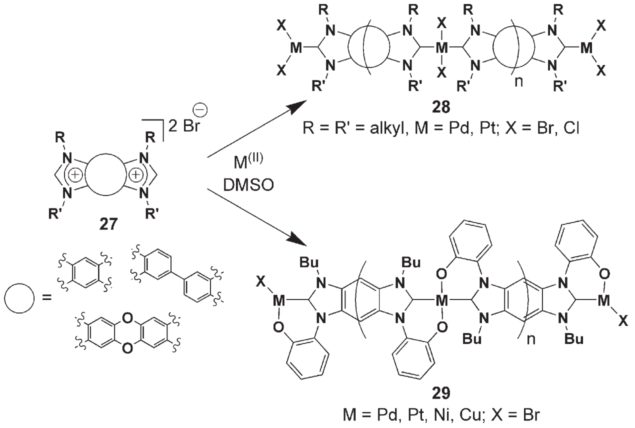

Fig. 15 Synthesis of main-chain organometallic polymers based on bis(NHC) frameworks from air- and moisture-stable monomers.

An advantage of using strongly donating monodentate ligands, such as NHCs, is that the metal center can remain coordinatively unsaturated, allowing additional ligands to coordinate various transition metal atoms. This feature can be used to tune the properties of the macromolecules post-polymerization. For example, addition of tricyclohexyl- or triphenylphosphine was found to effect dissolution of polymers that were otherwise insoluble in common organic solvents such as THF. Remarkably, the NHC ligands displayed such high affinities that macromolecular structure was not compromised even in the presence of excess phosphine.

3.2 Poly(metal acetylide)s

An interesting class of main-chain organometallic polymers under investigation since the 1970s is the poly(metal acetylide)s.[13] These systems generally involve group VIII to X transition metals, and within the same group, heavier metals typically lead to more stable macromolecules. For example, within group X-based polyynes, stability increases in the order of Ni < Pd < Pt, which can be ascribed to increasing ionic character of the M–C bond.

As opposed to the coordination polymers previously discussed, these polymers contain covalent carbon–metal σ-bonds in the main-chain. This bonding arrangement, combined with the conjugation provided by the diynes, results in rigid-rod structures. There is considerable electronic communication between the metal d-orbitals and the π-systems of the organic linkers which leads to extended conjugated structures, stimulating great interest in their synthesis and study. For example, extended π-conjugation in combination with highly polarizable metal centers often results in nonlinear optical (NLO) properties.[5] Another key property of these materials is their relatively high thermal and chemical stabilities. In the solid state, these polymers show decomposition temperatures under nitrogen of up to 350 °C. However, under air, the group X-based polymers exhibit explosive degradations at elevated temperatures.

Since the initial report by Hagihara and co-workers[13] on the preparation of Pd- and Pt-containing polyynes, considerable synthetic optimization and development has followed.[2,5] General synthetic avenues used to prepare poly(metal acetylide)s are depicted in Fig. 16. The first three methods (eqn (1)–(3)) utilize reactions of α,ω-diynes with metal(II) salts in accord with Path A (Fig. 9). A straightforward method to accomplish such polyyne syntheses is to deprotonate the diyne (*e.g.*, with ^{n}BuLi) and subsequently treat the dianion with a metal(II) salt. To avoid the use of strong bases and poor solubility from bis(acetylide) dianions, other milder methods have been developed that use transmetallation as a means to attach the alkyne ligands to the metal atoms. For example, *in situ* formation of Cu-acetylides (facilitated by exogenous bases such as amines) precedes transmetallation and subsequent polymerization (eqn (1) and (2)). Complete elimination of all bases (*e.g.*, alkyl lithiums or amines) can be accomplished by using preformed bis(stannane)s as the diyne comonomer. This is a particularly attractive methodology since decomposition of some transition metals is facilitated by amines. The tin acetylides undergo transmetallation to form new metal acetylides en route to polymer formation (eqn (3)). However, it is not necessary to form the metal acetylide bond as the key polymerization reaction. For example, an alternative approach uses preformed organometallic comonomers with terminal alkynes poised for alkyne dimerization (eqn (4)). A synthetic advantage of poly(metal acetylide)s is that these various access routes are, in general, each complimentary, with no one method being universally superior to the others.

Electronic and solubility tuning in these materials is usually achieved through functionalization of the arene linkers. For example, Fig. 17 depicts a series of Pt-based polymers (**30**) with varying conjugated linkers and lists their corresponding optical band gaps (E_g) (*i.e.*, the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital as determined by electronic absorption spectroscopy).[2] Alternatively, the physical properties of poly(metal acetylide)s can be varied by employing organometallic linkers, which ultimately clears a unique avenue to preparing bimetallic and multimetallic polymers.

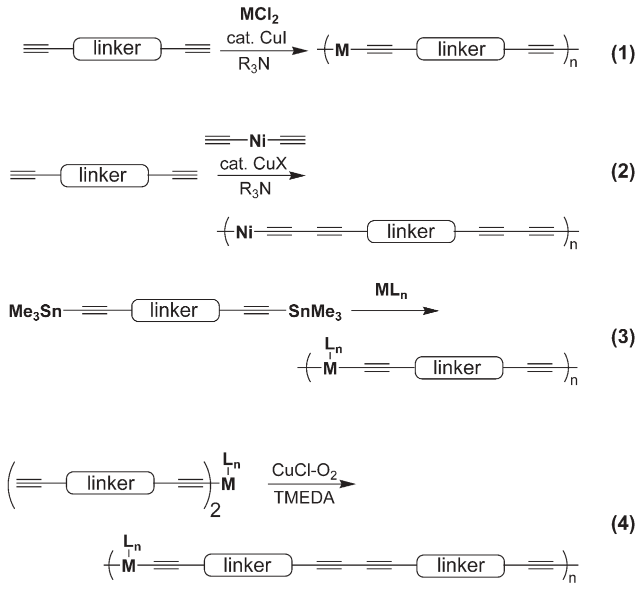

Fig. 16 General synthetic routes used to prepare poly(metal acetylide)s. Linkers are typically conjugated π-systems such as arylenes, vinylenes, and alkynes (selected examples are shown in Fig. 17).

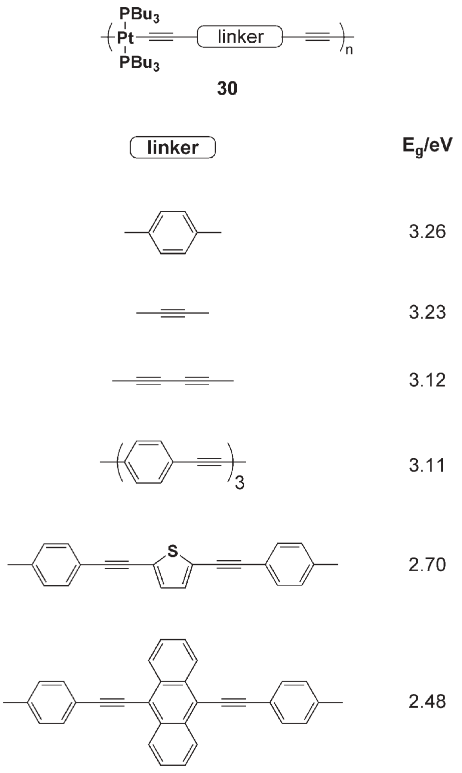

Fig. 17 A structurally varied series of Pt-based polyynes demonstrating tunable electronic properties. E_g/eV = energy of optical band gap in units of eV.

3.3 Poly(metallocene)s

Interestingly, the genesis of poly(metallocene)s can be traced back to the birth of organometallic polymers. The first organometallic polymer was reported by Arimoto and Haven in the 1950s.[1] In this founding report, radical polymerization of vinylferrocene **31** using various initiators successfully produced poly(vinylferrocene) **32** (Fig. 18). Since the initial report of this SGOP, poly(metallocene)s have experienced explosive growth and utility to become one of the most widely studied subclasses of metal-containing polymers.

Fig. 8 depicts some common main-chain poly(metallocene)s which are typically prepared using step-growth polymerizations. From a synthetic standpoint, it is important to consider the types of bonds that can be formed in order to prepare these materials. For most poly(metallocene)s, the bonds formed

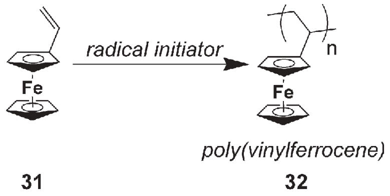

Fig. 18 Synthesis of poly(vinylferrocene) by Arimoto and Haven.

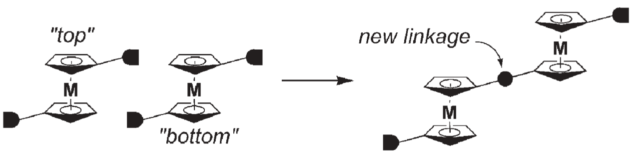

Fig. 19 Illustrative example of linkages formed between metallocene monomers during polymerization.

during polymerization are made from one arene to another. More specifically, Fig. 19 illustrates how the linkage of one monomer unit to another involves the connection of the "top" arene of one metallocene to the "bottom" arene of another unit. For example, reaction of 1,1′-bis(β-aminoethyl)ferrocene (**33**) with diacid chlorides or diisocyanates involves the condensation of amino groups on one ferrocene monomer with either an acid chloride or an isocyanate on the other. Ultimately, this results in the step-growth organometallic polyamides **34** and polyureas **35** in high yields with molecular weights up to 18000 Da (Fig. 20).[33] One exception to this more common architecture is the use of ditopic anionic linkers connected directly to the metal atom of a metallocene (*e.g.*, see polymer **12** in Fig. 8).[16]

Alternatively, metal–arene complexation can be used as the key polymerization reaction to prepare poly(metallocene)s (Fig. 21). This method generally provides polymers containing arenes such as biaryls and other polyaromatic hydrocarbons. One caveat to this approach, however, is that lower molecular weights are commonly observed and can be partially ascribed to the step-growth polymerization process (as opposed to a chain-growth) in combination with poor solubility of the intermediate oligomers.

More contemporary poly(metallocene) chemistry utilizes bridged metallocene monomers in ring-opening polymerization reactions (*i.e.*, Path C, Fig. 9). This powerful synthetic method was discovered by Brandt and Rauchfuss[34] and subsequently developed by Manners and co-workers.[2] Bridged (and often strained) metallocenes (*e.g.*, **36**) are transformed into main-chain poly(metallocene)s (**37**) (Fig. 22) using thermal, anionic, photo, and metal-mediated methods in solution or in the solid state. In addition, a remarkably broad range of metals have been successfully incorporated into poly(metallocene)s using this polymerization method. One of the most significant aspects of the ROP approach is that it proceeds *via* a chain-growth mechanism and polymers with extraordinarily high molecular weights (>10^6 Da) have been obtained.

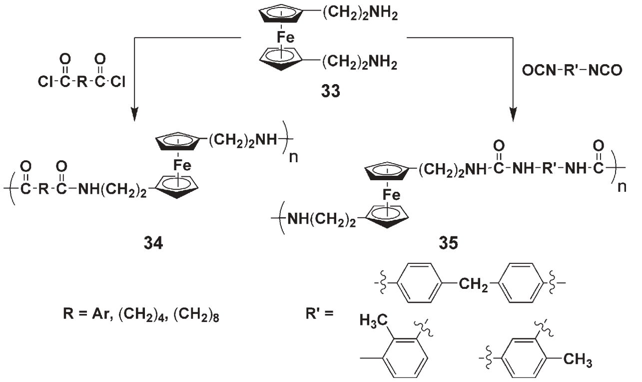

Fig. 20 Polycondensation routes employed to synthesize metallocene MCOPs.

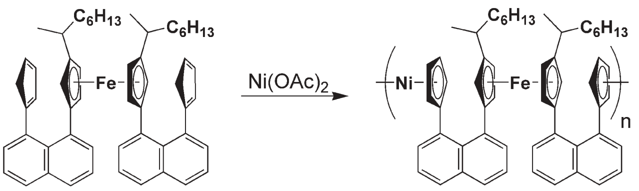

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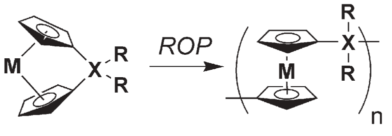
Fig. 21 Synthesis of a bimetallic poly(metallocene) using arene complexation as the polymerization event.



36 **37**

Fig. 22 General depiction of ring-opening polymerization method for synthesizing poly(metallocene)s.

In a related polymerization method, poly(ferrocene)s with conjugated linkers have been synthesized *via* ring-opening metathesis polymerization (ROMP) of ferrocenophanes. For example, Buretea and Tilley[35] and Grubbs and co-workers[36] have used ROMP of ferrocenophanes bridged by unsaturated alkyl chains such as ethylene and butadiene (**38** and **39**, respectively) to obtain highly conjugated poly(ferrocene)s **40** (Fig. 23). The solubility of these polymers can be tuned by incorporating alkyl groups in the unsaturated bridge. Using this modification, materials with molecular weights exceeding 3×10^5 Da were obtained and, interestingly, upon doping these polymers with I_2, they were found to exhibit conductivities of $\sigma = 10^{-5}$ S cm^{-1}.[37]

4 Characterization of main-chain organometallic polymers

The challenges associated with polymer characterization are unique beyond those of small molecules, and are often

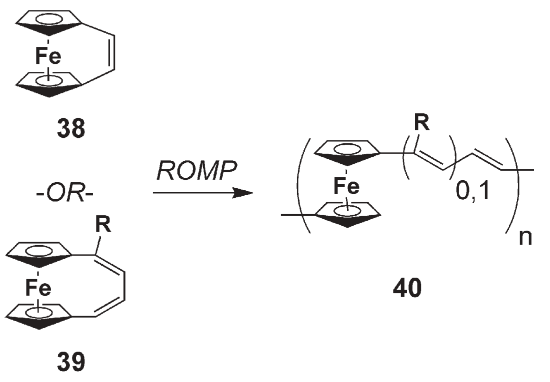


Fig. 23 Examples of a ROMP approach to highly conjugated poly(metallocene)s.

compounded by the presence of the incorporated metal centers. The repeat unit of a polymer chain can often be thought of as a small molecule in terms of determining its identity and structure. However, the challenge of ascertaining how many repeat units are actually incorporated into a polymer chain complicates characterization. Also, the macromolecular nature of polymeric materials can cause their physical properties to be drastically different than those of their monomer constituents.[7]

When characterizing a polymeric species, assuming the identity of the repeat unit is known, the molecular weight and polydispersity of the material are usually the primary descriptors. Most problems arise from poor solubilities,[38] depolymerization of labile coordination polymers upon dilution,[4] air or moisture sensitivity,[30] or a prohibitive interaction between the metal centers and the materials used for chromatographic separation.[39] Details regarding the unique challenges of trying to obtain accurate molecular weight data for MCOPs are discussed in this section, followed by an overview of other characterization techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), electronic absorption spectroscopy, and electrochemistry.

The most common technique for molecular weight determination of MCOPs is gel-permeation chromatography (GPC), which separates molecules based on their size. More specifically, it is the hydrodynamic volume of the polymer (*i.e.*, the volume of a hypothetical sphere that encapsulates the solution space of the molecule) that dictates its retention time. Regarding hydrodynamic volume and solubility parameters, if the metal present in the polymer results in a secondary structure in which the polymer folds back on itself, the hydrodynamic volume will decrease and the polymer will appear smaller than it actually is (and *vice versa*). The stiff linear shape adopted by many rigid-rod systems, for example, makes ascertaining accurate molecular weight data by GPC particularly subjective.[14] Another consideration is that GPC analysis utilizing refractive index (RI) or ultraviolet (UV) detectors does not provide exact molecular weight data; rather the data obtained is applied to a calibration curve constructed by organic standards, usually polystyrene or polyacrylates, of known molecular weights. Notably, there are no widely used organometallic standards for GPC analysis. The differences in the nature of the hydrocarbon standards and organometallic macromolecules can provide further discrepancies between relative and actual molecular weights. One detection method for determining exact molecular weights is light scattering, where particle size is measured directly based upon the intensity of the scattered light. However, organometallic polymers commonly absorb light in the visible region which complicates light scattering phenomena and often limits the use of this method for characterizing organometallic polymers.[38] NMR spectroscopy may also be used to measure the average molecular weight of (diamagnetic) MCOPs, but only if the end-groups can be accurately identified.[10,20]

Ultimately, it is important to note that because solution conformations vary greatly from one MCOP to another, accurate characterization protocols often require optimization on a "per polymer" basis. For example, GPC analysis requires that a polymer maintain consistent composition even under high dilution; accordingly, MCOPs comprised of relatively weak metal–ligand interactions may depolymerize under these conditions which may preclude this method of molecular weight determination.[23,30] Another example demonstrating complications in determining molecular weights of labile coordination polymers comes from a study where GPC and MALDI-MS (matrix assisted laser desorption ionization mass spectrometry) were used to characterize various terpyridine-based MCOPs.[39] The GPC data proved useful for determining relative molecular weights of these polymers, but the MALDI analysis caused considerable polymer fragmentation that was directly related to the applied laser intensity. A corollary to these findings is that one should be cautious when directly comparing molecular weights of MCOPs to polymer standards and/or other polymeric materials.

The thermal stability and physical characteristics of a polymer often contribute significantly in dictating the polymer's potential for application. Studying the temperature-dependent properties of a polymer often involves TGA and DSC studies. Both of these techniques involve heating a sample of the polymer (usually in the solid state) and monitoring for weight loss (TGA) or changes in heat flow (DSC). The former provides a means to measure decomposition temperatures while the latter provides information on important phase transitions.

Whereas TGA and DSC probe physical characteristics of a polymer, other techniques such as UV/Vis spectroscopy enable study of their electronic features. In general, UV/Vis (or electronic absorption) spectroscopy of MCOPs does not differ from that of other small- or macromolecular analytes. One notable caveat in which UV/Vis spectroscopy can be limited is in the analysis of labile coordination polymers. The problem arises simply from logistics. Typical concentrations for analysis range from 10^{-5} to 10^{-6} M. Polymers that display concentration-dependent molecular weights will depolymerize under such high dilution conditions, preventing an accurate measurement. This is particularly important since UV/Vis analysis of MCOPs is most commonly used to ascertain information about the electronic delocalization along an extended polymer chain (*i.e.*, over several repeat units). For example, whereas a monomeric palladium-bis(acetylide) (Fig. 24) displays an absorption maximum at 364 nm,[40] the corresponding polymer shows a maximum absorption at a longer wavelength (393 nm). The longer wavelength absorption suggests that the polymer structure contains an extended chromophore relative to the monomeric species. This key information supports two significant conclusions about the polymer's characteristics: (1) the polymer likely retains its macromolecular form even in dilute solutions, and (2) electronic communication extends over more than one repeat unit.

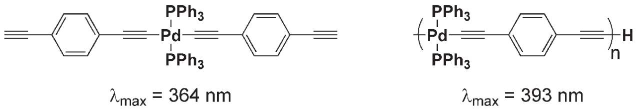


Fig. 24 Absorption maxima of a model metal-bis(acetylide) and its corresponding polymer.

Electronic characteristics can also be investigated through electrochemical analysis. Cyclic voltammetry provides a means to investigate the oxidation and reduction potentials of a system. Organometallic complexes are particularly interesting because they have multiple opportunities and sites for oxidation and reduction to occur. For example, oxidation and reduction can occur at the metal atom, or an ancillary ligand on the metal. Importantly, as one portion of the polymer is oxidized or reduced, it can significantly impact the electrochemical characteristics of the other moieties. When electrochemistry is used for studying systems with more than one metal (such is the case with MCOPs), the possibility of communication from one metal atom to another also becomes important.[41] Most commonly, electrochemistry (as an analytical tool) is used to investigate a MCOP's potential for use as a conductive material.[42] When a material conducts, it is successively oxidized and reduced as current (or electrons) flow through the material. More details regarding electrochemical analysis are discussed in the following section in the context of applications of conductive MCOPs.

5 Applications of main-chain organometallic polymers

The use of metal-containing polymers as functional materials has been in development for several decades, and commercial applications are on the horizon. While the metal atom clearly takes center stage in discussion of MCOPs, the organic linkers are often used as the sites for tuning physical properties (*e.g.*, solubilities, phase transitions, morphologies, liquid crystallinities, *etc.*), electronic characteristics (*e.g.*, conductivities), structural features (*e.g.*, chirality, tertiary structures, *etc.*), and mechanical properties. As such, the applications of MCOPs are largely dictated by the role and nature of the organic moieties linking and/or ligating to the incorporated transition metal atoms.

Swager has demonstrated that electrical conductivity in metal-containing polymers is a feature central to many applications including photoelectronics, molecular wires, electroluminescent devices, sensory materials, and various other applications that involve the bulk movement of charge through a material.[42] In some cases, materials that simply pass current are desired for use as organic–inorganic hybrids for electronic devices. In other applications, one form of energy is transformed into another (*e.g.*, light to current, or *vice versa*). In these situations, the conductive properties of the organometallic polymers facilitate the conversion, although it is important to note that other characteristics particular to the application must also be incorporated (*e.g.*, light absorptivity, oxidative stability, solubility, *etc.*) The mechanism by which electrons move through metal-containing polymeric materials is described in terms of how the metals interact with the organic framework as well as other metal atoms.

Classically, there are two descriptions taken from traditional inorganic chemistry that describe the mechanism of electron movement, namely outer- and inner-sphere electron transfer (Fig. 25). Outer-sphere electron transfer mechanisms are typically associated with side-group organometallic polymer motifs.[42] Regarding inner-sphere electron transfer, the important defining feature is that electron flow occurs between a metal atom and the attached bridging organic linker (and then onto the next metal center in the chain, and so on); thus, orbital overlap between the organic ligand and the metal atom is vital for conductivity to occur. For this reason, considerable attention is given to using metal atoms and organic linkers that have overlapping redox potentials, and accordingly are termed "redox matched." This condition facilitates electron transfer by assuring an optimal energy level agreement between the two interacting moieties. More specifically, electron conduction occurs more efficiently from a donating metal atom onto an organic ligand if the oxidation potential of the metal is at sufficient energy to match the reduction potential of the receiving ligand.[42]

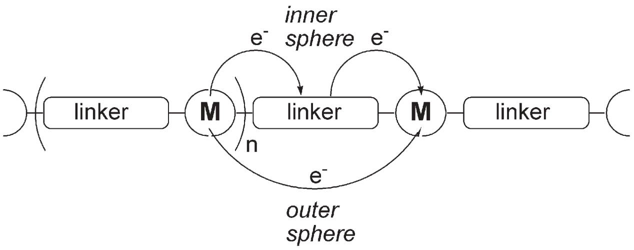
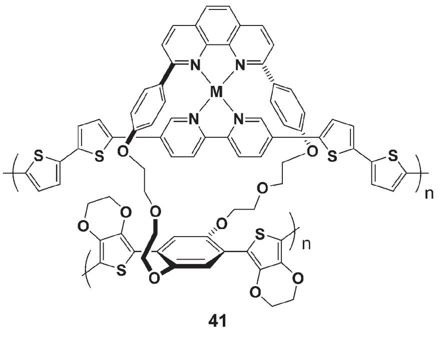


Fig. 25 Depiction of electron movement according to inner- and outer sphere mechanisms (top and bottom, respectively).

Recently, Swager has developed metallorotaxanes that show metal-dependent conductivities which may find utility in new sensory technologies.[42] The metallorotaxanes **41** (Fig. 26) are formed in the presence of metal salts *via* a self-assembly process to give conductive materials. When Cu(I) ions are incorporated, the materials were found to exhibit a high conductivity (σ = 38 S cm^{-1}). In contrast, when Zn(II) ions are incorporated, conductivity drops to 2 S cm^{-1}. The unique structural design may be described as a conductive polymer that is insulated by a nonconductive sheath, and is thus often referred to as an insulated molecular wire.

Organometallic polymers have features particularly attractive for NLO-applications as well. Orientation of the NLO chromophore is a control parameter that must be met for a NLO response to be observed. Requisite noncentrosymmetric arrangement is often achieved by exposure to an external electric field. Alignment by this method requires mobility of



41

M = Cu(I), Zn(II)

Fig. 26 Swager's metallorotaxane displaying metal-dependent conductive properties.

the NLO material, which can be accomplished for polymers in the solid state by conducting alignment at or above the T_g of the material. In ideal cases, the cooled NLO polymer retains its noncentrosymmetric orientation for extended (or indefinite) periods of time. Although this technique is not without certain caveats,[43] it offers a means of controlling chromophore alignment in inherently centrosymmetric materials (polymers). Of course, the synthetic aspects discussed above are also key to properties tuning when exploring MCOPs for NLO applications. In this regard, polymerization methods utilizing modular synthetic protocols will inevitably allow for broader control over their solubilities, processabilities, thermal stabilities, *etc.* Key for realization in electronic and optic devices, ferrocenes show very high thermal and photochemical stabilities.[2] As such, in addition to the poly(metal acetylide)s mentioned previously, poly(ferrocene)s have emerged as some of the most efficient organometallic molecules for NLO responses.[44]

Another application of MCOPs is their ability to be used as recoverable transition metal catalysts.[45] At first glance, it would appear that accessing metal centers within the polymer backbone would encumber catalysis. However, several polymeric systems are known to show activities that rival (or exceed) those of their small-molecule analogues. Of course, the primary objective in designing a polymer-supported (or incorporated) metal catalyst is to be able to recover the transition metal for reuse, thus increasing cost-efficiency and reducing metal contaminants in the waste stream. With this last consideration comes a criterion of stability. Specifically, in order for macromolecular structure to be conserved during the reaction, the polymeric catalyst must contain strong metal–ligand interactions such that depolymerization and metal leaching is minimized or eliminated completely.

In addition to the coordination polymer used by Ding (*e.g.*, see polymer **24** in Fig. 13), other approaches to obtain catalytically active MCOPs have used ionic bonding or combinations of ionic and coordinative bonds. Selected MCOPs reported by Sasai and Ding were recently highlighted as significant breakthroughs in recyclable catalyst technology.[46] These polymers make use of 1,1′:2,2′-binaphthol (binol) ligands with Al and Ti to form polymers of the general structure **42** (Fig. 27), which were synthesized by combining appropriate ligand precursors with readily available metal sources. These systems take advantage of the affinity of binol ligands for transition metals which, in these systems, contribute both ionic and coordinative metal ligation. Notably, in addition to increasing overall cost-efficiency through recyclability, the judicious choice of binol ligands provided a means for enantiocontrol over C–C bond forming reactions (Fig. 27). It was found that Al-based catalysts effectively gave up to 96% ee in Michael addition reactions, and Ti-based polymers catalyzed carbonyl–ene reactions with up to 99% ee. In each case, isolated yields were good to excellent, and the catalysts were active for up to five consecutive cycles. The heterogeneous MCOP catalysts were easily recovered at the completion of the reactions either by filtration in air (Ti-based), or by removal of supernatant and rinsing with fresh solvent under argon (Al-based).

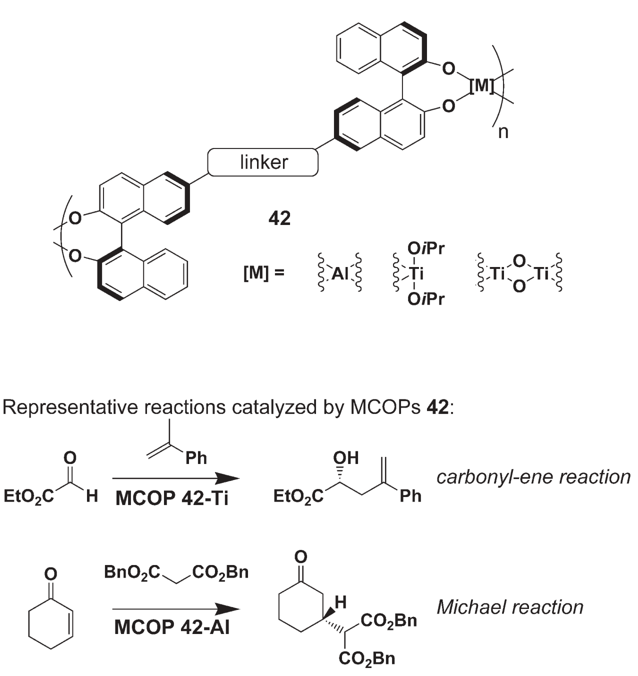
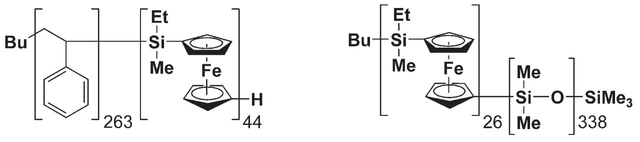


Fig. 27 Representative structure of binol-based MCOPs with applications as recyclable catalyst systems.

Carbon nanotubes (CNTs) hold great potential for applications in composite materials, nanoelectronics and nanoscale sensors. Because the properties of nanotubes are largely dependant on their size, research efforts are focused on preparing CNTs with very small structures. Recently MCOPs have been used to prepare CNTs with sub-nanometer dimensions.[47] Upon casting polystyrene-*b*-polyferrocenylsilane (PS-PFEMS) diblock copolymers (**43**) into thin films, these materials began to self-assemble into polyferrocenylsilane columns embedded in a polystyrene matrix. The inclusion of silicon in the iron-containing portion of the polymer limited the formation of iron clusters under the conditions required for nanotube growth and resulted in the formation of single-walled CNTs with diameters less than 1 nm. Additionally, the first organometallic nanotubes were prepared using MCOPs by simply allowing a poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (**44**) to self-assemble in hexanes (Fig. 28).[48]

6 Dynamic behavior in main-chain organometallic polymers

One of the most exciting new areas of macromolecular chemistry is the study of dynamic polymers.[49] Dynamic polymers may be defined as materials whose monomeric



43 **44**

Fig. 28 MCOPs utilized in the construction of organometallic nanotubes.

constituents are linked through reversible connections. As such, they undergo spontaneous structural reorganizations through assembly/disassembly processes in response to changes in external stimuli. Although polymer exchange reactions have long been documented (*e.g.*, transesterifications), the study of reversible polymerizations has received relatively little attention due to the difficulties in finding reactions with exquisitely controllable dynamic bonds. In fact, synthetic polymer methodology has historically been focused on specifically avoiding such exchange reactions and instead has sought to produce structurally well-defined, monodisperse polymers. The pursuit of polydisperse materials in dynamic equilibrium is a new direction and an emerging field in polymer chemistry with potential applications in self-healing materials, biomaterials, and synthetic self-replicating systems.

The equilibrium controlled processes that govern formation of coordination MCOPs makes these macromolecules particularly well-suited for studies in dynamic behavior. These unique systems respond to external stimuli by depolymerizing to return to organic ligand and metallic monomeric species. The constant formation and consumption of free ligand implies that it is advantageous to design systems in which the free ligands are relatively stable toward decomposition or other side-reactions after being liberated from a polymer chain. Other desirable features of a dynamic MCOP include a versatile ligand design and broad metal compatibility. Together, these two characteristics dictate the overall tunability of the system including the polymer shape, solubility, and conditions needed to facilitate polymerization/depolymerization processes.

Characterization of highly dynamic polymers can prove to be difficult because, by definition, the polymers are constantly changing their structural constituencies. For polymers that rapidly equilibrate under ambient conditions, molecular weights and viscosities are both concentration dependent. Thus, viscosity measurements have proven to be the most common method for characterization of these systems. While this method may not provide exact molecular weight data, relative molecular weights can be observed by studying a systematic series that varies in concentration. Discussed below are some examples that describe how MCOPs with various ligand–metal interactions may be used to control dynamic behavior and complications that arise during their characterization.

A series of dynamic polymers mentioned previously were reported by Craig *et al.*[23] and utilized palladium bimetallic species copolymerized with bipyridine units (see polymer **22** in Fig. 12). These polymers were studied in solution and found to exist as an equilibrium mixture of monomer, oligomer, and polymer. Polymer formation was observed by NMR spectroscopy and viscosity studies. An interesting feature of these materials is that the addition of monotopic pyridine-type ligands to solutions of polymer **22** reduces solution viscosity. This indicates that the polymers are reversible in solution, and that the equilibrium is shifted toward smaller polymeric species upon the addition of monotopic ligand, or other types of chain-transfer agents (CTAs).

Sijbesma and co-workers[8] have reported a series of Pd- and Pt-containing polymers based on bis(phosphine) linkers (see polymer **1** in Fig. 4). A significant feature of these coordination polymers is that despite using monodentate metal binding, they are strong enough to isolate in pure form and produce fibers. Their dynamic properties were probed through the use of trialkyl phosphines as CTAs. When solutions of the polymers were sonicated in the presence of up to 60 equivalents of CTA for eight hours, molecular weights were decreased from 10^5 to 10^4 Da. Interestingly, sonication alone (without CTA) also induced depolymerization, but to lesser extents.[8]

The ability to isolate and characterize dynamic polymers is facilitated by the strength of the ligand–metal interaction. As can be observed by comparison of Craig's and Sijbesma's systems, processability is often inversely related to dynamicity. That is, more easily depolymerizable systems are often harder to isolate and handle in the solid state. To realize the full range of potential for dynamic coordination polymers, robust systems still capable of depolymerization under reasonable conditions may be necessary. One class of MCOPs that meets these criteria is NHC-based macromolecules. Because of the high affinity of NHCs for various transition metals, stable high molecular weight polymers are attainable that show excellent thermal and chemical stability. Interestingly, bis(NHC)-based MCOPs **28** (Fig. 15) have also been shown to display dynamic behavior.[10] It was found that inclusion of (monotopic) benzimidazolium salts as CTAs during the polymerization reaction between bis(azolium) salts **27** and group X metals reduced their molecular weights. Pre-formed polymer was also found to decrease in molecular weight upon exposure to CTAs.

Beck and Rowan reported[50] the synthesis of a cross-linked organometallic polymer network based solely on metal–ligand coordination bonds (Fig. 29). Pyridines functionalized with benzimidazole groups at the 2,6-positions were connected through penta(ethylene glycol) spacer units to produce a ditopic ligand (**45**) capable of binding metals. With only Co(II) or Zn(II) present as the metal species, the resulting polymer adopts a linear shape with a 2 : 1 ligand to metal binding ratio. However, lanthanide ions were found to coordinate the ligands in a 3 : 1 ligand to metal ratio which enabled them to act as crosslinking agents. Thus, networked gels (**46**) were obtained

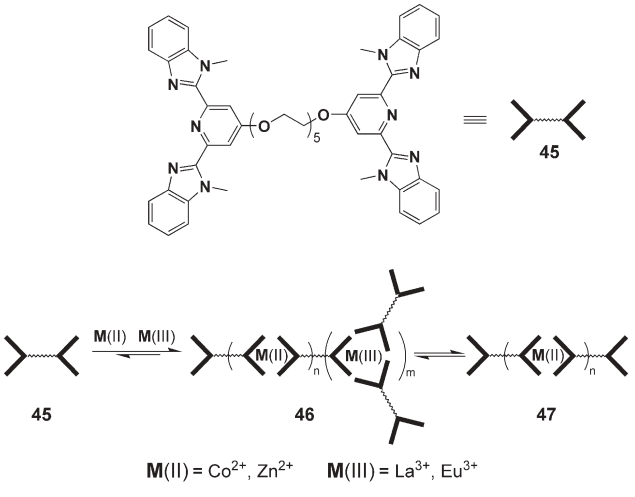


Fig. 29 Thermo- and mechano-responsive organometallic gels containing transition-metal and lanthanide ions.

upon the addition of La(III) and Eu(III). Because ligand coordination to the lanthanide ions is relatively weak, application of thermal or mechanical stress resulted in scission of the lanthanide-ligand coordination. This facilitated conversion of the networked gel to yield only linear Co(II) or Zn(II) polymer (**47**), as confirmed by UV-Vis spectrometry as well as visual observation of the transformation from gel to solution. Upon cooling or resting, the lanthanide ions were reincorporated into the material and a gel was reformed. Collectively, these stimuli-responsive materials hold outstanding potential for applications in biotechnology, separation science, and self-healing materials.

7 Conclusions and outlook

The field of organometallic polymer science has seen tremendous growth over the past five decades. Various design concepts have been utilized to incorporate metal centers into the main chains of polymers. This has included the development of new polymerization strategies that involve metal-containing monomers or the ligation of species which utilize metal-coordination as the key polymerization reaction. Incorporation of metals as an integral component of a polymer backbone remains a synthetic challenge that will undoubtedly be met with the development of new methodologies in polymer, inorganic, and organometallic chemistry.

A broad spectrum of potential applications has resulted from main-chain organometallic polymers, owing to their unique physical and electronic properties. It is worth noting that a conductive undoped all-organic polymer is yet to be reported. In contrast, many main-chain organometallic polymers display conductive or semi-conductive behavior even without the addition of dopants. Future studies will likely build upon the knowledge of redox-matching ligands with transition metals to further increase electrical conductivities exhibited by MCOPs. Recent breakthroughs in recyclable catalysts have involved the development of metal-containing polymers whose metal centers are specifically designed to facilitate organic transformations. The use of MCOPs in this manner is an emerging field that will undoubtedly continue to receive increasing consideration.

The influence of coordination polymers is expanding at an unprecedented pace as more researchers take advantage of the dynamic behavior of these materials. A vast continuum of coordination stability has been explored, ranging from materials whose macromolecular structure is immediately reverted to monomeric species upon dissolution to materials which are stable at extremely high temperatures. Recent advances in dynamic polymers with these systems will likely be aimed at development of materials that combine dynamic behavior with electronic and/or optical properties. Progress in this area may result in new applications in electronic systems or devices, such as self-healing circuits or new materials for molecular scale computing applications.

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