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Organometallic mediated radical polymerization**

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Keywords:
Controlled radical polymerization; Organometallic mediated radical polymerization; Cobalt mediated radical polymerization; Atom transfer radical polymerization; Reversible termination; Degenerative transfer

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Abstract

Controlled radical polymerization has become increasingly important over the past decade and a half, allowing for the facile synthesis of specific macromolecular architectures with excellent control over the chemical and physical properties. This article presents an organized and detailed review of one particular CRP technique, organometallic mediated radical polymerization (OMRP), focusing on the individual catalysts developed, their efficacy and monomer scope. Rhodium, cobalt, molybdenum, osmium, iron, palladium, titanium, chromium and vanadium mediated radical polymerizations are presented alongside organomain-group mediated reactions. A separate section reviews the types of copolymers which have been synthesized using OMRP techniques. An attempt is made to unify the many disparate names which have previously been used for OMRP by virtue of the common mechanistic aspects displayed by the different catalyst systems. A mechanistic discussion highlights the similarities and differences between these systems and examines the interplay between reversible termination and degenerative transfer OMRP and competing 1-electron redox processes.

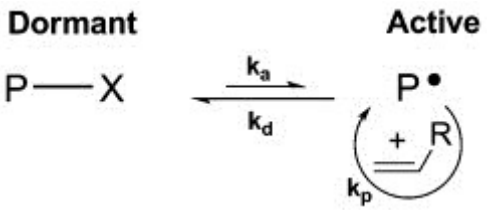
1. Introduction

Radical polymerizations are perhaps the most commonly employed industrial technique for the synthesis of polymeric materials, allowing the facile polymerization of a wide variety of vinyl monomers under mild conditions. The versatility of radical polymerizations is derived from their tolerance to functional groups, both within the monomer and in terms of external impurities. The highly active, growing radical species enable rapid polymerization but do not react with polar or protic compounds. However, this high reactivity results in bimolecular termination reactions between the neutral species, such as recombination and disproportionation. Initiation is slow relative to the extremely fast propagation rate, and the fast termination reactions mean that new chains are continually generated and control over the polymer molecular weight and polydispersity index is poor.[1]

The properties and applications of a polymer depend on the molecular weight distribution and molecular structure; the composition, topology and functionality of the polymer are all important.[2] Synthetic procedures which allow control over these parameters are therefore of great significance, particularly those which are not industrially demanding. One such process is controlled radical polymerization (CRP) which, through minimization of the side-reactions, has allowed the synthesis of novel functionalized materials with well-controlled molecular weights and molecular weight distributions.

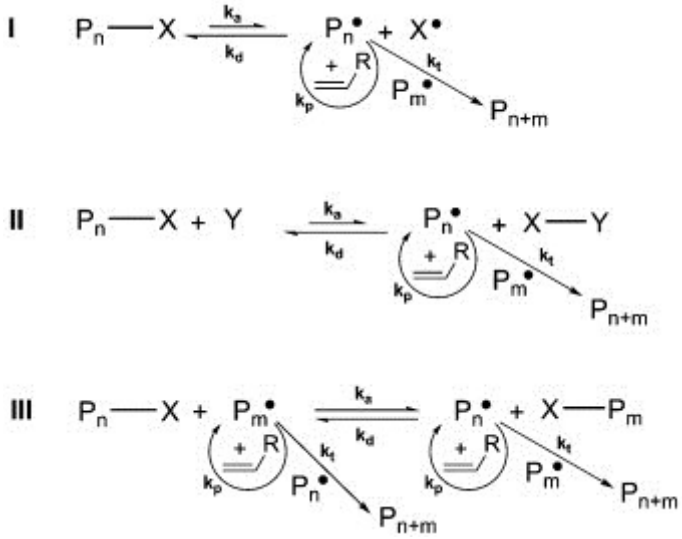
CRP techniques combine the precision polymer synthesis of a living polymerization with the versatility and tolerance of a free radical polymerization. The principle of equilibration between a growing radical chain and a dormant species (Scheme 1) is used to reduce chain breaking reactions and ensure quantitative initiation,

resulting in excellent control over molecular weights, polydispersities and end functionalities. Although termination is minimized, it is not eliminated and the presence of unavoidable termination reactions means that a truly living radical polymerization is still a goal aspired to by polymer chemists.



Scheme 1. Equilibrium between dormant and active species.

The position and dynamics of the equilibrium between the dormant and active species defines the rate of reaction, the molecular weight and the polydispersity of the polymer formed during a CRP. Mechanistically, there are three main types of CRP, differentiated by the nature of the deactivation process (Scheme 2).[3]



Scheme 2. Controlled radical polymerization mechanisms.

The first system is based on reversible deactivation through coupling, or reversible termination, (see **I** in Scheme 2) and involves homolytic cleavage of the dormant species into a propagating radical chain and a "stable" or persistent free radical. The persistent radical, $X^{\bullet}$, eventually becomes the dominant species, due to the persistent radical effect.[4] This results in a propensity for cross-termination between the propagating

species and the persistent radical, strongly inhibiting self-termination of the transient radicals and affording control of the polymerization. The earliest reports were of the versatile nitroxide-mediated polymerizations (NMP), which used persistent radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as the spin trap.[5] The spin trap should neither react with itself nor the monomer and does not actually have to be a radical species. In the case of thioketones,[6-7] phosphites,[8] reactive but non-polymerizable alkenes such as stilbene[9] and diphenylethylene[10] and certain transition metal compounds,[11-12] control over the polymerization is mediated by the reaction of the propagating radical with a species containing an even number of electrons. Much recent work has focused on organometallic mediated radical polymerization (OMRP) which allows control over polymerizations based on the reversible homolytic cleavage of the weak bond between an alkyl group and a transition metal catalyst.[13-18] It is worth noting that a stoichiometric amount of the mediating species is required in these systems because all of the propagating chains require an end-group.

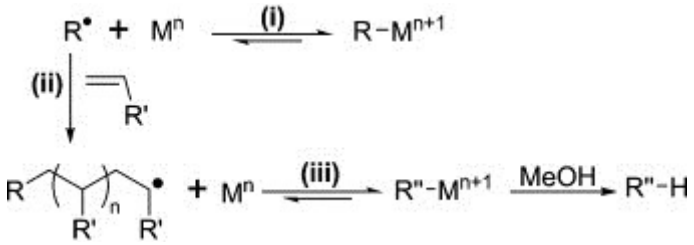
The second system employs reversible deactivation through atom transfer and involves a redox-active transition metal catalyst, typically used in conjunction with an alkyl halide initiator. The active radical species are generated through homolytic cleavage of carbon-halogen bonds via a reversible redox process catalyzed by the transition metal complex. The propagating radicals are temporarily deactivated through a halogen-transfer reaction with the oxidized complex, with the dynamic equilibrium between dormant and active species imparting control over the polymerization.[17, 19-23] Atom transfer radical polymerization (ATRP, see **II** in Scheme 2) has been reported for a wide variety of transition metal complexes.[15] This mechanism also relies on the persistent radical effect, but since the dormant species are capped by halogen atoms transferred by a metal catalyst, substoichiometric amounts of metal complex can be used.

The third process (**III** in Scheme 2) is known as degenerative transfer radical polymerization (DT) and is based on a thermodynamically neutral bimolecular exchange between a low concentration of growing radical chains and a dormant species.[17] The exchange may occur via atom or group transfer processes, with examples including alkyl iodides,[24] organotelluriums,[25-27] organostibines[25-27] and organobismuthines.[26] Addition-fragmentation chemistry also utilizes the degenerative transfer process with examples including reversible addition fragmentation chain transfer (RAFT) polymerization[28-30] and macromolecular architecture design by interchange of xanthates (MADIX).[31-32] These associative radical exchange systems are different to the first two processes shown in Scheme 2, because DT does not involve a persistent radical and the kinetics and rate of polymerization are therefore similar to a conventional free radical polymerization. The polymerization rate is proportional to the square root of the concentration of the radical initiator, rather than the concentration of the transfer agent,[15] and the exchange process usually takes place through short-lived intermediate species.

Controlled radical polymerization is unlikely to replace conventional radical polymerization for the production of large volume, commodity polymers.[33] However, there is a need for the production of

medium-to-high end specialty polymers with controlled architectures, with an anticipated market of greater than $20 billion per year.[34] CRP techniques have begun to fill this niche, with NMP, ATRP and DT polymerizations all developed for industrial use over the past 20 years.[35] Thus far, the commercialization of OMRP has been hindered by the limited monomer range and the high costs associated both with the metal complex and its removal from the polymer. Despite these drawbacks, OMRP is still an attractive technique because of the inherent scope of the system. With judicious choice of metal centre and careful ligand design, the metal-carbon bond strengths possess great tunability. By exploiting the steric effects of the ligand coordination sphere, it should be possible to adjust the metal-carbon bond strengths to suit any monomer. This will allow the controlled polymerization of a wide variety of monomers and promote the production of copolymers and advanced polymer architectures.

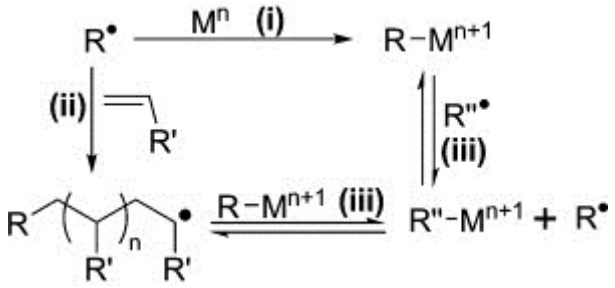
Organometallic mediated radical polymerization is based on the fast and reversible homolytic cleavage of a metal-carbon bond. This mechanism may proceed using the reversible termination (RT) principle, where the transition metal acts as a reversible spin-trap. RT OMRP is initiated by using conventional free radical initiators with a redox-active metal compound, or by utilizing a complex containing a pre-formed metal-carbon bond, and comprises three main steps. The growing, radical-terminated chain exists in equilibrium with the dormant species, which in the case of RT OMRP is metal-terminated. A low concentration of radical species present at any one time allows control over the molecular weight and polydispersity index (PDI), and so the equilibrium should favour the formation of the metal-carbon bonds of the deactivated polymer chain (Scheme 3). The free radical initiator decomposes homolytically to release carbon-based radicals, which can either react reversibly with the transition metal complex to form a dormant species with a weak metal-carbon bond, **(i)**, or enter the propagation stage, **(ii)**. Propagation continues until the growing, radical-terminated polymer chain reacts with the metal complex to form the dormant species in the deactivation step, **(iii)**. Reactions are often quenched by the addition of a protic solvent such as methanol, which can hydrolyze the metal-carbon bonds and yield polymer chains with saturated end groups.



Scheme 3. Reversible termination OMRP mechanism.

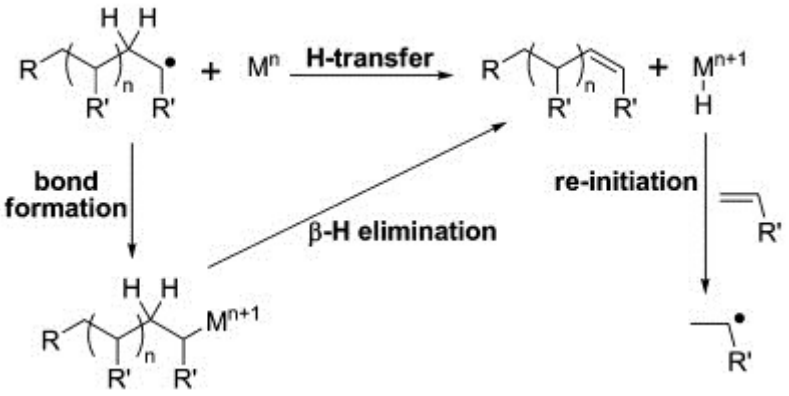
OMRP may also proceed through a degenerative transfer process (Scheme 4). In this case, the rate of polymerization is negligible until the concentration of radicals exceeds the concentration of the initial metal

species. The radicals formed from the initiation process react with the metal complex to form the dormant species, **(i)**, or with the monomer to form a propagating radical chain, **(ii)**. An associative exchange then takes place, with an active radical replacing the metal-bound radical of the dormant species, **(iii)**. These DT OMRP reactions are often characterized by long induction periods, during which time the initial radicals are converted to organometallic species.[36-37]



Scheme 4. Degenerative transfer OMRP mechanism.

An important side-reaction to consider in OMRP systems is catalytic chain transfer (CCT). CCT is a non-living process which can interfere with chain growth in pseudo-living polymerizations. CCT polymerization (CCTP) results from the intermolecular transfer of a hydride between the propagating radical and the metal complex. The mechanism is thought to involve conventional hydrogen transfer, but the possibility of bond formation followed by β-H elimination has not been discounted (Scheme 5).[38] Hydrogen abstraction from the growing polymer radical and transfer to another molecule of the monomer initiates a new propagating radical chain.[39] Thus, unlike controlled radical polymerizations, the amount of radical initiator does not determine the number of growing radical chains. CCT produces short-chain, olefin-terminated oligomers, with molecular weights largely independent of conversion. In OMRP, a low M-C bond dissociation energy will result in a relatively high radical concentration. The concentration of catalyst will also be high, thus potentially favouring a β-hydrogen abstraction reaction.[13]



Scheme 5. Catalytic chain transfer.

There are a variety of metal complexes active in OMRP and while the use of many different acronyms and terminology makes it difficult to compare and contrast the systems, the common denominator is that control over the polymerization is afforded by an organometallic species. The purpose of this review is therefore to discuss the different metal systems in terms of their efficacy, monomer scope and mechanism, to provide a comprehensive, stand-alone review of OMRP. While there is good coverage of OMRP in both more general reviews[15] and more specific reviews,[13-14, 17-18] this review includes detailed discussion on all metals engaging in OMRP, including main group. In addition, the development of OMRP for the synthesis of macromolecules is discussed. This review also attempts to unify many disparate names for organometallic mediated CRPs (which include stable free radical polymerization (SFRP), organometallic radical polymerization (OMRP), cobalt mediated radical polymerization (CMRP), organotellurium mediated radical polymerization (TERP), organostibine mediated radical polymerization (SBRP) and organobismuthine mediated radical polymerization (BIRP)) by recognizing their common mechanistic aspects.

2. Metals participating in OMRP

2.1. Early OMRP systems

2.1.1. Rhodium

The first example of OMRP was reported in 1992 by Wayland.[40] Two equivalents of tetramesitylporphyrinato rhodium(II) (Figure 1) reacted with an excess of the acrylate monomer to form a dirhodium species bridged by an alkyl chain, [(TMP)RhCH_2CH(CO_2X)CH(CO_2X)CH_2Rh(TMP)] (X = H, Me, Et), which could be fully characterized in the absence of light. Exposure of this complex to visible light homolytically cleaved one of the RhCH_2 bonds, resulting in the formation of [(TMP)Rh(II)]$^{\bullet}$, which did not initiate acrylate polymerization, and [(TMP)RhCH_2CH(CO_2X)CH(CO_2X)CH_2]$^{\bullet}$, which successfully initiated the polymerization of acrylic acid (AA), methyl acrylate (MA) and ethyl acrylate (EA). The growing radical chain was reversibly trapped by [(TMP)Rh(II)]$^{\bullet}$, with the exchange between dormant and active species imparting some control to the polymerization. However, the trapping species could also reinitiate polymerization, through formation of the bridged dirhodium initiator, resulting in the generation of new growing chains. This uncontrolled initiation, coupled with self-termination reactions between the growing chains, resulted in broadened PDIs of 1.75-2.75 for the polymerizations.

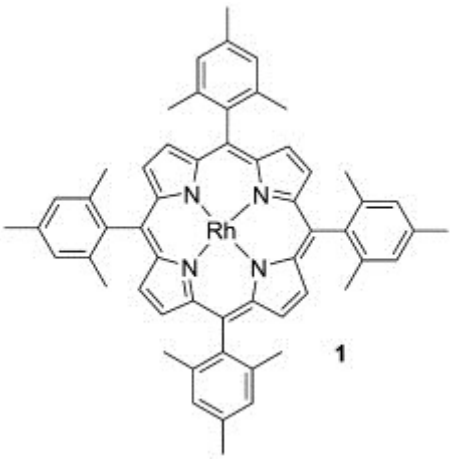
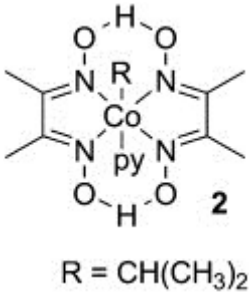


Figure 1. Tetramesitylporphyrinatorhodium(II).

2.1.2. Cobalt

Much recent work has been devoted to the development of CRP utilizing cobalt.[14] Early systems were based on porphyrins[41] and cobaloximes,[42] with isopropylpyridinato cobaloxime, $RCo(dmg)_2(py)$, **2**, shown to be an active photoinitiator for ethyl acrylate polymerization in chloroform. Molecular weights increased linearly with conversion, although there was a discrepancy between the observed and theoretical molecular weights above 40% conversion, with PDIs >1.5. Homolytic cleavage of the cobalt-carbon bond resulted in the formation of a persistent Co(II) radical and an unstable carbon-based radical which reacted with the monomer to initiate the polymerization. The reaction could be halted by removing the light source and the dormant chains reinitiated upon exposure to light.[42-43] The presence of unsaturated chain ends was ascribed to β-hydrogen transfer to cobalt as the concentration of monomer in the reaction decreased. Attempts to run the polymerizations in bulk or other solvents were unsuccessful, as chain transfer and termination reactions became competitive with propagation, resulting in low molecular weight polymers independent of conversion.[44] The steric environment of cobaloximes favours β-H abstraction, with many successful CCT polymerization catalysts based on cobaloximes.[45-46]



R = $CH(CH_3)_2$

Figure 2. (Isopropylpyridinato)cobaloxime.

Utilizing the tetramesitylporphyrin ligand, originally investigated for rhodium, in conjunction with cobalt resulted in a much more efficient OMRP system.[41] Organometallic derivatives of (TMP)Co (**3** in Fig. 3) initiated and controlled the polymerization of methyl acrylate, with living characteristics evidenced by the linear increase of molecular weight with conversion, PDIs of 1.1-1.3 and successful stop-start reactions. By heating the complexes to 60°C, the metal-carbon bond was homolytically cleaved, forming the persistent radical, [(TMP)Co(II)]$^{\bullet}$ and a carbon-based radical which initiated polymerization, before being reversibly trapped by the Co(II) species. Block copolymers could also be synthesized by introducing the second monomer feed after the reaction with methyl acrylate was complete. The steric bulk of the mesityl groups is important to prevent β-hydrogen elimination from the growing polymer chains and to disfavour dimerization of the complex, both of which would be detrimental to the control over the polymerization. Many cobalt porphyrin complexes have been reported which are extremely effective for catalytic chain transfer polymerization.[45-46]

Modification of the porphyrin ligand, through substitution of bromine groups on the pyrrole rings, resulted in the formation of a Co(II) system which retained control over the polymerization comparable to TMPCo, but with polymerization rates up to 30 times faster. Addition of electron-withdrawing groups on the ligand was proposed to stabilize the cobalt(II) oxidation state and reduce the metal-carbon bond dissociation enthalpy. A higher concentration of active radicals was formed from ($TMPBr_8$)Co (**4** in Fig. 3), in comparison to the same amount of TMPCo, and the shift in the equilibrium towards the active species resulted in a faster polymerization.[47] The weaker cobalt-carbon bond allowed the polymerization of methyl acrylate to be carried out lower temperatures and control over the system was maintained even at room temperature.[48]

A more convenient and practical procedure was discovered in 2004, using an organic radical source with [(TMP)Co(II)]$^{\bullet}$ to generate the Co(III) initiator *in situ* and produce polymers with extremely low PDIs.[49] At 60°C the $t_{1/2}$ of the initiator, 2,2'-azo-bis-(4-methoxy-2,4-dimethyl valeronitrile (V-70), is 11 minutes, making it a relatively short-lived radical source which converted the Co(II) species to [(TMP)Co(III)R] during an induction period. β-Hydrogen abstraction from the methyl group of the radical initiator formed an unsaturated olefin species and [(TMP)Co(III)H]. Addition of the monomer to the cobalt hydride complex formed [(TMP)Co(III)$CH(CO_2R)CH_3$], the desired initiating species for methyl acrylate polymerization. This organo-cobalt species controlled the concentration of polymer radicals and facilitated living polymerization, resulting in polymers with molecular weights that increased linearly with conversion and were very close to theoretical molecular weights, indicating that only 1 polymer chain per cobalt centre was formed. PDIs were very low (1.04-1.11) and block copolymers could be synthesized. Importantly, no β-H abstraction from the polymer radicals was observed.

It was noted that the polymerization rate was very slow if the concentration of the cobalt complex was greater than the concentration of radicals, but that even a slight excess of R$^{\bullet}$ significantly increased the rate, without loss of control. This drastic change in rate had important mechanistic implications for the cobalt porphyrin

systems. During the period of continuous radical influx, the polymerization is mediated by a degenerative transfer mechanism.[37] Approximately 90 minutes is required for the complete decay of the V-70 initiator at 60°C, during which time 1.2 radicals per molecule of initiator are released and a degenerative transfer mechanism operates. Once these radicals have been used up, a significant decrease in the polymerization rate occurs due to the reversible termination mechanism taking control. For polymerizations mediated solely by reversible termination, rates are extremely slow (0.7 eq. $R^{\bullet}$ reached 47% conversion in 62 hours, compared with 54% conversion in 150 minutes for 1.2 eq. $R^{\bullet}$ and 69% conversion in 105 minutes for 2.0 eq. $R^{\bullet}$, with all other polymerization conditions identical).[49] Exploitation of the degenerative transfer mechanism allowed less bulky porphyrin ligands to be used, as the low concentration of Co(II) radicals in solution prevents β-H abstraction. (TAP)Co, **5**, gives CCTP under reversible termination conditions (0.9 radicals per Co), but increasing the radical concentration to 1.1 equivalents per Co allowed OMRP to occur through the degenerative transfer mechanism, with high molecular polymers with PDIs of 1.1-1.15 formed.[37]

The robust nature of the cobalt porphyrin complexes prompted their application to the polymerization of more challenging monomers such as acylic acid and vinyl acetate (VAc). Water soluble $[(TMPS)Co(II)]^{\bullet}$, **6**, and $[(TSPP)Co(II)]^{\bullet}$, **7**, were used in conjunction with V-70 to control the polymerization of acrylic acid through a degenerative transfer OMRP.[50] As previously discussed, the DT mechanism operates for the first 90 minutes of the polymerization until the external radical source is used up. After this time, reversible termination becomes the only source of radicals, with a concomitant decrease in the polymerization rate. High molecular weight, low polydispersity poly(acrylic acid) was produced (M_n of 232,000, PDI of 1.2) in just 30 minutes using the TMPS cobalt system.

Controlled radical polymerization of vinyl acetate has long been recognized as a challenge facing polymer chemists, due to the difficulty in activating this monomer and then controlling the equilibrium between the unstabilized radical and the dormant species. $[(TMP)Co(II)]^{\bullet}$ was recently reported to control the polymerization of vinyl acetate, with living characteristics at low monomer conversions.[51-52] The strong $CoCH(OAc)CH_2R$ bond disfavours homolytic cleavage, resulting in a rate of reversible termination OMRP which is negligible. However, interchange of the radicals in solution with the organocobalt species through a degenerative transfer mechanism gives polymers with PDIs of 1.1-1.3, which exhibited first order rate kinetics at conversions below 20%. Both AIBN (2,2'-azobis(2-methylpropionitrile)) and V-70 were used in these investigations, as their vastly differing half-lives allowed a constant influx of radicals into solution. This decreased the induction period and prolonged the polymerization by constantly introducing radicals into the reaction. Above 20% conversion, deviations from CRP were observed as radical termination and chain transfer reactions were prevalent.

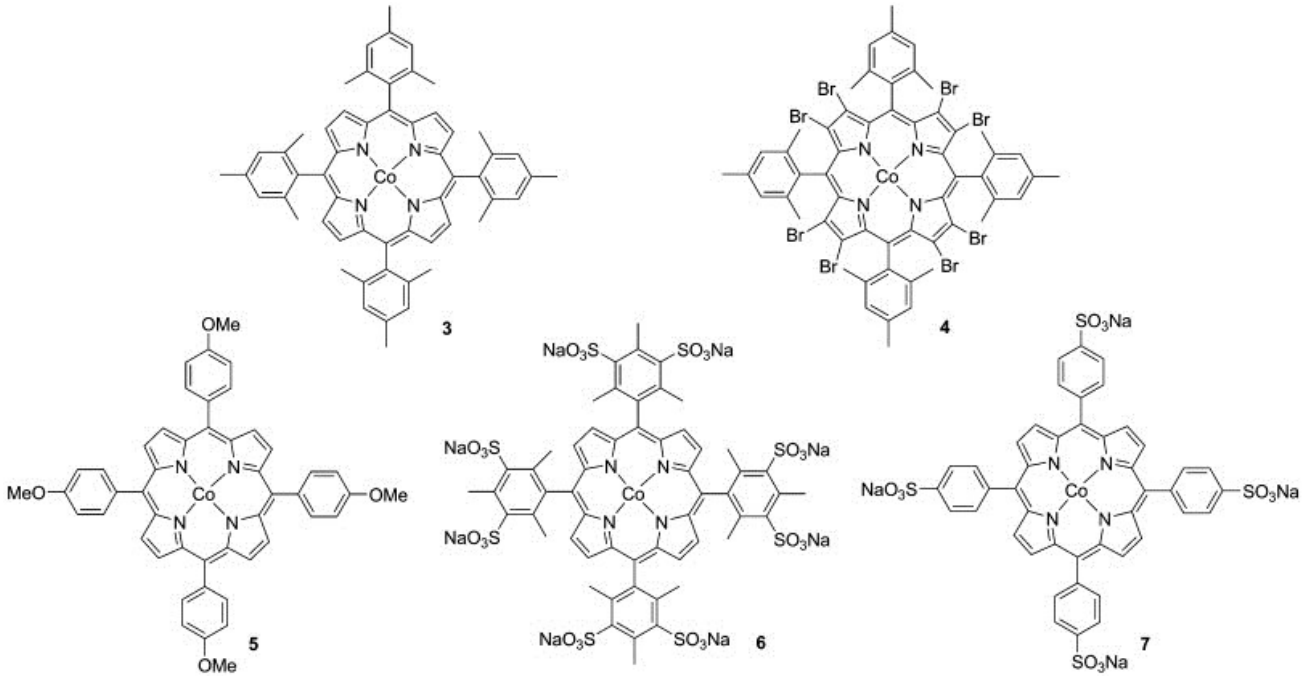


Figure 3. Co porphyrin complexes active in OMRP. (TMP)Co, **3**; ($TMPBr_8$)Co, **4**; (TAP)Co, **5**; (TMPS)Co, **6**; (TSPP)Co, **7**.

2.2. Development of Co-based OMRP systems

The first efficient OMRP of vinyl acetate was reported by Jérôme *et al.* in 2005. They used commercially available $Co(acac)_2$ (**8** in Fig. 4) and V-70 at 30°C for the bulk polymerization of vinyl acetate.[36] After a 12 hour induction period, during which time the colour of the reaction changed as the Co(II) precursor was oxidized to Co(III) organometallic species, a controlled polymerization progressed with first order kinetics, a linear increase in molecular weight with conversion and low PDIs of 1.1-1.2. Replacing V-70 with AIBN and running the polymerization at elevated temperatures (60°C) imparted some control, but molecular weights were higher than the theoretical values and PDIs were broad (2.0-3.5), indicating that irreversible chain termination was occurring.

The $Co(acac)_2$/V-70 system could also be extended for use in aqueous suspension[53] and miniemulsion[54] polymerization of vinyl acetate, with conversions of >95% reached in just 1 hour at 30°C. This allowed the synthesis of a range of PVAc latexes with targeted molar weights and PDIs as low as 1.3. Supported systems,[55] immobilizing the cobalt on silica and Merrifield resin, allowed the synthesis of well-controlled poly(vinyl acetate) without the coloured metal residues. Some loss of control was observed with the Merrifield resin, attributed to poor dispersion, but PDIs were generally between 1.3-1.4 and the supported systems also allowed facile catalyst recycling.

In order to address the inconvenient storage and handling of V-70, attempts were made to replace the organic initiator with a redox system capable of polymerizing VAc in the presence of $Co(acac)_2$.[56] The use of lauroyl or benzoyl peroxide as oxidants and $Co(acac)_2$ as the reducing agent was met with limited success. Although molecular weights increased linearly with conversion, PDIs broadened significantly above 20% conversion and were typically 1.7-2.6, with GPC traces showing bimodal distributions. Addition of ascorbic or citric acid as reducing agents improved the system. Despite inefficient initiation, which resulted in molecular weights higher than the theoretical values, PDIs remained low and the GPC traces were monomodal. The citric acid/lauroyl peroxide system reached 80% conversion in 3 hours, with high molecular weights (79,000 Da) and a PDI of 1.4

Originally, a reversible termination mechanism was proposed for the polymerization of VAc using $Co(acac)_2$.[36, 53-56] The initiation step was known to be different to acrylate polymerization using cobalt porphyrins, as there was no evidence for initial formation of a cobalt hydride species,[49] followed by hydrocobaltation of the first monomer unit. The presence of functional groups derived from V-70 at the α-chain end of the polymers confirmed that the polymerization was initiated by the thermal decomposition of V-70. Successful resumption of vinyl acetate polymerization from a PVAc-$Co(acac)_2$ macroinitiator supported the reversible termination mechanism.[36] However, the persistence of control, independent of whether 1 equivalent or 6.5 equivalents of V-70 were used,[57] prompted further studies. Reactivity, polymerization and computational studies led to the conclusion that vinyl acetate polymerization mediated by $Co(acac)_2$ and initiated by V-70 proceeds through degenerative transfer in the absence of Lewis bases, but the mechanism switches to reversible termination in the presence of electron donors such as water or pyridine.[58-59] In the absence of electron donors, a long induction period was observed during which an essentially irreversible reaction converting the Co(II) species to Co(III)R occurred. Towards the end of this transformation, the low concentration of Co(II) meant that the radicals generated from V-70 were not efficiently trapped and rapid polymerization occurred. The intervention of a degenerative transfer mechanism affords control over the polymerization, with excellent molecular weight control and PDIs of 1.1-1.2.[58]

PVAc-$Co(acac)_2$ macroinitiators could not reinitiate polymerization under strictly anhydrous and O_2-free conditions, but the addition of water to the purified macroinitiator allowed chain extension.[58] The water molecules were proposed to stabilize the Co(II) radical trap, favouring the homolytic cleavage of the cobalt-carbon bond and shifting the radical equilibrium, allowing the reversible termination OMRP to occur. Polymerizations carried out in the presence of 30 equivalents of pyridine with respect to Co(II) did not show the induction period typical of the degenerative transfer mechanism. However, although molecular weights did increase linearly with conversion, there was a loss of control as evidenced by molecular weights which deviated significantly from the theoretical values and broadened PDIs of 1.3-1.5. This was attributed to slow initiation and inefficient trapping by the $Co(acac)_2$(ED) species.[58-59] The presence of an electron donor (ED) such as water or pyridine blocks the coordination site on the Co(III) dormant species which is required

for an associative radical exchange, thus preventing degenerative transfer and favouring a reversible termination OMRP.

The $Co(acac)_2$/V-70 system has shown some efficacy in mediating the radical polymerization of other monomers. Vinyl chloroacetate (VClAc) and *N*-vinyl-2-pyrrolidone (NVP) were investigated by Matyjaszewski *et al.*,[60] who found that control over these monomers was inferior to that observed with vinyl acetate, with broadened PDIs of 1.7-2.2 at 50% conversion and molecular weights which were higher than the theoretical values. Control over the polymerization could be improved by copolymerization of these monomers with VAc. Improved control over NVP homopolymerization could be achieved by varying the V-70/Co ratio, with an optimal ratio of 8:1 giving polymers with PDIs as low as 1.3.[61]

The high reactivity of acrylonitrile (AN) means that it is a difficult monomer to control, as the reactive radical species undergo rapid propagation and termination reactions. Additionally, the low solubility of poly(acrylonitrile) often causes inhomogeneous reaction mixtures, which are less than ideal for controlled radical polymerizations. The use of the $Co(acac)_2$/V-70 system at 30°C in coordinating solvents gave promising results.[62] In DMF, molecular weights increased with conversion and although the observed molecular weights were higher than theoretical values, with PDIs of 1.6-1.9, this was attributed to poor initiation and low solubility of the polymer. Switching to DMSO improved the polymer solubility, but it was noted that the molecular weights were still significantly higher than theoretical values and did not increase linearly with conversion. Slow initiation was proposed to cause a change in the radical concentration during the polymerization, as more chains were formed, resulting in non-linear kinetics and broadened PDIs of 1.3-1.5. A more efficient initiating system proved to be $RCo(acac)_2$, where R was a poly(vinyl acetate) oligomer synthesized through DT OMRP.[59] Use of this Co(III) organometallic species resulted in acrylonitrile polymerization with no induction period, first order kinetics with respect to monomer and molecular weights which increased linearly with conversion. At 30°C the molecular weights were still somewhat higher than the theoretical values, with PDIs of 1.2-1.4. However, decreasing the polymerization temperature to 0°C gave molecular weights that were in good agreement with theoretical values and PDIs of *ca.* 1.15. DFT calculations and X-ray structure analysis supported the hypothesis that the solvation of the cobalt complex by DMF or DMSO changed its reactivity, weakening the cobalt-carbon bonds and allowing fast initiation. Good control over the polymerization is afforded by the RT OMRP mechanism which operates in the presence of external donors.

A similar approach was employed for ^{n}BA polymerization mediated by the $Co(acac)_2$/V-70 system.[63] Previous investigations had concluded that the less stable carbon-cobalt bond formed with this monomer favoured the active species, resulting in poorly controlled polymerizations.[57] By slowing down the monomer propagation with respect to the initiation step, better control could be achieved. After optimization of the initiating system, temperature and additives, polymerizations initiated by $RCo(acac)_2$ (where R was a poly(vinyl acetate) oligomer terminated by a V-70 fragment) followed a first order rate law and exhibited

molecular weights which increased linearly with conversion. PDIs were typically *ca.* 1.2-1.35, with a low molecular weight shoulder on the GPC trace attributed to slow initiation at 0°C.[63] Molecular weights were significantly higher than the theoretical values which were proposed to be due to low initiation efficiency, with significant amounts of the initiator not participating in the reaction under the experimental conditions. *n*-Butyl acrylate (^{n}BA) could also be polymerized using the lauroyl peroxide/$Co(acac)_2$ redox system. At 0°C, a 3 hour induction period was observed due to the time required for Co(II) to be converted into RCo(III). Molecular weights increased linearly with conversion and PDIs were <1.36, however the poor initiator efficiency for this system resulted in molecular weights which were again much higher than the theoretical values.

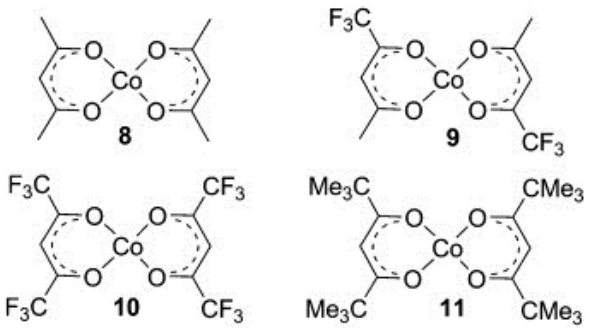
More recent work extended the scope of the $Co(acac)_2$ system to other vinyl esters.[64] Optimization of the redox system discussed above[56] used the sodium salt of citric acid in conjunction with lauroyl peroxide and the resulting poly(vinyl acetate) polymerization had an induction period of 1.5 hours, yielding well-controlled polymers with PDIs of 1.2-1.3. This system also controlled the polymerization of vinyl pivalate (VPv); at 30°C there was a 2.5 hour induction period, followed by a linear increase of molecular weights with conversion and PDIs of 1.2-1.3. The observation that molecular weights were much higher than the theoretical values was attributed to low initiator efficiency, with significantly fewer chains than 1 per Co formed. It was proposed that a substantial amount of the $Co(acac)_2$ participated in oxidative side reactions, as previously reported.[56] Polymerization of the less electron rich monomer vinyl benzoate (VBz) was much less efficient using this system. A shorter induction time of 0.25 hours was followed by a linear increase in molecular weight with conversion, but significant deviations from the theoretical molecular weights. The broad PDIs of 1.4-1.7 indicated that the propagating chains were not captured effectively by $Co(acac)_2$. It was proposed that the presence of a less electron-donating substituent adjacent to the propagating radical centre reduced the efficiency of Co(III)R formation and also decreased the tendency of the propagating chains to undergo nucleophilic degenerative transfer reactions with the organometallic species. This reduced the induction period and caused uneven initiation and propagation, leading to a loss of control over the polymerization.[64] The results obtained with vinyl benzoate are consistent with those obtained with vinyl chloroacetate[60] – electron poor vinyl esters are not effectively controlled by $Co(acac)_2$, but can undergo well-controlled copolymerization with other vinyl ester monomers.

Modification of the $Co(acac)_2$ system has been studied by a few groups. Matyjaszewski *et al.* investigated the effect of incorporating electron-withdrawing fluorine groups onto the backbone of the acac ligand and discovered that $Co(F_3\text{-acac})_2$, **9**, imparted reasonable control to the polymerization of VAc using 1 equivalent of V-70 at 30°C.[57] After an induction period comparable to that of the $Co(acac)_2$ system, molecular weights increased linearly with conversion and were in good agreement with theoretical values, with excellent PDIs of 1.1-1.2. In contrast, $Co(F_6\text{-acac})_2$, **10**, was a poor mediator of VAc polymerization, with molecular weights which were much higher than theoretical values and broad PDIs of 1.4-1.7. This was attributed to the slow

reaction of the propagating radicals with Co(F_6-acac)$_2$, resulting in inefficient deactivation and poor control over the polymerization.

Similar trends were observed when using these fluorinated systems with vinyl chloroacetate.[60] Polymerizations using Co(F_3-acac)$_2$ exhibited first order kinetics after a 5 hour induction period, molecular weights increased linearly with conversion and although PDIs were broad (1.7-2.0), control was improved compared to the original Co(acac)$_2$ complex. Use of Co(F_6-acac)$_2$ essentially resulted in an uncontrolled free radical polymerization of the monomer. No induction period was observed, indicating that no deactivation of the radical species occurred. Molecular weights were much higher than theoretical, with broad PDIs of 3.5-4.0.

Substitution of a bulky *tert*-butyl group into the acac backbone, forming the tetramethylheptadionato (tmhd) ligand, gave a complex which simultaneously controlled the polymerization of VAc through both DT and RT OMRP.[65] Polymerizations mediated by Co(tmhd)$_2$, **11**, and V-70 at 30°C had well-controlled molecular weights and PDIs of 1.1-1.5, at various ratios of Co/V-70. Interestingly, while DT OMRP halts after six half-lives of V-70, RT OMRP continues with a first-order rate law. Extended reaction times result in breakdown of this rate law and stagnating molecular weights, consistent with a competing CCT process. By decreasing the amount of V-70 used, the RT OMRP mechanism could be favoured over DT as the lower radical concentrations prevent the complete conversion of Co(II) to Co(III) required for the degenerative transfer mechanism to occur. DT OMRP could also be halted by diluting the reaction with toluene, again favouring RT. Finally, addition of an electron donor such as water or pyridine prevented DT by blocking the empty coordination site on the Co(III)R species, forcing RT OMRP. Successful chain growth from a macroinitiator prepared in a dilute polymerization, precipitated to remove traces of V-70 and reinitiated by the addition of VAc, toluene and heating to 30°C confirmed the RT OMRP mechanism. Comparison of the rate constants for polymerizations mediated by Co(acac)$_2$ and Co(tmhd)$_2$ revealed that in the absence of electron donors, the Co(tmhd)$_2$ system was faster than Co(acac)$_2$. However, this reactivity was reversed in the presence of electron donors, where the Co(acac)$_2$ system was approximately five times faster than Co(tmhd)$_2$. The authors rationalized this through competitive steric effects on the Co(III)R and Co(II)L bond strengths, supported by ^{1}H NMR studies and DFT calculations.[65]



← ***Figure 4.*** Bis acac cobalt complexes. Co(acac)$_2$, **8**; Co(F_3-acac)$_2$, **9**; Co(F_6-acac)$_2$, **10**; Co(tmhd)$_2$, **11**.

Substitution of one acac group for the readily modifiable 1,3-bis(2-pyridylimino)isoindolate (bpi) ligand, structurally related to porphyrins, but lacking a fourth *N*-donor, gave Co(II) complexes (**12** in Fig. 5) which were active for the OMRP of both MA and ^{n}BA.[66] Use of V-70 at 60°C in benzene resulted in well-controlled polymerizations with molecular weights which increased linearly with conversion and were in good agreement with theoretical molecular weights, with excellent PDIs of *ca.* 1.1. Despite the synthesis of a structurally diverse ligand set, incorporating electron withdrawing and electron donating groups onto the pyridyl and isoindoline groups, all polymerization data obtained were extremely similar. DFT calculations suggested that the Co(III)R bond was decoupled from the bpi substituents, meaning that the substitution pattern of the bpi ligand did not affect the polymerizations. The growth of the polymer chains was followed by liquid injection field desorption/ionization mass spectrometry (LIFDI-MS), allowing the detection of the initial organometallic species.[66] These data, coupled with ^{1}H NMR experiments, allowed the authors to conclude that it was unlikely that the Co(acac)(bpi) system operated via β-hydrogen abstraction from the initial radical species, as observed for the cobalt porphyrin systems.[49] The presence of functional groups derived from V-70 at the chain-ends supported a conventional initiation through thermal decomposition of the radical initiator.

Replacing both acac ligands with the isoelectronic β-ketoiminates provided versatility in terms of the steric and electronic modifications which could be made in close proximity to the cobalt centre. $Co(OC(Ph)CHC(Me)NAr)_2$, **13**, where Ar = Ph, 2,6-$Me_2C_6H_3$ and 4-$CF_3C_6H_4$, were utilized in the polymerization of vinyl acetate, initiated by V-70 at 30°C.[67] Use of 0.8 equivalents of V-70 resulted in a slow but reasonably well-controlled polymerization for all Co complexes, with molecular weights which increased linearly with conversion and PDIs of 1.2-1.4. Monomer consumption followed first order kinetics after *ca.* 60 hours (corresponding to the time taken for complete decomposition of V-70), commensurate with an RT OMRP mechanism. Molecular weights were typically higher than the theoretical values, indicating that the Co(II) complexes were not efficient radical traps and leading the authors to postulate that the increased steric crowding around the metal centre made these complexes less effective than $Co(acac)_2$ at mediating VAc polymerization. The fastest catalyst was R = 2,6-$Me_2C_6H_3$ and the steric bulk of the xylyl group was proposed to weaken the Co(III)R bond, favouring the active species. The use of 6 equivalents of V-70, to favour degenerative transfer, resulted in a faster polymerization with better control over molecular weight and PDIs of *ca.* 1.2 because the associative radical exchange occurred faster than addition of the propagating radical to the Co(II) species. At long reaction times molecular weights were lower than the theoretical values. This was attributed to the prevalence of CCT once the radical concentration had decreased. Interestingly, the addition of an electron donor such as pyridine to polymerizations mediated by the Ph-substituted complex had little effect, but quadrupled the rate of polymerization with the CF_3-substituted complex. Some control over the polymerization was lost, although PDIs remained below 1.3. ^{1}H NMR studies showed only very weak binding between pyridine and the Ph-substituted compound, whereas a significantly altered spectrum was obtained in the case of CF_3-substitution. The electron-poor cobalt centre binds more strongly to the electron donor,

shifting the OMRP equilibrium towards the active species and increasing the rate of polymerization. The authors concluded that the use of β-ketoiminate ligands instead of acac had two main effects. The cobalt centre was more electron-rich, due to the lower electronegativity of NAr, which stabilized the Co(III)R species. However, the presence of greater steric bulk around the metal centre weakened the cobalt-alkyl bond and the relative importance of these opposing effects depended on the precise nature of the ligand.

Recent reports extended this system to a tetradentate ketoiminate ligand. Bis(benzoylacetone)ethylenediaminato cobalt(II), **14**, was used in combination with 0.6 equivalents of V-70 at 50°C in toluene to control the polymerization of methyl acrylate.[68] The reaction was first order in monomer consumption for more than 6 half-lives of V-70, indicating that the radical concentration remained constant and that a reversible termination OMRP mechanism was operating. Increasing the V-70 concentration to 0.9 equivalents resulted in a 2.3 hour induction period, where polymerization rates were comparable to the previous experiments, followed by a rapid increase in rate as a degenerative transfer mechanism became dominant. Molecular weights were typically higher than theoretical, although increased linearly with conversion, and PDIs broadened throughout the reaction from 1.1-1.5. The gradual loss of control was attributed to non-reversible termination events, such as chain transfer. Synthesis of the Co(III)R analogue, where R = Et, produced a cobalt compound capable of both initiating and mediating the polymerization of methyl acrylate. Under the same conditions as previous experiments, but without the azo initiator, poly(methyl acrylate) was initially produced much more rapidly, with non-linear kinetics. After an hour, the rate decreased and monomer consumption became first-order. The homolytic cleavage of the Co(III)Et bond was concluded to be slower than the generation of radicals from a polymer chain bound to cobalt, so the initial concentration of Co(II) trapping species was lower, resulting in a faster polymerization. Once the initiator had been consumed and the concentration of Co(II) species was high, the formation of new radicals only occurred through the RT OMRP mechanism and the polymerization proceeded at the same rate as previously observed.[68]

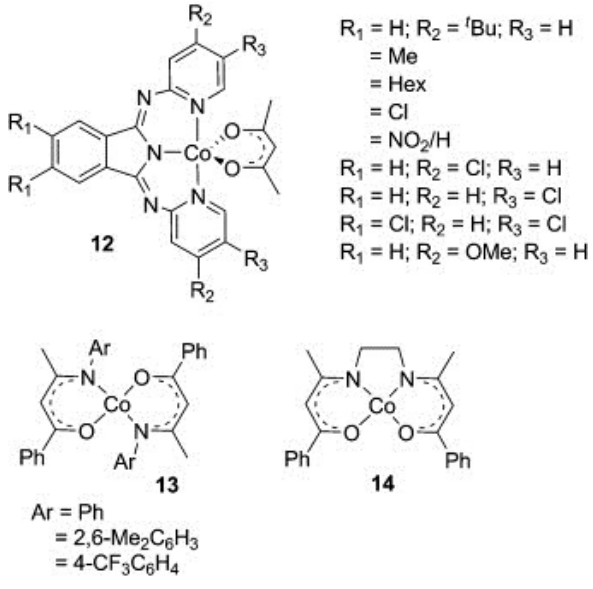


Figure 5. → Cobalt complexes with nitrogen donors. Co(acac)(bpi), **12**; $Co(OC(Ph)CHC(Me)NAr)_2$, **13**; Co(ketoiminato), **14**.

2.3. Extension to other transition metals

Despite the success of cobalt as a mediating species, the development of OMRP with other metals was slow. In contrast, ATRP has successfully utilized a wide variety of transition metal catalysts including Mo, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Cu.[15, 19-23] The screening of several of these complexes under OMRP conditions led to intriguing discoveries which examined interplay between metal-mediated CRP mechanisms and expanded the scope of metals with potential OMRP activity.

2.3.1. Molybdenum

Half-sandwich molybdenum(III) complexes were targeted by Poli *et al.* as representative species which should be able to control radical polymerization through both ATRP and OMRP regimes. For OMRP, reactivity is dependent on the strength of the metal-carbon bond, whereas in ATRP reactivity is dictated by the strengths of the metal-halogen and carbon-halogen bonds. Poli suggested that the behaviour of an organometallic compound should be predictable based on theoretical studies and used DFT calculations to anticipate which metal systems would be capable of controlling styrene polymerization through RT OMRP.[69] Calculation of the bond dissociation energies for a range of molybdenum complexes revealed that that the oxidative pathway which proceeds through halogen transfer was energetically competitive with organometallic bond formation between the metal centre and the propagating radical species. Consequently, experimental results confirmed that $CpMo(\eta^4\text{-}C_4H_6)Cl_2$, $CpMo(PMe_3)_2Cl_2$ and $CpMo(dppe)Cl_2$ (Figure 6, **15**-**17**) were all capable of controlling styrene (St) polymerization through an OMRP pathway, initiated by AIBN. Molecular weights increased linearly with conversion, with PDIs of 1.3-1.7, although low initiation efficiency resulted in a poor correlation of M_n with $M_{n,th}$ where molecular weights were consistently higher than expected. Saturated end groups were observed through ^1H NMR and MALDI-TOF studies, indicating that there was no contribution to the control through ATRP. Only the Mo(III)/Mo(IV) redox couple was active for OMRP; attempts to use the homolytic cleavage of a Mo(III)R bond to exploit the higher energy Mo(II)/Mo(III) redox couple of $CpMo(\eta^4\text{-}C_4H_6)(CH_2SiMe_3)_2$ were unsuccessful, most likely due to the high metal-carbon bond dissociation energy. The interplay between controlled radical polymerization mechanisms was demonstrated for the first time, as $CpMo(PMe_3)_2Cl_2$, **16**, and $CpMo(dppe)Cl_2$, **17**, were also capable of controlling styrene polymerization through ATRP. Interestingly, $CpMo(\eta^4\text{-}C_4H_6)Cl_2$, **15**, and $CpMo(\eta^4\text{-}C_4H_6)(CH_2SiMe_3)_2$, **18**, gave olefin-terminated, low molecular weight polymers independent of conversion, with broadened PDIs (1.4-2.5), when polymerization was initiated by an alkyl halide, indicating that CCT prevailed under ATRP conditions.[69]

Synthesis of the simple Mo(III) compounds $MoX_3(PMe_3)_3$, **19**, where X = Cl, Br and I, gave catalysts which were capable of controlling styrene through ATRP but which proved to be poor mediators of the polymerization under OMRP conditions.[70] Reactions carried out in toluene, with AIBN at 80°C resulted in

non-first order kinetics, molecular weights which were higher than the theoretical values and broad PDIs (1.5-2.5). Molecular weights did increase with conversion in the case of $MoCl_3(PMe_3)_3$, but the authors concluded that while this complex had a weak interaction with the propagating radical, it was not a competent enough spin trap to control the polymerization.

Further extension of this family of molybdenum compounds led to the synthesis of $CpMoCl_2(R_2\text{-dad})$ complexes, where R = Ph, 4-$CH_3C_6H_4$ (tol), 2,6-$^i Pr_2C_6H_3$ (dipp) and ^{i}Pr and dad = 1,4-diazadiene, RN=CH-CH=NR (**20** in Figure 6). The diazadienes were desirable target ligands due to their stability in air and facile synthesis, which offered a breadth of tunable steric and electronic properties. All of these complexes were efficient ATRP catalysts for the polymerization of styrene and $CpMoCl_2(dipp_2\text{-dad})$ was also active in the OMRP of styrene.[71] Polymerizations carried out with AIBN at 100°C had molecular weights which increased linearly with conversion and were in good agreement with theoretical values and moderate PDIs (<1.6). Use of the alkyl-substituted diazadiene compound, $CpMoCl_2(^i Pr_2\text{-dad})$, resulted in irreversible trapping of the organometallic species under OMRP conditions.[72] Styrene polymerizations initiated with AIBN halted at approximately 15% conversion, implying that a reaction which consumed the dormant species had occurred. Attempts to polymerize methyl acrylate under the same conditions resulted in no monomer conversion, indicating that consumption of the OMRP dormant species was more rapid for the PMA chain. The related $CpMoI_2(^i Pr_2\text{-dad})$ complex exhibited greater ATRP activity than the chloride analogue and also allowed polymerization of styrene and MA under OMRP conditions. However, the formation of Mo(IV)R was not sufficiently favourable and it was concluded that the ATRP equilibrium was actually exerting control over the polymerization, with OMRP and ATRP equilibria present simultaneously. This resulted in non-linear chain growth, yet molecular weights close to the theoretical values, with PDI values as low as 1.23.[72]

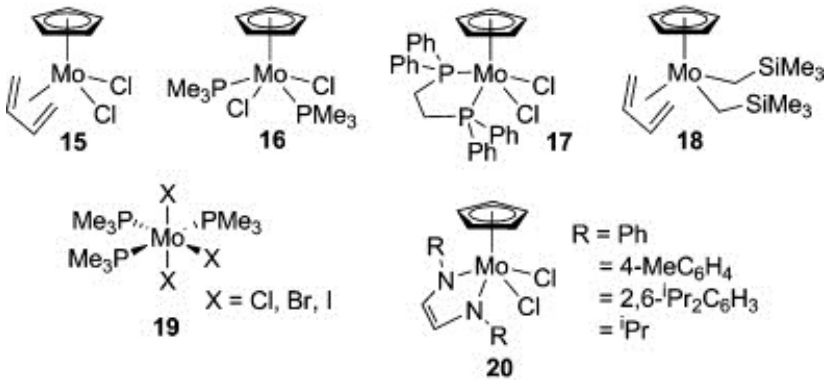


Figure 6. Half-sandwich molybdenum complexes used in OMRP.

2.3.2. Osmium

The coordinatively unsaturated compound $Os(PPh_3)_3Cl_2$, **21**, was found to be active in the OMRP of styrene in both DMF and toluene.[73] The use of a coordinating solvent did not affect the ability of the osmium species

to trap the propagating radical chains. Polymerizations initiated by AIBN at 100°C reached *ca.* 75% conversion in 48 hours, with molecular weights which increased linearly with conversion. PDIs were broad, at 2.8-3.2, which was attributed to the rapid decomposition of AIBN generating a high radical concentration which resulted in significant termination through radical coupling. A considerable number of dead chains, present from the beginning of the reaction, were evident in the bimodal GPC traces. This complex was also shown to be an excellent catalyst for the ATRP of styrene, methyl methacrylate (MMA) and butyl acrylate, giving another example of a compound which can operate in both ATRP and OMRP regimes.[73]

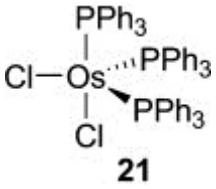


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Figure 7. Osmium complex active in OMRP.

2.3.3. Iron

Early studies on iron porphyrin (**22** in Fig. 8) phthalocyanine, **23**, and salen, **24**, compounds investigated the OMRP of styrene, initiated from an Fe(III) alkyl species prepared *in situ*.[74] Molecular weights were much higher than the theoretical values, potentially due to a low yield of the alkylated product. Initiation from the analogous Fe(II) phthalocyanine and salen complexes and a radical source (AIBN) at 80°C gave molecular weights which matched well with theoretical values and increased linearly with conversion, although PDIs were still reasonably broad (1.4-2.0). A maximum conversion of 40% was reached in all OMRP experiments, due to chain termination through coupling, disproportionation and β-H abstraction reactions. Higher conversions (*ca.* 70%) could be achieved by increasing the polymerization rate through the addition of aluminium salts, but this resulted in broadened PDIs of 1.5-2.4. The use of aluminum additives in ATRP has been shown to have a beneficial effect on both the rate of polymerization and the molecular weight distributions of several systems through acceleration of the activation and deactivation processes.[20, 70] As the aluminum additive may reduce the oxidized metal species,[20] in OMRP this could result in the equilibrium shifting towards the active radical species, causing a more rapid polymerization. While this would allow higher conversions to be reached, the higher radical concentrations result in a loss of control, as evidenced by the broadened PDIs. These complexes were also active for ATRP and excellent control over molecular weights and PDIs was achieved by using a 'double protection' procedure, where 0.5 equivalents of AIBN and 10 equivalents of 1-phenylethylbromide were used for initiation. Styrene polymerizations using the iron salen complex under these conditions reached >96% conversion in 6 hours, with good agreement between theoretical and observed molecular weights and PDIs of 1.2.

α-Diimine iron complexes, **25**, have also been investigated under both ATRP[75-78] and OMRP[79] conditions. A correlation between the metal spin state of the oxidized species and polymerization reactivity was reported,[77-78] with high-spin Fe(III) complexes corresponding to Fe(II) species which were effective catalysts for ATRP. Lower spin Fe(III) species accessed an organometallic pathway, leading to CCT, if the polymerizations were carried out under ATRP conditions. Under OMRP conditions,[79] styrene polymerizations were monomodal with PDIs as low as 1.4 only if 8 equivalents of catalyst was used. However, these reactions were very slow, reaching just 10% conversion in 48 hours. The instability of the iron alkyl species at the polymerization temperature of 120°C meant that excessive catalyst loadings were required, which retarded the polymerization rate. Initiation using V-70 at 70°C required an optimal 2 equivalents of catalyst, and the polymerizations proceeded with molecular weights which increased linearly with conversion and were in good agreement with theoretical values. PDIs were 1.3-1.5 depending on the catalyst used, with improved control derived from the lower spin complexes. Decomposition studies of L_nFeR species generated *in situ* showed that systems derived from the lower spin Fe(III) complexes exhibited increased stability over high spin Fe(III) derivatives. The rate of polymerization and the nature of the polymer formed were proposed to be dependent on the radical concentration generated by competing ATRP and OMRP equilibria. Halogenophilic catalysts, with high-spin Fe(III) analogues, resulted in fast monomer consumption and increased control over the polymerization. Chain transfer events were not kinetically relevant and so the ATRP equilibrium was dominant. Electron-withdrawing groups on the ligand decreased the halogenophilicity of the complexes and the slower rate of polymerization allowed the OMRP equilibrium to become involved, resulting in CCT and the formation of olefin-terminated polymer chains. The equilibrium disfavours the unstable Fe(III)R species, unless very high catalyst concentrations are used. Under ATRP conditions, the OMRP equilibrium is not dominant but rather provides a link to CCT.

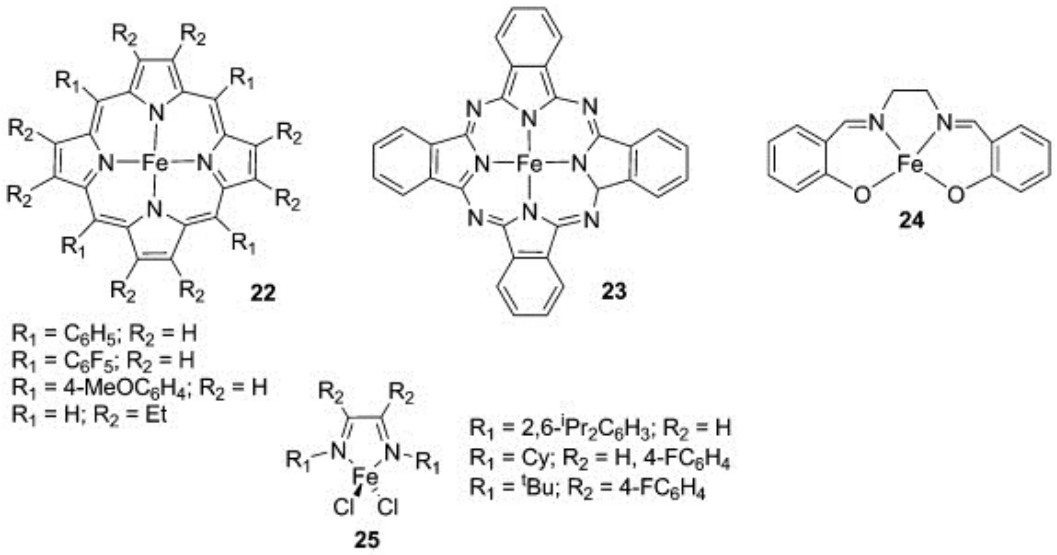

Figure 8. Iron complexes investigated for OMRP.

2.4. Expanding the scope of transition metals in OMRP

2.4.1. Group 10

Attempts to use palladium-based catalysts for controlled radical polymerization have met with limited success. The organometallic complexes **26**-**29** shown in Figure 9 are capable of initiating the polymerization of methyl acrylate, but do not efficiently control the reaction.[80-83] In the case of compounds **28**, initiation occurred through the insertion of methyl acrylate into the palladium-carbon bond, giving a species which could be isolated and characterized.[82] Propagation occurred through free radical polymerization, based on the reversible homolysis of the palladium-carbon bond but PDIs were very broad (1.5-6.8). Polymerization only occurred when these compounds were used in the presence of 1 equivalent of a monodentate phosphine or pyridine; catalyst decomposition was observed otherwise. The dormant PdR species were susceptible to β-H elimination, resulting in the formation of olefin-terminated polymer chains. Reinitiation occurred through monomer insertion into the PdH bond, but catalyst deactivation was linked to the decomposition of this species. Similar results were obtained using compounds **29**, which were active for the polymerization of methyl acrylate and butyl acrylate.[83] However, although conversions of up to 90% were achieved after 24 hours at room temperature, PDIs of 2.1-6.2 indicated a poorly controlled process. The propensity of these complexes to undergo β-H elimination is illustrated by their inability to polymerize MMA. The faster rate of β-H elimination from the methyl group, when compared to the methylene group of MA, resulted in a higher concentration of Pd-H and more rapid catalyst decomposition.

Organometallic nickel complexes **30** and **31** have been shown to initiate the radical polymerization of MMA, ^{n}BA and styrene through the homolytic cleavage of the metal-carbon bond, with more efficient systems generated through the addition of 3 equivalents of triphenylphosphine. Polymerization of MMA utilizing the nickel salicylaldiminato complex **30** yielded little polymer (<2% conversion) in the absence of PPh_3 but reached higher conversions (up to 50%) in its presence, although the polymerization did not exhibit living characteristics. Molecular weights were dependent on reaction temperature, with M_n at 10% conversion ranging from 8500 at 25ºC to 30,000 Da at 70ºC, with PDIs of 2.0-3.0. The nickel phosphinoenolate complex **31** initiated the radical polymerization of MMA in both the presence and absence of PPh_3, but only achieved 14% conversion in each case. Molecular weights were independent of conversion and PDIs were broad (2.1), indicating that the polymerization was poorly controlled. Polymerization of ^{n}BA was achieved using **30** in conjunction with PPh_3, although only moderate conversions (11%) were attained and high molecular weight polymers (135,000 Da) with broad PDIs (2.4) were obtained. In contrast, styrene did not require the presence of the additive and both **30** and **31** successfully initiated the polymerization of styrene at 70 ºC in bulk, reaching *ca.*14% conversion in 2 hours. Copolymerizations of the acrylate monomers with styrene and ethylene were also achieved, with the authors proposing that these nickel complexes operate through a dual reaction manifold, acting both as radical initiators and classical coordination-insertion catalysts. The reversible cleavage of the metal-carbon bond would allow ‘shuttling’ between the polymerization mechanisms

potentially allowing for the formation of multiblock copolymers of non-polar olefins and polar vinyl monomers, although control must first be improved.

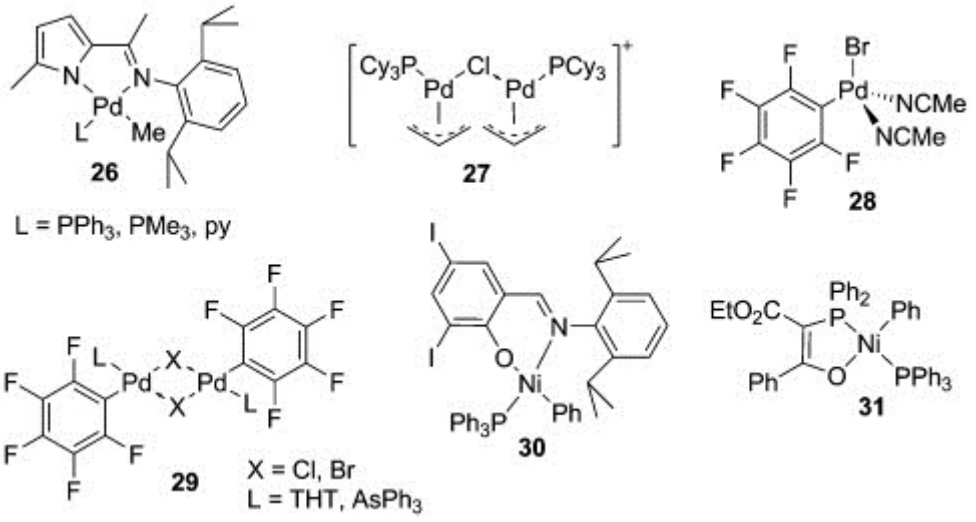

Figure 9. Group 10 complexes used to initiate radical polymerization.

2.4.2. Titanium

Early work reported that Cp_2TiCl_2 (**32** in Fig. 10) could be used as a chain growth regulator in the polymerization of MMA, initiated by AIBN.[84] While molecular weights did increase linearly with conversion, PDIs were broad (1.9-2.9) indicating that control over the polymerization was not ideal. Further investigation attempted mechanistic elucidation using DFT and EPR studies and it was discovered that formation of Ti(III) species had no significant thermodynamic restrictions.[85] EPR spectra showed the presence of Cp_2TiCl, which was proposed to mediate the polymerization through reversibly binding to the propagating radical.

In 2004 Asandei *et al.* reported that a system based on Cp_2TiCl_2/Zn/epoxide could be used to initiate and mediate the controlled radical polymerization of styrene.[86] Reduction of the metallocene by Zn formed the soluble metalorganic radical, Cp_2TiCl, which was active for the titanium-catalyzed radical ring opening of epoxides. Formation of $Cp_2TiCl(OR^{\bullet})$ gave a species capable of initiating styrene polymerization, while the presence of an additional equivalent of Cp_2TiCl efficiently mediated the polymerization through reversible trapping of the propagating chains. Control was also suggested to occur through degenerative transfer, where a propagating radical species displaced the bound polymer chain of Cp_2TiClR. The best initiator efficiency was achieved using monosubstituted, oxygen-rich, chelating diepoxides such as 1,4-butanediol diglycidyl ether (BDGE). The polymerization of styrene was first order in monomer and molecular weights increased linearly with conversion, with PDIs of 1.1-1.3. The polymerization of *para*-substituted styrenes could also be controlled by this system, with first order kinetics, a linear increase of molecular weights with conversion and

PDIs of 1.2-1.4 observed for both electron poor (4-chlorostyrene) and electron rich (4-methoxystyrene, 4-tert-butylstyrene) monomers.

Investigation of ligand effects showed that the titanocene system was more efficient than those based on alkoxides, bisketonates, scorpionates and half-sandwich compounds. While bisketonates[87] and scorpionates[88] did not control styrene polymerization effectively, alkoxides were capable of mediating the controlled radical polymerization of styrene.[87] Use of (^{i}PrO)$_2$TiCl$_2$, **33**, and (^{i}PrO)$_3$TiCl, **34**, as catalysts gave systems which displayed a linear increase in molecular weights with conversion but with PDIs of >1.4. The low initiator efficiency was attributed to decreased titanium oxophilicity which decreased the rate of radical ring opening, resulting in broadened PDIs. Facile ligand exchange was also proposed to occur, generating macromolecular Ti species which could not control the polymerization. The half-sandwich complexes CpTiCl$_3$, Cp*TiCl$_3$ and IndTiCl$_3$ (Figure 10, **35**-**37**) also proved less efficient at controlling styrene polymerization than Cp$_2$TiCl$_2$.[88] The electron-donating Cp* group strengthened the titanium-carbon bond, with temperatures of 110°C required for reversible bond homolysis and broadened PDIs of 1.7 observed. Control could be improved by increasing the steric bulk or by decreasing the electron donating ability of the ligands, with IndTiCl$_3$ and CpTiCl$_3$ both mediating controlled radical polymerization where molecular weights increased linearly with conversion and PDIs were relatively narrow (1.2-1.6). The authors concluded that as similar levels of control were observed for the IndTiCl$_3$ and CpTiCl$_3$ systems, the reaction was not sensitive to the steric effects of the ligands and the electronic contributions were more important.

This was investigated more extensively through the synthesis of a number of substituted metallocenes, with manipulation of the stereoelectronic effects anticipated to allow fine-tuning of the ability of the titanium catalyst to radically ring open the epoxide and reversibly cap the polymer chains.[89] While excellent control over styrene polymerization was displayed by L$_2$TiCl$_2$ (L = EtCp, ^{i}PrCp, ^{t}BuCp and Ind; Figure 10, **39**-**40**), with PDIs <1.2 and linear plots of molecular weight versus conversion, only subtle ligand effects were observed. Similar initiator efficiencies, PDIs and polymerization rates were displayed by all the aforementioned complexes, indicating that there was a balance between the steric and electronic effects. The titanium-carbon bond was strengthened as the electron donating ability of the ligand increased from Et to ^{i}Pr to ^{t}Bu, but this was counteracted by the increased steric repulsion from these bulkier groups. The effect of the halide substituent was more pronounced, with Cp$_2$TiCl$_2$, **32**, proving to be a more efficient catalyst than Cp$_2$TiBr$_2$, **34**, while the analogous Cp$_2$TiF$_2$ complex could not be reduced and so did not catalyze the polymerization. Improved rates of polymerization and better control over PDIs were attributed to faster initiation with the chloride system.[89]

Further optimization of the Cp$_2$TiCl$_2$ system investigated reaction variables including the effect of solvent, additives, ligands, *in situ* drying agents and reagent concentrations on the efficiency of styrene polymerization initiated by BDGE.[90] The nature of the reducing agent, effect of reaction temperature and reagent ratios were also studied.[91] Cp$_2$TiCl$_2$/Zn-catalyzed styrene polymerization could also be initiated using ketyl radicals, generated through the reduction of α,β-conjugated or aromatic aldehydes.[92] These reactions were

well-controlled, exhibiting first order kinetics, a linear increase of molecular weights with conversion and PDIs of 1.2. Peroxides were also efficient initiators, with a range of peroxides found to give similar rates of polymerization implying that initiation occurred primarily through the redox reaction of the peroxide with Ti(III), rather than through thermal decomposition of the peroxide.[93] The most effective initiator was benzoyl peroxide, which gave polymers with PDIs < 1.2 at a range of temperatures between 60-90°C. A comparison of the effect of reagent stoichiometry and temperature on the three initiator types revealed that the narrowest PDIs were obtained with a 2:1 ratio of titanium:initiator, with epoxide ring opening giving the fastest initiation.[94]

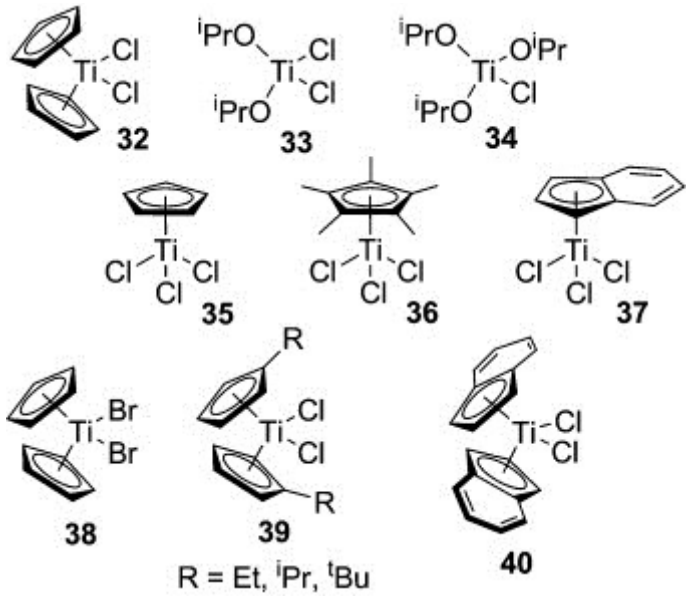

Figure 10. Efficient titanium complexes for CRP of styrene.

2.4.3. Chromium

The earliest attempts to use chromium complexes to control radical polymerization were in the 1970s when Minoura *et al.* used $Cr(acac)_2$ (**41** in Figure 11) and benzoyl peroxide to initiate the polymerization of a range of monomers in various solvents under a range of conditions.[95-98] Monomers including methyl methacrylate, methyl acrylate, acrylic acid and acrylonitrile were rapidly polymerized and both acrylonitrile and methyl acrylate exhibited molecular weights which increased with conversion and monomodal molecular weight distributions. The poor molecular weight control was attributed to a slow initiation, due to the unfavourably high redox potential of Cr(II)/Cr(III). Styrene, vinyl acetate and vinyl chloride could also be polymerized, albeit slowly, and the authors concluded that a "living" polymerization occurred at temperatures below 30°C but that conventional free radical polymerization took place above 40°C. This system was

developed several years later when $Cr(acac)_2$ and benzoyl peroxide were used in conjunction with polyamine ligands for the polymerization of MMA and VAc.[99] Some control over the molecular weight of the polymer was achieved, with PDIs as low as 1.5. However, the non-linear increase of molecular weight with conversion indicated that slow initiation was still a problem.

In 2008, Poli *et al.* reported the OMRP of VAc moderated by half-sandwich *β*-diketiminate Cr(II) complexes (**42**-**46** in Fig. 11), where the chromium-carbon bond strength could be tuned through modulation of the steric bulk of the *β*-diketiminate ligand.[12] The bulkiest system, with 2,6-di*iso*propylphenyl (dipp) substituents, showed reasonable activity for VAc polymerization, reaching 70% conversion in 46 hours when initiated with V-70 at 30°C. Molecular weights increased linearly with conversion, but were higher than theoretical values, and the PDIs were somewhat broad (1.4-1.8). Use of excess V-70 resulted in a faster but uncontrolled polymerization, with PDIs >2.4, indicating that the control in this system was derived from a reversible termination OMRP only. The lack of accessible coordination sites on the Cr(III) dormant species prevented an associative radical exchange and so degenerative transfer OMRP was not possible. The incorporation of less bulky aryl groups on the *β*-diketiminate ligand (**44** in Fig. 11) resulted in lower polymerization activity and DFT calculations correlated the steric bulk of these substituents with the Cr-C bond length and dissociation enthalpy. Bulkier groups resulted in longer, less energetic bonds, thus favouring the growing free radical and resulting in higher polymerization activity. Further experiments utilizing the dipp-substituted complex revealed that increasing the polymerization temperature decreased the rate and at 90°C only 34% conversion was reached after 84 hours.[100] Although molecular weights increased linearly with conversion and PDIs were as low as 1.2, molecular weights were much greater than the theoretical values. A deactivating side reaction was proposed to take place, involving acetate transfer to the chromium centre and resulting in the formation of an inactive thermal decomposition product. This irreversible deactivation occurred slowly at room temperature but more rapidly at elevated temperatures.

Electronic effects were also manifest in the *β*-diketiminate Cr(II) complexes, where isosteric mixed-aryl systems, **44**, were investigated through variation of the *para* substituent on the phenyl ring.[12] Although the incorporation of one dipp and one Ph group on the ligand did not sufficiently labilize the Cr(III)R bond to promote efficient polymerization, the *para* substituent was observed to affect the radical trapping ability of the Cr(II) complex. Both electron-withdrawing and electron-donating substituents (CF_3 and OMe) resulted in less efficient Cr(II) radical traps.

Synthesis of a well-defined Cr(III) alkyl species, $CpCrL(CH_2CMe_3)$ where L = 2,6-dimethylphenyl *β*-diketiminato, gave a single-component OMRP reagent (Fig. 11, **46**).[100] Room temperature polymerization of VAc had molecular weights which increased linearly with conversion and PDIs as low as 1.5. Good agreement between M_n and $M_{n,th}$ indicated improved initiator efficiency over the V-70 systems; however, a progressive decrease of the rate constant and broadened PDIs suggested that partial deactivation of the

growing chains occurred. This was supported by a maximum conversion of just 14% (after 400 hours) and the isolation of the chromium acetate species, which was also synthesized independently.

The interplay between ATRP and OMRP equilibria in the half-sandwich *β*-diketiminate Cr(II) complexes was also investigated, with this system proposed to be the first where OMRP trapping dominates.[101] Under OMRP conditions, a metal complex devoid of halogen ligands cannot participate in the ATRP equilibrium. However, under ATRP or RATRP conditions, the propagating chains may be trapped by either the oxidized M^{n+1}-X species from the (R)ATRP equilibrium or by M^n, thus entering the OMRP equilibrium. ATRP carried out at 50°C, using **42** (where R = dipp) and **43**, reached a maximum of 26% conversion with PDIs of 1.3-1.7, indicating that irreversible termination reactions were occurring. Similar results were obtained in reverse ATRP (RATRP) experiments carried out with V-70 and DFT calculations showed that OMRP trapping in these systems was both kinetically and thermodynamically favourable, leading the authors to conclude that the controlled features of the polymerization were derived from the OMRP equilibrium.

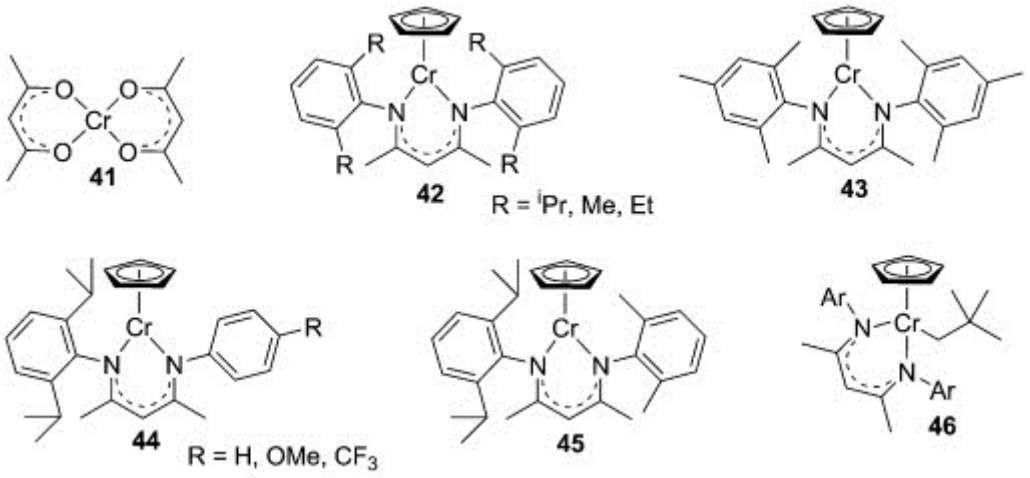

Figure 11. β-Diketonate and half-sandwich β-diketiminate chromium complexes.

2.4.4. Vanadium

Recently, the first controlled radical polymerization mediated by a vanadium complex was reported.[102] The bis(imino)pyridine complex [BIMPY]VCl_3, where [BIMPY] = 2,6-$(ArN{=}CMe)_2C_5H_3N$ (Ar = 2,6-$^{i}Pr_2C_6H_3$) (**47** in Fig. 12) was active for the OMRP of vinyl acetate, initiated by AIBN at 120°C. The polymerization was first order in monomer, molecular weights increased linearly with conversion and PDIs were *ca.* 1.3. The red, vanadium-terminated polymer could be used as a macroinitiator to restart polymerization and the absence of halogen-capped chains confirmed that control over the polymerization was not occurring through an ATRP regime. At lower temperatures, high molecular weights independent of conversion and broadened PDIs were

observed, suggesting that inferior initiation and chain exchange were occurring. The active catalyst was proposed to be a V(II) species, formed *in situ* from the reduction of the V(III) precursor by AIBN-derived radicals. Chlorine abstraction from [BIMPY]VCl_3 formed the trapping species, [BIMPY]VCl_2. Observed molecular weights supported this hypothesis, corresponding well with those predicted if the initiator produced only one propagating radical per molecule of AIBN. EPR analysis of the vanadium-capped polymer chain, however, suggested a V(IV) dormant species and further investigation through computational analysis examined a number of potential reaction scenarios.[103] It was concluded that for both styrene and vinyl acetate, halogen abstraction was irreversible and the ATRP equilibrium was not capable of mediating the polymerization. However, *in situ* formation of [BIMPY]VCl_2 enabled the OMRP equilibrium to be established through reaction with a radical species. Spin density calculations suggested that ligand non-innocence played a significant role in the electronic structure of these intermediates. Styrene polymerizations were inefficiently mediated, while excellent control over vinyl acetate was achieved as a result of both the higher reactivity of the VAc-derived radical and participation of the carbonyl oxygen of the ester group in the trapping step. Although the more reactive monomers such as MMA, AN and styrene were poorly controlled by this system, it was also active for other vinyl esters, with initial screening reactions of vinyl propionate, vinyl pivalate and vinyl benzoate showing good control over molecular weights and reasonable PDIs (1.3-1.6).

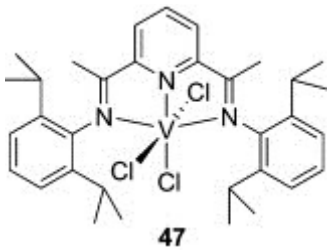

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Figure 12. Vanadium OMRP catalyst.

2.5. Main Group metals in OMRP

The metallic and metalloid main group elements can also control radical polymerizations through the formation of an organometallic intermediate. While they have traditionally been discussed as a separate class of CRP, their clear connection to d-block complexes through the reversible formation of carbon-metal bonds merits their inclusion in this discussion.

The ability of organotellurium compounds to undergo reversible tellurium-carbon bond cleavage[104] upon thermolysis and photolysis was applied to controlled radical polymerization in 2002 by Yamago *et al*.[105] The facile syntheses of the initiators and the ease of polymer end-group modifications made these compounds attractive, and excellent control was afforded by a range of organotellurium species (**48**-**51**, Figure 13).

Polymerization of styrene reached high conversions in 18 hours at 105°C, with molecular weights which increased linearly with conversion and PDIs of <1.2. Labelling experiments confirmed that the polymers were terminated with methyltellanyl groups. Functionalized styrenes could also be efficiently polymerized; *p*-methoxystyrene reactions were well-controlled, with PDIs of 1.2. Some loss of control was observed with *p*-chlorostyrene, where PDIs broadened to 1.4. These tellurium initiators were also active for the polymerization of a range of acrylates and methacrylates, including MMA, MA, ^{n}BA, *t*-butyl acrylate (^{t}BA), ethyl methacrylate (EMA) and 2-hydroxyethyl methacrylate (HEMA).[106] Polar monomers such as acrylonitrile, *N,N*-dimethylacrylamide (DMA) and 2-dimethylaminoethyl acrylate (DMAEA) could also be polymerized and all reactions proceeded with predictable molecular weights and PDIs of <1.23. The more reactive monomers (MMA, EMA and HEMA) showed improved control if 1 or 2 equivalents of $(MeTe)_2$ was added to the polymerization. A Te-capping mechanism was proposed, whereby the tellurium radical generated from the homolytic cleavage of the initiator forms dimethyl ditelluride, which reversibly caps the propagating radical chains. Increasing the concentration of $(MeTe)_2$ in the polymerization facilitated formation of the dormant species, preventing uncontrolled propagation of the more reactive monomers.[107]

Further elucidation of the polymerization mechanism was obtained through kinetic studies on this system using styrene, MMA and MA. It was proposed that thermal dissociation of the TeR species generates carbon-based radicals which undergo polymerization predominantly mediated by a degenerative transfer mechanism.[108-109] High temperatures were required for the initiation step and, by using a conventional radical initiator, well-controlled polymerizations could be achieved under milder conditions. Styrene polymerizations utilizing AIBN at 60°C required just 11 hours to reach conversions of greater than 80%, with PDIs <1.2. Use of V-70 allowed the temperature to be decreased further, with 23 hours at 40°C giving high conversions and PDIs of 1.2. These new, milder conditions could also be applied to the controlled polymerization of ^{n}BA and MMA, as well as monomers containing polar functional groups such as *N*-isopropylacrylamide (NIPAM), AN and HEMA.[108] This system was extended to use only shelf-stable reagents, eliminating the need for purification and handling of air-sensitive organotelluriums.[110] Some loss of control was observed, but styrene, ^{n}BA and MMA with PDIs <1.24 could be obtained through polymerization using AIBN and ditellurides, either through *in situ* generation of the organotellurium species (**50** in Fig. 13), followed by monomer addition, or through combination of AIBN, ditelluride and monomer directly.

Further development of organotellurium-mediated reactions included the use of conventional radical initiators for the polymerization of reactive monomers including NVP and NIPAM.[111] Polymerization of these monomers using ethyl-2-methyl-2-butyltellanylpropionate (EMA-TeBu, **51** when R = Bu) and 4,4'-azobis(4-cyanopentanoic acid) (ACP) or AIBN at 60°C reached conversions of >90% in 3 hours. A linear increase in molecular weights with conversion, good agreement of molecular weights with theoretical values and PDIs of 1.0-1.2 were observed.

The use of a hydrophobic organotellurium, EMA-TeBu, in conjunction with $(TeBu)_2$ and an azo initiator, allowed the miniemulsion polymerization of MMA.[112] Almost complete conversion was achieved in 6 hours at 60°C and the polymerization was first order in monomer. Molecular weights increased linearly with conversion and were in good agreement with theoretical values. Slightly broadened PDIs of 1.4-1.6 were attributed to the heterogeneous nature of the system and the lower exchange rate constant of butyl tellanyl compared with methyl tellanyl. Styrene and ^{n}BA could also be polymerized under these conditions, but without the added $(TeBu)_2$. High conversions were reached and stable latexes obtained, but some control over these reactions was lost, as evidenced by broadened PDIs and multimodal GPC traces.

A recent study investigated the effect of the tellanyl substituent on the rate and control of styrene polymerization.[113] A range of organotellurium compounds (Figure 13, **51**) were synthesized and employed in the bulk polymerization of styrene. In each case, high conversions (80-99%) were achieved after heating at 100°C for 24 hours. Molecular weights agreed well with theoretical values and PDIs were low (1.06-1.25). Use of 1 equivalent of AIBN increased the polymerization rate, with essentially quantitative conversion reached after 11 hours. Control over molecular weights was still good, but PDIs were slightly broadened (1.17-1.33). The effect of the tellanyl substituent was analyzed through kinetic experiments to obtain the exchange and thermal dissociation rate constants. Aryl substituents resulted in faster exchange rate constants, which allowed better control over the PDI. This was attributed to stabilization of the transition state through delocalization of the spin density on the Te atom.

Polymerization could also be initiated through direct photolysis of the Te-C bond of the dormant species.[114] Using ethyl-2-phenyltellanyl-2-methylpropionate, **51** if R = Ph, and a range of light conditions, the polymerization of ^{n}BA reached >85% conversion in 2 hours. Molecular weights were in good agreement with theoretical values, with PDIs of 1.09-1.18. No polymerization occurred in the dark and the use of unfiltered light resulted in a loss of control over the polymerization. Molecular weights were lower than theoretical values and PDIs of 1.87 were obtained, attributed to the loss of the phenyltellanyl polymer end group as a result of the high light intensity. This system was active for the polymerization of a range of acrylate and acrylamide monomers containing a variety of polar functional groups, including AA, NIPAM, NVP, 2-hydroxyethyl acrylate (HEA), *N*-vinylcarbazole (NVC) and *N*-vinylimidazole (NVI). In each case, excellent molecular weight control was displayed, conversions of >90% were achieved and PDIs were in the range 1.11-1.33. A reversible termination mechanism was proposed, with dissociation of RTe occurring upon irradiation. However, the role of degenerative transfer in this system has not yet been fully assessed and further studies are required.

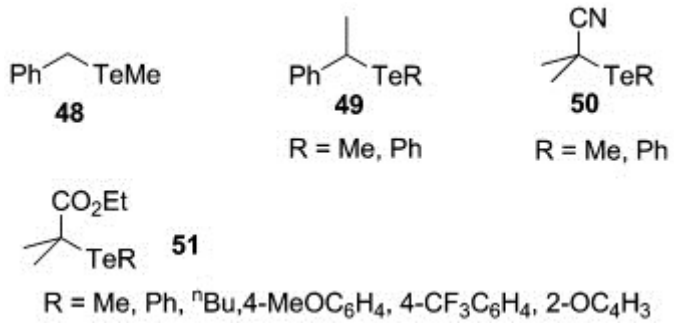


Figure 13. Organotellurium compounds used in controlled radical polymerization.

Yamago *et al.* extended their studies to antimony and discovered that organostibines were better precursors for carbon-centred radicals than organotelluriums and promoted highly controlled radical polymerization. The α-dimethylstibino ester, **52**, was active for styrene polymerization, reaching >80% conversion in 48 hours at 100°C.[115] Molecular weights were in excellent agreement with theoretical values and the PDI was 1.16. Addition of AIBN (0.1 – 1.0 eq.) significantly increased the rate of reaction and polymerizations using 0.5 eq. AIBN reached essentially quantitative conversion in 19 hours at 60°C. Molecular weights increased linearly as the styrene concentration was increased and also with conversion. PDIs were low, 1.14-1.23, and control experiments confirmed the presence of organostibine end-groups on the polymer. This system was active for a range of conjugated monomers, including ^{n}BA, MMA, NIPAM and AN, but also for unconjugated monomers such as NVP and VAc, indicating that organostibine mediated radical polymerization was also tolerant of polar functional groups within the monomer. For all of the monomers studied, complete conversion was achieved in fewer than 18 hours at 60°C, with excellent molecular weight control and PDIs of 1.06-1.26. Polymerization of NVP was investigated further, utilizing a range of organostibines (**52**-**54**, Fig. 14) for the production of the water soluble and biocompatible poly(*N*-vinyl-pyrrolidine). PDIs of *ca.* 1.1 were achieved at moderate molecular weights (up to 15,000 Da), but a broadening of PDI was observed as the target molecular weights were increased.[116] Kinetic experiments suggested a degenerative transfer mechanism, similar to that of the organotellurium species. However, the rate constant of degenerative transfer of Me_2Sb was found to be twice that of MeTe, providing a rationale for the improved control over polymerization exhibited by organostibines.[115] Excellent control could also be obtained through the use of organostibines **52** and **54** prepared *in situ* from the reaction of an azo initiator and tetramethylstibine.[117] Styrene, ^{n}BA, MMA and NVP were all polymerized to high conversions with excellent molecular weight control and PDIs of 1.07-1.36. The use of functionalized azo initiators allowed the preparation of organostibines containing ester, ether, alkene and alcohol groups (**55**-**58**).[117] Polymerization of MMA using these transfer agents resulted in the formation of PMMA containing ester, ether, alkene or alcohol α-end groups. Telechelic polymers could be obtained by selective transformation of the ω-end groups, with both homo- or hetero-telechelic species synthesized.

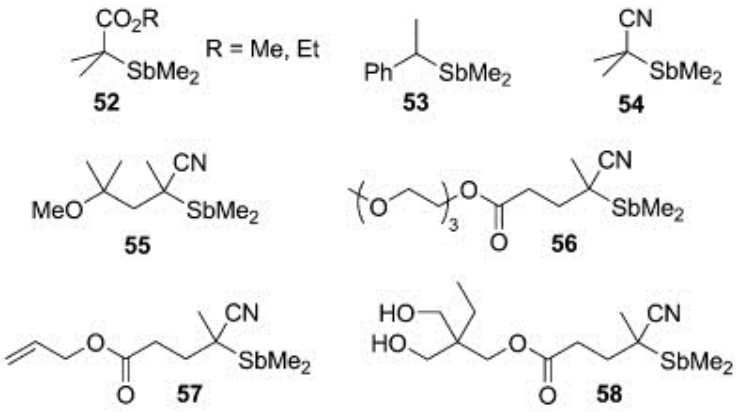


Figure 14. Organostibines used in controlled radical polymerization.

Organobismuthines were also discovered to be excellent precursors for carbon-based radicals, capable of mediating controlled radical polymerizations more efficiently than both Te and Sb-based systems. Compounds **59-60** (Figure 15) controlled the polymerization of styrene at 100°C, reaching high conversions in under 4 h, with well-controlled molecular weights and PDIs of <1.1.[118] The addition of 0.2 eq. of AIBN reduced the operating temperature to 60°C, with no loss of control and quantitative conversion achieved in 18 hours. The organobismuthines were versatile mediators, active for ^{n}BA, MMA, NIPAM and NVP polymerization. ^{n}BA, NIPAM and NVP required the use of AIBN for controlled radical polymerization, as the increased strength of the bismuth-carbon bonds, even at 100°C, resulted in a predominance of the dormant species otherwise. Kinetic studies confirmed that the mechanism of polymerization was mainly degenerative transfer, with a small contribution from the thermal dissociation mechanism. Larger rate constants were calculated for organobismuthines, both for degenerative transfer and thermal dissociation, suggesting that these species are better radical initiators and provide better control over polymerization when compared to organostibines and organotelluriums.

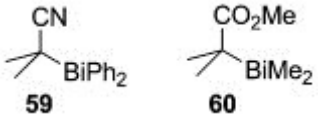


Figure 15. Organobismuthines used in controlled radical polymerization.

3. Copolymerization using OMRP

The recent development of new systems for OMRP has greatly expanded the monomer scope, presenting new opportunities for the synthesis of materials with well-defined structures and specific properties. By controlling

the length of the chains, the end-groups, architecture, composition and functionality of the polymer, materials can be tailored to particular applications. In particular, the ability of well-defined block copolymers to self-assemble under bulk or solution conditions to form nanostructures is becoming increasingly important. The ability of OMRP to yield advanced polymeric materials with predetermined molecular weights, low PDIs and controlled topology, composition and functional groups makes it increasingly valuable as the nano-technology market continues to escalate.

OMRP possesses a distinct advantage in copolymerization because of the ability of the metal complex to activate unreactive bonds, significantly expanding the monomer scope. ATRP methods have not been particularly successful for the polymerization of monomers which form unstabilized, reactive radicals (e.g. vinyl acetate) because these species form very strong carbon-halogen bonds which are difficult to activate further.[119] ATRP methods are more suitable for monomers which form stabilized radicals, and thus weaker carbon-halogen bonds, such as styrene and MMA. However, the OMRP equilibrium is eminently suitable for the regulation of highly reactive propagating radical species since activation relies only on the bond dissociation energy of the metal-carbon bond in the dormant state.[13] The synthetic organometallic chemist can investigate variables such as ligand design (steric bulk and electronics), choice of metal centre and oxidation state in order to achieve a system which will be suitable for the monomers of choice. As formation of the dormant species in OMRP requires the coordination of a propagating radical chain to the metal centre, OMRP is more sensitive to changes in the steric bulk of the ligand than ATRP, where a much smaller halogen radical is transferred. While obtaining appropriate experimental conditions for monomers of similar reactivity will be relatively straightforward, challenges exist when designing a catalyst which will be able to control the polymerization of monomers of significantly different reactivity. Choice of monomer sequence and initiation strategy is particularly important, as the following sections will highlight.

3.1. Acrylates

The synthesis of acrylate block copolymers through OMRP was first demonstrated by Wayland *et al.* in 1994.[41] The living nature of methyl acrylate polymerization mediated by cobalt porphyrin complexes was illustrated through the formation of poly(MA-*b*-^{n}BA) block copolymers. Addition of MA to (TMP)CoCH(CO_2CH_3)CH_3 at 60°C formed a (TMP)Co-terminated poly(MA) block. Removal of unreacted MA, followed by addition of ^{n}BA produced the corresponding block copolymer, with a well controlled PDI of 1.29. The brominated analogue, (Br_8TMP)Co-R, could also be used to form poly(MA-*b*-^{n}BA).[47] As in the case of acrylate homopolymerization, polymerization rates were faster with the brominated compound as a result of stabilization of the Co(II) species. Molecular weights increased linearly with conversion and PDIs of 1.09-1.11 showed improved control over the Co(TMP) system. The use of the azo initiator V-70 in conjunction with the (TMP)Co(II) complex also provided a route to increased polymerization rates and lower

PDIs.[49] Poly(MA-*b*-^{n}BA) was synthesized with PDIs of 1.05-1.07 at 60°C in benzene using this simplified approach. More recent work synthesized poly(MA-*b*-^{n}BA) using 4-methoxy substituted Co(acac)(bpi).[66] Excess monomer was removed after the formation of PMA and the Co-capped polymer was then dissolved in ^{n}BA and heated to 60°C. Molecular weights increased linearly with conversion and the PDIs of the block copolymers were typically <1.15.

The porphyrin complex (TMP)Co(II) could also be used to form block copolymers of methyl acrylate and vinyl acetate.[52] The PMA block, derived from the more reactive monomer, was synthesized first (M_n = 30,000 Da and PDI = 1.1), using AIBN as the radical source. The half life of the azo initiator is significantly longer than the 2 hours required for synthesis of the PMA-Co macroinitiator, leaving unreacted AIBN present in the reaction. Removal of the excess monomer, addition of vinyl acetate and heating to 60°C allowed the formation of well-defined poly(MA-*b*-VAc) with PDIs of 1.21 via DT OMRP. Conversion of VAc was low, *ca.* 9% in 90 min, as the porphyrin catalyst is not capable of mediating VAc polymerization to higher conversions.

Organo-main group initiators were also found to be efficient mediators for block copolymerization due to their wide monomer scope. Methyl 1-phenylethyltelluride was used to prepare ^{t}BA-Te macroinitiators which were then used for the polymerization of styrene and MMA.[106] Formation of poly(^{t}BA-*b*-St) and poly(^{t}BA-*b*-MMA) was accomplished in high yields with excellent control over molecular weights. Slightly broadened PDIs of 1.32-1.35 were attributed to the stronger carbon-tellurium bond formed in the P^{t}BA-Te macroinitiator, which resulted in a slight loss of control over the copolymerization. Poly(^{n}BA-*b*-St) was also prepared in miniemulsion using a macroinitiator prepared from EMA-TeBu.[112] Molecular weights were in good agreement with theoretical values and the PDI of 1.32 indicated a reasonable level of control was imparted to the copolymerization.

3.2. Vinyl esters

As discussed (*vide supra*), $Co(acac)_2$ is an efficient mediator of vinyl acetate OMRP. A wide range of copolymers of vinyl acetate have thus been investigated using this system, although the lower reactivity of vinyl esters when compared to other monomers means that block copolymers are most efficiently formed by utilizing a macroinitiator. By pre-forming the VAc block and using the metal-terminated poly(vinyl acetate) macroinitiator to initiate the polymerization of the second monomer, suitable VAc incorporation is ensured.

Early work looked at the copolymerization of ^{n}BA with VAc, using $Co(acac)_2$ and V70, showing that control over the polymerization increased as the VAc content increased. This was attributed to the greater efficiency of the cobalt complex in deactivating VAc-derived radicals, causing a shift in the equilibrium towards the dormant species.[57] Investigation of the composition of poly(VAc-*co*-^{n}BA) indicated a gradient sequence

distribution, and poly(VAc-*grad*-^{n}BA)-*b*-poly(VAc) containing 77% VAc could be prepared with PDIs below 1.3. Further optimization of the conditions required for efficient ^{n}BA copolymerization included studying the effect of the initiator, temperature and additives for the $Co(acac)_2$ system.[63] Use of an alkylcobalt(III) initiator in conjunction with 0.3 eq. $Co(acac)_2$ at 30°C gave poly(VAc-*co*-^{n}BA) with PDIs below 1.2, even at high conversions. Molecular weights showed improved control using this initiating system, proposed to be due to the increased initiator efficiency of the Co(III)R species in comparison to V-70. The presence of excess cobalt in the polymerization ensured efficient trapping of the propagating chains, shifting the equilibrium towards the dormant species and allowing control over the more reactive ^{n}BA monomer. Poly(VAc)-*b*-(^{n}BA) was prepared by using a Co-PVAc macroinitiator and a 1:1 mixture of VAc and ^{n}BA was also polymerized using the $Co(acac)_2$/LPO redox system, giving poly(VAc-*co*-^{n}BA) with molecular weights which increased linearly with conversion and PDIs of 1.2-1.3. In all cases, however, molecular weights were significantly higher than the theoretical values, which was attributed to the low initiator efficiencies observed with each of the initiating systems.

Synthesis of poly(VAc-*co*-NVP) was achieved using the $Co(acac)_2$/V-70 system, in the presence of 0, 20 and 50% VAc.[60] The rate of NVP consumption decreased and the induction period lengthened as the proportion of VAc in the reaction was increased, due to more efficient deactivation of VAc-terminated propagating chains. Molecular weights of the copolymer increased linearly with conversion and were in good agreement with theoretical values, but PDIs were broad (1.4-1.9) due to the lower deactivation rate of propagating chains terminated by PNVP. The poly(VAc-*co*-NVP) could be further functionalized by grafting onto a fullerene, forming nanohybrids with various compositions.[120] Hydrolysis of the acetate groups formed poly(VA-*co*-NVP)/C_{60}; hydrosoluble, biocompatible nanohybrids with potential applications as photosensitizers for photodynamic therapy. Poly(VAc-*b*-NVP) was synthesized using Co-PVAc macroinitiators of various chain lengths.[121] Reducing the temperature of the reaction improved the control over NVP polymerization and reactions were first order in monomer, with molecular weights which increased linearly with conversion and PDIs of 1.25-1.31 when the copolymerization was carried out at 20°C. The copolymer composition could be altered by varying the chain lengths through changing the VAc/Co and NVP/PVAc ratios and poly(PVA-*b*-NVP) could be obtained through hydrolysis of the acetate groups. This double amphiphilic polymer formed micellar aggregates in water, where the size of the micelles could be controlled through altering the molar mass of the PNVP block.

Co-PVAc macroinitiators were also used to synthesize poly(VAc-*b*-AN), with optimal control achieved by employing DMF as the solvent at 0°C for the RT OMRP of acrylonitrile.[122] To improve control over the reactive acrylonitrile monomer, low temperatures were used to reduce the propagation and termination rates, ensuring an appropriate equilibrium between dormant and active species. The optimized reaction conditions resulted in almost complete reinitiation, with only a trace of the PVAc macroinitiator remaining at the end of the polymerization. Molecular weights which increased linearly with conversion and extremely narrow PDIs of 1.15-1.20 illustrated the excellent control over this copolymerization, and a series of copolymers with

different molar masses and compositions were prepared. Partial hydrolysis of poly(VAc-*b*-AN) yielded poly(VA-*b*-AN), which could be used to stabilize silver nanoparticles in water.[123] The silver ions coordinate to the polar OH and CN groups and self-assembly of the copolymer in water resulted in the formation of spherical micelles with a poly(vinyl alcohol) shell and a poly(acrylonitrile) core loaded with silver ions, which were reduced to silver nanoparticles which exhibited high antibacterial activity. Complete hydrolysis of poly(VAc-*b*-AN) gave poly(VA-*b*-AA); another water-soluble, double amphiphilic copolymer.[122] Further investigation showed that this polymer was pH-responsive and formed aggregates at pH <3 due to hydrogen-bonding between the protonated poly(acrylic acid) and poly(vinyl alcohol) units. The role of the copolymerization solvent was further investigated and it was concluded that the use of a coordinating solvent increased the rate of RT OMRP, by occupying a coordination site of the cobalt centre and stabilizing the Co(II) species.[62] In non-coordinating solvents, Co-PVAc was an inefficient macroinitiator for AN polymerization because chelation of the carbonyl oxygen resulted in the slow release of radicals due to a stabilization of the cobalt-carbon bond of the dormant species. This system was further extended to the synthesis of triblock copolymers, utilizing OMRP for the initial synthesis of poly(VAc-*b*-AN), followed by reaction with a nitroxide species to end-cap the polymer chain.[124] Polymerization of styrene, ^{n}BA and 4-vinyl pyridine (VP) through NMP yielded poly(VAc-*b*-AN-*b*-St), poly(VAc-*b*-AN-*b*-^{n}BA) and poly(VAc-*b*-AN-*b*-VP) with well-controlled molecular weights and PDIs of *ca.* 1.2-1.3. Another synthesis of triblock copolymers from poly(VAc-*b*-AN) used isoprene assisted radical coupling to form symmetrical ABA copolymers with PDIs of <1.1.[125] Hydrolysis of the poly(VAc-*b*-AN-*b*-VAc) under different conditions gave poly(VA-*b*-AN-*b*-VA), an amphiphilic triblock copolymer, and also the fully hydrosoluble poly(VA-*b*-AA-*b*-VA).

Block copolymers of VAc and other vinyl esters can be achieved efficiently using the $Co(acac)_2$, lauroyl peroxide and citric acid trisodium salt redox system.[64] High molecular weight poly(VAc-*b*-VPv) and poly(VAc-*b*-VBz), with PDIs of *ca.* 1.3 and 1.6 respectively, were synthesized through sequential monomer addition. $Co(F_3\text{-acac})_2$ was used with V-70 for the copolymerization of VClAc with VAc, forming poly(VAc-*co*-VClAc) where molecular weights increased linearly with conversion and PDIs were *ca.* 1.4.[60] Optimization of the conditions allowed the synthesis of poly(VAc-*co*-VClAc) with PDIs <1.2, and removal of the cobalt end group through reaction with TEMPO produced a macroinitiator containing 5.5% vinyl chloroacetate.[126] These chlorine groups were used in the grafting-from ATRP of styrene, using copper-based catalysts, to synthesize poly(VAc-*graft*-St). Although molecular weights increased linearly with conversion, PDIs of >1.5 indicated poor control over the polymerization and it was proposed that intermolecular coupling reactions were occurring between the growing poly(styrene) grafts. A similar approach utilized $Co(acac)_2$/V-70 to form PVAc, with addition of a substituted nitroxide to the polymerization resulting in the formation of PVAc capped with a nitroxide group containing an α-bromoester.[127] These macroinitiators were used in the ATRP of styrene, MMA and EA, allowing the formation of poly(VAc-*b*-St), poly(VAc-*b*-MMA) and poly(VAc-*b*-EA). PDIs were well controlled for St and MMA (1.15-1.20) but broader

for the acrylate copolymer (1.50), where initiation was slow relative to propagation. Related research combined OMRP and RAFT for the synthesis of well-controlled poly(VAc-*b*-St), utilizing the $Co(acac)_2$ system for the vinyl acetate block and then replacing the cobalt ω-chain end with a dithioester which could be used to mediate the styrene polymerization.[128] Base-catalyzed methanolysis of poly(VAc-*b*-St) hydrolyzed the acetate groups of PVAc to alcohol functionalities (PVA), forming poly(VA-*b*-St); an amphiphilic block copolymer capable of self-associating in aqueous media to form micelles.[127-128]

Formation of poly(VAc-*b*-St) was also achieved using only OMRP.[129] $Co(acac)_2$ was used to form Co-PVAc macroinitiators of molar mass 7500, 11500 and 14500 Da, with PDIs of 1.1-1.2. Addition of styrene to the system and polymerization at 30°C resulted in the formation of block copolymers with high molecular weights and broad PDIs (1.65). The cobalt complex is inefficient at mediating styrene polymerization, as the stabilized styrenyl radicals are only partially deactivated by $Co(acac)_2$ and so polymerization of the second block is uncontrolled. Irreversible termination reactions also limited the styrene conversion to 45%. However, hydrolysis of the vinyl acetate groups gave poly(VA-*b*-St) which were used for the formation of spherical micelles and nanocups.

The versatile $Co(acac)_2$/V-70 system has also been used for the copolymerization of vinyl acetate with non-polar α-olefins such as octene (Oct) and ethylene (E), of particular interest for the design of new copolymers with novel architectures, properties and applications.[130] Poly(VAc-*co*-Oct) with molecular weights which increased linearly with conversion and PDIs of 1.1-1.3 was prepared, with ^{1}H NMR spectra indicating a gradient sequence distribution in the copolymer. The use of an isolated Co-PVAc macroinitiator allowed the synthesis of poly(VAc-*b*-Oct) with PDIs of 1.1-1.2, but octene conversion was limited to 14%. This was proposed to be due to chain transfer to the α-olefin which resulted in the formation of stable allylic radicals which were slow to reinitiate. Methanolysis of poly(VAc-*b*-Oct) gave the amphiphilic block copolymer poly(VA-*b*-Oct) which formed micelles with insoluble poly(octene) cores, stabilized by a solvated shell of the hydrophilic poly(vinyl alcohol) block. Copolymerization of ethylene with vinyl acetate proceeded more rapidly than the octene copolymerizations, forming poly(VAc-*co*-E) with high molecular weights and PDIs of *ca.* 2.4. The poor control over this polymerization was attributed to irreversible termination reactions, including chain transfer to the monomer and polymer. Use of a Co-PVAc macroinitiator allowed the formation of poly(VAc)-*b*-(VAc-*grad*-E) with M_n of 15900 Da and PDI of 1.14; however, only a small amount (*ca.* 10%) of ethylene was incorporated into the copolymer.

3.3. Styrenes

One of the most efficient catalyst systems for the OMRP of styrene is Cp_2TiCl_2/Zn, used in conjunction with a peroxide, epoxide or aldehyde initiator.[94] The radical ring opening of ethyl-3-methyl-3-phenyl glycidate by

Cp_2TiCl_2/Zn has been used to copolymerize styrene with 4-chlorostyrene (ClSt) and 4-*tert*-butylstyrene (^{t}BuSt), forming poly(St-*co*-4-ClSt-*co*-4-^{t}BuSt) with a molecular weight of 26,600 Da and PDI of 1.34.[86]

Another class of extremely efficient mediators of styrene OMRP are the main group organotellurides, organostibines and organobismuthines. As the same initiators control the polymerization of many different monomers under similar conditions, these species have proved proficient at the synthesis of a variety of copolymers. Methyl 1-phenylethyl telluride (Fig. 13; **49**, where R = Me) was used to form a PSt-Te macroinitiator, with M_n = 9200 Da and PDI = 1.17. Addition of 100 eq. of 4-methoxystyrene (MeOSt) resulted in the formation of well-controlled poly(St-*b*-4-MeOSt), with M_n = 18,000 Da and PDI = 1.19.[105] The same initiator could also be used to synthesize poly(St-*b*-MMA) and poly(St-*b*-^{t}BA) with PDIs of 1.25 and 1.18, respectively.[106] In each case, molecular weights were well controlled and agreed well with theoretical values. The system could be extended further, for the synthesis of triblock copolymers, and poly(St-*b*-MMA-*b*-^{t}BA) was synthesized in 69% yield from the diblock macroinitiator, with molecular weight of 22,600 Da and PDI of 1.27.

EMA-TeMe and EMA-TeBu (Fig. 13, **51** where R = Me and ^{n}Bu) were also used for the synthesis of poly(St-*b*-MMA).[109, 112] Formation of the block copolymer in aqueous dispersed systems resulted in some loss of control, as evidenced by the broadened PDI of 1.53 obtained under miniemulsion conditions.[112] However, molecular weights agreed well with theoretical values and EMA-TeBu could also be used for the preparation of well-controlled poly(St-*b*-^{n}BA).

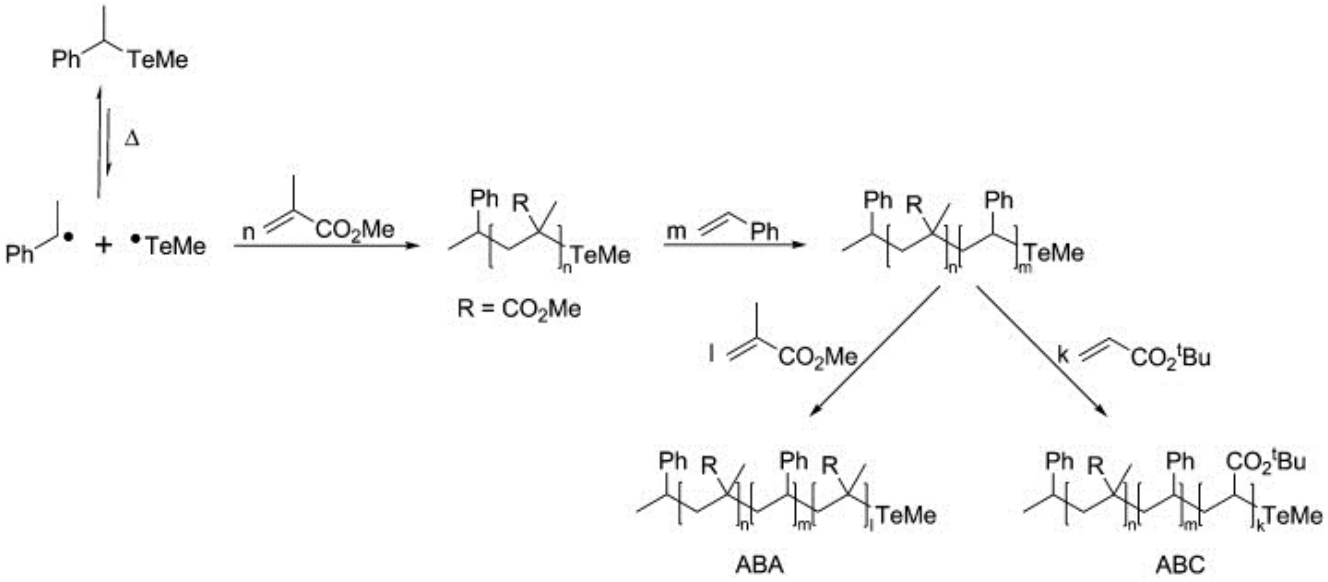
The versatility of the organo-main group elements in block copolymerization has been demonstrated by the formation of block copolymers comprising a non-polar styrene segment and a polar *N*-vinylpyrrolidone section. By combining conjugated and non-conjugated monomers in different compositions, polymers with interesting physical properties for a range of potential applications have been obtained. Use of a PSt-Bi macroinitiator, derived from **60** in Fig. 15, allowed the synthesis of poly(St-*b*-NVP) in 93% yield, with molecular weight of 15,000 Da and PDI of 1.16.[118] Organostibines **52** (where R = Et) and **53** (Fig. 14) were also used to form PSt-Sb macroinitiators for the synthesis of poly(St-*b*-NVP).[115-116] In each case, complete conversion of the macroinitiator to block copolymer was observed and the low PDIs of 1.05 illustrated the excellent control over the polymerization exerted by these species.

3.4. Methyl methacrylate

Polymerization using organotellurides has been proposed to occur through a single step degenerative transfer mechanism, via a hypervalent Te intermediate or transition state.[109] The absence of a kinetically important intermediate during the exchange means that the order of monomer addition in block copolymer formation is not particularly important. Exchange constants for homopolymerization versus copolymerization were found

to be very similar and this was attributed to the similarity in kinetic reactivity and thermodynamic stability of the exchanging radical species. The practical application of this is that a wide variety of well-controlled block copolymers can be prepared, regardless of which monomer is polymerized first.

Poly(MMA-*b*-St) has been synthesized utilizing methyl 1-phenylethyltelluride (**49** where R = Me in Fig. 13),[106] EMA-TeMe (**51** where R = Me in Fig. 13)[109] and EMA-TeBu (**51** where R = ^{n}Bu in Fig. 13)[112] to prepare the PMMA-Te macroinitiator. In each case, molecular weights increased linearly with conversion and were in good agreement with theoretical values. PDIs were *ca.* 1.1 under conventional conditions, but broadened slightly to 1.2 in miniemulsion. Poly(MMA-*b*-^{t}BA) could also be synthesized with predictable molecular weights and PDIs of 1.11.[106] Triblock copolymers of poly(MMA-*b*-St-*b*-MMA), poly(MMA-*b*-^{t}BA-*b*-MMA), poly(MMA-*b*-St-*b*-^{t}BA) and poly(MMA-*b*-^{t}BA-*b*-St) were synthesized using diblock macroinitiators obtained using methyl 1-phenylethyltelluride (Scheme 6).[106] Both the ABA and ABC triblock copolymers displayed excellent control over molecular weights and were synthesized in good yields with PDIs of 1.18-1.30.



Scheme 6. Tellurium-mediated synthesis of triblock copolymers poly(MMA-*b*-St-*b*-MMA) and poly(MMA-*b*-St-*b*-^{t}BA).

PMMA macroinitiators, based on organostibines **52** and **53** (Figure 14) were used to synthesize poly(MMA-*b*-NVP).[115-116] Complete conversion of the macroinitiator to the block copolymer resulted in high conversions, with PDIs of *ca.* 1.3. A low molecular weight shoulder in the GPC traces of the copolymers was

attributed to the fast propagation of NVP polymerization with respect to initiation from the PMMA-Sb, resulting in a slight broadening of the polydispersities.

3.5. N-vinylpyrrolidone

The organostibine initiator **53** (Figure 14) was also used to prepare poly(NVP-*b*-MMA),[116] illustrating that the order of monomer addition is generally unimportant in copolymerizations mediated by the organo-maingroup compounds. Excellent control over molecular weights and a PDI of 1.18 demonstrated that poly(NVP-*b*-MMA) could be prepared as efficiently as poly(MMA-*b*-NVP) (PDI of 1.31 using the same system).

3.6. N-isopropylacrylamide

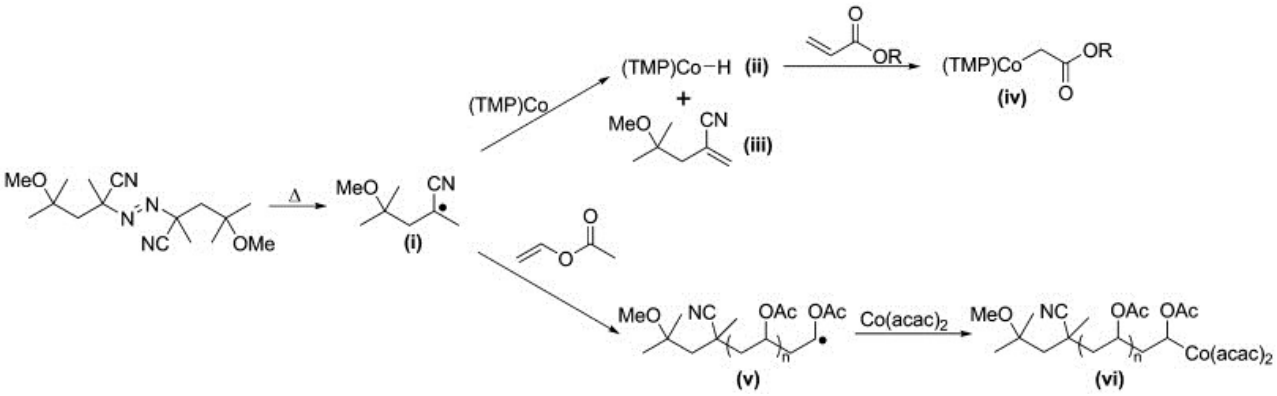
EMA-TeBu has been used to prepare thermoresponsive block copolymers of NIPAM and NVP.[111] Well-controlled PNIPAM-Te macroinitiators were used for the polymerization of NVP, forming poly(NIPAM-*b*-NVP) with various block lengths, dependent on monomer ratios. In each case, molecular weights increased linearly with conversion and were in excellent agreement with theoretical values with narrow PDIs of 1.09-1.15. The copolymers were soluble in water at room temperature but associated into micelle-like aggregates at increased temperatures, as the PNIPAM blocks dehydrated and formed the core. The association temperature was found to be dependent on the composition of the copolymer, with increased NVP content increasing the temperature at which aggregation occurred. Poly(NIPAM-*b*-NVP) could also be used to coat gold nanoparticles, by virtue of an interaction between the surface of the nanoparticle and the PNVP units. A temperature-dependent colour change was observed, due to heat-induced association of the copolymer-coated gold nanoparticles. These types of stimuli-responsive water-soluble polymer micelles are of particular interest as vehicles for drug delivery systems and other biological applications.

4. Mechanistic studies

While each of the aforementioned systems can effectively mediate radical polymerizations through the formation of an organometallic species, imparting control over the polymer properties, mechanistic similarities and differences are important to highlight.

The cobalt-mediated systems are the most extensively studied and OMRP using cobalt complexes may proceed through either reversible termination or degenerative transfer mechanisms.[14] When an azo radical initiator is used, the initiation step is slightly different for the two main classes of cobalt OMRP catalysts,

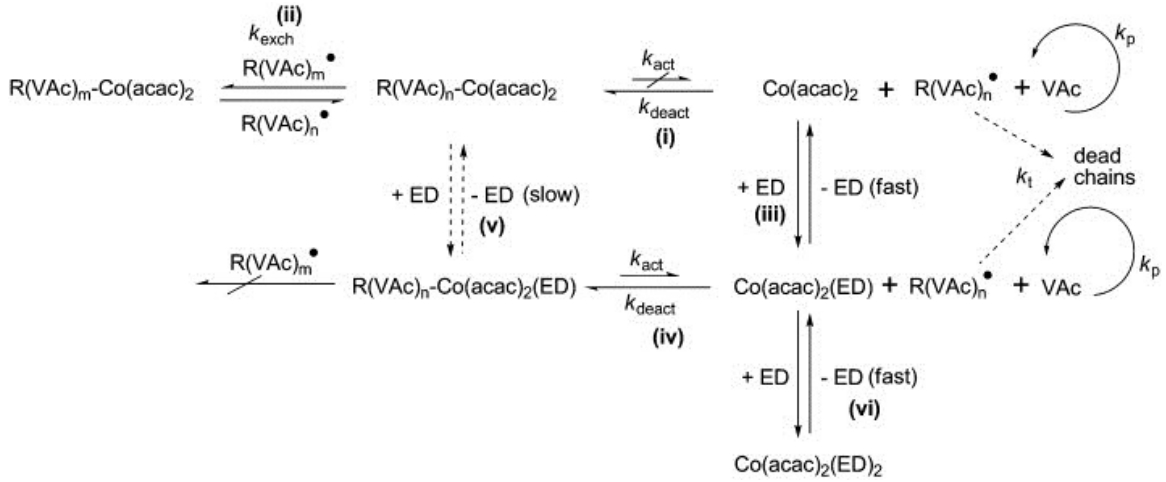
porphyrins and β-diketonato species (Scheme 7). Thermal decomposition of the initiator generates tertiary radicals, **(i)**, which initiate the polymerization **(v)** directly through reaction with the monomer when the catalyst is $Co(acac)_2$ or a derivative.[36, 53, 57, 65-68] The dormant species, **(vi)**, is formed through reaction of a radical with the metal complex, which will undergo either reversible termination or degenerative transfer OMRP depending on the reaction conditions. However, when the catalyst is a cobalt porphyrin, with greater propensity to participate in β-H elimination reactions, hydrogen abstraction from the α-methyl group of **(i)** generates a cobalt-hydride species, **(ii)**, and an olefin-terminated organic byproduct, **(iii)**. Addition of a monomer unit to the CoH complex forms the actual polymerization initiator, **(iv)**.[49]



Scheme 7. Differing initiation mechanisms for cobalt complexes.

Homolysis of the cobalt-carbon bond in **(iv)** would form the reversible termination OMRP equilibrium, whereby the radicals propagate through reaction with the monomer until they react with a Co(II) complex to form the dormant species. However, in the presence of even a slight excess of radicals with respect to cobalt, a degenerative transfer mechanism operates. The azo initiator provides a constant radical influx, which initiates tiny amounts of propagating chains throughout the polymerization. Rapid deactivation of these chains through reaction with a dormant CoR species provides control over the polymerization. Once the azo initiator has completely decomposed, the lack of new radicals results in a switch in polymerization mechanism to reversible termination, usually with a concomitant drop in polymerization rate.[37, 49]

The $Co(acac)_2$-based systems also operate through both DT and RT mechanisms, depending on the polymerization conditions.[58-59, 62, 65, 67-68] As with the porphyrin complexes, a higher concentration of radical initiator favours degenerative transfer. However, reversible termination can be favoured through decreasing the azo initiator concentration, diluting the reactions and also through the addition of an electron donor.



Scheme 8. Vinyl acetate OMRP using Co(acac)2 in the presence and absence of electron donors. Reproduced with permission from [58] 2007, Wiley VCH.

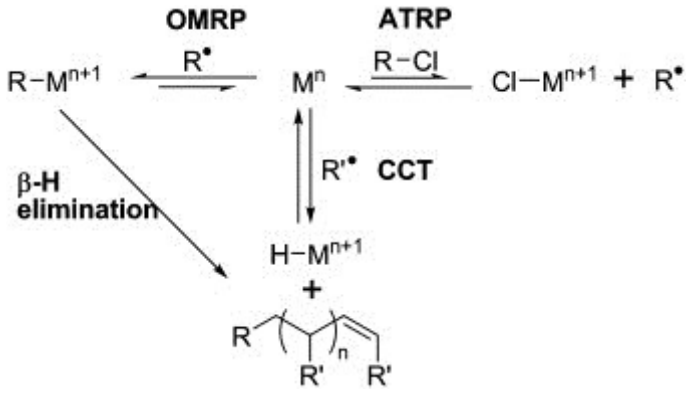
The presence of an electron donor, such as water or pyridine, blocks the coordination site on the cobalt centre required for associative radical exchange during the degenerative transfer mechanism (Scheme 8).[58-59] V-70 has a $t_{1/2}$ of 10 hours at 30°C and, in the absence of an electron donor group, the radicals slowly convert the $Co(acac)_2$ complex into $RCo(acac)_2$ in an essentially irreversible reaction, **(i)**. Towards the end of this transformation, the concentration of $Co(acac)_2$ is low, and so the new $R^\bullet$ are not efficiently trapped. These radicals begin to propagate, quickly generating polymer chains, and resulting in the observation of a rapid polymerization process after the induction period. The intervention of a degenerative transfer process, **(ii)**, ensures that the polymerization remains controlled. In the presence of an electron donor group, $Co(acac)_2(ED)$ is rapidly formed, **(iii)**, meaning that when the organometallic dormant species $RCo(acac)_2(ED)$ forms, **(iv)**, the coordination site needed for the degenerative transfer is blocked. The dissociation of the ED from dormant species, **(v)**, is slow, because the low-spin d^6 complex is relatively inert. Degenerative transfer will therefore only take place if the ED doesn't bind very strongly to the Co(III) dormant species and a significant amount of $RCo(acac)_2$ remains present at equilibrium. In the presence of a strong ED, polymerization occurs predominantly through RT OMRP and the electron donor addition/dissociation equilibrium, **(vi)**, between $Co(acac)_2(ED)$ and $Co(acac)_2(ED)_2$, stabilizes the Co(II) spin trap and accelerates the polymerization.

Organotellurides, organostibines and organobismuthines also show interplay between RT and DT OMRP.[25] In the absence of an azo initiator, the activation process occurs through homolysis of the organometallic bond of the mediating species to generate carbon-centred radicals.[105] Propagation through reaction with the monomer then occurs, with kinetic studies indicating that a bimolecular degenerative transfer process between active radicals and dormant species dominates the polymerization.[109] By including an azo initiator in the polymerization, initiating radicals are formed quickly under milder conditions and the polymerization occurs exclusively through degenerative transfer.[108]

Cp_2TiCl_2 has also been proposed to mediate polymerization through both RT and DT OMRP.[86] The capping of propagating chains through reaction with the Cp_2TiCl species generated *in situ* seems eminently possible. Less evidence has been provided for the degenerative transfer mechanism; presumably single-step DT must occur, analogous to the mechanism proposed for organo-main group compounds. However, unlike with the Co and main group species which show a switch to DT in the presence of excess radicals, the Ti system is less efficient when excess initiator is used.[94] Indeed, the presence of a substoichiometric amount of Ti results in an uncontrolled polymerization, presumably because RT OMRP is hindered. Radical polymerizations mediated by these Ti systems are not fully understood and further investigation into the mechanism is warranted.

Reversible termination OMRP dominates for other metal mediators. In the case of Mo, Fe, Os, Cr and V, trapping of the propagating radical through formation of an organometallic species imparts control to the polymerization. Lack of accessible coordination sites, the ability of metal-polymer macroinitiators to reinitiate polymerization and the loss of control observed when excess azo initiator is used all support the presence of RT OMRP, untainted by DT. However, many of these systems demonstrate interesting mechanistic interplay between OMRP, ATRP and CCT processes.

One of the earliest OMRP systems was based on half-sandwich molybdenum complexes. These complexes were active in both ATRP and OMRP equilibria, with the ancillary ligand determining which mechanism dominated.[69, 71-72] Mo(III) can reversibly trap the propagating radical under OMRP conditions, and since the concentration of Mo(III) remains high under ATRP conditions, both trapping mechanisms can occur simultaneously (Scheme 9). Several related complexes were found to operate by another mechanism under standard ATRP conditions, generating short-chain, olefin-terminated oligomers, with molecular weights independent of conversion, *i.e.* via CCT.

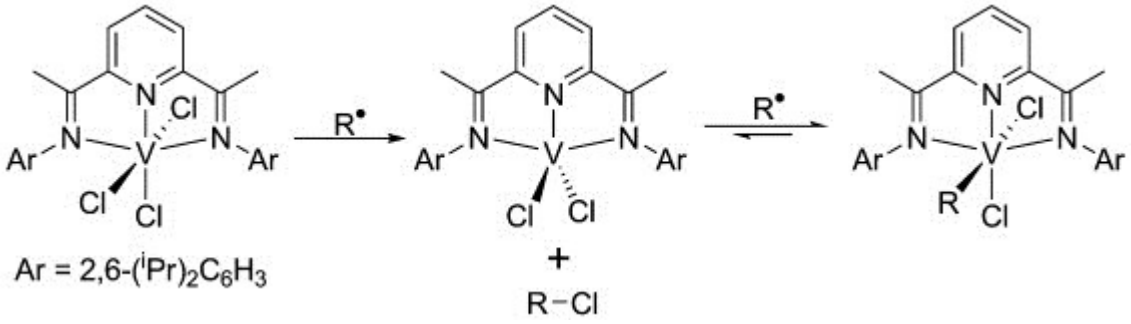


Scheme 9. Interplay between OMRP, ATRP and CCT for Mo and Fe catalysts.

Similar mechanistic interplay was demonstrated for a series of α-diimine iron complexes.[75-79] Again, the nature of the ligand determined the prevalent polymerization mechanism, with electron donating groups (EDG) favouring ATRP while electron withdrawing groups (EWG) favoured an organometallic regime. With polymerizations run under ATRP conditions, control was dependent on the halogenophilicity of the Fe(II) complexes. EDG resulted in efficient ATRP, giving halogen-terminated polymers with well-controlled molecular weights. EWG favoured the trapping of the propagating radical by the Fe(II) complex, establishing an OMRP equilibrium (Scheme 9). The instability of the Fe(III)R species formed resulted in β-hydrogen elimination to give low molecular weight, olefin-terminated polymers. If polymerizations were set up under OMRP conditions (using an azo initiator), OMRP could operate independently of the ATRP equilibrium and impart modest control over the polymerization. However, since most of the control was derived from the ATRP equilibrium, these catalysts were not efficient mediators of OMRP.[79]

Half-sandwich chromium complexes are mechanistically important because they represent examples of species where OMRP trapping dominates over ATRP.[12, 100-101] Despite the use of alkyl halide initiators, control over the polymerization was imparted through the OMRP regime.[101] DFT calculations showed that the ATRP dormant state was less favourable than the OMRP dormant state, as the energy barrier on going from the active radical to the ATRP dormant state was much greater than that leading to the OMRP dormant state. This energy difference was rationalized on the basis that OMRP trapping involves the formation of a single bond, whereas trapping through ATRP requires simultaneous bond-breaking and bond-forming processes in the transition state. Polymer chains were therefore trapped more rapidly by Cr(II) species than by Cr(III)Cl, establishing OMRP as the dominant mechanism.

The recently reported [BIMPY]VCl_3 system is another example of a catalyst system where OMRP trapping dominates over ATRP.[102-103] Vinyl acetate polymerization was well controlled when initiated with AIBN, using RATRP conditions. However, the lack of halogen-terminated polymer chains and the presence of vanadium in purified polymer samples suggested that OMRP was playing an important role. Experimental and computational studies support a 2-step process: irreversible halogen transfer from the parent $LVCl_3$ complex generates the active $LVCl_2$ species *in situ*. This complex does not participate in ATRP, but acts as a persistent radical and traps the propagating radical chains in a reversible termination OMRP process (Scheme 10). The energy difference between $LVCl_2$ and $LVCl_2R$, where R is a radical derived from vinyl acetate, was calculated to be just 4 kcal/mol. When R is a styrenyl radical, the energy difference is *ca.* 20 kcal/mol, and control over the polymerization is poor. Excellent control over VAc polymerization is not only due to the higher reactivity of the radical but also to chelation of the ester oxygen to the vanadium centre which increases the favourability of the trapping step.



Scheme 10. Two-step OMRP mechanism for vanadium species.

There are some clear correlations which can be made between OMRP catalysts and polymerization mechanism. While DT-OMRP dominates for cobalt and main group complexes, the degenerative transfer mechanism requires not only an excess of radical species with respect to the mediator but also a coordination environment around the oxidized metal species which can incorporate a further 1-electron ligand, both sterically and electronically. The $Co(acac)_2$ complex for VAc polymerization is an excellent example; the 4-coordinate, 15-electron Co(II) species is oxidized to the 5-coordinate, 16-electron RCo(III) dormant species. This compound is still coordinatively unsaturated, allowing an associative radical exchange to take place. If this site is blocked by another ligand, RT-OMRP occurs. This contrasts with the pentacoordinate Co(acac)(bpi) system,[66] which is a 17-electron species. Given that the dormant organometallic species is 6-coordinate, DT-OMRP requires that the metal centre accept a further ligand during the radical exchange event. It seems likely that this catalyst system would therefore operate through RT-OMRP, although the authors state that the mechanism gradually changes to a DT process, as indicated by the onset of a more rapid polymerization. Interestingly, the Co(acac)(bpi) complexes were excellent mediators for the polymerization of acrylate monomers, whereas $Co(acac)_2$ does not efficiently deactivate the acrylate radicals under standard reaction conditions, leading to uncontrolled polymerizations. Changing the coordination sphere of the metal directly affects the metal-carbon bond strengths and the increased steric crowding in the Co(acac)(bpi) system tunes the system for control over acrylate polymerization rather than vinyl acetate. In order for $Co(acac)_2$ to mediate the polymerization of more reactive monomers, such as acrylates and acrylonitrile, the reaction conditions must be modified to favour RT-OMRP. These include initiating from an organometallic species, decreasing the polymerization temperature, adding an excess of the control agent and using a coordinating solvent such as DMSO or DMF, all of which act to fine-tune the metal-carbon bond strength such that an appropriate dynamic equilibrium between dormant and active species can be achieved.

Another example where monomer type has a dramatic effect on the polymerization mechanism is that of (TMP)Co. Acrylate monomers can undergo both RT and DT OMRP, depending on the reaction conditions.[37] However, VAc can only be polymerized by this system through DT,[52] since a stronger metal-carbon bond is formed between the vinyl acetate radicals and the metal centre. The organo-cobalt

dissociation equilibrium constant is much lower for vinyl acetate because of the lower stability of the radical species and so RT OMRP is disfavoured. The rate constant for associative radical interchange was found to be the same for methyl acrylate and vinyl acetate, so DT OMRP proceeds in both cases.[131]

RT OMRP processes are also very dependent upon monomer reactivity, which plays an important role in determining the metal-carbon bond strengths. Half-sandwich chromium complexes are ineffective for the OMRP of styrene because the metal-carbon bonds are too weak, resulting in uncontrolled polymerizations.[12] These complexes are much more successful in controlling the polymerization of VAc, since stronger metal-carbon bonds are formed with the more reactive vinyl acetate radical. Additional investigations on these half-sandwich chromium complexes showed that the metal-carbon bond strengths could be further tuned by altering the aryl substituents on the ancillary ligand. As metal-carbon bond strengths tend to increase down a group, it is unsurprising that the half-sandwich molybdenum complexes are effective catalysts for the OMRP of styrene[69] and it would be anticipated that VAc polymerization would be unproductive. Iron shows similar reactivity to molybdenum, in that the OMRP of less reactive styrenyl radicals exhibits reasonably good control.[79] In contrast, the reactive vinyl acetate radicals form very strong metal-carbon bonds with iron and irreversible trapping occurs, with no productive polymerization observed.[132] Acrylonitrile-derived radicals form very weak bonds with iron, leading to high radical concentrations and uncontrolled polymerizations, with irreversible termination reactions. These observations led to the intelligent design of new catalysts: the higher redox potential of vanadium allows it to stabilize the more reactive radicals and activate unreactive bonds, with $BIMPYVCl_3$ proving an efficient catalyst for RT-OMRP of VAc.[102-103] The bonds formed between styrenyl radicals and vanadium are too weak, resulting in uncontrolled polymerizations; however, by altering the steric environment of the catalyst, it is possible that this could be tuned. The crowded environment around the metal centre favours RT OMRP processes, since the formation of 7-coordinate V(IV) species (required during associative radical exchange) is disfavoured.

5. Conclusions

This review presents a comprehensive discussion of metal complexes capable of controlling polymer molecular weights and PDIs through OMRP mechanisms. The diversity of metal species active in OMRP is ever-increasing, as are the families of monomers which can be efficiently controlled using these systems. While early work focused on acrylate polymerization mediated by cobalt porphyrins, extension to other cobalt systems with the ability to control a variety of different monomers represented significant progress in the utility of OMRP. Development of new systems based on metals including molybdenum, osmium, iron, palladium, titanium, chromium and, most recently, vanadium, has yielded new, tunable catalysts incorporating various ligand frameworks.

There are, however, several challenges which present themselves in the field of OMRP. The efficient design of new mediators is one issue. While recent research has significantly expanded the number of active systems, much of the periodic table remains unexplored. Ligand design also has a vital role to play in increasing the monomer scope and efficacy of OMRP catalysts, yet only a few investigations of systematic variation of ligand substituents have been reported. Better understanding of the role of the metal-carbon bond strengths, both in terms of the dormant species and organometallic initiating species, would facilitate improved control over polymerizations. While the effect of R-X bond dissociation enthalpies on ATRP initiation has been studied both experimentally and computationally, no such data have been compiled for OMRP systems and this in particular warrants further study. To improve control over copolymerization, catalysts which have switchable properties should be targeted. At the moment, $Co(acac)_2$ is the most efficient system for the copolymerization of monomers of different reactivities, but it requires a switch in polymerization mechanism through the addition of an additive, often with a concomitant reduction in reaction temperature. Designing a system with a preference for different monomers under varying thermal or irradiation conditions would allow facile copolymerization of monomers which vary significantly in reactivity.

Another significant challenge for groups involved with OMRP is to expand the scope of macromolecular architectures available. This may be achieved through exploiting existing catalysts, as the full scope of many of these systems has not yet been realized, or it may come through further catalyst design. In order to compete with other controlled radical polymerization techniques, the depth of applications available still needs to be improved.

The expanded monomer scope now available for OMRP allows a wide variety of advanced polymeric materials to be synthesized. Specific materials with precise topology, composition and functionality, in addition to targeted molecular weights and low PDIs, can be achieved. Better understanding of the mechanistic interplay which exists between competing reversible termination and degenerative transfer OMRP, ATRP and CCT processes will allow the design of more efficient catalysts, expansion to new metal systems and the production of specifically tailored macromolecular frameworks.

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