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ARTICLE TYPE

Reversible Deactivation Radical Polymerization in the Presence of Zero-Valent Metals: from Components to Precise Polymerization

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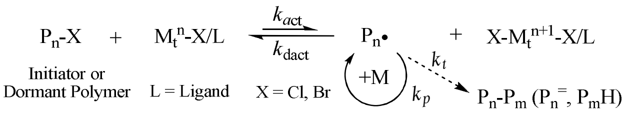
Typically, reversible deactivation radical polymerization (RDRP) in the presence of zero-valent metal contains monomer, initiator, zero-valent metal, ligand and solvent. RDRP in the presence of zero-valent metal has demonstrated many advantags, including well-controlled manners, low temperature, good retention of chain-end functionality, and readily recycle of metal. The development of zero-valent metal-mediated RDRP has profound impacts on precise polymer synthesis for its preparative characteristics of "green" RDRP, while still allowing excellent control over molecular weight and molecular weight distribution. Herein, we highlight recent work from the advent of zero-valent metal-mediated RDRP toward the advance of its components and synthesis of well-defined polymers.

1. Introduction

Over the past 30 years, controlled/"living" radical polymerization (CRP) (or named with reversible-deactivation radical polymerization, RDRP by IUPAC)[1] has become the most important and robust toolbox for polymer chemistry and macromolecular synthesis, which combines the advantages of traditional free radical polymerization and living ionic polymerization, *i.e.*, greater monomer diversity and less stringent reaction conditions.[2] Since the discovery of RDRP by Otsu in 1982,[3] many powerful RDRP techniques have been developed, including but not limited to nitroxide-mediated polymerization (NMP),[4] reversible addition-fragmentation transfer (RAFT) polymerization,[5] atom transfer radical polymerization (ATRP)[6, 7] and zero-valent metal mediated RDRP[8-10] *et al*.. In all RDRP techniques, an effective reversible deactivation between propagating radicals and dormant species is necessary for ensuring a low radical concentration, thereby largely reducing bimolecular termination and other side reactions.[11, 12] Based on the well developed concept over the past 30 years, RDRP can enable not only the production of polymers with precisely controlled molecular weight (MW) and narrow molecular weight distribution (M_w/M_n), but also the preparation every aspect of macromolecular architecture, *i.e.*, composition, topology and functionality.

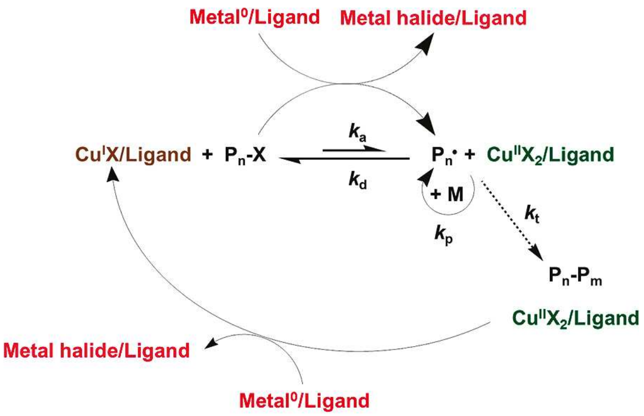
Metal-mediated RDRP, like ATRP, is a robust and versatile synthetic technique for preparation of polymers with well-defined architecture and site-specific functionality.[13, 14] The polymeric chain growth of ATRP, as a typical metal-mediated RDRP (transition metal-catalyzed living radical polymerization)[7, 15], is mediated by a transition-metal complex (Cu[14], Ru,[7] Fe,[16] *etc*.[17]). From Scheme 1, a low radical concentration, which facilitates the minimization of termination reaction, can be maintained by a dynamic equilibrium between the radical species (P_n•) and the dormant species (P_n-X) between the lower oxidation state (M_t^n-X/L) and higher oxidation state (X-M_t^{n+1}-X/L).[18] In metal-mediated RDRP, the zero-valent metal mediated RDRP, with abundantly available and readily reusable zero-valent metal as catalyst makes it a preferential choice for the synthesis of well-defined polymers.



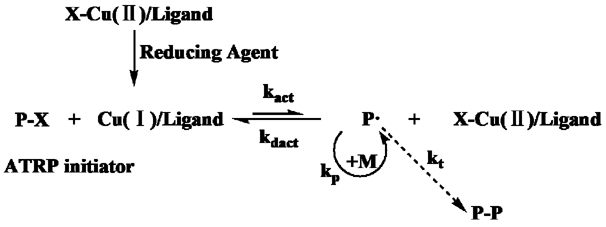
Scheme 1. Typical ATRP Mechanism.

Around 1970, many polymer chemists had reported radical polymerizations in the presence of activated metal powders (e.g., Ni(0), Co(0), Cu(0), Fe(0), *etc*.), however with unknown controllability.[18-20] In 1990, Otsu *et al*. also got an ill-defined poly(styrene) (PSt) with very high M_w/M_ns, initiated by reduced Ni(0)/benzyl halides.[21] Since the emerge of atom transfer radical addition in organic reaction,[22-25] a number of zero valent metals such as Cu(0),[26, 27] and Fe(0)[28-30] were found to be particularly active in ATRA process. After the invention of ATRP inspired by ATRA reaction, the utilization of Cu(0) in conjunction with a suitable ligand to scavenge the excess metal halide was firstly reported by Matyjaszewski *et al*. in 1997.[8] This work provided a ATRP with a significant reduction of the catalyst amount required to maintain reasonable polymerization rates.[31] The reduction in soluble catalyst concentration is a significant advancement in metal-mediated RDRP with simplified post treatment and many other desirable merits. When small amount of Cu(0) powder was added to ATRP of styrene (St) and (methyl)acrylates, a dramatic rate increase was observed. Toward practical applications and potential large production, ATRP has witnessed a vast development and can now be successfully conducted with very low amounts of catalyst, for example, initiators for continuous activator regeneration (ICAR) ATRP,[32] activators regenerated by electron transfer (ARGET) ATRP,[33, 34] electrochemically mediated atom transfer radical polymerization (eATRP).[35] In

ARGET ATRP (Scheme 2),[33, 34, 36, 40, 41] an excess of reducing agents, that do not form molecules capable of initiating an ATRP, is used. Zero-valent metals, which can react with alkyl halides and can initiate a polymerization, acted as a dual role of supplemental activator and reducing agent. Activators generated by electron transfer (AGET) ATRP has also[37, 38] been proposed by Matyjaszewski *et al*. by using reducing agent to reduce the higher oxidation state transition metal complex (Scheme 3).[39, 40] The addition of Cu(0) to the self-condensing vinyl polymerization of novel (meth)acrylic monomers using ATRP catalyst (Cu(II)) systems has also enabled a successful polymerization.[41] Similar to the cases of Cu(II)/Cu(0), Fe(III) halides were also used in the presence of Fe(0) to prepare the *in-situ* Fe(II).[31] The uses of zero-valent metal wire[42, 43] as a heterogeneous reducing agent facilitates the handling of the reducing agent and simplifies purification of the polymer.

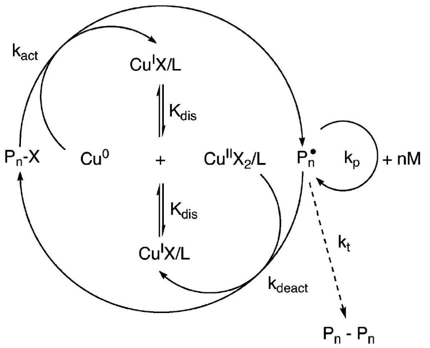


Scheme 2. Mechanism of ARGET ATRP with zero-valent metal as supplemental activator and reducing agent. (Reprinted with permission from {Y. Zhang, Y. Wang and K. Matyjaszewski, *Macromolecules*, 2011, **44**, 683-685.}. Copyright {2011} American Chemical Society.)[37]

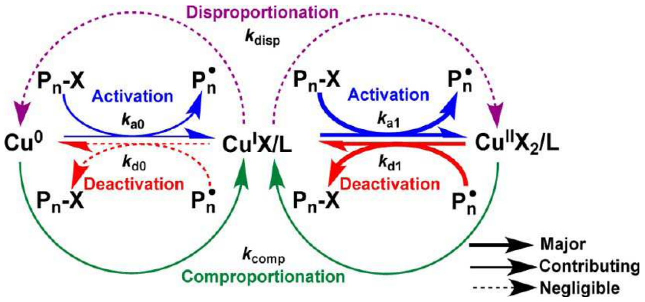


Scheme 3. Mechanism of AGET ATRP.

In 2006, single-electron transfer living radical polymerization (SET-LRP) proposed by Percec *et al.* demonstrated good control and relatively fast polymerization by using Cu(0) and tris(2-(dimethylamino)ethyl)amine (Me_6TREN) in dimethyl sulfoxide (DMSO).[9] As claimed by Percec *et al*. (Scheme 4) that in SET-LRP, Cu(0) species act as electron donor, and the initiator/dormant propagating species act as electron acceptor. Cu(0) donates an electron to P_n/P-X, resulting in a radical-anion. P_n•/P• is then generated from the heterolytic cleavage of the radical-anion intermediate $[P_n/PX]^{-•}$. The Cu(I) species generated during the formation of radicals spontaneously disproportionate into extremely reactive nascent atomic Cu(0) and $Cu(II)X_2/L$ species, which mediates the initiation and the reversible termination, respectively. Although many pieces of excellent work[44-46] was based on SET-LRP, the proposed mechanism by Percec *et al.* was argued with ARGET ATRP (Scheme 2) and a recently refined mechanism, named supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP) (Scheme 5).[47] According to SARA ATRP mechanism, Cu(I) acts as the major activator of alkyl halides with Cu(0) acting as a supplemental activator, and an inner-sphere electron transfer occurring during the activation step was proposed, disproportionation is very slow and limited in DMSO, Cu(0) is a very slow activator, and Cu(I) is the major activator. Meanwhile, slow activation of alkyl halides by Cu(0) and comproportionation of Cu(II) with Cu(0) for the small number of radicals lost to termination reactions in SARA ATRP.[47-51] As for the clarification of the mechanism, there has been a large body of mechanistic work, focusing on the following key questions (a) whether or not the alkyl halide forms a radical anion intermediate during the activation process,[9, 52, 53] (b) whether the role of Cu(0) is to act as a supplemental activator of alkyl halides and a reducing agent[38, 49-51] or if Cu(0) is the exclusive activator of alkyl halides[9, 54, 55] and (c) whether Cu(I)/L species participate in the activation of alkyl halides[38, 50, 51] or if they undergo instantaneous and complete disproportionation.[9, 56] Putting aside its mechanism, RDRP in the presence of Cu(0) or other zero valent metal has become an important RDRP technique and shown many desirable advantages, such as high polymerization rate at low temperature for monomers with relatively large k_p and good controllability under appropriate conditions. This mini-review will give a brief survey on RDRP in the presence of zero valent metal from three aspects, including components, advantages and precise polymer synthesis.



Scheme 4. Mechanism of SET-LRP by Percec *et al.* (Reprinted with permission from {V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro and S. Sahoo, *J. Am. Chem. Soc*, **2006**, 128, 14156-14165.}. Copyright {2006} American Chemical Society.)[9]



Scheme 5. Mechanism of SARA ARRP by Matyjaszewski *et al*. (Reprinted with permission from {D. Konkolewicz, Y. Wang, M. Zhong, P. Krys, A. A. Isse, A. Gennaro and K. Matyjaszewski, *Macromolecules*, 2013, **46**, 8749-8772.}. Copyright {2013} American Chemical Society.)[47]

2. Components of Zero-Valent Metal Mediated RDRP

As a typical zero-valent metal as catalyst in RDRP, monomer, catalyst system, initiator and solvent are essential. As following, this part will elaborate monomer, catalyst system, initiator and solvent, respectively.

2.1 Monomer

Various monomers have been successfully polymerized using zero-valent metal as catalyst in RDRP: (meth)acrylates, (meth)-acrylamides, acrylonitrile, vinyl chloride, styrene *etc*.. The rapid progress and proliferation has allowed a broad scope of vinyl monomers to be polymerized into well-defined polymers of controlled molecular weights and narrow MWDs. In this section, a variety of monomers for zero-valent metal as catalyst in RDRP at ambient temperature are described.

Acrylates and Acrylamides: Copper-based systems have been most extensively studied and effective in controlling the MWDs ($M_w/M_n < 1.30$) of poly(acrylate)s. As a typical monomer, zero-valent metal as catalyst in RDRP has been used in conjunction with acrylates and acrylamides, such as methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (*n*BA), *t*-butyl acrylate (*t*BA), solketal acrylate (SA) ((2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate),[57] 2-methoxyethyl acrylate (MEA),[58] poly(ethylene glycol) methyl ether acrylate (PEGMEA),[59] 2-ethylhexyl acrylate (2-EHA),[60] and *N*-isopropylacrylamide (NIPAM).[60, 61] For example, α,ω-di(bromo) PMA, PEA, and PBA with M_n ranging from 8500~35,000 g/mol were synthesized by Cu(0)/tris[2-(dimethylamino)ethyl] amine (Me_6TREN) at 25 ^oC in DMSO. These results accelerated strategies based on the TERMINI concept, synthesis of block copolymers, telechelics, and other polymers with complex architecture.[62] The application of copper(II) deactivator on Cu(0)-mediated RDRP of *t*BA can be achieved.[63] One-pot reduction/conjugation reaction enables post polymerization modification with functional MA and acrylamides (AM).[64] *N*,*N*-dimethylacrylamide (DMAA), NIPAM in protic[65-67] or dipolar aprotic solvents and surface-initiated RDRP of PNIPAM[68] can also be achieved by Cu(0)-mediated RDRP at 25 ^oC. Cu(0)-mediated RDRP of MA in the presence of classic 4-methoxyphenol free radical inhibitor was investigated.[69] Cu(0)/Me_6TREN-mediated RDRP of MA in hydrophobic media was enhanced by phenols.[70] A series of functional water-soluble polymers were successfully synthesized *via* RDRP mediated by prior disproportionation of CuBr/Me_6TREN in pure water with controlled chain length and narrow molecular weight distributions ($M_w/M_n \sim 1.10$), including PNIPAM, PDMAA, poly(ethylene glycol) acrylate (EGA), 2-hydroxyethyl acrylate (HEA), and an acrylamido glyco monomer.[71] Moreover, Cu(0) wire-mediated RDRP of HEA can be performed in solvents of methanol (MeOH) and DMSO using ethyl 2-bromoisobutyrate (EBiB) and Me_6TREN as initiator and ligand, respectively.[72]

Methyl Methacrylate: Cu(0)-mediated RDRP of MMA in DMSO has been performed.[73-76] Self-regulated Cu(0) catalyzed RDRP has been shown to be compatible with other methacrylate monomers such as butyl methacrylate (BMA). Because of the lower intrinsic k_p of methacrylates, zero-valent metal-mediated RDRP of MMA is about 5-10 times slower than zero-valent metal-mediated RDRP of MA under identical conditions. In our research, the RDRP of MMA is also feasible using 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN), a typical RAFT agent, as an initiator with Cu(0)/*N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA)[89] or Fe(0) as catalyst.[77] Meanwhile, Cu(0)/PMDETA catalyzed RDRP of MMA initiated with EBiB was also reported in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP),[78] which provided both enhanced rate of polymerization with well molecular weight evolution even at low temperatures ranging from -18 to 0 ^oC, and improved syndiotacticity (≈ 0.77), comparing with that of free radical polymerization. The active Cu(0) formed by the disproportionation of Cu(I) species in aqueous medium probably plays a vital role for a possible air-initiation of isobornyl methacrylate (IBMA) *via* Cu(0)-mediated RDRP, however with poor initiator efficiency due to the heterogeneous polymerization medium.[79] Methacrylate monomers were also successfully polymerized by ATRP utilizing copper wire as an *in situ* reducing agent at near-ambient temperatures (35 ^oC) in anisole.[80]

4-Vinylpyridine: In the presence or absence of ligand, well-controlled poly(4-vinylpyridine) (P4VP) was successfully obtained *via* Cu(0)-mediated RDRP with HFIP, a fuloroalcohol, as a solvent, which can strongly interact with 4-vinylpyridine (4VP) *via* hydrogen bonding. The equimolar 4VP and HFIP, and temperature (25 ^oC) favored a better hydrogen bonding interaction.[81] The presence of Me_6TREN facilitated faster polymerizations with more predictable number-average molecular weights ($M_{n,SEC}$) and narrower molecular weight distributions ($M_w/M_n < 1.25$) in comparison with those without hydrogen bonding interaction. Moreover, the hydrogen bonding had profound impacts on the stereoregulation during polymerization, which enabled P4VP with a highly syndiotactic (60.2%) and gave rise to a higher glass transition temperature (T_g) of P4VP.[82] Furthermore, reversible-deactivation radical copolymerization of 4VP and St was also successfully performed in HFIP, exhibiting a better controlled manner and a predominantly alternating monomer sequence. This well-regulated polymerization behavior as well as the monomer sequence were ascribed to electron induction and steric repulsion effects from the hydrogen bonding interaction between 4VP and HFIP.[83] Moreover, the alternating copolymer of 4VP and St obtained in HFIP showed a slightly higher glass transition temperature with respect to that of the random copolymer obtained in 2-propanol.

Styrene: Generally, higher temperature is often needed to realize the controlled polymerization due to the low propagation rate coefficient of St. In this regard, the controlled polymerization of St is very slow *via* zero-valent metal catalyzed RDRP at ambient temperature. For example, Subramanian *et al*. has reported a feasible Cu(0)/PMDETA catalyzed RDRP of St with 1-bromoethyl benzene (1-PEBr), EBiB, or diethyl-2-bromo-2-methyl malonate (DEBMM) as initiator in DMSO at 25 ^oC; however, a relatively broad polydispersity ($M_w/M_n>1.40$) was obtained.[84] They also claimed that the combination of Cu(0)-

mediated RDRP and RAFT polymerization could improve the living character of the reaction. The Cu(0)/PMDETA catalyzed RDRP of St initiated with DEBMM or *p*-toluenesulfonyl chloride (TsCl) combined with (2-ethoxy carbonyl)prop-2-yl-pyrrole-1-carbodithioate (CTA) in DMSO at 25 °C provides PSt with a lower polydispersity ($M_w/M_n \approx 1.20{\sim}1.26$). We recently reported a successful Cu(0)/PMDETA-mediated RDRP of St at room temperature with methyl-2-bromopropionate (MBP) or EBiB as initiator in DMF, but the polymerization rate was very low.[85] The reversible-deactivation radical copolymerization of St and other monomers could be easily realized. We have explored the Cu(0)/PMDETA mediated copolymerization of MMA and St in DMF at 25 °C.[86] The Cu(0)/Me_6TREN mediated copolymerization of 4VP and St was also suuceessfully performed at 25 °C in our group, with HFIP as solvent.[83] Perrier *et al*. have reported the controlled polymerization of St using Cu(0)/PMDETA as catalyst at 90 °C in toluene.[87] In our work, Fe(0) (powder or wire) and elemental bromine (Br_2) were used as the catalyst for RDRP of St without any additional initiator at 110 °C. The polymerization happened with controlled evidence at appropriate molar ratio of Fe(0)/Br_2.[88]

Acrylonitrile: Polyacrylonitrile (PAN) and its copolymer, such as the copolymers of St and AN (SAN), are commercially important polymers for its versatile and good performance including hardness and rigidity, chemical resistance, compatibility with polar substances, and low gas permeability. Well-defined PAN and SAN with predictable molecular weights, structures, and high chain-end functionalities would offer the polymers with high and unique performance. Therefore, the synthesis of controlled PAN and SAN has great significance for industrial applications. The feasibility of homo-polymerization of AN and copolymerization of St and AN by RDRP were investigated and well-defined PAN was prepared at room temperature explored by our group using $[\text{EBiB}]_0/[\text{Cu(0)}]_0/[\text{bipyridine (bpy)}]_0$ in DMSO.[89] RDRPs of AN initiated by 2-bromopropionitrile (BPN) using Cu(0)/Me_6TREN as a source of the catalyst in DMSO were also studied in detail by Li *et al.*.[90] Chen *et al*. reported that RDRP of AN can be catalyzed by Cu(0) powder with carbon tetrachloride (CCl_4) as the initiator and hexamethylenetetramine (HMT) as the ligand in *N*,*N*-dimethylformamide (DMF) or mixed solvent.[91] In addition, Zn(0)/$CuBr_2$ (10 ~ 50 ppm) was firstly used to catalyze radical polymerization of AN at ambient temperature reported by Liu *et al.*.[92]

Vinyl Chloride: RDRP of vinyl chloride (VC) has been a notable challenge to polymer chemistry, because the relatively stable gem-dihalide end groups have proven inert to most RDRP conditions.[93] The development of Cu(0)/tris(2-aminoethyl)amine (TREN)/$CuBr_2$ catalyzed RDRP of VC initiated with $CHBr_3$ in DMSO at 25 °C was reported by Percec *et al.*.[9, 94] The use of $CuBr_2$ additive allows for the first RDRP of controlled molecular weight of VC, low Cu(0) powder loading and improved I_{eff} with targeted degree of polymerization (DP) of 1,400. Without $CuBr_2$, RDRP of VC in DMSO was optimized by increasing the amount of TREN under these optimized conditions, target DP of 350 was achieved within 360 minutes producing PVC with $M_{n,\text{SEC}}$ = 25,900 g/mol (conversion = 86%, $M_w/M_n = 1.53$). Additionally, it is shown that Cu(0) wire can also be used as a simpler and more easily removed and recycled catalyst for the polymerization of VC at 25 °C.

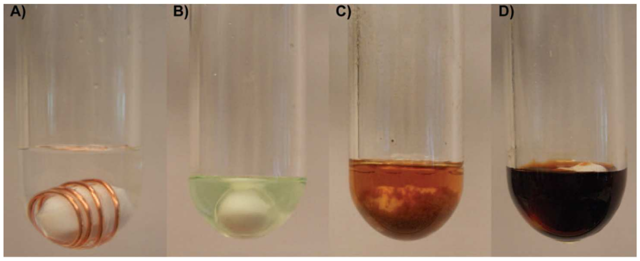
***N*-vinylcarbazole:** Carbazole-related polymers have attracted many attentions for their useful physical properties. For example, *N*-vinylcarbazole (NVC) based polymer is the first and most widely studied polymeric photoconductor, which has been polymerized successfully by cationic or free radical polymerization at higher temperature. The first report on the polymerization of carbazole-based monomers *via* zero-valent metal-mediated RDRP was reported by Haridharan *et al.*.[95] The ambient-temperature polymerization of NVC *via* Cu(0)/PMDETA-mediated RDRP method was possible in the presence or absence of CTA with $M_w/M_n < 1.25$, however the rate of polymerization was very slow. In the case of carbazole methacrylate (CMA), well-controlled polymerization with narrow molecular weight distribution ($M_w/M_n = 1.21{\sim}1.32$) was achieved in the presence of CTA, with moderate conversions.[66] Zero-valent metal-mediated RDRP method is a useful and simple tool for the synthesis of carbazole-based methacrylate polymers, although it gave poorer conversion compared with zero-valent metal-mediated RDRP of other common monomers. This may be attributed to the presence of CTA, which not only enables control but also decrease the polymerization rate.

2.2 Catalyst System

Cu(0) Powder & Wire: Cu(0)-mediated RDRP is significantly faster than other metal-catalyzed RDRP processes. A typical zero-valent metal-mediated RDRP of MA in DMSO at 25 °C ($[\text{MA}]_0/[\text{MBP}]_0/[\text{Cu(0)}]_0/[\text{Me}_6\text{TREN}]_0$ = 222/1/0.1/0.1) can achieve complete conversion within 50 min with approximate M_n of 20,000.[9] Cu(0) powder with Me_6TREN, PMDETA, TREN or bpy has been used in the zero-valent metal-mediated RDRP of MA, EA, BA, MMA, AN or VC initiated with chloro-, bromo-, or iodo-containing compounds.[9, 10, 55, 96-99] The catalytic activity depends on the structure of ligand used. The general order follows the following order: tetradentate (cyclic-bridged) > tetradentate (branched) > tetradentate (cyclic) > tridentate > tetradentate (linear) > bidentate ligands. The nature of N atoms is also important and follows the order pyridine ≥ aliphatic amine > imine. Ethylene is a better linkage for N atoms in the ligand than propylene.[100] A series of RAFT chain transfer agents can be efficiently synthesized by an one-step atom transfer radical addition-fragmentation (ATRAF) technique in the presence of Cu(0) powder.[101]

Effect of Cu(0) particle size on the kinetics of zero-valent metal-mediated RDRP in DMSO at 25 °C was also investigated by Percec *et al*., using Cu(0)/Me_6TREN catalyzed polymerization of MA initiated with MBP.[54] Decreasing the Cu(0) particle size results in a marked increase in the apparent rate constant of propagation (k_p^{app}). For example, decreasing the Cu(0) particle size from 425 nm to 50 nm increases the k_p^{app} by almost an order of magnitude. Regardless of the Cu(0) particle size used, an almost perfect zero-valent metal-mediated RDRP occurs with a first-order polymerization in growing species up to 100% conversion in DMSO; however, it should be noted that a relatively lower end-group functionality should be resulted from the faster polymerization.

The combined advantages of easier catalyst preparation, handling, uniformity, and simple recovery/recycling make Cu(0)-wire catalyzed RDRP to be an ideal RDRP methodology (Scheme 6). RDRP in the presence of Cu(0) wire demonstrated a RDRP with greater perfection, allowing for accurate determination of the external rate order for heterogeneous Cu(0) catalyst and accurate prediction of k_p^{app} from wire dimension. Cu(0) wire also exhibited a significantly greater control of molecular weight distribution than Cu(0) powder (Scheme 6).[9, 102-105] Cu(0) wire could also be used as a supplemental activator and reducing agent to accurately quantify the kinetics of the RDRP process.[47, 49-51] High-molecular-weight (co)polymers can be formed using ARGET ATRP with alkyl pseudohalide simultaneously as initiator and chain transfer agent, where Cu(0) wire can be used as reducing agent for several times without additional treatment.[106]



Scheme 6. Cu(0) wire mediated RDRP (Reprinted with permission from {Brad M. Rosen and Virgil Percec. *Chem. Rev.*, 2009, **109**, 5069-5119.}. Copyright {2009} American Chemical Society.)[10]

Copper Tubular Reactor: The use of copper tubing as both the reactor and as a catalyst source is demonstrated for continuous RDRP of MA at ambient temperature and at low solvent content of 30%.[75] The polymerizations proceeded quickly, reaching 67% conversion at a residence time. Lower ligand levels could be used without a precipitous decrease in reaction rate, offering the potential to balance the increased reactor volume (residence time) required with decreased raw material and post process purification costs. [107]

***In Situ* Cu(0):** RDRP was catalyzed by *in situ* Cu(0) generated from copper sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) and hydrazine hydrate ($N_2H_4{\cdot}H_2O$) at 25 °C. The polymerization occurred smoothly with moderate controllability: the polymerization rates increased by the increases of $N_2H_4{\cdot}H_2O$, and the initiator concentration had an optimal value on the polymerization rate; $M_{n,SEC}$ increased with monomer conversions and M_w/M_n were below 1.40. The $M_{n,SEC}$ deviated much from theoretical ones with about 50% polymer chain-end fidelities.[108] *In situ*-Cu(0) mediated RDRP of hydrophilic monomers were also exploited with full disproportionation of CuBr/Me_6TREN to Cu(0) powder and $CuBr_2$ in water prior to addition of both monomer and initiator.[71] *In situ* Cu(0)-mediated RDRP of MMA initiated with Ni(0)/EBiB/$CuBr_2$/PMDETA system exhibited almost optimal "living"/controlled nature and generated polymers with polydispersity index as low as 1.04 for 75.3% conversion and controlled molecular weights close to theoretical ones.[109] Also, a successful example of RDRP with $CuSO_4{\cdot}5H_2O$ as catalyst was reported in the presence of Fe(0) or ascorbic acid as reducing agent. $CuSO_4{\cdot}5H_2O$ produced a more controllable polymerization compared with the widely used $CuBr_2$.[110]

Other Zero-valent Metals: In 1999, Sawamoto *et al.* demonstrated a successful RDRP of methyl methacrylate (MMA) catalyzed with Ni(0)/PPh_3 using organic bromide as initiator in presence of Al(O*i*-Pr)$_3$ for the first time.[111] In our work, Fe(0) powder was used to catalyze the polymerization of MMA in the presence of RAFT agent, CPDN. Chen *et al.* synthesized PAN by RDRP using Fe(0) as catalyst and its desorption properties of Hg^{2+} was investigated after modified with $NH_2OH{\cdot}HCl$.[105] They also successfully reported a continuous RDRP of AN with iron tube as catalyst source without any ligand in *N*-methyl-2-pyrrolidone (NMP) and DMF.[112] Recently, the feasibility of Fe(0) powder-mediated polymerization of MMA and St with the addition of $CuBr_2$ as deactivator was investigated by our group at 25 °C, in which Fe(0) played a dual role of the activator for generation of active radical and the reducing agent for $CuBr_2$.[113, 114] Fe(0) (powder or wire) was demonstrated to remove/modify the thiocarbonylthio end group of the RAFT-made polymers.[115] Matyjaszewski and co-workers reported the zero-valent metal wire (zinc, magnesium, and iron) combined with $CuBr_2$-mediated polymerization of MA in DMSO at 25 °C.[37] Chen *et al.* also have dedicated to research a series of other zero-valent metal catalyzed RDRPs. For example, RDRPs of MMA with ytterbium powder (Yb(0))[116] and gadolinium powder (Gd(0))[117] as catalyst, respectively, and RDRPs of AN catalyzed with samarium powder (Sm(0)),[92] tin powder (Sn(0)),[118] lanthanum powder (La(0)),[119, 120] magnesium powder (Mg(0))[121] and so on. These all played a crucial role on the extension of RDRP applications.

2.3 Initiators

As with all metal-catalyzed RDRP processes, the appropriate choice of initiator is critical. A variety of monofunctional initiators, bifunctional initiators, multifunctional initiators, and macroinitiators have been used in zero-valent metal-mediated RDRP, like ATRP. Commonly, the leaving group is more or less exclusively a halogen in zero-valent metal-mediated RDRP, and thereby halogen compounds (R-X, X = halogen) are widely employed as initiators. Obviously, chlorine (Cl), bromine (Br), and iodine (I) are active as the halogen, while fluorine (F) is inactive for metal-catalyzed RDRP. The component R should contain some radical-stabilizing groups to facilitate radical generation, such as ester [-C(=O)OR], ketone [-C(=O)R], amide [-C(=O)NR_2], cyano (-C≡N), phenyl (-Ar), *etc.*.

***α*-Haloesters:** The most typical initiator for the polymerization of monofunctional acrylates is MBP, which has also been used as an initiator in the Cu(0)/Me_6TREN catalyzed RDRP of MA in DMSO.[9] Cu(0)-mediated RDRP of MMA initiated with the alkyl chlorides, methyl-2-chloropropionate (MCP) and catalyzed by Cu(0)/Me_6TREN/$CuCl_2$ in DMSO at 25 °C.[122] EBiB has been used in the Cu(0)/bpy catalyzed RDRP of MMA in DMSO[9] and the Cu(0)/PMDETA catalyzed RDRP of MMA in HFIP.[78] With EBiB as initiator, comproportionation was achieved in the initiation step of Cu(0)-mediated RDRP.[123] Additionally, alkyl 2-bromo-2-phenylacetates, a kind of initiator with synergistic phenyl and ester groups, such as ethyl 2-bromo-2-phenylacetate (EBPA), was ever reported as an effective initiator in metal-catalyzed RDRP of MMA.[124, 125] Recently, ligand-free Cu(0)-mediated polymerization of MMA by the selection of EBPA as initiator was realized.[74] The higher activation rate constants (k_{act}) of EBPA made the good control over polymerization even without any ligand. 2,2-Dichloroacetophenone (DCAP) was reported as an alternative effective initiator for the Cu(0)/PMDETA catalyzed RDRP of MMA in DMSO or HFIP at 25 °C in our group.[78]

Haloforms & Carbon Tetrachloride: Haloforms as initiators for Cu(0)-mediated RDRP can undergo subsequent functionalization to provide strategies for the synthesis of different block copolymers and other complex architectures. The haloforms of $CHCl_3$,[9, 122] $CHBr_3$,[9, 126] and CHI_3[9, 126] have been employed as initiators for the zero-valent metal-mediated RDRP of MA in DMSO at 25 °C. Among them, $CHCl_3$ and $CHBr_3$ are monofunctional initiators, however, CHI_3 is monofunctional initiator for PMA at low conversion but transitions to a bifunctional initiator at high conversion. $CHBr_3$ has also been demonstrated as an effective initiator for the zero-valent metal-mediated RDRP of VC in DMSO at 25 °C by Percec *et al.*.[9, 14] Using the inexpensive and readily available CCl_4 as initiator, the RDRP process was evaluated for the Cu(0) wire catalyzed polymerization of MMA, although the reaction time could be driven to completion in 10 h at 25 °C.[127] Chen *et al.* also reported some other zero-valent metal (such as Yb(0),[116] Sn(0),[118] La(0)[119, 120]) catalyzed RDRPs of MMA or AN with CCl_4 as initiator.

α-Halonitriles: α-Halonitriles are fast radical generators in metal-catalyzed RDRP, due to the presence of the strong electron-withdrawing cyano group. Moreover, the radical formed after halogen abstraction is sufficiently reactive, which leads to fast initiation through rapid radical addition to monomer. BPN resulted in polymers with the lowest polydispersities, is an effective initiator for the Cu(0)-mediated MA or AN in DMSO at 25 °C.[90] It was subsequently determined that an iodine-based initiator, 2-iodo-2-methylpropionitrile (CPI) was also effective initiator for the Cu(0)-mediated polymerization of MMA in the absence of ligand with DMSO as solvent.

Sulfonyl Halides: TsCl has been demonstrated to be an excellent radical initiator for the process of Cu(0)-mediated RDRP of MMA at 50 °C.[128] The first order kinetic dependency of the polymerization was preserved up to complete conversion. Polymerizations in MeOH could be significantly enhanced by the addition of small amounts of water. The molecular weights increased linearly with conversion and very narrow molecular weight distributions were obtained. In addition, phenoxybenzene-4,4'-disulfonyl chloride (PDSC) was used as an bifunctional initiator in conjunction with Cu(0)/bpy catalyzed RDRP of MMA at 25 °C in NMP.[9]

2.4. Solvents

DMSO: DMSO is one of most commonly used solvents for in ATRP and zero-valent metal-mediated RDRP, for its advantages of promoting the reaction. DMSO has a particularly high freezing point (18 °C), which is conducive to the freeze-pump-thaw process. DMSO enhances the polarity of the reaction system, thereby contributing to the electron transfer during the activation of alkyl halides by Cu(0).[9, 129-132] Matyjaszewski *et al.* evaluated the solvent effects with a thermodynamic scheme representing the ATRP equilibrium as the sum of an equilibrium involving carbon-halogen homolysis and three thermodynamic contributions related to the catalyst: the reduction/oxidation of (i) the metal complex and (ii) the halogen atom and (iii) the affinity of the higher oxidation state of the catalyst for halide anions (or "halidophilicity").[132] The experimental data agreed with the thermodynamic calculations, and DMSO is found to have greater ATRP equilibrium constant than acetone under identical conditions.[132]

DMF: It has been demonstrated that zero-valent metal-mediated RDRP can be performed effectively in a variety of solvents including DMF, NMP, propylene carbonate (PC), ethylene carbonate (EC), and dimethylacetamide (DMAC).[58] Addition of 5-10% H_2O to these solvents resulted in a linear enhancement of k_p^{app} and often a modest improvement in the molecular weight distribution. Interestingly, it was shown that DMF/H_2O mixture could be used as solvent for the zero-valent metal-mediated RDRP of hydrophilic monomers, such as NIPAM, PEGMEA and 2-EHA.[61] PAN have a good solubility in DMF, which make DMF a preferred solvent for zero-valent metal mediated RDRP of AN. Using DMF, RDRP of AN can be catalyzed by Cu(0) powder or Cu(0) wire.[89-92, 133]

Alcohols & Water: Alcohols including methanol, ethanol, 1-propanol, *tert*-butanol and methoxyethanol have been shown to be effective solvents for the Cu(0)/Me_6TREN catalyzed RDRP of MA at 25 °C.[9, 58, 134] The discovery of ethyl acetate-MeOH mixtures as effective solvents for Cu(0)-mediated RDRP is of particular interest for large-scale applications due to the low cost of ethyl acetate, as well as its distinct solubility profile as compared to the typical RDRP solvents.[135] Additionally, HFIP is a suitable solvent for the extremely rapid zero-valent metal-mediated RDRP of MMA[78] and AN[92] at very low temperature, providing dual control of molecular weight distribution and the polymer tacticity. Recently, Percec *et al.* reported the Cu(0)-mediated RDRP of a range of hydrophobic and hydrophilic acrylates, including MA, *n*BA, *t*BA, EHA and HEA using MBP and EBiB as initiators, Me_6TREN as ligand and 2,2,2-trifluoroethanol (TFE) as an efficient solvent.[136] Water is an environmentally friendly reaction medium. The apparent rate constant of the polymerization mediated by Cu(0) exhibits a linear increase with the addition of H_2O. According to Percec's theory, H_2O exhibits the highest equilibrium constant for disproportionation of Cu(I)X. Therefore, higher equilibrium constants for disproportionation generated by addition of H_2O to organic solvents (DMSO, DMF, DMAC, EC, PC, EtOH, MeOH, methoxyethanol, NMP, acetone) are found.[58] However, it was predicted by Kamlet-Taft relationship that H_2O had high ATRP equilibrium constant (K_{ATRP}, $\log K_{ATRP} \approx -4$).[132] This result can be also used to explain the rate enhancement by the addition of H_2O into organic solvent.[132] Cu(0)-mediated RDRP of MEA was achieved in H_2O catalyzed by sodium dithionate, which was first reported dealing with the synthesis of PMEA by RDRP approach in aqueous medium.[137] In aqueous, synthesis of zwitterionic polymer was achieved at 25 °C using 2-chloropropionamide as initiator and Cu(0) powder/Me_6TREN as catalyst system at room temperature.[67] Recently, Haddleton *et al.* gave an interesting work, which NIPAM was polymerized in a range of international beers, wine, ciders or spirits utilizing Cu(0)-mediated RDRP.[138]

Non-polar Solvent: Perrier *et al.* demonstrated the formation of well-defined PMMA homopolymer and block architectures *via* Cu(0)-mediated RDRP in toluene at 30 °C. Un-reacted Cu(0) in toluene is easily removed by filtration, centrifugation or sedimentation, which is likely to result in even lower copper concentrations. It provides a facile low-temperature route to the preparation of well-controlled poly(methacrylate)s using significantly less copper.[139] Then, Harrisson *et al*. have demonstrated that it is possible to control the polymerization of MA by using elemental copper and a conventional ATRP ligand/initiator at room temperature in a nonpolar solvent. It provides high chain end fidelity, as the polymers generated can be chain extended with 99% efficiency.[140]

Ionic Liquids: Ionic liquids are organic salts with melting point at or near room temperature. They have been extensively studied even as the solvent for polymerization processes because of their nonvolatility, high stability, high ion conductivity, and wide electrochemical activity. Using the ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) as solvent, a rapid Cu(0)/bpy catalyzed RDRP of MMA initiated by PDSC at 70 ^{o}C was reported.[73] All polymerization in $BMIMPF_6$ showed excellent predictability of molecular weight evolution and distribution ($M_w/M_n \approx 1.11\text{-}1.26$).

Acetic Acid: Percec *et al*. investigated the influence of acidity on Cu(0)-mediated RDRP of MMA in protic and dipolar aprotic solvents. It demonstrated that Cu(0)-mediated RDRP tolerated the addition of acetic acid to very high levels and preserves good control over the polymerization process, which sheds new light on the Cu(0)-mediated RDRP under acidic conditions.[141]

3. Toward Precise Control *via* Zero-Valent Metal Mediated RDRP

Some distinguishing characteristics and intrinsic advantages in normal RDRP, such as ATRP and RAFT, are also inherited by zero-valent metal mediated RDRP. Despite of vast developments of zero-valent metal catalyzed RDRP technique, the pursuits of precise control over macromolecular structure, including chain end functionality, tacticity and compatibility with other RDRP techniques, never stop. Also, the utilization of zero valent metal as catalyst can bring some intrinsic advantages arising from variable metal physical form and polymerization behavior.

3.1. Good Retention of Chain-end Functionality

In RDRPs, complete elimination of side reactions is difficult, and it gets more severe for polymerization with lower concentration of initiator or at high monomer conversions in polymerization. However, the good retention of chain-end functionality is necessary to achieve high molecular-weight polymers and allows for the synthesis of macroinitiators for block-copolymerization. The reaction temperature plays an important role in RDRPs. On one hand, the higher temperatures may improve the ratio of propagation to termination rate coefficients which favorables a high chain end functionality; On the other hand, lowering temperature would be useful for suppression of undesirable side reactions, such as backbiting in acrylates. Therefore, the temperature should be appropriately selected by balancing the above two concerns. The synthesis of a polymer with high chain-end functionality is very important for a successful zero-valent metal-mediated RDRP.[51, 142, 143] From these initial reports, a series of in-depth NMR, MALDI-TOF, and chain extension studies confirmed the high chain-end functionality.[9, 126, 144] And the polymers as macro-initiators from zero-valent metal-mediated RDRP can be used as chain extension reaction.[65] Improving initiation efficiency in the polymerization process can improve the chain-end functionality.[145] However, it should be noted that the formation of $Cu(II)X_2$/ligand complexes should inevitably lead to loss of halogen-end group functionality based on the mass balance relationship.[146] And, an increase of the generated $CuBr_2$/ligand complexes during polymerization process has been experimentally observed in literatures.[51, 97]

3.2. Simultaneous Control of Molecular Weight and Tacticity

The multiple controls of primary structures, such as molecular weight, stereochemistry, and monomer sequence, in synthetic polymers must lead to developments of more sophisticated functional polymers that would rival natural macromolecules with the uniform molecular weight, stereoregularity, and regulated monomer sequence. Recent years have witnessed a large number of novel RDRPs or catalysts that can precisely control either the molecular weight or the tacticity, and sometimes both of them, during various types of polymerizations.[147] Using low polymerization temperature, zero-valent metal-mediated RDRP may be quite proper and effective methods for the simultaneous control of the molecular weights and the tacticity for various types of monomers.

The controllability of molecular weight and tacticity of PMMA with Cu(0)/PMDETA as a catalyst system in a fluoroalcohol, HFIP as solvent was first achieved by our group.[78] Higher concentration of HFIP and lower reaction temperature produced higher syndiotactic ratio. Using HFIP as solvent, Chen *et al*. reported the Sm(0) powder catalyzed RDRP of AN with *N,N,N',N'*-tetramethylethylenediamine (TEMED) as ligand and BPN as initiator for simultaneous control of the molecular weights and the tacticity at 35 ^{o}C.[133] First-order kinetics of polymerization with respect to the monomer concentration, linear increase of the molecular weight with monomer conversion, and the highly syndiotactic PAN obtained indicated that the molecular weights and tacticity of PAN could be simultaneously controlled via zero-valent metal-mediated RDRP.

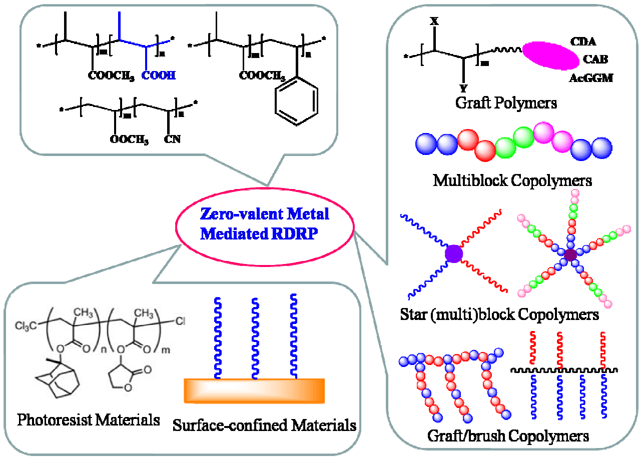
Recently, we illustrated a simultaneous control over molecular weight and tacticity of P4VP via a well-chosen RDRP technique and hydrogen bonding interaction. The optimal conditions for the hydrogen bonding interaction between 4VP and HFIP were screened *via* UV-vis spectroscopy. The results demonstrated that equimolar 4VP and HFIP and temperature at 25 ^{o}C favored a better hydrogen bonding interaction.[81] Guided by these primary results, the room-temperature Cu(0)-mediated RDRP was selected for the controlled polymerization of 4VP in the presence of equiv. HFIP. The polymerizations produced polymers with more predictable number-average molecular weights ($M_{n,SEC}$) and narrower molecular weight distributions ($M_w/M_n < 1.25$) in comparison with those without hydrogen bonding interaction. Moreover, the hydrogen bonding had profound impacts on the stereoregulation during polymerization, which enabled P4VP with a highly syndiotactic (60.2%) and gave rise to a higher glass transition temperature (T_g) of P4VP.[81, 82]

3.3. Compatibility with Other RDRP Techniques

Because the catalyst system in zero-valent metal-mediated RDRP can also be used as catalyst in "Click" Chemistry, zero-valent metal-mediated RDRP and "Click" Chemistry can take place at the same time in the same reaction system. This method provides a simple way to generate two different polymer chains at the same backbone. A clickable alkyne monomer, propargyl methacrylate (PgMA), was successfully polymerized in a well-controlled manner *via* single electron transfer initiation and propagation using EBiB/CTA/Cu(0)/PMDETA by our group.[148] The living nature of the polymerization was confirmed by the first-order kinetic plots, the linear relationships between molecular weights and the monomer conversions while keeping relatively narrow molecular weight distributions ($M_w/M_n \sim 1.55$), and the successful chain-extension with MMA. Moreover, a one-pot/one-step technique has been successfully employed to prepare the side-chain functionalized polymers. PSt-*b*-PEO-*b*-P*t*BA triblock copolymers were successfully synthesized *via* combination of zero-valent metal-mediated RDRP and "click" chemistry using Cu(0)/PMDETA as catalyst system by one-pot strategy.[149] Zero-valent metal-mediated RDRP has been successfully employed for the synthesis of tunable thermoresponsive protein–polymer conjugates *via* a combination of nucleophilic thiol–ene "click".[150] Discrete oligo(ethylene glycol) methacrylates were polymerized directly from a salmon calcitonin macroinitiator, readily synthesized in a one-pot protocol utilizing thiol–ene chemistry to yield well-defined conjugates. It should be noted that most of these structures have also been successfully produced by classical ATRP.[15]

Recently, the combination of zero-valent metal-mediated RDRP and nitroxide radical coupling reaction at ambient temperature was developed by Huang *et al.*, where the macroradicals generated by zero-valent metal-mediated RDRP mechanism are trapped by nitroxide radicals. This reaction is an alternative effective approach for coupling reaction under ambient conditions, which can be applicable to a variety of halogen-containing polymers, including PSt, PMA and PMMA with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) containing polymers. In addition, the room temperature inhibits side reactions such as thermal crosslinking, chain transfer and the β-H transfer of poly(methacrylate ester) macroradicals.[151] Moreover, the synthesis of ABC triblock copolymers were accomplished by Cu(0)-catalyzed one-pot strategy combining this reaction with "Click" chemistry.[152] First, the precursors, α,ω-heterofunctionalized poly(ethylene oxide) (PEO) with a TEMPO group and an alkyne group, PSt and P*t*BA with bromine or azide end group were designed and synthesized, respectively. Then, the one-pot coupling reactions between these precursors were carried out in the Cu(0)/Me$_6$TREN catalyzed system. The reaction between bromine group and nitroxide radical group with the simultaneous click coupling between azide and alkyne group produced ABC triblock copolymers. It was noticeable that Cu(I) generated from Cu(0) by zero-valent metal-mediated RDRP mechanism was utilized to catalyze click chemistry. To estimate the effect of Cu(0) on the one-pot reaction, a comparative analysis was performed in presence of different Cu(0) species. The result showed that Cu(0) with more active surface area could accelerate the one-pot reaction significantly. Our group also describes a facile removal/modification of thiocarbonylthio end groups of RAFT-made polymers by the utilization of Cu(0) powder/TEMPO under mild conditions, especially for PMMA. The utilization of Cu(0) wire can also remove the thiocarbonylthio end group effectively. Fe(0) (powder or wire) can be applied to remove/modify the thiocarbonylthio end group instead of Cu(0)/ligand with comparable results. This work provided an alternative and promising approach for an adjustable end group removal/modification of RAFT polymers, and would eventually strengthen and facilitate the potential large-scale application of RAFT-related polymers.[115]

4. Functional Polymers Prepared by Zero-Valent Metal Catalyzed RDRP



Scheme 7. Functional polymers designed by zero-valent metal mediated RDRP.

4.1 Controlled Copolymerization and Functional Copolymer *via* Zero-Valent Metal Catalyzed RDRP

Zero-valent metal mediated RDRP has developed as a reliable, robust and straightforward method for the construction well-defined copolymers. Percec *et al.* investigated the copolymerization of MMA and methacrylic acid (MAA) by zero-valent metal as catalyst. The kinetic plots of the polymerization for various MAA content were recorded and evaluated to estimate the copolymerization of MAA in MeOH/H$_2$O.[153] Our group investigated the copolymerization of MMA and St catalyzed by Cu(0) at room temperature. The reactivity ratios of MMA and St were calculated and compared with the systems mediated by other RDRP methods.[86] The Cu(0)-mediated RDRP of vinyl acetate (VAc) and AN at 25 °C proceeded smoothly in DMSO. The polymerization conveyed moderately controlled features at low VAc feed ratios. The reactivity ratios of VAc and AN in the system were found to be 0.003 and 1.605, respectively. It provided the copolymerization of AN and VAc, wherein VAc was an unavailable monomer for the Cu(0)-mediated RDRP.[88]

Native cellulose, with soluble esters or ethers in selected organic solvents, can be relatively easy to functionalize with various haloacyl groups, giving rise to polyfunctional macroinitiators. Vlcek *et al.* gave the first example of application of Cu(0)-mediated RDRP process to a controlled grafting of cellulose esters, cellulose diacetate (CDA), and cellulose acetate butyrate (CAB).[154] Chloro and bromo-functionalized macroinitiators were successfully prepared from the softwood hemicelluloses *O*-acetylated galactoglucomannan *via* Cu(0)-mediated RDRP.[155] A multifunctional macroinitiator for Cu(0)-mediated RDRP was designed from acetylated galactoglucomannan by α-bromoisobutyric acid functionalization of the anomeric hydroxyl groups on the heteropolysaccharide backbone.[156]

Whittaker *et al*. reported a new approach for the facile synthesis of high-order multiblock copolymers. The approach entailed sequential addition of different monomers *via* an iterative Cu(0)-mediated RDRP technique, allowing nearly perfect control over the copolymer microstructure. It is possible to synthesize high-order multiblock copolymers with unprecedented control, *i.e.*, P(MA-*b*-*n*BA-*b*-EA-*b*-2EHA-*b*-EA-*b*-*n*BA) copolymer, without any purification between iterative 24 h block formation steps.[157] Cu(0)-mediated RDRP was also successfully used to produce well-defined linear and star homo- and diblock-copolymers of poly(methyl acrylate-*b*-solketal acrylate) (PMA-*b*-PSA), and poly(methyl acrylate-*b*-glycolic acid) (P(MA-*b*-GA)$_n$) (where n = 1 or 4). Such vesicle structures have potential applications as delivery nanoscaled devices for drugs and other important biomolecules. Novel AB$_2$-type amphiphilic block copolymers of poly(ethylene glycol) (PEG) and PNIPAM, PEG-*b*-(PNIPAM)$_2$ were successfully synthesized through Cu(0)-mediated RDRP using a difunctional macroinitiator. The differential scanning calorimetry (DSC) measurement of PEG-*b*-(PNIPAM)$_2$ indicates the significant influence of the block copolymer molecular architecture on the phase transition.[158] Huang *et al*. have presented the synthesis of well-defined amphiphilic grafting copolymers containing poly(*N*-isopropylacrylamide)-*b*-poly(ethyl acrylate) (PNIPAM-*b*-PEA) backbone and hydrophobic poly(2-acryloyloxyethyl ferrocenecarboxylate) (PAEFC) side chains *via* the combination of Cu(0)-mediated RDRP and ATRP.[159] Triblock copolymers of polystyrene-*block*-poly(ethylene oxide)-*block*-poly(tert-butyl acrylate) (PSt-*b*-PEO-*b*-P*t*BA) were prepared via combination of Cu(0)-mediated RDRP with "click" chemistry using Cu(0)/PMDETA as the catalyst system, wherein the Cu(I) generated *in situ* was utilized directly to catalyze "click" chemistry.[149]

Meanwhile, Cu(0)-mediated RDRP was found to be promising for achieving comparable polymer layer thicknesses at lower reaction temperatures and shorter reaction times. The pH-responsive amphiphilic A$_2$B$_2$ miktoarm star block copolymer, poly(acrylic acid)$_2$-poly(vinyl acetate)$_2$ [(PAA)$_2$(PVAc)$_2$], with controlled molecular weight and well-defined structure was successfully synthesized *via* combination of Cu(0)-mediated RDRP and RAFT polymerization methods by our group.[160] The obtained well-defined miktoarm star block copolymer was further used to prepare the pH-responsive amphiphilic A$_2$B$_2$ miktoarm star block copolymers, which can self-assemble into spherical micelles possessing PVAc core and PAA shells; Recently, well-defined multi-block star copolymers *via* Cu(0)-mediated RDRP has been reported.[161] The technique involves a core first approach using a multi-functional initiator in connection with iterative Cu(0)-mediated RDRP steps. Noteworthy, the tedious purification is not required between the successive chain extension steps since complete monomer conversion can be achieved before the addition of each consecutive monomer type.[161]

Well-defined grafting copolymers poly[poly(ethylene glycol) methyl ether acrylate]-*g*-poly[poly(ethylene glycol) ethyl ether methacrylate] (PPEGMEA-*g*-PPEGEEMA) comprising two different hydrophilic side chains were synthesized *via* the combination of Cu(0)-mediated RDRP, ATRP, and the grafting-from strategy. The molecular weights of the backbone and the side chains were both controllable, and the molecular weight distributions were between 1.15 and 1.20.[162] A series of well-defined double hydrophilic graft copolymers, consisting of (PNIPAM-*b*-PEA) backbone and poly(2-vinylpyridine) side chains (PNIPAM-*b*-(PEA-*g*-P2VP)), were synthesized by successive Cu(0)-mediated RDRP and ATRP at 25 ^{o}C. Unimolecular micelles with PNIPAM-core formed in acidic environment (pH = 2) with elevated temperature (T > 32 ^{o}C), whereas the aggregates turned into spheres with PEA-*g*-P2VP-core accompanied with the lifting of pH values (pH > 5.3) at room temperature.[163] A versatile zero-valent metal-mediated RDRP process was developed and successfully used for the preparation of a series of hemicellulose-based graft-copolymers with tunable hydrophilicity. Acetylated galactoglucomannan (AcGGM) as a macroinitiator can be grafted in MMA, NIPAM and acrylamide (AcAm), respectively.[164] The cellulose nanocrystals (CNCs) were grafted with PNIPAM brushes *via* surface-initiated RDRP under various conditions at room temperature. It is expected that the suspension stability, interfacial interactions, friction, and other properties of grafted CNCs can be controlled by changes in temperature and can provide a unique platform for further development of stimuli-responsive nanomaterials.[165]

Amphiphilic heterograft copolymers poly(methyl methacrylate-*co*-2-(2-bromoisobutyryloxy)ethyl methacrylate)-graft-(poly(acrylic acid)/polystyrene) (P(MMA-*co*-BIEM)-*g*-(PAA/PSt)) were synthesized successfully by the combination of Cu(0)-mediated RDRP, Cu(0)-mediated RDRP-NRC, ATRP, and NMP *via* the "grafting from" approach. Self-assembly behaviors of the amphiphilic heterografting copolymers P(MMA-*co*-BIEM)-*g*-(PAA/PSt) in aqueous solution were investigated by atomic force microscopy (AFM) and dynamic light scattering (DLS), and the results demonstrated that the morphologies of the formed micelles were dependent on the grafting density.[166]

4.2 Dendrimers & Surface-Confined Zero-Valent Metal Catalyzed RDRPs

Dendrimers are monodisperse branched nonbiological macromolecules constructed *via* divergent or convergent synthesis that holds great promise for a variety of applications. In combination of terminal thio-bromo click reaction and acylation with 2-bromopropionyl bromide, Cu(0)-mediated RDRP of MA was shown to provide access to a three-step "branch" and "grow" divergent approach for preparing dendritic macromolecules wherein PMA connects the branching subunits.[62] This facile methodology can provide a diversity of dendritic macromolecular topologies and will ultimately provide the means to the development of self-organizable dendritic macromolecules. Moreover, four poly(amino (meth)acrylate) brushes, poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA), poly(2-(dimethylamino)ethyl acrylate) (PDMAEA), poly(2-(*tert*-butylamino)ethyl methacrylate) (PTBAEMA), has been synthesized *via* surface-confined RDRPs using surface-confined initiator from silane self-assembled monolayers (SAMs) on silicon wafer substrates by Walters *et al*..[167]

5. Conclusions

Zero-valent metal-mediated RDRP has been dramatically developed and becomes a robust and versatile synthetic technique for preparation of polymers with well-defined architecture and site specific functionality, such as stars, bottle brushes, block and gradient copolymers. Its intrinsic advantages by using zero-valent metal as catalyst can significantly simplify the polymerization procedure and facilitate for its potensial large-scale production.

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7. Notes and references

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