Transition Metal Catalysis in Controlled Radical Polymerization: Atom Transfer Radical Polymerization

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Abstract: This paper provides a brief survey of transition metal catalysis in controlled/„living“ radical polymerization with a special emphasis on copper-mediated atom transfer radical polymerization (ATRP). The scope and limitations of this technique are discussed, along with the most recent developments and future trends.

Keywords: catalysts · polymerizations · radical reactions · transition metals

Introduction

Radical polymerization is one of the most important methods for synthesizing polymers with nearly 50% of synthetic polymers prepared through radical processes.[1] The commercial success of radical polymerization has several origins. Firstly, a large number of monomers can undergo free radical polymerization; nearly all alkenes can be polymerized or copolymerized by a radical process. This is owing to the growing number of species that have a high tolerance of many functional groups, including acid, hydroxyl, and amino groups. Secondly, facile copolymerization can occur between various monomers. However, perhaps the most important is a convenient temperature range and very minimal requirements for purification of monomers, solvents, and so forth, which should only be deoxygenated. Radical polymerization can be carried out in bulk in solution, aqueous suspension, emulsion, dispersion, and so on.

There are, however, several limitations for a radical polymerization, especially in comparison with ionic processes. Anionic, and more recently also cationic, polymerization enables the preparation of well-defined polymers and copolymers with predetermined molecular weights and low polydispersities.[2–5] The main advantage of ionic reactions is the possibility of synthesizing segmented copolymers, such as block and graft copolymers, that microphase separate and can be used as thermoplastic elastomers, non-ionic surfactants, dispersants, lubricants, viscosity modifiers, special additives, and so on. These materials are prepared through so-called "living" polymerizations in which, after relatively fast initiation, chains only propagate and the contribution of chain-breaking reactions, such as transfer and termination, is negligible. Unfortunately, ionic polymerization is limited to a handful of monomers; it also requires very stringent drying, exclusion of moisture, and also very low temperatures ($< -70\,^{\circ}C$). On the other hand, until recently it was not possible to prepare the well-defined polymers and copolymers that were available from ionic reactions by radical methods. The main reason for this was the presence of unavoidable termination between growing radicals. In order to minimize the termination in conventional radicals systems, radicals are slowly and continuously generated by the thermal or photoinduced decomposition of suitable initiators such as peroxides or diazo compounds. This approach enables the synthesis of ill-defined high polymers, but not block copolymers. In recent years there has been a demand for the synthesis of the novel, well-defined materials available from ionic reactions but from techniques that require less stringent conditions. Radical polymerization is an obvious choice in this regard because of the facile reaction conditions and the large range of polymerizable monomers.

There are several approaches used to control radical polymerization and to suppress contribution of chain-breaking reactions together with assuring quantitative initiation.[6] All of them employ a dynamic equilibration between the propagating free radicals (with the rate constant of free radical propagation, k_p) and some kind of dormant species which is established through activation (k_a) and deactivation (k_d) steps. We prefer to classify these reactions as controlled radical polymerizations rather than living radical polymerizations because of the presence of unavoidable termination (k_t), which is inherently incompatible with the concept of living polymerization.[7, 8]

Currently three approaches seem to be the most successful for controlling radical polymerization:

1) Thermal homolytic cleavage of a weak bond in a covalent species that reversibly provides a growing radical and a less reactive radical (persistent or stable free radical, Scheme 1). There are several examples of persistent radicals but the most successful appear to be nitro-

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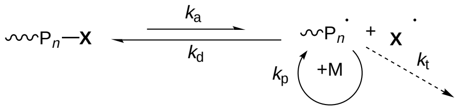
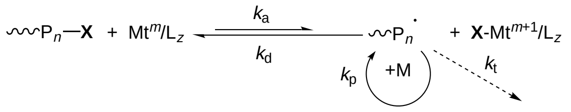


Scheme 1. Persistent or stable, free radical polymerization (M = monomer).

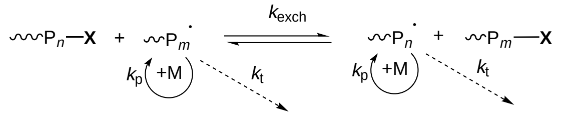
xides,[9–13] triazolinyl radicals,[14] some bulky organic radicals, e.g. trityl[15, 16], and organometallic species.[17]

2) Another approach is based on the catalyzed reversible cleavage of the covalent bond in the dormant species through a redox process (Scheme 2).[18, 19] The key step in controlling the polymerization is atom (or group) transfer between growing chains and a catalyst, and therefore was named atom transfer radical polymerization (ATRP).[19]



Scheme 2. Atom transfer radical polymerization (ATRP) (M = monomer, Mt = metal).

3) The third approach is based on a thermodynamically neutral exchange process between growing radicals present at very low concentrations and dormant species. This degenerative transfer process can employ alkyl iodides and also unsaturated methacrylate esters and thioesters.[20–22] The latter two processes operate by addition–fragmentation chemistry (Scheme 3).



Scheme 3. Polymerization by a thermodynamically neutral exchange process (M = monomer).

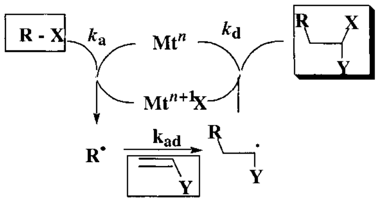
This Concepts article will summarize recent progress in ATRP, explain some fundamental steps involved in it, and also demonstrate some links to analogous processes in organic chemistry.

Discussion

Atom transfer radical addition (ATRA): The importance of radical reactions in organic synthesis is continuously increasing because of the tolerance of many functional groups exhibited by free radicals. It is possible to use radical processes in multistep cascade syntheses, which are based on the careful selection of reagents and make use of highly chemoselective and regioselective processes.[23, 24] The enhanced control relies on concepts of electrophilicity and nucleophilicity of organic radicals, and also on the persistent radical effect (PRE) in which the stationary concentration of reactive radicals is reduced and therefore minimizes the contribution of termination.[25] One of the most successful methods is the metal-catalyzed Kharasch addition[26] or atom transfer radical addition (ATRA),[23] so named because it employs atom transfer from an organic halide to a transition metal complex to generate the reactive radicals. This is followed by addition to the alkene, and then back transfer from the transition metal to a product radical to form the final product.

Abstract in Polish: *Przegląd ten jest poświęcony kontrolowanej polimeryzacji rodnikowej w obecności metali przejściowych, a w szczególności polimeryzacji rodnikowej z przeniesieniem atomu z udziałem związków miedzi. Przedyskutowany jest zakres i ograniczenia tej metody wraz z ostatnimi osiągnięciami i przyszłymi kierunkami rozwoju.*

In ATRA, a metal catalyst such as a copper(I) halide complexed by suitable ligands (although Ni, Pd, Ru, Fe, and other metals have been used as well) undergoes an inner sphere oxidation through abstraction of a halogen atom from a substrate (Scheme 4). This reaction generates a copper(II) complex and an organic radical. The radical may add to an alkene in an inter- or intramolecular fashion. It can also abstract the halogen atom from the copper(II) complex and return back to the original dormant organic halide species, or abstraction of the halogen may occur after addition to the alkene and thus form a desired product. The copper(I) complex is reformed, completing the catalytic cycle. The radical may also react with another radical, but because the steady-state concentration of radicals is very small, the contribution of termination is negligible. The substrates for ATRA should generate radicals much more easily than products and, therefore, should lead only to monoaddition.



Scheme 4. Atom transfer radical addition (M = monomer, Mt = metal).

From experimental evidence it is not fully clear whether the intermediate radicals are free radicals or coordinated to the metal center, but the most plausible mechanism based upon chemo-, regio-, and stereoselectivity suggests predominant involvement of free radicals. Nevertheless, the mechanism may change depending on the structure of metal compound, ligands, substrates, products, as well as solvents and temperature, and can include ionic intermediates, oxidative addition, organometallic species, or a simple transfer to the substrate without the catalyzed atom transfer step.

ATRA can be extended to atom transfer radical polymerization (ATRP) if the conditions can be modified such that more than one addition step occurs. Thus, if the radical species in Scheme 4 both before and after addition of the unsaturated substrate (monomer) possess comparable reactivity, then the activation–addition–deactivation cycle will repeat until all of monomer present is consumed. This process results in a chain-

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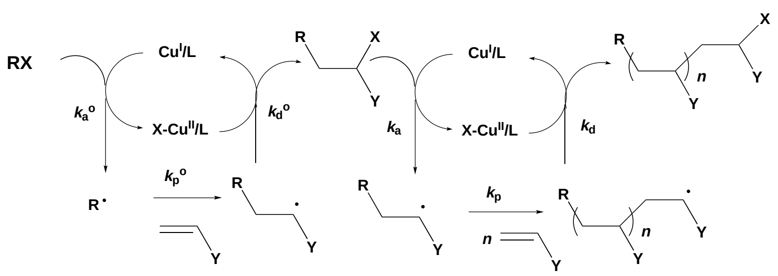


Scheme 5. Chain-growth polymerization.

growth polymerization (Scheme 5). However, not only one but several monomer molecules may add during one activation step. The precise number depends on the relative rates of propagation and deactivation and affects polydispersity of the obtained polymers.

Polymerization systems utilizing this concept have been developed with complexes of Cu, Ru, Ni, Pd, Rh and Fe to establish the ATRP equilibrium; however, the remainder of this survey will describe developments in copper-based ATRP.

Typical features of ATRP:[27] A successful ATRP process should meet several requirements:

1) It should consume the initiator at the early stages of polymerization and generate propagating chains leading to polymers with degrees of polymerization (DP) predetermined by the ratio of the concentrations of converted monomer (M) to the introduced initiator (I) ($\mathrm{DP} = \Delta[\mathrm{M}]/[\mathrm{I}]_o$).
2) The number of monomer molecules added during one activation step should be small, resulting in polymers with low polydispersities.
3) Finally, the contribution of chain-breaking reactions (transfer and termination) should be negligible so as to yield polymers with high degrees of end functionalities and allow the synthesis of block copolymers.

In order to reach these three goals, it is necessary to select appropriate reagents and appropriate reaction conditions. According to the general scheme of ATRP given above, the rate of polymerization can be derived, and is given by Equation (1).

$$R_p = k_p[\mathrm{M}][\mathrm{RX}]_o k_a[\mathrm{Cu^I}]/(k_d[\mathrm{X{-}Cu^{II}}]) \qquad (1)$$

Thus, the rate of polymerization should be internal first-order in monomer, external first-order with respect to initiator and activator, $\mathrm{Cu^I}$, and external negative first-order with respect to deactivator, $\mathrm{XCu^{II}}$.[27] However, the kinetics may be more complex owing to the formation of $\mathrm{XCu^{II}}$ species through PRE. Fractional orders with respect to the monomer and other components have been predicted for the idealized system with chain-length independent-termination rate coefficients.[28] The actual kinetics depends on many factors including the solubility of activator and deactivator, their possible interactions, and variations of their structures and reactivities with concentrations and composition of the reaction medium. It should be also noted that the contribution of PRE at the initial stages might be affected by the mixing method, crystallinity of the metal compound and ligand, and so forth.

One of the most important parameters in ATRP is the dynamics of exchange and, especially, the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional and uncontrolled radical polymerization. Polydispersities in ATRP are defined by Equation (2).

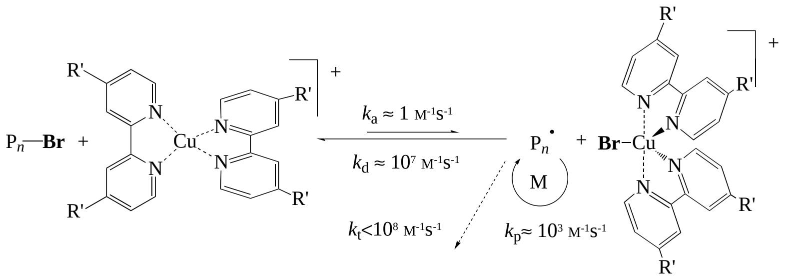
$$M_w/M_n = 1 + \{(k_p[\mathrm{RX}]_o)/(k_d[\mathrm{X{-}Cu^{II}}])\}(2/p - 1) \qquad (2)$$

Thus, polydispersities decrease with conversion (p), the rate constant of deactivation (k_d), and the concentration of deactivator ($[\mathrm{XCu^{II}}]$). However, they increase with the propagation rate constant (k_p) and the concentration of initiator ($[\mathrm{RX}]_o$). This means that more uniform polymers are obtained at higher conversions, when the concentration of deactivator in solution is high and the concentration of initiator is low.[29] Also, more uniform polymers are formed when the deactivator is very reactive (e.g., copper(II) complexed by 2,2′-bipyridine or pentamethyldiethylenetriamine rather than by water) and the monomer propagates slowly (styrene rather than acrylate).

Chain-breaking reactions do occur in controlled radical systems. Fortunately, at typical reaction temperatures the contribution of transfer is relatively small. For example, in polymerization of styrene, less than 10% of chains participate in transfer to monomer before reaching $M_n = 100\,000$. However, the contribution of transfer progressively increases with chain length, and therefore molecular weights must be limited by the appropriate ratio of monomer to initiator concentrations (for styrene $\Delta[\mathrm{M}]/[\mathrm{I}]_o < 1000$). Termination does occur in radical systems and currently can not be completely avoided. However, since termination is second-order with respect to radical concentration and propagation is first-order, the contribution of termination increases with radical concentration and, therefore, with the polymerization rate. Thus, most controlled radical polymerizations are designed to be slower than conventional systems. It is possible to generate relatively fast controlled radical polymerization, but only for the most reactive monomers, such as acrylates, and/or for relatively short chains. For short chains, the absolute concentration of terminated chains is still high, but their percentile in the total number of chains is small enough not to affect end functionalities and blocking efficiency. A typical proportion of terminated chains is between 1 and 10%; with the large domination of very short chains this may not markedly affect the properties of the synthesized polymers and copolymers. It is possible to measure the evolution of concentration of terminated chains by following the copper(II) species by

EPR.[30] Because termination rate coefficients decrease significantly with chain length and viscosity of the medium, the rate of termination also dramatically reduces; furthermore, the PRE also reduces this rate.

The radical nature of ATRP: A simplified picture of the ATRP equilibrium with a copper halide complex that contains two bipyridine ligands is shown in Scheme 6. Based on the X-ray structures of the corresponding isolated solids, the Cu^I cationic complex should have a slightly distorted tetrahedral coordination and Cu^{II} a trigonal bipyramidal coordination.[31]



Scheme 6. ATRP equilibrium with a copper halide complex that contains two bipyridine ligands.

However, this picture may not be fully correct in solution, especially in nonpolar solvents in which bridged species may participate.[32] The rate constants of the exchange process, propagation, and termination shown in Scheme 6 refer to styrene polymerization at 110 °C.[27, 33]

In analogy to ATRA, it is possible that not only free radicals but also other species may be involved in propagation. It was demonstrated that the ATRP mechanism operates in the polymerization of styrene and (meth)acrylates, catalyzed by copper halides complexed by 2,2′-bipyridine and the corresponding 4,4′-dialkyl substituted bipyridines.[34] This conclusion was reached based on several identical features of ATRP and conventional radical polymerizations. They include:

- chemoselectivity (reactivity ratios, effect of scavengers and additives selective for radical, ionic and organometallic reactions),[19, 35–39]
- regioselectivity (end groups, head-to-tail structures),[35]
- stereoselectivity (tacticity),[35]
- direct observation of radical coupling products (doubling of molecular weights, crosslinking for multifunctional systems, direct observation of copper(II) by EPR),[30]
- approaching the ATRP equilibria from the opposite site [e.g., azobisisobutyronitrile (AIBN) and XCu^{II} species], giving direct evidence that copper(II) deactivates growing radicals,[40–42]
- increasing rates and polydispersities by reducing concentration of copper(II), for example, by its lower solubility and by adding copper(0).[43]

Actually, none of these experiments prove unambiguously and unequivocally that a radical process operates. Nevertheless, when taken together they strongly indicated that the majority of monomer was consumed and that the polymer was predominantly formed by a free radical process.

Many features of copper-catalyzed atom transfer radical polymerization resemble closely those of other controlled radical systems, such as nitroxide-mediated processes,[12, 44] degenerative transfer[20] or those proceeding with organometallic intermediates.[17] Molecular weights increase linearly with conversion, polydispersities initially decrease with conversion, an excess of persistent radicals reduces polymerization rates, oxygen inhibits polymerization, and water generally does not affect polymerization. In addition, chemoselectivity (reactivity ratios and transfer coefficients), regioselectivity, and stereoselectivity (tacticity) are similar to those in conventional radical polymerizations. However, the presence of transition metals in the reaction requires very careful examination of the reactive intermediates and the mechanism of propagation.

It is possible that under certain conditions degenerative transfer and reversible formation of organometallic intermediates can supplement ATRP. It is also possible that ATRP may sometimes occur not by a concerted process with bridged intermediates but by two step process with the involvement of radical anions. For some monomers and some metal complexes, either oxidation or reduction of growing radicals to ionic species is possible and will usually induce loss of control owing to the high reaction temperature and the presence of adventitious water. However, it was found that although degenerative transfer operates with iodine, it does not with chlorine and bromine end groups. Also, a negligible effect of Cu(OTf) or $Cu(OTf)_2$ on rates and molecular weights in AIBN-initiated polymerization of styrene and acrylates suggests insignificant formation of organometallic intermediates.[45]

It is recommended that the involvement of radicals in metal-catalyzed polymerizations should always be tested using the above criteria, since even a small change in the monomer, ligand, temperature, or solvent may favor other reactions. For example, $Cu(PF_6)/4\,CH_3CN$ generates cationic polymerization of styrene,[46] analogously the CuBr/2 Bpy complex also yields a cationic polymerization of *p*-methoxystyrene,[47] whereas it generates carbanions from diethyl 2-bromomalonate.[32]

Recent developments in ATRP: There are three directions in the current development of ATRP. One is the preparation of various new materials;[48, 49] this will be briefly covered in the last section. The second one is the better understanding of the reaction mechanisms,[32] construction of the structure—reactivity correlation for monomers, alkyl halides and catalysts; these were discussed above. The third one is the continuous improvement of the catalytic systems, hopefully leading to better control, lower metal concentration, more selectivity, the expansion to new monomers, the use of environmentally friendly media such as water and carbon dioxide, and so on.

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Ligands and metals: The complexes of CuBr with bpy, originally adopted from organic chemists, were expanded to include alkyl-substituted bpy in order to increase solubility of catalysts and ensure fast deactivation. This resulted in the preparation of polymers with very low polydispersities, $M_w/M_n < 1.1$.[29] There are several similar approaches for other bidentate ligands such as pyridinimines[50] and phenanthrolines.[51] Another approach is to use multidentate ligands such as pentamethyldiethylenetriamine (PMDETA) and the corresponding permethylated tetramine.[52] PMDETA is an inexpensive ligand ($ 20/L), forms nearly colorless complexes with Cu^I, and also provides fast and efficient polymerization of styrene, acrylates, and methacrylates. The ATRP equilibrium is shifted towards the copper(II) species, possibily because the more electron-donating ligand complexes the stronger Lewis acid (cupric species) more efficiently. Even more efficient is the tripodal ligand tris(dimethylaminoethyl)-amine (Me_6TREN). Methyl acrylate polymerizes rapidly at room temperature with a low concentration of CuBr/Me_6TREN. After 1 h at 22 °C, 41 % conversion is reached and a polymer with $M_n = 9100$ and $M_w/M_n = 1.09$ is obtained from a ratio of monomer, initiator, and catalyst of 1000:5:0.5.[53] Some ligands used successfully in ATRP are shown in Figure 1.

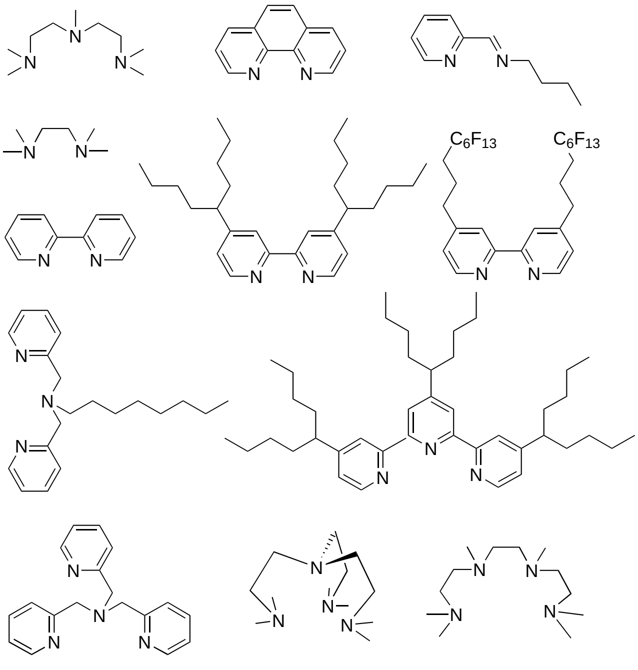

Figure 1. Some ligands used successfully in ATRP.

It is believed that the development of better ATRP catalytic systems will be a very exciting and rapidly developing area. The basic factors involved will include: cost, recovery and immobilization, efficiency (equilibrium constant and deactivation rate) and chemoselectivity (contribution of side reactions). Structurally, new improved catalysts should have a faster rate of formation of cupric species ($k_a \gg 1\,mol^{-1}L\,s^{-1}$), but with a preserved very fast deactivation ($k_d \gg 10^7\,mol^{-1}L\,s^{-1}$). The design of a catalyst should enable the expansion of the coordination sphere to accommodate atom transfer. Finally, the steric and electronic effects should selectively favor inner sphere electron transfer (ET) over any other process (β-H abstraction, outer sphere ET, formation of organometallic species, etc.).

An important role may be played not only by the multidentate amine ligands but also by the counterion. Some improvements have been noted by replacing Br and Cl in cuprous species by triflate,[54] carboxylate,[55] or PF_6.[56]

Although copper-based ATRP currently seems to be the most robust, other metals have been also successfully used (Ru,[18] Fe,[42, 57, 58] Ni,[59, 60] Pd,[61], Rh[62, 63]). The combination of a variety of metals, anions, and ligands may provide new, more efficient catalysts, which will expand the current limitations of ATRP. However, the precise mechanism of polymerization should also be carefully evaluated for each system.

Media/solvents: Radical polymerization is much less sensitive to solvent effects than ionic reactions. However, the structure and reactivity of the catalysts is strongly affected by solvents. For example, a remarkable effect of polar additives such as ethylene carbonate have been noted.[64] Also, dimethylformamide homogenizes CuBr/bpy systems.[65] It is expected that some additives may strongly affect the nature and reactivity of the catalyst by specific solvation.

Even more challenging is the use of water as medium for ATRP. Water can be used under both homogeneous conditions [e.g., water soluble poly(2-hydroxyethyl acrylate)][66] and under heterogeneous conditions (e.g., emulsions).[67] In both cases the proper catalytic system must be used. Activator and deactivator must be at the appropriate concentrations in the phase in which monomer is predominantly located and also in which polymerization occurs; similar rules apply to the initiator. A surfactant that does not interfere with ATRP should be used. For example, emulsion polymerization of styrene, butyl acrylate, and butyl methacrylate was successful in the presence of non-ionic surfactants, with CuBr complexed by 4,4′-dialkyl bpy as the catalyst and ethyl 2-bromoisobutyrate (added after monomer emulsion was formed) as initiator.[67] Other ligands, surfactants, initiators, and modes of addition often resulted in either unstable emulsions or poor control.

A similar approach was used for the polymerization of fluorinated (meth)acrylates and MMA (methyl methacrylate) in liquid CO_2. A special ligand with fluorinated groups used to solubilize catalytic systems is shown in Figure 1.[68]

Miscellaneous developments: There are several directions in which we can expand range of monomers, initiators, and reaction conditions. For example, the range of acrylic monomers have been expanded from the original primary alkyl esters to hydroxyethyl, glycidyl, dimethylaminoethyl, amido, and bromopropionyl derivatives and to tertiary esters convertible to acids; these can directly provide hyperbranched polymers[69] by self condensing vinyl polymerization.[70] Some examples of these monomers are shown in Figure 2.

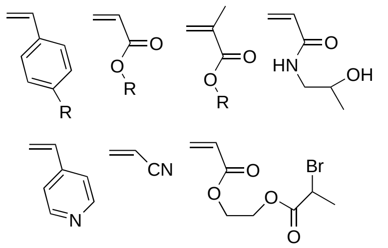

Figure 2. Some of the range of acrylic monomers that can be used in ATRP.

However, it is still difficult to homopolymerize some less reactive monomers such as vinyl acetate, vinyl chloride, and α-olefins, though their copolymerization has been successful in some cases.[32] Various initiators containing hydroxy, silyl, epoxy, amido, amino, cyano, halo, and unsaturated structures have been used to prepare end-functional polymers (Figure 3).[71]

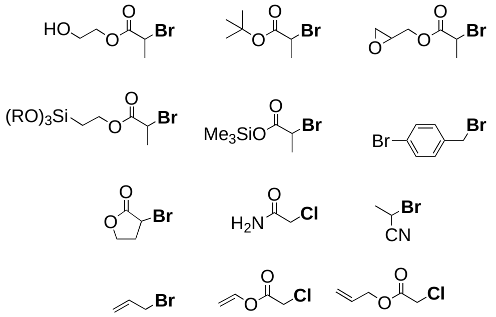

Figure 3. Various initiators used for the preparation of end-functional polymers.

Not only alkyl halides but also sulfonyl halides have been used successfully for many ATRP systems.[72–74] Moreover, it is possible to easily displace the halogen from the growing end group (Figure 4).[71]

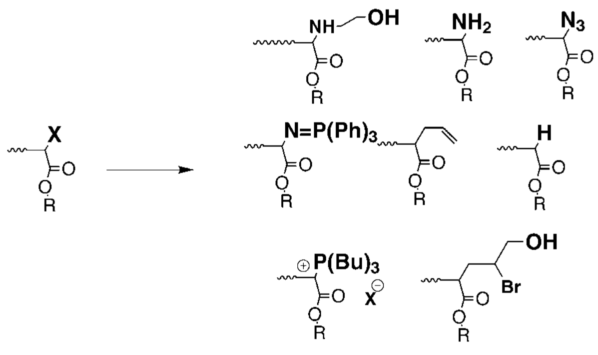

Figure 4. Example of the displacement of the halogen from the growing end group.

Active halogens can be incorporated at the chain ends of polymers prepared by other techniques such as cationic, anionic, ring-opening metathesis, and conventional radical processes to form macroinitiators. Such macroinitiators have been successfully used to chain extend by ATRP to form novel diblock, triblock, and graft copolymers.[75–78]

Recently, ATRP in the presence of metals in their zero oxidation state have been reported.[43] While they do not serve as catalysts themselves (radicals do not reduce Cu^{I} to Cu^{O}), they can act as precursors to the true catalysts and reduce the amount of ligands used by regenerating cuprous species from the cupric species. Moreover, the excess of Cu^{O} can be used to scavenge a limited amount of oxygen and inhibitor from the system, allowing some ATRP systems to be carried out just on a bench, without deoxygenation and/or inhibitor removal.[79]

New polymers and copolymers by ATRP:[48, 49] It is beyond the scope of this article to list and discuss all of the new materials made by ATRP. Generally, though, these materials can be grouped in three categories:

- new polymeric topology (Figure 5),
- new controlled compositions (Figure 6),
- new functionalities (Figure 7).

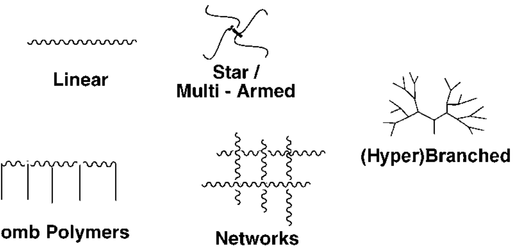

Figure 5. Schematic represetation of possible new polymeric topologies.

Figure 6. Schematic represetation of possible new controlled compositions.

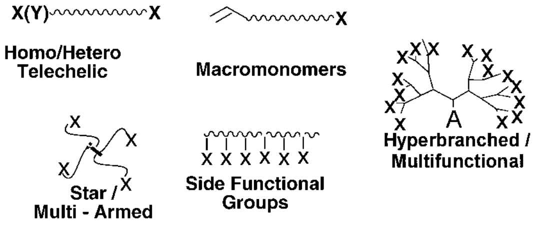

Figure 7. Schematic represetation of possible new functionalities.

These new, and often novel, materials have come about because of the large range of monomers and functionalities that can be utilized in ATRP. Other, more comprehensive reviews cover these structures prepared by ATRP in greater detail.[48, 49, 80, 81] However, it should be remembered that any controlled radical polymerization, ATRP included, is not as precise as some anionic polymerizations, although they may provide a larger variety of structures and encompass more monomers and useful functionalities.

Future Outlook

It is anticipated that controlled radical polymerization systems will become a commercial reality in a very near future, especially in the areas of specialties, coatings, surfactants, dispersants, and so on. From the previously discussed three methods used to control radical polymerizations, ATRP has several advantages which include:

- Br, Cl as the least expensive end groups (very important for short chains),
- a multitude of activated alkyl halides as functional initiators and macroinitiators for making novel block copolymers and hybrid materials,
- very facile removal of halogens, and their replacement by useful functional groups,
- very simple reaction set up and multitude of reaction conditions,
- possibility of adjusting rates and enhancing crosspropagation by selective catalysis,[82]
- and a large variation of the catalytic structures.

At the same time, the inherent part of ATRP is the transition metal catalyst, which should be removed and, ideally, recycled. In this area some successful approaches include selective absorption, precipitation, and immobilization techniques.

Mechanistically, the most exciting areas for future ATRP research include understanding the details of the process, especially the most crucial atom transfer step, and also a comprehensive structure–reactivity correlation for initiators, monomers, and catalysts. Synthetically, it is necessary to expand the range of monomers and initiators and better understand limits for the range of controlled molecular weights, crosspropagations, and end functionalities. Finally, one of the most attractive features is the preparation of many new functional polymers with novel and controlled compositions and topologies for structure–property relationship, and the better design of novel materials for special applications. ATRP is especially well suited for that purpose as a result of facile reaction conditions, a multitude of polymerizable monomers, and accessible chain functionalities.

Acknowledgments

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