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Atom Transfer Radical Polymerization

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Contents

I. Introduction

The synthesis of polymers with well-defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. Typically, living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination.[1−3] Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination, and ring-opening polymerizations. The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers.[4] Despite its tremendous industrial utility, CRP has not been realized until recently, largely due to the inevitable, near diffusion-controlled bimolecular radical coupling and disproportionation reactions.

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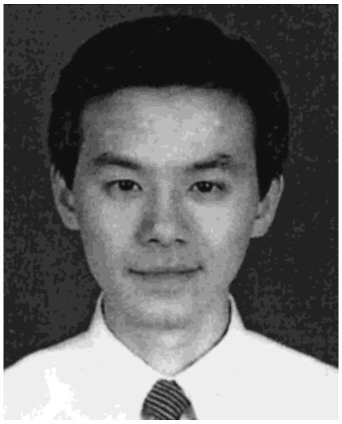
Krzysztof (Kris) Matyjaszewski was born in Konstantynow, Poland, in 1950. He obtained his Ph.D. degree in 1976 at the Polish Academy of Sciences in Lodz, Poland, working in the laboratories of Professor S. Penczek. He has received his Habilitation Degree in 1985 from Lodz Polytechnic, Poland. He stayed as a postdoctoral fellow at the University of Florida, working with Professor G. B. Butler. Since 1985 he has been at Carnegie Mellon University, where he has served as Chemistry Department Head (1994–1998) and is currently J. C. Warner Professor of Natural Sciences. He is also an adjunct professor at the Department of Petroleum and Chemical Engineering at the University of Pittsburgh and the Polish Academy of Sciences in Lodz, Poland. He served as Visiting Professor at the Universities in Paris, Strasbourg, Bordeaux, Bayreuth, Freiburg, Ulm, and Pisa. He is an editor of *Progress in Polymer Science* and serves on seven editorial boards of polymer journals. His main research interests include controlled/living polymerization with the most recent emphasis on free-radical systems. In 1995 he developed atom transfer radical polymerization (ATRP), one of the most successful methods for controlled/living radical polymerization (CRP) systems. During the last 5 years his group (25 postdoctoral fellows and 23 graduate and 26 undergraduate students) has published over 200 papers on ATRP and CRP. He holds over 20 U.S. and international patents. Close industrial interactions have been maintained by the ATRP Consortium (13 companies in 1996–2000) and newly established CRP Consortium (19 companies in 2001–2005). Research of Matyjaszewski group has received wide recognition, as evidenced by the ACS Carl S. Marvel Award for Creative Polymer Chemistry (1995), Elf Chair of French Academy of Sciences (1998), Humboldt Award for Senior US Scientists (1999), National Professorship of Poland (2000), Fellowship of ACS Division of Polymeric Materials and Engineering (2001), ACS Pittsburgh Award (2001), and ACS Award in Polymer Chemistry (2001).



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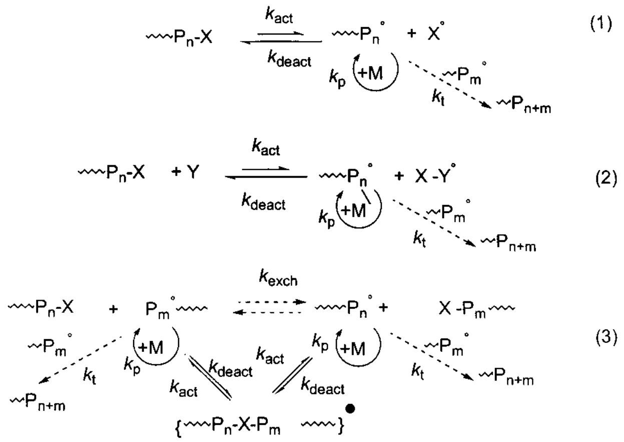
Scheme 1. General Scheme of CRP Methods



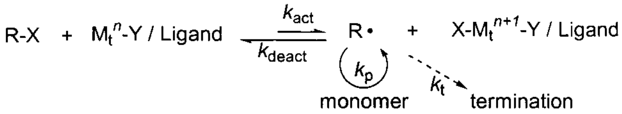
The past few years have witnessed the rapid growth in the development and understanding of new CRP methods.[5,6] All of these methods are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters, as in reversible addition fragmentation chain transfer processes (RAFT), alkoxyamines, as in nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP), and potentially even organometallic species. Free radicals may be generated by the spontaneous thermal process (NMP, SFRP) via a catalyzed reaction (ATRP) or reversibly via the degenerative exchange process with dormant species (DT, RAFT).

All of the CRP methods, shown in Scheme 1, include activation and deactivation steps (with rate constants k_{act} and k_{deact}), although in RAFT and DT the scheme may be formally simplified to just the exchange process with the apparent rate constant k_{exch}. Generated free radicals propagate and terminate (with rate constants k_p and k_t), as in a conventional free-radical polymerization. Thus, although termination occurs, under appropriate conditions its contribution will be small (less than a few percent of total number of chains) and these radical polymerizations behave as nearly living or controlled systems.

This review will focus on the fundamentals of transition metal catalyzed atom transfer radical polymerization (ATRP). We will discuss the current mechanistic understanding of this process and some synthetic applications that have resulted in a variety of well-defined materials. This review covers the literature from the beginning of this field (1995) until approximately the end of 2000. We primarily refer to papers published in peer-reviewed journals, unless the work appeared in nonpeer-reviewed literature and was not followed by a full publication.

A general mechanism for ATRP shown in Scheme 2 corresponds to case 2 from Scheme 1. The radicals, or the active species, are generated through a reversible redox process catalyzed by a transition metal

Scheme 2. Transition-Metal-Catalyzed ATRP



complex (M_t^n−Y/Ligand, where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, R−X. This process occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, X−M_t^{n+1}, as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination.[7] A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

The name atom transfer radical polymerization (ATRP) originates from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains, in the same way that the addition-fragmentation is the key step in the RAFT process. ATRP has its roots in atom transfer radical addition (ATRA), which targets the formation of 1:1 adducts of alkyl halides and alkenes, also catalyzed by transition metal complexes.[8] ATRA is a modification of Kharasch addition reaction, which usually occurs in the presence of light or conventional radical initiators.[9] Because of the involvement of transition metals in the activation and deactivation steps, chemo-, regio-, and stereoselectivities in ATRA and the Kharasch addition may be different. For example, under Kharasch conditions, in the reaction with chloroform the alkene will “insert” across the H−CCl_3 bond but in ATRA it will insert across the Cl−$CHCl_2$ bond, because the C−Cl bond is rapidly activated by the Fe(II) or Cu(I) complexes.[10]

ATRP also has roots in the transition metal catalyzed telomerization reactions.[11] These reactions, however, do not proceed with efficient exchange, which results in a nonlinear evolution of the molecular weights with conversions and polymers with high polydispersities. ATRP also has connections to the transition metal initiated redox processes as well as inhibition with transition metal compounds.[12−14] These two techniques allow for either an activation or deactivation process, however, without efficient reversibility. ATRP was developed by designing an appropriate catalyst (transition metal compound and ligands), using an initiator with the suitable structure, and adjusting the polymerization conditions such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process.[15−19] This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers.[17,20−24] Earlier attempts with heterogeneous catalyst and inefficient initiators were less successful.[25]

ATRP is among the most rapidly developing areas of chemistry, with the number of publications approximately doubling each year. According to SciFinder Scholar, 7 papers were published on ATRP in 1995, 47 in 1996, 111 in 1997, 150 in 1998, 318 in 1999, and more than 300 in 2000. In addition, many papers using the ATRP concept but not using the ATRP name are being published (alternative nomenclature include transition metal mediated living radical polymerization, transition metal catalyzed living free-radical polymerization, atom transfer polymerization, etc.).

II. Mechanistic Understandings of Atom Transfer Radical Polymerization

A. Components

As a multicomponent system, ATRP is composed of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration.

1. Monomers

A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals.[22,23] Ring-opening polymerization has been also successful.[26,27] Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) determines the polymerization rate. ATRP will not occur or occur very slowly if the equilibrium constant is too small. In contrast, too large an equilibrium constant will lead to a large amount of termination because of a high radical concentration. This will be accompanied by a large amount of deactivating higher oxidation state metal complex; which will shift the equilibrium toward dormant species and may result in the apparently slower polymerization.[28] Each monomer possesses its own intrinsic radical propagation rate. Thus, for a specific monomer, the concentration of propagating radicals and the rate of radical deactivation need to be adjusted to maintain polymerization control. However, since ATRP is a catalytic process, the overall position of the equilibrium not only depends

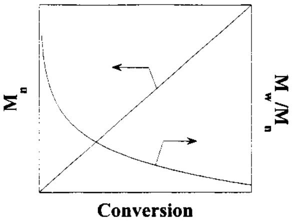


Figure 1. Schematic representation of the evolution of the molecular weights and polydispersities with conversion for a living polymerization.

on the radical (monomer) and the dormant species, but also can be adjusted by the amount and reactivity of the transition-metal catalyst added (cf. eq 2)

2. Initiators

The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization (eq 1).

$$\mathrm{DP} = [\mathrm{M}]_0/[\mathrm{initiator}]_0 \times \mathrm{conversion} \qquad (1)$$

Figure 1 illustrates a linear increase of molecular weights with conversion. Simultaneously, polydispersities (M_w/M_n) decrease with the conversion, depending on the relative rate of deactivation (cf. eq 3). In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is the best. Iodine works well for acrylate polymerizations in copper-mediated ATRP[29] and has been found to lead to controlled polymerization of styrene in ruthenium- and rhenium-based ATRP.[30,31] Fluorine is not used because the C−F bond is too strong to undergo homolytic cleavage. Some pseudohalogens, specifically thiocyanates and thiocarbamates, have been used successfully in the polymerization of acrylates and styrenes.[29,32,33]

Initiation should be fast and quantitative with a good initiator. In general, any alkyl halide with activating substituents on the α-carbon, such as aryl, carbonyl, or allyl groups, can potentially be used as ATRP initiators. Polyhalogenated compounds (e.g., CCl_4 and $CHCl_3$) and compounds with a weak R−X bond, such as N−X, S−X, and O−X, can also be used as ATRP initiators. When the initiating moiety is attached to macromolecular species, macroinitiators are formed and can be used to synthesize block/graft copolymers.[21] Similarly, the efficiency of block/graft copolymerization may be low if the apparent rate constant of cross-propagation is smaller than that of the subsequent homopolymerization.

It should be noted, however, that R−X bonds can be cleaved not only homolytically but also heterolytically, which depends mostly on the initiator structure and the choice of the transition metal catalyst. For example, side reactions are observed for copper-mediated ATRP of *p*-methoxystyrene, likely due to the heterolytic cleavage of C−X bond or oxidation of the radical to the corresponding carbocation.[14,34]

3. Catalysts

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth, the ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. A variety of transition-metal complexes have been studied as ATRP catalysts and will be discussed in more detail later in this paper.

4. Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used for different monomers. A solvent is sometimes necessary, especially when the obtained polymer is insoluble in its monomer (e.g., polyacrylonitrile). Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP)[35] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent,[36] should be minimized.

The possibility that the structure of the catalyst may change in different solvents should also be taken into consideration. For example, the ATRP of *n*-butyl acrylate with $CuBr(bpy)_3$ (bpy = 2,2′-bipyridine; here and below the notation of the complex reflects only the stoichiometry of added reagents and NOT the structure of the complex) as the catalyst carried out in ethylene carbonate was found to proceed much faster than in bulk.[37] A structural change from a dimeric halogen-bridged Cu(I) species in the bulk system to a monomeric Cu(I) species in ethylene carbonate was proposed to explain the rate difference. A similar rate enhancement in polar media was observed later from different studies.[38−40] Polar media can also help to dissolve the catalyst. For example, homogeneous ATRP using $CuBr(bpy)_3$ was achieved using 10% v/v DMF.[41]

5. Temperature and Reaction Time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures.[36,42] In general, the solubility of the catalyst increases at higher temperatures; however, catalyst decomposition may also occur with the temperature increase.[43,44] The optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight.

At high monomer conversions, the rate of propagation slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration independent. Prolonged reaction times leading to nearly complete monomer conversion may not increase the polydispersity of the final polymer but will induce loss of end groups.[45] Thus, to obtain polymers with high end-group functionality or to subsequently synthesize block copolymers, conversion must not exceed 95% to avoid end-group loss.

6. Additives

Additives are sometimes essential for a successful ATRP. For example, a Lewis acid, such as aluminum and other metal alkoxides, is needed for the controlled polymerization of MMA catalyzed by $RuCl_2(PPh_3)_3$ or other systems.[15,46,47] No or very slow polymerization was observed in the absence of the Lewis acid activator. Presumably, the aluminum compound can activate and stabilize the catalyst in the higher oxidation state.[46] Polymerization in the presence of very polar solvents such as water can be accelerated.[39] The presence of strong nucleophiles such as phosphines may sometimes terminate the process. [35]

B. Typical Phenomenology

1. Kinetics

The kinetics of ATRP is discussed here using copper-mediated ATRP as an example. Mechanistic investigations into ATRP based upon other metal systems are anticipated to yield similar results. According to Scheme 2 using the assumption that contribution of termination becomes insignificant due to the persistent radical effect[7,48] (PRE) (especially for the chain-length-dependent PRE[49]) and using a fast equilibrium approximation, which is necessary for observed low polydispersities, the rate law (eq 2, cf. Scheme 1 for the explanation of all symbols) for ATRP can be derived as follows.

$$R_p = k_p[M][P^*] = k_p K_{eq}[M][I]_0 \times [Cu^I]/[X - Cu^{II}] \quad (2)$$

Figure 2 shows a typical linear variation of conversion with time in semilogarithmic coordinates. Such a behavior indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. However, since termination occurs continuously, the concentration of the Cu(II) species increases and deviation from linearity may be observed. For the ideal case with chain length independent termination, PRE kinetics implies the semilogarithmic plot of monomer conversion vs time to the 2/3 exponent should be linear.[7] Nevertheless, a linear semilogarithmic plot is often observed. This may be due to an excess of the Cu(II) species present initially, a chain-length-dependent termination rate coefficient, and heterogeneity of the reaction system due to limited solubility of the copper complexes. It is also possible that self-initiation may continuously produce radicals and compensate for termination.[50,51] Similarly, external orders with respect to initiator and the Cu(I) species may also be affected by the PRE.[52]

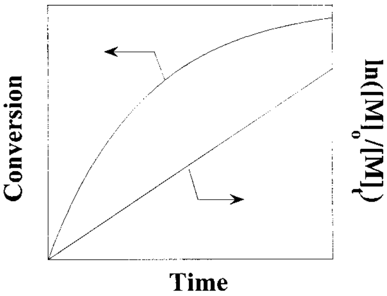


Figure 2. Schematic representation of the dependence of the conversion on time in linear and semilogarithmic coordinates.

Results from kinetic studies of ATRP for styrene,[35] methyl acrylate (MA),[53] and methyl methacrylate (MMA)[54,55] under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(l) complex concentrations. These observations are all consistent with the derived rate law (eq 2). The kinetically optimum ratio of ligand to copper in the polymerization of both styrene and MA was determined to be 2:1. Below this ratio the polymerization rate was usually slower, and above this ratio the polymerization rate remained constant. It should be noted that the optimum ratio can vary with regard to changes in the monomer, counterion, ligand, temperature, and other factors.[43,54,56]

The precise kinetic law for the deactivator ($X-Cu^{II}$) was more complex due to the spontaneous generation of Cu(II) via the persistent radical effect.[7,35,52] In the atom transfer step, a reactive organic radical is generated along with a stable Cu(II) species that can be regarded as a persistent metalloradical. If the initial concentration of deactivator Cu(II) in the polymerization is not sufficiently large to ensure a fast rate of deactivation (k_{deact}[Cu(II)]), then coupling of the organic radicals will occur, leading to an increase in the Cu(II) concentration. This process has been observed experimentally using ^{I}H NMR, UV−vis, EPR, and GC-MS techniques.[35,57] With each radical termination event, 2 equiv of Cu(II) will form irreversibly. Radical termination occurs rapidly until a sufficient amount of deactivator Cu(II) is formed and the radical concentration becomes low enough. Under such conditions, the rate at which radicals combine ($k_t[R^I]^2$) will become much slower than the

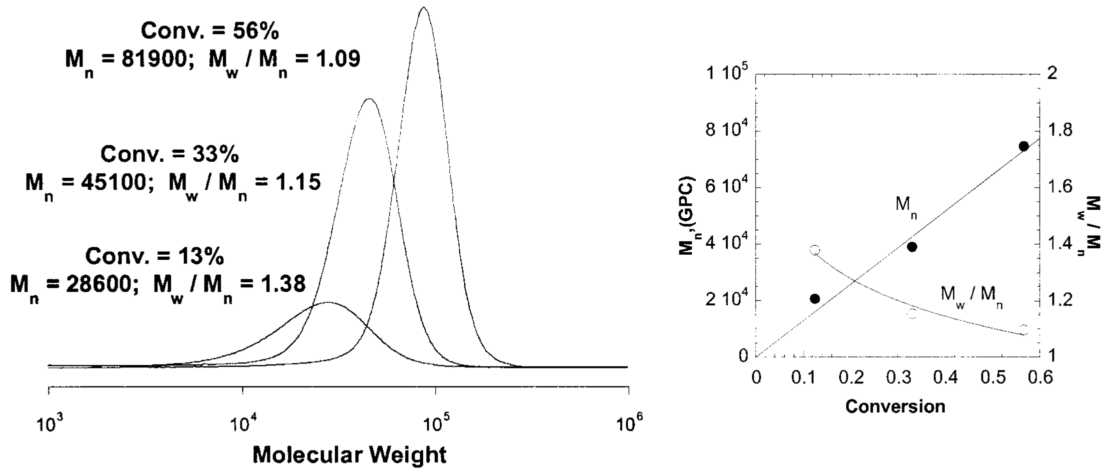


Figure 3. Evolution of molecular weight and polydispersity in the ATRP of MA: $T = 90$ °C; $[\mathrm{MA}]_o = 11.2$ M; $[\mathrm{MA}]_o/[\mathrm{MBP}]_o = 1513$ (MBP = methyl 2-bromopropionate); $[\mathrm{MBP}]_o/[\mathrm{CuBr}]_o/[\mathrm{dTbpy}]_o = 1/1/2$ (dTbpy = 4,4′-di-*tert*-butyl-2,2′-bypyridine).

rate at which radicals react with the copper(ll) complex ($k_{\mathrm{deact}}[\mathrm{R}^{\mathrm{l}}][\mathrm{Cu(II)}]$) in a deactivation process and a controlled/"living" polymerization will proceed. Typically, a small fraction (~5%) of the total growing polymer chains will be terminated during the early stage of the polymerization, but the majority of the chains (>90%) will continue to grow successfully. If a small amount of the deactivator (~10 mol %) is added initially to the polymerization, then the proportion of terminated chains can be greatly reduced.[20,57] The effect of Cu(II) on the polymerization may additionally be complicated by its poor solubility, by a slow reduction by reaction with monomers leading to 1,2-dihaloadducts, or from the self-initiated systems such as styrene and other monomers.[51,58]

2. Molecular Weight

Similarly to a typical living polymerization, the average molecular weight of the polymer made by a well-controlled ATRP can be predetermined by the ratio of consumed monomer and the initiator ($\mathrm{DP}_n = \Delta[\mathrm{M}]/[\mathrm{I}]_o$. DP = degree of polymerization) while maintaining a relatively narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$). In addition, precise control over the chemistry and the structure of the initiator and active end group allows for the synthesis of end-functionalized polymers and block copolymers. Well-defined polymers with molecular weights ranging from 1000 to 150 000 have been successfully synthesized. However, termination and other side reactions are also present in ATRP, and they become more prominent as higher molecular weight polymers are targeted. For example, in the copper-mediated ATRP of styrene, a slow termination process was observed arising mainly from the interaction of the copper(II) species with both the growing radical and the macromolecular alkyl halide. This effect is negligible for low molecular weight polystyrene but could result in an upper limit to styrene ATRP.[36]

Figure 3 shows a typical linear increase of the molecular weights with conversion in the ATRP of methyl acrylate.[53] Since the rate constants of propagation for acrylates are relatively large, initially, higher polydispersities were observed because several monomer units are added during each activation step. However, with the progress of the reaction, chains become more uniform due to continuous exchange reactions. The polydispersities drop with conversion, as predicted by eq 3. If k_p and the concentrations of initiator and deactivator are known, the rate constant of deactivation can be calculated from the evolution of polydispersities with conversion.

$$M_w/M_n = 1 + \left(\frac{[\mathrm{RX}]_0 k_p}{k_{\mathrm{deact}}[D]}\right)\left(\frac{2}{p} - 1\right) \tag{3}$$

3. Molecular Weight Distribution

The molecular weight distribution or polydispersity (M_w/M_n) is the index of the polymer chain-length distribution. In a well-controlled polymerization, M_w/M_n is usually less than 1.10. Equation 3 illustrates how the polydispersity index in ATRP in the absence of significant chain termination and transfer relates to the concentrations of initiator (RX) and deactivator (D), the rate constants of propagation (k_p) and deactivation (k_{deact}), and the monomer conversion (p).[59] This equation holds for conditions when initiator is completely consumed and degrees of polymerization are sufficiently high; otherwise the Poisson term should be added ($1/\mathrm{DP}_n$).

Thus, for the same monomer, a catalyst that deactivates the growing chains faster will result in polymers with lower polydispersities (smaller k_p/k_{deact}). Alternatively, polydispersities should decrease with an increasing concentration of deactivator, although at the cost of slower polymerization rates. For example, the addition of a small amount of Cu(II) halides in the copper-based ATRP leads to better controlled polymerizations with decreased polymerization rates.[53,60] Perhaps most important, however, is the propagation rate constant; higher polydispersities are usually found for polyacrylates than for polystyrene or polymethacrylates due to a much higher k_p for the former monomers.[61] Other predictions from eq 3 include higher polydispersities for shorter chains (higher $[\mathrm{RX}]_o$) and a decrease of the polydispersity with increasing monomer conversion. The implications of eq 3 are in agreement with the experimental results. It is also possible to correlate polydispersities with the rate constant of activation when they are plotted against time rather than conversion.[62]

The rate constant of deactivation (k_{deact}) is affected by a number of factors, such as the transition metal, the metal counterion, and the ligand. For the same catalytic system, an important factor is the lability of the X−M_t bond in the deactivator. $CuBr_2(dNbpy)_2$ (dNbpy = 4,4′-di(5-nonyl)-2,2′-bipyridine) yields faster deactivation than $CuCl_2(dNbpy)_2$. Similar results were obtained in earlier studies on the efficiency of inhibition of various metal salts.[13]

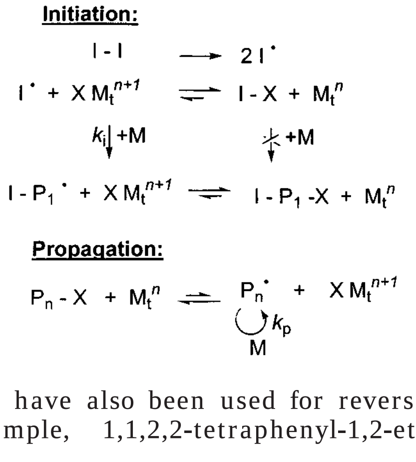
In ATRP, the concentration of deactivator increases sharply at the beginning of the polymerization and then increases slowly, but continuously, with monomer conversion.[63] The addition of a small amount of Cu(II) halides at the beginning of the polymerization can reduce the proportion of terminated chains and help establish the atom transfer equilibrium. Conversely, the addition of small amounts of copper(0) in copper-mediated ATRP can result in a faster polymerization rate, as “excess” copper(II) is reduced to copper(I) (cf. section II.G).[64]

It should be noted that deactivators may also participate in side reactions. For example, reduced molecular weights and termination were observed when the ATRP of styrene was carried out in the presence of a large amount of cupric triflate, likely due to the oxidation of growing radicals via an outer-sphere electron-transfer process.[65] Similarly, cuprous triflate and bromide may reduce the growing radicals in the polymerization of acrylonitrile[66] and methyl acrylate.[65]

4. Normal and Reverse ATRP

In a normal ATRP, the initiating radicals are generated from an alkyl halide in the presence of a transition metal in its lower oxidation state (e.g., $CuBr(dNbpy)_2$); however, conventional radical initiators can also be employed. For example, ATRP can be initiated using azobisisobutyronitrile (AIBN) with the transition-metal compound in its higher oxidation state (e.g., $CuBr_2(dNbpy)_2$). The latter approach has been named reverse ATRP and was successfully used for copper-based heterogeneous[67−70] and homogeneous[71] systems in solution and in emulsion[72] as well as for iron complexes.[73] Other conventional radical initiators have also been used for reverse ATRP. For example, 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED)[74] and diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS)[75] have been used successfully in the presence of $FeCl_3(PPh_3)_3$ for the reverse ATRP of MMA and styrene, respectively. For TPED, PMMA with M_n = 171 800 and M_w/M_n = 1.13 was obtained but the initiation efficiency was low (0.5). For DCDPS, the experimental molecular weights by size exclusion chromatography (SEC) were lower than the calculated values, assuming one molecule of DCDPS generated two living polymer chains. More recently, the reverse ATRP using tetraethylthiuram disulfide and $FeCl_3(PPh_3)_3$ as the initiating system resulted in the formation of PMMA with $M_n \approx 7000$ and $M_w/M_n = 1.05$ within 8 min at 90 °C in bulk.[76]

Scheme 3. Reverse ATRP Using AIBN as the Initiator



The reverse ATRP initiated by peroxides sometimes behaves quite differently than that based on the azo compounds. For instance, no control over the polymerization was observed for the homogeneous BPO/$CuBr_2(dNbpy)_2$ system (BPO = benzoyl peroxide). In contrast, controlled/“living” polymerization was observed when BPO was used together with $CuBr(dNbpy)_2$. The differences between the BPO and AIBN systems are ascribed to an electron transfer and the formation of a copper benzoate species.[70] In a heterogeneous system using bpy as the ligand, both CuBr and $CuBr_2$ yielded a controlled polymerization of styrene.[69]

5. Experimental Setup

ATRP can be carried out either in bulk or with a solvent. Solvents are often used to alleviate viscosity problems that arise at high conversions. As discussed previously, a variety of solvents can be used in ATRP. Environmentally friendly media, such as water[72,77−81] and carbon dioxide,[82] have been used. Depending on the initial conditions, ATRP can be performed in solution, suspension,[79,83] emulsion,[72,77,84] miniemulsion,[85] or dispersion.[82]

Kinetics of ATRP in emulsion is quite different from conventional emulsion polymerization.[86] Due to the slow growth of MW with conversion, the mechanism of nucleation changes entirely. Moreover, partition coefficients of both activators and deactivators in organic and aqueous phases become very important. The catalytic system should preferentially reside in the organic phase but should also be slightly soluble in water to transfer between monomer droplets and growing particles and also to scavenge radicals in water.[86] Both normal and reverse ATRP has been successful, although colloidal stability of latexes is higher and particle size smaller for the reverse ATRP.[86] The concept of compartmentalization, which is the essence of emulsion polymerization, is strongly related to the living polymerization. The proportion of terminated chains can be smaller than in bulk at the same overall rate of monomer consumption. However, only when the size of growing particles is smaller than 50 nm does the effect become significant.[87]

6. Catalyst Homogeneity

Both heterogeneous and homogeneous catalytic systems have been used in ATRP. Better solubility of the transition-metal complex is achieved by adding long alkyl substituents to the ligand.[35,43,88] Homogeneous systems allow for the detailed kinetic and mechanistic studies of the polymerization.[35,55,88] In addition, polymers with lower polydispersities are usually obtained with a homogeneous catalyst due to a higher concentration of deactivator in solution.[89]

Attempts have also been made using solid supported catalysts.[90−94] The usual procedure for removing the catalyst from a reaction on a laboratory scale involves precipitating the polymer or filtering the polymer solution through a column of aluminum oxide, which adsorbs the catalyst. Removal of the copper-based catalyst using an ion-exchange resin has also been reported.[95] The disadvantages of these techniques include cost, problems with scale-up, loss of polymer, and difficulties in separating the catalyst from functional polymers that interact with the copper complexes. Immobilization of the catalytic system on a solid support provides a more efficient way of separating and potentially recycling the catalyst. Thus, multidentate nitrogen donor ligands as well as Schiff base ligands have been covalently bounded to silica and cross linked polystyrene supports. In general, polymers with higher polydispersities ($M_w/M_n > 1.5$) were obtained using the solid supported catalysts. This was explained by slow deactivation of the growing radicals resulting from slow diffusion toward the metal center. Lower polydispersities were obtained when the catalyst was physically absorbed onto a solid support; however, only the controlled polymerization of methacrylates have been reported so far.[91,93,94] Other approaches involve the reversible adsorption of the transition-metal complex using ion-exchange resins,[95] a hybrid catalyst system consisting of majority of the immobilized catalyst and a minute amount of soluble more active catalyst,[96] or using ligands whose solubility is strongly dependent on the temperature.[97]

7. Summary and Outlook

The current understanding of the kinetics and mechanism of ATRP allows for a basic correlation of the effect of concentrations and structures of the involved reagents on the polymerization rates, molecular weights, and polydispersities. The structural effects will be discussed in more detail in the subsequent sections. ATRP is more complex than other CRP methods because it involves a complex, often heterogeneous catalytic system. The solubility, structure, concentration in solution, aggregation, effect of ion pairing, etc., may change not only with the overall catalyst composition and preparation method but also for each monomer, solvent, and temperature. Thus, more detailed information on the structure of both activator and deactivator in solution is needed. Additional complications appear in aqueous systems, both homogeneous and heterogeneous. In aqueous solution halogens can be displaced from transition metals (hydrolyze) and significantly reduce the concentration of the true deactivator ($X-M_t^{n+1}$ species). Complexes may be strongly solvated by water, reducing rates of activation and deactivation. Ligands may be more labile, enabling reorganization of the catalytic system.

In heterogeneous systems, especially emulsion, the behavior of ATRP and other CRPs is very different than conventional RP. Due to the slow growth of MW with conversion, the mechanism of nucleation changes entirely. Moreover, partition coefficients of both activator and deactivator in organic and aqueous phases become very important. Preferentially, the catalytic system should reside in the organic phase but should be also slightly soluble in water to scavenge radicals and transfer between monomer droplets and growing particles. The concept of compartmentalization, which is the essence of emulsion polymerization, has a strong effect in the living polymerization. It can potentially reduce the proportion of terminated chains; however, only when size of growing particles is smaller than 50 nm does the effect become significant, i.e., proportion of terminated chains becomes lower than in bulk at the same overall rate of monomer consumption.

Perhaps one of the main challenges for the commercialization of the ATRP process is the removal and recycling of the catalyst. There are several approaches being actively evaluated which are based on immobilization, biphasic systems with water, ionic liquids, and fluorinated solvents. More efficient methods of removal by extraction, filtration, etc., are needed. Another approach is to continuously increase the activity of the catalytic system, which may enable reducing the amount of the catalyst to a level that it may be left in the final polymer. Nearly all ATRP reactions are carried out in batch or semibatch systems, and conversion to continuous systems should be studied, perhaps using bulk monomer but reaching only partial monomer conversion in each cycle.

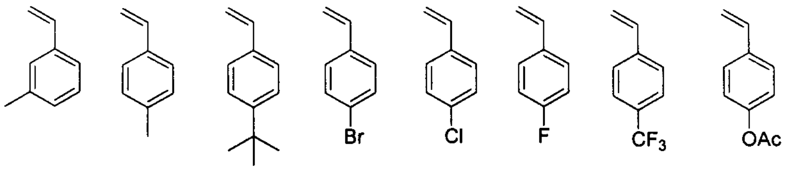
C. ATRP Monomers

Various monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, acrylonitrile, and other monomers which contain substituents that can stabilize the propagating radicals. Ring-opening polymerization is also possible. However, even using the same catalyst under the same conditions, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. The product of k_p and the equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) essentially determines the polymerization rate. ATRP will occur very slowly if the equilibrium constant is too small. This is plausibly the main reason why polymerization of less reactive monomers such as olefins, halogenated alkenes, and vinyl acetate has not yet been successful. Because each monomer has a specific equilibrium constant, optimal conditions for polymerization which include concentration and type of the catalyst, temperature, solvent, and some additives may be quite different. Therefore, we discuss ATRP monomers separating them into different groups starting from non-polar styrenes, followed by various (meth)acrylate esters, nitriles, amides, acids, and other monomers.

1. Styrenes

ATRP of styrene and its derivatives has been reported for the copper,[17−19,35] iron,[98] ruthenium,[31] and rhenium[30] catalytic systems; thus far the majority of the work has been performed using the copper-based systems.

Scheme 4. Various Styrenes Polymerized by ATRP



In addition to 1-phenylethyl halide and benzylic halides, a variety of compounds, such as allylic halides and functional α-haloesters,[99] polyhalogenated alkanes,[18,100] and arenesulfonyl chlorides,[55] have been used successfully as the initiators for the copper-mediated styrene ATRP. One of the most extensively studied systems is the polymerization of styrene conducted at 110 °C with CuBr(dNbpy)$_2$ as the catalyst and alkyl bromides as the initiators. A similar system for the chloride-mediated polymerization is conducted at 130 °C to obtain similar polymerization rates.[35] The reaction temperature can be lowered to 80−90 °C to produce well-defined polystyrenes in a reasonable time with the use of a more efficient catalyst, such as CuBr/PMDETA (PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine)[101] or CuOAc/CuBr/dNbpy.[60] However, to maintain a sufficiently large propagation rate, avoid vitrification at high conversion (for polystyrene $T_g \approx 100$ °C), and sometimes increase the solubility of the catalysts, higher reaction temperatures (>100 °C) are preferred for styrene ATRP. The reaction may be carried out in bulk or using a solvent, but the stability of the halide end group displays a pronounced solvent dependence as demonstrated by model studies using 1-phenylethyl bromide. As a result, nonpolar solvents are recommended for styrene ATRP.[36]

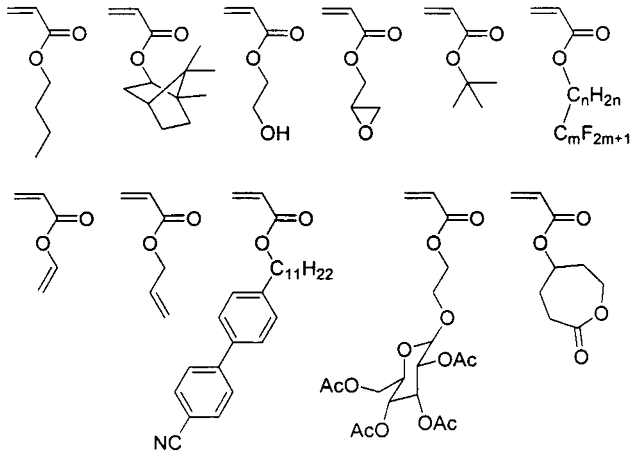
Polystyrenes with molecular weights (M_n) ranging from 1000 to 100 000 with low polydispersities have been prepared. Better molecular weight control is obtained at lower temperatures, presumably due to a lower contribution of the thermal self-initiation.[42,58] Additionally, a wide range of styrene derivatives with different substituents on the aromatic ring have been polymerized in a well-controlled fashion.[34] Well-defined *p*-acetoxystyrene was prepared, and subsequent hydrolysis afforded water-soluble poly(vinylphenol).[102] In general, styrenes with electron-withdrawing substituents polymerize faster. The Hammett correlation for ATRP of styrene provided $\rho = 1.5$ compared to $\rho = 0.5$ for the radical propagation constants. This indicates that the atom transfer equilibrium was more shifted toward the active species side for styrenic monomers bearing electron-withdrawing groups. This behavior was explained by the higher ATRP reactivity of secondary benzylic halides with electron-withdrawing groups.[103] Scheme 4 shows some styrene derivatives successfully polymerized by ATRP.

2. Acrylates

The controlled ATRP of acrylates has been reported for copper-,[16,18,53] ruthenium-,[104] and iron-based systems.[105] Copper appears to be superior over other transition metals in producing well-defined polyacrylates with low polydispersities in a relatively short time. This is partially due to the fast deactivation of the growing acrylic radicals by the cupric halides. Typically polymerizations were conducted in bulk with an alkyl 2-bromopropionate initiator. Well-defined polyacrylates with M_n up to 100 000 and $M_w/M_n < 1.1$ were prepared. Depending on the catalyst, a wide range of polymerization temperatures are possible to produce polymers within a reasonable time (e.g., $M_n = 20\,000$ in ca. 2 h). For example, using 0.05 mol % of CuBr/Me$_6$TREN (Me$_6$TREN = tris[2-(dimethylamino)ethyl]amine) as the catalyst, poly(MA) with $M_n = 12\,600$ and $M_w/M_n = 1.10$ was obtained in 1 h at ambient temperature.[106]

A wide range of acrylates with various side chains have been polymerized using ATRP (Scheme 5). For example, well-defined functional polymers were obtained by the ATRP of 2-hydroxyethyl acrylate (HEA)[80,107] and glycidyl acrylate.[108] Poly(*tert*-butyl acrylate) was also prepared in a well-controlled fashion.[109] Subsequent hydrolysis yields well-defined poly(acrylic acid). In addition, well-defined homopolymer and block copolymers with long alkyl chain[142] and fluorocarbon side chains have been prepared.[82,110] When allyl acrylate was subjected to ATRP conditions with bpy or dNbpy as the ligand, a cross-linking reaction occurred, even at 0 °C.[58]

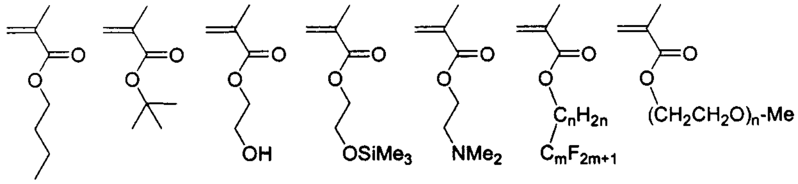
Scheme 5. Representative Acrylates Polymerized by ATRP



3. Methacrylates

ATRP of methyl methacrylate (MMA) has been reported for ruthenium,[15,104] copper,[111,112] nickel,[113−115] iron,[98,116,117] palladium,[118] and rhodium[119] catalytic systems. The facile polymerizability of MMA and the large range of available catalysts for the ATRP reaction is due to the relative ease of activation of the dormant species and the high values of the ATRP equilibrium constants. The equilibrium constants can sometimes be too high to obtain a controlled ATRP process, as is the case for the Me$_6$TREN ligands.[28] Using the known rate constant of propagation for

Scheme 6. Various Methacrylates Polymerized by ATRP



MMA, typical radical concentrations for the bulk and solution controlled ATRP of MMA are estimated to be between 10^{-7} and $l0^{-9}$ M.

Most polymerizations of MMA were carried out in solution at temperatures ranging from 70 to 90 °C. Solvents are necessary to solubilize the forming poly(MMA) (PMMA), which has a glass transition temperature $T_g > 100$ °C. In addition, solution polymerization helps to keep the concentration of growing radicals low. Under comparable conditions, the copper-mediated ATRP of MMA displays a significantly higher equilibrium constant when compared with styrene and MA. As a result, higher dilution and a lower catalyst concentration should be used for the MMA polymerization.

Initiation plays an important role in the ATRP of MMA. The best initiators include sulfonyl chlorides[111] and 2-halopropionitrile[98] because these initiators have sufficiently large apparent rate constants of initiation (high atom transfer equilibrium constants). Well-defined PMMA can be prepared within the molecular weight range from 1000 to 180 000. A series of initiators, including chloromethanes, α-chloroesters, α-chloroketones, and α-bromoesters, were studied in ruthenium-mediated ATRP of MMA.[120] CCl_3COCH_3, $CHCl_2COPh$, and dimethyl 2-bromo-2,4,4-trimethylglutarates were among the best initiators, yielding PMMA with controlled molecular weights and low polydispersities ($M_w/M_n = 1.1-1.2$). Similar studies were performed for Cu-based systems.[121,122] It should be noted that some of these initiators are too active for the copper-based systems and lead to excessive termination or other side reactions.[123]

Other methacrylic esters have also been successfully polymerized. These include *n*-butyl methacrylate,[55,77,88,124] 2-(dimethylamino)ethyl methacrylate (DMAEMA),[125] 2-hydroxyethyl methacrylate (HEMA)[104,126] and silyl-protected HEMA,[127] methacrylic acid in its alkyl protected form[128] or as its sodium salt,[129] methacrylates with an oligo(ethylene oxide) substituent,[39] and fluorinated methacrylic esters.[82,110,130] Scheme 6 illustrates examples of methacrylates polymerized by ATRP.

4. Acrylonitrile

Metal mediated controlled radical polymerization of acrylonitrile has so far only been reported for copper-mediated ATRP.[66,131,132] It is necessary to use a solvent because polyacrylonitrile is not soluble in its monomer. DMF is a good solvent for polyacrylonitrile; however, it may also complex with copper and deactivate the catalyst. Successful polymerizations have been carried out in ethylene carbonate in the presence of the $CuBr(bpy)_2$ complex using α-bromopropionitrile as the initiator at temperatures from 44 to 64 °C. The $CuBr(bpy)_2$ catalyst was soluble in the strongly polar polymerization medium, and the system was homogeneous. Well-defined polyacrylonitrile with $M_w/M_n < 1.05$ has been prepared within the molecular weight range from 1000 to 10 000. In all polymerizations there was significant curvature in the first-order kinetic plot of the monomer consumption. ^1H NMR spectroscopy and MALDI-TOF analysis showed that some halide end groups were irreversibly removed during the polymerization. It was proposed that the reduction of the propagating radical by the cuprous halide to form an anion was the major chain termination reaction.[66] Acrylonitrile has also been copolymerized with styrene in a well-controlled fashion to yield gradient copolymers with molecular weights ranging from 1000 to 15 000.[133]

5. (Meth)acrylamides

Polymers of acrylamide and its derivatives have found wide use in industry, agriculture, and medicine owing to their remarkable properties such as water solubility and potential biocompatibility. There are a few reports on the attempted ATRP of acrylamide. Using CuCl−bpy as the catalyst and surface-bound benzyl chloride as the initiator, Wirth et al. made poly(acrylamide) films from a silica surface.[134] The resulting materials provided good analytical separations; however, detailed proof for the controlled character of the polymerization was not provided. Li and Brittain also attempted the controlled polymerization of acrylamide by ATRP but did not obtain any polymers using $CuBr(bpy)_3$ as the catalyst and 1-(bromoethyl)benzene as the initiator at various temperatures.[135] It was shown using model compounds and kinetic studies that the polymerization of acrylamide under typical ATRP conditions displayed a much lower ATRP equilibrium constant than the acrylates or styrene.[136] The inactivation of the catalyst by complexation of copper by the forming polymer and displacement of the terminal halogen atom by the amide group are two potential side reactions. Interestingly, using 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam) as a ligand provided polymers in high yields in a short time. Unfortunately, the polymerization was not controlled and displayed slow deactivation characteristics. Loss of the chain-end halogen was considered previously[137] and recently confirmed by end-group analysis through the use of mass spectrometry.[138] The conclusion is that the presence of the metal as a Lewis acid in ATRP and its complexation to the amide functionality slows deactivation and makes the process an uncontrolled polymerization. Nevertheless, by using the Me_4Cyclam-based catalytic system and well-defined macroinitiators prepared by ATRP, block copolymers of poly(methyl acrylate-*b*-*N,N*-dimethylacrylamide) ($M_n = 4800$, $M_w/M_n = 1.33$) and poly(*n*-butyl acrylate-*b*-*N*-(2-hydroxypropyl)methacrylamide] ($M_n = 34\,000$, $M_w/M_n = 1.69$) were synthesized.[136] The best results for the ATRP of (meth)acrylamide were obtained using one of the most powerful catalytic systems (CuCl/Me$_6$TREN) due to its high equilibrium constant. Moreover, polymerizations were carried out using alkyl chlorides as the initiators at low temperature (20 °C) in a low polarity solvent (toluene) to minimize side reactions.[139] For example, poly(*N,N*-dimethylacrylamide) with molecular weight $M_n = 8400$ and polydispersity $M_w/M_n = 1.12$ was formed at room temperature in 50% toluene solution.

Metals other than copper have also been studied in the ATRP of acrylamide. For example, living polymerization of dimethylacrylamide (DMAA) is possible with the use of a bromide initiator such as CCl$_3$Br in conjunction with RuCl$_2$(PPh$_3$)$_3$ and Al(O*i*-Pr)$_3$ in toluene at 60 °C.[140] Polymers with relatively high polydispersities ($M_w/M_n = 1.6$) were obtained. Better control was achieved at lower temperatures, presumably due to a lower contribution of the side reactions.

A unique amide monomer, *N*-(2-hydroxypropyl) methacrylamide, was polymerized in a controlled manner using CuBr/Me$_4$Cyclam as the catalyst.[141] The polymerization was carried out in 1-butanol to yield a relatively well-defined polymer ($M_n = 21\,300$, $M_w/M_n = 1.38$) and block copolymers.

6. (Meth)acrylic Acids

Controlled polymerization of (meth)acrylic acid by ATRP presents a challenging problem because the acid monomers can poison the catalysts by coordinating to the transition metal. In addition, nitrogen-containing ligands can be protonated, which interferes with the metal complexation ability. Recently, Armes and co-workers reported the successful ATRP of sodium methacrylate in water using CuBr(bpy)$_3$ as the catalyst with a poly(ethylene oxide)-based macroinitiator.[129] Yields were moderate to good, molecular weight control was good, and the polydispersities were low ($M_w/M_n = 1.30$); however, high polydispersities were observed when the target $M_n > 10\,000$. The choice of pH and initiator was critical. The optimum pH lies between 8 and 9, as there appears to be a balance between the reduced propagation rate at high pH and competing protonation of the ligand at low pH. In addition, low conversion and initiator efficiency were obtained when sodium 2-bromoisobutyrate was used as the initiator. Other acidic monomers such as sodium vinylbenzoate were also successfully polymerized in aqueous media using a similar methodology.[143]

Alternatively, poly(meth)acrylic acids can be prepared by polymerization of protected monomers such as trimethylsilyl methacrylate, *tert*-butyl methacrylate, tetrahydropyranyl methacrylate, and benzyl methacrylate.[144]

7. Miscellaneous Monomers

Pyridine-containing polymers are useful for various applications such as water-soluble polymers and coordination reagents for transition metals. Both 4-vinylpyridine (4VP) and poly(4-vinylpyridine) (P4VP) can act as coordinating ligands for transition metals and compete for the binding of the metal catalysts in ATRP. By employing a strongly coordinating ligand such as Me$_6$TREN, well-defined P4VP has been obtained at 40 °C using a copper-based catalytic system.[145]

Alternating copolymers of isobutene with MA, BA, and AN have been prepared using CuBr(bpy)$_3$ as the catalyst and 1-phenylethyl bromide as the initiator at 50 °C.[146] The experimental molecular weights were close to the theoretical values, ranging from 4000 to 50 000. The polydispersities were relatively high ($M_w/M_n \approx 1.50$). Evidence of the alternating sequences and the tacticity of the isobutene with the MA was provided by ^{1}H NMR analysis. The prepared alternating copolymer with MA was an elastomer with a preponderant syndiotactic structure and a low glass transition temperature ($T_g \approx -30$ °C).

Alternating copolymerizations of maleimides with styrene[22,146−149] and MMA[150] have been carried out using copper-based ATRP. A linear increase of M_n with conversion was observed up to $M_n \approx 13\,000$, with M_w/M_n around 1.16−1.36. *N*-(2-acetoxyethyl)-maleimide was found to copolymerize faster than *N*-phenylmaleimide.[147]

Polymerization of vinylidene chloride and isoprene [17] by copper-mediated ATRP has also been carried out. Controlled polymerization of vinyl acetate (VOAc) by ATRP remains challenging, largely due to the small atom transfer equilibrium constant.[151] However, the successful copolymerization of VOAc with MA has been reported.[99] In addition, VOAc has been successfully block-copolymerized by combining ATRP with other polymerization processes.[151,152] ATRP of halogenated alkenes have not yet been reported in detail.

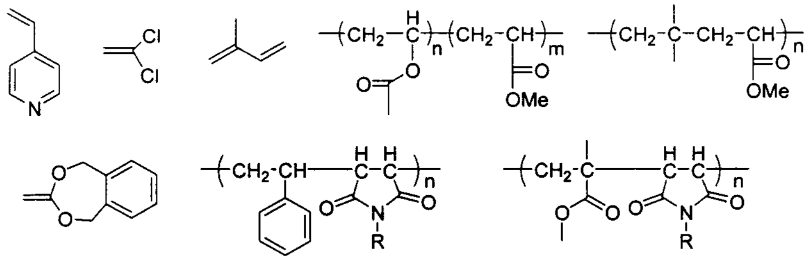
Ring-opening polymerization has been successful for several monomers, especially for those with radical-stabilizing substituents. Potential copolymerization of these monomers will lead to vinyl polymers with a hydrolyzable linkage in the main chain.[26,153] Some examples of other monomers (co)-polymerized by ATRP monomers are shown in Scheme 7.

In summary, a variety of monomers have been successfully polymerized under ATRP conditions to yield well-defined polymers. For a monomer to undergo ATRP, it is important to have stabilizing groups (e.g., phenyl or carbonyl) adjacent to the carbon radicals that produce a sufficiently large atom transfer equilibrium constant but do not interfere with the growing radical and the catalytic system. In addition, it is necessary to adjust the reaction conditions (concentrations, temperature, catalyst) to obtain a suitable radical concentration for a specific monomer.

8. Summary and Outlook

ATRP has been successful in controlling polymerization of many styrenes, acrylates, and methacrylates and several other relatively reactive monomers such as acrylamides, vinylpyridine, and acrylonitrile.

Scheme 7. Miscellaneous Monomers (co)Polymerized by ATRP



However, there are two major classes of monomers which have not yet been successfully polymerized by ATRP.

Acidic monomers fail since they can protonate ligands and form the corresponding carboxylate salts. There has been progress in this area, and methacrylic acid in the neutral form of the sodium salt has been polymerized. A similar approach has been reported for other acidic monomers. In principle, use of less basic ligands (oxygen and sulfur-based), which would also complex strongly, may prevent loss of ligands. Additionally, the acids may be used as ligands themselves: iron succinates or halides were reported as ATRP catalysts.

Halogenated alkenes, alkyl-substituted olefins, and vinyl esters are presently resistant to polymerization by ATRP. They belong to a class of monomers with very low intrinsic reactivity in radical polymerization and radical addition reactions and could have a very low ATRP equilibrium constant. To polymerize them, it will be necessary to use catalysts with very high reactivity and generally a very negative reduction potential, but this may be accompanied by reduction of the free radicals to carbanions and formation of organometallic species. Such species may react by a coordination pathway rather than via free radical intermediates. Those species may be also hydrolytically less stable and catalysts may be very sensitive to oxygen.

The range of monomers polymerizable by ATRP is greater than that accessible by nitroxide-mediated polymerization, since it includes the entire family of methacrylates. However, degenerative transfer processes, with the RAFT method being currently most often used, allows polymerization of more monomers than ATRP. Perhaps new ATRP catalysts may alleviate this problem. However, it must be stressed that each group of monomers may be best suited to a specific mechanism. For example, isobutene and vinyl ethers best fit cationic polymerization, α-olefins and perhaps dienes coordination, and/or anionic polymerization, whereas polar monomers such (meth)-acrylates seem to fit the free radical mechanism best.

D. ATRP Initiators

As discussed previously, the amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. Multifunctional initiators may provide chain growth in several directions (cf. section III.C). Fast initiation is important to obtain well-defined polymers with low polydispersities. A variety of initiators, typically alkyl halides, have been used successfully in ATRP. Many different types of halogenated compounds are potential initiators and are discussed below based on their structure.

1. Halogenated Alkanes

Halogenated alkanes, such as $CHCl_3$ or CCl_4, are typically used in atom transfer radical addition and were among the first studied as ATRP initiators.[15,16] In the ruthenium-catalyzed ATRP of MMA, molecular weights of the polymer increased linearly with the conversion; however, at high monomer conversion, the molecular weight deviated from the theoretical values.[124] The polymers obtained were monomodal with low polydispersities (ca. 1.3). In contrast, di- or monochloromethanes were not able to polymerize MMA under similar conditions.[120]

CCl_4 has also been used in other catalytic systems, including the Cu-based one.[18] When $CuCl(bpy)_3$ was used as the catalyst for the ATRP of styrene at 130 °C, CCl_4 was found to act as a bifunctional initiator.[121] Again, deviation of the molecular weights from the theoretic values was observed, and this was tentatively explained by additionally generated chains resulting from the activation of the central dichloromethylated moiety which undergoes β-scission.[121] Control of the molecular weight is possible using $CHCl_3$ for the $CuCl(bpy)_3$ system, whereas di- and monochloromethanes lead to uncontrolled polymerizations.[18] In homogeneous systems, CCl_4 is sometimes less efficient due to a potential outer-sphere electron-transfer (OSET) reaction and the reduction of the radicals to anions (cf. section II.I). Slow addition of the catalyst to the initiating system apparently improves the initiation efficiency.[42] With CCl_4 and $Ni\{o,o'\text{-}(CH_2NMe_2)_2C_6H_3\}Br$ as the catalyst, the experimental molecular weight of PMMA increased with monomer conversion but showed deviation at high conversions,[113] similar to the ruthenium system.[15] Deviation of molecular weight was also observed for the $FeCl_2(PPh_3)_2$ catalytic system.[116]

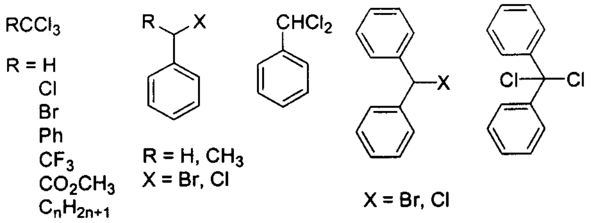
CCl_3Br successfully initiated the controlled polymerization of MMA catalyzed by $RuCl_2(PPh_3)_3$,[83] $NiBr_2(PPh_3)_2$,[44] $NiBr_2(PnBu_3)_2$,[114] or $Ni(PPh_3)_4$.[154] However, with the Ni(II)/$(PPh_3)_2$ system, other combinations of initiators and catalysts, such as $CCl_3Br/NiCl_2(PPh_3)_2$, $CCl_4/NiBr_2(PPh_3)_2$, or $CCl_4/NiCl_2(PPh_3)_2$, resulted in bimodal molecular weight distributions at high MMA conversions.[44]

2. Benzylic Halides

Benzyl-substituted halides are useful initiators for the polymerization of styrene and its derivatives due to their structural resemblance. However, they fail in the polymerization of more reactive monomers in ATRP such as MMA. For example, using CuCl(dNbpy)$_2$ as the catalyst, inefficient initiation was observed when 1-phenylethyl chloride was employed as the initiator for the polymerization of MMA.[123] PMMA with much higher molecular weights than the theoretic values and high polydispersities ($M_w/M_n = 1.5-1.8$) were obtained. In contrast, a well-controlled polymerization was realized with benzhydryl chloride (Ph_2CHCl) as the initiator under similar conditions. In fact, the radical generation was so fast that slow addition of benzhydryl chloride was necessary to avoid a significant contribution of irreversible biradical termination early in the polymerization.[123] Improvement of the initiation efficiency for the ATRP of MMA using primary and secondary benzylic halides is possible by employing the halogen exchange concept.[155]

Polyhalogenated benzylic halides have been used for the ATRP of MMA catalyzed by $RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$.[120] PMMA with very low polydispersities were obtained when Ph_2CCl_2 was used as the initiator. In contrast, $PhCCl_3$ led to a bimodal molecular weight distribution consisting of two narrowly distributed fractions, the higher of which was double the molecular weight of the other.[120] $PhCHCl_2$ has been also used in Cu-based ATRP of styrene and MMA, apparently providing two-directional growth of the polymeric chains.[156] Scheme 8 illustrates some examples of halogenated alkanes and benzylic halides used successfully in ATRP.

Scheme 8. Some Halogenated Alkanes and Benzylic Halides Used as ATRP Initiators

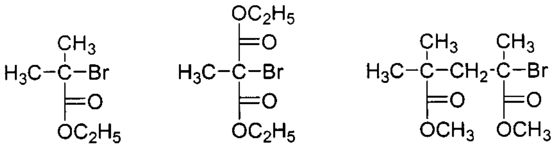


3. α-Haloesters

Various α-haloesters have been successfully employed to initiate well-controlled ATRP. In general, α-haloisobutyrates produce initiating radicals faster than the corresponding α-halopropionates due to better stabilization of the generated radicals after the halogen abstraction step. Thus, slow initiation will generally occur if α-halopropionates are used to initiate the polymerization of methacrylates. In contrast, α-bromopropionates are good initiators for the ATRP of acrylates due to their structural resemblance.

In their search for better initiators in ruthenium-mediated ATRP, Sawamoto et al. examined three α-bromoesters of different structures (Scheme 9).[120] The malonate with two geminal esters generates radicals faster than 2-bromoisobutyrate and leads to lower polydispersities. The dimeric model of the dormant chain end (dimethyl 2-bromo-2,4,4-trimethylglutarate) initiates a faster polymerization and provides PMMA with lower polydispersities than α-bromoisobutyrate, likely due to the back strain effect;[54,157,158] the release of the steric strain of the dormant species during rehybridization from the sp^3 to the sp^2 configuration leads to a higher equilibrium constant. The dimeric model has also been used in the ATRP of MMA catalyzed by $NiBr_2(PPh_3)_2$,[115] and the chloride analogue of the dimeric model compound leads to the controlled polymerization of MMA and styrene mediated by a half-metallocene-type ruthenium complexes.[159]

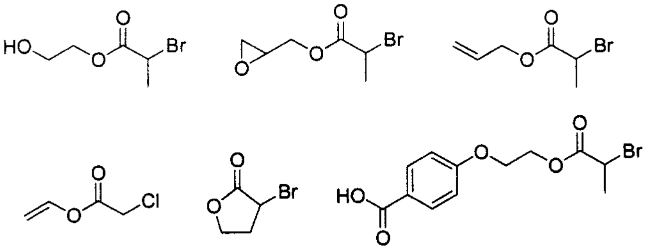
Scheme 9. Various α-Bromoesters Used in Ruthenium-Mediated ATRP of MMA



Malonate derivatives are less efficient in Cu-based ATRP, perhaps due to the previously mentioned OSET process. Slow addition of the catalyst to the initiator solution in monomer improves control tremendously.[42]

α-Haloesters with various functional groups attached can easily be prepared through a straightforward esterification reaction of the appropriate acid halides. Since ATRP can tolerate various functional groups, well-defined end-functional polymers have been conveniently prepared without the need for additional protecting reactions. A variety of functionalities, such as hydroxy, epoxy, allyl, vinyl, γ-lactone, and carboxylic acid have been introduced onto the α-end of the polymer by use of a functional initiator and will be discussed in later sections (Scheme 10).[99,128,160]

Scheme 10. Representative Functional Initiators Derived from α-Haloesters



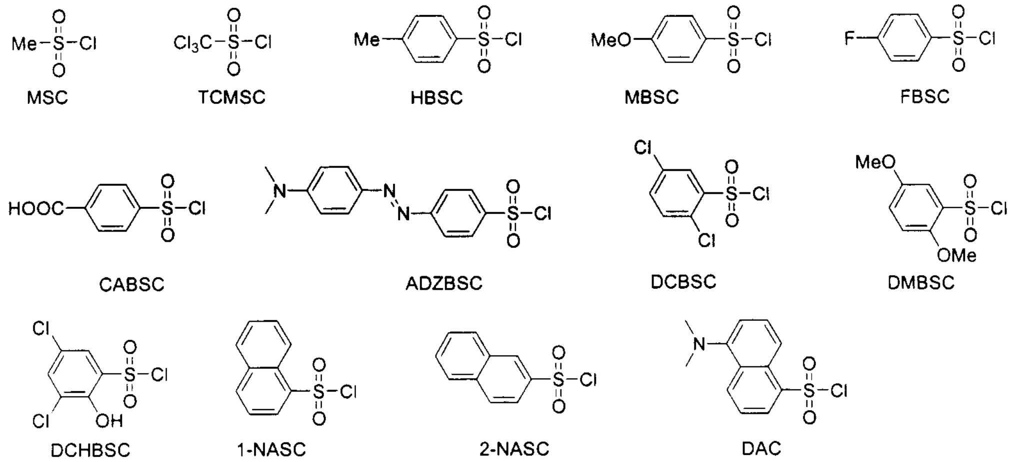
Polyhalogenated α-haloesters (e.g., $CCl_3CO_2CH_3$ and $CHCl_2CO_2CH_3$) have also been successfully applied as initiators for the ATRP of MMA catalyzed by $RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$.[120] Multiarm stars of PMMA are produced when multifunctional dichloroacetates are used in the ruthenium-catalyzed ATRP.[161,162]

Mixed benzyl and ester derivatives such as methyl α-bromophenylacetate were successfully used in the aqueous polymerization of 2-(dimethylamino)ethyl methacrylate.[163]

4. α-Haloketones

An α-bromoketone has been used to initiate the controlled polymerization of MMA catalyzed by Ni{*o*,*o*′-$(CH_2NMe_2)_2C_6H_3$}Br[113] and $Ni(PPh_3)_4$.[154] Polyhalogenated α-haloketones (e.g., CCl_3COCH_3 and $CHCl_2COPh$) are among the best initiators

Scheme 11. Examples of Sulfonyl Chlorides used as ATRP Initiators



for the ATRP of MMA catalyzed by ruthenium complexes.[83,120,159,164,165] Well-controlled polymers with low polydispersities ($M_w/M_n < 1.20$) have been obtained. The stronger electron-withdrawing power of the ketone's carbonyl induces further polarization of the carbon−chlorine bond, which is attributed to the faster initiation observed with the ketones than with the ester counterparts.

5. α-Halonitriles

α-Halonitriles are fast radical generators in ATRP, 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. Of the initiators studied for the polymerization of acrylonitrile catalyzed by copper complexes, 2-bromopropionitrile resulted in polymers with the lowest polydispersities.[131] 2-Bromopropionitrile is also the initiator of choice when a bromine initiator is desired in the iron-mediated ATRP of MMA.[98] However, α-halonitriles were not used in ruthenium-catalyzed ATRP as the cyano group deactivates the catalyst by forming a strong complex with ruthenium.[120]

6. Sulfonyl Halides

As ATRP initiators, sulfonyl chlorides yield a much faster rate of initiation than monomer propagation.[55] The apparent rate constants of initiation are about four (for styrene and methacrylates) and three (for acrylates) orders of magnitude higher than those for propagation. As a result, well-controlled polymerizations of a large number of monomers have been obtained in copper-catalyzed ATRP.[19,55] End-functional polymers have been prepared using sulfonyl chlorides where functionalities were introduced onto the aromatic ring.[166] The phenyl group substituent has only a small effect on the rate constant of initiation because the sulfonyl radical and its phenyl group are not related through conjugation.

A unique feature of the sulfonyl halides as initiators is that although they are easily generated, they only dimerize slowly to form disulfones and slowly disproportionate. Thus, they can react with the monomers and initiate the polymerization efficiently.[167]

When sulfonyl chlorides were used in the polymerization of MMA catalyzed by $RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$, S-shaped conversion vs time profiles were obtained.[168] Moreover, experimental molecular weights were higher than the theoretical values, indicating a low initiator efficiency. The polydispersities were around 1.2−1.5. The low initiator efficiency was explained by the formation of sulfonyl esters from sulfonyl chlorides and $Al(O\textit{i}Pr)_3$ during the early stages of the polymerization. Examples of sulfonyl chlorides used as ATRP initiators are shown in Scheme 11.

7. General Comments on the Initiator Structure in ATRP

Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized. Analogous to the "living" carbocationic systems, the main factors that determine the overall rate constants are the equilibrium constants rather than the absolute rate constants of addition.[169,170]

There are several general considerations for the initiator choice. (1) The stabilizing group order in the initiator is roughly CN > C(O)R > C(O)OR > Ph > Cl > Me. Multiple functional groups may increase the activity of the alkyl halide, e.g., carbon tetrachloride, benzhydryl derivatives, and malonates. Tertiary alkyl halides are better initiators than secondary ones, which are better than primary alkyl halides. These have been partially confirmed by recent measurements of activation rate constants.[171−173] Sulfonyl chlorides also provide faster initiation than propagation. (2) The general order of bond strength in the alkyl halides is R−Cl > R−Br > R−I. Thus, alkyl chlorides should be the least efficient initiators and alkyl iodides the most efficient. However, the use of alkyl iodides requires special precautions. They are light sensitive, can form metal iodide complexes with an unusual reactivity (e.g., CuI_2 is thermodynamically unstable and cannot be isolated), the R−I bond may possibly be cleaved heterolytically, and there are potential complications of the ATRP process by degenerative transfer.[174,175] By far, bromine and chlorine are the most frequently used halogens. In general, the same halogen is used in the initiator and the metal salt (e.g., RBr/CuBr); however, the halogen exchange can sometimes be used to obtain better polymerization control.[155] In a mixed halide initiating system, R−X/M_t−Y (X, Y = Br or Cl), the bulk of the polymer chains are terminated by chlorine due to the stronger alkyl−chloride bond. Thus, the rate of initiation is increased relative to propagation and ethyl 2-bromoisobutyrate/CuCl leads to a better-controlled polymerization of MMA in comparison to using ethyl 2-bromoisobutyrate/CuBr.[155] A similar result has also been observed in Ru-based ATRP.[176] The halogen exchange method also enables the use of alkyl halides of apparently lower reactivities in the polymerization of monomers with apparently higher equilibrium constants. This is especially important for the formation of block copolymers.[177−180] Pseudohalogens (e.g., SCN) have also been used in ATRP.[29,33] Initiation using benzyl thiocyanate is slow for both styrene and MA, and M_n higher than the theoretical values are obtained. Better results are obtained when alkyl halides are used as the initiators and CuSCN as the catalyst. Similarly, transition metal dithiocarbamates have been employed in the presence of AIBN to induce controlled reverse ATRP of styrene at 120 °C. Good agreement between theoretical and experimental M_n values were obtained with $M_w/M_n = 1.15-1.30$.[32] (3) Successful initiation in ATRP can depend strongly on the choice of catalyst. For example, 2-bromoisobutyrophenone initiates the controlled polymerization of MMA catalyzed by ruthenium or nickel complexes but has not been successfully used in the copper-mediated ATRP. This is ascribed to the reduction of the resulting electrophilic radical by the copper(I) species as the copper catalysts have lower redox potentials. (4) The method or order of reagent addition can be crucial. For example, slow addition of the benzhydryl chloride initiator to the CuCl(dNbpy)$_2$-catalyzed ATRP of MMA generates a lower concentration of benzhydryl radicals and thus reduces the rate of termination between the radicals. The diethyl 2-bromomalonate/CuBr system initiates the ATRP of styrene, and the polymerization was well controlled when the catalyst was added slowly to the initiator/monomer solution. This avoided the potential reduction of the malonyl radical by the copper(I) species. It may also be surprising, but the heterogeneous catalytic systems may provide more efficient initiation than homogeneous ones when very reactive alkyl halide initiators are used, most likely due to slow dissolution of the catalyst and hence its lower instantaneous concentration. For example, CCl_4 is a good initiator for styrene and MMA with CuBr(bpy)$_3$ as the catalyst,[18] but the same is not true using the CuBr(dNbpy)$_2$ catalytic system. The initiation efficiency increased when the catalyst solution was added slowly to the initiator solution.[42]

8. Summary and Outlook

Range of available initiators for ATRP is much larger than for other CRP methods. In fact, many NMP and RAFT reagents are prepared from ATRP initiators, i.e., activated alkyl halides by either nucleophilic displacement (RAFT) or radical trapping in the presence of Cu(0) (NMP). The basic requirement for a good ATRP initiator is that it should have reactivity at least comparable to that of the subsequently formed growing chains. This also indicates that not all initiators are good for all monomers. This is an extremely important criterion for the preparation of block copolymers. Very reactive initiators may produce too many radicals, which will terminate at early stages. This will reduce efficiency of initiation, produce too much of the deactivator, and slow the process. Perhaps one of the few exceptions is a class of sulfonyl halides which terminate relatively slowly by the irreversible radical termination.

It is necessary to better correlate structures of the alkyl halides with their ATRP reactivities. This includes both the alkyl part (electronic and steric effects) and (pseudo)halogens. The ATRP reactivity includes not only the BDE of the C−X bond, but also halogenophilicity of the transition metal. Thus, the structure−reactivity correlation should include both components as well as the effects of solvent and temperature. Comparison of model and macromolecular compounds is also important as well as extension to dense systems to compare intra- and intermolecular effects. This will be especially important for the macromolecular engineering of complex polymeric structures.

Halogen end groups are an inherent part of the ATRP systems. They can be replaced by many synthetic methods to provide more useful functionalities and provide halogen-free products. Pseudohalogens such as (iso)thiocyanate and azide groups have also been used as exchangeable end groups in ATRP and are quite attractive, since they may be hydrolytically more stable and can provide direct pathways to end-functional polymers. There are many multifunctional activated halides which enable simultaneous growth of chains in several direction, leading to star, comb, and brush macromolecules.

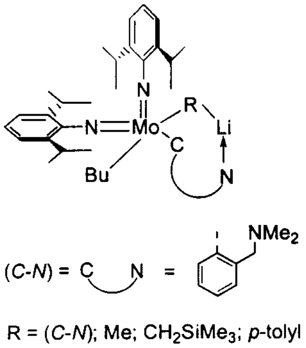
E. Transition Metal Complexes

A number of transition metal complexes have been applied in ATRP. As mentioned previously, to generate growing radicals, the metal center should undergo an electron transfer reaction with the abstraction of a (pseudo)halogen and expansion of the coordination sphere. In addition, to differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species. The applications and scope of the different transition-metal complexes are discussed following their periodic groups.

1. Group 6: Molybdenum and Chromium

A series of lithium molybdate(V) complexes [LiMo(NAr)$_2$(C−*N*)R] (C−*N* = $C_6H_4(CH_2NMe_2)$-2; R = (C−*N*), Me, CH_2SiMe_3, or *p*-tolyl), have been used in the ATRP of styrene using benzyl chloride as the initiator (Scheme 12).[181] The molybdate(V) complexes were generated in situ from the reaction of the corresponding molybdenum(VI) complexes [Mo(NAr)$_2$(C−*N*)R]. Relatively high polydispersities ($M_w/M_n \approx 1.5$) were obtained, and the efficiency of the benzyl chloride initiator was rather poor (6−18%), which was ascribed to the extreme air-sensitivity of the lithium

Scheme 12. Molybdate(V) Complexes used as ATRP Catalysts



molybdate(V) compounds. In addition, a side reaction occurred in ATRP; the lithium molybdate(V) reacted with (α-chloroethyl)benzene and (α-bromoethyl)benzene and resulted in the formation of LiCl and LiBr, respectively.

There has also been a report suggesting that chromium derivatives may act as ATRP catalysts, but there was no evidence to support a radical process, which could also have occurred through an anionic/coordination pathway.[182]

2. Group 7: Rhenium

Rhenium belongs to group 7 and shows the characteristics of both the early and late transition metals. Recently, rhenium(V) iododioxobis(triphenylphosphine) ($ReO_2I(PPh_3)_2$) in the presence of Al(O*i*Pr)$_3$ was reported to be an effective catalyst for the controlled polymerization of styrene using an alkyl iodide as the initiator.[30] Polymerizations were carried out at temperatures between 30 and 100 °C, with faster reactions at higher temperatures. Polydispersities were lower with decreasing temperature ($M_w/M_n \approx 1.50$ at 100 °C and 1.26 at 30 °C). Well-defined polystyrenes with M_n up to 40 000 and $M_w/M_n \approx 1.1-1.2$ were prepared in bulk at 80 °C. Of the iodide initiators studied, $(CH_3)_2C(CO_2Et)I$ and $CH_3CH(Ph)I$ resulted in lower polydispersities than $CH_3CH(CO_2Et)I$. In addition, $CH_3CH(CO_2Et)I$ as the initiator led to M_n slightly higher than the calculated values during the early stage of the polymerization, indicative of slow initiation from the acrylate-type initiators. ^{1}H NMR end-group analysis showed the presence of one initiator moiety (R) at the α-end and one iodine atom at the ω-end, both derived from the initiator R−I. Quenching experiments showed that adding methanol or water did not inhibit the polymerization, while 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) immediately and completely shut down the reaction. Interestingly, the polystyrene quenched with TEMPO did not show any TEMPO-related peaks in the ^{1}H NMR. ^{1}H and ^{13}C NMR analysis of a mixture of $ReO_2I(PPh_3)_2$ and TEMPO indicated a possible interaction between these two compounds. It was concluded that the polymerization does not proceed via an ionic mechanism, and a radical pathway was suggested. However, it is possible that the rhenium complexes slowly generate the initiating radicals but that control of the polymerization results from the degenerative transfer with the alkyl iodides.[175] It would be helpful to analyze the deactivation rates of the Re(VI) species.

3. Group 8: Ruthenium and Iron

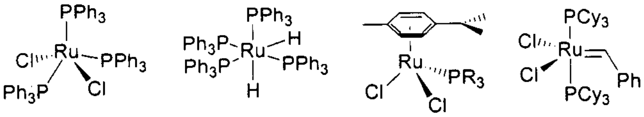
Ruthenium and iron belong to the group 8 transition metals and have been well studied in atom transfer radical addition reactions.

a. Ruthenium. The polymerization of MMA via ruthenium-catalyzed ATRP was first reported by Sawamoto et al. in 1995.[15] The polymerization was carried out using CCl_4 as the initiator, $RuCl_2$ complexed by 3 equiv of PPh_3 as the catalyst, and a Lewis acid such as methylaluminum bis(2,6-di-*tert*-butylphenoxide) as the activator in 75−80 vol % toluene at 60 °C. No polymerization was observed in the absence of the Lewis acid. A linear semilogarithmic plot of conversion vs time was obtained, indicating a constant number of propagating chains. The polymer molecular weights increased linearly with monomer conversion initially but deviated from the theoretical values at high conversions. Chain extension was observed upon addition of new monomer, indicating that polymerization had a “living” nature. The polymers produced were monomodal and had low polydispersities ($M_w/M_n \approx 1.3$). More controlled polymerizations were later obtained using $RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$ as the catalyst and α-haloesters, such as ethyl 2-bromoisobutyrate, as the initiator.[164]

The polymerization mediated by the ruthenium complex was proposed to follow a radical pathway based on several experimental data.[165] First, the polymerization was inhibited in the presence of TEMPO, galvinoxyl, and 1,1-diphenyl-2-picrylhydrazyl (DPPH). In contrast, the presence of H_2O or methanol did not affect the polymerization. In fact, well-defined PMMA was obtained through a suspension polymerization in water and alcohol.[83] Second, the presence of the initiator moiety at the α-end group was confirmed by ^{1}H NMR analysis, and the functionality was close to 1. The presence of the halogen atom at the ω-end group was confirmed by two different methods: ^{1}H NMR analysis and clean chain extension with a fresh feed of MMA using an unisolated and isolated macroinitiator. Third, the tacticity of the PMMA prepared by the ATRP catalyzed by the ruthenium complex had a slight preference for syndiotacticity which was similar to those prepared by a free-radical process. It should be noted that the intermediacy of a persistent Ru(III) radical was recently confirmed in the study of ATRP of MMA using a binuclear Ru(II) N_2-bridged complex, $[\{RuCl_2(NN'N)\}_2(\mu\text{-}N_2)]$ ($NN'N$ = 2,6-bis[(dimethylamino)methyl]pyridine).[183]

More reactive ruthenium-based ATRP catalysts employing carbon-centered ligands, i.e., 4-isopropyltoluene (*p*-cymene),[104,184,185] indenyl (Ind), and cyclopentadienyl (Cp),[159,186] have recently been reported (Scheme 13). A direct relationship between the arene ligand lability and the catalyst activity suggests that the *p*-cymene ligand is released in the ATRP process. Well-defined polystyrene as well as PMMA have been obtained using the new catalysts with $M_n \approx 40\ 000$ and $M_w/M_n \approx 1.1$. A halogen-free Ru(II) hydride complex, $RuH_2(PPh_3)_4$, is also more reactive than

Scheme 13. Ruthenium Complexes used as ATRP Catalysts



$RuCl_2(PPh_3)_3$. The polymerization of MMA can be carried out at or above room temperature without the use of additional aluminum compounds.[187]

Apparently, some Ru-based ROMP catalysts can directly catalyze the ATRP process while simultaneously being active in ROMP.[188]

b. Iron. In the presence of a preformed metal complex, $FeCl_2(PPh_3)_2$, CCl_4 induced the controlled polymerization of MMA at 80 °C in toluene.[116] The polymer molecular weights increased linearly with the monomer conversion initially, but deviation from the theoretical values was observed at higher conversions. Polydispersities were around 1.4. Addition of $Al(O\textit{i}Pr)_3$ accelerated the polymerization; however, molecular weight control was lost. The molecular weights decreased as the MMA was consumed with high molecular weight polymers obtained at low conversions. The polydispersity was high ($M_w/M_n \approx 3.0$).

A series of other organic halides, i.e., $CHCl_2COPh$, $(CH_3)_2CBrCO_2Et$, and $CH_3CBr(CO_2Et)_2$, were used as initiators in place of CCl_4 and led to the controlled polymerization of MMA with $M_w/M_n = 1.3-1.5$. With $CHCl_2COPh$ or $(CH_3)_2CBrCO_2Et$ as the initiator, the molecular weights obtained did not increase linearly with the monomer conversion and were higher than the theoretical values. When $CH_3CBr(CO_2Et)_2$ was used, a linear increase of the molecular weight with conversion was observed, however, the initiator efficiency was low. The authors attributed this to the interaction of $CH_3CBr(CO_2Et)_2$ with the $FeCl_2(PPh_3)_2$ catalyst to form a new iron complex.

Matyjaszewski et al. reported on several iron-based ATRP catalytic systems for the controlled polymerization of styrene and MMA.[98] As shown in Table 1, triethyl phosphite, a common ligand for iron in ATRA has a lower efficiency in ATRP. In contrast, dNbpy, $N(\textit{n}Bu)_3$, and $P(\textit{n}Bu)_3$ promote controlled polymerizations with high initiator efficiencies and leading to polymers with low polydispersities.

Table 1. Results of Bulk Polymerization of Styrene with Different Fe-Based Catalytic Systems at 110 °C

ligand	time (h)	conv (%)	$M_{n,Cal}$	$M_{n,SEC}$	M_w/M_n
$P(OEt)_3$[a]	15.0	87	9 200	30 500	6.14
PPh_3[a]	15.0	47	5 100	4 200	1.76
dNbpy[b]	21.0	64	6 800	6 500	1.27
$N(\textit{n}Bu)_3$[c]	10.0	78	16 800	17 000	1.24
$P(\textit{n}Bu)_3$[c]	6.0	81	16 900	17 500	1.38

[a] $PEBr/FeBr_2$/ligand/styrene = 1/1/3/100, where PEBr = (1-bromo)ethylbenzene. [b] $PEBr/FeBr_2$/ligand/styrene = 1/1/2/100. [c] $PEBr/FeBr_2$/ligand/styrene = 1/1/3/200.

The rate and polydispersity varied significantly depending on the catalytic system utilized for the ATRP of styrene. When dNbpy was used as the ligand, the polymerization proceeded quite slowly, with 64% monomer conversion after 21 h at 110 °C. The polydispersity of the polymers obtained was quite low ($M_w/M_n < 1.2$). $P(\textit{n}Bu)_3$ as the ligand led to a much faster polymerization with ca. 80% conversion of styrene in 6 h; however, the polydispersity was also higher ($M_w/M_n = 1.3-1.4$). Mixed ligands afforded an improved polymerization rate and polydispersity. For example, when a 1:1 mixture of dNbpy and $P(\textit{n}Bu)_3$ were used as the ligand, the ATRP of styrene proceeded with a comparable rate to that catalyzed by $FeBr_2-P(\textit{n}Bu)_3$ but with polydispersities similar to those prepared by $FeBr_2$(dNbpy). A mixed dNbpy and $N(\textit{n}Bu)_3$ system was used in a similar way. For the mixed-ligand system, it was proposed that all the catalytic species were in dynamic equilibrium with each other and that the ligands were likely to scramble between the active centers, contributing to the overall control of the polymerization.

Complexes of $FeBr_2$-dNbpy and $FeBr_2-N(\textit{n}Bu)_3$ both catalyzed the controlled ATRP of MMA to yield polymers with molecular weights up to 80 000 in 50 vol % *o*-xylene at 80 °C, but lower polydispersities were observed using dNbpy ($M_w/M_n \approx 1.2$) than when $N(\textit{n}Bu)_3$ ($M_w/M_n \approx 1.5$) was used as the ligand. Similar to the $FeCl_2(PPh_3)_2$ system, the choice of the initiator was important in the polymerization and fast initiation was essential to obtain well-defined PMMA. Ethyl 2-bromoisobutyrate (EB*i*B), 2-bromopropionitrile (BPN), and *p*-toluenesulfonyl chloride (*p*TsCl) yielded polymers with predictable molecular weights and low polydispersities (Table 2).

Table 2. Results of Iron-Mediated Polymerization of MMA with Different Initiating Systems at 90 °C[a]

initiator	conv (%)	$M_{n,Cal}$	$M_{n,SEC}$	M_w/M_n
BnBr	59.5	11 900	21 400	1.60
EB*i*B	72.3	14 500	15 200	1.38
BPN	60.6	12 100	12 800	1.25
*p*TsCl	53.0	10 600	10 700	1.24

[a] 50 vol % toluene, $[MMA]_o/[Initiator]_o/[FeBr_2]_o/[dNbpy]_o$ = 200/1/1/1.

Addition of 1 equiv of a radical inhibitor, such as galvinoxyl, completely inhibited the polymerization and the tacticity of the PMMA prepared by the iron catalyst closely resembled that prepared by a conventional free-radical polymerization.

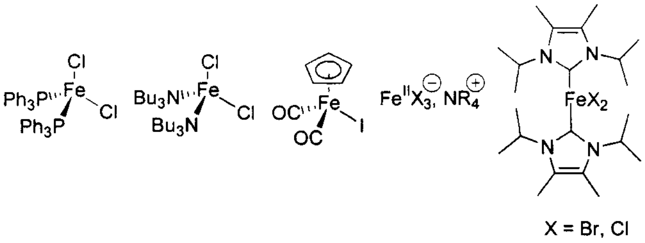
MMA has been polymerized using AIBN as the initiator in the presence of $FeCl_3/PPh_3$ at 85 °C either in bulk or in solution.[73] The polymerization was first order in monomer. An inhibition period was observed during the initial stage of the polymerization. This was attributed to the deactivation of the initiating/growing radicals by Fe(III) to form the alkyl halide dormant species and the generation of Fe(II) as indicated by the color change from deep orange to light yellow. The molecular weight increased linearly with conversion, and the polydispersities were quite low ($M_w/M_n < 1.3$). The initiator efficiency was lower when the polymerization was carried out in bulk rather than in solution, due to a larger proportion of termination in the bulk polymerization. The polymerization was significantly faster than that carried out using $CCl_4/FeCl_3/PPh_3$, with >95% yield after 2 h. ^1H NMR studies confirmed the presence of the

AIBN fragment moiety as the α-end group. ^1H NMR and chain extension experiments established that Cl atoms were present as the ω-end groups.

Ligands other than nitrogen- and phosphine-based ones have also been studied.[105,189,190] For example, a half-metallocene catalyst, $FeCp(CO)_2I$, yielded polystyrene with low polydispersities ($M_w/M_n = 1.1$). Interestingly, the addition of a metal alkoxide, either $Al(O\textit{i}Pr)_3$ or $Ti(O\textit{i}Pr)_4$, decreased the polymerization rate.[190] In another study, $FeBr_2$ complexed with ammonium and phosphonium chloride, bromide, or iodide salts induced the controlled polymerization of both styrene and methacrylates. In addition, well-defined poly(methyl acrylate) was produced for the first time using iron-based ATRP.[105] Reverse ATRP, initiated by AIBN/$FeBr_3$/onium salts, led to a controlled polymerization of both methyl methacrylate and methyl acrylate, while for styrene uncontrolled molecular weights and high polydispersities were obtained, presumably due to the involvement of the cationic polymerization.[105]

Recently, a ferrous halide complexed by 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Pr*i*Im) was found to be highly reactive and efficient in the ATRP of MMA and styrene (Scheme 14). The high catalyst activity was attributed to the high electron donacity of the ligand.[117]

Scheme 14. Iron Complexes used as ATRP Catalysts



4. Group 9: Rhodium

Rhodium belongs to the group 9 transition metals. Wilkinson's catalyst, $RhCl(PPh_3)_3$, which has found wide application as a homogeneous hydrogenation catalyst in organic chemistry, has been employed in the ATRP of styrene with a sulfonyl chloride as the initiator.[43] However, poor control and polymers with high polydispersities ($M_w/M_n \approx 1.8-3.2$) were obtained. In contrast, the successful ATRP of MMA was carried out using 2,2′-dichloroacetophenone as the initiator in the presence of $RhCl(PPh_3)_3$ and 7 equiv of PPh_3 in THF or a mixture of THF and H_2O.[119] The experimental molecular weights of PMMA agreed well with the predicted values up to 200 000, and the molecular weight distributions were relatively narrow ($M_w/M_n \approx 1.5$). A linear semilogarithmic plot of the monomer conversion vs time was observed. From the apparent polymerization rate and the propagation rate constant for MMA, the radical concentration of the polymerization reaction carried out in THF was estimated at 3.16×10^{-8} M. Interestingly, water was found to accelerate the polymerization significantly. Chain extension to *n*-butyl acrylate and MMA was successful after purification of the first block by precipitation into methanol. A lower initiator efficiency was observed when the polymerization of styrene was carried out using the same catalyst at 130 °C using *p*-methoxybenzenesulfonyl chloride as the initiator. The tacticity of the PMMA, inhibition studies (galvinoxyl), and end-group analysis indicated that radical intermediates were present in the polymerization.

5. Group 10: Nickel and Palladium

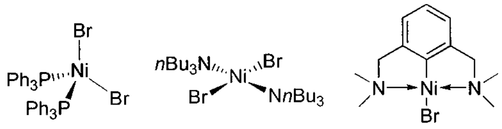
As group 10 late transition metals, nickel and palladium have been widely used in organometallic chemistry for carbon−carbon bond formation through the oxidative addition/reductive elimination mechanism. Complexes of nickel and palladium have also been studied as ATRP catalysts.

a. Nickel. One of the first attempts to use Ni(0) derivatives was undertaken by Otsu, however, with very low initiator efficiency.[25] Subsequently, one of the most reactive ATRA catalysts was used, $Ni\{o,o'\text{-}(CH_2NMe_2)_2C_6H_3\}X$ (denoted as Ni(NCN)Br), but initially failed to promote the ATRP of styrene due to its instability at high temperatures.[43] By lowering the reaction temperature to 80 °C, Ni(NCN)Br was successfully applied to the controlled polymerization of MMA with molecular weight up to 100 000. Polydispersities remained low ($M_w/M_n \approx 1.2$) throughout the reaction.[113] Interestingly, the molecular weight distribution broadened significantly when the polymerization was carried out in toluene under otherwise identical reaction conditions. The thermolysis of the obtained PMMA indicated the absence of abnormal linkages, such as the head to head linkages and vinylidene ends. The suspension polymerization of MMA was successful, with a high conversion of MMA and reasonable molecular weights. However, the polydispersity of the obtained polymer was relatively high ($M_w/M_n \approx 1.7$).

Despite the earlier proposal that ATRA catalyzed by Ni(NCN)Br may not proceed via a radical mechanism, as evidenced by the high regioselectivity of the final 1:1 adduct,[191] a radical pathway was proposed for the ATRP of methacrylates based on several lines of evidence.[113] First, the reaction was catalytic. When a catalyst-to-initiator ratio of 0.1 was used, the polymerization proceeded quite smoothly without sacrificing the molecular weight control but with slightly higher polydispersities. The oxidative addition/insertion/reductive elimination mechanism would require a stoichiometric amount of catalyst to initiator since each transition-metal center is permanently associated with the chain end. Second, the polymerization was inhibited by radical scavengers such as galvinoxyl. Third, end-group analysis indicated the presence of initiator moiety as the α-end group of the polymer chain and the halogen as the ω-end group. Finally, the tacticity of PMMA prepared using Ni(NCN)Br as the catalyst was similar to that prepared by conventional radical polymerizations.

Nickel halides complexed by phosphorus ligands have also been used for the ATRP of MMA (Scheme 15).[44,114,115] $CCl_3Br/NiBr_2(PPh_3)_2$ provided a smooth polymerization to yield polymers with predictable molecular weights and low polydispersities ($M_w/M_n \approx 1.20$) in the presence of $Al(\textit{i}OPr)_3$.[44] It was reported,

Scheme 15. Nickel Complexes used as ATRP Catalysts



however, that the $NiBr_2(PPh_3)_2$ complex was not stable or soluble in organic solvents. Decomposition of the catalyst was noted after prolonged use at high temperatures (60−80 °C), and the rate of polymerization decreased with time. In another paper, Teyssié et al. reported that $NiBr_2(PPh_3)_2$ catalyzed the ATRP of MMA in the absence of any Lewis acid additive.[115] A high monomer concentration and a large excess of the PPh_3 ligand helped preserve the control over the polymerization. The obtained PMMA displayed better thermal stability compared to that made by a conventional radical polymerization. In addition, the ATRP of *n*-butyl acrylate with $M_n \approx 35\,000$ and $M_w/M_n < 1.2$ was also successfully carried out.

Other nickel catalysts have also been studied. $NiBr_2(PnBu_3)_2$ was more thermally stable and soluble than $NiBr_2(PPh_3)_2$ and led to the controlled ATRP of both methacrylates and acrylates.[114] For methacrylates, $Al(iOPr)_3$ or other additives had no effect on the rate or control of the polymerization. More recently, a zerovalent nickel complex, $Ni(PPh_3)_4$, was reported to catalyze the controlled polymerization of MMA in the presence of $Al(iOPr)_3$.[154] The polymerization profile was similar to the $NiBr_2(PPh_3)_2/Al(iOPr)_3$ systems; however, a bimodal distribution was observed when a fresh feed of MMA was added to the reaction mixture after the initial monomer feed reached 90% conversion. This was attributed to excessive termination. A lower initiator efficiency was observed at a higher catalyst to initiator (Cl_3CBr) ratio, which was ascribed to the possible interaction between the catalyst and the initiator through an oxidative addition reaction. It was postulated that the real catalyst was likely a Ni(I) species, although the involvement of Ni(II) was not excluded.

The polymerization mediated by the nickel halides complexed by the phosphorus ligand was proposed to proceed via a radical mechanism based on inhibition studies (TEMPO), end-group measurements, and the tacticity analysis of the obtained polymers.[114] The study of the reactivity ratios of the MMA and *n*BA copolymerization also supports a radical mechanism.[115]

b. Palladium. PMMA with molecular weights up to 150 000 has been synthesized using $Pd(OAc)_2$ complexed by PPh_3 as the catalyst and CCl_4 as the initiator in 63 vol % toluene at 70 °C.[118] A good correlation between the theoretical and experimental molecular weights was observed when a 10-fold excess of the catalyst over the initiator was used. Lower ratios of catalyst to initiator (<10) resulted in high polydispersities and low initiator efficiencies, which was attributed to the low turnover of the palladium catalyst. The correct ratio of PPh_3 ligand to $Pd(OAc)_2$ was essential for the preparation of well-defined polymers. The absence of ligand led to an ill-controlled polymerization with very high molecular weights and polydispersities. In the presence of 4 equiv of ligand, the polymerization control was significantly improved. High conversion, high initiator efficiency (~1), and low polydispersities were obtained. However, the initiator efficiency decreased to 0.3 when a 10-fold excess of ligand relative to palladium was used. The polymerization temperature was also optimized. Slow initiation was observed at low temperatures (20 °C), while the catalyst was unstable at high temperatures (90 °C). The optimal polymerization reaction temperature was 70 °C. At this temperature a linear increase of the experimental molecular weights vs the monomer conversion was observed with an initiator efficiency close to unity. The relatively high polydispersity was likely due to either slow initiation or slow exchange between the active and dormant species. The polymerization was insensitive to water. A suspension polymerization has been carried out to yield PMMA of $M_n = 32\,500$ and $M_w/M_n = 1.55$. Inhibition studies (with 1,1-diphenyl-2-picrylhydrazyl or galvinoxyl), a composition study of poly(MMA-*b*-styrene), and the tacticity analysis of the obtained PMMA were used to support a radical mechanism for the polymerization.

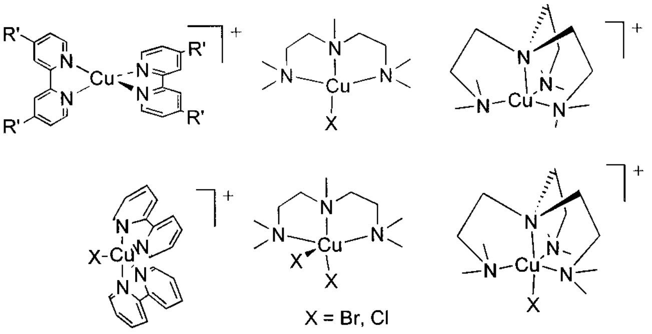
6. Group 11: Copper

Copper catalysts are superior in ATRP in terms of versatility and cost. Styrenes, (meth)acrylate esters and amides, and acrylonitrile have been successfully polymerized using copper-mediated ATRP.[22−24] The first copper-based ATRP system was reported in 1995.[16,18] Initially, cuprous halides complexed by three molecules of bpy were used as the catalysts. Controlled polymerizations with a linear increase of the molecular weight with conversion were achieved for styrene, MA, and MMA.[67] The polydispersities were fairly narrow ($M_w/M_n = 1.2-1.5$), and polymers with molecular weights up to 100 000 were prepared with good control. Well-defined polyacrylonitrile has also been prepared.[131,132]

It was proposed that the polymerization proceeded via a radical pathway based on several experimental data.[192] Thus, radical scavengers (e.g., galvinoxyl, TEMPO) terminated the polymerization. The polymerization was tolerant to a variety of functional groups, such as −OH and $-NH_2$, and insensitive to additives, such as H_2O, CH_3OH, and CH_3CN.[35] The tacticity of the PMMA prepared by ATRP catalyzed by copper complexes was similar to that prepared by a free-radical process. In addition, regio- and chemoselectivities were similar to those in conventional free-radical polymerizations. This is related to the microstructure of the polymers and the end groups, the reactivity ratios, and the sensitivity to transfer agents.[18,133,193] PRE results in the formation of a paramagnetic Cu(II) species detected by EPR.[57,63,194,195] Finally, the ATRP equilibrium can be approached from the other side, via reverse ATRP, using a CuX_2/L species and AIBN.[67,70,71]

Various polydentate ligands, such as phenanthroline and its derivatives,[196−198] substituted 2,2′:6′,2″-terpyridine,[199] and pyridineimines,[112,200] have been used for copper-mediated ATRP. The use of multidentate aliphatic amines as the ligand, both linear[79,101,201] and branched,[106,202] greatly reduced the

Scheme 16. Copper Complexes used as ATRP Catalysts



cost of the catalyst and dramatically increased the rate of the polymerization while still maintaining an overall good control. In addition, mutidentate picolylamines, which can easily be prepared and allow for further modifications and tuning of the catalyst, promoted well-controlled polymerizations of styrene and (meth)acrylates.[203] Branched tetradentate ligands, such as Me_6TREN and TPMA, provide the most strongly reducing ATRP catalysts.[106,203] Copper(I) prefers a tetrahedral or square planar configuration, which can be achieved in the cationic complexes with tetradentate ligands or with two bidentate ligands. Tridentate ligands presumably form neutral complexes. On the other hand, copper(II) forms cationic trigonal bipyramidal structures with tetradentate ligands or two bidentate ligands. Tridentate ligands apparently form square pyramidal neutral complexes with the longer Cu−X bond in the apical position.

Counterions other than halides have also been used.[33,53,60,204] With cuprous carboxylates such as cuprous acetate (CuOAc), the polymerization rate was significantly increased; however, the rate increase was accompanied by a decreased control over the polymerization, as indicated by higher than calculated experimental molecular weights and an increase of the polydispersities for the CuOAc-dNbpy catalytic system. Addition of a small amount of either the Cu(II) or Cu(I) halide to the cuprous carboxylate system yielded better controlled ATRP of styrene while still maintaining a fast polymerization.[60] A similar rate enhancement was observed for the ATRP of MA catalyzed by a $CuPF_6(dNbpy)_2$ complex.[53] Copper thiocyanate was used in ATRP of styrene, acrylates, and MMA.[29,33] Additionally, copper triflate was also successfully used with various ligands to promote controlled polymerizations.[204] Recently, CuY/bpy systems where Y = O, S, Se, Te were successfully applied in the ATRP of MMA in conjunction with alkyl halides.[205]

7. Summary and Outlook

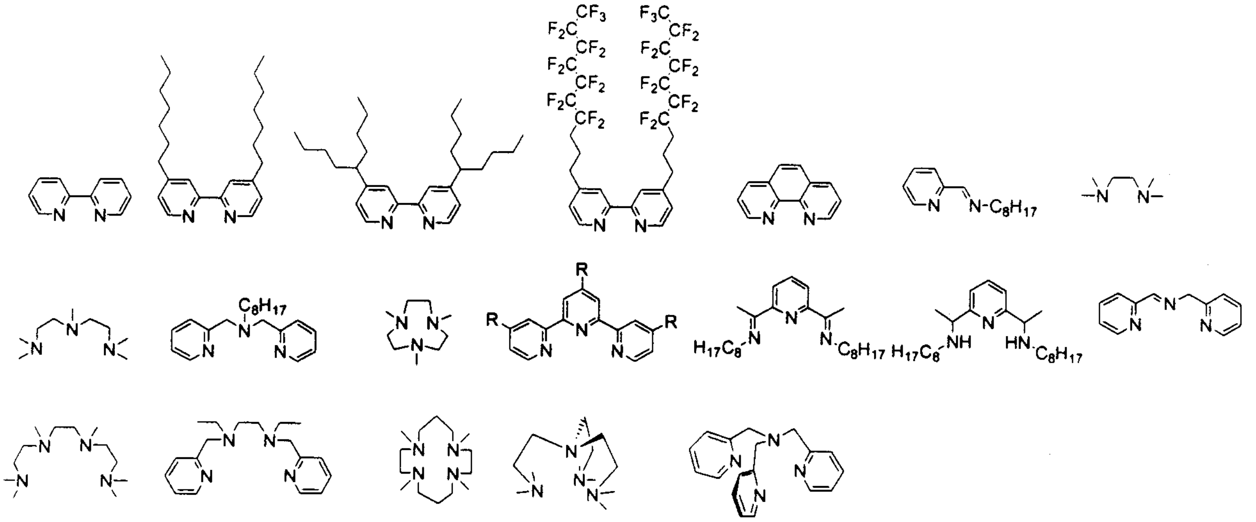
Transition metal complexes are perhaps the most important components of ATRP and also the most obscure. It is possible that some reported catalytic systems may lead not only to the free radical process but also to ionic and/or coordination polymerization. Some iodine-based systems may redox-initiate polymerization and attain control due to an iodine degenerative transfer process. Currently, complexes of late and middle transition metals are most efficient catalysts for ATRP. However, catalytic activity and selectivity is strongly ligand dependent. It is feasible that, as in single-site catalysts for coordination polymerization of olefins, the pendulum may swing from early to late and perhaps again back to early transition metals. This is possible by careful design of ligands, which dramatically increase selectivities and also activities of the involved complexes. Since CRP is very often used for polar monomers, early transition metals may be deactivated by (meth)acrylates due to their high oxophilicity and perhaps weaker halogenophilicity. They may also form direct bonds to carbon and abstract β-hydrogens. However, some ligands may provide high selectivity for halogen transfer over other pathways. It may be very interesting to explore lanthanides as potential catalysts due to the flexibility of the coordination sphere and large range of redox potentials.

The ideal catalyst for ATRP should be highly selective for atom transfer and should not participate in other reactions. It should deactivate extremely fast with diffusion-controlled rate constants, and it should have easily tunable activation rate constants to meet particular requirement for specific monomers. Thus, very active catalysts with equilibrium constants for styrenes and acrylates $K > 10^{-8}$ are not suitable for methacrylates. Polymerization of acrylamides requires higher activities (corresponding to $K > 10^{-7}$ for styrenes). Potential control of vinyl acetate and vinyl chloride may need catalysts with $K > 10^{-5}$ (for styrenes). These have not yet been developed.

The overall thermodynamic activity defined by the equilibrium constant is not sufficient to define the utility of the catalyst, and the aforementioned dynamics of exchange is of paramount importance. This requires facile rearrangement and expansion of the coordination sphere to accommodate incoming halogen. As will be discussed later, there is a correlation of the ATRP equilibrium constants and electrochemical redox potential for the outer-sphere electron transfer (OSET). However, the equilibrium constant depends also on the affinity of the complex to halogens. Thus, late transition-metal complexes are more reducing but have lower affinity to halogens. This may allow one to choose the appropriate complexes for different monomer groups to avoid side reactions associated with the oxidation and reduction of propagating free radicals.

It is expected that many new transition-metal complexes will be developed as very efficient ATRP catalysts. To make the quest for such catalysts more rational, it is necessary to better understand structures of both activators and deactivators and correlate them with the ATRP activities in model and macromolecular systems. It is possible to envisage that high-throughput methodologies will be applied for such research. However, it has to be realized that negative results (e.g., no polymerization) may indicate not only that a chosen catalytic system is not active enough, but also that it is too active and produces too many radicals which terminate at a very early stage. Thus, more systematic studies with either several monomers or catalysts/initiator ratios are needed to evaluate new catalytic systems.

Scheme 17. Examples of Ligands Used in Copper-Mediated ATRP



F. Ligand

The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer.[206] There are several guidelines for an efficient ATRP catalyst. First, fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkyl halide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third, fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth, relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of the radicals.

1. Nitrogen Ligands

Nitrogen ligands have been used in copper- and iron-mediated ATRP.[98,206] For copper-mediated ATRP, nitrogen-based ligands work particularly well. In contrast, sulfur, oxygen, or phosphorus ligands are less effective due to inappropriate electronic effects or unfavorable binding constants.

Both monodentate (e.g., $N(nBu)_3$) and bidentate (e.g., dNbpy) ligands have been applied to iron-mediated ATRP. For copper-based ATRP, the coordination chemistry of the transition-metal complex greatly affects the catalyst activity. Thus, although monodentate ligands are suitable for most of the transition metal salts employed in ATRA, they do not promote controlled copper-mediated ATRP. In contrast, a variety of multidentate nitrogen ligands have been successfully developed.[206] The electronic and steric effects of the ligands are important. Reduced catalytic activity or efficiency is observed when there is excessive steric hindrance around the metal center or the ligand has strongly electron-withdrawing substituents. A recent survey summarized different ligands employed in copper-mediated ATRP. The effect of the ligands and guidelines for ligand design were reviewed.[206] Activity of N-based ligands in ATRP decreases with the number of coordinating sites N4 > N3 >N2 ≫ N1 and with the number of linking C-atoms C2 > C3 ≫ C4. It also decreases in the order $R_2N- \approx$ PyrEnDash− > R−N= > Ph-N= > Ph−NR−. Activity is usually higher for bridged and cyclic systems than for linear analogues. Examples of some N-based ligands used successfully in Cu-based ATRP are shown in Scheme 17.

Ligands may participate in side reactions.[207] For example, Kubisa et al. studied the ATRP of several acrylates under conditions when low molecular weight polymers ($M_n = 2000$) were targeted using relatively high concentrations of the catalyst. MALDI TOF analysis of the polymer samples isolated at different stages of the polymerization revealed that in the course of the polymerization potentially active macromolecules terminated with bromine were gradually converted into inactive macromolecules devoid of terminal bromine. A possible chain transfer to the aliphatic amine ligand was proposed. Additionally, amines (and phosphines) react with alkyl halides by a nucleophilic substitution reaction, with loss of HX through a Hoffman elimination process.[208,209] For example, methyl 2-bromopropionate reacts with n-butylamine at 25 °C in DMSO with the rate constant $k = 0.0046\ M^{-1}\ s^{-1}$; the reaction with tertiary amines is slower and with amines complexed to CuBr so slow that it could not be detected.[209]

2. Phosphorus Ligands

Phosphorus-based ligands are used to complex most transition metals studied in ATRP, including rhenium,[30] ruthenium,[15,104] iron,[98,116] rhodium,[43,119] nickel,[44,114] and palladium,[118] however, not copper. PPh_3 is the most frequently used ligand and has been successfully applied to coordinate all the aforementioned transition metals. Another phosphorus ligand,

$P(nBu)_3$, has been used in nickel- and iron-based systems.

A series of phosphorus ligands have been studied for the $RuCl_2(p\text{-cymene})PR_3$-type catalyst.[104] Apparently only phosphines which are both strongly basic and possess a well-defined steric bulk ($160° < \theta < 170°$, θ = cone angle of the phosphine) display both high catalytic activity and good control of the polymerization.

3. Miscellaneous Ligands

Cyclopentadienyl, indenyl,[159,186] and 4-isopropyltoluene[104] have recently been used as ligands in ruthenium-based ATRP to yield more reactive catalysts than ruthenium complexed by phosphorus alone. Similarly, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Pr*i*Im) has been successfully used for iron-based ATRP. Oxygen-centered ligands such as phenol or carboxylic acids can also potentially be applied.[60,210] Chalcogenides, which can be considered as either ligands or counterions, may also affect the reactivity of Cu complexes.[205] In addition, iron complexed by halides can also promote the controlled polymerization of MMA.[105]

4. Summary and Outlook

As indicated in the previous section, ligands may be even more important than metal centers, since they can fine-tune selectivities and force the complex to participate in a one electron transfer process needed for ATRP in comparison with the preferred two-electron-transfer process, such as oxidative addition and reductive elimination for Ni or Pd complexes. Ligands serve several purposes. In addition to primary roles of tuning atom transfer equilibrium constants and dynamics as well as selectivities, they control solubilities in the reaction mixture and ensure stability of the complexes in different monomers, solvents, and temperatures. This is especially important in polymerization of acidic monomers and monomers which can strongly complex transition metals such as pyridine-, amide-, or amine-containing monomers. Proper design of ligands is especially important in polymerization under heterogeneous conditions, in water or ionic liquids. Partition coefficients and their dependence on temperature will define the efficiency of the catalyst for ATRP.

Ligands may also facilitate the removal and recycling of the catalyst. They may allow the immobilization of the catalyst and also distribution between two phases.

There are many redox-active enzymatic systems. Perhaps a closer look at their action, efficiency, and structure–reactivity correlation may inspire development of more powerful and more efficient ATRP catalysts.

G. Additives

ATRP is tolerant to a variety of functional groups. For example, addition of water, aliphatic alcohols, and polar compounds in copper-mediated ATRP had little effect on the control of polymerization.[35] The same phenomenon was observed for the ruthenium/aluminum alkoxide-mediated ATRP.[83] By taking advantage of the great tolerance toward functional groups in ATRP, a variety of well-defined functional polymers have been prepared without the need for protection and deprotection of the functionalities.[99] These observations support the intermediacy of radicals and excludes ionic or organocuprate intermediates in ATRP. However, addition of pyridine or PPh_3 to the copper-mediated ATRP led to a large decrease in the polymerization rate and an increase in the polydispersities, presumably due to competition with the ligand for coordination sites or the formation of less active complexes. A similar observation was reported for catalytic chain transfer.[211]

ATRP is moderately sensitive to oxygen. The polymerization will proceed in the presence of a small amount of oxygen, since small amounts of oxygen can be scavenged by the catalyst, which is present at a much higher concentration than the growing radicals.[212] However, oxidation of the catalyst reduces the catalyst concentration and slows down the polymerization. In some cases, oxygen may produce peroxides that can actually catalyze the reaction. The polymerization of methacrylates in the presence of small amounts of oxygen and Cu(I) or Cu(II) complexes has recently been reported to yield high molecular weight products with relatively low polydispersities. [51]

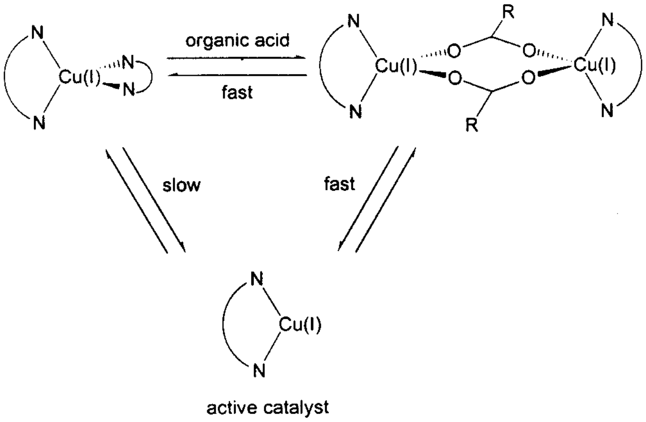
Thus, in some cases, additives can accelerate ATRP. When a small amount of copper(0) was added to the styrene and (meth)acrylates ATRP systems, a significant rate increase was observed.[64,213] For example, the polymerization of MA with a 1:0.2:0.4 ratio of MBP (MBP = methyl 2-bromopropionate), CuBr, and dNbpy in the presence of Cu(0) was 10 times faster than without Cu(0), with comparable control over the molecular weights and polydispersities in both cases. The addition of copper(0) to copper(II) dibromide in the presence of a solubilizing ligand also afforded a controlled polymerization with an increased rate. Similar rate enhancements were also observed in a phase transfer catalyzed process with Cu_2O/copper(0)/bpy as the catalyst.[214] Presumably, copper(0) reduces "excess" copper(II), generated mostly during the early stage of the polymerization through irreversible radical termination, to form in situ copper(I) by a simple electron transfer process. This process reduced the concentration of copper(II) and simultaneously increased the concentration of copper(I). As a result of the significant rate enhancement, the polymerizations can be carried out with a reduced amount of the catalyst. Copper(0) alone with the ligand also promoted ATRP but with less control over the polymerization. The addition of iron powder to salts of Fe(II) or Fe(III) resulted in a similar increased rate of polymerization.[64] Moreover, if a sufficient amount of zerovalent metal is present, the controlled radical polymerization can be carried out without the removal of any oxygen or inhibitor.[212] An induction period was observed, presumably due to the consumption of oxygen through oxidation of the catalyst. However, the presence of the zerovalent metal reduced the oxidized metal to regenerate the catalyst for a controlled polymerization. A similar effect can be achieved in the presence of other reducing agents such as sugars and aluminum alkoxides.[47]

Haddleton et al. investigated the ATRP of MMA catalyzed by CuBr/*N*-alkyl-2-pyridylmethanimine complexes using various phenols as additives and observed a small increase in the rate of polymerization.[215] Methyl hydroquinone as an additive has a similar effect and accelerates the polymerization by a factor of 3−4 at temperatures below 40 °C.[216] It appears that the rate increase is not at the expense of molecular weight control, and the polydispersities were typically <1.3. Several earlier studies clearly demonstrated that although phenols do affect the polymerization of styrene, their action on radical polymerization of (meth)acrylates in the absence of oxygen is very weak. For example, less than 1% retardation was observed for MMA polymerization with 0.2 M of hydroquinone. 4-Methoxyphenol even increased the polymerization rate initiated by AIBN at 45 °C. In the latter case, the transfer coefficient is $k_{tr}/k_p < 0.0005$.[217] The methyl acrylate system was similar, and inhibition was again insignificant at 50 °C, $k_x/k_p < 0.0002$.[218] Thus, the weak retardation/transfer effect of phenols on the polymerization of (meth)acrylates does not contradict the radical mechanism. Phenols may even accelerate the polymerization of MMA, which can be ascribed to a higher activity of the catalysts (larger equilibrium constants) with phenoxy ligands at the Cu center. A similar effect was observed for Cu carboxylates and $CuPF_6$.[29,60] The observed rate enhancement could additionally result from specific interactions of the phenol or methyl hydroquinone with the metal center, such as displacement of the ligand and conversion of the Cu(II) halide to a nondeactivating Cu(II) phenoxide. Furthermore, the stereochemistry of the polymers produced is consistent with that observed for a conventional free-radical polymerization, and the fraction of syndiotactic triads increases as the reaction temperature is lowered.

This rate increase was also observed when carboxylic acids were added to the polymerization of MMA catalyzed by (*N*-*n*-butyl-2-pyridylmethanimine)copper(I) bromide.[219] Although the polymerization rate progressively increased, the polydispersities increased with an increase in the benzoic acid-to-copper ratio. It was proposed that the active catalyst species formed through complexation of the added acid to the copper (Scheme 18).

However, the rate increase was not observed with the addition of benzoic acid to the CuCl−bpy system. In contrast, the addition of benzoic acid salts resulted in a rate enhancement.[220] The addition of a 1:1 mixture of benzoic acid and sodium carbonate also enhanced the rate, although the slow in situ formation of sodium benzoate led to a slower polymerization than when sodium benzoate was added directly. Electron-donating groups on the benzoate also increased the rate, which was also dependent on the electronegativity of the cation and increased in the order Li < Na ≈ K < Cs. This rate enhancement was attributed to the in situ formation of an active catalyst with carboxylate attached to the metal center. It was previously reported that higher rates were observed when Cu(I) carboxylates were used in place of copper(I) halides.[60]

Scheme 18. Proposed Copper(I) Intermediates in the Presence of Added Carboxylic Acid[219]

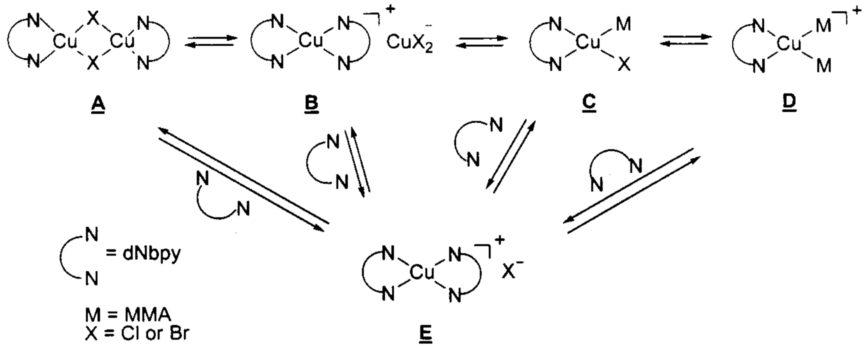


The presence of a Lewis acid, such as aluminum alkoxide, is essential for the controlled polymerization of MMA catalyzed by $RuCl_2(PPh_3)_3$.[15] The aluminum compound can presumably activate the polymerization by coordinating to the carbonyl group of the polymer chain end and the monomer. The added aluminum alkoxide can also lead to lower polydispersities but has no effect on the halogen exchange reactions.[176] Methylaluminum bis(2,6-di-*tert*-butylphenoxide), $MeAl(ODBP)_2$, led to a faster polymerization rate than $Al(iOPr)_3$.[124] This was attributed to the difference in the Lewis acidity. However, the polymerization rate in the presence of $MeAl(ODBP)_2$ decreased with time at 60 °C, which was attributed to the slow decomposition of the compound due to its instability at this temperature. When a difunctional initiator, bis(dichloroacetoxy)ethane, was used with $RuCl_2(PPh_3)_3$ as the catalyst, transesterification between the initiator and $Al(iOPr)_3$ occurred.[161] This led to polymers with a lower molecular weight than the theoretical ones. To avoid this problem, a weaker Lewis acid, aluminum acetylacetonate, was used. Recently, $Al(iOPr)_3$ has been applied to copper-mediated ATRP.[47,221] Using 1-phenylethyl bromide as the initiator, $[Cu(II)(4,4'\text{-dimethyl-}2,2'\text{-bipyridine})_3](PF_6)_2/Al(iOPr)_3$ successfully catalyzed the polymerization of styrene at 75 °C with M_n up to 50 000 and $M_w/M_n = 1.1-1.5$. The mechanism of the reaction remains unclear but could involve the in situ reduction of the Cu(II) to Cu(I) by the aluminum derivatives.

H. Catalyst Structure

The determination of the active catalyst structure remains a challenging task. Even in the most thoroughly studied copper/bpy catalytic system, the exact structure of the active species is not yet completely clear. Preliminary UV−vis studies of the Cu(I) and Cu(II) species and electron paramagnetic resonance (EPR) studies of the Cu(II) species suggest the species in polymerization solutions are quite complex.[222] Ligands on both the Cu(I) and Cu(II) species are labile in solution, and ^1H NMR studies indicate that there is fast exchange with the free ligand in solution on the Cu(I) coordinated by bpy.[58]

Scheme 19. Possible Catalyst Structures of CuX/dNbpy Complex[54]

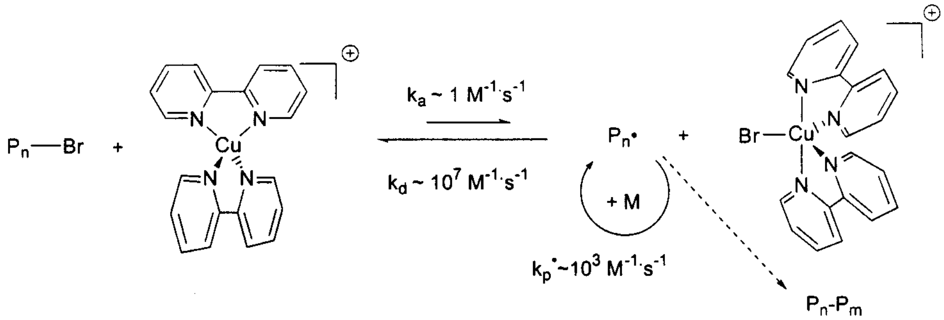


From the literature data on the coordination chemistry of copper complexes in polar solvents, the possible structures for the CuX/dNbpy complexes during the polymerization are illustrated in Scheme 19. In general, complexes of a one-to-one ratio of copper(I) halide to a bidentate ligand (e.g., bpy or phenanthroline) are either halogen-bridged dimers, LCu(μ-X)$_2$CuL (**A**), or copper(I) coordinated by two ligands with a dihalocuprate counteranion, (L_2Cu^+)-CuX_2^- (**B**).[223–225] In addition, Munakata suggested that the structures of CuX/bpy complexes in solution depend on the polarity of the solvent.[226] For example, in a polar solvent such as ethanol, the monomeric form $L_2Cu^+X^-$ (**E**) predominates while the bridged dimer LCu(μ-X)$_2$CuL (**A**) could exist in a less polar solvent such as acetone.

It was suggested that the CuX_2^- should not be the active catalyst during polymerization since the ATRP using N(*n*Bu)$_4^+$$CuX_2^-$ is very slow and not controlled.[35] In addition, a series of polymerizations was carried out with varying ratios of dNbpy to cuprous halide. The maximum rate of polymerization for styrene and MA was obtained when the dNbpy to cuprous halide ratio was 2,[35,53] suggesting $L_2Cu^+X^-$ (**E**) is the active form. For MMA, a dNbpy to cuprous halide ratio of 1 was sufficient to reach the maximum polymerization rate. However, when $CuPF_6$/dNbpy was used as the catalyst for the ATRP of MMA, which cannot form a bridged dimeric structure, the maximum rate of polymerization was observed with a dNbpy to copper(I) ratio of 2.[54] This implies that for $CuPF_6$/2dNbpy, $L_2Cu^+X^-$ (**E**) is the active form while LCu(μ-X)$_2$CuL (**A**) or Cu^+/2dNbpy/CuX_2^- $L_2Cu^+CuX_2^-$ (**B**) may be the dominating (not necessarily active) species for cuprous halide. One cannot rule out the possible coordination of one or two MMA molecules to the copper(I) species, making only 1 equiv of dNbpy sufficient to satisfy the coordination sphere of copper(I) (**C** and **D** in Scheme 19). However, recently isolated **B** displays similar activities in the styrene ATRP as the in situ formed CuBr(dNbpy)$_2$ catalyst.[56] The additional 1 equiv of ligand necessary for the maximum rate when using in situ catalyst formulations could be ascribed to solubility issues. Structure **B** may be most probable in nonpolar media,[227] while structure **C** is more likely in a polar media. The direct observation of structure **B** in styrene ATRP has recently been confirmed by extended X-ray absorption fine structure (EXAFS).[227,228] The equilibrium between **B** and **E** may strongly depend on the solvent polarity and its H-bonding ability. In less polar solvents, which cannot stabilize the X^- anions by hydrogen bonding, **B** and sometimes **A** may dominate. In polar protic solvents, **E** is preferred.

Perhaps even more complex is the structure of the relevant Cu(II) species. From the X-ray data and EXAFS, it appears that it should have a trigonal bipyramidal cationic structure [X−Cu(II)(bpy)$_2$]$^+$. However, in nonpolar media, a neutral distorted square planar structure X_2Cu(II)/bpy may be preferred over a pure Cu(II) species.[229] On the other hand, in the presence of Cu(I), it readily converts to [X−Cu(II)(bpy)$_2$]$^+$, which is accompanied by the anion [X_2Cu(I)]$^-$. In very polar and aqueous systems, the X−Cu(II) bond is quite labile and may be readily replaced by hydrating water molecules. Such a species will not deactivate ATRP, and consequently the polymerization rate increases, as already experimentally observed.[39] Thus, based on the literature data and ATRP model studies,[171,173] it seems that the copper species complexed by bpy derivatives and actively involved in the ATRP can be best represented by a tetrahedral Cu(I)(bpy)$_2$ and a trigonal bipyramidal XCu(II)(bpy)$_2$ (Scheme 20).

Scheme 20. Proposed Cu(I) and Cu(II) Species Using bpy as the Ligand



Analogous to the variety of structures proposed for the cuprous species, shown in 5, several different structures may also be put forth for the cupric species. MS,[230] EPR, and EXAFS analysis suggest that for the bpy ligands the preferred structure is a cationic trigonal bipyramid. The anion may vary, but in the presence of an excess of the Cu(I) species, it may be the linear X−Cu(I)−X anion. The pure CuX_2/bpy complex in nonpolar solvents preferentially has a neutral square planar structure, even when 2 equiv of bpy are used. The proportion of the cationic trigonal bipyramidal structure with the halide anion increases progressively with the polarity of the solvents and a decreasing temperature.

The X-ray and EXAFS structures of the cuprous halide/PMDETA complexes are shown in Figure 4.[228,231] The longer copper(II)−Br bond compared to the copper(II)−Cl bond is proposed to be responsible for the faster exchange and lower polydispersities in the bromine ATRP systems.

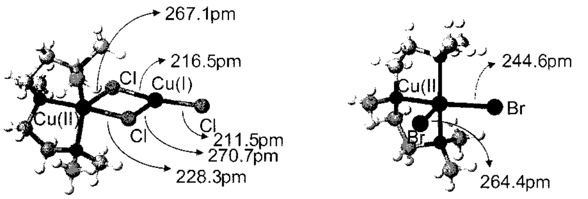


Figure 4. X-ray structure of the cuprous halide/PMDETA complexes.

There are more data on various bidentate, tridentate, and tetradentate copper complexes.[228,232] The direct observation of the dominating species in solution by EXAFS studies may help to better determine the structure of the activator and the deactivator in ATRP.[228] Nevertheless, more spectroscopic (UV, NMR, IR, EPR, MCD, etc.) and model kinetic studies are needed to fully understand the structures and activities of the various species which may change with temperature, solvent, and concentration.

I. Mechanism

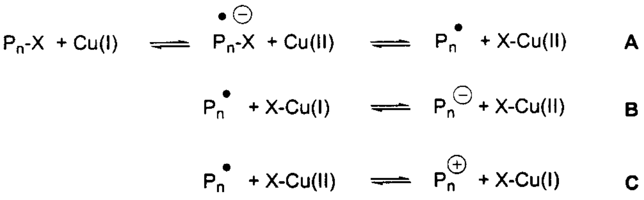
The general mechanism of ATRP was shown in Schemes 2 and 20. A radical pathway has been proposed in all the ATRP systems reported so far. However, the radical nature of the reactive or propagating species in ATRP requires very careful examination. The direct detection of growing radicals by EPR is often impossible due to the overwhelming presence of transition metals in the reaction. The *g*-values of the Cu(II) species and the propagating free radicals are too close to enable the direct detection of the radicals when they are present in minute amounts.

The existence of free radical has been proposed in copper-mediated ATRP based on several experimental observations.[192] (1) The ATRP equilibrium has been approached from both sides: RX/M_t^n and radicals/$X{-}M_t^{n+1}$ species (reverse ATRP). Thus, successful polymerizations have been carried out using conventional free radical initiators, such as AIBN and BPO, as well as organic halides.[16,70] (2) Chemoselectivity is similar to that for conventional radical polymerizations. Typical radical inhibitors, such as galvinoxyl and TEMPO, inhibit the polymerization, and the polymerization is retarded by the presence of a small amount of oxygen. In addition, ATRP is converted into a system which displays conventional radical polymerization characteristics upon addition of octanethiol as a chain transfer reagent.[193] Chain transfer in the BA polymerization also resembles the conventional radical process.[233] ATRP can be carried out in the presence of water[72,77] or other protonogenic reagents and is tolerant to a variety of functionalities.[99] Moreover, the reactivity ratios, which are very sensitive to the nature of the active centers, are nearly identical to those reported for the conventional radical polymerization but are very different from those for anionic, group transfer, and cationic systems.[133,234−237] (3) Regioselectivity and stereoselectivity are similar to and do not exceed that for a conventional radical polymerization. All the polymers formed by ATRP have regular head-to-tail structures with the dormant species of the typical secondary/tertiary alkyl halide structures, as evidenced by NMR.[18,165] In addition, polymers have the same tacticity as those prepared by a conventional free-radical process.[16,18] A recent racemization study using optically active alkyl halides also supports the radical intermediacy. Moreover, the rate constant of racemization of (*S*)-methyl 2-bromopropionate with CuBr/$(dNbpy)_2$ in toluene at 60 °C is similar to the rate constants of halogen exchange and scavenging free radicals with TEMPO ($k = 0.06$ mol^{-1} s^{-1} L). Similar rate constants indicate in all three reactions the same rate determining step proceeding by the common intermediate, i.e., involvement of free radicals in atom transfer radical processes.[238] (4) EPR studies have revealed the presence of X−Cu(II) species resulting from the persistent radical effect.[57,63,194,195,239,240] Additionally, the doubling of the molecular weight or cross-linking in multifunctional initiator systems as a result of radical−radical termination has been observed.[241] (5) Cross-exchange between different halogens and different polymerization systems (thermal and ATRP or nitroxide mediated and ATRP) demonstrates that they have the same intermediates and supports the radical mechanism.[155,242] Thus, equimolar mixtures of initiators for the nitroxide-mediated polymerization and the ATRP lead to polystyrene with a unimodal molecular weight distribution (MWD).[243] (6) Very recently, propagating free radicals were directly observed by EPR in ATRP of dimethacrylates catalyzed by CuBr/HMTETA. This has been possible due to the reduction of the termination coefficients resulting from the radicals trapping in the cross-linked matrix of the formed polymer.[244]

ATRP is typically described as proceeding through the reversible transfer of halogen atoms between growing chains and transition metals via an inner sphere electron transfer (ISET) process; however, as an alternative to the inner sphere process, outer sphere electron transfer (OSET)[42,245] may also occur. Scheme 21 illustrates several possible OSET processes that may occur in ATRP.

Path A concerns the formation of the intermediate radical anions followed by the halogen anion transfer

Scheme 21. Possible OSET Processes in ATRP



to the oxidized metal. This would result in a two-step rather than a concerted inner sphere process for the generation of radicals from initiators or polymer dormant species. Preliminary correlation studies between rates of atom transfer reactions and R−X bond energies and electron affinities suggest the predominant concerted process for many initiating and propagating species. Thus, for adducts with the same radical stabilizing substituent, tertiary alkyl halides are typically better initiators than secondary ones, which are better than primary alkyl halides. However, unexpectedly high rates even at the low temperatures found for some alkyl halides (e.g., haloacetonitrile) could indicate an outer sphere electron transfer process. This may happen with initiators having very high electron affinities (e.g., diethyl 2-bromomalonate or CCl_4) and may sometimes lead to side reactions that reduce the initiation efficiency. In contrast, the formation of radical anions by the outer sphere electron transfer process from Cu(I) to 1-phenylethyl bromide and other similar dormant species is not probable due to unfavorable redox potentials (cf. Figure 5).

Figure 5 illustrates the interrelations between the electrochemical potentials of the copper complexes and the organic radicals as well as the propagating radicals in styrene and acrylate polymerizations. Depending on the redox properties of both the transition metal complex and the corresponding organic radicals, reduction of the growing radicals to carbanions (Scheme 21, path B) or oxidation to carbocations (Scheme 21, path C) may happen under certain conditions and can sometimes become the dominant pathway.

For example, the ATRP of *p*-methoxystyrene using $Cu(I)/(dNbpy)_2$ was unsuccessful.[34] The oxidation of the *p*-methoxystyryl radical to cations (Scheme 21, path C) was postulated, yielding cationic intermediates responsible for an elimination process. Similarly, the presence of a large amount of cupric triflate in the conventional RP of styrene reduces the molecular weight and terminates the reaction, presumably through oxidation of the growing radicals via an outer-sphere electron-transfer process.[65] The observed slow termination reaction in the ATRP of styrene was attributed to the same process.[36] In addition, the cationic polymerization may occur using $CuPF_6(CH_3CN)_4$ complexes for styrene polymerizations,[246] which can be ascribed to the much stronger oxidation (and weaker reducing) power of this complex in comparison with the $Cu(I)/(bpy)_2$ complex.[247]

As shown in Figure 6, stronger reducing catalysts are also more active in ATRP. The activity of the catalysts in ATRP depends not only on the redox potential, but also on the halogenophilicity of the transition metal complexes. Both parameters are affected by the nature of the transition metal and ligand, including the complexation constants, the nucleophilicity, back-bonding, steric effects, etc. Scheme 22 represents the overall atom transfer equilibrium as a set of two redox processes, bond dissociation energy of alkyl halide and heterolytic cleavage of halogen−metal bond in the deactivator. The latter parameter is a measure of the halogenophilicity of the transition metal complex. Thus, it is possible to observe high values of atom transfer equilibrium, even if the transition metal complex is not very reducing but has high halogenophilicity (e.g., Ru vs Cu). For a series of nitrogen-based ligands in the Cu-based ATRP of methyl acrylate, a linear correlation between the polymerization rate (expressed by the apparent equilibrium constant, i.e., $K_{eq}^{app} = K_{eq}/[Cu(II)]$) and the redox potential of the complex in acetonitrile was found because of similar halogenophilicities.[172]

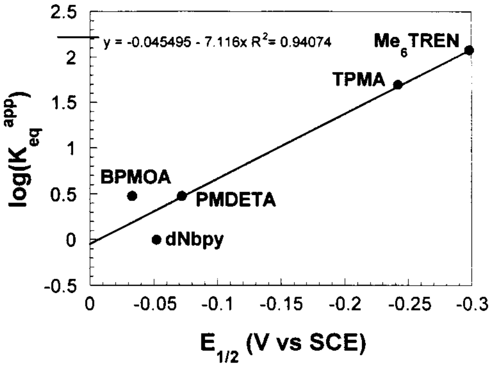


Figure 6. Correlation between the kinetics of the ATRP of MA and the redox potentials of the CuBr complexes in acetonitrile.[222]

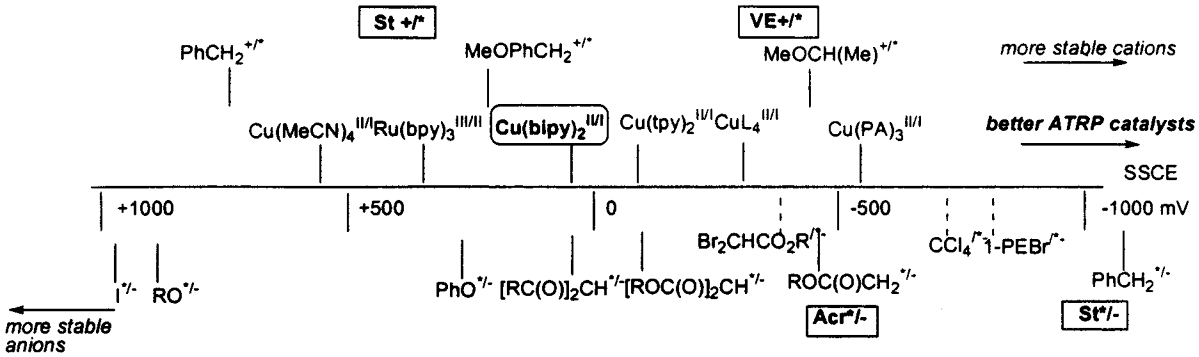
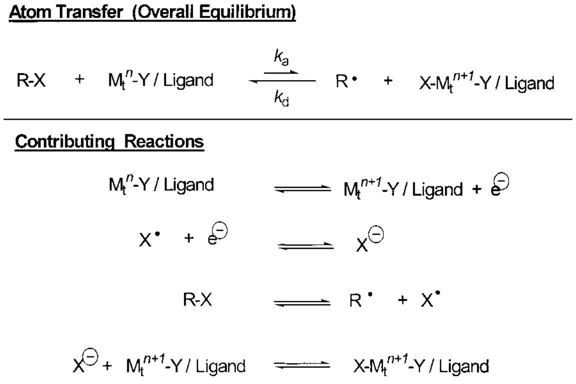


Figure 5. Redox potentials of some copper complexes.[192]

Scheme 22. Representation of Atom Transfer Equilibrium by Redox Processes, Homolytic Dissociation of Alkyl Halide, and Heterolytic Cleavage of $Cu^{(II)}-X$ Bond (i.e., Halogenophilicity)



Some radicals may react reversibly with metal centers, forming organometallic species, as reported previously.[248] This could happen with either the Cu(I) or Cu(II) species, especially in the absence ofligand.[249] It seems that these reactions are not very important in the styrene polymerization, since the rates of the conventional radical polymerization initiated by azo compounds or peroxides are not strongly affected by the addition of Cu(I)/$(dNbpy)_2$ or $Cu(OTf)_2(dNbpy)_2$.[65] Cupric triflate was used in these experiments instead of cupric bromide because the latter acts as an efficient inhibitor and results in reverse ATRP. For MA, the addition of cupric salts has no effect on the rates and molecular weights when using conventional initiators. However, the reaction rates decrease in the presence of $CuBr(dNbpy)_2$ and $CuOTf(dNbpy)_2$. This observation can be explained either by the formation of organometallic R−Cu(II) species, providing an additional pathway of control and supplementing the atom transfer process, or by the reversible reduction of growing radicals to the enolate anions, as discussed previously. The contribution of these reactions is, however, relatively small, since the polymerization of 2-hydroxyethyl acrylate is well controlled either in bulk or in aqueous solution.[80] The selectivity of atom transfer over formation of organometallic species depends on the spin state of some transition metals. Low spin species should favor atom transfer and M_t-X bonding, whereas high spin species favor the formation of M_t-C bond and organometallic species.

J. Overall Elementary Reactions

Similar to the conventional radical polymerizations, the elementary reactions in ATRP consist of initiation, propagation, and termination. For a well-controlled ATRP, initiation should be fast and quantitative. The apparent initiation rate constant ($k_i^{app} = k_i K_o$, where k_i and K_o refer to the absolute rate constant of addition of the initiating radical to the alkene and the atom transfer equilibrium constant for the initiating species, respectively) should be at least comparable to the apparent propagation rate constant ($k_p^{app} = k_p K_{eq}$, where k_p and K_{eq} refer to the absolute rate constant of propagation and the atom transfer equilibrium constant for the propagating species, respectively). If $k_i^{app} \ll k_p^{app}$, polymers with higher molecular weights than the theoretical values and higher polydispersities will be obtained. This behavior is based on the assumption that the system is equilibrated or there was deactivator added initially. The situation is more complex when the amount of the deactivator is small and the rate determining step of initiation is only activation. If initiation is too fast and a lot of radicals are generated during the initiation step, irreversible radical termination will reduce the initiator efficiency and slow the polymerization. A general guideline for choosing a suitable ATRP initiator is that the initiator should have a chemical structure similar to the dormant polymer species.

These rules also apply to the cross-propagation step. We refer to reactivities of monomer in ATRP in terms of k_p^{app}, which does not scale with the true k_p values. Efficient cross-propagation requires that the apparent rate constant of cross-propagation is at least as fast that of the subsequent propagation, unless halogen exchange is employed.

Polymer chains propagate by adding new monomer units to the growing chain ends. To obtain well-defined polymers with low polydispersities, it is crucial to rapidly deactivate the growing chains to form dormant species. Termination occurs through combination or disproportionation pathways and is most significant at the beginning of the polymerization. After a sufficient amount of the higher oxidation state metal complex has been built up by the irreversible termination reaction, the persistent radical effect predominates and radical termination is minimized.[7,48] It has been proposed that termination rate coefficients are chain length dependent and decrease during the polymerization to result in a steady rate of polymerization.[49] This helps to form well-defined polymers at higher conversions. However, when the monomer concentration becomes very low, propagation slows down but termination and other side reactions may still occur with the usual rate. Thus, there is a certain window of concentrations and conversions where the polymerization is well-controlled.

ATRP is a complex process based on several elementary reactions. Success depends on controlling all of them as well as on controlling the concentrations and reactivities of the involved species. The rate constants of radical propagation are systematically being evaluated by pulsed laser polymerization techniques.[61] The rate constants of termination are less accessible, as they depend on the chain length and the viscosity of the medium.[61] As discussed before, in ATRP perhaps most important are the rate constants for the activation and deactivation steps. They depend on the structure of monomer (i.e., the radical and the dormant species), on the halogen, and, obviously, on the transition-metal complexes. The values of the rate constants of some of these reactions have been reported for the polymeric species and some for the model systems, which mimic the structure of the dormant/active species.[171,173,250] Some values are shown in the Tables 3 and 4.

Scheme 23. Model Compounds Mimicking Polymeric Chains and Ligands Used in Kinetic Studies

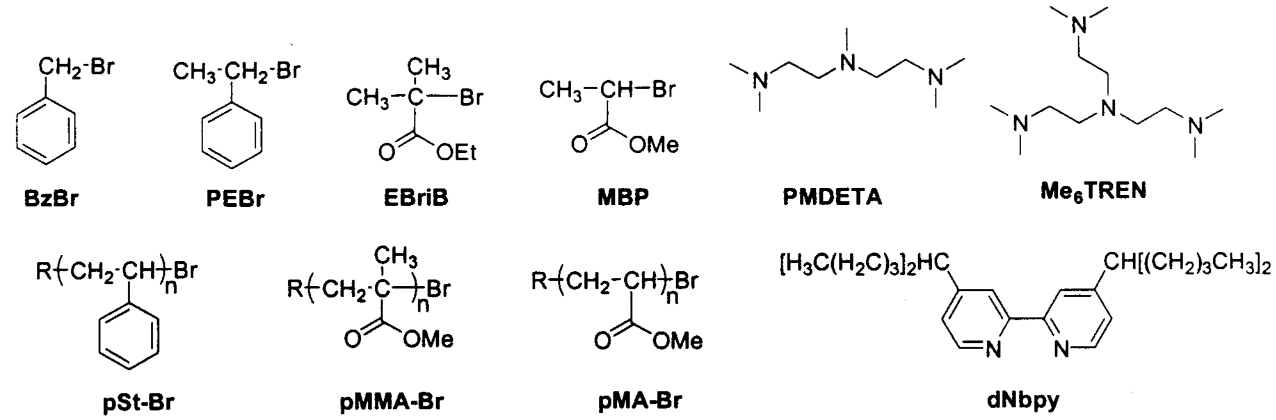


Table 3. Activation Rate Constants Measured under Various Conditions at 35 °C[172]

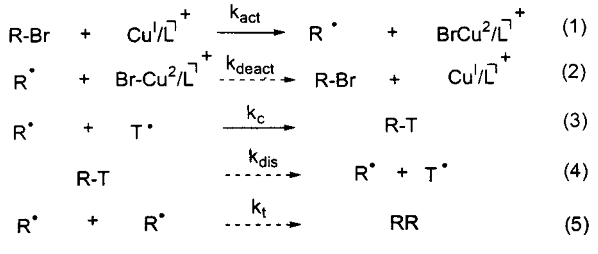
no.	RX	complex	solvent	k_{act} [M^{-1} s^{-1}]
1	PEBr	CuBr/2dNbpy	acetonitrile	0.085
2	MBrP	CuBr/2dNbpy	acetonitrile	0.052
3	EBriB	CuBr/2dNbpy	acetonitrile	0.60
4	BzBr	CuBr/2dNbpy	acetonitrile	0.043
5	PEBr	CuBr/PMDETA	acetonitrile	0.12
6	MBrP	CuBr/PMDETA	acetonitrile	0.11
7	EBriB	CuBr/PMDETA	acetonitrile	1.7
8	PECl	CuCl/Me$_{6TREN}$	acetonitrile	1.5
9	PEBr	CuBr/2dNbpy	ethyl acetate	0.016
10	PECl	CuCl/2dNbpy	acetonitrile	0.000056

Table 4. Deactivation Rate Constant Measured under Various Conditions at 75 °C[172]

no.	radical	complex	solvent	k_{deact} [M^{-1} s^{-1}]
1	PE	Cu(II)Br$_2$/2dNbpy	acetonitrile	2.5×10^7
2	PE	Cu(II)Br$_2$/PMDETA	acetonitrile	6.1×10^6
3[c]	PE	Cu(II)Br$_2$/Me$_6$TREN	acetonitrile	1.4×10^7
4	PE	Cu(II)Br$_2$/2dNbpy	ethyl acetate	2.4×10^8
5	PE	Cu(II)Cl$_2$/2dNbpy	acetonitrile	4.3×10^6

The structures of the corresponding reagents are shown in Scheme 23. The activation rate constants were measured using HPLC or GC under the kinetic isolation conditions achieved by trapping the generated radical with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as shown in Scheme 24 (broken arrows indicate reactions suppressed in the presence of excess TEMPO).

Scheme 24. Model Reactions for the Activation Rate Constant Measurements



The deactivation rate constants were determined by trapping 1-phenylethyl radicals using TEMPO in a competitive clock reaction (Scheme 25). The 1-phenylethyl radical was generated by the thermal decomposition of the 1-(*N*,*N*-(2-methylpropyl-1)(1-diethylphosphono-2,2-dimethyl-propyl-1-)-*N*-oxyl)-1-phenylethane (PESG1) alkoxyamine.

The following conclusions can be drawn from the model studies. At 35 °C, 2-bromoisobutyrate is approximately 10 times more reactive than the other alkyl halides and 1-phenylethyl bromide is 10^3 times more reactive than the corresponding chloride. This difference dramatically decreases at higher temperatures due to the higher activation energy for the latter. PMDETA forms more reactive Cu(I) complexes than dNbpy. Me$_6$TREN is $\sim 10^4$ times more active than the dNbpy-based complex. The reaction is faster in acetonitrile than in ethyl acetate.

In the deactivation process, the CuBr$_2$/dNbpy complex is more active in ethyl acetate than in acetonitrile. Deactivation is slower with CuCl$_2$ instead of CuBr$_2$. The reactivity of the CuBr$_2$/dNbpy complex is higher than with either Me$_6$TREN or PMDETA. Among the studied ligands, Me$_6$TREN appears to be most attractive since it promotes very fast activation but also sufficiently fast deactivation.

More systematic studies were performed with a series of N-based tridentate complexes shown in Figure 7 together with their reduction potentials.[172,251]

The rate constants of activation and deactivation for 1-phenylethyl bromide and the corresponding radical correlate well with the reduction potentials of the Cu(II) complexes. The catalytic activity of the complexes decreases in the order alkylamine $\approx$ pyridine $>$ alkyl imine $\gg$ aryl imine $>$ arylamine. The correlation between the activation and deactivation rate constants was approximately reciprocal, as shown in Figure 8. Thus, results with the Me$_6$TREN are quite unique, probably due to very small entropic constraints in the passage from the X−Cu(II) to the Cu(I) state.

Knowing the values of the rate constants of all the elementary reactions involved in ATRP will enhance the mechanistic understanding of ATRP, facilitate optimization of the reaction conditions for various monomers, and help in selecting the proper initiator and catalyst structures. Without this knowledge, efficient catalysts such as Me$_6$TREN-based complexes may lead to poorly controlled ATRP processes.[28]

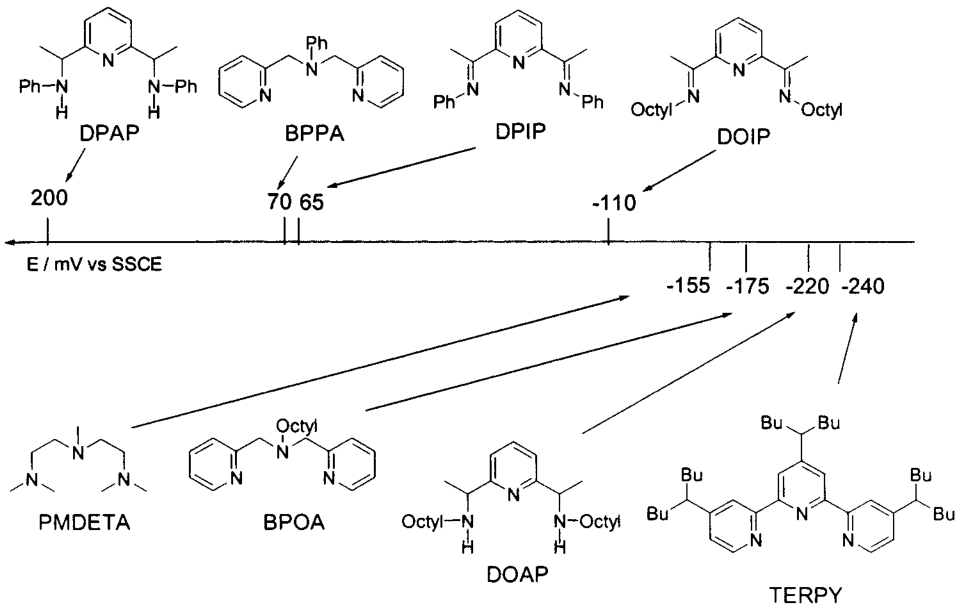
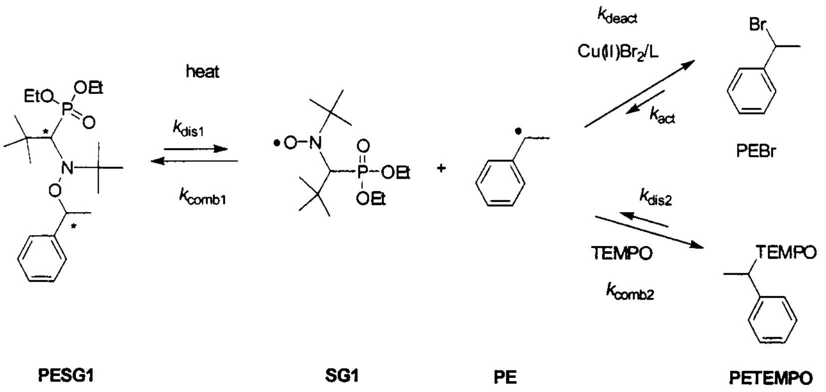


Figure 7. Reduction potentials of the series of $CuBr_2$ complexes in CH_3CN, 500 mV/s, 0.1 M $[NBu_4][PF_6]$, E vs SSCE.[172]

Scheme 25. Model Reactions for the Deactivation Rate Constant Measurements



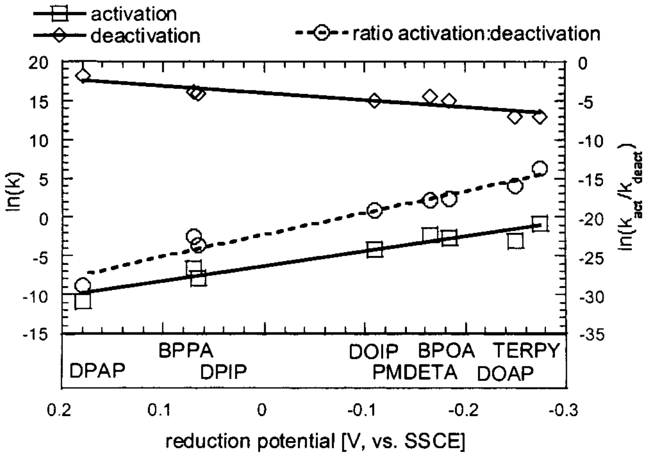


Figure 8. Dependence of the rate constants of activation for PEBr and deactivation for PE as well as their ratio (k_{act}/k_{deact}) on the reduction potential of the Cu(II) complexes. Rate constants of activation and deactivation were determined in acetonitrile at 35 and 75 °C, respectively.

III. Materials Made by ATRP

While the advent of atom transfer radical polymerization (ATRP) is relatively recent—the first publication was in 1995—the number of contributions with regard to materials synthesized at least in part using this technique is quite large. Below is a summary of the work appearing in the literature with regard to ATRP. The discussions have been divided into broad categories based on polymer functionality, composition, and architecture.

A. Functionality

Functionality can refer to many different aspects when describing a polymer. Those components relevant to ATRP are functional monomers, initiator fragments, and polymer termini shown in Figure 9. Each of these will be covered below, as recently reviewed.[252]

1. Monomer Functionality

A functionalized monomer may provide the material used directly to exploit the properties provided by the functional group (hydrophilicity, polarity, metal complexation, etc.) or via a derivative (i.e., protecting group) of a monomer which is not polymerizable by that mechanism. A survey of the literature reveals that both approaches have been used in the radical polymerization of functional monomers. Below is a description of such monomers, the motivations for their use, and results of ATRP using those compounds. Some of the generic classes

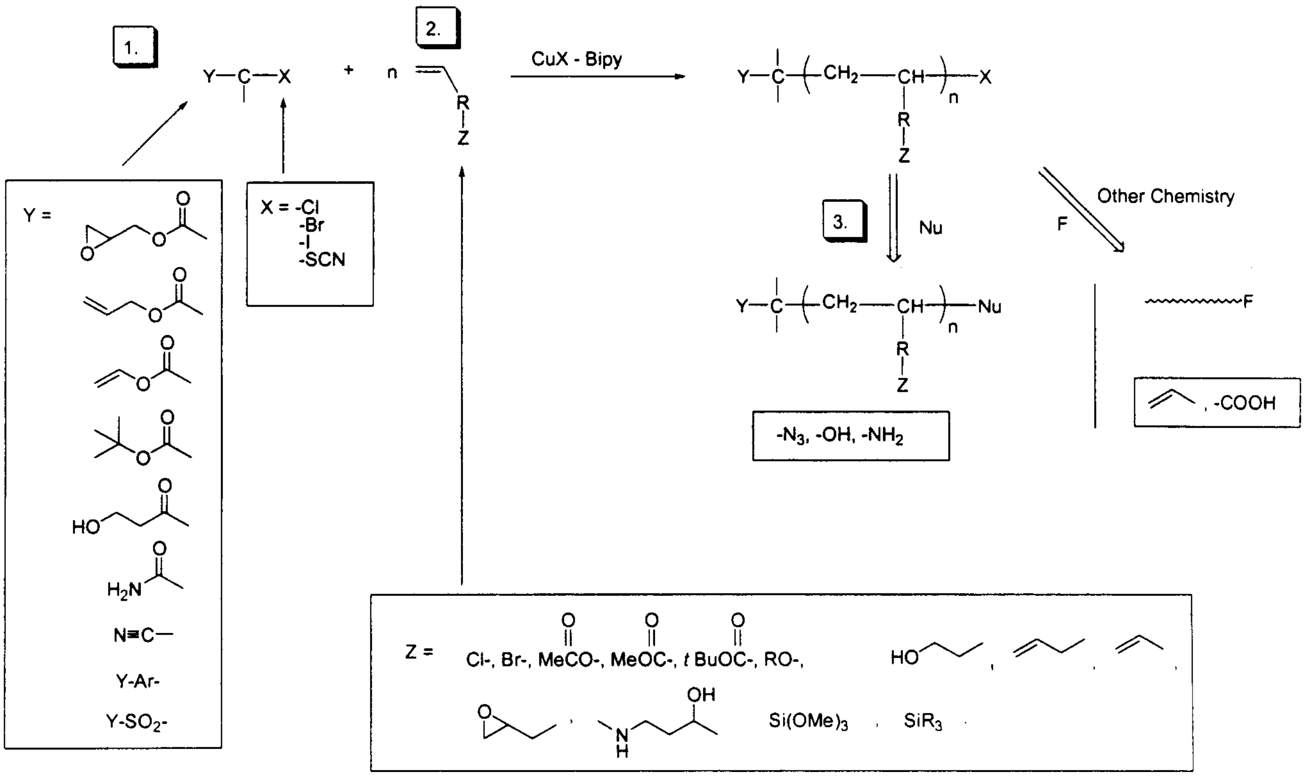


Figure 9. Possible routes to functionalized polymers by ATRP.

of monomers have already been discussed previously; here we focus only on functional monomers.

a. Styrene Derivatives. A number of ring-substituted styrenes was examined in a concerted study to determine the correlation between the monomer structure and the polymerization rate.[34] The various monomers studied and their Hammett σ values are listed in Table 5. Polymers with polydispersities $M_w/M_n < 1.3$ at high (~90%) conversion were prepared. Only 4-methoxystyrene did not form high polymer, with the reason being that in this system electron transfer dominated over atom transfer, resulting in a cationic oligomerization.

Table 5. σ Values for Substituted Styrenes Examined in the Hammett Study[34]

styrene ring substituent	σ^1	$M_{n,SEC}$	M_w/M_n
4-CF_3	0.54	65450	1.06
3-CF_3	0.43	12400	1.17
4-Br	0.23	10100	1.13
4-Cl	0.23	13310	1.12
4-F	0.06	7080	1.14
3-Me	−0.07	10800	1.17
4-Me	−0.17	4150	1.38
4-CMe_3	−0.20	6560	1.52
4-OMe	−0.27	oligomer	

[1] Positive σ − electron withdrawing substituent; negative σ − electron donating substituent

In another study, the polymerization of 4-acetoxystyrene was described.[102] The motivation for this project was synthesis of poly(4-vinylphenol), a water-soluble polymer that is not polymerizable by a free-radical mechanism. The difunctional initiator α,α′-*p*-dibromoxylene in bulk monomer with the heterogeneous $CuBr(bpy)_3$ catalyst system was used. The kinetic indicating plots obeyed first-order conservation of radicals until ~75% conversion.

Considering the reasonable agreement between theoretical and observed molecular weights and the relatively narrow molecular weight distribution, the authors attributed the nonlinearity in the kinetic measurements at high conversion to a diffusion-controlled process. However, a reasonable assertion is that when the concentration of monomer is depleted under bulk conditions, termination takes place, causing an irreversible loss of the active species and, therefore, lowering R_p and increasing the polydispersity. There were no attempts to quantify the functionality of the purified polymer. The polymer at the end of the reaction had a measured molecular weight within 10% of the theoretical value and a polydispersity less than 1.2.

Vinyl benzoic acid in its sodium salt form was also successfully polymerized in aqueous media.[143] In general, styrenes are easily polymerized by Cu-based and many other transition-metal complexes.

4-Vinylpyridine (VP) is structurally similar to styrene. The resulting polymers can be used as polymeric multidentate ligands for the coordination of transition metals and in water purification and emulsification processes. VP has been successfully polymerized by ATRP using cuprous halides complexed by Me_6TREN. Other ligands were less successful. In the polymerizations, differences in the kinetics and end-group functionality were observed between the bromine and chlorine end groups.[145] With a Cl-based initiator and a CuCl catalyst, first order kinetics were observed to high monomer conversion. The polymerizations with bromine showed a decreasing slope in the semilogarithmic plot of monomer consumption, indicating a loss of control either through radical termination or a nucleophilic displacement reaction[36,209] between the chain end and the pyridine nitrogen. The polymerizations improved when conducted in 2-propanol, presumably due to the ability of the alcohol to hydrogen bond with the pyridine nitrogen, thereby preventing complexation of the monomer or the polymer to the catalyst. Under appropriate conditions, a linear increase of the molecular weights with conversion was observed, but the molecular weight estimated by SEC using polystyrene or PMMA standards was nearly double that predicted from the monomer-to-initiator ratio. Polydispersities were below 1.2 throughout that reaction.

b. (Meth)acrylate Derivatives. A number of functional acrylates have been studied in ATRP reactions. One monomer examined in depth was 2-hydroxyethyl acrylate (HEA).[80,107] While many common monomers such as styrene, butyl acrylate, and methyl methacrylate do not require stringent purification measures for use in ATRP reactions, HEA contains acrylic acid and a diacrylate as impurities. The former can poison the catalyst, while the latter will cause cross-linking in the reaction. Therefore, HEA must be purified by an extraction/distillation procedure from the inhibited reagent prior to use. When purified, the ATRP of HEA is well controlled, both in bulk and in water. The kinetic plots are linear, obeying a first-order relation with respect to monomer consumption, and molecular weights increase linearly with conversion. Polydispersities decrease to below 1.2 over the same period. However, the molecular weights measured by SEC using polystyrene or PMMA standards are often 50% greater than those predicted by the ratio of consumed monomer to initially infused initiator. ^{1}H NMR and MALDI-TOF MS studies have determined that the M_n of the polymers is much closer to the theoretical values, as shown in Table 6. The reason for the difference in the SEC measurements is most likely due to deviations between the hydrodynamic volumes of poly(HEA) and the linear polystyrene standards used to generate the SEC calibration curve.

Table 6. SEC, ^{1}H NMR, and MALDI-TOF Molecular Weight Results for Poly(HEA) Initiated by Diethylmethylbromomalonate (DEMBM) and Methyl 2-Bromopropionate (MBP)[80]

initiator	$M_{n,th}$	method	$M_{n,exp}$	M_w/M_n
DEMBM	3100	SEC	6270	1.22
		^{1}H NMR		
		MALDI-TOF MS	3200	1.25
MBP	4100	SEC	9860	1.17
		^{1}H NMR	4200	
		MALDI-TOF MS	4842	1.19

Due to poor solubility of the poly(HEA) in less polar solvents, the monomer is often polymerized in its protected form, 2-trimethylsilyloxyethyl acrylate (HEA-TMS).[107,110] The resulting polymer is more compatible with organic media, especially when used for the synthesis of block copolymers.

The methacrylate analogue of HEA 2-hydroxyethyl methacrylate (HEMA) was also used. The polymerization in bulk at room temperature led to polymers with high polydispersity[126] ($M_w/M_n = 1.5$), and an insoluble gel was obtained when water was used as the solvent at 20 °C.[253] Well-defined poly(HEMA) could be prepared using mixed solvents, either a 70/30 mixture of methyl ethyl ketone and 1-propanol[126] or a 50/50 mixture of methanol and water.[254] In the first case, an alkyl bromide initiator was used in conjunction with CuCl(bpy)$_2$, and in the second case, an oligo(ethylene oxide)-based initiator was used. The ATRP of the trimethylsilyl-protected HEMA monomer has also been studied.[110,126,127] The protected form was used in the polymerization due to its improved compatibility in organic systems. In these studies, the material was either used for the synthesis of block copolymers followed by deprotection to make amphiphilic materials[110] or homopolymerized then followed by a transesterification with 2-bromoisobutyryl bromide to subsequently prepare graft copolymers, leading to polymer brushes.[127]

Another water-soluble acrylic monomer polymerized was 2-(dimethylamino)ethyl methacrylate (DMAEMA).[125] Conservation of radicals was maintained throughout the reactions, and molecular weights increased linearly with conversion. Deviation between the measured and the theoretical molecular weights was observed due to a low initiator efficiency from 2-bromoisobutyrate and tosyl chloride and differences in the hydrodynamic volumes between the PDMAEMA and the PMMA calibration standards. 2-Bromopropionitrile showed the highest initiation efficiency, and when used, polydispersities remained below 1.25 throughout the reaction. This monomer was also polymerized directly in water.[163]

The polymerization of oligo(ethylene oxide) methacrylate by ATRP has recently been reported. When the reaction was conducted in aqueous media, fast and well-controlled polymerizations were obtained at ambient temperature using water-soluble initiators.[81] The significant rate increase was ascribed to the polar media, which could affect the catalyst structure.

Armes et al. studied the ATRP of a number of hydrophilic monomers in aqueous media.[129,143,253] Methacrylic acid was polymerized in its sodium salt form at pH 8, although the reaction rate is slow even at 90 °C (only 70−80% conversion is achieved after 21 h).[129] In contrast, the ATRP of sodium 4-vinylbenzoate was rapid at 20 °C, with 95% yield obtained within 25 min.[143] Polydispersities were around 1.30 in both cases, as determined by aqueous SEC studies. Another anionic monomer, ammonium 2-sulfatoethyl methacrylate, was also rapidly polymerized via ATRP in aqueous media (87% conversion within 3 h at 20 °C). On the other hand, monomer decomposition, possibly via hydrolytic cleavage of the ester bond, seemed present for potassium 3-sulfopropyl methacrylate.[254] The polymerization stopped after ∼40% conversion. Two quaternized monomers, vinylbenzyltrimethylammonium chloride and the hydrochloride salt of 2-aminoethyl methacrylate, were also successfully polymerized in aqueous ATRP to high conversion (95%); however, an aqueous SEC analysis showed a relatively high polydispersity ($M_w/M_n \approx 2.2$) for poly(vinylbenzyltrimethylammonium chloride).

Other water-soluble monomers such as *N*-vinylpyrrolidinone and sodium 4-styrenesulfonate were studied, but their ATRP was less successful.[254] Very slow polymerization occurred at room temperature for *N*-vinylpyrrolidinone, whereas rapid but relatively uncontrolled polymerization was observed for 4-styrenesulfonate. A hydrophilic–hydrophobic block copolymer of sodium 4-vinylbenzoate and oligo(ethylene oxide) methacrylate was prepared in “one-pot” in aqueous media. Dynamic light scattering studies indicated that micellization occurred in aqueous media on adjusting the solution pH from 8 to 3.

A number of other functional polyacrylates have been synthesized by ATRP (cf. Scheme 5). The motivation for the polymerization of glycidyl acrylate[108] was for the attachment of various functional groups, as macroinitiators for other polymerizations that could lead to graft copolymers, or as monomeric species in cross-linking reactions. Allyl[255] and vinyl acrylate[255] could be used as reactive species in curing reactions for coatings. *tert*-Butyl acrylate (tBA)[109] serves as a protected acrylic acid, while isobornyl acrylate is a commercially available monomer leading to a polymer with an unusually high T_g compared to other polyacrylates. 11-(4′-Cyanophenyl-4″-phenoxy)-undecyl acrylate[256] has been used as a monomer to produce side-chain liquid crystalline polymers. Similarly, cinnamic acid derivatives were polymerized by ATRP using a “core first” approach.[257] Two acrylate monomers, i.e., 4-methoxyphenyl 4-{[2-(1-oxo-2- propenyloxy)ethyl]oxy} benzoate and 4-methoxyphenyl 4-{[6-(1-oxo-2- propenyloxy)hexyl]oxy} benzoate, were successfully polymerized using hyperbranched poly(*p*-chloromethylstyrene) as an initiator by ATRP. The mesophase behavior of these dendritic copolymers essentially depends on the chemical nature of the polyacrylates. [258] Recently, an acrylate–lactone monomer, 4-(acryloyloxy)ϵ-caprolactone, has been prepared.[259] This new difunctional monomer can be selectively polymerized in a controlled/“living” way by both ATRP and ring-opening polymerization (ROP). Well-defined poly[(2-*β*-D-glucopyranosyloxy)ethyl acrylate] was prepared from 2-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)ethyl acrylate after hydrolysis using dilute CH_3ONa solution in $CHCl_3/CH_3OH$.[260] The ATRP of methacrylates containing biologically active groups such as 5′-methacryloyluridine and 5′-methacryloyladenosine as well as sugar-containing groups 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose and 2-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)ethyl acrylate have been successful and also led to the formation of the corresponding block copolymers.[260–262]

c. Macromonomers. Macromonomers are polymer chains which contain a double bond (or other polymerizable group) at a chain end which can be (co)polymerized in a separate reaction to yield graft copolymers. They will be discussed in more detail in section III.C.1 on controlling chain topologies. Macromonomers have been both prepared and copolymerized by ATRP.

For example, vinyl chloroacetate was used as an initiator for the ATRP of styrene.[263] Macromonomers of molecular weights $M_n = 5000$, 10 000, and 15 000 were synthesized with polydispersities below 1.2. No polymerization of the vinyl acetate segment was observed due to the inability of that moiety to copolymerize with styrene. The macromonomers were subsequently copolymerized with *N*-vinylpyrrolidinone for the synthesis of hydrogels.[263]

Allyl bromide and chloride were used as initiators for the ATRP of styrene using the heterogeneous copper–bipyridine complex where the halogen on the metal complex matched that on the initiator.[264] For both initiators, good agreement between the theoretical and measured molecular weights was observed. The polydispersity for the bromine system ($M_w/M_n = 1.2$) was lower than in the case of chlorine ($M_w/M_n = 1.3$), consistent with results using initiators such as benzyl bromide or chloride under similar reaction conditions.[18] Similarly, allyl end-functionalized macromonomers of DMAEMA have been prepared using either allyl 2-bromoisobutyrate or allyl trichloroacetamide.[265] The macromonomers were quaternized with methyl iodide and copolymerized with acrylamide under conventional free radical conditions to yield comb-branched polyelectrolytes. No copolymerization of these macromonomers with, e.g., α-olefins was yet reported. On the other hand, ATRP was used for the homopolymerization of macromonomers prepared by cationic polymerization.[266] In this study, the polymerization of methacrylate terminal poly(isobutylvinyl ether) yielded a densely grafted brush copolymer. The copolymerization of MMA-terminated polyMMA with BA by ATRP lead to well-defined grafts with a more uniform distribution of grafts than achieved by either the conventional radical process or an anionic polymerization.[267,268]

2. Initiator Functionality

In ATRP, initiation is accomplished through homolytic cleavage of activated halogen-containing compounds and addition of the generated radicals to alkenes. The radical-stabilizing group should reside on the α-C atom (aryl, carbonyl, nitrile, multiple halogens) or involve weak bonding with heteroatoms (S, N, O). Direct bonding of the halogen to an aryl or carbonyl group does not facilitate radical generation, and since vinyl, acyl halides, or haloarenes are bad ATRP initiators, ATRP can be carried out, e.g., in chlorobenzene. The fragment that forms the α-end of the polymer chain can contain a number of functional groups tolerant to ATRP catalysts and radicals.

a. Activated Alkyl Halides. A number of functional initiators were used for the ATRP of styrene and methyl acrylate.[99,146] The general rules for the selection of the appropriate initiators were discussed in section II.D. The product of the apparent equilibrium constant and the rate constant of the addition to monomer for the initiation step should be similar to or larger than that for the propagation step. In addition, any functionalities in the initiator should not interfere with ATRP (i.e., should be inert toward both the catalyst and the alkyl halide). ATRP of MA was faster due to higher concentration of initiator and catalyst.

Thus, polymerizations with initiators or monomers containing carboxylic acids are more difficult because

Scheme 26. Synthesis of Macromonomers by ATRP

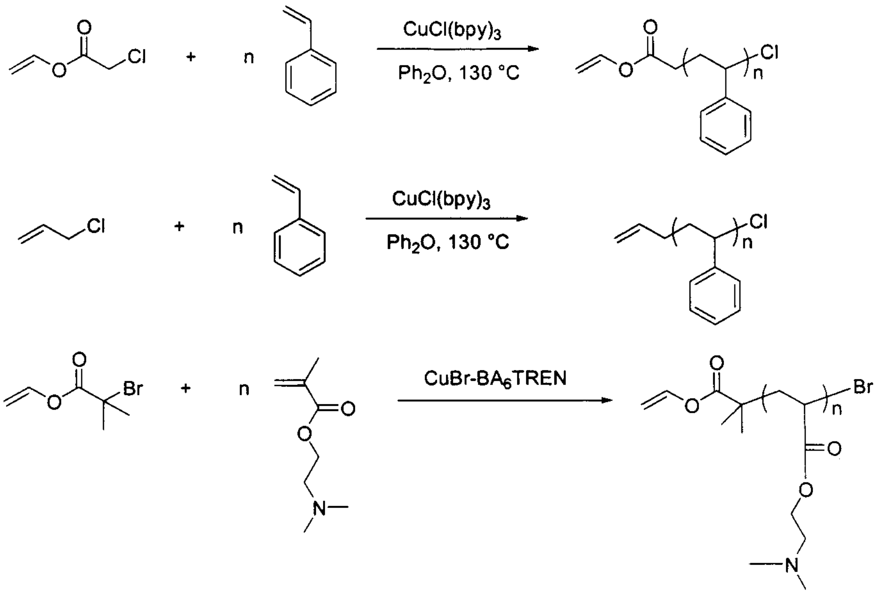
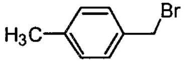
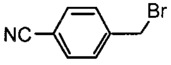
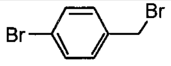
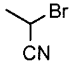
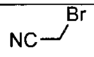
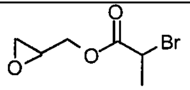
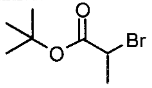
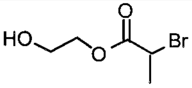
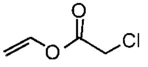
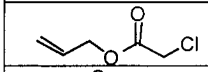
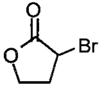
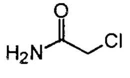


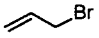
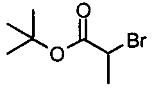
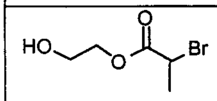
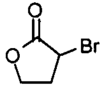
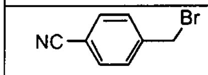
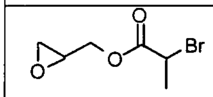
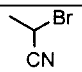
Table 7. ATRP of Styrene[a] from Various Functionalized Initiators[99]

Initiator Structure	Initiator Name	$M_{n,Cal}$	$M_{n,SEC}$	M_w/M_n
	4-Methylbenzyl bromide	5110	4400	1.17
	4-Cyanobenzyl bromide	4760	5500	1.10
	4-Bromobenzyl bromide	4750	4500	1.16
	2-Bromopropionitrile	4800	5100	1.09
	Bromoacetonitrile	4750	4500	1.10
	Glycidol 2-bromopropionate	6190	6800	1.12
	*tert*-Butyl 2-bromopropionate	4110	4000	1.17
	Hydroxyethyl 2-bromopropionate	4810	7500	1.10
	Vinyl chloroacetate	9400	5800	1.12
	Allyl chloroacetate	1430	2600	1.77
	α-Bromo-γ-butyrolactone	4050	4000	1.17
	2-Chloroacetamide	1200	4000	1.51

[a] 110 °C; bulk, $[S]_o/[I]_o = 96$; $[I]_o/[CuBr]_o/[dNbpy]_o = 1/1/2$; time= 3.0 h.

the acid functionality may poison the catalyst.[269,270] However, the ATRP of MMA using 2-bromoisobutyric acid has been demonstrated.[219] The results indicated a linear growth of the molecular weights with conversion but at higher levels than those predicted by the ratio of the concentrations of monomer to initiator. The lower initiation efficiency of the carboxylic acids was later confirmed in the $NiBr_2(PPh_3)_2$-

Table 8. ATRP of Methyl Acrylate[a] from Various Functionalized Initiators[99]

Initiator Structure	Initiator Name	$M_{n,Cal}$	$M_{n,SEC}$	M_w/M_n
	Allyl bromide	4430	6200	1.34
	*tert*-Butyl 2-bromopropionate	4650	4700	1.22
	Hydroxyethyl 2-bromopropionate	4850	6800	1.30
	α-Bromo-γ-butyrolactone	4165	4800	1.13
	4-Cyanobenzyl bromide	3720	4100	1.13
	Glycidol 2-bromopropionate	3710	4000	1.23
	2-Bromopropionitrile	3280	3500	1.10

[a] 110 °C; bulk, $[MA]_o/[I]_o = 58$; $[I]_o/[CuBr]_o/[dNbpy]_o = 1/0.3/0.6$; time= 1.7 h.

mediated polymerization of MMA[115] and the CuBr(PMDETA)-mediated polymerization of styrene.[128]

A number of protected carboxylic acid initiators were studied. [128] Hydrolysis of the protecting groups liberates the free terminal carboxylic acid functionalities. Although the initiator efficiency was low (0.6) with trimethylsilyl as the protecting group, the initiator efficiency increased using *tert*-butyl and *tert*-butyldimethylsilyl groups. When carboxylic acid initiators with remote halogens such as 4-(1-bromoethyl)benzoic acid were used, well-defined polystyrene with initiator efficiencies close to 0.7 was prepared.[128] The molecular weights measured by SEC were more than double those determined from either ^{1}H NMR or MALDI-TOF MS,[271] however, which could be due to interactions between the acid groups and the SEC columns.

Hydroxy derivatives of (meth)acrylates are efficient initiators for ATRP (cf. Tables 7 and 8). For the MMA polymerization, 2-hydroxyethyl 2′-bromoisobutyrate was also efficient.[160] MALDI-TOF MS of a low molecular weight PMMA sample exclusively showed a series of peaks corresponding to PMMA oligomers containing the hydroxyl initiating fragment. Similar results were reported for a poly(methyl acrylate) sample. [272]

Other functionalities have also been incorporated into the ATRP initiators. Initiators with anhydride and oxazoline functionalities have been utilized in the ATRP of styrene.[271] The resulting reactive polymers may be applicable as blend compatibilizers. A bromopropionate derivative of anthracene, the difunctional compound 9,10-bis(1-bromoethylcarbalkoxymethyl)anthracene, was synthesized for use in the ATRP of styrene.[273] The chromophore placed in the center of a polymer chain enabled studies of local chain dynamics by fluorescence depolarization techniques. Through the use of a thiophene-containing initiator, thiophene end-capped PMMA was prepared by ATRP.[274] The resulting polymer was subjected to electrolysis in the presence of pyrrole to result in electrically conducting graft copolymers. More recently, uridine- and adenosine-functionalized initiators were used to prepare polystyrene and PMMA with potential applications in the biorecognition field.[262,275] The same group synthesized a number of carbohydrate-based initiators which were used to prepare star polymers with a carbohydrate core, glucose end-functionalized polymer chains, and span functionalized amphiphilic polymers efficiently.[276]

b. Activated Sulfonyl Halides. Another class of initiators for ATRP are sulfonyl halides.[19,55] Various substituted aromatic and aliphatic sulfonyl chlorides were examined as initiators for the ATRP of styrene, MMA, and *n*-butyl methacrylate (BMA) with the heterogeneous $CuCl(bpy)_3$ system.[166] The initiators listed in Scheme 11 displayed linear first-order kinetic plots with molecular weights that increased linearly with monomer conversion. Initiation, and, therefore, incorporation of the functionalities, appears to be efficient and nearly quantitative, resulting in polymers with a variety of novel moieties

Table 9. Experimental Rate Constants of Propagation (k_p^{exp}) and the Concentration of Propagating Radicals ([P•]) for the CuCl/bpy-Catalyzed Radical Polymerization of Styrene, (5.9 M), Methyl Methacrylate, (6.22 M), and *n*-Butyl Methacrylate, (4.9 M) Initiated with Substituted Arenesulfonyl Chlorides[a,b] [166]

M	I	M_w/M_n (conv., %)	T (°C)	k_p^{exp} (10^{-4} s^{-1})	[P•] (10^{-7} M)[c]
S	CABSC	1.38 (96)	130	0.50	0.19
S	DCHBSC	1.40 (85)	130	0.53	0.20
S	HBSC	1.53 (90)	130	0.36	0.14
S	MBSC	1.25 (93)	130	0.39	0.15
S	MSC	1.49 (89)	130	0.59	0.23
MMA	CABSC	1.22 (88)	90	1.83	1.13
MMA	DCHBSC	1.19 (76)	90	0.92	0.57
MMA	HBSC	1.27 (89)	90	1.50	0.93
MMA	TCMSC	1.21 (91)	90	1.50	0.93
MMA	DCBSC	1.14 (96)	90	1.58	0.98
MMA	1-NASC	1.19 (97)	90	2.44	1.51
MMA	2-NASC	1.22 (97)	90	2.97	1.84
MMA	MBSC	1.18 (94)	90	2.44	1.51
MMA	DMBSC	1.20 (92)	90	1.81	1.12
MMA	ADZBSC	1.25 (93)	90	2.08	1.29
MMA	DAC	1.60 (93)	90	0.54	0.33
MMA	MSC	1.35 (89)	90	2.87	1.76
BMA	CABSC	1.26 (92)	120	3.42	1.09
BMA	MBSC	1.24 (98)	120	3.42	1.09
BMA	MSC	1.27 (94)	120	7.50	2.40

[a] Cf. Scheme 11 for the initiator structures. [b] [M]/[I]/[CuCl]/[bpy] = 200/1/1/3 molar ratio. [c] [P•] = k_p^{exp}/k_p^{rad}. For S: k_p^{rad} = 2609 L mol^{-1} s^{-1}; for MMA: k_p^{rad} = 1616 L mol^{-1} s^{-1}; for BMA: k_p^{rad} = 3127 L mol^{-1} s^{-1}; recalculated using data from van Herk, A. M. *J. Macromol. Sci., Rev.* **1997**, *C37*, 633.

located at one chain end. The aryl sulfonyl chlorides have been called a “universal class of ATRP initiators”[55] due to their relatively high rates of initiation over propagation. They are excellent initiators for MMA and other methacrylates.[111] However, polymerizations of acrylates is slow and may result in higher than predicted molecular weights and higher polydispersities.[55] Similarly, polydispersities for styrene are higher than with 1-phenylethyl halides and were generally greater than 1.3.[166] Mono-, di-, and multifunctional sulfonyl halides initiators have also been used, leading to star polymers.[167]

c. Macroinitiators. When a polymer chain contains an end group with an activated halogen atom, it can be used as ATRP initiator or as a macroinitiator. Macroinitiators have been prepared via different methods including cationic, anionic, coordination, conventional radical, and even polycondensation processes.[277] They will be discussed in detail in section III.B.2.b together with mechanistic transformations. ATRP initiators and macroinitiators were also immobilized on surfaces leading to a uniform growth of the chains from both flat and spherical surfaces (cf. section III.B.2).[134,278−280]

3. Chain End Functionality

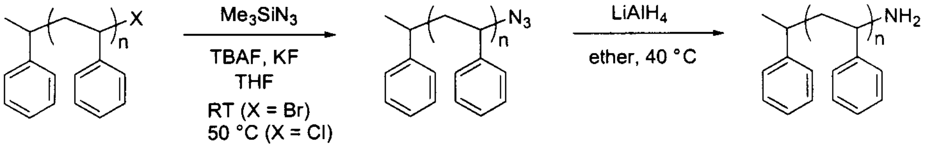
One of the criteria for the “livingness” of polymers synthesized by ATRP is the preservation of end groups throughout a polymerization. ^{1}H NMR has been used to verify the presence of the carbon−halogen bond.[18,19,124] MS was also used to confirm degree of remaining functionality, although the data may be less reliable due to sensitivities that depend on the structure of the end groups and the low stability of the alkyl halides, especially under MALDI conditions.[252] In most cases nearly quantitative functionality was observed (>95%). In the case of the methyl acrylate polymerization, the functionality was determined by comparing the NMR integrations of the methine proton on the terminal acrylate carbon with the phenyl ring protons of the 1-phenylethyl halide initiator fragment.[18] For polystyrene, a comparison between the integration for the terminal methine proton and the methyl protons of the toluenesulfonyl tail group was used.[19] Comparison of methine proton integration with the allyl initiator fragment was also effective.[264] Similar studies were performed for polyacrylonitrile.[66,131] For MMA, comparison of the ratio of the terminal and the chain methoxy protons relative to the size exclusion chromatography (SEC) results elucidated the polymer functionality.[124]

It is possible to control which halogen resides on the polymer chain end in some cases. An example has been given in the ATRP of MMA. In a mixed halogen environment, i.e., an alkyl bromide in the presence of copper chloride or vice versa, carbon will preferentially bond to chlorine over bromine.[155,281] However, the position of the equilibrium depends on the ligand and the transition metal. For example, in the ATRP of MMA initiated by α-bromoesters and catalyzed by a stoichiometric amount of a ruthenium chloride complex, nearly equimolar amounts of the alkyl chloride and bromide were needed.[176]

Thus, in ATRP, nearly every chain should contain a halogen atom at its headgroup, if termination and transfer are essentially absent. This halogen atom can be replaced through a variety of reactions leading to end functional polymers. Due to the increasing concern over the presence of halogens in the environment, the first consideration may be removal of those species from the chain ends after the polymerization is completed. A common method of dehalogenation of organic compounds, the reaction with trialkyltin hydrides,[282] was applied to polymers prepared by ATRP.[283] Using a radical reaction that can be employed either with an isolated polymer or in situ at the end of a polymerization, the addition of tributyltin hydride to the polymeric alkyl halide in the presence of a radical source (AIBN, polymeric radical, or Cu(I) complex) leads to a saturated hydrogen-terminated polymer. Such substitutions are often desirable for high-temperature applications where some evidence for halogen loss has been described.[256,284] By replacing tributyltin hydride with allyl tri-*n*-butylstannane, polymers with allyl end groups were produced.[285]

The terminal halogen can also be displaced by nucleophilic substitution, free-radical chemistry, or electrophilic addition catalyzed by Lewis acids. The first example of a chemical transformation of the halogen end group involved bromo- and chloro-terminated polystyrene.[286] Scheme 27 illustrates the reactions used to replace the halogens with azides leading to, in turn, amine groups. The nucleophilic substitution reaction with trimethylsilyl azide yielded the azide terminal polymer. This was followed by a

Scheme 27. Synthesis of End-Functional Polystyrenes[286]

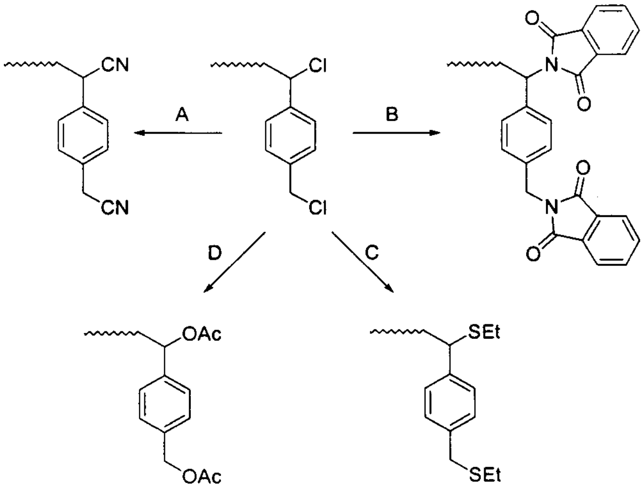


reduction with lithium aluminum hydride to afford the primary amino-functionalized chain end. Verification of the transformations was obtained by ^{1}H NMR, where the terminal methine resonance shifted quantitatively from 4.50 to 4.00 to 3.40 ppm, corresponding to the benzyl halide, azide, and amine, respectively. As a final confirmation that the transformation had taken place, α,ω-diamino-terminal polystyrene (M_n = 5100, M_w/M_n = 1.2) was reacted with terephthaloyl chloride in a step growth polymerization that yielded a polystyrene with several amido linkages with M_n = 23 000, M_w/M_n = 2.5.[286]

This method of transformation was later expanded to include the transformation of halo-terminated acrylates to azide- and amine-terminal polymers.[287] The nucleophilic displacement can be carried out also with NaN_3 in a DMF solution. Since the methylene protons α to the ester are difficult to analyze by ^{1}H NMR, a quantitative IR technique was used to evaluate the selectivity of the reactions. Since reduction with $LiAlH_4$ cannot be performed for acrylates, conversion to the phosphoranimines and subsequent hydrolysis produced the amines.[287]

Halogen atom displacement reactions from hyperbranched polystyrene and polyacrylate have also been reported.[146,288] Upon heating or UV irradiation, the hyperbranched polyacrylate with azide groups cross-linked.[146] Other examples are depicted in Scheme 28 for a terminal unit on a hyperbranched polystyrene.[288] Reactions A and B were attempted to produce intermediates that could be converted to amines. In reaction A some HCl elimination was observed. In reaction B, potassium phthalimide provided only partial substitution. Reduction to the amine via the Gabriel synthesis resulted in gelation. In reaction C, the polymer was stirred with sodium ethyl sulfide, resulting in 89% conversion. Finally, in D, exposing the benzyl chloride groups to potassium acetate under phase-transfer catalysis conditions yielded the acetate-modified hyperbranched polymer in 76% conversion.

Scheme 28. End-Functionalization of Hyperbranched Polystyrenes[288]



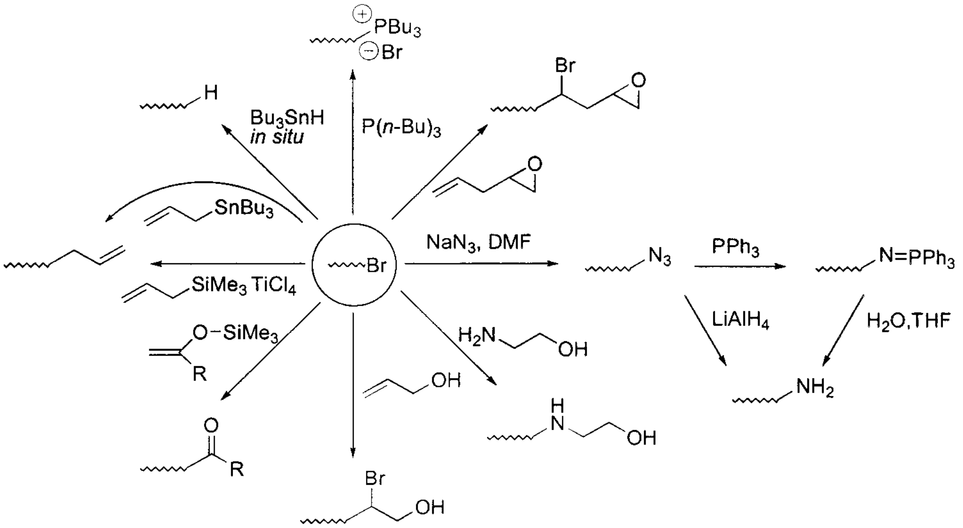
Elimination was also reported in the attempted alcoholysis, but better results were obtained by using functional initiators.[271] Reactions with amines and phosphines are also accompanied by an elimination process, especially at higher temperatures and for the more bulky triphenylphosphine.[208,209]

Another approach involves the atom transfer radical addition reaction. It should lead exclusively to monoaddition if monofunctional polymers are targeted. Thus, nonpolymerizable monomers by ATRP should be used. For example, the addition of an excess allyl alcohol near the end of an acrylate polymerization resulted in the monoaddition of this less reactive monomer. The new alkyl halide chain end no longer participated in the ATRP process due to the very low reactivity of the carbon−halogen bond.[272] The concept of end-functionalization through the addition of a nonpolymerizable monomer resembles earlier telomerization experiments[289] and was also applied to incorporate 1,2-epoxy-5-hexene[285] and maleic anhydride.[290,292] In the former case, hyperbranched polyacrylates were used, resulting in polymers with multiple epoxy groups. By reacting bromo-terminated polymers with C_{60} under ATRP conditions, C_{60}-terminated polystyrene and PMMA were prepared.[291] The fluorescence quenching using triethylamine or fumaronitrile showed that C_{60} still kept its strong electron-accepting and strong electron-donating properties after it was modified by the macromolecules.

Some end-group transformation reactions developed in the area of living cationic polymerizations have been adopted to ATRP. One example is the reaction of an alkyl chloride with silyl enol ethers.[167,293] The method has been adopted to the ATRP of MMA synthesized by the ruthenium dichloride tris(triphenyl phosphine) complex.[294] At the end of the polymerization, addition of either α-(trimethylsilyloxy)-styrene or *p*-methoxy-α-(trimethylsilyloxy)styrene to the reaction mixture resulted in a ketone-functionalized polymer chain end and released chlorotrimethylsilane. The functionality of the polymers, determined by ^{1}H NMR, was >0.97. Another example is the transformation of the halo-terminated polystyrenes to the allyl derivatives in the presence of allylsilanes and strong Lewis acids such as $TiCl_4$.[252]

Polymeric diols hold value in step growth copolymerizations. Inclusion of styrenes and acrylates into those copolymers could, therefore, expand the applications of materials such as polyesters and polyurethanes.[295] The first hydroxy group can be incorporated by using hydroxy-functional initiator derivatives based on 2-bromoisobutyrates and 2-bromopro-

Scheme 29. Examples of the Displacement of the Terminal Halogen in ATRP Polymers Using Electrophilic, Nucleophilic, and Radical Reactions



pionates.[160,272] For the second group, two approaches to functionalization have been employed. The first one involved the direct substitution of the halogen with an amino alcohol such as aminoethanol.[272] The reaction was successful with polystyrene, but multiple additions to the backbone ester groups were observed with poly(methyl acrylate). Using 4-aminobutanol in place of aminoethanol alleviated the latter problem. The other approach employs allyl alcohol.[272]

Diols can also be made by coupling the chains initiated by hydroxy group containing initiators. For example, sulfide linkage between two chains with hydroxy terminal structures can be accomplished through the coupling of the polymeric alkyl halides with sodium sulfide.[296] The low basicity and high nucleophilicity of the RS anion reduces elimination, and its higher reactivity than Na_2S ensures high functionality. In a similar way reaction with α-methylstyrene leads to formation of the monoadduct, cumyl halides, which are thermally unstable, decompose, and react in the second addition, leading to chain coupling. [295]

Aside from the more obvious aspects of ATRP (predictable molecular weights, narrow polydispersities), one of the most important and exciting features of this type of polymerization is the nearly quantitative preservation of the halogen end groups. The number of known reactions that involve halogens (radical or ionic) makes it likely that ATRP will be propelled into numerous applications that are not currently envisioned. For these reasons, the importance of transformation reactions cannot be stressed enough. A summary of several routes to displace the terminal halogen using electrophilic, nucleophilic, and radical transformations is shown in Scheme 29.

4. Summary and Outlook

As discussed in this section, ATRP is the most versatile CRP technique to precisely and inexpensively control chain-end functionalities. This is especially important in the synthesis of reactive and functional polymers of relatively low molecular weight. For example, in the reactive difunctional oligomer of DP ~10, end groups contribute to 20 mol %. Such oligomers may be used as building blocks for currently targeted high solid coatings and perhaps the next generation of solventless coatings. Halogen end groups are much less expensive than nitroxides and/or dithioesters. Due to commercial availability of many activated alkyl halides with various functionalities, it is very easy to prepare end-functional polymers. Moreover, the activated alkyl halides can be incorporated to the chain ends of many polymers prepared by other techniques and open the routes toward novel block copolymers. Attachment of initiator fragments to organic or inorganic surfaces can be used as means to modify the surface. This modification can be performed under very undemanding conditions of free radical polymerization to yield biocompatible surfaces, and surfaces with improved lubrication or scratch resistance by incorporation of a well-defined nanoscale polymer layer

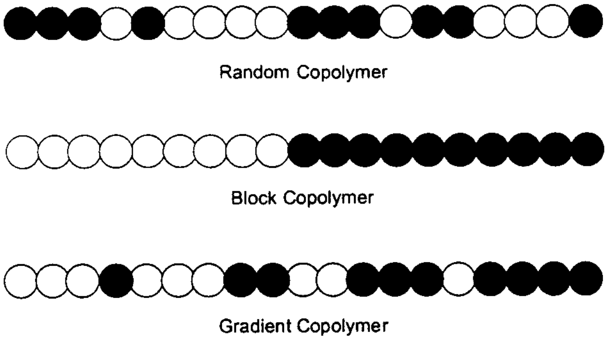
Halogen end groups may be replaced using many different organic transformations such as nucleophilic substitution, electrophilic addition, radical addition, etc. Especially important may be synthesis of well-defined mono-, di-, and multifunctional oligomers with hydroxy, amino, and acidic functionality for coatings and segments for polyesters, polyamides, and polyurethanes. These new applications will require very precise control of functionalities.

Many examples provided in this section show some feasibility studies which should be quantified and the conditions for the highest control of functionalities should be optimized. Here, some high-throughput techniques may be very helpful. Finally, a detailed structure–property correlation is needed to optimize properties of materials prepared with available functionalities.

B. Composition

In this section we will cover the combinations of monomers arranged in a linear polymer motif. Differentiation will be made between the relative posi-

Scheme 30. Schematic Representation of Random, Block and Gradient Copolymers



tion of monomers (i.e. statistical, gradient, or block) along a chain. Copolymers with a nonlinear structure will be discussed in section III.C devoted to chain topology.

1. Gradient/Statistical Copolymers

Aside from advantages such as tolerance to functional groups and mild reaction conditions, free-radical polymerizations are attractive because of the wider variety of monomers that can be homo- and copolymerized relative to other ionic techniques. The statistical (or random) copolymerization of multiple monomers in a single reaction is well established, and as a result, a plethora of monomer reactivity ratios have been measured for the prediction of polymer composition and characteristics.[297] The slow rate of initiation relative to propagation in conventional radical systems composed of two or more monomers leads to chains which have differing compositions depending on when they were grown. This results in a composition variation *among the chains* and, in the extreme cases, may result in a mixture of two homopolymers. In ATRP, all the chains are initiated early in the reaction and, under proper conditions, remain active over the entire course of the reaction. Therefore, changes in the instantaneous composition arising from variations in the relative concentrations of monomers is reflected *along all chains*. In the extreme case of very different reactivity ratios, this may lead to block copolymers. At the end of the reaction, the cumulative compositions of the conventional and controlled reactions should be the same, but in the conventional case a variety of compositions will be observed between the chains, while in ATRP all chains will have a similar structure, although they may not be symmetrical. This will result in the gradient of composition along the chain.[133] Such gradient copolymers are expected to have properties unlike other copolymers (block or random), making them candidates for applications such as blend compatibilizers and pressure sensitive adhesives.[133,298] The shape of the gradient depends on the reactivity ratios and on the composition of the monomer feed. However, ATRP (and other controlled radical polymerization techniques) enables the synthesis of not only spontaneous gradient but also forced gradient copolymers. In the latter system, the addition of one monomer is metered into a reactor already containing another monomer in a semibatch mode.

Due to the relative infancy of ATRP, only a limited number of gradient copolymers have been reported.[133] The first example was a spontaneous and forced gradient copolymerization of styrene and MMA.[299] The molecular weight was predictable, polydispersities $M_w/M_n < 1.25$, and the composition of styrene relative to MMA decreased as MMA was added. In another study examining the forced gradient copolymerization of methyl acrylate (MA) and styrene, changes in the feed rate of MA (0.085 vs 0.050 mL/min) resulted in differences in the instantaneous composition of MA in the copolymer. At a higher feed rate, there was more MA incorporated into the chains at a given fractional chain length (conversion). Thermal and mechanical studies on the block, statistical, and forced gradient copolymers of styrene and methyl acrylate with molecular weights, polydispersities, and compositions listed in Table 10 are shown in Figure 10.[133] The DSC and dynamic mechanical results indicate that the block copolymer has significantly different properties from the gradient copolymers. The DSC traces show that the forced gradient copolymer behavior depends on the thermal history. The lower modulus (G') of the forced gradient compared to the statistical gradient copolymer demonstrates that materials with different properties were produced.

Table 10. Composition and Molecular Weight Data[133]

copolymer	% MA	M_n	M_w/M_n
block (B1)	40	16 000	1.42
random (R1)	57	22 000	1.18
gradient (G2)[a]	55	12 000	1.19

[a] MA added to styrene at 0.05 mL/min.

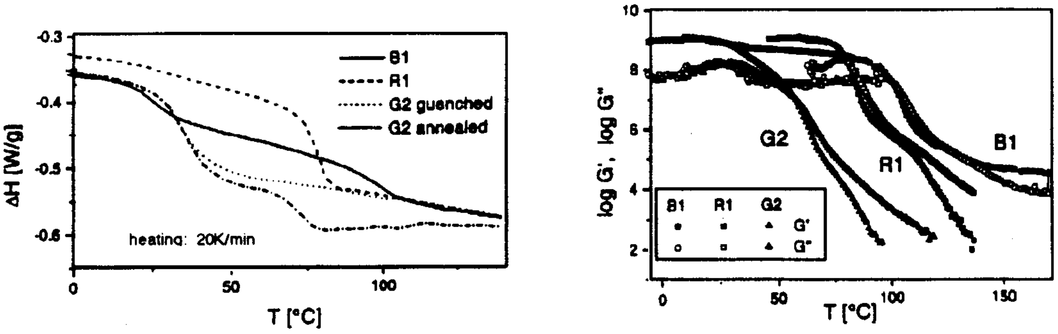


Figure 10. Differential scanning calorimetry and dynamic mechanical analysis data for copolymers described in Table 10.[133]

The synthesis of forced gradients of styrene and acrylonitrile[133] as well as spontaneous gradients of styrene and *n*-butyl acrylate have been reported.[235,237] In the latter case, a nonlinear least-squares regression analysis showed that the accepted reactivity ratios for styrene and *n*-butyl acrylate found in conventional radical polymerization[300] fell within the joint confidence intervals (JCI) of the copolymers prepared by ATRP.[235,237] These data along with ^{13}C NMR data[237] on the acrylate carbonyl group absorption confirm the radical nature of ATRP.

Figure 11 shows the results of small angle X-ray scattering of two S/AN gradient copolymers with the same content of AN (59 mol %) with low polydispersities but different MW. The higher MW sample displayed a periodicity of 22.4 nm but the lower MW sample only 13.4 nm. The higher MW sample stayed in the phase separated regime at $T > 200$ °C, but for the lower MW sample the order decreased with temperature and a single phase was formed at $T > 150$ °C. Thus, it is possible to manipulate phase transitions by changing MW and perhaps compositions and the shape of the gradient.

Other examples of spontaneous copolymerization have been reported in the literature. One describes copolymerization of styrene with 4-acetoxystyrene.[301] Copolymerization of a 1:1 molar ratio of the two monomers using the heterogeneous CuBr(bpy)$_3$ catalyst system in bulk at 110 °C leads to copolymers in quantitative yield with $M_n = 9000$, $M_w/M_n = 1.14$.

Epoxystyrene[302] and trimethylsilylstyrene[303] were also successfully copolymerized with styrene. Copolymerizations with styrene were conducted using both the nitroxide-mediated and ATRP approaches. In the ATRP reactions monomodal molecular weight distributions were obtained in polymerizations where the measured and calculated chain lengths were in reasonable agreement. The composition of the copolymer agreed with the feed ratios of the two monomers, and NMR analysis showed that the epoxide ring was unaffected under the polymerization conditions. Such preservation was important to prevent cross-linking reactions during polymerization and to optimize the properties of the material for use in adhesive, coatings, and lithography applications.

Statistical copolymerizations of MMA and *n*-butyl methacrylate (BMA) have been conducted to determine the reactivity ratios and attempt to ascertain the mechanisms of propagation of a number of polymerization systems.[234] The polymerizations studied were conventional free-radical polymerization (CFRP), catalytic chain transfer polymerization (CCTP), group transfer polymerization (GTP), anionic polymerization (anionic), lithium alkyl/aluminum alkyl anionic polymerization (Li/Al), and atom transfer radical polymerization (ATRP). The hypothesis was that values of the reactivity ratios of BMA and MMA that were similar must belong to polymerization systems which operate by similar mechanisms (ionic, radical, etc.).[234] The results indicate that there are three groups of separate reactivity ratio (*r*) values. These are grouped according to radical (CFRP, CCTP, ATRP), ionic (anionic, Li/Al), and GTP mechanisms. Two of the conclusions the authors cite are (1) ATRP proceeds by propagation through a radical species and (2) GTP proceeds by a mechanism that is not like either radical or ionic polymerizations.

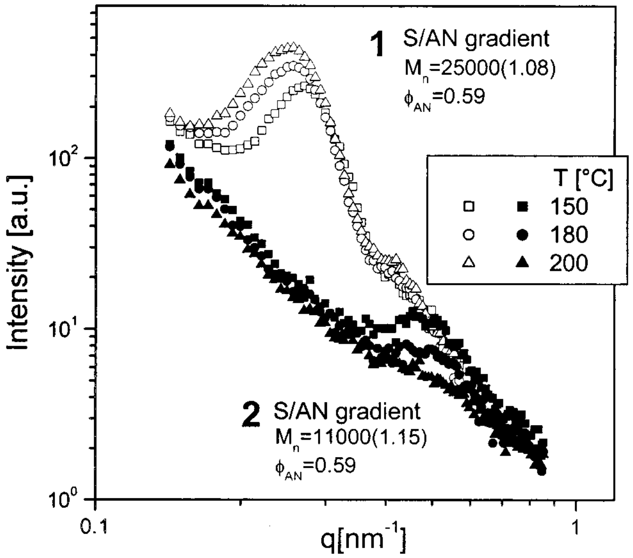


Figure 11. Small angle X-ray scattering of two S/AN gradient copolymers. Both copolymers contained 59% (mol) AN; gradient 1: M_n = 25 000 and M_w/M_n = 1.08; gradient 2: M_n = 11 000 and M_w/M_n = 1.15.

The copolymerization of MMA with *n*-butyl acrylate by both a conventional radical polymerization and ATRP was studied.[115,236] The reactivity ratios for the two polymerization techniques were similar and independent of the structure of the catalytic system.[236] This led to the suggestion that ATRP proceeds via a radical propagation mechanism, although some differences could arise from preferential monomer complexation by a catalyst. Differences may also appear due to incomparable reaction conditions such as conversion, temperature, solvent, and methods of measurement and data analysis, which can differ significantly between the conventional and ATRP experiments.[192] Sawamoto et al. also reported statistical copolymerizations of MMA with either *n*-butyl or methyl acrylate.[114] No reactivity ratio values were provided.

A series of sequential styrene/MMA statistical copolymerizations was conducted within the same reactor from the same chains toward the synthesis of ABC "block-random" copolymers.[304] Since the rates of polymerization of the two monomers are similar, the composition of the copolymer could be defined by the initial monomer feed ratios. Over the course of the reaction, the feed composition of styrene/MMA was changed from 3/1 to 1/1 to 1/4 by the addition of more MMA. The polydispersity of the copolymer was ~1.5, higher than that found in the ATRP of MMA alone using the same ruthenium complex.[124]

The synthesis of both spontaneous and forced gradient copolymers is in its infancy using controlled free radical polymerization techniques, but significant contributions are expected in the future. Results from these studies will elucidate mechanistic aspects of controlled free radical polymerizations and generate data in studies (in comparison to theory) on the ability of these macromolecules to serve as novel materials.

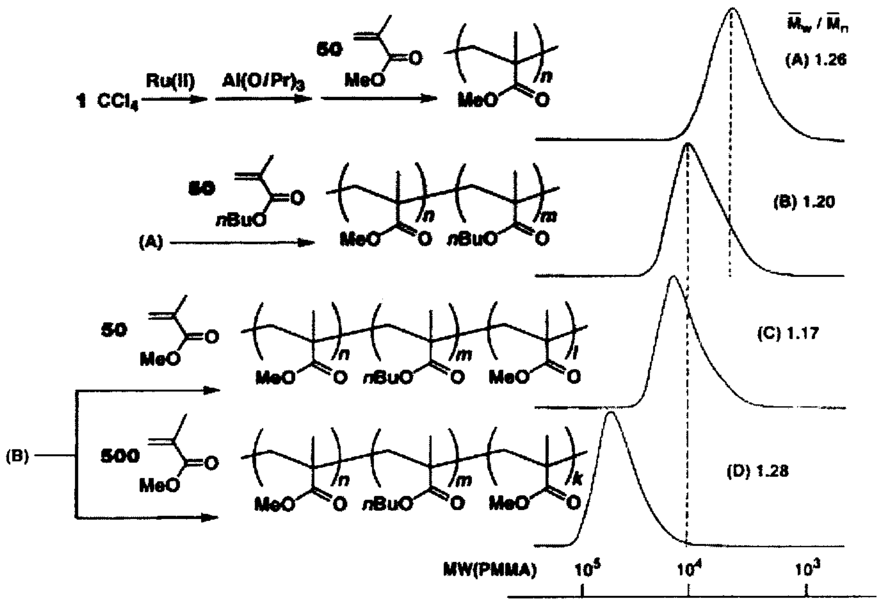


Figure 12. SEC chromatograms of the various segments in the synthesis of polyMMA-*b*-polyBMA-*b*-polyMMA.[124]

Table 11. Molecular Weight Data for the Synthesis of Triblock Copolymers of Styrene and 4-Acetoxystyrene[301]

exp[a]	initiator mole	monomer mole	T (°C)	time (h)	yield (%)	$M_n \times 10^{-3}$	M_w/M_n
1	DBX[1] 6.8×10^{-4}	Sty 0.052	110	18	94	10.0	1.24
2	Br−St-Br[2] 2.1×10^{-4}	AcOSt 0.039	90	15.5	73	21.0	1.15
3	DBX[1] 6.5×10^{-4}	AcOSt 0.033	90	1.7	58	4.8	1.11
4	Br−P(AcOSt)-Br[3] 3.8×10^{-4}	Sty 0.052	110	19	80	25.2	1.16

[a] (1) α,α′-*p*-Dibromoxylene, (2) initiator = polymer synthesized in exp 1, (3) initiator = polymer synthesized in exp 3.

2. Block Copolymers

The presence of an activated alkyl halide at a polymer chain end enables ATRP to synthesize di-, tri-, or multiblock copolymers. Block copolymers can be generated from a macroinitiator synthesized by either ATRP or a different mechanism altogether.[21] Furthermore, the growth of subsequent blocks can be achieved from an isolated macroinitiator or by in situ addition of a second monomer to a reaction near completion. The examples below will summarize many of the block copolymers synthesized to date and give motivations for their generation and an overall flavor for the variety of structures that can be produced through very rudimentary reactions.

a. Block Copolymers Synthesized (Strictly) by ATRP. Shortly after the discovery of ATRP, it was recognized that the wide variety of monomers, conservation of end groups, and control over molecular weights and polydispersities could facilitate the synthesis of block copolymers.[17] The first example of such a reaction was the synthesis of poly(methyl acrylate)-*b*-polystyrene) and polystyrene-*b*-poly(methyl acrylate).[16,299] Since then, a number of di- and triblock copolymers have been well documented and will be discussed in more detail.

i. Comonomers Belonging to the Same Class. The switch from one block to another may sometimes be difficult and should be performed according to certain rules. The simplest is block copolymerization within the same class of monomers such as methacrylates, acrylates, or styrenes. Two early examples were the syntheses of poly(butyl methacrylate)-*b*-poly(methyl methacrylate) diblock[113] and poly(methyl methacrylate)-*b*-poly(butyl methacrylate)-*b*-poly(methyl methacrylate) triblock[124] copolymers prepared by sequential monomer addition. Formation of the diblock copolymer was confirmed by overlaying the SEC traces of the poly(butyl methacrylate) segment with diblock copolymer. The polydispersities of the homo- and diblock copolymers were both low, $M_w/M_n < 1.2$.[113] For the triblock copolymer, ^{1}H NMR determination of end groups at the conclusion of the polymerization of each segment demonstrated that the majority of chains remained active. Furthermore, addition of an excess of MMA to the chlorine terminal PMMA-*b*-PBMA diblock macroinitiator provided a triblock copolymer where an unambiguous evaluation of the amount of unreacted diblock could be made. Figure 12 shows that the amount of this remaining material is insignificant.[124]

In another effort, polystyrene-*b*-poly(4-acetoxystyrene)-*b*-polystyrene and poly(4-acetoxystyrene)-*b*-polystyrene-*b*-poly(4-acetoxystyrene) were synthesized in order to produce amphiphilic triblock copolymers after hydrolysis of the acetate groups.[301] Table 11 lists the molecular weights and distribution results for polymers initiated by α,α′-*p*-dibromoxylene. The table shows that polydispersity remains low in the transition from one block to the other, and the process appears to work well regardless of the order of the segments polymerized. However, SEC traces of both of the purified triblock copolymers showed a low molecular weight tail indicative of either a small degree of irreversible termination or inefficient initiation/loss of halogen chain ends during either the purification of the macroinitiator or the onset of block copolymerization. Nevertheless, the polydispersities are quite low, indicating well-defined materials. No data was given on the hydrolysis of the acetoxy groups.

The synthesis of amphiphilic block copolymers based on acrylic segments has been disclosed. Diblock and triblock copolymers of *n*-butyl acrylate and HEA were polymerized by chain extension of poly(*n*-butyl acrylate) with HEA-TMS.[107] The amphiphilic materials were obtained by deprotection of the trimethylsilyl group with HCl in THF. Qualitative studies showed that varying the ratio of hydrophile to hydrophobe as well as the arrangement of the various segments in the copolymer (AB, ABA, BAB, and statistical copolymers) influenced the behavior of the material in water. Homopolymerizations of unprotected HEA were also discussed; M_n, measured by ^{1}H NMR, agreed with theoretical values but polydispersities, measured by SEC in DMF, were higher ($M_w/M_n = 1.5-1.7$) than those observed in the polymerization of the protected monomer.

ATRP was also used to produce amphiphilic block copolymers as stabilizers for suspension polymerization in supercritical carbon dioxide.[110] These diblock copolymers consist of a CO_2-philic block and a CO_2-phobic segment. The challenge in these systems, similar to the polyacrylonitrile block copolymerizations,[132] is that the CO_2-philic segment, poly(perfluorooctyl methacrylate) (PFOMA), is poorly soluble in organic solvents, making synthesis and characterization difficult. Therefore, the PFOMA block was polymerized from an organic macroinitiator as shown in Table 12. Similarly, ATRP was used to prepare block copolymers comprised of fluorinated (meth)acrylates and polyMMA and polyDMAEMA (DMAEMA = 2-(dimethylamino)ethyl methacrylate) using bpy ligands with long fluoroalkyl groups in homogeneous $scCO_2$.[82]

Table 12. Synthesis of Hydrocarbon/Fluorocarbon Diblock Copolymers[110]

hydrocarbon block	M_n 10^{-3}	M_w/M_n	fluorocarbon block	M_n 10^{-3}
PMMA	8.1	1.3	PFOMA	55.9
P(*t*BA)	5.0	1.6	PFOMA	52.6
PHEMA-TMS	4.0	1.5	PFOMA	40.0

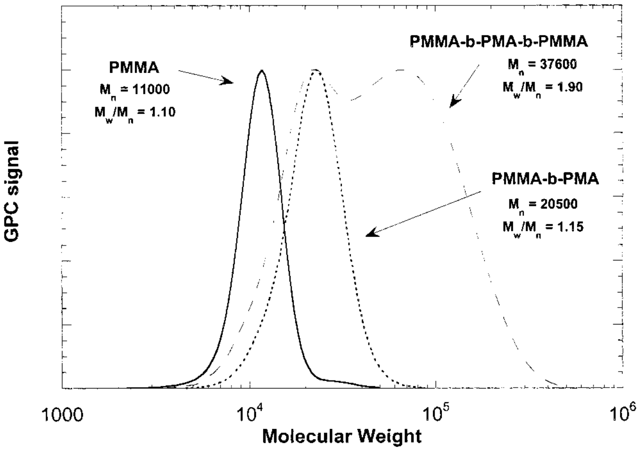


Figure 13. Overlaid SEC traces depicting the efficiency of blocking reactions in the synthesis of block copolymers composed of PMMA and PMA.[177]

ii. Comonomers Belonging to Different Classes. A series of experiments was designed to examine the blocking efficiency in methacrylate and acrylate polymerizations as a function of macroinitiator composition, end group, and activating transition metal complex.[177] The data, depicted graphically in Figure 13, showed that initiation of MMA from a chlorine terminal poly(methyl acrylate) macroinitiator resulted in poor initiation efficiency. However, when the PMMA was used to initiate the polymerization of the acrylate, a uniform shift of the entire SEC trace to higher molecular weight occurred. Chain extension of this diblock copolymer with MMA again showed poor initiation efficiency. Finally, the ATRP of MMA from bromine terminal poly(methyl acrylate) mediated by a copper chloride complex showed fast initiation. The conclusions derived from these studies were that when the acrylate macroinitiator contained a chlorine end group, propagation of MMA was faster than initiation, leading to a bimodal molecular weight distribution. The rate of cross-propagation from a bromine-terminal acrylate, however, was at least comparable to that of propagation of MMA mediated by chlorine. Since the previous model studies showed that, in a mixed halogen environment, the alkyl halide will contain predominantly chlorine,[155] chain extension of the bromine terminal polyacrylate with MMA mediated by a copper chloride complex provides high initiation efficiency. This study enabled the efficient synthesis of poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate) ABA triblock copolymer by polymerization of the MMA segments from a difunctional poly(*n*-butyl acrylate) macroinitiator.[177] The exchange improved the efficiency of block copolymerization significantly. The polydispersities of the hard block in all acrylic thermoplastic elastomers have a great effect on the morphology and rheological properties, as recently reported.[178−180]

Thus, the chain extension is efficient if the apparent rate constant of crosspropagation is at least as fast as that of the subsequent propagation. This means that the product of the equilibrium constant and the rate constant of addition for the switch should be at least comparable to that for the continuation of the growth of the second block. According to the homopolymerization and model studies, the following order can be proposed AN > MMA > St ≈ MA. The structure of the ester group (e.g., methyl vs butyl, etc.) is less important. This indicates that an order of addition for styrenes and acrylates is not important, but methacrylates and acrylonitrile should not follow polystyrene or polyacrylate blocks. If, for some reason, such an order of block introduction is required, a halogen exchange should be used. Starting from bromo-terminated chains and switching to chloro-terminated ones in the presence of CuCl alters equilibrium constants, which are much higher for Br than for Cl derivatives. Similar rules apply for the choice of efficient initiators for the homopolymerizations. They simply follow the strength of C−X bonds. As will be showed later, violation of these rules leads to lower blocking efficiency.

A possibility to avoid halogen exchange is to add the second more reactive comonomer before the first one is consumed. A small amount of the first, less reactive, comonomer in the reaction mixture can act as a kinetic “compatibilizer”, preventing an uncontrolled growth of the second block. This will result in the formation of the random outer block (it may have a tapered structure). Mechanical properties of the resulting block copolymers with outer tapered segments are dramatically different from those of the pure block copolymers.[305] Thus, although this approach simplifies synthesis, it leads to entirely different products!

The halogen exchange was also useful for the block copolymerization of DMAEMA using well-defined PMMA, PMA, and polystyrene as macroinitiators. The polydispersities of the block copolymers are lower with the halogen exchange ($M_w/M_n = 1.2$).[306]

On the other hand, the exchange was not necessary for the block copolymerization of 4-vinylpyridine from PMMA-Cl. Me$_6$TREN was used as a ligand to avoid motel decomplexation in the presence of poly(vinylpyridine).[145]

Other styrene/(meth)acrylate block copolymers have also been prepared. One study involved the use of chlorine terminal macroinitiators of either polystyrene or poly(*n*-butyl acrylate) in the ATRP of either *n*-butyl acrylate or styrene, respectively, for polymerizations mediated by a CuCl/bpy complex in the presence of DMF.[307] From the reactions, linear semilogarithmic plots of monomer consumption were obtained along with descriptions of molecular weight with conversion. However, polydispersity increased with the addition of each successive block, most likely due to end-group loss occurring through termination or some side reaction.[36] In another study, the preparation of block polystyrene-*b*-poly(*p*-nitrophenyl methacrylate) and its hydrolysis and amino substitution products, polystyrene-*b*-poly(methacrylic acid) and polystyrene-*b*-poly(*N*-butyl methacrylamide), were described.[308] Polystyrene-*b*-poly(*p*-nitrophenyl methacrylate) formed micelles in chloroform with polystyrene as shell and poly(nitrophenyl methacrylate) as core but formed inverse micelles in dimethyl sulfoxide. However, because the methacrylate was used as the second block, the polydispersities of the block copolymers were higher than that of the starting polystyrene.

Synthesis of triblock copolymers composed of polyacrylonitrile (PAN) peripheral blocks was also difficult.[132] Block copolymers consisting of PAN and other vinyl monomers is challenging due to the relative insolubility of the former in common organic solvents. Furthermore, other polymers soluble in common solvents often exhibit limited solubility in ethylene and propylene carbonate, two diluents found to be particularly good for the ATRP of acrylonitrile. A compromise was diphenyl ether. Triblock copolymers were generated from difunctional poly(*n*-butyl acrylate) and poly(ethylhexyl acrylate), which were synthesized by the ATRP of the acrylate initiated by α,α′-*p*-dibromoxylene. The polymerization of acrylonitrile from the macroinitiator resulted in molecular weights that increased linearly with conversion.

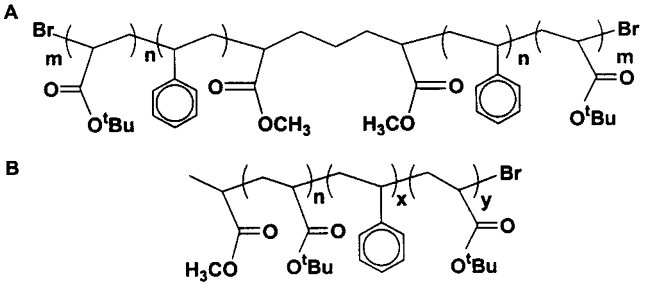


Figure 14. Structure of (A) symmetrical difunctional P*t*BA-*b*-PS-*b*-P*t*BA and (B) unsymmetrical monofunctional P*t*BA-*b*-PS-*b*-P*t*BA.

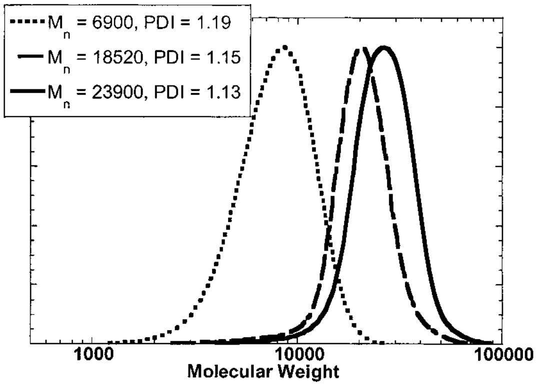


Figure 15. SEC traces of (A) difunctional PS (- - -) and P*t*BA-*b*-PS-*b*-P*t*BA (−) and (B) P*t*BA (• • •), P*t*BA-*b*-PS (- - -), and P*t*BA-*b*-PS-*b*-P*t*BA (−) in THF at 35 °C.

Block copolymers from PMMA and polystyrene macroinitiators were examined in experiments studying ATRP at ambient temperature mediated by CuBr/bpy complexes in acetonitrile.[38] PMMA-*b*-PS, PMMA-*b*-PHEMA), and PS-*b*-PHEMA) block copolymers were synthesized with polydispersities below 1.5 at high conversion of the second block.

Polystyrene and polyacrylate block copolymers can be grown from either type of macroinitiator. This has been demonstrated for the synthesis of various SA, AS, SAS, and ASA diblock and triblock copolymers between styrene and *tert*-butyl acrylate.[109,144] The latter triblock has been prepared either using a difunctional initiator with chain extension from both ends of the polystyrene to the polyacrylate or by crossing from a monofunctional acrylate to styrene and back to the acrylate. The final structures are illustrated in Figure 14, and the SEC traces are shown in Figure 15.[144] Similar systems have been used for *n*-butyl acrylate as described in simple experiments for the undergraduate laboratories.[309,310]

ATRP has been used successfully for the preparation of ABC triblock copolymers (terpolymers) as well as the corresponding ABCBA pentablocks and even (ABC)$_3$Z nonablock copolymers (terpolymers) using trifunctional cores (cf. section III.C.3). In the synthesis of ABC systems, the order of block formation is important and should generally follow the rules

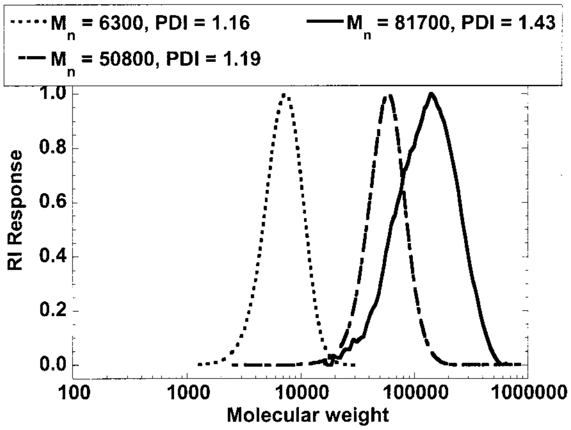


Figure 16. SEC traces of difunctional PtBA (· · ·) in THF, PMMA-*b*-PtBA-*b*-PMMA (- - -) in THF, and P4VP-*b*-PMMA-*b*-PtBA-*b*-PMMA-*b*-P4VP (—) in DMF.

(AN ≥ MMA ≥ S, A). It is possible, however, to change this order by using the halogen exchange methodology. For example, a triblock system has been prepared using a bromine-terminated difunctional poly(*tert*-butyl acrylate) macroinitiator, which was chain extended with MMA using a CuCl-based catalyst to invoke the halogen switch. This was subsequently chain extended with 4VP using the CuCl/Me$_6$TREN catalyst system to generate the ABCBA block copolymer.[311] The SEC traces are shown in Figure 16.

The thermal stability of polystyrene containing halogen termini was enhanced by block copolymerization of styrene with substituted norbornadiene (Scheme 31).[284] This monomer was also homopolymerized by ATRP ($M_n = 2900$, $M_w/M_n = 1.17$) using a CuCl/bpy catalyst. In the copolymerization, chloroterminated polystyrene ($M_n = 10\,300$, $M_w/M_n = 1.36$) was chain extended with substituted norbornadiene. The molecular weight of the block copolymer was $M_n = 14\,400$, $M_w/M_n = 1.24$, indicating that 5% (mol) of the bicyclic species was incorporated into the macromolecule. Thermogravimetric analyses (TGA) of Cl-terminal polystyrene and polystyrene-*b*-poly(norbornadiene) synthesized by ATRP and polystyrene synthesized by classic free radical polymerization showed that chlorine-capped polystyrene underwent decomposition at a temperature 50 °C lower than the analogous homopolymer without Cl end groups. Removal of the Cl from the polystyrene terminus by formation of a block copolymer increased the thermal stability.

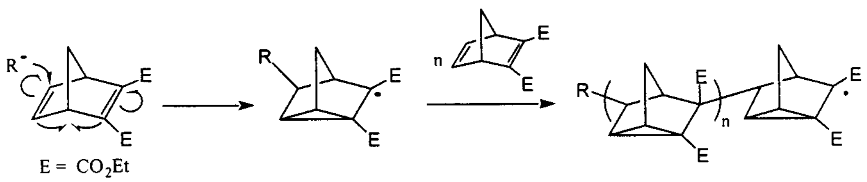
However, the thermal stability of PMMA prepared by ATRP mediated by a nickel bromide complex showed different results.[113] The onset of degradation in the TGA measurement occurred at 375 °C, much higher than the 165 °C found in the same thermolysis of PMMA prepared by a conventional radical polymerization. Different results were obtained using the CuBr/bpy catalytic system.[312] The TGA data indicate that the catalyst should be removed for higher thermal stability.[113,256,284,312]

b. Mechanistic Transformations. A polymer synthesized by one mechanism can be used, either directly or after a simple organic transformation reaction, as a macroinitiator for the ATRP of vinyl monomers. Efficient ATRP macroinitiators were prepared by cationic, anionic, ring-opening metathesis (ROMP), conventional radical, and step growth polymerizations.

i. Cationic to ATRP. Aside from purity issues associated with ionic polymerizations, transformation from cationic polymerization to ATRP can be considered in many respects the most simple because the counteranion of the active species is often a halogen atom. Therefore, ensuring that the halogen is bonded to an organic fragment that is able to undergo bond homolysis in the presence of the appropriate copper(I) salt is the only variable necessary to have a viable macroinitiator.

The first, and most straightforward, example of such a transformation is from the cationic polymerization of styrene.[313] As shown in Scheme 32 initiation of the styrene polymerization with SnCl$_4$ produces an active species with chlorine as the counterion. Termination of the reaction yields 1-phenylalkyl chloride terminal polystyrene. After purification, ATRP with either methyl acrylate, methyl methacrylate, or styrene in conjunction with a soluble CuCl(dNbpy)$_2$ catalyst yields the diblock copolymers. For all three monomers, the molecular weights increased according to the predetermined ratio of monomer to initiator. The polydispersities were quite low for styrene and methyl acrylate ($M_w/M_n = 1.2$) but were significantly higher for MMA ($M_w/M_n = 1.6$). The higher polydispersity was most likely due to slow initiation of MMA polymerization relative to propagation based on model studies initiating an MMA polymerization from benzyl chloride.[123] A demonstration of this method in a one-pot process by the addition of methyl acrylate to the living polystyryl chloride to deactivate the cationic system was also

Scheme 31. Radical Polymerization of Norbornadienes[284]



Scheme 32. Transformation from Carbocationic Polymerization to ATRP[313]

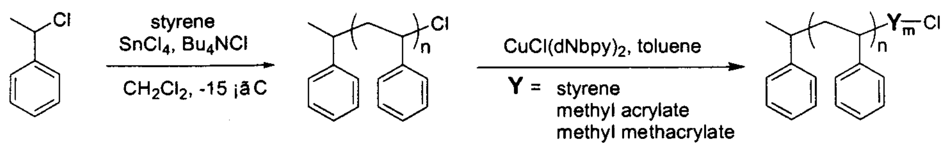


Table 13. Synthesis of ABA Triblock Copolymers from Cl-Sty-PIB-Sty-Cl Macroinitiators[315]

monomer	$M_{n,th}$	$M_{n,exp}$	M_w/M_n
styrene[a]	13 370	13 350	1.18
methyl acrylate[a]	11 800	12 200	1.41
methyl methacrylate[a]	23 100	22 500	1.45
isobornyl acrylate[a]	17 270	18 850	1.44
styrene[b]	48 000	48 820	1.14
methyl acrylate[b]	32 000	31 810	1.42
methyl methacrylate[b]	33 000	33 500	1.47
isobornyl acrylate[b]	48 000	49 500	1.21

[a] Macroinitiator $M_n = 7800$, $M_w/M_n = 1.31$. [b] Macroinitiator $M_n = 28800$, $M_w/M_n = 1.31$.

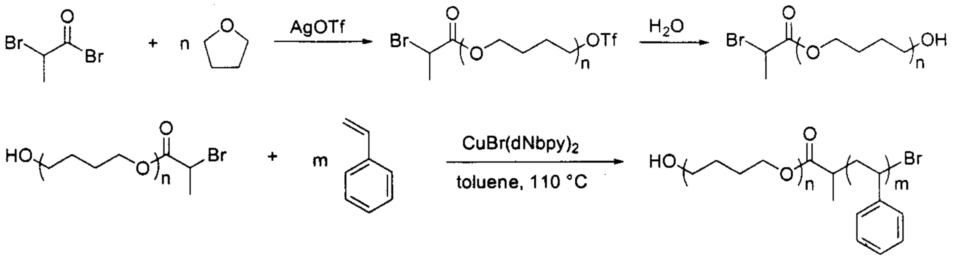
described. It should be noted that in the SEC traces of the block copolymers with poly(meth)acrylates there was a small low molecular weight shoulder, most likely corresponding to polystyrene chains which did not initiate the polymerization. Qualitative assessment of these chains indicates that they represent less than 10% of the total concentration of polymer.

Similar studies were performed simultaneously by the Kops[314] and Matyjaszewski[315] groups regarding the preparation of difunctional polyisobutene macroinitiators for use in ATRP. Because the *tert*-butyl chloride terminal fragments are not efficient initiators for ATRP, at the end of the cationic polymerization, a low concentration of styrene was added to the living cationic polyisobutene to ensure that α-phenylalkyl chloride moieties were located at the chain termini.[315,316] Polymerization of styrene[313,314] and *p*-acetoxystyrene[314] by ATRP then proceeded in both studies. The Kops group used the heterogeneous $CuCl(bpy)_3$ catalyst, while Coca and Matyjaszewski used the homogeneous $CuCl(dNbpy)_2$ system. Efficient initiation was observed in styrene[313,314] polymerization, but with *p*-acetoxystyrene[314] residual macroinitiator was observed in the SEC traces. This was attributed to poor compatibility between the monomer and the macroinitiator.[314] The Matyjaszewski contribution also described the polymerizations of methyl acrylate, methyl methacrylate, isobornyl acrylate, and styrene. The results in Table 13 show that the polydispersities were somewhat larger than for block copolymerizations from polystyrene macroinitiators.[315] However, the polydispersities of the macroinitiators in this study were also larger than in the previous case. Later, the Kops group introduced another polyisobutylene macroinitiator by substituting the Cl-terminal telechelic homopolymer with a phenol followed by esterification of the alcohol with 2-bromopropionyl chloride.[317] The polymerization of styrene was performed, but the use of the bromine end group in conjunction with a $CuBr(bpy)_3$ catalyst allowed for the polymerization to be conducted at 110 °C instead of 130 °C without a significant decrease in the reaction rate.

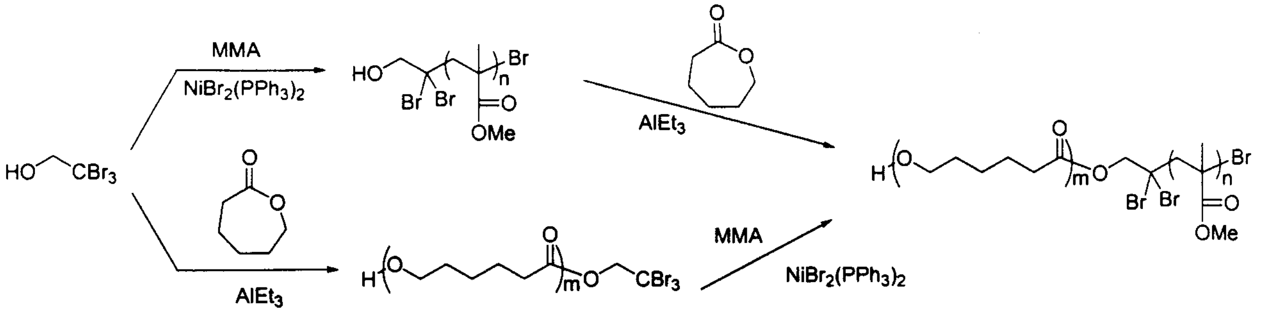
Transformation from living cationic ring-opening polymerization to ATRP was realized using polyTHF as the macroinitiator.[318] The monofunctional macroinitiator was synthesized directly by the cationic ring-opening polymerization of THF initiated by 2-bromopropionyl bromide/AgOTf followed by termination with water. For the difunctional macroinitiator, termination with the attachable ATRP initiator sodium 2-bromopropionate following propagation initiated by triflic anhydride was necessary. The ATRP of styrene, methyl acrylate, and methyl methacrylate from the monofunctional polyTHF macroinitiator varied strongly with temperature and the ratio of monomer to initiator. However, conditions could be found for each monomer that yielded diblock copolymers with predetermined molecular weights and moderate polydispersities, $M_w/M_n < 1.5$. The difunctional initiator gave poorer control than the monofunctional analogue. The MMA polymerization was well controlled, with molecular weights less than 20% over those predicted and polydispersities reduced from $M_w/M_n = 1.71$ for the macroinitiator to $M_w/M_n = 1.34$ for the triblock copolymer. The monofunctional initiator contains a hydroxyl group at the other polyTHF terminus, which can be converted to an ATRP initiator for polymerization of a different monomer to yield asymmetric ABC triblock copolymer. Conversely, block copolymers have also been prepared using a mechanism transformation from ATRP to cationic polymerization. Thus, polystyrene PS with end-terminal bromine (Br−PS−Br) was synthesized by ATRP using the difunctional initiator 1,2-bis(2′-bromobutyryloxy)ethane. The resulting polymer was treated with silver perchlorate at −78 °C to initiate the polymerization of tetrahydrofuran. Triblock poly(tetrahydrofuran)−polystyrene−poly(tetrahydrofuran) (PTHF−PS-PTHF) diol was obtained after propagation at −15 °C.[319] Similarly, polymeric radicals, generated by bromine terminated PS under ATRP conditions, were oxidized to the corresponding carbocations using iodonium salts, such as Ph_2IPF_6, to initiate the polymerization of cyclohexene oxide.[320]

The combination of cationic polymerization and ATRP can also be achieved using difunctional initiators. For example, 2-hydroxyethyl-2-bromobutyrate was used to produce polystyrene in the presence of $CuBr(bpy)_3$. The resulting polymer was then used as a chain-transfer agent in the cationic ring-opening

Scheme 33. Transformation from Cationic ROP to ATRP[318]



Scheme 34. Transformation from Anionic ROP to ATRP[322]



polymerization of 1,3-dioxepane with triflic acid as the initiator.[321]

ii. Anionic to ATRP. In a one-pot reaction, a commercially available functionalized initiator has been used for the ring-opening polymerization (ROP) of ϵ-caprolactone as well as the ATRP of styrene and MMA.[322] Scheme 34 shows that diblock copolymers could be synthesized by one of two routes: polymerization of styrene or MMA by ATRP followed by ROP of ϵ-caprolactone or, conversely, ROP of the cyclic ester followed by the ATRP reactions. In either case, diblock copolymers were produced exhibiting monomodal molecular weight distributions with little evidence of unreacted starting material. To test the "livingness" of the system, a polycaprolactone macroinitiator was used for ATRP of *n*-butyl acrylate. The diblock copolymer was chain extended with MMA to yield an ABC triblock copolymer.

An amphiphilic copolymer, poly(ϵ-caprolactone)-*b*-poly(*tert*-butyl acrylate), was recently described. PCL-*b*-PAA was prepared from the selective hydrolysis of a poly(ϵ-caprolactone)-*b*-poly(*tert*-butyl acrylate) precursor, which was synthesized by anionic ring-opening polymerization (ROP) of ϵ-caprolactone followed by ATRP of *tert*-butyl acrylate (*t*BA). Self-assembly of PCL-*b*-PAA into polymer micelles followed by cross-linking of the hydrophilic shell layer via condensation reactions between the carboxylic acid functionalities of PAA and a diamine afforded shell-cross-linked nanoparticles. Finally, nanocage structures were produced after the selective hydrolysis of the polyester (PCL) core domain.[323]

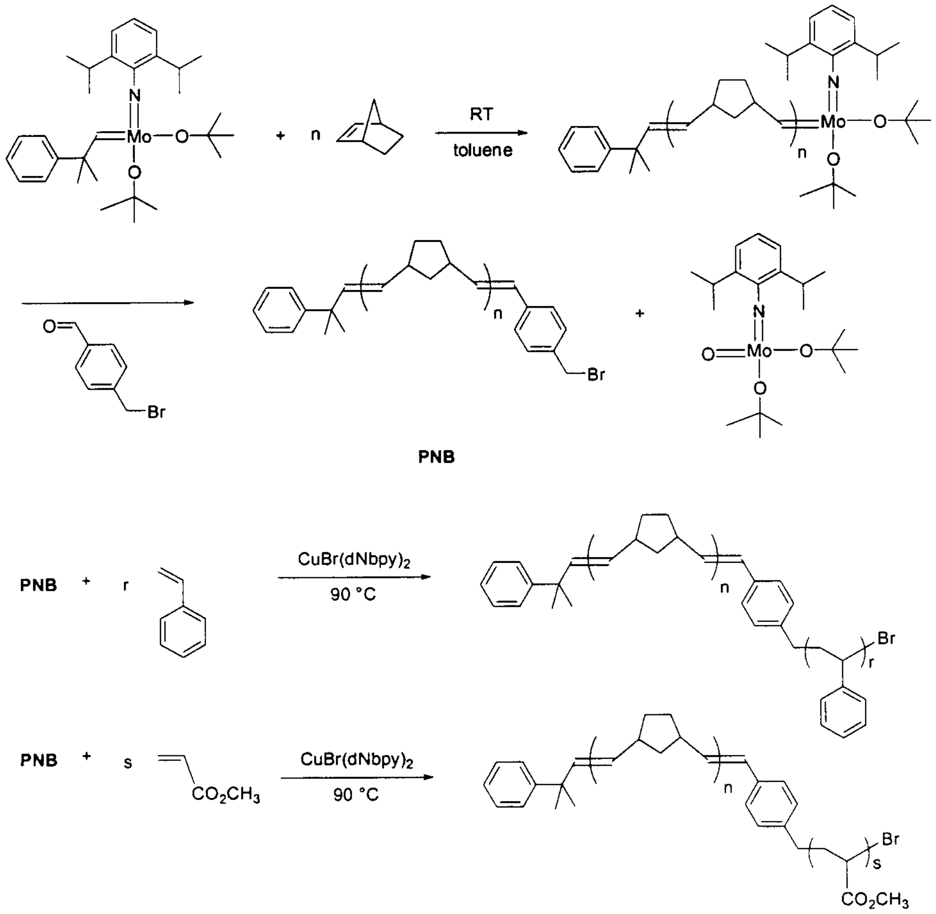
One of the more thoroughly studied classes of block copolymers are those containing poly(ethylene oxide) (PEO). Currently, mono-[324,325] and difunctional[326-328] PEO macroinitiators containing α-haloesters have been used in polymerizations of styrene,[324-327] methyl methacrylate,[325,328] and *tert*-butyl acrylate.[328] Studies examining styrene polymerizations were conducted with the CuX/bpy (X = Br, Cl) catalyst system. Polymerizations initiated with the 2-chloropropionate end group and catalyzed with the copper chloride showed lower polydispersities, either in bulk or solution, than the corresponding bromide functional initiator/catalyst, due to halogen exchange.[326,327] The effect of the substituent on the α-carbon of chloroacetate functional initiators was examined.[325] Model studies showed the following order of polymerization rate phenyl acetate > propionate > acetate. Similar results were obtained from polymerizations with MMA.[325] The polymerization of *tert*-butyl acrylate from 2-bromopropionate functional PEO was part of a study to examine amphiphilic copolymers by MALDI-TOF mass spectrometry.[328] SEC evaluation showed that experimental molecular weight agreed with theory but polydispersities increased to $M_w/M_n = 1.3$ from the macroinitiator of $M_w/M_n = 1.1$. In the MMA polymerization from the 2-bromopropionate functional PEO, higher efficiencies were observed in the more polar solvents.[328]

Transformation from anionic vinyl polymerization is also possible. Thus, living anionic polystyryllithium was end-capped with styrene oxide and terminated with 2-bromoisobutyryl bromide.[329] The styrene oxide was used to reduce the nucleophilicity of the active species and to prevent attack at the carbonyl group of the isobutyrate required to initiate ATRP. The purified macroinitiator was then used in the ATRP of styrene, methyl acrylate, *n*-butyl acrylate, and a mixture of styrene/acrylonitrile. In each case there was a linear increase of molecular weight with conversion, and SEC measurements of M_n were within 20% of the theoretically predicted values. Polydispersities were $M_w/M_n < 1.2$. Using the same synthetic methodology, a poly(styrene-*b*-isoprene) macroinitiator was prepared.

Kops et al. published data on another amphiphilic block copolymer system, namely, poly(ethylene-*co*-butylene)-*b*-poly(4-hydroxystyrene).[330] The macroinitiator was obtained by anionic polymerization, quenching with EO, subsequent hydrogenation, and esterification of monohydroxy terminal poly(ethylene-*co*-butylene) (Kraton polymer) with 2-bromopropionyl chloride. ATRP of styrene and 4-acetoxystyrene were conducted with a CuBr salt ligated by either bpy or 1,1,4,7,10,10-hexamethyltriethylenetetraamine. For styrene, the polymerization could be conducted in bulk, but with the substituted monomer, xylene was required to improve the solubility of the macroinitiator. In both cases, polydispersity was $M_w/M_n < 1.3$. DSC analyses showed two glass transitions for the Kraton ($T_g = -63$ °C) and either the PS ($T_g = 93$ °C) or poly(4-acetoxystyrene) ($T_g = 85$ °C) segments. Hydrolysis of the acetoxy group to a hydroxyl fragment was performed with hydrazine hydrate in xylene.

Recently, the synthesis of polyisoprene-*b*-polystyrene block copolymers bearing a fluorescent dye at the junction by the combination of living anionic polymerization and ATRP has been reported. In the synthesis, the polyisoprene carbanion was first reacted with a 1-aryl-1-phenylethylene derivative and

Scheme 35. Transformation from ROMP to ATRP[333]



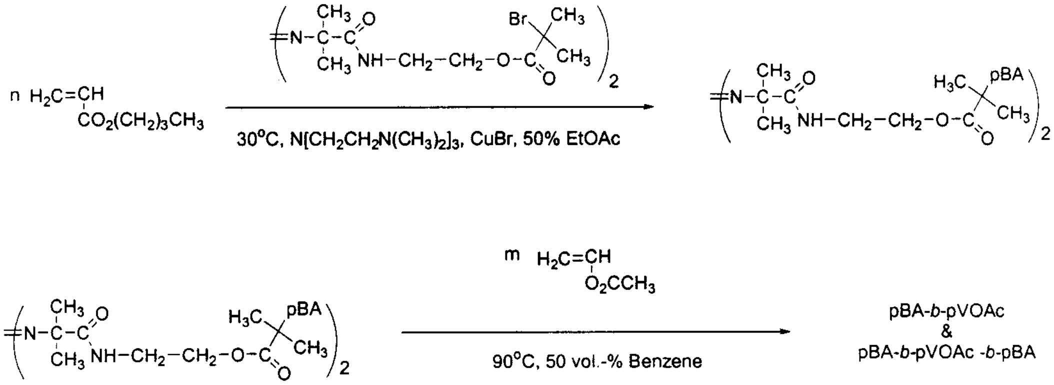
then treated with an excess of α,α′-dihalo-*p*-xylene to generate the ATRP initiator moiety. Subsequent ATRP of styrene yielded the target block copolymer.[331] A similar approach was used for the block copolymers of methacrylates and acrylates. [332]

iii. ROMP to ATRP. There have been a few reports on the transformation from ring-opening metathesis polymerization (ROMP) to ATRP. Macroinitiators were synthesized by polymerization of norbornene or dicyclopentadiene from a molybdenum carbene initiator followed by termination with *p*-(bromomethyl)-benzaldehyde (Scheme 35). The terminal benzyl bromide moieties were then exploited in the ATRP of vinyl monomers.[333] Polymerization of styrene and methyl acrylate from a polynorbornene macroinitiator (M_n = 30 500, M_w/M_n = 1.09) yielded polynorbornene-*b*-polystyrene (M_n = 110 400, M_w/M_n = 1.06) and polynorbornene-*b*-poly(methyl acrylate) (M_n = 85 100, M_w/M_n = 1.07). In addition, the ATRP of the same two monomers from a poly(dicyclopentadiene) macroinitiator (M_n = 12 100, M_w/M_n = 1.24) produced poly(dicyclopentadiene)-*b*-polystyrene (M_n = 20 100, M_w/M_n = 1.37) and poly(dicyclopentadiene)-*b*-poly(methyl acrylate) (M_n = 25 300, M_w/M_n = 1.47). The increased polydispersity from the poly(dicyclopentadiene) system is possibly due to a mixture of mono- and difunctionalities in the dicyclopentadiene during ROMP. In all of the polymerizations, two glass transition temperatures were observed indicating microphase separation of the two segments of the blocks.

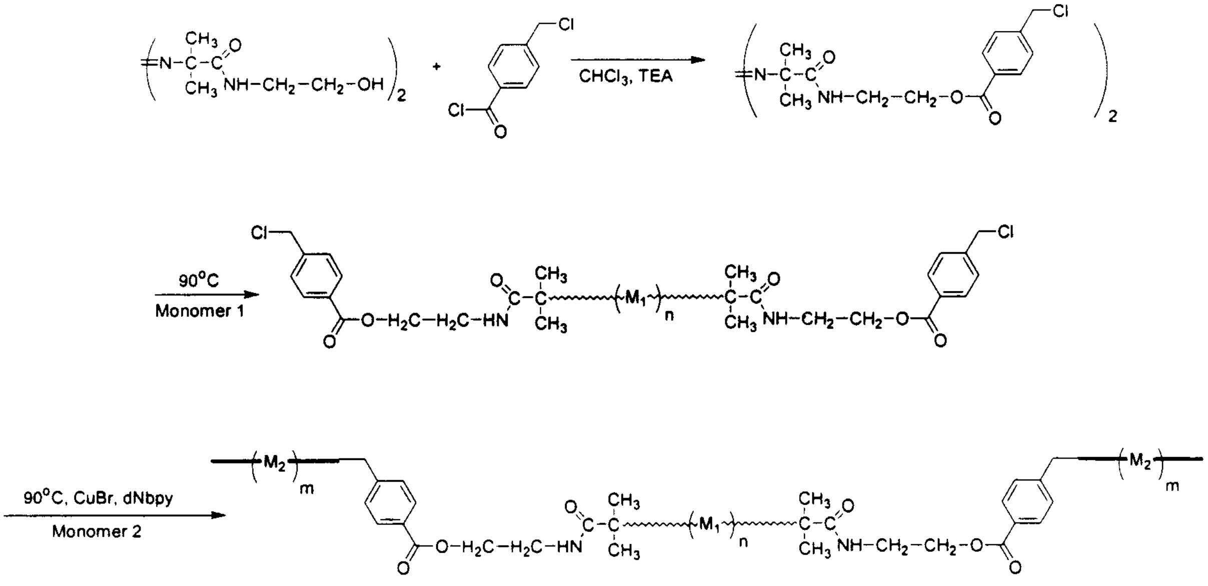
In another account, the synthesis of polystyrene-*b*-polybutadiene-*b*-polystyrene and poly(methyl methacrylate)-*b*-polybutadiene-*b*-poly(methyl methacrylate) triblock copolymers with the center polybutadiene segments containing 100% 1,4-microstructure was described.[334] Chain transfer in the ROMP of 1,5-cyclooctadiene to vinyl compounds with ATRP initiating sites generated the difunctional macroinitiators. Triblock structure was confirmed by selective polybutadiene degradation using OsO_4/H_2O_2. It seems that ROMP catalysts are also active in ATRP, and simultaneous growth of cyclooctadiene and an acrylate was achieved using one single catalytic system.[188,334]

iv. Conventional Radical Polymerization to ATRP. Monomers without radical stabilizing substituents have not yet been successfully homopolymerized by ATRP. To this group will belong vinylidine chloride, vinyl acetate (VOAc), ethylene, etc. However, they have been efficiently incorporated into block copolymers with the second block built by ATRP. For example, block copolymers of VOAc were prepared using four different methods.[152] The first two employed azo compounds containing activated halogen atoms. ATRP was carried before (Scheme 36) or after the conventional free-radical polymerization (Scheme 37) depending on the choice of initiator and reaction conditions. In the first case, low-temperature (30 °C) ATRP of *n*BA in the presence of CuBr/Me$_6$TREN complex was completed first, without destroying the diazene. The resulting P*n*BA (M_n = 7500; M_w/M_n =

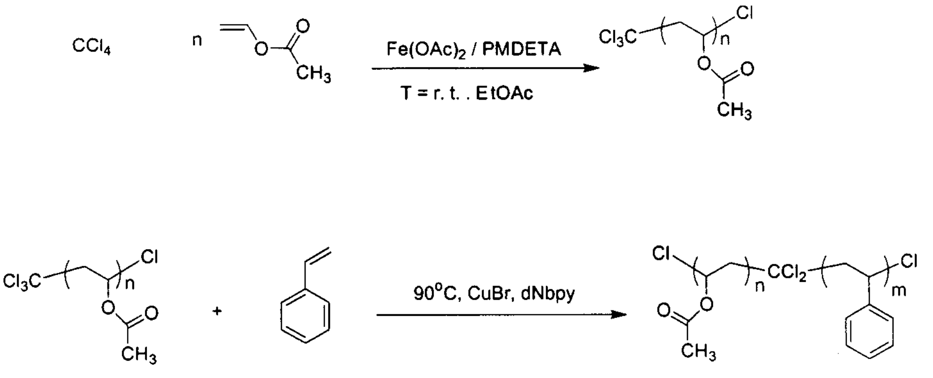
Scheme 36. Low-Temperature ATRP Followed by Conventional Radical Polymerization



Scheme 37. Transformation from Conventional Radical Polymerization to ATRP



Scheme 38. Telomerization Followed by ATRP

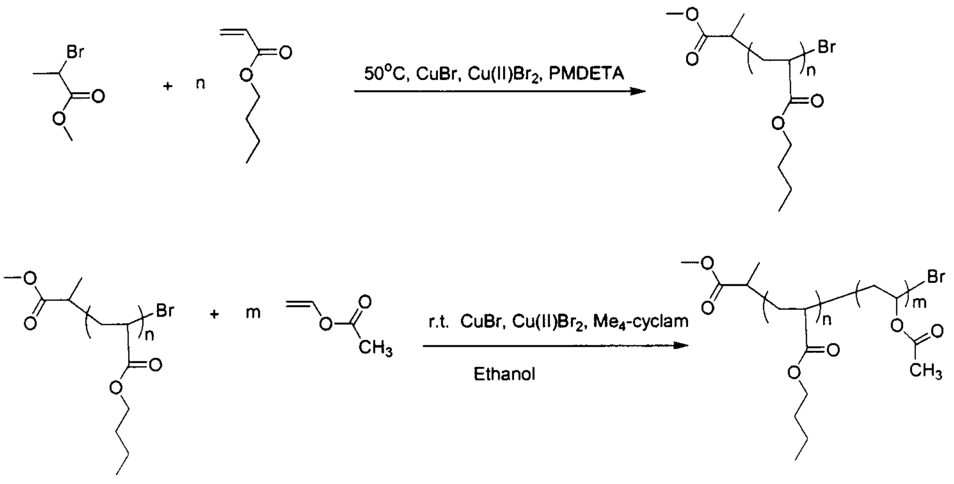


1.15) with the preserved central azo unit was dissolved in VOAc and extended to a block copolymer (M_n = 41 800; M_w/M_n = 3.56).

In the second method, 2,2′-azobis[2-methyl-*N*-(2-(4-chloromethylbenzoyloxy)ethyl) propionamide] was used to initiate the polymerization of vinyl acetate at 90 °C first. The resulting PVOAc with a Cl-terminal group (M_n = 47 900; M_w/M_n = 2.21) was subsequently used as a macroinitiator for the ATRP of styrene to yield PVOAc-*b*-PS (M_n = 91 600; M_w/M_n = 1.80).

Alternatively, ATRP has been combined with a redox-initiated system. In the third method, VOAc was polymerized in the presence of $CCl_4/Fe(OAc)_2$/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) to yield PVOAc with trichloromethyl end groups (M_n = 3600; M_w/M_n = 1.81). The polymer obtained was dissolved in styrene and block copolymerized by ATRP to form PVOAc-*b*-PS (M_n = 24 300; M_w/M_n = 1.42). In the fourth approach, P*n*BA with a bromine end group (M_n = 2460; M_w/M_n = 1.32), as prepared by ATRP, was dissolved in the VOAc together with CuBr/1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam) to initiate VOAc polymerization. A block copolymer with M_n = 4450 and M_w/M_n = 2.58 was prepared. In the presence of

Scheme 39. ATRP Followed by Radical Polymerization



20 mol % of $CuBr_2$, the polydispersity was further reduced to 1.73. Free radical telomerization has been combined with ATRP in several other instances. A difunctional macroinitiator was synthesized by the di-*tert*-butyl peroxide-initiated radical polymerization of vinylidene fluoride in the presence of 1,2-dibromotetrafluoroethane. From the difunctional bromine-terminated macroinitiator, the ATRP of styrene was continued. Linear increases of the molecular weights with conversion were observed, but the polydispersity also increased from $M_w/M_n = 1.4$ to 1.7 over the course of the reaction. SEC chromatograms of the macroinitiator and final reaction sample showed no residual homo-PVDF, indicating that all of the starting material participated in the ATRP process.[335] In a similar way, vinylidene fluoride CCl_3-terminated telomers (T) were synthesized and used to initiate the ATRP of styrene, MMA, MA, and *n*BA. By varying $[CHCl_3]_0/[VDF]_0$ and $[M]_0/[T]_0$ ratios in the telomerization and ATRP steps, the chain length of both blocks and the copolymer composition was controlled.[336,337]

The combination of redox telomerization with ATRP has also been used in the synthesis of block copolymers of other polymers that could have been prepared by ATRP such as polyacrylates, polymethacrylates, and polystyrene.[121,122] During the controlled growth by ATRP, the polydispersity decreased from 2.3 to 1.6 showing the addition of a segment with a well-defined chain length.

v. Step Growth to ATRP. There are a few examples of well-defined block copolymers composed of blocks made by step growth polymerization and segments consisting of vinyl monomers without significant contamination by the corresponding homopolymers.

The formation of ABA triblock copolymers synthesized from a difunctional polysulfone macroinitiator has been described.[338] The α,ω-dihydroxy terminal polysulfone was synthesized by the reaction of 4-fluorophenyl sulfone with an excess (<10%) of bisphenol A in the presence potassium bicarbonate at temperatures in excess of 140 °C. The polysulfone was esterified with 2-bromopropionyl bromide in the presence of pyridine to yield the difunctional ATRP macroinitiator with $M_n = 4030$, $M_w/M_n = 1.5$. Polymerization of styrene or *n*-butyl acrylate using the $CuBr(dNbpy)_2$ catalyst system at 110 °C yielded 67% and 95% conversions of styrene and *n*-butyl acrylate after 7 h, respectively. Following typical ATRP behavior, the molecular weights of the triblock copolymers increased with concomitant decreases in the molecular weight distributions: $M_n = 15\,300$, $M_w/M_n = 1.2$ for polystyrene and $M_n = 10\,700$, $M_w/M_n = 1.1$ for *n*-butyl acrylate. The triblock copolymer with a central polysulfone segment (25 w%) organizes in supramolecular aggregates with a periodicity from 10 to 12 nm. According to SAXS, the periodicity remains even above 250 °C, although DMA indicates that the triblock copolymer "melts" at about 100 °C. This temperature corresponds to a structural relaxation of the linear poly(*n*-butyl acrylate) with a molecular weight of a few million, confirming a high degree of aggregation. Similar to the synthesis of the difunctional polysulfone macroinitiator, a polyester was used in the synthesis of block copolymers by ATRP.[339] The α,ω-dihydroxy terminal polymer was synthesized by the transesterification of 1,6-hexanediol with dimethyl adipate. The end groups were then esterified with 2-bromopropionyl bromide, and the ATRP of styrene yielded the ABA triblock copolymers.

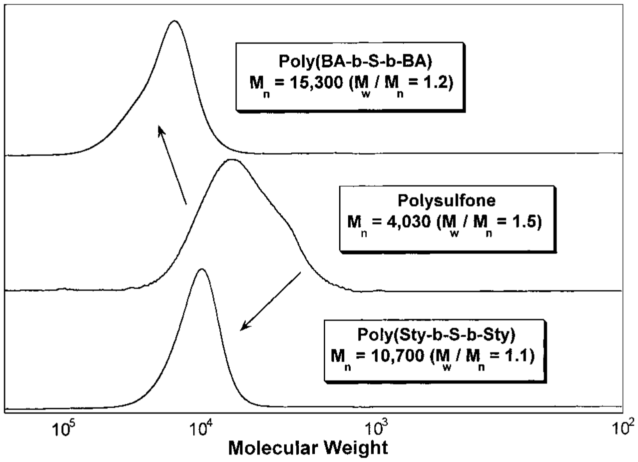
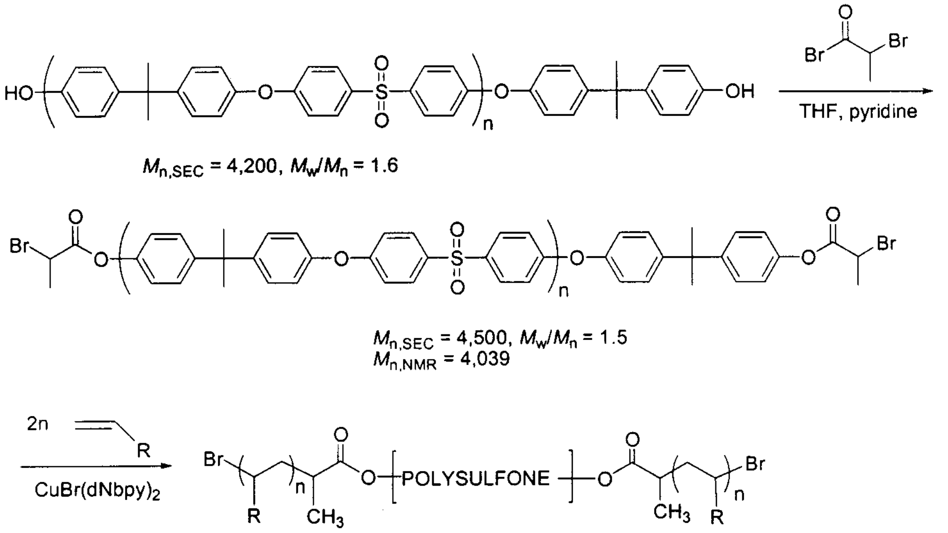


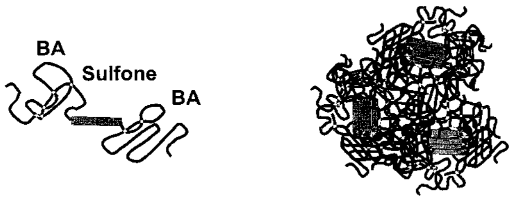
Figure 17. SEC chromatograms of a polysulfone macroinitiator and ABA block copolymers of polysulfone (S) with polystyrene (Sty) or poly(*n*-butyl acrylate) (*n*BA).

Recently, the synthesis of rigid-flexible triblock copolymers, with a rigid central part and possessing

Scheme 40. Preparation of the Polysulfone Macroinitiator and Triblock Copolymer with Polystyrene (R = Ph) and Poly(*n*-butyl acrylate) (R = C(O)-O-*n*Bu)



Scheme 41. Supramolecular Aggregates of Polysulfone-*b*-Poly(*n*-butyl acrylate) Block Copolymer



photoluminescence, has been described.[340] First, Suzuki coupling was applied to prepare α,ω-acetoxy-functionalized oligophenylenes with five or seven rings. Hydrolysis of these acetoxy end groups and esterification of the resulting hydroxy end groups with acyl chlorides led to molecules capable of acting as ATRP initiators. The final rigid–flexible copolymers of styrene displayed low polydispersities and showed blue light emission.

vi. Dendritic Initiators for ATRP. Dendrimers are monomodal and, therefore, are not always considered polymeric in nature. However, at increasing generation number, the molecules achieve high molecular weights and display thermal properties, such as glass transition temperatures, indicative of polymeric systems. Furthermore, when used as initiators for linear polymers, the dendrons can occupy significant fractions of the total weight of the polymer.

The primary example utilized benzyl ether dendron initiators of generations 1–4. The third-generation initiator is shown in Scheme 42.[341] The benzyl chloride moiety is located at the focal point of the molecule. ATRP of styrene from the initiators proceeds in a controlled fashion below M_n = 30 000, M_w/M_n < 1.3. Above M_n = 30 000, deviations from the theoretical molecular weights are observed and polydispersities increase. This was attributed to an HCl elimination reaction occurring early in the polymerization. However, the formation of a nonpolymerizable species is also possible due to some form of bimolecular termination resulting from establishment of the equilibrium at low monomer conversion (<5%). Thermal analysis of the block copolymers reveals one T_g indicating miscibility of the two fragments, while a blend of the homopolymer and dendron shows two glass transitions. Furthermore, for a given polystyrene block length, an increase in the dendron generation number caused a decrease in the T_g.

In a related study, benzyl ether dendrons with ethyl ester terminal groups and benzyl bromide initiator fragments at the dendron focal points were examined.[342] ATRP of styrene from the initiators of generations 0–3 proceeded with slightly better control at higher molecular weights than those seen with the benzyl chloride analogues. The ethyl ester moieties were then converted to carboxylic acid, [G-1]-dendron ester, butyl amide, and methyl alcohol functionalities. Interestingly, ^{1}H NMR of the block copolymers containing the hydrophilic dendron in $CDCl_3$ showed resonances only for the polystyrene segment, while a spectrum measured in deuterated DMF elucidated signals for both the dendron and polystyrene protons, as a result of aggregation of the hydrophilic moieties in the nonpolar solvent with the long relaxation time.

3. Inorganic/Organic Hybrids

While the inorganic segments of inorganic/organic hybrids are synthesized by mechanisms other than ATRP (anionic, condensation, etc.), these polymers have been grouped into their own category due to their unique composition relative to organic polymers produced by other methods.[343] Several studies on the preparation of poly(dimethylsiloxane) (PDMS) block copolymers via ATRP have been reported. Difunctional PDMS macroinitiators were synthesized by hydrosilylation of vinyl or hydrosilyl terminal PDMS with a hydrosilyl- or vinyl-functionalized molecule containing a benzyl chloride moiety.[146,344,345] Initiation of a number of vinyl monomers yields polymers with increased molecular weights and relatively low polydispersities (Table 14).

In another study, hydrosilylation of commercially available difunctional hydrosilyl terminal PDMS (M_w/M_n > 1.3) with allyl- or 3-butenyl 2-bromoisobutyrate

Scheme 42. Use of a Dendritic Initiator in the ATRP of Styrene

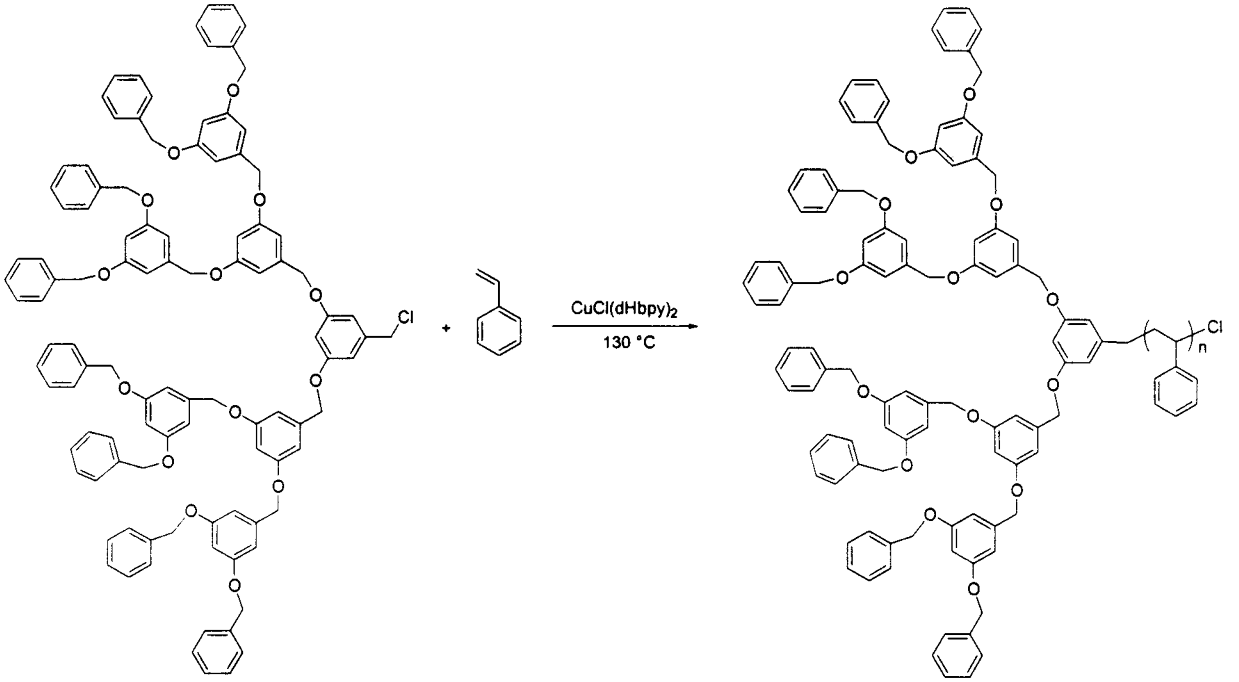


Table 14. ATRP of Vinyl Monomers from Difunctional PDMS Macroinitiators [146]

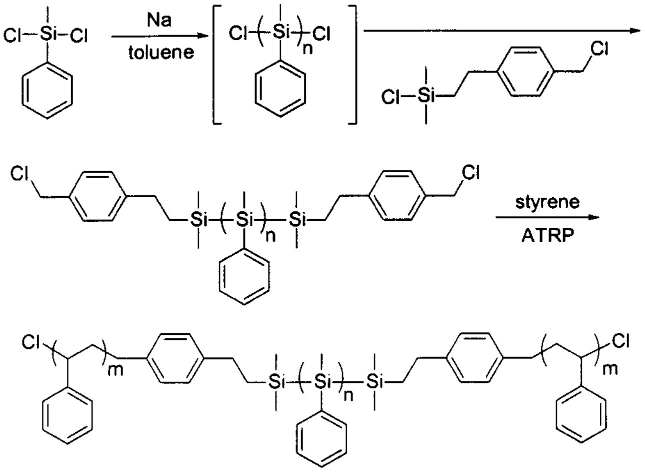
PDMS M_n	M_w/M_n	monomer	M_n[a]	M_w/M_n[a]
4500	1.2	styrene	9 800	1.2
9800	2.4	styrene	20 700	1.6
2600	1.2	methyl acrylate	4 600	1.3
4500	1.2	isobornyl acrylate	13 700	1.6
9800	2.4	*n*-butyl acrylate	24 000	1.6

[a] Values for triblock copolymer.

resulted in the ATRP macroinitiators.[346] Linear increase of M_n with monomer conversion was observed with the use of well-defined monofunctional, low-polydispersity PDMS macroinitiators synthesized by the anionic ring-opening polymerization of hexamethylcyclotrisiloxane. In addition, a monofunctional polystyrene-*b*-poly(dimethylsiloxane) macroinitiator was used to initiate ATRP of *n*-butyl acrylate and methyl methacrylate, forming ABC organic/inorganic hybrid triblock copolymers.[346] In a similar way, 2-bromoisobutyrate groups were attached to amino end-functional PDMS to generate growth of polymethacrylate blocks in two directions.[347] Grafting of hydrophilic polymers from PDMS backbone resulted in amphiphilic copolymers for cosmetic and hair applications.[348]

Jones et al. reported the preparation of a hybrid block copolymer utilizing initiation of ATRP from chloromethylphenyl terminal telechelic poly(methylphenylsilylene) (PMPS).[349] The synthetic method of the macroinitiator and subsequent ABA triblock copolymers is shown in Scheme 43. The attachable initiator, (4-chloromethylphenylethyl)dimethylchlorosilane, was added to the reductive coupling reaction of methylphenyldichlorosilane at the end of the polymerization. The material was then used in the ATRP of styrene following purification by precipitation in methanol. ^{29}Si NMR showed the presence of methoxysilane species in the polymer resulting from

Scheme 43. Transformation from Polysilanes Prepared by Wurtz Coupling to ATRP



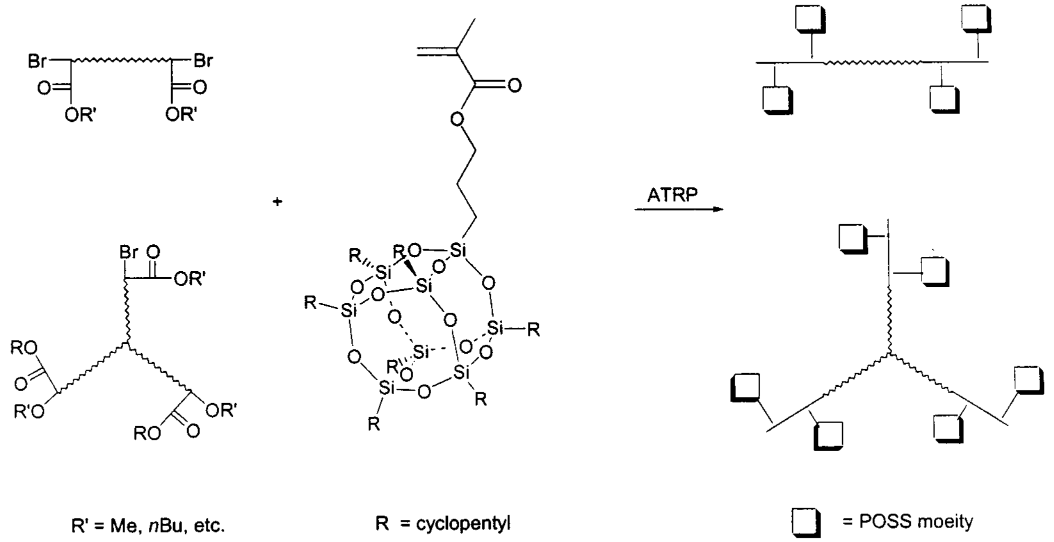
condensation of unreacted silyl chloride with the methanol precipitant. Nevertheless, SEC confirmed the formation of the block copolymer by increasing molecular weight.

A novel class of well-defined hybrid (co)polymers based on polyhedral oligomeric silsesquioxanes (POSS) has been prepared by ATRP.[350] Homopolymers of MA-POSS, poly(MA-POSS)-*b*-poly(*n*BA)-*b*-poly(MA-POSS), and a star-shaped block copolymers of poly(methyl acrylate) and poly(MA-POSS) have been prepared (cf. Scheme 44).

4. Summary and Outlook

Conventional radical polymerization has been used for many years to synthesize a myriad of different statistical copolymers. This is due to reactivity ratios relatively close to unity. At the same time conventional radical polymerization was totally inefficient in the formation of block copolymers, due to the very short lifetime of the growing chain and the continu-

Scheme 44. POSS-Containing Organic Inorganic Hybrid Polymers



ously occurring initiation process. ATRP and other CRP methods build upon strengths of conventional radical polymerization. However, by extending the life of propagating chains to hours and enabling nearly instantaneous initiation; for the first time CRPs also provide access to well-defined segmented copolymers with block and graft structures.

In fact, the composition of each chain of statistical copolymers in conventional and controlled radical polymerization is different. Since essentially every chain in ATRP survives from the very early to the final stage of polymerization, any variation of the monomer feed and resulting rates of incorporation of the consumed comonomers is recorded along the chain length. This leads to the formation of a new class of polymers, gradient copolymers. These copolymers form a bridge between conventionally prepared statistical copolymers, in which a composition varies between the chains, and block copolymers, with a composition that changes in a regular fashion along each polymer chain. Gradient copolymers have physical properties different from random and block copolymers of the same overall composition. They can show microphase separation but with a lower order–disorder temperature than block copolymers. They may find uses as adhesives, vibration dampening materials, blend compatibilizers, specialty surfactants, dispersants, etc.

ATRP was the first CRP technique to provide a variety of block copolymers from monomers polymerized by a free-radical mechanism. Because the efficiency of cross-propagation depends on the structure of involved comonomers, it is important to understand relative reactivities of chain ends. In most CRP methods it is possible to extend a chain from a more reactive to less reactive system, e.g., from polymethacrylate to polyacrylate. ATRP provides an additional, and unique, handle to move “uphill” from polyacrylate to polymethacrylate by halogen exchange. Thus, it is possible to grow soft difunctional polyacrylate central segment and extend it with two hard polymethacrylate side blocks to form thermoplastic elastomers. Many variations of ABC triblock and pentablocks have also been prepared using this technique.

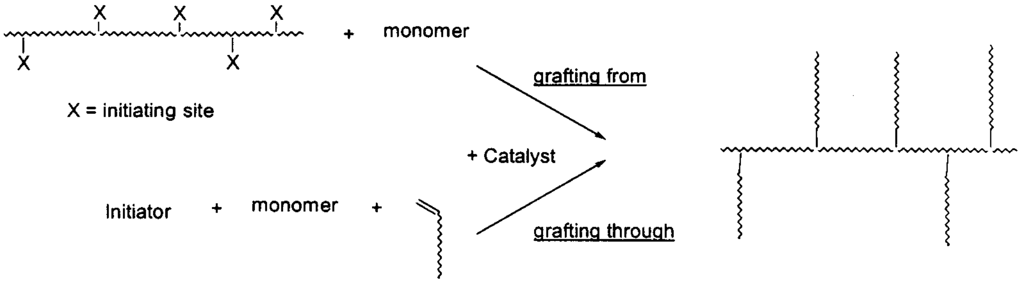
As indicated earlier in this section, most of the block copolymers prepared by ATRP are not as well defined as those prepared by anionic polymerization, although they are formed from a larger range of comonomers and under less demanding conditions. Thus, careful structure–property evaluation is needed to thoroughly explore properties and find suitable applications. Such studies are even more critical for gradient copolymers and gradient/block copolymers which are relatively virgin materials.

The facile incorporation of activated alkyl halides to the chain ends or side groups of polymers prepared by other mechanisms enabled synthesis of copolymers with well-defined segments by ATRP and other segments formed by carbocationic, carbanionic, coordination, metathesis, ionic ring-opening polymerization, condensation polymerization, and also conventional radical processes. Additionally, natural products and inorganic materials may be “decorated” with well-defined blocks prepared by ATRP to form many novel hybrid systems.

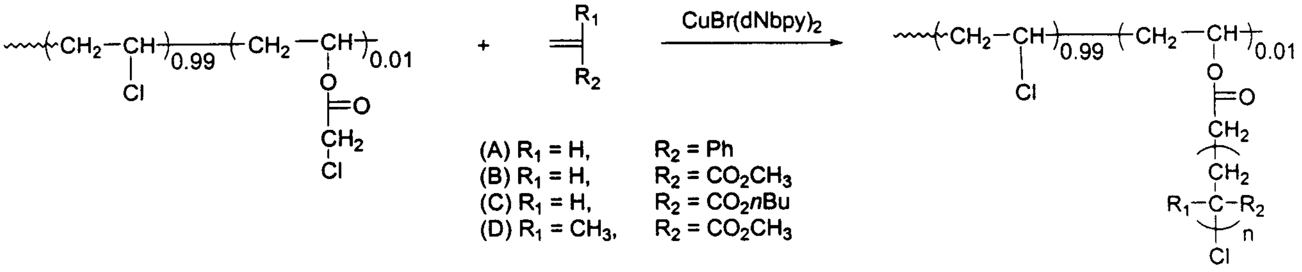
Due to simple preparative techniques for block copolymers, it is expected that many new materials will be prepared. They may include blocks with amphiphilic properties, blocks which will be entirely water soluble (for crystal engineering), and blocks which may carry special functionalities and coordinate catalysts, contain electro- or photoconductive segments, or carry biofunctionality. Perhaps, the efficient preparation of block and graft copolymers between polyolefins and polar monomers will be one of the first challenges explored.

Until now, most of the block copolymers studied by polymer physicists were prepared by anionic means and were essentially limited to styrene and dienes. A variety of new segmented copolymers made by ATRP and other CRP techniques need to be thoroughly evaluated to comprehend correlation between their molecular structure and macroscopic properties. Since some morphologies in these systems may be kinetically trapped, it will be important to

Scheme 45. Grafting from and Grafting through Processes



Scheme 46. Grafting from Poly(vinyl chloride)



expand these studies to incorporate also the effect of processing on final properties. The segmented, gradient, and periodic copolymers phase separate on nanoscale dimensions and may become important building blocks for many new nanomaterials.

C. Topology

The control over molecular weight and functionality obtained in ATRP has allowed for the synthesis of numerous materials with many novel topologies. With the exception of linear polymers, architectural differences lie in branched structures with regard to the number of branches and their relative placement in the macromolecule. However, these variations, in conjunction with changes in composition, may provide dramatic differences in the properties of the materials. The following examples only serve as starting points for even more well-defined materials in the future.

1. Graft Copolymers

The synthesis of graft copolymers can be accomplished through one of three routes: "grafting from" reactions (utilizing polymerization of grafts from a macroinitiator with pendant functionality), "grafting through" processes (operating by homo- or copolymerization of a macromonomer) and "grafting onto" (occurring when the growing chain is attached to a polymer backbone). The first two methods have been used in conjunction with ATRP in the design of graft copolymers and underscore the versatility of this controlled radical polymerization technique to synthesize a variety of (co)polymers.

a. Organic Grafts from an Organic Backbone. *i. "Grafting from".* An early example of graft copolymers utilizes the ATRP of vinyl monomers from pendant-functionalized poly(vinyl chloride) (PVC) macroinitiators.[351] The purpose of the study was to chemically incorporate another monomer into the PVC matrix to reduce the brittle nature of that polymer. Traditionally used plasticizers suffer from problems such as leaching and phase separation. Polymerization of the grafts is initiated by chloroacetate moieties attached to the polymeric backbone. Commercial PVC containing 1% (mol) chloroacetate groups was used in ATRP of styrene, MA, *n*BA, and MMA. The results of the study, summarized in Table 15, demonstrate that in each case the molecular weight of the copolymer increased above that of the macroinitiator yet the polydispersity remained essentially the same. The polydispersity did not decrease because of the variable quantity of initiating sites per chain. The large increase in the molecular weight distribution for the MMA polymerization may originate from slow ATRP initiation of MMA from the primary alkyl halide sites. Most important, however, was the influence on the glass transition temperatures after incorporation of the grafts. The decreased T_g of the copolymers containing MA and *n*BA indicates that self-plasticized PVC has been synthesized. This is especially well illustrated by systems with an increasing content of p*n*BA (Table 16). One T_g indicates no microphase separation for these copolymers.

Table 15. Characterization Data for the ATRP of Vinyl Monomers from PVC Macroinitiators[351]

second monomer	M_n (SEC)	M_w/M_n	mole % second monomer	T_g (°C)
	47 400	2.66	0	83
styrene	99 500	3.72	80	80
MA	57 700	2.40	50	21
MMA	83 600	4.94	60	111
BA	81 400	2.44	65	−19

Another example of using ATRP to prepare such copolymers by grafting from is the ATRP of styrene,[146,352] isobornyl acrylate,[146] and MMA[353] grafts from EXXPRO, a commercially available poly(isobutylene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene). The use of ATRP allowed for control over the composition of the copolymer. DSC analysis of the

Table 16. Results of Graft Copolymerization of PVC with *n*-Butyl Acrylate (*n*BA)[a]

time (h)	M_n (SEC)	M_w/M_n (SEC)	M_n (NMR)	content of *n*BA (mol-%)	T_g (°C)
0	47 400	2.66		0	83
2.0	61 500	2.28	114 900	41	−4
4.3	79 500	2.42	166 100	55	−11
9.5	81 400	2.44	227 000	65	−19

[a] [n-Butyl acrylate]$_o$ = 6.98 M, [CuBr]$_o$ = [dNbpy]$_o$/2 = 3.49 × 10^{-2} M, [PVC-1]$_o$ = 1.0 × 10^{-3} M, T = 90 °C.

graft copolymer showed two glass transition temperatures indicative of a microphase-separated system.[146,352] When the graft copolymer contained 6% (w) polystyrene, reversible elongations of up to 500% were observed, indicating thermoplastic elastomeric behavior.[352]

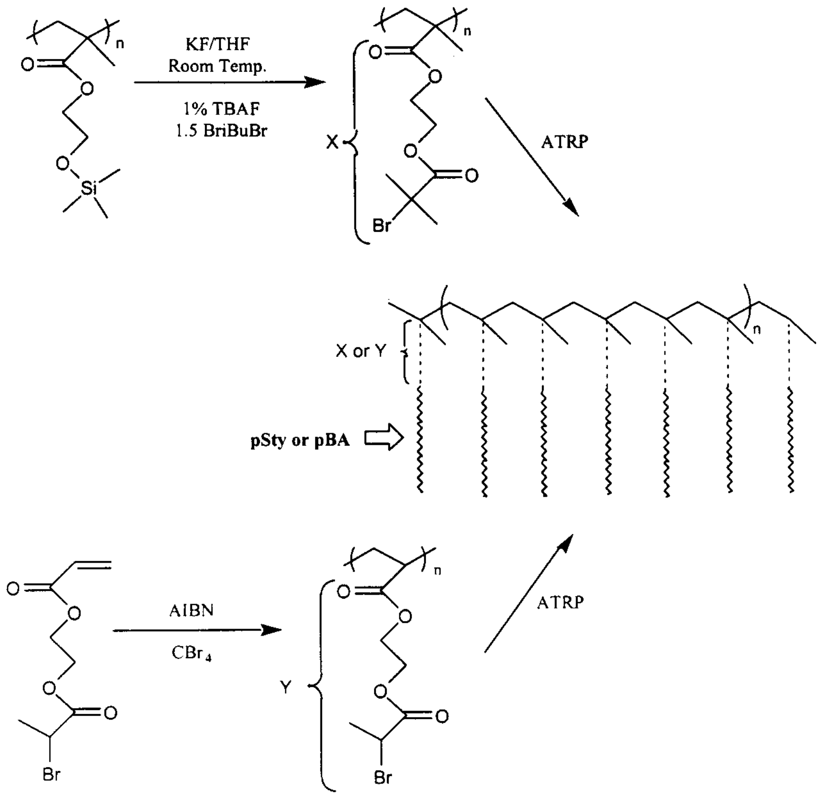
In a similar way, ATRP was used to graft well-defined polymers from the polyethylene. In one example, a commercial copolymer of ethylene with glycidyl methacrylate was used.[354] The epoxy groups were transformed into the α-bromoesters, which initiated ATRP of styrene and (meth)acrylates. In the second example, polyethylene or its copolymer with styrene was brominated and the generated alkyl bromides initiated ATRP process which was catalyzed by CuBr/PMDETA.[355] In a similar way, syndiotactic polystyrene was brominated and grafted with pMMA, pMA and pS.[356]

Bromination of pendant allylic groups with *N*-bromosuccinimide has been used to synthesize an ATRP macroinitiator from an ethylene−propylene−diene terpolymer.[357] The allyl bromide groups served as initiating species for the polymerization of MMA. Grafting efficiencies of up to 93% were obtained. Little or no grafting through the unsaturation in the polymer backbone was observed. Similarly, chemical modification of commercially available monodisperse Kraton polymer was carried out to introduce benzyl bromide ATRP initiating sites.[358] Subsequent ATRP of ethyl methacrylate produced a block-graft copolymers composed of polystyrene-*b*-poly(ethylene-*co*-propylene) and poly(ethyl methacrylate).

A practical application of amphiphilic graft copolymers has been disclosed in the area of personal care products. Various (meth)acrylates, methacrylic acid, and *p*-chloromethylstyrene were copolymerized by a conventional free-radical copolymerization. “Grafting from” the chloromethylphenyl groups within the polysiloxane or polystyrene chains with either methacrylic acid[348] t-BA or HEMA-TMS[359] by ATRP yielded the amphiphilic graft copolymers. When HEMA-TMS was used, deprotection was required.[359]

The field of densely grafted copolymers has received considerable attention in recent years. The materials (also called bottle-brush copolymers) contain a grafted chain at each repeat unit of the polymer backbone. As a result, the macromolecules adopt a more elongated conformation. Within the context of ATRP, examples of brush copolymers have been provided.[127,266,360] In one study, the copolymers were assembled by grafting from a linear backbone (Scheme 47). Synthesis of the macroinitiator was achieved through one of two approaches. One method used conventional radical polymerization of 2-(2-bromopropionyloxy)ethyl acrylate in the presence of CBr_4 to produce a macroinitiator with M_n = 27 300 and high polydispersity M_w/M_n = 2.3. The alternative involved ATRP of 2-trimethylsilyloxyethyl methacrylate followed by esterification of the protected alcohol

Scheme 47. Dense Grafting by ATRP leading to Polymeric Bottle Brushes[127]



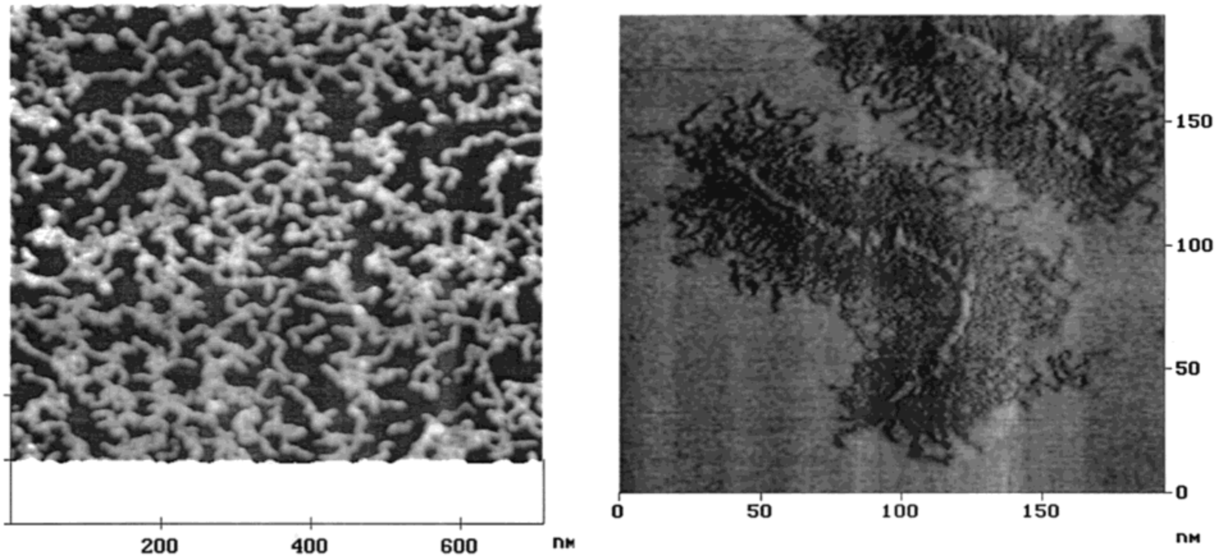


Figure 18. AFM images of polystyrene and poly(*n*-butyl acrylate) brushes on mica surface.

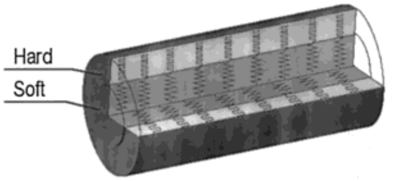


Figure 19. Cylindrical core/shell bottle brushes.

with 2-bromopropionyl bromide. While synthetically more challenging, the latter method provided a macroinitiator of well-defined structure ($M_n = 55\,500$, $M_w/M_n = 1.3$) leading to a brush synthesized entirely by a controlled process. From either macroinitiator, the ATRP of styrene and *n*-butyl acrylate was conducted leading to the desired densely grafted structures. The grafting reactions were found to be very sensitive to reaction conditions; additional deactivator, high concentrations of monomer, and reduced temperatures were all necessary in arriving at the desired materials.

Since the aspect ratio and size of the macromolecules were so large, individual chains were observed by atomic force microscopy (AFM) (Figure 18). The brushes with polystyrene side chains form elongated structures on a mica surface with an average length of 100 nm, a width of 10 nm, and a height of 3 nm. Poly(*n*-butyl acrylate) absorbs well onto the mica surface and forms spectacular single molecule brushes in which the backbone and side chains can be visualized using tapping mode AFM. Similarly, core–shell cylindrical brushes were prepared via block copolymerization. They consist of the soft poly(*n*-butyl acrylate) cores and hard polystyrene shells (Figure 19).[360] The high-resolution AFM micrographs of the block copolymer brushes PBPEM-*graft*-(P*n*BA-*b*-PS) brushes show a necklace morphology.[360] The undulating backbone with a thin film surrounding it is clearly visible. The two cross-sectional profiles in Figure 20d and c were recorded along the molecular backbone and perpendicular to it, respectively. A tentative interpretation of the undulations is presented in Figure 20e and f. In contrast to the homopolymer brushes, the PS tails in the block copolymer brushes tend to aggregate to reduce the interfacial energy between the PS and P*n*BA blocks as well as between the PS and the air. While the aggregation occurs, the P*n*BA chain fragments remain tightly adsorbed to the substrate, as illustrated by the edge view in Figure 20e and by the side view in Figure 20f.

The synthesis of well-defined brush block copolymers demonstrates the synthetic power of ATRP. It was used to create a well-defined backbone with DP ≈ 500, followed by the transesterification and the subsequent grafting of P*n*BA chains with a final chain extension with S to produce the block copolymers.

Patten et al. recently described a similar methodology for the formation of less densely packed backbone, where grafted polymers (macromolecules derived from only one monomer) were prepared strictly by ATRP.[361] The copolymerization of 4-acetoxymethyl- or 4-methoxymethylstyrene with styrene yielded a pendant functional macroinitiator with “latent initiation sites”. Transformation of the ester or ether to benzyl bromide substituents provided the alkyl halide necessary for the grafting reactions. Increased polydispersities above 20% conversion were attributed to internal coupling reactions between the grafted chains.

Triblock copolymers with densely grafted styrenic end blocks from a polyisobutylene macroinitiator were recently reported.[362] The macroinitiator was prepared from a triblock copolymer of polyisobutylene with end blocks of poly(*p*-methylstyrene) by bromination to obtain initiating bromomethyl groups. Controlled polymerizations of styrene and *p*-acetoxystyrene yielded new triblock copolymer structures with densely grafted end blocks. For the polymerization of styrene, SEC analysis with the light-scattering detector revealed a small fraction of very high molecular weight polymer produced from cross-linking by coupling reactions, which was not noticeable with either refractive index or intrinsic viscosity detectors. It was also found that the thermally initiated polymerizations occurred simultaneously for both styrene and *p*-acetoxystyrene, which were also

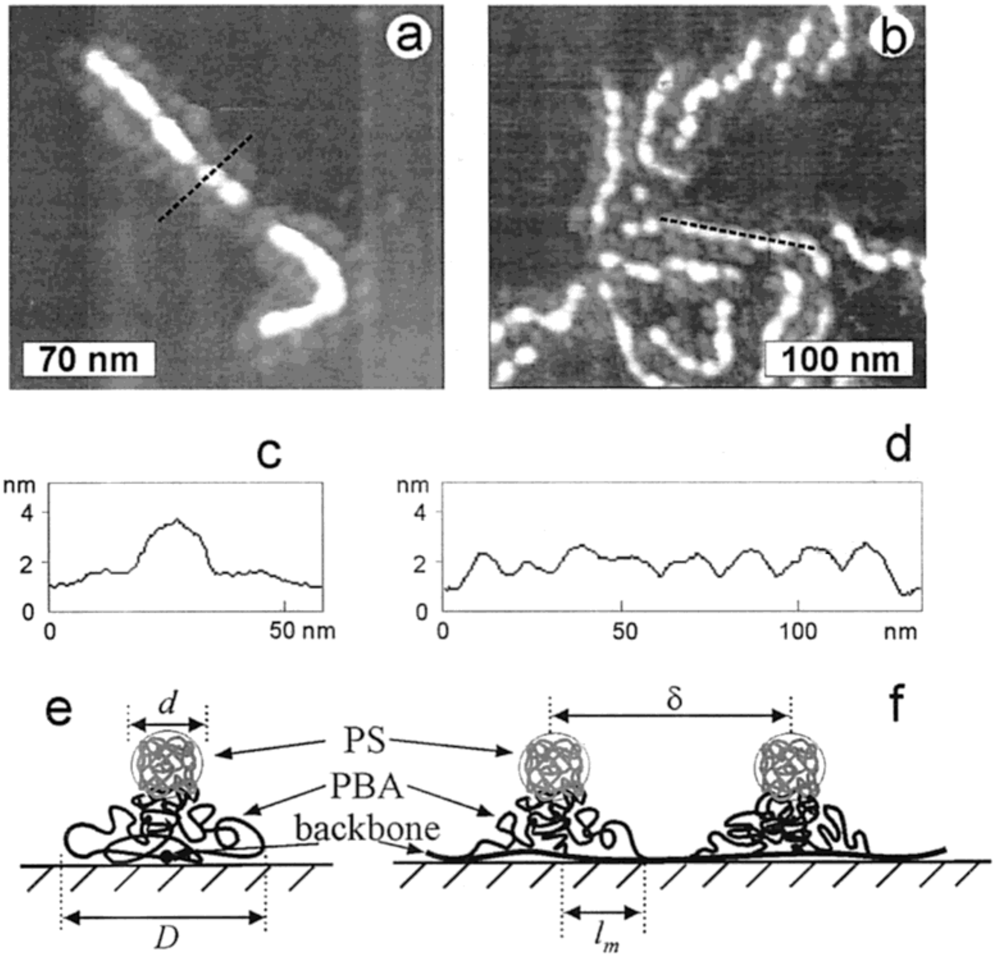


Figure 20. AFM micrographs of single molecules of PBPEM-*graft*-(P*n*BA-*b*-PS) brushes VII (a) and V (b). The cross sectional profiles (c and d) were drawn perpendicular and parallel to the molecular contour along the dotted lines in a and b, respectively. The corresponding cartoons explain the necklace morphology while looking at the molecule from the edge (e) and from the side (f).[360]

controlled, yielding low molecular weight polymers with narrow distributions.

An architecturally interesting example reported is dendrigraft polymers.[363] These materials are synthesized by the combination of nitroxide mediated controlled free radical polymerization and ATRP. Copolymerization of *p*-(4′-chloromethylbenzyloxymethyl)-styrene with styrene initiated by 1-phenylethyl-TEMPO yields a linear polymer with pendant benzyl chloride moieties. Nucleophilic substitution with 2-hydroxy-1-phenylethyl-TEMPO results in a macroinitiator which will commence polymerization of a mixture of *p*-(4′-chloromethylbenzyloxymethyl)styrene and styrene again. Following this reaction, the ATRP of vinyl monomers yields the dendrigraft copolymers. The first two steps of the reaction were performed under control with only a small quantity (<10%) of polymer observed originating from the thermally initiated polymerization of styrene. From the graft copolymers, the ATRP of styrene and *n*-butyl methacrylate yielded the dendrigraft structures with the lowest polydispersities, $M_w/M_n = 1.38$. Molecular weights measured by SEC versus linear polystyrene standards ($M_w = 480\,000$) were significantly smaller than those from absolute methods ($M_w = 1\,140\,000$), indicating that the macromolecules adopted compact structures in solution.

A "tandem polymerization" technique has recently been reported where the copolymerization of 4-(2-bromoisobutyryloxy) ϵ-caprolactone with MMA and ϵ-caprolactone resulted in the synthesis of a series of architecturally complex structures.[364,365] When the monomer was copolymerized with ϵ-caprolactone, an ATRP macroinitiator was synthesized. "Grafting from" the MMA yielded the desired graft copolymer. Likewise, use of the compound to initiate the ATRP of MMA yielded a macromonomer which was copolymerized with ϵ-caprolactone in a "grafting through" reaction. The authors were also able to perform these two polymerizations simultaneously to obtain a branched structure.

ii. "Grafting through". The combination of hydrophobic and hydrophilic segments may yield materials swelling dramatically in water without chemical crosslinking. These hydrogels aggregate in aqueous media, forming physical crosslinks through their hydrophobic domains, while the hydrophilic moieties are present in sufficient concentration to absorb water. Such hydrogels should have a hydrophilic backbone and hydrophobic combs.

The first example of hydrogels made by ATRP involved graft copolymers of polystyrene with *N*-vinyl pyrrolidinone (NVP).[263] The method of graft copolymer formation was the copolymerization of vinyl ester

Scheme 48. Grafting through Process with Macromonomers Prepared by ATRP

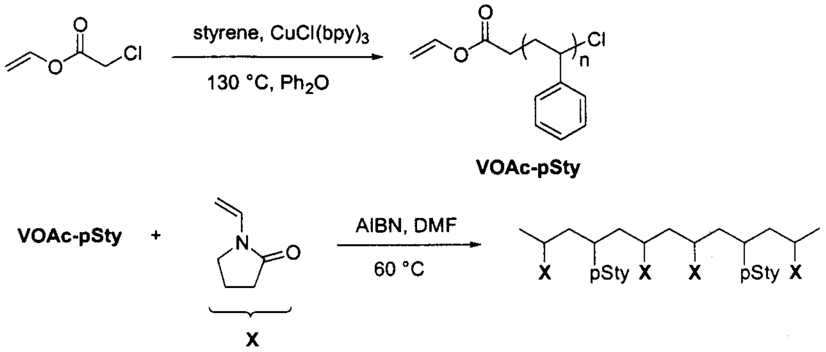


Table 17. Compositional Data of Copolymers Synthesized from Macromonomers[a] (M_n = 5800)[263]

theoretical wt % Sty	actual wt % Sty	M_n copolymer	PDI	% yield	avg. no. of grafts per chain	% conv MM	% conv NVP
50	35.4	95 500	2.80	19.6	5.8	14	25
40	34.2	316 000	5.90	48.9	18.6	42	53
30	19.2	264 000	2.36	15.8	8.7	10	18
20	13.0	219 000	2.45	20.0	4.9	12	21
10	7.7	185 000	1.81	22.1	2.5	16	23

[a] Copolymer was not isolated since it formed a surfactant

Table 18. Swelling Parameters of Graft Copolymers Containing Grafts with M_n = 5800[263]

	wt % Sty				
	35.4	34.2	19.2*	13.0	7.73
^1Q (%)[a]	387	661	538	1228	3311
^2H (%)[b]	74.1	84.9	81.4	91.9	97.0

[a] $^1Q = W_{wet}/W_{dry} \times 100\%$. [b] $^2H = (W_{wet} - W_{dry})/W_{wet} \times 100\%$.

terminal polystyrene macromonomers with NVP by a conventional free-radical polymerization. Synthesis of the macromonomers was achieved by the ATRP of styrene initiated by vinyl chloroacetate. Molecular weights were predetermined, and polydispersities were low, $M_w/M_n < 1.2$. Polymerization through the vinyl acetate double bond was not observed, due to low degrees of styrene polymerization and the reactivity ratios of the two comonomers. Three different molecular weight macromonomers were examined in the graft copolymerizations (M_n = 5800, 11 900, and 15 900) with varying theoretical weight fractions (10−50%) of styrene designed for the copolymers. Graft copolymer formation was performed using an AIBN-initiated polymerization in DMF at 60 °C. Representative results for the graft copolymers are shown in Table 17. As the macromonomer molecular weight increased, the graft density decreased. Polymerizations attempted with a high molecular weight macromonomer (M_n = 15 900) showed no incorporation of polystyrene grafts. Excluding the 40% (w) macromonomer shown, the data in Table 17 also demonstrate that with increasing loadings of styrene, the graft copolymers contained a higher concentration of the hydrophobic segments while maintaining the same number of grafts per chain. This was possible because the molecular weight decreased with increasing amount of macromonomer in the feed. For the lower molecular weight macromonomer, the observed content of styrene, copolymer molecular weight, and graft density all increased with hydrophobe content. All of the materials behaved as hydrogels absorbing significant amounts of water as indicated by the equilibrium water content (*H*) and the equilibrium state of swelling (*Q*) in Table 18.

The "grafting through" approach using ATRP has also been applied in the copolymerization of *n*BA and PMMA macromonomers. [267,268] In contrast to a conventional copolymerization where the relative reactivity of the macromonomer is significantly lower than that of the MMA, the relative reactivity of the macromonomer is much closer to that of MMA in ATRP. This was explained by the longer time scale of monomer addition in ATRP (seconds) than in conventional polymerization (milliseconds). The graft copolymers obtained by ATRP also had lower polydispersities.[268] Similar results were obtained for PDMS macromonomers, which in ATRP had reactivity ratios much closer to MMA than in a conventional process under similar conditions (r_{PDMS} = 0.82 vs 0.34). Even better results were obtained using PDMS macroinitiators, especially in less diluted systems. The PDMS macroinitiator compatibilizes the growing chain and prevents phase segregation.[366]

The other example of brush copolymers utilizes the "grafting through" approach where vinyl terminal macromonomers are synthesized first followed by polymerization through those double bonds to produce the densely grafted macromolecules. In that work, the zinc iodide-mediated polymerization of isobutylvinyl ether was initiated by the hydrogen chloride adduct of 2-(vinyloxyethyl) methacrylate to yield a methacrylate terminal poly(isobutylvinyl ether) macromonomer.[266] In the ATRP of the macromonomers, linear increases of the molecular weights with conversion were observed. Polydispersity remained low $M_w/M_n < 1.2$ throughout the reaction. The study has shown that well-defined materials could be produced from components that were themselves synthesized by living polymerization techniques.

b. Organic Grafts from Inorganic Backbones. The first example reported of an inorganic/organic hybrid graft copolymer consisted of polystyrene grafts from a PDMS backbone.[344] The pendant-functionalized PDMS macroinitiator was synthesized in an analogous fashion to the terminal difunctional macroinitiator described earlier, hydrosilylation of poly(vinylmethylsiloxane-*stat*-dimethylsiloxane) with a compound containing hydrosilyl and benzyl chloride moieties. ATRP of styrene from a macroinitiator with pendant benzyl chloride groups ($M_n = 6600$, $M_w/M_n = 1.76$) resulted in a copolymer with $M_n = 14\,800$, $M_w/M_n = 2.10$. In a similar way, amphiphilic side chains were grafted from PDMS backbone.[359] An alternative method involves grafting through by using PDMS macroinitiators.[366]

Side polystyrene chains were grafted from a polysilylene backbone by ATRP.[367] The graft copolymer has improved mechanical properties compared to the homopolymer, and the optoelectronic properties of the polysilylene were preserved. In this account, 35% of the phenyl rings of poly(methylphenylsilylene) (PMPS) were bromomethylated in a Friedel−Crafts reaction. ATRP of styrene from the macroinitiator using the heterogeneous CuBr(bpy)$_3$ catalyst system provided the graft copolymers. Evidence for graft formation was obtained from SEC using a UV detector collecting data at 254 nm (selective for polystyrene segments) and 339 nm (selective for the polysilylene segments). The considerable overlap of the two peaks demonstrated that the two components of the system are present within the same molecules. ^{1}H NMR measurement of the purified copolymer gives a ratio of polystyrene to PMPS of 12.5:1. A lower than expected T_g of 80 °C was explained by the authors to be due to “considerable free volume of the multiple chain ends”.[367] The ^{1}H NMR spectrum of the product showed that some unreacted benzyl bromide moieties were still present on the PMPS backbone.

2. Grafts from Surfaces

Growth of polymers at interfaces by ATRP, be it from planar surfaces or spherical particles, holds promise in fields such as lithography, lubrication, and chromatography. The use of classic free-radical initiators with azo moieties have been demonstrated,[368,369] but there is poor control over chain length and terminal chain functionality. In ATRP, a monofunctional initiator molecule can be attached to a surface ensuring that, in the absence of chain transfer or thermal self-initiation, chains can be grown solely from that surface. Such is the case with a study by Wirth et al. where polyacrylamide was grown from functionalized silica particles.[370] While no information was given on the controlled growth of films, attachment of the polyacrylamide to the surface was confirmed by elemental analysis. When packed into an HPLC column, the modified silica particles were found to be effective in the fast, efficient separation of basic proteins.[370] The authors later extended the surface initiated acrylamide polymerization to silicon wafers where they demonstrated that film thickness could be controlled by the concentration of monomer in the reaction.[134]

Spherical silica particles containing surface ethoxysilyl groups were functionalized with 2-(4-chloromethylphenyl)ethyldimethylethoxysilane by the Stöber process.[371] Following the ATRP of styrene, dynamic light scattering confirmed that the size of the particles had nearly doubled. Cleavage of the core allowed for SEC analysis of the arms—“high” molecular weight polymer was obtained with polydispersities as low as $M_w/M_n = 1.14$. Similarly, (11′-chlorodimethylsilylundecyl)-2-chloro-2-phenylacetate was attached to a silica gel surface to initiate the ATRP of styrene.[372] ATRP also enables the synthesis of block copolymers from such particles. Functional nanoparticles were prepared where approximately 1000 functional silanes bearing 2-bromoisobutyrate initiating groups were condensed onto the nanoparticle surface. The ATRP of styrene and subsequently benzyl acrylate was conducted enabling the synthesis of homo- and block copolymers tethered to a colloidal core. Particle size increased from 24 to 30 and to 55 nm by AFM and from 25 to 52 and to 106 nm by dynamic light scattering, correspondingly. SEC of the chains cleaved from the surface by destruction of particles with HF shows a progressive increase of molecular weights from $M_n = 5250$ to 27 280 on extension from polystyrene to polystyrene-*b*-poly(benzyl acrylate) while preserving low polydispersities.[373]

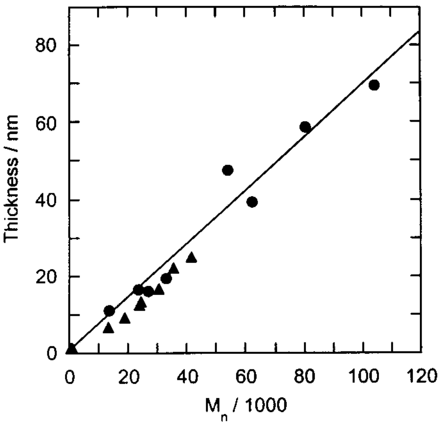
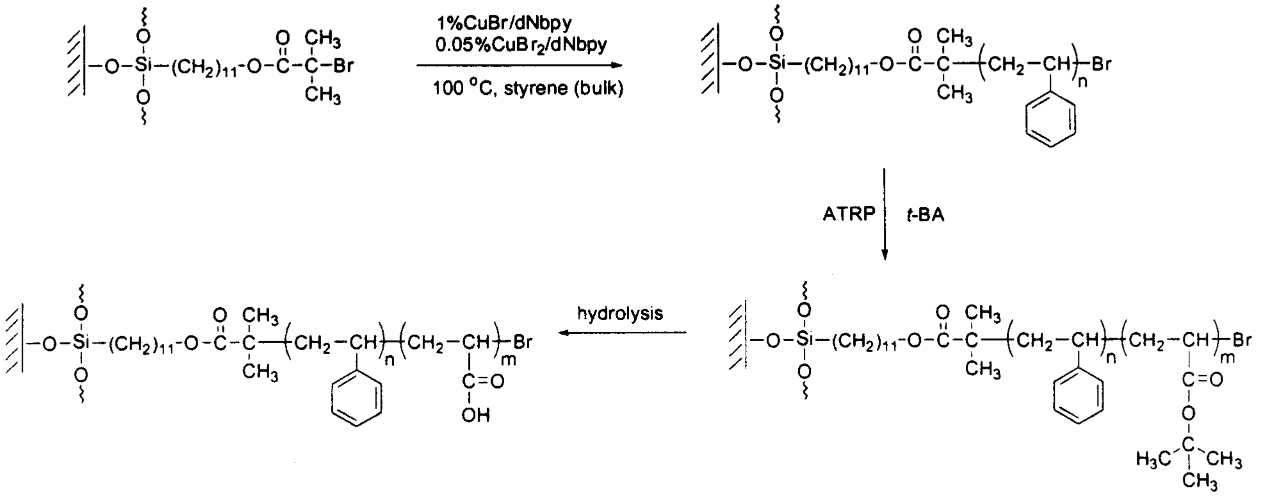


Figure 21. Relationship between the thickness of a PMMA film grown from a silicon surface and the molecular weight of chains polymerized in solution.[278]

There are several accounts of grafting from flat surfaces such as silicon wafers by ATRP. In one system, Langmuir−Blodgett techniques were used to condense a monolayer of 4-(2-trimethoxysilylethyl)phenylsulfonyl chloride onto the surface.[278] The ATRP of MMA mediated by a CuBr/alkyl bipyridine complex with a “sacrificial” initiator, i.e., untethered *p*-toluenesufonyl chloride, showed linear increases in film thickness with the molecular weight of chains in solution (Figure 21).

Another study utilized chlorosilanes in the self-assembly of (5′-trichlorosilyl)pentyl 2-bromoisobutyrate on an oxidized silicon wafer.[374] In the NiBr(PPh$_3$)$_2$-mediated polymerization of MMA, linear increases of film thickness with the length of untethered chains polymerized from ethyl 2-bromoisobutyrate was observed. The authors of both studies emphasize that the free initiator was necessary to provide control of the surface polymerization as the deactivator was provided by termination of short chains very early in the reactions. A sugar-

Scheme 49. Grafting from Flat Surfaces by ATRP, Followed by Block Copolymerization and Deprotection



carrying methacrylate, 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIpGlc), was recently grafted on a silica surface using a monolayer of the initiator, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, which was immobilized by the Langmuir–Blodgett technique.[375]

ATRP has also been used for the synthesis of block copolymers from a modified silicon surface. A polystyrene layer was grown from the surface by living cationic polymerization.[279] The terminal secondary benzyl chloride groups were then used in the ATRP of MMA using a CuBr/PMDETA complex.[101] The efficiency of blocking was not evaluated. Under homogeneous conditions, the blocking efficiency should be very low, because benzyl halides are poor initiators for ATRP of MMA, especially without the halogen exchange.[123] Nevertheless, incorporation of some PMMA onto the macroinitiator was confirmed by reflectance FTIR and water contact angle measurements. In the latter case, changes in contact angle were observed for data measured after immersion of the wafers in solvents selective for either the polystyrene or PMMA segments. The films were responsive to their environment and nanopattern formation occurred, perhaps due to a low brush density.[279,376] The same group also attached an azo-functional trichlorosilane to the silica surface and used reverse ATRP to prepare similar block copolymers.[377]

Block copolymers of polystyrene-*b*-poly(*tert*-butyl acrylate) on silica wafer also have been prepared exclusively by ATRP.[280] Modification of the hydrophilicity of the surface layer was achieved by hydrolysis of the *tert*-butyl ester to form polystyrene-*b*-poly(acrylic acid) and confirmed by a decrease in water contact angle from 86° to 18°. On the other hand, high contact angles were obtained when fluoroacrylates were polymerized from the surface (119°). It was also demonstrated that the presence of a small amount of cupric halide prior to the commencement of the polymerization can result in a sufficient deactivator concentration, thus eliminating the need for the “sacrificial initiator”. Ambient temperature ATRP of MMA using 2-bromoisobutyrates attached to a gold surface with CuBr–tris[2-(dimethylamino)ethyl]amine as the catalysts led to densely chemically bound PMMA brushes on gold surface.[378,379]

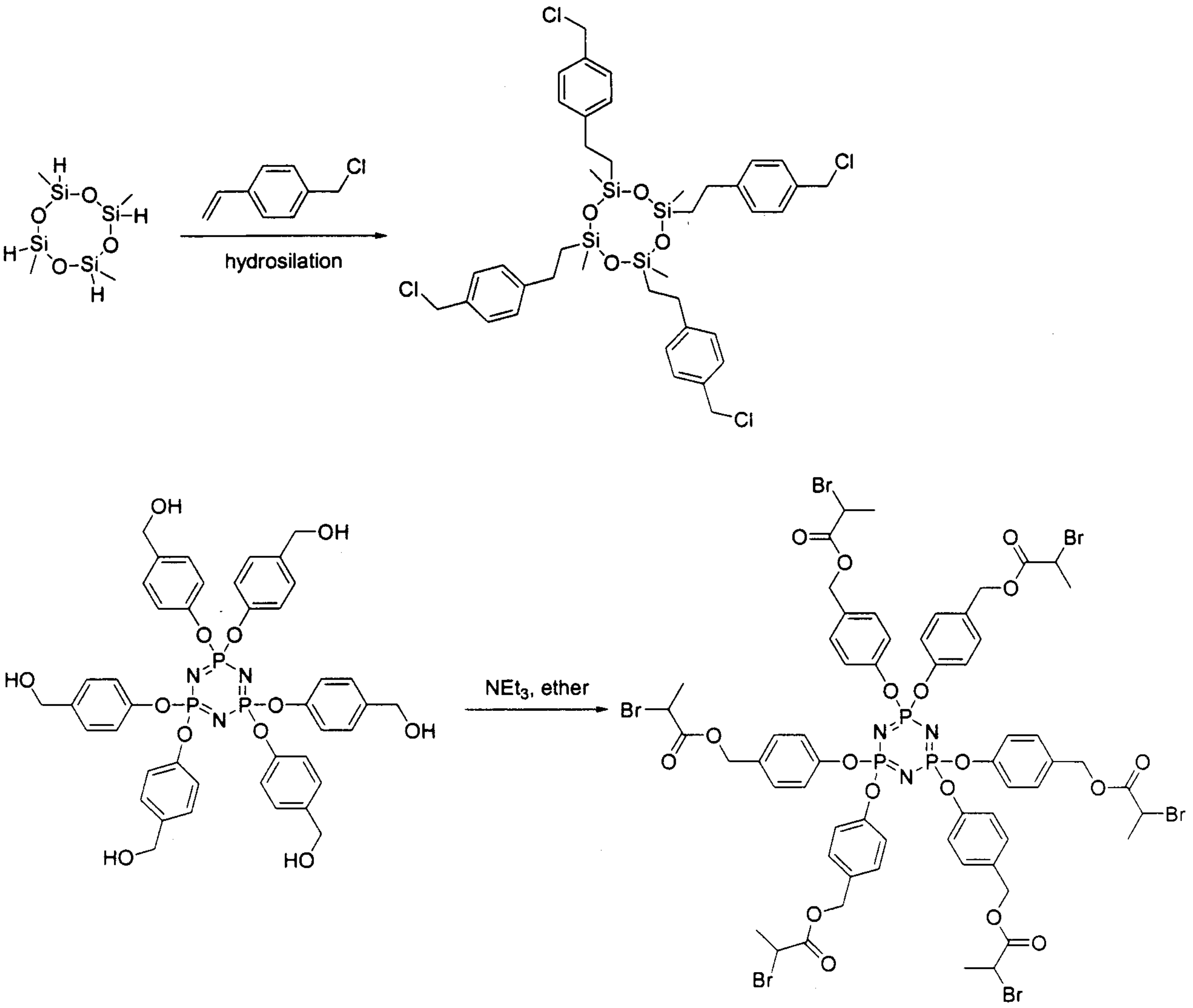
Recently, ATRP has been used to amplify initiators, patterned on films of gold by microcontact printing, into polymeric barriers that can serve as robust barriers to a range of wet chemical etchants.[380] The use of ATRP permits a high level of control over the thickness and functionality of polymer brushes and makes tailoring of the physical properties of the brushes such as their wettability and etching resistance possible.

3. Star Polymers

The use of multifunctional small molecule initiators to synthesize star polymers was recognized shortly after the advent of ATRP. The first example was polymerization of styrene from hexakis(bromomethyl)benzene.[299] The molecular weights correlated with the theoretical values ($M_{n,exp}$ = 62 400, $M_{n,th}$ = 60 000), and the polydispersity was low (M_w/M_n = 1.23). Since that time, additional examples have been reported in the literature. A study was published on comparison of mono-, di-, and trifunctional dichloroacetate initiators for ATRP of MMA using a Ru(II) catalyst system.[161] Both aromatic and aliphatic analogues of the initiators were examined. Both SEC and ^{1}H NMR confirmed quantitative initiation by all three sites in the trifunctional compound. Polydispersities were low, $M_w/M_n = 1.2-1.3$. When $Al(O\textit{i}Pr)_3$ was used, deviation from the theoretical molecular weight was observed for the multifunctional initiators. Reactions with aluminum tris(acetyl acetonate) avoided this problem. ^{1}H NMR studies determined that the more basic $Al(O\textit{i}Pr)_3$ was promoting a transesterification reaction with (1) the initiator to alter the monomer-to-initiator ratio and (2) the methacrylate repeat units to poison the catalyst.

Another study involving three-arm star polymers was performed in the area of side chain liquid crystalline polymers.[256] Linear and star polymers of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate were prepared with predetermined molecular weights and narrow molecular weight distributions. The broadening of the isotropization temperature of the polymer prepared by the conventional free radical polymerization was due to an inhomogeneity in the chain length (polydispersity) and from contamination by

Scheme 50. Synthesis of Star Polymers from Inorganic Core[345]



branched architectures as a result of chain transfer to polymer observed at high monomer conversions.

Other examples of star polymers include those derived from initiators bearing inorganic heterocyclic fragments.[345,381] Shown in Scheme 50 are the reactions used to prepare tetra- and hexafunctional initiators from cyclotetrasiloxanes and cyclotriphosphazenes, respectively. Polymerizations of styrene and acrylates from these initiators yielded polymers with low polydispersities. In both cases the molecular weights measured by SEC using linear polystyrene standards were lower than those predicted theoretically due to differences in the hydrodynamic volume of the stars versus the linear standards. However, the absolute molecular weights measured by light scattering and viscometry showed a good correlation with the theoretical values. In addition, the first six armed star-block copolymer composed of a poly(methyl acrylate) core and poly(isobornyl acrylate) shell was synthesized.[345,381]

Two groups have reported the use of functional calixarenes as initiators for ATRP. The first study examined dichloroacetate-substituted calixarenes with functionalities of four, six, and eight. Polymerizations of MMA and *n*-butyl acrylate were well-controlled as demonstrated by the agreement between the theoretical and measured arm molecular weight following cleavage of the core.[162] A star-block copolymer of PMMA and poly(*n*-butyl methacrylate) was also synthesized from the octafunctional initiator.

The ATRP of styrene from octafunctional 2-bromopropionate-modified calixarenes was the focus of the second study.[382] Below 20% conversion the polymerization was controlled by agreement between measured and theoretical molecular weight. Above that conversion, high molecular weight shoulders were observed by on-line light scattering measurements which the authors attributed to coupling between stars. However, under the proper conditions of high dilution and cessation of the polymerization at low conversion, stars with molecular weights as high as $M_n = 340\,000$ were formed. Agreement between the free arm chain length and the theoretically predicted values was obtained.

In a similar way, multifunctional initiators with three, four, six, and eight sulfonyl halide groups were used to prepare star polymers with methacrylates and styrene.[167]

Dendrimer-forming moieties were used to synthesize hexa- and dodecafunctionalized initiators composed of 2-bromoisobutyrates.[383] The molecular weights of the PMMA were lower than those pre-

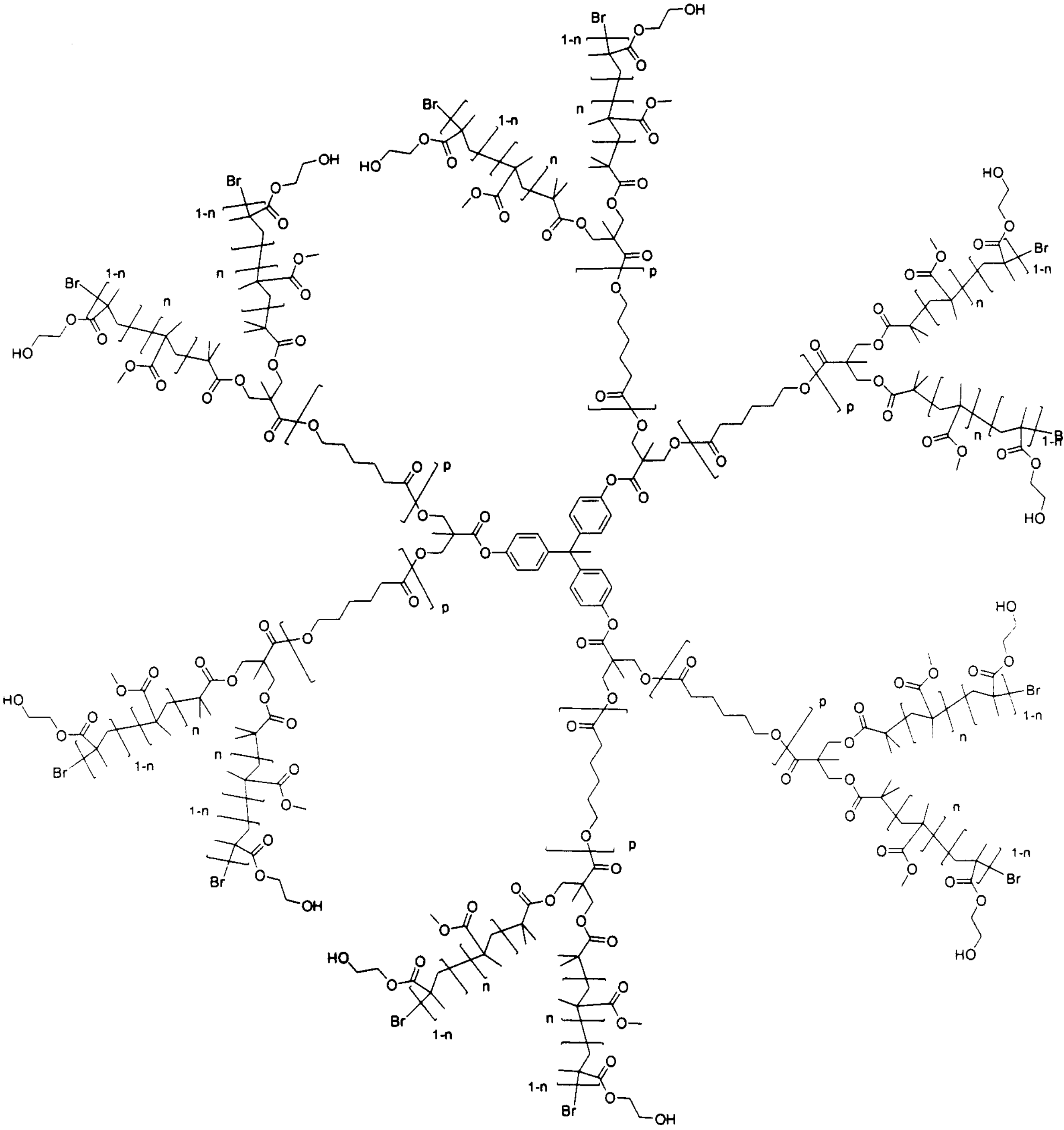
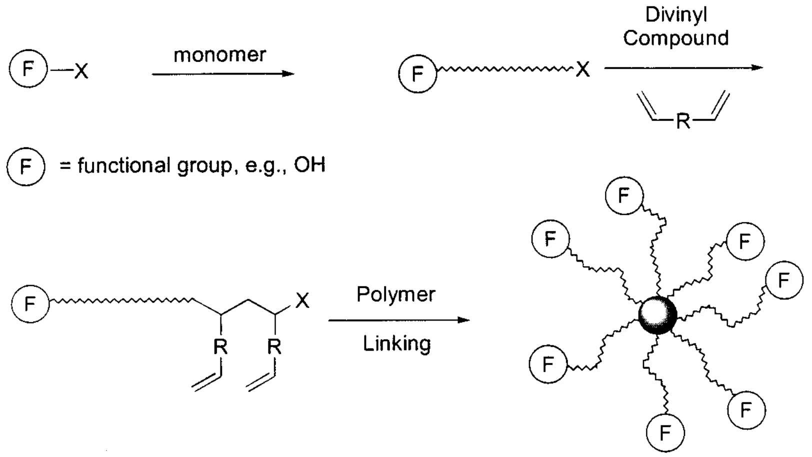


Figure 22. Dendrimer-like star-block copolymer composed of a poly(ϵ-caprolactone) and a poly(MMA-*co*-HEMA) shell.[387]

dicted by theory, but ^{1}H NMR measurements showed better agreement. Polydispersities were quite low, $M_w/M_n < 1.12$. The same initiators were used in the synthesis of star-block copolymers composed of *tert*-butyl acrylate and MMA in both orders extending from the core.[384] Following hydrolysis of the *tert*-butyl esters to acrylic acid, ^{1}H NMR studies showed that the stars formed unimolecular micelles; the structure changed its conformation based on the selectivity of the solvent toward the two segments of the copolymer. Similarly, star-block copolymers of MMA and HEMA were prepared.[385] ^{1}H NMR studies using deuterated monomer showed incomplete initiation for initiators with a higher number of arms (e.g., 12), which was speculated to be due to steric effects.[386] The resulting copolymers were used to produce nanophase separated inorganic/organic hybrids by templating the vitrification of methylsilsesquioxane, and nanoporous thin films were generated by the subsequent thermal degradation of the organic polymer. It was expected that these polymers would find applications as novel templating materials for the preparation of porous low dielectric constant films. Stars were also prepared based on multifunctional sulfonyl halides.[167]

The "dendrimer-like" star-block copolymers have been synthesized from initiators produced by dendrimer techniques.[387] Synthesis of this multibranched macromolecule began with ϵ-caprolactone polymerization from a hexafunctional initiator. Each hydroxyl end group was then chemically transformed into two 2-bromoisobutyrate moieties, which were used to initiate the ATRP of either MMA or a mixture of MMA/HEMA to give the structure shown in Figure 22. The thermal and mechanical studies of the caprolactone/MMA system showed that the material

Scheme 51. Functional Star Polymers by the "Arm-First" Approach



was phase separated. The hydroxyl groups from HEMA in the statistical copolymer were used to initiate the ring-opening polymerization of ethylene oxide to yield an amphiphilic star–*block*–graft copolymer.[387]

The IBM group has also used the "tandem polymerization" approach to synthesize a four-arm star polymer where the arms consist of PMMA synthesized by ATRP from poly(di-*n*-hexylfluorene).[388] The macroinitiator was obtained by esterification of the aryl dihydroxy terminal units of the macroinitiator with 2-bromoisobutyryl bromide.

Haddleton et al. recently reported on the esterification of the natural products D-glucose and β-cyclodextrin with 2-bromoisobutyryl bromide.[389] The products, with functionality of 5 and 21, respectively, were used as initiators for the ATRP of styrene and MMA. From the glucose derivative, both polymerizations resulted in molecular weights that were close to the theoretically predicted values based on linear standards, which is surprising for a multifunctional stars. The polydispersity for the PMMA star was M_w/M_n =1.18, but a higher value of M_w/M_n =1.70 was obtained for the styrene polymerization. For the more highly branched β-cyclodextrin star, the SEC trace of the PMMA sample was multimodal. In the styrene polymerization, a network resulted due to coupling of the arms.

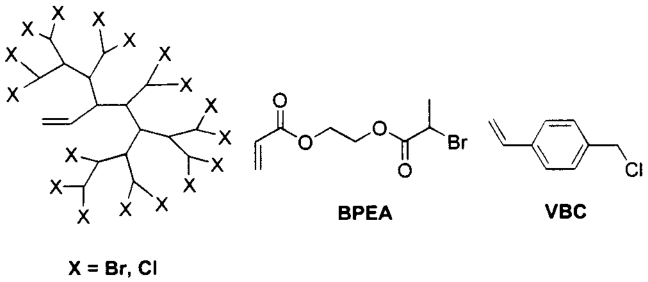
Coordination chemistry has been used in the synthesis of star polymers with up to six arms per molecule.[390] 4,4′-Bis(chloromethyl)-2,2′-bipyridine or mixtures of that ligand with unsubstituted bipyridine was coordinated to ruthenium(II) such that complexes with two, four, or six alkyl halide moieties per metal complex were obtained. The 4-chloromethyl groups on the ligand were then used to initiate the copper-mediated ATRP of styrene or nickel-catalyzed ATRP of methyl acrylate. A convergent approach has recently been reported where 2,2′-bipyridines substituted by polystyrene prepared by ATRP were made before coordination took place.[391]

All of the aforementioned literature reports showed star polymer formation originating from a core. The so-called "arm-first" approach has also been demonstrated. Linear polymers of polystyrene[392] or poly(*tert*-butyl acrylate)[241] were first prepared by ATRP. The resulting polymers were subsequently allowed to react with a cross-linking reagents such as divinyl benzene, 1,4-butanediol diacrylate, and ethylene glycol dimethacrylate to form cross-linked cores. Several factors pertinent to star polymer formation, including the choice of the exchanging halogen and solvent, the addition of a copper(II) species, the ratio of the coupling reagent to the macroinitiator, and thereaction time for the star formation, are crucial for efficient star formation. The highest efficiency (~95%) was observed with 10- to 15-fold excess of the difunctional monomer over chain ends. Functional initiators were used to directly prepare arms with α-functionalities since ATRP is highly tolerant to functional groups. End-functional star polymers with hydroxy, epoxy, amino, cyano, and bromine groups on the outer layers were successfully synthesized.[241] An alternative approach to end-functional stars can employ a chain end transformation process, such as a radical addition reaction to incorporate epoxy or hydroxy groups.[285] When a difunctional initiator was first used followed by reaction with difunctional monomer, crosslinked polymer gels were formed.[393] The studies of the swelling equilibrium of different parts of the same sample showed that these gels were fairly homogeneous.

4. Hyperbranched Polymers

Within the context of ATRP, hyperbranched polymers are prepared by the self-condensing vinyl polymerization (SCVP)[394] of AB* star monomers by a controlled free-radical process. The result, under certain conditions, is a highly branched, soluble polymer that contains one double bond and, in the absence of irreversible termination, a large quantity of halogen end groups equal to the degree of polymerization (Scheme 52). The AB* monomers, similar to AB_2 monomers proposed by Flory,[395] are so named because they contain two active species, the double bond A group and the initiator fragments B*. Two examples explored in detail by ATRP are vinyl benzyl chloride (VBC, *p*-chloromethylstyrene)[396] and 2-(2-bromopropionyloxy)ethyl acrylate (BPEA),[397] both depicted in Scheme 52. Several other (meth)acrylates with either 2-bromopropionate or 2-bromoisobutyrate groups were also used.[398] It should be noted that under certain conditions linear homopolymers of the

Scheme 52. Schematic Representation of Hyperbranched Polymer and AB* Monomers[396]



AB* monomers can be synthesized as intermediates toward other chain architectures.[127,363,399]

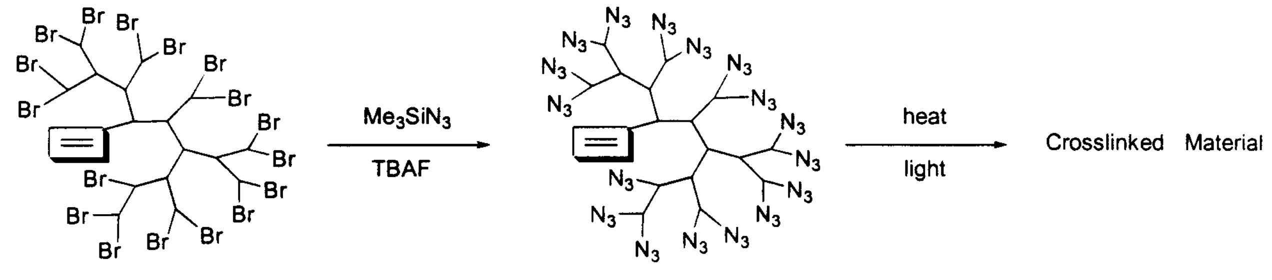
The first hyperbranched polymer synthesized by ATRP was VBC. In two studies[288,396] different results were obtained in terms of the actual structure of the polymers formed as a function of reaction conditions. In the first report,[396] a low catalyst concentration (5%) was used relative to monomer (i.e., initiator). In a later report,[288] a significantly higher quantity of catalyst was used (>20%). Apparently, in the presence of larger amounts of the catalyst, more deactivator is formed, leading to faster deactivation and a higher degree of branching (vide infra). However, in the presence of more catalyst, more radicals are also formed, leading to more termination and resulting in an additional source of branching via radical coupling.

The synthesis of hyperbranched polymers from BPEA provides more information on conditions leading to either branched or linear polymers.[397,399,400] Molecular weight does not dramatically increase until conversions greater than 50%.[399] This is in accord with a step-growth polymerization and values predicted by theoretical treatments of the system.[400,401] Since the secondary 2-bromopropionate dormant species formed during the reaction should have a similar (if not equivalent) reactivity to the 2-bromopropionate found on the monomer, theory[402] predicts that a macromolecule with a maximum degree of branching (DB), 0.46, should be formed. The value measured by ^{1}H NMR was 0.49. The polydispersity of the system is significantly lower than that predicted by theory, which should be similar to the degree of polymerization.[400] A theoretical treatment using multifunctional initiators in an SCVP reaction led to the possibility that intramolecular cyclization may lead to a molecule with a lower polydispersity.[403] Another study identified that certain catalyst systems could influence the formation of linear polymers over branched structures or produce such an active polymerization that too much irreversible termination occurs and the reaction effectively shuts down.[399] Later studies showed that inclusion of Cu(0) in the reaction allowed for polymerizations to continue.[398] Furthermore, the solubility of the deactivator play a dramatic role in determining the topology of the polymers.[400] When more $CuBr_2$ complex was in solution, deactivation was faster, allowing for more a random initiation from the various alkyl halide species in the macromolecules, which lead to higher branching. With less deactivator, multiple monomer additions per active species can occur, thereby decreasing the degree of branching.

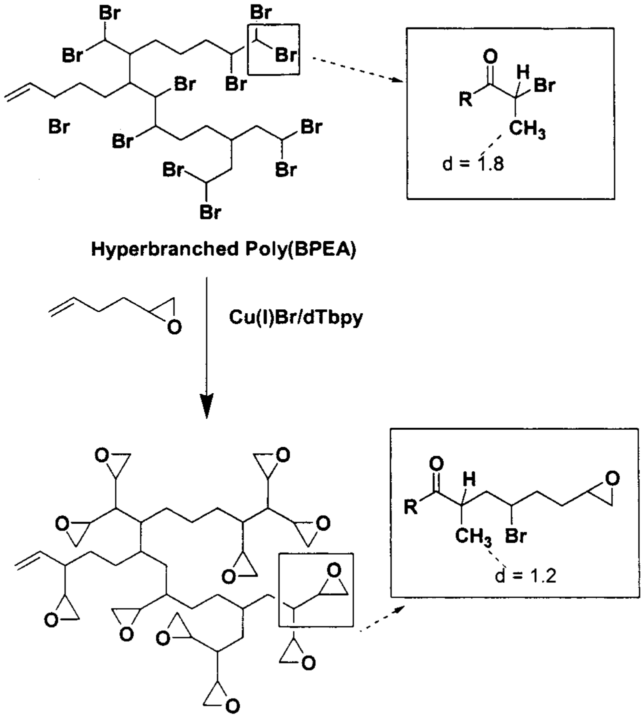
Hyperbranched polymers synthesized by ATRP using “mixed monomers”, structures that contain combinations of (meth)acrylates with α-haloesters,[398] has also been reported. For example, 2-(2-bromopropionyloxy)ethyl methacrylate (BPEM) contains the methacrylate and bromopropionate groups which form tertiary and secondary radicals, respectively. Likewise, the monomer 2-(2-bromoisobutyryloxy)ethyl acrylate (BIEA) contains the secondary acrylate group with a tertiary 2-bromoisobutyrate fragment. With these monomers, branched macromolecules were obtained. In a similar way, macroinitiators were used to reduce the proportion of branched units.[404]

The terminal halogens in hyperbranched polymers have been replaced by more useful functionalities, such as azido, amino, hydroxy, and epoxy, using radical addition reactions.[285] For example, terminal bromines in the hyperbranched poly(2-bromopropionyloxy-2-ethyl acrylate) (PBPEA) were displaced by azide anions. The resulting polyacrylates with ∼80 functional groups have been thermally (at ∼200 °C) or photochemically crosslinked. The labile bromines in PBPEA were used to insert nonpolymerizable monomers by ATRP such as allyl alcohol and 1,2-epoxy-5-hexene via an ATRA reaction. The resulting multifunctional polyols and polyepoxides can be potentially used in thermosetting technologies. Hydrophilic poly(ethylene glycol) or pentaerythritol ethoxylate cores with hyperbranched polystyrene arms were prepared by reacting PEG or pentaerythritol ethoxylate with 2-bromopropionyl bromide followed by the ATRP of the macroinitiator and chloromethylstyrene to produce the amphiphilic hyperbranched polymer. Depending on the functionality of the macroinitiator, the products have either a dumbbell or 4-arm starburst structure. The dumbbell polymers tend to have higher molecular weights, while the starburst polymers have rather low molecular weights.[405]

Scheme 53. Displacement of Bromines by Azides in Hyperbranched Poly(2-bromopropionyloxy-2-ethyl acrylate)



Scheme 54. Addition of 1,2-Epoxy-5-hexene to the Hyperbranched Poly(2-bromopropionyloxy-2-ethyl acrylate)



Heat-resistant hyperbranched copolymers of VBC and *N*-cyclohexylmaleimide have been synthesized by ATRP. Under the identical polymerization conditions and after the same reaction time, high monomer conversions occurred near the equimolar feed composition, indicating the formation of charge-transfer complexes between VBC (electron donor) and maleimide (electron acceptor). As expected, the T_g of the copolymer increased with an increasing content of maleimide in the feed.[406]

Hyperbranched polymers can further initiate polymerizations forming dendrigraft polymers. Thus, hyperbranched polymers from vinyl benzyl chloride were used to initiate the ATRP of *n*-butyl acrylate[146] and styrene.[407] Dendrigraft polystyrene was found to display a lower intrinsic viscosity and higher thermal stability than linear polystyrenes.[407] Recently, hyperbranched polyglycerol prepared by ring-opening multibranching polymerization was esterified with 2-bromoisobutyryl bromide. Such macroinitiators were used to initiate the ATRP of MA, resulting in multiarm block copolymers with polyether core and ~50 PMA arms.[408]

By combining the concept of SCVP and “simultaneous living polymerization”, hyperbranched polymers have been prepared using monomers containing both a polymerizable group and initiating site, but the polymerizable group and the initiating site undergo different polymerization mechanisms (Scheme 55).[409] The molecular architecture can be conveniently altered by adding monomers which can be polymerized by only one of the mechanisms.

5. Summary and Outlook

Due to an easy access to multifunctional initiators, ATRP and other CRP methods are readily suited to synthesize polymers with novel topologies such as stars, combs, dendritic, or well-defined networks. However, special attention must be paid due to unavoidable termination via biradical coupling. Thus, 5% of termination may be easily tolerated for most of the linear chains; however, it may lead to a catastrophic change in behavior for multifunctional complex architecture. Thus, for the polymer chains growing in five directions, 5% of intermolecular coupling will lead to 25% of chains linked together but for chains growing in 20 directions may lead to the complete cross linking and gelation. Of course, intramolecular coupling and disproportionation may diminish this effect, but the danger of the cross-linking will always exist. Therefore it is very important to better understand and control the termination process. The synthesis of well-defined multifunctional stars and densely grafted molecular brushes is typically carried out slowly, to low conversion, under high dilution and using excess of deactivator. Applications might range from rheology and impact modifiers to materials for controlled release of drugs.

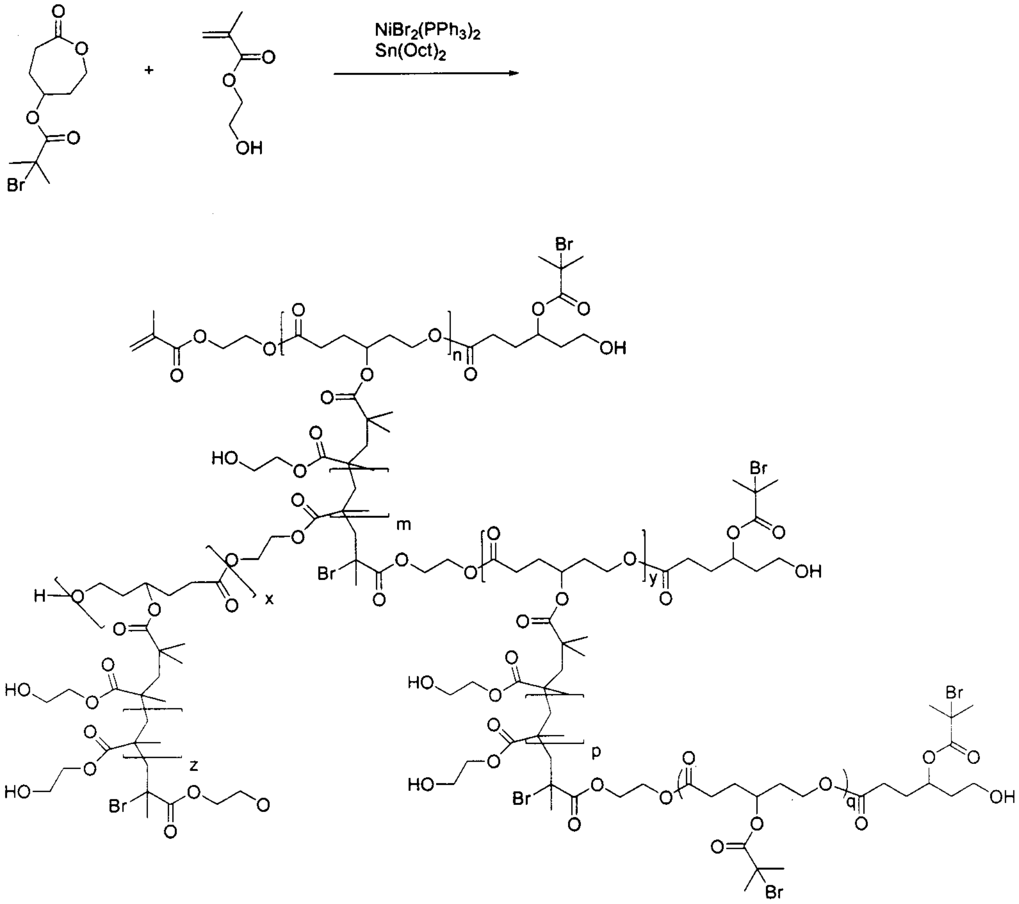
IV. Conclusions

This review has summarized the research activity in the field of ATRP, since the first reports in 1995 to the end of 2000. As evidenced by the discussed literature, a basic understanding of the mechanism and kinetics of this process has enabled the synthesis of various polymeric materials with novel functionalities, compositions, and architectures which are schematically represented in Scheme 56. However, since ATRP is a complex multicomponent system, it is important to understand and to consider all of its components to make full use of this methodology and find the optimum polymerization conditions for the preparation of specific materials for particular applications. This understanding will allow ATRP processes to continue to evolve and provide lower cost commercially viable systems. A spectrum of physical properties will be developed for the expanded range of materials prepared by CRP to allow industry to target products to meet the requirements of specific applications.

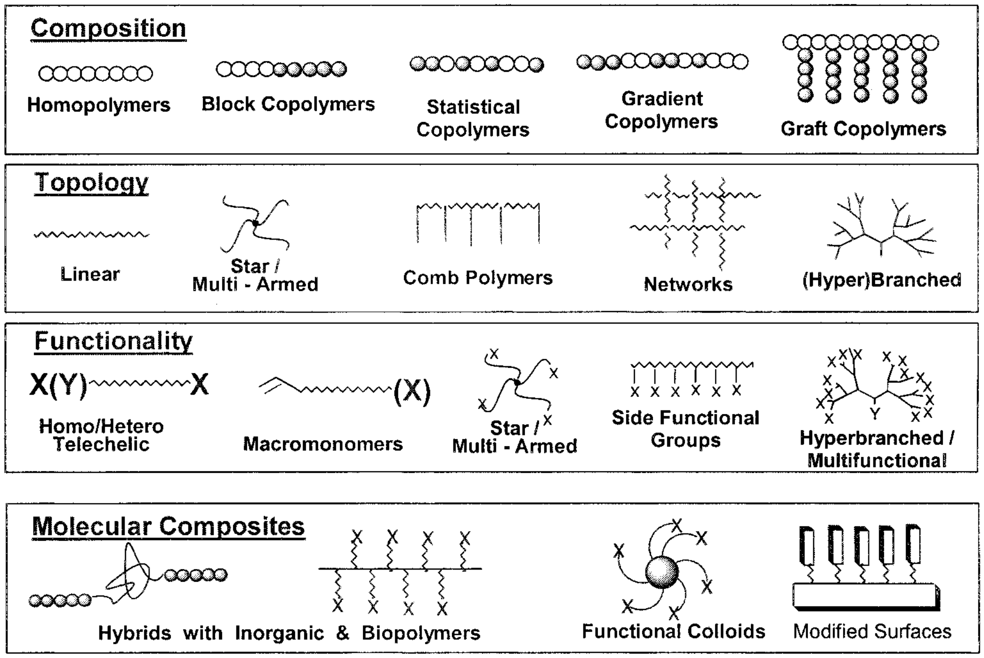
It is anticipated that future research in ATRP will be focused on three areas: (1) construction of a structure−reactivity correlation for all components of an ATRP process; (2) development of new, more efficient, more selective, less expensive, and environmentally sound ATRP catalytic systems; and (3) building a relationship between molecular structure and macroscopic properties for materials made by ATRP.

A detailed knowledge of the structure and interactions of the involved reagents and correlation between their configuration and reactivity is needed. The desired level of information on rate constants of propagation and termination is presently available only for a few monomers from PLP measurements. Precise information on the variation of the rate coefficients of termination with chain length and viscosity must be obtained to properly model ATRP and other CRP processes. Precise activation and deactivation rate constants will have to be measured

Scheme 55. Hyperbranched Polymers by Combination of Anionic ROP and ATRP[409]



Scheme 56. Schematic Representation of Controlled Topologies, Compositions, and Functionalities and Molecular Composites Prepared by ATRP



for many catalytic systems under different conditions (monomer, solvent, temperature for both model and macromolecular systems), since only preliminary information on dynamics of atom transfer equilibria is currently available. As we start to understand the influence of the involved reagents, alkyl group, (pseudo)halogen, transition metal, ligand, solvent, and temperature on these reactions, our ability to prepare materials with desired properties will expand.

The transition metal catalyst is the core component of ATRP systems. The search for more active and more selective catalysts will continue and may get inspiration from enzymatic systems. Expansion of ATRP catalysts to earlier transition metals and lanthanides will require special tuning of the properties of the metal centers by suitable ligands. New catalysts are required to expand the range of monomers polymerizable by ATRP to include acidic and also less reactive monomers such as vinyl halides, esters, or even α-olefins. We are still at an embryonic stage in the development of systems for catalyst removal, regeneration, and recycling. Challenges remain related to extension of ATRP to heterogeneous systems such as emulsion, suspension, or dispersion polymerization in aqueous media. Other biphasic systems such as use of supported catalysts, ionic liquids, or other nonsolvents may assist in catalyst recycle.

Many new functional polymers with novel and controlled compositions and topologies have been prepared by ATRP, and a complete structure−property relationship has to be developed to allow a correlation of molecular structure with macroscopic properties. The degree of end functionality must be precisely measured, although this is not an easy task, especially for higher molecular weight products. Efficiency of block and graft copolymerization must also be precisely known; perhaps 2D-chromatography techniques can provide more information than currently used SEC. We still do not know how to define the quality and a shape of a gradient copolymer on the molecular level and how the gradient affects properties. More information on the effect on properties resulting from control of topologies in complex architectures such as stars, molecular brushes, hyperbranched systems, and networks is also needed. A combination of this information with a systematic variation of molecular weights (shape of molecular weight distribution and not only overall polydispersities), composition (including gradients), end functionalities, and topologies should provide access to the needed comprehensive structure−property correlation. However, since morphologies may also be kinetically trapped, processing, i.e., mechanical stresses, solvent removal, and thermal history may affect the final properties of the materials. Thus, processing should also be taken into consideration during the development of this comprehensive composition/property correlation. Semiempirical simulations will be employed to assist in the construction of this comprehensive picture by modeling of entire routes including synthesis and processing to ultimately obtain materials with desired function for a targeted application. We have stressed the role of ATRP for the preparation of end functional low molar mass polymers, “difficult” block copolymers, multiarm stars, and combs, but we also included hybrid materials with polymers prepared by different mechanisms or attached to inorganic or biomaterials, partly to define the capabilities of ATRP, in the belief that such hybrid systems can phase separate at nanoscale dimensions, thereby generating entirely new materials for variety of special applications.

Although ATRP may be the most versatile system among the recently developed CRP methods, we recognize that for some targeted materials nitroxide or degenerative systems (RAFT) may be equally or even better suited. Regardless, the development of CRP techniques should have a tremendous impact on the range of commercial products prepared by a free radical method. While materials prepared by CRP may replace products made by some other techniques such as group transfer or anionic polymerization, opportunities lie in defining markets for entirely new materials. The first products prepared by controlled radical polymerization might be introduced already in 2001, and it is anticipated that the others will quickly follow. Patent activity indicates market targets include coatings, adhesives, elastomers, sealants, lubricants, imaging materials, powder binder compositions, pigment dispersants, personal care compositions, detergents, water treatment chemicals, and telechelic materials with hydroxy, epoxy, carboxy, and amine functionality in addition to amphiphilic block copolymers. Higher value applications include photopaternable materials and biological sensors.

In summary, ATRP is a valuable tool for the design and synthesis of novel materials. These materials can be employed to meet the requirement of numerous applications. The polymers can be prepared under facile reaction conditions, using a multitude of available polymerizable monomers with accessible chain functionalities. The types of materials produced by ATRP will be limited only by the imagination of those generating the materials.

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