Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Mechanistic and Synthetic Aspects of Atom Transfer Radical Polymerization

Krzysztof Matyjaszewski[a]
[a] Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA

To cite this Article Matyjaszewski, Krzysztof(1997) 'Mechanistic and Synthetic Aspects of Atom Transfer Radical Polymerization', Journal of Macromolecular Science, Part A, 34: 10, 1785 — 1801
To link to this Article: DOI: 10.1080/10601329708010308
URL: http://dx.doi.org/10.1080/10601329708010308

J.M.S.—PURE APPL. CHEM., A34(10), pp. 1785–1801 (1997)

MECHANISTIC AND SYNTHETIC ASPECTS OF ATOM TRANSFER RADICAL POLYMERIZATION

Krzysztof Matyjaszewski
Department of Chemistry
Carnegie Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213

ABSTRACT

Mechanistic and synthetic aspects of atom transfer radical polymerization (ATRP) are reviewed. This controlled/"living" system polymerizes many monomers including styrenes, (meth)acrylates, acrylonitrile and dienes. The halogen end groups can be converted to other functional groups such as amines and azides. In addition to producing well-defined linear homopolymers, statistical copolymers, block copolymers, and gradient copolymers, ATRP can be used to synthesize graft and hyperbranched copolymers through copolymerization with functionalized monomers. Selection of appropriate conditions for ATRP depends on targeted molecular weight and degree of polymer chain end-functionality and includes considering the monomer(s) to be polymerized, initiator structure/reactivity, amount of catalyst/deactivator used, halogen end-group used, and temperature.

INTRODUCTION

Though radical reactions are a potentially powerful synthetic tool, they have found limited application in synthesis due to the difficulty in controlling unavoidable termination reactions between radicals and low yield of desired addition and substitution products. However, several new methodologies have been used to prepare addition, substitution and cross-coupling products in high yields [1]. These systems are based on a persistent radical effect which reduces stationary concentrations of reacting radicals, lowering the contribution of termination reactions [2]. Stable (persistent) radicals can be derived from organometallic species or some organic radicals. One of the most useful systems employs atom transfer radical reactions with middle and transition metals such as Cu, Ni, Pd, Ru, Fe and others [3].

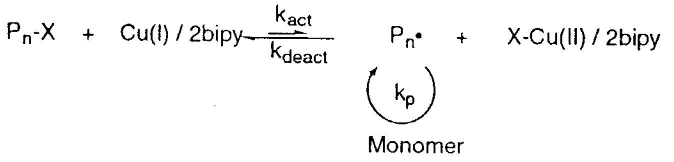
Radical polymerization has been the most important commercial polymerization process during the last 50 years. Nevertheless, much academic and industrial research in chain growth polymerization has been focused on coordination, cationic, anionic and ring-opening polymerizations, due to much better control of macromolecular structure in these processes [4]. However, concurrent with the progress in radical organic chemistry, controlled radical polymerizations have been developed [5]. Originally, inifer or iniferter methodology was used [6], followed by stable free radicals such as TEMPO [7-9], various organometallic species, with cobalt-porphyrines being most successful [10], degenerative transfer [11] and atom transfer radical polymerization (ATRP) [12-15].

ATRP seems to be the most robust of these systems. and can be used for the largest number of monomers. ATRP also gives good control over chain topologies, compositions and functionalities and uses many initiators and macroinitiators with halogen atoms activated by aryl, allyl, sulfone or carbonyl groups. Moreover, since ATRP is *catalytic*, the proportion of radicals (polymerization rate) can be easily controlled by the amount and activity of the catalyst.

The purpose of this paper is to explain mechanistic features of the ATRP process and analyze the role of the reaction components and conditions. Synthetic advantages of ATRP are discussed and examples of materials synthesized by ATRP are given.

Mechanism of ATRP

Analogous to atom transfer radical addition reactions, ATRP occurs as a repetitive addition of a monomer to growing radicals generated from dormant alkyl (pseudo)halides by a reversible redox process catalyzed by transition metal compounds, such as cuprous halides complexed by two 2,2'-bipyridine (bipy) molecules [15, 16] (Equation 1).



$$P_n\text{-}X + Cu(I)/2bipy \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} \underset{\underset{\text{Monomer}}{\circlearrowleft k_p}}{P_n^{\bullet}} + X\text{-}Cu(II)/2bipy \quad (1)$$

Control and properties of the resulting polymers depend on the stationary concentration of growing radicals and the relative rates of propagation and deactivation. Consequently, during one activation step, several monomers may be added, affecting polydispersities of the polymer being formed. If the deactivation process is very slow or does not exist, ATRP becomes a conventional redox initiated radical polymerization. When one or less than one monomer unit is incorporated at each activation step, the process is well controlled and may be considered as an "insertion" proceeding via radical intermediates, consistent with results from trapping experiments, reactivity ratios, and regio and stereochemistry of addition products [16].

Since the catalyst is not bound to the growing chain, ATRP behaves in a similar way in homogeneous (using homogenizing ligands such as 4,4'-di-(5-nonyl)-2,2'-bipyridine, dNbipy) and heterogeneous systems [15, 16]. Slightly higher polydispersities in heterogeneous systems are due to a lower concentration of deactivator (X-M_t^{n+1} species) and a slower deactivation process. However, differences with homogeneous systems are not dramatic. For instance, in the bulk styrene polymerization at 100°C with 0.5 mol% of 1-phenylethyl bromide $M_w/M_n \approx 1.1$ using CuBr/2dNbipy versus 1.3 using CuBr/2bpy.

Results from kinetic studies of polymerizations using homogeneous catalytic systems are more meaningful. The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by two bipyridine ligands (catalyst) [17]. The reaction is usually negative first order with respect to the deactivator ($CuBr_2$/2dNbipy) (Equation 2).

$$R_p = k_{app}[M] = k_p[P\bullet][M] = k_p K_{eq}[In]\frac{[Cu(I)]}{[Cu(II)X]}[M] \quad (2)$$

The precise kinetic law for the deactivator is more complex, since some deactivator is spontaneously formed (when it is not present at the beginning of the reaction), establishing a persistent radical effect. For example, in the bulk polymerization of styrene at 110°C, using RBr and CuBr/dNbipy, the equilibrium constant is approximately $K_{eq}=k_{act}/k_{deact}=4\times10^{-8}$. Therefore, if $[RBr]_o \approx [Cu(I)]_o \approx 0.1$ mol/L, the product of concentrations of radicals and deactivator should be equal: $[R\cdot]\,[CuBr_2]=K_{eq}\,[RX]\,[CuBr]=4\ 10^{-10}\ mol^2\ L^{-2}$. Thus, at the very beginning of the reaction, both radicals and deactivator reach very high concentrations $\approx 10^{-5}$ mol/L. However, some radicals rapidly recombine, reducing their concentration to 10^{-7} mol/L, and lead to large excess of the deactivator ($\approx 5\ 10^{-3}$ mol/L). Consequently, approximately 5% of chains are terminated during the first short non-stationary process but this also means that ≈95% of chains continue polymerization successfully. If a small amount of the deactivator (5%) is added at the very beginning, the proportion of dead chains is significantly reduced.

The Role of Components and Reaction Conditions in ATRP

ATRP is a multicomponent system consisting of an alkyl halide (initiator) a redox-active transition metal in its lower oxidation state (M_t^n), ligands, a deactivator (XM_t^{n+1} species) either formed spontaneously or present from the very beginning of the reaction, monomer and growing chains, and additives (solvent). Reactions are performed in bulk or in solution at elevated temperatures and reaction times of 1 to 10 hours.

Alkyl (Pseudo)halide RX

The main role of the alkyl halide (RX) species is to quantitatively generate growing chains. The structure of the alkyl group R should be similar to the structure of the growing chain. Thus, 1-phenylethyl derivatives resemble growing polystyrene chains, 2-halo propionates model growing acrylate chains, and 2-halo propionitriles are appropriate initiatiors for acrylonitrile polymerization. To choose a good initiator, the ratio of the apparent initiation rate constant ($k_i^{app}=k_i\ K_0$, where k_i and K_0 refer to the absolute rate constant of the addition of the initiating radical to alkene and the equilibrium constant for the initiating species) to the apparent propagation rate constant ($k_p^{app}=k_p\ K$) must be considered. If $k_i^{app}<<k_p^{app}$, initiation is incomplete, too high molecular weights are observed and polydispersities are high. Also, in block copolymerizations the efficiency of block copolymer formation may be low if the apparent rate constant of crosspropagation is smaller than that of the subsequent homopropagation. For initiation, it is better to use less reactive radicals which are formed with relatively higher efficiency than growing radicals. For example, 2-chloroisobutyrates and chlorosulfonates are good initiators for styrene and (meth)acrylates, however, chloroacetates, 2-chloropropionates and 1-phenylethyl chloride are inefficient initiators in polymerization of methyl methacrylate (cf. Figure 1). However, there is a limit in increasing stability of initiating radicals and trityl derivatives are inefficient initiators.

Any alkyl halide with activated substituents on the α–carbon such as aryl, carbonyl, or allyl can be used as well as polyhalogenated compounds (CCl_4, $HCCl_3$) and compounds with a weak X bonding such as N-X, S-X, and O-X. This includes not only low molar mass molecules but also macromolecular species which can be used to synthesize block/graft copolymers.

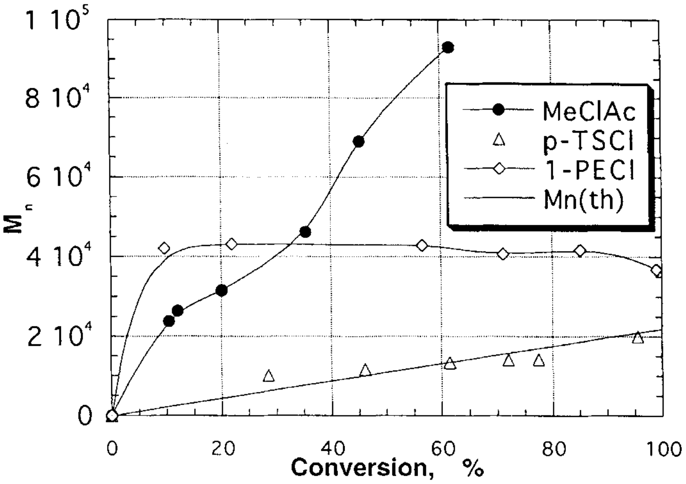


Figure 1. Dependence of M_n on conversion for ATRP of methyl methacrylate $[MMA]_0 = 4.7$ M, initiated by methyl chloroacetate $[MeClAc]_0 = 0.024$ M (●), p-toluene chlorosulfonate $[p\text{-}TSCl]_0=0.024$ M (Δ) and 1-phenylethyl chloride $[1\text{-}PECl]_0= 0.024$ M (◊) and catalyzed by $[CuBr/2dNbipy]_0=0.012$, Temp. = 90°C in diphenyl ether.

Group X must rapidly and selectively migrate between the growing chain and transition metal. Bromine and chlorine seem to work best. Fluorine is bound too strongly and iodine is involved in side reactions in the polymerization of styrene, although it is a good leaving group for polymerizing acrylates. Pseudohalogens have also been used, for example thiocyanates in polymerization of acrylates and styrenes.

R-X bonds can be cleaved not only homolytically but also heterolytically, depending on the substituents on R, nucleophilicity of X, Lewis acidity of transition metal complex, solvent and temperature. Thus, some groups X work well for R with electron-withdrawing substituents but fail with electron-donating substituents (e.g. alkyl iodides are successful with acrylates but not with styrenes). Conversely, side reactions are noticeable for malonate derivatives, presumably due to their reduction to the corresponding carbanions.

Polymerization rates in ATRP are first order with respect to [RX] and molecular weights scale reciprocally with $[RX]_0$.

Transition Metal and Ligands (Mt^nL_x)

This species is key for successful ATRP. Basic requirements for the good catalyst are high selectivity towards atom transfer process and high lability of the resulting X-M_t^{n+1} species. The metal should participate in a one-electron transfer redox cycle rather than a two-electron process which would result in oxidative addition/reductive elimination but not in the atom transfer process. Additionally, the metal should have a high affinity for atom/group X but a low affinity for hydrogen and alkyl radicals. Otherwise, transfer reactions (ß-H elimination) and the formation of organometallic derivatives may be observed, reducing selectivity of propagation and control (livingness) of the process.

The most important factors in selecting good ATRP catalysts are the equilibrium position and dynamics of exchange between dormant and active species. These parameters are related to the redox cycle Mt^n/M_t^{n+1}, but it must be remembered that ATRP is not an electron transfer but an atom transfer process. Thus, the inner coordination sphere of M_t^n must expand to accommodate a new X ligand. Expansion from tetra to pentacoordinated structure Cu^I/2bipy -> X- Cu^{II}/2bipy or penta to hexacoordinated structure $X_2Fe^{II}/3PR_3$ -> $X_3Fe^{III}/3PR_3$ must be possible.

The values of equilibrium constants needed for successful polymerization of (meth)acrylates, styrene and acrylonitrile should be in the range $K \approx 10^{-8\pm2}$. Therefore, a similar value should be observed for model reactions between transition metal complexes and benzyl halides at 100°C. The successful polymerization of monomers with weaker stabilizing substituents such as vinyl chloride, vinyl acetate, and potentially ethylene will require much higher values of the equilibrium constants in reference to benzyl halide ($K \approx 10^{-6\pm2}$). However, it is not only the value of the equilibrium constant but also the *dynamics* of the exchange that are important. The deactivation process must be very fast, $k_d \approx 10^{7\pm1}$ $mol^{-1}Ls^{-1}$ otherwise poor control of molecular weights, high polydispersities, and in the limiting case, conventional redox initiation will be observed.

The role of ligands is three-fold. They affect the redox chemistry by their electronic effects, they control selectivity by steric/electronic effects and they also solubilize catalytic systems. A few comparative data are helpful to illustrate these points:

•The overall polymerization rate and control with heterogeneous catalytic system (bulk polymerization of styrene, CuBr/2bipy) is slower and leads to polymers with higher polydispersities than with the homogeneous system (CuBr/2dNbipy). This is due to lower concentration of the catalyst and deactivator in the heterogenous case. Polymerization is negative first or fractional order with respect to $[CuBr_2]_o$ [17].

•The polymerization of methyl acrylate in the presence of CuBr/2dtBbipy (4,4'-di-t-butyl derivative) has a fractional order in $[CuBr]_o$ but is not affected by $[CuBr_2]_o$ due to its low solubility [18].

•Steric effects are manifested by complete inactivity of 6,6'-disubstituted bipy in ATRP. Molecular models indicate that there is no space for the halogen atom to approach metal and form X- Cu^{II}/2bipy species.

•When bipy with electron donating substituents (4,4'-dicarbomethoxy) is used, polymerization is 10 times slower than with unsubstituted bipy. Apparently, electron-poor ligands stabilize Cu^{I} and destabilize Cu^{II} reducing the corresponding equilibrium constant.

•Use of acetonitrile instead of bipy increases Lewis acidity of copper halides and leads to heterolytic cleavage of C-X bond, side reactions, and in some cases cationic polymerization.

In the case of copper, the most active system is one with two dNbipy. The polymerization rate is first order with respect to Cu^{I}/2dNbipy and the molecular weight does NOT depend on [Cu^{I}/2dNbipy]. It seems that radicals do not interact with [Cu^{I}/2dNbipy], since neither polymerization rate nor molecular weights were significantly affected when [Cu^{I}/2dNbipy] was added to polymerization initiated by conventional organic peroxides [19].

Deactivators

The deactivator is a vital part of the catalytic system. The deactivators reduce polymerization rate and polydispersities but may also participate in side reactions. Thus, the structure and amount of the deactivator are extremely important.

Polydispersities in systems with relatively slow exchange decrease with conversion as follows:

$$\mathbf{M_w/M_n = 1 + (2/p - 1)\{([RX]_o - [RX])k_p\} / (k_{deact}[D])} \qquad (3)$$

This equation can be simplified for complete conversion (p=1) and complete initiation [20, 21]:

$$\mathbf{M_w/M_n = 1 + ([RX]_o k_p) / (k_{deact}[D])} \qquad (4)$$

Thus, polydispersities are higher for shorter chains (higher $[RX]_o$), and for higher k_p/k_{deact} ratios. This is in agreement with experimental observation that poly-

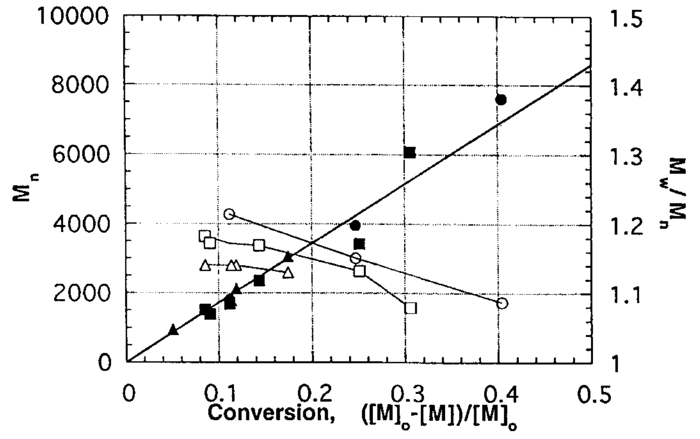


Figure 2. Dependence of M_n and M_w/M_n on conversion for polymerization of methyl acrylate $[MA]_0=11.1$ M initiated by methyl 2-bromopropionate $[MBP]_0 = 0.055$ M, and catalyzed by $[CuBr/2dNbipy]_0=0.055$ M, in the presence of different amounts of $[CuBr_2/2dNbipy]_0= 0.0055$ M (▲△), 0.0027 M (■ □), 0.0014 M (●○) at 90°C.

dispersities are higher in the polymerization of acrylates than styrene, which polymerizes much slower. At the same time polydispersities should decrease with increasing deactivator concentration ($[D]=[X\text{-}Cu^{II}/2dNbipy]$). Indeed, lower polydispersities are seen with progressively added deactivator (cf. Figure 2).

An important factor is the lability of $X\text{-}M_t$ bond in the deactivator. Much lower polydispersities are observed with $CuBr_2$/2dNbipy than with $CuCl_2$/2dNbipy, consistent with earlier studies on the efficiency of inhibition of various metal salts. $CuBr_2$/DMF was approximately two times more efficient an inhibitor than $CuCl_2$/DMF in polymerization of methyl methacrylate [22].

Addition of a small quantity of the deactivator at the very beginning of polymerization can be beneficial, reducing the proportion of terminated chains sacrificed to generate a persistent radical effect. Polymerization with highly purified catalyst (no CuX_2) leads to polymers with higher initial polydispersities due to high molecular weight fraction (noticeable as a tail in GPC traces) formed at the initial stages.

CuX_2 is highly reactive and may react not only by atom transfer but also by electron transfer, by H-abstraction, and also by direct addition to alkene. Indeed, when styrene is refluxed over solid $CuBr_2$, the 1,2-dibromo adduct is formed [23].

However, no adduct formation was observed when either bipy or dNbipy was present [19].

CuX_2 is a relatively strong Lewis acid and may catalyze heterolytic cleavage of C-X bond. The contribution of this reaction depends on ligands (nucleophilic ligands reduce Lewis acidity), on nature of X (iodides are easily cleaved heterolytically), on nature of the α-substituents at the terminal C-atom (electron donating groups like OR, PhOR accelerate this reaction) and on solvent (heterolytic cleavage occurs faster in polar solvents). CuX_2 may react with radicals not only via transfer of halogen atom but also by formation of the short lived Cu^{III} species, which may decompose by hydrogen abstraction. Thus, it is necessary to control the concentration of deactivator. It is indispensable for controlled polymerization but its excess may reduce polymerization rate and lead to side reactions.

Monomers

ATRP can be used for many vinyl monomers including styrenes, (meth)-acrylates, acrylonitrile, and dienes. The currently available catalytic system is not yet efficient enough to polymerize less reactive monomers which produce non-stabilized, very reactive radicals such as ethylene, α-olefins, vinyl chloride and vinyl acetate.

There are some limitations in the monomer structure as well. For example, polymerization of *p*-methoxystyrene is accompanied by severe side reactions and the structure of oligomers formed suggests involvement of cationic intermediates. It is possible that not only homolytic but also heterolytic cleavage of the R-X bond occurs. Alternatively, the growing radical might be oxidized to the corresponding cation. The same type of reaction is feasible for styrene. Indeed, at T>110°C it is difficult to obtain polystyrenes with $M_n>50{,}000$. Higher molecular weight polymers can be formed at lower temperatures and preferentially with R-Cl rather than R-Br as initiators.

Another class of monomers which can not be polymerized are acids. Thus, neither acrylic nor methacrylic acid can be polymerized with currently available ATRP catalyst. This is due to the rapid formation of Cu^{II} carboxylates which are inefficient deactivators and can not be reduced to active Cu^{I} species. However, polymerization of the corresponding *tert*-butyl esters, which are easily hydrolyzed, was successful (cf. Figure 3).

Hydroxy derivative such as HEA and HEMA can be polymerized to high molecular weight products by ATRP (cf. Figure 4).

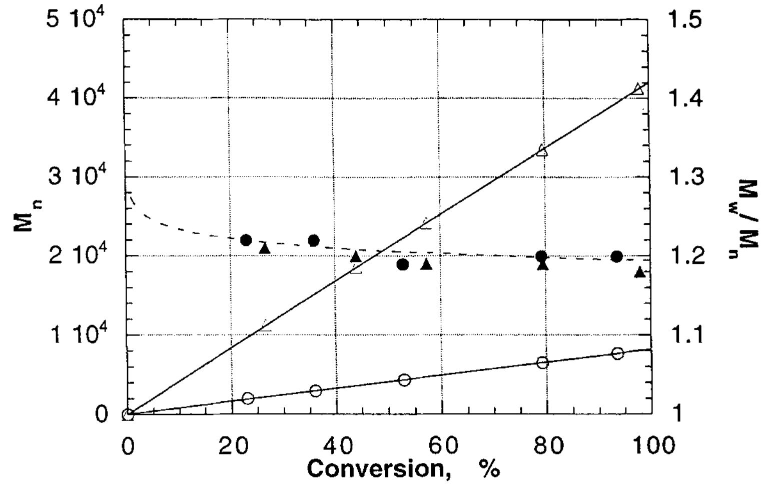


Figure 3. Dependence of M_n and M_w/M_n on conversion for different $[\text{monomer}]_0/[\text{initiator}]_0$ ratios for bulk ATRP of t-butyl acrylate $[\text{tBA}]_0 = 6.83$ M, initiated by methyl 2-bromopropionate $[\text{MBP}]_0 = 0.10$ M ((△▲), 0.22 M (○●), Temp. = 90°C.

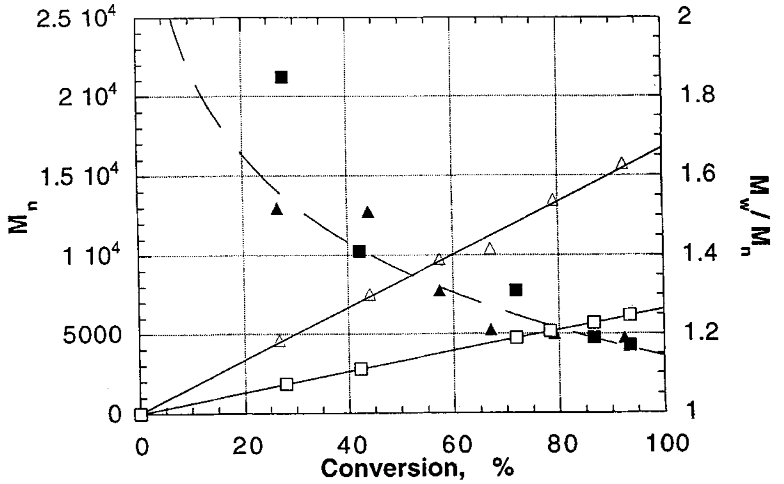


Figure 4. Dependence of M_n and M_w/M_n on conversion for different $[\text{monomer}]_0/[\text{initiator}]_0$ ratios for bulk ATRP of 2-hydroxyethyl acrylate $[\text{HEA}]_0 = 8.57$ M, initiated by methyl 2-bromopropionate $[\text{MBP}]_0 = 0.32\text{M}$ (□ ■), 0.17 M (△▲), and catalyzed by $[\text{CuBr/2dNbipy}]_0$=,Temp. = 90°C.

Solvents and Additives

Most ATRPs are performed in bulk. Since polymerization is first order in R-X and Cu^I/2dNbipy, 50% dilution leads to four times slower rate compared to bulk polymerization. Typically, polymerizations are carried out in relatively non-polar solvents such as benzene, *p*-dimethoxybenzene or diphenyl ether. However, more polar solvents such as ethylene carbonate, propylene carbonate and water have been successfully used [24]. Solvent choice should be dictated by the potential for chain transfer, the limiting factor being the desired molecular weight. When low molar mass polymer is targeted (M_n<20,000), even toluene or xylene can be used. Additionally, solvent interactions with the catalytic system should be considered.

Specific interactions with the catalyst should be avoided. Thus, polymerizations catalyzed by CuBr in DMF and acetonitrile are only moderately successful, whereas addition of 5 vol% of pyridine slows down reaction significantly. Two equivalents of triphenylphosphine entirely deactivate Cu-based ATRP process .

The polymerization is moderately sensitive to oxygen. Small amounts of oxygen can be scavenged by the catalyst which is present at much higher concentration than growing radicals. This however, reduces catalyst concentration and may produce an excess of transition metal conjugate, a deactivator.

Temperature and Reaction Time

Temperature has several effects on ATRP. The rate of polymerization increases with increasing temperature due to the increase of both radical propagation rate constants and the equilibrium constant. For styrene R-Br/CuBr/dNbipy $\Delta H^\ddagger$=4.8 kcal/mol and 6.3 kcal/mol for Cl based system. The formation of radicals in polymerization of methyl acrylate is more endothermic, $\Delta H^\ddagger \approx 12$ kcal/mol. This correlates with the higher reactivity of acrylate radical in comparison with styryl radical.

Energy of activation for propagation is higher than that for termination. Therefore, higher k_p/k_t ratios and better control (livingness) are observed at higher temperatures. Concurrently, at elevated temperatures transfer and other side reactions become more important. The optimal temperature depends on monomer and catalytic system (ligands, X group) as well as on the targeted molecular weight, and on the chemist's patience. If only ratio of termination to propagation is considered, better control is observed for slower reactions, but at higher temperatures.

Once the monomer is nearly consumed, propagation rate is very slow but side reactions which do not depend on monomer concentration may still proceed. Under such conditions, polydispersities may be very low but loss of functionalities may occur. Thus, for the synthesis of block copolymers conversion must not exceed 95% to avoid functional group loss.

New Materials by ATRP

One benefit of ATRP is that polymers with complex topologies and compositions can be made by simple polymerization techniques. The following discussion highlights polymers and copolymers synthesized by ATRP. Some of these materials have either never been made before, their synthesis required multiple steps under stringent reaction conditions, or if they have been prepared before, were not well-defined materials.

Homopolymerizations

The list of successfully polymerized monomers include styrenes (*p*-H, *p*-Me, *p*-*t*-Bu, *p*-Cl, *p*-Br, *p*-CF_3, *m*-CF_3, *p*-OAc), methacrylates and acrylates (Me, Et, *n*-Bu, *t*-Bu, ethylhexyl, 2-hydroxyethyl, glycidyl, and fluoroalkyl), acrylonitrile and methacrylonitrile and acrylamide [25]. Molecular weights are usually less than $M_n \approx 100{,}000$ and resulting polydispersities $1.03 < M_w/M_n < 1.5$.

Random/Gradient Copolymerizations

Radical polymerization allows for synthesizing many random copolymers due to relatively similar reactivity of various monomers. In conventional free radical polymerizations, the polymer composition varies from chain to chain depending on conversion, unless "azeotropic" conditions are established. Due to the "living" nature of the polymerization, in ATRP all chains have similar amounts of comonomers. Statistical copolymers have been prepared between (meth)acrylates, acrylonitrile, vinylidene chloride and styrene. In "living" polymerizations, all of the polymer chains grow at similar rates. By changing the composition of the monomer feed during the polymerization, the composition of the polymer backbone will also change. Slowly altering the reaction medium from one monomer to another forms a compositional gradient along the chain. Various shapes of the gradient can be designed and can include blocks of each monomer at the chain ends [26]. This has been demonstrated using copolymerizations of methyl acrylate/styrene [27], methyl methacrylate/styrene, and acrylonitrile/styrene. These copolymers might be used as blend compatibilizers and as novel materials for vibration and noise dampening.

Periodic Copolymers

Alternating copolymers with isobutene and methyl acrylate have been synthesized [28]. These copolymers exhibit good agreement of experimental molecular weights with theoretical (predicted from the ratio of concentrations of reacted monomers to the introduced initiator), relatively low polydispersites and glass transition approximately $T_g \approx -30^oC$.

Block Copolymers

ATRP can be applied to block copolymer synthesis in two ways. The first is the simple addition of a second monomer to the reaction medium after nearly complete consumption of the first monomer. The second method involves the isolation and purification of the first polymer, then using it as a macrointiator. ABA block copolymers can be synthesized by using difunctional initiators for ATRP to synthesize the central block, followed by addition of a second monomer to form the A blocks. Thermoplastic elastomers have been prepared in this way using *n*-butyl acrylate, methyl acrylate, or 2-ethylhexyl acrylate as the central, soft block with styrene, methyl methacrylate, or acrylonitrile comprising the hard A blocks [24, 29].

Block copolymers have also been synthesized where one of the blocks has been prepared by a polymerization technique other than radical polymerization. Isobutene has been polymerized cationically and, at the chain ends, capped with small amounts of styrene. These polymers have then been isolated and used as macroinitiators for the polymerization of block copolymers with styrene, methyl acrylate, and methyl methacrylate.

Condensation polymers have been used as central blocks in ABA copolymers. Polysulfone was synthesized with an excess of bisphenol A, resulting in polymers with phenolic end groups. Treatment of the polymer with 2-bromopropionyl bromide results in a macroinitiator consisting of polysulfone with 2-bromopropionyloxy end groups, M_n=4,000, M_w/M_n=1.5. The macroinitiator was used to synthesize ABA block copolymers with styrene, M_n=10,700, M_w/M_n=1.1, and *n*-butyl acrylate, M_n=15,300, M_w/M_n=1.2.

The use of a macroinitiator has been extended to polymers prepared by other methods but modified to contain active halogens capable of acting as initiators for ATRP. Such examples include the use of poly(dimethyl siloxane) with benzyl chloride end/side groups. These were successfully used to synthesize ABA block and graft copolymers, where A = styrene or *n*-butyl acrylate and B = PDMS [30].

Functionalized Polymers

Since the polymer chain has a halogen end group (more than one if a di-, tri-, or *n* functional initiator is used), simple organic chemistry can be employed to change the halogen to another functional group. This transformation has been demonstrated by preparing telechelic styrene with amine end groups. α,α'-*p*-Dibromoxylene was used to initiate the oligomerization of styrene by ATRP (M_n=3,800). The α,ω-bromine end groups were then transformed to azide end groups by reaction with trimethylsilyl azide. Reduction of the azide end groups yielded the telechelic, amine terminated polystyrene [31]. This polymer was then condensed by reaction with terephthaloyl chloride to synthesize higher molecular weight polystyrene with internal amide groups, M_n=19,200.

Hyperbranched/Branched Polymers

The vinyl A=B-C* monomer, *p*-chloromethylstyrene, was shown to form a hyperbranched polymer when homopolymerized by ATRP [32]. An acrylic A=B-C* monomer, 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) has been synthesized and used in homopolymerizations and copolymerizations to generate hyperbranched or branched polymers, respectively [33]. After polymerization by ATRP, a viscous solid was obtained. $M_{n,GPC}$=4,800, M_w/M_n=2.8; $M_{n,NMR}$=19,600. By using ATRP to copolymerize BPEA with a conventional vinyl monomer, branched polymers are obtained. The branching density can be controlled by varying the amount of BPEA added to the reaction mixture. Branched copolymers were prepared using methyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, and styrene.

Graft /Comb Polymers

Copolymerization of BPEA with *n*-butyl acrylate using a conventional free radical initiator such as AIBN leads to linear copolymers with pendent bromine groups. These groups can then be used to initiate ATRP. This copolymer was used as a macrointiator for the synthesis of graft/comb copolymers. By synthesizing polymers with soft backbones and hard grafts, thermoplastic elastomers were prepared. The soft backbones consisted of *n*-butyl acrylate, 2-ethylhexyl acrylate or methyl acrylate. The hard segments were prepared by ATRP of MMA or styrene. Another approach includes polystyrene macomonomer with vinyl acetate end group. Copolymerization of the macromonomer with N-vinylpyrrolidone led to the formation of high molecular weight graft copolymers (M_n>200,000) soluble in DMF and THF but which behave as efficient hydrogels with equilibrium water content varying from 70 to 95%, depending on the length of macromonomers and number of grafts per chain [34].

CONCLUSIONS

Atom transfer radical polymerization, ATRP, is a robust polymerization system that can polymerize styrenes, (meth)acrylates, acrylonitrile, and dienes. The reaction conditions are not stringent; only the absence of oxygen is required to carry out the polymerization. The halogen end groups can be converted to other functional groups, such as amines and carboxylic acids. In addition to producing well-defined linear homopolymers, statistical copolymers, block copolymers, and gradient copolymers, ATRP can be used to synthesize graft and hyperbranched copolymers through copolymerization with functionalized monomers. Selecting appropriate conditions for ATRP includes considering the monomer(s) to be polymerized, degree of functionality within the monomer(s), initiator structure/reacivity, amount of catalyst/deactivator used, halogen end-group used, and temperature.

ACKNOWLEDGMENTS

Partial support from the National Science Foundation, Army Research Office and Industrial Sponsors of ATRP Consortium at CMU is acknowledged.

REFERENCES

[1] D. P. Curran, *Comprehensive Organic Synthesis*, B. M. Trost and I. Fleming, Eds., Pergamon Press, Oxford, Vol. 4, (1991).
[2] H. Fischer, *J. Am. Chem. Soc., 108,* 3925 (1986).
[3] J. Iqbal, B. Bhatia, and N. K. Nayyar, *Chem. Rev., 94,* 519 (1994).
[4] O. Webster, *Science, 251,* 887 (1991).
[5] D. Greszta, D. Mardare, and K. Matyjaszewski, *Macromolecules, 27,* 638 (1994).
[6] T. Otsu and M. Yoshida, *Makromol. Chem., Rapid Commun., 3,* 133 (1982).
[7] D. H. Solomon , E. Rizzardo, and P. Cacioli, *U. S. Patent, 4, 581, 429* (1986).
[8] M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, and G. K. Hamer, *Macromolecules, 26,* 2987 (1993).

[9] K. Matyjaszewski, S. Gaynor, D. Greszta, D. Mardare, and T. Shigemoto, *J. Phys. Org. Chem., 8,* 306 (1995).

[10] B. B. Wayland, G. Pszmik, S. L. Mukerjee, and M. Fryd, *J. Am. Chem. Soc., 116,* 7943 (1994).

[11] S. Gaynor, J. S. Wang, and K. Matyjaszewski, *Macromolecules, 28,* 8051 (1995).

[12] J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc., 117,* 5614 (1995).

[13] M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura, *Macromolecules, 28,* 1721 (1995).

[14] V. Percec and B. Barboiu, *Macromolecules, 28,* 7970 (1995).

[15] T. E. Patten, J. Xia, T. Abernathy, and K. Matyjaszewski, *Science, 272,* 866 (1996).

[16] J. S. Wang and K. Matyjaszewski, *Macromolecules, 28*, 7901 (1995).

[17] J. Xia and K. Matyjaszewski, *ACS Polym. Preprints, 37(2),* 513 (1996).

[18] H. Paik and K. Matyjaszewski, *ACS Polym. Preprints, 37(2),* 274 (1996).

[19] K. Matyjaszewski, T. Patten, and J. Xia, *J. Am. Chem. Soc., 119*, 674 (1997).

[20] K. Matyjaszewski and C.-H. Lin, *Makromol. Chem. Macromol. Symp., 47*, 221 (1991).

[21] A. H. E. Mueller, R. Zhuang, D. Yan, and G. Litvinienko, *Macromolecules, 28*, 4326 (1995).

[22] W. I. Bengough and W. H. Fairservice, *Trans. Faraday Soc., 67,* 414 (1971).

[23] M. Asscher and D. Vofsi, *J. Chem. Soc., 1963,* 1887 (1963).

[24] S. M. Jo, S. G. Gaynor, and K. Matyjaszewski, *ACS Polymer Preprints, 37 (2)*, 272 (1996).

[25] K. Matyjaszewski and S. Wang, *WO 96/30421* (1996).

[26] T. Pakula and K. Matyjaszewski, *Macromol. Theory & Simulat., 5,* 987 (1996).

[27] D. Greszta and K. Matyjaszewski, *ACS Polym. Preprints, 37(1),* 569 (1996).

[28] S. Coca and K. Matyjaszewski, *ACS Polym. Preprints, 37(1),* 573 (1996).

[29] J. S. Wang, D. Greszta, and K. Matyjaszewski, *Polym. Mater. Sci. Eng., 73*, 416 (1995).

[30] Y. Nakagawa and K. Matyjaszewski, *ACS Polym. Preprints, 37(2),* 270 (1996).

[31] Y. Nakagawa, S. G. Gaynor, and K. Matyjaszewski, *ACS Polym. Preprints, 37(1)*, 577 (1996).

[32] S. G. Gaynor and K. Matyjaszewski, *Macromolecules, 29*, 1079 (1996).

[33] S. G. Gaynor, S. Z. Edelman, A. Kulfan, and K. Matyjaszewski, *ACS Polymer Preprints, 37(2),* 413 (1996).

[34] K. L. Beers, S. G. Gaynor, and K. Matyjaszewski, *ACS Polym. Preprints, 37(1)*, 571 (1996).