ADVANCED MATERIALS

Atom Transfer Radical Polymerization and the Synthesis of Polymeric Materials**

By Timothy E. Patten* and Krzysztof Matyjaszewski

1. Introduction

The development of new polymeric materials is based on the availability of methods, principally living polymerizations,[1–3] that allow well-defined polymers to be prepared. Living polymerizations are chain-growth polymerizations that proceed in the absence of irreversible chain transfer and chain termination.[4–7] Provided that initiation is complete and exchange between species of various reactivities is fast, one can adjust the final average molecular weight of the polymer by varying the initial monomer-to-initiator ratio ($DP_n = \Delta[M]/[I]_0$) while maintaining a narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$).[8,9] Also, one has control over the chemistry and structure of the initiator and active end group, so polymers can be end-functionalized and block copolymerized with other monomers. Thus, using only a few monomers and a living polymerization, one can create many new materials[10] with vastly differing properties simply by varying the topology of the polymer (i.e., comb, star, dendritic, etc.), the composition of the polymer (i.e., random, periodic, graft, etc.), or the functional groups at various sites on the polymer (i.e., end, center, side, etc.) (Fig. 1). Examples of such materials prepared by atom transfer radical polymerization (ATRP) are shown later in this review.

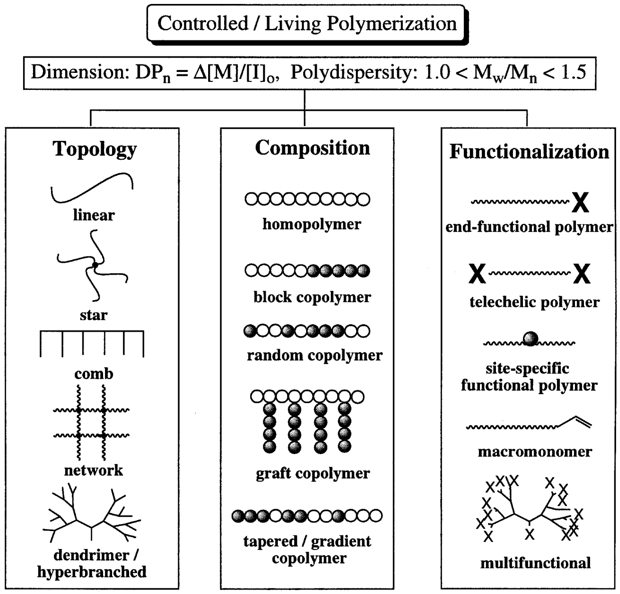

Fig. 1. A schematic representation of how new polymers and materials can be prepared from a few monomers using controlled/living polymerizations.

Much of the academic and industrial research on materials development has focused on coordination, cationic, anionic, and ring-opening polymerizations due to the availability of controlled/living polymerizations of these types. Free-radical polymerizations accounted for approximately half of the total production of polymers in the United States in 1995.[11] Despite its tremendous utility, a significant drawback to free-radical polymerization is the lack of macromolecular structure control due to near diffusion-controlled radical coupling and disproportionation. Therefore, the development of controlled/living[12] radical polymerization methods has been a long-standing goal in polymer chemistry. The last five years have seen the realization of this goal and the rapid growth in the development and understanding of new controlled radical polymerizations. In this discussion, we give a brief overview of recent developments in controlled radical polymerizations and describe in more depth the progress that has been made in the development of ATRP.

2. Controlled/Living Radical Polymerization

The bimolecular rate constants for coupling and disproportionation for most organic radicals are near the diffusion-controlled limit (10^8 to 10^{10} $M^{-1}s^{-1}$),[13] so the apparent rates of these processes become relatively slow only at radical concentrations below 10^{-7} M. The kinetic chain length of a radical polymerization is proportional to the ratios of the monomer-to-radical concentrations and of the propagation-to-termination rate constants.[14] Thus, it

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[*] Dr. T. E. Patten
Department of Chemistry
University of California at Davis
One Shields Avenue, Davis, CA 95616 (USA)
Prof. K. Matyjaszewski
Department of Chemistry
Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh, PA 15213 (USA)

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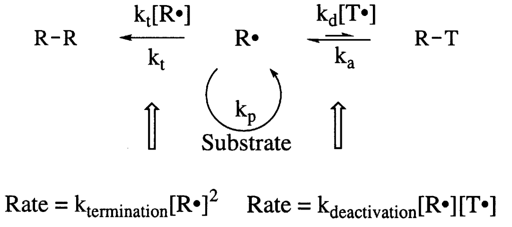
seems that with a controlled free-radical polymerization it would be possible only to prepare a small concentration of polymer chains of a very high molecular weight. Such a polymerization yielding lower molar mass polymer would involve the paradoxical requirements of a large concentration of polymer chains but a small concentration of radicals.

This problem of contradictory requirements can be circumvented by preempting irreversible termination with fast, reversible deactivation to a dormant species (Scheme 1). This dormant species can then be activated reversibly to yield free radicals capable of propagating the polymerization. In this manner, a small concentration of radicals can be employed to propagate a large number of chains. For this equilibrium to be effective in controlling a radical polymerization, there are two necessary conditions. First, the equilibrium between dormant and active (free-radical) species must lie strongly to the side of the dormant species to assure that the overall concentration of radicals will remain very low and that the rate of irreversible termination will be negligible relative to the apparent rate of polymerization. Second, the rate of exchange between dormant and active species must be faster than the rate of propagation to assure that all polymer chains have an equal probability of adding monomer. If these stipulations are met, then a living radical polymerization yielding polymers with a wide range of molecular weights is possible.



Scheme 1. Mechanistic strategy for reducing the contribution of termination in free-radical polymerization.

There are two caveats for living radical polymerizations. The first is that irreversible termination is only minimized in these polymerizations and not excluded from the mechanism. Therefore, these polymerizations do not meet the strict definition of a *living* polymerization and are more properly termed controlled/living polymerizations to reflect the uncertainty regarding the contribution of unavoidable irreversible termination. Second, above some molecular weight value specific to the polymerization of each monomer, all controlled/living radical polymerizations can no longer be considered controlled, because slower termination, transfer, and other side reactions become significant.

All of the known controlled/living radical polymerizations can be categorized into three subgroups based upon the general mechanism of radical generation. The first such mechanism involves the reversible capture of the polymeric radical by some species to form a stable, persistent radical (Eq. 1). This mechanism was proposed in the aluminum/TEMPO-mediated[15] (where TEMPO is the 2,2,6,6-tetramethyl-1-piperidinyloxy free radical) as well as the phosphite-mediated[16] polymerization of vinyl acetate and in the "aged" chromium-acetate-mediated polymerization of methacrylates.[17]

$$PX^{\bullet} \rightleftharpoons P^{\bullet} + X \qquad (1)$$

Timothy E. Patten was born in New York in 1967. He received his BA in chemistry from La Salle University (1989) and his Ph.D. in chemistry from the University of California, Berkeley (1994) for his work on living organotitanium(IV)-catalyzed polymerizations of isocyanates under the supervision of Bruce M. Novak. After a postdoctoral research assistantship with Krzysztof Matyjaszewski at Carnegie Mellon University, he joined the Department of Chemistry at the University of California, Davis, in 1996, where he is currently an assistant professor. His current research interests include the development of controlled/living radical polymerization methodology and its use in the preparation of well-defined polymeric materials and the preparation of hybrid organic/inorganic nanoparticles.

Krzysztof Matyjaszewski was born in Poland in 1950. He received his Ph.D. from the Polish Academy of Sciences (1976) for his work on the cationic polymerization of tetrahydrofuran and D.Sc. from the Technical University in Lodz, Poland (1985). He joined the Department of Chemistry at Carnegie Mellon University in 1985, where he is currently a professor and head of the department. His current research interests include the synthesis of well-defined macromolecules via living and controlled polymerizations, and the synthesis and uses of inorganic and organometallic polymers as nonlinear optical materials, photoconductors, photoresists, and precursors to ceramics.

The second mechanism involves the rapid degenerative transfer of a functional group between dormant and active polymer chain ends (Eq. 2). An example of controlled/living radical polymerizations that function via this mechanism is the iodine-atom-mediated radical polymerization of acrylates and styrene.[18]

$$P{-}X + P'^{\bullet} \rightleftharpoons P^{\bullet} + P'{-}X \qquad (2)$$

The third mechanism involves the reversible homolytic cleavage of a dormant chain end adduct into the corresponding polymeric radical and a stable, persistent radical that cannot undergo addition to monomer (Eq. 3). This mechanism is the most commonly occurring of the three, and the radical-forming equilibrium can be established via either the application of thermal energy or the addition of a catalyst.

$$P{-}X \underset{\text{Catalyst}}{\overset{\Delta\text{ or}}{\rightleftharpoons}} P^{\bullet} + X^{\bullet} \qquad (3)$$

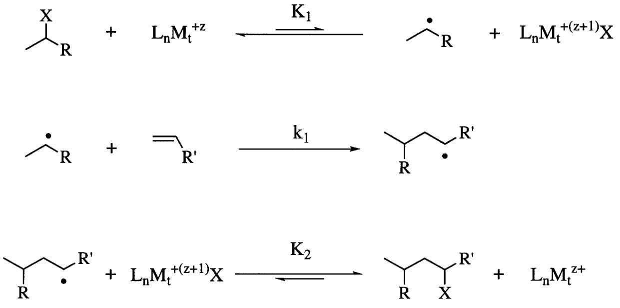
Examples of controlled/living radical polymerizations that function via an uncatalyzed homolytic cleavage mechanism include the diarylalkyl- or triarylalkyl-mediated polymerization of methacrylates,[19,20] the dithiocarbamate-mediated polymerization of acrylates, methacrylates, and styrene,[21] the TEMPO-mediated polymerization of styrenes,[22–25] and the cobalt-macrocycle-mediated polymerization of acrylates.[26,27] The remainder of this discussion will be devoted to discussions of polymerizations that function using catalyzed homolytic cleavage mechanisms.

3. Atom Transfer Radical Polymerization

Previously, radical reactions had found limited application in organic synthesis due to the low yields of desired addition and substitution products caused by radical termination reactions. The usefulness of these reactions increased dramatically after the discovery that persistent radicals[28] could be used to reduce the stationary concentration of reacting radicals and thereby minimize the contribution of termination.[29–31] Of the methods developed based on this concept, one of the most useful is atom transfer radical addition (ATRA),[32,33] so named because it employs atom transfer from an organic halide to a transition-metal complex to generate the reacting radicals, followed by back transfer from the transition metal to a product radical to form the final product.

In ATRA a metal catalyst, usually a complex of a copper(I) halide and 2,2′-bipyridyl[30,32,34–36] (although Ni,[37] Pd,[38] Ru,[39,40] Fe,[29] and other metals[31] have been used as well), undergoes a one-electron oxidation with concomitant abstraction of a halogen atom from a substrate (Scheme 2).

This reaction generates an organic radical and a copper(II) complex. One requirement for the reaction to occur is that substituents must be present on the organic halide that will stabilize the resultant radical. From the experimental evidence it is not fully clear whether the intermediate radicals are free radicals, in a solvent cage, or coordinated to the metal center, but the most plausible mechanism based upon experimental evidence involves free radicals. The resultant organic radical can add to an unsaturated compound in an inter- or intramolecular fashion, or it can abstract the halogen atom from the copper(II) complex and revert back to the original dormant organic halide species. The copper(I) complex is reformed, completing the catalytic cycle. The radical may also react with another radical, but because the concentration of propagating radicals is very small, the contribution from termination reactions to the products formed is minimal. The substrates for this reaction are typically chosen such that if addition occurs, then the newly formed radical is much less stabilized relative to the initial radical and will essentially react irreversibly with the copper(II) complex to form an inactive alkyl halide product ($K_2 \gg K_1$). Therefore, in ATRA usually only one addition step occurs.



Scheme 2. The general mechanism of ATRA.

Atom transfer radical addition can be extended to atom transfer radical polymerization if the conditions can be modified such that more than one addition step is possible. Thus, if the radical species in Scheme 2 before and after addition of the unsaturated substrate possess comparable stabilization, then the activation–addition–deactivation cycle will repeat until all of the unsaturated substrate present is consumed. This process results in a chain-growth polymerization. Polymerization systems utilizing this concept have been developed using Cu^{I},[41–46] Ni^{II},[47,48] Ru^{II}/$Al(OR)_3$,[49,50] and Fe^{II}[51,52] complexes to catalyze the radical-forming equilibrium.

4. Kinetics and Mechanism of ATRP

An ATRP system consists of an initiator, a metal halide complexed with some ligand(s), and of course, monomer. Thus far, the copper-based ATRP system has been adapted successfully for the controlled/living polymerization of styrenes, acrylates, methacrylates, acrylonitrile, and other monomers (Fig. 2). The ruthenium/aluminum alkoxide–based ATRP system has been demonstrated to work with methacrylates; however, a recent symposium report in-

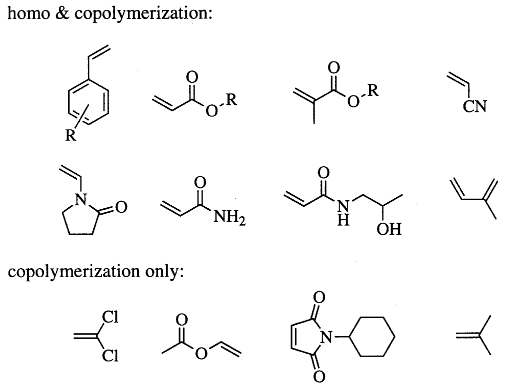


Fig. 2. Monomer types that can be polymerized using ATRP.

dicates that the system has been adapted for acrylates and styrene as well.[53] The iron-based ATRP system has been demonstrated to work with styrenes and methacrylates, while the nickel-based ATRP systems have been shown to work for methacrylates. The choice of monomer to be polymerized dictates the types of other components that can be used. The initiator usually, but not always, should have a structure homologous to the corresponding polymer end group. Also, the halogen atom in the initiator and metal complex should correspond with one other, but again, in some cases this is not necessary. For copper-based ATRP, typically two equivalents of a bidentate ligand is added per copper center. The most effective ligands are derivatives of 2,2′-bipyridine (bipy),[41,42] other π-accepting, chelating nitrogen-based ligands such as 2-iminopyridines,[46] and some aliphatic polyamines (Fig. 3).[54]

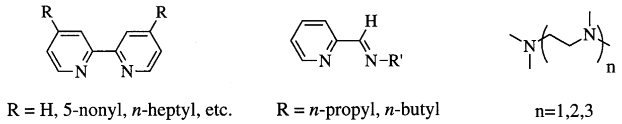
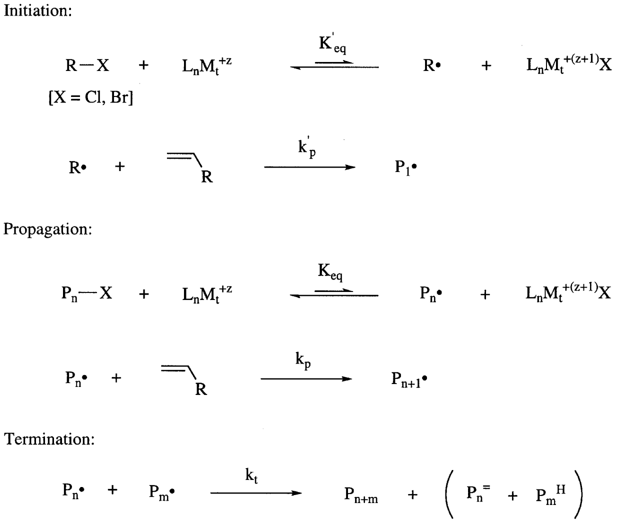


Fig. 3. Ligands for copper(I) halides that can be used for ATRP.

As complexes of bipy with copper(I) halides are largely insoluble in the non-polar media of bulk polymerizations, long alkyl chain substituents at the 4,4′-positions of the bipyridine ligand serve to increase the solubility of the resulting copper complex.[44,45] The ruthenium/aluminum alkoxide–based ATRP systems use triarylphosphine ligands.[49] The nickel-based ATRP systems use either triarylphosphines[48] or bisiminoaryl ligands.[47] The iron-based ATRP systems employ trialkylphosphines,[51] trialkylamines,[52] or a mixture of a trialkyl amine with a 2,2′-bipyridine.[52]

The mechanism of ATRP adapted from that of ATRA is shown in Scheme 3. The mechanism consists of initiation and propagation processes that are phenomenologically related. These sequences are comprised of an atom transfer equilibrium and an addition of the intermediate radical to a monomer. Termination by radical coupling and disproportionation is included in the mechanistic scheme because of the magnitude of the associated rate constant, but only a few percent of the polymer chains in ATRP undergo bimolecular termination. Additionally, some other side reactions may limit the achievable molecular weights.[55] The intermediacy of radicals in the mechanism is consistent with experimental results from trapping experiments,[42,56] copolymerization reactivity ratios,[57,58] and the regio- and stereochemistry of polymerization.[42] Thus, the net propagation sequence can be considered an "insertion" process proceeding via radical intermediates. In the case of copper-based ATRP, a "reverse ATRP" experiment confirmed that the higher oxidation state metal (i.e., the copper(II) complex formed after atom transfer) is also an intermediate in ATRP.[59–61] In reverse ATRP, the polymerization is entered from the right-hand side of the atom transfer equilibrium by generating radicals, for this example, in the presence of CuBr$_2$/2 4,4′-di-(5-nonyl)-2,2′-dipyridyl (dNbipy) and monomer. As in the case of "forward ATRP" a controlled/living polymerization ensues.



Scheme 3. The general mechanism of ATRP, as adapted from the mechanism of ATRA.

The kinetics and mechanism of ATRP will be discussed using copper-based ATRP as an example. It is anticipated that mechanistic investigations into ATRP based upon other metal systems will yield analogous results. The rate law (Eq. 4) for this mechanism can be derived by omitting the termination step (it is recognized that, in ATRP and other controlled radical polymerizations, termination always occurs but it becomes insignificant due to the persistent radical effect) and using a fast equilibrium approximation.[60] A fast pre-equilibrium is a necessary condition for observing low polydispersities.[62]

$$R_\mathrm{p} = k_\mathrm{app}\,[\mathrm{M}] = k_\mathrm{p}[\mathrm{P}^\bullet][\mathrm{M}] = k_\mathrm{p}K_\mathrm{eq}[\mathrm{In}]\frac{[\mathrm{Cu^I}]}{[\mathrm{Cu^{II}X}]}[\mathrm{M}] \qquad (4)$$

where $K_\mathrm{eq} = \dfrac{k_\mathrm{act}}{k_\mathrm{deact}} = \dfrac{[\mathrm{P}^\bullet][\mathrm{Cu^{II}X}]}{[\mathrm{Cu^I}][\mathrm{PX}]}$

Results from kinetic studies of ATRP using soluble catalyst systems indicate that the rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and copper(I) complex concentrations.[60] These observations are all consistent with the derived rate law. The kinetically optimum ratio of ligand to copper in polymerization of styrene was determined to be two to one, but the ratio can vary with changes to the monomer, counterion, ligand, temperature, and other factors.[60] Below this ratio the polymerization rate was usually much slower, and above this ratio the polymerization rate remained constant.

Determining the precise kinetic order with respect to the deactivator concentration was complicated due to the spontaneous generation of copper(II) via the persistent radical effect.[60] In the atom transfer step, a reactive organic radical is generated along with a stable copper(II) species that can be regarded as a persistent metalloradical. If the initial concentration of copper(II) in the polymerization is not sufficiently large to ensure that the rate of deactivation ($k_{\mathrm{deact}}[\mathrm{Cu^{II}}]$) is fast, then coupling of the organic radicals will occur, leading to an increase in the deactivator concentration. Consider the following: in the bulk polymerization of styrene using 1-phenylethyl bromide (1-PEBr) initiator and CuBr/2 dNbipy as the catalyst, the equilibrium constant, $K_{\mathrm{eq}} = k_{\mathrm{act}}/k_{\mathrm{deact}}$, is approximately 4×10^{-8} at 110 °C.[60] The initial concentrations of all the species are $[\mathrm{RBr}]_0 = [\mathrm{Cu^I}]_0 = 0.1$ M and $[\mathrm{R^\bullet}]_0 = [\mathrm{Cu^{II}}]_0 = 0$ M. The concentrations of $\mathrm{Cu^I}$ and halide end groups will remain approximately constant throughout the polymerization, and therefore the product of the radical and deactivator concentrations must be constant and equal to $[\mathrm{R^\bullet}][\mathrm{CuBr_2}] = K_{\mathrm{eq}}[\mathrm{RX}][\mathrm{CuBr}] = 4 \times 10^{-10}\ \mathrm{M^2}$. During the initial stages of the reaction, the radical and deactivator concentrations will increase to approximately 10^{-6} M. At these concentrations the radicals will couple rapidly, and with each combination event two equivalents of deactivator will form irreversibly. This process has been observed experimentally using ^{1}H NMR, UV-vis, and GC-MS techniques.[60] More radicals and deactivator will be formed and more radical combination will occur until a radical concentration of 10^{-7} M and a deactivator concentration of 10^{-3} M are reached. At these concentrations the rate at which radicals combine ($k_{\mathrm{term}}[\mathrm{R^\bullet}]^2$) will be much slower than the rate at which radicals will react with the copper(II) complex ($k_{\mathrm{deact}}[\mathrm{R^\bullet}][\mathrm{Cu^{II}}]$) in a deactivation process, and a controlled/living polymerization will ensue. Under the aforementioned conditions, approximately five percent of the polymer chains will be terminated during this initial, short, non-stationary process, but the majority of the chains (>90 %) will continue the polymerization successfully. If a small amount of the deactivator (~10 mol.-%) is added initially to the polymerization, then the proportion of terminated chains will be reduced greatly.[63]

In a polymerization based upon the ATRP catalytic cycle, the control of the polymerization and the definition of the resulting polymers will depend not only upon the stationary concentration of the growing radicals but also upon the relative rates of propagation and deactivation. During one activation step any number of equivalents of monomer can be added to the polymer chain with varying effects upon the polydispersities of the polymers formed. At the limit where the deactivation process is very slow or does not occur ($k_{\mathrm{deact}} \ll k_{\mathrm{p}}$), ATRP simply becomes a conventional redox-initiated radical polymerization and high polydispersities are observed.[64] At the limit where an average of one or fewer monomers is added per activation step ($k_{\mathrm{deact}} \gg k_{\mathrm{p}}$), then the polymerization is well controlled and the polydispersities can approach a Poisson distribution.

5. The ATRP of Various Monomers

Due to a number of factors, the ATRP of each type of monomer requires a specific set of conditions. Each monomer possesses an intrinsic radical propagation rate, so the concentration of propagating radicals and the rate of radical deactivation may need to be adjusted to maintain polymerization control. How such adjustments should be made is monomer specific as well. For the polymerization of each monomer, the corresponding alkyl halide end group will possess its own unique redox potential. Therefore, in combination with the same metal catalyst, each end group will exhibit a different atom transfer equilibrium constant, deactivation rate constant, and corresponding concentration of propagating radicals. To vary the aforementioned factors, one component of ATRP that can be modified is the metal center, so the coordination sphere and the initial concentration of the metal complex are useful tools for fine tuning ATRP. Another useful tool is the initiator, which, depending upon the propagation rate constant for a particular monomer and the equilibrium constant for the end group/catalyst pair, can be varied to assure that the apparent rate of initiation is faster than the apparent rate of propagation.

5.1. Styrene

Styrene ATRP has been reported for the copper[41–45,60] and iron[52] catalyst systems; thus far the majority of work has been performed using the copper-based system.

In styrene ATRP, polymerizations are conducted at 110 °C for bromide-mediated polymerization and 130 °C for chloride-mediated polymerization. The corresponding 1-phenylethyl halide is usually used as the initiator; however, a wide variety of compounds have been used successfully as initiators for copper-mediated styrene ATRP,[42,43] such as benzylic halides, allylic halides, α-bromoesters, polyhalogenated alkanes, and arenesulfonyl chlorides. Solvents may be used for styrene ATRP, but the stability of the halide end group displays a pronounced solvent dependence as demonstrated by model studies using 1-phenylethyl bromide.[55] Therefore, non-polar solvents are recommended for styrene ATRP. Well-defined polystyrenes can be prepared within the molecular weight range of 1000 to 90 000. In the region from 1000 to 30 000 the polydispersities (M_w/M_n) are less than 1.10, and above 30 000 the polydispersities fall within the range of 1.10 to 1.50. A wide range of styrene derivatives were polymerized in a controlled fashion using this method (Fig. 4);[65] however, there are some limitations to monomer structure. For example, the polymerization of *p*-methoxystyrene is accompanied by side reactions, and the structure of the oligomers formed suggests the involvement of cationic intermediates.[65] It is possible that heterolytic cleavage of the carbon–halogen bond occurs in addition to homolytic cleavage. Alternatively, the growing radical for this polymerization is very electron rich and might be oxidized by the copper catalyst.

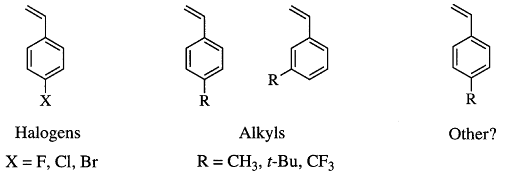


Fig. 4. Various styrenes that can be polymerized using ATRP.

Under conditions in which the polymerization rate is slow (i.e., dilute polymerization conditions) a slow termination process is observed in styrene ATRP, and this process is more pronounced in bromine-mediated ATRP than in chlorine-mediated ATRP.[55] Model studies of this process showed that hydrogen halide was eliminated from the end group and that this process was promoted by both polar solvents and the copper(II) complex.[55] For the copper-mediated elimination, two possible mechanisms were implicated: electron transfer from the polymeric radical to the copper(II) complex and abstraction of a halogen anion by the Lewis acidic copper(II) complex. The rate of elimination in the model reaction is most likely greater than the same in ATRP due to steric differences between the model end group and the polymeric end group. Regardless, the studies showed that the reaction of the polymeric radical with the copper(II) complex is highly chemoselective for deactivation over halide abstraction/electron transfer. Overall, the effect of this side reaction upon the molecular weight control is negligible for the lower molecular weight ranges (1000 to 30 000), but may contribute to the upper molecular weight limit observed in styrene ATRP. Higher molecular weight polystyrene (up to 90 000) can be formed at lower temperatures and preferentially using chlorine-mediated ATRP rather than bromine-mediated ATRP.

Table 1 shows current kinetic data for the various styrene ATRP systems, and using the known rate constant for styrene radical propagation (k_p = 1.6 × 10^3 $M^{-1}s^{-1}$ at 110 °C)[66] one can calculate the concentration of propagating radicals for styrene ATRP. In particular, the first two entries in Table 1 yield typical radical concentrations for bulk and solution polymerizations: bulk = 1.0 × 10^{-7} M, solution = 2.4 × 10^{-8} M. If the corresponding polymerizations are conducted with an initial 10 mol.-% excess of copper(II) complex relative to Cu^I, in order to keep the deactivator concentration relatively constant (electron spin resonance (ESR) experiments show that approximately 5 % $CuBr_2$ is formed under these conditions),[67] then the atom transfer equilibrium constants can be estimated: K_{eq} = 3.9 × 10^{-8} (bromide-mediated ATRP) and K_{eq} = 2.1 × 10^{-8} (chloride-mediated ATRP).

5.2. Methyl Methacrylate

Methyl methacrylate (MMA) ATRP has been reported for the copper,[42,46,68,69] ruthenium/aluminum alkoxide,[49,50] iron,[51,52] and nickel[47,48] catalyst systems.

The radical propagation rate for MMA (k_p = 1.6 × 10^3 M^{-1} s^{-1} at 90 °C)[66,70] is greater than that for styrene (k_p = 8.95 × 10^2 $M^{-1}s^{-1}$ at 90 °C),[66,71] so it is important to keep the concentration of propagating radicals low by adjusting the atom transfer equilibrium. In the case of copper-mediated MMA ATRP, the use of copper bromide instead of copper chloride leads to more rapidly decreasing polydispersities (*p*-toluenesulfonyl chloride/copper chloride (*p*-TsCl/CuCl) conversion = 25 %, M_n = 8500, M_w/M_n = 2, while for *p*-TsCl/CuBr for the same conversion, M_n = 7800, M_w/M_n = 1.18),[68,69] due to the better efficiency of bromine in the deactivation step as observed by Bengough and Fairservice in studies of the inhibition of MMA polymerization in dimethylformamide (DMF).[72,73] In addition, the polymerization is less controlled when bipy is used instead of dNbipy due to the low solubility of the deactivator. The best initiators for MMA ATRP are *p*-toluenesulfonyl chloride, benzhydryl chloride, and dialkyl 2-bromo-2-methylmalonates because with these initiators the appar-

Table 1. Published kinetic data for the ATRP of styrene using various soluble catalyst systems [a].

Catalyst	Initiator	$[Monomer]_0$	$[Catalyst]_0$	$[Initiator]_0$	k_{obs} [s^{-1}]	*T* [°C]
CuBr / 2 dNbipy [60]	1-PEBr	8.7 M	0.087 M	0.087 M	1.6 × 10^{-4}	110
CuBr / 2 dNbipy [60]	1-PEBr	4.5 M [b]	0.045 M	0.045 M	3.9 × 10^{-5}	110
CuCl / 2 bpy9 [45]	*p*-methoxybenzenesulfonyl chloride	5.77 M [c]	0.058 M	0.058 M	2.3 × 10^{-5}	130
$FeBr_2$ / 3 Bu_3P [52]	1-PEBr	8.7 M	0.044 M	0.044 M	8.3 × 10^{-5}	110
$FeBr_2$ / Bu_3P / dNbipy [52]	1-PEBr	8.7 M	0.087 M	0.087 M	8.8 × 10^{-5}	110
$FeBr_2$ / Bu_3N / dNbipy [52]	1-PEBr	8.7 M	0.087 M	0.087 M	6.7 × 10^{-5}	110

[a] dNbipy = 4,4′-di-(5-nonyl)-2,2′-bipyridyl. bpy9 = 4,4′-di-(*n*-nonyl)-2,2′-bipyridyl. 1-PEBr = 1-phenylethyl bromide. [b] In diphenyl ether. [c] In xylene.

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ent rate constant of initiation is larger than that of propagation.

Well-defined poly(methyl methacrylate) can be prepared within the molecular weight range of 1000 to 180 000, and in analogy to acrylate esters, potentially a wide variety of methacrylate esters can be polymerized using ATRP. The ranges within which the resulting polymer retains a narrow molecular weight distribution ($M_w/M_n < 1.5$) varies between catalyst systems. Table 2 shows known kinetic data for MMA ATRP. Using the known rate constant for MMA radical propagation one can calculate the concentrations of propagating radicals: typical radical concentrations for bulk and solution MMA polymerizations are on the order of 10^{-7} M for bulk polymerizations and 10^{-8} M for solution polymerizations.

5.3. Methyl Acrylate

Methyl acrylate (MA) ATRP has been reported for the copper[42,44,74] catalyst system. The standard conditions for methyl acrylate (MA) ATRP are similar to those of styrene ATRP except that the polymerizations are conducted at 90 °C. Typically, an alkyl bromopropionate is used as the initiator, because its structure is homologous to that of the polymer end group. Well-defined poly(methyl acrylate) with polydispersities of less than 1.10 can be prepared within the molecular weight range of 1000 to 80 000. Above 90 000 the polydispersities fall within a range above 1.3. A wide range of polyacrylates with differing side chains can be prepared using ATRP (Fig. 5). Thus far, acrylates with primary, secondary, and tertiary alkyl groups have been polymerized successfully, as well as those with alcohol,[75] epoxide,[76] and vinyl groups.[77]

5.4. Acrylonitrile

Acrylonitrile ATRP has been reported for the copper[78] catalyst system. The ATRP of acrylonitrile is necessarily conducted using a solvent, because polyacrylonitrile is not soluble in its monomer. Thus, acrylonitrile can be polymerized using a 33 % solution in ethylene carbonate, 0.1 mol.-% 2-bromopropionitrile initiator, and 0.01 to 0.05 mol.-% copper(I) catalyst. The polymerizations are conducted at 44 to 64 °C. α-Halopropionitriles are the best initiators for these polymerizations, because, again, they are homologous to the structure of the dormant polymer end group. Benzylic halides have been examined as initiators for these polymerizations, but polymers with higher than predicted molecular weights and broad polydispersities are obtained. Presumably these results are due to a much slower apparent rate of initiation relative to propagation in the case of the benzylic halides. Well-defined polyacrylonitrile with polydispersities of less than 1.05 can be prepared within the molecular weight range of 1000 to 10 000. Higher molecular weights have not yet been achieved due to the slow deactivation of the copper catalyst with polyacrylonitrile over time. Acrylonitrile also can be copolymerized with styrene in a well-controlled fashion to yield gradient copolymers with molecular weights ranging from 1000 to 15 000.[57,79]

6. The Role of Components and Reaction Conditions in ATRP

The previous discussion of the ATRP of different monomers serves to highlight the fact that in ATRP one set of conditions cannot be applied to every monomer class.

Table 2. Published kinetic data for the ATRP of methyl methacrylate using various soluble catalyst systems [a].

Catalyst	Initiator	$[\text{Monomer}]_0$	$[\text{Catalyst}]_0$	$[\text{Initiator}]_0$	k_{obs} [s^{-1}]	T [°C]
$RuCl_2(PPh_3)_3$ / 4 $Al(O^iPr)_3$ [50]	CCl_3COCH_3	2.0 M [b]	0.01 M	0.02 M	2.0×10^{-5}	80
$RuCl_2(PPh_3)_3$ / 4 $Al(O^iPr)_3$ [50]	$CHCl_2COC_6H_5$	2.0 M [b]	0.01 M	0.02 M	1.4×10^{-5}	80
$RuCl_2(PPh_3)_3$ / 4 $Al(O^iPr)_3$ [50]	$(CH_3)_2CBrCO_2CH_2CH_3$	2.0 M [b]	0.01 M	0.02 M	1.1×10^{-5}	80
$RuCl_2(PPh_3)_3$ / 4 $MeAl(ODBP)_2$ [49]	CCl_4	2.0 M [b]	0.01 M	0.02 M	1.4×10^{-4}	60
$FeCl_2(PPh_3)_2$ [51]	CCl_4	2.0 M [b]	0.01 M	0.02 M	2.4×10^{-5} [d]	80
$FeBr_2$ / dNbipy [52]	*p*-toluenesulfonyl chloride	4.7 M [c]	0.03 M	0.03 M	9.3×10^{-5}	90
$FeBr_2$ / 2 $(octyl)_3N$ [52]	*p*-toluenesulfonyl chloride	4.7 M [c]	0.016 M	0.016 M	3.6×10^{-5}	80
$Ni[C_6H_3(CH_2NMe_2)_2]Br$ [47]	CCl_4	8.2 M [b]	0.04 M	0.017 M	5.6×10^{-6}	74
CuBr / 2 dNbipy [68]	*p*-toluenesulfonyl chloride	4.7 M [d]	0.011 M	0.021 M	8.1×10^{-5}	90
CuCl / 1.4 bpy9 [81]	*p*-methoxybenzenesulfonyl chloride	6.25 M [c]	0.019 M	0.063 M	1.0×10^{-5}	80
CuBr / 3 (2-pyridinecarbaldehyde *n*-propylimine) [46]	$(CH_3)_2CBrCO_2CH_2CH_3$	3.1 M [c]	0.016 M	0.016 M	6.1×10^{-5}	90

[a] dNbipy = 4,4′-di-(5-nonyl)-2,2′-bipyridyl. bpy9 = 4,4′-di-(*n*-nonyl)-2,2′-bipyridyl. ODBP = 2,6-di-*tert*-butylphenoxide. [b] In toluene. [c] In *o*-xylene. [d] In diphenyl ether. [e] Estimated from conversion plot.

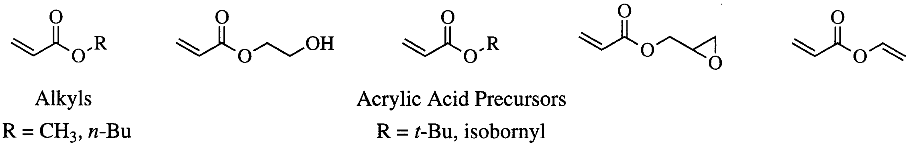

Fig. 5. Various acrylates that can be polymerized using ATRP.

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A unique combination of initiator, metal, ligands, deactivator, temperature, reaction time, and solvent must be employed for the ATRP of each particular monomer. Therefore, understanding the role of each component of ATRP is crucial for obtaining well-defined polymers and for expanding the scope of ATRP to other monomers.

6.1. Alkyl (Pseudo)Halides

The main role of the alkyl halide (RX) species is to determine the number of initiated chains. The polymerization rates in ATRP are first order with respect to the concentration of RX, and the molecular weights scale reciprocally with the initial concentration of initiator.[42,60] The (pseudo)halide group, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex. Thus far, bromine and chlorine are the halogens that afford the best molecular weight control.[41,42,44,60] Iodine works well for acrylate polymerizations; however, in styrene polymerizations the heterolytic elimination of hydrogen iodide is too fast at high temperatures.[80] As for other X groups, some pseudohalogens, specifically thiocyanates, have been used successfully in polymerization of acrylates and styrenes.[80]

For the selection of a good initiator, the ratio of the apparent initiation rate constant (k_iK_0, where k_i and K_0 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) to the apparent propagation rate constant (k_pK_{eq}, where k_p and K_{eq} refer to the absolute rate constant of propagation and the atom transfer equilibrium constant for the dormant chain, respectively) must be considered.[81] If the product k_iK_0 is much less than k_pK_{eq}, then initiation will be incomplete during the polymerization, and the molecular weights and polydispersities will be too high.

To a first approximation, the structure of the alkyl group, R, in the initiator should be similar to the structure of the dormant polymer species. Thus, 1-phenylethyl halides resemble dormant polystyrene chain ends, α-halopropionates approximate dormant acrylate end groups, and α-halopropionitriles are homologous to dormant acrylonitrile chain ends. This guideline holds true for secondary radicals but not quite for tertiary radicals. For example, isobutyrates are not the best initiators for MMA, most likely due to the β-strain effect.[82] For the selection of initiators that are not structurally related to the dormant polymer chain end, it is better to use organic (pseudo)halides that form less reactive radicals with higher efficiency than the dormant polymer chain ends. For example, alkyl 2-chloroisobutyrates and arenesulfonyl chlorides are good initiators for styrene, alkyl acrylates, and alkyl methacrylate ATRP, but chloroacetates, 2-chloropropionates, and 1-phenylethyl chloride are poor initiators for the polymerization of methyl methacrylate.

In general, any alkyl halide with activating substituents on the α-carbon, such as aryl, carbonyl, and allyl groups, can potentially be used as ATRP initiators. Polyhalogenated compounds (CCl_4 and $CHCl_3$) and compounds with a weak R–X bond, such as N–X, S–X, and O–X, can also presumably be used as ATRP initiators. There is, however, an upper limit to the stability of the initiating radicals beyond which it also becomes an inefficient initiator. For example, trityl halides are poor initiators for ATRP. The list of potential ATRP initiators includes not only small molecules but also macromolecular species that can be used to synthesize block/graft copolymers.

6.2. Transition Metals and Ligands

In general, the rate of polymerization is first order with respect to the concentration of ATRP catalyst, and the molecular weights *do not* depend upon its concentration. There are several requirements for an effective ATRP catalyst. First, the metal complex must have an accessible one-electron redox couple to promote atom transfer, but this requirement alone is not sufficient, because as its name indicates ATRP is an atom transfer not an electron transfer process. Therefore, a second requirement is that upon one-electron oxidation, the coordination number of the metal center must increase by one in order to accommodate a new ligand, X. A brief review of known copper-based ATRP catalysts shows that in most systems the lower oxidation state of the metal is presumed to be tetracoordinate and the higher oxidation state is presumed to be pentacoordinate. Clearly, more information is needed on the structure of the active metal complexes in ATRP. A third requirement for a good ATRP catalyst is that the catalyst must show selectivity for atom transfer and therefore possess a low affinity for alkyl radicals and the hydrogen atoms on alkyl groups. If not, then transfer reactions, such as β-H elimination and the formation of organometallic derivatives, may be observed. These reactions would reduce the selectivity of the propagation step and the control, or rather the "livingness", of the polymerization. Finally, the metal center must not be a strong Lewis acid, otherwise the ionization of certain initiators/end groups to carbocations may occur.

The most important system variables in selecting or designing good ATRP catalysts are the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. As mentioned above, adjusting the chemistry of the metal catalyst will serve to achieve this aim. The position of equilibrium depends upon the nature of the metal and ligands. Generally, more electron donating ligands better stabilize the higher oxidation state of the metal and accelerate the polymerization. Weakly coordinating and bidentate anionic ligands may strongly affect polymerization as observed for $[Cu(CH_3CN)_4]^+PF_6^-$ and copper carboxylate derivatives.[80,83] The range of equilibrium constant values required for the successful polymerization of methacrylates, styrenes, acrylates, and acrylonitrile is from 10^{-6} to 10^{-10}. However, not only the value of the equilibrium constant but also the *dynamics* of exchange between dormant and active species is important for a controlled/living radical polymerization. The deactivation step must be very fast, ($k_d \approx 10^{7\pm1}$ M^{-1} s^{-1}), otherwise the polymerization will display poor control over molecular weights and yield polymer with high polydispersity.

For ATRP catalysts that are insoluble in relatively nonpolar media such as styrene and methyl methacrylate, ligands that possess long alkyl chains serve to increase the complex's solubility. For example, when bipy is used in copper-mediated ATRP, the copper halide is sparingly soluble in the polymerization medium and the polymerization is heterogeneous. Bipyridyl ligands with long alkyl chains at the 4,4′-positions (such as dNbipy) completely solubilize the copper halide.[44,45] Qualitatively, ATRP behaves in a similar manner whether or not the catalyst is highly soluble in the polymerization medium, because the catalyst is not bound to the growing chain. Thus, somewhat higher polydispersities are observed in heterogeneous copper-mediated ATRP due to the lower concentration of the Cu^{II} complex (deactivator) and consequently a slower deactivation process; however, the overall difference is not too dramatic. For instance, in the bulk polymerization of styrene (at 100 °C with 0.5 mol.-% of 1-PEBr initiator) the polydispersity, M_w/M_n, averages around 1.1 when CuBr/2 dNbipy is the catalyst, versus 1.3 when CuBr/2 bipy is the catalyst.

In the case of copper-mediated ATRP, the roles of the copper(I) and copper(II) species were investigated. The role of the copper(I) complex is the generation of radicals via atom transfer. A series of experiments were performed by adding 2 dNbipy/CuX to dicumyl peroxide–initiated free-radical polymerizations of styrene and monitoring the kinetics of the polymerizations and the molecular weights and polydispersities of the resulting polymers.[60] The polymerizations with and without added copper(I) behaved similarly, which demonstrated that the copper(I) complex does not react reversibly with the growing radicals in any manner that results in polymerization control. In a similar experiment, $\text{Cu}^{\text{II}}(\text{OTf})_2$ (OTf = triflate) had no effect on the radical polymerization of methyl acrylate (OTf cannot be transferred to organic radicals), indicating the absence of specific interactions of growing radicals with copper(II).[63] Thus, the exclusive role of the copper(II) complex is to deactivate active radicals via atom transfer.

6.3. Deactivator

The deactivator in ATRP is the higher oxidation state metal complex formed after atom transfer, and it plays a vital role in ATRP in reducing the polymerization rate and the polydispersity of the final polymer. Equation 5 relates how the polydispersities in polymerization systems with relatively fast exchange decrease with conversion, where p is the polymerization conversion, $[\text{RX}]_0$ is the concentration of initiator, [RX] is the concentration of dormant polymer chains, and [D] is the concentration of deactivator.

$$\frac{M_w}{M_n} = 1 + \left(\frac{2}{p} - 1\right)\left(\frac{\left([\text{RX}]_0 - [\text{RX}]_t\right)k_p}{k_{\text{deact}}[\text{D}]}\right) \tag{5}$$

This equation can be simplified for complete conversion ($p = 1$) and complete initiation (Eq. 6).

$$\frac{M_w}{M_n} = 1 + \left(\frac{[\text{RX}]_0 k_p}{k_{\text{deact}}[\text{D}]}\right) \tag{6}$$

A number of conclusions can be drawn from Equation 6. First, the final polydispersities should be higher for shorter polymer chains, because of the higher value of $[\text{RX}]_0$. This result can be rationalized by the fact that relative to longer chains, the growth of smaller chains involves fewer activation–deactivation steps and therefore fewer opportunities for controlled growth. Second, the final polydispersities should be higher for higher values of the ratio, k_p/k_{deact}, and in the limit where the rate of deactivation is too slow or zero, ATRP simply becomes a redox-initiated polymerization. Thus, for the hypothetical polymerization of two monomers with different k_p values, such as methyl acrylate and styrene, and the same k_{deact}, the polymerization with the larger k_p, methyl acrylate in this case, will yield polymer with the higher polydispersity. Third, the polydispersity of the final polymer should decrease with an increasing concentration of deactivator, which is in fact observed.[68]

In ATRP the concentration of deactivator continuously, but slowly, increases in concentration with conversion due to the persistent radical effect. While the final molecular weights do not depend upon the concentration of deactivator, the rate of polymerization will decrease with its increasing concentration. In the case of copper-mediated ATRP, it is possible to increase the observed polymerization rate by adding a small amount of metallic copper(0), which conproportionates with copper(II) to regenerate copper(I). This approach also allows for a significant reduction in the amount of catalyst required for polymerization.[84]

6.4. Monomers

As discussed previously, ATRP can be used for many vinyl monomers, including styrenes, acrylates, methacrylates, acrylonitrile, and dienes. The current generation of catalyst systems is not sufficiently efficient to polymerize less reactive monomers, such as ethylene, α-olefins, vinyl

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chloride, and vinyl acetate, which produce non-stabilized, highly reactive radicals. Acrylic and methacrylic acid cannot be polymerized with currently available ATRP catalysts, because these monomers react rapidly with the metal complexes to form metal carboxylates that are inefficient deactivators and cannot be reduced to active ATRP catalysts. A better understanding of the transition-metal chemistry involved in ATRP and better ligand design may allow these monomers to be polymerized directly. Nevertheless, the corresponding *tert*-butyl esters of these monomers, which are easily hydrolyzed, can be polymerized using ATRP.[85]

6.5. Solvents and Additives

Typically, ATRP is conducted in bulk, but solvents may be used and are sometimes necessary when the polymer is insoluble in its monomer. Solution polymerizations are slower relative to bulk polymerizations using the same amounts of reagents due to the reaction orders of each component. When solvents are used they are usually non-polar, such as *p*-xylene, *p*-dimethoxybenzene, and diphenyl ether, but some polar solvents, such as ethylene carbonate and propylene carbonate, have been used successfully. Solvent choice should be dictated by several factors. First, with some solvents there is the potential for chain transfer, depending upon the corresponding transfer constant, C_s. Second, solvent interactions with the catalyst system should be considered. Specific interactions with the catalyst, such as solvolysis of the halogen ligand or displacement of spectator ligands, should be avoided. Third, certain polymer end groups, such as polystyryl halides, can undergo solvolysis or elimination of HX at 110 to 130 °C in many polar solvents.

The polymerization is rather sensitive to oxygen. ATRP will proceed when a small amount of oxygen is present, because the oxygen can be scavenged by the catalyst, which is present at much higher concentration than the polymeric radicals. However, oxidation of the catalyst reduces the metal complex concentration, potentially forms an excess of deactivator, and therefore reduces the rate of polymerization.

Other additives have varying effects upon ATRP. Matyjaszewski et al. showed that the addition of moderate concentrations of water, aliphatic alcohols, and polar compounds had little or no effect upon copper-mediated ATRP.[60] Nishikawa et al. showed the same for ruthenium/aluminum alkoxide–mediated ATRP.[56] The addition of amine and phosphine ligands to copper-mediated ATRP inhibited the polymerization, presumably by saturating the coordinating sphere of the active copper(I) complex or by forming copper(I) complexes that were inactive to atom transfer. In some cases additives can accelerate ATRP. Haddleton et al.[86] investigated MMA ATRP using various phenols as additives and observed a small increase in the rate of polymerization. The absence of polymerization inhibition was consistent with observations of the effect of phenols on free-radical polymerizations of MMA. For example, less than 1 % retardation was observed for the 2,2′-azobisisobutyronitrile- (AIBN-) initiated polymerization of MMA with 0.2 M hydroquinone;[87] the presence of 4-methoxyphenol actually increased the polymerization rate at 45 °C. In the latter case, the transfer coefficient was measured to be $k_{tr}/k_p < 0.0005$. A similar observation was made for methyl acrylate,[88] where inhibition was again insignificant at 50 °C since $k_x/k_p < 0.0002$. The absence of a retardation/transfer effect of phenols in the polymerization of methacrylates and acrylates supports the intermediacy of free radicals and excludes the intermediacy of nucleophilic organocuprates in ATRP, which should be sensistive to the relatively acidic phenols. The small observed rate enhancement likely can be attributed to specific interactions of the phenol with the metal center, such as ligand exchange. A similar effect was noticed for ATRP catalyzed using copper carboxylates and $Cu[(CH_3CN)_4]^+PF_6^-$.[80,83]

6.6. Temperature and Reaction Time

In ATRP, the observed rate of polymerization increases with increasing temperature due to increases in both the rate constant for radical propagation and the atom transfer equilibrium constant. The energy of activation for radical propagation is appreciably higher than that for termination by radical combination and disproportionation. Consequently, at higher temperatures the ratio k_p/k_t will be higher and therefore better polymerization control (i.e., "livingness") will be observed. If only the ratio of termination to propagation is considered, the best control will be observed for slower reactions at higher temperatures, but at elevated temperatures the rate of chain transfer and other side reactions become faster. Thus, an optimum temperature for each type of ATRP must be found. The atom transfer enthalpies for styrene ATRP have been measured for the copper-based ATRP system: ΔH^0 = 4.8 kcal mol^{-1} (ΔS^0 = –22 kcal mol^{-1}) for the bromine-mediated process and ΔH^0 = 6.3 kcal mol^{-1} (ΔS^0 = –20 kcal mol^{-1}) for the chlorine-mediated process.[60] In the bromine-mediated ATRP of methyl acrylate, $\Delta H^0 \approx 12$ kcal mol^{-1}, which indicates that the formation of radicals is more endothermic in comparison to the styrene system.[74] This result correlates well with the higher reactivity of the acrylate radical relative to the styryl radical. For polymerization of methyl methacrylate an intermediate value was determined ($\Delta H^0 \approx 10$ kcal mol^{-1}).[63]

The most important effect of reaction time in ATRP occurs at high conversions. At high monomer conversions the rate of propagation is very slow; however, the rate of most side reactions does not depend upon monomer concentration, so such processes may still proceed at their normal rate. Even though the rate of such side reactions may be perceived as slow, they can have a significant effect upon the structure of the final polymer, because upon continued heating after complete monomer conversion, the loss of end group functionality may occur. That the polydispersity of the final polymer may be very low may be misleading. Therefore, when conducting ATRP in which maintaining the end group functionality is a concern (i.e., in the preparation of block copolymers), the polymerization conversion should not exceed 95 % in order to avoid potential end group loss.

7. The Synthesis of Polymers with Application to Materials and the Synthesis of New Materials Using ATRP

Controlled/living radical polymerizations, including ATRP, provide three powerful tools for macromolecular design: the synthesis of novel statistical and segmented copolymers by the controlled addition of monomers, the synthesis of end-functional polymers by selective termination of the chain ends with various reagents, and the synthesis of polymers with new topologies by using either multifunctional initiators, macroinitiators, or inimers (i.e., molecules serving both as initiators (ini) and monomers (mers)). The conditions for conducting ATRP are not very stringent, as they can be conducted using “off-the-shelf” reagents and require only the exclusion of efficient radical scavengers. These distinctions, combined with the fact that many polar monomers can be polymerized using radical intermediates, point towards ATRP being a useful new tool for the synthesis of new materials. Unique materials applications of this method are likely to be found in the synthesis of specialty polymers, such as the grafting/blocking from commodity polymers, and in copolymer synthesis, for which compositional heterogeneity and too high polydispersities lead to processing and coating problems.

Given the recent development of these methods, most explorations using ATRP have involved the synthesis of polymeric materials with varying compositions, functionalities, and topologies.[89,90] Some of these polymeric materials have been prepared previously using multistep methods and rather stringent reaction conditions, while others have been prepared for the first time. The application of ATRP and other living radical polymerizations to materials synthesis is a future direction of this research area. The potential of ATRP as a technique for the preparation of new materials is a consequence of the simplicity of the method, the range of monomers that can be used in these polymerizations, and the control afforded over end group functionality.

7.1. Functional Polymers

In addition to the polymerization of functionalized monomers, polymers prepared using ATRP can be chain end-functionalized. This conversion can be accomplished through the use of functionalized initiators, chemical transformation of the terminating chain end, or both. Functionalized initiators, including α-haloesters and benzyl halides that contain hydroxy, amino, ester, amide, epoxy, vinyl, allyl, and cyclophosphazine groups, have been used successfully to initiate ATRP.[91–94] To functionalize the terminating end of the polymer chain, azide displacement reactions have been the most successful approach.[95,96] The bromide end groups of polystyrene and poly(methyl acrylate) prepared using ATRP were transformed to azide end groups by reaction with trimethylsilyl azide in the presence of tetra-*n*-butylammonium fluoride. Subsequent reduction of the azide end groups with $LiAlH_4$ yielded the corresponding amine-terminated polystyrene, and reaction with triphenyl phosphine produced the corresponding phosphoranimine. Hydrolysis of the phosphoranimine also yielded the amine-terminated polymers. Novel resins containing well-defined polystyrene and poly(methyl acrylate) segments have been synthesized by preparing amine-terminated telechelic oligomers using a bis-initiator and the above method, and then condensing these oligomers with diacid chlorides.[95]

7.2. Random, Alternating, and Gradient Copolymerizations

ATRP has been used to copolymerize monomers that will undergo radical homopolymerization as well as combinations of these monomers with olefins that will not undergo radical homopolymerization. The list of monomers that have been used in such copolymerizations includes all of the previously discussed monomers for ATRP homopolymerization as well as vinyl acetate, vinylidene chloride, isobutene, maleic anhydride, and *N*-cyclohexylmaleimide (in the latter three cases, the olefins will not undergo radical homopolymerizations).[97]

In conventional free-radical copolymerizations, the composition of polymer chains within a sample is quite variable from chain to chain. Due to chain termination, the relative amounts of incorporated comonomers vary with conversion, unless “azeotropic” conditions are used.[14] Thus, chains formed early in the polymerization have very different compositions than those formed during the later stages. In contrast, all polymer chains within a sample prepared using ATRP have a similar composition, due to the absence of chain-breaking reactions and the fact that the polymer chains grow at similar rates. Furthermore, it is possible to change the composition of the polymer backbone from random to gradient simply by varying the composition of the monomer fed during the polymerization (Fig. 6).[57,79,98,99] Various shapes of the gradient can be designed, including one in which the chain ends are homopolymer blocks. This gradient control in ATRP copolymerizations has been demonstrated using monomer pairs, including methyl acrylate/styrene, methyl methacrylate/styrene, and acrylonitrile/styrene.

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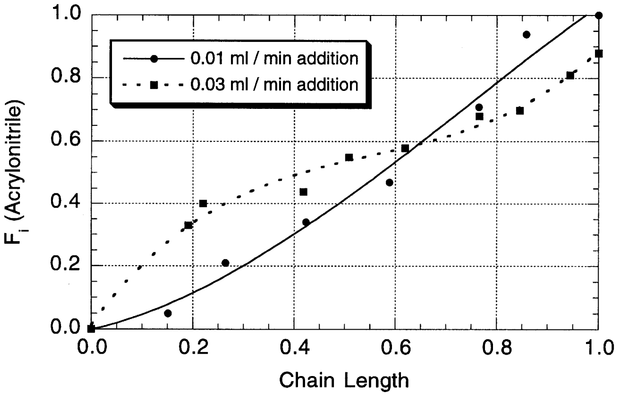


Fig. 6. Dependence of the shape of the gradient on the rate of addition in the atom transfer radical copolymerization of styrene and acrylonitrile. Acrylonitrile was added to a batch of styrene at a rate of 0.01 mL/min (●) and 0.03 mL/min (■). $[ST]_0 = 8.7$ M (10 mL), $[1\text{-PEBr}]_0 = 0.1$ M, $[CuBr]_0 = 0.1$ M, $[bipy]_0 = 0.2$ M, 80 °C.

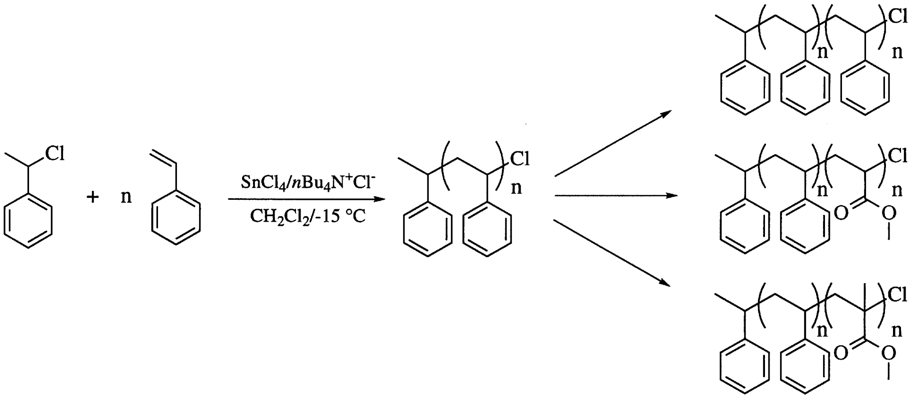
The physical properties of gradient copolymers were found to differ considerably from those of the corresponding block and random copolymers.[100] The main effects observed were related to differences in local dynamics, which in the case of the gradient copolymers with their broad range of local compositions manifests itself in an extremely broad spectrum of relaxation times of segmental motions. Qualitatively, in gradient polymers the temperature dependencies of their dynamic properties and of their microphase separation morphologies remain the same as compared to diblock copolymers, but changes in the composition gradients will alter the microphase separation transition temperature continuously along the temperature scale. The experimental data also suggest a strong dependence of the morphological and dynamic states of the gradient copolymer samples on their temperature and thermal history. Simulations[98] of the interfacial effects of incompatible polymers modified by the presence of gradient copolymers indicate that gradient copolymers are effective compatibilizers, combining the advantageous properties of both diblock and random copolymers. Therefore, gradient copolymers can potentially be used as compatibilizers, surfactants, and novel materials for vibration and noise dampening.

7.3. Block Copolymers

Linear diblock copolymers have long been studied for their microphase separation behavior and their ability in polymer blends to disperse incompatible phases and to increase interfacial adhesion. Diblock copolymers have been prepared using ATRP via two routes: by the sequential addition of two monomers to the polymerization medium and by using isolated, purified ATRP homopolymers as macroinitiators.[42,47,101] When bifunctional initiators are used, ABA triblock copolymers can be prepared using these methods, including thermoplastic elastomers in which the central "A" segments are soft blocks such as *n*-butyl acrylate, methyl acrylate, and 2-ethylhexyl acrylate, and the outer "B" segments are hard blocks such as styrene, methyl methacrylate, and acrylonitrile.[102] These types of block copolymers can also be synthesized by preparing segments using other polymerization techniques and then crossing over to ATRP. Crossover has been achieved from cationic polymerizations (Scheme 4),[103,104] certain step-growth polymerizations,[105] inorganic polymers,[93,106] dendrimers,[107,108] and ring-opening metathesis polymerization (ROMP).[109]

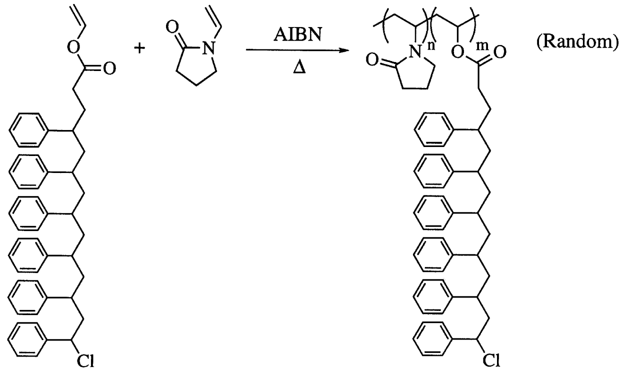
7.4. Graft/Comb Polymers

Several different approaches have been used to prepare graft/comb polymers using ATRP, but all share the common theme of using orthogonal initiating groups or polymerization methods to prepare the two segments. Several approaches have involved using other polymerization methods to polymerize and copolymerize monomers possessing functional groups capable of initiating ATRP. The resulting polymer was then used as a macroinitiator for the ATRP of various monomers. Conventional free-radical copolymerizations of (2-bromopropionyloxy)ethyl acrylate (BPEA) with butyl acrylate or vinyl chloride with vinyl chloroacetate led to linear copolymers with pendent ATRP initiating sites,[110,111] and these copolymers were used as macroinitiators in ATRP to yield graft/comb copolymers.



Scheme 4. Block copolymer synthesis via the crossover from controlled/living cationic polymerization to ATRP.

Those combinations involving soft polymer backbone segments (i.e., *n*-butyl acrylate, 2-ethylhexyl acrylate, or methyl acrylate) and hard graft polymer segments (i.e., methyl methacrylate or styrene) yielded thermoplastic elastomers. Another approach used different controlled/living radical polymerization methods to prepare the two segments of the graft copolymer. Grubbs et al.[112] prepared backbone polymers using controlled/living radical polymerization methods. Subsequent polymerizations using these macroinitiators and ATRP/nitroxyl radical–mediated polymerization conditions yielded well-defined graft and dendrigraft copolymers of styrene and alkyl methacrylates. Some approaches involved modification of a functional polymer backbone with initiators for ATRP, and then conducting ATRP to graft polymer chains from the parent polymer. The hydrosilation of poly(methyl vinyl siloxane) side chains with silane benzyl chloride groups[106] yielded macroinitiators that were used to prepare graft copolymers of polysiloxanes with styrene and butyl acrylate. The final reported route into graft/comb polymers employed the macromonomer approach. Polystyrene macromonomers were prepared using ATRP and vinyl chloroacetate initiator and then were copolymerized with *N*-vinylpyrrolidinone to form high molecular weight graft copolymers (Scheme 5).[113]

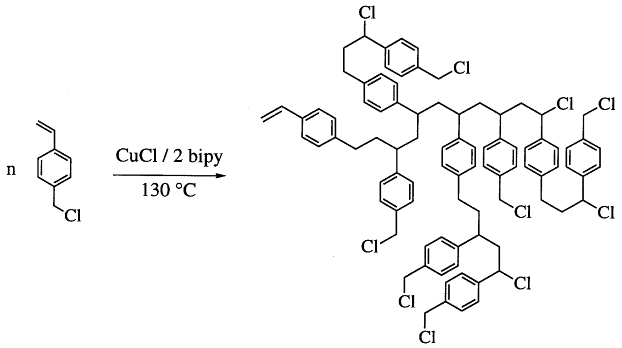


Scheme 5. Preparation of high molecular weight graft copolymers.

Due to the opposite hydrophilicities of the two segments, these copolymers dissolved in DMF but only swelled in hydrocarbons or water. These materials exhibited swellabilities in water exceeding 95 % and equilibrium water contents over 50 %, depending upon the amount of styrene incorporated into the copolymer. These types of materials and their variations could find application as superabsorbant materials.

7.5. Hyperbranched/Branched Polymers

A recent subject in polymer/materials synthesis is the preparation of hyperbranched polymers via self-condensing vinyl polymerizations.[114,115] The introduction of branching into a polymer can dramatically alter its properties, with dendrimers being the extreme example, so the preparation of these types of macromolecules is of interest to the polymer/materials community. In 1952 Flory[116] proposed that the polymerization of AB_2 monomers would lead to branched, but not crosslinked (network), structures. In self-condensing vinyl polymerizations, AB* monomers are the subject of polymerization: "A" represents a vinyl group, while "B*" represents a functional group that can be activated and can initiate the polymerization of the double bonds. Hybrid monomers, AB*, containing both a polymerizable vinyl group, A, and an activated halogen atom, B*, can be homopolymerized using ATRP to yield hyperbranched polymers. The copolymerization of AB* monomers with conventional monomers yields macromolecules with branched structures. These methods have been developed for the ATRP of *p*-chloromethylstyrene (Scheme 6),[117] *p*-chloromethylstyrene/styrene,[117] and 2-(2-bromopropionyloxy)ethyl acrylate (BPEA).[118–120]



Scheme 6. ATRP of *p*-chloromethylstyrene.

8. Conclusions

The combination of synthetic versatility and simplicity makes ATRP a powerful technique for use in the design and synthesis of new polymeric materials with novel structures. ATRP can be used to polymerize and copolymerize a wide variety of monomers, including styrenes, methacrylates, acrylates, and acrylonitrile, with accurate control over the molecular weight and molecular weight distribution of the final polymer. The reaction conditions are not very stringent, because only the absence of efficient radical scavengers is required to conduct the polymerization, and many types of functional groups and polymerization additives can be tolerated. The composition, functionality, and architecture of the final polymer all can be controlled through variations in the side groups, end groups, and initiator structure.

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