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Krzysztof Matyjaszewski [a]

[a] Carnegie Mellon University, Fifth Avenue Pittsburgh, PA, USA

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NEW MATERIALS BY ATOM TRANSFER RADICAL POLYMERIZATION

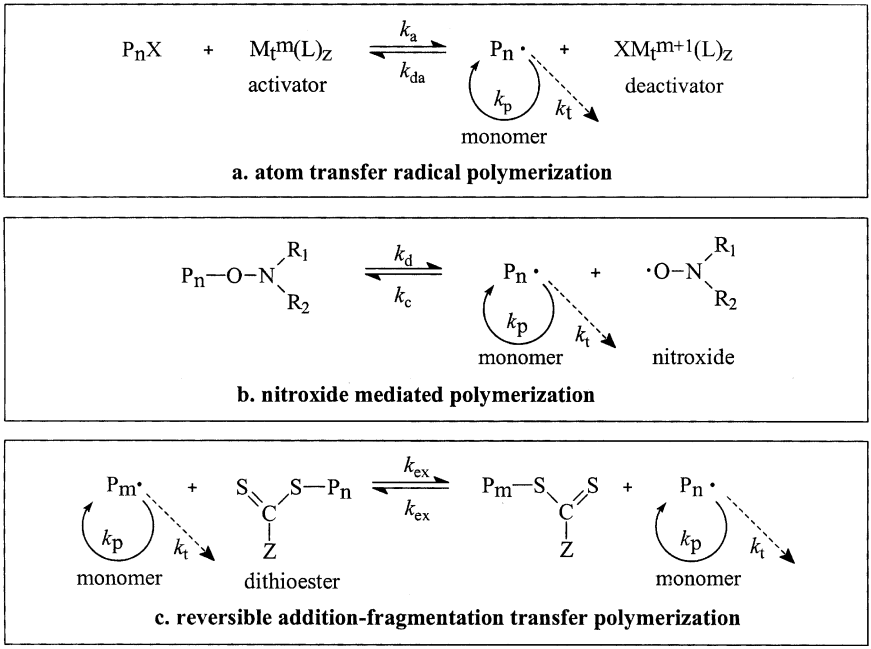
Krzysztof Matyjaszewski
Carnegie Mellon University, 4400 Fifth Avenue Pittsburgh, PA, 15213, USA

Fundamentals of atom transfer radical polymerization (ATRP) and other controlled/living radical polymerizations are discussed. Several new polymer materials with controlled topology, composition, and functionality prepared by ATRP are presented.

INTRODUCTION

The development of controlled/living radical polymerizations (CRP) is among the most important advances in polymer chemistry of the last decade [1]. Several methods allowing control of radical polymerization have been reported. Among them, the most studied and promising are: atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and degenerative transfer with dithioesters via reversible addition-fragmentation transfer polymerization (RAFT). These three main methods are based on the same simple concept, an equilibrium between a low concentration of active propagating chains and a predominant amount of dormant chains, which are unable to propagate or self-terminate. Thus, the probability of bimolecular termination reactions decreases and the radical polymerization behaves as a living system. Therefore CRP offers possibility of synthesizing various homopolymers and copolymers with molecular weight predetermined by the ratio of consumed monomer to the introduced initiator, low polydispersities, controlled compositions, functionalities and chain topologies. Each system employs different chemistry: ATRP involves a reversible atom transfer with a simultaneous redox process, NMP relies on a reversible homolytic cleavage of alkoxyamines and RAFT uses a reversible addition-fragmentation with dithioesters as shown in Scheme 1.

Address correspondence to Krzysztof Matyjaszewski, Carnegie Mellon University, 4400 Fifth Avenue Pittsburgh, PA, 15213, USA. E-mail: km3b@andrew.cmu.edu



SCHEME 1

The field of controlled/living radical polymerization (CRP) is among the most rapidly developing areas of polymer science. Figure 1 illustrates number of papers published in the generic field of CRP and more specific ATRP, NMP and various degenerative transfer (DT) processes, including alkyl iodides, RAFT and catalytic chain transfer (CCT). The first paper on ATRP appeared in 1995 and at present, on now every week more than 10 papers are published on ATRP. The main reason for such an explosive development of CRP is its simplicity and an unusual power to prepare tailor-made functional macromolecules for many special applications which is predicted to affect $20 billion/year market.

FUNDAMENTALS OF CONTROLLED/LIVING RADICAL POLYMERIZATION (CRP)

The great expectations for the controlled/living radical polymerization (CRP) have their origins in the dominating position of the free radical technique, by far the most common method of making polymeric materials (nearly 50% of all polymers are made this way) [1]. This is due to the large number of available vinyl monomers (e.g., there are nearly 300 different

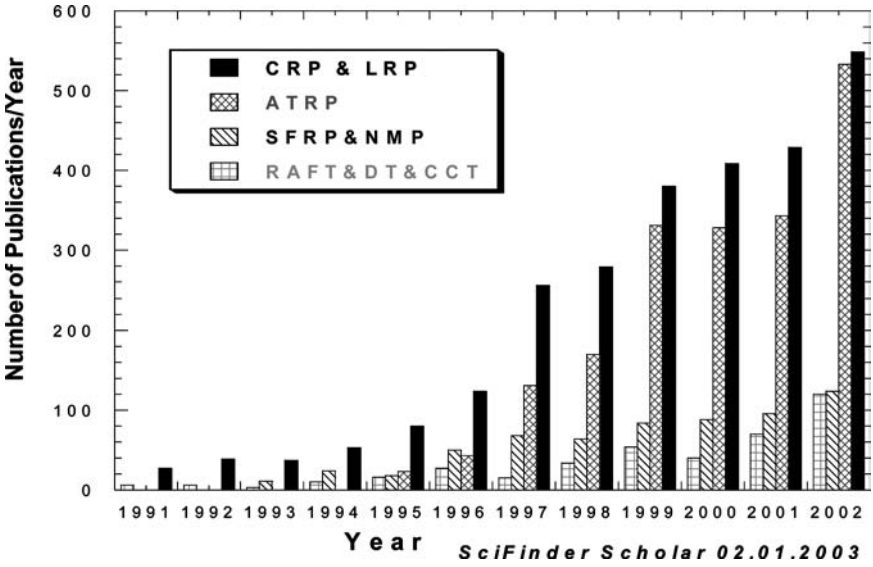


FIGURE 1 Number of publications on ATRP, NMP DT (including RAFT) and generic CRP, according to SciFinder Scholar.

methacrylates available commercially) which can be easily homopolymerized and copolymerized. Reaction conditions are undemanding and only require moderate heating, deoxygenation, and are tolerant to moisture and protic impurities. However, in contrast to many ionic reactions, until recently, it was impossible to make well-defined polymers through a conventional radical process. The advent of CRP enables preparation of many new materials such as well-defined components of coatings (with narrow MWD, precisely controlled functionalities and reduced volatile organic compounds -VOCs), non ionic surfactants, polar thermoplastic elastomers, entirely water soluble block copolymers (potentially for crystal engineering), gels and hydrogels, lubricants and additives, surface modifiers, hybrids with natural and inorganic polymers, various biomaterials and electronic materials. In this section we describe the fundamentals of CRP. Extensive discussion of more detailed aspects, such as the monomers, initiators, catalysts, media, etc., can be found in a recent review [2].

Mechanistically, new controlled/living systems are quite similar to conventional radical polymerizations. Polymeric radicals grow and terminate with similar rate constants. The main difference between the two systems is only how the radicals are generated. They are generated slowly and irreversibly in the conventional processes through dissociation of peroxides or diazo compounds which typically have a half-lifetime in the range of 10

hours. Propagation is rapid with an approximate frequency of monomer addition of $\sim$1 ms. This means that within 1 s, a polymer chain with DP $\sim$1000 is typically formed. Within approximately the same time, chains terminate by either coupling or disproportionation. During such a short time, it is not possible to perform any kind of macromolecular engineering by adding another monomer, functionalizing reagent, etc.

The controlled/living reactions are quite similar to the conventional ones, however, the radical formation is reversible. Similar values for the equilibrium constants during initiation and propagation, ensure that the initiator is consumed at the early stages of the polymerization, generating chains which slowly and continuously grow, as in a living process. There are a number of critical differences between conventional and controlled/living radical reactions:

- Perhaps the most important difference between the two approaches is the lifetime of the propagating chains, which is extended from $\sim$1 s to more than 1h.
- The second major difference is the very significant increase in the initiation rate, which enables simultaneous growth of all the polymer chains. Both parameters allow various macromolecular engineering techniques to be applied, such as making well-defined star polymers, block and grafts, end functional polymers and many other well-defined materials.
- Termination processes cannot be avoided in CRPs. Thus, CRP is generally less precise than the anionic polymerization. Termination is the most dangerous chain breaking reaction in CRPs. Since it is a bimolecular process, increasing the polymerization rate increases the concentration of radicals and enhances the termination process. Termination also becomes more significant for longer chains and at higher conversion. However, this process is somehow self tuned, since termination is chain length dependent.
- Polymers prepared by CRPs will never have 100% functionality and 100% blocking efficiency. For monomers with low values of rate constants of radical propagation (k_p) such as dienes, styrenes and methacrylates, it is necessary to slow down the polymerization rate to avoid excessive termination; for those with high k_p value such as acrylates this is less important.
- Since propagating species are free radicals, chemo-, regio- and stereoselectivities are similar to those found in conventional radical polymerizations. This means that similar reactivity ratios, similar sensitivity to transfer reagents and similar tacticities are observed.

The key feature of the controlled/living radical polymerization is the dynamic equilibration between the active radicals and various types of

dormant species. Currently three systems seem to be most efficient: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and degenerative transfer processes, such as reversible addition-fragmentation transfer RAFT [3].

Each of the CRPs has some limitations and some special advantages, and it is expected that each technique may find special areas where it would be best suited synthetically. For example, NMP carried out in the presence of bulky nitroxides cannot be applied to the polymerization of methacrylates due to fast β-H abstraction. ATRP can not yet be used for the polymerization of acidic monomers, which can protonate the ligands and complex with copper. RAFT is very slow for the synthesis of low MW polymers due to retardation effects, and may provide branching due to trapping of growing radicals by the intermediate radicals. At the same time, each technique has some special advantages. Terminal alkoxyamines may act as additional stabilizers for some polymers. ATRP enables the synthesis of special block copolymers by utilizing a halogen exchange and has an inexpensive halogen at the chain end [4]. RAFT can be applied to the polymerization of many unreactive monomers, such as vinyl acetate [5].

Three general prerequisites should be fulfilled for CRP: initiation should be fast in comparison with propagation, degrees of polymerization should be predefined by the $\Delta[M]/[I]_o$ ratio and low enough to minimize the effect of chain breaking reactions (transfer and termination) and equilibrium should be established between growing radicals and dormant chains. The equilibrium constant and dynamics of exchange are among the most important features of CRP.

TYPICAL FEATURES OF ATRP

A successful ATRP process should meet several requirements:

- Initiator should be consumed at the early stages of polymerization to form polymers with degrees of polymerization predetermined by the ratio of the concentrations of converted monomer to the introduced initiator ($DP = \Delta[M]/[I]_o$).
- The number of monomer molecules added during one activation step should be small, resulting in polymers with low polydispersities.
- The contribution of chain breaking reactions (transfer and termination) should be negligible to yield polymers with high degrees of end-functionalities, and allow the synthesis of block copolymers.

In order to reach these three goals, it is necessary to select appropriate reagents and appropriate reaction conditions.

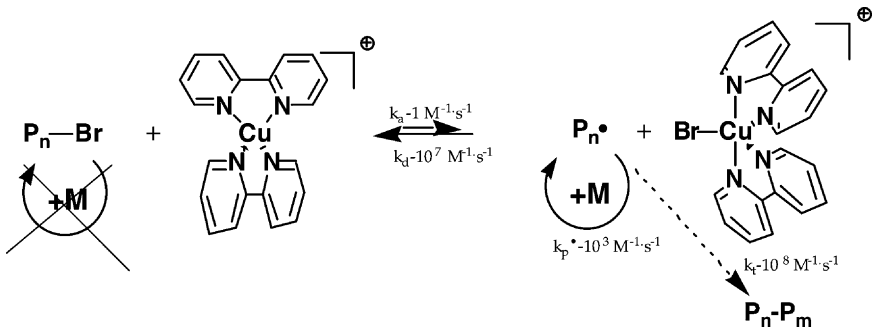
ATRP is based on the reversible transfer of an atom or group from a dormant polymer chain (R-X) to a transition metal (M_t^n/Ligand) to form a radical ($R^{\bullet}$), which can initiate the polymerization, and a metal-halide whose oxidation state has increased by one (X-M_t^{n+1}/Ligand); the transferred atom or group is covalently bound to the transition metal. (Scheme 2) A catalytic system employing copper (I) halides (M_t^n/Ligand) complexed with substituted 2,2′-bipyridines (bpy) has proven to be quite robust, successfully polymerizing styrenes, various (meth)acrylates, acrylonitrile and other monomers [6]. Other metal centers have been used, such as ruthenium, nickel and iron based systems [2,7]. Copper salts with various anions and polydentate complexing ligands were used, such as substituted bipyridines, pyridines, and linear polyamines.

The rate constants of the exchange process, propagation and termination shown in Scheme to bulk styrene polymerization at 110°C.

According to this general ATRP scheme, the rate of polymerization is given by Eq. (1):

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

Thus, the rate of polymerization is internally first order in monomer, externally first order with respect to initiator and activator, Cu(I), and negative first order with respect to deactivator, XCu(II). However, the kinetics may be more complex due to the formation of XCu(II) species via the persistent radical effect (PRE). The actual kinetics depend on many factors, including the solubility of activator and deactivator, their possible interactions, and variations of their structures and reactivities with concentrations and composition of the reaction medium. It should be also noted that the contribution of PRE at the initial stages might be affected by the mixing method, crystallinity of the metal compound and ligand, solubility of the reagents in the polymerization locus, etc [8].



SCHEME 2

One of the most important parameters in ATRP is the dynamics of exchange, and especially the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates, leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP are defined by Eq. (2), when the contribution of chain breaking reactions is small and initiation is complete:

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

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

MATERIALS CONTROLLABLE BY ATRP

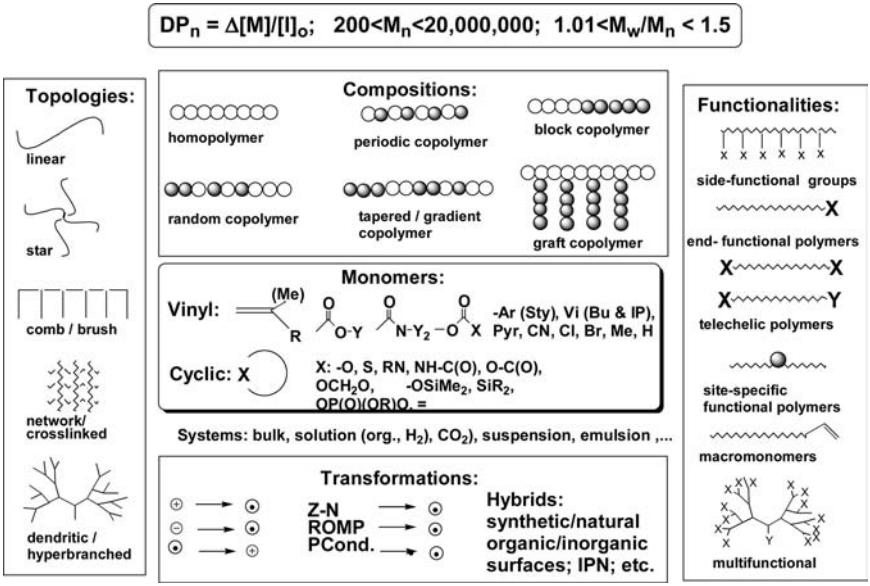
The most important benefit of controlled/"living" polymerizations is that they allow preparation of new macromolecules with varying compositions (homopolymers, random, periodic, block, graft and gradient copolymers), novel topologies (linear, star, comb, (hyper)branched, networks, etc.), and functionalities placed at different parts of macromolecules or various combinations of these [9].

Scheme 3 illustrates some examples of polymer chain topologies, compositions and functionalities which have been prepared using ATRP or one or several of the aforementioned polymerization methods.

In addition, ATRP and other CRP methods can be combines with other living polymerizations via mechanistic transformation and generate many hybrid materials shown in the Scheme. This can be extended to the hybrids with inorganic compounds but also with natural products. More detailed structures are outlined below.

CONTROLLED COMPOSITIONS BY ATRP

One of the driving forces for the development of a controlled / "living" radical polymerization is to allow for the copolymerization of two or more



SCHEME 3

monomers [10]. This has been demonstrated with ATRP by copolymerization of various combinations of styrene, methyl or butyl acrylate, methyl or butyl methacrylate, and acrylonitrile [11]. ATRP allows for the copolymerization of these monomers using all feed compositions without loss of control of the polymerization; this is in contrast to the use of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), which must contain a significant amount of styrene as comonomer to retain control of the polymerization. This restriction does not apply to polymerizations mediated by new nitroxides [12]. The statistical copolymers prepared by living polymerizations are not the same as those prepared by conventional radical polymerizations due to the differences in polymerization mechanism. During a copolymerization, one monomer is generally consumed faster than the other, resulting in a constantly changing monomer feed composition during the polymerization; the preference is dependent on the reactivity ratios of the two (or more) monomers. In conventional radical polymerization, where the polymer chains are continuously initiated and are irreversibly terminated, the change in monomer feed is recorded in the individual polymer chains, whose composition will vary from chain to chain, depending on when the chain was formed, i.e., at the beginning or near the end of the reaction. However, since ATRP is a controlled/"living" polymerization system, the vast majority of polymer chains do not irreversibly terminate, but grow

gradually throughout the polymerization. The change in monomer feed is recorded in the polymer chain itself and not from chain to chain. The drifting of composition along the polymer chain is expected to yield gradient copolymers with novel properties, such as blend compatibilization and vibration dampening [13].

Block copolymers can be formed by addition of a second vinyl monomer to a macroinitiator which contains halide groups that participate in the atom transfer process. Most notably this has been demonstrated by successive addition of a second monomer at the end of the polymerization of a first monomer by ATRP. In this manner, AB and ABA block copolymers have been prepared with various combinations of styrene, acrylates, methacrylates, and acrylonitrile. It is very important to select the right order of monomer addition. For example, polyacrylates can be efficiently initiated by the poly(methyl methacrylate)-Br/CuBr/L system. However, the opposite is not true because concentration of radicals and overall reactivity of acrylates is generally too low to efficiently initiate MMA polymerization. Halogen exchange comes to the rescue; bromo-terminated polyacrylate in the presence of CuCl/L is an efficient initiator for MMA polymerization due to reduced polymerization rate of PMMA-Cl species which are predominantly formed after the exchange process [14].

ATRP can be also employed for block copolymer synthesis from monomers which are not polymerizable radically. Macroinitiators can be prepared from materials that are not vinyl monomers. It should be stressed that the only requirement for a macroinitiator is that it contains at least one radically transferable atom, such as benzylic halides or α-halo ketones, esters, and nitriles. By appropriate modification of the end groups of polymers prepared using other polymerization systems, numerous block copolymers have been prepared. These include block and graft copolymers of polysiloxanes [15] and polysulfone (step-growth polymerization) [16], polynorbornene and poly(dicyclopentadiene) (ROMP) [17], polyisobutene (cationic polymerization) [18], poly(vinyl chloride) [19] and poly(THF) (cationic ring opening polymerization) [20]. These block copolymers are only a small sampling of what is possible and numerous combinations of various (co)polymers with vinyl polymers can be synthesized. The block copolymers may find use as blend compatibilizers, surfactants, adhesives, thermoplastic elastomers, etc.

CONTROLLED TOPOLOGIES BY ATRP

ATRP has also allowed for the preparation of polymers with topologies other than linear polymers, such as graft and (hyper)branched polymers. The graft copolymers have been prepared by two different methods. The

first involves the copolymerization of macromonomers with a vinyl monomer (grafting-through). ATRP was used to prepare a polystyrene macromonomer with a vinyl acetate end group, which was then copolymerized with N-vinyl pyrrolidinone to give the water swellable copolymer, poly(N-vinyl pyrrolidinone-g-styrene) [21]. Macromonomers have been also copolymerized by ATRP providing better control of the copolymer than conventional methods [22]. The second method involves growing the grafts from the polymer backbone by using a polymer with pendent activated alkyl halide groups as macroinitiators for ATRP. In this way densely grafted molecular brushes were prepared [23].

The polymerization of AB* monomers (A = double bond, B* = latent initiator group) can lead to branched and hyperbranched polymers. This is possible by activation of the B* group to form a radical, which can then initiate the polymerization of the double bond. Upon deactivation of the propagating radical, after addition of one or more double bonds, a new, potential active site is formed, A*. Monomer can now be added at either site, which can lead to branching in the polymer chain. Also, each macromolecule should contain only one double bond which can be incorporated into a growing polymer chain. The (hyper)branched polymers using ATRP were formed from p-chloromethylstyrene (p-CMS) and 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) with 1 mol% of Cu(I)Br/2dTbpy (dTbpy = 4,4′-di(t-butyl)-2,2′-bipyridine) [24]. In the latter case higher degree of branching was found due to secondary structures of both A* and B* units.

CONTROLLED FUNCTIONALITIES BY ATRP

In ATRP, at the end of the polymerization the polymer chains are capped with a halogen atom that can be replaced with a more useful functional group. For example, polystyrene was polymerized using α, α'-dibromoxylene to prepare a α, ω-dibromopolystyrene. This polymer was then treated with trimethylsilyl azide in the presence of tetrabutylammonium fluoride to produce the azido-functional polystyrene, which was further reduced using $LiAlH_4$ to prepare α, ω-diaminopolystyrene, $M_n = 5{,}100$; $M_w/M_n = 1.2$. This telechelic polymer was then used in a polycondensation reaction by treating with an equimolar amount of terephthaloyl chloride to produce a polystyrene with internal amide linkages, $M_n = 23{,}000$; $M_w/M_n = 2.5$ [25].

Functionality can also be introduced into the polymer by other methods. Because of the radical nature of the polymerization, a wide number of functional groups can be tolerated. Alkyl halide initiators containing a functional group that does not participate in the polymerization can also be used. These are widely available and many different types are

commercially available. Some end-functional polymers that have been prepared have contained epoxide, azido, amino, hydroxyl, cyano, and allyl end groups. In addition, functional groups can be present on the monomer itself as was demonstrated for various styrenes and acrylates [26].

To conclude, atom transfer radical polymerization is a robust method for preparing well-defined polymers and novel materials with unique compositions and architectures. Although significant progress has been made in the past few years since the development of ATRP, continuous research on the better mechanistic understanding of ATRP and the preparation of more efficient catalyst systems to yield more well-defined polymers and polymerize new monomers is needed. The syntheses of new materials need to be optimized and their properties should be studied.

It is anticipated that the new controlled/living radical polymerization techniques will help to provide many new well-defined polymers via macromolecular engineering.

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