# From cationic ring-opening polymerization to atom transfer radical polymerization

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*Dedicated to Professor Stanislaw Penczek on the occasion of his 80th birthday*

**Abstract**: Roots of controlled radical polymerization, including atom transfer radical polymerization (ATRP), originate in living ionic polymerizations accompanied by reversible deactivation, such as cationic ring-opening polymerization of tetrahydrofuran and other heterocyclics. Recent developments in ATRP, including mechanistic understanding, synthesis of polymers with precisely controlled architecture and some applications of polymers prepared by ATRP are presented.

**Keywords**: cationic ring-opening polymerization, tetrahydrofuran, atom transfer radical polymerization, ATRP, controlled radical polymerization, block copolymers.

## Od kationowej polimeryzacji z otwarciem pierścienia do polimeryzacji rodnikowej z przeniesieniem atomu

**Streszczenie**: Artykuł stanowi przegląd literaturowy dotyczący kontrolowanej polimeryzacji rodnikowej, w tym w szczególności kontrolowanej polimeryzacji rodnikowej z przeniesieniem atomu (ATRP), wywodzącej się z jonowej polimeryzacji żyjącej, której towarzyszy odwracalna dezaktywacja. Omówiono rozwój wspomnianych metod polimeryzacji, monomery, inicjatory i warunki reakcji syntezy polimerów o precyzyjnie kontrolowanej architekturze, a także zastosowanie materiałów o różnorodnych właściwościach, uzyskiwanych z wykorzystaniem ATRP.

**Słowa kluczowe**: kationowa polimeryzacja z otwarciem pierścienia, tetrahydrofuran, rodnikowa polimeryzacja z przeniesieniem atomu, ATRP, kontrolowana polimeryzacja rodnikowa, kopolimery blokowe.

### INTRODUCTION

This short mini-review is intended to show how a concept, developed for cationic ring-opening polymerization of cyclic ethers in the laboratory of Professor Penczek at Polish Academy of Sciences, has been applied to controlled polymerization systems, comprising several radical polymerizations and, in particular, atom transfer radical polymerization (ATRP).

Current progress in polymer science is enabled by new synthetic avenues, permitting precise control over molecular architecture [1]. Indeed, controlled polymer synthesis is the first and the most important prerequisite to prepare polymeric materials for targeted applications. When supplemented with an appropriate processing, it forms basis of macromolecular engineering. Preparation of well-defined, essentially tailor-made, functional polymers enables their organization into many nanostructured functional materials for advanced applications, ranging from thermoplastic elastomers, coatings, various sealants, adhesives, dispersants, health and beauty products to materials for electronics and biomedical or drug delivery systems [2, 3].

For a long time, anionic polymerization of non-polar vinyl monomers such as styrene and dienes was the only synthetic method to prepare polymers with precisely controlled structure and low dispersity [4—6]. It was subsequently used to synthesize various segmented copolymers and macromolecules with more sophisticated architecture, including cyclics, combs, stars, pom-poms and many others [7]. For a long time it was considered to be impossible to extend the concept of living polymerization without chain-breaking polymerizations, introduced by Szwarc, to cationic vinyl polymerization and especially radical polymerization, characterized by significant transfer or unavoidable radical termination reactions, respectively. However, a strong suppression of chain breaking reactions under appropriate conditions has been successively demonstrated for essentially all polymerization mechanisms, including carbocationic, coordination, radical, and various ring opening processes (cationic, anionic and metathesis) [9]. Nearly all of these advances are based on dynamic exchange between tiny amount of propagating active centers and dominating amount of dormant species [10]. Cationic ring-opening polymerization

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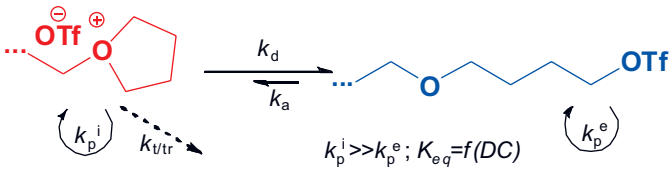
of tetrahydrofuran studied in Professor Penczek laboratory was perhaps the first system in which kinetics, thermodynamics and dynamics of exchange reactions was established in great detail and with high precision [11]. Subsequently, similar concepts have been extended to essentially all controlled/living polymerization systems.

## CATIONIC RING-OPENING POLYMERIZATION OF TETRAHYDROFURAN

I joined Professor Penczek's laboratory in 1972 and started to work under direct supervision of Dr. Kubisa. At that time, new very strong acids (or superacids) such as triflic (trifluoromethanesulfonic) and fluorosulfonic acids were introduced and used in polymerization of tetrahydrofuran (THF). This generated a significant interest in academia and also in industry, resulting in commercial products including polyTHF diols, which were subsequently used in specialty polyesters and polyurethanes [12—16]. Initially it was not realized that under such conditions two types of growing chain ends can be in equilibrium. We originally studied the kinetics of THF polymerization in various solvents using various initiators under classic dilatometric techniques. Polymerizations employing relatively stable complex counterions such as $BF_4$, $PF_6$, $SbCl_6$, $AsF_6$, or $SbF_6$, all had similar polymerization rates but relatively higher than those with triflate derivatives. Moreover, the rates of polymerization with these complex anions were not significantly affected by solvents but the rates of polymerizations conducted with triflate anions clearly increased with solvent polarity. Thus, a hypothesis was born that complex anions are counterions of propagating oxonium ions, whereas triflate anions can also form covalent esters that are much less reactive, which meant that esters could ionize more efficiently in solvents displaying higher dielectric constants and form a higher proportion of more reactive oxonium ions.

In order to verify this hypothesis, it was necessary to perform NMR spectroscopic studies to explore the structure of polymer end groups present at very low concentrations. At that time, high field NMR was not available in Poland and Professor Penczek decided to collaborate with Professor Goethals from University of Ghent, Belgium, who had access to the first 300 MHz NMR machine in Europe. Thus, after barely finishing my first year in the laboratory of Professor Penczek, I took a portable vacuum line, NMR tubes, all necessary reagents and went for a two-week intense research project to Belgium, preparing samples under high vacuum, sealing off NMR tubes and studying structure of the end groups of polytetrahydrofuran initiated by triflic esters in various solvents [17—19]. Accordingly, we established effect of solvent polarity on the equilibrium between propagating oxonium ions and dormant esters [20]. Subsequently, during my second stay in Ghent, we were able to extend these studies to cover not only effects of temperature, *i.e.*




**Scheme A. Ion/ester equilibrium in cationic ring-opening polymerization of tetrahydrofuran**

thermodynamics of ion-ester equilibrium, but also the dynamics of these equilibrium by rapidly changing the sample temperature and were able to directly measure the rate constants of ionization of esters to oxonium ions (activation, $k_a$ in Scheme A) and their temporary termination (deactivation back to the dormant state, $k_d$ in Scheme A). Since access to NMR was quite limited, most of these studies were performed at nights and evenings in collaboration with members of Professor Goethals' group. The results of these studies were published in several papers that revealed effect of temperature and solvents and subsequently nature of counterions on the ion-ester equilibria [22, 23]. Similar studies were also carried out, in parallel, in several laboratories in the USA and also in Japan [12—16, 23, 24].

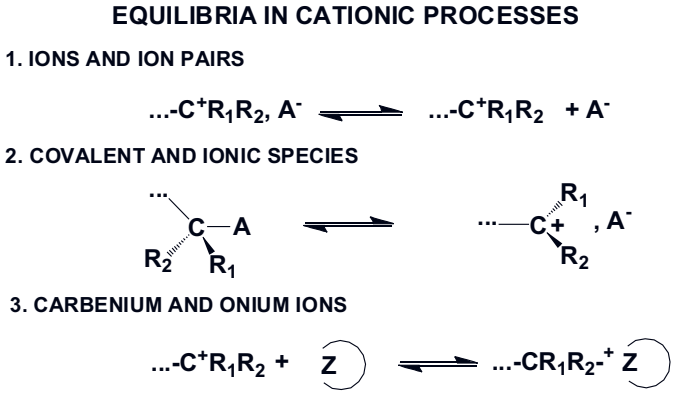
The studies focused on ion-ester equilibrium were later extended to equilibria between ion pairs and free ions in a collaborative effort with Prof. Slomkowski [25, 26]. Surprisingly, for the first time in ionic polymerization, similar reactivities for all ionic species were observed. The information collected on the thermodynamics and kinetics of polymerization of THF provided a very complete molecular picture and permitted a precise description of all molecular events in these systems [11]. The activation of esters occurred predominantly *via* an intramolecular process in low-strained five membered ring of THF but *via* external bimolecular ionization in more strained seven-membered oxepane [27]. While access to high resolution NMR was at that time limited, access to heteronuclear NMR, especially $^{31}P$ NMR was available in Lodz. We, therefore developed an ion trapping procedure to quantitatively determine the structure and concentration of growing chain ends in various polymerization systems [28, 29].

Subsequently, the studies of cationic ring-opening polymerization of cyclic ethers were extended to cyclic amines, iminoethers, sulfides, acetals and orthoesters which resulted in establishment of a general theory for the cationic ring-opening polymerization of heterocyclics [30—32]. Reactivity of monomers scaled reciprocally with the reactivity of onium ions and the rate constants of propagation were determined by onium ions reactivities rather than those of monomers. Ions and ion pairs had similar reactivities and active — dormant species equilibria were affected by monomers nucleophilicities, ring strain and nucleofugacity of leaving groups as well as solvent and temperature [33—36]. After completing the studies on cationic ring-opening polymerization of hete-

rocyclics [37—40], I turned my attention to cationic vinyl polymerization, whereas the laboratory of Professor Penczek continued studies on ring-opening polymerizations [41] and focused more on anionic/coordination polymerization, especially of polymerization of cyclic esters, where they made many ground-breaking discoveries [42].

## CARBOCATIONIC POLYMERIZATION

At that time cationic polymerization of styrene was considered to be impossible to control, due to several chain breaking reactions and, especially, the very fast rate of propagation [8, 43]. I started my research on carbocationic polymerizations in the laboratory of Professor Sigwalt in Paris, where I studied structure of carbocations and their reactivities using various spectroscopic techniques. At that time, a so called pseudocationic polymerization was proposed to operate in polymerization of styrene initiated by strong acids such as perchloric or triflic acids [44—50]. It had been postulated earlier, that styrene polymerization occurred in this system by means of a multicenter rearrangement, without involvement of carbocations [51]. A similar mechanism was proposed for the polymerization of isobutene in the presence of Lewis acids and also for polymerization of vinyl ethers, where polarized covalent bonds where postulated to be the active species in contrast to carbocations [52, 53]. Nevertheless based on various mechanistic and spectroscopic studies we proposed a unified theory of carbocationic polymerization in which carbocations (free ions or ion pairs – also with intrinsically similar reactivities, as in CROP) were solely responsible for polymerization [54, 55]. This was in excellent agreement with very profound studies made by Professor Mayr on electrophilic additions of carbocations to alkenes [56—58]. Covalent dormant species could not react with monomers due to their $sp^3$ hybridization [59, 60]. Thus, tiny amounts of carbocations (well below 1 % of chain ends) were responsible for the entire polymerization and the dynamics of exchange between active and dormant species affected the degree of control [61, 62]. Scheme B presents the three fundamental equilibria present in carbocationic systems. In addition to the equilibrium between free ions and ion pairs, equilibria between carbocations and covalent species and/or onium ions are responsible for the controlled chain growth.




**Scheme B. Equilibria in the carbocationic polymerization of alkenes**

These studies were continued after I moved to Carnegie Mellon University in 1985. However, since research funding in U.S.A. is quite different from the European principles, I had to broaden my research activities to organometallic and inorganic polymers due to their potential applications as electronic and biomedical materials so that I could secure support for my research. Initially, we developed new synthetic pathways to polysilanes using ultrasonication, and also ring-opening polymerization to prepare well-defined polysilanes and corresponding block copolymers [63—70]. In addition, we also discovered new routes to polyphosphazenes *via* phosphine azides and phosphoranimines [71—80]. While the results of our research were quite well recognized, a program officer from one of the funding agencies told me that they were no longer interested in polysilanes, and he very much appreciated our accomplishments, he encouraged me to apply for some "wild" or "crazy" project that could have a real impact on polymer /materials science. Thus, in 1992 I was analyzing major challenges in synthetic polymer chemistry and decided that we should try to apply principles of exchange between active and dormant species [81, 82] to improve control in radical polymerization.

## EARLY STAGES OF CONTROLLED RADICAL POLYMERIZATION

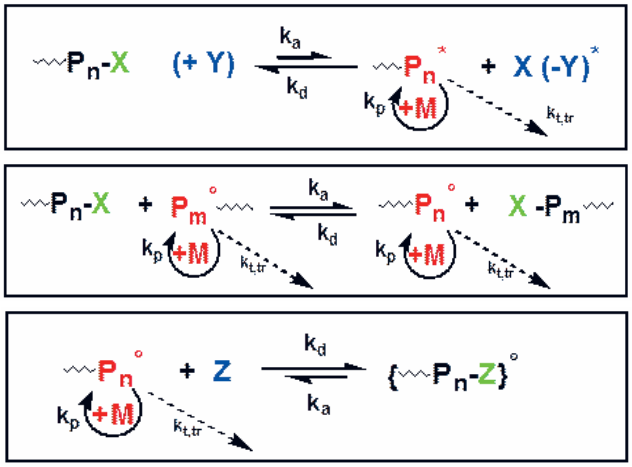
"Living" radical polymerization (IUPAC recommends a term reversible-deactivation radical polymerization) [83] was proposed already before 1980s by Borsig, Braun or Minoura and was then more intensely studied by Otsu, who was brave enough to drop the quotation marks and used the term living radical polymerization for polymerization of methyl methacrylate (MMA) and styrene (St) mediated by benzyl dithiocarbamate, a system not that far from a modern RAFT process.

The first evidence of reversible deactivation in radical polymerization was reported by Borsig [84, 85] who used diaryl and triaryl capping groups in polymerizations of MMA and observed an increase of molecular weights with conversion and also formation of block copolymers. This system was later studied by Braun, [86] however, dispersities were always relatively high, initiation efficiencies low and the molecular weights (*MW*) did not evolve linearly with conversion. In the seventies, Minoura reported that MMA polymerization initiated by peroxides in the presence of chromium (II) acetate led to a monotonous increase of molecular weight with conversion [87]. He attributed this to a "living" propagation *via* radicals coordinated to Cr which were not able to terminate. Later, this system was critically evaluated by Banderman

[88] who demonstrated that the system conforms to conventional radical polymerization, and the apparent control resulted from a combination of the dead-end and gel effects. Indeed, efficiency of initiation was very low, often below 10 %.

In 1982 Otsu, for the first time, used the term living radical polymerization to describe a radical polymerization in the presence of dithiocarbamates [89, 90]. In analogy with the inifers used in carbocationic systems, he proposed that dithiocarbamates acted as iniferters, *i.e*. agents which initiate, transfer and terminate. Unfortunately, as with the previously discussed systems, dispersities were always relatively high, molecular weights did not evolve linearly with conversion and initiation efficiency was low. A new system for controlling radical polymerizations, based on nitroxides as mediating stable radicals, appeared in the patent literature in 1985 [91]. Unfortunately, the work of Rizzardo and Solomon was not sufficiently recognized at that time and it was not until 1993 when Georges published his first paper on controlling the bulk radical polymerization of styrene in the presence of TEMPO that interest in controlled radical polymerization was revitalized [92, 93]. TEMPO-mediated systems have been generally limited to styrene and its copolymers and other nitroxides were needed for polymerization of acrylates and other monomers.

The timing for Georges' paper was perfect for our group, as we already received funding for research on controlled radical polymerization. We analyzed possibilities and limitations of "living" radical polymerization based on principles known from other "living" polymerizations in which a small proportion of terminated chains existed but could be tolerated [94]. This allows selecting conditions under which the highest degree of chain end functionality could be preserved: high initial monomer concentration, relatively low targeted *MW*, high temperature and pressure to maximize $k_p/k_t$ ratio, compartmentalization and polymerization of monomers with intrinsically high $k_p$, such as acrylates [94]. We also discussed three types of exchange reactions, including degenerative exchange, a concept that we introduced at that time. Scheme C shows three types of equilibria between active and dormant species in controlled/living radical polymerizations *via*: (i) spontaneous or catalyzed reversible activation of dormant species, (ii) degenerative exchange and (iii) reversible trapping of propagating radicals. Subsequently, all of these concepts have been implemented in many controlled radical polymerizations [95—98]. We used TEMPO in thermal, AIBN (azoisobutyronitrile) and BPO (benzoyl peroxide) — initiated polymerization of styrene, used various substituted nitroxides, *e.g*. 4-phosphonoxy TEMPO derivative and nitronyl-nitroxides to accelerate polymerization, phosphites and organometallic derivatives to control the polymerization of several vinyl monomers [99]. Another approach was based on degenerative transfer with alkyl iodides [99, 100]. It should be stressed that although we estimated at that time what values of rate constants and equilibrium constants are needed for efficient exchange between active and dormant species [94] we were in a continuous search for better systems, hopefully catalytic, to control radical polymerization.

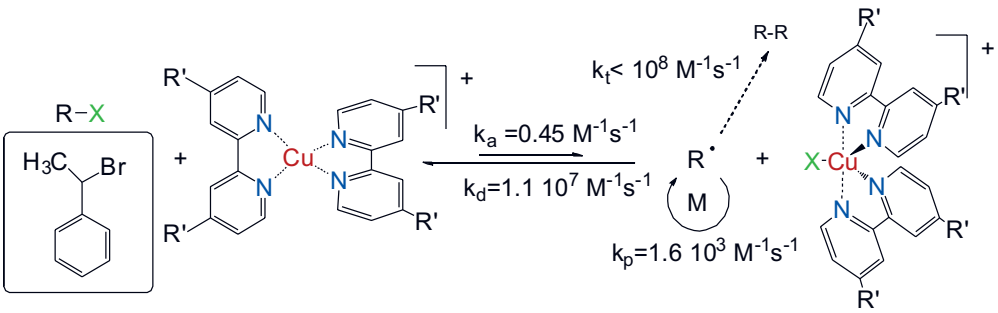



**Scheme C. Three types of equilibria between active and dormant species in controlled/living radical polymerization proceeding by spontaneous/catalyzed reversible activation of dormant species, degenerative exchange and reversible trapping of propagating radicals**

## ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

In 1995 two promising systems for controlling radical polymerization were reported. They were based on catalytic systems used for atom transfer radical additions [101] and therefore were named atom transfer radical polymerization (ATRP). One of these systems was based on the $RuCl_2/(PPh_3)_2$ catalyst which was used for polymerization of MMA initiated by $CCl_4$ [102]. However, this catalytic system was inactive alone and required activation by aluminum alkoxides as cocatalysts. The exact nature of this activation has not yet been established but could involve reduction of $Ru^{III}$ species or exchange of ligands on Ru complexes. The second system was based on the CuX/bpy catalyst (bpy: 2,2′-bipyridyne) which had been used in most efficient atom transfer radical addition reactions [103]. The Cu based ATRP system was successfully applied to the polymerization of styrene, (meth)acrylates, acrylonitrile and several other monomers and comonomers. Various alkyl halides and pseudohalides were used as initiators. Originally, complexes with bpy ligands provided heterogeneous systems and were later replaced by bpy substituted with alkyl groups such as dHbpy (4,4′-diheptyl-2,2′-bipyridine) and dNbpy (4,4′-di(5-nonyl)-2,2′-bipyridine) to provide a homogeneous catalytic system. This considerably improved control and provided polystyrenes with very low dispersities, $M_w/M_n$<1.05 [104].

ATRP has progressively expanded during the last 15 years resulting in development of a very robust and




**Scheme D. Bulk ATRP of styrene at 110 °C catalyzed by $Cu^{I}$/bpy derivatives**

powerful synthetic technique. The research has been developing in three different directions. Mechanistic/kinetic studies focused on searching for new and more efficient catalytic systems and reduction of the amount of Cu catalyst. They are accompanied by expansion of range of polymerizable monomers, media and reactions conditions. The second direction is towards enhanced control of macromolecular architecture: preparation of statistical, gradient, alternating, block and graft copolymer, stars, combs, brushes, (hyper)branched (co)polymers or even networks and supplementing them with various site specific incorporation of functionalities. One of the most rapidly developing areas involves various hybrids and bioconjugates. The third direction is application of tailored materials prepared by ATRP as advanced materials for optoelectronics, health and beauty products, biomedical materials, coatings, sealants, *etc.*, often in collaboration with industry. The three areas will be very briefly reviewed in the next sections. The purpose of this summary is not to provide an extensive discussion but rather to present an overview of ATRP and facilitate an interested reader in locating the original source of information.

## ATRP components

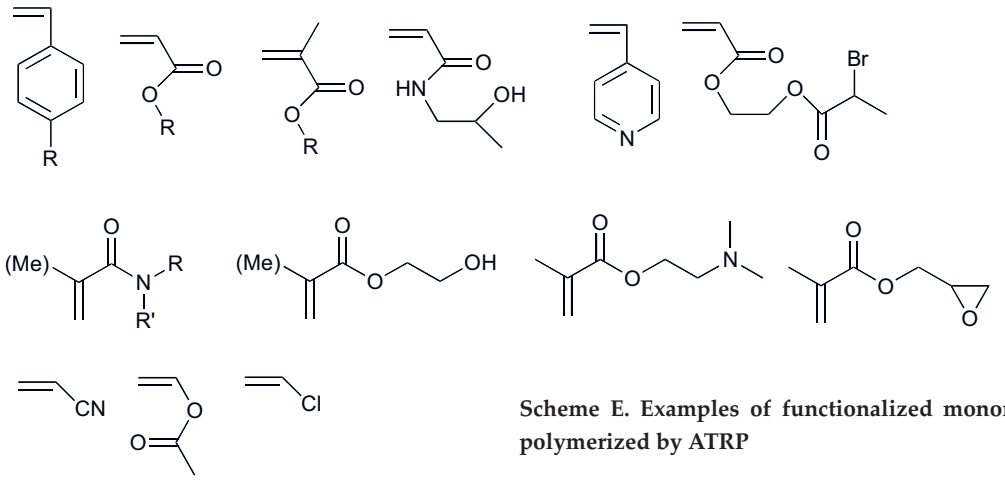
ATRP generally proceeds by inducing a homolytic cleavage of an alkyl-halogen bond (R-X) by a $Cu^{I}$/ligand complex, generating an alkyl radical and a corresponding $Cu^{II}$/ligand complex, other transition metal complexes can be employed. The newly formed radical can initiate polymerization by addition of a vinyl monomer, but can also propagate and terminate by either coupling or disproportionation, or be reversibly deactivated by the $Cu^{II}$/ligand complex. In ATRP, formation of radicals is reversible and one should seek to maintain a low stationary radical concentration and shift the equilibrium between the activation ($k_a$) and deactivation ($k_d$) processes, $K_{ATRP}=k_a/k_d$, strongly to the left-hand side ($k_a<k_d$). This reduces the fraction of terminated chains and enables synthesis of polymers with predetermined molecular weights, narrow molecular weight distributions and high retention of functionalities [105]. This is shown above in Scheme D for ATRP of styrene.

Below, basic components of ATRP will be briefly illustrated.

## Monomers

Copper catalyzed ATRP is applicable to a wide range of monomers that contain α-stabilizing substituents adjacent to the transferable atom or group (Scheme E).

Such substituents provide efficient activation of the dormant chains. The initial range of monomers that could be polymerized by ATRP included styrenes [103], (meth)acrylates [106], meth(acrylamides) [107, 108], and acrylonitrile [109—113]. Subsequently, ATRP was expanded to include several functional monomers including 4-vinylpyridine [114—117], monomers containing



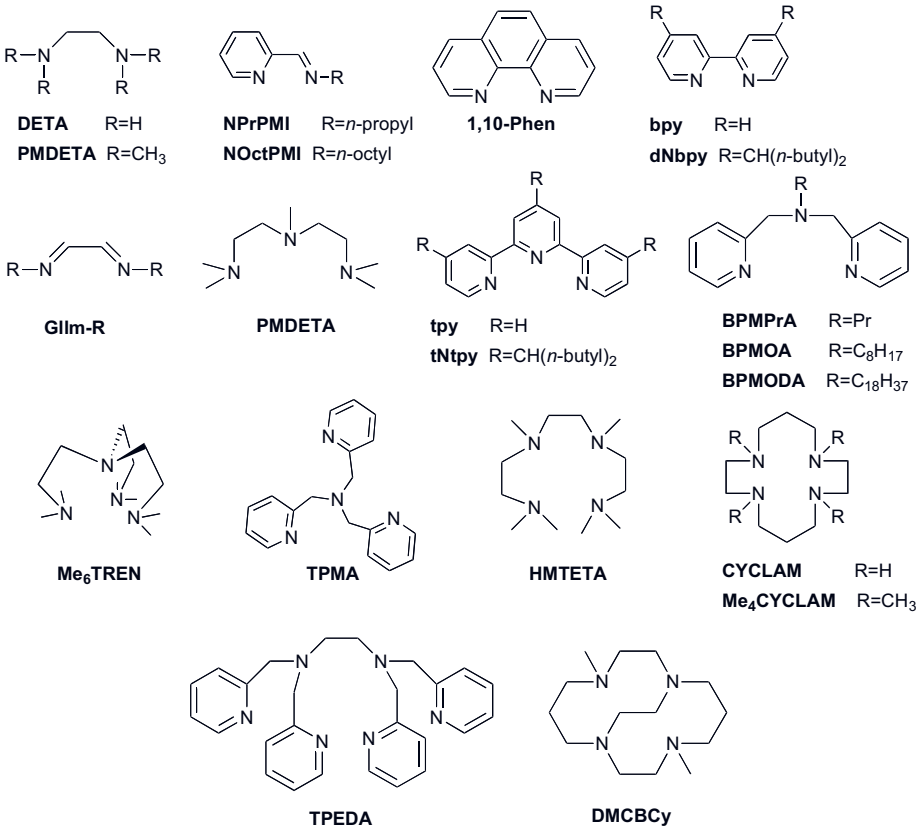

**Scheme E. Examples of functionalized monomers that can be polymerized by ATRP**

OH-group, such as 2-hydroxyethyl acrylate (HEA) [118], 2-hydroxyethyl methacrylate (HEMA) [119—121], and glycidyl acrylate [111, 121—123], and precursors of ionic monomers [124] including dimethylaminoethyl methacrylate (DMAEMA) [125—127], 2-(trimethylammonium)ethyl methacrylate, trifluoromethanesulfonate and 2-(dimethylammonium)ethyl methacrylate bromide [128] or ionic liquid monomers [129, 130]. Glycidyl acrylate [124] has also been copolymerized by ATRP yielding well-defined polymers containing the reactive glycidyl group that can be used as a precursor for other functional groups [123]. Furthermore, both neutral and ionic water-soluble monomers can be polymerized in a controlled fashion by ATRP in protic (aqueous) media [131]. Several macromonomers have been either homopolymerized or copolymerized by ATRP [132—134]. Additionally, simple alkenes have been copolymerized by ATRP with polar monomers [135—138]. Recent improvements in catalysis and expansion of suitable transferable atoms or groups has also allowed successful ATRP of *N*-vinylpyrrolidone [139], vinyl acetate [140] and vinyl chloride [141].

**Initiators**

The polymer chains in ATRP start growing by homolytic cleavage of a carbon-halogen bond in an initiator. The initiator in ATRP can be either a small molecule, macromolecule, or a functionalized surface of any topology, with one or more radically transferable atoms or groups [142]. The best results have been obtained when X has been either a chlorine or bromine, but iodine has also been successful for acrylates, vinyl acetate and vinyl chloride [140, 143—146].

An appropriate combination of the initiator, catalyst and reaction conditions must be selected in order to conduct a successful ATRP. The primary reason is to provide high efficiency of the initiation reaction [147]. Generally, activation rate constants are highest for tertiary alkyl halides, followed by secondary ones. The activity of alkyl bromides is several times larger than that of the analogous alkyl chlorides in reactions mediated by the same catalyst complex. Additionally, polymers prepared by other polymerization processes can be functionalized at the termini or along the backbone and incorporated into an ATRP as macroinitiators [148—152]. This methodology leads to the preparation of well-defined block and graft copolymers comprising a broader range of monomers. Furthermore, the initiator(s) can be attached to any type of polymer, solid surface [153] (particle [154], fiber [155], porous material [156], *etc.*) leading to chain growth in several directions. A functional initiator may carry a second non-initiating functionality, in addition to a radically transferable atom or group, to yield hetero-telechelic materials [157—159], and since ATRP is a radical process, many functional groups can be tolerated in the initiator molecule including hydroxy, epoxy, amino,




**Scheme F. Examples of *N*-based complexing ligands for ATRP**

amido, cyano and azido. Additionally, several other ones can be incorporated in a protected form.

**Ligands for copper catalyzed ATRP**

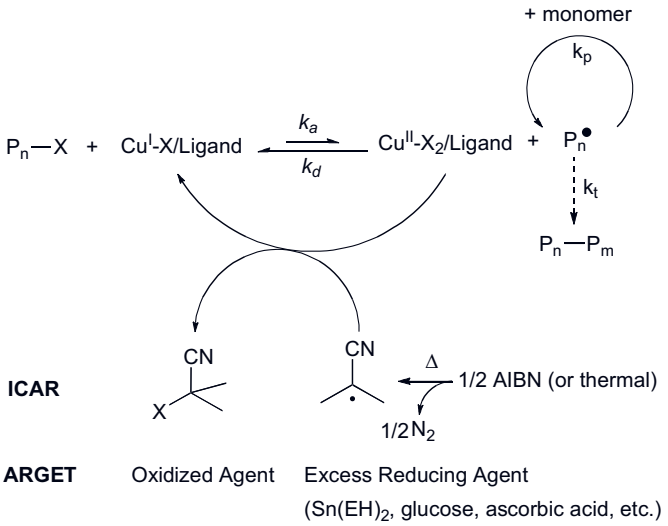
The primary role of the complexing ligand in an ATRP is to solubilize the copper salts and tune the catalytic activity to optimally conduct a well-controlled polymerization. Neutral nitrogen based ligands are typically used in copper catalyzed ATRP. Some representative examples are shown in Scheme F. Depending on the type of amine ligand, the complexes are either neutral (triamines) or ionic (bpy and tetramines) [160].

General order of activity of the copper complex formed with specific type of ligand is: branched > cyclic > linear; N4 > N3 > N2; alkyl amines ~ pyridines > imines > aryl amines. Anionic ligands form stable and active neutral copper complexes, but their deactivation rate constants are lower [161, 162]. Because of the high stability of copper(I) and copper(II) complexes formed with TPMA, this catalyst is particularly suitable for ARGET (activators regenerated by electron transfer) and ICAR ATRP (initiators for continuous activator regeneration), as discussed in the next section [163]. More detailed information about structural and mechanistic aspects of copper catalyzed ATRA (atom transfer radical addition) and ATRP can be found in several recently published review articles [164—168]. ATRP has been successfully mediated by a variety of metals but copper complexes have been the most thoroughly investigated in ATRP and are the most efficient catalysts based on broad range of monomers that can be polymerized and applicability to diverse reaction media, including water, ionic liquids or $CO_2$.

**Methods to initiate an ATRP**

There are several methods to reach ATRP equilibrium, including normal ATRP, shown in Scheme D and the upper part of Scheme G. The same equilibrium can be attained from the opposite side, using conventional radical initiators and $Cu^{II}$/ligand species, as demonstrated in reverse ATRP [169].

An improved reverse ATRP was developed to take advantage of the ability to use more active or readily oxidized complexes [170, 171]. This procedure was named simultaneous reverse and normal initiation (SR&NI) because the activator and a small fraction of initiating chains were formed in a "reverse" ATRP reaction, while the majority of the growing polymer chains were initiated from the added normal ATRP initiator molecule. The limitation of normal and simultaneous reverse initiation in copper mediated ATRP is evident in the inability of these techniques to produce clean block copolymers. This problem was resolved in AGET (activators generated by electron transfer) ATRP, where stoichiometric amounts of the reducing agents are added to the reaction mixture containing alkyl halide, monomer and the air stable deac-




**Scheme G. Regeneration of copper(I) complex in ARGET and ICAR ATRP**

tivator (X-$Cu^{II}$), to regenerate the activator ($Cu^I$). After the regeneration of the activator ($Cu^I$), the polymerization kinetics resemble the kinetics of conventional ATRP. AGET ATRP utilizes reducing agents that are unable to initiate new polymer chains such as zero valent copper, tin(II) 2-ethylhexanoate, ascorbic acid or triethylamine [131, 172—176]. This technique has been shown to be particularly useful in aqueous and miniemulsion systems where it simplifies the set-up procedure [172, 177—184].

**ATRP with ppm Cu catalysts**

Sufficiently stable and active ATRP catalyst could be used at very low concentrations. However, as a result of unavoidable radical termination reactions, the $Cu^I$ complex is converted to a higher oxidation state complex (X-$Cu^{II}$). Therefore, the deactivator (X-$Cu^{II}$) will accumulate in the system as the propagation and termination proceed and reaction would stop at low conversion. This could be avoided if the $Cu^I$ activator could be regenerated as in ARGET or ICAR ATRP in the presence of the reducing agent or radical initiator as shown in the lower part of Scheme G [185—187].

**Thermodynamics and kinetics of ATRP**

ATRP is a radical process, and the chemoselectivity [188], cross-propagation kinetics [189], kinetic isotope effects [190], the reactivity ratios [189, 191—195], and regio- and stereo-selectivity [106, 192, 196, 197] are similar to free radical polymerizations. ATRP can be conducted in the presence of water or other protic solvents, and is tolerant to a wide variety of functionalities present in the (co)monomers [198, 199]. Cross-exchange between different halogens [200] and different polymerization systems (thermal and ATRP or nitroxide mediated polymerization and ATRP) demonstrates that these reactions have

the same intermediates and supports a common radical mechanism [201]. ATRP can be converted to a system that displays conventional radical polymerization by the addition of octanethiol as a chain transfer reagent [202]. Chain transfer in *n*-butyl acrylate polymerization also resembles the conventional radical process [203], although backbiting could be less pronounced [204—206]. Lastly, racemization studies using optically active alkyl halides [207], direct observation of deactivator species (transition metal complexes in the higher oxidation state, *i.e.* $Cu^{II}$) [208—212] and propagating free radicals in the polymerization of dimethylacrylates [213] by EPR also supports a radical mechanism.

Mechanistically, atom transfer radical process occurs *via* an inner sphere electron transfer (ISET) process, *i.e.* atom transfer passing through a Cu-X-C transition state, which is formally also a single electron transfer process. According to Marcus analysis of electron transfer processes, outer sphere electron transfer (OSET) should be approximately $10^{10}$ times slower than ISET [214].

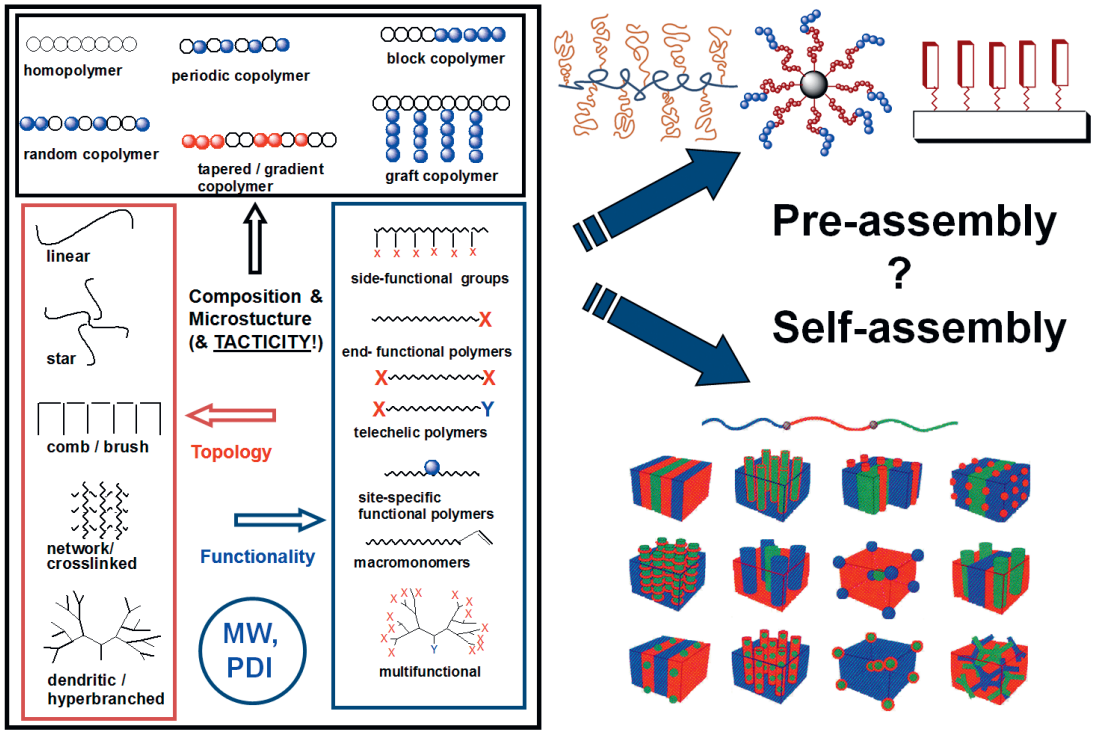
Perhaps, the most important reaction parameters in an ATRP are the activation ($k_a$) and deactivation ($k_d$) rate constants, and consequently the equilibrium constant for atom transfer ($K_{ATRP} = k_a/k_d$). They depend on the structure of the alkyl halide/monomer, the structure of the copper complex, the solvent, temperature, and pressure [215—231]. Systematic evaluation of $K_{ATRP}$, $k_a$ and $k_d$ is crucial for further understanding of the ATRP mechanism and can provide information about the nature and reactivity of active intermediates, and factors needed to design more active catalysts that can be used in lower concentrations and also polymerize currently inactive monomers.

ATRP can be carried out in bulk, in organic solvents, and in aqueous media under homogeneous conditions or in dispersed media.

## Control of polymer architecture

ATRP is a versatile tool for preparation of various polymers with precisely controlled macromolecular architectures. Scheme H illustrates some examples of polymers with controlled chain composition, topology and functionality that have been prepared using ATRP.

Concerning composition, one can prepare homopolymers and statistical (random) copolymers from monomers with similar reactivities. However, if the reactivities of the comonomers are different, then gradient copolymers can be formed [193, 232—236]. Gradient copolymers with continuously varied composition along the polymer chain can also be formed from comonomers with the same reactivity by using a feeding technique [237, 238]. Copolymerization of comonomers with very low reactivity ratios can lead to alternating or periodic copolymers. They can also be formed if one less reactive comonomer (such as simple alkene) is used in large excess. Sometimes, complexation with Lewis acid can additionally enhance tendency for alternation [239, 240]. Nevertheless, the most common products are segmented copolymers such as block and graft copolymers. The former can be formed by sequential addition of comonomers and also by segmental coupling (using *e.g.* click chemistry), mechanistic transformation (from/to ATRP and ionic, coordination or polycondensation) or even 2-directional concurrent growth by different polymerization mecha-




**Scheme H. Controlled molecular structures accessible by ATRP**

nisms [241—250]. Appropriate sequence of comonomer addition is very important when preparing block copolymerization solely by ATRP, but sometimes cross propagation from less readily activated monomer to more readily activated monomer can be additionally enhanced by halogen exchange process. Radical polymerization is generally not efficient for the control of stereochemistry and polymer tacticity. However, in the presence of Lewis acids such as $Y(OTf)_3$ and $Yb(OTf)_3$ poly(dimethylacrylamide) with strongly enhanced isotacticity was prepared as well as the first block copolymers with atactic and isotactic segments [251].

There are many examples of controlling polymer chain topology using not only linear but also branched architectures. They can include synthesis of star polymers using either the core-first or arm-first approaches [246, 252—261]. The latter relies on using macroinitiators or macromonomers and divinyl crosslinking agents. Stars are formed in high yield and with high uniformity under appropriate conditions, instead of macroscopic gels/networks. Gels prepared by ATRP are different from those made by conventional RP, due to higher chain uniformity; they swell more and can be degraded easier when degradable crosslinkers are used [262—268]. One can also prepare comb-like polymers by grafting from, onto and through using macromonomers. Very dense grafting along the polymer backbone results in formation of macromolecular bottle-brush structures. They can be very large macromolecules with $M_n$ values exceeding several millions that can not only be visualized by AFM as single molecules but also used as various sensors and model tensile machines [269—278]. ATRP has been also used for synthesis of randomly branched and hyperbranched polymers and even for dendritic systems [279—282] and, cyclic polymers have been prepared by ATRP or ATRP and nitroxide coupling.

ATRP is tolerant of many functional groups such as hydroxy, cyano, amino, amido, esters and others but acids should be protected to prevent ligand protonation. This can be accomplished at higher pH or in the presence of amines that scavenge protons. Functionality can be incorporated *via* monomers, or initiators [283—285]. One of many advantages of ATRP is the availability of various functional initiators and facile preparation of multifunctional systems by simple esterification of precursor molecules to form 2-bromopropionates or 2-bromoisobutyrates. These precursor molecules not only include simple organic polyols, but also natural products and flat, concave and convex inorganic surfaces. Moreover, displacement of halides from the chain ends provide not only a variety of homo and hetero telechelics but also many multifunctional stars or (hyper)branched systems.

The properties of many materials are defined not only by the architecture a single macromolecule but by their self-assembly to various nanostructured materials. In addition, various pre-assembly procedures are also possible by surface patterning, grafting from various functional surfaces and even from linear polymer chains. There are many morphologies available for block copolymers, depending on the block order, interactions parameters and volume fractions, that result in formation of spheres, cylinders, lamellae and bicontinuous structures in various combinations [286—289].

Molecular hybrids comprise synthetic polymers covalently tethered to inorganic materials and natural products [290—292]. The well-defined organic-inorganic hybrids can be formed by grafting from flat, convex, concave or irregular surfaces [293, 294]. Surfaces of gold, silicon, silica, iron and other inorganic substrates were functionalized with bromoesters to initiate growth of polystyrene, poly(meth)acrylates, polyacrylonitrile or polyacrylamide chains *via* ATRP [295]. It is possible to vary grafting density and prepare very densely grafted films, with density approaching ~0.5 to 1 chain/$nm^2$ [296, 297]. Grafting density can be continuously varied along the substrate to prepare surfaces with a macroscopic gradient [298]. Very dense grafting is not possible *via* grafting onto, since attached polymer chains collapse on the surface and prevent other chains in the solution from reaching the surface. Furthermore non-uniform growth cannot provide high grafting density. It is only when polymer chains grow by adding a few monomer units during each activity period that high grafting density is possible. The resulting hybrids have many new and unusual properties related to their unique compressability, lubrication properties and, reduced swelling or interpenetration [297]. Grafting can be performed by normal ATRP but also by ARGET [299].

It is also possible to graft polymers and block copolymers onto inorganic surfaces. For example, poly(methacrylic acid)-*block*-poly(methyl methacrylate)-*block*-poly(sodium styrenesulfonate) prepared by ATRP was grafted onto ~200 nm diameter iron particles to destroy residual chlorinated pollutants [300].

The slower controlled chain growth in ATRP facilitates better control in templated systems. Mesoporous silica was functionalized with bromoesters and used to grow polyacrylonitrile, polystyrene or poly(meth)acrylates. The growth of polymer chains was followed by TGA, porosity and analysis of detached polymers. Highly uniform growth was achieved on the molecular level (as evidenced by low dispersity of detached polymers analyzed by GPC) but also macroscopically (overall porosity measurements).

Functional groups in natural products have been converted to ATRP initiators ($NH_2$ or OH groups converted to bromoamides and bromoesters) [155, 291, 301]. In order to retain the properties of the natural product the original substrate should not interfere with the ATRP process during the polymerization and the functionality and properties of the natural products should not be affected by ATRP. Alternatively, chains prepared by CRP containing functionalities ($NH_2$ or OH) can be used to grow polypeptides or DNA. It is also possible to fuse functio-

nalized natural products and organic polymers together either with click reactions, by biotin-avidin chemistry or from genetically modified peptides [291, 302—315].

**Applications of materials prepared by ATRP**

Block copolymers based on acrylates and other polar monomers could find application as polar thermoplastic elastomers [316] in automotive applications, as they do not swell in hydrocarbons. However, they can also be used for much more sophisticated applications such as controlled drug-release in cardiovascular stents [317]. Amphiphilic block copolymers with water soluble segments were successfully used as very efficient surfactants [318] and were also used for higher end applications including pigment dispersants [319, 320], various additives, and as components of health and beauty products. Segmented copolymers with nanostructured morphologies are being evaluated in microelectronic devices [283, 321].

Graft copolymers have been used as compatibilizers for polymer blends and may be used in many applications described for block copolymers [322]. Gradient copolymers display promise in applications ranging from surfactants to noise and vibration dampening materials [193, 323, 324]. Designed branching allows precise control over melt viscosity and polymer processing while comb and star polymers can be used as viscosity modifiers and lubricants [325].

The ultimate example of controlled topology might be molecular bottlebrushes [326]. Such polymers, when lightly crosslinked, result in supersoft elastomers [327]. Environmentally stable materials were synthesized with moduli ~ 1 kPa, in the range attainable by hydrogels. Molecular brushes are swollen by their own short side chains that do not entangle and never leach. These materials can have very high ionic conductivities, reaching 1 mS/cm for Li cations at room temperature [328]. Brushes were used as a core-shell cylindrical templates to prepare various nanostructured materials [329—331].

ATRP offers unprecedented control over chain end functionality. End functional polyacrylates are excellent components of sealants for out-door and automotive applications [332, 333]. Multifunctional low *MW* polymers are desirable components in coatings with a low organic solvent content important for VOC reduction [334]. Incorporation of degradable units into the backbone of vinyl polymers allows controlled cleavage and degradation/recycling of such polymers.

Molecular hybrids with a covalent attachment of well-defined functional polymer to either an inorganic component or a natural product can provide materials with previously unattainable properties. Such hybrids allow better dispersability of inorganic components (pigments, carbon black, carbon nanotubes, nanoparticles), they dramatically enhance the stability of such dispersions, and they allow the formation of molecular nanocomposites. Also, dense polymer layers improve lubrication, prevent corrosion, and facilitate surface patterning. Precise grafting from chromatographic packing enables enhanced chromatographic resolution of oligopeptides and synthetic prions [335].

Other potential applications include microelectronics, microfluidics and optoelectronics, as well as biomedical applications such as components of tissue and bone engineering, controlled drug release and drug targeting, antimicrobial surfaces [336], steering enzyme activity [291, 314, 337—339], and many others.

At Carnegie Mellon University, we formed two consecutive research consortia focused on ATRP and then on broader aspects of controlled radical polymerization with participation of over 50 international industrial companies. We have signed 16 licensing for production of advanced polymers using ATRP technologies and commercial products prepared by ATRP have been introduced to the market since 2004 in Japan, US and Europe.

In summary, the process of intermittent activation of dormant species, initially studied in the laboratory of Professor Penczek at Polish Academy of Sciences in Lodz in 1970s has been expanded to many other controlled polymerization processes. This procedure is the essence of controlled radical polymerization processes, including ATRP, and provides a simple but powerful and efficient technique to prepare polymers with controlled composition and architecture that are of increasing commercial relevance and importance.

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