New (Co)polymers by Atom Transfer Radical Polymerization

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SUMMARY: The fundamentals of atom transfer radical polymerization (ATRP) are presented. This includes the mechanistic considerations including structure of active and dormant species and structural features of the catalyst and reaction conditions as well as the nature of initiation and propagation steps. Extension of homogeneous polymerization to heterogeneous systems including emulsion polymerization is presented. Synthesis of (co)polymers with predefined molecular weights and low polydispersites as well as with controlled compositions, functionalities and architectures is reviewed.

Introduction

Controlled radical polymerization (CRP) is a new synthetic method which enables preparation of well-defined polymers from radically polymerizable monomers.[1] Like in other controlled/"living" systems, evolution of molecular weights is proportional with conversion ($DP_n = \Delta[M]/[I]_0$), polymers have narrow molecular weight distributions ($M_w/M_n < 1.5$) and precisely controlled end functionalities. It is also possible to synthesize block and graft copolymers and prepare macromolecules with novel architectures such as stars, combs, hyperbranched, etc. in sharp contrast to conventional radical systems.[2]

Three general prerequisites should be fulfilled for CRP: initiation should be fast in comparison with propagation, degrees of polymerization should be predefined by $\Delta[M]/[I]_0$ ratio

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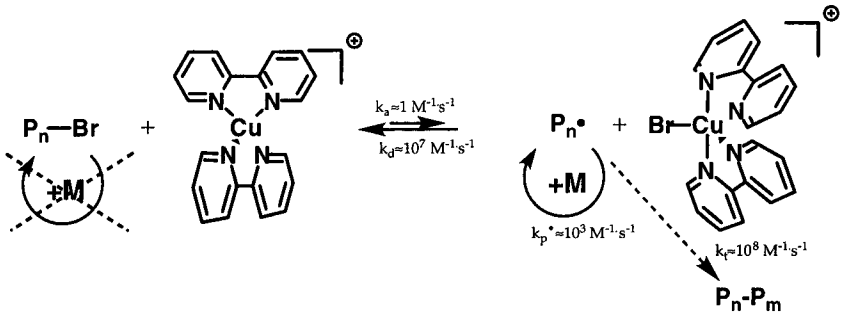
and low enough to minimize effect of chain breaking reactions (transfer and termination) and equilibrium between growing radicals and dormant chains should be establish. The equilibrium constant and dynamics of exchange is among the most important features of CRP. Three general approaches towards equilibrium can be used: degenerative transfer, reversible formation of persistant radicals and reversible cleavage of covalent bonds to produce growing radicals and stable radicals.[3] There are two very successful systems which employ the last approach, they are based on non-catalyzed homolytic cleavage of alkoxyamines[4,5] and transition metal catalyzed cleavage of alkyl halides, i. e., atom transfer radical polymerization, ATRP.[6,7]

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·), 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. ATRP is a simple extension of the well known atom transfer radical addition (ATRA) reactions that have been widely used in organic chemistry.[8] A similar equilibria are established at the propagation stage:



A catalytic system employing copper (I) halides (M_t^n/Ligand) complexed with 2,2'-bipyridines (bpy) has proven to be quite robust, successfully polymerizing styrenes,[7,9-11] various (meth)acrylates,[9,12,13] acrylonitrile [14] and other monomers.[15] Other metal centers have been used, such as ruthenium,[6] nickel[16,17] and iron [18,19] based systems. Copper salts with various anions[20] and polydentate complexing ligands were used, such as substitued bpys,[21] pyridines,[13] and linear polyamines.[22]

Mechanism

Based on the proposed mechanism, the kinetics of the polymerization is expected to conform to the rate law in equation 1. When sufficiently large amount of the deactivator is added, the polymerization is first order in monomer, initiator (R-X), metal catalyst, and inversely proportional in deactivator. Although initial studies indicated that the kinetics were not first order with respect to the catalyst, but only fractional, this was apparently due to the incomplete solubility of the catalyst using the simple bpy ligand. When more soluble catalyst systems were used, i.e., with 4,4'-dialkyl substituted bipyridines, the reaction followed first order kinetics with respect to the copper (I) catalyst.[23]

$$R_p = k_p[M]\frac{k_a}{k_d}[R-X]_o\frac{[M_t^n]}{[X-M_t^{n+1}]} \quad (1)$$

Obtaining the external order with respect to the deactivator has proven to be more complicated due to its generation in situ, resulting from a small proportion of bimolecular termination. The rate of the deactivator formation progressively slows down as the concentration of radicals is lowered due to the higher concentration of the deactivator; the equilibrium is shifted towards the dormant species. This persistent radical effect is responsible for self-regulation by the catalyst system.[24] The effect of externally added deactivator becomes apparent only when the amount of added deactivator is greater than that formed spontaneously by the polymerization system.[23] When no deactivator is added, a fractional orders may be observed, dependent on the effect of the chain lengthon the rate constants involved.

The dynamics of equilibration process has been measured by the evaluation of polydispersities, direct rates of the activation process and measurements of the equilibrium constants from the kinetics of propagation.[23,25]

Determinating if the polymerization is truly based on a free radical or is mediated by the metal center has not been straightforward. There is really no one reaction which unequivocally determines the reaction mechanism. However, there are numerous criteria, when taken together, can be helpful to determine the nature of the propagating species. These include

chemoselectivity (the reactivity ratios for copolymerizations,[26] the effect of added reagents, such as protic solvents, radical scavengers, transfer agents), stereoselectivity (the tacticity of the resulting polymer), regioselectivity (structure of end groups and proportion of head-to-head structures) and elucidation of the mode of termination, i.e., coupling/disproportionation and the concurrent formation of Cu(II) species.[27]

Additional support for a radical mechanism has been the development of "reverse ATRP." In this system, the transition metal catalyst is, initially, the high oxidation state metal halide, e.g., $Cu(II)Cl_2/L$.[28] In the presence of a conventional free radical initiator, i.e., AIBN, the radical reacts with the metal halide to form the alkyl halide and the lower oxidation state metal. After nearly all of the initiator and metal halide have been consumed, the controlled / "living" radical polymerization begins. Significant improvements in control and polydispersities were observed when a soluble catalyst system (ligand: 4,4'-di(5-nonyl)-2,2'-bipyridine = dNbpy) was used when compared to a heterogeneous system (bpy).[29] The addition of CuCl/2dNbpy to the AIBN initiated radical polymerization of styrene had no effect on the kinetics of the polymerization or on the final molecular weight of the resulting polymer. This indicates that the propagating radicals do not interact significantly with the copper (I) complex in the polymerization of styrene. [23] However, some rate reduction observed in the presence of Cu(I) species in the AIBN initiated polymerization of methyl acrylate, may indicate some interactions of electrophilic radicals with Cu(I).

ATRP is a radical polymerization system which is based on the reversible activation and deactivation of propagating radicals. Activation occurs by an inner sphere electron transfer reaction between an alkyl halide (R-X) and a transition metal (M_t^n) to form a radical and a metal halide ($X\text{-}M_t^{n+1}$) with rate constant $k_a \approx 10^{-1\pm1}$ $M^{-1}s^{-1}$; deactivation occurs when the propagating radical reacts with the metal halide to reform the alkyl halide and the lower oxidation state transition metal, with rate constant $k_d \approx 10^{7\pm1}$ $M^{-1}s^{-1}$. The equilibrium constant, $K = k_a/k_d$, and the rate constants of the exchange are dependent on the polymerization system and vary with monomer/halogen/metal/ligand/temperature/solvent. The fast deactivation process is responsible for obtaining good control of the molecular weight and low polydispersities in ATRP which depend not only on the rate constants of propagation and deactivation but also on the

concentration, i.e. solubility of the deactivator (Cu(II) species). Reactivity of the deactivator may be fine tuned by the ligands and halogen atoms. Typically, Br is exchanged faster than Cl.[23] Recent results indicate that significantly faster and better controlled polymerization can be achieved by replacing substituted bipyridines with linear triamines and tetraamines [22] and with Me_6TREN ligands:

Table 1.

Bulk ATRP of Methyl Acrylate with CuBr/Me_6TREN at 22° C and $[MA]_0/[2\text{-EBP}]_0 = 232$

entry	$[catalyst]_0/[2\text{-EBP}]_0$	time (h)	conv (%)	$M_{n,\,Cal}$	$M_{n,\,SEC}$	f^a	M_w/M_n
1	1.0	0.50	66	13200	17900	0.74	1.24
2	0.2	1.00	57	11400	12600	0.90	1.10
3	0.1	1.00	41	8200	9100	0.90	1.09
4[b]	0.1	0.10	8	1600	773500	0.002	2.98

[a] $f = M_{n,\,Cal}/M_{n,\,SEC}$. [b] unsubstituted TREN was used as the ligand

It seems that it is possible to prepare well defined poly(methyl acrylate) with low catalyst concentration (10 mol% in respect to initiator) at room temperature when methylated TREN is used as ligand. Non-methylated TREN leads to uncontrolled polymerization with low yield and very high molecular weight.

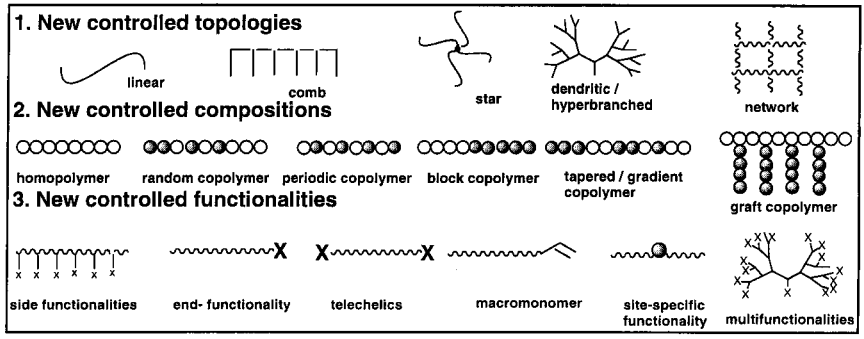
Additional significant improvement has been recently accomplished in ATRP systems by application of zerovalent metals which can reduce concentration of the deactivator.[30] Polymerization rate increases strongly but control is still maintained. The efficient system requires relatively large size of copper (-100 mesh or even copper turning) since a large surface metal powder (copper, 1 μm) results in a too fast disproportionation of copper(II) with copper(0) to form copper(I) and a loss of control. In the presence of Cu(O), controlled ATRP can be conducted for unpurified monomers containing inhibitors and finite amount of oxygen.

Recently, ATRP has been also extended to emulsions, suspension, dispersion and homogeneous aqueous media. For example, well defined polymers in the range of molecular

weights M_n=10,000 to 20,000 and low polydispersities M_w/M_n= 1.11 (poly(butyl acrylate)), 1.07 (polystyrene) and 1.19 (poly(butyl methacrylate)) were prepared in aqueous emulsions using Brij® 98 as emulsion stabilizer, ethyl 2-bromoisobutyrate as initiator and CuBr/2dNbpy as a catalyst. With Brij® 98 emulsions were stable for a few days, however, with Brij® 97 coagulation was observed although molecular weight and polydispersities control was also quite successful. Particle size distribution is relatively narrow (≈1.2) and the particle size is in the range 0.1 to 1 nm, depending on the surfactant, initiator, temperature, monomer, etc.

Materials

The most important benefit of controlled/"living" polymerizations is that they allow to prepare new macromolecules with novel topologies (linear, star, comb, (hyper)branched, notworks, etc.), varying compositions (homopolymers, random, periodic, block, graft and gradient copolymers), and functionalities placed at different parts of macromolecules or various combinations of these. Some of the possibilities are outlined below.



The extent of the control of polymerization is defined by how low a polydispersity and how high a molecular weight can be obtained for a given monomer. Well-defined polystyrenes and poly(meth)acrylates as well as polyacrylontrile have all been prepared with chain lengths ranging from oligomers (DP_n < 10) to high polymer, M_n ≈ 100,000, and with polydispersities significantly below M_w/M_n = 1.5, in some cases M_w/M_n < 1.1. The control of the polymerization is limited by side reactions including: diradical termination, elimination of HX from the chain end, and oxidation/reduction of the radical to the corresponding cation/anion.[31] Understanding

and avoiding these side reactions will be of prime importance in the future development of higher molecular weight polymers, $M_n > 100{,}000$, with low polydispersities, $M_w/M_n < 1.1$.

Monomers which generate very reactive radicals which are not stabilzed by resonance, such as α-olefins, vinyl acetate and vinyl chloride produce very low concentration of radicals due to low equilibrium constants and polymerize very slowly although copolymerization is more successful. Some other monomers, such as acrylic acid, interfere with the catalyst and lead to limited polymer yields.

Controlled Compositions by ATRP Another driving force for the development of a controlled / "living" radical polymerization is to allow for the copolymerization of two or more monomers. This has been demonstrated with ATRP by copolymerization of various combinations of styrene, methyl or butyl acrylate, methyl or butyl methacrylate, and acrylonitrile.[32,33] ATRP allows for the copolymerization of these monomers using all feed compostions without loss of control of the polymerization; this is in contrast to the use of nitroxides in controlled radical polymerizations, which must contain a significant amount of styrene as comonomer to retain control of the polymerization.[34] 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 compatiblization and vibration dampening. [32]

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 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; bromoterminated polyacrylate in the presence of CuCl/L is an efficient iniator for MMA polymerization due to reduced polymerization rate of PMMA-Cl species which are predominantly formed after the exchange process.[35]

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[36] and polysulfone[37] (step-growth polymerization), polynorbornene and poly(dicyclopentadiene) (ROMP),[38] polyisobutene (cationic polymerization),[39] poly(vinyl chloride)[40] and poly(THF) (cationic ring opening polymerization). 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).[41] 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.

The polymerization of AB* monomers (A = double bond, B* = latent initiator group) can lead to branched and hyperbranched polymers.[42] 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)[43] and 2-(2-bromopropionyloxy) ethyl acrylate (BPEA) with 1 mol% of Cu(I)Br/2dTbpy (dTbpy = 4,4'-di(t-butyl)-2,2'-bipyridine).[44] 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 tetrabutyl ammonium 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.[45]

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.[46]

To conclude, atom transfer radical polymerization, ATRP is a robust method for preparing well-defined polymers and novel materials with unique compositions and architectures. This paper discusses the basic mechanism of ATRP, some of new catalytic systems and conditions, and has provided a sampling of the broad range of materials that have been prepared. Although significant progress has been made in the past few years since the development of ATRP, a continuous research on the better mechanistic understandingof ATRP, preparation of more efficient catalyst systems to yield more well-defined polymers and polymerize new monomers is needed. Synthesis of new materials need to be optimized and their properties should be studied.

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