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Progress in controlled/living polymerization in aqueous media***)

Part I. PRINCIPLES AND METHODS

Summary — A review with 113 references covering fundamentals, principal phenomena, general features and experimental criteria for CLP, *viz.*, (*i*) fullfilment of the first-order reaction kinetics (*i.e.*, ln(monomer concentration), or $\ln([M]_0/[M])$, is a linear function of time; no termination; constant concentration of active centers); (*ii*) number-average *M* is a linear function of the degree of monomer conversion; (*iii*) narrow *MWD*; (*iv*) long lifetime of polymer chains able to propagate (owing to absence of chain transfer and termination). CLP methods are presented, *viz.*, anionic polymerization including group transfer polymerization (GTP), cationic polymerization, which is much more difficult to carry out; ring opening metathesis polymerization; coordination polymerization; radical polymerization (involving stable free radicals (SFRP); atom transfer (ATRP); and utilizing the degenerative chain transfer reaction with chain transfer agent used in excess over radical initiator).

Key words: controlled/living polymerization, living anionic polymerization, group-transfer polymerization (GTP), living cationic polymerization, living ring-opening metathesis polymerization (ROMP), living coordination polymerization, living radical polymerization.

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Since Staudinger [1] introduced eight decades ago the concept of a chain polymerization and the basic structure of a polymer molecule, polymer science and technology has experienced an immense development that revolutionized the world and the life of human beings. Numerous polymeric materials have been created owing to the continuous progress in understanding the

fundamentals of polymerization. One of the greatest contributions to this field from synthetic polymer chemists is the living polymerization methodology, which allows the preparation of macromolecules with the maximum degree of structural and compositional homogeneity. As a consequence, well-defined polymers with precise molecular weights, compositions, topologies and functionalities can be tailor-made. This is a significant step toward the ultimate goal of polymer synthesis, when the design of novel materials is only limited by the imagination of human beings.

DEFINITION

The terms "living polymerization" and "living polymers" were introduced by Szwarc [2] in 1956, although prior to his classical work, Ziegler [3] and Flory [4] also described similar systems. By definition, living polymerization is a chain polymerization that proceeds with no irreversible chain breaking processes, *i.e.*, neither chain transfer nor termination. This ideal case, however, has been achieved only in a few anionic polymerization systems [5, 6]. In reality, most of the so-called living polymerizations, especially those proceeding *via* a cationic or radical mechanism, are not free from chain transfer or termination. To differentiate these imperfect polymerizations from the ideal living polymerization, terms such as controlled, "living", pseudo-living, quasi-living and many others have been used in the literature, which initiate an on-going debate on the nomenclature [7]. Before a uniform terminology is settled, we use the term "controlled/living polymerization" (CLP) to describe all the polymerization processes from which polymers with predetermined molecular weights, low polydispersities and high functionalities can be obtained.

GENERAL FEATURES AND EXPERIMENTAL CRITERIA FOR CLP

It is widely accepted that CLP should display the following features [6, 8, 9]:

Feature 1. The first-order kinetic behavior, *i.e.*, the logarithm of monomer concentration ([M]) is a linear function of time. This is due to the lack of termination, so that the concentration of the active propagating species ([P*]) is constant.

$$R_p = \frac{-d[M]}{dt} = k_p[P^*][M] \quad (1)$$

$$\ln\frac{[M]_0}{[M]} = k_p[P^*]t = k_p^{app}t \quad (2)$$

R_p and k_p are the propagation rate and the propagation rate constant, respectively. Equation (2) is presented graphically in Fig. 1. This semilogarithmic plot is very sensitive to changes in the concentration of the propagating species. The straight line represents the case of constant [P*] and an upward curvature indicates an increasing [P*] — the case of slow initiation. On the other hand, a downward curvature suggests the decrease of [P*], resulting from either termination or other side reactions that slow down the generation of active species, *e.g.*, poisoning of a catalytic system.

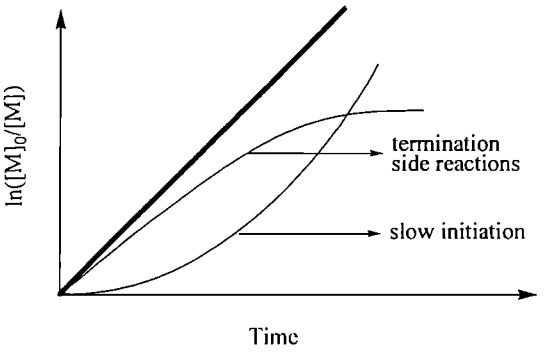


Fig. 1. Illustrative graph of $ln([M]_0/[M])$ vs. time

In conventional polymerizations, where termination occurs readily, a first-order kinetics could also be observed. The origin of the straight line, however, is that the termination is compensated by continuous generation of active species, occurring at a rate equal to the rate of termination, so that the concentration of the active species remains constant. The semilogarithmic plot is insensitive to a chain transfer process or to a low exchange between different active species, since they do not affect the number of the active propagating species.

Feature 2. The predetermined degree of polymerization (X_n), *i.e.*, the number-average molecular weight (M_n), is a linear function of monomer conversion.

$$X_n = \frac{M_n}{M_0} = \frac{\Delta[M]}{[I]_0} = \frac{[M]_0}{[I]_0} = (\text{conversion}) \quad (3)$$

M_0 is the molecular weight of the monomer unit. The above result is due to the constant number of chains existing throughout the polymerization, and requires the following two conditions to be met: (*i*) initiation should be sufficiently fast so that the chains start to grow simultaneously; (*ii*) no chain transfer occurs to increase the total number of chains. Figure 2 illustrates

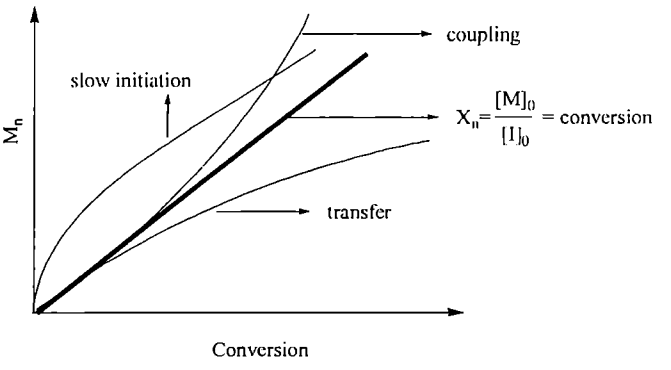


Fig. 2. Illustrative graph of molecular weight vs. conversion

the ideal growth of molecular weights with conversion, as well as the effects of slow initiation and chain transfer on the molecular weight evolution.

Importantly, the evolution of molecular weights is not very sensitive to chain termination, since the number of chains remains unchanged. Only when the coupling reaction plays a significant role is the effect of termination observable on the plot.

Penczek *et al.* [9] combined both Feature 1 and 2 into a single equation:

$$\ln\left(1-\frac{[I]_0}{[M]_0}X_n\right) = -k_p[I]_0 \cdot t \tag{4}$$

The linearity of the plot of the left-hand side of eq. 4 *vs* time t becomes a sufficient criterion to exclude both chain termination and transfer reactions.

Feature 3. Narrow molecular weight distribution. Although this feature is very desirable, it is not necessarily inherent in the living polymerization, which requires only the absence of chain transfer and termination, but ignores the rate of initiation, exchange and depropagation. Studies [6, 8, 10] indicate that in order to obtain a polymer with a narrow molecular weight distribution, each of the following five requirements should be fullfilled: (*i*) The rate of initiation is at least comparable with the rate of propagation. This condition allows all the polymer chains to grow simultaneously. (*ii*) The exchange between species of different reactivities is fast as compared with propagation. This condition ensures that all the active chain termini are equally susceptible to the reaction with the monomer for a uniform growth. (*iii*) Chain transfer and termination must be negligible. (*iv*) The rate of depropagation is substantially lower than that of propagation. This guarantees polymerization is irreversible. (*v*) The system is homogeneous and mixing is sufficiently fast. Therefore, all the active centers are introduced at the onset of polymerization.

Under such conditions, a polymer with a Poisson distribution can be formed, as quantified in eq. 4, where $X_w(M_w)$ and $X_n(M_n)$ represent the weight and number-average degrees of polymerization (molecular weight), respectively.

$$\frac{X_w}{X_n} = \frac{M_w}{M_n} = 1+\frac{X_n}{(X_n+1)^2} = 1+\frac{1}{X_n} \tag{5}$$

According to eq. 5, polydispersity (M_w/M_n) decreases as the molecular weight is increased. A polymerization that satisfies all five prerequisites listed above is expected to have a final polymer with a polydispersity less than 1.1 at X_n greater than 10.

Feature 4. Long-lived polymer chains [11]. This is the consequence of the negligible chain transfer and termination. Hence, all the chains retain their capabilities of further growth after the monomer has been fully consumed. Propagation resumes upon an additional monomer has been introduced. This unique feature enables block copolymers to be prepared by sequential monomer addition.

APPLICATIONS OF CLP

The significance of CLP as a synthetic tool has been widely recognized. With polymers having uniform and predictable chain lengths readily available, it provides the best opportunity to control the bulk properties by variations introduced at the molecular level. Furthermore, a variety of novel polymer materials (Table 1) can be generated by using this powerful technique.

T a b l e 1. Polymers available by CLP techniques

Composition	Topology	Functionality
Homopolymer	Linear	Side-functional groups
Periodic copolymer	Comb/brush	End-functional groups
Block copolymer	Star	Telechelic polymers
Random copolymer	Ladder	Site-specific functional polymers
Gradient copolymer	Cyclic	Macromonomers
Graft copolymer	Network/ Crosslinked	Multifunctional polymers
	Dendritic/ Hyperbranched	

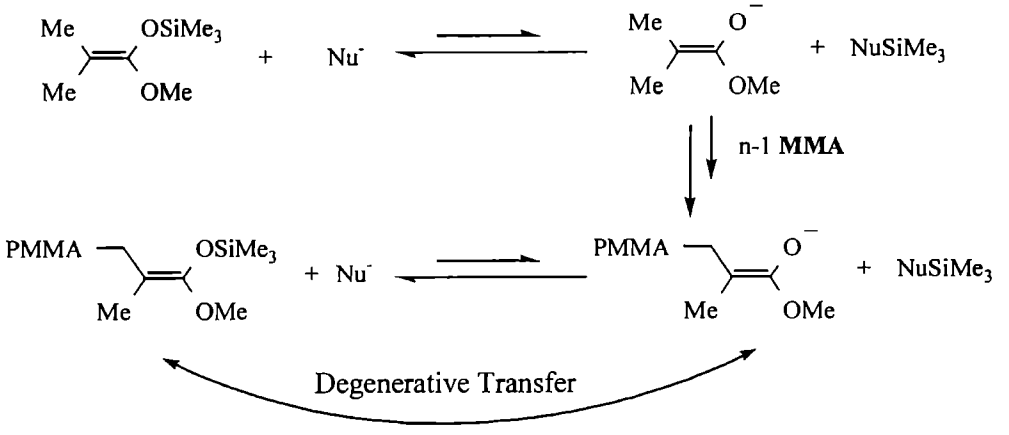
CLP METHODS

For nearly 30 years after Szwarc reported his insightful work, living polymerization of vinyl monomers had been restricted to anionic polymerization systems only. On the other hand, in the 1960s and 1970s, several cationic ring-opening polymerizations of heterocyclic monomers were found to proceed with most undesirable side reactions virtually absent [12, 13]. A dynamic equilibrium between the active and the dormant species was discovered for the tuning of polymerization of tetrahydrofuran (THF) [14, 15]. In the early 1980s this concept of equilibrium was eventually extended to vinyl monomers, triggering the breakthrough discovery of cationic vinyl polymerizations that proceeded in a controlled fashion under certain restrictive conditions [16]. Since then, extensive investigations on CLP *via* various mechanisms have been conducted [17]. In the late 1980s and throughout the 1990s, the scope of CLP has been rapidly expanded. At the present moment, several major classes of chain polymerization like anionic [6, 18], cationic [19], ring-opening metathesis [20, 21], coordination [22, 23] and radical polymerization [24], can become living or controlled under appropriate conditions.

Ionic polymerization

Living anionic polymerization has been applied to styrenes, dienes, (meth)acrylates, epoxides, episulfides, cyclic siloxanes and lactones [6, 18]. The polymerizations of styrene and 1,3-dienes are almost perfectly living provided they are carried out at low temperatures. However, these simple systems composed only of the monomer and the initiator are intolerant to most proton-donating or electrophilic functional groups, such as hydroxy, amino, cyano and carbonyl groups. This is so because of the serious side reactions between these functional groups and the initiators or the propagating anions. For a similar reason, the living polymerization of polar monomers such as (meth)acrylics has been a long-standing problem. An additional reason for the lack of control of these polymerizations is that the propagation rate also becomes too fast if only ionic species are present. There are in general two strategies to overcome these difficulties. The first is to protect the functional groups during the polymerization followed by deprotection. The second is to reduce the nucleophilicity of the carbanion at the chain end, thus slowing down the propagation rate as well as suppressing the side reactions. This can be achieved by a very careful selection of initiator, solvent and temperature. A bulky and less nucleophilic initiator is generally desired [25]. LiCl [26] or a larger and polarizable counterion [27] such as Bu_4N^+ also has a remarkable effect on stabilizing the chain end, whereby the side reactions are suppressed.

Group transfer polymerization (GTP) provides a more efficient method to polymerize polar monomers in a living fashion [28]. The elementary reaction is a catalyzed Michael addition of a silyl ketene acetal to a monomer in the presence of a variety of onium salts or Lewis acids. The lack of side reactions in the system is attributed to a small concentration of enolate anions as well as large counterions involved. The enolate anions are in a rapid exchange with abundant silyl ketene chain-end [29] (Scheme 1). Degenerative exchange may also take place in this process. Such a fast equilibrium between the active species and the dormant species, rather than a direct transfer of the silyl group to the incoming monomer, is the key to achieve the living nature in GTP.

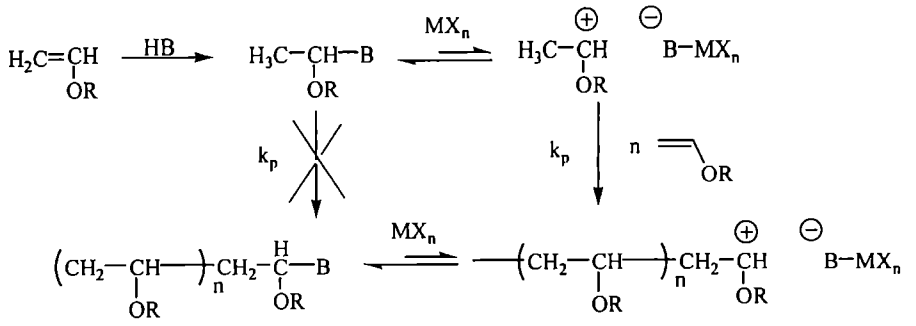


Scheme 1. Group transfer polymerization (GTP) of methyl methacrylate (MMA)

The same concept also applies in many polymerizations proceeding by other mechanisms. This will be described later in more detail.

GTP works best with methacrylates. Polymerizations of other polar monomers such as acrylates, (meth)acrylonitrile, *N,N*-dimethylacrylamide, *etc.* have also been reported but the success was limited [30]. Ambient temperatures (0—50°C) are preferred, the polymerization must be conducted in a dry atmosphere, and protic solvents cannot be used.

As compared with anionic polymerization, it is much



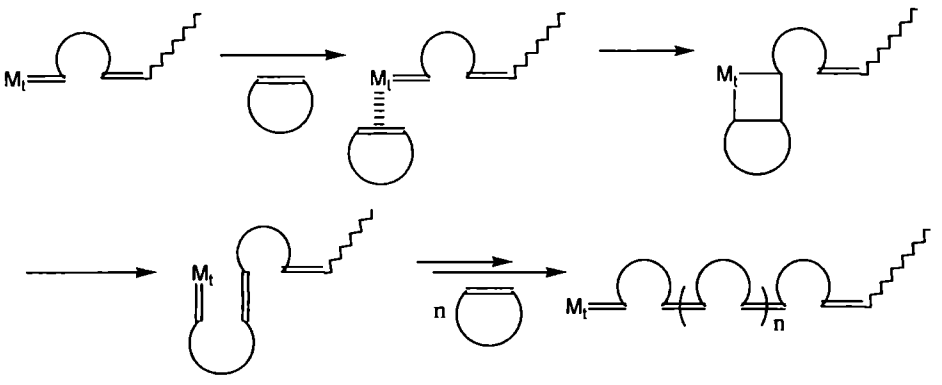
Scheme 2. The principle of living cationic polymerization

harder to achieve livingness in the cationic vinyl polymerization [8]. The major obstacles are: (*i*) Facile chain transfer reaction, which arises from the abstraction of the β-H next to the carbocationic center by monomers, counterions or other nucleophiles in the system. (*ii*) Slow initiation compared with the extremely fast propagation. (*iii*) Coexistence of several active species of different activities and lifetimes, which strongly affects the polydispersity of the synthesized polymer. In order to avoid these problems, it is necessary to reduce both the lifetime and the concentration of the carbocations. At the same time, the lifetime of the propagating chain needs to be maintained as long as possible. The concentration of the propagating chains should also be large enough to achieve the molecular weight control. Introducing a rapid equilibrium between the active carbocation and a dormant covalent species solved this controversy, as shown in Scheme 2 [31].

The growing species are in the carbocationic form only for a short period of time; for most of time they are in the dormant form. As a consequence, propagation slows down, accompanied by the prolonged lifetime of the growing chains. This makes it much easier to achieve a relatively fast initiation and exchange rate relative to the propagation rate. The above strategy is generally realized through the following approaches: (*i*) Using a relatively weak Lewis acid to partially ionize the covalent species in a rapid and reversible way. (*ii*) Adding weak nucleophiles to form reversibly the onium ions with the growing carbocations. (*iii*) Adding salts that suppress the free ions and potentially modify the nature of the Lewis acids.

Up to date, virtually all classes of cationically polymerizable vinyl compounds including vinyl ethers, isobutene, styrenes and *N*-vinylcarbazole, can be polymerized in a controlled way by using the aforementioned strategies. The polymerization procedure generally requires low temperatures (-80°C to 0°C), high purity of the monomer, solvents and other reagents, as well as a dry and inert gas atmosphere [32].

In addition to vinyl monomers, several cyclic monomers can be polymerized in a living fashion through cationic ring-opening polymerizations [33]. These include monomers with bulky substituents [13, 34, 35] such as *N*-*t*-butylaziridine, conidine, 1,3,3-trimethylazetidine and 3,4-dihydro-2H-benzo[4,5]imidazo[2,1-b]oxazine. Steric hindrance around the heteroatom increases the k_p/k_{tr} ratio remarkably, and thus inhibits the chain transfer to polymer; the high ring-strain prevents depropagation; the high nucleophilicity of the heteroatom makes fast initiation with a number of initiators possible; and the stability of the active species reduces the sensitivity of the systems to impurities. The last two factors are most likely responsible for the CLP of lactones [36] and cyclic (thio)carbonates [37], although these monomers do not have bulky substituents or high ring-strain. Tetrahydrofuran (THF) represents another type of cyclic monomers with which an equilibrium of cation and covalent species can be achieved during the propagation [14]. As a consequence, the lifetime of the



Scheme 3. Mechanism of metathesis polymerization

active species is longer than the time needed to achieve complete conversion of the monomer. However, at high conversions, a narrow molecular weight distribution cannot be attained owing to the reversibility of propagation. Recently, Patten *et al.* [35] have reported on the controlled polymerization of 6,8-dioxabicyclo[3.2.1]-octane, also based on the principle of equilibrium between active—dormant species. The initiating/activating system was the same as that used in the living cationic polymerization of isobutyl vinyl ether (IBVE).

Ring opening metathesis polymerization (ROMP) and coordination polymerization

In the ring opening metathesis polymerization (ROMP), a metal carbene species at the growing polymer end reacts with the double bond of the monomer. The resulting 4-membered ring subsequently opens to generate a new metal carbene and a new double bond on the chain backbone. The process is illustrated in Scheme 3.

The major obstacle to achieve living polymerization by this method lies in the high activity of most classical catalysts for the metathesis of ordinary olefins. As a consequence, the metal carbene at the chain end not only reacts with the carbon-carbon double bond of the monomer, but also with those on the chain backbone, either intramolecularly or intermolecularly, to give cyclic or linear oligomers. This, together with a generally observed slow initiation, broadens the molecular weight distribution. Hence, the key to a controlled polymerization is first to have a monomer with a strained ring so that the double bond of the monomer is more reactive than the ordinary double bond; secondly, to find a catalyst with a moderate activity that reacts only with the monomer, and the corresponding alkylidene complex is formed quantitatively, followed by rapid decomposition. Both requirements are fulfilled in the polymerizations of norbornenes and norbornadienes. Successful catalysts include complexes of titanium [38], tantalum [39], tungsten [40] and molybdenum [41] with bulky and electron-donating ligands in order to stabilize the metal carbene against side reactions. With molybdenum complexes as the catalysts, the polymerizations are even tolerant to a variety of functional groups on the monomer [21]. Living ROMP of cyclooctatetraene provides a route to prepare well-defined conjugated polyacetylenes that contain up to 15 double bonds [42]. It is noteworthy that acetylenes can also directly polymerize in a living fashion using Mo- [43] or Nb-based [44] initiators. The living polymerization of other alkynes such as 2-butyne has also been reported under the catalysis of a tantalum complex [44]. These polymerizations all proceed *via* a metathesis mechanism.

Coordination polymerization differs from metathesis polymerization in that the propagation takes place *via* the insertion of the monomer between a single metal-X bond (X can be a carbon, oxygen or sulfur atom), rather than a (2 + 2) cycloaddition. Due to the high activities of the catalysts, a major concern for living polymerization is how to prevent β-hydride transfer. The ligands are thus usually sterically hindered or strongly chelating to decrease the reactivity of the catalyst. Upon appropriate choice of transition metal complexes, the living coordination polymerizations of α-olefins [23, 45], butadiene [46], (di)isocyanides [47], isocyanates [48] and norbornene [49] have been reported to occur. For polar monomers such as acrylates, methacrylates, olefin oxides, lactones and lactides, living polymerization has been achieved by using aluminum porphyrin or alkoxide complexes as initiators [50]. The bulkiness of the ligands helps to prevent β-hydride abstraction. A rapid and reversible formation of a covalent bond between the growing polymer and the metal atom ensures a fast initiation relative to propagation.

Radical polymerization

For a controlled/living radical polymerization, the biggest challenge is how to reduce the termination between radicals, which is diffusion controlled. The strategy is similar to that used for controlled/living cationic polymerization, *i.e.*, to introduce a dormant species that does not propagate by itself, but may convert reversibly to a radical to propagate. Therefore, both the radicals and the dormant species contribute to the total number of propagating chains. The instantaneous proportion of terminated chains can then be expressed as

$$\text{termination (\%)} = \frac{[\text{terminated radicals}]}{[\text{terminated radicals}] + [\text{growing chains}]} = \frac{[\text{terminated radicals}]}{[\text{terminated radicals}] + [\text{radicals}] + [\text{dormant species}]} \quad (6)$$

According to this equation, the larger the proportion of the dormant species, the lower the percentage of the radical termination. In conventional radical polymerization, the concentration of the dormant species can be regarded as zero. Hence, each terminated radical makes a significant contribution to the fraction of the dead chains. When the concentration of the dormant species predominates, as is the case in all controlled radical polymerizations, the overall impact of termination is largely suppressed, even if the absolute number of terminated radicals remains the same as it does in the conventional radical polymerization. This is an important conclusion indicating that the well-controlled polymerization can be achieved without sacrificing the polymerization rate.

Among many available controlled/living radical polymerization methods [24], three approaches are most successful and extensively studied.

The first one is to use a stable radical (X$^\bullet$) to couple the active radical and to form reversibly a dormant covalent species (P-X, eq. 7); k_a and k_d are the rate constants of activation and deactivation, respectively.

$$P\text{-}X \underset{k_d}{\overset{k_a}{\rightleftharpoons}} P^{\bullet} + X^{\bullet} \quad (7)$$

This method is often called the stable free radical polymerization (SFRP) in the literature. The stable radicals used include various nitroxides [51, 52], triazolinyl radicals [53], dithiocarbamates [54], trityl [55] and benzhydryl derivatives [56], as well as organometallic species [57]. The nitroxide mediated polymerization (NMP) is usually more efficient than others are. However, the monomers that can be polymerized by NMP are limited to styrenes, acrylates and acrylamides. Polymerization can be carried out by using either a unimolecular alkoxamine initiator [58] or combination of a conventional radical initiator and a nitroxide radical [52, 59].

The second technique involves a catalyzed reversible redox process (eq. 8).

$$P\text{-}X + M_t^n/L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} P^{\bullet} + X\text{-}M_t^{n+1}/L \quad (8)$$

Since the key step to control the polymerization involves the atom transfer reaction, this method is termed the atom transfer radical polymerization (ATRP). Ru [60], Cu [61], Fe [62], Ni [63] and other transition metal complexes [64] are used as catalysts. A variety of monomers can be polymerized by using ATRP [65] ranging from styrenes, (meth)acrylates, acrylonitrile to (meth)acrylamides, methacrylic acid and some water soluble monomers such as 4-vinylpyridine. One unique advantage of ATRP comes from the use of many commercially available initiators (P-X), including various alkyl halides as well as any compound with a weak halogen-heteroatom bond, such as sulfonyl halides. They provide the polymers with simple halogen as the end groups, which can be easily converted to other useful functionalities [66]. ATRP can also be conducted in an alternative way, *viz.*, to start the polymerization with a conventional radical initiator and a metal complex at the higher oxidation-state (from right to left in eq. 8). This process is called the reverse ATRP [67].

Both SFRP and ATRP follow the same principle called the persistent radical effect (PRE) [68] which describes the self-regulation of the concentration of an active radical in the presence of a stable radical. The third successful controlled/living radical polymerization technique does not conform to this model. Instead, it is based on the degenerative transfer (eq. 9),

$$P_n\text{-}X + P_m^{\bullet} \overset{k_{exchange}}{\rightleftharpoons} P_n^{\bullet} + X\text{-}P_m \quad (9)$$

The large excess of the transfer agent over the radical initiator provides the dominating dormant species. A constant radical concentration comes from a slow and steady decomposition of a radical initiator. As long as the exchange between dormant species and radicals is much faster than the propagation, narrow molecular weight distribution of the final polymer can be obtained. The proper choice of the transfer agent is therefore the key to the polymerization control. So far three types of transfer agents are employed, *viz.*, alkyl iodides [69], unsaturated methacrylate esters [70] and thiocarbonylthio compounds [71, 72]. The latter two processes operate *via* the addition—fragmentation chemistry, in particular, the last one is called the reversible addition—fragmentation chain transfer polymerization (RAFT). The degenerative transfer systems can be potentially applied to any radical polymerizable monomer endowed with low reactivity such as vinyl acetate [73] that still remains a challenge for other controlled/living radical polymerizations. The drawback to this method is that significant retardation may occur in some cases, particularly in synthesizing low molecular weight polymers [72]. Moreover, the gel effect cannot be entirely avoided at high conversions to the continuous supply of low molecular weight radicals, while in ATRP and SFRP systems such a problem does not exist.

SUMMARY

Of all the CLP methods, the anionic polymerization in general appears to give the most precise control over the molecular weight. In addition, stereospecific polymers are also available in these systems [74]. On the other hand, radical polymerization recently has been attracting more and more attention because of its ability to (co)polymerize a wide range of monomers. Furthermore, radical polymerization is more tolerant to impurities and can be performed in protic and aqueous media, which are preferable industrially. The latter point is discussed at more length in Part II.

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