"Living" Radical Polymerization. 1. Possibilities and Limitations

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ABSTRACT: The possibility of the synthesis of well-defined polymers by radical polymerization is discussed. Kinetic analysis demonstrates that the preparation of polymers with controlled macromolecular structure in a "living" radical process requires a low stationary concentration of growing radicals which are in a dynamic equilibrium with the dormant species. Three approaches are described: first, when growing radicals react reversibly with scavenging radicals to form covalent species, second, when growing radicals react reversibly with covalent species to produce persistent radicals, and third, when growing radicals participate in the degenerative transfer reaction which regenerates the same type of radicals. Some of the reported "living" radical systems are critically evaluated.

Introduction

Synthetic polymer chemistry has been recently focused on the control of macromolecular and supramolecular structures. This includes the preparation of polymers with novel architectures such as cyclic, threaded, and ladder structures as well as various types of block and star polymers and copolymers which may microphase separate into domains of various geometries. Synthesis of well-defined polymers requires high chemoselectivity, regioselectivity, and stereoselectivity. High chemoselectivity is observed in living polymerizations when chain growth is not disturbed by any chain breaking reactions. Chemoselectivity is probably the most important parameter because it affects macromolecular dimensions, defines the end groups of polymer chains, and is a prerequisite for the formation of block copolymers. If initiation is fast, then the degree of polymerization is defined by the ratio of the concentration of reacted monomer to that of the introduced initiator:

$$DP_n = \Delta[M]/[I]_0 \quad (1)$$

Living polymerization is most often observed in chain reactions which proceed with polar growing species such as ions or organometallic compounds. In these systems, active species react with monomer and sometimes may terminate in reactions with impurities or intentionally added terminators. Chain ends do not react one with another due to electrostatic repulsions. On the other hand, free radicals, which are the growing species in radical polymerization, very easily react with one another via coupling and/or disproportionation. Thus, it is inherently impossible to imagine a living radical polymerization. However, by careful adjustment of the reaction conditions it is possible to prepare well-defined polymers by a radical mechanism as will be shown in this article. Because the termination cannot be completely excluded we will refer to this system as "living".

Recent Developments in Living Polymerization with the Special Emphasis on Carbocationic Polymerization

Living polymerization was initially reported for the anionic polymerization of alkenes and dienes in which the growing carbanions survive for a period of time greatly exceeding that necessary for complete monomer conversion.[1] Quite good living systems were also described for the anionic ring opening polymerization of epoxides and the cationic ring opening polymerization of various heterocyclics (ethers, sulfides, amines, imino ethers, etc.) in which olate and onium ions are quite stable.[2,3] Living polymerization was recently extended to systems which are more difficult to control such as polymerization of (meth)acrylates,[4-6] metathesis polymerization of cycloolefins,[7] and others. Various living systems are discussed in a recent review.[8]

Recently, well-defined polymers have been prepared by the cationic polymerization of alkenes.[9-11] This process was historically difficult to control and even thought to be impossible to convert into a living system. It is instructive to look closer at this system because some methods used to improve the "livingness" of the cationic polymerization may be used successfully in radical systems.[12] Progress in the cationic polymerization of alkenes can be ascribed to the better understanding of the reaction mechanism and to the correct choice of initiator, additives, and reaction temperature. Transfer is the major chain breaking reaction in this system due to the facile elimination of β-H atoms (partially positively charged) from the growing carbocations. The reactions carried out in the absence of basic components (counterions, solvent, additives) provide better defined systems due to the suppression of the unimolecular (spontaneous) transfer. However, transfer to monomer still exists and can be reduced only at sufficiently low temperatures. The proportion of chains marked by transfer increases with conversion and with the polymerization degree (DP). In the case of spontaneous transfer (for example, in cationic polymerization transfer to solvent, counterion, etc.), the ratio of the observed number average DP to the theoretical DP ($DP_{(T)}$, no transfer) decreases with conversion p and with the product of the concentration of initiator times ratio of the rate constants of transfer to propagation:

$$DP/DP_{(T)} = 1/\{1 + \ln[1/(1-p)](k_{tr}/k_p)/[I]_0\} \quad (2)$$

As shown in Figure 1 the ratio $DP/DP_{(T)}$ decreases monotonously with conversion. The drop is the most pronounced for the highest value of the parameter $[k_{tr}/k_p]/[I]_0$. The ratio of the rate constants is given by "chemistry" i.e. mechanism, counterion, monomer, solvent, temperature, etc. However, the concentration of initiator can be easily controlled and "poor" systems with, e.g., experimental DP 4 times lower than theoretically expected ($b = 1$ in Figure 1) can be converted to well-defined systems

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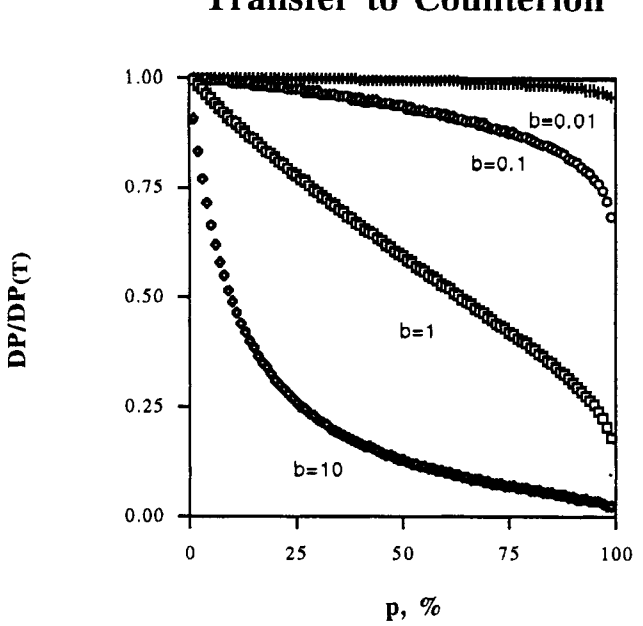


Figure 1. Effect of the unimolecular transfer on polymerization degrees as a function of conversion for various ratios $b = (k_{tr}/k_p)/[I]_0$ in the cationic polymerization.

($b = 0.1$ or $b = 0.01$) by increasing the concentration of initiator by 10- or 100-fold. This necessitates the synthesis of shorter chains. For sufficiently short chains, transfer may not be noticed. Thus, polymerization degrees corresponding to those described by eq 1 may be obtained if initiation is fast in comparison with propagation and DP low enought not to be marked by transfer. This requires relatively high concentrations of the initiator ($[I]_0 \geq 10^{-2}$ mol·L^{-1}). Carbocations react very rapidly with alkenes ($k_p \approx 10^5$ mol^{-1}·L·s^{-1} at $\approx$20 °C). Thus, if all growing chains will be in the form of carbocations, polymerization may be finished in a fraction of a second and may be difficult to control or even explosive. In order to reduce polymerization rates, a dynamic equilibrium between reactive carbocations and dormant species was used. Reversible ionization of covalent species and reversible formation of onium ions provides well-defined systems with the number of chains (or M_n) defined by the total concentration of growing and dormant species ($[I]_0 \approx 10^{-2}$ mol·L^{-1}) but with the rates proportional to the concentration of carbocations present at very low amounts ($[C^+] \approx 10^{-7}$ mol·L^{-1})

Fundamentals of Radical Polymerization

Radical polymerization includes four elementary reactions: (1) slow initiation by the homolytic cleavage of a molecule with low thermal stability (peroxide, diazo compound) ($k_d < 10^{-5}$ s^{-1}),

$$\mathrm{I{-}I} \xrightarrow{k_d} 2\mathrm{I}^{\bullet} \qquad (3a)$$

(2) relatively fast reaction of primary radicals with monomer to generate the first growing species (because $k_d < k_i[M]$, the decomposition is the rate determining step)

$$\mathrm{I}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1^{\bullet} \qquad (3b)$$

(3) fast propagation with moderate regioselectivity and low stereoselectivity ($k_p \approx 10^3$ mol^{-1}·L·s^{-1}),

$$\mathrm{P}_n^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1}^{\bullet} \qquad (3c)$$

(4) very fast termination between growing radicals ($k_t \approx 10^7$ mol^{-1}·L·s^{-1}),

$$\mathrm{P}_n^{\bullet} + \mathrm{P}_m^{\bullet} \xrightarrow{k_t} \mathrm{P}_{n+m}/(\mathrm{P}_n{=} + \mathrm{P}_m{-}\mathrm{H}) \qquad (3d)$$

Transfer reactions are usually less important, unless transfer agents are added.

A typical synthesis of high molecular weight polymers requires slow initiation, producing a low momentary concentration of growing radicals which terminate in a bimolecular process. Because termination is bimolecular, higher radical concentrations would produce shorter chains. The proportion of chains marked by any side reaction (transfer in cationic process and termination in a radical process) increases with chain length. Therefore, well-defined polymers by radical polymerization may be formed only if chains are relatively short *and* the concentration of free radicals is low enough. These two requirements are in an apparent contradiction but can be accommodated via reversible deactivation of growing free radicals in a way similar to the aforementioned deactivation of growing carbocations. Another possibility to fulfill the requirements for a low stationary concentration of radicals and short chains is to use conventional initiating systems with very efficient transfer reagents which will regenerate the same (or similar) growing radicals; see next sections.

Kinetic Requirements for a "Living" Radical Polymerization

Living polymerization should provide well-defined polymers with a negligible amount of chain breaking. The criteria of livingness have not been well-defined but it has been stressed that the chain breaking should not be observable (<5%) at the time of complete conversion of a monomer (>99%) for a synthetically convenient reaction time (>10 min). The time criterion is more important for ionic reactions which are usually much faster than radical reactions and will not be discussed here.

In Figure 1, the top two curves correspond to 5% deactivation of chains at 99% conversion and 10% deactivation at 70% conversion. The behavior of radical systems is different from cationic. The most important chain breaking reaction in the latter is transfer (cf. Figure 1) which has little or no effect on rates and leads to a higher number of chains (lower molecular weights) than expected. In radical reactions, termination is the most important chain breaking process. With fast initiation, the total number of chains is constant (assuming termination by disproportionation) and molecular weights close to theoretical ones are expected. At the same time, termination reduces the number of active chains, resulting in the decrease in polymerization rates, which will be accompanied by an increase in polydispersities.

From the point of view of the synthesis of well-defined polymers, block copolymers and end-functional polymers, any chain breaking reaction is disallowed. However, termination and transfer will lead to different deviations from the behavior of ideal systems (either lower rates or lower DP).

As discussed in the previous section, the synthesis of well-defined polymers by living polymerization should occur in systems with a low momentary (stationary) concentration of growing radicals which should be *reversibly* deactivated to provide a relatively large number of macromolecules. To control molecular weights in a sufficient way, the initiation rate should be at least comparable to that of propagation. Thus, let's assume that the initiator of the structure P–R is the adduct of the model of growing radical P$^{\bullet}$ and a scavenging radical R$^{\bullet}$.

R• can react only with P• but not with monomer (M) and cannot initiate polymerization. The covalent adduct homolytically cleaves to P• and R• with the rate constant of activation k_{act} and reforms with the rate constant of deactivation k_{deact}:

$$P\text{–}R \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} P^{\bullet} + R^{\bullet} \quad (4)$$

The role of a scavenger of the growing radicals may also be played by a neutral species. In that case, a stable adduct with an odd number of electrons (a persistent radical) will be reversibly formed:

$$\{P\text{–}X\}^{\bullet} \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} P^{\bullet} + X \quad (5)$$

The kinetic requirements for this case (II) are identical to those for the previously discussed case (I) (eq 4).

There is another possibility for the synthesis of well-defined polymers. Radicals present at certain low concentrations, or formed continuously during slow initiation, may react in the transfer process with some agents which will reform radicals of the same or similar structure as growing radicals. This transfer is thermodynamically neutral and may be considered as the degenerative exchange process. If the exchange (transfer) is fast and the ratio of terminated chains to the total amount of chains is low, then a well-defined system (III) may be formed:

$$P_n^{\bullet} + P_1\text{–}R \overset{k_{tr}}{\rightleftarrows} P_1^{\bullet} + P_n\text{–}R \quad (6)$$

In this case, the main requirement for a "living" system is that a growing radical (P_n•) reacts rapidly and selectively with a transfer agent (P_1–R) to exchange the R and form a dormant species P_n–R and a new radical P_1• capable of chain growth. The latter after addition of $m-1$ monomer units (P_m•) will react again with a transfer agent (P_n–R) to generate P_m–R and P_n•. If this exchange is fast, polymers with a narrow MWD can be prepared. Degrees of polymerization will be defined by the ratio $\Delta[M]/[P\text{–}R]$ = DP and the reaction rate by a low stationary concentration of radicals P•. This concentration has to be kept low enough to reduce the possibility of bimolecular termination.

Thus, small differences exist between the previously discussed systems I and II and the case III. In case I, a dormant species (P_n–R) is homolytically cleaved to a scavenger and a growing radical (R• and P_n•). In cases II and III the growing radical reacts with a nonradical (species with an even number of electrons); in case II, the concentration of these species is approximately equal to that of the growing species and the resulting persistent radical is at a very high concentration. In case III, the concentration of the growing species is much lower than that of the transfer agent and the unstable radicals ([P_n–R–P_m]•) might be formed only as an intermediate product. If the small amount of growing chains is deactivated in cases I and II, then the concentration of scavengers increases and this should result in the decrease of the ratio of active to dormant species and therefore in the reduction of the polymerization rate. The constant ratio of active to dormant species is permitted for cases I and II, providing that either no deactivation occurs or that there is a large excess of scavenger over growing radicals at the beginning of the reaction.

The kinetic analysis for case I is given below. The treatment for case II is very similar.

Assuming a steady state for the concentration of dormant chains:

$$-d[P\text{–}R] = k_{act}[P\text{–}R] - k_{deact}[P^{\bullet}][R^{\bullet}] \approx 0 \quad (7)$$

$$[P^{\bullet}]_{st} = k_{act}[P\text{–}R]/(k_{deact}[R^{\bullet}]) \quad (8)$$

or, if $[P^{\bullet}] = [R^{\bullet}]$:

$$[P^{\bullet}]_{st} = (k_{act}[P\text{–}R]/k_{deact})^{1/2} \quad (9)$$

Growing radicals will also participate in propagation (no concentration change) and in the undesirable irreversible termination:

$$-d[P^{\bullet}]/dt = k_t[P^{\bullet}]^2 + k_{deact}[P^{\bullet}][R^{\bullet}] - k_{act}[P\text{–}R] \quad (10)$$

The deactivation is not considered as a chain breaking because it is reversible. Irreversible termination produces entirely inactive chains by either coupling or disproportionation of growing radicals P•. The stationary concentration of growing radicals is constant because, although some chains are terminated, the radicals are easily reformed from the large pool of dormant species (dormant species are at least 1 million times more populous than growing radicals). Because we are concerned mostly with "living" systems, only a small fraction of the growing chains (dormant and active) can be deactivated (≈5%). This 5% of the chains will terminate within time τ_t:

$$0.05[P\text{–}R]_0 = k_t[P^{\bullet}]^2_{st}\tau_t \quad (11)$$

This approximate equation will be valid only for a relatively low proportion of terminated chains (≤10%), after which the decrease of [P–R] has to be accounted for. Equation 11 is valid when [R•] does not change significantly in time. This may happen for the degenerative transfer (cf. eq 6), for systems with a strong tendency to form dimers R–R, and also for systems in which radicals R• are present in a large excess in comparison with P• from the beginning of the reaction. If this is not the case, each deactivated chain will provide one molecule of R• and the decrease of the polymerization rate should be observed due to the drop of the concentration of growing radicals. Therefore, if the apparent rate constant of polymerization does not change with conversion (straight kinetic plot in semilogarithmic coordinates), then the system is based on either degenerative transfer or initially a significant excess of scavenging radicals is present.

Monomer is consumed with a rate proportional to the concentration of the monomer and growing radicals and to the rate constant of propagation k_p:

$$-d[M]/dt = k_p[P^{\bullet}][M] \quad (12)$$

A total of 99% of monomer will be consumed at time τ_p, which for a good "living" system should be comparable or shorter than the time when 5% of chains terminate (τ_t):

$$\ln([M]_0/0.01[M]_0) = k_p[P^{\bullet}]_{st}\tau_p \quad (13)$$

Combination of eqs 11 and 13 leads to

$$[P^{\bullet}]_{st}/[P\text{–}R]_0 \approx k_p/100k_t \quad (14)$$

If less rigorous living criteria are set (10% of chains terminated within a time of 70% monomer conversion), then

$$[P^{\bullet}]_{st}/[P\text{–}R]_0 \approx k_p/10k_t \quad (15)$$

Thus, depending on the quality of the system, either eq 14 or 15 may be used.

The analysis of the polymerization of styrene for which kinetic parameters are well-known is given below. At 60 °C, $k_p \approx 10^2$ mol^{-1}·L·s^{-1} and $k_t \approx 10^7$ mol^{-1}·L·s^{-1}.[14] The

stationary concentration of growing radicals is estimated as

$$[P^\bullet]_{st} = [P-R]_0 k_p/k_t 100 \approx 10^{-9}\ \text{mol}\cdot\text{L}^{-1} \quad (16)$$

when a better defined system (eq 14) is targeted, using $[M]_0 = 1\ \text{mol}\cdot\text{L}^{-1}$, and synthesizing a polymer with DP = 100 ($[P-R]_0 = [M]_0/DP = 10^{-2}\ \text{mol}\cdot\text{L}^{-1}$).

At such a low $[P^\bullet]_{st}$, a 99% conversion will be reached after $\approx 4 \times 10^7$ s, which is more than *1 year*!

The dynamics of the activation (homolytic cleavage) and deactivation (recombination with a scavenger) is very important. The upper limit for the rate constant of the recombination reaction between growing radicals and scavenging radicals is set by diffusion ($k_{deact} \approx 10^9\ \text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$). If no excess scavenger is present ($[P^\bullet] \approx [R^\bullet] \approx 10^{-9}\ \text{mol}\cdot\text{L}^{-1}$), then

$$k_{act} = k_{deact}[P^\bullet][R^\bullet]/[P-R] \approx k_{deact}[P^\bullet]^2/[P-R] \approx 10^{-7}\ \text{s}^{-1} \quad (17)$$

Therefore, the activation is extremely slow and 90% of the dormant species would be consumed only after more than *0.5 year*! If the structure of the initiator is very similar to that of the dormant growing species, the rates of the homolytic cleavage of the initiator and of the dormant growing species will be also very similar and initiation may be incomplete. Additionally, polydispersities in these systems will depend on the relative rate of initiation as well as on the rate of exchange between active and dormant species (activation/deactivation)[13] and may be relatively high in slowly exchanging systems.

Thus, the first estimates of the possibilities for a "living" radical polymerization for styrene are not very optimistic. A good system providing well-defined polymers requires extremely lengthy reactions and precludes practical applications. However, there are possibilities to improve the "living" radical polymerization systems.

Possible Improvements for "Living" Radical Systems

The slow overall polymerization rate, limited by a low stationary concentration of growing radicals, makes the "living" radical polymerization impractically slow. Very low values of the rate constants of activation (≈initiation) disable preparation of well-defined systems because of the incomplete initiation. This will lead to higher than expected molecular weights and a broader molecular weight distribution due to slow initiation and slow exchange between dormant and growing species.

There are three approaches to make "living" polymerization faster. The first method is based on lowering the criteria for the well-defined system. Thus, using eq 5 (10% deactivation at 70% conversion) will reduce polymerization time 10-fold in comparison with eq 14 (5% deactivation at 99% conversion). For the previously discussed case of styrene, polymerization time can be reduced from 1 year to 1 month. Potentially, the reaction time can be further reduced, however, at the expense of the loss of the macromolecular control.

The second approach is based on the increase of $[P-R]_0$. Increasing $[P-R]_0$ will, however, reduce DP unless it is accompanied by the corresponding increase of $[M]_0$. Thus, working in bulk ($[M]_0 \approx 10\ \text{mol}\cdot\text{L}^{-1}$) will enable a 10 times increase of $[P-R]_0$ and 10 times faster polymerization than in a more dilute system ($[M]_0 \approx 1\ \text{mol}\cdot\text{L}^{-1}$) without decreasing DP. This may lead to a reduction in the polymerization time from 1 month to 3 days. Of course, the polymerization must be slower if higher molecular weight polymers are desired.

The third approach is based on the increase of the k_p/k_t ratio. Once again, there are a few methods to do that. The first one is to increase the polymerization temperature. Since the activation energy of propagation is always higher than that of termination, the k_p/k_t ratio will increase with temperature. There is, however, a limit to use this approach since at temperatures above 100 °C a spontaneous thermal initiation occurs for vinyl monomers. The second possibility for the enhancement of the k_p/k_t ratio is an increase of pressure. Propagation has a negative volume of activation, termination has a positive one (mostly due to the viscosity effect), and propagation will be favored at higher pressures. The third possibility is also related to viscosity. Polymerization in bulk will provide more viscous systems with a higher k_p/k_t ratio. Additionally, similar effects may be accomplished by the correct choice of solvents and reaction media. The Tromsdorff effect is not expected in living radical systems because radicals will be predominantly consumed in the reaction with a low molecular weight scavenger. Finally, the k_p/k_t ratio changes strongly with the monomer structure. For example, the k_p/k_t ratio increases in the order ethylene < styrene < methyl methacrylate < vinyl acetate < methyl acrylate [$(0.0005 < 0.03 < 0.2 < 1 < 2.1) \times 10^{-4}$] at 60 °C.[14]

Thus, methyl acrylate allows a 70 times higher stationary concentration of growing radicals than styrene under otherwise similar conditions. This may lead to a reduction in the polymerization time to hours, which is comparable to conventional radical polymerization.

One comment should be added on the potential participation of solvent cage effects. It is possible that the homolytic cleavage of dormant chains will be accompanied by a very fast recombination of the growing radical with a scavenger within a solvent cage rather than with one arriving from the outside. This may lead to recombination faster than diffusion controlled rates and also to an enhanced k_p/k_t ratio due to the easier penetration of the solvent cage by a small monomer molecule rather than by the growing radical. This could allow synthesis of well-defined systems at higher stationary concentrations of radicals and shorter reaction times than in the "classic" systems without contribution of the solvent cage. In fact, the solvent cage may be interpreted as a selective insertion of the monomer into the P–R bond and only some trapping experiments, solvent effects or copolymerization studies may confirm the true radical nature of propagation. The limiting case for these systems may be a radical-coordinative polymerization in which a nearly concerted process can take place.

The dynamics of the exchange should eventually be enhanced and initiation accelerated. This can be accomplished by the more facile homolytic cleavage (higher k_{act}) and by the simultaneous shift of the equilibrium to the same low stationary concentration of the growing radicals with the scavenger used in excess.

These scavengers should be selective in the reaction with growing radicals but should not react with an alkene and should not initiate polymerization. They might dimerize but some radicals are sufficiently stable and do not dimerize (TEMPO, galvinoxyl, etc.).

The second approach, based on the formation of persistent radicals, is best realized with organometallic compounds. However, some of them may have a high affinity toward hydrogen and may lead to the undesired and uncontrolled transfer.

The third approach, based on transfer reagents, requires very selective compounds which will exclusively provide thermodynamically neutral degenerative transfer with rates comparable to or faster than that of propagation. Because transfer agents are present at concentrations much lower than that of the monomer, ($[P-R]_0 \approx [M]_0/DP$), rate constants of transfer must be faster than the propagation rate constants.

Brief Review of Reported Living Radical Systems

This section does not pretend to be comprehensive, but to be rather selective in discussing a few systems which may be interesting from the point of view of the aforementioned approach to living systems.

All of the systems are based (sometimes by chance) on a lower stationary concentration of growing radicals and suppression of the termination process by various means. This may include physical means (precipitation, emulsions, inclusion complexes, template polymerization, stiff chains, viscous media) or chemical means such as a decrease of the concentration of growing radicals by the reversible termination with scavengers.[15]

Unfortunately, some of the systems used are far from being ideal: initiation is slow, scavengers react with monomers, reversibility is not observed except under photochemical conditions, and some side reactions lead to decomposition products. Criteria for living systems are often not obeyed, and most reactions were limited only to low conversions (<10%). Molecular weights do not increase linearly with conversion and polydispersities are broad. Nevertheless, in some systems block copolymers have been prepared but, as will be discussed later, probably not via chain extension reactions.

The discussion will be based on three types of living systems described above.

System I Based on Reversible Recombination of Growing Radicals with Scavenging Radicals. This system is very often postulated as the main operating system in the thermal polymerization with alkoxyamines or with alkyl dithiocarbamates. However, both of these systems, conform also to case III (degenerative transfer).

Probably the best example of case I is the photochemical polymerization with dithiocarbamate derivatives, usually tetraalkylthiuram disulfide. In the early 1980s, Otsu reported a living radical polymerization of alkenes with this compound and described its action as inifer or iniferter which means that it acted as *ini*tiator, trans*fer* agent and *ter*minator.[16] The systems with thiuram disulfide as iniferter are usually characterized by the initial rapid growth and then a monotonous increase in molecular weight with conversion. In some cases, molecular weights do not increase linearly with conversion, however. The polymerization obeys a first order kinetics in monomer, as often observed for stationary state conditions. Molecular weight distribution remains fairly constant but usually not below $\bar{M}_w/\bar{M}_n \approx 2$.

Systems initiated with dithiocarbamate derivatives behave differently when initiated thermally and photochemically. Thiuram disulfide is a poor photochemical initiator and starts to act efficiently only at temperatures above 90 °C:[17]

$$R_2N-C(S)-S-S-C(S)-NR_2 \rightleftarrows 2R_2N-C(S)-S^{\bullet} \quad (18)$$

$$R_2N-C(S)-S^{\bullet} + M \rightarrow P_1^{\bullet} \quad \text{(slow)} \quad (19)$$

This may be ascribed to low reactivity of the primary radicals $R_2N-C(S)-S^{\bullet}$. These radicals slowly initiate polymerization and rapidly scavenge growing radicals to form dithiocarbamate end groups which are quite thermally stable but which cleave homolytically in the presence of light:

$$R_2N-C(S)-S^{\bullet} + P_n^{\bullet} \rightarrow R_2N-C(S)-S-P_n \quad \text{(reversible with } h\nu) \quad (20)$$

Growing radicals may also react with dithiocarbamate end groups in two different ways: by a transfer process

$$R_2N-C(S)-S-P_n + P_m^{\bullet} \rightarrow R_2N-C(S)-S-P_m + P_n^{\bullet} \quad (21)$$

and additionally by irreversibly forming head-to-head end groups and producing thiocarbamate radicals of low reactivity. The latter reaction reported by Sigwalt is very important in thermal polymerization of acrylates:[18,19]

$$R_2N-C(S)-S-P_n + P_m^{\bullet} \rightarrow R_2N-C(S)-S^{\bullet} + P_m-P_n \quad (22)$$

Thermal polymerization of acrylates in the presence of benzyl dithiocarbamate is slower (!) than spontaneous thermal polymerization.[19] This means that the degradative transfer is the main operating reaction. On the other hand, photochemical cleavage of the NC(S)S–C bond may provide reversible systems conforming to system I.[17]

In addition, side reactions such as the evolution of CS_2 were reported and lead to additional complications:[20]

$$R_2N-C(S)-S^{\bullet} \rightarrow R_2N^{\bullet} + CS_2 \quad (23)$$

Another class of thermal initiators which provide systems of type I is based on tetraarylethanes[21,22] and (phenylazo)triphenylmethane:[23]

$$Ar_2CR-P_n-RCAr_2 \rightleftarrows Ar_2CR-P_n^{\bullet} + {}^{\bullet}CRAr_2 \quad (24)$$

$$Ar-N=N-CAr_3 + nM \rightarrow Ar-P_n-CAr_3 \rightleftarrows Ar-P_n^{\bullet} + {}^{\bullet}CAr_3 \quad (25)$$

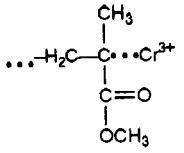
The bulky $Ar_2RC^{\bullet}$ or $Ar_3C^{\bullet}$ species plays a role of scavenging radicals. A good living system should require fast initiation which is usually not fulfilled in these systems. Most studies with these compounds provided poly(methyl methacrylate) with relatively poor control of molecular weights and polydispersities.

Recently, a new series of initiators, generated from hyponitrite, aryl diazoate or cyanate anions by reaction with electron acceptors such as aryl diazonium ions or activated alkyl halides, have been shown to provide long-lived oxygen-centered radicals.[24] The "living" nature of these polymerizations was partially demonstrated by a quasi-linear increase in DP_n with conversion or by synthesis of block copolymers of the type poly(methyl methacrylate)–poly(butyl acrylate). However, broad polydispersities (2.0–3.0) and low conversions were obtained:

$$Ar^{\bullet\bullet}ON=NAr \xrightarrow{n CH_2=CHCO_2R} Ar(CH_2-CHCO_2R)_nON=NAr \quad (26)$$

System II Based on the Reaction of Growing Radicals To Reversibly Form Persistent Radicals. There are several papers describing radical polymerization of acrylic monomers (methyl methacrylate, acrylonitrile, methyl acrylate, acrylamide) by initiation with "aged" chromium acetate (Cr^{2+}) and benzoyl peroxide (BPO), suggesting that a "living" polymerization occurs at temperatures below 30 °C.[25] An important factor is the presence of strong electron donors such as DMF or HMPA.

The mechanism of this radical polymerization is discussed in terms of a transition metal complex (Cr^{3+}) stabilizing the growing radicals:



(27)

These systems have very low activity toward styrene, vinyl acetate, and vinyl chloride.[25]

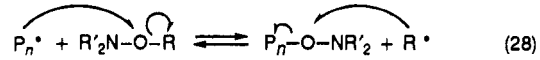
Organometallic derivatives of Ni(0), oxidized in a one-electron transfer process in the presence of certain organic halides (R–X), are useful initiators (iniferters) in unconventional free radical polymerization of styrene and methyl methacrylate, allowing the synthesis of block copolymers of the type polystyrene–poly(methyl methacrylate).[26]

The main problem with derivatives of transition metals is their high affinity toward hydrogen which results in β-hydrogen elimination from growing radicals and formation of the unsaturated chain ends. This is the case of Co^{2+} used successfully as a chain-transfer reagent in free-radical polymerization of acrylic monomers.[27,28]

Nevertheless, if the affinity of transition metals toward hydrogen could be reduced by a proper choice of ligands, systems based on organometallic compounds are among the most promising.

System III Based on the Degenerative Transfer. The concept of the thermodynamically neutral degenerative transfer has not been intentionally used yet. In fact, it is very similar to the inifer system but the species are not initiator per se and require the use of true radical initiators. These initiators can be added in controlled amounts like in the polymerization with alkoxyamines as transfer agents.[29] The role of the initiator may be also played by impurities or even by the product of decomposition of transfer agents (alkyl dithiocarbamates).[16]

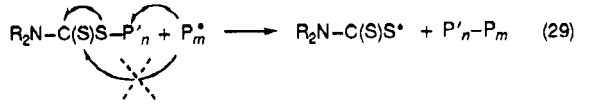
Some of the best controlled polymers obtained by radical polymerization are prepared with preformed alkoxyamines or even those prepared in situ.[29,30] Alkoxyamines alone are inefficient initiators, unless at high temperatures, but they might react easily with radicals. Thus, radical polymerization initiated by classic initiators (AIBN, peroxides, etc.) in the presence of alkoxyamines provides polymers with molecular weights determined by the number of alkoxyamines and rates determined by the stationary concentration of growing free radicals. This is possible when a macromolecular radical ($P_n^{\bullet}$) attacks alkoxyamine selectively at the oxygen atom, forming a macromolecular alkoxyamine, and releases a radical R$^{\bullet}$ capable of initiation of new chains:



(28)

This is probably the main reaction responsible for the formation of well-defined polymers in these systems. Indeed, successful polymerizations with TEMPO and alkoxyamines require an excess of radical initiator. Alkoxyamine may be prepared in advance or generated in situ by the reaction between TEMPO and initiator in the presence of monomer.

As discussed previously, dithiocarbamates are poor thermal initiators because they initiate slowly, do not reversibly form radicals, and participate in the degradative rather than in the degenerative transfer. According to the results of Sigwalt,[18,19] alkyl dithiocarbamate reduces the rate of spontaneous thermal polymerization of butyl acrylate but allows some control of molecular weights. This has been explained by the degradative transfer (top arrows):



(29)

This type of transfer may also lead to the formation of block copolymers with the macromolecular dithiocarbamate.[31] Thus, block copolymers may not be formed via a typical chain extension process but rather via coupling of a growing polyB with a polyA terminated with a dithiocarbamate moiety. The synthesis of the well-defined polymers will require very high chemoselectivity of the degenerative transfer (bottom arrow) and a very small contribution of the degradative transfer.

The prerequisite for a good degenerative transfer agent is high chemoselectivity (no β-H abstraction) and transfer rapid in comparison with propagation. In that case all chains will grow simultaneously and polymers with narrow molecular weight distribution may be prepared.

In the paper which follows this introductory article, the new approach based on the reversible deactivation of growing radicals with organoaluminum compounds will be presented. This system provides well-defined poly(vinyl acetates) with $\bar{M}_w/\bar{M}_n < 1.2$ and molecular weights up to $\bar{M}_n \approx 10\,000$[32] as well as block copolymers between poly(vinyl acetate) and various alkenes.[33]

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