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Fundamentals and some practical synthetic aspects of controlled radical polymerization will be discussed in the lecture. Effect of slow initiation, termination, and transfer on kinetics, molecular weights and polydispersities will be described in the quantitative way. Conditions for typical radical polymerization and for controlled radical polymerization will be compared. The concept of reversible deactivation of growing radicals in order to control molecular weights, polydispersities and terminal functionalities will be presented.

Four systems will be discussed in detail:

1. Reversible cleavage of covalent species
2. Reversible formation of persistent radicals
3. Reversible redox systems
4. Degenerative group and atom transfer

In all four systems the effect of dynamics of exchange between dormant and active species on kinetics as well as on the evolution of molecular weights and polydispersities with conversion will be presented.

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Fundamentals and Practical Aspects of "Living" Radical Polymerization

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Introduction

Living radical polymerization is very difficult if not impossible to realize. Complete elimination of chain breaking reactions, especially termination, is not possible in radical processes. Therefore quotation marks are used for a term of "living" radical polymerization. However, well-defined polymers with predetermined molecular weights, low polydispersities and terminal functionalities as well as block copolymers can be prepared via radical polymerization. Thus, although complete suppression of termination is not possible, preparation of controlled polymers with relatively low molecular weights has been successful. In this article fundamentals and some practical synthetic aspects of controlled radical polymerization will be discussed.

Effect of Slow Initiation, Termination, and Transfer on Kinetics, Molecular Weights and Polydispersities.

Well-defined polymers and block copolymers with the polymerization degrees predetermined by the ratio of concentrations of reacted monomer to the introduced initiator, $DP=\Delta[M]/[I]_o$, and with low polydispersities, $M_w/M_n<1.1$, are usually prepared in living systems, i.e. in chain growth processes without chain breaking reactions. However, the absence of chain breaking reactions is not a sufficient condition for the synthesis of well defined polymers. For example, slow initiation may lead to molecular weights much higher than expected and also to larger polydispersities; slow exchange between species of different reactivities and different lifetimes may result in polymodal molecular weight distributions, even if no irreversible chain breaking reactions are present. Two graphs shown below (Figure 1 and Figure 2) present the quantitative effect of slow initiation, unimolecular termination and transfer to monomer on kinetics and evolution of molecular weights with conversion.

In the ideal living system, with one type of active center which is formed by fast initiation and without chain breaking reactions, straight semilogarithmic kinetic plots and linear evolution of molecular weight with conversion is expected. However, an increase in the slope of the semilogarithmic anamorphoses and initially higher than predicted molecular weights are observed with slow initiation.

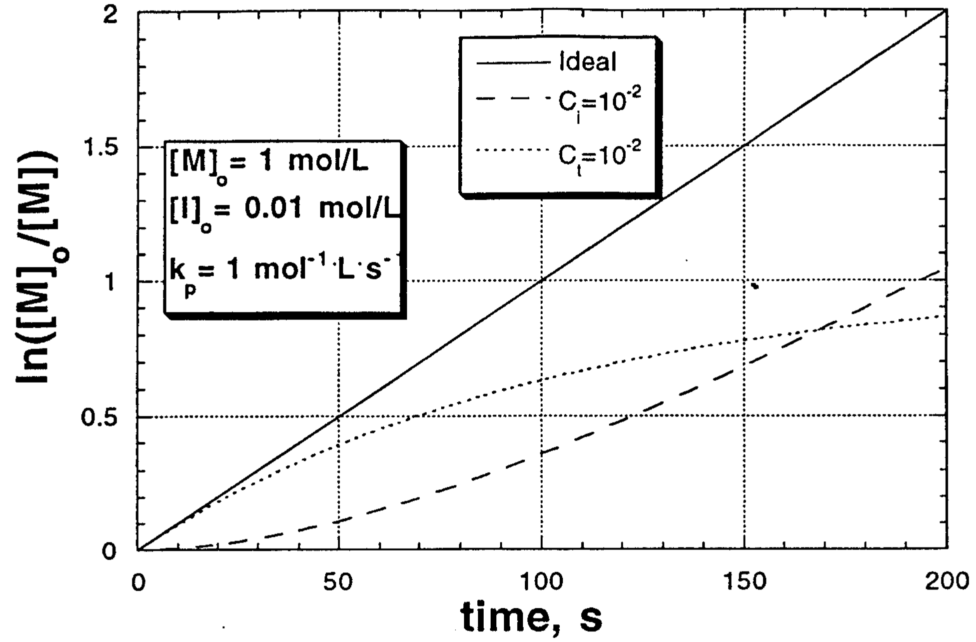


Fig.1. Effect of slow initiation and termination on kinetics of chain polymerization

This is also accompanied by enhanced polydispersities and can be assigned to the continuous increase of the number of growing chains. On the other hand, termination reduces the number of growing chains and decreases the polymerization rate, sometimes even to limited conversions, depending on k_p/k_t and $[M]_o/[I]_o$ ratios.

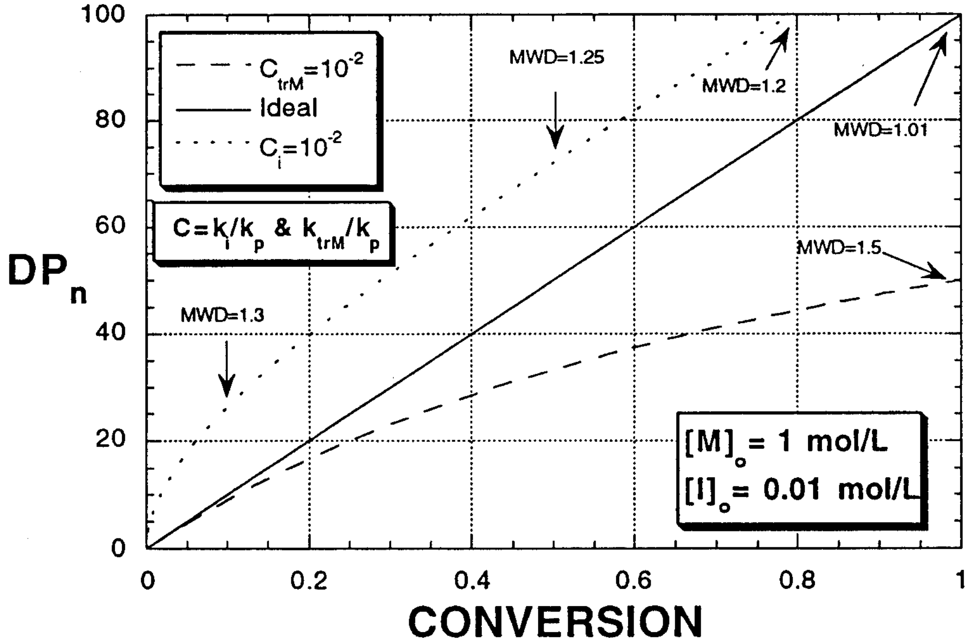


Fig.2. Effect of slow initiation and transfer to monomer on molecular weights

The total number of chains in systems with unimolecular termination and with termination by disproportionation in radical polymerization remains constant and therefore a linear increase of molecular weights with conversion is preserved provided that initiation is fast. Transfer usually has no effect on kinetics but it generates an increasing number of dead chains leading to lower than expected molecular weights.

Figure 3 shows the dependence of the ratio of chains which have been irreversibly deactivated by either termination or transfer to monomer, to the total number of chains. If this ratio equals zero, all chains are active and potentially functionalizable; if the ratio equals 1, then all chains are deactivated. In order to prepare well-defined block copolymers and end-functionalized polymers, the proportion of deactivated chains must be very small, <5%. As shown in Figure 3, the proportion of deactivated chains increases with chain length and also with the ratio $k_{t/tr}/k_p$. The proportion of deactivated chains can be significantly reduced for the same transfer/termination coefficient, if low molecular weight polymers are synthesized.

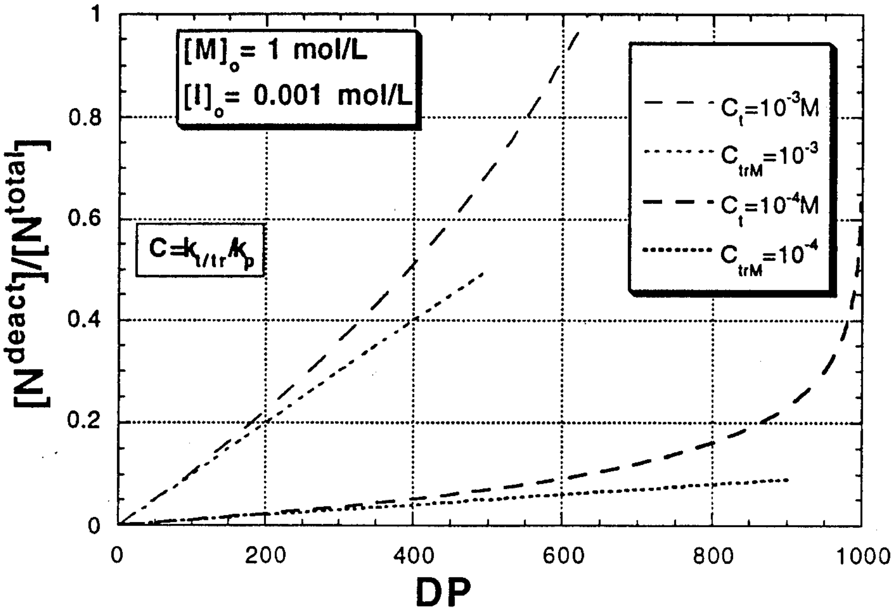


Fig.3. Proportion of chains deactivated by termination and transfer to monomer as a function of DP.

In the case of transfer to monomer, the proportion of deactivated chains increases monotonously with conversion up to a certain value at the final conversion. For the case of termination, it is necessary to stop the reaction at an appropriate stage; otherwise all chains will become deactivated.

Polydispersities are also reduced for shorter chains even for the same ratio of rate constants of propagation and transfer. Fig. 4 shows the reduction of polydispersities in the hypothetical systems with fast initiation, no termination and transfer to monomer, $k_p/k_{trM} = 10^{-3}$, as a function of $[M]_o/[I]_o$ at complete conversion. Polydispersities can be reduced from $M_w/M_n = 2$ for the ratio $[M]_o/[I]_o = 10^{-4}$, to $M_w/M_n = 1.5$ for the ratio 10^{-3} and down to $M_w/M_n = 1.1$ for the ratio $[M]_o/[I]_o = 10^{-2}$.

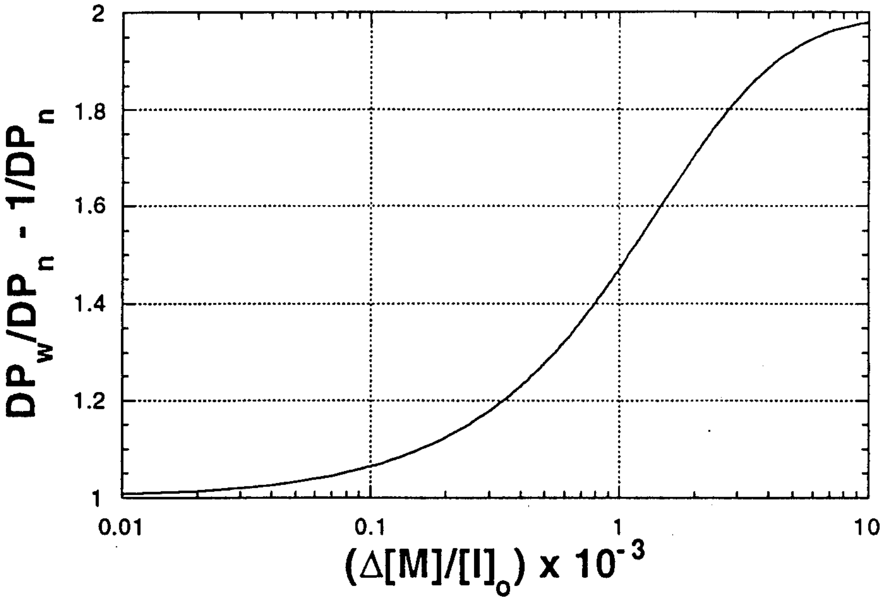


Fig.4. Dependence of polydispersities at complete conversion on $[M]_o/[I]_o$ ratios for systems with fast initiation and transfer to monomer, $k_p/k_{trM} = 10^{-3}$.

Both figures demonstrate that polymers with a low proportion of deactivated chains and with very narrow polydispersities can be prepared in the presence of chain breaking reactions such as transfer and termination, if molecular weights are limited to a relatively low range. Many well-defined polymers prepared recently have rather low molecular weights, indicating that control is due to a careful selection of the polymerization conditions rather than to the substantial increase in chemoselectivities and new polymerization mechanisms.

Basis of Radical Polymerization.

Radical polymerization includes five elementary reactions:

-slow homolytic cleavage of a peroxide, diazo, or other similar compounds; $k_d < 10^{-5 \pm 1}\ s^{-1}$,

$$\mathbf{I\text{-}I} \xrightarrow{k_d} \mathbf{2\,I^{\bullet}} \tag{1}$$

-relatively fast reaction of primary radicals with monomer to generate the first growing species; because $k_d < k_o[M]$, the decomposition is the rate determining step in the initiation process:

$$\mathbf{I^\bullet + M \xrightarrow{k_o} P_1^\bullet} \tag{2}$$

-fast propagation ; $k_p \approx 10^{3\pm1}$ $mol^{-1} \cdot L \cdot s^{-1}$,

$$\mathbf{P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet} \tag{3}$$

-very fast termination between growing radicals via coupling or disproportionation; $k_t \approx 10^{7\pm1}$ $mol^{-1} \cdot L \cdot s^{-1}$,

$$\mathbf{P_n^\bullet + P_m^\bullet \xrightarrow{k_t} P_{n+m} \;/\; (\,P_n^{=} \;+\; P_m\text{-}H)} \tag{4}$$

-transfer reactions including transfer to monomer, initiator, solvent, polymer, and specially added transfer agents.

$$\mathbf{P_n^\bullet + X \xrightarrow{k_{tr}} P_n \;\; + X^\bullet} \tag{5}$$

Usually high molecular weight polymers are formed because contribution of transfer is small, initiation is slow and produces a low stationary concentration of growing radicals ($[P^\bullet] \approx 10^{-7\pm1}$ mol/L) which terminate in a bimolecular way. Ratio of the rate of propagation to that of termination ("livingness") decreases with $[P^\bullet]$, because propagation is first order but termination is second order in respect to $[P^\bullet]$. However, as demonstrated in Fig. 3, the proportion of chains marked by termination increases with chain length. Therefore, well defined polymers may be formed in radical polymerization only if chains are relatively short and concentration of free radicals is low enough. There is an apparent contradiction between these two requirements because usually a decrease of the concentration of radicals leads to higher molecular weights. However, the two conditions can be accommodated in systems with reversible deactivation of growing radicals.

Reversible Deactivation of Growing Radicals in the Controlled Radical Polymerization.

As discussed in the previous sections, controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weights sufficiently low. This necessitates a relatively high concentration of the initiator or, in other words, low $[M]_o/[I]_o$ ratios. However, because termination is bimolecular, the contribution of termination becomes more significant at high $[I]_o$, when a large concentration of radicals, $[P^\bullet]$, is generated.

In order to solve the discrepancy between high $[I]_o$ and low $[P^\bullet]$, it is necessary to establish an exchange between dormant and active species. The concentration of the dormant species can be equal to $[I]_o$ and the concentration of momentarily growing species to $[P^\bullet]$. The total number of growing chains will be equal to $[I]_0$ ($\approx [P\text{-}R]_0 + [P^\bullet]$), and radicals would be present at a very low stationary concentration, $[P^\bullet]$, and therefore the contribution of termination and the proportion of irreversibly terminated chains should be very low. There are three possibilities to realize the concept of controlled radical polymerization.

1. Reversible homolytic cleavage of covalent species:

$$\text{P-R} \underset{k_{\text{deact}}}{\overset{k_{\text{act}}}{\rightleftharpoons}} \text{P}^\bullet + \text{R}^\bullet \qquad (6)$$

The covalent species P-R can reversibly and homolytically cleave to produce the growing radical $P^\bullet$, capable of propagation, and the dormant radical $R^\bullet$, which, ideally, should react only with $P^\bullet$ but not with the monomer or with itself to form inactive dimers. $P^\bullet$ can react not only with M and $R^\bullet$ but also with another $P^\bullet$, leading to termination. Because termination rate is proportional to $[P^\bullet]^2$, and propagation rate to $[P^\bullet]$, the contribution of termination and the proportion of deactivated chains increases with $[P^\bullet]$.

This case is probably most frequently postulated in controlled radical polymerizations. As examples of $R^\bullet$, dithiocarbamate radicals,[1, 2] nitroxyl radicals,[3, 4, 5, 6] and also bulky organic radicals such as triarylmethyl and substituted diarylmethyl species can be used [7, 8]. The problems with most of them, except nitroxyl radicals, is that the scavenging radicals can initiate the polymerization themselves and that they participate in side reactions leading to the degradative transfer. Some systems involving nitroxyl radicals will be discussed in detail later. The degenerative transfer (cf. infra) may be also present in some of these systems.

2. Reversible homolytic cleavage of persistent radicals:

$$\mathbf{P^\bullet + X} \rightleftharpoons \mathbf{\{P\text{-}X\}^\bullet} \qquad (7)$$

The persistent radical $\{P\text{-}X\}^\bullet$ should only cleave homolytically to form $P^\bullet$ and the species X, but it should not react with monomer. X should be an inert compound capable only of reacting with $P^\bullet$. $P^\bullet$, as in the previous case, is a typical growing radical which can react with X, with M, and with $P^\bullet$. As before, if $[P^\bullet]$ is very low, the proportion of deactivated chains is low as well.

The role of X can be played by some elementoorganic or organometallic species with an even number of electrons. Some success has been reported with group XIII and XV elements such as aluminum [9] and phosphorus [10] as well as with organometallic derivatives of Co,[11, 12] Cr,[13, 14, 15] and other transition metals. In some cases, metal with an odd number of electrons acts as a scavenger. In some cases not only radical but also ionic and / or coordinative polymerization may occur, and it is necessary to carefully evaluate the mechanism of the polymerization. In some systems, it may happen that both mechanisms can operate simultaneously. That is, not only homolytic but also heterolytic bond cleavage may take place. The proportion of each pathway will depend on the nature of the metal or element, ligands and medium effects.

3. Degenerative transfer:

$$P_n^\bullet + P_1\text{-}R \overset{k}{\rightleftarrows} P_1^\bullet + P_n\text{-}R \qquad (8)$$

The concept of degenerative transfer is based on a thermodynamically neutral exchange reaction between active and dormant species. This can be visualized as transfer of the R moiety between all chains in such a way that the concentration of $P^\bullet$ remains very low and number of chains roughly corresponds to [P-R]. P-R can not react directly with monomer and P-R can not react with one another; it can react only with $P^\bullet$. $P^\bullet$ would be generated by a classic radical initiating system such as AIBN, BPO, redox, etc. $P^\bullet$ can react with monomer, for propagation, with P-R, for degenerative transfer, and can also react one with another, for termination. The latter reaction can not be completely avoided, although its contribution will depend on the concentration of $P^\bullet$, as described previously. Nevertheless, the maximum amount of deactivated chains would be equal to that of the introduced initiator, $[I]_o$. If the concentration of the transfer agent is much higher than that of the initiator, $[P\text{-}R]_o >> [I]_o$, then the proportion of deactivated chains will be low enough and controlled polymerization can be accomplished. This additionally requires fast exchange between growing radicals, $P^\bullet$, and the dormant species, P-R. Fast initiation is not required in this case. There are only a few examples of such reactions, and one of them, based on alkyl iodides, will be discussed later.

4. Mixed systems

Degenerative transfer may operate simultaneously with the reversible cleavage of covalent species and persistent radicals. This means that in addition to unimolecular exchange, the bimolecular process based on the degenerative transfer may take place. For example, the use of alkoxyamines together with classic radical initiators pose the possibility of both reactions 1 and 3.

Reversible Cleavage of Covalent Species

The successful unimolecular exchange requires the equilibrium (eq. 6) to be strongly shifted to the side of the dormant species in order to maintain a low stationary concentration of radicals. In addition, the scavenger should not initiate polymerization and should not be involved in side reactions.

Some potential scavengers such as dithiocarbamyl and trityl radicals react with alkenes and also decompose, e.g. $R_2NC(S)S^\bullet$ to $R_2N^\bullet$ and CS_2 [16]. On the other hand, nitroxyl radicals do not react directly with alkenes (or they react extremely slowly). They are relatively stable even at elevated temperatures, but they react very rapidly with most organic radicals [17] to form alkoxyamines.

Alkoxyamines have been used in the polymerization of methacrylates and acrylates as initiators, either alone or together with peroxy initiators at temperatures <100 °C [3]. More recently, this system has been extended to the polymerization of styrene [4]. Alkoxyamines were prepared in situ from the nitroxyl radical, TEMPO, and benzoyl peroxide. A small excess of benzoyl peroxide was used so that the concentration of the produced radicals would exceed the concentration of the scavenger, and thereby initiate polymerization. However, temperatures above 120 °C were required to break the $C\text{-}ONR_2$ bond. At temperatures >100 °C, styrene polymerizes by self-initiation via formation of the Diels-Alder adduct which is further aromatized, generating radicals.

Thus, radicals are slowly formed also during the polymerization. Radicals formed by self-initiation are initially trapped by scavengers and then, when the concentration of scavengers is low enough and the concentration of growing radicals high enough, polymerization starts. This is evidenced by long induction periods [18]. Thus, for the polymerization of styrene moderated by nitroxyl radicals, it is not necessary to use radical initiators.

Kinetics of the polymerization of bulk styrene at 120 °C in the presence of TEMPO initiated by benzoyl peroxide and AIBN as well as the self-initiated system is quite similar and the amount of the added initiator regulates the length of induction periods. Slopes in semilogarithmic coordinates depend on the concentration of added scavenger.

Figures 5 and 6 show typical SEC traces obtained in the polymerization of styrene initiated by an excess of AIBN (0.03 mol/L) over scavenger (0.01 mol/L) and with its equimolar amount (0.03 mol/L). It can be noted that the peak values continuously move to higher molecular weights. M_n corresponds always to the total number of chains produced by the initiating radicals, but M_{peak} values corresponds to the dormant chains which are reversibly activated. In the latter case, both M_n and M_{peak} values are similar because only a very small proportion of chains have been irreversibly deactivated by bimolecular termination between growing / initiating radicals.

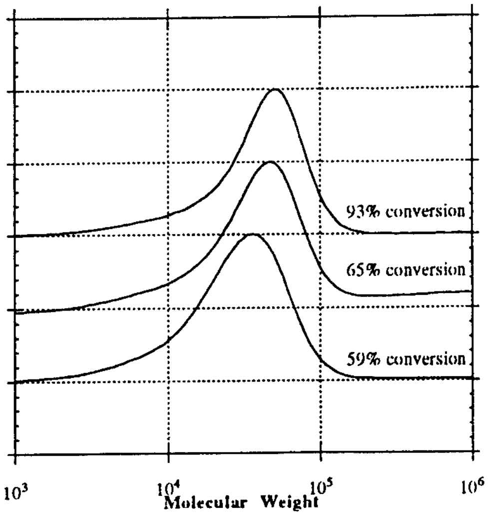


Fig. 5 Bulk polymerization of styrene with $[AIBN]_0$=0.03 mol/L and $[TEMPO]_0$=0.01 mol/L at 120 °C.

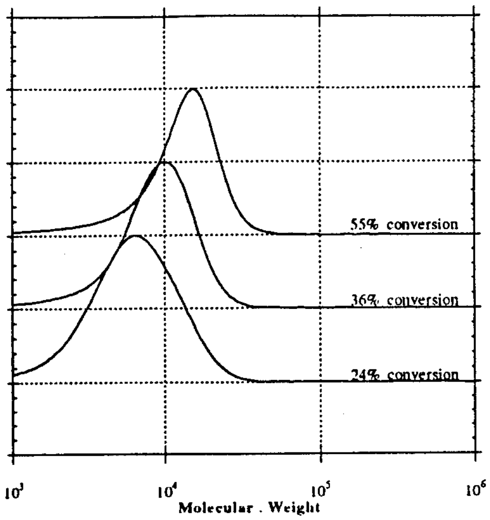
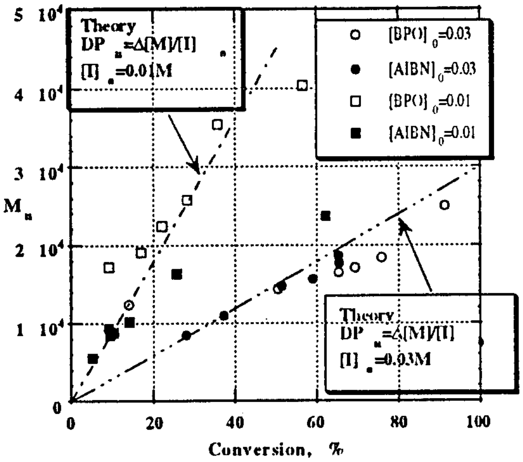


Fig. 6 Bulk polymerization of styrene with $[AIBN]_0$=0.03 mol/L and $[TEMPO]_0$= 0.03 mol/L at 120 °C.

This is illustrated in Figs.7 and 8. Fig. 7 shows that M_n values depend on the concentration of the initiator (≈ 50% efficiency of initiation), if a relatively small concentration of scavenger is used. However, the M_{peak} values, shown in Fig. 8, correlate to the scavenger concentration because it defines the concentration of chains which are in their dormant state and which are capable of growth.



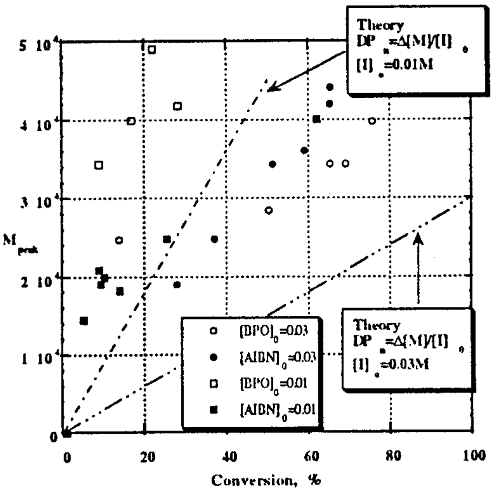


Fig.7 M_n dependence on conversion in bulk polymerization of styrene at 120 °C with BPO/AIBN and $[TEMPO]_0$=0.01 mol/L.

Fig.8 M_{peak} dependence on conversion in bulk polymerization of styrene at 120 °C with BPO/AIBN and $[TEMPO]_0$=0.01 mol/L.

On the other hand, if the scavenger is used in excess, then both M_n and M_{peak} values are defined by the scavenger concentration because polymerization starts only when the concentration of radicals formed from the initiator and by self-initiation becomes comparable to the initial scavenger concentration.

Polydispersities either increase or decrease with conversion. The former trend can be assigned to slow but continuous self-initiation and termination of radicals produced in excess of the scavenger. The decrease of polydispersities with conversion can be explained by the reduction of the proportion of uncontrolled chains terminated at the early stages with the excess of radicals. Sometimes, a reduction of polydispersities may also happen if the exchange between active and dormant species is slow in comparison with propagation. Nevertheless, most polydispersities at high conversions are in the range of $M_w/M_n \approx 1.4 \pm 0.1$, which is much less than that obtained in the classic thermal radical polymerization.

Spontaneous self-initiation in the polymerization of styrene starts at elevated temperatures and could be avoided if the rate of the homolytic cleavage is accelerated. It seems that 4-phosphonooxy-TEMPO provides much faster polymerization than either TEMPO or 4-hydroxy-TEMPO. This is shown in Fig. 9. Higher rates could be due not only to a shift in the equilibrium position, but also due to less efficient scavenging. However, the total number of chains with 4-phosphonooxy-TEMPO is nearly the same as with other nitroxyl radicals. (Fig. 10)

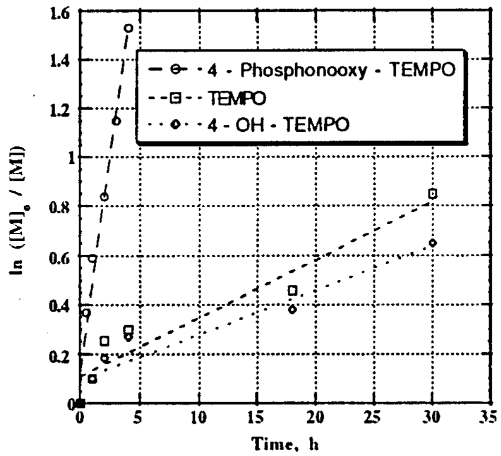


Fig. 9 Kinetics of styrene polymerizations at 110 °C with TEMPO derivatives.

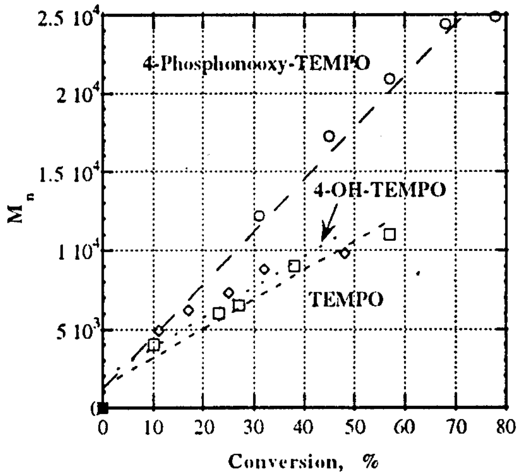
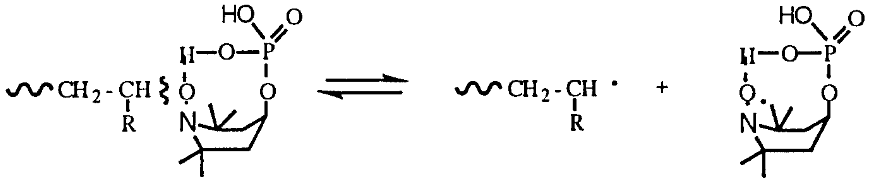


Fig. 10 M_n dependence on conversion in the bulk polymerization of styrene at 120 °C with various TEMPO derivatives.

The exact nature of the shift of the equilibrium is not known and it may be due to either faster homolytic cleavage or a slower trapping process. It is possible that the hydrogen bonding from the remote phosphoric acid to the nucleophilic oxygen promotes cleavage and also stabilizes the resulting nitroxyl radical



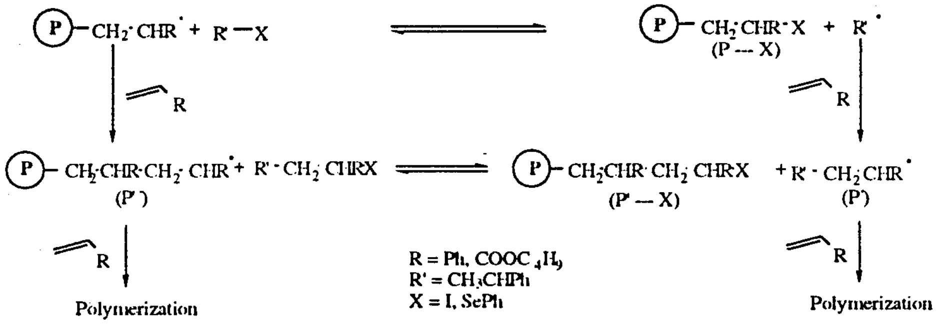
(9)

The fine tuning of the equilibrium constant by structural effects in the scavenger molecule and potentially by medium and additives is one of the most important research directions in this area. It is especially important for the polymerization of monomers which do not self-initiate and can not match-up an excess of scavenger if the initiator is not added in sufficient amount. This is the case of acrylates, vinyl acetate and other alkenes.

Degenerative Transfer

In degenerative transfer, Scheme 1, a transfer agent, R' - X, reacts with a propagating radical ,P$^\bullet$, to form a dormant polymer chain, P - X. The new radical, R'$^\bullet$, can then reinitiate polymerization. Because of this, the number of polymer chains is equal to the concentration of the transfer agent. The newly formed polymer chain, P'$^\bullet$, can then react with the dormant polymer chain, P - X, to form P' - X and P$^\bullet$. Optimally, the exchange reaction between the dormant and active radical species should be a thermodynamically neutral reaction. In order for this to be obtained, the transfer agent should resemble the polymer chain end. The compound which was initially employed was 1 - phenylethyl iodide, 1 - PEI.

Scheme 1



The basic requirement for the effective degenerative transfer is the sufficient thermal stability of P-R and fast exchange with P$^\bullet$ in comparison with propagation. This means that the transfer coefficients should be similar to or larger than 1. This is necessary for the preparation of well defined polymers, especially when $[M]_0 >> [P\text{-}R]_0$. Additionally, the reactivity of the P_1-R species in the initially added transfer agent should be similar to or higher than that in the macromolecular species P_n-R. Thus, $P_1^\bullet$ should be similar to the growing radical $P_n^\bullet$. Inspection of transfer coefficients indicates that large k_{tr}/k_p values are found for compounds with very labile E-Z bonds such as S-S, Si-H, P-H or Br_3C-Br. As mentioned before, the degenerative nature of the process requires that P$^\bullet$ must be a carbon centered species, i.e., a 1-phenylethyl derivative for styrene polymerization. Of course, the C-H bond is not sufficiently labile. Apparently, 1-phenylethyl sulfides are not reactive enough either. Thus, in addition to considering organometallic species, the corresponding alkyl iodides were examined by our group for use as the P-R species. Similarly, iodine and selenium compounds have been used successfully in organic synthesis in radical addition reactions to various vinyl compounds [19], [20] Fig. 11 shows the kinetics of the bulk polymerization of butyl acrylate and styrene under various conditions.

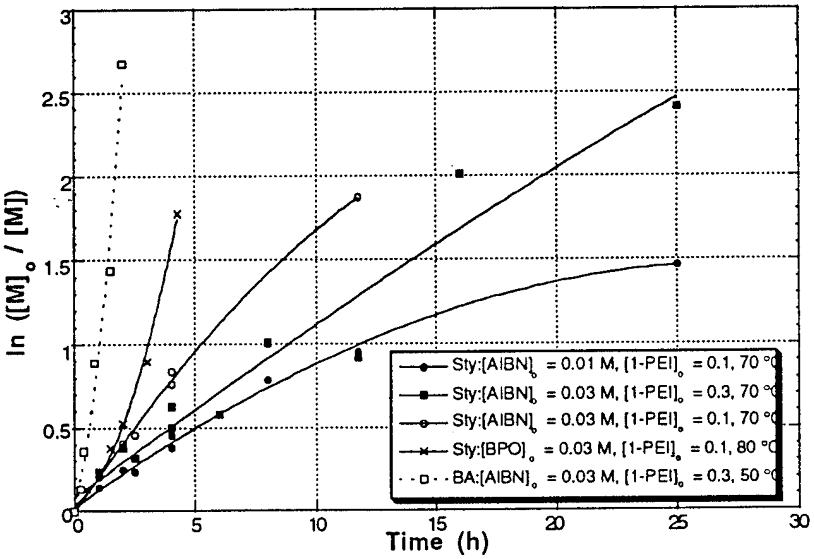


Fig. 11 Kinetics of bulk polymerization of styrene and butyl acrylate at various conditions.

The polymerization of butyl acrylate was too fast at 70 °C and although it was carried out at 50 °C was faster than polymerization of styrene at 70 °C. The bulk polymerization of butyl acrylate exhibited a rate acceleration at higher conversions. This may be due to an increase in the viscosity of the reaction mixture which reduced termination rate like in the Trommsdorff effect. The polymerization of styrene at 80 °C initiated by BPO showed again that the rate of polymerization increased with time as the reaction reached higher conversions.

However, for styrene polymerizations initiated by AIBN semilogarithmic plots were decreasing with time. This could be due to the fact that [AIBN] was substantially reduced when the styrene polymerization had reached high conversions. After 20 hours, the concentration of AIBN would have been ≈5% of the original value, resulting in a rate of polymerization ≈20% the original. The apparent linearity of the kinetic plots at higher initiator concentrations, may be due to the simultaneous actions of both effects, i. e., rate reduction due to initiator depletion and rate acceleration due to increased viscosity. Increasing the amount of transfer agent, 1 - PEI, resulted in a slower polymerization. As shown in Fig. 11, when $[1 - \mathrm{PEI}]_0 = 0.1$ M was used, the reaction was 63 % complete in twelve hours, while the reaction using $[1 - \mathrm{PEI}]_0 = 0.3$ M required sixteen hours to reach similar conversions.

Nevertheless, the main advantage of these systems is the control of molecular weights which increase with conversion and approach the theoretical value of $DP_n = \Delta[M] / [R' - X]_0$, as shown in Fig. 12.

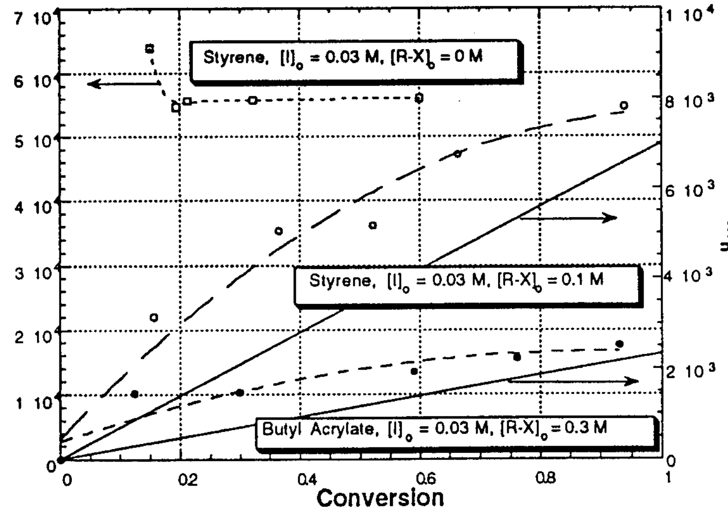


Fig. 12 Molecular weight dependence upon conversion for the bulk polymerization of styrene and butyl acrylate at 70 °C. [I] = AIBN, [R-X] = 1-Phenylethyl iodide.

The higher molecular weights at the outset than predicted indicate that the rate of exchange of iodine between the propagating radical and the transfer agent is slow in comparison to the rate of propagation. The polydispersities were < 1.5 even at conversions greater than 90%. This is in sharp contrast to the polymerization of styrene without the transfer agent, $M_n / M_w > 2$. When no transfer agent was used, the molecular weight, $M_n \approx 60{,}000$, did not increase with conversion. Butyl acrylate also provides controlled polymers with AIBN/PEI initiating system.

The rates of polymerization increased with temperature. At 70 and 90 °C, there was no significant effect on the evolution of molecular weights with conversion. However, when the polymerization was carried out at 50 °C, the molecular weights and polydispersities were higher than at the higher temperatures indicating that transfer between the propagating radical and the transfer agent was relatively slower.

Various transfer agents were used to explore the effect of R' on the control of molecular weights. The following iodine compounds were used in addition to 1 - phenylethyl iodide: perfluorohexyl iodide, perfluoroisopropyl iodide, iodoacetonitrile, isopropyl iodide, n - propyl iodide and phenyl iodide. Of these, only primary alkyl and aryl iodides showed no or very weak effect on molecular weights.

Although the C-I bond can also be cleaved heterolytically, this does not happen for styrene derivatives below 100 °C. Spontaneous, homolytic cleavage does not happen either at reasonable rates for $T < 100$ °C, as proved in blank experiments. However, addition of 1 - phenylethyl iodide to the polymerization of styrene initiated by AIBN had a tremendous effect on the evolution of molecular weight with conversion and on polydispersities.

Thus, the radical polymerization of styrene and butyl acrylate in the presence of degenerative transfer agents followed typical behavior of controlled polymerization such as low polydispersities and a linear evolution of molecular weight with conversion, although it was initiated by classic radical initiators. Moreover, addition of a new portion of monomer or addition of another monomer extends chain growth leading to block copolymers as in the case of polystyrene and poly(butyl acrylate).

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