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SYNTHESIS OF WELL DEFINED POLYMERS BY CONTROLLED RADICAL POLYMERIZATIONS

by

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SYNTHESIS OF WELL DEFINED POLYMERS BY CONTROLLED RADICAL POLYMERIZATION

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ABSTRACT

Controlled radical polymerizations can be achieved by using either unimolecular or bimolecular exchange between growing radicals and dormant chains. Dormant chains can be represented as either covalent species or organometallic compounds. Systems based on alkoxyamines, organochromium, organoaluminum compounds, and alkyl iodides are discussed in detail. In many systems, straight semilogarithmic plots indicate a constant number of growing radicals. A linear increase of molecular weights with conversion indicates a constant number of chains capable of growth but being predominantly in the dormant state. Some of these systems can be used in the synthesis of block copolymers and for end-functionalization.

INTRODUCTION

The radical polymerization of vinyl monomers usually provides polymers with broad molecular weight distributions, $M_w / M_n \approx 2$, especially at higher conversions. It does not allow, however, end group control, unless in telomerization, and rarely can it lead to block copolymers. Molecular weight control in radical polymerization is difficult to achieve and molecular weights are adjusted by employing transfer agents. This contrasts with ionic polymerizations which, in many cases, provide well-defined polymers with narrow molecular weight distribution, $M_w / M_n < 1.1$, precisely controlled degrees of polymerization, $DP_n = \Delta[M] / [I]_o$, desired terminal functionalities by using special initiators and terminating agents, and a variety of block copolymers. Because experimental conditions for radical polymerizations are more easily realized commercially than those for ionic polymerizations, which often require complete elimination of moisture, it is very tempting to extend the concept of controlled polymerization to radical systems.

Most reports on the synthesis of well-defined polymers refer to living polymerizations, which are chain growth processes without chain breaking reactions (Ref. 1). However, it has been noted that well defined polymers can be also prepared in systems in which transfer and/or termination has been present but their contribution was sufficiently small that it did not affect the properties of the obtained polymers (Ref. 2). Moreover, it has also been found that polymers with polymodal, or at least broad distributions, have been obtained without chain breaking reactions but when exchange between species of different activities, or of different lifetimes, was slow in comparison with propagation (Ref. 3). Also slow initiation prevented the synthesis of polymers with degrees of polymerization predetermined by the simple equation $DP_n = \Delta[M] / [I]_o$. Thus, controlled and living polymerizations are two different categories, although in many cases, they may overlap.

Termination reactions in radical polymerizations carried out in solution can not be avoided entirely. Therefore, radical polymerizations can not truly be living. However, as will be demonstrated later, careful adjustment of the reaction conditions and through the use of special initiators, deactivators, and transfer agents, one may obtain controlled polymerizations resulting in well defined polymers and block copolymers.

BASICS OF RADICAL POLYMERIZATION AND CONTROLLED POLYMERIZATION

Radical polymerizations typically consist of three elementary reactions: initiation, propagation and termination. Transfer, in many cases is not as important as in ionic reactions but can be enhanced, if so desired, in the presence of intentionally added agents.

Initiation is typically carried out with diazo or peroxy compounds which decompose slowly with half lifetimes in the range of a few hours. Very often, only a small fraction of the initiator is consumed at nearly complete monomer conversion.

Propagation is relatively fast, although slower than most ionic reactions; $k_p \approx 10^{3\pm1}$ $mol^{-1} \cdot L \cdot s^{-1}$ at $\approx 70\ ^{\circ}C$. Activation energies of propagation are in the range of $E_p \approx 6 \pm 2$ kcal / mol.

Growing radicals terminate bimolecularly very rapidly by either coupling or disproportionation, $k_t \approx 10^{8\pm1}$ $mol^{-1} \cdot L \cdot s^{-1}$ at $\approx 70\ ^{\circ}C$. Termination is nearly diffusion controlled with rather small activation energies, $E_t \approx 3 \pm 2$ kcal / mol.

Typical radical polymerizations are based on the slow generation of radicals which grow and rapidly terminate. In order to grow sufficiently high polymer, it is necessary to keep the concentration of growing radicals very low, usually in the range of $[P^*] \approx 10^{-7\pm1}$ mol / L. Because the termination rate is proportional to $[P^*]^2$ and the rate of propagation to $[P^*]$, the relative contribution of termination increases with $[P^*]$.

Controlled polymerizations require fast initiation, in order to assure that all chains start growing with the same probability, fast exchange between sites of various activities, and a low contribution of chain breaking reactions. As shown in Fig. 1, the proportion of chains deactivated by either transfer or termination increases with chain length. Transfer to monomer and unimolecular termination was simulated in Fig. 1 but the same is qualitatively true for a bimolecular termination and transfer to a transfer agent.

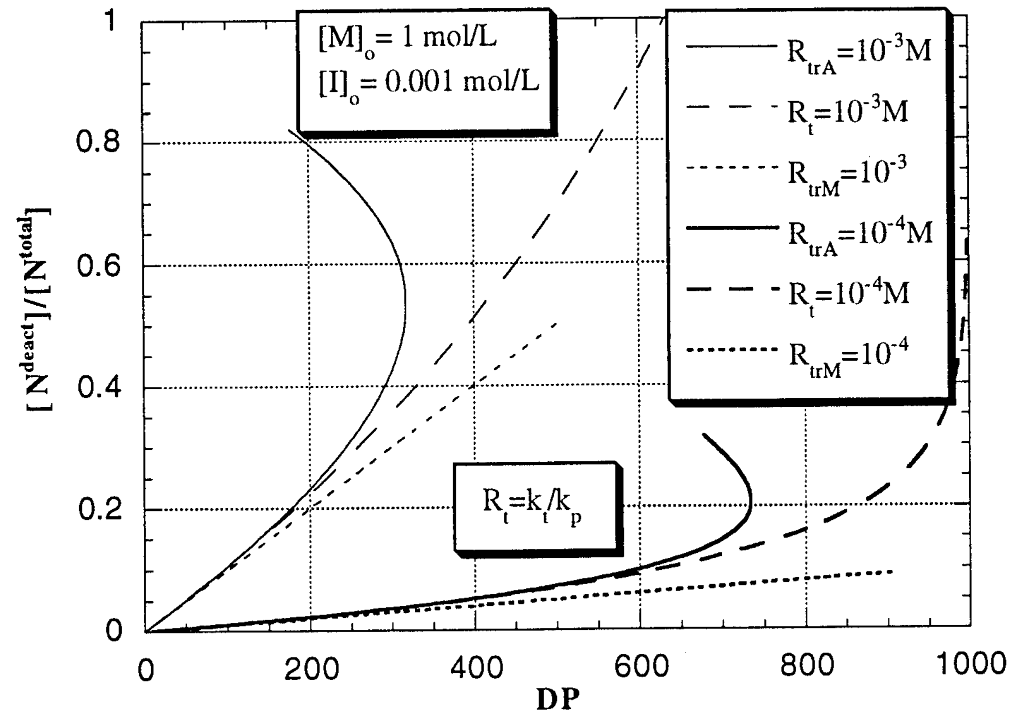


Fig. 1. The effect of degree of polymerization, DP, on the proportion of chains deactivated by chain breaking reactions.

The proportion of deactivated chains increases with the transfer / termination coefficient, and it also strongly increases with the degree of polymerization for the same values of $k_{tr/t} / k_p$. Therefore, the synthesis of controlled polymers should be limited to relatively low degrees of polymerization.

Typical radical polymerizations do not yield controlled polymers because initiation is slow, and the low concentration of radicals, which is necessary to avoid termination, results in very high, uncontrolled, degrees of polymerization. It is, however, possible to accommodate the requirement of a low concentration of growing radicals and a high concentration of propagating chains if the latter are predominantly in their dormant state but are dynamically interconverting with a minute amount of the growing free radicals.

There are two possible exchange reactions between dormant chains and growing radicals. Dormant chains can cleave homolytically to give growing species and scavengers in a unimolecular way (Eq. 1), or they can exchange with growing radicals in the bimolecular fashion (Eq. 2).

$$\mathbf{P\text{-}R} \quad \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} \quad \mathbf{P}^{\bullet} + \mathbf{R}^{\bullet} \qquad (1)$$

$$\mathbf{P}_n^{\bullet} + \mathbf{P}_1\!-\!\mathbf{R} \quad \overset{k_{tr}}{\rightleftharpoons} \quad \mathbf{P}_1^{\bullet} + \mathbf{P}_n\!-\!\mathbf{R} \qquad (2)$$

Typically, dormant species are compounds with an even number of electrons but it may also happen that the role of the dormant species is played by persistent radicals which reversibly release growing radicals (Eq. 3).

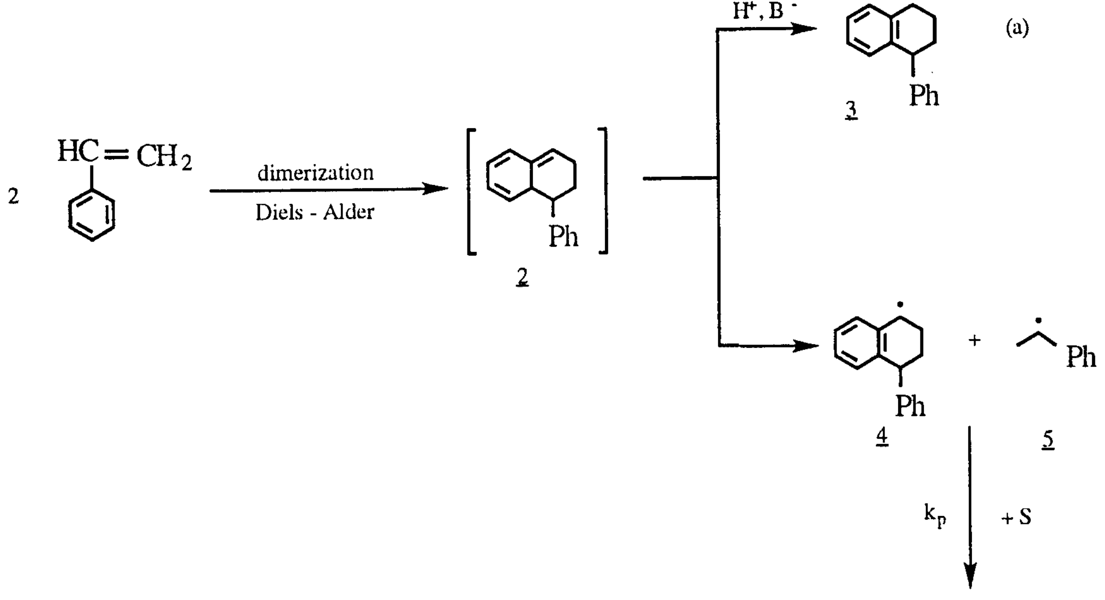
$$\mathbf{P}^{\bullet} + \mathbf{X} \quad \rightleftharpoons \quad \{\mathbf{P} - \mathbf{X}\}^{\bullet} \qquad (3)$$

UNIMOLECULAR EXCHANGE BETWEEN GROWING RADICALS AND DORMANT ALKOXYAMINES

The successful operation of the unimolecular exchange process requires the equilibrium, described by Eq. 1, to be strongly shifted to the side of the dormant species in order to maintain a low momentary concentration of radicals. It also requires that the scavenger does not initiate polymerization and that it remains unchanged during the polymerization process.

Among many reported covalent species, alkoxyamines behave in the cleanest way (Ref. 4). Nitroxyl radicals do not react directly with alkenes, or they react extremely slowly, they are relatively stable even at elevated temperatures, and they react with diffusion controlled rates with most organic radicals. Some other potential scavengers such as dithiocarbamates or trityl radicals do react with alkenes and also decompose, e.g. $R_2NC(S)S^*$ to R_2N^* and CS_2 (Ref. 5, 6).

Alkoxyamines have been used in the polymerization of methacrylates and acrylates as initiators, either alone or together with peroxy initiators at temperatures <100 °C (Ref. 7). More recently, this system has been extended to the polymerization of styrene (Ref. 8). However, temperatures above 120 °C were required to break the $C-ONR_2$ bond. In Ref. 8, alkoxyamines were prepared in situ from the nitroxyl radical, 2, 2, 6, 6 - tetramethyl - 1-piperidinyloxy, 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. At temperatures >100 °C, styrene polymerizes by self-initiation via formation of the Diels-Alder adduct which is further aromatized, generating radicals (Eq.4).



(4)

Thus, radicals are slowly formed even during the polymerization. However, because propagation is first order in monomer and spontaneous initiation is second or third order in monomer, contribution of self-initiation decreases with conversion, provided that the growing species are not irreversibly terminated. In order to reduce self-initiation, protonic acids have been added (Ref. 9); acids, however, promote dimerization and may also lead to indanic dimers.

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 (Ref. 10). Thus, in principle, for the polymerization of styrene, it is not necessary to use radical initiators in systems moderated by nitroxyl radicals.

Fig. 2 shows the kinetic plots of the polymerization of bulk styrene at 120 °C in the presence of TEMPO, $[TEMPO]_0 = 0.01$ mol / L, initiated by benzoyl peroxide, $[BPO]_0 = 0.01$ and 0.03 mol / L, and AIBN, $[AIBN]_0 = 0.01$ and 0.03 mol / L, as well as the self-initiated system.

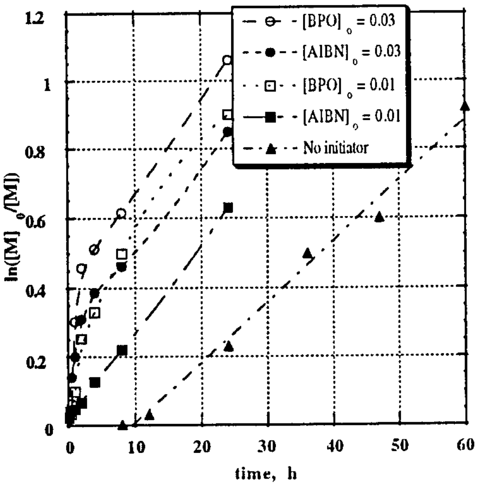


Fig. 2 Kinetics of the bulk polymerization of styrene at 120 °C with BPO / AIBN and $TEMPO]_0 = 0.01$ mol / L.

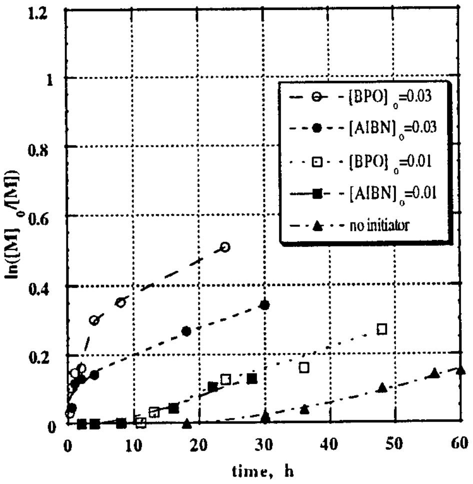


Fig. 3 Kinetics of the bulk polymerization of styrene at 120 °C with BPO / AIBN and $[TEMPO]_0 = 0.03$ mol / L.

Initially, non - stationary periods were observed in some of the systems. However, subsequently similar slopes of the kinetic plots have been found. This indicates that the same stationary conditions are reached, regardless of the nature and concentration of the initiator. Polymerizations initiated by BPO have higher initial rates, presumably due to the higher efficiency of initiation, than systems initiated by AIBN.

Fig. 3 presents similar plots but with a higher scavenger concentration, $[\mathrm{TEMPO}]_o = 0.03$ mol / L. Now, induction periods are observed not only for the self-initiated system, but also when the concentration of radicals generated by thermal decomposition of the initiator is inferior to the scavenger concentration.

If a simple equilibrium between alkoxyamines and growing radicals is assumed:

$$P_n \wr \text{O-NR}_2 \rightleftharpoons P_n^{\bullet} + {}^{\bullet}\text{O-NR}_2 \qquad (5)$$

then,

$$K = [P_n^*]\,[ONR_2^*] / [P_n\text{-}ONR_2] \qquad (6)$$

The concentration of growing radicals, as estimated from the kinetic plots, is much lower than that of the dormant chains $[P_n^*] << [P_n\text{-}ONR_2]$, the latter being close to the initial concentration of the scavenger. The slopes of the semilogarithmic plots are equal to:

$$-d\ln[M] / dt = k = k_p^*\,[P_n^*] = k_p^{app}\,[P_n\text{-}ONR_2] \qquad (7)$$

Combination of Eqs. (6) and (7) gives an estimate of the equilibrium constant, K.

$$K = [ONR_2^*]\,k_p^{app} / k_p^* \qquad (8)$$

The estimates of the equilibrium constant are in the range of $K \approx 10^{-9\pm1}$ mol / L. These are based on the observed rate coefficients $k \approx 10^{-5}\ s^{-1}$, radical propagation rate constant $k_p^* \approx 10^3\ mol^{-1}{\cdot}L{\cdot}s^{-1}$, number of dormant chains similar to the introduced scavenger, and ≈ 10% remaining scavenger in the systems (UV). Because the equilibrium constant is defined by the ratio of the rate constants of the homolytic cleavage and the diffusion controlled trapping of the growing radicals, $\approx 10^9\ mol^{-1}{\cdot}L{\cdot}s^{-1}$, the value of the former should be in the range of $k \approx 10^{0\pm1}\ s^{-1}$.

Figures 4 and 5 show typical SEC traces obtained from 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. In the former case, M_n corresponds to the total number of chains produced by the initaiting 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. This is illustrated in Figs. 6, 7, 8 and 9.

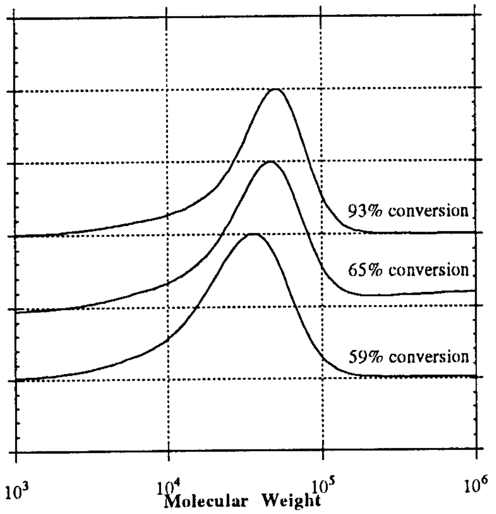


Fig. 4 Bulk polymerization of styrene with $[AIBN]_0 = 0.03$ mol / L and $[TEMPO]_0 = 0.01$ mol / L at 120 °C.

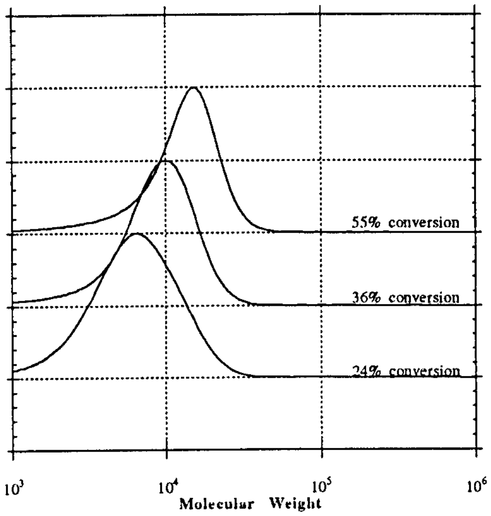


Fig. 5 Bulk polymerization of styrene with $[AIBN]_0 = 0.03$ mol / L and $[TEMPO]_0 = 0.03$ mol / L at 120 °C.

Fig. 6 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. 7, correlate to the scavenger concentration because it defines the concentration of chains which are in their dormant state and which are capable of growth.

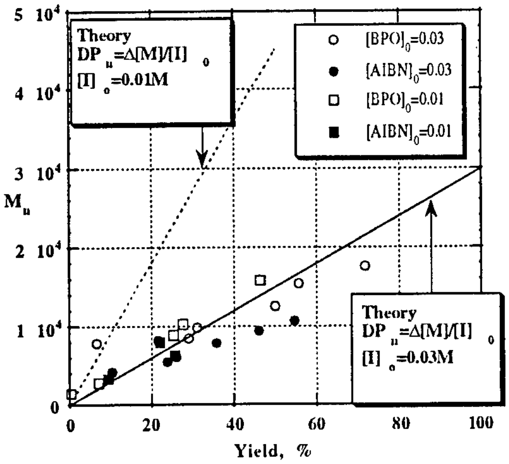


Fig. 6 M_n dependence upon conversion in the bulk polymerization of styrene at 120 °C with BPO / AIBN and $[TEMPO]_0 = 0.03$ mol / L.

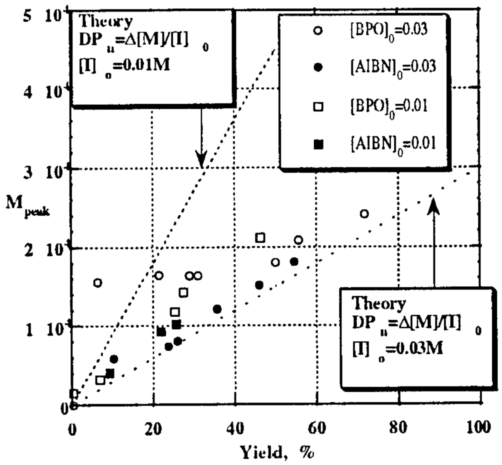


Fig. 7 M_{peak} dependence upon conversion in the bulk polymerization of styrene at 120 °C with BPO/AIBN and $[TEMPO]_0 = 0.03$ mol/L.

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 (Figs. 8 and 9), because polymerization starts only when the concentration of radicals formed from the initiator and by self-initiation becomes comparable to the initial scavenger concentration.

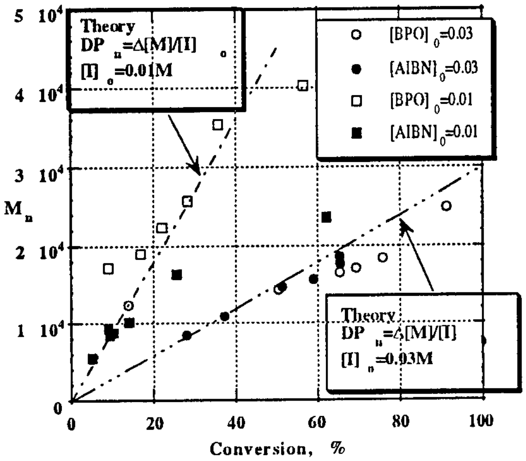


Fig. 8 M_n dependence upon conversion in the bulk polymerization of styrene at 120 °C with BPO / AIBN and $[TEMPO]_0 = 0.01$ mol / L.

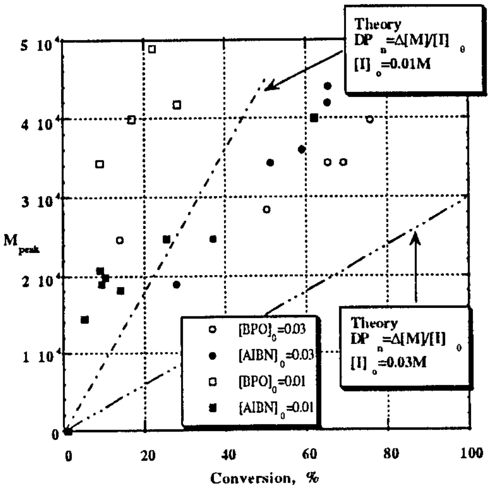


Fig. 9 M_{peak} dependence upon conversion in the bulk polymerization of styrene at 120 °C with BPO/AIBN and $[TEMPO]_0 = 0.01$ mol/L.

Polydispersities either increase or decrease with conversion. The former 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. (Figs. 10, 11).

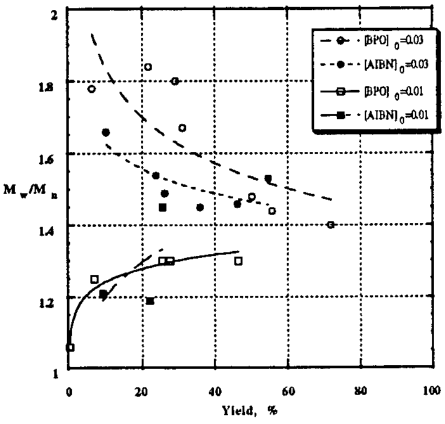


Fig. 10 Polydispersity dependence upon conversion in the bulk polymerization of styrene at 120 °C with BPO / AIBN and $[TEMPO]_0 = 0.03$ mol / L.

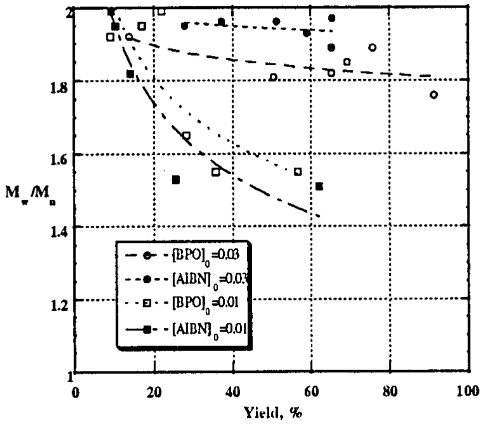
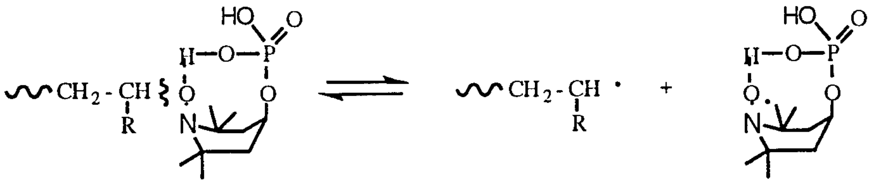


Fig. 11 Polydispersity dependence upon conversion in the bulk polymerization of styrene at 120 °C with BPO / AIBN and $[TEMPO]_0 = 0.01$ mol / L.

Spontaneous self-initiation in the polymerization of styrene starts at elevated temperatures and could be avoided if the rate of the homolytic cleavage could be accelerated. We studied the effect of different nitroxyl radicals and found that 4-phosphonooxy-TEMPO provides much faster polymerization than either TEMPO or 4-hydroxy-TEMPO. This is shown in Fig. 12.

Higher rates could be due not only to a shift in the equilibrium position, but also in less efficient scavenging. However, the total number of chains with 4-phosphonooxy-TEMPO is nearly the same as with other nitroxyl radicals. (Fig. 13)

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 (Eq. 9).



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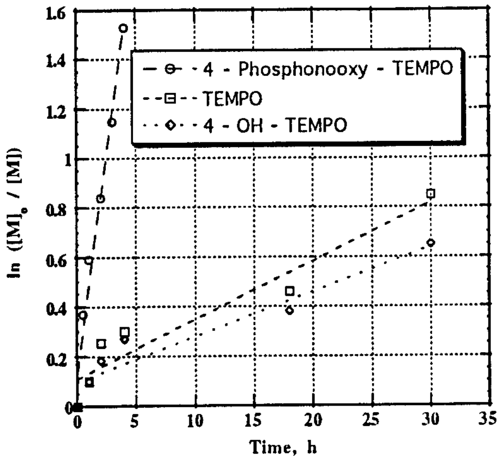


Fig. 12 Kinetics of styrene polymerizations at 110 °C with various TEMPO derivatives.

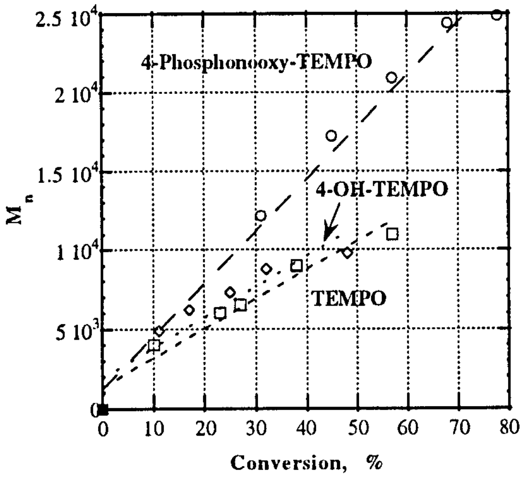


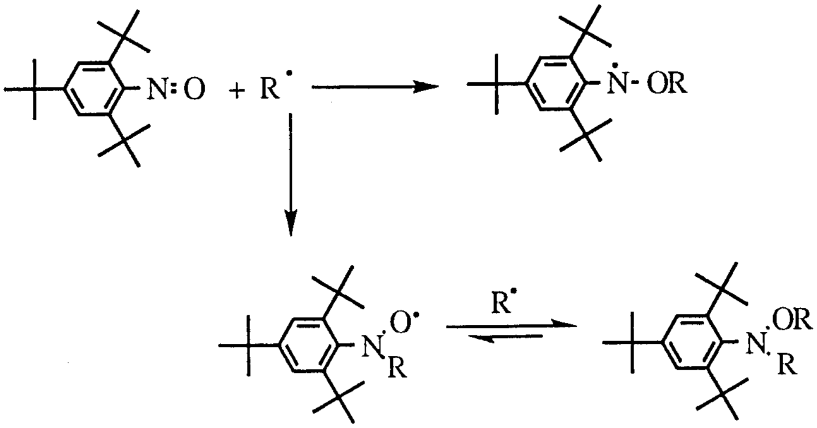
Fig. 13 M_n dependence upon conversion in the bulk polymerization of styrene at 120 °C with various TEMPO derivatives.

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. This 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.

One potential method of preparing new nitroxyl radicals is based on the in situ generation of scavenging nitroxyl radicals from nitroso compounds. We used 2-methyl-2-nitrosopropane, MNP, and 2, 4, 6-tri(tert-butyl)nitrosobenzene, TBNB, compounds in the presence of variable amounts of AIBN used as initiators. It is expected that for the 100% efficiency of AIBN, equimolar amounts of the initiator, and nitroso species are necessary to produce alkoxyamine. Excess of the initiator may be necessary to assure sufficiently fast polymerization.

The polymerization was very slow when an equimolar ratio of MNP and AIBN was used, and a two fold excess of AIBN was required to observe a significant rate of polymerization of MMA at 80 °C. On the other hand, a 1:1 ratio of TBNB and AIBN gave a relatively rapid polymerization with an uncontrolled initial period. A two fold excess of AIBN extended this non stationary period considerably.

This indicates that the efficiency of the initial trapping is dependent on the structure of nitroso compound and nitroxyl radical. For example, the much less reactive anilino radicals can be produced (Eq. 10). In addition, the equilibrium position between active and dormant species may be affected by substituents in the nitroxyl radical. Protected by three tert-butyl groups, α-aromatic substituents may either reduce the reactivity of the nitroxyl radical or accelerate homolytic cleavage of the corresponding alkoxyamines.



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EXCHANGE BETWEEN GROWING RADICALS AND DORMANT ORGANOMETALLIC SPECIES

The reversible reaction of organic radicals with cobaloxime is probably the most well known radical reaction involving organometallic species (Ref. 11). This process was successfully transferred from biological systems to polymer chemistry (Ref. 12) to prepare unsaturated poly(methyl methacrylate) oligomers with catalytic amounts of cobaloxime. Apparently, for less sterically demanding acrylate radicals, reversible formation of dormant species is observed, without loss of β-H atoms (Ref. 13). Another class of organometallic compounds used successfully for radical polymerization are Cr^{III} species which lead to controlled radical polymerization of MMA initiated by redox reaction with BPO (Ref. 14).

We have extended the latter system to the polymerization of vinyl acetate (Ref. 15) by changing the ligands around chromium and have found a monotonous increase of molecular weights with conversion for 1, 4, 7, 10, 13, 16 - hexaazacyclooctadecane trisulfate, N_6, H^+, as shown in Fig. 14.

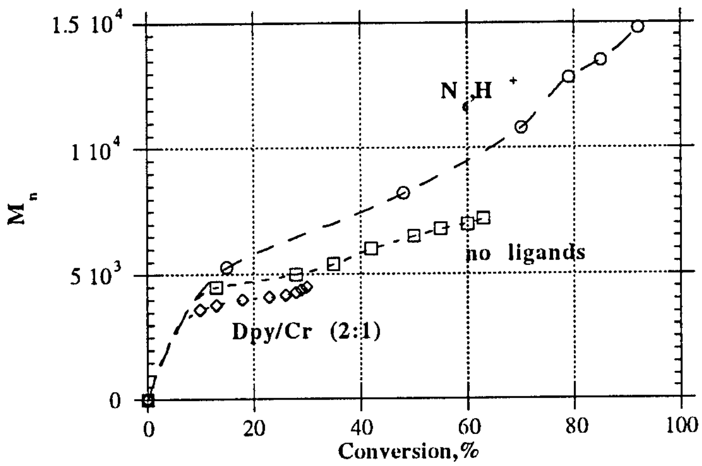


Fig. 14 M_n dependence upon conversion in the polymerization of vinyl acetate with chromium acetate and various ligands in THF at 20 °C.

The N_6, H^+ ligand leads also to the fastest polymerization, probably due to better solubility of the initial chromium diacetate and a faster electron transfer process as well as the potential ligand exchange between acetate / benzoate and sulfate species. Apparently, dipyrydyl did not improve this system.

Another electron transfer source may be provided by p - chlorophenyl diazonium tetraflouroborate salts. In these cases, the reactions are faster and the molecular weights increase linearly with conversion for $Co(OAc)_2$, $Cr(OAc)_2$ and $Ce(OAc)_3$, as shown in Fig. 15. Apparently, the molecular weights were initially higher than expected for $Rh(OAc)_2$ which may indicate slow initiation. Nevertheless, polydispersities for the latter system were relatively low, $M_w / M_n \approx 1.25$ to 1.45.

The last system which will be discussed is based on the ternary mixture of trialkyl aluminum, a complexing ligand such as 2, 2' - dipyridyl, and a stable radical such as TEMPO. This initiating system has been reported previously as a successful one in the polymerization of vinyl acetate and other monomers (Ref. 16, 17). The ternary initiating system $Al(i\text{-}Bu)_3$ / DPy / 2 TEMPO has also been used in the preparation of block copolymers. However, as in most organoaluminum species, it is very sensitive to moisture

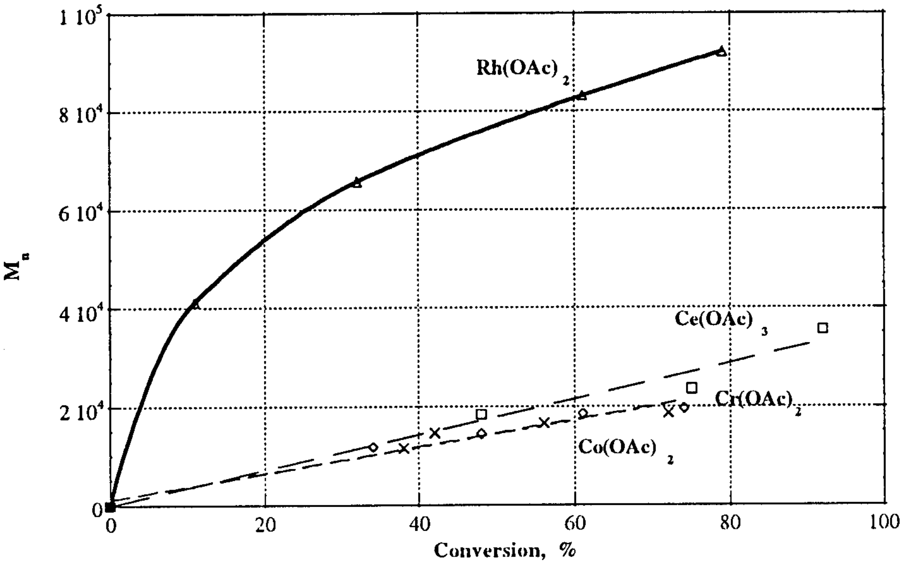


Fig. 15 M_n dependence upon conversion in the polymerization of methyl methacrylate using a diazonium salt and transition metal catalyst.

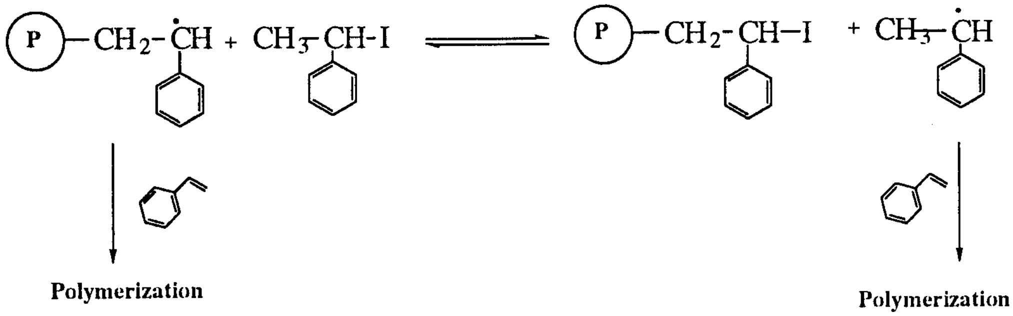
and oxygen. Apparently, small amounts of moisture and oxygen improve the polymerization system but larger quantities of moisture and oxygen terminate polymerization. The detailed studies on the effect of both reagents will be reported elsewhere.

Reactions with organometallic compounds may proceed not only via homolytic cleavage of the Mt-C bond but also by heterolytic cleavage leading, for example, to enolate anions in polymerization of MMA. The coordinative polymerization and insertion of monomer into Mt-C bond is also feasible. In order to have a deeper insight into the mechanism of these reactions, it is necessary to study effect of various quenching reagents and the reactivity ratios in copolymerization. It may happen, however, that scavengers, such as TEMPO, modify or even destroy the reactive sites as observed in polymerization of VAc initiated by the aforementioned ternary system. The copolymerization rates may be strongly affected by the equilibria involving both growing radicals, especially if one is more electrophilic and the other more nucleophilic. The scavenger / copolymerization studies are, however, necessary to understand the nature of the growing species involved in these reactions.

BIMOLECULAR EXCHANGE BETWEEN GROWING RADICALS AND DORMANT SPECIES

As shown in Eq. 2, not only unimolecular but also bimolecular exchange between the growing and dormant species may take place. The potential advantage of the bimolecular exchange system is that it may be based on the classic initiator added in small amounts to the efficient transfer agent. The ideal bimolecular exchange should involve a thermodynamically neutral transfer. This means that the transfer agent should contain a P species resembling the growing radical P*. In such a case, the transfer may be considered as a degenerative process. The prerequisites for the successful degenerative transfer agent also include its stability to homolytic cleavage, otherwise a unimolecular process will take place, and a sufficient lability of the P-R bond. Similar reaction are known in synthetic organic chemistry (Ref. 18).

We have used an alkyl iodide, 1-phenylethyl iodide, in the polymerization of several alkenes as degenerative transfer reagents and have found that it is successful in controlling the polymerization of styrene, and butyl acrylate.



(12)

The radicals generated by the initiator, AIBN, propagate and exchange iodine from the majority of the other chains relatively rapidly. This is evidenced by the observation that the molecular weights correspond to the concentration of transfer agents rather than initiator. Without the transfer agent, the molecular weight of the polystyrene was rather constant throughout the reaction at around $M_n = 60{,}000$. However, in the presence of the transfer agent, 1-phenylethyl iodide, the molecular weights drop to levels which are approximately equal to $DP_n = \Delta[M] / [X]_0$. Also, the molecular weight of the polymer increases with conversion in contrast with the sample without the transfer agent.

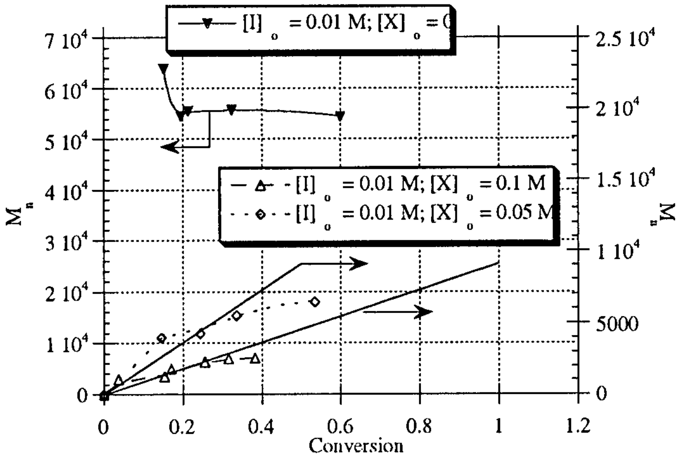


Fig. 16 Dependence of M_n upon conversion in the bulk polymerization of styrene in the presence of AIBN, $[I]_o$, and 1-phenylethyl iodide, $[X]_o$. The solid lines indicate the theoretical M_n based upon $DP_n = \Delta[M] / [X]_o$.

CONCLUSIONS

Controlled radical polymerizations have been achieved by using either unimolecular or bimolecular exchange between the growing radicals and dormant chains. Dormant chains have been represented by either covalent species or organometallic compounds. In many systems, straight semilogarithmic plots indicated a constant number of growing radicals and an increase in molecular weights with conversion indicated a constant number of chains capable of growth but being predominantly in the dormant state.

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