'LIVING' AND CONTROLLED RADICAL POLYMERIZATION

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Radical polymerizations cannot truly be 'living' because of the inevitable termination between growing radicals. However, relatively good control of molecular weights, polydispersities and terminal functionalities can be achieved by using either unimolecular or bimolecular exchange between growing radicals and dormant chains. The dormant chains can be in the form of either covalent species or organometallic compounds. Some systems based on alkoxyamines, organochromium compounds, organoaluminum compounds and alkyl iodides were studied and are discussed in detail.

INTRODUCTION

The importance of radical polymerizations can be ascribed to a large variety of monomers which can be polymerized and copolymerized radically and to the undemanding experimental conditions. Radical polymerizations require the absence of oxygen but can be carried out in the presence of water, e.g. suspension or emulsion polymerization, and in a convenient temperature range, ≈ 0 to $100\,°C$. However, the control over macromolecular structure in radical polymerizations is poor and much worse than in ionic polymerizations. Since the possibility of controlling molecular weights, polydispersities and terminal functionalities is very attractive for the preparation of new materials, it is desirable to improve the control of macromolecular structure in radical processes.

Well defined polymers are prepared in living systems without chain-breaking reactions. However, it has recently been noted that controlled polymerizations can also be obtained in systems in which transfer and/or termination reactions are present but molecular weights have been adjusted to a level where contribution of these reactions could be neglected.[1]

Termination is the most important chain breaking process in radical polymerization. The contribution of termination increases with the concentration of growing radicals, $[P^\bullet]$, because termination is second order in $[P^\bullet]$ and propagation is first order in $[P^\bullet]$. The proportion of deactivated chains increases with increasing chain length. Therefore, the synthesis of well defined polymers by controlled radical polymerization requires a low momentary, or stationary, concentration of growing radicals which should reversibly deactivate to provide a large number of relatively short chains In addition, initiation rates should be at least comparable to that of propagation to appropriately control molecular weights.

Three possibilities of controlling radical polymerization have been discussed in a recent review:[2]

1. Deactivation of a growing radical with a stable radical by the reversible formation of dormant covalent species, followed by their homolytic cleavage

$$P - R \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P^\bullet + R^\bullet \qquad (1)$$
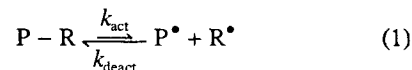
A dormant species, P-R, is the adduct of the growing radical $P^\bullet$ and a scavenging radical $R^\bullet$. $R^\bullet$ can react only with $P^\bullet$ but not with the monomer, M, and cannot initiate polymerization. The covalent adduct cleaves homolytically to $P^\bullet$ and $R^\bullet$ with the rate constant of activation, k_{act} and P-R is reformed with the rate constant of deactivation, k_{deact}.

2. Reversible deactivation of a growing radical with a 'non-radical' species through the formation of a dormant persistent radical [equation (2)]. In this case, a stable adduct with an odd number of electrons, a

persistent radical, is reversibly formed:

$$P^{\bullet} + X \rightleftharpoons \{P - X\}^{\bullet} \qquad (2)$$
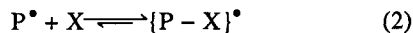
3. Reversible degenerative transfer based on thermodynamically neutral exchange reactions between growing radicals and transfer agents:

$$P_n^{\bullet} + P_1 - R \xrightarrow{k_{tr}} P_1^{\bullet} + P_n - R \qquad (3)$$
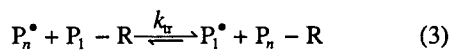
Here, the basic requirement for a 'living', or controlled, system is that a growing $P_n^{\bullet}$, reacts rapidly and selectively with a transfer agent, P_1–R, to exchange ligand R and to form a dormant species P_n–R and a new radical $P_1^{\bullet}$ capable of chain growth. The latter, after addition of $m - 1$ monomer units, $P_m^{\bullet}$, will react again with a transfer agent, P_n–R, to form P_m–R and $P_n^{\bullet}$. If the exchange is fast, polymers with a narrow molecular weight distribution can be prepared. The degree of polymerization is defined by the ratio $DP = \Delta[\text{M}]/[\text{P}-\text{R}]$ and the reaction rate by a low concentration of stationary radicals $[\text{P}^{\bullet}]$. This concentration has to be kept low enough to reduce the possibility of bimolecular termination.

In the first category, nitroxyl radicals, protected phenoxyl radicals, dithiocarbamate, trityl and benzhydryl derivatives have been used with variable success. The second category is generally based on organometallic compounds which form stabilized hypercoordinated radicals. The third group requires very rapid and 'clean' transfer without any side reactions.

The control of a polymerization process is enhanced due to (i) a reduction in the ratio of the rate of termination to that of propagation, owing to low instantaneous concentration of growing radicals; (ii) similar rates of initiation and propagation due to application of initiators resembling polymer end groups in their dormant state; and (iii) a low proportion of chains marked by uncontrolled termination and/or transfer due to relatively low molecular weights.

Below, some examples of the synthesis of polymers by radical polymerization with enhanced control are discussed.

REVERSIBLE DEACTIVATION BY NITROXYL RADICALS

The first announcement of a 'living' radical polymerization appeared in 1982 when Otsu and Yoshida[3] reported an increase of molecular weight with conversion in the polymerization of styrene and methacrylates in the presence of dithiocarbamates. Later, more detailed studies indicated that in addition to the proposed iniferter action, some side reactions occurred. The term iniferter stands for a compound which acts at the same time as an *ini*tiator, trans*fer* agent and *ter*minator. The side reactions include decomposition of the

dithiocarbamates and degradative transfer by formation of head-to-head polymers and dithiocarbamate radicals [equation (4)].[4,5] The latter can reinitiate polymerization, although very slowly.

$$R_2N \cdot C(S) S \cdot P'_n \;\; + \;\; P_m^{\bullet} \longrightarrow R_2N \cdot C(S) S^{\bullet} \;\; + \;\; P'_n - P_m \qquad (4)$$
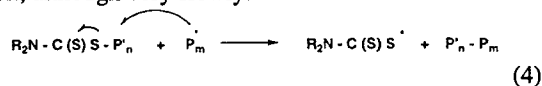
In some other systems, based on relatively stable trityl and benzhydryl radicals, side-reactions and initiation with scavenging radicals also occur.[6,7] In fact, the increase in molecular weight with conversion in the polymerization of methyl methacrylate initiated by 3,3,4,4-tetraphenylhexane might be the first report on controlled radical polymerization.[6]

Probably the best system described in the literature employs nitroxyl radicals such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and its derivatives. These radicals are stable to above 100 °C, do not initiate polymerization and react very rapidly with C-based radicals such as the growing species in the radical polymerization of alkenes. Alkoxyamines, which are the products of these reactions decompose reversibly at elevated temperatures:

$$P_n \, \S \, O - NR_2 \rightleftharpoons P_n^{\bullet} + {}^{\bullet}O - NR_2 \qquad (5)$$
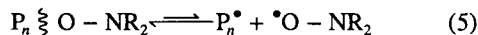
The position of the equilibrium depends on the nature of the radicals, solvent and temperature. Originally, polymerization of acrylates and methacrylates was initiated by a mixture of alkoxyamines prepared in advance and by classical initiators for radical polymerization.[8] The excess of radicals might exchange via degenerative transfer [equation (3)].

More recently, alkoxyamines have been generated in the polymerization of styrene *in situ* from benzoyl peroxide (BPO) and a small excess of TEMPO ($[\text{TEMPO}]_0/[\text{BPO}]_0 \approx 1.2$).[9] The polymerization of styrene in the presence of TEMPO requires relatively high temperatures, *ca.* 120 °C at which point spontaneous thermal initiation of styrene becomes significant. Apparently, BPO decomposition was accelerated in the presence of TEMPO.[10] Acidic additives have been used to reduce thermal self-initiation.[9,11]

We have previously reported that the spontaneous thermal polymerization of styrene could also be controlled through the use of various stable radicals.[12] Initially, polymerization was inhibited by these radicals and started after an induction period, when nearly all stable radicals were consumed. The induction periods and the rates of the subsequent controlled propagation depended on temperature and on the concentrations of scavenging radicals. Molecular weights were controlled by the amount of the scavenger and polydispersities were lower than in the usual radical polymerization, $M_w/M_n \approx 1.3$.

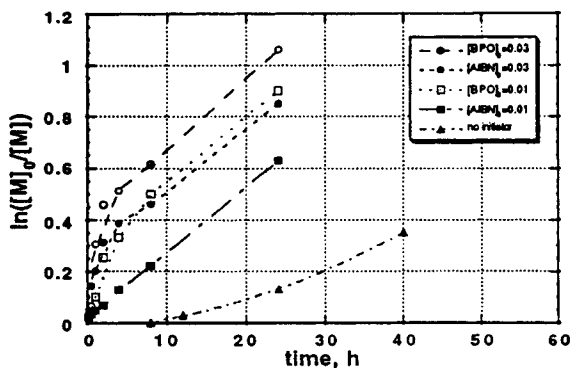The polymerization of styrene in the presence of nitroxyl radicals occurred regardless of the source of

Figure 1. Kinetics of bulk polymerization of styrene at 120 °C in the presence of [TEMPO]$_0$ = 0·01 M and [BPO]$_0$ = 0·03 and 0·01 M, [AIBN]$_0$ 0·03 and 0·01 M, and also without initiator

the radicals. Radicals may be formed by the spontaneous thermal initiation. by the redox process with BPO, but this is less important at 120° C. Initiation may also occur by the thermal decomposition of the initiator [azobisisobutyronitrile (AIBN) and also BPO].[13] However, the degree of control depends on the amount of radicals and also on the dynamics of exchange.

The amount of the scavenger controlled the polymerization rates and molecular weights. The rate of polymerization decreased with an increase in the concentration of the initial scavenger. This possibly indicated the presence of a relatively high stationary concentration of the scavenger. The amount of the initiator regulated the induction period and if used in excess over scavenger, it also affected M_n (Figure 2). When the initiator was used in excess over the scavenger, initially fast polymerization was observed during which uncontrolled, high molecular weight polymers were formed. Subsequently, stationary conditions were reached which were independent of the structure and concentration of the initiator.

For a simple equilibrium between alkoxyamines and growing radicals described by equation (5), the equilibrium constant is given by

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

The concentration of growing radicals can be estimated from the kinetic plots. It is much lower than that of the dormant chains $[P_n^*] \ll [P_n - ONR_2]$. The latter is close to the initial concentration of the scavenger. The slopes of the kinetic plots are

$$-d \ln[M]/dt = k = k_p^*[P_n^*] \qquad (7)$$

The equilibrium constant, K, can be estimated by combination of equations (6) and (7):

$$K = [ONR_2^*]k/k_p^* [P_n - ONR_2] \qquad (8)$$

The values of the equilibrium constant, estimated in the polymerization of styrene at 120 °C, were in the range $K < 10^{-10}$ mol l^{-1}. They were based on the observed rate coefficients $k \approx 10^{-5}$ s^{-1}, a radical propagation rate constant $k_p^* \approx 10^3$ mol^{-1} l s^{-1}, the number of dormant chains similar to the introduced scavenger and less than 1% of the scavenger remaining 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, ca 10^9 mol^{-1} l^{-1} s^{-1}, the rate constant of the cleavage should be in the range of $k_{act} < 10^{-1}$ s^{-1}. However, direct NMR studies indicate that P–ONR$_2$ decomposes much slower, $k_{act} = 10^{-5}$ s^{-1} at 120 °C.

The position of the maximum on gel permeation chromatographic (GPC) traces, M_{peak} closely follows the values predicted for the number of chains deactivated by TEMPO in the form of alkoxyamines. However, as shown in Figure 2, M_n values correspond to the total number of chains and are reasonably proportional to the concentration of the initiator, corrected for self-initiation and the coupling/disproportionation of the growing chains. The polydispersities remained relatively low and in some cases they decreased with conversion, especially when excess initiator was used. The polydispersities also were affected by the dynamics of the exchange reactions.

The dynamics and thermodynamics of the exchange reactions depended on the structure of growing radicals and nitroxyl radicals, and also on some additives, solvents and temperature. The structure of TEMPO-like radical scavenger used in the polymerization of styrene initiated by AIBN strongly affected polymerization rates, molecular weights and the molecular weight distribution of polymers. Figures 3 and 4 show the kinetic plots and the evolution of molecular weight with conversion for the polymelization of styrene initiated by AIBN in the
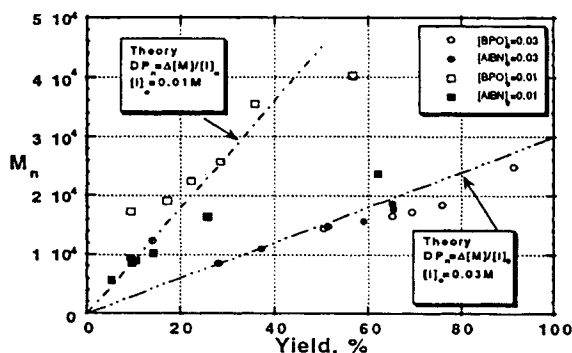

Figure 2. Evolution of molecular weight with conversion in the bulk polymerization of styrene at 120 °C in the presence of [TEMPO]$_0$ = 0·01 M and [BPO]$_0$ = 0·03 and 0·01 M, [AIBN]$_0$ = 0·03 and 0·01 M
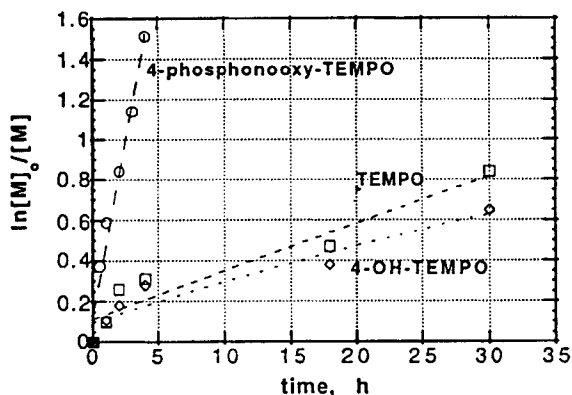
Figure 3. First-order–time-conversion plots in the radical polymerization of styrene initiated by AIBN (0·03 M)/TEMPO-based nitroxyl radicals (0·03 M) at 120 °C
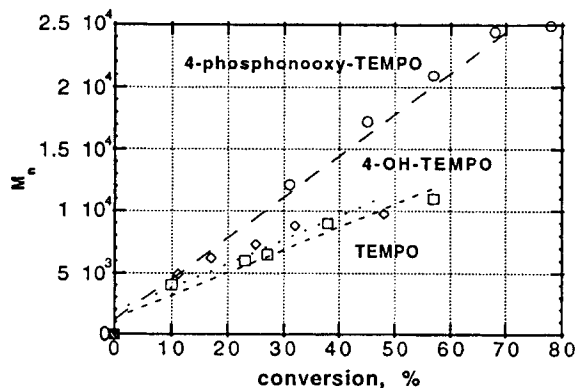

Figure 4. M_n–conversion dependence in the radical polymerization of styrene initiated by AIBN (0·03 M)–TEMPO-based nitroxyl radicals (0·03 M) at 120 °C

presence of TEMPO, 4-hydroxy-TEMPO and 4-phosphonooxy-TEMPO as radical scavengers.

The polymerization rates increased approximately tenfold in the presence of 4-phosphonooxy-TEMPO and decreased slightly in the presence of 4-hydroxy-TEMPO, when compared with unsubstituted TEMPO. The molecular weights increase linearly with conversion in all cases, but had higher values in the presence of 4-phosphonooxy-TEMPO, at the same initial concentrations of initiator, AIBN, and radical scavenger.

The faster reaction with 4-phosphonooxy-TEMPO may be explained by the shifting of the equilibrium towards growing radicals. This would be due to faster homolytic cleavage of the deactivated species or due to

the lower reactivity of the scavenger. These effects might be ascribed to the hydrogen bonding of the phosphoric acid moiety to the nitroxyl oxygen [equation (9)]

$$(9)$$
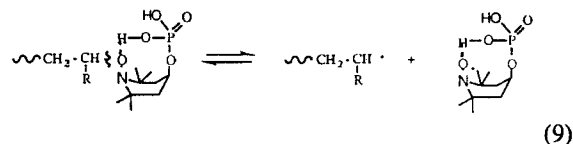
Another possibility affecting the exchange between growing and dormant species may involve the coordination of nitronyl nitroxides.[14] Manganese(II) hexafluoroacetylacetonate was used in the synthesis of mixed-ligand complexes with 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide as the nitronyl nitroxide species [equation (10)].
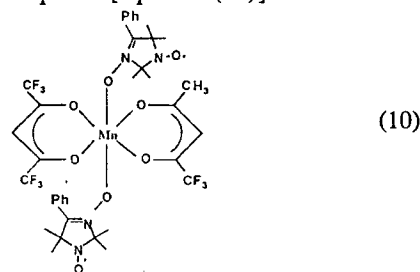

$$(10)$$

Figure 5 shows the kinetic plots for the radical polymerization of MMA and styrene initiated by AIBN, in the presence of the above radical scavenger, with and without complexation with $Mn(hfac)_2$. In the presence of the complexed radical scavenger (1 and 3 in Figure 5) the polymerization rates were higher than using the uncomplexed scavenger (2 and 4 in Figure 5).

It was possible to polymerize styrene at temperatures below 100 °C. The molecular weights of both polymers grew linearly with conversion (Figure 6).

The structure of the organic radicals, or parent monomers, also affects the polymerization rates and the relevant equilibria. It seemed that polymerization of polar vinyl monomers such as vinyl acetate (VAc), methyl methacrylate (MMA) and methyl acrylate (MA) is faster at 80 °C than the polymerization of styrene at 120 °C (Figure 7) under otherwise similar conditions (bulk, AIBN, 0.03 M–TEMPO, 0.03 M).

In most cases, except for methyl methacrylate, the molecular weights increased with conversion as shown in Figure 8 and were defined by the amount of alkoxyamine formed by recombination of TEMPO with the growing radicals. It was possible that the tertiary radicals in the polymerization of MMA participated in transfer reactions which limited molecular weights at lower levels than for the secondary radicals derived from styrene, acrylates and vinyl acetate.

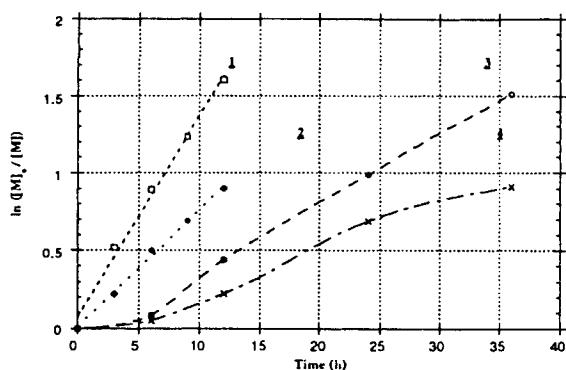Radical polymerizations are not strongly affected by

Figure 5. Kinetic plots for the radical polymerization of MMA and S at 80 °C. (1) MMA [AIBN–4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide–manganese(II) hexafluoroacetylacetonate trihydrate (1 : 1 : 1)]; (2) MMA [AIBN–4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide (1 : 1)]; (3) styrene [AIBN–4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide–manganese(II)hexafluoroacetyl-acetonate trihydrate (1 : 1 : 1)]; (4) styrene [AIBN–4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide (1 : 1)]
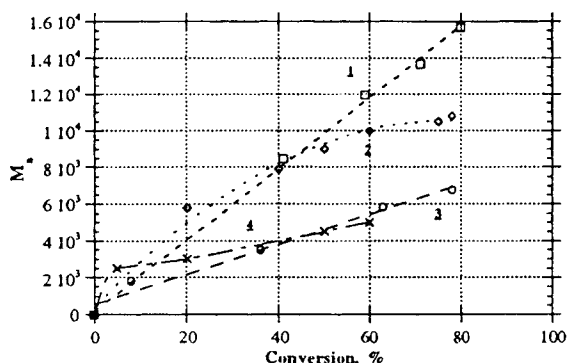

Figure 6. M_n–conversion dependence in radical polymerization of MMA and S at 80 °C. (1) MMA [AIBN–4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide–manganese(II) hexafluoroacetylacetonate trihydrate (1 : 1 : 1)]; (2) MMA [AIBN–4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide (1 : 1)]; (3) styrene [AIBN– 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide– manganese(II) hexafluoroacetylacetonate trihydrate(1 : 1 : 1)]; (4) styrene [AIBN–4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxide (1 : 1)]

the polarity of the solvents, under comparable conditions. However, in the thermal polymerization of styrene in the presence of TEMPO as a radical scavenger, the polymerization rates decreased in the order of bulk > decalin > diglyme. The longest induction period was noticed in the polar solvent, diglyme. In decalin, the initial rates were comparable to those in bulk polymerization, although they later levelled off. The solvent
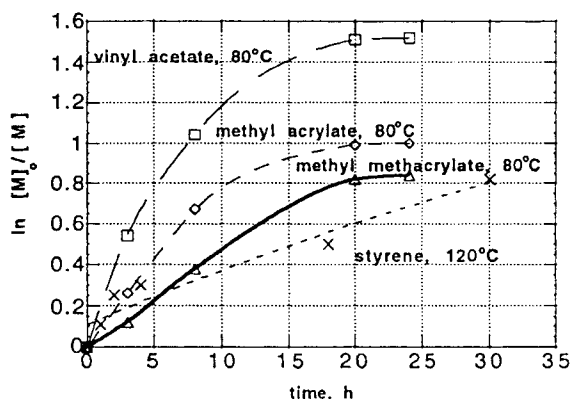

Figure 7. Kinetic plots in the radical polymerization of VAc, MMA, MA and styrene, initiated by AIBN (0·03 M)–TEMPO (0·03 M)
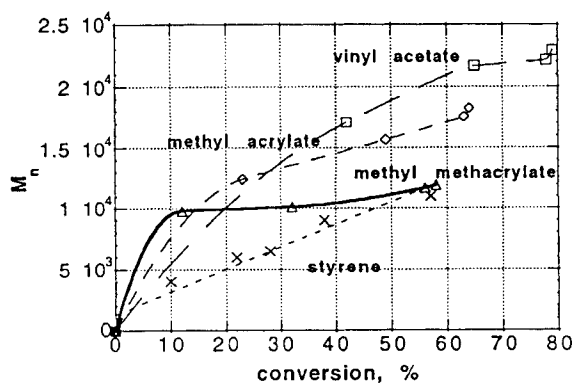

Figure 8. M_n–conversion dependence in radical polymerizations of VAc, MMA and MA, initiated by AIBN (0·03 M)–TEMPO (0·03 M)

effect on the evolution of molecular weights with conversion was very minor.

REVERSIBLE DEACTIVATION WITH ORGANOMETALLIC COMPOUNDS

Transition metals

Reversible reactions of carbon-based radicals with organometallic compounds play an important role in biological systems.[15]Cobaloximes and Co-porphyrins react reversibly with primary and secondary alkyl radicals.[16] They have been used successfully for the controlled polymerization of acrylates.[17,18] On the other hand, a reaction with tertiary radicals was accompanied by β-hydrogen abstraction. Therefore, Co derivatives have been used as efficient chain-transfer reagents in the polymerization of methyl methacrylate.[19,20]

Some transition metal acetylacetonates based on Ni(II) and V(III) have been used as initiators for the living polymerization of acrylic monomers in the presence of aluminium alkyls or alumoxanes.[21,22] The role of aluminium derivatives is not yet clear, although they could be considered as alkylating reagents as in coordinative polymerization. In the absence of the Al derivatives, polymerization could not be completed[21] or did not work in a controlled manner.[22] Controlled polymerization of electron-accepting monomers, methyl methacrylate and di-2-ethylhexyl itaconate, was achieved using lanthanum versatate–diazonium salts. EPR measurements indicated formation of metal-stabilized radicals in these systems.[23]

Initiating systems based on chromium acetate and organic peroxides in DMF as the solvent have already been reported for the radical polymerization of MMA.[24] At temperatures below 30 °C, molecular weights increased monotonously with monomer conversion. These initiating systems have not been used successfully in the polymerization of other vinyl monomers such as vinyl acetate or styrene.

Macrocyclic polyamines such as 1,4,7,10-tetraazacyclododecane (12-ane-4) and 1,4,7,10,13,16-hexaazacyclooctadecane (18-ane-6)[25] and related methyl-substituted derivatives are known as good complexing ligands for many transition metals. The ligand sphere and the coordination geometry have a large influence on the kinetic, thermodynamic and electronic properties of transition metal complexes. In some cases the macrocyclic ligand stabilizes the highest metal oxidation state leading to exceptionally negative values for the metal$^{(n+1)+/n+}$ redox couples,

The controlled polymerization of VAc and MMA in THF was achieved using as the initiator a redox system based on BPO and chromium diacetate in the presence of different N-based ligands [2,2'-dipyridyl(Dpy), 18-ane-6 trisulfate (N_6,H^+) and hexamethyl-18-ane-6 (N_6-CH_3)].[26] Figure 9 shows time–conversion plots obtained in the polymerization of VAc in the presence of different ligands, or without ligands, and also in methanol as the solvent. The highest conversion, up to 90%, obtained in the shortest time, 30 hours, was found in the presence of N_6,H^+ as the ligand.

Figure 10 shows the evolution of molecular weight with conversion for the same three systems. In the case of the macrocyclic ligand N_6,H^+, a monotonous increase in M_n with conversion was observed. However, initially, up to 20% conversion, the increase was faster than at later stages.

In the absence of any ligands, a curvature in the M_n-conversion dependence indicated poor control of molecular weights. However, the molecular weights were significantly lower than those obtained by initiation with BPO alone, in the absence of chromium acetate, suggesting presence of chain transfer reactions.
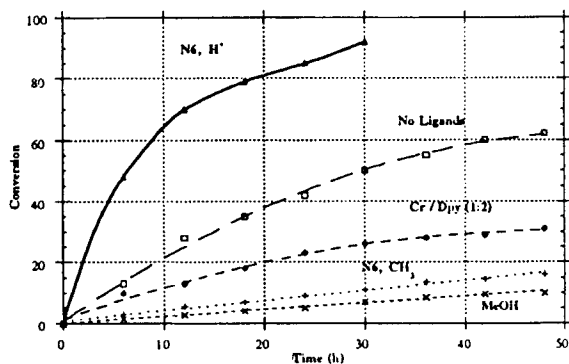

Figure 9. Time–conversion plots in the polymerization of vinyl acetate initiated by BPO–Cr(OAc)$_2$ in the presence of different ligands and solvents
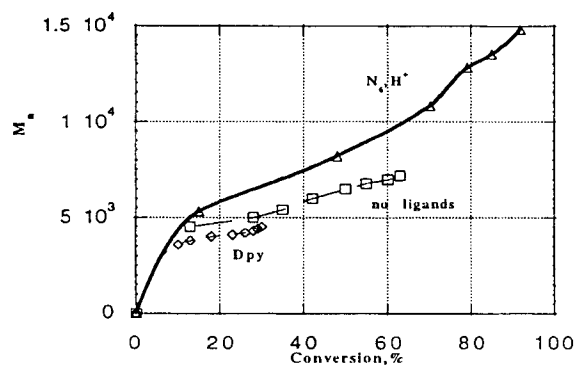

Figure 10. M_n-conversion dependence in the polymerization of vinyl acetate initiated by BPO–Cr(OAc)$_2$ in the presence of different ligands
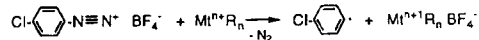
Hence, the reactivity of the system is strongly dependent on the chromium solvation shell and coordination ligands used. Apparently, the reaction between chromium diacetate and BPO is a redox process in which chromium(III) species are generated along with benzoate anion and benzoyloxy radical:[27]

$$Ph\text{-}C(=O)\text{-}O\text{-}O\text{-}C(=O)\text{-}Ph + Cr^{2+}(OAc)_2 \xrightarrow[20°C]{THF} PhCOO^- + Cr^{3+}(OAc)_2(OBz)$$
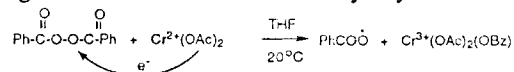
(11)

It was previously proposed that Cr(III) species were complexing the growing PMMA radicals. Such a complex would normally produce Cr(IV) species, which may have lower stability than the Cr(III) compounds. Another possibility is that the Cr(II) species formed complexes with the growing radicals, thus forming Cr(III) species. In that case, Cr(II) will have a dual role: as a redox co-initiator and the reversible scavenger of growing species.

Polymerization of some acrylic monomers can be redox initiated by mixtures (1:1) of transition metal derivatives (acetates, metallocenes) and arenediazonium salts (DS):[28]

$$Cl\text{-}\langle\bigcirc\rangle\text{-}N\equiv N^+ \; BF_4^- \; + \; Mt^{n+}R_n \xrightarrow{-N_2} \; Cl\text{-}\langle\bigcirc\rangle\cdot \; + \; Mt^{n+1}R_n \, BF_4^-$$

$Mt = Rh^{II}, Cr^{II}, Co^{II}, Ce^{III}, Ru^{II}, Zr^{IV}$

$R = OAc$, cyclopentadienyl

Figures 11 and 12 show typical behavior of the (12) polymerization of MMA initiated by mixtures of transition metal acetates with p-chlorobenzenediazonium tetrafluoroborate. The fastest polymerization was observed with the initiating system based on $Ce(OAc)_3$–DS, 90% conversion after 6 h. With $Rh(OAc)_2$–DS, an induction period was found during the first 2–3 hours. Molecular weights increased monotonously with conversion. The highest values were observed with $Rh(OAc)_2$–DS. It seemed that the number of chains was constant for Ce-, Co-, and Cr-based initiating systems but it increased with $Rh(OAc)_2$–DS.
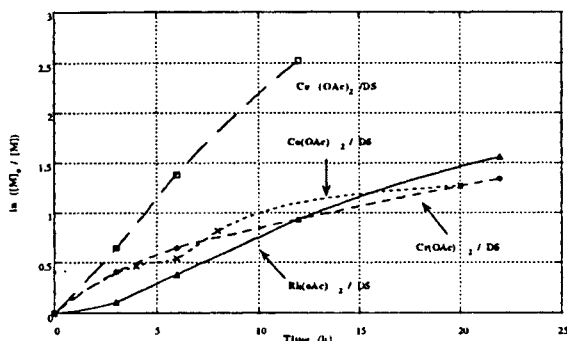

Figure 11. Time–conversion plots in semilogarithmic coordinates for polymerization of MMA initiated by $Mt^{n+}(OAc)_n$–p-chlorobenzenediazonium tetrafluoroborate (1:1); $[MMA]_0 = 5\cdot0$ M, $[I]_0 = 0\cdot125$ M, THF–acetone (1:1), 40 °C
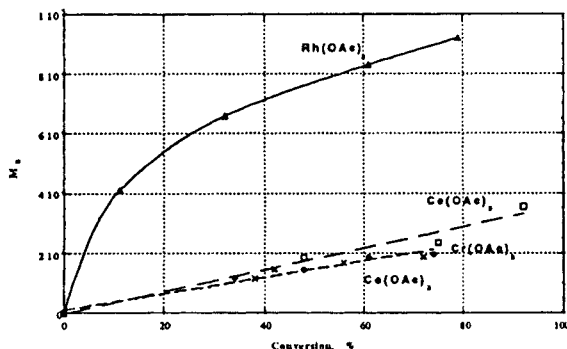

Figure 12. M_n–conversion dependence in polymerization of MMA initiated by $Mt^{n+}(OAc)_n$–p-chlorobenzenediazonium tetrafluoroborate (1:1). $[MMA]_0 = SM_1$ $[I]_0 = 0\cdot12$ M, THF–acetone (1:1), 40 °C

Despite slow initiation, $Rh(OAc)_2$–DS yielded polymers with the lowest polydispersities $(M_w/M_n = 1\cdot2-1\cdot45)$. Three other systems provided polymers with higher polydispersities, although the molecular weights grew linearly with conversion, indicating a low contribution of transfer In most cases, molecular weights increased with conversion and polydispersities were lower than in a typical radical or anionic polymerization at these temperatures. Trapping experiments and relative monomer reactivities based on copolymerization studies indicated that these polymerizations proceeded via a radical mechanism rather than through the anionic coordination pathway. For example, when a mixture of water and acetone was used as the solvent, no effect on the polymerization was observed. The improved polymerization control could be ascribed to an equilibrium between growing radicals and dormant persistent radicals.

In addition to metal acetates, various metallocenes have been reacted with diazonium salts in order to initiate the polymerization of acrylic monomers, acrylates, and methacrylates. Among various metallocenes based on Zr(IV), Ru(II), Cr(II) and Ni(II), dicyclopentadienylchromium, Cp_2Cr, appeared to have the best control of the polymerization of both methyl acrylate and MMA (e.g. PMMA, $M_{n,theor} = 20,000$, $M_w/M_n = 1\cdot24$).

A tentatively plausible mechanism for the initiation of the polymerization of MMA with Cp_2Cr-p-chlorobenzenediazonium tetrafluoroborate is shown in equation (13).

(13)
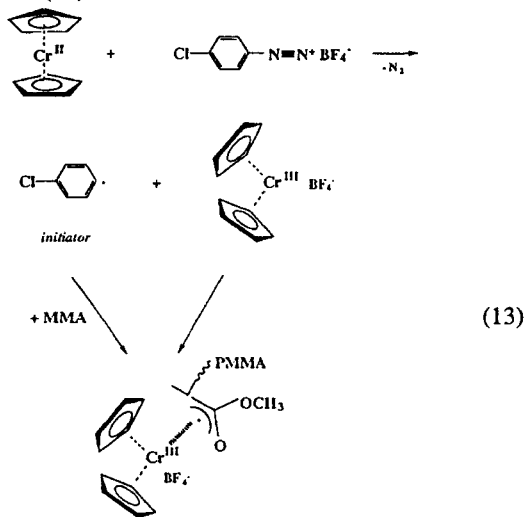
Organoaluminum compounds complexed by ligands and activated by stable radicals

Organoaluminum compounds complexed by various N- or O-based donor ligands such as pyridines,[29] dipyridyl (2,2'- or 4,4'-)[30] or semiquinones[31] produce radicals

which can initiate polymerization. Another method of generating the initiating radicals is through the reaction of organoaluminum compounds with nitroxyl radicals.[32] However, in both of these systems, no control of polymerization has been reported. We used a three-component system based on organoaluminum compounds complexed by 2,2'-dipyridyl and activated by TEMPO.[33,34]

This system had the advantage of fast generation of propagating radicals. This was probably based on the reversible formation of hypercoordinated aluminum radicals which release reversibly propagating radicals. The system is, however, sensitive to moisture and oxygen and its activity depended strongly on the monomer structure. This may be explained by various affinities of the propagating radicals, which may be more or less nucleophilic or electrophilic towards the scavenging species. In addition to the radical pathway, coordination polymerization may also take place. The impurities may catalyze the polymerization but they may also suppress one or more processes. In addition, the effect of time (aging) is important.[33,35]

The polymerization of vinyl acetate in benzene initiated by triisobutylaluminum-2,2'-dipyridyl–TEMPO (1:1:2) at temperatures ranging from 20 to 60 °C, proceeded according to first-order kinetics in monomer and at an apparently constant concentration of growing species.[33] The initial rates of polymerization depended strongly on the Al:TEMPO ratio and seemed to be optimum at a ratio of 1:2. Molecular weights increased linearly with conversion (Figure 13) and the polydispersities remained low (1·2–1·3). Apparently, the lowest polydispersities were observed at the highest temperatures. This may be ascribed to the higher activation energy of propagation
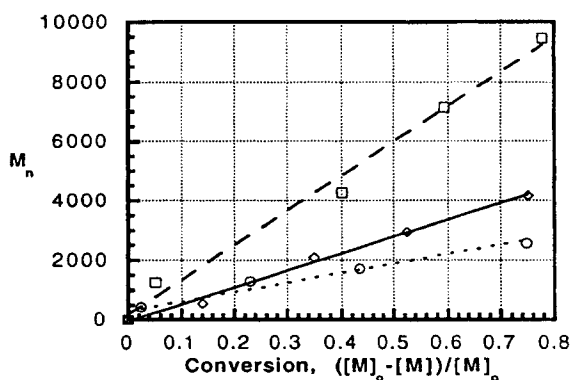
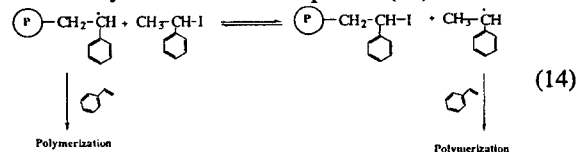than that of termination and the decrease in the proportion of termination with increase in temperature.

The three-component initiating system was also efficient for the polymerization of styrene and MMA. In the latter case, the polymerization rate was a few orders of magnitude faster than for vinyl acetate and polymerization was completed in a few minutes rather than in a few hours under similar conditions.[36]

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 bonds is also feasible. In order to understand the mechanism of these reactions, it is necessary to study the effects of various quenching reagents and the reactivity ratios in copolymerization. It may happen, however, that scavengers, such as TEMPO, modify or destroy the reactive sites of one type, leading to erroneous conclusions. 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.

DEGENERATIVE TRANSFER

As shown in equation (3), not only unimolecular but also bimolecular exchange between the growing and dormant species may take place. The potential advantage of a system with bimolecular exchange is that it may employ a classical initiator added in small amounts to an efficient transfer agent. The ideal bimolecular exchange should involve a thermodynamically neutral transfer. This means that the transfer agent should contain a P moiety resembling the growing radical P·. In such a case, the transfer may be considered 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 reactions involving alkyl iodides and phenylselenides are known in synthetic organic chemistry.[37]

We have successfully used several alkyl iodides as degenerative transfer reagents in the polymerization of various alkenes, including acrylates and styrenes. An example of using 1-phenylethyl iodide in polymerization of styrene is shown in equation (14).

Figure 13. Molecular weight–conversion dependence in polymerization of VAc ([M]₀ 2·5 M) with Al(i-Bu)₃–Dpy–TEMPO (1:1:2) in benzene, at different concentrations of initiator and temperatures: (□) [I]₀ = 0·05 M, 20 C; (◇) [I]₀ 0·05 M, 60 °C; (O) [I]₀ = 0·3 M, 60 °C
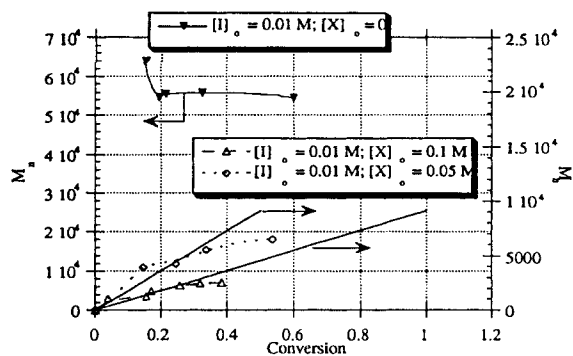
$$\text{(14)}$$

Figure 14. Dependence of Mn upon conversion in the bulk polymerization of styrene in the presence of AIBN (I) and 1-phenylethyl iodide (X). The solid lines indicate the theoretical M_n based on $DP_n = \Delta[M]/[X]_0$

The radicals generated by the initiator, AIBN or BPO, propagate and exchange iodine from the majority of the other chains relatively rapidly. This was evidenced by the observation that the molecular weights corresponded to the concentration of transfer agents rather than initiator. Without the transfer agent, the molecular weight of polystyrene and poly(butyl acrylate) were fairly constant throughout the reaction at around $M_n = 50,000-100,000$. However, in the presence of the transfer agent, X, the molecular weights dropped to levels which were approximately equal to $DP_n = \Delta[M]/[X]_0$ (M_n up to 5000). Also, as shown in Figure 14, the molecular weights increased with conversion in contrast to the sample without the transfer agent.

CONCLUSIONS

Radical polymerizations cannot be truly 'living' because of the inevitable termination between growing radicals. However, relatively good control of molecular weights, polydispersities and terminal functionalities can be achieved by using unimolecular and bimolecular exchange between growing radicals and dormant chains. Covalent species or organometallic compounds can play the role of dormant species. 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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