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CONTROLLED RADICAL POLYMERIZATION

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ABSTRACT

Various methods which lead to the control of molecular weight and polydispersities, and which allow for the preparation of block copolymers by radical polymerization are discussed. Thermal polymerization of styrenes in the presence of stable radicals, polymerization of vinyl acetate and methyl methacrylate in the presence of chromium complexed by macrocyclic ligands polymerization of vinyl acetate initiated by organoaluminum compounds complexed by dipyrindyl and activated by stable radicals, as well as in the presence of phosphites, are described in detail.

INTRODUCTION

Radical polymerization is probably the most important commercial process leading to high molecular weight polymers. This is due to the large variety of monomers which can be polymerized and copolymerized radically and to relatively simple experimental conditions which require the absence of oxygen but which can be carried out in the presence of water, e.g., as in suspension or emulsion polymerization, and at a convenient temperature range, typically 0 to 100°C. However, the degree of control over macromolecular structure in radical polymerization is inferior to that of the less frequently used ionic polymerization methods. The latter gives access to well-defined polymers, end-functional polymers, and block copolymers, but has to be carried out with nearly complete exclusion of oxygen and moisture (<10 ppm), and often at very low temperatures. The possibility of controlling molecular weights, polydispersities, and terminal functionalities is very

attractive for tuning various properties of polymers and preparation of new materials with novel characteristics. Thus, it is very desirable to extend the control of macromolecular structure from ionic to radical processes.

The synthesis of well-defined polymers is usually accomplished in living systems when the contribution of transfer and termination is below detection levels. However, controlled polymers have been recently prepared in systems in which transfer and/or termination reactions were detected and quantitatively determined [1, 2]. In ionic reactions the contribution of chain-breaking reactions increases with chain length and can be negligible for polymers with sufficiently low molecular weights.

Termination seems to be inevitable for radical reactions. Two growing radicals must recombine or disproportionate, in contrast to two cationic or two anionic chain ends in ionic polymerization. Thus, a truly living free-radical polymerization cannot be realized. However, there are some reports on the preparation of well-defined low and medium molecular weight polymers, $M_n < 30,000$, by radical processes [3, 4]. In this article we describe some of the new systems in which radical polymerization provides polymers with a controlled structure.

Usually, most of these systems are based on the reversible termination of growing radicals with various scavengers, X. The reversibility allows for a large total number of chains, equal to $\{P-X\}^*$, and at the same time, for a low, stationary concentration of growing macromolecular radicals, P^* . Scavenger X may have an even or odd number of electrons. In the latter case, instead of the persistent radical $\{P-X\}^*$, covalent species $P-X$ is formed:



In the ideal case, this results in the continuous growth of all chains but at a rate much slower than a "normal" radical polymerization.

Propagation in this system is the reaction between growing radicals P^* and monomer M (Eq. 2), whereas termination is the bimolecular reaction between growing radicals, P^* , via coupling or via disproportionation (Eq. 3):



The reversible Reaction (1) is not considered termination because it only temporarily deactivates growing chains. Rate of termination increases with the second power of the concentration of radicals, but the rate of propagation with the first power. Thus, the contribution of termination and the proportion of terminated chains increases with the concentration of free radicals:

$$R_t/R_p = k_t[P^*]^2/k_p[P^*][M] \approx [P^*] \quad (4)$$

The control of macromolecular structure requires low ratios of R_t/R_p and low $[P^*]$. Molecular weight usually increases with a decrease of the concentration of the growing species. However, this includes not only the active but the dormant, temporarily deactivated species as well:

$$DP \approx \Delta[M]/([P^*] + \{\{P-X\}^*\}) \quad (5)$$

The above equation is accurate, provided that exchange between both species is fast and the contributions of termination and transfer are small.

Preparation of polymers with controlled molecular weights and low polydis-

persity requires relatively fast initiation to enable growth of all chains at the same time. Initiation is usually very slow in radical polymerization, and only a fraction of the initiator is used at complete monomer conversion. The instantaneous initiation in the "normal" radical process would lead to a very high concentration of radicals and would result in a very fast termination rate proportional to $[P^*]^2$. On the other hand, fast initiation is easily realized in systems with reversible termination. In that case, a low and steady momentary concentration of radicals can be generated when initiation is as fast as propagation.

In this article we discuss four different approaches which enhance control of radical polymerization. These methods provide routes to polymers with low polydispersities and, in some instances, to block copolymers.

THERMAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF NITROXIDES AS STABLE RADICAL SCAVENGERS

It was observed that radical polymerization initiated by classic initiators (organic peroxides, dialkylperoxalates) in the presence of alkoxyamines, either preformed or prepared in situ, provides well-defined polymers. These polymers demonstrated molecular weights reciprocal to the concentration of alkoxyamines, and the rates were determined by the stationary concentration of the growing radicals [5].

Recently, low polydispersity polystyrene was prepared by initiation with systems based on benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) at various molar ratios at temperatures of 125–140°C [6, 7]. The unusually narrow polydispersities were attributed to fast initiation by a redox process in which phenyl radicals were formed by decomposition of BPO promoted by TEMPO [8]. Growing polystyryl chains were proposed to be "reversibly" deactivated by scavenging TEMPO radicals, thus substantially reducing irreversible termination that prematurely stops chain growth. It was assumed that new initiating radicals generated by thermal processes should have no effect on molecular weights and polydispersities. We decided to simplify this system by using nitroxyl radicals in the thermal polymerization of styrene, in the absence of any added radical initiators.

Figure 1 presents kinetic data for the thermal polymerization of styrene, 120°C, at concentrations of $[\text{TEMPO}]_0$ in the 0.02 to 0.12 M range. With the increase of $[\text{TEMPO}]_0$, induction periods increased and the reaction became slower, following a typical pattern for the inhibition. The radicals generated thermally were initially scavenged by TEMPO, forming alkoxyamines bonded by oligomeric polystyrene growing chains. When the concentration of thermally generated radicals became comparable to, or exceeded, $[\text{TEMPO}]_0$, polymerization could proceed. Alkoxyamines are thermally unstable at temperatures higher than 120°C and can reversibly decompose, generating polystyryl radicals and releasing TEMPO. After addition of the first monomer molecules, polystyryl radicals were reversibly trapped by TEMPO to form dormant alkoxyamines. Because radicals are continuously generated, it is also possible that they may react with dormant alkoxyamines in the degenerative transfer processes (Scheme 1).

The unimolecular and bimolecular exchange reactions allow the simultaneous and almost linear growth of all chains with conversion (Fig. 2) and the preparation of polymers with low polydispersities (Fig. 3). Apparently the molecular weight of the polymer can be adjusted to higher or lower values by using varying amounts of

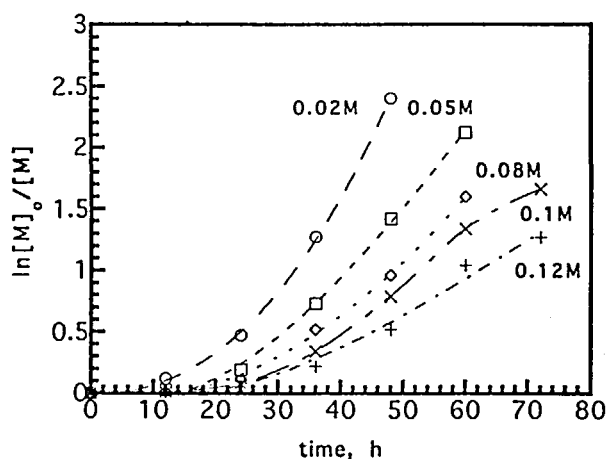
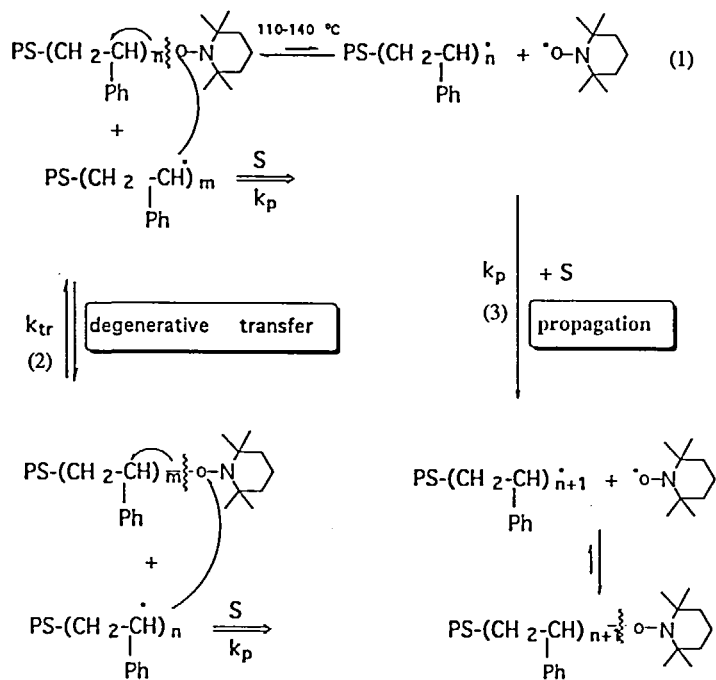


FIG. 1. Time-conversion plots in semilogarithmic coordinates for the thermal polymerization of styrene, in bulk, 120°C, at concentrations of TEMPO in the range 0.02-0.12 M.



SCHEME 1.

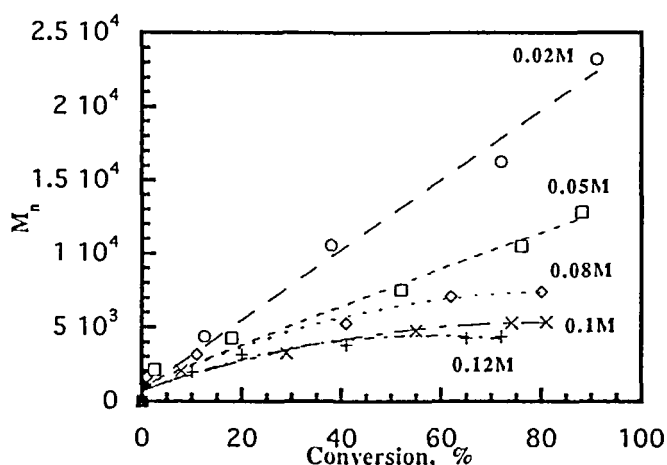


FIG. 2. M_n -conversion dependence for the thermal polymerization of styrene, in bulk, 120°C, at concentrations of TEMPO in the range of 0.02–0.12 M.

$[\text{TEMPO}]_0$; however, a limitation to the range $M_n \approx 12,000$ was observed. The increase of polydispersities with conversion may indicate an increase of the proportion of chains irreversibly terminated by recombination or involved in transfer. At higher temperature, 130°C, an increase in polymerization rates was accompanied by curvature of the kinetic plots, indicating variations of the number of growing radicals (Fig. 4).

Radicals formed continuously during thermal initiation may react in the transfer processes with polymeric alkoxyamines. In this thermodynamically neutral process, newly generated radicals will react with the alkoxyamines, dormant species, reforming radicals of the same structure as growing radicals and alkoxyamines, also

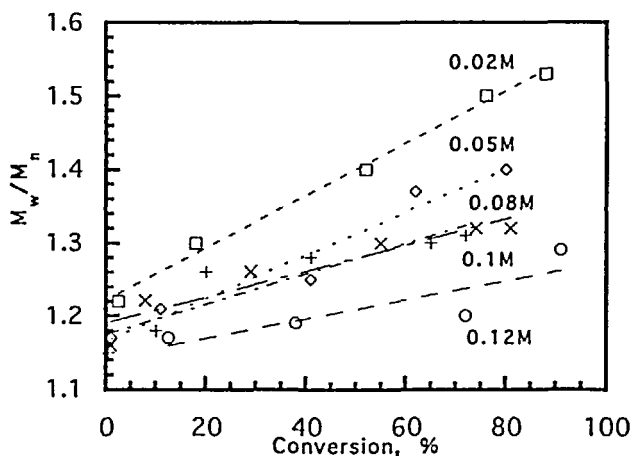


FIG. 3. M_w/M_n -conversion plots for the thermal polymerization of styrene, 120°C, in bulk, at concentrations of TEMPO in the range 0.02–0.12 M.

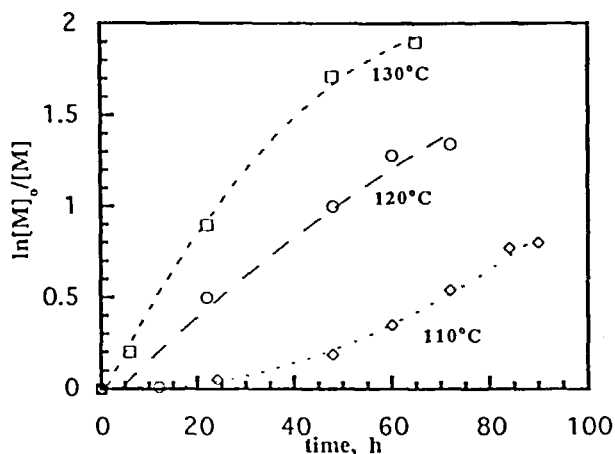


FIG. 4. Time-conversion plots in semilogarithmic coordinates for the thermal polymerization of styrene, at different temperatures. $[\text{TEMPO}]_0 = 10^{-1} \text{ M}$.

of the same structure. If the exchange process (Scheme 1, Eqs. 1 and 2) is fast enough and the ratio of terminated chains to the total number of chains is low, a controlled radical polymerization may occur. However, at conversions higher than 75% and higher temperature, 130°C, spontaneous thermal initiation and termination seem to dominate over propagation. Therefore, broader polydispersities at the final stages have been found. Various stable radicals behave in different ways in the polymerization of styrene (Table 1).

Nitroxyl radicals have provided the lowest molecular weights and polydispersities. Radicals with bulky substituents such as 2,6-di-*tert*-butyl phenoxyl radicals were not very efficient. This could be ascribed to either some irreversible side reactions or slower degenerative transfer due to steric hindrances preventing a bimolecular process.

TABLE 1. Thermal Polymerization of Styrene in the Presence of Different Stable Radicals, 10^{-1} M , $T = 120^\circ\text{C}$, 48 Hours

Radical	M_n	M_w/M_n	Conversion, %
—	196,000	2.62	87
TEMPO	4,240	1.26	80
4-OH-TEMPO	3,915	1.27	62
4-Oxo-TEMPO	6,830	1.38	74
2,2,3,4,5,5-Hexamethyl-3-imidazolinium-1-yloxy methyl sulfate	4,367	1.31	78
DPPH	3,444	1.76	36
Galvinoxyl	43,157	1.5	57

**POLYMERIZATION OF VINYL ACETATE IN THE
PRESENCE OF ORGANOCHROMIUM COMPOUNDS
COMPLEXED BY VARIOUS LIGANDS**

Metal stabilized propagating radicals based on Co and Cr have been described previously [9, 10]. Poor control of molecular weights and the facile chain transfer processes could be attributed to the reversibility of the redox couples $\text{Co}^{3+/2+}$ and $\text{Cr}^{3+/2+}$ due to their positive redox potentials and to β -hydrogen abstractions in the formation of metal hydrides.

Reversible reactions of carbon-based radicals with organometallic compounds play an important role in biological processes but can also be applied in polymer synthesis. For example, cobaloximes have been used as efficient chain-transfer reagents in order to regulate molecular weights of various polymers synthesized by radical processes [9, 11].

Initiating systems based on chromium acetate and organic peroxides in DMF have been previously reported for the radical polymerization of MMA [12]. At temperatures below 30°C, molecular weights increased monotonously with monomer conversion. These initiating systems have been unsuccessfully used in the polymerization of other vinyl monomers such as vinyl acetate or styrene.

Macrocyclic polyamines such as 1,4,7,10-tetraazacyclododecane (12-and-4) and 1,4,7,10,13,16-hexaazacyclooctadecane (18-ane-6) [13] and related methyl-substituted derivatives are known as the best 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^{3+/2+} redox couples.

The controlled polymerization of vinyl acetate (VAc) and methyl methacrylate (MMA) in THF was achieved by using redox systems based on benzoyl peroxide (BPO) and chromium diacetate as the initiators. This was done in the presence of different N-based ligands [2,2'-dipyridyl (Dpy), 18-ane-6 trisulfate (N_6H^+), and hexamethyl 18-ane-6 ($\text{N}_6\text{-CH}_3$)].

Figure 5 shows time-conversion plots obtained from the polymerization of VAc in the presence of different ligands, or without ligands, as well as in methanol as solvent. The highest conversion, up to 90%, obtained in the shortest time, 30 hours, was found in the presence of N_6H^+ as ligand. In the presence of ligands known to stabilize the lower oxidation states, e.g., Dpy and $\text{N}_6\text{-CH}_3$, polymerization rates were reduced and lower conversions were observed. The presence of methanol as solvent enhanced the redox initiation rate. This was observed by rapid change of the color, but only 10% conversion was found after 48 hours.

Figure 6 shows the evolution of molecular weight as a function of conversion for the same three systems. In the case of macrocyclic ligand N_6H^+ , a monotonous increase of M_n with conversion was observed (Δ). Although initially there was up to 20% conversion, the increase was faster than at later stages.

In the absence of any ligands, a curvature in M_n -conversion dependence (\square) indicated poor control of molecular weight. In the presence of Dpy as ligand for Cr(II), the molecule weight was the lowest and did not vary with conversion. Probably a combination of slow initiation, fast propagation, and fast chain-transfer reactions may operate in this system.

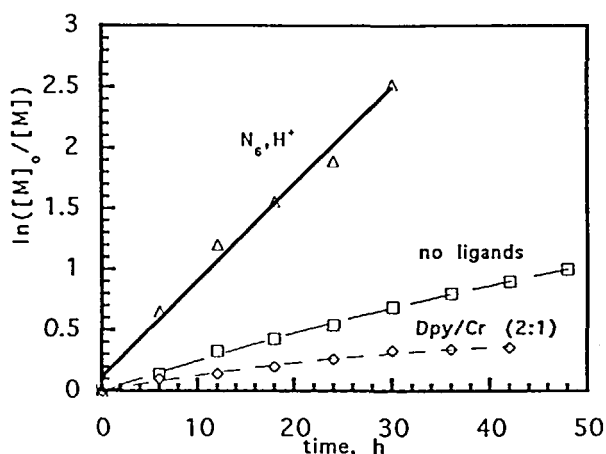


FIG. 5. Time-conversion plots in the polymerization of VAc with $\text{Cr}(\text{OAc})_2/\text{BPO}$, THF, 20°C , $[\text{VAc}]_0 = 5 \text{ M}$, $[\text{Cr}^{2+}]_0 = [\text{BPO}]_0 = 0.25 \text{ M}$, $[\text{Lig}]_0 = [\text{Cr}^{2+}]_0$.

Figure 7 shows the variation of polydispersities for the same three systems. In the presence of macrocyclic ligand N_6, H^+ , polydispersities have the lowest values, $M_w/M_n = 1.54$ to 1.63 , with an increase at higher conversions and higher molecular weights. In the absence of any ligand, polydispersities were higher, with an increase at the end of the reaction, $M_w/M_n = 1.62$ to 1.76 . In the presence of Dpy as ligand, the highest polydispersities, $M_w/M_n = 1.7$ to 1.84 , there was increasing conversion at constant molecular weights, thus confirming the major contribution of chain-transfer reactions. It was possible that chromium hydrides were formed by elimination of $\beta\text{-H}$ atoms from the growing radicals.

Thus, the reactivity of chromium is strongly dependent on its solvation shell and the coordination ligands used. Apparently the reaction between chromium diacetate

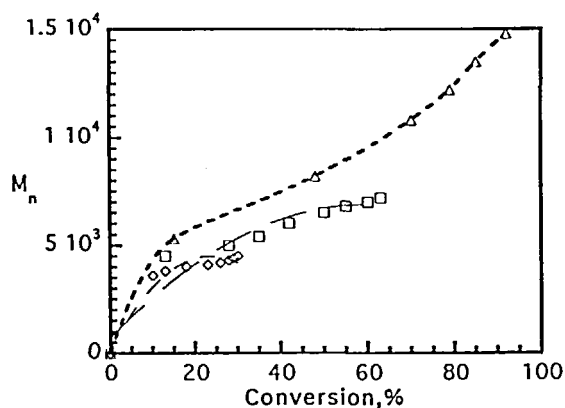


FIG. 6. M_n -conversion dependence in the polymerization of VAc with $\text{Cr}(\text{OAc})_2/\text{BPO}$, THF, 20°C , $[\text{VAc}]_0 = 5 \text{ M}$, $[\text{Cr}^{2+}]_0 = [\text{BPO}]_0 = 0.25 \text{ M}$, $[\text{Lig}]_0 = [\text{Cr}^{2+}]_0$.

The mechanism for controlled polymerization with chromium compounds is not yet clear. It was previously proposed that Cr(III) species were complexing with the growing PMMA radicals [15]. Such a complex will formally produce Cr(IV) species which may have lower stability than Cr(III) compounds. Another possibility is that Cr(II) species complex growing radicals formed Cr(III) species. In that case Cr(II) will have a dual role: as a redox coinitiator and as the reversible scavenger of growing species. We are currently investigating this system and are searching for more efficient ligands to control the polymerization of vinyl acetate and other vinyl monomers.

ORGANOALUMINUM COMPOUNDS COMPLEXED BY LIGANDS AND ACTIVATED BY STABLE RADICALS

Organoaluminum compounds complexed by various N- or O-based donor ligands, such as pyridines [16], dipyriddy (2,2'- or 4,4'-) [17], and semiquinones [18], produce radicals which can initiate polymerization. Another method of generation of the initiating radicals is the reaction of organoaluminum compounds with nitroxyl radicals [19]. However, in both of these systems, no control of polymerization has been reported. We have used a tricomponent system based on organoaluminum compounds complexed by 2,2'-dipyridyl and activated by TEMPO. This system has the advantage of the fast generation of propagating radicals and is 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 strongly depends on the monomer structure. This may be explained by various affinities of the propagating radicals, which may be more or less nucleophilic or electrophilic toward the scavenging species.

Polymerization of vinyl acetate in benzene 20 to 60°C initiated by triisobutylaluminum/2,2'-dipyridyl/TEMPO (1:1:2) proceeded according to first-order kinetics in monomer and at an apparently constant concentration of growing species (Fig. 8). Initial rates of polymerization depend strongly on the Al:TEMPO ratio and seem to be optimal at a 1:2 ratio (Fig. 9).

Molecular weight increased linearly with conversion (Fig. 10) and polydispersities remained low (Fig. 11). Apparently the lowest polydispersities were observed at the highest temperatures. This may be ascribed to a higher activation energy of propagation than that of termination and to a decrease in the proportion of termination with temperature.

The tricomponent initiating system was also efficient for the polymerization of styrene and MMA. In the latter case the polymerization rate was much faster than for vinyl acetate and polymerization was completed in a few minutes rather than in a few hours under similar conditions (Fig. 12).

The ability to use the same initiating system for MMA, styrene, and vinyl acetate allowed the preparation of block copolymers. Table 2 presents the results of copolymerization of vinyl acetate with styrene, MMA, and butyl acrylate.

Better results were obtained using vinyl acetate as the first monomer. This was due to a slower and better controlled polymerization than when using MMA. Figure 13 shows SEC traces for PVAc-PMMA block copolymers before and after addition

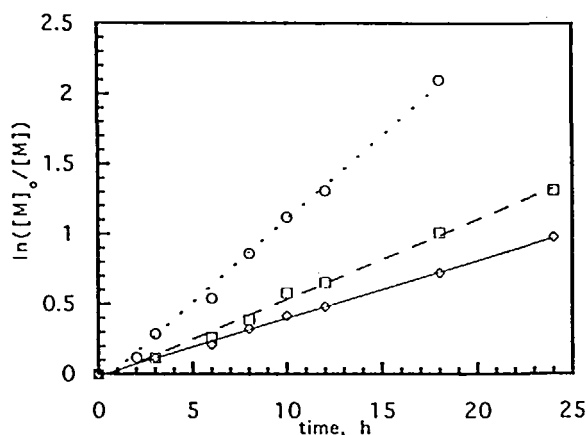


FIG. 8. Time-conversion plots in semilogarithmic coordinates in the polymerization of VAc ($[M]_0 = 2.5$ M), with $\text{Al}(\text{iBu})_3/\text{Dpy}/\text{TEMPO}$ (1:1:2) in benzene, 60°C , at different concentrations of initiator: 0.3 M (\circ), 0.05 M (\square), 0.01 M (\diamond).

of the second monomer. In some cases a trace of the first block (PVAc) remained, indicating incomplete blocking efficiency.

POLYMERIZATION OF VINYL ACETATE INITIATED BY PEROXIDES IN THE PRESENCE OF TRIALKYLPHOSPHITES

Reactions between free radicals and trivalent phosphorus compounds, such as alkyl (aryl) phosphine or phosphite products, lead to pentavalent phosphoranyl radicals, **1**. These may undergo subsequent α - or β -scissions (Scheme 3) [20, 21].

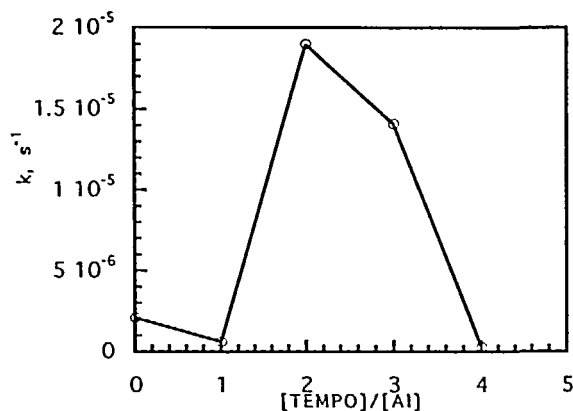


FIG. 9. The effect of the ratios $[\text{TEMPO}]/[\text{Al}]$ on rate coefficients, k , in the polymerization of VAc, ($[M]_0 = 2.5$ M), with $\text{Al}(\text{iBu})_3/\text{Dpy}/\text{TEMPO}$ (1:1:2), $[I]_0 = 0.3$ M, in benzene, 60°C .

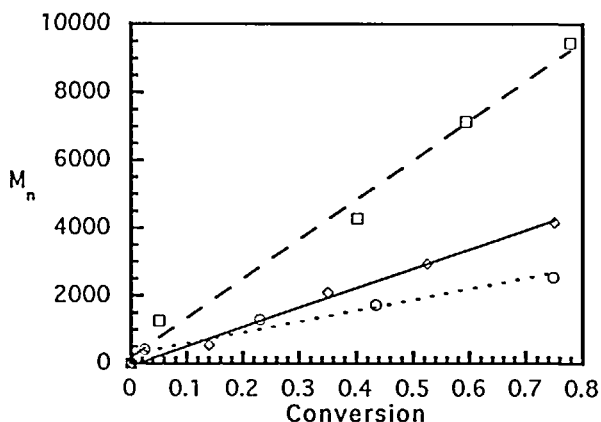


FIG. 10. Molecular weight-conversion dependence in the polymerization of VAc, ($[M]_0 = 2.5\text{ M}$), with $\text{Al}(\text{iBu})_3/\text{Dpy}/\text{TEMPO}$ (1:1:2) in benzene, at different concentrations of initiator and temperatures: $[I]_0 = 0.05\text{ M}$, 20°C (\diamond); $[I]_0 = 0.05\text{ M}$, 60°C (\square); $[I]_0 = 0.3\text{ M}$, 60°C (\circ).

There are a few examples of radical polymerization of acrylic monomers, methyl methacrylate and acrylonitrile, in the presence of trivalent phosphorus compounds, phosphines and phosphites [22, 23]. It was supposed that both the polymerization mechanism and the chain composition were influenced by the P-centered radicals formed in these processes.

Figure 14 shows that the polymerization of VAc initiated by BPO is accelerated by the presence of tris(2,2,2-trifluoroethyl)phosphite (TFEP). The kinetic plots obtained in the presence of phosphite were linear, indicating that the concentration of the growing radicals did not vary during polymerization. Model ^{31}P -NMR studies

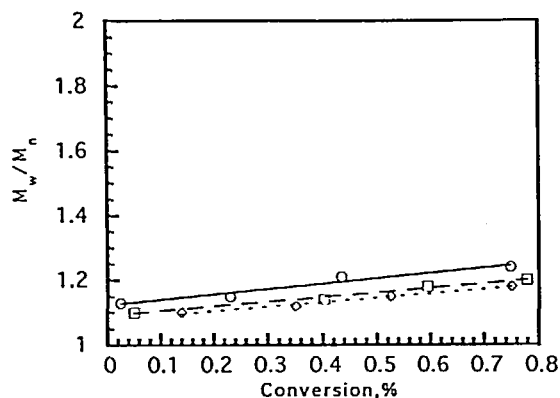


FIG. 11. Variation of polydispersities with conversion in the polymerization of VAc, ($[M]_0 = 2.5\text{ M}$), with $\text{Al}(\text{iBu})_3/\text{Dpy}/\text{TEMPO}$ (1:1:2) in benzene, at different concentrations of initiator and temperatures: $[I]_0 = 0.05\text{ M}$, 30°C (\circ); $[I]_0 = 0.05\text{ M}$, 60°C (\square); $[I]_0 = 0.3\text{ M}$, 60°C (\diamond).

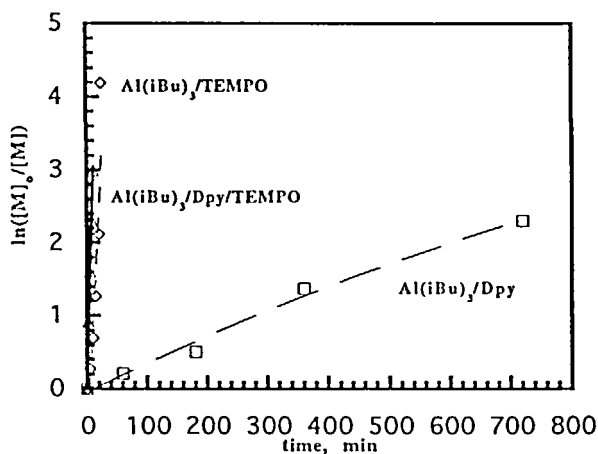


FIG. 12. Time-conversion plots in semilogarithmic coordinates in the polymerization of MMA initiated by $\text{Al}(\text{iBu})_3/\text{TEMPO}$ (1:1), $\text{Al}(\text{iBu})_3/\text{Dpy}$ (1:1), and $\text{Al}(\text{iBu})_3/\text{Dpy}/\text{TEMPO}$ (1:1:2).

TABLE 2. Radical Block Copolymerization of Vinyl Acetate with Styrene and MMA^a

Initiator	Monomer	Time, hours	$M_{n,\text{calc}}$	$M_{n,\text{GPC}}$	M_w/M_n
$\text{Al}(\text{iBu})_3/\text{dipyridyl}/2$ TEMPO	VAc	24	5,000	4,900	1.16
	MMA	6	10,000	15,300	1.48
$\text{Al}(\text{iBu})_3/\text{dipyridyl}/2$ TEMPO	MMA	0.5	10,000	14,400	1.24
	VAc	24	15,000	18,800	1.27
$\text{Al}(\text{iBu})_3/\text{dipyridyl}/2$ TEMPO	VAc	24	10,000	26,900	1.21
	Styrene	6	23,000	41,700	1.32

^a $[\text{M}]_0 = 2 \text{ mol/L}$, $[\text{I}]_0 = \text{variable}$, $T = 25^\circ\text{C}$, benzene.

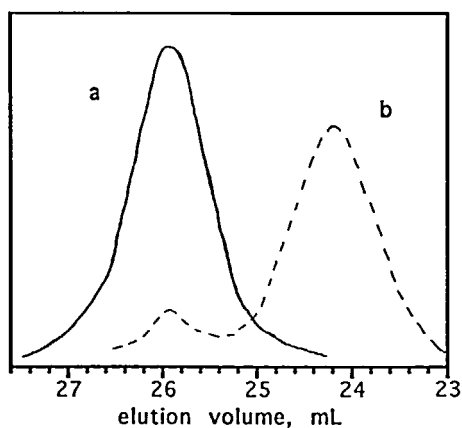
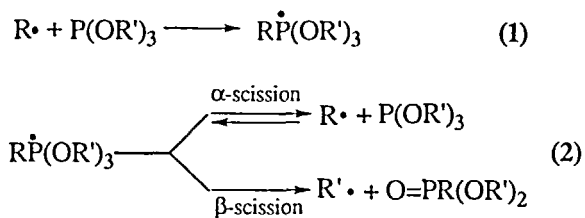


FIG. 13. SEC curves for block copolymers PVAc-PMMA: (a) PVAc homopolymer, $M_{n,\text{GPC}} = 5000$, $M_w/M_n = 1.16$; (b) PVAc-PMMA block copolymer, $M_{n,\text{GPC}} = 15,300$, $M_w/M_n = 1.48$.



SCHEME 3.

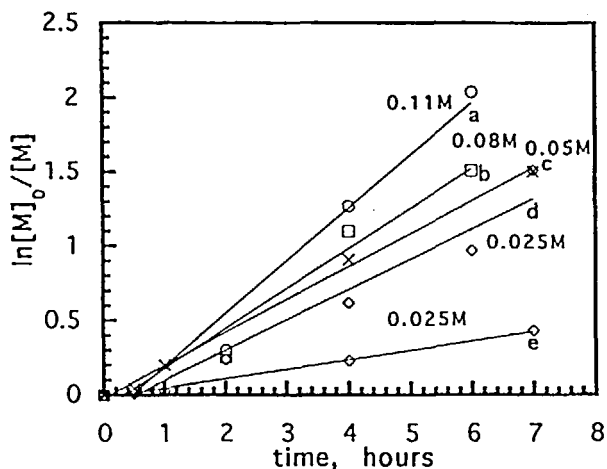
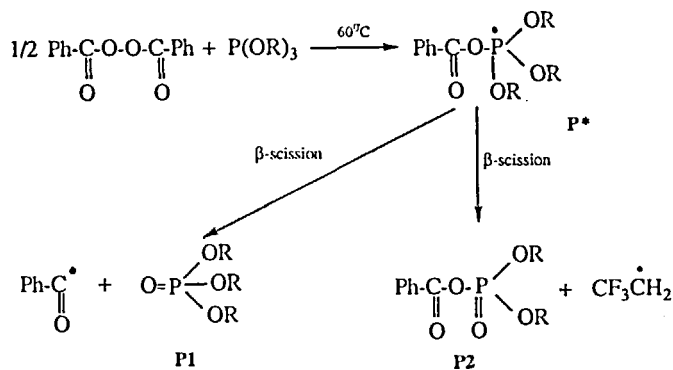


FIG. 14. Time-conversion plots in semilogarithmic coordinates in the polymerization of VAc initiated by TFEP/BPO, $[VAc]_0 = 5.4$ M, benzene, 60°C , $[BPO]:[TFEP] = 1:1.5$. (a) $[BPO]_0 = 0.11$ M, (b) $[BPO]_0 = 0.08$ M, (c) $[BPO]_0 = 0.05$ M, (d) $[BPO]_0 = 0.025$ M, (e) $[BPO]_0 = 0.025$ M, no TFEP.



SCHEME 4.

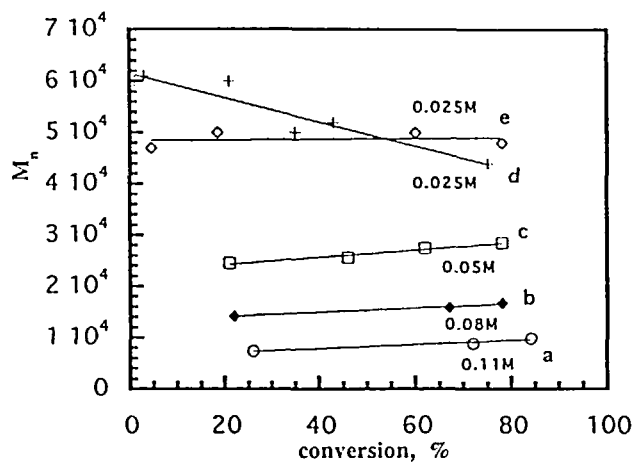


FIG. 15. M_n -conversion dependence in the polymerization of VAc initiated by TFEP/BPO, $[VAc]_0 = 5.4$ M, benzene, 60°C , $[BPO]:[TFEP] = 1:1.5$. (a) $[BPO]_0 = 0.11$ M, (b) $[BPO]_0 = 0.08$ M, (c) $[BPO]_0 = 0.05$ M, (d) $[BPO]_0 = 0.025$ M, (e) $[BPO]_0 = 0.025$ M, no TFEP.

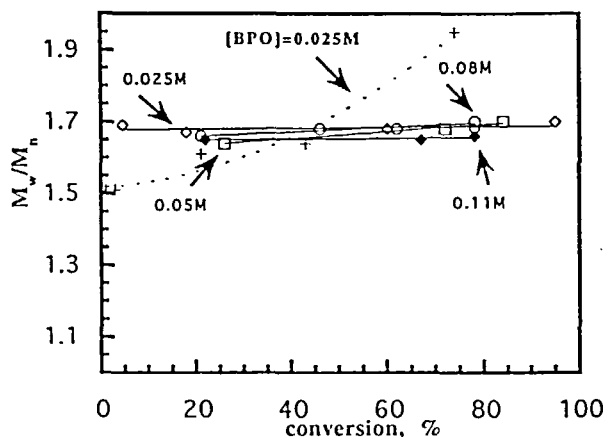


FIG. 16. M_w/M_n -conversion dependence in the polymerization of VAc initiated by TFEP/BPO (1.5/1).

TABLE 3. Effect of the Structure of Phosphites on Polymerization of Vinyl Acetate in Benzene at 60°C ^a

Phosphite	M_n	M_w/M_n	Conversion, %
$(\text{CH}_3\text{O})_3\text{P}$	99,000	1.55	18
$(n\text{-C}_4\text{H}_9\text{O})_3\text{P}$	84,000	1.56	5
$(i\text{-C}_3\text{H}_7\text{O})_3\text{P}$	—	—	<0.5
$(\text{CF}_3\text{CH}_2\text{O})_3\text{P}^b$	63,000	1.39	85

^a $[\text{P}(\text{OR})_3]/[\text{BPO}] = 1.5/1$, $[\text{BPO}]_0 = 0.025$ mol/L, $[\text{VAc}]_0 = 7$ mol/L, 24 hours.

^bTime = 6 hours.

of BPO/phosphite mixtures indicated relatively rapid formation of phosphates (P1 or P2) and suggested that the reaction may proceed via phosphoranyl intermediates, (P*) (Scheme 4).

Figure 15 shows that the molecular weights from the polymerization of VAc initiated by BPO in the presence of phosphites remain constant up to high monomer conversion. This is in contrast to polymerization initiated by BPO alone, where a strong decrease of molecular weights was observed. The constant value of the molecular weights also leads to lower polydispersities than in the BPO system (Fig. 16). One possible explanation for the constant value of molecular weights with conversion is that the ratio of the rates of initiation and propagation did not change with conversion. This might indicate that the monomer was involved in the rate-limiting step in the initiation process; for example, in the reaction with the phosphoranyl radical.

It is possible that growing radicals may interact with the phosphite and form reversibly P-centered radicals. However, whereas polymerization rates are slightly retarded, molecular weights are not affected by the excess phosphite in the system. Thus, the interactions may be relatively weak. It was observed that the structure of the phosphite strongly affects the efficiency of the system (Table 3).

More sterically hindered alkyl substituents in the phosphite apparently reduced the polymerization rate. This may support the bimolecular reaction of the phosphoranyl radical with a monomer as the rate-determining step in initiation. Electronic effects must also be important because tris(2,2,2-trifluoroethyl)phosphite is more sterically hindered than trimethyl or triethyl phosphite but leads to faster polymerization.

CONCLUSIONS

It was shown that there are several possibilities for improving control in radical polymerizations. Although these systems are far from true living polymerizations, they allow for the preparation of polymers with predictable molecular weights and low polydispersities, and also the synthesis of block copolymers.

In all of these systems, with the possible exception of phosphite/BPO, there is an equilibrium between dormant and active species. The equilibrium may be achieved by homolytic cleavage of the covalent species, alkoxyamines, or by the reversible reaction of growing radicals with organometallic compounds such as organoaluminum or chromium derivatives. The equilibrium and the degree of control depend strongly on the substituents and ligands stabilizing the metal center as well as on the propagating radicals. Degenerative transfer between dormant and active species may additionally reduce polydispersities.

The controlled system should be based on relatively fast initiation, reversible deactivation, and should be carried out at a sufficiently low concentration of growing radicals and a sufficiently high concentration of dormant species. This was done in order to decrease the contribution of the inevitable termination between growing radicals. Some additional narrowing of the molecular weight distribution may be achieved by adjusting the relative rates of propagation with those of initiation and/or transfer, as shown for BPO/phosphites. It seems that the search for a controlled radical polymerization should be continued by the adjustment of the equilibria

between dormant and active species and suppression of such side reactions as β -hydrogen abstraction and electron transfer. Control of molecular weights additionally requires fast initiation, which should be accomplished by the formation of the initiating species *in situ* or just prior to polymerization. Work at higher temperatures is preferred due to the higher energy of activation of propagation in comparison with that of termination, which is the main, and most difficult to avoid, chain-breaking reaction in radical polymerization, provided that the contribution of transfer is low enough.

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Note added in proof:

The kinetic plots and evolutions of molecular weights with conversion presented in Figures 1–4 are slightly different from those reported before [24]. The recrystallized TEMPO was used in these studies, in contrast to the earlier studies [24] in which the scavenger was used as received from Aldrich.