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FROM “LIVING” CARBOCATIONIC TO “LIVING” RADICAL POLYMERIZATION

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ABSTRACT

“Living” carbocationic polymerization is compared to the “living” radical process. Similarities and differences are discussed. “Living” radical polymerization of vinyl acetate and methyl methacrylate to provide polymers with controlled molecular weights and narrow molecular weight distribution ($M_w/M_n < 1.2$) are presented.

INTRODUCTION

Living polymerization enables preparation of well-defined polymers with controlled macromolecular and sometimes even supramolecular structure. Polymers with novel topologies such as cyclic, star, and ladder as well as various types of copolymers which may microphase separately have been prepared via living processes. Living polymerization requires high chemoselectivity when chain growth is not disturbed by any chain-breaking reactions. If initiation is fast, then the degree of polymerization equals the ratio of the consumed monomer to the introduced initiator:

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

Living polymerization is usually observed in chain processes with polar growing species such as ions or organometallic compounds. Carbocations are very reactive, and in addition to the electrophilic addition to double bonds (propagation), may also participate in various side reactions such as elimination (transfer), substi-

tution (termination), and rearrangements. Due to instability of the growing carbocations, the cationic polymerization of alkenes has been considered for a long time as impossible to realize in the living system [1]. However, very extensive research carried out by Professor Kennedy and other researchers in the field of carbocationic polymerization led to the preparation of well-defined polymers and copolymers by the cationic process [2, 3].

In ionic polymerizations, chain ends do not react with one another because of electrostatic repulsions. On the other hand, free radicals, which are the growing species in radical polymerization, very easily react with one another via coupling and/or disproportionation. Thus, termination as a chain-breaking process cannot be avoided in radical polymerization. Nevertheless, as demonstrated in this paper, under appropriate conditions it is possible to prepare well-defined polymers by controlled radical polymerization, too. We will discuss in more detail the preparation of well-defined poly(vinyl acetate) and poly(methyl methacrylate) as examples of this process.

CONCEPT OF LIVING POLYMERIZATION

Living polymerization is classically defined as a chain reaction during which no termination and transfer occur, with the consequence that all macromolecules in the system are capable of growth as long as monomer is present [4]. But since no polymerization is perfectly living, it was proposed that "polymers are considered to be living if they retain their capacity of growth for a time needed for the completion of a desired task" [5]. A ranking of the livingness of the various systems has been proposed, based on the values of the ratios of the termination/transfer to the propagation rate constant (k_t/k_p and k_{tr}/k_p) [6]. This ranking enables the upper limit of the DP of the well-defined polymer to be determined with the ratio of the corresponding rate constants. If only a $DP_n \approx 100$ is planned, the well-defined polymer can be prepared even at the $k_{tr}/k_p \approx 10^{-4}$ mol/L ratio, but if the goal is a $DP_n \approx 10,000$, this value should be nearer to 10^{-6} mol/L.

Control of molecular weights in the living process as defined in Eq. (1), additionally requires fast initiation. If initiation is much slower than propagation, then higher than expected (Eq. 1) degrees of polymerization will be observed.

In ionic reactions, active species with various reactivities coexist (free ions, ion pairs, aggregates, covalent species, etc.). If they propagate simultaneously but with different rate constants, then polymodal molecular weight distribution may result. The polydispersity in that case will depend on the rate of the exchange between these species. In the case of the exchange being faster than propagation, very narrow (Poisson) distribution is expected.

Thus, the concept of living polymerization allows the presence of species with various reactivities and, in the extreme case, even entirely dormant (inactive) species. Polymers with low polydispersities can be produced if exchange between the active and dormant species is fast.

In real systems, chain-breaking reactions do occur and cannot be entirely avoided; bimolecular termination between growing radicals might be the best example. On the other hand, these nonliving systems may still provide well-defined

polymers if the appropriate reaction conditions are chosen. We therefore refer to these systems as apparently living, “living,” or controlled systems.

LIVING CARBOCATIONIC POLYMERIZATION

Progress in the cationic polymerization of alkenes can be ascribed to a better understanding of the reaction mechanism and to the correct choice of initiator, additives, and other reaction conditions. The main four characteristic features of carbocationic polymerization are discussed below.

1. A positive charge in carbocations is located mainly on the sp^2 hybridized C atom (20 to 30%), but a significant amount of charge is also located on the β -H atoms (5 to 10%). Thus, transfer is the major chain-breaking reaction due to the facile elimination of β -H atoms from the growing carbocations. Reactions carried out in the absence of basic components (counterions, solvent, additives) provide better defined systems due to the suppression of unimolecular (spontaneous) transfer. However, transfer to monomer still exists and can be reduced only at sufficiently low temperatures. The proportion of chains marked by transfer increases with conversion and with the degree of polymerization (DP). In the case of transfer to monomer, the ratio of the observed number-average DP to the theoretical DP^T (no transfer) decreases with conversion p according to the following expression:

$$DP/DP^T = 1/\{1 + (k_{trM}/k_p) \cdot [M]_0/[I]_0 \cdot p\} \quad (2)$$

As shown in Fig. 1, the ratio DP/DP^T decreases monotonously with conversion. The drop is most pronounced for the highest value of the parameter $a = (k_{trM}/k_p) \cdot [M]_0/[I]_0$.

Figure 2 show how polydispersity of the polymers obtained at complete monomer conversion changes with the value of parameter a . A semilogarithmic scale was used to better visualize the dependence of polydispersity on a . The calculations were based on the approach presented in Reference 7.

It seems that well-defined systems can be easily obtained for $a < 0.1$. The value of a depends on the ratio of rate constants of transfer to propagation *and* also on the ratio of the concentration of monomer to that of the initiator. The ratio of the rate constants is given by “chemistry,” i.e., mechanism, counterion, monomer, solvent, temperature, etc. However, the concentration of initiator can be easily controlled and “poor” systems with, e.g., experimental DP twice lower than theoretically expected can be converted to well-defined systems by increasing the concentration of initiator by 10- or 100-fold. This necessitates the synthesis of shorter chains. For sufficiently short chains, transfer may not be noticed. Thus, degrees of polymerization corresponding to those described by Eq. (1) may be obtained if initiation is fast in comparison with propagation and DP is low enough not to be marked by transfer. This requires relatively high concentrations of the initiator ($[I]_0 \geq 10^{-2}$ mol/L for $k_{trM}/k_p \approx 10^{-3}$ and $[M]_0 \approx 1$ mol/L).

2. Carbocations react very rapidly with alkenes ($k_p \approx 10^5$ mol⁻¹·L·s⁻¹ at $\approx 20^\circ\text{C}$) [8]. Thus, if all growing chains will be in the form of carbocations, and the concentration of the initiator will be high ($[I]_0 \geq 10^{-2}$ mol/L), then polymerization may be finished in a fraction of a second and may be difficult to control or may even be explosive. In order to reduce polymerization rates, a dynamic equilib-

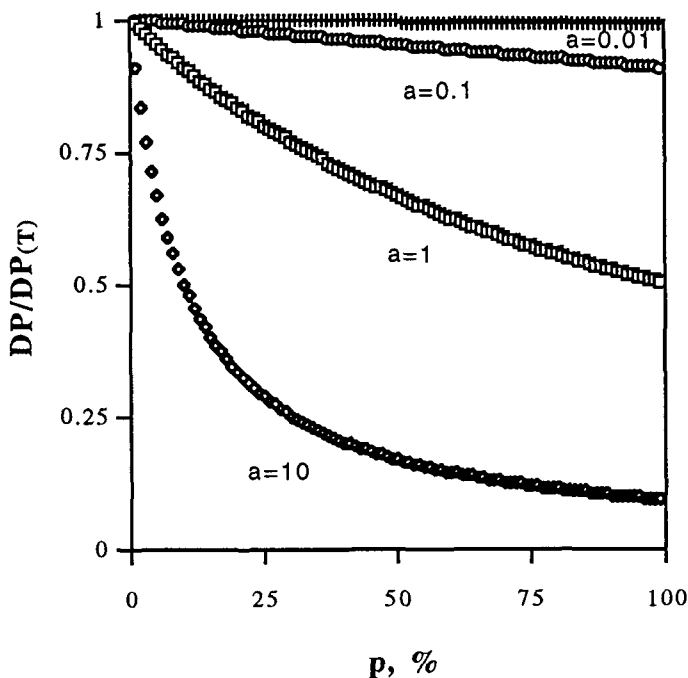


FIG. 1. Effect of the transfer to monomer on polymerization degrees as a function of conversion for various parameters $a = (k_{trM}/k_p) \cdot [M]_0/[I]_0$.

rium between reactive carbocations and dormant species was used. Reversible ionization of covalent species and reversible formation of onium ions provides well-defined systems with the number of chains (M_n) defined by the total concentration of growing and dormant species ($[I]_0 \approx 10^{-2}$ mol/L) but with the rates proportional to the concentration of carbocations present in very low amounts ($[C^+] \approx 10^{-7}$ mol/L):

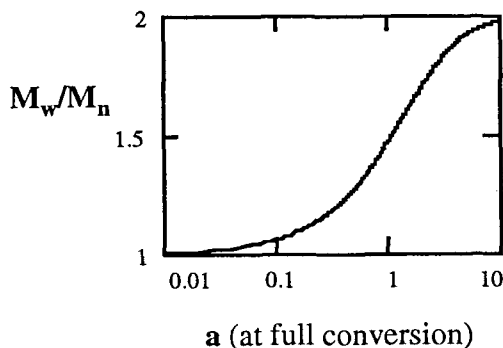


FIG. 2. Effect of the transfer to monomer on polydispersity at complete conversion for various parameters $a = (k_{trM}/k_p) \cdot [M]_0/[I]_0$.

BASIS OF RADICAL POLYMERIZATION

Radical polymerization includes four elementary reactions.

1. Slow initiation via the homolytic cleavage of a peroxide, diazo, or other similar compounds; $k_d < 10^{-5} \text{ s}^{-1}$;



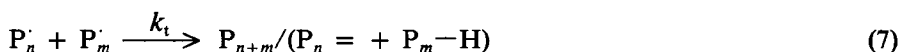
2. Relatively fast reaction of primary radicals with monomer to generate the first growing species; because $k_d < k_0[\text{M}]$, the decomposition remains the rate-determining step:



3. Fast propagation; $k_p \approx 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$:



4. Very fast termination between growing radicals via coupling or disproportionation; $k_t \approx 10^7 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$:



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

A synthesis of high molecular weight polymers requires slow initiation to produce a low momentary concentration of growing radicals ($[\text{P}\cdot] \approx 10^{-7} \text{ mol/L}$) which terminate in a bimolecular process. The ratio of the rate of propagation to that of termination ("livingness") decreases with $[\text{P}\cdot]$ because propagation is a first-order process but termination is a second-order process with respect to $[\text{P}\cdot]$. The proportion of chains marked by termination increases with chain length. Therefore, well-defined polymers from radical polymerization may be formed only if chains are relatively short *and* the concentration of free radicals is low enough. These two requirements are in an apparent contradiction but can be accommodated via reversible deactivation of growing free radicals in a way similar to the deactivation of growing carbocations.

KINETICS OF "LIVING" RADICAL POLYMERIZATION

Living polymerization should provide well-defined polymers with a negligible amount of chain breaking (<5%) at high monomer conversion (>99%). In Fig. 1 the top two curves correspond approximately to 5% deactivation of chains at 99% conversion and 10% deactivation at 70% conversion. The behavior of radical systems is different from that of cationic systems. The most important chain-breaking reaction is not transfer but termination. From the point of view of the synthesis of well-defined polymers, block copolymers, and end-functional polymers, any chain-breaking reaction is disallowed. However, termination and transfer lead to

different deviations from the behavior of ideal systems (either lower rates or lower DP).

The synthesis of well-defined polymers by radical polymerization requires a low stationary concentration of growing radicals which should be *reversibly* deactivated to provide a relatively large number of macromolecules. There are two ways of deactivation of growing radical P'. The first one is with a scavenging radical R': R' should react with P' but not with monomer (M), and should not initiate polymerization. The second approach is based on the nonradical scavenger which provides reversibly persistent (“dormant”) radicals. To control molecular weights in a sufficient way, the initiation rate should be comparable to that of propagation and, therefore, the structure of the initiator should be similar to that of the dormant species P-R. In the first system the covalent adduct homolytically cleaves to P' and R' with the rate constant of initiation k_i and regenerates with the rate constant of recombination k_r :



Assuming a steady state for the concentration of dormant chains:

$$-d[P-R] = k_i[P-R] - k_r[P'][R'] \approx 0 \quad (9)$$

$$[P']_{st} = k_i[P-R]/(k_t[R']) \quad (10)$$

The recombination of [P'] with [R'] is not considered to be chain breaking because it is reversible. Irreversible termination produces entirely inactive chains by either coupling or disproportionation of growing radicals P'. The stationary concentration of growing radicals is nearly constant because although some chains are terminated, the radicals are easily reformed from the large pool of dormant species. Nevertheless, some chains will terminate; 5% of the chains will irreversibly terminate after time (τ_t):

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

Monomer is consumed at a rate proportional to its concentration, that of the growing radicals, and to the rate constant of propagation k_p :

$$-d[M]/dt = k_p[P'][M] \quad (12)$$

99% of monomer will be consumed after time τ_p , which for a well-defined system should be comparable or shorter than the time when 5% of chains terminate (τ_t):

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

Consequently:

$$[P']_{st}/[P-R]_0 \leq k_p/100k_t \quad (14)$$

For the polymerization of styrene at 60°C: $k_p \approx 10^2 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_t \approx 10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$ [13]. To make a polymer with DP ≈ 100 in bulk ($[M]_0 \approx 10 \text{ mol}\cdot\text{L}^{-1}$), the concentration of the initiator should be equal to $[P-R]_0 = [M]_0/\text{DP} = 10^{-1} \text{ mol}\cdot\text{L}^{-1}$ and the stationary radical concentration:

$$[P']_{st} = [P-R]_0 \cdot k_p/k_t \cdot 100 \approx 10^{-8} \text{ mol}\cdot\text{L}^{-1} \quad (15)$$

At such a low $[P]_{st}$, a 99% conversion will be reached after $\approx 4 \times 10^6$ s, which is more than 1 month. However, the k_p/k_t ratio for other monomers, such as vinyl acetate or acrylates, is higher than for styrene (30 and 60 times, respectively) [13]. This allows an increase of the concentration of growing radicals at the same level of chain breaking and decreases the reaction time to approximately 1 day.

A comment should be added on the potential participation of solvent cage effects. The homolytic cleavage of dormant chains and a very fast recombination of the growing radical with a scavenger might occur within a solvent cage. A small monomer molecule may diffuse into the solvent cage relatively faster than the growing radical, leading to a k_p/k_t ratio apparently higher than discussed before. This could allow synthesis of well-defined systems at higher stationary concentrations of radicals and shorter reaction times than in the "classic" systems without contribution of the solvent cage.

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

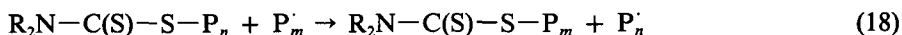


The kinetic requirements for this case are identical to those discussed previously. This approach is best realized with organometallic compounds. However, some of them may have a high affinity toward hydrogen and may lead to the undesired and uncontrolled transfer [14, 15].

There are a few systems postulated as living radical ones in which growing radicals are reversibly deactivated by radical scavengers. The best results are in the thermal polymerization of styrene and methacrylate initiated with alkoxyamines [16, 17] or with alkyl dithiocarbamates [18]. However, the former system requires an excess of radicals and is based on thermoneutral transfer; the latter one is accompanied by various side reactions, including the evolution of CS_2 [19].



Growing radicals may react with dithiocarbamate end-groups in two different ways. By a transfer process as suggested by Otsu [18]:



and additionally by irreversibly forming head-to-head end-groups and producing thiocarbamate radicals of low reactivity. The latter reaction, reported by Sigwalt, is very important in the polymerization of acrylates [20, 21].

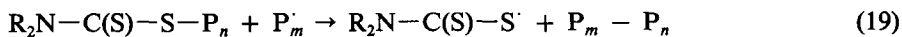


Photo polymerization of acrylates in the presence of benzyl dithiocarbamate is slower (!) than spontaneous photo polymerization [20]. This means that degradative transfer is the main operating reaction.

"LIVING" POLYMERIZATION OF VINYL ACETATE

The monomer vinyl acetate has been polymerized, at least so far, via a radical mechanism. Thus, vinyl acetate is a very good test-monomer for a "living" radical process.

The initiator is based on an organometallic compound which is complexed by ligands and then activated by some stable (or not) radicals. Here we will describe results with triisobutylaluminum, complexed by 2,2'-dipyridyl (DPy) and activated by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). A typical composition is 1:1:2. Excess TEMPO (≥ 4) stops the reaction, thereby confirming the radical character of the process [22].

Figure 3 presents three kinetic plots obtained at 20°C in benzene at three different concentrations of initiator. Straight lines in the semilogarithmic coordinates indicate first-order kinetics in the monomer. Thus, monomer is involved in the rate-limiting step. The straight lines also indicate a constant concentration of the active species. This information, together with molecular weight data, prove that initiation is rapid and the contribution of termination is very low.

Figure 4 shows three typical plots of the evolution of molecular weights with conversion. Straight lines passing through the origin have been obtained. The molecular weight distribution stays very low, usually below $M_w/M_n < 1.3$ (Fig. 5).

The highest obtained molecular weights were $M_n \approx 50,000$. This limit is probably not set by termination but rather by transfer.

The initiating system is quite complex and changes activity at various proportions of TEMPO. Polymerization occurs slowly even without TEMPO. Preliminary EPR studies indicate the presence of radicals in the $Al(iBu)_3:DPy$ complex at this stage. However, polymerization is slow and semilog plots are sigmoidal, indicating slow initiation. Molecular weights are higher than predicted for living systems, as expected for incomplete initiation. Polymerization is strongly accelerated in the presence of two equivalents of TEMPO, and it is entirely inhibited by four equivalents of TEMPO. The initiator was prepared by mixing the organoaluminum compound with DPy (a strong red color was observed), and the TEMPO was added with the formation of a more intense color.

The maximum coordination number of aluminum is six. If three valences are occupied by alkyl groups, two by DPy, only one TEMPO can be accommodated to form a stable delocalized radical:

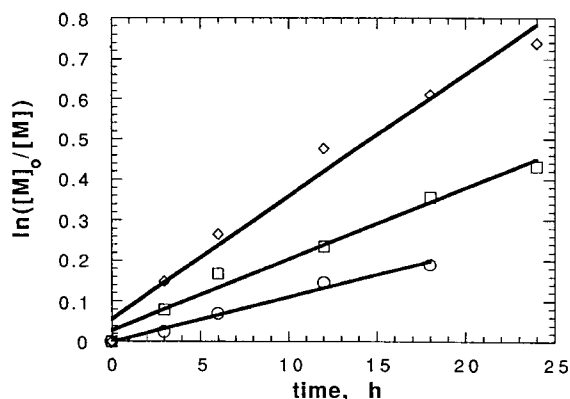


FIG. 3. The kinetics of the polymerization of vinyl acetate ($[M]_0 = 2.5$ mol/L) at 20°C in C_6H_6 at variable concentration of the initiator: (\diamond) $[I]_0 = 0.30$ mol/L; (\square) $[I]_0 = 0.05$ mol/L; (\circ) $[I]_0 = 0.01$ mol/L.

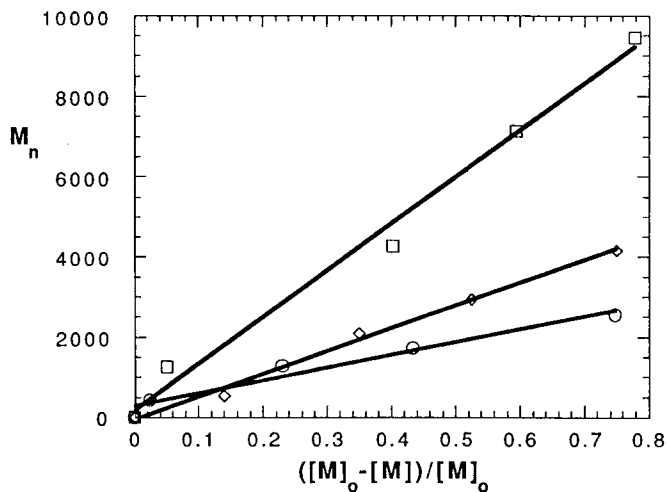


FIG. 4. The effect of conversion on molecular weights in the polymerization of vinyl acetate in C_6H_6 : (\square) $60^\circ C$, $[I]_0 = 0.05$ mol/L; (\diamond) $60^\circ C$, $[I]_0 = 0.30$ mol/L; (\circ) $20^\circ C$, $[I]_0 = 0.05$ mol/L.

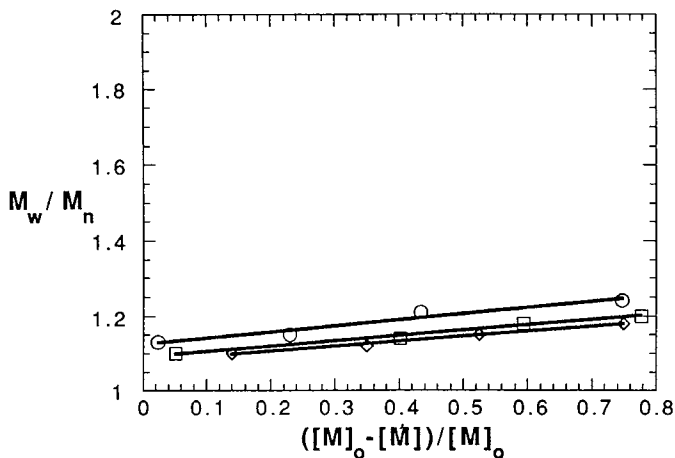
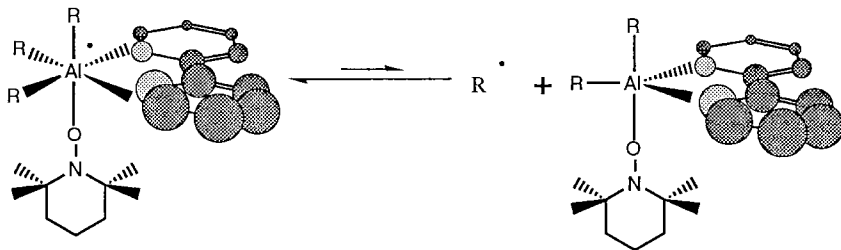


FIG. 5. The effect of temperature and the concentration of the initiator on polydispersities of poly(vinyl acetate) prepared in C_6H_6 : (\diamond) $60^\circ C$, $[I]_0 = 0.05$ mol/L; (\square) $60^\circ C$, $[I]_0 = 0.30$ mol/L; (\circ) $20^\circ C$, $[I]_0 = 0.05$ mol/L.



(20)

The stable delocalized radical could be in equilibrium with a tiny amount of a very reactive radical R^{\cdot} , capable of initiation and subsequent propagation. Better results with two equivalents of TEMPO may indicate better delocalization of electrons within a persistent radical with two TEMPO ligands. The real natures of the active and the dormant species are not yet precisely known and will be the subject of subsequent studies.

The kinetic results indicate that the reaction is first order in monomer, meaning that it is involved in the rate-determining step. The fractional order in the initiating system (≈ 0.4) suggests that a radical C^{\cdot} is formed reversibly from the dormant species $C-Z^{\cdot}$. It is reactive enough to initiate polymerization and subsequently to propagate:



If we assume that the rate constants of propagation and bimolecular termination in this particular system are similar to those in a homogenous radical polymerization of vinyl acetate [13], we may estimate the stationary concentration of growing radicals:

$$d \ln [M]/dt = k = k_p^{\cdot} [C^{\cdot}]_{st} \quad (23)$$

$$[C^{\cdot}]_{st} = k/k_p^{\cdot} \approx 10^{-8} \text{ mol/L} \quad (24)$$

This low estimated stationary concentration of growing radicals prevents bimolecular termination and allows the preparation of well-defined polymers. We are currently investigating systems with different ligands and activators which provide faster overall polymerization and, presumably, a higher stationary concentration of growing radicals. If these systems still remain well defined, with low polydispersity and no termination, this would indicate that the k_p/k_t ratio is apparently higher than deduced from the homogenous systems. If the reaction occurs in a solvent cage, it is possible to imagine that a monomer penetrates the cage relatively faster than another growing radical.

Polymerization of methyl methacrylate with the same initiating system is not controlled. Very rapid polymerization and higher than predicted molecular weights are obtained. However, manipulation of the substituents and ligands on aluminum allows the preparation of well-defined systems. Thus, instead of the AlR_3/Dpy complex, an organoaluminum amide, $Al(NPh_2)_2$, could be used. This compound alone leads to slow and uncontrolled anionic-coordinative polymerization of methyl methacrylate at ambient temperatures, but in the presence of TEMPO it provides well-defined poly(methyl methacrylates) [23].

CONCLUSIONS

The concept of reversible deactivation of the growing species which led to the successful synthesis of well-defined polymers via carbocationic polymerization has been applied to radical polymerization. Polymerization of vinyl acetate and methyl

methacrylate in the presence of organoaluminum compounds activated by stable radicals provides polymers with narrow molecular weight distributions ($M_w/M_n < 1.3$). The efficiency of the initiating system depends on substituents and coordinated ligands around aluminum, which should be adjusted for the corresponding monomer.

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