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"Living" Radical Polymerization of Vinyl Acetate

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ABSTRACT: The synthesis of well-defined poly(vinyl acetate) in "living" radical polymerization is reported. Straight lines in semilogarithmic plots up to >90% conversion indicate internal first order in monomer and a constant concentration of growing species. Molecular weights increase linearly with conversion. The initiating system might involve persistent radical formed by the ternary complexes of organoaluminum compounds with Lewis bases and stable radicals. This article focuses on the Al(*i*Bu)$_3$:BPy:TEMPO system. The effect of the composition of the initiating system and its aging is described.

Introduction

The classic definition of living polymerization requires absence of chain breaking reactions.[1,2] The nearly complete suppression of transfer and termination has been successfully accomplished in polymerization with polar active species such as carbanions, olate anions, oxonium ions, and also various organometallic compounds.[2,3] Recently, living carbocationic polymerization has also been announced, although carbocations always do participate in transfer reactions by β-H atom elimination from carbocations.[4–6] However, well-defined polymers can be prepared in this system, if molecular weights are not too high. Control has been achieved in the cationic polymerization of alkenes by dynamic equilibration of the growing carbocations with dormant onium ions and/or covalent species.[6] If exchange is fast, polymers with narrow molecular weight distributions can be prepared.[7,8]

The concept of the living radical polymerization has often been criticized because it is impossible to entirely suppress bimolecular termination between growing radicals. However, in a fashion similar to "living" (quotation marks are used to recognize the presence of chain breaking reactions) carbocationic polymerization, well-defined polymers can be prepared if the concentration of growing radicals is sufficiently low and the molecular weights not too high. The theoretical bases of "living" radical polymerization and three possible scenarios for the realization of this concept have been discussed together with a brief review of the most important "living" radical systems in the preceding article.[9]

In this paper, we will describe our results for the polymerization of vinyl acetate (VAc) initiated by triisobutylaluminum (Al(*i*Bu)$_3$) complexed by a bidentate ligand, 2,2′-bipyridyl (Bpy), and activated by a stable radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The typical composition is 1:1.2. Vinyl acetate is a monomer which has been, at least so far, polymerized via a radical mechanism. This is in contrast to styrene and acrylates, two monomers primarily studied to date in "living" radical polymerizations, but also successfully polymerized anionically and/or cationically(styrene). In order to test the degree of control of our new initiating system, we studied not only the dependence of the molecular weights on conversion (in which linearity does not preclude termination if initiation is fast) but also polydispersity and the kinetics of polymerization, up to above 90% conversion. Linear plots in semilogarithmic coordinates indicate that only a small proportion of termination exists in the reported system. We would like to emphasize that the observed linear correlation between molecular weights and conversion, low polydispersities, and straight lines in the kinetic plots up to very high conversions and in the low range of molecular weights are quite unique in this field. Most of the previous studies were limited to <10% conversion and nonlinear correlations were found at initial stages.

Experimental Section

Materials. Triisobutylaluminum, Al(*i*Bu)$_3$, was used as a 1 M solution in toluene (Aldrich). 2,2′-Bipyridyl, bpy, and 2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO, were used as received (Aldrich). In some cases TEMPO was sublimed. Benzene was refluxed overnight over CaH$_2$ and freshly distilled before use. Vinyl acetate, VAc, was washed with 2% alkali solution to remove a stabilizer, dried over anhydrous MgSO$_4$, and distilled over CaH$_2$.

Preparation of Initiator Al(*i*Bu)$_3$/Bpy/TEMPO. To a three-necked round-bottomed flask (100 mL), equipped with magnetic stirrer and containing Al(*i*Bu)$_3$ (1 mmol), was added 1 mL of a 1 M solution of BPy (1 mmol) in benzene, by means of a hypodermic syringe, in an argon atmosphere. The mixture was stirred for 10 min at room temperature. A deep-red complex of Al(*i*Bu)$_3$:BPy was formed immediately, in a fast, exothermic reaction. Then 2 mL of 1 M solution of TEMPO (2 mmol) in benzene was added to this complex; the exothermic complexation was noticed.

Polymerization. All polymerizations were performed in dried glassware, under an argon atmosphere. Apparently, traces of moisture or oxygen may catalyze polymerization. The polymerization solvent (benzene) was cannulated via a double-ended needle to a round bottom flask pressured with argon and equipped with a magnetic stirrer and rubber septum. The calculated amount of freshly prepared initiator was syringed into the flask, and then the purified monomer was slowly added to the initiator solution. The polymerization reactions were performed at temperatures ranging from 20 to 60 °C, for 12–24 h. Polymers were precipitated into a large excess of hexane, filtered, and dried under reduced pressure at room temperature. The orange color in the precipitated polymers disappeared after treatment with alkali solutions.

Measurements. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters 510 HPLC equipped with a 410 differential refractometer and UV detector with THF as an eluent and a flow rate of 1.0 mL·min^{-1} and with three Ultrastyragel columns (100 Å, 500 Å, and linear) in series. The molecular weight calibration curve was obtained using polystyrene standards.

Kinetic measurements were performed using dilatometric techniques. The reaction components were introduced by syringes in the following order: solvent, initiator, monomer. The content of the dilatometer was vigorously stirred during the addition process. After filling, the dilatometer was closed and

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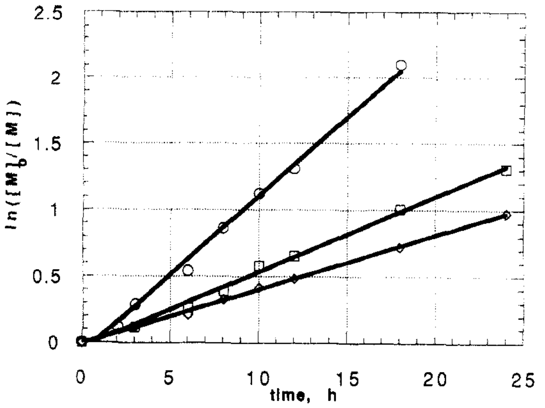


Figure 1. First order time–conversion plots in the polymerization of VAc ($[M]_0 = 2.5$ M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2) in benzene, 60 °C, at different concentrations of initiator: 0.3 M (○); 0.05 M (□); 0.01 M (◇).

placed in a thermostat bath controlled to <0.01 °C. The contraction was followed by a cathetometer.

Results and Discussion

Kinetic Studies. In order to better understand the mechanism of propagation and control rates of polymerization, we performed basic kinetic experiments. The internal order in monomer and external order in initiator, as well as the effect of temperature, were investigated. Because the initiating system is quite complex, we also studied the effect of the composition of the initiator and its aging on the kinetics of polymerization.

Figure 1 presents three kinetic plots obtained at 60 °C in benzene, at three different concentrations of initiator. Straight lines in the semilogarithmic coordinates indicate first order in 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 the molecular weight data prove that initiation is rapid and the contribution of termination is minimal.

The slopes of the semilogarithmic anamorphoses allow the calculation of rate coefficients (k) and the determination of the external order in initiator, as well as the apparent rate constants of propagation:

$$d[M]/dt = k[M] = k_p^{app}[M][I]^n \qquad (1)$$

$$\Delta \ln [M]/\Delta t = k = k_p^{app}[I]^n \qquad (2)$$

$$\ln k = \ln k_p^{app} + n \ln [I] \qquad (3)$$

The dependence of the logarithm of the rate coefficient on the logarithm of the initial concentration of initiator is shown in Figure 2 for 60 and 20 °C. The fractional orders observed in this graph ($n \approx 0.3$) will be discussed in a later section.

The Arrhenius plots of the apparent rate constants of propagation (k_p^{app}) and the logarithmic dependence of the rate coefficients (k) obtained at the same concentration of initiator at three different temperatures, versus the reciprocal absolute temperature is shown in Figure 3. The apparent energy of activation obtained from these plots is $E_a^{app} = 6.7$ kcal/mol and is higher than that for the radical propagation of vinyl acetate ($E_a = 4.5$ kcal/mol).[10] The higher E_a^{app} value indicates that this is probably a composite value consisting of the true activation energy of radical propagation and the enthalpy of the equilibrium between dormant and active species.

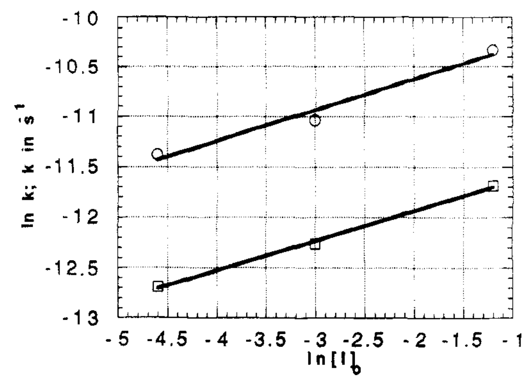


Figure 2. Dependence of rate coefficient (k) on the initiator concentration in the polymerization of VAc ($[M]_0 = 2.5$ M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2) in benzene, at different temperatures: 20 °C (□); 60 °C (○).

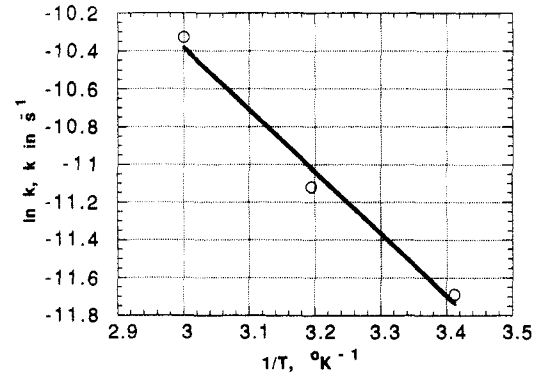


Figure 3. Dependence of rate coefficients (k) on temperature in the polymerization of VAc ($[M]_0 = 2.5$ M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2) in benzene, for $[I]_0 = 0.3$ M.

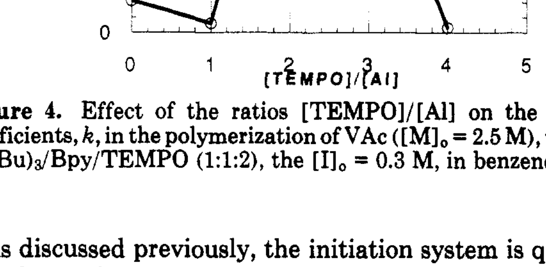


Figure 4. Effect of the ratios [TEMPO]/[Al] on the rate coefficients, k, in the polymerization of VAc ($[M]_0 = 2.5$ M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2), the $[I]_0 = 0.3$ M, in benzene, 60 °C.

As discussed previously, the initiation system is quite complex and its activity varies with the proportion of TEMPO. Figure 4 shows the dependence of the rate coefficient (slope of the semilogarithmic anamorphoses) at a constant concentration of the complex (Al(iBu)$_3$:BPy and at various ratios of TEMPO to complex. Polymerization occurs slowly even without TEMPO but it is strongly accelerated in the presence of 2 equiv of TEMPO. Polymerization without added TEMPO proceeds with an acceleration, and the maximum rate is similar to that with 1 equiv of TEMPO. Polymerization is nearly entirely inhibited by 4 equiv of TEMPO which may confirm the radical character of the process. Straight kinetic plots have been observed only for the ratio 2. For the ratio 3, the initial rate was very similar to that observed for the ratio 2, but the rate subsequently decreased.

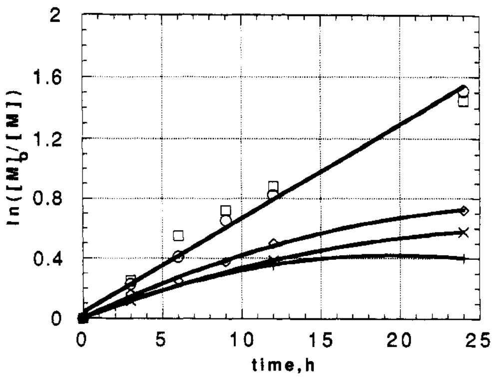


Figure 5. Effect of aging on kinetics in the polymerization of VAc ($[M]_0 = 2.5$ M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2), $[I]_0 = 0.3$ M, in benzene, 60 °C: $t = 0$ min (○); $t = 2$ min (□); $t = 10$ min (◇); $t = 30$ min (×); $t = 60$ min (+).

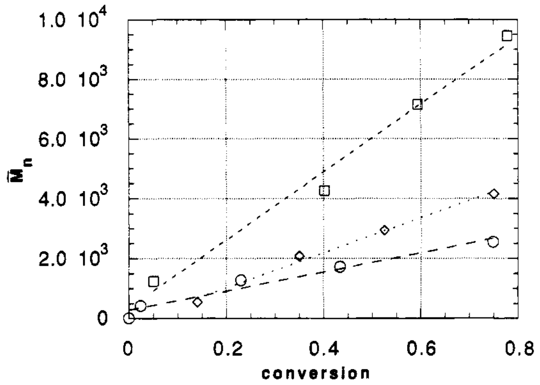


Figure 6. Molecular weight–conversion dependence in the polymerization of VAc ($[M]_0$ - 2.5 M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2) in benzene, at different concentrations of initiator and temperatures: $[I]_0 = 0.05$ M, 20 °C (○); $[I]_0 = 0.05$ M, 60 °C (□); $[I]_0 = 0.3$ M, 60 °C (◇).

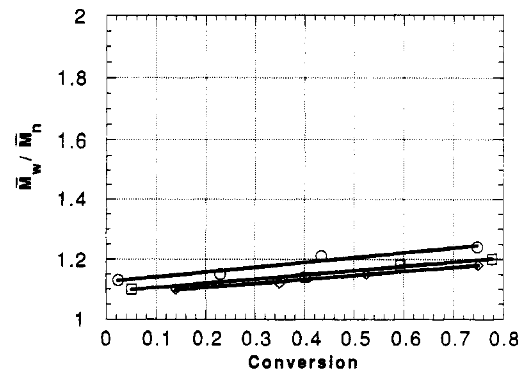


Figure 7. Variation of polydispersities with conversion in polymerization of VAc ($[M]_0 = 2.5$ M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2) in benzene, at different concentrations of initiator and temperatures: $[I]_0 = 0.05$ M, 20 °C (○); $[I]_0 = 0.05$ M, 60 °C (□); $[I]_0 = 0.3$ M, 60 °C (◇).

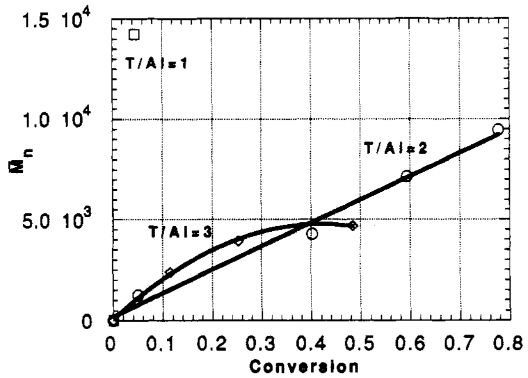


Figure 8. Dependence of molecular weight on the ratio [TEMPO]/[Al] in the polymerization of VAc ($[M]_0 = 2.5$ M), $[I]_0 = 0.3$ M, with Al(iBu)$_3$/Bpy/TEMPO (1:1:2) in benzene, 60 °C.

Aging of the initiating system is another important parameter, affecting the kinetics and molecular weights. The aging time is defined as the time between the addition of TEMPO to the Al(iBu)$_3$:BPy complex and the addition of the initiating system to the monomer solution. The aging time "zero" is when TEMPO was added last to the mixture of monomer and the Al(iBu)$_3$:BPy complex. Figure 5 shows the effect of aging of the initiating system based on 1:1:2 composition (Al(iBu)$_3$:BPy:TEMPO) on the rate coefficients at 20 °C. Apparently, longer aging times decrease polymerization rates and lead to deviation from linearity in the semilogarithmic plots. This is in contrast to the polymerization initiated by "fresh" systems in which termination is not observed even at longer times. This may indicate that either the presence of the monomer and/or polymer reduces termination, or that the growing radicals are more stable than the initiating radicals. It is also possible that the active species are slowly destroyed by the moisture or oxygen diffusing to the reaction mixture.

Molecular Weights. As discussed in the preceding article, the preparation of well-defined polymers by a radical polymerization is possible at a sufficiently low stationary concentration of growing radicals, in order to reduce the rate of bimolecular termination in comparison to propagation (unimolecular in respect to a radical). The low concentration of radicals means that the overall polymerization rates are also low, as shown in the previous section. The chain breaking reactions are usually less evident for low molecular weight polymers, which are produced faster than higher molecular weight polymers.

Figure 6 shows three typical plots of the evolution of molecular weights with conversion. Almost straight lines passing through the origin have been obtained. The molecular weight distribution stays very low, usually below $\bar{M}_w/\bar{M}_n < 1.3$ (Figure 7). The highest molecular weights obtained were $\bar{M}_n \approx 30\,000$. This limit is probably set by transfer.[10]

Figure 8 shows the dependence of molecular weights on conversion at different TEMPO/{Al(iBu)$_3$:BPy} ratios. Molecular weights higher than expected for a living process have been observed at a low proportion of TEMPO, indicating incomplete initiation. On the other hand, at the ratio 3, the molecular weights do not increase in the expected way. This may indicate the contribution of transfer at this ratio.

Figure 9 shows the effect of aging on molecular weights and demonstrates the decrease in initiator efficiency with an increase of the aging time. These data are in good correlation with the kinetic studies already presented.

In all of the discussed systems the initiation is not complete and molecular weights are higher than theoretically predicted (assuming one chain per aluminum atom). The reasons for the variation in efficiency of initiation is not known and may be ascribed to the cocatalysis by moisture or oxygen.

Discussion of the Plausible Polymerization Mechanism. Although the real nature of the growing and dormant species is not yet known and the exact mechanism of propagation not yet confirmed, we will attempt to discuss plausible mechanistic features of this process. The complete formulation of the mechanism requires spectroscopic characterization of the active intermediates such as polarized or "free" radicals, the structure of the

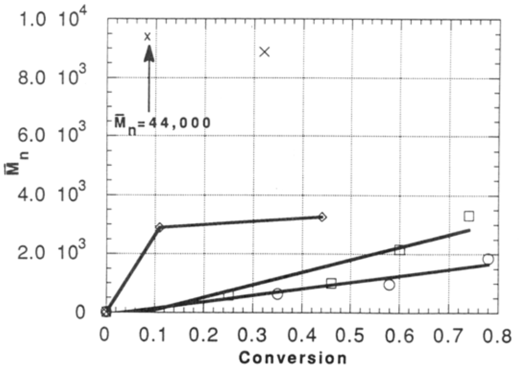


Figure 9. Effect of aging on molecular weight in the polymerization of VAc ($[M]_o = 2.5$ M), with Al(iBu)$_3$/Bpy/TEMPO (1:1:2), $[I]_o = 0.3$ M, in benzene, 60 °C: $t = 0$ min (○); $t = 10$ min (□); $t = 30$ min (◇); $t = 60$ min (×).

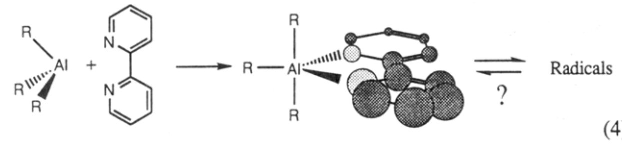
persistent dormant radicals, determination of the contribution of the solvent cage, dynamics of exchange, and the microstructure of the polymer including end groups.

There are several earlier reports describing the synthesis and characterization of crystalline, neutral complexes of organoaluminum derivatives and mono- or bidentate N-based ligands such as triethylamine, pyridine, 2,2′-bipyridyl, 1,10-phenanthroline, and N,N,N',N'-tetramethylethylenediamine.[11–13] The Al coordination numbers (4 in complexes with monodentate and 5 in complexes with bidentate Lewis bases) have been established on the basis of cryoscopic molecular weight studies. Persistent radicals have been produced by a single electron transfer reaction of R_2AlH to bipyridyl (2,2′- or 4,4′-) or pyrazine[16] or by reduction of the complexes with alkali metals.[17,18] Persistent radicals with fluxional or bidentate structures have been also observed for $AlEt_nCl_{3-n}$ complexes with semiquinones.[19]

Complexes between aluminum halides, AlX_3, and stable radicals (e.g. TEMPO, di-*tert*-butyl nitroxide) have been observed by EPR.[20–22] Therefore, similar to transition metal compounds,[23] organoaluminum compounds of the type $AlR_{3-n}X_n$ are highly effective acceptors of the free nitroxide radicals.[24,25] Organoaluminum alkyls are known as efficient chain transfer reagents.[26,27] This suggests that they may form relatively unstable complexed radicals. Apparently, their stability may be enhanced by changing the aluminum coordination number from 4 (or 5) to 6 in the presence of ligands containing heteroatoms as electron donors.

According to our knowledge, interactions between stable radicals such as TEMPO and organoaluminum compounds coordinated with Lewis bases have not yet been reported. A tentative mechanistic proposal involving the following steps is presented below.

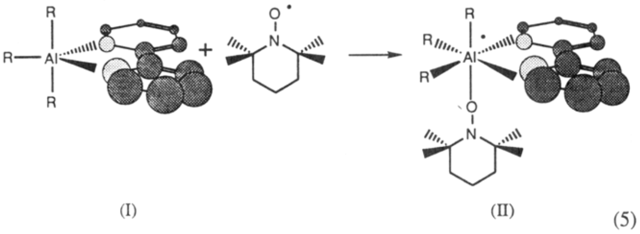
(i) The pentacoordinated complexes **I** are formed between Al(iBu)$_3$ and BPy, at a molar ratio 1:1 (BPy is probably bound coordinatively to Al):



(I) (4)

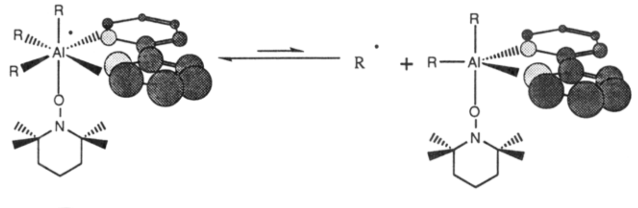
Our preliminary EPR studies indicate that radicals have already been formed at this stage. They could resemble radicals $\{R_2Al{:}BPy\}^\bullet$, reported in ref 16. The complex was used as an initiator in the polymerization of vinyl acetate (at the ratio TEMPO/Al = 0). After 48 h, poly(vinyl acetate) was obtained (yield ≈ 80%); GPC indicates $\bar{M}_n = 27\,000$ ($\bar{M}_n^T = \Delta[M]/[I]_o = 10\,000$) and a relatively narrow polydispersity, $\bar{M}_w/\bar{M}_n = 1.23$. Low overall rates, acceleration periods, and higher than expected molecular weights indicate a low proportion of radicals.

(ii) The irreversible attack of TEMPO on the pentacoordinated complex Al(iBu)$_3$:BPy (I) leads to a relatively stable and delocalized radical (II):



(I) (II) (5)

TEMPO may also react with some short-lived radicals present at stage (i) to form alkoxyamines and pentacoordinated complexes of the type IV. The radical II could be in equilibrium with a tiny amount of a very reactive radical $R^\bullet$ (III), capable of initiation and subsequent propagation:

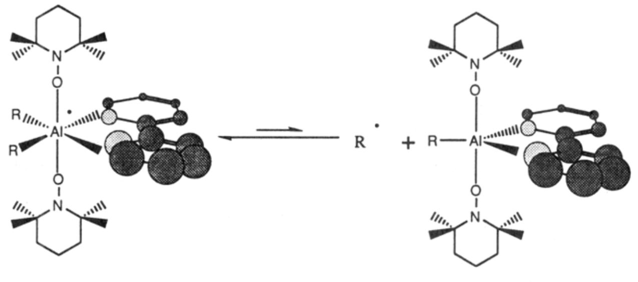


(II) (III) (IV) (6)

This equilibrium might be in apparent contradiction with the stability of TEMPO$^\bullet$ and $R^\bullet$ (as individual species), but it is in agreement with the energies of Al–C and Al–O bonds. The latter is much stronger due to its polar character and is difficult to cleave homolytically.

The proposed geometries of the high-coordinated structures (II or IV) are only tentative. For example, IV might have a trigonal bipyramid or square pyramid geometry, and TEMPO might be located at either the apical or the equatorial position. In the hexacoordinated structures shown in eqs 5–7 three substituents should be connected via true covalent bonds, however, the fourth one (and BPy) formally via coordinative type bonding.

Kinetic measurements indicate that the reactivity of the system with only one TEMPO ligand (structure II) is low, but it dramatically increases with two TEMPO ligands (structure IIa):



(IIa) (III) (IVa) (7)

The second equivalent of TEMPO could scavenge the growing radicals III, unless it is again preferentially bound to aluminum with the release of the alkyl radical. Alkyl radicals present at high concentrations must either couple, disproportionate, or be annihilated in some other way. The addition of the third equivalent of TEMPO provides pentacoordinated species with three TEMPO ligands and the return of the radical R$^\bullet$ may be difficult due to steric effects.

The addition of the fourth equivalent inhibits polymerization. Under such conditions, either three or four valences at aluminum are occupied by TEMPO ligands. TEMPO is a very powerful scavenger, but a very poor initiator for a radical polymerization. Therefore, the efficiency of the discussed initiating system indicates that no free TEMPO is present and no TEMPO is cleaved from the dormant species.

It should be noted that organoaluminum alkyls without Lewis bases, complexed by TEMPO are not efficient as initiators for VAc, although they initiate a very fast and exothermic polymerization of methyl methacrylate.[26]

In the preceding article, we proposed three approaches to "living" radical polymerization based on (1) the homolytic cleavage of species with labile C–Z bonds, to a growing radical C$^\bullet$ and a scavenging radical Z$^\bullet$, (2) the reversible reaction of the growing radical C$^\bullet$ with a scavenger Z to produce a stabilized radical C–Z$^\bullet$, and (3) the degenerative transfer process between growing radicals $C_n^\bullet$ and transfer agents C_m–Z.

We tentatively assume, on the basis of the preliminary kinetic data, that the discussed system belongs to case 2. The reason for the unusual stability of the dormant radical (IVa) could be attributed both to a favored steric environment at the aluminum atom and to enhanced electron delocalization over all organic substituents bonded or coordinated by aluminum.

The kinetic results indicate first order in monomer, meaning that it is involved in the rate determining step. The fractional order in the initiating system suggests that a radical C$^\bullet$ is cleaved homolytically from the dormant species C–Z$^\bullet$ (k_{act}) in the reversible mode (k_{deact}). Radical C$^\bullet$ is reactive enough to initiate polymerization and subsequently to propagate:

$$\text{C–Z}^\bullet \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} \text{C}^\bullet + \text{Z} \qquad (8)$$

$$\text{C}_n^\bullet + \text{M} \xrightarrow{k_p} \text{C}_{n+1} \qquad (9)$$

If we can assume that the rate constants of the elementary reactions such as propagation and bimolecular termination in this particular system are similar to those in a homogeneous radical polymerization of vinyl acetate,[10] we may estimate the stationary concentration of growing radicals which depends on the relative rate constants of activation and deactivation:

$$\Delta \ln [\text{M}]/\Delta t = k = k_p^\bullet[\text{C}^\bullet]_{st} \qquad (10)$$

$$[\text{C}^\bullet]_{st} = k/k_p^\bullet \approx 10^{-8}\ \text{mol/L} \qquad (11)$$

This low estimated stationary concentration of growing radicals prevents bimolecular termination and enables preparation of well-defined polymers.

Conclusions

In this paper, we report the synthesis of well-defined poly(vinyl acetate) via the radical polymerization using a tricomponent system comprising an organoaluminum compound complexed by Lewis bases and activated by stable radicals. In the absence of TEMPO, the coordination complex Al(iBu)$_3$:Bpy initiates a very slow, but controlled, polymerization of VAc, whereas the excess of TEMPO inhibits this polymerization. Polymerization of VAc initiated by the complex Al(iBu)$_3$/Bpy/TEMPO (1:1:2) is first order in monomer and fractional order in the initiating system. Molecular weights increase linearly with conversion and polydispersities remain low but initiator efficiency is not complete. Chains could be extended by new monomer addition, and block copolymers have been prepared with styrene and methyl methacrylate.[28] The reported results indicate that the overall rate of initiation is comparable to that of propagation, that contribution of the irreversible bimolecular termination of the growing radicals is negligible under chosen conditions, and that growing radicals are in dynamic equilibrium with dormant species. The real nature of the active and the dormant species is not yet precisely known and will be a subject of the subsequent studies.

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