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"LIVING" RADICAL POLYMERIZATION OF VINYL ACETATE' by

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"Living" Radical Polymerization of Vinyl Acetate

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Abstract:

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 constant concentration of growing species. Molecular weights increase linearly with conversion. The initiating system is based on the persistent radicals formed by the ternary complexes of organoaluminum compounds with Lewis bases and stable radicals. This article focuses on Al(iBu)₃:DPy:TEMPO system. The effect of the composition of the initiating system and its aging is described. It is proposed that propagation involves reversible cleavage of growing radicals from persistent complexed radicals based on hexacoordinated organoaluminum species.

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INTRODUCTION

The classic definition of the living polymerization requires no 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 with various organometallic compounds^{2,3}. Recently, living carbocationic polymerization has been also announced, although carbocations always do participate in transfer reactions by β -H atom elimination from carbocations^{4,5,6}. However, well defined polymers can be prepared in this system, if molecular weights are not too high. The control in the cationic polymerization of alkenes has been achieved by the dynamic equilibration of the growing carbocations with dormant onium ions and/or covalent species⁶. If exchange is fast, polymers with narrow molecular weight distributions can be prepared^{7,8}.

The concept of the living radical polymerization has been often criticized because it is impossible to entirely suppress bimolecular termination between growing radicals. However, in a way similar to the living carbocationic polymerization, well defined polymers can be prepared if concentration of the growing radicals is sufficiently low and the molecular weights not too high. The theoretical bases of the 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 article⁹.

In this paper we will describe our results in polymerization of vinyl acetate (VAc) initiated by triisobutylaluminum (Al(iBu)₃), complexed by a bidentate ligand, 2,2'-dipyridyl (Dpy) and activated by a stable radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a typical composition being 1:1:2. Vinyl acetate is a monomer which has been, at least so far, polymerized only via radical mechanism. This is in a big contrast to styrene and acrylates, two monomers

mainly studied until now 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 (which linearity does not preclude termination, if initiation is fast), but also polydispersity and kinetics of polymerization, up to above 90% conversion. Linear plots in semilogarithmic coordinates indicate very small proportion of termination 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 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% conversions and nonlinear correlations were found at initial stages.

EXPERIMENTAL

Materials

Triisobutylaluminum, Al(iBu)₃, was used as 1M solution in toluene (Aldrich). 2,2'-Dipyridyl, Dpy, and 2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO, were used as received (Aldrich). Benzene was refluxed overnight over CaH₂ and freshly distilled before use. Vinyl acetate, VAc, was washed with 2% alkali solution to remove a stabilizer, dried over anhydrous MgSO₄, and distilled over CaH₂.

Preparation of Initiator Al(iBu)3/Dpy/TEMPO

To a three-necked round-bottomed flask (100 mL), equipped with magnetic stirrer and containing Al(iBu)₃ (1mmol), was added 1 mL 1M solution in benzene of DPy (1mmol), by means of a hypodermic syringe in a dry argon atmosphere. The mixture was stirred for 10 minutes, at room temperature. A

deep-red colored complex of the type Al(iBu)3:DPy was formed immediately, in a fast, exothermic reaction. Then, 2mL of 1M solution in benzene of TEMPO (2mmoles), were added to this complex; the same exothermic complexation was noticed.

Polymerization

All polymerizations were performed in carefully dried glassware, under a purified argon atmosphere. The polymerization solvent (benzene) was canulated 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 initiator just prepared was syringed into the flask and then, the purified monomer was slowly added to the initiator solution. The polymerization reactions were performed in a temperature range of 20-60°C, during typically 12 to 24 hours. Polymers were precipitated into a large excess of hexane, filtered and dried under reduced pressure, at room temperature.

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, using THF as eluent with 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 standard polystyrenes.

Kinetic measurements were performed using dilatometric techniques. All operations involved in the purification of the individual chemicals and in the introducing of the reaction components into the dilatometer were performed in purified argon atmosphere. The reaction components were dosed by syringes in the following order: solvent, initiator, monomer and during dosing, the content of the dilatometer was vigorously stirred. After filling, the dilatometer was closed and placed in a thermostat bath controlled to <0.01°C. The contraction was followed by means of 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 the 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 constant concentration of the active species. This information, together with the molecular weight data prove that initiation is rapid and contribution of termination is very low.

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

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

$$d\ln[M]/dt = k = k_{\rm p}^{\rm app} \cdot [I]^{\rm n}$$
⁽²⁾

$$\ln k = \ln k_0^{app} + n \ln [I]$$
(3)

Dependence of the logarithm of the rate coefficient on the logarithm of the initial concentration of the initiator is shown in Figure 2 for 60 and 20°C. The fractional orders observed in this graph ($n\approx0.3$) will be discussed in the later section.

The Arrhenius plots of the apparent rate constants of the propagation (k_p^{app}) and the logarithmic dependence of the rate coefficients (k) obtained at the same concentration of the 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 for the radical propagation of vinyl acetate $(E_a=4.5 \text{ kcal/mol})^{10}$. The higher E_a^{app} value indicates that this is probably a composite value consisting of the true activation energy of the radical propagation and the enthalpy of the equilibrium between dormant and active species.

As discussed previously, the initiation system is quite complex and is active at various proportions of TEMPO. Figure 4 shows the dependence of the rate coefficient (slope of the semilogarithmic anamorphoses) at constant concentration of the complex Al(iBu)₃:DPy and varied ratios of TEMPO to the complex. Polymerization occurs slowly even without TEMPO but it is strongly accelerated in the presence of two equivalents of TEMPO. Polymerization without added TEMPO proceeds with strong acceleration and the maximum rate is nearly the same as with 1 equivalent of TEMPO. Polymerization is nearly entirely inhibited by four equivalents of TEMPO which confirms a 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, probably, due to the termination process.

Aging of the initiating system is another important parameter, affecting kinetics and molecular weights. The aging time is defined as a time between addition of TEMPO to the Al(iBu)₃:DPy complex and addition of the initiating system to a monomer solution. The aging time "zero" is when TEMPO was added last to the mixture of monomer and the Al(iBu)₃:DPy complex. Figure 5 shows the effect of aging of the initiating system based on 1:1:2 composition (Al(iBu)₃:DPy:TEMPO) on the rate coefficients, at 20°C. Apparently, longer aging times decrease polymerization rates and lead to the deviation from the linearity in semilogarithmic plots. This is in contrast to the polymerization initiated by "fresh" systems in which termination is not observed even at longer times. This indicates that either the presence of the monomer and/or polymer reduces termination, or that the growing radicals are more stable than the initiating radicals.

Molecular Weights

As discussed in the preceding article, the preparation of well defined polymers by a radical polymerization is possible at sufficiently low stationary concentration of growing radicals, in order to reduce the rate of the bimolecular termination in comparison with 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. Straight lines passing through origin have been obtained. Molecular weight distribution stays very low, usually below $M_w/M_n < 1.2$

(Figure 7). The highest obtained molecular weights were $M_n \approx 30,000$. This limit is probably set not by termination, but rather by transfer and is typical for a radical process¹⁰.

Figure 8 shows the dependence of molecular weights on conversion at different TEMPO/ {Al(iBu)3:DPy} ratios. Molecular weights higher than expected for a living process have been observed at 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 contribution of transfer at this ratio.

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

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 the process. The complete formulation of the mechanism requires spectroscopic characterization of the active intermediates such as polarized or "free" radicals, structure of persistent dormant radicals, determination of the contribution of the solvent cage, dynamics of exchange, etc.

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'dipyridyl, 1,10-phenanthroline, N,N,N',N'-tetramethylethylenediamine^{11,12,13}. The Al coordination numbers (4 in complexes with monodentate and 5 in complexes with bidentate Lewis bases) have been established based on crioscopic molecular weight studies. Persistent radicals have been produced by a single electron transfer reaction of R₂AlH to dipyridyl (2,2'- or 4,4'-) or pyrazine¹⁶, 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} complexed with semiguinones¹⁹.

Complexes between aluminum halides, AlX₃, and stable radicals (e.g. TEMPO, di-tert-butylnitroxide) have been observed by EPR 20,21,22. Therefore, similar to transition metal compounds²³, 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 radical. 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 were not yet reported. Below, a tentative mechanistic proposal, involving the following steps is presented:

(i) Formation of the pentacoordinated stable complexes I between Al(iBu)₃ and DPy, at a molar ratio 1:1 (DPy is bound coordinatively to Al):



Our preliminary EPR studies indicate the presence of small amount of radicals already at this stage. The complex was used as the initiator in polymerization of vinyl acetate (at the ratio TEMPO/A1=0). After 48 hours, poly(vinyl acetate) was obtained (yield $\approx 80\%$); GPC indicates $M_n = 27,000 (M_n^T = 10,000)$, and a relatively narrow polydispersity, $M_W/M_n = 1.23$. Low overall rates, acceleration periods and higher than expected molecular weights indicate slow initiation and low proportion of radicals. Nevertheless, radicals are present in Al(iBu)3:DPy complex, even in the absence of alkali metals.

(ii) The irreversible attack of TEMPO on the pentacoordinated complex Al(iBu)3:DPy (I), leading to a relatively stable and delocalized radical (II):



TEMPO may also react with some short-lived radicals present at the stage (i) to form alkoxy amines 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:



This equilibrium might be in apparent contradiction with the stability of

TEMPO• and R• (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 can be hardly homolytically broken.

The proposed geometries of the high-coordinated structures (II or IV) are only tentative. For example, it is not yet known, whether (IV) has a trigonal bipyramid or square pyramid geometry, or if TEMPO is located at the apical or the equatorial position. In the hexacoordinated structures shown in eqs 5, 6, and 7 three substituents are connected via true covalent bonds, however, the fourth one (and DPy) are connected formally via coordinative type bonding.

Kinetic measurements indicate that the reactivity of the system with only one TEMPO as ligand (structure II) is low, but it dramatically increases with two TEMPO ligands (structure 2a):



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 provices pentacoordinated species with three TEMPO ligands and the return of the radical R• may be difficult due to steric effects.

The addition of the fourth equivalent inhibits polymerization entirely. 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 of any monomer. Therefore, the efficiency of the described 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.

In the preceding article, we proposed three approaches to "living" radical polymerization, based on:

- the homolytic cleavage of species with labile C-Z bond, to a growing radical C• and a scavenging radical Z•,

- the reversible reaction of the growing radical C• with a scavenger Z to produce a stabilized radical C-Z•,

- the degenerative transfer process between growing radicals C_n • and transfer agents C_m -Z.

According to the discussion above and the kinetic results, the studied system conforms best to the case 2. The reason for the unusual stability of the dormant radical (IVa) could be attributed both to a favored steric environment at aluminum atom, and to an enhanced electron delocalization over all organic substituents bonded or coordinated by aluminum.

The kinetic results indicate the 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• is reversibly cleaved homolytically from the dormant species C-Z•. It is reactive enough to initiate polymerization and subsequently to propagate:

$$C-Z \bullet \xleftarrow{k_i} C \bullet + Z \tag{7}$$

 $C_{n^{\bullet}} + M \xrightarrow{k_{\rho}} C_{n+1}$ (8)

If we can assume that the rate constants of elementary reactions such as propagation and bimolecular termination in this particular system are similar to those in a homogenous radical polymerization of vinyl acetate¹⁰, we may estimate the stationary concentration of growing radicals:

$$d\ln[M]/dt = k = k_p^{\bullet} [C^{\bullet}]_{st}$$
⁽⁹⁾

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

This low estimated stationary concentration of growing radicals prevents bimolecular termination and allows to prepare well-defined polymers. At present, we investigate systems with different ligands and activators which provide faster overall polymerization and, presumably, higher stationary concentration of the 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.

CONCLUSIONS

In this paper we report 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:Dpy 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/Dpy/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. Chains could be extended by new monomer addition and block copolymers have been prepared with styrene and methyl methacrylate²⁸. The reported results indicate that the rate of initiation is at least 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 a dynamic equilibriu..n 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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CAPTIONS FOR FIGURES

Fig. 1. Kinetics of Polymerization of Vinyl Acetate ($[M]_0=2.5 \text{ mol/L}$) at 60°C in C₆H₆ at variable concentration of the initiator.

Fig. 2. Dependence of the Rate Coefficient (k) on the Initiator Concentration in C_6H_6 at 20°C and 60°C.

Fig. 3. Effect of Temperature on Rate Coefficients in C_6H_6 at $[I]_0=0.3$. mol/L.

Fig. 4. Effect of the Ratio [TEMPO]/[Al] on Rate Coefficients in C₆H₆ at 60°C.

Fig. 5. Effect of Aging on Kinetics in C₆H₆ at 60°C.

Fig. 6. Effect of Conversion of Molecular Weights in C₆H₆ at 20°C and 60°C and Variable Concentration of the Initiator.

Fig. 7. Effect of Temperature and the Concentration of the Initiator on Polydispersities.

Fig. 8. Effect of the Ratio [TEMPO]/[Al] on Molecular Weights in C6H6 at 60°C.

Fig. 9. Effect of Aging on Molecular Weights in C₆H₆ at 60°C.



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Effect of Aging on Kinetics at 60 °C





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