

Investigation of Methyl Methacrylate and Vinyl Acetate Polymerization Promoted by $\text{Al}(\text{iBu})_3/2,2'$ -Bipyridine and $\text{Al}(\text{iBu})_3/2,2'$ -Bipyridine/TEMPO Complexes

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ABSTRACT: Results of methyl methacrylate (MMA) and vinyl acetate (VOAc) polymerization using the $\text{Al}(\text{iBu})_3/2,2'$ -bipyridine/TEMPO initiating system at room temperature failed to confirm the “living” radical mechanism reported earlier. Several species apparently propagate without control in a normal free radical process and only above a critical initiator concentration. No evidence was found for the penta- and hexacoordinated aluminum species previously suggested, but high conversion to an alkoxyamine was observed. Additionally, mixing $\text{Al}(\text{iBu})_3$ and BIPY promotes a variety of reactions involving alkyl and hydride transfers to the aromatic rings forming reduced BIPY products, along with a persistent organoaluminum radical. All these results illustrate that the process is considerably more complicated than postulated before. Conversely, at -78°C , a single active species excluding the participation of TEMPO has been put in evidence, displaying some “living” characteristics. Several experiments support its anionic nature, as previously suggested by Ikeda.

Introduction

The concept that stable free radicals, such as nitroxides, could be used as an efficient reversible terminating agent to control radical polymerization, without initiating new chains, was first introduced by the pioneering work of Solomon and Rizzardo.¹ These findings were renewed by Georges et al.,² who were able to prepare relatively high molecular weight (MW) polystyrene with a molecular weight distribution (MWD) lower than the theoretical limit of 1.5 ($M_w/M_n < 1.3$). These encouraging results from the Xerox research group were the beginning of a large number of publications concerning “living” free radical polymerization and copolymerization of styrene derivatives, dienes,³ and polar monomers, such as acrylates,⁴ mediated by stable nitroxides. A related approach has used cobalt(III) porphyrin alkyl compounds to polymerize acrylates,^{5,6} in a controlled way to predictable MW and narrow MWD. More recently, atom transfer radical polymerization of polar and nonpolar monomers initiated by alkyl and arylsulfonfyl halides in the presence of copper, ruthenium, and nickel catalysts has been proposed by several groups.^{7–9}

The first example of “living” polymerization of vinyl acetate (VOAc) was reported by one of the present authors (K.M.).^{10–12} Aluminum alkyls of the type $\text{R}_n\text{AlCl}_{3-n}$ complexed with 2,2'-bipyridine and stable nitroxide radicals (e.g., TEMPO) were used as initiating

systems for MMA and styrene as well as VOAc homo- and copolymerization. A persistent delocalized hexacoordinated aluminum radical was postulated as the dormant species in the tentative mechanism. The hexacoordinated aluminum radicals have rarely been reported before.¹³ However, tetracoordinated persistent aluminum and zinc radicals formed in the reaction of α -diimine-type ligands (e.g., 2,2'-bipyridine, 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene) with R_3Al or R_2Zn have been observed by ESR spectroscopy.^{14–16} An electron-transfer mechanism has been proposed with the overall reaction being transfer of one alkyl group or hydrogen atom from the metal to the ligand. A reduced α -diimine-ligand coordinated to the mono or dialkylmetal (major products) in addition to a persistent radical (minor product) were observed by NMR. Moreover, aluminum derivatives of semiquinones exist as pairs of persistent radicals and alkyl radicals. The alkyl radicals could initiate polymerization of vinyl monomers as shown by Davies et al.¹⁷ Pasynkiewicz and co-workers¹⁸ have shown that homolytic cleavage of the aluminum–oxygen bond of organoaluminum phenoxides occurs in the presence of oxygen, but rather than the butylated hydroxytoluene radical being produced, unidentified persistent aluminum-containing radicals were also formed.

Among the number of systems which provide “living” anionic polymerization of methacrylic monomers in the presence of aluminum derivatives in conjunction with a cocatalyst/co-initiator,^{19–21} Ikeda et al.²² suggested 20 years ago that polymerization of methacrylates in toluene at room temperature with R_3Al and Lewis base adduct (e.g., 2,2'-bipyridine, triphenylphosphine) proceeds according to an anionic coordinative mechanism. Korshun and Mazurek²³ reported that methacrylate

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Table 1. Effect of Temperature on the MMA Polymerization Initiated by TIBA/BIPY Complex (Molar Ratio: 1/1) in Toluene

entry	$[I]_0 \times 10^2$ (mol L ⁻¹)	M/I	time (h)	T (°C)	yield (%)	M_n^e (g/mol)	M_w/M_n	$f^{a,b}$	% S	% H	% I
1	8.4	29	1	room temperature	7	7400	1.47	0.027	72	27	1
			16		42	6600	1.45	0.18			
			113		80	6000	1.46	0.38			
2 ^b	8.5	58	1	room temperature	22	6900	1.53	0.18			
			24		26						
3	8.4	29	1.3	-23	100	37500	2.17	0.077	74	24	2
4	8.4	29	1.3	-45	100	57000	1.81	0.050	79	20	1
5	8.4	29	1	-78	100	125000	1.35	0.023	80	20	0
6 ^c	8.4	29	1	-78	94	155000	1.55	0.017			
7 ^d	8.4	29	4	-78	0						
8	2.4	88	1	-78	0						

^a $f = M_{n,th}/M_{n,exp}$; $M_{n,th} = M/I \times 100 \times \% \text{ conv}$; $M/I = M/Al$ (molar ratio). ^b Benzyl chloride (dried over CaH₂) was added in excess relative to aluminum 1 h after MMA addition. ^c TIBA and BIPY were aged 16 h at room temperature before MMA addition. ^d TIBA and BIPY were previously mixed at -78 °C before MMA addition. ^e Calculated from GPC using PSt standards for calibration.

monomers were polymerized within temperature range from +25 to -60 °C in the presence of R₃Al/BIPY/Cr(acac)₃ with M_n increasing linearly with conversion. "Long-lived" anionic active centers are invoked, and block copolymers were prepared. This system is similar to the ^tBu₃Al/2,2'-bipyridine/TEMPO (TIBA/BIPY/TEMPO) system if we consider the organic nitroxyl radical as being replaced by the inorganic Cr(III) (d³) radical.

The experimental and mechanistic inconsistencies prompted us to reinvestigate the MMA and VOAc polymerization promoted by ^tBu₃Al/2,2'-bipyridine (TIBA/BIPY) and TIBA/BIPY/TEMPO initiator systems in toluene within temperature range from -78 to +25 °C. To shed more light on the studied systems, we also carried out a detailed spectroscopic study of the reaction in the absence of monomers in an attempt to obtain a better characterized initiating system.

Experimental Section

Materials. MMA and VOAc from Aldrich were first distilled over CaH₂ and then stored under nitrogen at -20 °C. They then had TEA added until a persistent yellowish color was observed and were distilled under reduced pressure just prior to polymerization.

Toluene was purified by refluxing over sodium-benzophenone complex under dry nitrogen for several days and was freshly distilled from polystyryllithium. Benzene was first distilled from CaH₂ and then dried over metallic sodium mirror just prior to polymerization.

2,2'-Bipyridine (BIPY, 2,2'-dipyridyl) and 2,2,6,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were used as received from Aldrich. Triisobutylaluminum (TIBA) in toluene solution from Aldrich was used without further purification.

Polymerizations. The MMA and VOAc polymerizations were carried out under nitrogen atmosphere in a previously flamed glassware reactor. Monomers, solvents, and catalyst solutions were transferred by syringes and stainless steel capillaries.

To the toluene solution of BIPY was added the toluene TIBA solution, and the mixture was then stirred at room temperature for 1 to 10 min. A deep red color was noticed. The MMA-TEMPO mixture was then added, and the color was still observed.

Polymerization was stopped with acidified methanol, and the polymer was recovered by precipitation into cold heptane, kept in the freezer for several hours, filtered, and dried under vacuum at 60 °C overnight. Additional confirmation of negative experiments was provided by evaporation of some of the precipitation mixtures.

Characterizations. ¹H NMR spectra were recorded in CDCl₃ with a Bruker AM400 apparatus at 25 °C. ²⁷Al NMR

spectra were recorded in CDCl₃ with a Bruker AM300 apparatus at 25 °C. Size exclusion chromatography was performed in THF using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractometer detector. Columns were calibrated with polystyrene standards.

Results and Discussion

1. Study of the Initiating System ^tBu₃Al/2,2'-Bipyridine (TIBA/BIPY). (a) **Temperature Effect on the MMA Polymerization in Toluene.** The reaction product from mixing TIBA and BIPY at room temperature initiates polymerization of methyl methacrylate. As can be seen in Table 1, polymerizations carried out at room temperature were very similar to those described previously by Ikeda and co-workers.²² Approximately 80% yield was reached after 4 days, although increasing the monomer concentration resulted in 22% yield after 1 h ($[M]_0 = 4.9$ mol L⁻¹) instead of 7% within the same reaction time when $[M]_0 = 2.4$ mol L⁻¹. The activity strongly depends on the nature of the alkyl group of the aluminum compound as previously shown.²⁴ Even though the yield gradually increases over the relatively large time scale, the molecular weight *does not* increase, indicating that under these conditions this is not a controlled system. Nevertheless, the molecular weight distribution (MWD) remains below $M_w/M_n < 1.5$ and the initiator efficiency substantially improves with time, suggesting that the number of propagating species increases gradually during the course of polymerization.

When the temperature is reduced to below -23 °C, a quantitative yield is recorded within 1 h. Polydispersity first increases, e.g., $M_w/M_n = 2.17$ at -23 °C, and then decreases at -78 °C, e.g., $M_w/M_n = 1.35$ with a monomodal distribution (Figure 1). The initiator efficiency calculated relative to the aluminum atom is very low at -78 °C, e.g., $f = 0.023$ (reaction 5). The reaction mixture develops an intense deep red color immediately upon mixing; to be active, that solution has to be kept 5–10 min at room temperature, but further aging time has little influence on the subsequent polymerization (see entry 6, Table 1). In contrast, when the components are mixed at -78 °C, a yellow color is observed with no MMA polymerization occurring after 1 h while the reaction mixture remains yellow (entry 7).

At room temperature, cyclization involving the anti-penultimate ester group of the growing chain is one of the main termination processes in anionic MMA poly-

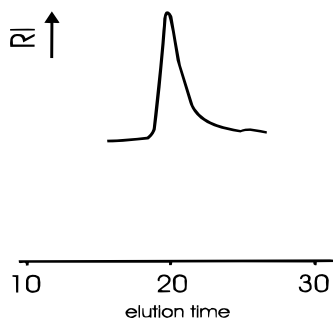


Figure 1. MWD curve of a poly(MMA) prepared with $t\text{-Bu}_3\text{Al}$ /2,2'-bipyridine at $-78\text{ }^\circ\text{C}$. $[t\text{-Bu}_3\text{Al}]_0 = [2,2'\text{-bipyridine}]_0 = 8.4 \times 10^{-2} \text{ mol L}^{-1}$, $[\text{MMA}]_0 = 2.35 \text{ mol L}^{-1}$, $M_{n,\text{exp}} = 274\,000 \text{ g mol}^{-1}$, $M_w/M_n = 1.3$, and $f = 0.009$.

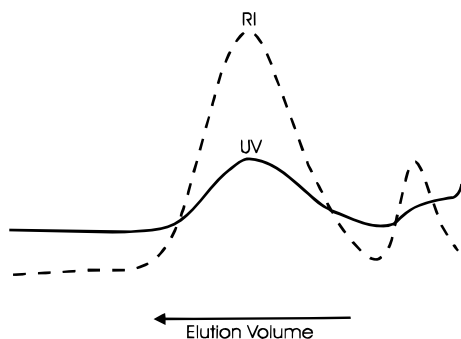


Figure 2. Comparison of SEC MWD curves obtained by UV and RI detection of poly(MMA) prepared with $t\text{-Bu}_3\text{Al}$ /2,2'-bipyridine at room temperature. $[t\text{-Bu}_3\text{Al}]_0 = [2,2'\text{-bipyridine}]_0 = 8.5 \times 10^{-2} \text{ mol L}^{-1}$, $[\text{MMA}]_0 = 4.93 \text{ mol L}^{-1}$, $M_{n,\text{exp}} = 6900 \text{ g mol}^{-1}$, $M_w/M_n = 1.5$, and $f = 0.18$.

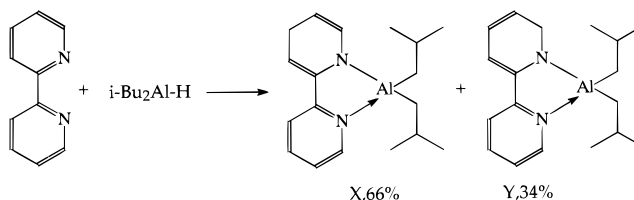
merization. Therefore, a higher activity is recorded when polymerizations are performed below $-23\text{ }^\circ\text{C}$ because propagation is favored against termination reactions. Moreover, an equilibrium existing between different ionic species could be shifted to the more reactive one when the temperature decreases,^{25,26} which is the only kind of propagation center resulting in a low polydispersity. Furthermore, aggregation between TIBA/BIPY complexes is expected to be modified by the added MMA. The very low initiator efficiency might thus be explained by a slow initiation with respect to propagation.

As previously reported,²⁴ the microstructure of the polymer shows some stereoselectivity with $rr = 72\%$, slightly higher than PMMA from a true radical initiation at room temperature. To clarify the mechanism, a labeling experiment using dry benzyl chloride was carried out at room temperature on propagating PMMA. After addition of the end-capping agent, the reaction terminates (entry 2 in Table 1) while an excellent overlap of both the UV at 254 nm and RI signals is observed by SEC, thus indicating that nucleophilic substitution occurred (Figure 2).

In the studied system, a high initiator concentration is required; otherwise, traces of water in the reaction medium are responsible for the absence of polymerization (entry 8, Table 1). Around 3% of active species are generated when $[\text{I}]_0 = 2.4 \times 10^{-2} \text{ mol L}^{-1}$; thus as little as ca. 10 ppm of water is enough to prevent polymerization.

For purposes of comparison, a coordinative anionic mechanism in which Et_2Al^+ acts as a counteranion was suggested for the MMA polymerization promoted by $\text{PPh}_3/\text{AlR}_3$ in toluene at low temperature.²⁷ PMMA with

Scheme 1. Reaction of Diisobutylaluminum Hydride with Bipyridine



molecular characteristics and stereochemistry similar to those obtained in the presence of the BIPY/TIBA initiating system has been synthesized.

(b) Investigation of the Nature of the Lewis Base–Aluminum Alkyl Adduct. To attempt to understand the polymerization mechanism, the interaction of aluminum alkyls with coordinating Lewis bases was examined using different spectroscopic techniques. Reacting of TIBA and BIPY results in a complicated product mixture containing diamagnetic species and broad peaks associated with paramagnetism as observed by NMR.

^1H NMR Study. Dissociation of $t\text{-Bu}_3\text{Al}$ into isobutene and $t\text{-Bu}_2\text{Al-H}$ is well documented and is indeed the basis for the synthesis of a wide range of n -alkyl aluminum compounds by reaction of Bu_3Al and the appropriate alkene.²⁸ For purpose of simplification in assigning some of the products of this reaction we replaced $t\text{-Bu}_3\text{Al}$ with $t\text{-Bu}_2\text{Al-H}$. This reaction indeed produces a simplified ^1H NMR spectrum. Two major products are observed with reduction of one of the aromatic rings with addition of Al-H both para (X) and ortho (Y), both fully assigned by ^1H and ^{13}C NMR (Scheme 1 and Appendices 1–4, Supporting Information). The products thus contain three normal covalent bonds to aluminum and a fourth one through a two electron donation from the aromatic pyridyl nitrogen.

Reduction of the aromatic ring also occurs when bipyridine is replaced with 4,4'-dimethyl-2,2'-bipyridine. In this case the ratio of the products is altered such that 75% of the product is reduced ortho and only 25% is para. When phenanthroline is used in place of bipyridine, equal amounts of the para and ortho products are observed. With phenanthroline all 16 multiplets between 3.8 and 7.7 ppm are individually resolved and assigned by a combination of decoupling and NOE experiments (Figure 3 and Appendix 5, Supporting Information).

On leaving the above reaction mixture, in the apparent absence of air, for 2 weeks (in a Young's tap NMR tube) further reaction is observed with both bipyridine and 4,4'-dimethyl-2,2'-bipyridine to give mixtures of X and Z (wherein one ring is reduced, leaving only one double bond and a hydroxy substituent on the meta position relative to nitrogen) (Scheme 2; $\text{R} = \text{Me}, \text{H}$).

Of particular note are the multiplets from the vinyl protons around 3.8–5.5 ppm which are due to non-aromatic vinyl protons. Reexamination of the ^1H NMR spectra from the reaction between $t\text{-Bu}_3\text{Al}$ and bipyridine reveals that the major diamagnetic products are of both X and Y accompanied by the evolution of isobutene, presumably proceeding via an aluminum hydride. In addition to X and Y a minor product A is observed, from the ortho addition of Al-t-Bu_3 to one of the aryl rings (Scheme 3).

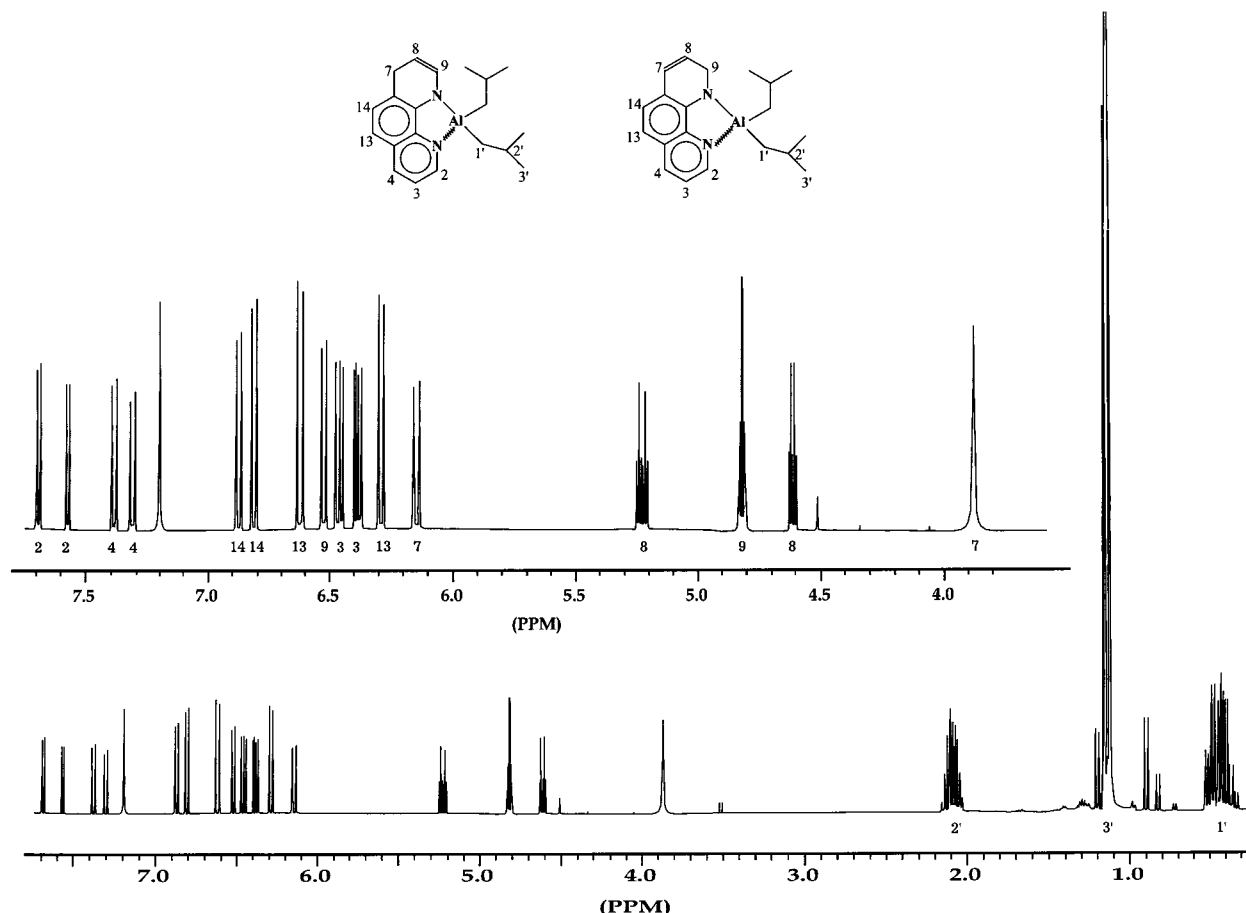
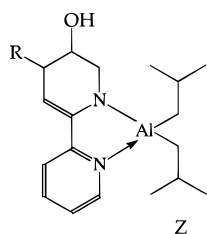
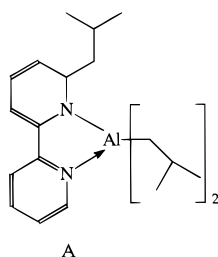


Figure 3. 400 MHz ^1H NMR spectrum of the reaction mixture of phenanthroline and diisobutyl aluminumhydride in benzene at ambient temperature.

Scheme 2. Oxidation Product from the Reaction of Reduced Bipyridine Diisobutylaluminum Complex with Air (Trace)



Scheme 3. Additional Product Observed from the Reaction of Triisobutylaluminum with Bipyridine, Involving Addition of Aluminum Alkyl across the Double Bond



Thus reaction of $^i\text{Bu}_3\text{Al}$ with bipyridine at room temperature surprisingly results in a complex mixture of products in which a range of ring reduction products predominate. All assigned products are tetracoordinate and not a Lewis acid–Lewis base pentacoordinated complex as previously reported.^{10,11,22} When $^i\text{Bu}_2\text{Al}-\text{D}$ is used, the deuterium is found in both the para and

Table 2. ^{27}Al NMR Parameters of the Components of the Initiating System TIBA/BIPY/TEMPO^a

compound	d (ppm)	$\nu_{1/2}$ (Hz) ^b	CN
TIBA	280	5600	3
	154	5200	4
TIBA/BIPY	149	92	4
TIBA/BIPY/TEMPO (0.5:1:2)	no change	no change	no change

^a Hexane, 1 mol L⁻¹, 20 °C, Al(acac)₃ as an external standard.

^b Peak width at half-height.

ortho positions indicating that both H and isobutyl radicals are formed during the reaction. The product mixture does vary with time and is also susceptible to reaction with trace oxygen and moisture.

^{27}Al NMR Study. ^{27}Al NMR spectroscopy was used to provide information about the coordination number and symmetry of aluminum complexes. Below are shown the results of ^{27}Al NMR measurements recorded for TIBA and complexes with different stoichiometries (Table 2).

^{27}Al NMR spectra are shown in Figure 4. The spectra of aluminum compounds, i.e., the chemical shift and the width at half-height ($\nu_{1/2}$) depend primarily on the coordination number (CN) of aluminum.²⁹ In the spectrum of TIBA a monomeric species and species with CN = 4 can be observed. The species with CN = 4 are probably not dimers, because Al(^iBu)₃ does not dimerize in hexane solution.²⁹ Most likely, it is an aluminoxane Al_nO_m(^iBu)_{3x}, a hydrolysis product.

The spectrum changes dramatically upon addition of BIPY: only one upfield narrow signal (≈ 100 Hz) is

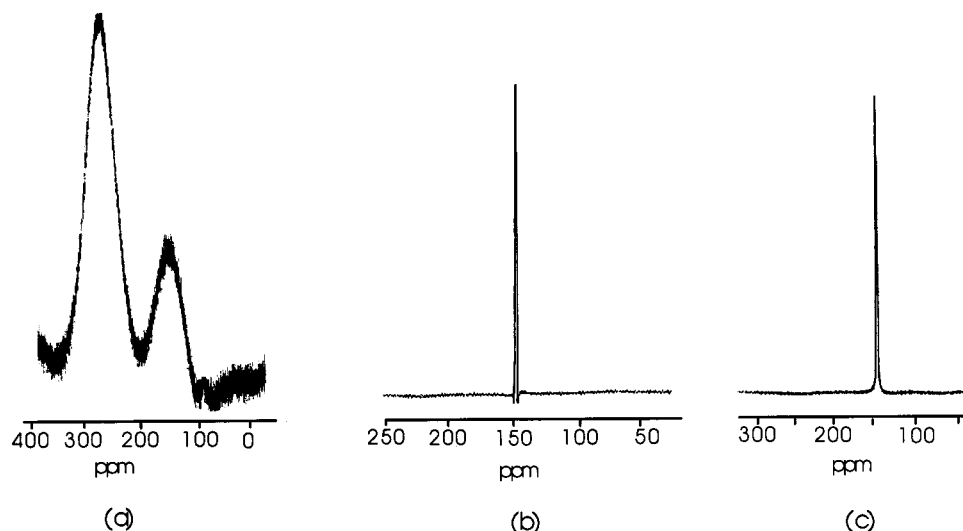


Figure 4. ^{27}Al NMR spectra: (a) $(t\text{Bu})_3\text{Al}$; (b) $(t\text{Bu})_3\text{Al} + \text{BIPY}$; (c) $(t\text{Bu})_3\text{Al} + \text{BIPY} + \text{TEMPO}$ (0.5/1/2). All spectra were recorded in hexane, 1 mol L^{-1} , at 20°C , with $\text{Al}(\text{acac})_3$ as an external standard. The glass signal from the NMR tube was subtracted from each spectrum.

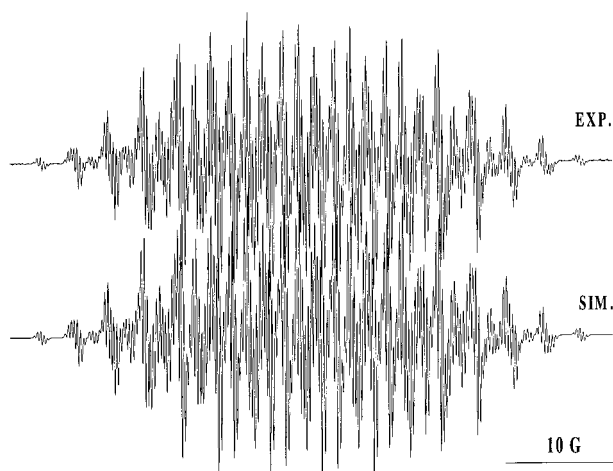


Figure 5. Experimental (Exp.) and Simulated (Sim.) ESR spectra of 2,2'-dipyridyl/ $\text{Al}(t\text{Bu})_2$.

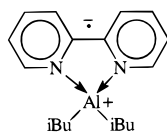


Figure 6. Possible structure of the radical complex between BIPY and TIBA.

observed (Figure 4b). This suggests that both species react with BIPY to form a tetracoordinated complex (i.e., $\text{Al}/\text{reduced BIPY}$; see above). No pentacoordinated complex around 50 ppm was observed, indicating that the tetracoordinated species was predominantly formed in this reaction (the unusual narrowness of the signal might also indicate a paramagnetic nature of the complexes, such as a radical anion shown in Figure 6). The addition of TEMPO to the reaction mixture results in no noticeable changes in the ^{27}Al NMR spectrum (Figure 4c).

ESR Study. The reaction also produces a persistent radical coupled to aluminum which remains ESR active over several weeks when air is excluded. The identification of the species was aided by the strong interaction between the ^{27}Al nucleus ($I = 5/2$; isotopic abundance 100%) and the unpaired electron.

Table 3. ESR Parameters of Paramagnetic BIPY/AlR_2 Species in Toluene at Room Temperature (Coupling Constants in mT)

AlR_3	$\text{H}-\text{Al}(t\text{Bu})_2$ (ref 30)	$\text{Al}(t\text{Bu})_3$ (obtd values)
g		2.0031
a_N	0.304	0.305
a_{H3}	0.028	0.029
a_{H4}	0.263	0.260
a_{H5}	0.304	0.306
a_{H6}	0.028	0.024
a_{Al}	0.437	0.437

The ESR spectrum of the $\text{BIPY}(\text{AlR}_2)^\circ$ is shown in Figure 5 and the spectroscopic parameters are compared with those of the same persistent radical produced from the reaction between $t\text{Bu}_2\text{Al}-\text{H}$ and BIPY³⁰ in Table 3. The ESR spectrum resembles closely the spectrum previously reported,¹¹ which was obtained after mixing TIBA with BIPY at room temperature in benzene solution. However, the resolution is now much improved due to lower concentration of the reagents and enables full assignment of the ESR signals.

The reactions between BIPY and TIBA were conducted in THF, benzene, or toluene; the formation of the radical is not solvent dependent; as would be expected for a free uncharged radical. This is in accord with Kaim's finding.³⁰ Moreover, after the formation of the radical at room temperature, the ESR spectrum remains almost unaffected by a temperature decrease down to -78°C .

At room temperature, the ease of formation of the radical represented in Figure 6 may be explained by its high persistency. However, the intensely colored radical is not formed when reagents are mixed together at -78°C , and no polymerization occurred after monomer addition. Reaction of aliphatic diimine and Et_3Al has been reported to initially form a complex with monodentate bonding mode via one N-donor site of the ligand in the s-trans configuration,¹⁵ which might explain this phenomenon at low temperature. When a solution of the 1/1 complex is warmed, the reaction involving alkyl and/or hydride transfer to the ligand skeleton together with formation of the organometallic radical arises, and MMA polymerization can take place.

Table 4. Vinyl Acetate (VOAc) Polymerization in Toluene Solution Initiated by TIBA/BIPY/TEMPO (Molar Ratio = 1/1/2)

[VOAc]/[Al] ^a	T (°C)	time (h)	yield (%)	M _{n,exp} (g/mol)
50 ^d	60	72	trace	122
50 ^d	60	72	trace	491
50 ^d	30	24	trace	605
50 ^d	30	24	trace	566
30 ^d	30	24	trace	483
10 ^d	30	24	trace	156
100 ^e	60	7	10	401
100 ^e	60	23	100	5500
100 ^e	60	72	27	6800
100 ^{b,e}	60	32	30	1300
100 ^e	25	24	79	19000
120 ^{c,d}	60	24	trace	

^a Molar ratio. ^b Phenantroline used instead of BIPY. ^c Benzene was used as solvent; TEMPO was purified by sublimation before use. ^d Experiments performed at U.Lg and U. W. C., under high purity conditions. ^e Experiments performed at C. M. U., not excluding trace O₂ and H₂O.

When MMA is introduced into the ESR tubes under nitrogen atmosphere at a range of temperatures, an immediate disappearance of the ESR signal along with a fast polymerization at -78°C takes place.

This observation suggests that the polymerization may originate from the persistent organometallic radical. However, the persistent radical is not able to initiate the polymerization by itself because of its low reactivity. Therefore, an electron transfer from the paramagnetic species to the monomer followed by recombination of the MMA anion-radical into the dianion associated with Al^+Bu_2 as counteraction might further induce the polymerization. Another plausible explanation could be that the 2,2'-bipyridine anion-radical is sufficiently nucleophilic to promote polymerization. Accordingly, it is well-known that such anion-radicals tend to form tight ion pairs with alkali-metal cations.³¹ Further studies are currently in progress in our laboratories to identify unambiguously the different species involved in the initiation mechanism.

The products characterized by NMR and ESR spectroscopy imply that the tentative mechanism previously proposed¹⁰ did not accurately describe all of the reactions occurring in solution between 2,2'-bipyridine and Bu_3Al and that the predominant aluminum species are tetracoordinated and not penta- or hexacoordinated. The tetracoordinated species may include those outlined in Schemes 1 and 2 as well as a paramagnetic complex (Figure 6). Furthermore, in their mechanistic considerations Ikeda et al.²² did not take into account the involvement of the persistent organometallic radical $\text{BIPY}(\text{Bu}_2\text{Al})^\circ$ which may play a significant role in the initiation step.

2. Study of the Initiating System $\text{Bu}_3\text{Al}/2,2'$ -Bipyridine/TEMPO (TIBA/BIPY/TEMPO). It has been previously proposed that addition of TEMPO to the bicomponent system TIBA/BIPY improves the control of polymerization of MMA and VOAc wherein the growing macroradical recombines reversibly with the aluminum complex, thus generating a persistent hexacoordinated aluminum radical as a dormant species.

(a) Vinyl Acetate (VOAc) Polymerization. Polymerization experiments were carried out under conditions similar to employed before ($[\text{VOAc}]/[\text{Al}] = 10/120$ molar ratio with a molar ratio TIBA/BIPY/TEMPO of 1/1/2 at 60°C). In contrast with the previous reports, results summarized in Table 4 lead to irreproducible

and usually very low polymer formation. A number of attempts under high purity conditions, and including variation of temperature, $[\text{VOAc}]/[\text{Al}]$ molar ratio, addition order, aging process, alkyl group and N-donor ligand structure (and even the source of monomer) all led to the same negative results. Finally, it has been recently reported³² that polymerization kinetics and structures of the obtained products are very sensitive to minute amounts of impurities such as water and oxygen which may lead to the formation of alumoxanes or aluminum peroxides responsible for a noncontrolled polymerization.

(b) Methyl Methacrylate (MMA) Polymerization. Changing the monomer from VOAc to MMA resulted in polymerization (Table 5). Detailed investigation of this reaction showed that the mechanism is not "living". Broad and even multimodal molecular weight distributions are obtained, and reinitiation on addition of a second aliquot of monomer is not observed. Furthermore, conversion strongly depends on the initiator concentration (assuming an aluminum-based initiator), leading to almost quantitative yield at concentrations above ca. $6.7 \times 10^{-2} \text{ mol L}^{-1}$ (or a monomer to aluminum molar ratio lower than 30) after 1 h polymerization time at room temperature (entry 3 in Table 5).

When conversion is plotted against initiator concentration while monomer concentration and temperature are kept constant, a straight line is recorded with a correlation coefficient close to unity (ca. 0.995), in Figure 7. High initiator concentration seems to be necessary in order to obtain a quantitative polymer yield, suggesting a considerable amount of termination reactions. Moreover, the multimodal molecular weight distribution observed indicates the presence of more than one active propagating species. It is important to notice the bicomponent systems TIBA/BIPY and TIBA/TEMPO may also act as initiators for MMA polymerization at room temperature. Indeed TIBA/TEMPO in a 1/2 molar ratio results in an almost quantitative yield after 1 h with a bimodal MWD, i.e., $M_{n,\text{exp}} = 41\,600 \text{ g/mol}$ and $M_w/M_n = 2.7$, while TIBA/BIPY (molar ratio = 1) provides less than 10% yield under the same reaction conditions.

All of these observations are indicative of normal free radical polymerization not fulfilling the characteristics of a "living"/controlled polymerization of MMA at room temperature. Conversely, some features of "living" systems were observed when MMA polymerization was promoted by the tricomponent system (entries 5 and 6 in Table 5) at a temperature lower than -78°C . Quantitative yields were still obtained within 1 h with monomodal MWD (Figure 8), indicating only one propagating species. Nevertheless, initiator efficiency based on aluminum containing species is very low, e.g., $f = 0.01$. The PMMA syndiotactic content at this temperature is 81%, typical of an anionic process.

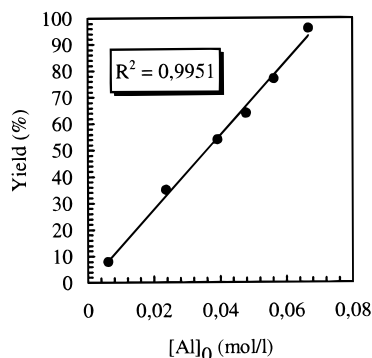
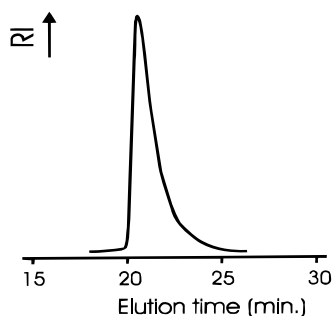
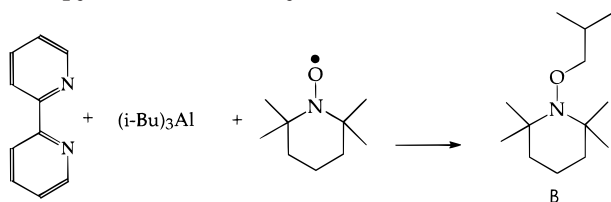
Since MWD, initiator efficiency and stereochemistry of the obtained PMMA are quite similar to those prepared with the TIBA/BIPY system at -78°C , it seems reasonable to admit that the TIBA/BIPY complex is the only one responsible for MMA polymerization at low temperature with this initiating system; i.e., TEMPO is just an inert compound at this temperature.

(c) Investigation of the Reaction Products Related to the Tricomponent System TIBA/BIPY/TEMPO. ^1H NMR Study. When 2 equiv of TEMPO is added to a hydrocarbon solution of Bu_3Al and bipyridine (molar ratio = 1:1) the major product is B

Table 5. Effect of Temperature and Initiator Concentration on the MMA Polymerization in Toluene Initiated by TIBA/BIPY/TEMPO (Molar Ratio = 1/1/2)^e

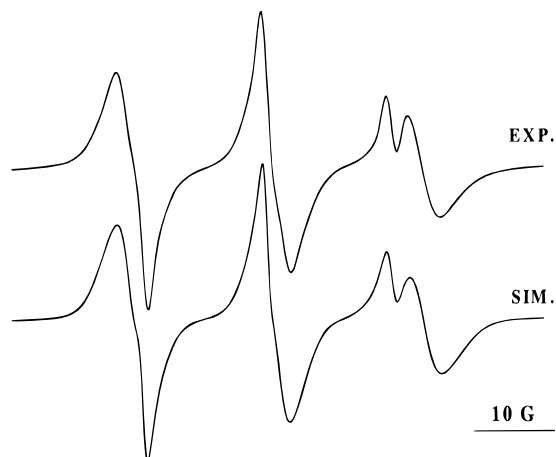
entry	[I] ₀ × 10 ² (mol L ⁻¹)	M/I ^a	T (°C)	yield (%)	M _n ^b (g/mol)	M _w /M _n	"f" ^c	% S	% H	% I
1	0.73	262	room temp	32	65 700	5.9 (m)				
2	2.36	84	room temp	35	171 800	3 (m)				
3	6.67	29	room temp	96	40 000	4.9 (m)		67	29	4
4	8.40	29	-15	91	54 400	4.9 (m)		65	31	5
5	8.40	29	-78	92	238 000	1.2	0.011	81	18	1
6 ^d	5.90	33	< -78	90	71 500	1.1	0.041			

^a Molar ratio. ^b Calculated from GPC using PSt standards for calibration. ^c $f = M_{n,th}/M_{n,exp}$; $M_{n,th} = M/I \times 100 \times \% \text{ conv} = M/Al \times 100 \times \% \text{ conv}$. ^d MMA was distilled under vacuum from TEA over TIBA/BIPY complex in toluene. ^e Polymerization time = 1 h; m = multimodal.

**Figure 7.** Dependence of the conversion versus initiator concentration for selected MMA polymerizations carried out in toluene at room temperature with the tricomponent system ^tBu₃Al/2,2'-bipyridine/TEMPO (molar ratio = 1/1/2). [MMA]₀ = 1.95 mol L⁻¹, and [^tBu₃Al]₀ = 0.62–6.67 × 10⁻² mol L⁻¹.**Figure 8.** MWD curve of a poly(MMA) prepared with ^tBu₃Al/2,2'-bipyridine/TEMPO (molar ratio = 1/1/2) at -78 °C. [^tBu₃Al]₀ = 8.4 × 10⁻² mol L⁻¹, [MMA]₀ = 2.4 mol L⁻¹, M_{n,exp} = 238 000 g mol⁻¹, M_w/M_n = 1.2, and "f" = 0.011.**Scheme 4. Main Product from the Reaction between Dipyrindine, Triisobutylaluminum, and TEMPO**

(Scheme 4) with minor dialkyl recombination products. No aluminum alkyl is visible in the NMR spectrum, indicating that all of the alkyl groups have reacted (Appendix 6, Supporting Information). Note that there is little evidence for any of the reduced products observed in the absence of TEMPO, as described above, and bipyridine is present in the spectrum. Similar results are observed when ^tBu₃Al is replaced by Et₃Al in the reaction.

The reaction of triisobutyl aluminum alkyl with bipyridine results in the reduction of bipyridine. This

**Figure 9.** Experimental (Exp.) and Simulated (Sim.) ESR spectra of a Al/TEMPO complex and TEMPO mixture.

complex promotes evolution of alkyl radicals which combine with TEMPO to give alkoxyamines in almost quantitative yield. Alkoxyamines have already been reported by Solomon et al.¹ to be effective in living radical polymerization of acrylics and styrene. Our results suggest that the combination of TIBA/BIPY/TEMPO produces in situ a system similar to that previously reported.

ESR Study. The addition of TIBA to BIPY results in a deep red solution. On adding this solution to TEMPO, the mixture changes color within seconds to orange-brown. The typical ESR signal of the nitroxyl radical completely disappeared in few minutes at room temperature confirming the formation of an alkoxyamine. These data further indicate that the expected hyper-valent persistent Al-centered radical (dormant species), which should be present in relatively large amounts in the formerly proposed mechanism, is not formed. We were unable to detect any paramagnetic species showing hyperfine structure by ²⁷Al even at low temperatures. However, the mixture of TEMPO and BIPY/TIBA complex at -78 °C consists of a superposition of two overlapping spectra from Al/TEMPO complex ($a_N = 18.54$ G; 90%) and free nitroxide ($a_N = 15.77$ G; 10%) as confirmed by computer simulation (Figure 9). Molecular complexes between some group III and IV Lewis acids and aliphatic nitroxides which behave as Lewis bases were previously reported.^{33,34} Addition of a stronger Lewis base such as MMA displaces the TEMPO giving an ESR signal of the uncomplexed nitroxyl ($a_N = 15.78$ G; $g = 2.00616$) (Figure 10). Furthermore, the MMA polymerization is not inhibited by the presence of nitroxyl as shown by the constant intensity of the ESR signal during the whole course of the reactions. Even though, the rate of radical trapping (k deactivation) is still very fast at -78 °C, i.e., 4.9×10^8 mol⁻¹ L

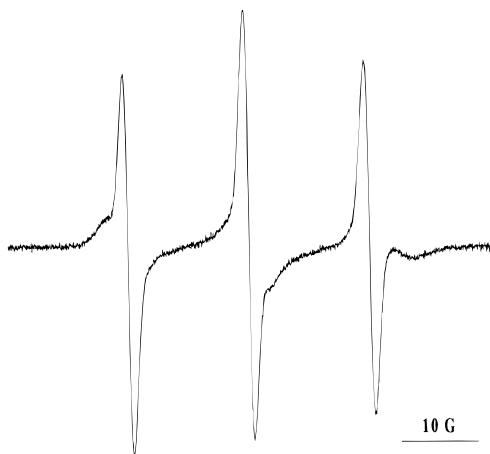


Figure 10. ESR spectrum of TEMPO.

s^{-1} as calculated from the relationship proposed by Bowry and al.³⁵

General Discussion

The results of polymerization of MMA or VOAc with the $\text{Al}(\text{tBu}_3)/2,2'$ -bipyridine/TEMPO system at room temperature do not confirm the "living" radical mechanism proposed earlier.^{10,11} Several species likely propagate at ambient temperature, and a critical initiator concentration is necessary to achieve quantitative conversion of the monomer. When TIBA and BIPY are mixed, a variety of reactions involving alkyl and hydride transfer to the dipyridyl ring, thus forming reduced BIPY products along with a persistent organoaluminum radical, illustrate that the process is considerably more complicated than previously postulated. NMR and ESR studies do not provide evidence for a penta- or hexa-coordinated aluminum species but indicate high conversion to an alkoxyamine. It is plausible that impurities such as O_2 and H_2O might affect the course of the reaction and lead to the formation of aluminum peroxides and/or aluminoxanes, which may activate the dormant alkoxyamine or just generate free radicals by themselves,³⁶ all resulting in a polymerization process difficult to reproduce. Meanwhile VOAc "living" radical polymerization has been achieved by using degenerative iodine transfer.³⁷

On the other hand, at -78°C we have put in evidence a single active species related to the $\text{Al}(\text{tBu}_3)/2,2'$ -bipyridine initiating system initially proposed by Ikeda and displaying some "living" character. The mechanism involved, excluding participation of TEMPO, is most probably an anionic one as shown by the influence of temperature, by the PMMA end-capping in the presence of benzyl chloride, and to some extent by the relatively high syndiotactic content. We are currently further investigating the different species involved in those reactions.

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Supporting Information Available: Tables of ^1H NMR and ^{13}C NMR spectroscopic data (Appendices 1–6) for the products resulting from the reaction of diisobutylaluminum hydride with bipyridine, phenanthroline, and bipyridine in the

presence of TEMPO (6 pages). Ordering and Internet access information is given on any current masthead page.

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