

Is FeEt₂(2,2'-dipyridyl)₂ a Ziegler Catalyst for Polymerization of the Polar Monomer Acrylonitrile?

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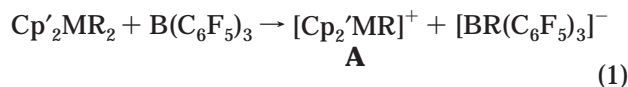
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Received January 14, 2004

This paper describes a reinvestigation into the putative role of a Ziegler process during polymerization of acrylonitrile by the compound FeEt₂(2,2'-dipyridyl)₂. For this very efficient polymerization initiator, acrylonitrile coordination is reported to be a precondition for polymerization, seemingly more compatible with a Ziegler than with a conventional radical process. Consistent with the previous observations, we do indeed find evidence for a sequence of events in which acrylonitrile displaces a dipy ligand of FeEt₂(dipy)₂, coordinating via the C=C bond in η²-fashion rather than via the nitrogen. Subsequent steps involve β-hydrogen elimination from one of the ethyl groups to give a hydrido-ethylene-ethyl intermediate, followed by concomitant reductive elimination of ethane and hydride migration to the acrylonitrile to form a 2-cyanoethyliron compound. The latter then undergoes iron–carbon bond homolysis, the resulting cyanoethyl radical initiating a conventional but possibly living radical chain polymerization process. Investigated as possible ethylene polymerization catalysts are FeEt₂(dipy)₂ “activated” with B(C₆F₅)₃ and [Ph₃C][B(C₆F₅)₄], and both FeCl₂(dipy)₂ and FeCl₂(dmby) (dmby = 6,6'-dimethyl-2,2'-dipyridyl) activated with AlMe₃, AlEt₃, and MAO. Some of these related, potentially catalytic systems polymerize acrylonitrile, but none initiate ethylene polymerization, probably ruling out the possibility of a Ziegler process by this system for any monomer.

Introduction

There have in recent years been numerous investigations into the use of group 4 organometallic complexes as homogeneous catalysts for the polymerization of olefins via a Ziegler (coordination) mechanism.¹ The most studied and successful of the precursor compounds have been metallocenes of the type Cp'₂MR₂ (M = Ti, Zr, Hf; R = alkyl; Cp' = substituted cyclopentadienyl), which undergo alkyl carbanion abstraction on reaction with Lewis acid cocatalysts such as the borane B(C₆F₅)₃ (eq 1) to give the formally 14-electron, cationic species [Cp'₂MR]⁺ (A), which are believed to be the actual catalysts.



Similar species are apparently formed on treating, for example, metallocene dihalides with methylalumoxane (MAO), and commercially viable polyolefin processes are based on use of this cocatalyst.¹

In contrast, early transition metal metallocene catalyst systems have not normally been found useful for either the homopolymerization of polar olefins such as acrylates, methacrylates, vinyl halides, and vinylamines or the copolymerization of these monomers with, for example, ethylene or propylene.² In general, it seems that the Lewis base sites in all such candidate monomers coordinate preferentially to the highly Lewis acidic metal ions, thus precluding the migratory insertion processes necessary for Ziegler polymerization. Where polymerization of, for example, methyl methacrylate has been found to be induced by cationic metallocene species, the mechanism has involved not a Ziegler process but a group transfer mechanism.³

While homopolymers of many polar monomers may, of course, be readily prepared via radical and ionic processes,³ the resulting polymeric products are generally atactic in nature. Thus the design of Ziegler catalysts that might through their chirality induce the formation of new polymers exhibiting significant tacticity is an obviously desirable goal. Similarly, since ethylene and propylene are not readily polymerized via radical or ionic processes, there are as yet no generally satisfactory routes to the formation of, for example,

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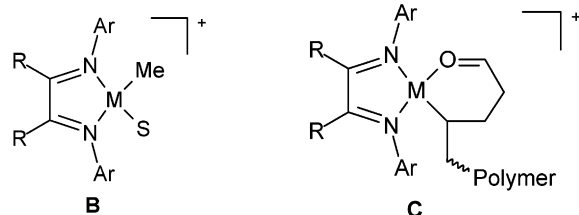
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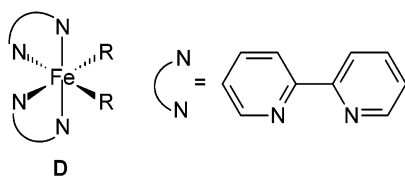
ethylene- or propylene-polar monomer copolymers. Given the properties that polyolefins functionalized in this way are expected to exhibit,^{2,4} it is not surprising that research in this area has been intense.²

One potential solution to the problem of coordination of the "wrong end" of a polar monomer is to utilize poorly electrophilic metal complexes, and thus considerable research has been carried out with late metal catalysts, especially of palladium.⁵ Cationic α -diimine complexes of the type $[\text{PdMe}(\text{S})(\alpha\text{-diimine})]^+$ (**B**, S = solvent), which are excellent catalysts for the polymerization of ethylene, do indeed catalyze the copolymerization of ethylene with acrylates and methacrylates.⁵ However the efficacies of such catalyst systems are affected adversely by the proclivity of incorporated ester-containing units to chelate as in **C**, and the polymeric products tend to have the ester moieties only at the polymer ends.



Attempts to use similar catalysts to polymerize vinyl chloride also resulted in an initial 1,2-vinyl chloride insertion into the Pd-methyl bond, but the thus formed Pd- CH_2CHClMe species undergoes facile β -chlorine migration to the metal to form propylene and catalytically inactive chloropalladium compounds.⁶

Given this background, we were intrigued by reports by Yamamoto et al. from the 1970s⁷ that several polar olefins (acrylonitrile, methacrylonitrile, acrolein, methyl acrylate, methyl vinyl ketone) are polymerized by *inter alia* compounds of the type *cis*- $\text{FeR}_2(\text{dipy})_2$ (**D**: R = Me, Et, n-Pr; dipy = 2,2'-dipyridyl).⁸

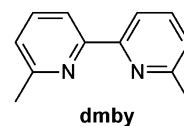


These polymerization reactions involved no induction period and gave at least one copolymer (acrylonitrile-methyl methacrylate) of composition said to be very different from that formed via typical radical and anionic processes. This information, coupled with ob-

servations that styrene was not polymerized by $\text{FeEt}_2(\text{dipy})_2$ and that thermal decomposition of this ethyl-iron compound gave a species of reduced catalytic activity, was taken as evidence that conventional free radical and anionic processes were not involved.^{7,8}

Interestingly, however, polymerization in strongly coordinating solvents or in the presence of free dipyridyl resulted in reduced rates and reduced molecular weights. These findings, in addition to a kinetics study, led to the conclusion that the polymerization reactions involved Ziegler processes in which a dipyridyl ligand dissociated one or both nitrogen donor atoms to generate a vacant site to which an olefin could coordinate and undergo migratory insertion.^{7,8}

Yamamoto's research was reported in an era when polymerization of polar monomers had not yet begun to be viewed with widespread interest, and the conclusions appear not to have been widely noted. In addition this research was carried out before the importance of cationic initiators of types such as **A** and **B** was generally recognized, and indeed before the role of MAO as a cocatalyst had been discovered.⁹ We have therefore reinvestigated the abilities of the compounds $\text{FeR}_2(\text{dipy})_2$ (R = Me, Et) to polymerize acrylonitrile, and also ethylene and styrene. In addition, we have also carried out related studies of the possible catalytic properties of the cationic species $[\text{FeEt}(\text{dipy})_2]^+$, formed on treating $\text{FeEt}_2(\text{dipy})_2$ with the well-known^{1,2} carbanion abstractors $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, and of the species formed on treating $\text{FeCl}_2(\text{dipy})_2$ with AlMe_3 , AlEt_3 , and MAO. With a view to possibly stacking the deck in favor of a Ziegler process by decreasing the number of ancillary ligands on the metal, we have also prepared, characterized, and investigated for catalytic activity the new tetrahedral compound $\text{FeCl}_2(\text{dmby})$ (dmby = 6,6'-dimethyl-2,2'-dipyridyl).



We present here our results, which unfortunately seem best interpreted in terms of non-Ziegler polymerization processes by these iron compounds.

Experimental Section

All reactions were carried out under purified argon using standard Schlenk line techniques. The solvents toluene, pentane, diethyl ether, hexanes, and tetrahydrofuran were dried by refluxing over sodium/benzophenone; dichloromethane was dried by refluxing over calcium hydride. Toluene- d_6 and benzene- d_6 were dried over sodium/benzophenone, CD_2Cl_2 over calcium hydride, and CDCl_3 and $\text{DMSO}-d_6$ over 4 Å molecular sieves. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were run on Bruker AV300, -400, or -500 spectrometers, chemical shifts being referenced to the residual proton signals of the deuterated solvents. Electrospray mass spectrometry experiments were run in positive and negative ion modes on a Quattro VG with nitrogen as the nebulizing gas.

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Table 1. Acrylonitrile Polymerizations Using $\text{FeX}_2(\text{dipy})_2$ (X = Me, Et, Cl)

exp no.	catalyst	cocatalyst	conversion (%)	no. polymer chains per Fe	M_w (M_w/M_n)
1	$\text{FeMe}_2(\text{dipy})_2^a$	none	<1		
2	$\text{FeEt}_2(\text{dipy})_2^a$	none	42		
3	$\text{FeEt}_2(\text{dipy})_2^b$	none	10		
4	$\text{FeEt}_2(\text{dipy})_2^c$	none	98		
5	$\text{FeCl}_2(\text{dipy})_2^a$	none	0		
6	$\text{FeCl}_2(\text{dipy})_2^a$	MAO (9.0 mmol)	0		
7	$\text{FeCl}_2(\text{dipy})_2^a$	AlMe_3 (2.0 mmol)	10	4.5	758 (1.05)
8	$\text{FeCl}_2(\text{dipy})_2^a$	AlMe_3 (8.0 mmol)	19	9.0	741 (1.02)
9	$\text{FeCl}_2(\text{dipy})_2^a$	AlEt_3 (1.9 mmol)	45	19.8	804 (1.02)
10	$\text{FeCl}_2(\text{dipy})_2^a$	AlEt_3 (7.6 mmol)	74	34.8	756 (1.02)
11	$\text{FeCl}_2(\text{dmby})^a$	MAO (6.0 mmol)	2		
12	$\text{FeCl}_2(\text{dmby})^a$	AlMe_3 (8.0 mmol)	18		

^a In acrylonitrile as solvent. ^b In toluene. ^c In DMF.

MALDI-TOF experiments were carried using an Applied Biosystems Voyager DE-STR Biospec workstation. In a typical experiment, 0.3 mg of 4-hydroxybenzylidene malononitrile, used as a matrix, was dissolved in 300 μL of acetone, and 2 mg of polyacrylonitrile was dissolved in 200 μL of DMF. A thin layer of the matrix solution (0.5 μL) was placed on a stainless steel target and air-dried, and then 0.5 μL of the sample solution was placed on the matrix layer and air-dried. The mixture was washed with 2 μL of distilled water and dried, and 0.5 μL of a doping salt solution (0.1 M NH_4HCO_3) was added to enhance cationization.

The compound $\text{FeCl}_2(\text{dipy})_2$ was prepared from $[\text{Fe}(\text{dipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$, and both were prepared using modifications of the literature methods.¹⁰ In particular, $\text{FeCl}_2(\text{dipy})_2$ was prepared by heating $[\text{Fe}(\text{dipy})_3]\text{Cl}_2$ at 80 °C under reduced pressure in a sublimation apparatus for 20 h, the released dipyriddy being collected on a coldfinger. The conversion was accompanied by a change in color from red to deep blue, and the product obtained was washed well with pentanes to remove all remaining free dipyriddy. ¹H NMR of $\text{FeCl}_2(\text{dipy})_2$ (DMSO-*d*₆): δ 8.90, 8.23, 7.53, and 7.40 (all broad singlets of equal intensities). The compound $\text{FeMe}_2(\text{dipy})_2$ was prepared as in the literature in 80% yield via the reaction of $\text{FeCl}_2(\text{dipy})_2$ with methylolithium in toluene at -78 °C. ¹H NMR (benzene-*d*₆): δ 6.0–9.5 (m, 16H dipyriddy), 0.89 (s, 6H, Me).^{11a} The compound $\text{FeEt}_2(\text{dipy})_2$ was synthesized using the reaction of $\text{FeCl}_2(\text{dipy})_2$ with ethyllithium^{11a} and, preferably, via reaction of $\text{Fe}(\text{acac})_3$ with dipyriddy and AlEt_2OEt .^{8b,c,11b} The latter procedure was found to give purer product in higher yields (65%). ¹H NMR (benzene-*d*₆): δ 6.0–9.5 (m, 16H, dipyriddy), 2.23 (2H, m, CH_2), 1.95 (2H, m, CH_2), 0.56 (6H, t, ³*J*_{HH} 7.0 Hz, Me). The compounds dmby (6,6'-dimethyl-2,2'-dipyriddy),^{12a,b} $\text{FeCl}_2(\text{dmby})$,^{12c} and $\text{B}(\text{C}_6\text{F}_5)_3$ ¹³ were prepared as in the literature, while $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was purchased from Asahi Glass Company Ltd., Tokyo. Acrylonitrile and styrene were dried over 4 Å molecular sieves followed by vacuum distillation to remove inhibitors. Polymerization grade ethylene (99+% purity) was purchased from Air Products and dried prior to use by passage through 4 Å molecular sieves.

Polymerizations were carried out in Schlenk flasks under purified argon in solutions cooled in an ice bath. The results of these and other polymerization experiments are shown in Table 1, which lists conversions and, where possible, molecular weight data (MALDI-TOF).

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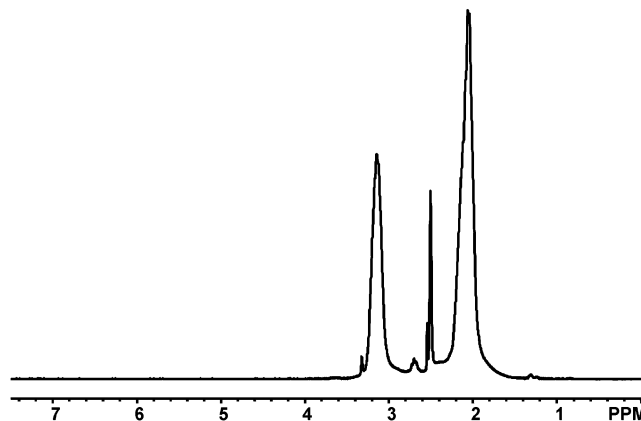


Figure 1. ¹H NMR spectrum of polyacrylonitrile formed using $\text{FeEt}_2(\text{dipy})_2$ (experiment 4 of Table 1).

Polymerization of Acrylonitrile Using $\text{FeR}_2(\text{dipy})_2$ (R = Me, Et). As a general procedure, 4 mL of acrylonitrile (0.06 mol) was added slowly to 30.0 mg of $\text{FeMe}_2(\text{dipy})_2$ or $\text{FeEt}_2(\text{dipy})_2$ (~70 μmol), either as the solid or dissolved in 10 mL of toluene or DMF. Both $\text{FeMe}_2(\text{dipy})_2$ and $\text{FeEt}_2(\text{dipy})_2$ give brown solutions in acrylonitrile, although neither is very soluble; while both are soluble in toluene, the intense blue colors changed within a few minutes to red on the addition of acrylonitrile. In DMF, the blue color of the $\text{FeEt}_2(\text{dipy})_2$ changed to brown on the addition of acrylonitrile and the solution warmed as a gel-like material appeared within 10 min. The reaction mixtures were all stirred for 3 h and were then quenched by the addition of 50 mL of acidified methanol (10 v/v % HCl). Some of the reactions gave pale yellow powdery polyacrylonitrile, which was filtered, washed with methanol, and purified by being dissolved in a minimum amount of DMSO and then reprecipitated by the slow addition of the polymer solution to ~100 mL of rapidly stirred methanol. The precipitated white powders were filtered, dried in vacuo, and characterized by ¹H (Figure 1) and ¹³C{¹H} (Figure 2) NMR spectroscopy.

Copolymerization of Acrylonitrile and Styrene Using $\text{FeEt}_2(\text{dipy})_2$. To a solution of 45 mg of $\text{FeEt}_2(\text{dipy})_2$ (114 μmol) in 4 mL of styrene was added 4 mL of acrylonitrile. The blue solution turned to a viscous brown gel immediately after the addition of acrylonitrile. The mixture was stirred for 3 h, when acidified methanol was added to terminate the polymerization. A pale yellow powder was collected and separated into chloroform-soluble and chloroform-insoluble fractions, which were characterized by ¹H NMR spectroscopy.

Attempted Polymerization of Acrylonitrile Using $\text{FeEt}_2(\text{dipy})_2$ Combined with $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. To a mixture of 30 mg of $\text{FeEt}_2(\text{dipy})_2$ (~70 μmol) and an equivalent amount of $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was added 4 mL (0.06 mol) of acrylonitrile. Both solutions turned red,

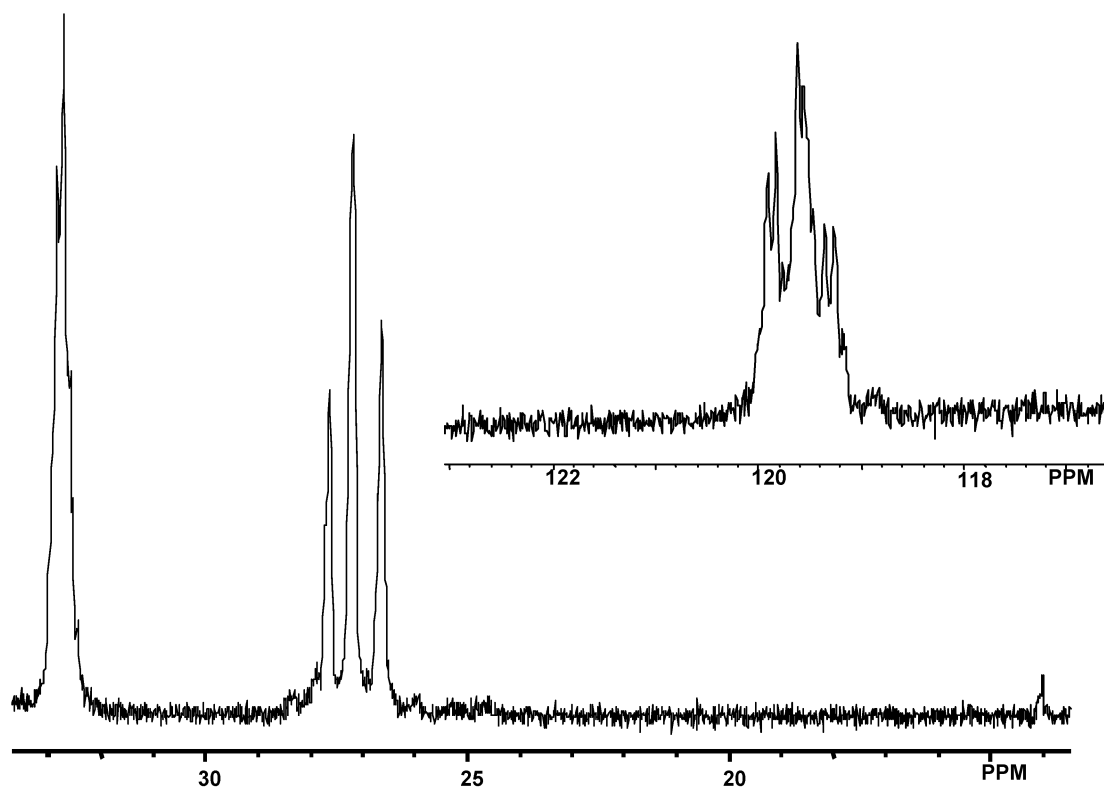


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polyacrylonitrile formed using $\text{FeEt}_2(\text{dipy})_2$ (experiment 4 of Table 1).

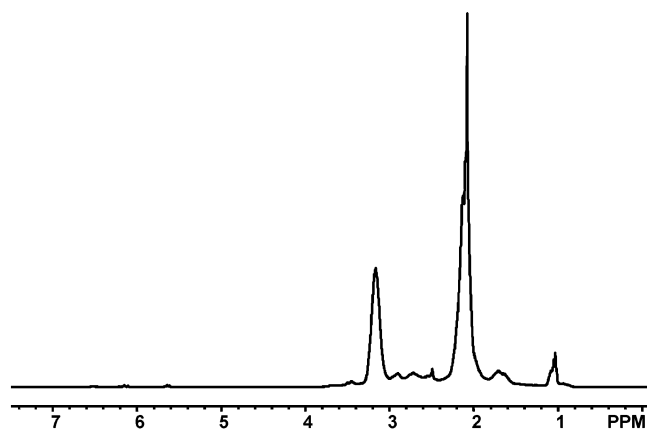


Figure 3. ^1H NMR spectrum of the polyacrylonitrile formed using $\text{FeCl}_2(\text{dipy})_2/\text{AlMe}_3$ (experiment 7 of Table 1).

but there was no evolution of heat or formation of precipitate. No precipitates formed when 50 mL of methanol was added to the solutions after 3 h.

Polymerization of Acrylonitrile Using $\text{FeCl}_2(\text{dipy})_2/\text{AlR}_3$ (R = Me, Et) or MAO. A suspension of 40.0 mg of $\text{FeCl}_2(\text{dipy})_2$ ($\sim 90 \mu\text{mol}$) in 4 mL of acrylonitrile (0.06 mol) was treated with approximately 100-fold molar excesses of trimethylaluminum, triethylaluminum, or MAO, and the mixtures were stirred for 3 h. The addition of AlMe_3 or AlEt_3 resulted in immediate heating of the solutions, which turned orange-red, and the precipitation of polymer, which was purified and characterized as above. This was characterized by NMR spectroscopy (Figure 3) and mass spectrometry (Figure 4). Under these conditions, no polymerization was observed using MAO.

Copolymerization of Acrylonitrile and Styrene Using $\text{FeCl}_2(\text{dipy})_2/\text{AlMe}_3$. The addition of 4 mL of AlMe_3 (2.0 M in hexane, 8.0 mmol) to a mixture of 50 mg of $\text{FeCl}_2(\text{dipy})_2$ (0.114 mmol) and 4 mL of styrene (35 mmol) in 4 mL of acrylonitrile (60 mmol) resulted in immediate warming of the mixture and

a change in the color of the suspension from dark blue to brick red. The mixture remained warm for ~ 30 min and was stirred for 3 h when acidified methanol was added to stop the polymerization. A pale yellow powder was collected and was separated into chloroform-soluble and chloroform-insoluble fractions, which were characterized by ^1H NMR spectroscopy (Figure 5).

Attempted Polymerization of Ethylene. A mixture of 40 mg of $\text{FeCl}_2(\text{dipy})_2$ ($\sim 90 \mu\text{mol}$) in 10 mL of toluene was saturated with ethylene by bubbling for 10 min, and 4 mL of AlMe_3 (2.0 M in hexane, 8.0 mmol) was then added. No temperature change was noticed, but ethylene was continually bubbled through the mixture for 3 h. The addition of 50 mL of acidified methanol resulted in the precipitation of no polyethylene. In similar experiments, ethylene-saturated solutions of 30 mg of $\text{FeEt}_2(\text{dipy})_2$ (70 μmol) in 10 mL of toluene were treated with 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in 5 mL of toluene. Again no temperature change was observed and no polymer was formed after 3 h. In addition, removal of all volatiles under reduced pressure and examination of the residue by ^1H NMR spectroscopy revealed no resonances attributable to oligomeric hydrocarbons. In a complementary experiment, an ethylene-saturated solution of $\text{FeEt}_2(\text{dipy})_2$ in THF was treated with 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, and after 10 min, the solution was examined by ESMS in an effort to identify the species in solution.

Attempted Polymerizations Using $\text{FeCl}_2(\text{dmby})$. A solution of 32 mg of $\text{FeCl}_2(\text{dmby})$ (0.1 mmol) and 15 equiv of MAO in 4 mL of acrylonitrile was stirred for 6 h. The solution turned orange, but the addition of acidified methanol yielded only a small amount of polyacrylonitrile. A similar reaction using $\text{FeCl}_2(\text{dmby})$ and 2 equiv of AlMe_3 resulted in the precipitation of 600 mg of polyacrylonitrile (Table 1), but an attempted polymerization of ethylene (1 atm) using $\text{FeCl}_2(\text{dmby})/\text{MAO}$ in toluene yielded no polymer.

Reaction of $\text{FeEt}_2(\text{dipy})_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$. A solution of 36 mg of $\text{B}(\text{C}_6\text{F}_5)_3$ (70.4 μmol) in 5 mL of toluene was added to a solution of 30 mg of $\text{FeEt}_2(\text{dipy})_2$ (70.4 μmol) in 20 mL of toluene, resulting in a color change from blue to red and

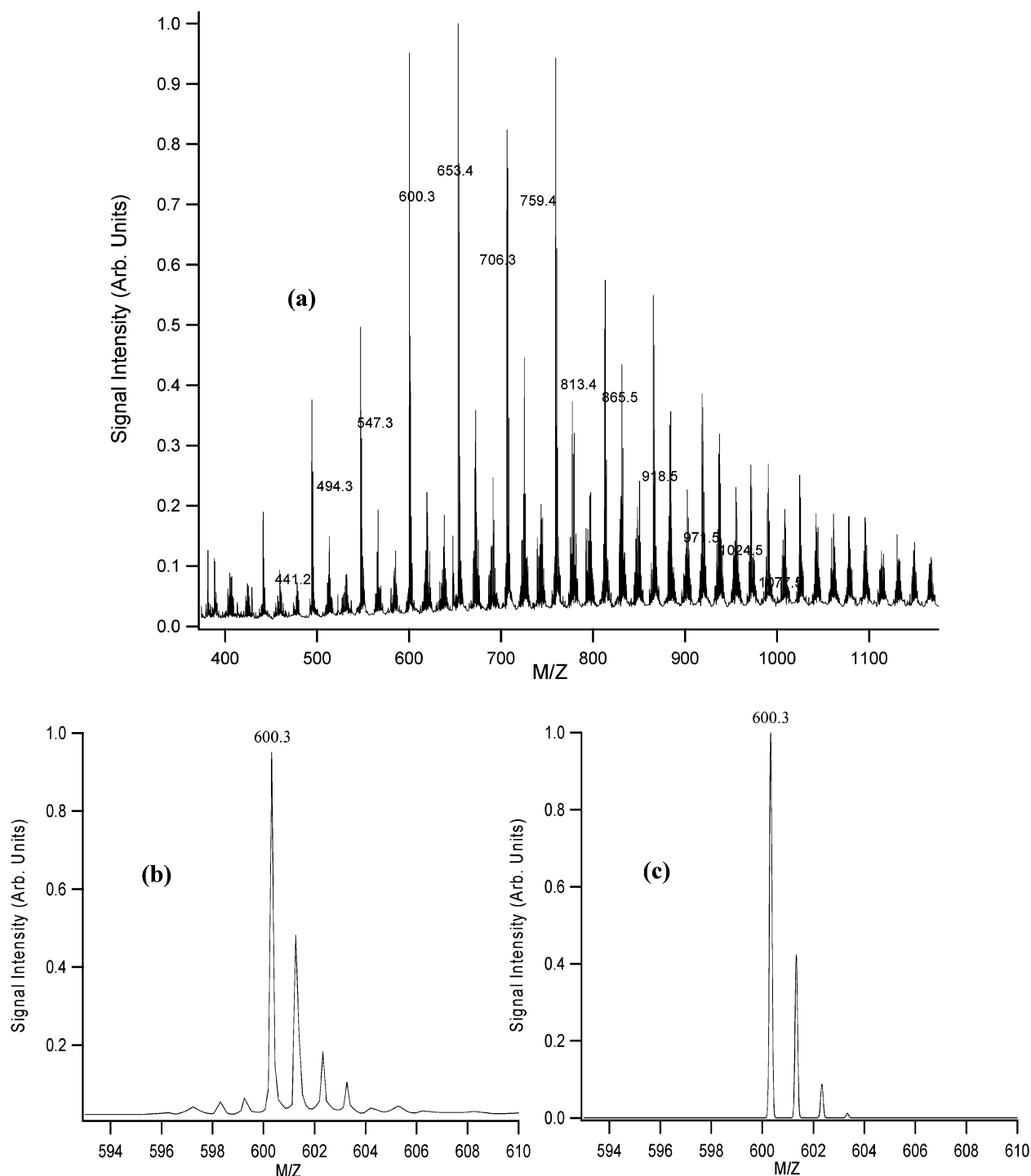


Figure 4. MALDI-TOF mass spectrum of the polyacrylonitrile formed using $\text{FeCl}_2(\text{dipy})_2/\text{AlMe}_3$ (experiment 7 of Table 1): (a) mass spectrum of polyacrylonitrile, (b) expanded peak at M/Z 600, (c) theoretical peak at m/z 600 ($\text{C}_{34}\text{H}_{38}\text{N}_{11}$).

precipitation of a red oil. The supernatant was decanted, and the red oil was pumped on overnight and characterized by ESMS and ^1H NMR spectroscopy. ^1H NMR (20 °C, CD_2Cl_2): δ 7.18–8.40 (16H, dipyridyl), 1.08 (2H, br s, $\text{CH}_3\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3^-$), 0.49 (3H, br s, $\text{CH}_3\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3^-$). In a separate experiment, 4 mg of $\text{FeEt}_2(\text{dipy})_2$ and an approximately equivalent amount of $\text{B}(\text{C}_6\text{F}_5)_3$ were placed in an NMR tube. After the NMR tube was sealed with a rubber septum and cooled to -78 °C, 0.5 mL of $\text{THF-}d_8$ was added and the tube was immediately placed in the precooled probe of a 500 MHz NMR spectrometer. ^1H NMR data were collected from -68 to 22 °C.

Reaction of $\text{FeEt}_2(\text{dipy})_2$ with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. A solution of 32 mg of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (35.2 μmol) in 5 mL of toluene was added to a solution of 30 mg of $\text{FeEt}_2(\text{dipy})_2$ (70.4 μmol)

in 20 mL of toluene. A red oily material precipitated immediately and was freed of solvent as above. A ^1H NMR spectrum (CD_2Cl_2 , 20 °C) was essentially identical to that obtained in the reaction except that the $[\text{CH}_3\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$ resonances were missing.

Results and Discussion

Acrylonitrile Polymerization. We first confirmed the reported activities of $\text{FeMe}_2(\text{dipy})_2$ and $\text{FeEt}_2(\text{dipy})_2$ as catalytic initiators for the polymerization of acrylonitrile^{7,8} in DMF, toluene, and/or pure acrylonitrile. As can be seen from Table 1, conversion using FeEt_2 -

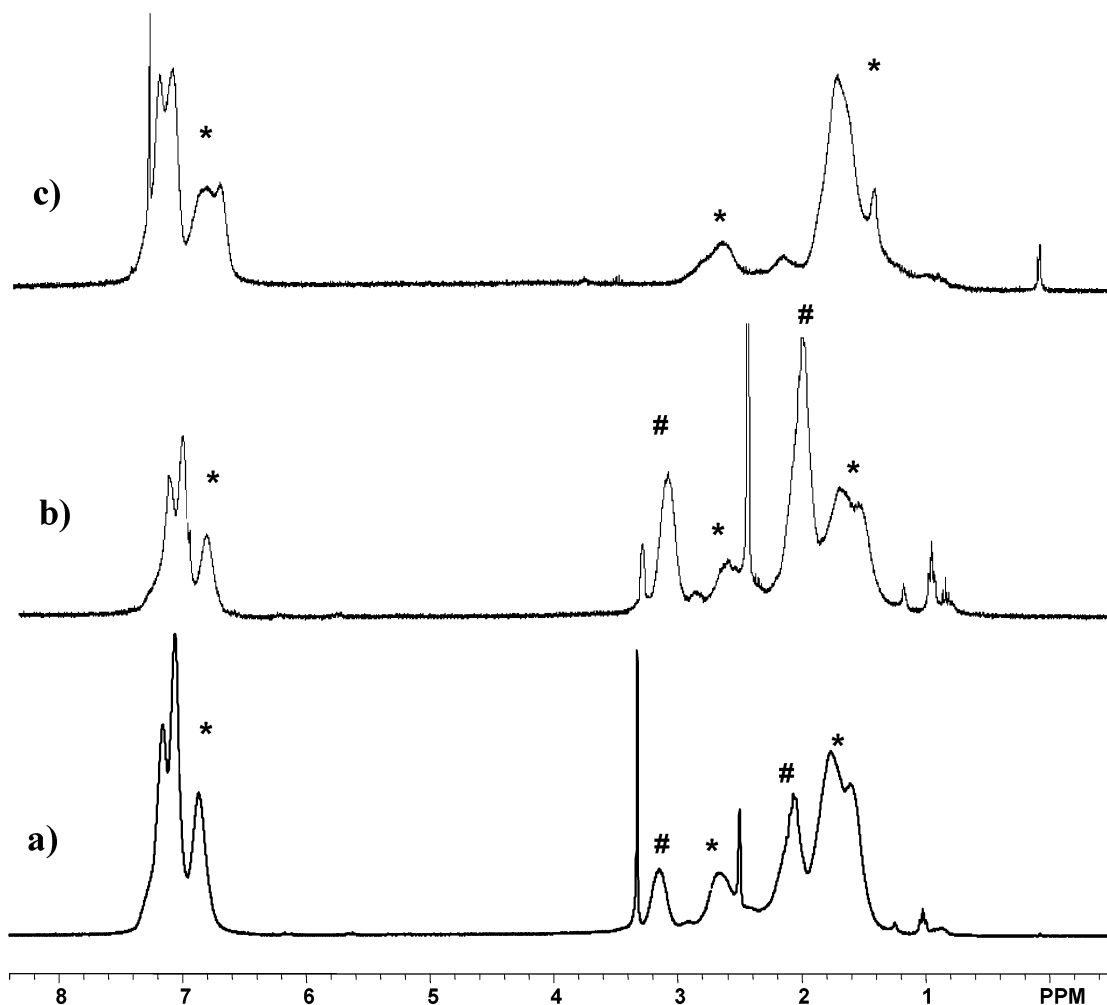


Figure 5. ^1H NMR spectra of (a) the crude polymeric material obtained on copolymerization of acrylonitrile and styrene, (b) the material insoluble in chloroform, and (c) the material soluble in chloroform. Styrene peaks are marked *, acrylonitrile peaks #.

(dipy) $_2$ was essentially quantitative in DMF within 3 h, but only $\sim 10\%$ in toluene and 42% in the absence of any solvent. The differences in conversion may be related in part to differences in solubilities of the catalysts and polyacrylonitrile in the three solvents.⁸ $\text{FeMe}_2(\text{dipy})_2$, $\text{FeEt}_2(\text{dipy})_2$, and polyacrylonitrile are all soluble in DMF, and thus the polymerization reactions are maintained throughout in a genuinely homogeneous albeit gel-like mode. In contrast, $\text{FeMe}_2(\text{dipy})_2$ and $\text{FeEt}_2(\text{dipy})_2$ are soluble in toluene, but polyacrylonitrile is not, while none are very soluble in acrylonitrile. Thus, neither catalyst is readily available in neat acrylonitrile, while in both toluene and neat acrylonitrile precipitation of polyacrylonitrile might well result in entrapment of catalyst and hence in the effective loss of active catalytic centers.

We also carried out experiments in which we treated $\text{FeCl}_2(\text{dipy})_2$ with various alkyl aluminum compounds in bulk acrylonitrile. Conditions of the polymerization reactions and workup procedures were as above. In control experiments, it was found that no polyacrylonitrile was formed over 3 h in the presence of $\text{FeCl}_2(\text{dipy})_2$, AlMe_3 , or MAO alone, although a trace amount was formed by AlEt_3 and low conversions (~ 0.5 g) were obtained by using AlMe_3 over a 6 h period. While the combination of $\text{FeCl}_2(\text{dipy})_2$ and MAO was also surpris-

ingly inactive, significant amounts of polyacrylonitrile were formed when $\text{FeCl}_2(\text{dipy})_2$ was activated with AlMe_3 or AlEt_3 . Indeed, the conversions, especially with AlEt_3 , are comparable with those obtained using $\text{FeEt}_2(\text{dipy})_2$ alone in bulk acrylonitrile.

To assess the possible role of free radical chain processes in these polymerization reactions, we attempted the homopolymerization of styrene and the copolymerization of acrylonitrile and styrene by $\text{FeMe}_2(\text{dipy})_2$ and the $\text{FeCl}_2(\text{dipy})_2/\text{AlEt}_3$ system. Acrylonitrile and styrene are both readily homopolymerized via radical chain processes,¹⁴ and it was an observation that $\text{FeMe}_2(\text{dipy})_2$ does not induce styrene polymerization that was originally taken as evidence that the compound is not a radical polymerization initiator.^{8a} We have confirmed that $\text{FeMe}_2(\text{dipy})_2$ is a very poor initiator of styrene polymerization, as only a small amount of polystyrene was obtained.

Pale yellow polymeric materials were obtained, however, during attempted copolymerizations of acrylonitrile and styrene using $\text{FeMe}_2(\text{dipy})_2$ or $\text{FeCl}_2(\text{dipy})_2/\text{AlEt}_3$, and ^1H NMR spectra ($\text{DMSO}-d_6$) of the crude

(14) (a) Barton, J.; Borsig, E. *Complexes in Free Radical Polymerization*; Elsevier Science Inc.: New York, 1988. (b) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 1700.

products showed the presence of both styrene (δ 6.6–7.4, \sim 2.7, \sim 1.7) and acrylonitrile (δ \sim 3.1, \sim 2.0) resonances. Figure 5a shows a ^1H NMR spectrum that is representative of the products formed in all copolymerization experiments carried out. Since polystyrene is soluble in chloroform while polyacrylonitrile-*co*-polystyrene and polyacrylonitrile are not,¹⁵ chloroform extractions of the polymeric products were carried out and found to produce a small amount of soluble white polymer, which was shown by ^1H NMR spectroscopy (Figure 5c) to be polystyrene. However, most of the material was insoluble in chloroform and was shown by ^1H NMR spectroscopy (Figure 5b) to consist of a considerable proportion of styrene units in addition to acrylonitrile. Thus a significant part of the product was a copolymer.

These results are clearly consistent with a radical polymerization process, and we note that a somewhat similar result has been observed during copolymerization of acrylonitrile and styrene induced by dibenzoyl peroxide/ AlEt_3 ; styrene is not polymerized by this initiator system except in the presence of polar monomers such as acrylonitrile.^{14a} We briefly assessed the possibility that acrylonitrile polymerization by $\text{FeCl}_2(\text{dipy})_2/\text{AlEt}_3$ might be affected by radical scavengers, and our interest was initially aroused when we observed partial inhibition by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), which has been used previously in this way.¹⁶ However, we subsequently found that TEMPO reacts with both AlEt_3 and $\text{FeEt}_2(\text{dipy})_2$, and thus this result became meaningless. Similarly, phenolic scavengers such as 4-methoxyphenol, the stabilizer in commercial acrylonitrile, could not be used because they react with $\text{FeEt}_2(\text{dipy})_2$ to form aryloxy compounds.^{8f}

On the other hand, AlR_3 has been reported to initiate the radical polymerization of several vinyl monomers including acrylonitrile,^{14a,17} although our results (Table 1) suggest that it is not very effective over 3 h, at any rate. It thus seems likely that the combination of $\text{FeCl}_2(\text{dipy})_2$ and AlEt_3 facilitates significantly the increased formation of radicals, and we note as precedent that iron(II) compounds such as $\text{FeCl}_2(\text{PPh}_3)_2$ play roles in radical polymerization of methyl methacrylate.^{15,18}

Characterization of Acrylonitrile Homopolymers Using MALDI-TOF Mass Spectrometry and NMR Spectroscopy. The polyacrylonitrile samples obtained here were all too insoluble in conventional GPC solvents (THF, toluene) for molecular weight measurements in the equipment available, and therefore MALDI-TOF mass spectrometry experiments were carried out in an effort to obtain molecular weight information. See Table 1 for the M_w and polydispersity data obtained. Interestingly, the polymeric samples obtained using $\text{FeMe}_2(\text{dipy})_2$ and $\text{FeEt}_2(\text{dipy})_2$ were quite different from those obtained using $\text{FeCl}_2(\text{dipy})_2$ activated with AlMe_3 or AlEt_3 . The latter were relatively soluble in the solvent used (DMF), and mass spectra were easily obtained. As

a representative example, we show in Figure 4a the MALDI-TOF mass spectrum of the material obtained in experiment 7, in which $\text{FeCl}_2(\text{dipy})_2$ was activated with AlMe_3 .

As can be seen, the spectrum exhibits a manifold of peaks in the range 441–1024, all separated by 53 amu, the molecular weight of acrylonitrile. There are also much weaker multiplets between the main peaks, possibly indicative of structural irregularities, although they seem not to be readily interpretable. The major peaks all exhibit an isotope distribution (see Figure 4b,c for peak at 600.4) that is consistent with identification of the polymeric units as being of the type $\text{CH}_3(\text{CH}_2\text{-CHCN})_x\text{CH}_2\text{CH}_2\text{CN}$ ($x = 7\text{--}18$), cationization in the series being effected by H^+ . The ^1H NMR spectrum of the polymer (Figure 3) is consistent with this formulation, exhibiting at $\delta \sim 1.1$ a methyl resonance, which is coupled to resonances that are part of the broad multiplet at $\delta \sim 1.75$; thus a terminal ethyl group seems likely. However, the polymer clearly contains irregularities, as the spectrum also exhibits broad, weak multiplets at $\delta \sim 2.7$, ~ 2.9 , and ~ 3.4 , which presumably are to be associated with the minor multiplets in the mass spectrum. We have not attempted to assign these resonances, but note that NMR spectra of polyacrylonitrile prepared via anionic processes exhibit similar features, tentatively believed to arise from branched or cyclized structures.¹⁹ We note also only very weak olefinic resonances in the region δ 5.5–6.5, consistent with the lack of evidence in the mass spectrum for unsaturation. The intensity of the methyl resonance at $\delta \sim 1.1$ relative to those of the main chain resonances ($\delta \sim 2.05$, 3.1) yields an M_n value of ~ 700 , consistent with the MS data.

These results, coupled with the above-mentioned observations that $\text{FeCl}_2(\text{dipy})_2$ and AlMe_3 alone are poor initiators, suggest that polymerization of acrylonitrile involves initial transfer of methyl groups from aluminum to iron followed by methyl transfer to monomer, either as an anion or as a radical. Anionic or radical polymerization ensues until termination by hydrogen abstraction, possibly from an iron hydride formed from thermal decomposition of alkyl-iron species.^{8c} Conventional radical polymerizations of acrylonitrile are believed to involve termination via coupling rather than disproportionation,²⁰ but the latter process cannot be important here because polymers containing odd numbers of incorporated monomer are quite apparent in the mass spectrum. Whether this result points to an anionic mechanism or whether a novel mode of radical termination is involved is not clear. The mass spectrum of the polymer formed by activating $\text{FeCl}_2(\text{dipy})_2$ with AlEt_3 (experiment 9 in Table 1) was similar, albeit in this case with the expected propyl headgroup.

In contrast, the polymer formed in high conversion using $\text{FeEt}_2(\text{dipy})_2$ in DMF as initiator (experiment 4 in Table 1) was seemingly of much higher molecular weight, as it was much less soluble than those described above, and a MALDI-TOF mass spectrum could not be obtained. Consistent with this, Yamamoto et al. showed via viscometry measurements^{8b-d} that molecular weights

(15) Brandrup, J.; Immergut, E. H.; Grulke, E. *Polymer Handbook*, 4th ed.; John Wiley & Sons: Toronto, 1999.

(16) (a) Bevington, J. C.; Hunt, B. J.; Warburton, J. *Polymer* **2003**, *44*, 3469. (b) Bevington, J. C.; Hunt, B. J. *Polym. Mater.* **2002**, *19*, 113.

(17) (a) Tsuchihara, K.; Suzuki, Y.; Asai, M.; Soga, K. *Chem. Lett.* **1999**, 891. (b) Tsuchihara, K.; Suzuki, Y.; Asai, M.; Soga, K. *Polym. J.* **2000**, *32*, 700.

(18) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.

(19) Pai Verneker V. R.; Shaha, B. *Macromolecules* **1986**, *19*, 1851.

(20) Stevens, M. P. *Polymer Chemistry*; Oxford University Press: New York, 1999; p 177.

of polyacrylonitrile made in this way were in the range 8000–20 000, depending on the conditions of the polymer synthesis. A ^1H NMR spectrum of the material in $\text{DMSO}-d_6$ is shown in Figure 1. As can be seen, in addition to the main chain resonances at $\delta \sim 2.05$ (CH_2) and ~ 3.1 (CH), there is only an apparent triplet at δ 1.3 (actually a double doublet) and a weak multiplet at δ 2.7 and no olefinic resonances. The doublets at δ 1.3 are in the region expected for an end group of the type $\text{P}\sim\text{CH}_2\text{CH}(\text{CN})\text{Me}$ and have been noted previously for acrylonitrile polymerization initiated by 2-halopropionitriles and catalyzed by copper(I) compounds in atom transfer radical polymerization (ATRP) processes.²¹ We find that the 1-methyl resonance of 2-cyanobutane also occurs at δ 1.3, in contrast to the 4-methyl resonance which is observed at δ 1.1. A COSY spectrum demonstrated the presence of coupling of the methyl resonances with a resonance at about δ 3.0, on the high-frequency side of the broad CH backbone resonance (and comparable with δ 2.65 for the 2-H of 2-cyanobutane). Thus the resonances at δ 1.3 are indeed attributable to methyl groups coupled to the single hydrogen of a $\text{CH}(\text{CN})$ moiety, the pair of resonances arising because of the presence of diastereomers in the $\text{P}\sim(\text{CH}_2\text{C}^*\text{HCN})\text{-(CH}_2\text{C}^*\text{HCN})\text{Me}$ chain end. On the assumption that every polymer chain contains a $(\text{CH}_2\text{C}^*\text{HCN})\text{Me}$ end group, M_n is found to be ~ 20 000, reasonably consistent with Yamamoto's earlier findings.^{8d}

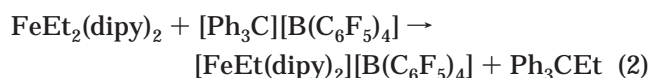
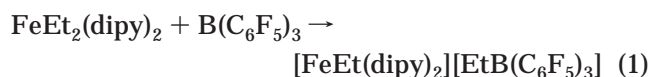
The weak multiplet at δ 2.7 correlates with a CH_2 resonance at δ 2.0 and appears to various extents in the ^1H NMR spectra of all of the polymers listed in Table 1, although it does not appear in published ^1H NMR spectra of polyacrylonitrile formed via ATRP.²¹ It is tentatively assigned to groups such as $\text{P}\sim\sim(\text{CH}_2\text{CHCN})\text{-(CHCNCH}_2)\sim\text{P}$ since ^1H NMR spectra of vicinal dinitriles of the types R-CHCN-CHCN-R' ($\text{R} = \text{alkyl}$) exhibit CHCN resonances in the region δ 2.5–3.0, depending on the solvent.²² The resonance may also be indicative of termination of radical polymerization via coupling,²¹ of tail-to-tail coupling during polymerization, or of branching in the polymer. While tail-to-tail coupling is not of course anticipated for free radical polymerizations of a monomer such as acrylonitrile,²⁰ low levels of tail-to-tail coupling have precedent.²³

Other than the weak resonances noted above, the NMR spectrum is remarkably clean, suggesting a very regular structure for the polymer. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is shown in Figure 2, the CH_2 ($\delta \sim 32.7$) and CH ($\delta \sim 26.8$) and CN ($\delta \sim 119$) multiplets being consistent with a highly atactic material.²⁴ There are also weak resonances at δ 13.9, attributable to the methyl of the $\text{P}\sim\text{CHCNCH}_3$ end group, and δ 33.9, tentatively assigned to the methyne carbon of the same end group.

Tests for Ziegler Activity. We then carried out a complementary series of experiments designed to assess

the system for Ziegler activity of any kind. As tests for Ziegler processes, we attempted polymerizations of ethylene using $\text{FeEt}_2(\text{dipy})_2$ only, using $\text{FeEt}_2(\text{dipy})_2$ activated by $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, using $\text{FeCl}_2(\text{dipy})_2/\text{AlMe}_3$, and using $\text{FeCl}_2(\text{dmby})$ in the presence of AlMe_3 , AlEt_3 , and MAO.

We readily confirmed Yamamoto's report^{8f} that ethylene is not polymerized by $\text{FeEt}_2(\text{dipy})_2$ alone. We also failed to polymerize ethylene using $\text{FeCl}_2(\text{dmby})$ or $\text{FeCl}_2(\text{dipy})_2$ in the presence of the conventional Ziegler activators AlMe_3 , AlEt_3 , and MAO, and using $\text{FeEt}_2(\text{dipy})_2$ treated with $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. The latter reactions are expected to produce the cationic species $[\text{FeEt}(\text{dipy})_2]^+$, as in eqs 1 and 2, and are discussed further below.



These results cast considerable doubt on the suggestion that $\text{FeEt}_2(\text{dipy})_2$ can behave as a Ziegler catalyst.^{7,8} Of all the commonly used monomers and using both early¹ and late⁵ transition metal catalysts, ethylene seems to be the most readily polymerized via a Ziegler process,¹ and thus any putative Ziegler catalyst must *de rigueur* catalyze at least the oligomerization of ethylene. However, no oligo- or polyethylene has been detected in any of the systems studied here, a result that casts serious doubt on the possibility that either $\text{FeEt}_2(\text{dipy})_2$ or $[\text{FeEt}(\text{dipy})_2]^+$ can behave as a Ziegler catalyst.

Reactions of $\text{FeEt}_2(\text{dipy})_2$ with the Ethyl-Abstracting Species $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. Keeping in mind the apparently general importance of cationic catalysts containing a vacant site created by abstraction of the alkyl ligand,^{1,5} we investigated the reactions of $\text{FeEt}_2(\text{dipy})_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. We anticipated that the cationic species $[\text{FeEt}(\text{dipy})_2]^+$ would be produced as in eqs 1 and 2 and wished to investigate its formation and properties.

However, the best choice of solvent for the abstraction reactions was not immediately obvious. The compound $\text{FeEt}_2(\text{dipy})_2$ reacts with dichloromethane, in which the reactants and products are soluble, and so toluene was used. Reaction of a 1:1 mixture of $\text{FeEt}_2(\text{dipy})_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in this solvent is rapid, the deep blue of the soluble diethyl compound giving way immediately to a deep red oil, which by separating out provided inferential evidence that an ionic compound had been formed. The supernatant solution was removed by syringe and the oil was pumped on at room temperature overnight, leaving a red powder. The latter was dissolved in dichloromethane, and a positive mode ES mass spectrum exhibited a weak peak at 397 Da/e with an isotope pattern consistent with the formulation of $[\text{FeEt}(\text{dipy})_2]^+(\text{C}_{22}\text{H}_{21}\text{FeN}_4)$. There was also in the negative mode mass spectrum a strong peak at 541 Da/e, exhibiting an isotope pattern consistent with the formulation of $[\text{EtB}(\text{C}_6\text{F}_5)_3]-(\text{C}_{20}\text{H}_5\text{BF}_{15})$, and thus the mass spectral data appeared to be consistent with the reaction shown in eq 1.

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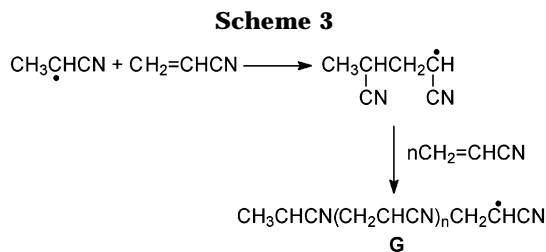
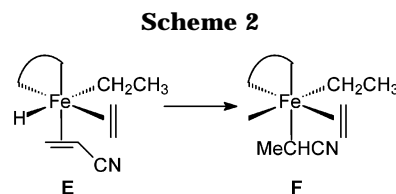
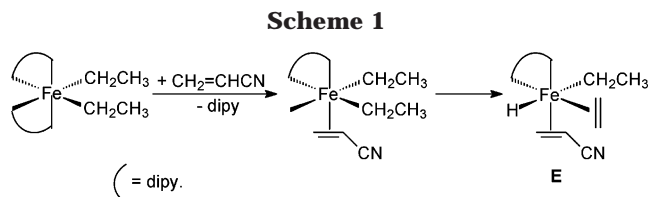
(c) Bamford, C. H. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon Press: New York, 1989; Vol. 3, p 219.

(24) (a) Minagawa, M.; Ute, K.; Kitayama, T.; Hatada, K. *Macromolecules* **1994**, *27*, 3669. (b) Katsuraya, K.; Hatanaka, K.; Matsuzaki, K.; Minagawa, M. *Polymers* **2001**, *42*, 6323. (c) Barboiu, B.; Percec, V. *Macromolecules* **2001**, *34*, 8626.

A ^1H NMR spectrum of the red powder in CD_2Cl_2 at room temperature was not, however, consistent with the presence of $[\text{FeEt}(\text{dipy})_2][\text{EtB}(\text{C}_6\text{F}_5)_3]$. The spectrum exhibited only a single set of dipyrindyl resonances, consistent with the presence of a single product, in addition to broadened resonances at δ 1.08 (2H) and 0.49 (3H), attributable to the ethyl hydrogens of the anion $[\text{EtB}(\text{C}_6\text{F}_5)_3]^-$.²⁸ However contamination with residual toluene rendered integrations meaningless. Surprisingly, there were no resonances attributable to an ethyl group bonded to iron. A similar experiment involving $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in toluene also resulted in an oil, which was dried in the same way. The ^1H NMR spectrum was very similar, except that the borate ethyl resonances were missing. All attempts to grow crystallographically useful crystals from the $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ systems via CH_2Cl_2 /hexane layering experiments failed. Attempts to clarify matters by monitoring the reaction in $\text{THF}-d_8$ at low temperatures and with various borane:iron ratios resulted in the observation of a major resonance at δ 5.34, corresponding to ethylene, and a very weak hydride resonance at δ -7.6, suggesting decomposition via β -elimination. While other resonances could not be identified, none could be attributed to $[\text{EtB}(\text{C}_6\text{F}_5)_3]^-$, and this approach was abandoned.

Mechanism of Polymerization of Acrylonitrile by $\text{FeEt}_2(\text{dipy})_2$. Although the mechanism of polymer initiation and propagation in the presence of $\text{FeEt}_2(\text{dipy})_2$ was initially quite unclear, radical processes seemed likely for reasons given above. Similar conclusions were reached for acrylonitrile polymerization by the isoelectronic cobalt complexes $[\text{CoR}_2(\text{dipy})_2]^+$ ($\text{R} = \text{Me}, \text{PhCH}_2$)²⁵ while this work was in progress. However, as noted above, several apparent incongruities reported by Yamamoto^{7,8} must be rationalized. These are as follows: (1) addition of free dipyrindyl and use of coordinating solvents during polymerization result in inhibition, presumably by blocking a needed coordination site; (2) ethylene and *smaller* amounts of ethane are evolved during polymerization of acrylonitrile by $\text{FeEt}_2(\text{dipy})_2$; and (3) ethylene and ethane are also products of the slower thermal decomposition of $\text{FeEt}_2(\text{dipy})_2$ in the absence of acrylonitrile.

The most obvious free radical polymerization initiator in this system would be the ethyl radical, formed via thermal homolysis of $\text{FeEt}_2(\text{dipy})_2$; in this case, polymers of the type $\text{Et}(\text{CH}_2\text{CHCN})_n\text{CH}_2\text{CH}_2\text{CN}$ would result. However, while the observed ethylene and ethane are the products expected of ethyl radical disproportionation (albeit in a 1:1 ratio), significant amounts of *n*-butane would also result from ethyl radical coupling,²⁶ and this was not observed.^{7,8} Furthermore, of course, our end group analyses are inconsistent with the presence of an *n*-propyl end group. Also seemingly incompatible with simple homolysis followed by ethyl radical initiated polymerization, Yamamoto's observations require initial displacement of a dipyrindyl ligand by acrylonitrile. Furthermore, we find that while addition of acrylonitrile to a DMF solution of $\text{FeEt}_2(\text{dipy})_2$ results in almost immediate discharge of the intense blue color of this



compound, solutions of $\text{FeEt}_2(\text{dipy})_2$ in acetonitrile retain their blue color for an hour or more. Thus coordination of the acrylonitrile must occur not via the nitrile group but *via the C=C bond*, and a sequence as in Scheme 1 seems likely.

Consistent with Scheme 1, ethylene formation would involve β -hydrogen elimination from an ethyl group after a coordination site is opened up by dipyrindyl dissociation, and ethane formation would result from reductive elimination from a species such as **E**. However, since the molar ratio of ethane:ethylene is less than 1:1, it follows that not all of the hydride ligand is utilized in this way and it is likely that migratory insertion of the acrylonitrile also occurs (Scheme 2).

It is expected that 2,1-insertion, as in **F**, will result,²⁷ that homolysis of the resulting iron-carbon σ bond would give the stable cyanoethyl radical $\cdot\text{CHMeCN}$ could be facile, and that homolysis in the presence of acrylonitrile would result in the formation of polymer containing the cyanoethyl headgroup (Scheme 3).

Termination to give a saturated end group would then involve hydrogen atom abstraction by **G** from solvent or from another polymer chain, but the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances of the resulting saturated end group would likely be obscured by the much stronger backbone resonances. There is no need to consider chain transfer, as Yamamoto has shown that the number of chains of polyacrylonitrile formed per iron is less than one.^{8d}

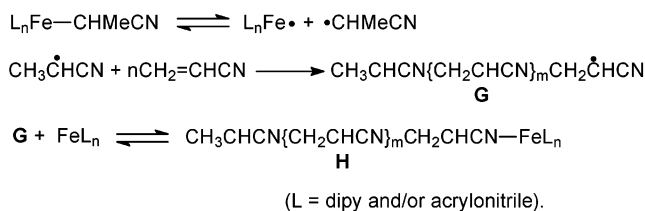
Attempts to monitor by NMR spectroscopy the course of the reaction of $\text{FeEt}_2(\text{dipy})_2$ with small excesses of acrylonitrile in benzene- d_6 , toluene- d_8 , and chlorobenzene- d_5 all failed because of the rapid gel formation, and

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Scheme 4



thus we have been unable to verify the relevance of the chemistry of Schemes 1–3. However, it seems likely that 2-cyanoethyl-metal compounds in general²⁷ may undergo thermal homolysis and thereby induce acrylonitrile polymerization, and we are investigating other such compounds for this property. Another intriguing possibility is that homolysis of an intermediate such as **F** may be reversible and that the formally iron(I) product of homolysis, perhaps stabilized by coordination of a second acrylonitrile or by recoordination of dipy, may also couple reversibly with a growing polymer chain **G** (Scheme 4).

In this way the growing polymer chain could be maintained much of the time as a dormant alkyl-iron species **H**, and the overall, possibly living polymerization process would have much in common with the well-known atom transfer radical polymerization (ATRP) and radical addition-transfer chain transfer (RAFT) processes for living radical polymerization.²⁹

Similar processes involving the living radical polymerization of acrylates initiated and controlled by organocobalt porphyrin complexes have been reported,³⁰ although most such polymerization reactions seem to be dominated by chain transfer processes involving hydrogen abstraction from the growing polymer chains by the metal-centered radicals.³¹ Chain transfer reactions of this type would proceed as in Scheme 5 and would result in unsaturated end groups. Clearly this does not happen in this iron system.

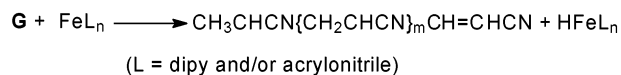
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Scheme 5



Within hours of our submission of this article, there appeared an ASAP article, by Jordan et al., describing a very similar investigation of the role(s) of FeEt₂(dipy)₂ in the polymerization of acrylonitrile.³² A Ziegler process was ruled out, as it is here, but a radical process was also ruled out because vinyl chloride was not polymerized. Instead an anionic polymerization process was considered, in part by default and in part because the structure of the polymeric material obtained was consistent with this conclusion. However, the preliminary steps hypothesized above in Schemes 1–4 were not considered, and since all of these proposed steps would have to be successfully negotiated by the iron system before it can initiate polymerization, a negative result for one monomer does not rule out a radical process for another. Indeed, for the above-mentioned and related organocobalt porphyrin complexes, there seems to be a fine line between systems that encourage chain growth and those that function as efficient chain transfer agents; different monomers also can behave quite differently.^{30,31,33}

Because of low solubility of polyacrylonitrile, we have not been able to assess whether the polymerization process is living, although the apparent lack of chain transfer is consistent with a living process, as are the very low polydispersities of some of the products (Table 1). However, FeMe₂(dipy)₂ and FeEt₂(dipy)₂ have also been reported to induce polymerization of other polar monomers such as methylvinyl ketone, methyl acrylate, methyl methacrylate, and vinyl acetate.^{7,8} The resulting polymer processes would be much more amenable to, for example, tests of living character and in situ monitoring by IR and NMR spectroscopy, and research is in progress on the mechanisms of these reactions.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council, Bayer Inc., Queen's University, and the Canadian Foundation for Innovation for support of this research.

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