

***N,N*-Bis(triethylaluminio)ethylenediamine- and *N,N*-Bis(trimethylaluminio)ethylenediamine-Derived Organometallic Precursors to Aluminum Nitride: Syntheses, Structures, and Pyrolyses**

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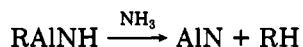
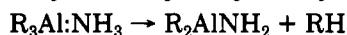
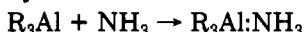
The reactions of triethylaluminum or trimethylaluminum with ethylenediamine (en) in a 2:1 molar ratio have been studied. Pyrolysis of the initially formed adducts under nitrogen yields polymeric amides and imides. Evidence was also obtained for the formation of novel en-chelated organoaluminum intermediates during the conversion of the adducts to the amides. The structures and properties of the adducts, as well as their pyrolysis products, have been studied with ^1H and ^{13}C NMR, FT-IR, GC, DSC, TGA, elemental analysis, and XRD methods. AlN powder has been obtained by the pyrolysis of the imides at 1000 °C in NH_3 . Preliminary studies were also carried out on the fabrication of AlN thin films on Si substrates by solution coating, using a solution of the bis(diethylaluminio)ethylenediamine in benzene, followed by pyrolysis under NH_3 .

Introduction

The high intrinsic thermal conductivity and electrical resistivity of AlN and its closely matched thermal expansion to Si, along with other properties (high decomposition temperature, high oxidative stability, hardness, etc.), make it an excellent candidate for use both as a substrate for Si-based electronics and as a high-temperature structural ceramic material.¹⁻⁵ Many of these desirable properties are dependent on the control of the purity and stoichiometry of the aluminum nitride; in particular, small amounts of impurities (e.g., oxygen) lead to a substantial reduction in the thermal conductivity.⁵ Furthermore, the successful application of AlN also requires the ability to prepare it in desired forms (powder, monolith, fiber, thin film, etc.), often at low temperature.

The current methods for producing AlN include reaction of aluminum metal with N_2 or NH_3 or reduction of aluminum oxide with carbon in the presence of nitrogen or ammonia. These methods generally yield AlN that is contaminated with aluminum, oxygen, carbon, or other impurities and cannot be used to prepare AlN fiber or thin films.

Recently, organometallic aluminum compounds have been used as precursors to AlN in various final forms. High-purity AlN powder has been prepared by reaction of ammonia with trialkylaluminum compounds and subsequent thermolysis in an ammonia atmosphere.⁶



where R = CH_3 , C_2H_5 , $i\text{-C}_4\text{H}_9$, etc.

Polycrystalline aluminum nitride thin films were also made by chemical vapor deposition using the volatile organoaluminum amide, $[\text{Me}_2\text{AlNH}_2]_3$,⁷ or azide, $[\text{Et}_2\text{AlN}_3]_3$,⁸

(1) Slack, G. A.; Tanzilli, R. A.; Pohl, R. O.; Vandersande, J. W. *J. Phys. Chem. Solids* 1987, 48, 641.

(2) Slack, G. A.; McNelly, T. F. *J. Cryst. Growth* 1976, 34, 263.

(3) Slack, G. A.; McNelly, T. F. *J. Cryst. Growth* 1977, 42, 560.

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(6) Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C.; Lee, W.; Slack, G. A. *Mater. Res. Soc. Symp. Proc.* 1986, 73, 359.

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An effective solution-based precursor system to AlN films would present an attractive alternative to these vapor-phase processes. The Et_3Al -modified ethylaluminum amide $[\text{EtAlNH}]_m[\text{Et}_2\text{AlNH}_2]_n\text{Et}_3\text{Al}$ has been employed to produce AlN fiber.^{9,10} The full and effective implementation of these and other applications for AlN precursors will require a better understanding of the chemistry of such Al-N compounds as well as the development of new precursor systems.

In 1968, Gilbert and Smith¹¹ reported the results of a study of the interaction of ethylenediamine and triethylaluminum in a 1:1 molar ratio. Their work indicated that the initially formed liquid adduct, after undergoing two decomposition processes at 50 and 130 °C was converted into a soluble polymeric solid, $[\text{EtAl}(\text{NHCH}_2\text{CH}_2\text{NH})]_x$. However no structural information regarding the final and intermediate products of these thermolysis reactions was given nor was the pyrolysis of these compounds to AlN performed. Beachley and Racette¹² studied the factors affecting the formation of chelated monomeric or unchelated dimeric organoaluminum-nitrogen compounds derived from 1:1 reactions between R_3Al and various substituted ethylenediamine derivatives (i.e., $\text{HR}'\text{NCH}_2\text{CH}_2\text{NRR}''$; R = H, Me, Et, Ph; R', R'' = Me, Et). Their studies showed that factors such as steric effects of R, R', and R'', ligand base strength, and chelate ring size controlled the position of the monomer-dimer equilibrium.

In this paper, we report detailed studies of the reactions of ethylenediamine with triethylaluminum or trimethylaluminum in a 1:2 ratio. These studies have resulted in a better understanding of the chemistry of the (trialkylaluminio)ethylenediamine system, as well as the development of a new method for the fabrication of AlN films. Studies of the corresponding 1:1 reactions are in progress.

Experimental Section

General Methods. All of the syntheses and manipulations were carried out in a N_2 -filled drybox or in Schlenk glassware under N_2 because trimethylaluminum, triethylaluminum, and their compounds with ethylenediamine are air and moisture sensitive.

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(9) Tebbe, F. N. U.S. Patent 4,696,968.

(10) Tebbe, F. N. Eur. Pat. APPL. EP 259164.

(11) Gilbert, J. K.; Smith, J. D. *J. Chem. Soc. A* 1968, 233.

(12) Beachley, Jr., O. T.; Racette, K. C. *Inorg. Chem.* 1976, 15, 2110.

(Caution: these trialkylaluminum compounds are highly inflammable; Me_3Al , in particular, inflames when exposed to air.). Ethylenediamine was distilled from KOH under N_2 ; toluene and benzene were refluxed overnight over sodium under nitrogen and distilled before use. Triethylaluminum was purified by vacuum distillation. Trimethylaluminum, benzene- d_6 , and toluene- d_8 (99%, 99.5%, and 99% pure, respectively, Aldrich Chemical Co.) were used as received.

^1H and ^{13}C NMR spectra were obtained on a Varian XL-200 NMR spectrometer with benzene- d_6 or toluene- d_8 as solvents. An interpulse of zero was used as delay time for all the spectra. ^1H NMR spectra were obtained at 200 MHz by using the residual protons in deuterobenzene ($\delta = 7.15$ ppm) or deuterotoluene ($\delta = 2.09$ ppm) as reference. In cases where quantitation was important, appropriate delays between acquisitions were employed. ^{13}C spectra were obtained on the same instrument at 50.3 MHz. The benzene peak at $\delta = 128.0$ ppm or toluene peak at $\delta = 20.4$ ppm was used as reference. IR spectra were determined with a Perkin-Elmer FT-1800 infrared spectrometer in KBr pellet samples or as neat films between NaCl single-crystal plates. DSC and TGA measurements of the compounds were carried out with a Perkin-Elmer DSC7/TGA7 thermal analysis system with heating rates of 10 $^{\circ}\text{C}/\text{min}$. The atmosphere was either nitrogen that had been passed through a BTS catalyst (BASF Co.) and a molecular sieve column to remove O_2 and H_2O , respectively, or electronic grade ammonia. In all cases the samples were loaded under a dry nitrogen atmosphere. This was accomplished in the case of the TGA measurements by using a specially designed Lexan glovebox that was constructed to enclose the TGA instrument. For the DSC measurements Cu-gasket-sealed, stainless steel DSC cells supplied by the instrument manufacturer were loaded in a glovebox and weighed with a microbalance before and after the loading operation to determine the sample weight. Gas evolution studies were done by heating the precursor with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2 atmosphere and analyzing the volatile fractions by using a Shimadzu GC-9A gas chromatograph with a 6-ft VZ-10 column (Alltech Associates, Inc.). X-ray powder diffraction patterns were measured with a Philips diffractometer employing $\text{Cu K}\alpha$ radiation and a Ni filter. Elemental analyses were obtained from Schwarzkopf Microanalytical Lab. The composition of an AlN thin film sample was measured with a Perkin-Elmer PHI 545C scanning Auger microprobe. This instrument employs a 3-kV Ar^+ ion beam for depth profiling. Al, N, C, O, and Si atomic concentrations were monitored as a function of sputtering time. Sputtering was done with the Ar^+ beam over a 2-mm diameter. A piece of single-crystal AlN was used as a standard to calibrate the sensitivity factors for the calculation of the atomic concentrations during the Auger depth profile. An estimate of sputtering rate was obtained from sputtering a CVD-grown AlN thin film of known thickness. 7 With use of this resulting rate (200 $\text{\AA}/\text{min}$), the film thickness was determined.

Preparation of N,N' -Bis(triethylaluminio)ethylenediamine (Adduct), $[\text{Et}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlEt}_3]$ (I). To a solution of 22.83 g of triethylaluminum (0.2 mol) in 20 mL of benzene at ca -10 $^{\circ}\text{C}$ was added 35 mL of a benzene solution containing 6.01 g (0.1 mol) of ethylenediamine. The mixture was evacuated at room temperature until all the solvent was removed, leaving a colorless clear oil (I). The oil was unstable at room temperature, so it was stored at -10 $^{\circ}\text{C}$. Due to its instability, elemental analysis was not carried out. Characterization is based on the results of ^1H and ^{13}C NMR studies. ^1H NMR (C_6D_6) δ 1.316 (t, 18 H, $J = 8.20$ Hz), -0.031 (q, 12 H, $J = 8.20$ Hz), 1.550 (br, $\text{NCH}_2\text{CH}_2\text{N}$, 4 H), 0.821 (br, NH_2 , 4 H). ^{13}C NMR (C_6D_6) δ 9.74 (AlCH_2CH_3), -0.80 (AlCH_2CH_3), 40.67 ($\text{NCH}_2\text{CH}_2\text{N}$).

Preparation of N,N' -Bis(diethylaluminio)ethylenediamine (Polymeric Amide), $[\text{Et}_2\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NHAlEt}_2]$ (II). A solution of 5 g of the N,N' -bis(triethylaluminio)ethylenediamine adduct (I) from the preceding reaction in 20 mL of benzene was refluxed for 12 h. The resultant product (II), after removal of benzene by evacuation at 60 $^{\circ}\text{C}$, was a colorless and viscous oil, highly soluble in benzene or toluene. Anal. Calcd for $\text{C}_{10}\text{H}_{26}\text{N}_2\text{Al}_2$:

C, 52.63; H, 11.40; N, 12.28; Al, 23.68. Found: C, 52.77; H, 11.38; N, 12.64; Al, 23.28. ^1H NMR, δ 1.35 (br, AlCH_2CH_3), 0.22 (br, AlCH_2CH_3), 0.56 (br, NH), 2.80, 2.39 (br, $\text{NCH}_2\text{CH}_2\text{N}$). ^{13}C NMR, δ 10.03 (s, AlCH_2CH_3), 0.05 (m, AlCH_2CH_3), 45.51 (m, $\text{NCH}_2\text{CH}_2\text{N}$).

The average molecular weight of the polymeric ethylaluminum amide (II) was determined cryoscopically under N_2 with benzene as the solvent. Three concentrations were used for the measurements ($W_{\text{polymer}}/W_{\text{benzene}} = 0.078, 0.091, 0.212$). The corresponding freezing point depressions were found to be 0.26, 0.29, and 0.54 $^{\circ}\text{C}$ as compared with the freezing point of pure benzene, resulting in calculated molecular weights of 1565, 1595 and 2010.

Preparation of N,N' -Bis(ethylaluminio)ethylenediamine (Polymeric Imide), $[\text{EtAINH}_2\text{CH}_2\text{CH}_2\text{NAlEt}_2]$ (III). The polymeric amide II (3 g) was heated at 230 $^{\circ}\text{C}$ under N_2 for about 10 min. During this period the evolution of ethane was observed by GC analysis and the amide became increasingly viscous. Finally a colorless, clear, glassy solid (III) was obtained. Anal. Calcd for $\text{C}_6\text{H}_{14}\text{N}_2\text{Al}_2$: C, 42.85; H, 8.3; N, 16.66; Al, 32.14. Found: C, 45.05; H, 8.97; N, 15.63; Al, 28.38. This solid was insoluble in hydrocarbon solvents; further heating to 400 $^{\circ}\text{C}$ under N_2 gave a dark-brown solid.

Preparation of N,N' -Bis(trimethylaluminio)ethylenediamine (Adduct), $[\text{Me}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlMe}_3]$ (IV). A solution of 6.01 g of ethylenediamine (0.1 mol) in 20 mL of toluene was added dropwise to 55 mL of a toluene solution containing 14.40 g of trimethylaluminum (0.2 mol) that was cooled in a dry ice-isopropyl alcohol bath (-75 $^{\circ}\text{C}$). The resultant white powder (IV) was filtered off and dried under reduced pressure at ambient temperature. Anal. Calcd for $\text{C}_8\text{H}_{26}\text{Al}_2\text{N}_2$: C, 47.06; H, 12.75; Al, 26.47; N, 13.73. Found: C, 46.60; H, 12.48; Al, 26.65; N, 14.17. ^1H NMR δ -0.56 (AlCH_3 , 18 H), 0.60 (br, NH_2 , 4 H), 1.45 (br, $\text{NCH}_2\text{CH}_2\text{N}$, 4 H).

Preparation of N,N' -Bis(dimethylaluminio)ethylenediamine (Polymeric Amide), $[\text{Me}_2\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NAlMe}_2]$ (V). A mixture of 5 g of the adduct (IV) with 20 mL of benzene was refluxed for 12 h. Evolution of a gas was observed at the beginning of the reflux, which as identified as methane by gas chromatographic analysis. After refluxing for 12 h, a solid remained in suspension; the solvent was removed by evacuation at 60 $^{\circ}\text{C}$, yielding a white solid (V) that was insoluble in benzene and toluene. Anal. Calcd for $\text{C}_6\text{H}_{18}\text{Al}_2\text{N}_2$: C, 41.86; H, 10.47; Al, 31.40; N, 16.28. Found: C, 42.54; H, 10.73; Al, 30.80; N, 15.94.

Preparation of N,N' -Bis(methylaluminio)ethylenediamine (Polymeric Imide), $[\text{MeAlNH}_2\text{CH}_2\text{CH}_2\text{NAlMe}]$ (VI). The polymeric amide V (2 g) was heated at 240 $^{\circ}\text{C}$; an oil bubbler allowed methane generated from the decomposition to escape. After 10 min, gas evolution ceased, and a colorless glassy solid (VI) remained. Anal. Calcd for $\text{C}_4\text{H}_{10}\text{Al}_2\text{N}_2$: C, 34.29; H, 7.14; Al, 38.57; N, 20.00. Found: C, 36.08; H, 7.95; Al, 36.93; N, 19.07. Like its ethylaluminum counterpart, it is insoluble in hydrocarbon solvents, and further heating to 400 $^{\circ}\text{C}$ yields a dark-brown solid.

Conversion of the Bis(triethylaluminio)ethylenediamine Adduct I to the Adduct-Amide Intermediate VII. A solution of the adduct I in benzene was heated at 75 $^{\circ}\text{C}$ for 15 min. During the heating, ^{13}C NMR spectra were taken periodically. In a similar experiment, ^1H NMR spectra were taken for a solution heated at 70 $^{\circ}\text{C}$ for various times. The ^{13}C and ^1H NMR spectra observed in this manner were attributed to an adduct-amide intermediate (VII). ^{13}C NMR δ -1.90, -1.03, 0.42, 8.72, 8.88, 10.60, 41.51, 43.39 ppm. ^1H NMR δ 1.548 (t, 9 H), 1.003 (q, 6 H), 0.254 (q, 6 H), -0.148 (two q, 4 H).

Quantitative Measurement of Ethane Produced during the Conversion of the Bis(triethylaluminio) Adduct I to the Adduct-Amide Intermediate VII. A 2.345-g (1.00×10^{-2} mol) sample of the adduct I was heated at 55 $^{\circ}\text{C}$ for 10 min. The ethane generated from the decomposition was trapped in a liquid nitrogen trap in a calibrated volume of a vacuum line containing a Hg manometer. Its amount (0.172 g, 5.73×10^{-3} mol) was calculated from the ideal gas law. The ^1H NMR spectra for the sample before and after the heating indicated that 83% of the adduct had transformed into the adduct-amide intermediate VII, which suggests that 0.202 g (6.73×10^{-3} mol) of ethane should have been generated.

Pyrolyses of the Polymeric Ethylaluminum and Methylaluminum Imides. In separate experiments, the polymeric

(13) Sauls, F. C.; Interrante, L. V.; Jiang, Z. Me_3AlNH_3 Formation and Pyrolytic Methane Loss; Thermodynamics, Kinetics and Mechanism. *Inorg. Chem.*, in press.

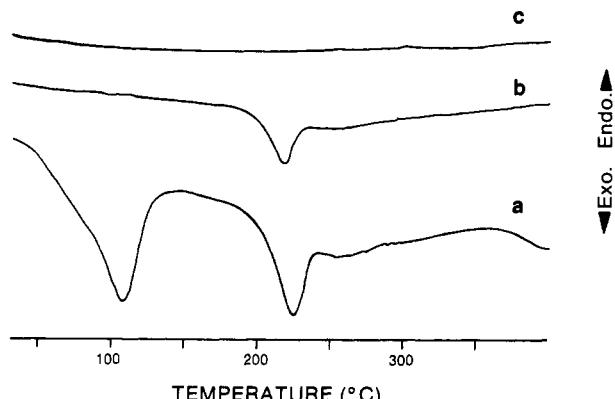


Figure 1. DSC curves for (a) $\text{Et}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{Et}_3$ (I), (b) $\text{Et}_2\text{AlNHCH}_2\text{CH}_2\text{NHAIEt}_2$ (II), (c) $\text{EtAlNCH}_2\text{CH}_2\text{NAlEt}$ (III).

imides III and VI were loaded into tungsten boats and inserted into a quartz tube. The quartz tube was heated at 450, 600, or 1000 °C for 12 h under a flow of purified N_2 or NH_3 in a programmable furnace. The pyrolysis products were unloaded in the glovebox and ground with a mortar and pestle for X-ray diffraction measurements.

Fabrication of Aluminum Nitride Thin Films. In a N_2 -filled glovebox, a solution of the bis(diethylaluminio)-en amide II in benzene (3–7%, by weight) was dropped onto a Si(100) wafer section, and the excess solution was drained off. The wafer was then heated at 100 °C on a hot plate for 5 min. The resultant sample was placed in a quartz tube and heated at 900 °C for 24 h under a flow of NH_3 . A smooth, thin coating had formed on the Si substrate. The composition of this coating was determined by Auger electron spectroscopy, and the thickness was estimated by Auger depth profiling, with Ar^+ sputtering.

Results and Discussion

***N,N'*-Bis(Triethylaluminio)ethylenediamine System.** The bis(triethylaluminio)-en adduct, $\text{Et}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlEt}_3$ (I), slowly decomposes at room temperature, accompanied by the evolution of a gas. Figure 1a shows the results of DSC studies of the adduct from 40 to 400 °C, which indicates that the adduct undergoes two exothermic processes (one at 30–130 °C, the second at 180–240 °C). Figure 2 shows the results of analyses of the evolved gases by gas chromatography. Ethane is clearly the principal component of the gaseous products in both temperature ranges with the relative amount of ethylene becoming significant only beyond ca. 250 °C. Prior DSC studies of the $\text{R}_{3-x}\text{AlNH}_{3-x}$ ($\text{R} = \text{Me}$, Et, *i*-Bu) compounds have yielded enthalpies for the adduct-to-amide or amide-to-imide conversions (one alkane molecule is lost in each of the above processes) in the range –70 to –80 kJ/mol.⁶ In the case of the bis(triethylaluminio)-en adduct (I), a ΔH of –130.5 kJ/mol was observed for the first exothermic process, which corresponds reasonably well with the assumption that 2 mol of ethane is lost during this reaction, especially considering the instability of the adduct and the likelihood that it was partially converted to the amide in the process of loading the DSC sample cell. Further confirmation of the stoichiometry of this reaction is obtained from the NMR spectra of the adduct and amide as well as elemental analysis of the amide product obtained after extended reflux of the adduct in benzene solution. Therefore, we associate the first exothermic process in the DSC to the loss of the first 2 equiv of ethane in the conversion of the adduct to amide (eq 1).

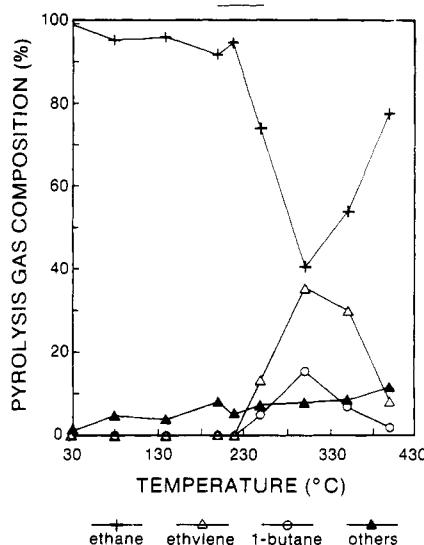
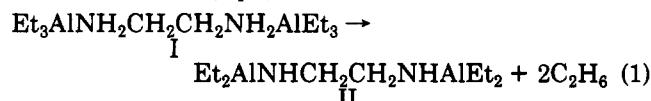
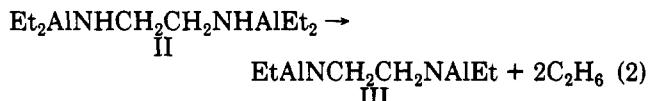


Figure 2. Relative amounts of the volatile products observed by GC analysis on heating $\text{Et}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlEt}_3$ (I) from room temperature to 400 °C at 10 °C/min.

The as-synthesized amide is a highly viscous material from which fiber is easily pulled. Its high viscosity and molecular weight (ca. 1600) suggests an oligomeric or polymeric structure in which Al–N bonding has linked the $\text{Et}_2\text{Al}-\text{en}-\text{AlEt}_2$ units into extended chains. The solubility of the amide in hydrocarbon solvents suggests further the prospect of its application as a solution-based precursor for AlN fiber or thin films. Indeed, our preliminary studies indicate that it can be used to generate AlN films on Si and other substrates (vide infra).

In comparison with the adduct I, the DSC trace for the amide II (Figure 1b) shows a similar exothermic peak at ca. 190–235 °C, without the peak at lower temperature associated with the adduct → amide transformation (Figure 1a). The heat evolved during the 190–235 °C transition ($\Delta H = -127.6$ kJ/mol) again corresponds reasonably well to the expected exotherm associated with the loss of two alkane molecules and the further extension of the Al–N bonding network.⁶ This latter transition is thus attributed to the next stage of the precursor thermolysis process, the conversion of the amide to the imide (eq 2).



In this case the product is a glassy solid that is insoluble in hydrocarbon solvents. Its elemental analysis is again consistent with the expected imide composition II, although the presence of a small amount of unconverted amide is suggested by both the analysis and the IR spectrum, to be discussed in more detail later.

The effects of further heating of this imide product under nitrogen and ammonia were investigated by using thermal gravimetric analysis (TGA). Figure 3a shows the TGA of the imide under a flow of N_2 . The small weight loss below 180 °C is attributed to evaporation of some low molecular weight oligomers or solvent or decomposition of the amide remaining in the sample (obtained by heating the amide). The actual decomposition appears to start near 180 °C and ends at about 430 °C. As is indicated by the data in Figure 2, ethane continues to be the major component of the gaseous byproducts, although ethylene and higher hydrocarbons are also produced in substantial amounts in the region of the major weight loss for the

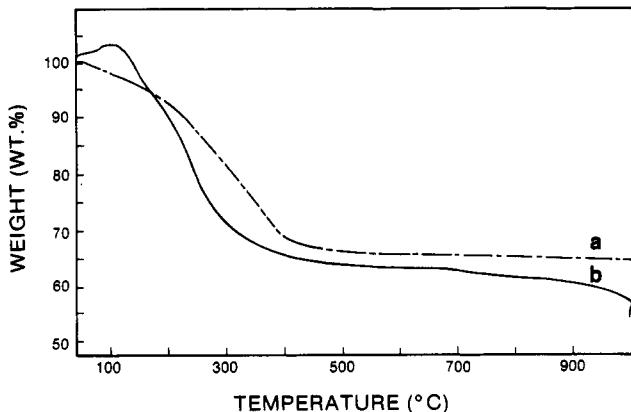


Figure 3. TGA results for $\text{EtAlNCH}_2\text{CH}_2\text{NAIET}$ (III) under (a) nitrogen, (b) ammonia. Note: the temperature was held at 1000 °C for 1 h in experiment b.

amide (ca. 200–400 °C). A possible source of the ethylene is the following β -elimination process:



This reaction has considerable precedent in earlier studies of the thermal decompositions of organoaluminum compounds.^{14,15} In the latter portion of this weight loss region, beyond ca. 300 °C, it seems from Figure 2 that ethane again takes over as the predominant product. However, it should be noted that any hydrogen produced would not have been detected by the analysis procedure employed; moreover, the amount of gas evolved beyond 300 °C is likely to be substantially less than that produced below this temperature (Figure 3a).

The higher TGA yield than expected (the theoretical yield for the imide to AlN conversion is 48.8%, whereas a 64% ceramic yield is observed) along with the black color of the pyrolysis product suggests that carbon is retained in the solid on pyrolysis of the imide under nitrogen.

It is notable that no obvious thermal effect is observed in the DSC (Figure 1c) trace of the imide even though a significant weight loss is found from its TGA curve below 400 °C. Similar observations were made in prior DSC studies of the corresponding $[\text{EtAlNH}]_x$ and $[\text{MeAlNH}]_x$ imide systems, suggesting that this last pyrolysis step is fundamentally different from the adduct–amide and amide–imide conversions.⁶

The TGA (Figure 3b) curve of the imide III under a flow of NH_3 shows two important differences when compared with that under N_2 . First, the weight of the TGA sample increases at low temperature and then starts to decrease after 115 °C. Second, unlike the corresponding TGA under N_2 , where weight loss is complete at about 430 °C, the TGA of the imide in NH_3 shows a further weight loss above 670 °C. To account for the initial weight gain, the following experiment was carried out: NH_3 gas was added to a flask containing some imide at room temperature. After 5 min, a liquid was found in the flask that was identified as ethylenediamine by ^1H NMR. The above experiment indicates that ammonia displaces ethylenediamine from the polymeric imide, presumably forming an ethylaluminum imide product. Therefore, the increase in the TGA sample weight is attributed to the addition of ammonia into the system. The weight starts to decrease when the ethylenediamine is vaporized and/or the new

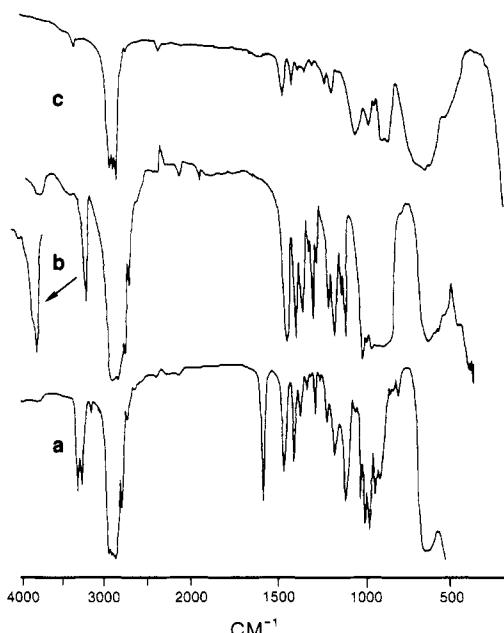


Figure 4. FT-IR spectra of (a) $\text{Et}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlEt}_3$ (I), (b) $\text{Et}_2\text{AlNHCH}_2\text{CH}_2\text{NHAIET}_2$ (II), (c) $\text{EtAlNCH}_2\text{CH}_2\text{NAIET}$ (III).

product (presumably polymeric EtAlNH) starts to decompose.

Further investigation into the structures of these compounds and their pyrolysis products was carried out by infrared spectral measurements. The spectrum of the adduct I (Figure 4a) shows three strong peaks that correspond to the asymmetric stretching (3320 cm^{-1}), symmetric stretching (3260 cm^{-1}), and bending vibrations (1585 cm^{-1}) of the NH_2 groups in the adduct. In the spectrum of the amide II (Figure 4b) the occurrence of a sharp peak near 3250 cm^{-1} and the disappearance of the peak at 1585 cm^{-1} indicate the conversion of NH_2 to N-H . The observation of a large shoulder on the high-frequency side of the N-H stretching band is attributed to the presence of different isomeric units in the polymeric amide; for instance, in the case of a ring-chain polymer (vide infra), cis and trans isomers would be expected. The spectrum of the imide IV (Figure 4c) shows a small peak at 3359 cm^{-1} , which is attributed to the stretching vibration of some residual N-H groups. This result is consistent with the TGA of the imide and its elemental analysis.

In an effort to obtain information regarding the mechanism of the adduct-to-amide decomposition, as well as the structures of any intermediates, ^1H and ^{13}C NMR spectra of solutions of the adduct heated at different temperatures for varying amounts of time were determined. Figure 5 shows the ^{13}C NMR spectra of the as-synthesized adduct as well as those of samples heated at 75 °C for 5 and 10 min. These spectra show a decrease in the relative intensities of the peaks attributed to the adduct I (-0.80 , 9.74 , and 40.67 ppm) with increasing heating time. At the same time, new peaks at -1.90 , -1.03 , 0.42 , 8.72 , 8.88 , 10.60 , 41.51 , and 43.39 ppm grow in. With further heating these peaks are eventually replaced by those characteristic of the amide II. The corresponding changes in the ^1H NMR spectra as the adduct is refluxed in benzene are shown in Figure 6. Again, a new set of peaks, at 1.548 (t), 1.003 (q), 0.254 (q), and -0.148 ppm (2q) grow in as the corresponding adduct peaks disappear. As with the ^{13}C NMR spectra, the new peaks remain in the same position and in a constant integration ratio during the entire decomposition process. These new peaks in the ^{13}C and ^1H NMR spectra are attributed to an intermediate

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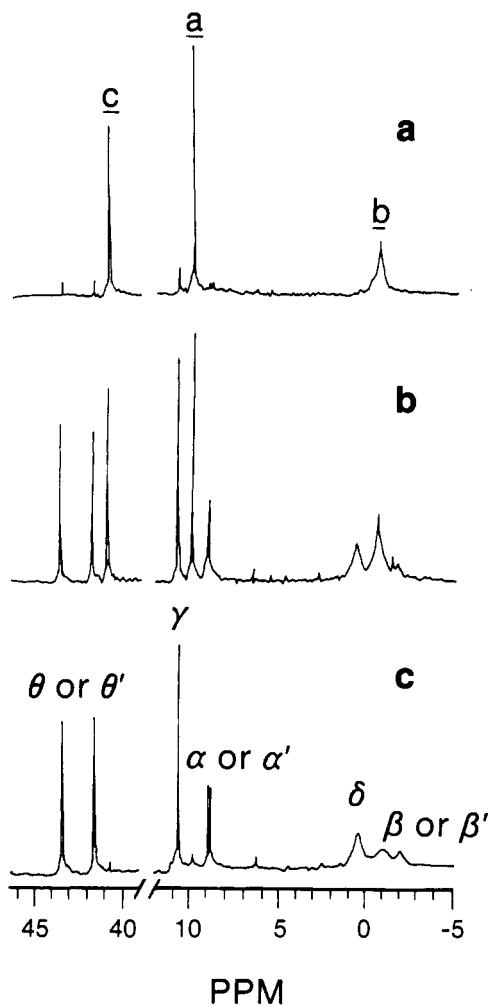
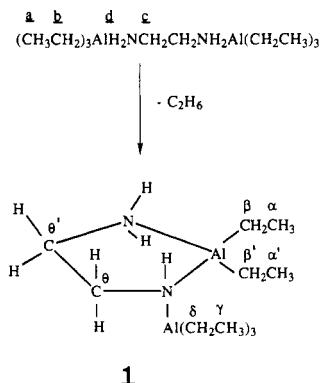


Figure 5. ^{13}C NMR spectra of $\text{Et}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlEt}_3$ (I) in C_6D_6 , (a) as-synthesized, (b) after heating at $75\text{ }^\circ\text{C}$ for 5 min, (c) after heating at $75\text{ }^\circ\text{C}$ for 10 min. Note: a-d and all the Greek letters refer to both H and C atoms on the structures; all spectra were obtained at $10\text{ }^\circ\text{C}$.

(VII) in the conversion of the adduct to the amide.

The structural assignment for this intermediate (1) is based on a consideration of the chemical shift values, the



splitting pattern, and the relative intensities of the ^{13}C and ^1H NMR peaks. Thus, in Figure 5 the peaks labeled γ and α, α' are in the same chemical shift region as the α peaks in the spectrum of the adduct, which were attributed to the CH_3 C atoms of the ethyl groups on Al. Similarly, the δ and β, β' peaks appear to replace the β peak of the adduct, which was assigned to the CH_2 C atom attached to Al. The peaks at lowest field, labeled c in the spectrum of the adduct, are clearly associated with the ethylenediamine CH_2 groups and are replaced by the θ, θ' peaks of

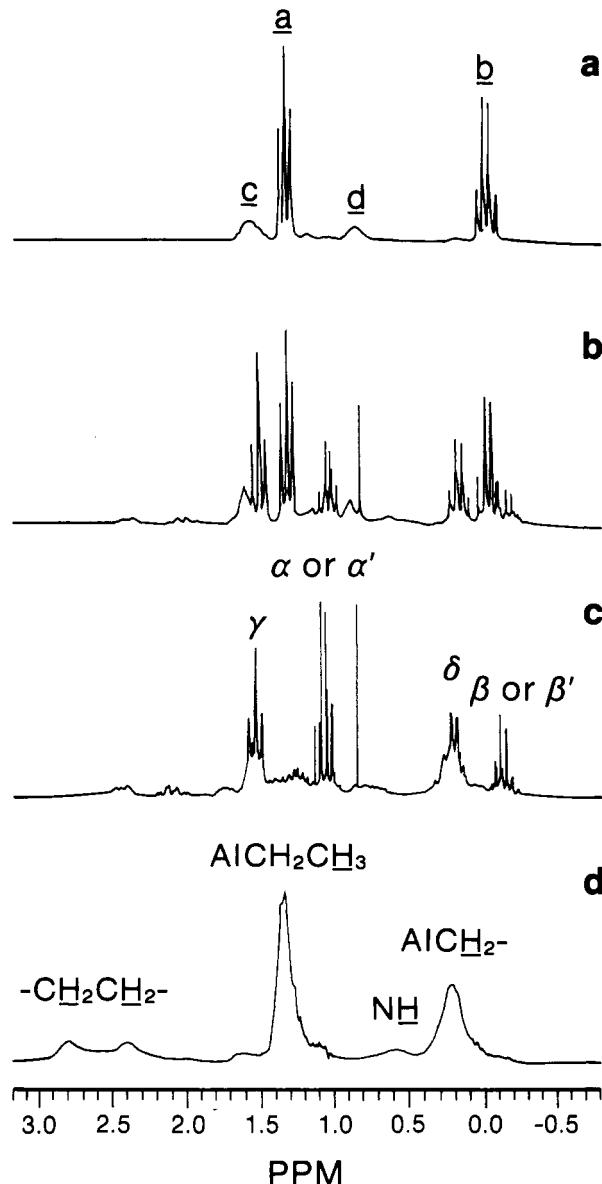


Figure 6. ^1H NMR spectra of $\text{Et}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlEt}_3$ (I) in C_6D_6 , (a) as-synthesized, (b) after heating at $70\text{ }^\circ\text{C}$ for 3 min, (c) after heating at $70\text{ }^\circ\text{C}$ for 10 min, (d) refluxed in benzene for 12 h. (See Figure 5 for peak assignments). Note: all spectra were obtained at $10\text{ }^\circ\text{C}$.

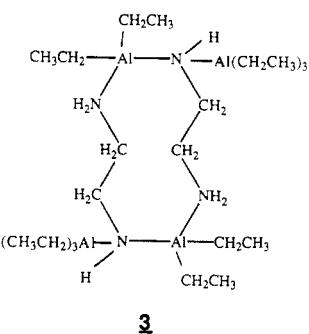
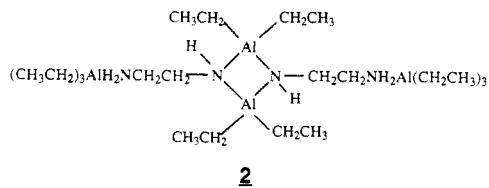
the intermediate. The fact that the γ peak appears on the low-field side of the α peak of the adduct whereas the α and α' peaks occur at higher field, is consistent with the expected deshielding of the $\text{Al}-\text{CH}_2\text{CH}_3$ carbon as the electron density on N is shared with the second Al atom of the five-membered ring, and the increased shielding of the α, α' carbons in the relatively more electron-rich environment provided by the two N atoms in this ring. Similarly, the δ and β, β' peaks in the ^{13}C spectrum, as well as the corresponding ^1H NMR peaks associated with these $\text{Al}(\text{CH}_2\text{CH}_3)_x$ groups, show the same shifts to lower and higher field as would be expected on the basis of this structural assignment. The doubling of the α, α' and β, β' peaks is consistent with the unsymmetrical environment of the two $(\text{Al})-\text{CH}_2\text{CH}_3$ groups in the chelate ring structure shown in 1. Thus, the apparent quartet in the ^1H NMR spectrum at 1.08 ppm (Figure 6c) is attributed to the combination of two closely spaced triplets, as would be expected for the α and α' H atoms in this structure. The peaks associated with the θ and θ' CH_2 groups are not clearly resolved in the ^1H NMR spectrum but are tenta-

tively assigned to the complex multiplets observed in the vicinities of 2.1 and 2.4 ppm in the spectrum shown in Figure 6c.

The intensity ratios of the respective γ and α , α' , and δ and β , β' peaks in the ^1H NMR spectrum and even in the ^{13}C spectrum are close to the expected 3:2 for this five-membered ring structure. Similarly, selective proton decoupling experiments provide confirmation for the respective ^1H and ^{13}C NMR peak assignments.

From the above NMR studies we propose that the adduct initially transforms into a metastable adduct-amide intermediate, releasing only 1 equiv of ethane prior to further decomposition. In support of this conclusion, a quantitative analysis of the ethane produced during the conversion of the adduct to the intermediate yielded approximately 85% of the expected 1 mol of ethane/mol of adduct. Unfortunately, this intermediate is unstable at room temperature, converting gradually to the polymeric amide, which has rendered its isolation and detailed characterization quite difficult. Efforts to determine its molecular weight by cryoscopy measurements in benzene were unsuccessful, yielding highly irreproducible results.

In the absence of molecular weight measurements, alternative structures containing unchelated ethylenediamine units, e.g., dimeric species of the composition $(Et_2Al)_2(Et_3Al)_2(en)_2$, involving either open (2) or bridging (3) en ligands, cannot be ruled out by the stoichiometry considerations noted above.



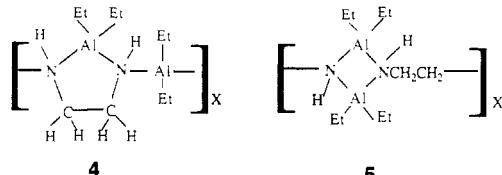
However, on the basis of the NMR spectra and entropy considerations, such structures are viewed as less likely than the chelated monomeric structure 1. In the case of 2, which can have cis and trans isomers, a total of three different environments for the Et groups of the AlEt_2 functionalities would be expected, assuming that both isomers are present. The observed NMR spectra indicate only two AlEt_2 -Et environments, which would be expected only if the cis isomer was the exclusive product. Such a situation does have precedent in the earlier work of Beachley and Racette on alkyl-substituted ethylenediamine derivatives of the type $[\text{R}_2\text{AlR}'\text{NCH}_2\text{CH}_2\text{NR}'']_x$.¹² In this case a dimeric structure ($x = 2$) was evidenced for certain combinations of R, R', and R'' by molecular weight measurements. On the basis of the spectral data obtained, a molecular structure analogous to that of 2 but without the terminal AlR_3 groups was suggested for these dimers in which the cis conformation was apparently strongly preferred. It is therefore possible that such a structure

pertains to the adduct-amide intermediate that we have evidenced; however, an additional argument against this structure and in favor of the monomeric chelated structure 1, which also has precedent in the work of Beachley and Racette,¹² is provided by the chemical shift data obtained for the intermediate VII and its adduct precursor I. In particular, it is difficult to rationalize on the basis of structure 2 the substantial chemical shift difference observed (0.3 ppm) in the ^1H NMR spectrum for the terminal AlEt_3 groups of the intermediate relative to that found for the adduct. Indeed, we would expect that the environment of the Et groups for these AlR_3 groups should be quite similar, in the absence of some extraordinary association between the terminal NH_2AlEt_3 groups in the dimer.

Higher oligomers of 2, such the trimer, would have much more complicated NMR spectra than those observed, due to the various structural isomers expected. As for the other dimeric species 3, although NMR spectra similar to that of 1 would be expected, the 10-membered ring structure appears less likely on the basis of entropy considerations.

In Figure 6d the ^1H NMR spectrum of a benzene solution of the adduct after 12 h of reflux is shown. At this stage essentially all of the adduct has transformed into the polymeric amide, $[\text{Et}_2\text{AlNHCH}_2\text{CH}_2\text{NHAIEt}_2]_x$, which is suggested by the ^1H NMR assignments (Figure 6d) and the FT-IR spectrum (Figure 4b).

The fact that the amide is very soluble in benzene or toluene and that fibers can be pulled easily from the neat liquid suggests that it has a long-chain polymeric structure. Cryoscopic measurements in benzene indicate that its average molecular weight is around 1600. The two alternative structures 4 and 5 are proposed.



Structure 4 would be formed if a pendant AlEt_3 group of the proposed five-membered ring intermediate 1 reacts with the NH_2 functionality in another five-membered ring compound, with the loss of 1 equiv of ethane. Structure 5 is an isomer of 4, in which the chelating ethylenediamide is converted to a bridging group that links four-membered Al_2N_2 rings. The available evidence does not permit a decision between these or other alternative structures; however, the four-membered Al_2N_2 rings in the latter structure are at least consistent with prior observations on N-alkyl-substituted diorganoaluminum amides.¹⁶⁻¹⁸ The splitting of the peaks in the ^1H NMR spectrum assigned to the methyl groups (labeled in Figure 6d) could be attributed to the different environments of the bridging AlEt_2 and ring AlEt_2 units of structure 4 or to the presence of cis and trans configurations in structure 5. The potential existence of cis and trans isomers in either structure may also explain the existence of the shoulder on the N-H stretching band and the observation of separate resonances for the two methylene groups of the CH_2CH_2 linkage in the ^1H NMR spectrum. The degree of polymerization, i.e. x , would be 7.4 on the basis of the above proposed structures and the average molecular weight of 1600.

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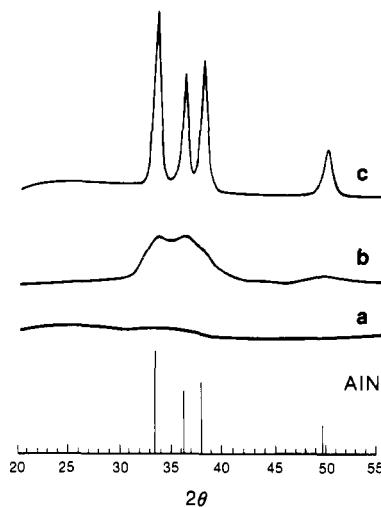


Figure 7. XRD patterns for $\text{EtAlNCH}_2\text{CH}_2\text{NAlEt}$ (III) after heating under ammonia for 12 h at (a) 450, (b) 600, (c) 1000 °C.

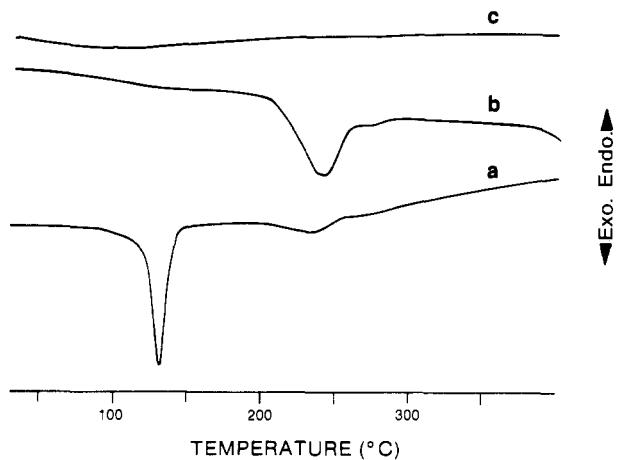


Figure 8. DSC curves for (a) $\text{Me}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlMe}_3$ (IV), (b) $\text{Me}_2\text{AlNHCH}_2\text{CH}_2\text{NAlMe}_2$ (V), (c) $\text{MeAlNCH}_2\text{CH}_2\text{NAlMe}$ (VI).

The conversion of the imide to AlN on pyrolysis in ammonia was confirmed by powder XRD studies of the product. The pyrolysis products obtained on heating at 450 and 600 °C under either nitrogen or ammonia are yellow solids; however, the product after heating to 1000 °C for 12 h in ammonia is an off-white material, whereas under nitrogen a black solid is obtained after the 1000 °C heating. X-ray diffraction studies of the ammonia pyrolysis products (Figure 7) show that a crystalline AlN phase (2H) is formed between 450 and 600 °C under these conditions. Further heating under ammonia at 1000 °C for 12 h results in improved crystallinity. In contrast, XRD studies of the pyrolysis product obtained after heating at 1000 °C for 12 h under a flow of nitrogen does not indicate the presence of any crystalline phases.

A uniform, adherent, thin film was obtained by solution coating of the amide in benzene on a silicon wafer and subsequent pyrolysis under ammonia at 900 °C. The composition of this thin film as determined by Auger electron spectroscopy, after Ar^+ ion sputtering to remove surface contamination, approximated that of AlN with a small amount of residual carbon and oxygen (i.e., 4.6 and 5.3 at. %, respectively). The thickness of the film was estimated to be ca. 200 Å on the basis of an Auger depth profile study.

***N,N'*-Bis(trimethylaluminio)ethylenediamine System.** As compared with the triethylaluminum system,

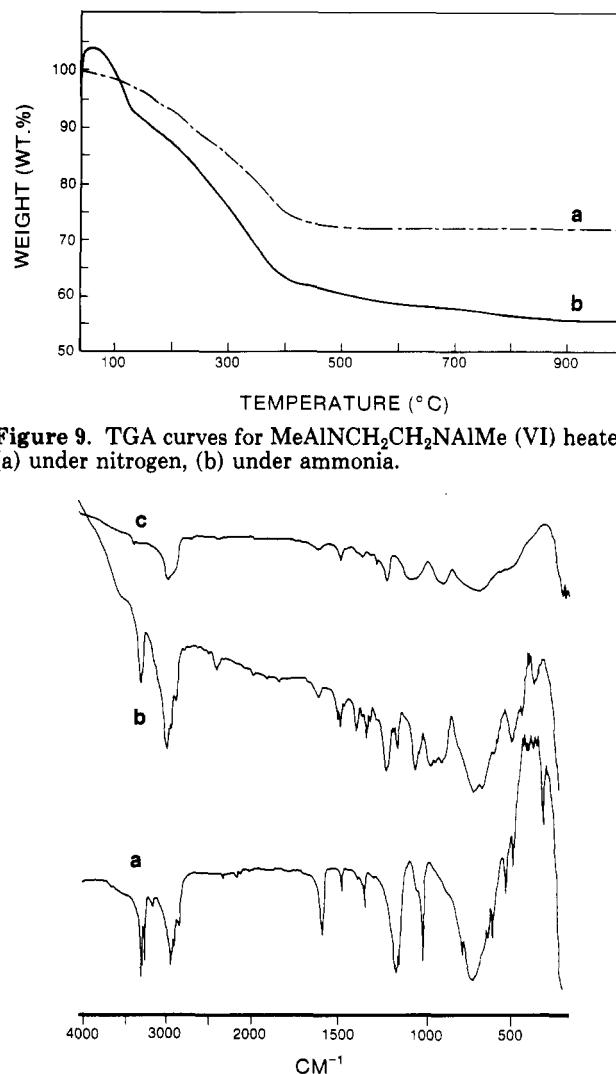


Figure 9. TGA curves for $\text{MeAlNCH}_2\text{CH}_2\text{NAlMe}$ (VI) heated (a) under nitrogen, (b) under ammonia.

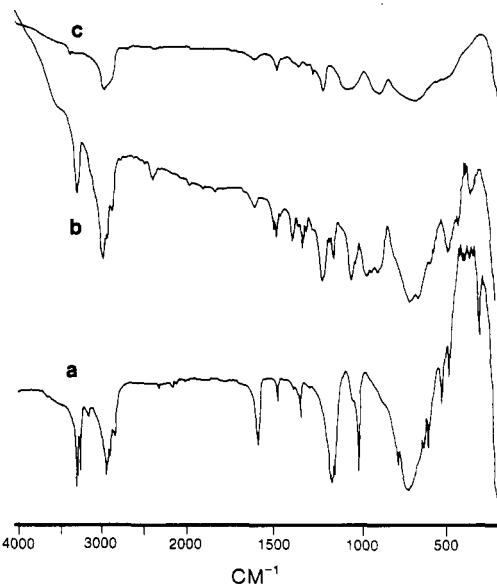
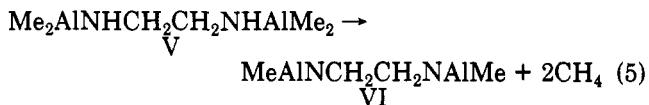
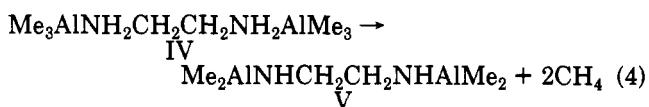


Figure 10. FT-IR spectra of (a) $\text{Me}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlMe}_3$ (IV), (b) $\text{Me}_2\text{AlNHCH}_2\text{CH}_2\text{NAlMe}_2$ (V), (c) $\text{MeAlNCH}_2\text{CH}_2\text{NAlMe}$ (VI).

the trimethylaluminum adduct IV and amide V are solids rather than liquids. The solubility of these compounds in hydrocarbon solvents is very low. However, the adduct, polymeric amide, and imide VI show very similar chemistry compared with their triethylaluminum counterparts. Figure 8 shows the results of the DSC studies for these three compounds. As in the triethylaluminum system, the adduct experiences two exothermic processes below 400 °C that are attributed to the following decomposition reactions:



The enthalpies are -142.4 kJ/mol (calculated from the first peak of Figure 8a) and -135.3 kJ/mol (calculated from Figure 8b), respectively, which suggests that 2 equiv of methane molecules are lost in each exothermic process.⁶ From the DSC curve of the adduct IV we can see that the adduct starts to decompose above 90 °C, i.e., it is much more stable than its triethylaluminum counterpart, which decomposes at a significant rate even at room temperature.

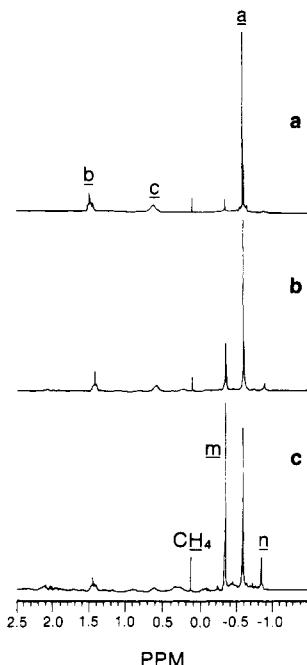


Figure 11. ^1H NMR spectra of $\text{Me}_3\text{AlNH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{AlMe}_3$ (IV) in C_6D_6 , (a) as-synthesized, a $\text{Al}(\text{CH}_3)_3$, b $\text{NCH}_2\text{CH}_2\text{N}$, c NH_2 , (b) heated at 80°C for 3 min, (c) heated at 80°C for 15 min. *m* and *n* are attributed to an intermediate.

The same trend is also observed for both the $\text{Me}_3\text{Al}:\text{NH}_3$ and $\text{Et}_3\text{Al}:\text{NH}_3$ systems; here the Me compound decomposes at its melting point of ca. 60°C , whereas the Et compound decomposes below room temperature.⁶ Figure 8b indicates that the polymeric amide V begins to decompose at 190°C , which is the same temperature as observed for the triethylaluminum polymeric amide. However, this decomposition for the ethyl compound finishes about 25°C lower than for the methyl derivative. Also analogous to the ethyl system, no thermal effect is observed for the methyl imide below 400°C . Figure 9 shows the TGA curves of the imide under nitrogen and ammonia. The TGA under ammonia shows a good quantitative conversion of the imide to AlN (theoretical yield, 58%; found, 56%), whereas an appreciably higher ceramic yield is observed

on heating to 1000°C under nitrogen.

Figure 10 shows the IR spectra of the adduct IV, amide V, and imide VI. The IR absorption peaks in the N-H stretching and bending region for these three spectra are, in general, as expected for the appropriate $\text{Me}_{3-x}\text{AlNH}_{2-x}\text{CH}_2\text{CH}_2\text{NH}_{2-x}\text{AlMe}_{3-x}$ ($x = 0-2$) structure. However, a small broad peak near 1587 cm^{-1} is found in Figure 10b, which corresponds to the NH_2 bending vibration. This suggests that some adduct is still left in the polymeric amide after 12 h of reflux in benzene. Moreover, a small amount of the amide is found in the imide, which can be seen from the small N-H stretching vibration near 3350 cm^{-1} in the spectrum of the imide (Figure 10c).

^1H NMR studies were carried out in an effort to determine if an intermediate analogous to that observed for the *N,N*-bis(triethylaluminio)ethylenediamine compound occurs in the conversion of the Me adduct to the amide. Figure 11 shows that two peaks (-0.84 , -0.30 ppm) start to grow in when the adduct solution is heated; we attribute these two peaks to an intermediate decomposition product. The intensity ratio (3:1) of these two peaks, which does not change during the heating process, is not consistent with the en-chelated structure proposed for the ethyl aluminum adduct-amide intermediate 1, nor is it consistent with either of the alternative structures 2 or 3. Unfortunately, the solubility of the adduct, as well as that of the decomposition product, is so low that determination of the ^{13}C NMR spectra was not possible. Similarly, attempts to obtain single crystals suitable for a structure determination were not successful. Therefore, we lack sufficient evidence to propose a structure at the present time.

Finally, as with the ethyl compound, highly crystalline AlN was obtained on pyrolysis of the polymeric methyl imide at 1000°C for 12 h under a flow of ammonia.

Acknowledgment. We thank Bingxi Sun for the Auger analysis of the AlN thin film. Financial support for this work was provided by the Air Force Office of Scientific Research (AFOSR) and the Office of Naval Research.

Registry No. I, 127971-40-8; II, 127971-33-9; III, 127971-35-1; IV, 127971-41-9; V, 127971-37-3; VI, 127971-39-5; VII, 127971-42-0; triethylaluminum, 97-93-8; ethylenediamine, 107-15-3; trimethylaluminum, 75-24-1.