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Shaping potentialities of aluminum nitride polymeric precursors Preparation of thin coatings and 1D nanostructures in liquid phase

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Abstract

The present paper is focused on the synthesis of a series of poly[*N*-(alkylimino)alanes] of the type $[HAlNR]_n$ as preceramic polymers for the preparation of aluminum nitride (AlN). Polymers were characterized by means of Fourier transform infrared spectra (FT-IR), liquid-state ^1H and ^{13}C NMR spectrometry and elemental analyses. The polymers were prepared in different physical states going from viscous liquid to solid (soluble and/or fusible) compounds with the decrease of the carbon content in the polymer chain. Such properties offer potentialities in the preparation of complex forms of ceramics including thin coatings and 1D nanostructures. AlN thin coatings and 1D nanostructures were obtained from a solution of poly[*N*-(isopropylimino)alane] in toluene followed by heat-treatment in flowing ammonia up to 1000 °C resulting in a ceramic yield of 50.6%. Subsequent heat-treatment to 1800 °C in flowing nitrogen allowed the production of crystalline AlN coatings and nanorods identified by Raman spectrometry and X-ray diffraction.

Keywords: Poly[*N*-(alkylimino)alane]; FT-IR; NMR; Thin coatings; Nanostructures

1. Introduction

Pyrolytic conversion of preceramic polymers displaying metal–nitrogen and/or metal–carbon bonds has been intensively investigated since the early 1990s for the preparation of nitride or carbide-based non-oxide ceramics, most of them being silicon nitride (Si_3N_4) and silicon carbide (SiC)[1,2]. The composition of such preceramic compounds can be adjusted at the molecular scale to design the composition and the microstructure of the derived ceramics in a way not known from classical methods. In addition, by tailoring the synthesis procedure and functionality of such polymers, it is possible to control their physical state, i.e., liquid or solid (soluble and/or fusible), for the preparation of ceramics with a desired shape (nanofiber, thin coating, ...) using conventional shaping processes. Aluminum nitride (AlN) is one of the most important nitride-based ceramics which exhibits a very high thermal conductivity[3,4] and an electric insulation (large energy gap[5]). Such properties are interesting for the preparation of AlN nanoreinforced-organic polymers (i.e., for increasing the thermal conductivity of polymers) or AlN coated-structures (i.e., for producing radiation-transparent structures). Among polymeric precursors containing Al–N bonds, poly[*N*-(alkylimino)alanes] of the type $[HAlNR]_n$ represent a well-known cage/cyclic-type compound historically proposed by Ruff and Hawthorne[6]. Such compounds represent a source of both aluminum and nitrogen elements with the correct aluminum-to-nitrogen ratio and a postulated cage/cyclic-type structure which should undergo limited structural rearrangements to prepare AlN in its hexagonal structure[6–11].

Some of the poly[*N*-(alkylimino)alanes] of the type $[HAlNR]_n$ ($R = H$, Et, ^{i}Pr) have been already used as precursor source of AlN[10–12], but little efforts have been focused on both the synthesis of such polymers and their potentialities for shaping process. For example, whereas most of AlN thin coatings have been obtained by vapour deposition techniques[12], only one example dedicated to dip-coating in a solution derived from bis(diethylaluminio)ethylenediamine has been reported by Jiang and Interrante[13]. Besides, no work reports the potentialities of poly[*N*-(alkylimino)alanes] as precursors for nanostructured AlN.

It is therefore the aim of this paper to describe the synthesis and the characterization of a series of poly[*N*-

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Table 1
Properties of polymers **1**–**6**

R	State	Chemical formulae[a]
1: CH_3	Solid	$[Al_{1.0}N_{1.5}C_{1.8}H_{7.2}Li_{1.2}Cl_{0.8}]_n$
2: CH_2CH_3	Solid	$[Al_{1.0}N_{0.9}C_{2.1}H_{6.8}]_n$
3: $CH(CH_3)_2$	Solid	$[Al_{1.0}N_{0.9}C_{2.8}H_{8.1}]_n$
4: $CH_2CH(CH_3)_2$	Solid	$[Al_{1.0}N_{1.0}C_{4.3}H_{10.8}]_n$
5: $(CH_2)_4CH_3$	Liquid	$[Al_{1.0}N_{0.9}C_{5.7}H_{14.1}]_n$
6: $(CH_2)_7CH_3$	Liquid	$[Al_{1.0}N_{0.8}C_{7.7}H_{20.1}]_n$

[a] Empirical formulas standardized at $Al_{1.0}$. Oxygen is <2% and omitted.

(alkylimino)alanes] suitable as precursors of thin coatings and nanostructures in the soluble state.

2. Experimental procedure

2.1. Reagents and solvents

Synthesis procedures were carried out in flowing purified argon using Schlenk techniques. Lithium aluminum hydride (95%) was obtained from Sigma–Aldrich as pellets. Alkylammonium chloride compounds were home made by the reaction of primary alkylamine with hydrochloric acid, and then dried at 120 °C prior to use. Diethyl ether was purified by distillation from sodium and calcium chloride. Ammonia and nitrogen were used in their as-received state (>99.999%).

2.2. Polymer and ceramic preparation

Poly[*N*-(alkylimino)alane] of the type $[HAlNR]_n$ was prepared according to the following reaction:

$$n\,LiAlH_4 + n\,RNH_3Cl \xrightarrow[T=-78\,^\circ C]{Et_2O} 1/n[HAlNR]_n + 3n\,H_2 + n\,LiCl$$

Fine powders of $LiAlH_4$ were carefully dissolved in Et_2O, and then added dropwise to a solution of an excess of RNH_3Cl in Et_2O at −78 °C under vigorous stirring. Lithium chloride precipitated immediately and hydrogen was removed. After the complete addition of alkylammonium chloride, the mixture was stirred for 10 min more at −78 °C, and then, allowed to warm up to RT overnight. The solution was filtered through a pad of Celite, then concentrated in a high vacuum (RT/10^{-2} mbar) to produce six poly[*N*-(alkylimino)alanes] $[HAlNR]_n$ going from **1** to **6** (Table 1) as air- and moisture-sensitive compounds at RT. Polymer-to-ceramic conversion of such compounds was first carried out in a silica tube furnace in flowing ammonia from 25 to 1000 °C (60 °C/h; dwell time of 2 h). A second thermal step was performed in a graphite furnace in flowing nitrogen from 25 to 1800 °C (100 °C/h; dwell time of 2 h).

2.3. Characterization

Polymers were analyzed at RT with respect to their IR and NMR spectra. Fourier transform infrared spectra (FT-IR) were obtained from a Nicolet Magna 550 Fourier transform-infrared spectrometer in a KBr matrix for solids (dried at 120 °C in air) and between CsI windows for viscous liquids. Liquid-state ^1H and ^{13}C NMR spectra were obtained in C_6D_6 at 300 and 75 MHz, respectively. Chemical analyses were made at the *Service Central de Microanalyse du CNRS* (Vernaison, France). Thermogravimetric analyses (TGA, Setaram TGA 92 16-18) of the polymer decomposition was carried out in a mixture of ammonia and nitrogen atmosphere (50 cm^3/min) from 25 to 1000 °C (1 °C/min) in silicate crucibles.

3. Results and discussion

3.1. Polymer synthesis

Following the synthesis procedure described in Section 2, poly[*N*-(alkylimino)alanes] are recovered as viscous liquids or solids depending on the nature of the R pendent group in $[HAlNR]_n$. Change in the physical state (from solid to liquid) of polymers with increasing R is caused by the steric hindrance around the amino function in alkylammonium chloride which probably restricts the reaction with $LiAlH_4$. Table 1 gives some properties of polymers **1**–**6**.

It should be mentioned that the synthetic pathway described above is not suitable for the preparation of $[HAlNCH_3]_n$ (poly[*N*-(methylimino)alane] **1**). This compound is insoluble in all common organic solvents, and it is difficult to separate the polymer from the chloride residue as illustrated with the identification of chloride impurities by elemental analysis (Table 1). This problem has been already reported for the preparation of a polymer with R = H [9]. The yields found for compounds **2**–**6** are high in accordance with their excellent solubility (>86% by weight).

3.2. Polymer characterization

The data obtained from IR and NMR spectra performed on the studied polymers are consistent with those previously published for poly[*N*-(alkylimino)alanes] $[HAlNR]_n$ (R = H, Et, ^{i}Pr)[9–11]. FT-IR spectra recorded on polymers **2**–**6** (Fig. 1) show the expected bands as follows: $\nu_{N\text{–}H}$ (∼3450 cm^{-1}), $\nu_{C\text{–}H}$ (2963–2872 cm^{-1}), $\nu_{Al\text{–}H}$ (∼1850 cm^{-1}),

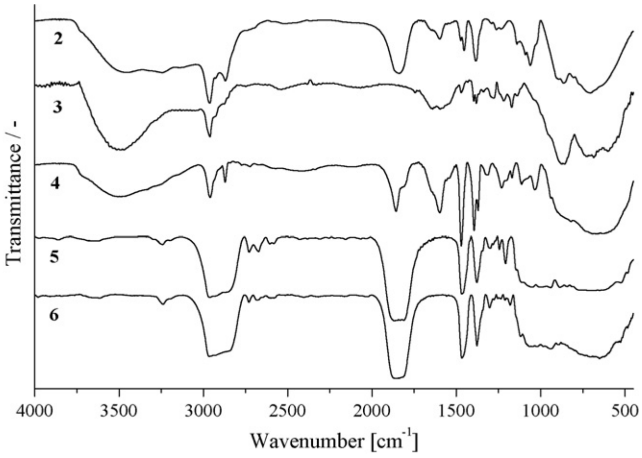

Fig. 1. IR spectra for poly[*N*-(alkylimino)alanes] going from **2** (R = CH_3) to **6** (R = $(CH_2)_7CH_3$).

δ_{asCH_3} (1468–1450 cm^{-1}), δ_{sCH_3} (1389–1372 cm^{-1}), $\nu_{C–N}$ (~1095 cm^{-1}) and $\nu_{Al–N}$ (706–674 cm^{-1}).

The band at ~1595 cm^{-1} ascribed to the bending vibration of the NH groups which appears in some of the spectra suggests that poly[*N*-(alkylimino)alanes] are probably composed of linear parts in the polymer network with peripheral N(H)R groups. This result points to the fact that polymerization reaction is incomplete, probably due to the steric hindrance of *N*-pentyl and *N*-octyl pendent groups. Corresponding elongation and bending bands of such groups display poor intensities.

^{1}H NMR analyses are in good accordance with FT-IR data. The presence of Al–***H*** bonds is confirmed by the appearance of a very broad singulet at δ = 4.2–4.63 ppm, the chemical shift depending on the nature of the R group. A multiplet signal centred at δ = 3.6 ppm is attributed to the proton in C***H*** group found in *N*-isopropyl- and *N*-isobutyl-containing polymers. The protons in C***H***$_2$ groups linked to nitrogen atoms are represented by a broad signal at δ = 3.2 ppm for polymers **2**, **4**–**6**. The protons in C***H***$_2$ groups bonded to carbon atoms in *N*-pentyl and *N*-octyl containing polymers are located in a range of chemical shift between δ = 1.8 and 2.4 ppm. Finally, the presence of two sets of signal in the range δ = 0.9–1.5 ppm is assigned to protons in C***H***$_3$ groups. ^{13}C NMR data are in good agreement with such results. The signals emerging at δ = 48.9 ppm (***C***H) and δ = 28.1 ppm (***C***H$_3$) for polymer **3** as well as the signals at δ = 19.7–21.5 ppm (***C***H$_3$), 41.3–42.4 ppm (***C***H$_2$) for **2** are consistent with the chemical shifts reported for cage-type hexamer $[HAlN^{i}Pr]_n$ and octamer $[HAlNEt]_n$[8]. Signals at δ = 50.2 ppm (polymer **4**) and 46.4 ppm (polymers **5**–**6**) can be attributed to carbon atoms in ***C***H$_2$ groups bonded to nitrogen. Signals in the range δ = 27.1–34.2 ppm for polymers **5**–**6** are assigned to carbon atoms in ***C***H$_2$ groups which display various atomic environments in the alkyl chain. In addition, the signal value at δ = 14.4 ppm found in polymers **5**–**6** spectra is consistent with the chemical shift values for carbon atoms in ***C***H$_3$ groups. Signals at 33.6 and 20.4 ppm are attributed to carbon atoms in ***C***H and ***C***H$_3$ groups in polymer **4**, respectively.

Chemical formulas are consistent with the reaction pathway depicted in Section 2. As an illustration, the aluminum-to-nitrogen ratio is found to be close to that expected (Al:N = 1) and the carbon content decreases going from **6** to **2** in accordance with the reduction of the length of the alkyl chain. In contrast, the percentage in hydrogen is found to be higher than expected most probably due to the presence of terminal alkylamino groups in the polymer network as suggested by FT-IR. This is especially the case for polymers **5**–**6**, i.e., with a high alkyl chain length causing steric hindrance. Therefore, we can conclude that the degree of branching of the latter is low. This is reflected by TGA experiments.

Table 2
TGA data for polymers **2**–**6**

Polymers	ΔT (°C)[a]	Ceramic yield (%)[b]
2	30–900	53.7
3	30–870	50.6
4	30–800	40.1
5	50–700	38.1
6	50–600	23.2

[a] Temperature range where weight loss occurs.
[b] Ceramic yield calculated from the weight loss measured at 1000 °C.

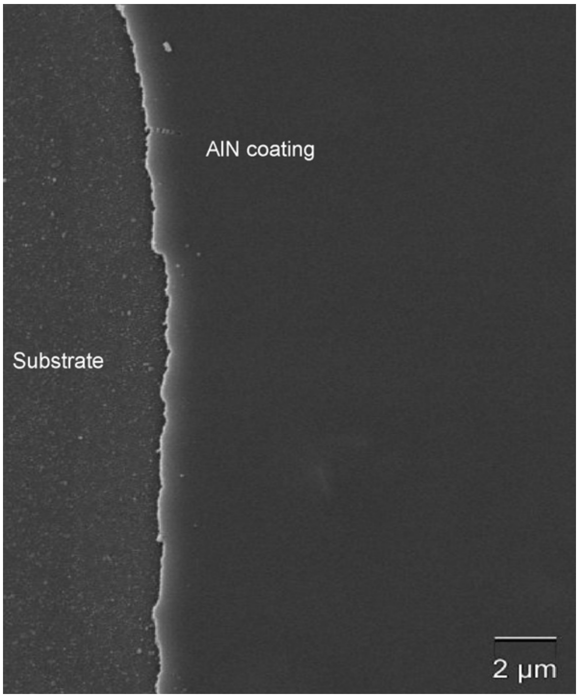

Fig. 2. SEM images of AlN thin coating obtained at 1800 °C.

These polymers are decomposed into ceramics by pyrolysis at 1000 °C using ammonia as controlled atmosphere. Table 2 reports TGA data for polymers **2**–**6**. It should be mentioned that TGA data for **1** were not retained due to the presence of chloride impurities. As expected, ceramic yields are found to decrease from 53.7% (**2**) to 23.2% (**6**), thereby with increasing alkyl chain length.

3.3. *Shaping potentialities in liquid state*

One of the main advantages of preceramic polymers is their shaping potentiality to generate complex-shaped ceramics[14,15]. Poly[*N*-(alkylimino)alanes] in common distilled organic solvent such as toluene and tetrahydrofuran (THF) can be shaped to produce thin coatings and 1D nanostructures using dip-coating and templating processes, respectively. Shaping examples are provided for the representative polymer **3**, but it should be mentioned that other compounds can be shaped in a similar way.

3.3.1. *Preparation of thin coatings*

A dense graphite substrate was dipped once into a low viscous polymer solution of polymer **3** in toluene (10% by weight) before its heating in flowing ammonia up to 1000 °C and then in flowing nitrogen from RT to 1800 °C to generate well crystalline AlN. SEM observations (SEM, Hitachi S800 operating at 150 kV) of the surface show a regular coating in which some defects such as cracks and defoliating can be only identified at high magnification (Fig. 2). On the presented sample, the film thickness can be estimated to about 500 nm. Depending on the

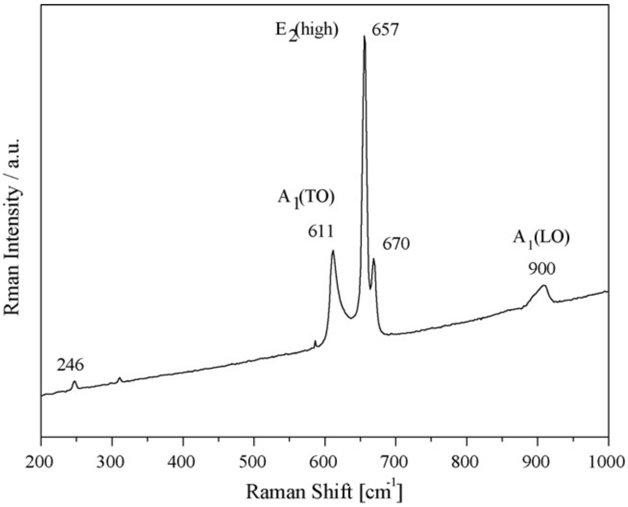

Fig. 3. Corresponding Raman pattern of AlN coatings.

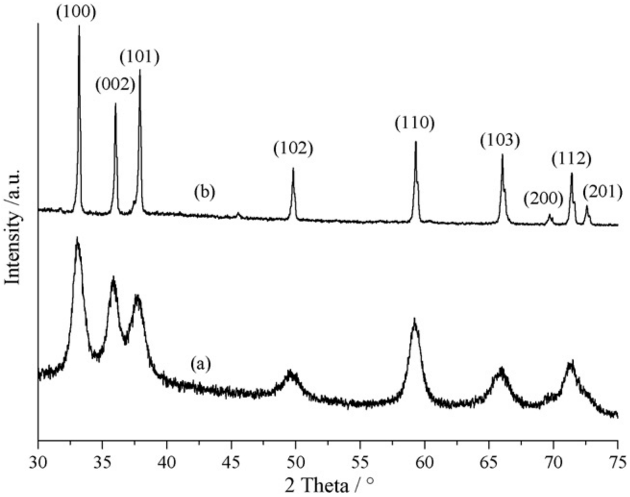

Fig. 4. XRD patterns of AlN produced at 1200 °C (a), then 1800 °C (b).

polymer concentration and the number of deposit, the thickness of the coating can be controlled and adjusted from 500 nm to 2 μm. The residual porosity of the coating due to both the weight loss (49.4%) and the density increase which occur during the polymer-to-ceramic conversion can be filled by combining this polymer approach with the gaseous one (CVD) and prepare dense coating.

Achievement of aluminum nitride was evidenced by Raman spectroscopy (Raman Renishaw RM 1000). The Raman scattering spectrum (Fig. 3) performed on the sample heated at 1800 °C was recorded using the 514.5 nm line of Ar^+ ion laser as excitation source.

The spectrum shows four well-defined peaks corresponding exactly to the signature of wurtzite-AlN (w-AlN) as reported for bulk material[16]. Peaks at 611, 657, 670 and 900 cm^{-1} are attributed to the A_1 (TO), E_2 (high), E_1 (TO) and A_1 (LO) vibration modes, respectively.

3.3.2. Preparation of 1D nanostructures

The template-directed synthesis is an elegant chemical approach to prepare nanomaterials[17]. This technique consists in the filling of a nanoporous membrane constituted of numerous straight cylindrical pores with a narrow size distribution by a liquid, a gas or a meltable solid. Sneddon and co-workers[18–20], Interrante and co-workers[21] and our team[22] have been the first to report the successful preparation of nanostructured B_4C, SiC and BN using this templating process, respectively.

Using a poly[*N*-(isopropylimino)alane]-to-toluene ratio of 1:3 in weight, it is possible to infiltrate a commercially available aluminum oxide filter membrane (Anodisc 47, 0.2 μm nominal pore diameter from Whatman®) with the solution. Alumina mold was preferred according to its homogeneous distribution of pore size and its thermal stability which allows to retain the pore morphology during the polymer-to-ceramic conversion. The membrane (dried at 120 °C prior use) was filled with the solution at RT in flowing argon. When the membrane was saturated with the solution and a covering coating was formed, the sample was treated in flowing ammonia to 1000 °C (60 °C/h), and then in flowing nitrogen to 1200 °C (100 °C/h) to proceed to the conversion of the soluble polymer inside the pores of the membrane into an aluminum nitride-filled membrane. The aluminum oxide template was, then, dissolved at RT in 48% hydrofluoric acid for 48 h and finally washed thoroughly with deionised water, methanol, and acetone to generate poorly crystallized aluminum nitride as suggested by X-ray diffraction (Philipps PW 3040/60 X'Pert PRO X-ray diffraction system operating at 30 mA and 40 kV, Fig. 4a). The latter underwent heat-treatments in flowing nitrogen to 1800 °C (100 °C/h) to produce w-AlN with an increased grain size as illustrated in Fig. 4b through the strong decrease of the FWHM of the (1 0 0) and (0 0 2) peaks. Preliminary results show that alumina is not totally removed most probably due to a short time of etching (Fig. 5), but it is interesting to observe that w-AlN is shaped into a close packed array

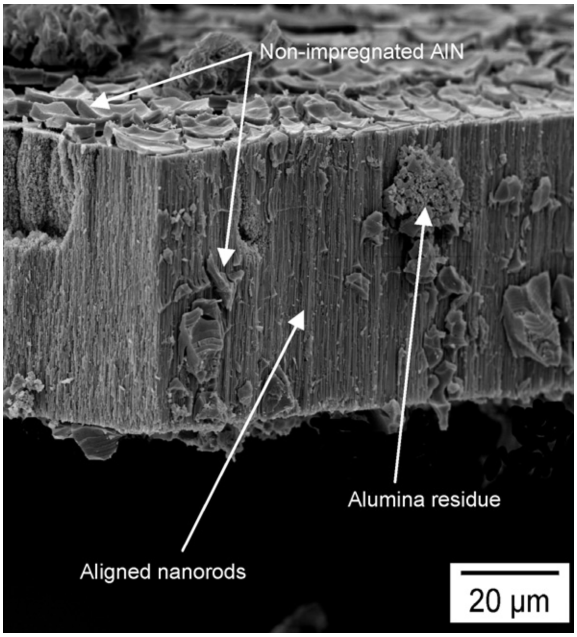

Fig. 5. SEM images of nanostructured AlN obtained at 1800 °C.

of highly ordered nanorods 200 nm in diameter supported by a thin film.

Further works are under investigation to completely remove alumina from AlN nanostructures and infiltrate membrane in molten state.

According to the fact that AlN is the widest direct-bandgap semiconductors, such AlN nanorods could be used as ultraviolet LEDs and laser diodes substrate.[23]

4. Conclusion

We have reported the synthesis and characterization of a series of poly[*N*-(alkylimino)alanes], $[HAlNR]_n$, from lithium aluminum hydride and various alkylammonium chloride. Depending on the nature of the carbon-based pendant groups, polymers display various physical states going from viscous liquid to soluble solid. Such properties offer interesting possibilities in the preparation of complex-shaped ceramics including thin coatings and 1D nanostructures. Polymers were shaped by dip-coating and templating processes and the resulting shaped green bodies were converted by heat-treatment in an ammonia atmosphere at 1000 °C, then in a nitrogen atmosphere at 1800 °C into AlN thin coatings and 1D nanostructures. An alternative method currently under study consists in the investigation of the shaping potentialities of solid poly[*N*-(alkylimino)alanes] in their molten state.

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