Modification of PAN by Titanium Dialkylamides: Precursors for Titanium Carbide

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INTRODUCTION

Advanced ceramics (e.g., carbides, nitrides, and borides) are materials having desirable properties for a variety of applications. Their key properties are high hardness and strength along with resistance to heat, corrosion, and wear.[1] Methods for producing these materials, particularly in fiber form, require unconventional processing techniques. We have focused on the Ti–C–N systems in our attempts to obtain fibers of such materials. Our approach to producing such fibers is analogous to the processing of organic polymers into carbon fibers.[2] Synthesizing the above-mentioned ceramics by the pyrolysis of organometallic polymers, or other precursors,[3] has particularly facilitated the fabrication of such ceramic fibers.

In our attempt toward such fibers, we felt that if we utilized organic polymers (as a source of carbon) and suitably modified it with an organotitanium complex at the molecular level, we would have a system containing the right ingredients, i.e., Ti and C. Such a polymeric system could conceivably be processed into a fiber. Two such systems immediately caught our attention. $TiCl_4$ and alkyl cyanides are reported to form complexes of the type $(R-C\equiv N)_2 \cdot TiCl_4$ and titanium amides $(R_2N)_4Ti$ also complex with the $-C\equiv N$ group.[5] Polyacrylonitrile (PAN) has pendant nitrile groups and therefore was selected as a prime candidate for modification of organotitanium complexes. PAN can also be easily fabricated into fibers and processed at elevated temperatures to produce "carbon" which can simultaneously undergo a "solid state" reaction with titanium. Under appropriate processing conditions it was envisaged that Ti–C would be the main constituent of the end product.

Thus far we have synthesized organometallic monomers and organic polymers along with their modification; the fabrication of such modified organic polymers into fibers is followed by their thermal processing into ceramics.

EXPERIMENTAL

Materials and Equipment

In the synthesis of the monomers, operations were conducted under an inert atmosphere using Schlenk tube techniques. Diethyl ether was distilled from sodium–benzophenone ketyl under argon. Benzene was freshly distilled from

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calcium hydride. Diethylamine was dried over barium oxide and the center cut used. Methyl lithium and dimethylamine in diethyl ether (Alfa) were used as received.

Viscosities were obtained in a Cannon-Ubbelohde viscometer. ^{1}H-NMR spectra were recorded on a 200 MHz (IBM-Bruker) spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer interfaced with a data station. DSC scans were made on a Perkin Elmer DSC-2 calorimeter also interfaced with a data station. TGA analyses were similarly made on a Perkin-Elmer TGS-2 system, generally at a heating rate of 10–20°C/min in a nitrogen atmosphere. Polymers were pyrolyzed in a quartz combustion tube in a Lindberg Model 54252 tube furnace interfaced with a Eurotherm micro-processor-controller Model 810. SEM-EDAX studies were accomplished on a JEOL 840 equipped with a Tracor Northern TN 550 computerized EDAX system. Scanning Auger-ESCA were performed on a Perkin-Elmer 590 system.

Synthesis

Tetrakisdimethylaminotitanium was prepared by the method reported by Lappert et al.[6] Yd. 91%. ^{1}H-NMR (benzene d_6)δ 3.0 for methyl protons. IR (NaCl) (cm^{-1}): 2967, 2861, 2773, 1452, 1417, 1152, 1075, 1055, 943.

Tetrakisdiethylaminotitanium was prepared by the method reported by Bradley and Thomas.[7] Yd. 88%. ^{1}H-NMR (benzene d_6)δ 2.7(q); 1.0(t) for ethyl protons. The IR spectrum was similar to that of tetrakisdimethylaminotitanium.

The above yields are those of the crude products. Before analysis and reactions, the crude products were vacuum distilled directly into the reaction vessels. This was necessary, as direct transfer of the viscous liquids was difficult.

Polymerization of Acrylonitrile. Polyacrylonitrile was prepared by precipitation polymerization techniques.[8] The molecular weight was approximately 18,000.

Fibers

Wet Spinning of Polyacrylonitrile. Polyacrylonitrile (1.75 g) was dissolved in 25 mL of DMF. The viscous solution was placed in a syringe fitted with a fine needle which dipped in a cold water tray. Pressure was applied to the piston of the syringe. Polymer solution flowed through the needle and immediately began to solidify in the tray in the form of fiber. The as-spun fiber was drawn, before drying in a hot water bath maintained at about 70°C, and dried overnight in an air oven at 60°C under tension.

Chemical Modification of PAN Fibers. The drawn fibers were immersed in dilute and concentrated solutions of Ti(NEt$_2$)$_4$ in benzene and neat Ti(NMe$_2$)$_4$, in a Schlenk flask. The fibers were generally dipped for 48 h under argon. They were then quickly transferred to an alumina boat and immediately pyrolyzed in a quartz tube in a furnace at different temperatures and periods in various reactive/inert gases.

TABLE I

Processing Conditions and Thermal Analysis of PAN Fibers Modified by Ti(NEt$_2$)$_4$

Sample no.	Ti(NEt$_2$)$_4$ benzene[a]	Thermal processing conditions	IDT[b] (°C)	Weight loss[c] (%)
1	Concd	Directly heated to 1000°C in argon	519	18% at 850°C
2		Sample 1 reheated to 560°C for 1 h and then 1150°C in argon	654	16% at 850°C
3	Concd	Heated to 1050°C for 2 h in argon	—	No weight loss
4	Dilute	Directly heated to 560°C for 1 h and then to 1150°C in argon	552	64% at 850°C
5	Dilute	Directly heated to 1000°C in argon	510	18% at 600°C
7	PAN powder + dilute Ti(NEt$_2$)$_4$	Heated to 560°C for 1 h and 1050°C for 1 h	620	7%

[a] Concd: neat Ti(NEt$_2$)$_4$; dilute: Ti(NEt$_2$)$_4$ + benzene.
[b] IDT: Initial decomposition temperature.
[c] Determined by thermogravimetric analysis.

TABLE II

Processing Conditions and Thermal Analysis of Pan Modified by Ti(NMe$_2$)$_4$

Sample no.	Sample description	Thermal processing conditions	Weight loss (%)
8	Ti(NMe$_2$)$_4$(neat)	Heated in argon to 1000°C for 1 h and then to 1200°C	No weight loss
9	PAN powder + Ti(NMe$_2$)$_4$(neat)	Heated in argon to 500°C for 1 h, then to 1000°C for 1 h, and finally to 1200°C	9.2%
10	PAN powder Ti(NMe$_2$)$_4$(neat)	Heated in ammonia for 1 h, then to 900°C to also in ammonia; finally from 900°C to 1200°C in nitrogen	
11	PAN fiber + Ti(NMe$_2$)$_4$(neat)	Heated in ammonia to 560°C for 1 h; then to 900°C also in ammonia; finally from 900°C to 1200°C in nitrogen	No weight loss

Chemical Modification of PAN Powder. Polyacrylonitrile was powdered and dipped as above in Ti(NEt$_2$)$_4$ and Ti(NMe$_2$)$_4$ for 24 h and then pyrolyzed at different temperatures and times.

The conditions are summarized in Tables I and II.

RESULTS AND DISCUSSION

Synthesis: Model Systems

Titanium containing monomers, tetrakis(dialkylamino)titanium (R$_2$N)$_4$Ti (R = C$_2$H$_5$, CH$_3$) were synthesized by a slight modification of the procedure reported in the literature.[6,7] In general, first the lithium dialkylamides (LDA) were obtained by reacting methyl lithium in diethyl ether with the appropriate dialkylamine at low temperatures (-20°C). To the resulting LDA was then added TiCl$_4$ in benzene, the temperature being maintained below 10°C. These reactions were conducted in an argon environment to exclude
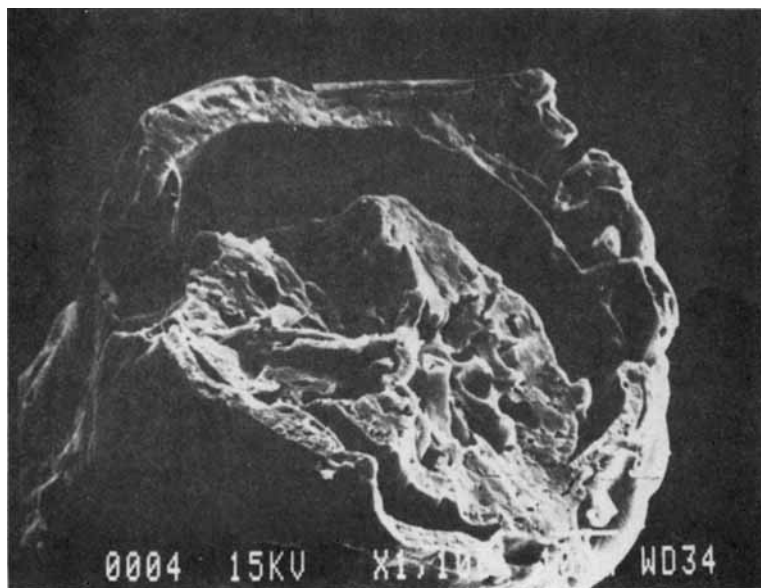
moisture and air. In both instances the titanium monomers are high boiling viscous fluids. The above sequence of reactions are presented below in Scheme 1:

$$R_2NH + CH_3Li \xrightarrow[\text{temp} < -20°C]{\text{diethyl ether}} R_2NLi + CH_4$$

$$TiCl_4 + R_2NLi \xrightarrow[\text{temp} < 10°C]{\text{benzene}} (R_2N)_4Ti + LiCl$$

$$[R = CH_3, C_2H_5—]$$

Scheme 1.

Polyacrylonitrile (PAN) was prepared by known procedures.[8] Purified acrylonitrile was polymerized with a redox initiator system in water by precipitation polymerization. The intrinsic viscosity η was determined at 25°C in DMF, and the molecular weights calculated from the Mark-Houwink equation ranged between 18,000 and 20,000, suitable for fiber spinning.

Preliminary investigation regarding the feasibility of these monomers as potential sources of "active Ti" in solid state reactions was conducted prior to fiber fabrication and processing studies. The titanium monomer $[(CH_3)_2N]_4Ti$, on pyrolysis from ambient to 1200°C, in an argon atmosphere left a black residue. On a chemical analysis it was observed that the residue contained 61% titanium. The residue was also found to contain carbon, nitrogen, and oxygen. In a parallel experiment, polyacrylonitrile powder (PAN) and the monomer $Ti[N(CH_3)_2]_4$ in a 10:1 ratio by weight, mixed under argon for 24 h, was similarly pyrolyzed in argon. A black residue was obtained which contained 23% Ti, 61% C, and 7% N, along with oxygen. It can be assumed that a mixture of $Ti(O, C, N)$ and carbon are present. The total weight loss in both experiments was ca. 40%. The above pyrolyses are summarized in Scheme 2:

$$Ti(NR_2)_4 \xrightarrow[\text{ambient} \to 1200°C]{\text{argon}} \begin{array}{c} Ti(C, N, O) \\ [Ti\ 60\%] \end{array}$$

$$Ti(NR_2)_4 + —[CH_2—\underset{\underset{CN}{|}}{CH}—]_n— \xrightarrow[\text{ambient} \to 1200°C]{\text{argon}} \begin{array}{c} Ti(C, N, O) + C \\ [Ti\ 23\%] \end{array}$$

Scheme 2.

From these initial experiments it was concluded that these monomers could provide the titanium, a crucial source for reaction with carbon. The production of titanium with excess carbon in the latter experiment was critical as it was anticipated that an analogous solid state reaction would occur in the titanium-modified PAN fibers.

Fiber Processing

PAN powder was dissolved in dimethylformamide (DMF) and the "dope" extruded into a chilled water bath to coagulate the polymer. The as-spun fibers were drawn in a hot water bath before drying. The drawn fibers were

Fig. 1.   SEM micrograph (1100 ×): cross section of fiber modified by Ti(NMe$_2$)$_4$) at ambient temperature and pyrolyzed in NH$_3$–N$_2$.

dried overnight in an oven at 60°C, under tension. It may be mentioned that the PAN fibers were porous to enable the titanium monomers to diffuse sufficiently into the inner core to provide a homogeneous fiber. The titanium monomer was expected to percolate through these pores and channels and form intimate molecular level complexes with the abundant reactive pendant cyano groups of PAN.

Modification of the PAN fiber was done after drawing and drying. The fibers were immersed in solution of Ti(NEt$_2$)$_4$/benzene for 48 h at 10°C. The concentration of Ti(NEt$_2$)$_4$ in benzene was varied to determine the effect on fiber structure. The modified fibers were pyrolyzed under different conditions which are summarized in Table I. The presence of a "skin" and an "inner core" along with substantial voids made the fibers extremely brittle. Table II summarizes the modification of PAN fibers by the monomer Ti(NMe$_2$)$_4$. Here no solvent was used, as the monomer was less viscous and easier to handle. Figure 1 is an SEM micrograph of a cross section of a fiber pyrolyzed in ammonia. The voids, compared to fibers pyrolyzed in argon, were substantially reduced, and the fiber was consequently less brittle.

Thermal Analysis

The results of thermogravimetric analyses (TGA) of the fibers and powders are also summarized in Tables I and II. A perusal of the thermal stability of these fibers indicates that processing conditions are vital not only to ultimate mechanical fiber properties but also to their thermal stability. Sample 3 showed no weight loss until 800°C in a nitrogen atmosphere. Similarly sample 8 and 11 showed no weight losses until 850°C; however, sample 8 showed weight gain at 430–550°C, possibly nitridation.
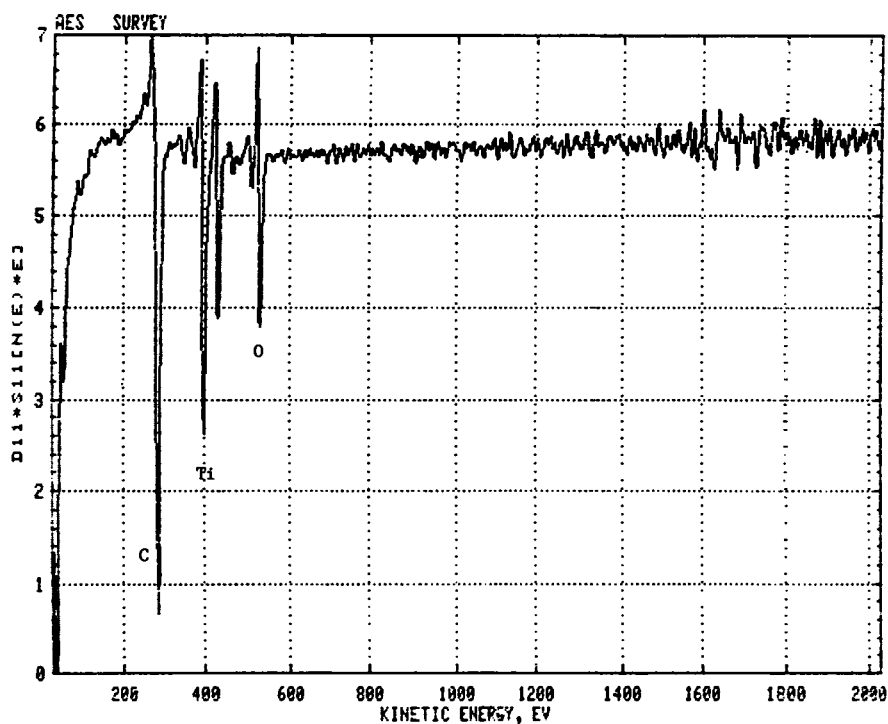
Fig. 2.   AES survey of powdered fiber (sample 11).

Materials Characterization

Scanning Auger electron spectroscopy (AES) was performed on a finely powdered single fiber mounted on a copper backed adhesive tape. The AES survey of the powder is given in Figure 2. The Auger transitions of the major elemental constituents of the fiber, i.e., C and Ti, are evident. Contributions from the carbon and oxygen of the adhesive are possible as copper signals were observed in the ESCA survey. From these initial AES and ESCA surveys, it appears that the fibers are composed of Ti(C, O).

Semiquantitative elemental analysis was performed on the fiber samples by SEM–EDAX. The Ti content on the surface ranged around 90–95% and in the interior from 65 to 90%, depending on the conditions of PAN fiber modification. The inner core contained a higher percentage of titanium when the modifications were performed at 20°C, compared to −10°C. Thus temperature possibly affects the rate of titanium monomer diffusion as well as reaction rate of the —C≡N group and the titanium monomer.

We are currently attempting to densify the fiber by conducting the pyrolysis in reducing hydrocarbon atmospheres and increasing the maximum processing temperature to 1700–2000°C. Tensile testing of these fibers will be reported subsequently.

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