

Alumina–Carbon Composite Fibers from Poly[(acyloxy)aloxane]s

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SYNOPSIS

The alumina–carbon composite fibers were obtained from poly[(acyloxy)aloxane] (PAA) with 3-ethoxypropanoic (EPA) and *m*-anisic acids (*m*-AA) legands. This preceramic polymer can be dissolved in *p*-xylene–methanol–EPA mixed solvent, and the concentrated solution exhibited an excellent spinnability. During the pyrolysis and sintering processes, aliphatic carboxylate in the side groups was easily decomposed and eliminated. The aromatic carboxylate, however, seems to be converted and migrated to a carbon domain in the alumina matrix into which aloxane repetition was converted. The fibers pyrolyzed up to 800 and 1000°C have electrical conductivities that monotonically increase with increasing temperature. The fiber pyrolyzed up to 1200°C showed the electrical conductivity in a rather complicated manner.

INTRODUCTION

Various combinations including polymer–polymer, polymer–metal, polymer–ceramics, metal–ceramics, and ceramics–ceramics have been utilized to obtain the composite materials.¹ Generally, these composite materials are obtained by the addition or mixing of two or more materials with different properties. The composites obtained from the block or graft copolymers alone can be included in the other category in the sense that they are molecularly designed to form composite structures.²

We have made a molecular design of the precursor polymers for the ceramics aiming to the ceramics–ceramics composite material. Poly[(acyloxy)aloxane], which consists of Al–O repetition as its backbone and aliphatic carboxyl side groups, has been utilized as a precursor polymer for alumina Al₂O₃.^{3–7} To obtain ceramics–ceramics composite material in this precursor polymer method, aromatic carboxylic acids, which can be converted and migrated to a carbon domain, were introduced as well as aliphatic carboxylic acid onto aloxane repetition of poly[(acyloxy)aloxane], which is converted into

alumina after pyrolysis. The ceramics obtained is expected to be an alumina–carbon composite material.

The removal of the organic residue and the simultaneous conversion of the aromatics and Al–O repetition into carbon and alumina during the pyrolysis have not been studied, and the structure and properties of the resulting composite materials are not known so far.

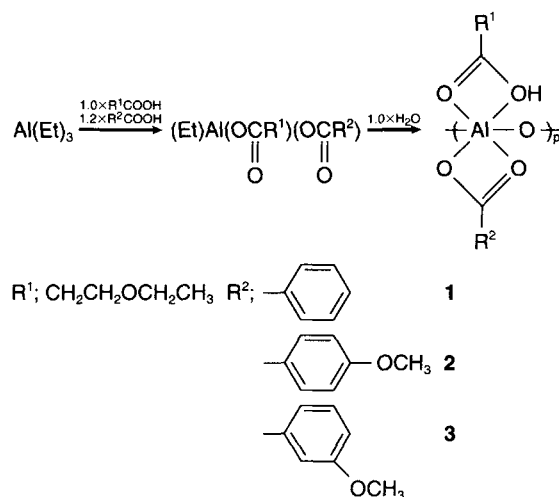
This study revealed the course of the pyrolysis of the poly[(acyloxy)aloxane], which has aromatics in its side group by tracing with IR and electron spectroscopy for chemical analysis (ESCA). Furthermore the structure and properties of the alumina–carbon composite fibers obtained were studied by using scanning electron microscopy (SEM) and wide-angle X-ray diffraction (WAXD) and the measurements of the electrical conductivity.

EXPERIMENTALS

Materials

Triethylaluminum (TEA) was provided by Toso-Akzo Chemical Corp. (Tokyo, Japan) and was used without further purification. Tetrahydrofuran (THF), toluene (TOL), and 1,4-dioxane (DOX)

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Scheme 1

were distilled over sodium metal under a nitrogen atmosphere. 3-Ethoxypropanoic acid (EPA) was synthesized by Michael reaction from ethyl acrylate and ethanol and purified by distillation under reduced pressure. Benzoic (BA), *p*-anisic (*p*-AA), and *m*-anisic acids (*m*-AA) were supplied by Nakalai Tesque Inc. (Tokyo, Japan) and were purified by recrystallization in the diethyl ether.

Synthesis of Poly(acyloxyaloxane)s

Poly(acyloxyaloxane)s were prepared by a two- or three-stage reaction of TEA with carboxylic acids and water³⁻⁶ (Schemes 1 and 2).

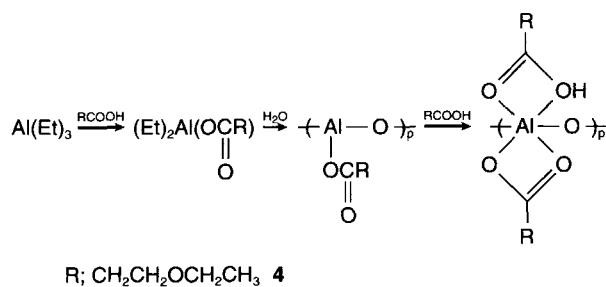
Poly[(((benzoyl)oxy)aloxane] 1

A solution of 7.083 g (58 mmol) of BA and 8.222 g (69.6 mmol, 1.2 equivalent of TEA) of EPA in 24 mL of TOL were added dropwise to the solution of 7.96 mL (58 mmol) of TEA in 24 mL of TOL at -20°C .

After the addition this solution was kept stirred at room temperature for 1 h to complete the reaction. Then a solution of 1.044 g (58 mmol) of water in 9.4 mL of DOX was added dropwise at -20°C . This solution was allowed to stand at room temperature overnight. The product **1** was precipitated in a large excess of *n*-hexane and then dried at 50°C under vacuum.

Poly[(((4-methoxybenzoyl)oxy)aloxane] 2

A solution of 8.825 g (58 mmol) of *p*-AA and 8.222 g (69.6 mmol, 1.2 equivalent of TEA) of EPA in 80 mL of THF were added dropwise to the solution of 7.96 mL (58 mmol) of TEA in 24 mL of THF at -20°C . After the addition, stirring was continued at room temperature for 1 h to complete the reaction. Then a solution of 1.044 g (58 mmol) of water in 10.6 mL of THF was added dropwise at -20°C . This solution was allowed to stand at room temperature overnight, and the product **2** was purified by the same way as **1**.



Scheme 2

Poly[((3-ethoxybenzoyl)oxy)aloxane] 3

By the similar reaction of TEA with EPA, *p*-AA, and water to the synthesis of **2**, poly[((3-ethoxybenzoyl)oxy)aloxane], **3** was obtained.

Poly[((3-ethoxypropanoyl)oxy)aloxane] 4

A solution of 23.63 g (0.2 mol) of EPA in 50 mL of TOL was added dropwise to the solution of an equimolar amount of TEA in 81 mL of TOL at -20°C . After the addition was over, the solution was kept stirred at room temperature for 1 h to complete the reaction. The solution of 3.6 g (0.2 mol) of water in 31.4 mL of DOX was added dropwise at -20°C . After the addition, the product was kept stirred for 2 h and then allowed to stand at room temperature overnight. To this solution, 11.81 g (0.1 mol) of EPA in 23 mL of TOL was added and stirred thoroughly at 70°C . Again this solution was allowed to stand at room temperature overnight. The product was precipitated in a large excess of *n*-hexane, and dried at 50°C under vacuum.

Dry Spinning

A 30 wt % solution of poly(acyloxyaloxane) was loaded in a syringe equipped with a capillary of 3 mm in length and 0.7 mm in inner diameter and degassed as complete as possible. The syringe was fixed on a laboratory feeding instrument (JP-100G, Furue Science, Tokyo, Japan). The solution was emerged at a constant rate. The extrudate was passed through a drying column at 70°C and taken up on a roll at 32 m/min.

Pyrolysis of the Precursor Fiber

The precursor fiber was cut into 100-mm-long pieces and inserted into an alumina tube of 100 mm in length and 0.8 mm in inner diameter. Several of these were placed on a alumina boat and pyrolyzed in a tubular electric furnace (CT-4C, Advantec, Tokyo, Japan) with flowing nitrogen. The temperature of the furnace was controlled by a digital programmable controller (DP-1110-00, Chino, Tokyo, Japan) with a thyristor regulator (SF-W12, Chino, Tokyo, Japan).

MEASUREMENTS AND OBSERVATIONS

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were recorded under an

air or a nitrogen atmosphere on Shimadzu DT-30 and Shimadzu TG-30 thermal analyzers, respectively. The rate of heating was set at $10^{\circ}\text{C}/\text{min}$ for a 5.0-mg sample. Scanning electron micrographs of the fibers were taken on a JASCO TSM-25S II microscope. IR spectra of the precursor, and pyrolyzed fibers were obtained in IR spectrometer (Firis 100, Fuji Electric, Tokyo, Japan). Surface analyses were carried out with ESCA (ESCA750, Shimadzu, Kyoto, Japan) operated at 8 kV and 20 mA. An instrumental vacuum less than 5×10^{-7} torr was used. The data were analyzed on the spectra of C_{1s} , O_{1s} , and Al_{2p} regions. For the samples pyrolyzed up to 600°C or higher, the surface was etched with argon ion sputtering. Wide angle X-ray diffraction (WAXS) patterns were obtained with a X-ray generator (DXGETS-F, JEOL, Tokyo, Japan) operated at 40 kV and 20 mA on a flat film. Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) was radiated for 4 h. The electrical conductivity of the pyrolyzed fiber as a function of temperature was evaluated by 4192F LF impedance analyzer (Yokogawa-Hewlett-Packard, Tokyo, Japan) at 100 kHz with the four-terminal device schematically described in Figure 1.

RESULTS AND DISCUSSION

Characterization of the Precursor Polymers

The four products **1**, **2**, **3**, and **4** were white powdery solids with the reduced viscosity η_{sp}/c ($c = 0.4 \text{ g/dL}$ in phenol-1,1,2,2-tetrachloroethane mixed solvent⁷ at 30°C) listed in Table I. According to the preliminary experiment for the solubility, it was

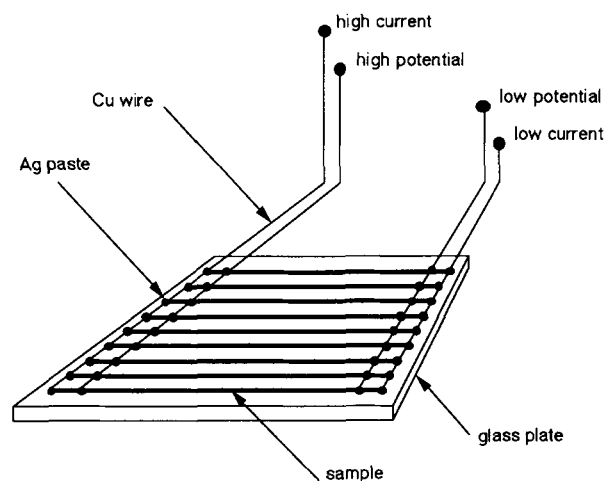

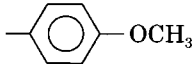
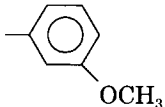


Figure 1 Four-terminal device used in the electrical conductivity measurements of the pyrolyzed fibers.

Table I Characteristics of Poly[(acyloxy) aloxane]s with Various Ligands

Designation	R ¹	η_{sp}/C^a	Solubility in <i>p</i> -xylene–MeOH Mixed Solvent	Spinnability of Conc. Solution in <i>p</i> -xylene–MeOH–EPA Mixed Solvent
1		5.80	Gel	–
2		2.09	+	+
3		2.11	+	++
4	–CH ₂ CH ₂ OCH ₂ CH ₃	0.50	+	++

^a0.4 g/dL in C₆H₅OH/(CHCl₂)₂ at 30°C.

found that **2**, **3**, and **4** can be dissolved in *p*-xylene–methanol mixed solvent. However **1** did not dissolve in any common organic solvents and tended to be a gel in *p*-xylene–methanol mixed solvent. Furthermore, the addition of a small amount of EPA in the solution was found to enhance the spinnability of the concentrated solution of **2**, **3**, and **4**. Since **3** showed the best spinnability, **3** was chosen as a precursor polymer thereafter, and **4**, which does not have aromatics in its ligand, was utilized for comparative purpose.

Typical DTA and TGA curves for **3** performed under a nitrogen atmosphere were shown in Figure 2. An endothermic peak was recorded around 290°C in DTA. This peak was accompanied by a sharp weight loss between 200 and 300°C as detected by TGA, indicating the thermal decomposition starts

at this temperature region and elimination of the organic residue occurs. These results taught that it is necessary to pyrolyze the precursor polymer at a temperature lower than 290°C, where the rate of decomposition is rather low, to obtain alumina–carbon composite ceramics, and the heating pattern in the pyrolysis process was decided to be a temperature raise at 10°C/min up to 250°C and holding at that temperature for 1 h, and then another temperature raise at 10°C/min up to the temperature desired.

Fiber Spinning

Product **3** dissolved in *p*-xylene–methanol–EPA (90/5/5 wt %) to be a 30 wt % solution was prepared as a spinning dope. Continuous filament of 20–30

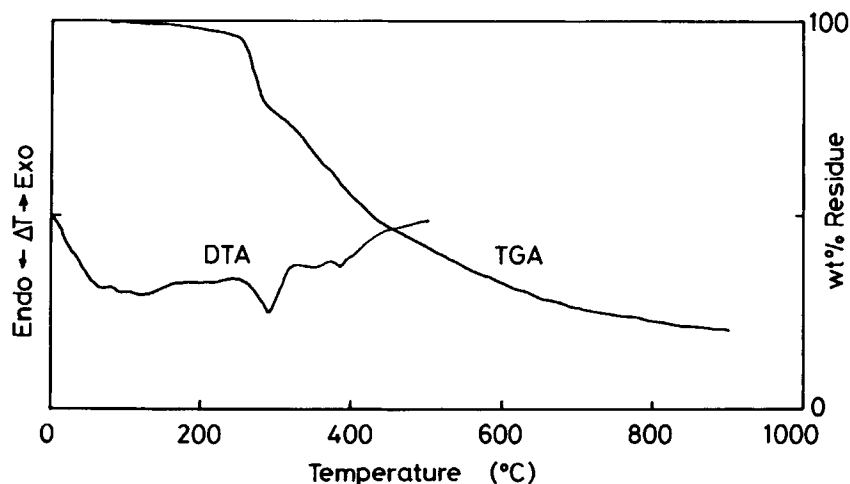


Figure 2 DTA and TGA curves of **3** in streaming nitrogen.

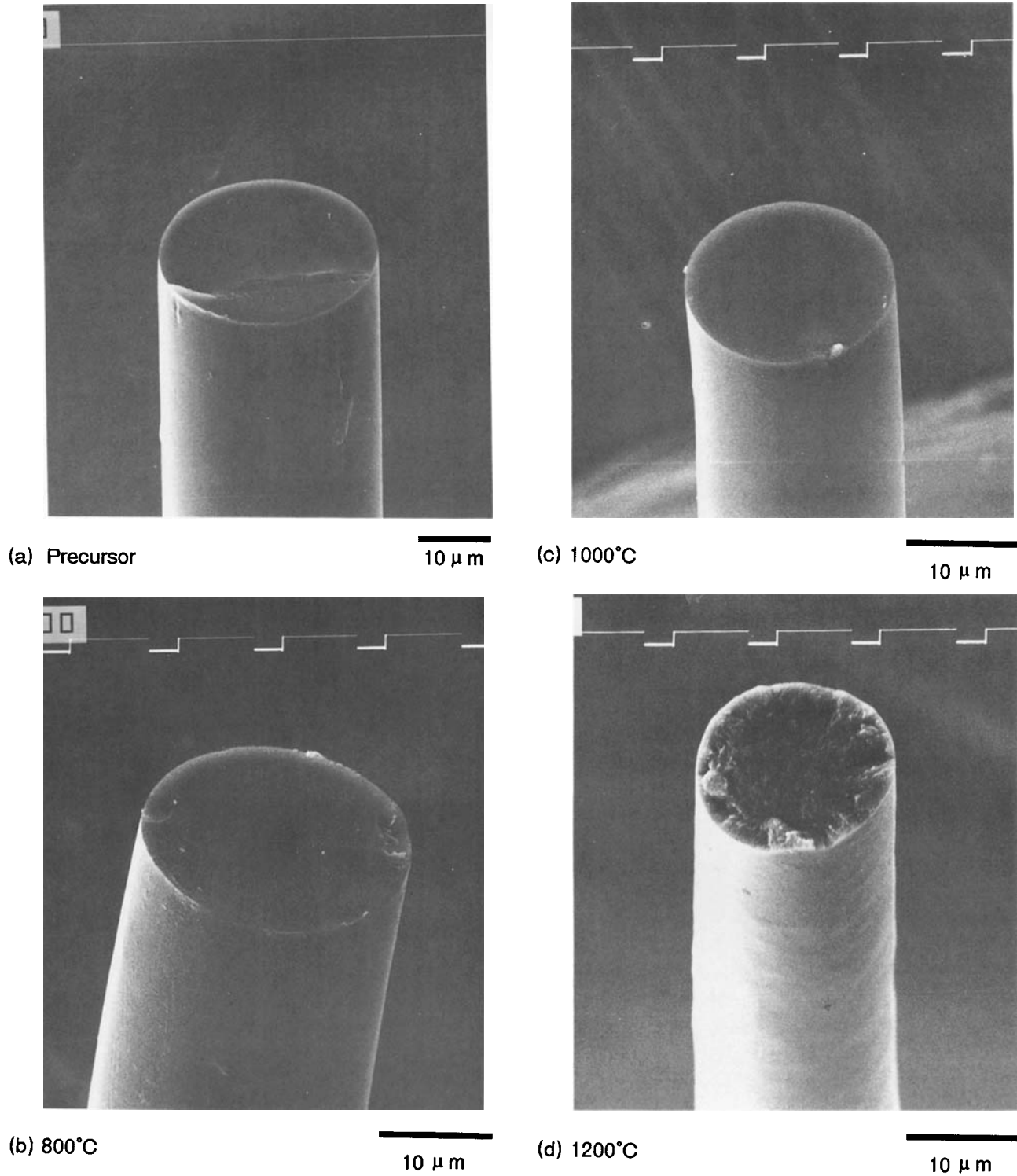


Figure 3 SEM photographs of the precursor fiber and the fibers pyrolyzed up to the temperatures indicated.

μ m in diameter were easily obtained by dry spinning. Prior to the pyrolysis, as spun fibers they were dried at 50°C under vacuum to eliminate the residual solvent as much as possible.

Pyrolysis of the Fibers

Fibers pyrolyzed up to higher than 600°C under the heating conditions mentioned earlier were all black,

which is due to the carbon distributed in the alumina matrix. The typical SEM photos of the precursor fiber and fibers pyrolyzed up to the temperature indicated are shown in Figure 3. Precursor fiber has a smooth surface and a dense cross section. Such appearance of the fiber was kept even after the pyrolyzed process up to 1000°C. The fiber pyrolyzed up to 1200°C, however, has a rough surface and a cross section. It may be due to the overgrowth of the alumina crystal. Similar phenomenon has been observed when alumina fiber was prepared from a preceramic polymer.⁶ There is another reason that may cause this defect in the fiber. It is well known that the carbon materials have a smaller thermal expansion coefficient than those of other ceramics.⁸ The difference of the expansion between alumina matrix and carbon domain at an elevated temperature may cause a local thermal stress.

The change in the IR spectrum during the pyrolysis of the precursor polymer up to 400°C is shown in Figure 4. It has been reported that the thermal scission at the ethoxy group in EPA initially occurred followed by the decomposition at the carboxylate bonded to aluminum when only EPA was

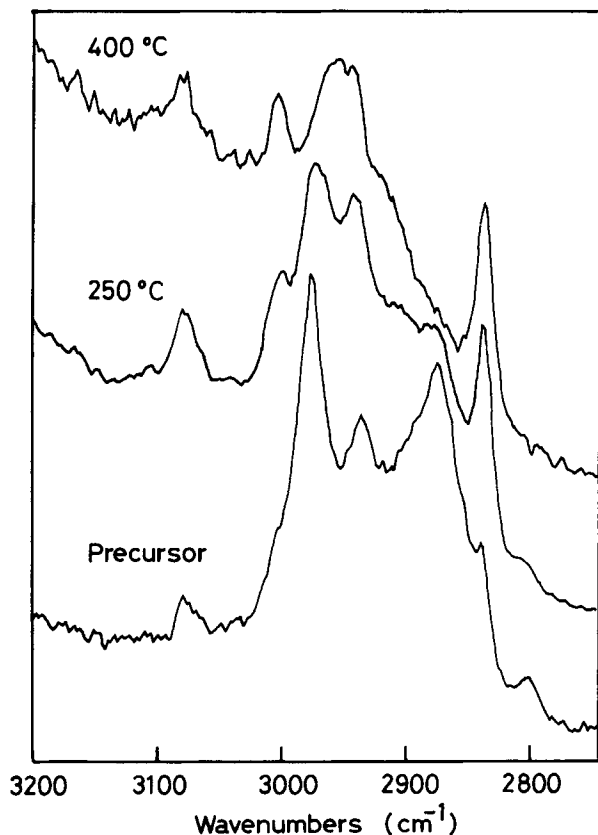


Figure 4 Change in IR spectrum of the precursor polymer 3 during pyrolysis up to 400°C.

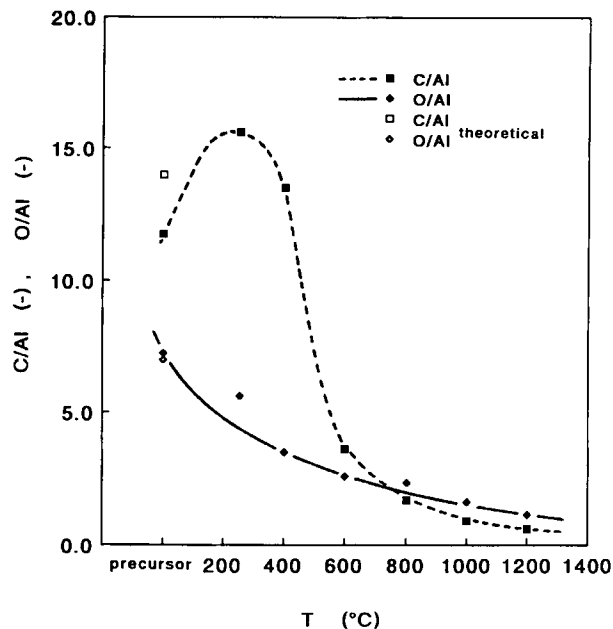


Figure 5 The molar ratios of carbon and oxygen to aluminum as functions of the pyrolysis temperature.

introduced to the precursor polymer.⁹ The IR spectrum obtained from the precursor polymer that contain both EPA and *m*-AA has peaks at 3080 cm^{-1} (ν_{CH} of aromatics, *m*-AA), 2980 and 2873 cm^{-1} (ν_{CH} of $-\text{CH}_3$, EPA), 2935 cm^{-1} (ν_{CH} of $-\text{CH}_2-$, EPA), and 2840 cm^{-1} as a shoulder (ν_{CH} of $-\text{OCH}_3$, *m*-AA). Even after pyrolysis of the precursor polymer up to 250°C and holding it for 1 h, the peak area at 3080 cm^{-1} stayed almost unchanged, and the shoulder at 2840 cm^{-1} changed to a sharp peak, while the peaks at 2980, 2935, and 2873 cm^{-1} tended to be smaller. This tendency was stronger after the precursor polymer was further heated up to 400°C, indicating that the thermal decomposition at EPA proceeded by this temperature, whereas *m*-AA was still relatively stable.

The molar ratios of carbon and oxygen in the fibers to the aluminum, C-Al and O-Al obtained from the peak areas of ESCA spectra as functions of the pyrolysis temperature are plotted in Figure 5. C-Al and O-Al in the precursor fiber were close to the theoretical values calculated, assuming 1.2 equivalent of EPA and 1.0 equivalent of *m*-anisic acid were reacted to TEA. O-Al decreases gradually with the pyrolysis temperature and nearly corresponded to the value of the alumina Al_2O_3 (O-Al = 1.5) when the fiber was heated up to 1000°C. Further heating up to 1200°C reduced O-Al to lower than 1.5, suggesting either that the alumina was reduced to the metallic aluminum oxidizing the carbon

or that the aluminum reacted with carbon to the aluminum carbide. On the other hand, C-Al initially increased probably due to the carbon or the organic residue pyrolyzed and migrated near the fiber surface, and then decreased at a temperature range between 400 and 600°C. At higher pyrolysis temperature, C-Al decreased gradually.

Assuming the fibers pyrolyzed up to higher than 800°C contain only alumina and carbon, the carbon contents averaged to the fiber radial direction can be obtained from the weight loss during the heating of these fibers in air until no weight loss occurs. Comparing the carbon contents in the fibers pyrolyzed up to 800, 1000, and 1200°C obtained in this method with those obtained in ESCA measurements, the latter are 35–50% lower than the former (see Table II). This is attributable to the fact that the carbon near the fiber surface, which ESCA can detect, is more easily eliminated during the pyrolysis, and there exists a distribution of the carbon content in the radial direction.

ESCA spectrum of the aluminum in the fiber pyrolyzed up to 1200°C shown in Figure 6 was obtained after the fiber surface was etched by the argon ion. No clear shoulder of the metallic aluminum at 72.5–72.8 eV¹⁰ was detected in this measurement on the strong peak of the alumina at 74.5 eV. WAXS pattern of the fiber pyrolyzed up to 1200°C is shown in Figure 7. In addition to the peaks at $2\theta = 37.8^\circ$ from α -alumina¹¹ and at $2\theta = 45.9^\circ$ from γ -alumina,¹¹ two peaks at $2\theta = 40.4^\circ$ and 32.0° are detected indicating the presence of the aluminum carbide.¹¹ These results give a fiber structure; carbon and a small amount of aluminum carbide are distributed in the alumina matrix.

Electrical Conductivity

Figure 8 shows the temperature dependence of the electrical conductivity of the fibers pyrolyzed up to the temperatures indicated. The electrical conductivity was ranged from 10^0 – 10^2 S/cm, which tended to increase with the temperature of the measure-

Table II Carbon Content in Pyrolyzed Fibers Obtained in TGA and ESCA

Pyrolysis Temperature (°C)	Carbon Content TGA (wt %)	Carbon Content ESCA (wt %)
800	64.3	23.7
1000	47.1	17.1
1200	25.9	13.5

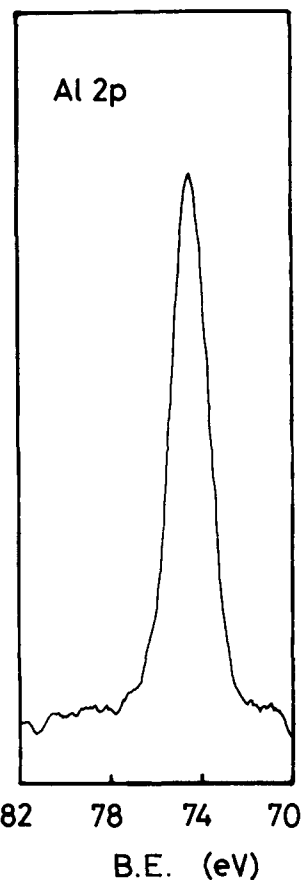


Figure 6 ESCA spectrum of the fiber pyrolyzed up to 1200°C obtained at Al_{2p} region.

ment, typical of the semiconductor. It is clear from Figure 8 that the introduction of the aromatics in the side chain of the precursor polymer is more effective to the electrical conductivity than that of the

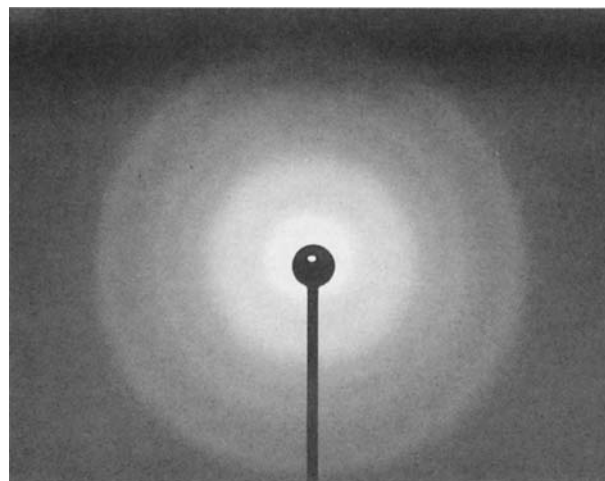


Figure 7 WAXS pattern of the fiber pyrolyzed up to 1200°C.

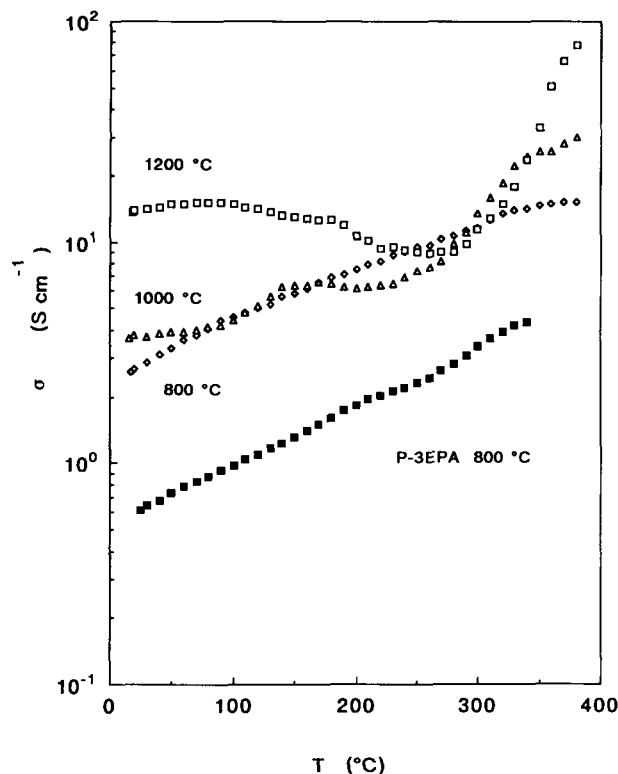


Figure 8 Electrical conductivity of the fibers pyrolyzed up to the temperature indicated. \diamond \triangle \square : precursor polymer 3, \blacksquare : precursor polymer 4.

aliphatics. The higher the pyrolysis temperature, the higher the electrical conductivity at any given temperature of the measurement. The fibers pyrolyzed up to 800 and 1000°C have electrical conductivity that monotonically increase with increasing temperature. The fiber pyrolyzed up to 1200°C showed an electrical property in a rather complicated manner, almost constant between room temperature and 180°C, and then decreased up to 250°C, followed by a sudden increase at a higher temperature region. This may suggest the mechanism of the electrical conduction in this fiber changes with temperature.

Comparing the electrical conductivities of the fibers with the carbon contents in these fibers listed in Table II, the fiber pyrolyzed up to the higher temperature, which has a lower carbon content, showed a higher electrical conductivity. This is considered to be an indication of the formation of the more graphitelike carbon structure in the fiber when pyrolyzed up to higher temperatures. Furthermore, in addition to the carbon itself, the presence of Al_4C_3 in the fiber pyrolyzed up to 1200°C as detected by WAXS may contribute to the electrical conductivity. The organic side chains, especially those having aromatics, were probably converted into a continuous

carbon structure in the alumina matrix rather than being eliminated in the course of the decomposition.

CONCLUSIONS

Poly[[(3-ethoxybenzoyl)oxy]aloxane] in which both aliphatic and aromatic carboxylic acids were introduced as ligands were synthesized. The aloxane backbone units in this inorganic polymer were converted into alumina and a matrix was constructed after pyrolysis. The aromatic side groups distributed randomly in the molecular level on the main chain were converted into carbon and migrated to be some continuous phase in fiber direction which give rise to the electrical conductivity. The carbon content near the fiber surface was found to be lower than that inside of the fiber. This fact suggests a possibility to eliminate the carbon near the surface, which act as a insulating layer of this electrically conductive ceramic fiber.

The authors would like to express their gratitude to Toso-Akzo Chemical Corp. for its kind supply of TEA and to Chemical Research Lab of Nippon Steel for the use of its ESCA instrument. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

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Received November 7, 1990

Accepted April 24, 1991