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Synthesis of Poly[(acyloxy)aloxane] with Carboxyl Ligand and Its Utilization for the Processing of Alumina Fiber

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ABSTRACT: This paper describes the preparation of poly[(propanoyloxy)aloxane] and poly[((3-ethoxypropanoyl)oxy)aloxane] by a three-stage reaction of triethylaluminum (TEA) with water and the relevant carboxylic acids. TEA was first reacted with an equimolar amount of propanoic (PA) and 3-ethoxypropanoic acids (EPA) to produce diethyl(propanoato)aluminum and diethyl(3-ethoxypropanoato)aluminum, respectively, with evolution of 1 equiv mol of ethane. They were hydrolyzed by an equimolar amount of water and gave 1.8 equiv mol of ethane (relative to TEA) and oligo[(acyloxy)aloxanes] having both ethyl and hydroxo terminals. These products aggregated by intermolecular coordination and became gel in the reaction solvents. In the third stage, they were further reacted with PA and EPA, respectively. On evolution of 0.2 equiv mol of ethane (relative to TEA), poly[(acyloxy)aloxanes] with higher solubility and higher degree of polymerization were produced. The structures of the final products were identified by spectroscopic and other analytical data. The ^{27}Al NMR spectra indicated that all Al atoms take a hexacoordinated structure by the complexation of PA and EPA. Thus, poly[(propanoyloxy)aloxane] was the most stabilized when each unit had one PA ligand. Its Al centers have double chelates of the carboxylate and the carboxyl groups of PA and are stacked with bonding oxygens to form a uniaxial sandwich-type configuration. Poly[((3-ethoxypropanoyl)oxy)aloxane], on the other hand, took one EPA ligand in every two units to accomplish the hexacoordination of Al since EPA, with an ethoxy group, is a tridentate ligand. Its configuration is more complex with a fluxional exchange of Al–ethoxy ligand bonds. The concentrated solution of the latter product showed excellent fiber-forming properties and was subjected to conventional dry spinning to prepare a continuous precursor filament. The filament obtained was then pyrolyzed up to 1000 °C in a furnace. After decomposition of the organic residue the filament was sintered to γ-alumina with a satisfactory strength. From these results it was shown that poly[(acyloxy)aloxane] with carboxyl ligand is a good polymer precursor for alumina fiber.

Introduction

The method of making ceramics by pyrolysis of organometallic or inorganic polymers has recently been studied extensively.[1-3] This method is generally called the precursor method or chemical conversion method, by which graphite[4] and silicon carbide fibers[5] are now produced from polyacrylonitrile and polyorganosilane precursors, respectively. The performance of these ceramic fibers obtained by pyrolysis is determined in part by the properties of their precursors[6-9] which must contain the same elements as the product ceramics. Therefore, one of the key steps in the method should be preparation of precursor polymers which are both processable and calcine to the desired ceramics.

Recently, alumina fibers have been produced by the precursor method. The precursors utilized are polymeric ion species 1 formed from hydroxoaluminum chloride[10] and poly(aloxane) 2 by hydrolysis of organoaluminum com-

$$\underset{\textbf{1}}{[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}} \qquad \underset{\textbf{2},\ X\,=\,\text{alkyl, etc.}}{-(Al(-X)-O)_p-}$$

pounds.[2,11] Since both polymers are built up from an Al–O backbone, they presumably have a strong tendency to calcine to alumina. However, the yield of alumina fibers from the polymers is not so high because of the lower processability of the precursors during spinning. In particular, 2 is unstable and easily decomposes to gel during spinning. In addition, its structure is so complex[12-14] that it has not been well characterized yet.

In this paper we describe the synthesis of new poly[(acyloxy)aloxanes][15] **5** with carboxylic acid ligands that are well characterized and useful as alumina precursors. They are readily prepared by a one-pot, three-stage reaction of triethylaluminum with both water and carboxylic acids (Scheme I). A solution of **5** showed good fiber-forming properties and was subjected to an experimental dry spinning. The fibers obtained were then pyrolyzed to alumina at 1000 °C to demonstrate the feasibility of using the polymers for the production of alumina fiber.

Experimental Section

Materials. Triethylaluminum (TEA) was provided by Toyo-Stoffer Chemical Corp. (Tokyo, Japan) and was used without further purification. Tetrahydrofuran (THF), toluene (TOL), and 1,4-dioxane (DOX) were distilled over sodium metal under a

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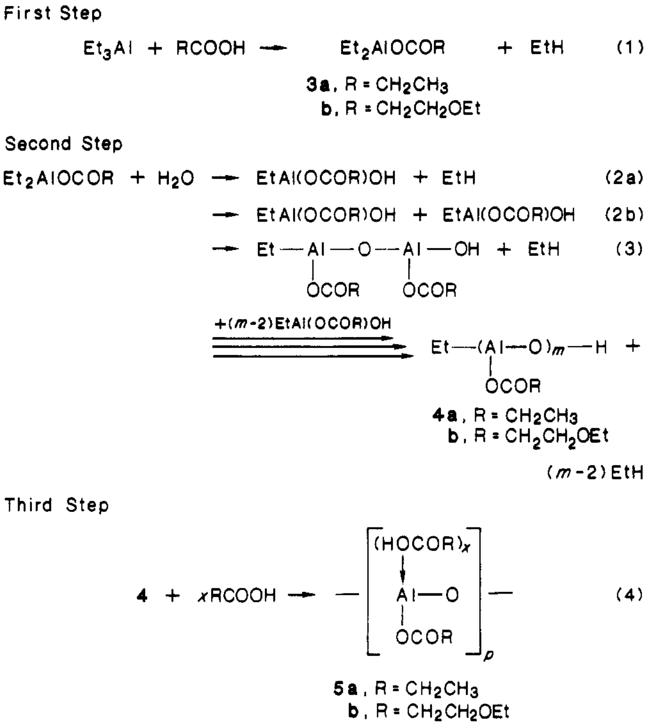
Scheme I



nitrogen atmosphere. Propanoic (PA) and 3-ethoxypropanoic acids (EPA) were supplied from Tokyo-Kasei Kogyo, Ltd. (Tokyo, Japan), and purified by distillation under reduced pressure.

Measurements. ^{27}Al NMR spectra were measured at 20.7 MHz on a Varian FT-80 spectrometer. The chemical shift of the signals[16] was recorded by δ value relative to an external standard: hexaaquaaluminum chloride $[Al(OD_2)_6]^{3+}Cl_3$ in D_2O (50 wt %) at pD = 1. ^{1}H NMR spectra were measured at 200 MHz by a Varian XL-200 spectrometer with tetramethylsilane (TMS) as the internal standard. IR spectra were measured by a JASCO IRA-1 spectrometer. DTA and TGA analyses were recorded in a nitrogen atmosphere on Shimazu DT-30 and Shimazu TG-30 thermal analyzers, respectively. The rate of heating was set at 15 °C/min for a 5.0-mg sample. Wide-angle X-ray scattering (WAXS) was measured by an X-ray diffractometer ADG-301 (Toshiba, Tokyo, Japan) with Ni-filtered Cu Kα radiation (operated at 35 kV and 16 mA). Scanning electron micrographs (SEM) were recorded on a JASCO TSM-25S II microscope. Elemental analyses were made by The Laboratory for Organic Elemental Microanalysis, Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto, Japan. Dilute solution viscosity was measured with a Ubbelohde type viscometer at 30 °C for solutions (4.0 g/dL) of the polymer in a mixture of 1/1 (w/w) phenol (PhOH)/1,1,2,2-tetrachloroethane (TCE).

Diethyl(propanoato)aluminum (3a). A solution of 4.30 g (58 mmol) of PA in 10 mL of TOL was added to the solution of an equimolar amount of TEA in 24 mL of TOL at −20 °C. The ethane gas produced was collected in a graduated tube which was conventionally devised to connect with a glycerol depot at an equilibrium atmospheric pressure for volume measurement. After the addition was over the solution was stirred at room temperature for a half hour to complete the reaction. The final volume of ethane was ca. 1300 cm^3 (58 mmol). The solvent was then removed in vacuo to isolate a colorless liquid product. It was identified as **3a** by the following data: ^{1}H NMR (C_6D_6) δ 0.36 (q, $AlCH_2$, 4 H), 1.23 (m, CH_3, 9 H), 2.5 (t, $COCH_2$, 2 H); ^{27}Al NMR (C_6D_6) δ −0.4; IR (Nujol) 1580, 1470 cm^{-1} (CO_2^-). This product was spectroscopically pure although it was not further purified. It was unstable in air and decomposed during distillation.

Diethyl(3-ethoxypropanoato)aluminum (3b). EPA was reacted with TEA by the same procedure as above. **3b**: ^{1}H NMR (C_6D_6) δ 0.36 (q, $AlCH_2$, 4 H), 1.23 (m, CH_3, 9 H), 2.5 (t, $COCH_2$, 2 H), 3.6 (m, CH_2OCH_2, 4 H); ^{27}Al NMR (C_6D_6) δ −10.8; IR (Nujol) 1580, 1470 (CO_2^-), 1100 (ν_{C-O}) cm^{-1}.

Poly[(propanoyloxy)aloxane] (5a). A solution of 4.30 g (58 mmol) of PA in 10 mL of THF was added dropwise to a solution of an equimolar amount (6.62 g) of TEA in 24 mL of THF with stirring at −20 °C under a nitrogen atmosphere. After the addition, stirring was continued at room temperature for 1 h. It was then cooled to 0 °C again in the second stage and the solution of 1.04 g (58 mmol) of water in 10 mL of THF was added dropwise over a period of 3 h. After the addition was over stirring was continued at room temperature for 2 h. During this time the solution became a gel. To this gel, in the third stage, 4.30 g (58 mmol) of PA in 10 mL of THF was added and mixed thoroughly at room temperature. The system became a homogeneous viscous solution again and was allowed to stand at room temperature overnight. In these reactions the evolved ethane was collected and measured as above. The solution was then poured into a large excess of *n*-hexane to precipitate the polymeric product, which was isolated by filtration and dried in vacuo. The white powdery product thus obtained (11.0 g) was further extracted with *n*-hexane in a Soxhlet extractor for 24 h. After drying the product whose weight was reduced to 10.3 g was analyzed by spectroscopies and elemental analysis. **5a**: ^{1}H NMR (D_2O) δ 1.13 (t, CH_3, 6 H), 2.36 (q, $COCH_2$, 4 H); ^{27}Al NMR (C_6D_6) δ 2.1 (half-width, 1600 Hz); IR (KBr) 1580, 1430 (CO_2^-), 980 (ν_{Al-O}) cm^{-1}. Anal. Calcd for $[C_3H_5AlO_3\cdot(C_3H_6O_2)_{1.0}]_n$: C, 37.90; H, 5.83. Found: C, 37.67; H, 5.89.

Poly[((3-ethoxypropanoyl)oxy)aloxane] (5b). By a similar reaction of TEA with EPA and water **5b** was obtained. The data for the product obtained by adding 0.5 equiv mol of EPA (relative to TEA) in the third stage was as follows: ^{1}H NMR (C_6D_6) δ 1.2 (t, CH_3, 4.5 H), 2.5 (m, $COCH_2$, 3.0 H), 3.6 (m, CH_2OCH_2, 6.0 H); ^{27}Al NMR (C_6D_6) δ 1.4 (half-width, 1600 Hz); IR (KBr) 1580, 1430 (CO_2^-), 1100 (ν_{C-O}), 980 (ν_{Al-O}) cm^{-1}. Anal. Calcd for $[C_5H_9AlO_4\cdot(C_5H_{10}O_3)_{0.5}]_n$: C, 41.10; H, 6.44. Found: C, 41.14; H, 6.86.

Dry Spinning. In a syringe equipped with a needle (3-mm length, 0.5-mm diameter) with an orifice of 0.25-mm i.d., a 10–20 wt % solution of **5b** in toluene was charged and degassed completely. The syringe was fitted with a micro feeding machine (Furue Science (Tokyo, Japan), JP-100G) and the solution was extruded at a constant rate of 0.1 mL/min. The extrudate was taken up at a constant rate and was passed through a drying column kept at 60 °C. The half-dried filament was wound on a roll of paper. It was dried further in an air oven at 100 °C to give a white continuous filament of 16-μm diameter.

Pyrolysis of the Precursor Filament. The above filament was cut to staple fibers of 100-mm length. Several pieces were placed on an alumina boat and pyrolyzed in a tubular electric furnace fitted with silicon carbide heaters with flowing nitrogen. The temperature of the furnace was raised at a constant rate of 5 °C/min and kept at 1000 °C for 0.5 h. After the pyrolysis the furnace was cooled to room temperature slowly (3–5 h). The fibers obtained had decreased in size to 8.2 μm in diameter and 55 mm in length. Their weight had also decreased to 23% of the original.

Results and Discussion

Preparation of Poly[(propanoyloxy)aloxane]. In Table I some results of the one-pot three-stage reaction of TEA with PA and H_2O are shown. In the first stage TEA was reacted with an equimolar amount of PA to form diethyl(propanoato)aluminum (**3a**) and an equimolar amount of ethane (see Experimental Section). In the second stage **3a** was hydrolyzed in situ with an equimolar amount of water. The system became a gel with evolution of 1.8 equiv mol of ethane (relative to TEA). The product isolated from this system was insoluble in any of the organic solvents used (runs 1 and 6). In the third stage PA was added to the gel system and reacted at room temperature. Very quickly, ethane gas was produced in an amount equal to 0.2 equiv of TEA. The gel system was inhomogeneous when the amount of PA was relatively low. However, it yielded a very viscous homogeneous sol in THF, when the amount of PA exceeded 1.0 mol relative to TEA. In the same condition using TOL–DOX system white solids were formed in the gel and precipitated. The products isolated by reprecipitation were crystalline white solids whose yields are shown by the crude yield in Table I. They were further extracted with *n*-hexane for purifi-

Table I
Preparation of Poly[(propanoyloxy)aloxane] by Three-Stage Reaction[a]

			product		
run	PA ratio[b]	solvent	crude yield,[c] g	net yield,[d] g (%)	η_{sp}/C,[e] dL/g
1[f]	0	THF	7.9	6.7	insol
2	0.2	THF	8.3	7.4	insol
3	0.5	THF	10.1	8.7	insol
4	1.0	THF	11.0	10.3 (93)	2.26
5	2.0	THF	12.3	10.6 (96)	0.59
6[f]	0	TOL-DOX[g]	7.5	6.7	insol
7	1.0	TOL-DOX[g]	11.3	10.3 (93)	2.38

[a] [TEA] = [PA] = [H_2O] = 58 mmol in the first and the second stages. [b] In the third stage; in molar ratio of PA to TEA. [c] After reprecipitation. [d] After extraction with *n*-hexane. The theoretical yield of **5a** with an equimolar amount of PA is 11.0 g, on which the percent yield in the parenthesis was calculated. [e] At 4.0 g/dL in phenol (50)–1,1,2,2-tetrachloroethane (50) at 30 °C. [f] Product of the second-stage reaction. [g] The solvent used in the first and the third stages was toluene and that of the second stage was 1,4-dioxane.

cation. The yields after purification are shown as the net yield in the same table, which, in some cases, decreased by more than 20 wt % compared to the crude yield after PA involved in excess was removed. There were some cases that more than 10% of the products themselves were lost from the filter container of the Soxhlet extractor to decrease the yields more than expected. However, it was noted that with increasing amounts of PA in the third stage the crude yield was increased linearly, but the net yield reached a limit in the runs (no. 4, 5, and 7) where the molar ratios of PA to TEA were over 1.0 (vide infra). The solubility of the isolated product was also dependent on the amount of PA reacted. When the molar ratio of PA in the third stage was over 1.0 relative to TEA, all the products were soluble in very polar solvents such as the PhOH–TCE mixture. When it was less than 1.0 the products were insoluble in any of the organic solvents tried. The solution viscosities were the highest in runs 4 and 7, in which the ratio of PA in the third stage was just 1.0 (relative to TEA). It became lower in run 5 when a higher ratio of PA was used.

Preparation of Poly[((3-ethoxypropanoyl)oxy)aloxane]. Table II summarizes the results of the three stage reaction of TEA with EPA and H_2O. In this series diethyl(3-ethoxypropanoato)aluminum (**3b**) was formed in situ in the first stage (see Experimental Section) and was hydrolyzed by an equimolar amount of H_2O in the second stage. The volumes of ethane produced in both stages were almost identical with those of the former cases using PA as acid. After the hydrolysis the system became a gel but the product isolated was soluble in the PhOH–TCE mixture. In the third stage the hydrolysis product was further reacted with EPA. When the molar ratio of EPA to TEA was over 0.5, the gel system became a homogeneous viscous solution in both THF and TOL–DOX. As in the case of TEA–PA–H_2O, the yield of the crude product after reprecipitation was increased with increasing amounts of EPA, but the net yield of the extracted product was limited to ca. 11 g if the molar ratio of EPA to TEA was over 0.5. The products of runs 8, 9, 14, and 15, where the EPA ratio was below 0.5, were soluble only in the PhOH–TCE mixture. In the other runs, the products were all soluble in common organic solvents like THF, TOL, DOX, benzene, chloroform, dimethylformamide, and also the PhOH–TCE mixture. The solution viscosity of the products was highest when the molar ratio of EPA to TEA was 0.5.

Table II
Preparation of Poly[((3-ethoxypropanoyl)oxy)aloxane] by Three-Stage Reaction[a]

			product		
run	EPA ratio[b]	solvent	crude yield,[c] g	net yield,[d] g (%)	η_{sp}/C,[e] dL/g
8[f]	0	THF	9.0	8.8	0.22
9	0.2	THF	10.1	9.8	0.36
10	0.5	THF	10.8	10.7 (84)	0.68
11	0.7	THF	13.1	11.0 (87)	0.67
12	1.0	THF	13.8	10.8 (85)	0.30
13	2.0	THF	18.4	11.1 (87)	0.23
14[f]	0	TOL-DOX[g]	9.3	9.2	0.18
15	0.2	TOL-DOX	10.3	10.1	0.39
16	0.5	TOL-DOX	12.2	11.0 (87)	0.45
17	0.7	TOL-DOX	13.3	10.8 (85)	0.45
18	1.0	TOL-DOX	15.5	11.9 (94)	0.29

[a] [TEA] = [EPA] = [H_2O] = 58 mmol in the first and the second stages. [b] In the third stage; in molar ratio of EPA to TEA. [c] After reprecipitation. [d] After extraction with *n*-hexane. The theoretical yield of **5b** with EPA:TEA mole ratio of 0.5 is 12.7 g, on which the percent yield in the parenthesis was calculated. [e] At 4.0 g/dL in phenol (50)–1,1,2,2-tetrachloroethane (50) at 30 °C. [f] Product of the second-stage reaction. [g] The solvent used in the first and the third stages was toluene and that of the second stage was 1,4-dioxane.

Structure of Hydrolysis Product 4. It is known that poly(ethylaloxane) is formed by partial hydrolysis of TEA.[12-14] However, the product is either an oligomer with a degree of polymerization less than 10 or a heavily cross-linked gel. In the present study, one ethyl group of TEA was replaced by a carboxylate group to stabilize one bond of trivalent aluminum compound against hydrolysis[12] as **3**. Then the remaining diethyl group was to be selectively hydrolyzed to form a linear chain of aloxane with carboxylato pendants. In the practical hydrolysis of **3**, however, least soluble gel products were produced instead of the intended linear polymer (eq 2 and 3 in Scheme I).

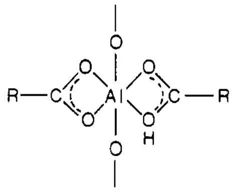
In the case where **3b** was reacted with water in TOL at −20 °C gel was formed when ca. 90% of the H_2O had been added. In the same reaction in THF the system remained homogeneous at −20 °C after all the H_2O had been applied. It became gel while it was worked up at room temperature. Thus, for obtaining clear ^1H and ^{27}Al NMR spectra of the hydrolysis product **4b**, **3b** was hydrolyzed in deuteriated THF and the system just before gelation was directly subjected to the measurements. The results were as follows: ^1H NMR (THF-d_8) δ 0.36 (small q, $AlCH_2$, ca. 0.2 H), 1.0 (small s, AlOH, ca. 0.1 H), 1.2 (m, CH_3, ca. 3.3 H), 2.5 (t, $COCH_2$, 2 H), 3.6 (m, CH_2OCH_2, 4 H); ^{27}Al NMR (THF-d_8) δ 3.2 (line width, 140 Hz). The small upfield signals in the ^1H NMR spectrum are assigned to ethyl and hydroxo groups,[14c] respectively. These signals were detected even after the solution became gel, though the peaks were much broader. The other signals are assigned to the EPA residue. The presence of the ethyl group in the product was supported by the fact that the total amount of ethane produced by the hydrolysis was 1.8 equiv mol of TEA. It was considerably less than the theoretical value of 2.0 obtained by assuming all ethyl groups of **3b** are hydrolyzed.[14c] The product was soluble in a PhOH–TCE mixture but the relative viscosities of the solution were about 0.2 dL/g (runs 8 and 14). The IR spectra of the isolated product showed the characteristic absorptions of hydroxy (3450 cm^{-1}), carboxylate (1580, 1470 cm^{-1}), and ether groups (1100 cm^{-1}). From these data the structure of the hydrolysis product is considered to have an oligomeric chain **4b** in which several (propanoyloxy)aloxane units are bonded linearly and terminated by both ethyl and hydroxo groups. The chains, however, should aggregate with each other to form gel in the reaction solvents. As indicated by the high-field shift of the ^{27}Al NMR signal,[16] the Al atoms of the aloxane units have a hexacoordinated structure. Each Al center of the unit is bonded with two oxygen atoms and one carboxylato group. So the remaining vacant sites for coordination should be filled by coordination of the terminal groups and the pendant carboxylate groups and, sometimes, solvent molecules. In fact, the terminal hydroxo group is known to form a strong coordination bond of the type Al–O(–H)–Al.[17] By these coordinations the chains aggregate strongly to form the gel state. This type of aggregation was possibly untied in very polar solvent like a PhOH–TCE mixture to solubilize the product **4b**.

By the hydrolysis of **3a** the gel product was likewise obtained, although it was insoluble in any solvents due to the tight aggregation and the higher crystallinity. The structure was similarly identified as **4a** by the following data: ^{1}H NMR (THF-d_8) δ 0.34 (small q, AlCH$_2$, 0.2 H), 1.0 (small s, AlOH, 0.1 H), 1.2 (m, CH$_3$, 3.3 H), 2.4 (q, COCH$_2$, 2 H); ^{27}Al NMR (THF-d_8) δ 1.4 (line width, 80 Hz); IR (KBr) 3450 (OH), 1580, 1470 (COO$^-$). It also involves both hydroxo and ethyl terminals.

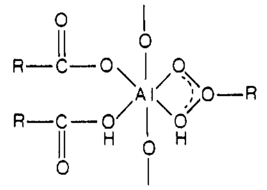
The above results indicate that the condensation of AlEt and AlOH terminals to form AlOAl is inhibited by the mutual aggregation of the oligomer chains of **4**. For attaining the higher degree of polymerization this aggregation should be dispersed so as to allow their intermolecular reactions.

Structure of the Poly[(acyloxy)aloxane] 5 with Carboxyl Ligand. In the third stage of the synthesis the hydrolysis products **4a** and **4b** were reacted with PA and EPA, respectively. In both cases, ethane was produced in ca. 0.2 molar ratio to TEA, which corresponds to the remaining AlEt groups in **4**. When the mole ratio of acid was 1.0 relative to TEA for **4a** and 0.5 for **4b**, the gels of the hydrolysis products were solubilized to form homogeneous viscous solutions. The products isolated from each system became soluble in common organic solvents and their solution viscosities were the highest. Therefore, both of the products were first characterized, which are shown in the Experimental Section.

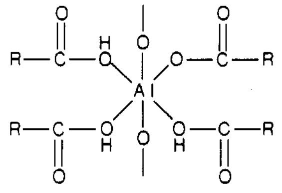
The product **5a** from **4a** showed one ethyl signal due to the propanoyloxy residues in the ^{1}H NMR spectrum and single absorption of the carboxylate group in the IR spectrum. These results indicated that the PA reacted in the first and the third stages are not discriminated and both the propanoate and the propanoic acid ligands are complexed with Al by equivalent bonds. **5a** showed the absorption[18] of $\nu_{\text{Al-O}}$ at 980 cm^{-1}, which was very small in **4a**. The data of elemental analysis of **5a** was coincident with the calculated value assuming a 1:1 complexation of PA with the each (propanoyloxy)aloxane unit. Furthermore, the chemical shift of the ^{27}Al NMR signal of **5a**, appearing in the neighborhood of 0 ppm,[16] indicated the hexacoordination of Al center, and its broad line shape was indicative of the polymeric structure.[16a] In this product, therefore, two of the six coordination sites of Al are occupied by oxygen atoms of the aloxane backbone and the other four can be filled with carboxylate and carboxyl groups of PA, which are both bidentate ligands.[19] The propanoate and propanoic acid ligands are equivalent by proton exchange to form double chelates on the equatorial positions of AlO backbone as depicted in **6a-1**. By uniaxial stacking of these planar units, which are separated by oxygen atoms, the sandwich-type polymer chains are formed. A similar configuration has recently been reported in other oxygenated metal polymers.[20]



6a-1, R = Et
b-1, R = CH$_2$CH$_2$OEt



6a-2
b-2

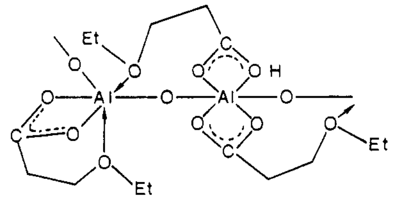


6a-3
b-3

The product **5a** containing PA ligand in a higher molar ratio than 1.0 per unit, e.g., the crude product of run 5, also showed similar spectroscopic data. They are considered to keep the similar hexacoordinated structure to the above with a different mode of complexation. Some of the carboxylate and the carboxyl groups in coordination work as monodentate ligands and two or three carboxylic acids can sit on one unit as shown in **6a-2** or **6a-3**. These products were more soluble in organic solvents because of the increased flexibility of the chain. These units are easily converted to the more stable unit **6a-1** by removal of the excess acid by extraction. Therefore, the products after the purification (run 5) consisted preferentially of the units **6a-1** as those of runs 4 and 7. Based on the composition of **6a-1**, the net yields in the parentheses of Table I were calculated. They were over 90% in the three runs.

In the products with a lower PA ratio than 1.0 per unit, all the coordination sites of Al atoms are not saturated by the ligands. For attaining the hexacoordination these products must aggregate by mutual complexation or bridge formation[17] as **4a**, and become insoluble. With increasing molar ratio of PA the degree of aggregation was decreased and the product was more soluble.

The structure of the product produced by the reaction of **4b** with $^1/_2$ equiv mol of EPA (relative to TEA) is considered to have a similar structure to **5b** from the data in the Experimental Section, although it is somewhat complex. Since EPA is a tridentate ligand with an ethoxy group, the hexacoordination of the aloxane unit is accomplished when every two ((3-ethoxypropanoyl)oxy)aloxane monomeric units are complexed with one EPA in minimum. These cases were the products of runs 10 and 16 where $^1/_2$ equiv mol of PEA was added to **4b**. From the elemental analyses of the isolated products, the EPA ratio per monomeric unit was calculated as 0.5. The chemical shift of the ^{27}Al NMR signals indicated that they have a similar hexacoordinated structure. Therefore, in these products the bidentate carboxylate and carboxyl groups of EPA form the chelates as in **5a** and the ethoxy branches of EPA fill the remaining vacant sites of the Al center. The typical structure is shown as **6b-4**, in which ethoxy groups



6b-4

coordinate the aloxane units that their carboxylate and carboxyl groups coordinate or those adjacent to them. The coordination of the ethoxy groups, however, is rather labile and rapid intra- and/or intermolecular exchange of the metal–ligand bonds should occur in the product. Therefore, the chains of **5b** take a random coil instead of the linear chains like **5a**. These chains have also hydroxo terminals since a very small singlet due to AlOH was detected at δ 1.0 ppm in their ^{1}H NMR spectra. They may also participate in the coordination and increase the solution viscosity of **5b**.

In the products with a higher EPA ratio than 0.5 per unit (runs 11 and 17), the ethoxy ligands are replaced by carboxyl groups of EPA and the units of **6b-1** involving the double chelates of carboxylate and carboxyl groups increase in ratio. The products with EPA ligands in just 1.0 molar ratio per unit (runs 12 and 18) consist mainly of **6b-1** like the product of **5a** with PA in the same ratio. If the ratio of EPA is over 1.0, the units **6b-2** and **6b-3** with two and three EPA ligands, respectively, are involved (run 13). These units are also converted to **6b-4** by extraction of excess EPA. Therefore, the EPA ratio per unit became 0.5 in each of the purified products of runs 11–13, 17, and 18. Their net yields based on this composition are shown in the parentheses of Table II. It should be noted that the yields were as high as 85% although their solution viscosity was relatively low. The products with a smaller EPA ratio than 0.5 should have an unsaturation in the hexacoordination which causes a cross-linking of the product just as **4b**.

The above results indicated that **4a** and **4b** can be set free from aggregation by the complexation with an appropriate amount of carboxylic acid. Then, the reaction can be allowed between the freed hydroxo terminals and Al(OCOR)$_2$ groups that should be produced from the ethyl terminals of **4**. It should be reversible:

$$\text{-Al(-OCOR)-OH} + \text{-Al(-OCOR)-OCOR} \rightleftharpoons \text{-Al(-OCOR)-O-Al(-OCOR)} + \text{RCOOH} \quad (5)$$

The forward condensation leads to the chain extension as observed in runs 4, 7, 10, and 16, while the reverse reaction decreases the molecular weight of the product, as in runs 5 and 13. Therefore, the solution viscosities of **5a** and **5b** were the highest when the ratios of PA and EPA were just 1.0 and 0.5, respectively, at which the hexacoordination of each aloxane unit is accomplished.

The above condensation reaction was supported by the ^{1}H NMR spectroscopy for the aforementioned reaction system of **4b** in deuteriated THF. To the gel of **4b** was added an equimolar amount of EPA (relative to TEA) for the third stage reaction. On addition the broad signals of AlEt (at δ 0.36) disappeared with evolution of ethane, as expected from the rapid reaction of the terminal AlEt with the acid. After a while the system became a viscous solution with dissolution of the gel and the signal due to the other terminal group AlOH (broad singlet at δ 1.0) weakened. In addition, the IR absorbance of $\nu_{\text{O-H}}$ of the isolated products of **5a** and **5b** was much smaller than that of **4a** and **4b** while the absorbance of $\nu_{\text{Al-O}}$ increased in intensity in the former. These observations support the condensation reaction between the terminal OH and Al(OCOR)$_2$ occurring by the action of carboxylic acids.

As mentioned above, the carboxylate and carboxyl ligands of **5** are equivalently complexed with Al atom even in the products with a higher ratio of carboxyl ligands. Most of the carboxyl groups in coordination have a strong nature of ion and the protons freed from them may migrate on the six ligand oxygen atoms around the Al center. The presence of such a proton was supported by the small but sharp IR absorption at 3720 cm^{-1} which is generally assigned to the monomeric OH group. Due to this ionic nature of the products the responsible molecular weight could not be determined by the conventional methods. GPC gave no reproducible data either.

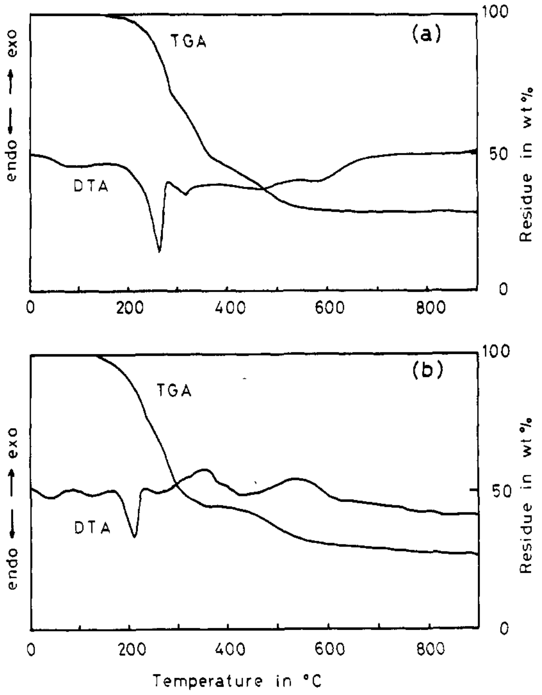
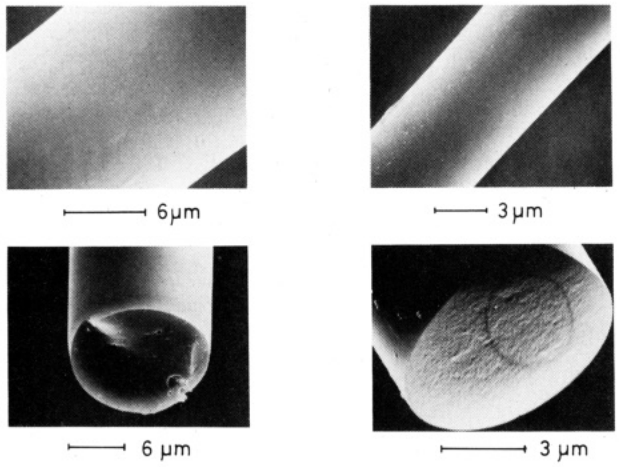


Figure 1. DTA and TGA traces for (a) **5a** with PA ligand in 1.0 molar ratio per aloxane monomer unit and (b) **5b** with EPA ligand in 0.5 molar ratio per aloxane monomer unit (measured in nitrogen atmosphere).

Thermal Properties. Parts a and b of Figure 1 show the typical DTA and TGA curves for **5a** with PA ratio of 1.0 and for **5b** with EPA ratio of 0.5 per monomeric unit, respectively. In DTA endothermic peaks were recorded at 260 °C for **5a** and at 220 °C for **5b**. These peaks were accompanied by sharp weight losses in TGA. Therefore, the thermal decomposition of both polymers start at these temperature regions with eliminating the organic residues. At temperatures of 300–500 °C a milder endothermic process with a slower weight loss was recorded for both polymers, which is attributed to the secondary decomposition of the residues. At over 500 °C little change was shown for both polymers. These results indicate that poly[(acyloxy)aloxanes] **5** are converted to an inorganic material at 500–600 °C. At 900 °C the residues were 30% for **5a** and 29% for **5b**, which were a little higher than the theoretical values of 26.8% and 23.3%, assuming their complete conversion to Al$_2$O$_3$, respectively. The pyrolysates at 900 °C were greyish powders and they might be contaminated by carbon derived from organic residues. When they were further pyrolyzed in air at over 1200 °C pure α-alumina powders were obtained with theoretical yields.

Spinning and Pyrolysis of the Filament of 5b. Poly[(acyloxy)aloxane] **5b** with EPA ligand is soluble in common organic solvents like toluene and forms a very viscous solution with an excellent thread-forming property. In the present study, **5b** with EPA ligand in molar ratio of 0.7 per monomeric unit was used and its 20 wt % solution in toluene was prepared as dope. It was subjected to the conventional dry spinning to give a continuous monofilament with ca. 20-μm diameter quite smoothly. Figure 2a shows the typical SEM micrographs of the filament (16-μm diameter). The surface shows a smooth phase although some holes are shown in the cross-sectional



(a) (b)

Figure 2. Scanning electron micrographs for (a) the precursor fibers and (b) the alumina fibers sintered up to 1000 °C.

view. The defects inside the fiber came from the incomplete desolvation which should be avoided by optimization of the spinning condition. The tensile strength and modulus of the filament were 11 MPa and 0.4 GPa, respectively. So, they were somewhat fragile in handling. The dope of **5b** with EPA ratio of 0.5 per monomeric unit, which was of the highest viscosity, resulted in solution fracture during extrusion. With increasing content of EPA ligand the flow of the extrudate was smoother and the spinnability of the dope became higher.

The filament thus obtained was pyrolyzed to alumina. In this pyrolysis we faced two major difficulties.[21] The one was the large shrinkage of filament (ca. 50% in length), which is expected due to loss of the organic residue and densification of the filament, i.e., from a density of ca. 1.0 (for organics) to 3.0–4.0 (for alumina) during sintering. The other was that the filament contains more than 75 wt % of organic residue that could be carbonized during pyrolysis. Once the filament was contaminated by carbon it was hard to remove by burning. During the pyrolysis, therefore, many defects occurred in the filaments and sometimes the fibrous form was broken. In general, these are avoided by slowing the heating rate and by changing the environmental gas. Through many trials and errors we found that the present precursor fiber can be sintered to alumina with a satisfactory strength by pyrolyzing it up to 1000 °C in flowing nitrogen gas at a heating rate below 10 °C/min.

Figure 2b shows the SEM photographs of the alumina fiber thus obtained. The fiber has homogeneous cross section and surface as does the precursor, in spite of its large shrinkage (49% in diameter and 55% in length). Its tensile strength and modulus were 940 MPa and 60 GPa, respectively, which were somewhat lower than those of the alumina fibers that have recently been commercialized[2,22] (1000–2000 MPa in strength and 300 GPa in modulus). This can be attributed to the abrupt transition of crystalline phase and the uneven grain growth which generally occur at the sintering of pure alumina.[10b] According to the literature,[2,10b] these phenomena may be avoided by adding a small amount of silica and magnesia to the precursor as the sintering agents. The same method will be examined to improve the properties of the above fibers.

The WAXS of the sintered fiber showed principal diffractions[10b] at $2\theta = 67.0°$, 45.9°, and 39.5°. Therefore, its crystalline state was in the γ-phase.[2] Since the transition temperature from the amorphous phase to the γ-phase is ca. 970 °C, the fiber should have undergone the abrupt crystallization, which might give some microcracks and defects inside the fiber. The details will be discussed elsewhere.

In the present experiments we have demonstrated the possibility for developing alumina fiber by using **5b** as the precursor polymer. EPA used is a very characteristic acid ligand in that it gives an excellent solubility and spinnability to poly[(acyloxy)aloxane]. We are studying potential applications of this interesting ligand to other types of organoaluminum polymers.

Registry No. **3a**, 22880-63-3; **3b**, 94190-67-7; **4a**, 109889-87-4; **4b**, 109889-88-5; **5a**, 24767-89-3; **5b**, 109889-89-6; Al_2O_3, 1344-28-1.

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