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(23) The difficulty encountered in the isolation of covalently cross-linked systems after treatment with diamines is due to the limited choice of suitable solvents and the fact that, in solvents such as dimethyl sulfoxide, salt formation precedes covalent coupling. Condensation cross-linking with diols or triols in the presence of dicyclohexylcarbodiimide is difficult to accomplish because of the persistent presence of traces of water in the reactants.

Novel Melt-Processable Poly[(acyloxy)aloxane] as Alumina Precursor

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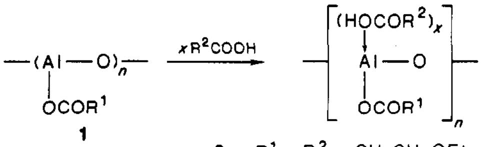
ABSTRACT: A poly[(acyloxy)aloxane] with both *n*-dodecanoic acid (DA) and 3-ethoxypropanoic acid (EPA) ligands was prepared by the sequential reaction of triethylaluminum (TEA) with DA, water, and EPA, respectively. The hydrolytic polymerization of the first-stage product, diethyl(dodecanoato)aluminum, yielded a less soluble cross-linked oligomer of poly[(dodecanoyloxy)aloxane] (PDA). Further reaction with EPA afforded soluble thermoplastics of poly[(acyloxy)aloxane] with DA and EPA mixed ligands. The viscosity of the polymers was found to be dependent on the EPA to TEA ratio when the DA to TEA ratio was kept at unity. The maximum inherent viscosity, 0.58 dL/g, was observed at an EPA to TEA ratio of 0.8. The structure of these polymers was confirmed by ^{27}Al NMR, as well as other spectroscopic techniques and elemental analyses. The hexacoordination states of the aloxane, characteristic of the polymers, were due to the chelation of both the carboxylate and carboxyl groups of DA and EPA. Even for the products with less than 1.0 molar ratio of EPA per repeat unit, the ethoxy group of EPA also participates in the coordination. Since the polymers melted at ca. 200 °C, they could be melt-spun into thin fibers with a ram extruder having an orifice of 0.5 mm in diameter. Both spinnability and the quality of the filaments obtained were found to be best for the polymer with an EPA to TEA ratio of 0.8, whose molecular weight was higher than that of the other polymer samples. The as-spun fibers of this polymer were annealed at 160 °C in a flow of air and then pyrolyzed in a flow of nitrogen from 160 to 700 °C. Above 700 °C the flow was changed to air again, and the fiber was sintered up to 1400 °C. In the course of this multistep pyrolysis the fiber was subjected not only to shrinkage but also to the phase transition of alumina. Hence, the physical properties and the morphology of the fiber were greatly dependent on the pyrolysis temperature. The highest strength and modulus of the sintered fiber were 520 MPa and 48 GPa, respectively. These values ought to increase upon suppression of the abrupt phase transitions. On the bases of these data, poly[(acyloxy)aloxane] with DA and EPA mixed ligands was proven to be versatile as a melt-processable preceramic polymer for alumina.

Introduction

Poly[(acyloxy)aloxane] **1** consists of an Al–O backbone and carboxylate side group. The aluminum can be "properly coordinated" by an appropriate amount of carboxylic acid (eq 1), with the hexacoordination state of the aloxane unit as accomplished in **2**.[1,2] This poly[(acyloxy)aloxane] with carboxy ligands, **2**, becomes more soluble, higher in molecular weight, and better in solution processability than the original polymer **1**. With **2** as a preceramic polymer, the preparation of high-performance alumina fiber has been demonstrated.[1] However, **2** was not melt-processable like other alumina preceramic polymers reported so far,[3] and much effort was necessary in making the precursor fiber with good quality. In this paper we report a novel poly[(acyloxy)aloxane] **2c** with melt-processability and for which a high efficiency in spinning is obtained.



$$-\!\!\left(\underset{\underset{\displaystyle OCOR^1}{|}}{Al}-O\right)_{\!n}\!- \xrightarrow{x\,R^2COOH} -\!\!\left[\begin{array}{c}(HOCOR^2)_x\\ \downarrow\\ Al-O\\ |\\ OCOR^1\end{array}\right]_n\!\!- \qquad (1)$$

1

2a, $R^1 = R^2 = CH_2CH_2OEt$
2b, $R^1 = R^2 = (CH_2)_{10}CH_3$
3c, $R^1 = (CH_2)_{10}CH_3$, $R^2 = CH_2CH_2OEt$

The principle of molecular design for such melt-processable poly[(acyloxy)aloxane] can be explained with the aid of the two derivatives of the series discussed below. One derivative is poly[(3-ethoxypropanoyl)oxy)aloxane], **2a**, having the 3-ethoxypropanoic acid (EPA) ligand to monomer ratio of 0.5,[1] and the other derivative is poly[(*n*-dodecanoyloxy)aloxane], **2b**, having one *n*-dodecanoic acid (DA) per repeat unit.[4] The former is characterized by a good dry-spinnability of its solution, and the latter, having a longer alkyl chain, is characterized by a thermoplastic property despite its poor spinnability. As both characteristics can be attributed to their own ligands, a

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polymer containing both EPA and DA ligands ought to have both thermoplasticity and spinnability.[3] On the basis of this hypothesis poly[(*n*-dodecanoyloxy)aloxane] with EPA ligands was prepared by a sequential reaction of TEA with DA, water, and EPA, similar to the method recently reported by us.[1] The polymer was then subjected to the conventional melt-spinning process and pyrolysis to demonstrate its feasibility in the processing of alumina fiber.

Experimental Section

Materials. Triethylaluminum (TEA) was provided by Toyo-Stowfer Chemical Corp. (Tokyo, Japan) and was used without further purification. Toluene (TOL), 1,4-dioxane (DOX), and tetrahydrofuran (THF) were distilled over sodium metal under a nitrogen atmosphere. *n*-Dodecanoic (DA) 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 was recorded by value relative to the external standard, deuteriated hexaaquaaluminum chloride $[(Al(OD_2)_6]Cl_3$ in D_2O (50 wt %) at pD 1. ^{1}H NMR spectra were measured at 200 MHz on a Varian XL-200 spectrometer with tetramethylsilane as an internal standard. IR spectra were measured by a JASCO IRA-1 spectrometer. DTA and TGA analyses were recorded under a nitrogen atmosphere on Shimazu DT-30 and Shimazu TG-30 thermal analyzers, respectively. The rate of heating was set at 10 °C/min for a 5.0-mg sample. From the endothermic peak of the DTA curve the melting point of the product was determined. Wide-angle X-ray scattering (WAXS) was measured on 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 taken with a JASCO TSM-25S II microscope. Elemental analyses were made by The Laboratory for Organic Elemental Microanalysis, Faculty of Pharmaceutical Science, Kyoto University (Kyoto, Japan). Dilute solution viscosity was measured with an Ubbelohde type viscometer at 30 °C for solutions (0.4 g/dL) of the polymer in toluene. The density of fiber was measured by the sink–float method (Archimedean principle) with a mixture of diiodomethane and benzene. For the fibers with a density over 3.3 g/cm^3 the aqueous solution of thallium formate malonate (Wako Chemical Corp., Japan) was used as the reference liquid.

Tensile Measurement of Fibers. Because of the very brittle character of specimen, test pieces were made as follows. A single filament was placed in the center of a paper frame of 20 mm × 30 mm, having a square window of 10 mm × 10 mm, and then fixed with an ethyl α-cyanoacrylate adhesive. After the both upper and lower parts of the frame were grasped by the jaws of the tensile tester (type TOM 200D (Shinko Tsushin, Tokyo, Japan)), both of the side edges were cut by scissors. Then the tensile measurements were made as usual[5] at a cross-head speed of 0.5 mm/min.

Diethyl(dodecanoato)aluminum (3b). A solution of 11.6 g (58 mmol) of DA in 10 mL of TOL was added to a stirred solution of an equimolar amount (6.62 g) of TEA in 24 mL of TOL at −20 °C under a nitrogen atmosphere. After the addition was over, stirring was continued at room temperature for 30 min to complete the reaction. The volume of ethane collected as the reaction proceeded reached ca. 1300 mL, which corresponds to 58 mmol. The solvent was then removed in vacuo, and the product was isolated in a quantitative yield (16.5 g) as white flakes. **3b**: ^{1}H NMR (C_6D_6) δ 0.4 (q, $AlCH_2$, 4 H), 1.3 (m, CH_3, 9 H), 1.5 (m, CCH_2C, 18 H), 2.6 (m, CH_2COO, 2 H); ^{27}Al NMR (C_6D_6) δ −11 (half-width = 160 Hz); IR (nujol) 2920 (CH_2), 1580, 1470 (CO_2^-) cm^{-1}. This product was not purified further because it was quite sensitive to moisture and temperature.

Poly[(*n*-dodecanoyloxy)aloxane] (1b). Without isolation of **3b** the reaction solution was cooled to 0 °C for the second step of the reaction scheme. The solution was kept stirred under a nitrogen atmosphere, and 1.04 g (58 mmol) of water dissolved in 10 mL of DOX 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 period the solution became gelatinous and turbid. The ethane gas evolved from this reaction was 1.8 equiv relative to TEA. The solvent was evaporated to dryness in vacuo to isolate a white powdery product. Its yield was 14.5 g, which was slightly higher than the theoretical yield (14.1 g) assuming the complete conversion of **3b** to the aloxane units. **1b**: mp 228 °C (by DTA); ^{1}H NMR (THF-d_8) δ 0.4 (q, $AlCH_2$, ca. 0.1 H), 1.1 (s, AlOH, 0.1 H), 1.2 (m, CH_3, ca. 3.2 H), 1.5 (m, CCH_2C, 18 H), 2.6 (m, CH_2COO, 2 H); ^{27}Al NMR (THF-d_8) δ ~2 (half-width = ~600 Hz); IR (nujol) 3450 (OH) 2940 (CH_2), 1570, 1450 (CO_2^-) cm^{-1}. This product was less soluble in common organic solvents and underwent further hydrolysis in air with the evolution of ethane. From ^{1}H NMR the integral ratio of the signal at δ 0.4 to that at δ 2.6, the degree of polymerization of **1b** was calculated to be slightly less than 20.

Poly[(dodecanoyloxy)aloxane] with EPA Ligands (2c). The gellish solution of **1b** resulting from the above reaction was directly subjected to the third stage of the reaction with EPA. The solution was agitated mechanically at room temperature under a nitrogen atmosphere, and 6.85 g (58 mmol) of EPA was added portionwise. Upon the addition of the first portion, 0.2 equiv of ethane relative to TEA was produced. Thereafter no ethane evolved. When approximately half of the EPA had been added, the solution became homogenous and very viscous. After all EPA had been reacted for 5 h, the solution was evaporated to dryness in vacuo. The white residue obtained was washed twice thoroughly with a small portion of *n*-pentane, dried in vacuo, and weighed. The amount of the product obtained was 21.0 g (99%), which was almost quantitative in yield.

Since this product was soluble in most organic solvents, even in *n*-hexane, it was not purified by the usual reprecipitation or exhaustive washing. **2c** ($x = 1$): mp 197 °C; $\eta_{sp}/C = 0.32$ dL/g; ^{1}H NMR (C_6D_6) δ 1.2 (m, CH_3, 6 H), 1.5 (m, CCH_2C, 18 H), 2.6 (m, CH_2COO, 4 H), 3.8 (m, CH_2O, 4 H); ^{27}Al NMR (C_6D_6) δ ~0 (half width = ~2000 Hz); IR (KBr) 2920 (CH_2), 1570, 1450 (CO_2^-), 1100 (CO), 980 (AlO) cm^{-1}. Anal. Calcd for $[C_{12}H_{23}AlO_3(C_5H_{10}O_3)]$: C, 56.65; H, 9.23. Found: C, 56.27; H, 9.38. These data confirmed that EPA reacted quantitatively.

Polymers having a different content of EPA were prepared in a similar manner, e.g., **2c** ($x = 0.8$): mp 199 °C; $\eta_{sp}/C = 0.58$ dL/g. Anal. Calcd for $[C_{12}H_{23}AlO_3(C_5H_{10}O_3)_{0.8}]$: C, 57.03; H, 9.27. Found: C, 56.62; H, 9.48. The spectroscopic data were quite similar to those of **2c** ($x = 1$) except for the integral ratios of ^{1}H NMR.

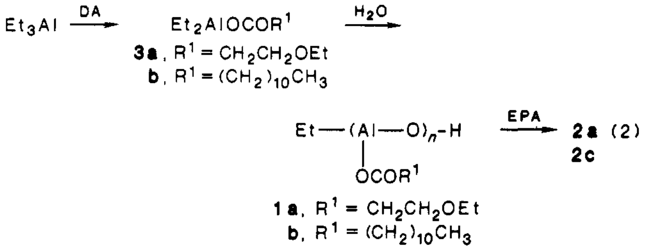
Melt Spinning. The powdered polymer sample (ca. 3 g) was placed in a stainless steel ram extruder that consisted of a cylinder (200-mm length and 20-mm o.d.), a piston rod (10-mm diameter), and a spinneret having a nozzle of 0.5 mm in diameter. The extruder was installed with a micropressing machine (Furue Science, Tokyo, Japan) and heated slowly to 205 °C. Prior to the extrusion the piston was pressed lightly and then released several times to remove the gas included in the melt. Then, the melt was extruded through the nozzle at a constant rate of ca. 0.1 cm^3/min at a constant temperature of 205 °C. The filament was taken on a bobbin under atmospheric conditions at a predetermined velocity of 30–100 m/min. The diameter of the as-spun filament was ranged from 20 to 30 μm.

Pyrolysis of the Filaments. The above precursor filament was cut into short fibers of 100 mm in length. Several pieces of the fibers were placed on an alumina boat and put into a tubular electric furnace (Toyo CT-4C, Tokyo, Japan) with a stream of air (10 cm^3/min) flowing through the furnace. The temperature of the furnace was kept at 160 °C for 6 h during the annealing of the fibers. Then the flowing gas was changed from air to nitrogen (50 cm^3/min), and the temperature was raised to 200 °C for a period of 15 min. Above 200 °C, the temperature was raised stepwise to 700 °C at the rate of 50 °C in an interval of every 15 min. When the temperature reached 700 °C, the nitrogen flow was changed to an air flow (20 cm^3/min) again, with the heating rate kept constant. When the predetermined temperature above 1000 °C was reached, it was held constant for 15 min and then cooled down to room temperature over a period of 3–5 h. The pyrolyzed fibers were found to have decreased in weight and size as compared to the precursors.

Results and Discussion

Preparation of Poly[(acyloxy)aloxane] with Mixed

Ligands. Poly[(acyloxy)aloxane] can be readily prepared by the one-pot sequential reaction of organoaluminum compounds with water and carboxylic acids (eq 2). Trialkyl-[1] and trialkoxyaluminums[2] are useful as the starting materials. In the present study TEA was utilized because the reaction proceeds at low temperatures and the conversion of each of the three steps in eq 2 is quantitative. First, TEA was reacted with an equimolar amount of DA to produce **3b** and ethane in quantitative yields. Compound **3b** as formed was then reacted with an equimolar amount of H_2O to promote the hydrolytic polymerization. In compound **3b**, one of the trivalent aluminum atoms is stabilized so that selective hydrolysis of the ethyl groups was possible. However, the practical reaction system turned gelatinous after evolution of 1.8 equiv of ethane relative to TEA. The product was the less soluble oligomer **1b**, which was insoluble in TOL, DOX, diethyl ether, or chloroform, partly soluble in THF, and soluble in a phenol (PhOH)–tetrachloroethane (TCE) mixture (50/50 in weight). Its IR spectrum showed the characteristic absorptions of the carboxylate groups on the side chains. The ^{1}H NMR spectrum revealed that the product was terminated by both ethyl and hydroxo groups, having a degree of polymerization less than 20 (see Experimental Section). The presence of the ethyl groups in the product was reasonable considering that the total amount of ethane produced by the hydrolysis was 1.8 equiv relative to TEA. It was considerably less than the theoretical value of 2.0 obtained by assuming all ethyl groups of **3b** are hydrolyzed. The relative viscosity of the product was ca. 0.1 dL/g (in a PhOH–TCE mixture). These data indicated that the hydrolysis product is an oligomer consisting of (dodecanoyloxy)aloxane units and terminated by both ethyl and hydroxo groups. The oligomeric chains, however, aggregated with each other to form a gel in the reaction solvent. Its ^{27}Al NMR spectrum in deuteriated THF showed a broad signal centered at 0 ppm, which is a proof of the hexacoordination state of the aluminum atoms.[6] The broadness of the signal may be attributed to the asymmetric environments of the aluminum neclei with quadrapole.[6a] Each Al center of the aloxane 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. These coordinations should lead to the chain aggregation to form the gel state. The similar hexacoordination structures generated by the intermolecular aggregation have been known for basic aluminum chloride with a polymeric chain[6b] and alumino silicates[6c] and also for aluminum salts such as aluminum tricarboxylates[6d,7] and trialkoxides.[6a] All of them exhibit the ^{27}Al NMR signals around 0 ppm. The similar cross-linked structure of **1b** was also found in the case of poly[((3-ethoxypropanoyl)oxy)aloxane] (**1a**) that was previously[1] reported for the hydrolytic polymerization of diethyl(3-ethoxypropanoato)aluminum (**3a**). In these oligomers the condensation of AlEt and AlOH terminals was inhibited, and the polymeric chain of Al–O–Al could not be formed.



$$Et_3Al \xrightarrow{DA} Et_2AlOCOR^1 \xrightarrow{H_2O} Et{-}(\underset{\displaystyle OCOR^1}{Al}{-}O)_n{-}H \xrightarrow{EPA} \mathbf{2a},\ \mathbf{2c} \quad (2)$$

3a, $R^1 = CH_2CH_2OEt$
b, $R^1 = (CH_2)_{10}CH_3$

1a, $R^1 = CH_2CH_2OEt$
b, $R^1 = (CH_2)_{10}CH_3$

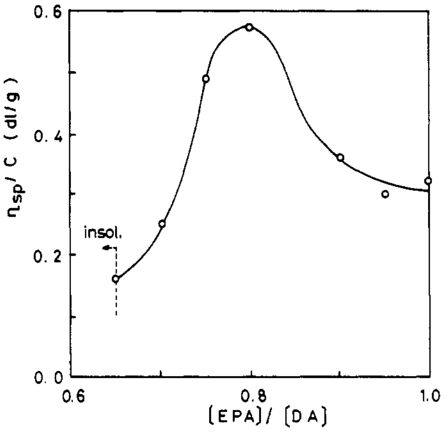


Figure 1. Effect of ligand composition of EPA on the viscosity of **2c**.

In the third stage EPA was added directly to the "gellish" solution of **1b**. It reacted first with the ethyl groups remaining in **1b** to yield 0.2 equiv of ethane relative to TEA, as illustrated in the Experimental Section. EPA then reacted with the internal units of the polymer chains. When the amount of EPA added reached a level greater than 0.65 relative to TEA, the system turned to a viscous sol from the gel state. The product was finally obtained from this sol in a quantitative yield. From the reaction with an equimolar amount of EPA relative to TEA, the product **2c** ($x = 1$) comprising DA and EPA ligands in a 1:1 ratio was obtained. The structure of this product was confirmed by spectroscopies and elemental analyses. The important data for the structural determination were the strong IR absorption[2] at 980 cm^{-1} due to the ν_{Al-O} and the broad signal centered at ca. 0 ppm in the ^{27}Al NMR spectrum.[6] As described above, this suggested that the product should keep a hexacoordination structure within the aloxane unit. The extremely large half-width ($\sim$2000 Hz) of the signal may be attributed to the polymeric structure of **2c** with high viscosity. Since the product was highly soluble, such intermolecular aggregation as in **1b** must have been untied by the coordination of EPA in the vacant sites of the hexacoordinated aluminum atom of the aloxane units. Therefore, the polymers, comprising the units of saturated coordination and thus freed from the cross-linking , could get into a chain growth by the mutual reaction of their terminals.[1] The most probable structure of the polymers produced is that depicted in **4a**, in which the Al(III) of the Al–O backbone is chelated by both the carboxylate and carboxyl groups of EPA and DA. Since the carboxyl and carboxylate groups have a similar nature when coordinated, both ligand types are thought to be equivalent with a fast proton scrambling. This postulate was supported by the observation of the sole carboxylate absorption in the IR spectrum. However, the placement and sequence of both the carboxyl and carboxylate groups on the chain were not clarified yet. It should be most probable to consider a random sequence because the large half-width of the ^{27}Al NMR should be ascribed not only to the viscosity effect but also to the multiple environments of the aloxane units.

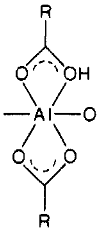
Products with EPA to TEA ratios of less than unity were also prepared. These were accomplished by decreasing the amount of EPA over the range of 1.0–0.65 relative to TEA or DA. At the values below 0.65 the gel of **1b** did not turn into a sol, and insoluble products were obtained. The ligand ratios in the isolated products were found to be identical with the EPA to DA feed ratio by ^{1}H NMR spectroscopy. Figure 1 shows the change in the solution viscosity of **2c** as a function of the EPA to TEA ratio, x.

Table I
Results of Melt-Spinning of Poly[(acyloxy)aloxanes] and the Properties of the Precursor Fibers

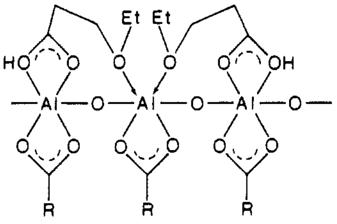
							tensile properties		
run	polym (x^a)	η_{sp}/C,[b] dL/g	mp, °C	spinning temp, °C	max melt-draw ratio[c]	filament[d] diam, μm	strength, MPa	elongation, %	modulus, GPa
1	**1b** (0)	insol	228	235	35	81	1	1.1	0.07
2	**2c** (0.8)	0.58	199	205	>100	25	24	1.8	1.4
3	**2c** (1.0)	0.32	197	205	>100	27	17	1.9	0.9

[a] EPA ratio per monomer unit. [b] In toluene (C = 0.4 g/dL). [c] V_L/V_0 where V_L is the maximum take-up velocity of the fiber (m/min) and V_0 is the extrusion velocity of the melt (m/min). [d] Of the typical as-spun filaments.

The viscosity sharply increased as x increased above 0.65 and reached a maximum 0.58 dL/g at x = 0.8. Thereafter the viscosity decreased once more. Since the carboxyl and carboxylate ligands are bidentate[7] in nature, the six coordination sites of the aluminum atoms in **2c** with x = 1 are completely filled by these ligands and the two Al–O bonds. However, in **2c** with $x < 1$ some of the coordination sites are vacant and should be filled by the ethoxy groups of EPA, which is a much weaker coordination ligand. In general, the highest viscosity for the poly[(acyloxy)aloxane] was obtained when the number of coordination sites was balanced with the number of ligands.[1,2] Thus, for all aluminum atoms of **2c** to be in a full-coordination state the theoretical ratio of EPA to monomer unit should be 0.67; two sites are occupied by two Al–O bonds, two by DA, 1.33 by the EPA carboxyl, and 0.67 by the EPA ethoxy group. However, this would be an ideal case because a special ligand placement and a specific chain conformation would be necessary for all the ethoxy groups of EPA to participate in the coordination. In practice, **2c** would have a ramdom sequence of the acid groups as mentioned earlier and involves units having either two DA ligands, two EPA ligands, or one DA ligand and one EPA ligand. Therefore, the full balance between coordination sites and ligands was obtained at x = 0.8 to achieve the highest molecular weight.[8] The product **2c** with $x < 2$ is believed to contain units such as those in **4b**, in which the coordination of the ethoxy groups of EPA to a unit having only one carboxylate group is involved. Such coordinations may also occur intermolecularly.



4a



4b

R = CH_2CH_2OEt or $(CH_2)_{10}CH_3$

Thermal Properties. Figure 2 shows the DTA curves of **1b** and **2c** with different ratios of EPA ligands to TEA. Each curve shows an endothermic peak below 230 °C which can be ascribed to the fusion of the polymer crystals. In the cooling experiment, the crystallization reoccurred at a temperature well below the melting point because of the supercooling for each sample. These results supported the thermoplastic character of the three polymers. There was a tendency for the endotherm to become sharper and lower in temperature as the amount of EPA ligands contained in the samples was increased. The melting points of **1b** containing no EPA ligands was much higher than that for **2c**, which contained EPA. The thermal fusion of **1b** could occur after the intermolecular aggregation was dissociated at a higher temperature. The exothermic peaks noted in the three curves over the temperature range of 250–500 °C are due to the decomposition of the organic residues. Above 500 °C several broad endothermic peaks were observed, indicating the calcination of the inorganic residues.

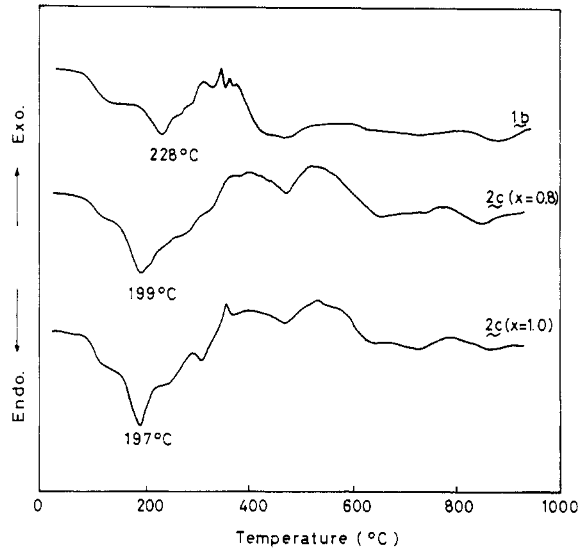


Figure 2. DTA curves of poly[(acyloxy)aloxanes] **1b** and **2c** with different EPA ratios, x.

TGA analyses of these samples indicated that the final residual weight fractions at 1000 °C were 23 wt % for **1b**, 17 wt % for **2c** (x = 0.8), and 16 wt % for **2c** (x = 1.0). Since the theoretical yields of aluminum oxide from the three are 21.0%, 15.1%, and 14.1%, respectively, the final residual weights obtained in TGA are slightly higher. This may be attributed to the carbon remaining inside the ceramic residues.

Melt-Spinnability. The three polymers shown above were subjected to melt spinning at a temperature slightly above their melting points. During the spinning process, the melt was extruded at a constant rate and drawn into a thin fiber by applying tension. The spinnability was evaluated by the maximum melt–draw ratio, V_L/V_0, where V_0 and V_L are the extrusion velocity of the melt and the maximum take-up velocity at which the running filament breaks, respectively.[9] The results, including those of the fiber properties, are summarized in Table I. The maximum melt–draw ratio of **2c** was much higher than that of **1b** containing no EPA ligands and even surpassed the maximum velocity of the winder used. The filament diameters of **2c** shown in Table I were those determined for the fibers that were obtained at the melt–draw ratio of ca. 100. The fiber of **2c** can be spun thinner as to have a diameter of ca. 9 μm, while it was not possible to make that of **1b** thinner than 50 μm in diameter. In addition, the fiber of **1b** was found to have a wrinkled surface by SEM, which should be derived from the large shrinkage due to the intermolecular aggregation recurring by solidification of the polymer melt. The fiber of **2c**, in turn, showed an ordinary smooth surface.

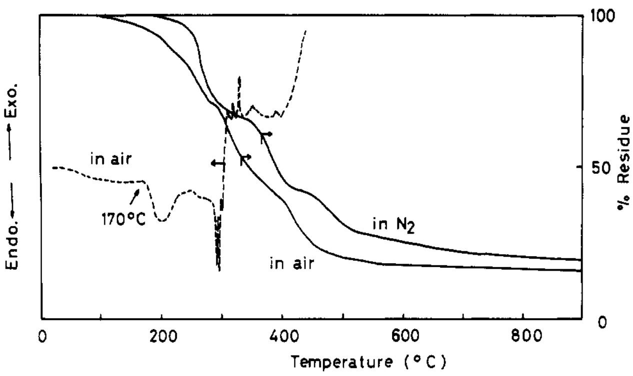


Figure 3. DTA and TGA curves of **2c** ($x = 0.8$) under a flow of air and TGA curve of **2c** under a flow of nitrogen.

The drawing of these as-spun fibers was not studied because they were all brittle, like other preceramic fibers thus far.[10] The highest mechanical properties were shown by the fiber of **2c** ($x = 0.8$), although the values were not so high. The tensile properties of this fiber were almost 1.5 times those of the fibers obtained from **2c** ($x = 2.0$) and even 20 times those of **1b**. This tendency is compatible with their viscosity and molecular weight differences. On the basis of the above data, the fiber made from poly[(acyloxy)aloxane] with an EPA to DA ratio of 0.8, **2c** ($x = 0.8$), was chosen as the precursor for processing of alumina fiber.

Pyrolysis. The pyrolysis of the precursor fiber was divided into three processes: annealing, thermolysis, and sintering, according to the thermal properties of **2c** ($x = 0.8$). Since the melt-spun fiber of **2c** ($x = 0.8$) is thermoplastic, it must be made infusible by proper annealing before pyrolytic calcination at high temperature. Figure 3 shows the typical DTA and TGA curves of **2c** ($x = 0.8$) in air and the TGA curve measured under a stream of nitrogen for comparison. The DTA showed that the polymer began to decompose in air at a temperature below the melting point and calcined to alumina at a much higher rate than it did in nitrogen. The oxygen and moisture in the air probably hastened the decomposition. The DTA taken in air was also quite different from that in nitrogen (the middle curve in Figure 2). It showed a relatively small endothermic peak around the melting point and a large exothermic peak above 290 °C due to the oxidative decomposition of the organic residue portion. Since the endothermic peak began to decline at 170 °C, the polymer should maintain its solid state at 160 °C in spite of decomposition occurring very slowly. Thus, an attempt of the annealing of the fiber was made at 160 °C by exposing it to a stream of air for 6 h. After this treatment the fiber was found to be less fusible, even at over 200 °C.

The fiber thus heat-set was pyrolyzed in a stream of nitrogen at a sufficiently slow rate of heating so as to obtain a decrease in weight not exceeding 1 wt % per minute. This thermolysis process covered the temperature range 160–700 °C. When the pyrolysis was performed in air, an exothermic thermolysis was observed as indicated in the DTA and caused an extraordinary weight loss as well as the formation of cracks inside the fiber.[11] After the intensive survey for the appropriate heating rate, it was found that the stepwise heating of 50 °C in 15-min intervals, corresponding to 3.3 °C/min on average, was adequate for the manual control of the temperature of the furnace. The details will appear elsewhere. In this step most of the organic residue of **2c** ($x = 0.8$) was removed as proven by the TGA analysis under nitrogen.

Above 700 °C the nitrogen stream was changed to a stream of air once again, and the heating was continued at the same rate. In this sintering step a trace of carbon residue generated from the organic residue was burned off, and the fiber was sintered to a solid ceramic. During this period, the inner structural changes of the fiber, such as grain growth, should have occurred with the change of crystalline states. Through these three carefully controlled processes the precursor fiber was successfully converted to alumina.

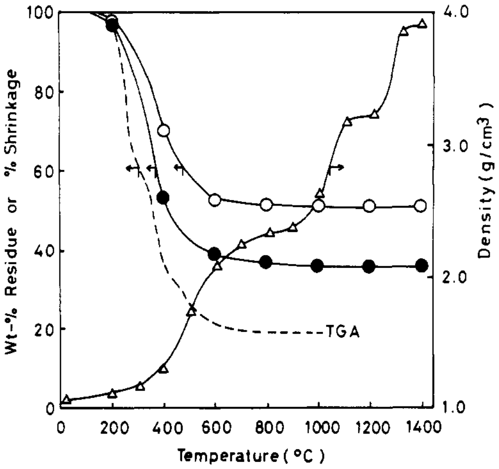


Figure 4. Changes in length (○), diameter (●), and density (△) of the filament as a function of pyrolysis temperature, as compared to the TGA curve under nitrogen (dotted line).

Fiber Properties. During the above pyrolysis enormous shrinkage was incurred by the fiber because it had lost more than 80% of the mass and had increased in specific gravity, i.e., from a value of 1.1 of the organic precursor to 3.0–4.0 of the ceramic product. Figure 4 shows the changes in filament shrinkage and in filament density during the course of the present pyrolysis. Most of the filament shrinkage occurred during the thermolysis process at the temperatures between 200 and 700 °C where most of the organic residue was removed (see TGA curve). The annealing process induced little change in the appearance of the fiber. During the sintering process the filament diameter continued to decrease at a relatively lower rate while its length was kept almost unchanged. The length and diameter of the fiber obtained at 1400 °C were 51% and 35% of those of the original fiber, respectively. The smaller the ratio of shrinkage in length to that in diameter may be due to the molecular orientation in the precursor fiber, although the crystal orientation was not detected by the X-ray diffraction.

As for the density of the fiber, three well-defined stages were noted. Below 400 °C the density was lower than 1.5, indicating the organic nature of the fiber. Following the first increase in density by calcination, the fiber became inorganic, and a density of ca. 2.2 persisted over the temperature range 600–900 °C. In this region the fiber should be amorphous alumina (*a*-alumina). The second increase in density then occurred together with the phase transition of alumina, i.e., from *a*-alumina to γ-alumina.[12] The density became constant again at a value of 3.2 for the γ-alumina at 1100–1200°C. Above 1200 °C there was the third sharp increase in density up to 3.8–3.9, and this can be attributed to the transition of the γ-alumina to α-alumina. The transition temperatures of *a* → γ and γ → α are known to be 970 and 1100–1200 °C, respectively.[12b] These are quite comparable with the above two increasing regions in the density–temperature profile. These phase transitions were also supported by the variation in the WAXS patterns as the increases in the density of the fibers were transcended.

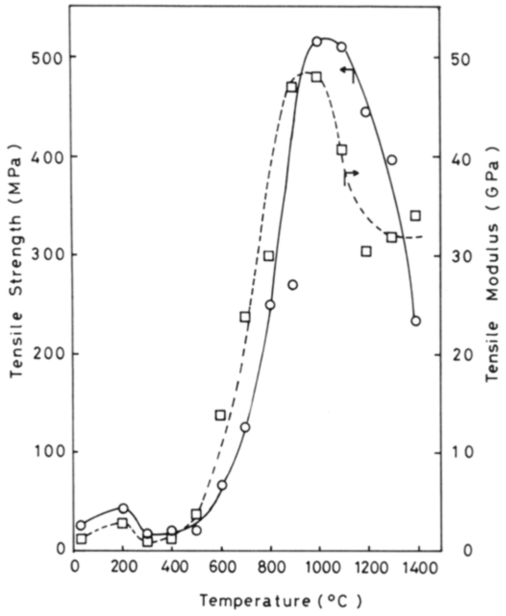
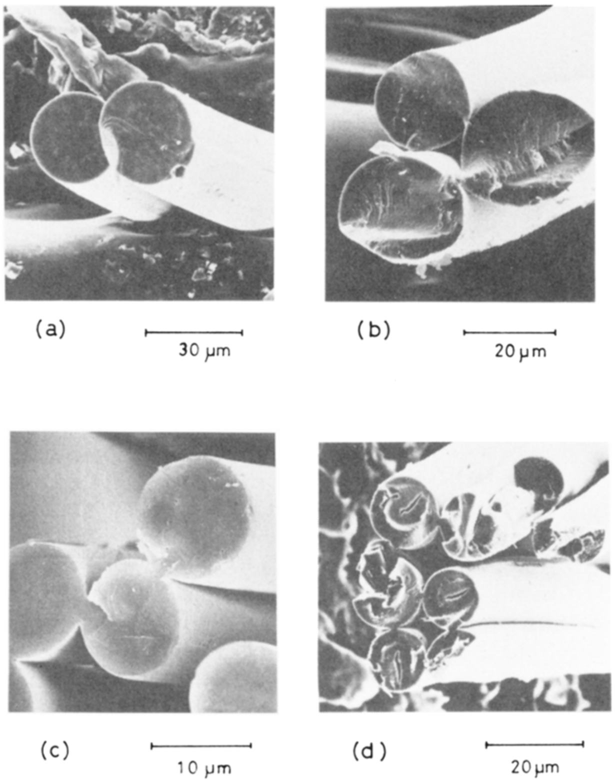


Figure 5. Changes in mechanical properties with pyrolysis temperature.

The WAXS of the fiber pyrolyzed at 600 °C showed only a broad halo, indicating the amorphous nature. In the WAXS of the fiber sintered at 1100 °C, three reflections were recorded at $2\theta = 67.0, 45.9$, and 39.5°, which correspond to those of γ-alumina.[12b] The fiber sintered at 1400 °C showed the same WAXS pattern with α-alumina[12b] whose diffractions appear at $2\theta = 57.6, 43.5, 35.1, 25.7$°, etc. These phase transitions generally have a great influence on the mechanical properties and morphologies of the fiber.

Figure 5 shows the changes in the mechanical properties of the fiber with pyrolysis temperature. The tensile strength and the modulus of the precursor fiber increased slightly after annealing. In the earlier stages of the thermolysis process, however, the mechanical properties of the precursor fiber showed a tendency of deterioration. The mechanical properties became lower than those of the precursor, perhaps owing to the thermal degradation of the fiber. Above 500 °C, once most of the organic residue had been removed, a great increase in mechanical properties was exhibited. The fiber strength reached a maximum at 1000 °C. This should be ascribed to the densification of fiber with sintering. When the fiber was pyrolyzed in air, in the temperature range of 160–700 °C, the maximum strength observed was at least 20% lower than that of the fiber sintered in nitrogen. This result was probably because of the inner defects occurring during the exothermic process (vide supra). Above 1000 °C, the fiber decreased in the mechanical strength in spite of the increasing density of the fiber. This deterioration may be associated with the aforementioned phase transitions of alumina $a \to \gamma \to \alpha$. Since the crystallization of ceramics is a rapid process above the transition temperatures, it is generally followed by an abrupt shrinkage and a grain growth in the fiber, and sometimes microcracks prevail in the boundaries of the grains, causing strength deterioration. Therefore, these abrupt phase changes must be suppressed to obtain a high-performance fiber, for example, by mixing sintering agents in the precursor.[3] In the present experiments such a control was not attempted, and the strength and the modulus were lowered abruptly above the phase transitions of alumina.



(a) (b) (c) (d)

Figure 6. Scanning electron micrographs of (a) the precursor fiber and the alumina fibers calcined at (b) 600, (c) 1000, and (d) 1400 °C.

The maximum strength and modulus obtained were 520 MPa and 48 GPa at 1000 °C, respectively. These values were considerably lower than those of the alumina fibers that have recently been commercialized[3] (1–2 GPa in strength and 300 GPa in modulus, modified with silica and magnesia as the sintering agents).

Morphology. Figure 6 shows the scanning electron micrographs of the precursor fiber and of the calcined fibers at three representative temperatures. The precursor fiber had small holes in the cross-sectional area, which were due to the incomplete degassing from the polymer melt in spite of efforts to degas the melt prior to extrusion. It is felt that those holes could be removed by improving the spinning method, e.g., by use of a screw extruder.[9] The fiber calcined at 600 °C exhibited a phase similar to that of the precursor, even though large amounts of shrinkage had occurred. Since the holes in the cross section did not seem to increase in number, they must have originated from those in the precursor. In other words, cracks and defects should not have been induced in the fiber during the removal of organic residue. At 1000 °C more homogeneous phases were formed although interfilament sticking happened to occur in this case. On the other hand, the fiber sintered at 1400 °C showed large cracks inside the fiber, which were induced by the abrupt shrinkage following the phase transition. The presence of these cracks resulted in the aforementioned deterioration of the fiber properties.

In conclusion, the possibility of developing alumina fiber was demonstrated with thermoplastic poly[(acyloxy)aloxane] **2c** as the preceramic polymer. **2c** showed a good melt-spinnability, being equal to that of ordinary organic polymers. The melt-spun fiber was annealed and pyrolyzed successfully to give alumina fiber with a considerably high strength. We are currently improving the method by adding some sintering agents to the precursor to produce a high-performance ceramic fiber.

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Carbonation and Related Reactions of Poly(styryl)lithium

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ABSTRACT: The carbonation of polymeric organolithium compounds using carbon dioxide has been studied by a combination of acid titration, size-exclusion and thin-layer chromatography, and infrared and ultraviolet spectral analysis. In hydrocarbon solution, the hydrolysis products of this reaction were the carboxylated polymer, the corresponding ketone (dimer) and alcohol (trimer). In general, the addition of a Lewis base (e.g., tetrahydrofuran) was found to attenuate the yield of the dimeric and trimeric products. However, the total elimination of these higher molecular weight products was accomplished by the carbonation of freeze-dried material where the active centers were complexed with one or two molecules of *N,N,N′,N′*-tetramethylethylenediamine.

Introduction

Alkyllithium-initiated anionic polymerizations of certain monomers can be performed without the incursion of spontaneous termination or chain-transfer reactions.[1–4] When suitable initiators and procedures are used, these polymerizations yield polymers with predictable molecular weights and narrow molecular weight distributions.[1] Because of the absence of termination and chain-transfer reactions, these polymerizations generate stable, carbanionic chain ends which allow controlled termination reactions to be effected.[2] In principal, chains with a variety of functional groups at one or both ends can be prepared.[5] However, many of the reported examples of anionic chain-end functionalizations have not been well characterized.[2]

The carbonation of polymeric carbanions using carbon dioxide is one of the most useful and widely used functionalization reactions.[2] However, there are special problems associated with the simple carbonation of polymeric organolithium compounds. For example, it has been reported that the resulting carboxylated polymer is contaminated with significant amounts of the corresponding ketone (dimer) and tertiary alcohol (trimer) as shown in eq 1.[6,7]

$$\mathrm{PLi} \xrightarrow{\mathrm{CO_2}} \xrightarrow{\mathrm{H_3O^+}} \mathrm{PCO_2H} + \mathrm{P_2CO} + \mathrm{P_3COH} \qquad (1)$$

We previously reported results of a study of the carbonation of polymeric organolithium compounds using high vacuum techniques and high-purity, gaseous carbon dioxide.[8] Carbonations of poly(styryl)lithium, poly(isoprenyl)lithium, and poly(styrene-*b*-isoprenyl)lithium in benzene were reported to produce a mixture of the polymer carboxylic acids (60% yields) and the corresponding ketone dimers (40% yields), but no tertiary alcohols were detected by size exclusion chromatography.[8] When analogous carbonations were carried out in the presence of 25/75 tetrahydrofuran (THF)/benzene (v/v) mixtures to eliminate chain-end association,[2] the carboxylation occurred essentially quantitatively (eq 2).[8] Furthermore, when a

$$\mathrm{PLi} \xrightarrow{\mathrm{CO_2}} \xrightarrow{\mathrm{H_3O^+}} \underset{100\%}{\mathrm{PCO_2H}} \qquad (2)$$

freeze-dried sample of poly(styryl)lithium was carboxylated, it was reported that the ketone could be efficiently prepared (eq 3).[9]

$$\mathrm{PsLi} \xrightarrow[\text{freeze-drying from benzene}]{} \xrightarrow{\mathrm{CO_2}} \xrightarrow{\mathrm{H_3O^+}} \underset{90\%}{\mathrm{(Ps)_2CO}} \qquad (3)$$

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