Preparation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-ZrO}_2$ Fibers from Polyaluminosiloxanes and Polyzirconosiloxanes*

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ポリアルミノシロキサン及びポリジルコノシロキサンからの $\text{SiO}_2\text{-Al}_2\text{O}_3$ 及び $\text{SiO}_2\text{-ZrO}_2$ 繊維の調製*

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$\text{SiO}_2\text{-Al}_2\text{O}_3$ fibers and $\text{SiO}_2\text{-ZrO}_2$ fibers were prepared by a new method via polyaluminosiloxanes (PAS) and polyzirconosiloxanes (PZS) prepared from silicic acid and metal chelates. Silicic acid was brought to reaction with 2, 4-pentanedionatoaluminum diisopropoxide and bis (2, 4-pentanedionato) (ethyl 3-oxobutanato) zirconium isopropoxide to give PAS and PZS with spinnability and stability against condensations. Precursor fibers were obtained by dry spinning of PAS and PZS. $\text{SiO}_2\text{-Al}_2\text{O}_3$ fibers and $\text{SiO}_2\text{-ZrO}_2$ fibers were formed by pyrolysis of the precursor fibers at 1000°C.

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1. Introduction

As it is well known, precursor method is one of the routes for preparing ceramic fibers. Recent interests have been focused on the method using organometallic polymer precursors derived from organometallic compounds through their polymerization. In the method, the formation of organometallic polymers soluble in solvents is the key process for preparing ceramic fibers from organometallic compounds: it allows us to prepare precursor fibers from the polymer solutions by dry spinning. Hydrolytic polycondensation is the reaction to prepare precursors for M_xO_y (and $\text{SiO}_2\text{-M}_x\text{O}_y$) fibers using organometallic compounds such as triethylaluminum, diethylaluminum monocarboxylate and titanium tetraalkoxide. $\text{SiO}_2\text{-M}_x\text{O}_y$ fibers have been also prepared by cohydrolysis of two component-metal alkoxide systems such as $\text{Si}(\text{OEt})_4\text{-Al}(\text{OR})_3^{1)}$, $\text{Ti}(\text{OR})_4^{2)}$ and $\text{Zr}(\text{OR})_4^{3)}$. However, the methods tend to provide polymetalloxanes which undergo further condensation to form gels: metal alkoxides are highly sensitive to hydrolysis and have a func-

tionality more than two which, in turn, makes it difficult to direct the reaction toward controlled polymerization. Chemical modification and/or derivatization of metal alkoxides would allow to regulate their functionality or hydrolysis and consequently polymerization reaction. We have found that polytitanosiloxanes with good spinnability are obtained by the reaction of silicic acid with titanium chelates.⁴⁾

In this paper, we wish to report that polyaluminum- and zirconosiloxane with an appreciable spinnability are formed by the reaction of silicic acid with aluminum and zirconium chelates derived by modification of the metal alkoxides, and $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-ZrO}_2$ fibers are prepared by pyrolysis of the precursor fibers made by dry spinning of polymer solutions.

2. Experiment

2.1 Materials

Silicic acid ($\text{HO}[-\text{Si}(\text{OH})_2-\text{O}]_n\text{-H}$, SA) was prepared from sodium metasilicate as a 0.85 mol/l SiO_2 -tetrahydrofuran solution by method described in the previous paper.⁵⁾

Aluminum chelate, (2,4-pentanedionato) aluminum diisopropoxide (PAP), was prepared according to the literature.⁶⁾

Zirconium chelate, bis (2, 4-pentanedionato)

* Studies on the Syntheses of Polymetalloxanes and Their Properties as a Precursor for Amorphous Oxide (Part 2)
ポリメタロキシサンの合成及びそれらの非晶質酸化物前駆体としての性質についての研究 (第2報)

(ethyl 3-oxobutanato) zirconium isopropoxide (PEZP), was prepared by the reaction of bis (2, 4-pentanedionato) zirconium diisopropoxide with ethyl 3-oxobutanate at the 1 : 1 molar ratio.

2.2 Preparation of polyalumino- and zirco-nosiloxanes

Polyaluminosiloxanes (PAS) and polyzirconosiloxanes (PZS) were prepared by the reaction of SA with PAP or PEZP in methanol. The reaction was carried out at various molar ratios of SA to PAP (SA/PAP=0.25, 0.5, 1.0, 2.0) or PEZP (SA/PEZP=0.5, 1.0, 2.0). The SA/THF solution (5.9 ml, 0.01 mol) and methanol (20 ml) was added into PAP or PEZP in the molar ratio mentioned above, and then refluxed for a period of a certain time. The resultant mixture was concentrated *in vacuo* to give a highly viscous solution or gel. Highly viscous solutions were obtained at the molar ratios SA/PAP=0.25 and 0.5, or SA/PEZP=0.5 and 1.0. The polymers were isolated by the reprecipitation method : they were once dissolved in 5 ml of acetone and poured into 200 ml of hexane under vigorous stirring followed by filtration and drying *in vacuo* to give white or slightly yellow powders.

2.3 Preparation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ fibers and $\text{SiO}_2\text{-ZrO}_2$ fibers

$\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-ZrO}_2$ precursor fibers were obtained by dry spinning of a highly viscous solution of PAS (SA/PAP=0.5) and PZS (SA/PEZP=1.0), followed by pyrolysis at 900°, 1000° or 1200°C for 1 h to give $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-ZrO}_2$ fibers.

2.4 Measurements

The IR spectra of PAS and PZS were measured with KBr disk method using Hitachi IR spectrophotometer model 260-50. The NMR spectra were measured using JEOL model JNM-PMX 60 SI. TG and DTA curves were measured using Rigaku Denki Thermoflex (high temperature type). The X-ray diffractogram of $\text{SiO}_2\text{-Al}_2\text{O}_3$ fibers and $\text{SiO}_2\text{-ZrO}_2$ fibers were measured using Rigaku Denki model RAD-II A.

3. Results

3.1 Formation of polyalumino- and zirco-nosiloxanes

Spinnability was estimated by measuring the length of fiber formed by dipping a glass rod (5 ϕ mm) in the solution and pulling it up. A fiber of 40 cm long was obtained from PAS at the molar ratio SA/PAP=0.25 and without refluxing. Spinnability of PAS was remarkably dependent on the molar ratio SA/PAP and reaction time, and it was observed that it decreased with an increase in the molar ratio or reaction time. On

the other hand, the reaction in the molar ratio SA/PEZP=0.5 and 1.0 gave a highly viscous brown solution. A fiber of 155 cm long was obtained at the molar ratio SA/PEZP=0.5 and reaction time 0.5 h. Spinnability of PZS showed no remarkable dependency on molar ratio or reaction time. Comparing the spinnability of PAS with that of PZS or PTS (polytitanosiloxane reported in earlier letter⁴⁾), PAS shows appreciably low spinnability in a narrow range of molar ratio and reaction time, while PZS shows almost the same tendency as PTS. Furthermore, there appears maximum in the plot of spinnability versus molar ratio or reaction time in the case of PZS, whereas in the case of PAS spinnability decreases as the molar ratio or reaction time increases.

The IR spectra of isolated PAS and PZS are shown in Figs. 1 and 2, which show absorption peaks due to silanol group (ν_{SiOH} 3400 cm^{-1}), 2, 4-pentanedionato group or ethyl 3-oxobutanato group ($\nu_{\text{C=O}}$ 2900 cm^{-1} , $\nu_{\text{C=O}}$ 1610 cm^{-1} , 1540 cm^{-1}), and linkages of Si-O-Si ($\nu_{\text{Si-O-Si}}$ 1070 cm^{-1}), Si-O-Al ($\nu_{\text{Si-O-Al}}$ 1030 cm^{-1})⁷⁾ or Si-O-Zr ($\nu_{\text{Si-O-Zr}}$ 1020 cm^{-1}).⁷⁾ The NMR spectra showed peaks due to 2,4-pentanedionato group (δ 1.88 ppm, δ 5.18 ppm), silanol group (δ 3.5 ppm) and ethyl 3-oxobutanato group (δ 2.00 ppm). These spectra indicate that PAS and PZS are composed of Si-O-Si and Si-O-Al or Si-O-Zr linkages with silanol and 2, 4-pentanedionato or ethyl 3-oxobutanato group as

Fig. 1. IR spectrum of PAS (SA/PAP=0.5).

Fig. 2. IR spectrum of PZS (SA/PEZP=1.0).

Fig. 3. TG and DTA curves of PAS (SA/PAP=0.5).

Fig. 4. TG and DTA curves of PZS (SA/PEZP=1.0).

pendants.

3.2 Preparation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-ZrO}_2$ fibers

Dry spinning and thermal property measurements of PAS and PZS were conducted to obtain precursor fibers and oxide fibers. Dry spinning of both viscous PAS (SA/PAP=0.5) and PZS (SA/PEZP=1.0) solution provided slightly yellow precursor fibers. Figs. 3 and 4 are the TG and DTA curves of PAS and PZS. These figures show broad exothermic peaks with weight loss at 150°–600°C (Fig. 3) and 150°–510°C (Fig. 4) due to removal of organic groups and peaks with or without weight loss at 980°C (Fig. 3) and 1150°C (Fig. 4). On the other hand, the precursor fibers from PAS and PZS are subjected to pyrolysis at 900°, 1000° (PAS and PZS) and 1200°C (PZS) followed by X-ray analysis. The fibers from PAS formed black and white fibers when heated at 900° and 1000°C, respectively. While the fibers from PZS formed black fibers at 900° and 1000°C, and white fibers at 1200°C. From X-ray analysis, these fibers were confirmed to be amorphous at 900°C and crystallized at 1000° or 1200°C. Figs. 5

and 6 show X-ray diffractogram of the fibers heated at 1000°C. These figures indicated diffraction patterns due to mullite (Fig. 5) and mixture of tetragonal and monoclinic ZrO_2 (Fig. 6). The latter pattern was also observed for the fibers at

Fig. 5. X-ray diffractogram of $\text{SiO}_2\text{-Al}_2\text{O}_3$ fibers heated at 1000°C.

Fig. 6. X-ray diffractogram of $\text{SiO}_2\text{-ZrO}_2$ fibers heated at 1000°C.

1200°C from PZS. From these results, the peak at 980°C in Fig. 3 is due to crystallization of alumina whereas the peak at 1150°C in Fig. 4 may be ascribed to removal of carbons.

4. Conclusion

(1) $\text{SiO}_2\text{-Al}_2\text{O}_3$ fibers and $\text{SiO}_2\text{-ZrO}_2$ fibers were prepared by a new method via polymetalloxanes PAS and PZS prepared from silicic acid and metal chelates.

(2) PAS and PZS, precursors for oxide fibers, were stable to further condensation and showed spinnability.

(3) The back bone of PAS and PZS were composed of Si-O-Si linkage and Si-O-Al or Si-O-Zr linkage having silanol and ligand group as pendants.

(4) $\text{SiO}_2\text{-Al}_2\text{O}_3$ (SA/PAP=0.5) and $\text{SiO}_2\text{-ZrO}_2$ (SA/PEZP=1.0) fibers were obtained by dry spinning of PAS and PZS precursor fibers followed by pyrolysis at 900°, 1000° and 1200°C.

(5) $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-ZrO}_2$ fibers were amorphous at 900°C while crystallized at 1000° and 1200°C.

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