Preparation of Polysiloxazanes and Their Transformation to Silicon Oxynitride

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ポリシロキサザンの調製とその窒化酸化ケイ素への変換過程

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Cyclic and bicyclic oligosiloxazanes were synthesized by the reaction of 1,3-diamino-1,3-di-*t*-butoxy-1,3-dimethyldisiloxane with 1,1,3,3-tetraisocyanato-1,3-dimethyl-1,3-disiloxane (M-TIDS) in 1 : 1 and 1 : 2 molar ratios, respectively. Based on these results, polysiloxazane M-PSZ was prepared by the ammonolysis of M-TIDS in tetrahydrofuran (THF) at 213 K. The structure and stability against the gelation of M-PSZ were found to be dependent on the temperature and polarity of the solvents. The molecular weight of M-PSZ was increased by aging a THF solution of M-PSZ at room temperature. A maximum weight average molecular weight of 70000 was observed for M-PSZ, for which a dilute solution was stable over 6 months. Silicon oxynitride was prepared by the pyrolysis of M-PSZ under an ammonia atmosphere. The ceramization process was monitored by infrared and nuclear magnetic resonance spectra, which showed the replacement of a methyl group with an amino group following a condensation reaction to provide silicon oxynitride at 1173 K.

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1. Introduction

Silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) has been expected to perform as a heat-resistant, anti-oxidative, and anti-corrosive ceramic in the forms of fibers,^{1)–3)} thin films,⁴⁾ and fine powders.^{5),6)} Such silicon oxynitrides are molded by liquid-phase sintering in the presence of alumina or yttria to aid pyrolysis, as they do not respond well to melting or sintering in fabrication processes.^{5),7),8)}

It is desirable for precursor polymers to have good solubility, stability with easy handling, and simple structures, as well as to contain elements suitable for ceramics. For example, silicon oxynitride is prepared from polysiloxazanes that consist of silicon, nitrogen, and oxygen.^{3),6)} These polysiloxazanes are synthesized by the copolymerization of polysiloxanes and polysilazanes;^{9)–13)} hydrolysis of chlorosilane in the presence of hydrazine derivatives,¹⁴⁾ or ammonolysis of polysiloxanes.⁵⁾ These compounds are problematic, however, in that the molar ratios of silicon, oxygen, and nitrogen are not desirable for the formation of silicon oxynitride.

In this paper, the reaction of 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane (DS-2B) with ammonia will be reported as a model reaction to synthesize polysiloxazanes (M-PSZ) according to the Eqs. (1) and (2). In addition, the preparation of M-PSZ by the ammonolysis of 1,1,3,3-tetraisocyanato-1,3-dimethyldisiloxane (M-TIDS) and its transformation to ceramics according to the Eq. (3) will be presented. Because M-TIDS consists of silicon, nitrogen, and oxygen in molar ratios appropriate to the synthesis of silicon oxynitride, it would be a good precursor to silicon oxynitride by the precursor method.

2. Experimental

Reagents

M-TIDS and 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane (M-DIDB) were synthesized according to the literature.¹⁵⁾ Ammonia (Nihon Sanso Co., Ltd.) was used after passing it through a column packed with potassium hydroxide. *t*-Butyl alcohol (Wako Pure Chemical Co., Ltd.), tetrahydrofuran (THF, Wako Pure Chemical Co., Ltd.), diethyl ether (Wako Pure Chemical Co., Ltd.), and 1,4-dioxane (Wako Pure Chemical Co., Ltd.), hexane (Wako Pure Chemical Co., Ltd.), and triethylamine (Wako Pure Chemical Co., Ltd.) were dried by conventional methods and distilled before use.

Synthesis of 1,3-diamino-1,3-di-*t*-butoxy-1,3-dimethyldisiloxane (M-DADB)

A four-necked flask equipped with a thermometer, dropping funnel, and magnetic stirrer was cooled to 213 K and 110 g (6.47 mol) of ammonia was trapped. 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane 32.7 g (0.098 mol) was dissolved in THF 100 mL and then dropped into the mixture within 30 min. After the addition, the temperature was

raised to 236 K and then stirred for 5 h. The temperature was slowly raised to room temperature, after which ammonium cyanate was filtered. M-DADB was isolated by distillation under reduced pressure.

M-DADB: bp (K/kPa): 370.7–371.7/1.47; ^1H NMR (CDCl_3 , δ , ppm): 0.11–0.14 (q, 3H, Si-CH₃), 0.89 (s, 2H, Si-NH₂), 1.31 (s, 9H, C(CH₃)₃); ^{13}C NMR (CDCl_3 , δ , ppm): –0.1 (Si-CH₃), 31.8 (C(CH₃)₃), 72.1 (C(CH₃)₃); ^{29}Si NMR (CDCl_3 , δ , ppm): –43.1; IR (CCl₄ soln. method, cm^{–1}): 3370 (ν_{NH}), 2980 (ν_{CH}), 2330 (ν_{NCO}), 2300 (ν_{NCO}), 1180 (δ_{NH}), 1110 ($\nu_{\text{Si-O-Si}}$); MS (EI 70 eV, m/z): 281 ($\text{M}^+ - 72$).

Synthesis of 2,8-di-*t*-butoxy-4,6-diisocyanato-2,4,6,8-tetramethyl-3,7-diaza-1,5-dioxo-2,4,6,8-tetrasilacyclooctane (CSZ)

M-DADB 19.7 g (0.07 mol), triethylamine 3.0 g (0.03 mol), and THF 100 mL were charged into a flask and cooled to 213 K. A mixture of M-TIDS 18.9 g (0.07 mol) and THF 100 mL was added and then subjected to reflux for 2 h. CSZ was isolated by distillation under reduced pressure. CSZ: bp (K/kPa): 439.6–440.7/1.47; ^1H NMR (CDCl_3 , δ , ppm): 0.01–0.24 (m, 6H, Si-CH₃), 1.19–1.31 (s, 2H, Si-NH₂), 1.30 (s, 9H, C(CH₃)₃); ^{13}C NMR (CDCl_3 , δ , ppm): –0.2 (Si-CH₃), 32.5 (C(CH₃)₃), 72.1 (C(CH₃)₃), 123.1 (NCO); ^{29}Si NMR (CDCl_3 , δ , ppm): –41.0–43.6; IR (CCl₄ soln. method, cm^{–1}): 3370 (ν_{NH}), 2980 (ν_{CH}), 2330 (ν_{NCO}), 1180 (δ_{NH}), 1110 ($\nu_{\text{Si-O-Si}}$), 1050 ($\delta_{\text{Si-N-Si}}$); MS (EI 70 eV, m/z): 467 ($\text{M}^+ - 72$).

Synthesis of 3,5,9,11-tetra-*t*-butoxy-1,3,5,7,9,11-hexamethyl-2,6,8,12-tetraaza-4,10,13-trioxa-1,3,5,7,9,11-hexasilabicyclo[5.5.1]tridecane (BCSZ)

M-TIDS 7.0 g (0.025 mol), triethylamine 0.3 g (0.003 mol), and THF 100 mL were charged into a flask and cooled to 213 K. A mixture of M-DADB 3.38 g (0.0125 mol) and THF 100 mL was added and then subjected to reflux for 2 h. BCSZ was isolated by distillation under reduced pressure.

BCSZ: bp (K/kPa): 460.2–460.7/1.47; ^1H NMR (CDCl_3 , δ , ppm): 0.07–0.20 (m, 9H, Si-CH₃), 1.12 (s, 2H, Si-NH₂), 1.31 (s, 18H, C(CH₃)₃); ^{13}C NMR (CDCl_3 , δ , ppm): –0.2 (Si-CH₃), 32.5 (C(CH₃)₃), 72.1 (C(CH₃)₃); ^{29}Si NMR (CDCl_3 , δ , ppm): –38.2–42.3; IR (CCl₄ soln. method, cm^{–1}): 3370 (ν_{NH}), 2980 (ν_{CH}), 1180 (ν_{NH}), 1110 ($\nu_{\text{Si-O-Si}}$), 1050 ($\delta_{\text{Si-N-Si}}$); MS (EI 70 eV, m/z): 527 ($\text{M}^+ - 15$).

Polymerization of M-PSZ

All experiments were carried out under nitrogen atmosphere.

M-TIDS 13.5 g (0.05 mol) and THF, diethyl ether, or 1,4-dioxane 100 mL were charged in a flask equipped with a gas inlet tube and cooled to 293 K or 213 K. Ammonia gas was trapped in a test tube at 263 K and then introduced to the flask through a gas inlet tube as a mixture with nitrogen. The reaction mixture was stirred for 5 h, after which cyanuric acid was filtered at 263 K. The filtrate was condensed to 30 mass% solution at 293 K and poured into hexane 100 mL with vigorous stirring. After filtration and drying, M-PSZ was isolated as a white powder.

In contrast, after the filtration of cyanuric acid, the filtrate was condensed to 30–60 mass% at 293 K and stirred at 293 K with monitoring of the molecular weight by GPC.

Pyrolysis of M-PSZ

M-PSZ powder was put into an alumina boat and heated under nitrogen or ammonia atmosphere in a tube-type electric heater at a rate of 5 K/min. After the target temperature was reached, it was held for a certain period and then cooled to room temperature at a rate of 5 K/min.

Analysis

Infrared (IR) spectra were recorded by JASCO FT-IR-400 by the carbon tetrachloride solution method or the KBr disk method.

^1H , ^{13}C , and ^{29}Si nuclear magnetic resonance (NMR) spectra were acquired by a JEOL JNM-EX400 in chloroform-*d* or THF-*d*₈.

^{29}Si { ^1H } Cross polarization/magic angle spinning (CP/MAS) NMR spectra and ^{29}Si { ^1H } gated dipole-dipole/magic angle spinning (gated DD/MAS) NMR spectra were acquired by a JEOL JNM-EX300. The chemical shift was referred to polydimethylsilane as a standard.

Gas chromatography (GC) was carried out using a GL Science GC390 equipped with a column of SE-30. Carrier gas: He. Temp.: 353–563 K. Heating rate: 15 K/min.

Gel permeation chromatography (GPC) was measured by a Hitachi liquid chromatography system composed of a pump L-6200 and a refractive index detector L-3300. Tetrahydrofuran was selected as a mobile phase for the directly connected columns GL-R420, GL-R430, and GL-R440 (Hitachi Chemical Co., Ltd.). Molecular weights were calculated based on the standard polystyrenes.

The silicon content was determined by a wet method. Sample (0.2 g) was weighed in a Kjeldahl flask and heated in the presence of ammonium sulfate (1 g), ammonium nitrate (1 g), and sulfuric acid (20 mL). The residue was poured into 100 g of ice, followed by filtration. The filtrate was subjected to firing in a crucible, followed by weighing as SiO₂.

3. Results and discussion

Reaction of M-TIDS with M-DADB

The reaction of M-TIDS with M-DADB was tried as a model reaction of M-TIDS with ammonia. Because the substitution reaction of isocyanatosilanes with amines occurs preferable to the addition reaction at 213 K,¹⁶⁾ the reaction of M-TIDS with M-DADB was carried out at 213 K. The molar ratio of M-TIDS to D-DADB was changed as 1 and 2 in the synthesis of CSZ and BCSZ, respectively.

In the reaction of M-TIDS with M-DADB in 1 : 1 molar ratio, cyclic oligosiloxazane CSZ was predominantly formed. The progress of the reaction was monitored by the production of cyanuric acid as a white precipitate just after the addition of M-DADB to M-TIDS. Triethylamine acts as a catalyst to polymerize cyanuric acid to form cyanuric acid, in addition to activation of the substitution reaction by increasing basicity of the solution. CSZ was isolated as a colorless liquid in 31% yield. The relatively low yield of CSZ was due to the formation of polysiloxazanes with high molecular weight. CSZ was highly hydrolysable and provided gel when exposed to air.

When M-TIDS was subjected to the reaction with M-DADB in a 1 : 2 molar ratio, bicyclic oligosiloxazane BCSZ was formed. The reaction was monitored by gas chromatography, which showed decreasing peak intensities due to M-TIDS and M-DADB and an increasing peak intensity of CSZ at the initial stage of the reaction. The peak intensity due to CSZ decreased with increasing peak intensity due to BCSZ at the middle and final stages of the reaction. The variation of these peak intensities suggests the stepwise polymerization of M-TIDS with M-DADB. BCSZ was isolated as a colorless viscous liquid in 53% yield. CSZ was easily hydrolysable but more stable than CSZ.

Ammonolysis of M-TIDS

Since M-TIDS was found to react with M-DADB to provide ladder-type oligosiloxazanes, M-TIDS was subjected to the reaction with ammonia to prepare polysiloxazane M-PSZs.

Table 1. Results of the Preparation of M-PSZ

No.	Solvent ^{a)}	Temp./ K	M-PSZ yield/ %	Cyanuric acid yield/ %	Gel time ^{b)/} day
1	THF	293	90	96	3
2		213	99	96	9
3	Diethyl ether	293	88	88	2
4		213	96	93	8
5	1,4-Dioxane	293	88	88	2
6		213	97	96	8

a) Scale in operation: M-TIDS: 13.5 g (0.05 mol), NH₃: 9.7 mL (0.45 mol), Solvent: 100 mL. Time: 5 h.

b) M-PSZ/THF 10 mass% solution aging at 293 K.

Table 2. Molecular Weight of M-PSZ (No. 2) on Aging^{a)}

Aging time/ h	$M_w^{b)/10^3}$	$M_w/M_n^{b)}$
0	2.5	2.7
5	3.3	4.0
10	5.0	5.5
24	7.9	6.6
40	9.0	10.8
80	16.0	14.0
105	28.0	15.2
120	34.0	15.8
130	45.0	16.0
140	58.0	16.4
150	70.0	16.7

a) Scale in operation: M-TIDS: 13.5 g (0.05 mol), NH₃: 9.7 mL (0.45 mol).

50 mass% THF solution at room temp.

b) GPC. Based on standard polystyrene.

The results of the ammonolysis of M-TIDS are summarized in **Table 1**. Under every condition, cyanuric acid was produced just after the introduction of ammonia as a byproduct. M-PSZs were isolated as white powders in almost quantitative yield for the reaction at 213 K (Nos. 2, 4, 6), while they decreased slightly for the reaction at 293 K (Nos. 1, 3, 5). The yields of ammonium cyanate were quantitative for Nos. 1, 2, 4, and 6, while they decreased slightly for Nos. 3 and 5. Since isolated M-PSZ by reprecipitation was insoluble in organic solvents, the filtrate was concentrated to form a 30 mass% THF solution and subjected to aging at 293 K: M-PSZ (Nos. 1, 3, 5) provided gel after aging for 2–3 days, while the gel time was 8–9 days for M-PSZ (Nos. 2, 4, 6). The molecular structure of M-PSZ would be highly dependent on the temperature and polarity of solvents. M-PSZ (1, 2, 3) would consist of an amide structure in the main chain, as the addition reaction of isocyanatosilanes with amines occurs preferably to the substitution reaction, which results in low recovery of cyanuric acid in M-PSZs (3, 5) and a shorter gel time in M-PSZs (1, 3, 5). The relatively long gel time for M-PSZs (1, 2) was due to the polarity of the solvent, as THF is the most polar solvent among the three solvents in Table 1. The amino group might be stabilized by the high polarity of THF to retard the polymerization or gel formation.

The analytical data for M-PSZ (No. 2) are shown in **Table 2**, and the NMR spectra are shown in **Figs. 1** and **2**. In the ¹H NMR spectrum, relatively sharp signals due to Si–CH₃ and a broad signal due to Si–NH were observed at 0.14 ppm and 1.15 ppm, respectively. In the ²⁹Si NMR spectrum, three broad signals due to SiOMe(NH)₂, SiOMe(NH₂)(NH), and SiOMe(NCO)(NH) were observed with a peak area ratio of 9 : 10 : 1. In the IR spectrum, absorption peaks due to ν_{SiOSi}, ν_{SiNSi}, and ν_{Si–C} were observed. The silicon content was 41.5%, which is almost consistent with the calculated value 39.9% for the structure [SiMe(NH)OSiMe(NH)_{0.5}(NH₂)]₁₂. The molecular weight was calculated by GPC analysis for the

Fig. 1. ¹H NMR spectrum of M-PSZ (No. 2). Fig. 2. ²⁹Si NMR spectrum of M-PSZ (No. 2).

as-prepared M-PSZ solution to be $M_w=900$, and the polydispersity was $M_w/M_n=1.3$. These data suggest the average formula of M-PSZ as [SiMe(NH)OSiMe(NH)_{0.5}(NH₂)]₁₂.

Molecular weight of M-PSZ on aging

The preparation of M-PSZs of various molecular weights were prepared by aging a THF solution of M-PSZ at 293 K. **Figure 3** and **Table 3** summarize the results of the aging of M-PSZ in THF with concentrations of 30, 40, 50, and 60 mass%. Upon aging of the 30 mass% solution, M_w increased gradually to 5000 after 150 h. Upon aging of the 40 mass% solution, M_w increased rapidly to provide M-PSZ of $M_w=35000$ after 150 h. The M_w of M-PSZ increased to 28000 for the 50 mass% solution after 105 h. Since the viscosity was increased significantly, another 3 mL of THF was added, and aging continued. The M_w was 50000 after 150 h, 70000 with further aging, and finally the M-PSZ gelled. With increases in the aging time of the 50 mass% solution, the M_n was almost constant to increase the polydispersity M_w/M_n , which is typical for condensation polymerization. When the 60 mass% solution was aged, the M_w increased rapidly, and the solution gelled after 24 h.

The M-PSZ with $M_w=70000$ was diluted to 1 mass% THF solution and aged at 20 K under nitrogen atmosphere. No gel formation occurred for this solution over 6 months. It therefore appears that the molecular weight of M-PSZ can be simply controlled by the concentration and aging period of a THF solution. In addition, M-PSZ can be stored as a diluted solu-

Fig. 3. Weight average molecular weight of M-PSZ in THF on aging at 293 K.

Table 3. Yield and Spectral and Analytical Data of M-PSZ (No. 2)

Yield ^{a)} / %	96	
¹ H NMR (THF- <i>d</i> ₆ , δ, ppm)	0.14 1.15	(b, 12H, SiCH ₃) (b, 6.63H, NH)
¹³ C NMR (THF- <i>d</i> ₆ , δ, ppm)	-0.20 123.3	(SiCH ₃) (NCO)
²⁹ Si NMR (THF- <i>d</i> ₆ , δ, ppm)	-31.0~38.0 -38.0~44.0 -48.0	(SiO(CH ₃)(NH) ₂) (SiO(CH ₃)(NH ₂)(NH)) (SiO(CH ₃)(NCO)(NH))
IR (CCl ₄ soln. method, cm ⁻¹)	910	(V _{Si-NH-Si})
	1050	(V _{Si-O-Si})
	1280	(V _{Si-CH₃})
	2180	(V _{NCO})
	2980	(V _{C-H})
<i>M_w</i> (<i>M_w</i> / <i>M_n</i>) (GPC)	3390	(V _{N-H})
	900	(1.3)
Si analysis (Calcd.) (wet method, %)	41.5	(39.9)

a) Based on the unit structure of [SiMe(NH)OSiMe(NH)_{0.5}(NH₂)_{0.5}].

Table 4. Ceramic Conversion of M-PSZ at 1673 K

Atmosphere ^{b)}	Ceramic yield/ %	Si% ^{a)}	N% ^{a)}	Color of residue
Nitrogen	83.6	50.0	22.7	Black / gray
Ammonia	72.1	53.4	28.6	White / gray

a) Calcd. values for Si₂N₂O: Si: 56.0%, N: 28.0%.

tion for long periods without gelation.

Preparation of silicon oxynitride from M-PSZ

Results regarding the pyrolysis of M-PSZ under nitrogen or ammonia atmosphere to 1673 K are summarized in Table 4. The ratio of the residual weight and the loaded weight is referred to as the ceramic yield. After the pyrolysis in nitrogen, black and partly gray powder was recovered in ceramic yield 83.6%. The silicon and nitrogen contents were 50.0% and 22.7%, respectively, which were lower than the calculated values of 56.0% for silicon and 28.0% for nitrogen in Si₂N₂O. The color of the sample after pyrolysis suggests the contamination of carbon. On the other hand, slightly gray powder was recovered after the pyrolysis at 1673 K in ammonia in ceramic yield of 72.1%. The silicon and nitrogen contents were 53.4% and 28.6%, respectively, which were close to the calculated values for silicon oxynitride Si₂N₂O. Pyrolysis under ammonia atmosphere is preferable to that of nitrogen

Table 5. Ceramic Yield and Color on the Pyrolysis of M-PSZ in Ammonia

Temperature/ K	Ceramic yield/ %	Color of the residue
293	100.0	White
423	97.6	White
523	96.3	Yellowish white
623	94.9	Yellowish white
723	92.3	Light yellow
773	89.1	Light yellow
873	86.1	Black/ white
973	79.0	Gray/ white
1073	72.6	Gray/ white
1373	72.1	Gray/ white
1673	72.1	Gray/ white

Fig. 4. Ceramic yield of M-PSZ upon pyrolysis under ammonia atmosphere.

for the preparation of silicon oxynitride from M-PSZ.

The ceramization process of M-PSZ under ammonia was monitored by the weight and color of the sample after pyrolysis at certain temperatures. Table 5 and Fig. 4 summarize the ceramic yield and color of the pyrolyzed M-PSZ. The weight differences at the temperatures 293–523 K, 523–723 K, 723–873 K, and 873–1173 K were 3.7%, 4.0%, 6.2%, and 13.5%, respectively. No weight change was observed above a temperature of 1173 K. In addition, the color of the residue changed from black to gray at temperatures of 873–973 K. These data suggest the formation of silicon oxynitride ceramics at 1173 K.

The pyrolysis of M-PSZ was monitored by IR and NMR spectra, as shown in Figs. 5 and 6, respectively. The ²⁹Si {¹H} CP/MAS NMR spectra, while the ²⁹Si {¹H} gated DD/MAS NMR spectra were acquired below and above the temperature of 873 K, respectively. In the IR spectrum of M-PSZ, absorption peaks due to Si–NH–Si, Si–O–Si, Si–C, and C–H linkages and Si–CH₃ and NCO groups were observed. For the pyrolysis up to 773 K, the peak due to the NCO group disappeared and the peak intensity due to the N–H bond decreased. When the temperature increased to 873 K, the peaks due to the C–H bond and Si–CH₃ group disappeared, while the peaks due to Si–N–Si and Si–O–Si remained. An absorption peak due to the Si–C linkage disappeared at 1173 K. With increases in temperature to 1673 K, peak intensities due to Si–N–Si and Si–O–Si increased, which supported the formation of silicon oxynitride. On the other hand, in the ²⁹Si {¹H} CP/MAS NMR spectrum of M-PSZ, two strong signals due to SiOMe(NH)₂ and SiOMe(NH₂)(NH) units were observed, but the signal due to the SiOMe(NCO)(NH) unit was weak. At 423 K, the signal due to the SiOMe(NH)₂ unit was decreased while new signals due to SiOMe(NCO)(NH), SiO(NH₂)(NH)₂, and

Fig. 5

Fig. 6

Fig. 5. IR spectra of M-PSZ upon pyrolysis under ammonia atmosphere. (KBr disk method).

Fig. 6. ^{29}Si $\{^1\text{H}\}$ CP/MAS and ^{29}Si $\{^1\text{H}\}$ gated DD/MAS NMR spectra of M-PSZ upon pyrolysis under ammonia atmosphere.

$\text{SiO}(\text{NH})_3$ units appeared at -50 , -65 , and -69 ppm, respectively. Because most of the methyl groups were replaced with amino groups, the signals due to $\text{SiOMe}(\text{NH})_2$ and $\text{SiOMe}(\text{NH}_2)(\text{NH})$ units became weak to produce a relatively weak peak due to the $\text{SiOMe}(\text{NCO})(\text{NH})$ unit. At temperatures of 523 and 623 K, the signal due to $\text{SiOMe}(\text{NCO})(\text{NH})$ unit was decreased and then disappeared, which is consistent with the disappearance of the absorption peak in Fig. 5. At 773 K, only a signal due to $\text{SiO}(\text{NH})_3$ was observed. In the spectra obtained at 873 and 1173 K, ^{29}Si $\{^1\text{H}\}$ gated DD/MAS NMR provided signals because the proton content decreased significantly at these temperatures, which is supported by the observations of ceramic yield and color, as shown in Table 5. The signals due to SiON_3 , SiO_2N_2 , and SiO_3N units were observed with chemical shifts of -59 ,¹⁷⁾ -73 ,¹⁷⁾ and -86 ¹⁸⁾ ppm, respectively, at a temperature of 873 K. At 1173 K, the signals due to SiON_3 and SiO_2N_2 were increased to collapse the three signals.

The ceramization process can be summarized as follows: polysiloxazane M-PSZ with the average structure $[\text{Si}(\text{CH}_3)(\text{NH})\text{OSi}(\text{CH}_3)(\text{NH}_2)(\text{NH})_{0.5}]_n$ is prepared by the ammonolysis of M-TIDS. Upon pyrolysis of M-PSZ under ammonia atmosphere, the silylmethyl group is replaced with an amino group at 423–473 K. With increases in temperature to 773 K, replacement of the methyl group and condensation of the amino group are almost complete to form a silicon oxynitride precursor polymer in the plausible formula $[\text{Si}(\text{NH})_{1.5}\text{O}_{0.5}]_n$. The ceramization to silicon oxynitride with the estimated formula of $\text{Si}_2\text{N}_2\text{O}$ is completed at 1173 K.

4. Conclusion

Cyclic oligosiloxazane was synthesized by the reaction of 1,3-diamino-1,3-di-*t*-butoxy-1,3-dimethyldisiloxane (M-DADB) with 1,1,3,3-tetraisocyanato-1,3-dimethyl-1,3-disiloxane (M-TIDS) in a molar ratio of 1 : 1 in tetrahydrofuran (THF). Bicyclic oligosiloxazane was synthesized by the reaction of M-DADB with M-TIDS in a molar ratio of 1 : 2 in THF.

Polysiloxazane M-PSZ was prepared by the ammonolysis of M-TIDS in THF at 213 K. The structure and stability against gelation of M-PSZ were dependent on the temperature and polarity of the solvents. The molecular weight of M-PSZ was increased by aging a THF solution of M-PSZ at room temperature. M-PSZ with a maximum weight average molecular weight of 75000 was prepared, for which dilute solution was stable for a long period without gelation.

Silicon oxynitride was prepared by the pyrolysis of M-PSZ under ammonia atmosphere. The methyl group is replaced with an amino group, and the condensation reaction between amino groups then provided a silicon oxynitride prepolymer. Further pyrolysis of prepolymer provided silicon oxynitride at 1173 K.

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