Instructions for use

Paper

Substituent effects on the glass transition phenomena of polyorganosilsesquioxane particles prepared by two-step acid–base catalyzed sol–gel process

Kenji TAKAHASHI, Kiyoharu TADANAGA,[†] Akitoshi HAYASHI and Masahiro TATSUMISAGO

Department of Applied Chemistry, Graduate School of Engineering Osaka Prefecture University, Sakai, Osaka 599–8531

Polyorganosilsesquioxanes ($RSiO_{3/2}$) (R: organic group) particles with different organic groups such as alkyl and aryl groups were prepared using a two-step acid–base catalyzed sol–gel process. Spherical particles were formed at room temperature using the two-step acid–base catalyzed sol–gel process in which trifunctional organoalkoxysilanes with R = methyl, *n*-propyl, *n*-butyl, phenyl, and benzyl were used as starting materials. Polyorganosilsesquioxanes with longer alkyl groups or phenethyl group prepared by the two-step acid–base catalyzed sol–gel process were oily material at room temperature. Polyorganosilsesquioxanes with shorter alkyl or aryl groups exhibited the glass transition. In contrast, polyorganosilsesquioxanes with longer alkyl groups showed no glass transition behavior. The occurrence of glass transition phenomena of polyorganosilsesquioxanes was concluded to be strongly dependent on the chain length of organic substituents.

1. Introduction

Particles of glassy materials are used for a large variety of applications such as sealing or joining of glasses, ceramics and metals, passivation of semiconductors, sintering of ceramics and so on. Glassy powders are usually prepared by grounding or milling. However, control of particles size or glass transition behavior of glassy powders must be important for an advanced use of those materials in colloidal processes.

On the other hand, various kinds of inorganic–organic hybrid materials have attracted considerable interest because they have excellent properties, which can not be exhibited by inorganic or organic materials themselves.[1),2)] Among the inorganic–organic hybrid materials, much attention has been paid to polyorgano-silsesquioxanes ($RSiO_{3/2}$) (R: organic group) because of their unique thermal, optical, and mechanical properties.[3),4)] In these materials, polyorganosilsesquioxanes with aryl groups such as polyphenylsilsesquioxane ($PhSiO_{3/2}$), polybenzylsilsesquioxane [$C_6H_5CH_2$–$SiO_{3/2}$ ($BnSiO_{3/2}$)], and polyphenethylsilsesquioxane [$C_6H_5(CH_2)_2$–$SiO_{3/2}$ (Phenethyl-$SiO_{3/2}$)], prepared using the sol–gel process, were found to exhibit the glass transition.[5),6)] However, few reports have described polyorganosilsesquioxanes with no benzene rings, which exhibited the glass transition. Arkhireeva et al.[7)] claimed that polymethylsilsesquioxane ($MeSiO_{3/2}$) and polyvinylsilsesquioxane showed a glass transition temperature (T_g), but that report presented no evidence for the glass transition. In addition, to the best of our knowledge, the reason that these polyorganosilsesquioxanes with aryl groups exhibited the glass transition has not yet been clarified. A systematic study of polyorganosilsesquioxanes with different organic groups forming gels was reported by Loy et al.,[4)] where

polyorganosilsesquioxanes with different organic groups were prepared under acidic, neutral, and basic conditions. However, as far as we know, no report has described the systematic study of glass transition phenomena of polyorganosilsesquioxanes. The elucidation of glass transition phenomena of polyorgano-silsesquioxanes should engender the design of new glassy hybrid materials. Especially, particles of those materials can be used for electrophoretic deposition, precise shaping, and so on, and thus, the preparation of particles using several techniques has been studied. The sol–gel method using trifunctional organoalkoxysilanes [$RSi(OR')_3$] (R: organic group, OR': alkoxy group (OCH_3 (OMe), OCH_2CH_3 (OEt))) is usually used as a preparation of polyorganosilsesquioxane particles.[7)–17)] Preparation of various polyorganosilsesquioxane particles like $MeSiO_{3/2}$,[9)] $PhSiO_{3/2}$,[10),12),13)] $BnSiO_{3/2}$,[9),13)] polyaminophenylsilsesquioxane,[14)] and polymercaptopropylsilsesquioxane,[11)] using a two-step acid–base catalyzed sol–gel process, have already been reported.

We demonstrated that $PhSiO_{3/2}$ and $BnSiO_{3/2}$ particles prepared using the two-step acid–base catalyzed sol–gel process exhibit the glass transition and that particles are thermally softened by heating at temperatures greater than T_g.[13)] Using the thermal softening behavior of these particles, $PhSiO_{3/2}$ and $BnSiO_{3/2}$ thick films with high transparency or microlens arrays were formed by electrophoretic deposition of the particles and subsequent heat treatment.[18)–20)]

In this study, we have prepared polyorganosilsesquioxanes with different organic groups from $RSi(OR')_3$ using the two-step acid–base catalyzed sol–gel process. First, the ability of $RSi(OR')_3$ to form particles with different organic groups using the two-step process was investigated systematically. Then, the thermal properties, especially glass transition phenomena, of those polyorganosilsesquioxanes were examined. The polyorga-nosilsesquioxanes prepared in this work are classifiable into two types based on the organic groups that are bound directly to Si

† Corresponding author: K. Tadanaga; E-mail: tadanaga@chem. osakafu-u.ac.jp

JCS-Japan

Takahashi et al.: Substituent effects on the glass transition phenomena of polyorganosilsesquioxane particles prepared by two-step acid–base catalyzed sol–gel process

atoms. One is the polyorganosilsesquioxanes with aryl groups; the other is those with alkyl groups. Effects of the chain length and the size of organic groups on the properties are discussed.

2. Experimental

2.1 Preparation of polyorganosilsesquioxane particles

Methyltriethoxysilane [MeSi(OEt)$_3$], normal-propyltriethoxysilane [n-PrSi(OEt)$_3$], normal-butyltrimethoxysilane [n-BuSi(OMe)$_3$], iso-butyltriethoxysilane [i-BuSi(OEt)$_3$], normal-pentyltriethoxysilane [Pentyl-Si(OEt)$_3$], normal-octyltriethoxysilane [Octyl-Si(OEt)$_3$], phenyltriethoxysilane [PhSi(OEt)$_3$], benzyltriethoxysilane [BnSi(OEt)$_3$], and phenethyltrimethoxysilane [Phenethyl-Si(OMe)$_3$] were used as starting alkoxides. Phenethyl-Si(OMe)$_3$ and the others were purchased respectively from Gelest Inc. and Shin-Etsu Chemical Co. Ltd.

The two-step acid–base catalyzed sol–gel process was used to prepare all samples. First, RSi(OR′)$_3$ dissolved in ethanol (EtOH) was hydrolyzed with 0.01 mass % hydrochloric acid at room temperature for 3 h. The resultant RSi(OR′)$_3$ sol was then added all at once to 4 mass % ammonia water. Microparticles were formed after the addition of the sol to the ammonia water, thereby yielding an opaque sol. The sol was stirred for an additional 2 h at room temperature at a stirring rate of around 1300 rpm. The mole ratio of RSi(OR′)$_3$:EtOH:H$_2$O (in hydrochloric acid):H$_2$O (in ammonia water) was fixed at 1:20: 20:180. The samples were collected from the sol by centrifugation and dried under vacuum.

2.2 Characterization of polyorganosilsesquioxane particles

Scanning electron microscopy (SEM) (JSM-5300; JEOL) was used for observation of the shape and the size of the particles. Thermal behavior of the polyorganosilsesquioxanes was examined using differential scanning calorimetry (DSC) curves of repeated heating and cooling runs under 5°C/min or 20°C/min (Pyris1 DSC; PerkinElmer). Differential thermal analysis (DTA) and thermogravimetry (TG) (Thermo plus 8120; Rigaku Corp.) of the polyorganosilsesquioxanes were performed at a heating rate of 10°C/min under air flow. Gel permeation chromatography (GPC) measurements were performed using a pump (LC-10AD; Shimadzu Corp.), a detector (RID-6A; Shimadzu Corp.), and a column oven (CTO-10A; Shimadzu Corp.). A combination of two silica-gel columns (CF-310HQ and GF-7MHQ, Shodex; Showa Denko K.K.) was used, with THF as an eluent, at 40°C. For GPC measurements, the polyorganosilsesquioxanes were dissolved in THF and the solution was filtered through a membrane filter with 0.45 μm pore size. The concentration of the polyorganosilsesquioxanes in the GPC measurements was fixed at 0.2 mass %.

3. Results and discussion

3.1 Characterization of polyorganosilsesquioxanes with aryl groups

Table 1 summarizes the appearances and the thermal properties of polyorganosilsesquioxanes with aryl groups. The samples prepared from PhSi(OEt)$_3$ and BnSi(OEt)$_3$ were powders, whereas the sample prepared from Phenethyl-Si(OMe)$_3$ was oily. **Figure 1** shows SEM photographs of the samples prepared from (a) PhSi(OEt)$_3$ and (b) BnSi(OEt)$_3$. As depicted in Fig. 1, both powder samples comprise aggregates of spherical particles with average diameters of 500 nm. Linear oligomers such as hydrolyzed monomer, dimer, and trimer are known to be formed mainly under acidic conditions.[21] When transparent sols prepared under acidic conditions are added to ammonia water,

Table 1. Appearances and thermal properties of polyorganosilsesquioxanes with aryl groups

RSi(OR′)$_3$	Appearance	Onset temperature for oxidation of organic groups/°C	Glass transition temperature*/°C	Solidification temperature*/°C
PhSi(OEt)$_3$	Powder	530	100	×
BnSi(OEt)$_3$	Powder	280	35	×
Phenethyl-Si(OMe)$_3$	Oil	210	−5	−40

*Solidification temperature: the temperature at which an exothermic peak due to the solidification was observed in the cooling process of DSC measurements.
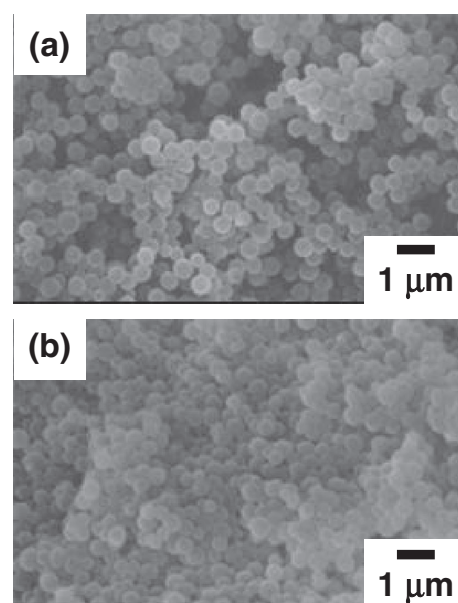×: Not observed.

Fig. 1. SEM photographs of samples prepared from (a) PhSi(OEt)$_3$ and (b) BnSi(OEt)$_3$.

opaque sols are obtained; emulsion droplets including the linear oligomers (oil phase) would be formed in the aqueous phase. The three-dimensional siloxane networks of the oligomers are developed rapidly under basic conditions. The emulsion droplets are surrounded by the ammonia water; thereby, three-dimensional networks of the oligomers are developed at the surface of the emulsion droplets through hydrolysis and condensation reactions. Generally, larger organic groups (R) of RSi(OR′)$_3$ are known to decrease the rates of hydrolysis and condensation because of steric effects, leading to the suppression of polymerization.[21] In other words, with increasing length of methylene chains between a benzene ring and a silicon atom, hydrolysis and condensation reactions should be prevented; the development of three-dimensional siloxane networks is suppressed because of the increased steric effects. Actually, we confirmed that the sample prepared from PhSi(OEt)$_3$ polymerized more sufficiently than that prepared from BnSi(OEt)$_3$. [GPC curves will be shown later (Fig. 5).] It is presumed that solid particles (powder samples) are obtainable when the polymerization of oligomers proceeds sufficiently. Therefore, the sample prepared from Phenethyl-Si(OMe)$_3$ did not form powder samples at room temperature, as shown in Table 1.
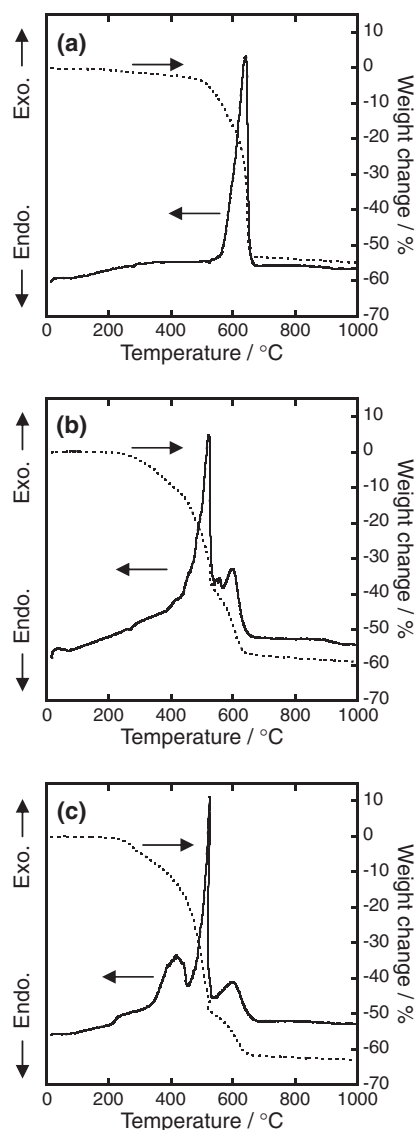
Fig. 2. DTA and TG curves up to 1000°C for samples prepared from (a) PhSi(OEt)₃, (b) BnSi(OEt)₃, and (c) Phenethyl-Si(OMe)₃.

Figure 2 shows DTA and TG curves up to 1000°C for samples prepared from (a) PhSi(OEt)$_3$, (b) BnSi(OEt)$_3$, and (c) Phenethyl-Si(OMe)$_3$. For the sample prepared from PhSi(OEt)$_3$, an exothermic peak accompanied with weight loss is observed in the DTA and TG curves. For samples prepared from BnSi(OEt)$_3$ and Phenethyl-Si(OMe)$_3$, exothermic peaks accompanied with weight losses are observed in wide temperature ranges. These exothermic peaks are attributable to the oxidation of the organic groups, so that these samples should become silica by heating to temperatures greater than the oxidation temperature of the organic groups. The onset temperatures for oxidation, which are listed in Table 1, shift to lower temperatures with increased length of methylene chains between a benzene ring and a silicon atom; the onset temperature for the oxidation shifts from around 530°C for the sample prepared from PhSi(OEt)$_3$ [Fig. 2(a)] to around 210°C for the sample prepared from Phenethyl-Si(OMe)$_3$ [Fig. 2(c)].

Our previous studies demonstrated that particles prepared from PhSi(OEt)$_3$ and BnSi(OEt)$_3$[13)] using the two-step acid–base catalyzed sol–gel process exhibited the apparent glass transition. The glass transition temperature of the particles prepared from PhSi(OEt)$_3$ and BnSi(OEt)$_3$ under the present experimental
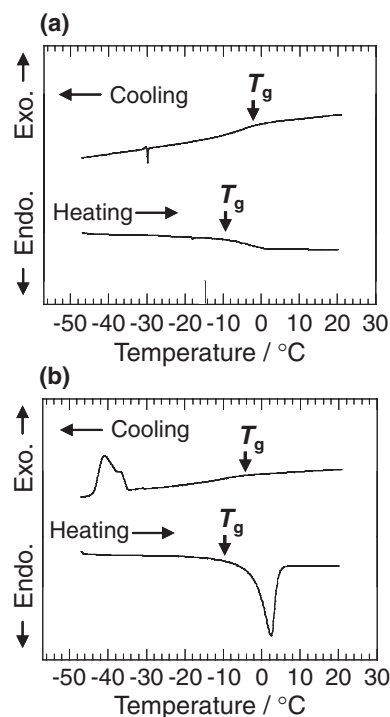

Fig. 3. DSC cooling and heating curves from −50 to 25°C at cooling and heating rate of 5°C/min for (a) transparent and (b) opaque samples prepared from Phenethyl-Si(OMe)₃.

conditions is summarized in Table 1. The PhSiO$_{3/2}$ particles showed T_g at much higher temperatures than the BnSiO$_{3/2}$ particles. In Phenethyl-Si(OMe)$_3$, white precipitates were collected from the colloidal sol after centrifugation. Table 1 shows that the appearance of the precipitates after drying under vacuum was that of a high-viscosity oil. Moreover, the Phenethyl-SiO$_{3/2}$ precipitates were separated spontaneously into two parts during the drying process under vacuum: one was a transparent region (major part), and the other was a white region (minor part) (referred to respectively as *transparent sample* and *opaque sample*). The DSC measurements of the two regions were performed separately. **Figure 3** shows DSC cooling and heating curves from −50 to 25°C at cooling and heating rate of 5°C/min for the (a) transparent and (b) opaque samples. The measurements were started with the cooling process from 25°C. In the transparent sample [Fig. 3(a)], endothermic changes resulting from the glass transition are observed at around −5°C in the cooling and heating processes. In contrast, in the opaque sample [Fig. 3(b)], exothermic and endothermic peaks attributable to solidification and the melting are primarily observed, respectively, at around −40 and 2°C in the cooling and heating processes. Endothermic changes attributable to the glass transition are also observed at around −5°C in the cooling and heating processes, as shown in Fig. 3(b). The appearance in the glass transition of the opaque sample is probably attributable to the small amounts of residual transparent samples; it was difficult to remove the transparent region from the opaque region completely. These results indicate that the structures of the two regions (transparent and opaque samples) are inherently different. Shimojima et al.[22)] reported that RSi(OR′)$_3$-derived species with long alkyl chains were self-organized according to their hydrophobic-hydrophilic interactions. It is therefore suggested that the sample prepared from Phenethyl-Si(OMe)$_3$ partially includes an ordered structure because of the self-organization of Phenethyl-Si(OMe)$_3$-derived

JCS-Japan

Takahashi et al.: Substituent effects on the glass transition phenomena of polyorganosilsesquioxane particles prepared by two-step acid–base catalyzed sol–gel process

Table 2. Appearances and thermal properties of polyorganosilsesquioxanes with alkyl groups

RSi(OR′)$_3$	Appearance	Onset temperature for oxidation of organic groups/°C	Glass transition temperature* /°C	Solidification temperature* /°C
MeSi(OEt)$_3$	Powder	430	×	×
PrSi(OEt)$_3$	Powder	220	<200	×
n-BuSi (OMe)$_3$	Powder	190	95	×
i-BuSi(OEt)$_3$	Oil	190	10	×
Pentyl-Si (OEt)$_3$	Oil	—	×	−45
Octyl-Si (OEt)$_3$	Oil	—	×	−40

*Solidification temperature: the temperature at which an exothermic peak due to the solidification was observed in the cooling process of DSC measurements.

×: Not observed, —: Not measured.

species. We can conclude that the sample prepared from Phenethyl-Si(OMe)$_3$ is composed mainly of amorphous components that exhibit the glass transition, but that it consists partially of crystalline products.

The glass transition temperature of the samples prepared from PhSi(OEt)$_3$, BnSi(OEt)$_3$, and Phenethyl-Si(OMe)$_3$ was increased in the order: Phenethyl-Si(OMe)$_3$ < BnSi(OEt)$_3$ < PhSi(OEt)$_3$. As described above, a similar tendency was observed in the formation of solid particles. Our previous work[23] showed that T_g of the PhSiO$_{3/2}$ particles prepared from PhSi(OEt)$_3$ was increased with increased molecular weight: T_g is dependent primarily on the degree of polymerization. The difference in T_g shown in Table 1 must be brought about by the difference in the polymerization degree. Schneider et al.[5] also reported a similar tendency: T_g of samples prepared from phenethyltriethoxysilane [Phenethyl-Si(OEt)$_3$], BnSi(OEt)$_3$, and PhSi(OEt)$_3$ were increased in the same order of this study, irrespective of hydrolysis and condensation conditions such as acidic and basic conditions.

It can be summarized that polyorganosilsesquioxanes with aryl groups, prepared using the two-step acid–base catalyzed sol–gel process, have a powerful tendency to exhibit the glass transition.

3.2 Characterization of polyorganosilsesquioxanes with alkyl groups

Table 2 summarizes the appearances and the thermal properties of polyorganosilsesquioxanes with alkyl groups. RSi(OR′)$_3$ with shorter alkyl groups (R: methyl, n-propyl, n-butyl) forms powder samples, whereas RSi(OR′)$_3$ with bulkier or longer alkyl groups (R: i-butyl, pentyl, octyl) does not form powder samples at room temperature. An increase in the chain length of alkyl groups prevented the development of three-dimensional siloxane networks because of steric effects. Consequently, powder samples (solid particles) were not obtained from RSi(OR′)$_3$ with bulkier or longer alkyl groups, as shown in Table 2. **Figure 4** shows SEM photographs of samples prepared from (a) MeSi(OEt)$_3$ and (b) n-PrSi(OEt)$_3$. It is apparent that both samples comprise aggregates of spherical particles. The MeSiO$_{3/2}$ particles size is around 800 nm, and the n-PrSiO$_{3/2}$ particles' size range is 100–500 nm. However, the powder sample prepared from n-BuSi(OMe)$_3$ did not consist of the aggregates of spherical particles.

Here, we discuss the effects of benzene rings on the formation of solid particles. **Figure 5** shows GPC curves of the samples
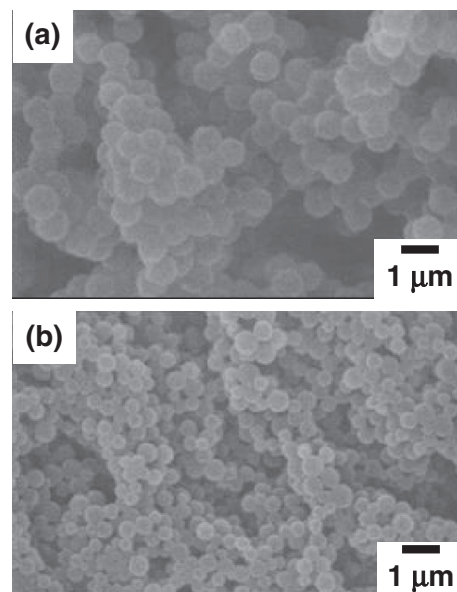
Fig. 4. SEM photographs of samples prepared from (a) MeSi(OEt)$_3$ and (b) n-PrSi(OEt)$_3$.
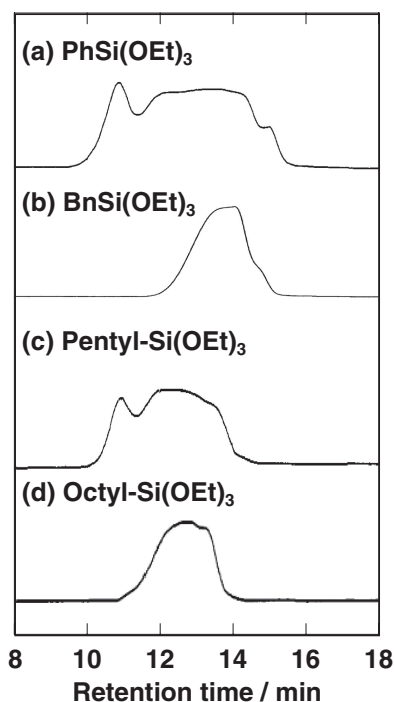
Fig. 5. GPC curves of samples prepared from (a) PhSi(OEt)$_3$, (b) BnSi(OEt)$_3$, (c) Pentyl-Si(OEt)$_3$, and (d) Octyl-Si(OEt)$_3$.

prepared from (a) PhSi(OEt)$_3$, (b) BnSi(OEt)$_3$, (c) Pentyl-Si(OEt)$_3$, and (d) Octyl-Si(OEt)$_3$. The peaks of the sample prepared from PhSi(OEt)$_3$ are observed at shorter retention times than those of the sample prepared from BnSi(OEt)$_3$. This result means that the former consists of species with larger molecular weight than the latter; benzyl groups hinder the development of three-dimensional siloxane networks more than that of phenyl groups. Similar phenomena are visible for samples prepared from pentyl-Si(OEt)$_3$ and octyl-Si(OEt)$_3$; octyl groups suppress the polymerization of the samples more than pentyl groups do. On the other hand, the molecular weights of PhSi(OEt)$_3$ and
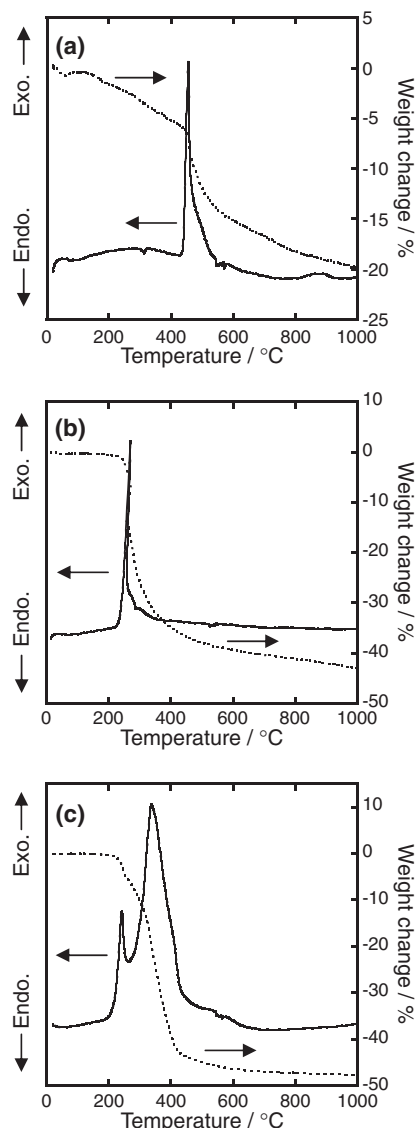
Fig. 6. DTA and TG curves up to 1000°C for samples prepared from (a) MeSi(OEt)$_3$, (b) n-PrSi(OEt)$_3$, and (c) n-BuSi(OMe)$_3$.
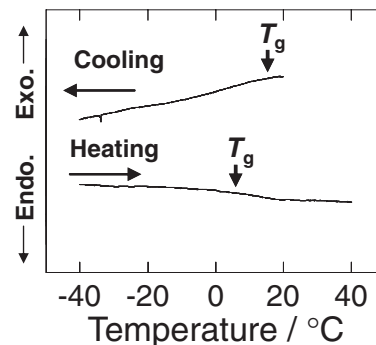

Fig. 7. DSC cooling and heating curves from −50 to 50°C at cooling and heating rate of 5°C/min for the sample prepared from i-BuSi(OEt)$_3$.
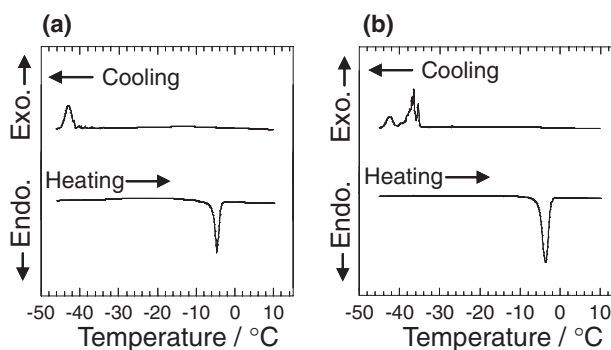

Fig. 8. DSC cooling and heating curves from −50 to 25°C at cooling and heating rate of 5°C/min for the samples prepared from (a) Pentyl-Si(OEt)$_3$ and (b) Octyl-Si(OEt)$_3$.

BnSi(OEt)$_3$ are similar to those of Pentyl-Si(OEt)$_3$ and Octyl-Si(OEt)$_3$, respectively [PhSi(OEt)$_3$: 240.4, BnSi(OEt)$_3$: 254.4, Pentyl-Si(OEt)$_3$: 234.4, Octyl-Si(OEt)$_3$: 276.5]. In Fig. 5, the peaks of the samples prepared from Pentyl-Si(OEt)$_3$ and Octyl-Si(OEt)$_3$ are observed respectively at shorter retention times than those of the samples prepared from PhSi(OEt)$_3$ and BnSi(OEt)$_3$. This result indicates that the former two samples comprise more polymerized species than the latter two samples, respectively, and that benzene rings suppress polymerization because of bulky substituents. However, as described previously, the samples with benzene rings such as phenyl and benzyl groups were powders (solid particles), whereas the samples prepared from Pentyl-Si(OEt)$_3$ and Octyl-Si(OEt)$_3$ were oily, suggesting that the solid particles are obtainable with the poor polymerization degree when benzene rings exist. Interactions among benzene rings probably play an important role in the formation of solid particles. The intramolecular and/or intermolecular interactions between the silsesquioxane chains with benzene rings may cause the increase in melting point.

Figure 6 shows DTA and TG curves up to 1000°C for samples prepared from (a) MeSi(OEt)$_3$, (b) n-PrSi(OEt)$_3$, and (c) n-

BuSi(OMe)$_3$. For all samples, a sharp or split exothermic peak accompanied with weight losses is observed in the DTA and TG curves. These exothermic peaks are assigned to the oxidation of the organic groups. The onset temperatures for the oxidation, which are listed in Table 2, shift to lower temperatures with an increase in the chain length of alkyl groups; the onset temperature for the oxidation shifts from around 430°C for the sample prepared from MeSi(OEt)$_3$ [Fig. 6(a)] to around 190°C for the sample prepared from n-BuSi(OMe)$_3$ [Fig. 6(c)].

As presented in Table 2, samples prepared from n-PrSi(OEt)$_3$, n-BuSi(OMe)$_3$, and i-BuSi(OEt)$_3$ exhibited the glass transition, whereas the samples prepared from Pentyl-Si(OEt)$_3$ and Octyl-Si(OEt)$_3$ showed solidification. **Figure 7** shows DSC cooling and heating curves from −50 to 50°C at cooling and heating rate of 5°C/min for the sample prepared from i-BuSi(OEt)$_3$. The measurement was started with the cooling process from 25°C. Very small endothermic changes resulting from the glass transition are observed at around 10°C in the cooling and heating processes. Table 2 shows that T_g of the sample prepared from i-BuSi(OEt)$_3$ (ca. 10°C) is much lower than that of the sample prepared from n-Bu(OMe)$_3$ (ca. 95°C). The glass transition temperature is primarily dependent on the degree of polymerization;[23] T_g is increased with the increased degree of polymerization. i-BuSi(OEt)$_3$ has a larger organic substituent (R) and a larger alkoxy group (OR′) than n-Bu(OMe)$_3$; consequently, the development of three-dimensional siloxane networks of the sample prepared from i-BuSi(OEt)$_3$ should be prevented. The sample prepared from i-BuSi(OEt)$_3$ showed T_g at lower temperatures. **Figure 8** shows DSC cooling and heating curves from −50 to 25°C at cooling and heating rate of 5°C/min for the samples prepared from (a) Pentyl-Si(OEt)$_3$ and (b) Octyl-Si(OEt)$_3$.
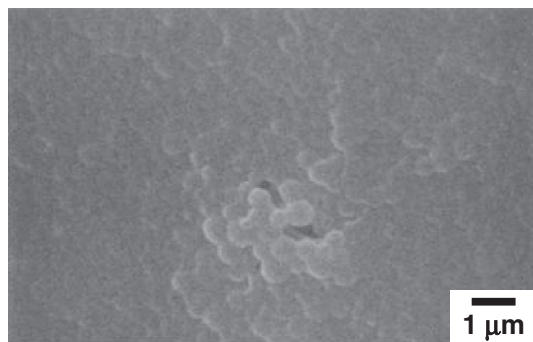
JCS-Japan

Takahashi et al.: Substituent effects on the glass transition phenomena of polyorganosilsesquioxane particles prepared by two-step acid–base catalyzed sol–gel process

Fig. 9. SEM photograph of the n-PrSiO$_{3/2}$ particles after heat treatment at 200°C for 10 min.

Fig. 10. SEM photograph of the MeSiO$_{3/2}$ particles after heat treatment at 400°C for 10 min.

Measurements were started with the cooling process from 25°C. In both samples, exothermic and endothermic peaks attributable to solidification and melting are observed in the cooling and heating processes, respectively, indicating that these samples consist of crystalline products without amorphous components that exhibit the glass transition. The crystallization is probably brought about by the self-organization of RSi(OR')$_3$-derived species, as reported by Shimojima et al.[22] However, cooling rates from molten liquids to solid states are known to be an important factor for the formation of glasses.[24] The cooling rate was 5°C/min under the present experimental condition; thereby, the samples prepared from Pentyl-Si(OEt)$_3$ and Octyl-Si(OEt)$_3$ might achieve a glassy state through a rapid cooling process.

Figure 6 shows that the oxidation of propyl groups in the polypropylsilsesquioxane (n-PrSiO$_{3/2}$) particles started at around 220°C. Consequently, the DSC measurements of the particles were conducted at 25–200°C at heating and cooling rate of 20°C/min, but no appreciable thermal change attributable to the glass transition was observed in this temperature range. However, the particles are markedly softened by heat treatment at 200°C for 10 min as shown in **Fig. 9**, indicating that the n-PrSiO$_{3/2}$ particles apparently exhibit the glass transition. In general, silica glasses are thermally softened, but it is difficult to observe T_g of pure silica glasses because they show little change in heat capacity at T_g.[25] The n-PrSiO$_{3/2}$ particles are presumed to have an identical tendency to that of silica glasses.

Figure 10 shows an SEM photograph of the MeSiO$_{3/2}$ particles after heat treatment at 400°C for 10 min. No large difference is visible in the particle morphology before [Fig. 4(a)] and after heat treatment (Fig. 10). This result means that the MeSiO$_{3/2}$ particles show no glass transition behavior below the oxidation temperature of methyl groups (ca. 430°C). Furthermore, no exothermic or endothermic peaks attributable to the solidification and the melting were observed in DTA and TG curves [Fig. 6(a)]. However, the MeSiO$_{3/2}$ particles might show glass transition behavior at higher temperatures than the oxidation temperature of methyl groups when the particles are heat-treated under an inert atmosphere to suppress the oxidation of methyl groups.

From these results in the system of polyorganosilsesquioxanes with alkyl groups, it can be concluded that polyorganosilsesquioxanes with shorter alkyl groups exhibit the glass transition, whereas polyorganosilsesquioxanes with longer alkyl groups show no glass transition behavior because of easy crystallization. The crystallization would be caused by the self-organization of RSi(OR')$_3$-derived species.

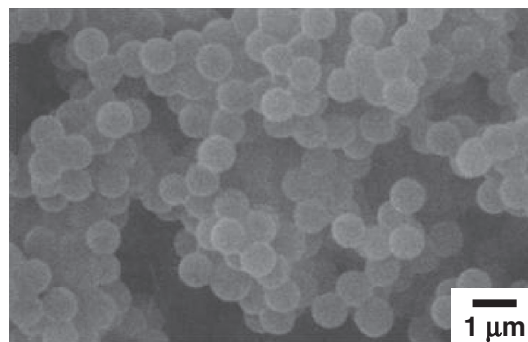Polyorganosilsesquioxanes that exhibit the glass transition are expected to serve as new glassy hybrid materials that can replace inorganic glasses and organic polymers. Our findings will open the door to design of new inorganic–organic hybrids with thermal softening behavior. They are anticipated to be applicable to various fields such as micro-optics, electronics, and ionics.

4. Conclusions

Polyorganosilsesquioxanes with different organic groups were prepared by the two-step acid–base catalyzed sol–gel process. Particles were obtained from MeSi(OEt)$_3$, n-PrSi(OEt)$_3$, n-BuSi(OMe)$_3$, PhSi(OEt)$_3$, and BnSi(OEt)$_3$, which were used as starting alkoxides. Polyorganosilsesquioxanes with aryl groups exhibited a powerful tendency to display the glass transition. It was also clarified that polyorganosilsesquioxanes with shorter alkyl groups prepared from n-PrSi(OEt)$_3$, n-BuSi(OMe)$_3$, and i-BuSi(OEt)$_3$ exhibited the glass transition. The MeSiO$_{3/2}$ particles showed no glass transition behavior from heat treatment below the oxidation temperature of methyl groups. However, the particles might show glass transition behavior by heat treatment under an inert atmosphere to suppress the oxidation of methyl groups. Polyorganosilsesquioxanes with longer alkyl groups prepared from Pentyl-Si(OEt)$_3$ and Octyl-Si(OEt)$_3$ also showed no glass transition behavior because they were composed of crystalline components attributable to the self-organization of RSi(OR')$_3$-derived species.

References

1) A. P. Wight and M. E. Davis, *Chem. Rev.*, **102**, 3589 (2002).
2) C. Sanchez, B. Lebeau, F. Chaput and J.-P. Boilot, *Adv. Mater.*, **15**, 1969 (2003).
3) R. H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, **95**, 1409 (1995).
4) D. A. Loy, B. M. Baugher, C. R. Baugher, D. A. Schneider and K. Rahimian, *Chem. Mater.*, **12**, 3624 (2000).
5) D. A. Schneider, D. A. Loy, B. M. Baugher, D. R. Wheeler, R. A. Assink, T. M. Alam and R. Saunders, *Polymer Prepr.*, **39**, 513 (1998).
6) H. Masai, M. Takahashi, Y. Tokuda and T. Yoko, *J. Mater. Res.*, **20**, 1234 (2005).
7) A. Arkhireeva, J. N. Hay and W. Oware, *J. Non-Cryst. Solids*, **351**, 1688 (2005).
8) J. Y. Choi, C. H. Kim and D. K. Kim, *J. Am. Ceram. Soc.*, **81**, 1184 (1998).
9) A. Matsuda, T. Tanaka, K. Tadanaga, T. Minami and M. Tatsumisago, *J. Mater. Sci.*, **39**, 903 (2004).

10) S. Shibata, M. Yamane, K. Kamada, K. Ohta, K. Sasaki and H. Masuhara, *J. Sol-Gel Sci. Technol.*, 8, 959 (1997).

11) C. R. Miller, R. Vogel, P. P. T. Surawski, K. S. Jack, S. R. Corrie and M. Trau, *Langmuir*, 21, 9733 (2005).

12) K. Katagiri, K. Hasegawa, A. Matsuda, M. Tatsumisago and T. Minami, *J. Am. Ceram. Soc.*, 81, 2501 (1998).

13) A. Matsuda, T. Sasaki, K. Hasegawa, M. Tatsumisago and T. Minami, *J. Ceram. Soc. Japan*, 108, 830 (2000).

14) K. Takahashi, K. Tadanaga, A. Hayashi and M. Tatsumisago, *Chem. Lett.*, 36, 324 (2007).

15) T. Matsumoto, Y. Takayama, N. Wada, H. Onoda, K. Kojima, H. Yamada and H. Wakabayashi, *J. Mater. Chem.*, 13, 1764 (2003).

16) A. Arkhireeva and J. N. Hay, *J. Mater. Chem.*, 13, 3122 (2003).

17) A. Arkhireeva, J. N. Hay and M. Manzano, *Chem. Mater.*, 17, 875 (2005).

18) A. Matsuda, T. Sasaki, K. Hasegawa, M. Tatsumisago and T. Minami, *J. Am. Ceram. Soc.*, 84, 775 (2001).

19) K. Takahashi, K. Tadanaga, A. Hayashi, A. Matsuda and M. Tatsumisago, *J. Mater. Res.*, 21, 1255 (2006).

20) K. Takahashi, K. Tadanaga, A. Matsuda, A. Hayashi and M. Tatsumisago, *J. Am. Ceram. Soc.*, 89, 3832 (2006).

21) C. J. Brinker and G. W. Scherer, "Sol–Gel Science", Academic Press Inc., Boston (1990).

22) A. Shimojima, Y. Sugahara and K. Kuroda, *Bull. Chem. Soc. Jpn.*, 70, 2847 (1997).

23) K. Takahashi, K. Tadanaga, A. Hayashi, A. Matsuda and M. Tatsumisago, *J. Ceram. Soc. Japan*, 115, 131 (2007).

24) M. Tatsumisago, T. Minami and M. Tanaka, *J. Am. Ceram. Soc.*, 64, C97 (1981).

25) J. Wong and C. A. Angell, "Glass Structure by Spectroscopy", Marcel Dekker, New York (1976).