Thermal Softening Behavior of Poly(phenylsilsesquioxane) and Poly(benzylsilsesquioxane) Particles

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ポリフェニルシルセスキオキサン及びポリベンジルシルセスキオキサン微粒子の熱軟化挙動

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The thermal softening behavior of poly(phenylsilsesquioxane) ($\text{PhSiO}_{3/2}$) and poly(benzylsilsesquioxane) ($\text{BnSiO}_{3/2}$) particles during heat treatment has been investigated from the results of gel permeation chromatography, thermal and structural analyses of the particles. Both $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles thermally softened, and the on-set temperature of thermal sintering was about 140 and 50°C for $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$, respectively. The thermal sintering of the $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles was caused by the decrease of viscosity at temperatures higher than the glass transition temperatures. Glass transition was observed for $\text{BnSiO}_{3/2}$ in the repeated heating runs, while for $\text{PhSiO}_{3/2}$ glass transition was appreciable only in the first heating run. From ^{29}Si nuclear magnetic resonance spectra, the development of siloxane network during heat treatment was found to be more significant in $\text{PhSiO}_{3/2}$ than in $\text{BnSiO}_{3/2}$. The difference in the structural evolution during heat treatment makes $\text{PhSiO}_{3/2}$ particles thermosetting and $\text{BnSiO}_{3/2}$ ones thermoplastic.

[Received May 15, 2000; Accepted June, 21, 2000]

Key-words: Phenylsilsesquioxane, Benzylsilsesquioxane, Thermal softening, Sintering, Glass transition, Thick film

1. Introduction

We have developed a new technique to form transparent thick films on substrates by using poly(phenylsilsesquioxane) ($\text{PhSiO}_{3/2}$) and poly(benzylsilsesquioxane) ($\text{BnSiO}_{3/2}$) in the electrophoretic sol-gel deposition for the application to micro-optic devices.^{1)–3)} The process of the technique developed is as follows: (1) preparation of $\text{PhSiO}_{3/2}$ or $\text{BnSiO}_{3/2}$ micro-particles from corresponding organoalkoxysilanes by the sol-gel method, (2) electrophoretic deposition of the particles in sol on the substrate used as an electrode, and (3) improvement in transparency of the deposited film on the substrate due to the thermal sintering of the particles by a heat treatment. Patterned thick films with a convex shape for optical component can be fabricated on glass substrates with patterned indium tin oxide (ITO) coating when the particles dispersed in the sol are selectively deposited on the patterned area at which dc voltage is applied.³⁾ The most important point to obtain transparent, thick films by this process is the thermal sintering of the particles during a heat treatment, which causes the morphological change of the films from the aggregate of the poly(silsesquioxane) particles to monolith. We have investigated the thermal properties of the several kinds of organosilsesquioxane particles which were prepared by the sol-gel method and found that the thermal sintering of the particles was a unique phenomenon for $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$, so far. Therefore the comparison of the thermal softening behaviors for $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles affords useful information to control the sintering of organosilsesquioxanes for the fabrication of highly transparent, thick films in this process.

In this study, we have performed gel permeation chromatography and thermal analyses for the particles, and also measured the X-ray diffraction patterns and ^{29}Si nuclear magnetic resonance (NMR) of the particles. The thermal softening behaviors of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles with

heat treatment are compared on the basis of these characterizations.

2. Experimental procedure

2.1 Preparation of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles

Preparation procedures of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles were essentially the same as described in the preceding papers.^{1)–3)} Phenyltriethoxysilane and benzyltriethoxysilane were used as starting materials for the preparation of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles, respectively. Hydrochloric acid (0.01 mass%) was added to phenyltriethoxysilane and benzyltriethoxysilane for hydrolysis and the mixtures were respectively stirred at 25°C for 7 and 15 h until the mixtures became homogeneous. The hydrolyzed phenyltriethoxysilane and benzyltriethoxysilane solutions obtained were then added to 4 and 1 mass% ammonia water, and the resultant solutions were stirred for 14 and 10 h, respectively. The mole ratio of organoalkoxysilane/ H_2O (in hydrochloric acid)/ H_2O (in ammonia water) was fixed to be 1/20/180. The $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles formed in the solutions were collected by centrifugation and were dried under vacuum at room temperature for 3 h.

2.2 Characterization of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles

Refractive indexes of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles were evaluated using refractive index standard liquids (Cargille Laboratories, Series AAA, AA and A). The weight average molecular weight of the particles was measured using a gel permeation chromatography (GPC) with tetrahydrofuran as the eluent at 40°C. Differential thermal analysis (DTA) and thermogravimetry (TG) of the particles were performed under 10°C·min⁻¹. FT-IR spectra and X-ray diffraction patterns of the particles were also obtained.

Thermal softening behaviors of the particles with respect to the sintering were observed using a scanning electron microscope (SEM). Penetration tests were also carried out

using a thermomechanical analyzer (TMA). The monolithic plate samples of about 0.3 mm in thickness for the TMA were prepared from acetone solutions, in which $\text{PhSiO}_{3/2}$ or $\text{BnSiO}_{3/2}$ particles were dissolved, by casting the solutions in a glass dish and being dried. Glass transition temperatures of the particles were obtained from differential scanning calorimetry (DSC) curves of repeated heating and cooling runs under $20^\circ\text{C}\cdot\text{min}^{-1}$. Structural changes in the particles with heat treatment were examined from ^{29}Si cross polarization magic-angle spinning (CPMAS)-NMR.

3. Results

3.1 Refractive index and molecular weight

The diameters of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles prepared under these conditions were 0.2 to $1\ \mu\text{m}$. Refractive indexes of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles after drying in vacuum for 3 h were 1.57 and 1.62, respectively.

Figure 1 shows GPC elution curves of (a) $\text{PhSiO}_{3/2}$ and (b) $\text{BnSiO}_{3/2}$ particles. It can be seen that the GPC curve of $\text{PhSiO}_{3/2}$ (a) shows a broader band at shorter retain time than that of $\text{BnSiO}_{3/2}$ (b), indicating that $\text{PhSiO}_{3/2}$ consists of polymerized species with larger molecular weights than those in $\text{BnSiO}_{3/2}$ particles. The weight average molecular weight of the particles was evaluated to be 5.0×10^3 for $\text{PhSiO}_{3/2}$ and 2.2×10^3 for $\text{BnSiO}_{3/2}$ according to the polystyrene standard.

3.2 Thermal stability of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$

Figures 2(a) and (b) show DTA and TG curves for $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles, respectively. An exothermic peak with a shoulder is seen in the DTA curve for $\text{PhSiO}_{3/2}$ (a) at 615°C and the total weight loss in the TG curve (a) after heating up to 1000°C is about 53%. On the other hand, two exothermic peaks are clearly observed in the DTA curve of $\text{BnSiO}_{3/2}$ (b) at 505 and 610°C and the total weight loss in the TG curve (b) after heating up to 1000°C is about 50%. The thermal decomposition of phenyl and benzyl groups in the particles at these temperatures was also confirmed by the FT-IR spectra.

3.3 Structural ordering

Figures 3(a) and (b) show changes in the X-ray diffraction patterns of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles when the particles were heat-treated at various temperatures for 2 h. The X-ray diffraction patterns of $\text{PhSiO}_{3/2}$ (Fig. 3(a)) show a relatively sharper and intense peak at 7° and a very broad

one at around 18° , indicating that the structural ordering with spacings of 1.3 and 0.5 nm is present in the $\text{PhSiO}_{3/2}$ particles. It can be seen that the intensity of the sharper peak slightly increases with increasing the heat treatment temperature from 200 to 400°C . The X-ray diffraction patterns of $\text{BnSiO}_{3/2}$ (Fig. 3(b)) also display a sharper peak at 7° and a very broad peak at 21° , which correspond to the structural ordering with spacings of 1.3 and 0.4 nm, respectively. The intensity and half width of the peak remain almost constant during the heat treatment.

3.4 On-set temperature of the thermal sintering of the particles

Morphological changes of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles with heat treatment are shown in Figs. 4(a)–(f). Figures 4(a), (b), and (c) are SEM images for the $\text{PhSiO}_{3/2}$ particles before heat treatment, after heat treatment at 100°C for 30 min, and at 140°C for 30 min, respectively; Figs. 4(d), (e), and (f) are for the $\text{BnSiO}_{3/2}$ particles before heat treatment, after heat treatment at 40°C for 30 min, and at 50°C for 30 min, respectively. The aggregates of spherical $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles of 0.2 to $1\ \mu\text{m}$ in diameter are seen before heat treatment in Figs. 4(a) and (d). Although the spherical shapes of the particles are kept after a heat treatment at 100°C for $\text{PhSiO}_{3/2}$ (Fig. 4(b)) and at 40°C for $\text{BnSiO}_{3/2}$ (Fig. 4(e)), necking among the particles is seen after a heat treatment at 140°C for $\text{PhSiO}_{3/2}$ (Fig. 4(c)) and at 50°C for $\text{BnSiO}_{3/2}$ (Fig. 4(f)). These results typically indicate that both of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles are thermally softened and the on-set temperatures of the thermal

Fig. 1. GPC elution curves of (a) $\text{PhSiO}_{3/2}$ and (b) $\text{BnSiO}_{3/2}$ particles.

Fig. 2. DTA and TG curves for (a) $\text{PhSiO}_{3/2}$ and (b) $\text{BnSiO}_{3/2}$ particles at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

Fig. 3. Changes in the X-ray diffraction patterns of (a) $\text{PhSiO}_{3/2}$ and (b) $\text{BnSiO}_{3/2}$ particles when the particles were heat-treated at various temperatures for 2 h.

Fig. 4. Morphological changes of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles during heat treatment. (a), (b) and (c) are SEM images for the $\text{PhSiO}_{3/2}$ particles before heat treatment, after heat treatment at 100°C for 30 min and at 140°C for 30 min; (d), (e) and (f) are for the $\text{BnSiO}_{3/2}$ particles before heat treatment, after heat treatment at 40°C for 30 min and at 50°C for 30 min, respectively.

sintering for $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles are about 140 and 50°C, respectively.

3.5 Thermomechanical analysis of softening behavior

The penetration ratios of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ monoliths under a probe load of 0.5 g and a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ are shown in Figs. 5(a) and (b), respectively. The penetration ratio was defined as the percentage of the penetration depth to the thickness of the monolithic plate

sample of about 0.3 mm in thickness. While the penetration ratio of $\text{PhSiO}_{3/2}$ increases to be about 60% at temperatures from 140 to 240°C, the ratio slightly decreases from 240 to 400°C. The increase in the penetration ratio reflects the softening and decrease in viscosity of $\text{PhSiO}_{3/2}$. The slight decrease from 240 to 400°C can be ascribed to thermal expansion of hardened $\text{PhSiO}_{3/2}$ monolith on the glass substrate. The penetration began at about 140°C for $\text{PhSiO}_{3/2}$

Fig. 5. The penetration ratios of (a) $\text{PhSiO}_{3/2}$ and (b) $\text{BnSiO}_{3/2}$ monoliths under a probe load of 0.5 g and a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The penetration ratio was defined as the percentage of the penetration depth to the thickness of the monolithic sample.

regardless of the heating rate, whereas the ratio increased with an increase in the heating rate. On the other hand, the ratio of $\text{BnSiO}_{3/2}$ drastically increases at 47°C to become about 90% at 100°C , and monotonically increases from 100 to 160°C .

3.6 Glass transition of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles

Figures 6(a) and (b) show DSC heating curves of $\text{PhSiO}_{3/2}$ particles from 30 to 120°C and $\text{BnSiO}_{3/2}$ particles from 30 to 70°C on repeated runs, respectively. The thermal sintering between the particles was observed for both $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles after the repeated heating and cooling runs in the above temperature ranges, as expected from Fig. 4. Although an endothermic peak due to glass transition is clearly observed at around 100°C in the first heating of $\text{PhSiO}_{3/2}$ particles, such a peak is not appreciable in the second and third runs. In contrast, an endothermic peak due to glass transition is observable at around 40°C in all the DSC curves of the repeated heating runs for the $\text{BnSiO}_{3/2}$ particles.

In the repeated heating curves of DSC for $\text{PhSiO}_{3/2}$ particles from 30 to 200°C after the first heating up to 130°C , endothermic peaks due to the glass transition were not appreciable, either.

3.7 Development of the structural unit

Solid-state NMR spectroscopy is a powerful method to

Fig. 6. DSC heating curves of (a) $\text{PhSiO}_{3/2}$ particles from 30 to 120°C and (b) $\text{BnSiO}_{3/2}$ particles from 30 to 70°C on repeated runs at heating and cooling rates of $20^\circ\text{C}\cdot\text{min}^{-1}$.

characterize the chemical structure of the poly(organosilsesquioxane) particles.⁴⁾ The ^{29}Si CPMAS-NMR spectra of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles heat-treated at various temperatures for 2 h are shown in Figs. 7(a) and (b), respectively. In Fig. 7(a) for $\text{PhSiO}_{3/2}$, two peaks are observed at -76 and -85 ppm, which are assigned to T_2 units with two bridging oxygens and T_3 units with three bridging oxygens, respectively. The relative intensity of T_2 to T_3 units of $\text{PhSiO}_{3/2}$ particles markedly decreases when the particles were heat-treated at 200°C , which is higher by about 100°C than the glass transition temperature. The peak due to T_2 units almost disappears after a heat treatment at 400°C . In the spectra of $\text{BnSiO}_{3/2}$ (Fig. 7(b)), two peaks at -65 ppm due to T_2 units and at -78 ppm due to T_3 units are observable. The relative intensity of T_2 to T_3 units of $\text{BnSiO}_{3/2}$ particles decreases with an increase in the heat treatment temperature. Although the relative intensity of T_2 to T_3 units of $\text{BnSiO}_{3/2}$ is comparable to that of $\text{PhSiO}_{3/2}$ before the heat treatment, the intensity of T_2 units of $\text{BnSiO}_{3/2}$ is larger than that of $\text{PhSiO}_{3/2}$ after a heat treatment at 200°C and is still appreciable even after a heat treatment at 300°C .

4. Discussion

Refractive indexes of 1.57 for $\text{PhSiO}_{3/2}$ and 1.62 for $\text{BnSiO}_{3/2}$ particles are relatively high compared with those of poly(alkylsilsesquioxanes).⁵⁾ The high refractive index of the particles can be ascribed to a large dielectric constant of phenyl and benzyl groups due to their π -electrons in the ben-

Fig. 7. ^{29}Si CPMAS-NMR spectra of (a) $\text{PhSiO}_{3/2}$ and (b) $\text{BnSiO}_{3/2}$ particles heat-treated at various temperatures for 2 h.

zene ring. Transparent inorganic-organic materials with high refractive index can be obtained after the thermal sintering of the particles, and hence $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ are promising materials for micro-optic components such as micro-lens arrays and gratings.⁶⁾

The weight average molecular weight of $\text{BnSiO}_{3/2}$ particles evaluated using GPC was lower than that of $\text{PhSiO}_{3/2}$ particles, so that benzyl groups should prevent the development of siloxane chains in the particles than phenyl groups. An exothermic peak with a shoulder at 615°C in the DTA curve for $\text{PhSiO}_{3/2}$ corresponds to the thermal decomposition of phenyl groups. The total weight loss of $\text{PhSiO}_{3/2}$ particles after heating up to 1000°C is about 53%, which agrees with the calculated value for the weight loss from $\text{PhSiO}_{3/2}$ to SiO_2 . On the other hand, two exothermic peaks were observed in the DTA curve of $\text{BnSiO}_{3/2}$ at 505 and 610°C, which probably reflect the decomposition of benzyl groups

at the surface and inside of the particles, respectively. The total weight loss of about 50% for $\text{BnSiO}_{3/2}$ after heating up to 1000°C is slightly smaller than the calculated value of 58% for the change from $\text{BnSiO}_{3/2}$ to SiO_2 . This discrepancy in weight loss should be ascribed to the residual carbons.⁷⁾ $\text{PhSiO}_{3/2}$ has a higher thermal stability against decomposition by about 100°C than $\text{BnSiO}_{3/2}$.

The structural ordering of 1.3 and 0.5 nm in $\text{PhSiO}_{3/2}$ is reported to be assigned to the chain-to-chain distance and to intra-chain distances for a stereoregular double chain structure like a ladder of $\text{PhSiO}_{3/2}$, respectively.^{8),9)} The structure of $\text{BnSiO}_{3/2}$ is probably analogous to the double chain structure of $\text{PhSiO}_{3/2}$.

$\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles were thermally softened and the on-set temperatures of thermal sintering for $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles were about 140 and 50°C, respectively. Penetration ratios increased at 138°C to be 63% for $\text{PhSiO}_{3/2}$ and at 47°C to be 98% for $\text{BnSiO}_{3/2}$. These results of the penetration ratio measurements agree with the morphological changes of the particles due to the fusion during the heat treatment and also suggest that the viscosity of the particles significantly decreases at these temperatures. The penetration ratio of $\text{BnSiO}_{3/2}$ was larger than that of the $\text{PhSiO}_{3/2}$, indicating that $\text{PhSiO}_{3/2}$ hardened during the heating. From the comparison of the penetration curves, the increase in the penetration ratio of $\text{BnSiO}_{3/2}$ during heating was found to be more drastic than that of $\text{PhSiO}_{3/2}$, suggesting that the viscosity of $\text{BnSiO}_{3/2}$ was considerably lower than that of $\text{PhSiO}_{3/2}$ at temperatures around their on-set temperatures of the thermal sintering. We have recently found that the thermal sintering on-set temperatures of the $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles can be controlled by changing the molecular weight of the particles from the preparation conditions. The relationship between the on-set temperature and molecular weight of each particle will be reported in detail elsewhere.

Endothermic peaks due to glass transition were observed in the first heating DSC curves of both $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles, whereas the glass transition was unappreciable for $\text{PhSiO}_{3/2}$ and observable for $\text{BnSiO}_{3/2}$ on the repeated heating and cooling runs. When the $\text{PhSiO}_{3/2}$ particles were heated at temperatures higher than the glass transition temperature, the viscosity of the particles first decreased due to the thermal softening of the particles and then the polymerization degree and distribution of the molecular weight of the $\text{PhSiO}_{3/2}$ increased. These phenomena probably make the glass transition of $\text{PhSiO}_{3/2}$ particles unappreciable on the repeated heating and cooling runs. Glass transition was reversible for the $\text{BnSiO}_{3/2}$ particles, so that the polymerization degree and distribution of the molecular weight of the thermally sintered $\text{BnSiO}_{3/2}$ tended to remain constant at around the thermal sintering on-set temperature. The difference of changes in polymerization degree and distribution of the molecular weight at around the thermal sintering on-set temperature should provide the $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles with thermosetting and thermoplastic properties, respectively.

The ^{29}Si CPMAS-NMR spectra indicated that the flexible T_2 units were transformed into rigid T_3 units in both $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles at temperatures higher than the glass transition temperature. It was found from the comparison of the NMR spectra of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles that the development of siloxane network, i.e., hardening during heat treatment was more significant in $\text{PhSiO}_{3/2}$ than in $\text{BnSiO}_{3/2}$. The significant development of siloxane network must cause the increases in the polymerization degree and distribution of the molecular weight of $\text{PhSiO}_{3/2}$, and hence it makes the glass transition of $\text{PhSiO}_{3/2}$ unappreciable as discussed above.

We have shown in the previous papers^{1),2)} that a high heating rate was indispensable to transform the opaque thick film composed of aggregated $\text{PhSiO}_{3/2}$ particles, which were deposited by electrophoresis, into the transparent, continuous layer of $\text{PhSiO}_{3/2}$. From the results of DSC, TMA and NMR in this work, the decrease in viscosity due to the thermal softening and sintering behaviors of the $\text{PhSiO}_{3/2}$ particles was considered to be a competitive process to the hardening due to the development of siloxane network caused by the transformation of flexible T_2 units to rigid T_3 units during the heat treatment. Thus the high heating rate can achieve the thermal sintering of the $\text{PhSiO}_{3/2}$ particles before hardening of the particles, leading to the successful formation of the highly transparent, thick films.

5. Conclusions

Transparent, thick films were fabricable on substrates by electrophoretic deposition using $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles prepared by the sol-gel method. The transparency of the thick films was governed by the thermal softening and sintering behaviors of these particles. The on-set temperatures of the thermal sintering were identified from SEM observation to be 140°C for $\text{PhSiO}_{3/2}$ and 50°C for $\text{BnSiO}_{3/2}$ particles, respectively. Significant increases in penetration ratio were also observed at 138°C for $\text{PhSiO}_{3/2}$ and at 47°C for $\text{BnSiO}_{3/2}$ particles. These phenomena corresponded to the drastic decrease in viscosity at temperatures higher than the glass transition temperatures of the $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles. Although the glass transition was observed at around 100°C for $\text{PhSiO}_{3/2}$ only in the first heating DSC curve of the repeated runs, that was observed at 38°C for $\text{BnSiO}_{3/2}$ in all the repeated runs. The development of siloxane network during heat treatment was more significant in $\text{PhSiO}_{3/2}$ than in $\text{BnSiO}_{3/2}$. The difference in the structural evolution during heat treatment above made glass

transition unappreciable for $\text{PhSiO}_{3/2}$ and reversible for $\text{BnSiO}_{3/2}$ in the repeated heating runs, and also provided $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles with thermosetting and thermoplastic properties, respectively. Hybridization of $\text{PhSiO}_{3/2}$ and $\text{BnSiO}_{3/2}$ particles should permit the controlled thermal sintering behavior of the resultant poly (phenyl-benzylsilsesquioxane) and the improved transparency of the resultant thick films deposited by the electrophoresis for their application to micro-optics components.

Acknowledgment This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

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