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Synthesis of polysiloxane-modified silica hybrid particles by a high temperature water technology

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ABSTRACT

Polysiloxane-modified silica hybrid particles were synthesized by hydrolysis and subsequent polycondensation of phenyltrimethoxysilane in the presence of colloidal silica at above 220 °C. The process variables include pH of the colloid, [silica]/[phenyltrimethoxysilane] molar ratio, reaction temperature, and reaction time. The products were characterized by solvent extraction, TGA, GPC, TEM, and ^{29}Si NMR. The degree of surface modification (DOM) ranged between 5 and 35 wt.% by tuning the process variables when a neutral colloid was used. On the other hand, the DOM proved to be strongly dependent on temperature and becomes essentially zero when the synthesis was conducted with an acidic colloid at temperatures as high as 350 °C. TEM analysis suggested that each silica particle was surface modified resulting in minimal aggregation of the particles. The hybridization mechanism was studied by the DOM and the molecular weight of ungrafted polysiloxane.

1. Introduction

High temperature water (HTW) technology has been studied as an attractive reaction route during the last two decades because of tunable physical properties such as dielectric constant, ion product, and density by controlling temperature and pressure, and non-hazardous nature of the reaction medium [1]. Majority of the HTW research targeted HTW-assisted oxidative degradation of various materials such as hazardous industrial waste [2] while material synthesis including metal oxide fine particle formation has been actively investigated during the last decade [3]. We have been studying HTW technology as a new environmentally benign process for silicone industry. We have thus far demonstrated a catalyst-free polysiloxane synthesis by subcritical water technology in 2005 [4,5]. The primary process involves hydrolysis and subsequent polycondensation of organoalkoxysilanes yielding polysiloxanes. As this water-assisted polysiloxane synthesis is attractive from environmental friendliness and process simplicity, we started applying HTW process to develop nanohybrid materials. Nanohybrid materials in which inorganic nanosize particles are well dispersed in a polymeric matrix are important class of materials with significant interests from both academia and industries [6]. It is well known that the surface modification of particles is a very critical step in developing practical hybridized materials. For the silicone industry, silica is the most important type of nanoparticle materials.

The basic idea for the present hybridization technology is to simultaneously polymerize organoalkoxysilanes and modify the surface of silica. Use of silane coupling agent is a very well known approach to modify the surface of silica [7,8]. However, surface modification by polymeric materials, especially with polysiloxanes, was only studied by few [9] although several modification methods for solid particle [10–13] and colloidal particles [14–16] with carbon-based polymers have been demonstrated yielding particles with controlled polymer structure and molecular weight. We expected that in our new approach, the residual silanol and/or methoxy groups on the polysiloxane molecules function as reaction sites yielding Si–O–Si bonds connecting silica and polysiloxanes. From this standpoint, the subcritical water-assisted process yielding relatively high contents of silanol and methoxy groups on the resultant polysiloxane [5] may be preferable for grafting on silica particles. While it is possible to add water as a reactant to a mixture of silica and a polysiloxane precursor, aqueous colloidal silica, which is a dispersion of nanometer size silica in water, should be a good substrate for preparing nanometer scale hybrid particles.

In this report, we describe a study of simplified hybridization using colloidal silica and phenyltrimethoxysilane (PTMS) yielding polysiloxane–silica hybrids. We focused on how the reaction

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conditions affect formation of phenylsilsesquioxane-modified hybrid silica particles to confirm the feasibility of the synthetic process.

2. Experimental section

2.1. Equipment

A custom made cylindrically shaped reactor with an internal volume of 10 mL was made using 1/2″ SUS 316 BA pipe. Swagelok connectors were used to cap the two ends. A salt bath heated by an electric furnace with the temperature stability within +/− 1 °C was used as a heat source.

2.2. Materials and characterization methods

PTMS supplied by Dow Corning Toray Co. Ltd. was used without further purification. Following three colloidal silica dispersions were used as received: (a) "Snowtex O": supplied by Nissan Chemical; silica content: 20 wt.%; pH: ca. 3; particle size: 10–20 nm, (b) "PL-1": supplied by Fuso Chemical; silica content: 12 wt.%; pH: ca. 7; particle size: 10 nm; and (c) "Snowtex 30": supplied by Nissan Chemical; silica content: 30 wt.%; pH: ca. 10; particle size: 10–20 nm.

Solution inCD_3COCD_3 and solid state ^{29}Si NMR spectra were recorded by a single pulse mode with a Bruker AC300P spectrometer. Tetramethylsilane and 3-trimethylsilyl-1-propanesulfonic acid sodium salt were used as external standards for the solution and the solid state measurements, respectively. Chromium acetylacetonate [$Cr(acac)_3$] was used as a relaxation agent for the solution ^{29}Si NMR measurements. FT-IR spectroscopic measurements were obtained in a transmission mode using a JASCO FT/IR-670 Plus.

TEM analysis of hybrid materials was made with a Hitachi H-8100 microscope. The observation was performed at an accelerating voltage of 100 keV. The specimen was prepared by embedding in an epoxy resin followed by slicing with a microtome in a frozen state. Gel permeation chromatography (GPC) was performed using chloroform as an eluent using a Shimadzu LC-VP GPC system equipped with four Shodex K-G, K-800D, K-804L, K-803L columns and a refractometer. The weight average molecular weight (*M*w) and the polydispersity were calculated using polystyrene standards. Thermogravimetric differential thermal analysis (TG-DTA) was conducted using Rigaku Thermoflex TAS200-TG8110D at a heating rate of 10 °C/min in air.

2.3. A typical example of in situ hybridization process

Neutral silica dispersion (PL-1; 2.0 mL; 0.256 g of silica) and PTMS (0.38 mL) were placed in a one-end capped reactor and then the other end was capped. The reactor was placed in a preheated salt bath at 300 °C to start the reaction as depicted schematically in Fig. 1.

After heating for 10 min, the reactor was pulled out of the salt bath and placed into a water bath to terminate the reaction. The product composed of colorless solid and liquid. The solid product was filtered then dried *in vacuo* at 80 °C to yield a colorless powder. (0.46 g; 90%).

As will be described in the "Results and Discussion", the solid products are composed of insoluble poly(phenylsilsesquioxane)-silica hybrid particles and toluene-soluble "ungrafted" poly(phenylsilsesquioxane). Extraction of the solid product with toluene was carried out to remove the polymer. A part of the product (100 mg) was mixed with toluene (3 mL) and stirred for half an hour at room temperature. The insoluble material was separated by centrifugation and this process was repeated three times. The solid thus obtained was dried at 80 °C *in vacuo*.

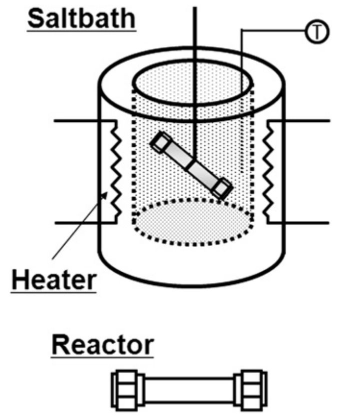


Fig. 1. Reaction system used in the present study.

3. Results and discussion

3.1. Stability of various colloidal silicas at elevated temperatures

Our primary silica source for the polysiloxane–silica hybrid particles in the present study is aqueous colloidal silica. We selected three colloidal silicas as summarized in the experimental section to identify the suitable substrate for the present HTW process.

First, the stability of the colloids at elevated temperatures was examined in a SUS 316 sealed tube. The results are summarized in Table 1.

The temperature range was determined by referring to the results of the polysiloxane synthesis [4]. It is important to note that the acidic colloid proved to be essentially stable even at 300 °C while the neutral and basic colloids are quite unstable at above 250 °C resulting in precipitation of solid silica. All the three colloids were stable at 200 °C. Influence of the pressure on the stability at 300 °C for the acidic colloid is interesting. This may be because when the pressure is 5 MPa, water in the colloid can be at a gas state because the pressure was below the saturated vapor pressure called SVP. Obviously, the colloid cannot exist in a gas state. On the other hand, the colloid should essentially remain at a liquid state when the pressure was as high as 10 MPa, which is higher than SVP.

Table 1
Stability of colloidal silicas at elevated temperatures[a]

Silica's name	Temp (°C)	Pressure (MPa)[b]	pH[c]	Product appearance
Snowtex O	200	10	5–6	Liquid[d]
	250	10	5–6	Liquid[d]
	300	5		Colorless solid
	300	10	5–6	Liquid[d]
PL-1	200	10	7–8	Liquid[d]
	250	10		Colorless solid
	300	5		Colorless solid
	300	10		Colorless solid
Snowtex 30	200	10	10–11	Liquid[d]
	250	10		Colorless solid
	300	5		Colorless solid
	300	10		Colorless solid

[a] Heated in a salt bath for 10 min and then quenched in a water bath.
[b] Pressure of the mixture: calculated value.
[c] pH: measured for liquid products.
[d] A trace amount of solid was also formed.

Water transitionally becomes vapor before temperatures reach the intended values, and this should cause the formation of the small amount of solid under various temperature conditions.

As for the stability, the acidic colloid proved to the highest. In addition, the acidic colloid is worth being examined due to the potential accelerating effect of the acid on a hydrolysis rate of the polysiloxane precursor. On the other hand, the neutral colloid is better than other two from the practical standpoint because we can eliminate a neutralization step in the synthetic process. As for the basic colloid, the stability is very similar to that of the neutral colloid. Hence, we could not identify any advantages by using the basic colloid. Taking these observations into account, we focused on the acidic and neutral colloidal silicas for the following hybridization study. A potential hurdle for the effective hybridization will be controlling the rates of surface modification and silica precipitation.

3.2. *Hybridization using colloidal silica and PTMS*

Surface modification of colloidal silica by polymeric species has widely been studied by Yoshinaga and co-workers [14–16] in which carbon-based polymers with a terminal trimethoxysilyl group were reacted with colloidal silica in an organic solvent. As described in "Introduction", the notable feature of our hybridization approach includes (1) a simplified process, and (2) *in situ* surface modification of silica by silanol and/or methoxysilyl groups of a polysiloxane formed by polymerization of PTMS without any catalyst. In the present study, the hybridization between silica and PTMS is called "*in situ* hybridization".

Since both colloids were essentially stable at 200 °C, we examined the hybridization reaction at temperatures above 250 °C. First, the impact of the [Silica]/[Polymer] ratio on the hybridization reaction was examined at 300 °C. The results are summarized in Table 2 along with those for PTMS polymerization under the same conditions as a reference.

As the polymerization of PTMS yields water-insoluble, but organic solvent-soluble solid in high yield [4], one can expect that the solid product yield is high in *in situ* hybridization process if precipitation of silica occurs. The precipitation is caused by changes in the nature of silica surface via hybridization of silica with PTMS or by changes in reaction medium from water to aqueous methanol formed as a result of hydrolysis of PTMS. It was found that batches with the neutral colloid essentially yielded solid products while the products in batches containing acidic colloid were strongly affected by the [Silica]/[Polymer] ratio. Batches #1, 7, 8, and "Ref" resulted in phase separated products. The liquid thus formed proved to be a mixture of water and methanol formed by the polymerization of PTMS. In batches #2, 3, and 9–12, the solid product was swelled by the liquid because the amount of liquid was relatively small. Taking high colloid stability of the acid colloid into account, high solid product yields suggest that the *in situ* hybridization took place in at least batches #2 and #3. The internal pressure is unknown because of the following reasons: (1) an accurate amount of MeOH formed by the reaction is unknown and (2) MeOH forms a homogeneous mixture with water in a reaction medium. Silanol and/or methoxy groups on polysiloxane must interact with silica in the reaction medium resulting in hybridization as shown in Scheme 1. The hybrids thus formed were characterized focusing on "the degree of surface modification" as an important parameter to discuss the structural difference of the hybrids.

Table 2
In situ hybridization between silica and PTMS.[a]

Batch #	Silica source	[Silica]/[Polymer][b]	Product	Yield[c]
1	Snowtex O	25/75	Mixture: colorless solid and liquid	88
2		50/50	Colorless solid swollen in liquid	77
3		67/33	Colorless solid swollen in liquid	82
4		75/25	Mixture: gel-like solid and liquid	49
5		83/17	Liquid and a trace amount of solid	10
6		90/10	Liquid and a trace amount of solid	4
7	PL-1	25/75	Mixture: colorless solid and liquid	93
8		50/50	Mixture: colorless solid and liquid	90
9		67/33	Colorless solid swollen in liquid	86
10		75/25	Colorless solid swollen in liquid	95
11		83/17	Colorless solid swollen in liquid	96
12		90/10	Colorless solid swollen in liquid	97
Ref	None	0/100	Mixture: colorless solid and liquid	93

[a] Silica content in each colloid: 12 wt.%; and heating time: 10 min.

[b] Weight ratio based on the silica's weight and the theoretical polymer weight.

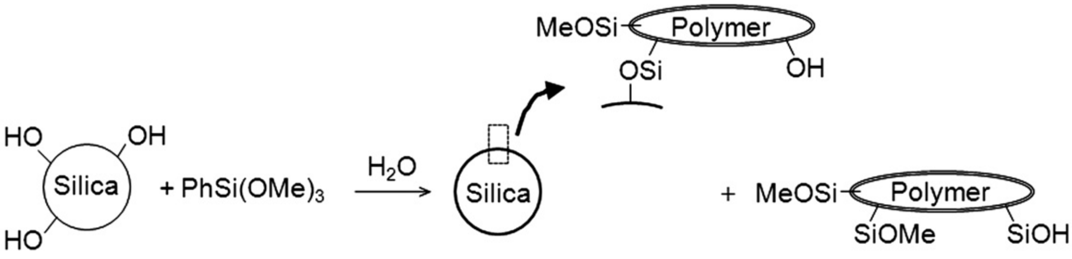
[c] Isolated solid product yield in percent based on the sum of silica's weight and the theoretical polymer weight.

3.3. *Characterization of the resultant hybrids*

The solid product in batch #8 was characterized by TEM to see the morphology. The TEM micrograph is shown in Fig. 2 in which each silica particle seems to be dispersed in a matrix without significant agglomeration. This may suggest that the silica particle's surface is well covered with polysiloxane formed by the intended *in situ* surface modification. The product was then characterized by FT-IR spectroscopy to see how the particle's surface had changed by the *in situ* hybridization. It was expected that the hybridization yields both polysiloxanes grafted on silica surface and ungrafted polysiloxanes. The ungrafted polysiloxane, poly(phenylsilsesquioxane) in fact, formed by the process is organic solvent-soluble [4] while polysiloxanes grafted on silica surface are likely to be insoluble. This is because the silica's inherent nature of insolubility due to the infinite molecular weight is probably not affected by some degree of surface modification. The hybridization product then underwent solvent extraction with toluene before characterization to remove the ungrafted soluble polysiloxane. The IR spectrum of the insoluble material as an extraction residue is depicted in Fig. 3 along with those of soluble polysiloxane and unmodified silica.

Besides several broad absorptions due to silica, distinct absorption bands assignable to phenyl groups were recorded at 1430, 760, and 700 cm^{-1} on the spectrum of the hybrid. This indicates that the *in situ* hybridization product has phenyl groups on the surface.

The insoluble hybridization product from batch #8 was also characterized by a solid state ^{29}Si NMR spectroscopy as depicted in Fig. 4. In addition to an intense resonance at −116 ppm assignable to silica's SiO_2 structure, there are two discernible resonances at −83 and −75 ppm assignable to a $PhSiO_{3/2}$ unit and $Ph(RO)SiO_{2/2}$ units (R: Me or H), respectively. This indicates that the insoluble material is composed of phenyl-containing siloxane and silica components. Because soluble "ungrafted" polysiloxanes were removed by solvent extraction, the product should have chemically bonded phenylsilsesquioxane structure on the silica surface. According to the integral ratio, the [Silica]/[Polysiloxane] molar ratio was 86/14 for batch #8. This can be converted to the [Silica]/[Polymer] weight ratio of 74/26. In addition, the $[Ph(RO)SiO_{2/2}]/[PhSiO_{3/2} + Ph(RO)SiO_{2/2}]$ molar ratio was 29/100. This is within the $Ph(RO)SiO_{2/2}$ content range observed for poly(phenylsilsesquioxane) synthesis reported elsewhere [4].



Scheme 1. Surface modification mechanism in the present hybridization.

Present characterization results suggest that the solid product derived from the HTW reaction of colloidal silica and PTMS is a hybrid material in which a part of the soluble polysiloxanes became insoluble by reacting with silica. In other words, surface modification of silica is achieved *in situ* by the present synthesis. Insoluble solid products obtained by other batches in Table 2 showed FT-IR and ^{29}Si NMR spectra being very similar to those of batch #8 although the [Silica]/[Polymer] ratios were different from each other. These results indicate that the present method yields hybrid materials with an essentially similar chemical structure.

3.4. The degree of surface modification: DOM

Thermogravimetric analysis (TGA) of the insoluble solid after solvent extraction was conducted to gain information about the degree of surface modification (DOM). TGA profile of the insoluble solid in batch #8 is depicted in Fig. 5 while the definition of DOM in this study is as follows.

$$[\text{Weight of grafted polymer}]/[\text{Weight of insoluble solid}] \times 100$$

The weight loss of the solid observed until around 700 °C is due to loss of the surface groups, but the observed weight loss does not represent the weight of the grafted polymer because part of the siloxane polymer is converted to silica and remains upon heating in air at 700 °C. Hence, it is necessary to determine the residual weight percentage of siloxane polymer as a control experiment. Assuming that the weight loss behavior of the grafted polymer on a silica surface is identical to that of the "ungrafted" polymer, the DOM can be determined from the following equation

$$\text{DOM} = \text{WL}_\text{H}/\text{WL}_\text{P} \times 100$$

where WL_H is percent weight loss of the insoluble hybrid and WL_P is percent weight loss of the soluble polymer synthesized by the present HTW method. The value of WL_P was determined to be 55.

The DOM of an insoluble solid for Batch #8 calculated by this method was 18% which corresponds to the [Silica]/[Polysiloxane] weight ratio of 82/18. This is very different from the value determined by analyzing ^{29}Si NMR spectrum described in the previous section. This inconsistency may be due to the fact that each analytical method has its own cause for experimental uncertainty such as unoptimized T1 relaxation time in the ^{29}Si NMR.

Since solid state ^{29}Si NMR requires more than three days to collect data, we decided to focus on TGA for estimation of DOM to study the hybridization mechanism.

3.5. DOM as a function of silica content of the hybrids

The DOM values of the silica/polysiloxane hybrids listed in Table 2 were determined by the TGA method. The results are depicted in Fig. 6.

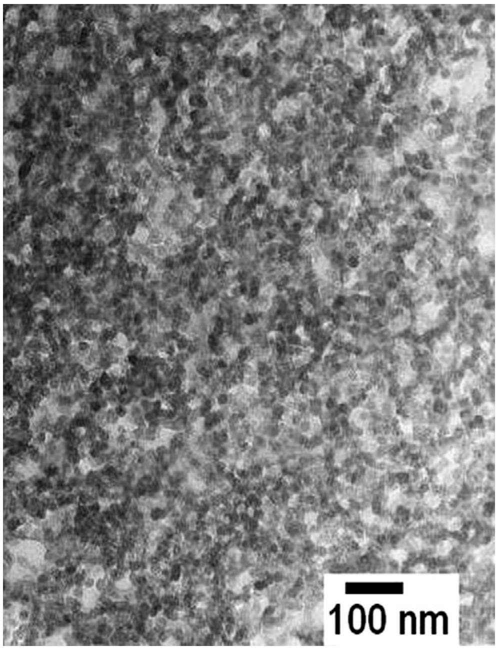


Fig. 2. TEM micrograph of batch #8 product in Table 2.

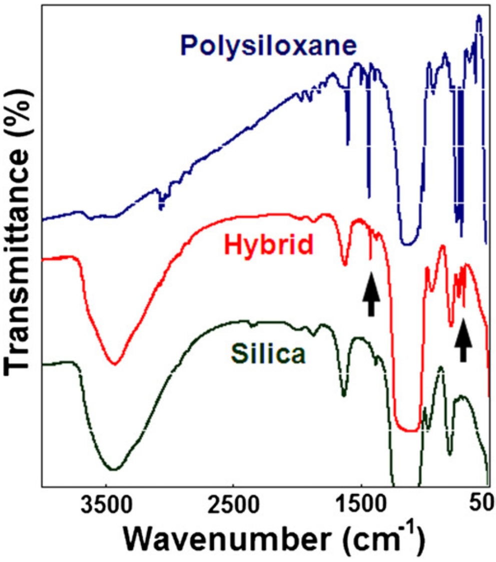


Fig. 3. FT-IR spectra of the insoluble hybrid, soluble polysiloxane, and unmodified silica.

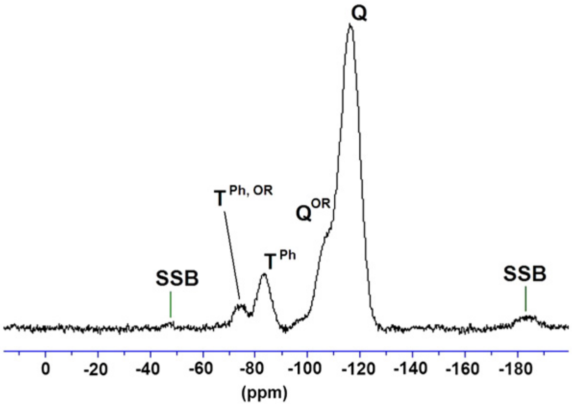


Fig. 4. Solid state single pulse ^{29}Si NMR spectrum of the insoluble hybrid.

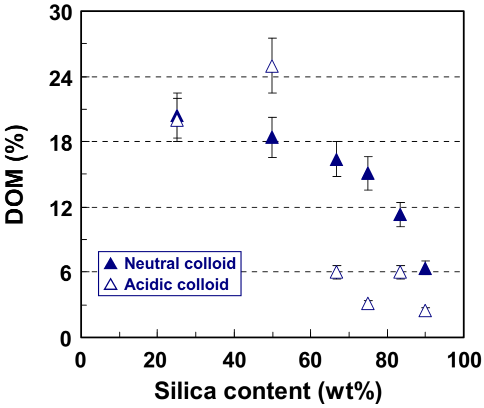


Fig. 6. DOM as a function of silica content in the hybrids.

The DOM values monotonously decreased as the silica content in the mixture increased when the neutral colloid was used as the silica source. This is as expected because the relative amount of PTMS is small when the silica content is high. On the other hand, when the acidic colloid was used, the trend seen in DOM profile was definitely different from that of the neutral colloid. The solid yield for three batches at the silica content of 75, 83, 90 wt.% was very low (see Table 2) due to the higher colloid stability of the colloid as described in the previous section. Hence, the DOM at these high silica content should not be compared with other three at the lower silica content of 25, 50, 67 wt.%.

One can also discuss how much polymer combines with silica yielding a grafted polymer to better understand the *in situ* hybridization process. The grafted polymer ratio (GPR) is defined as [Weight of grafted polymer]/[Weight of whole polymer]×100. Fig. 7 illustrates the trend for GPR as a function of the silica content.

The GPR for the hybrids derived from the neutral silica colloid increased with increasing silica content. This may be due to the silica's larger surface area available for surface modification. On the other hand, the GPR profile for the hybrids derived from the acidic colloid was characterized by a distinct decrease when the silica content was greater than the critical value between 40 and 67 wt.%. The root cause for the low GPR values at higher silica contents is the high colloid stability of the acidic colloidal silica as described above.

3.6. *The effect of reaction temperature on DOM*

Understanding of the *in situ* hybridization was further studied by measuring DOM under various reaction conditions. The effect of temperature on DOM for the hybrids with the silica content of 50 wt.% (formulations #2 and #8) is depicted in Fig. 8.

The DOM for the hybrids derived from the neutral colloid was found not to depend on the reaction temperature except at 350 °C. The reason for the plural data points at 350 °C is discussed later. Further characterization of the hybrids synthesized at various temperatures was conducted by ^{29}Si NMR spectroscopy to gain insights into the structural units present as well as the residual alkoxy & silanol groups. The results are summarized in Table 3.

Although the DOM values are very similar to each other, definite differences were observed among the materials. First, one can discuss the $[T^{\mathrm{Ph,OR}}+T^{\mathrm{Ph}}]/[Q^{\mathrm{OR}}+Q]$ ratio which should strongly correlate to the DOM. The ratio for the material synthesized at 380 °C is larger than those for two materials synthesized at lower temperatures indicating that the DOM for the former is definitely larger than those for the latter. This is probably due to higher activation toward silica's surface OH groups whose reactivity is low. The $[T^{\mathrm{Ph,OR}}]/[T^{\mathrm{Ph,OR}}+\mathrm{T}^{\mathrm{Ph}}]$ ratio is also of interest. This value decreases as the temperature increases suggesting that the degree of polymerization increases with increasing temperatures [17]. This is quite reasonable. The NMR study supports that the temperature is indeed an important factor controlling the hybridization reaction.

On the other hand, the profile with the acidic colloid proved to be temperature dependent (see Fig. 8). The DOM value significantly

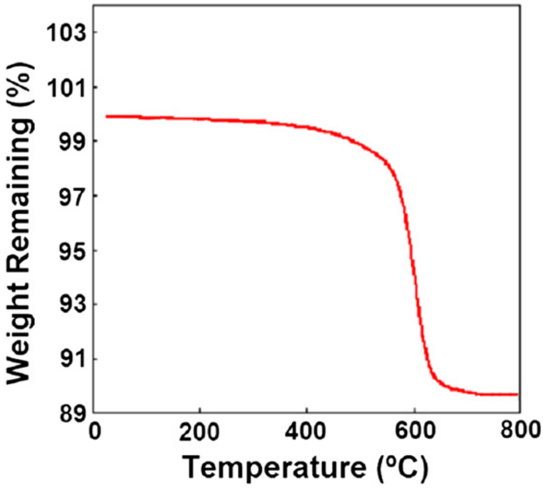


Fig. 5. TGA profile of the insoluble solid for batch #8.

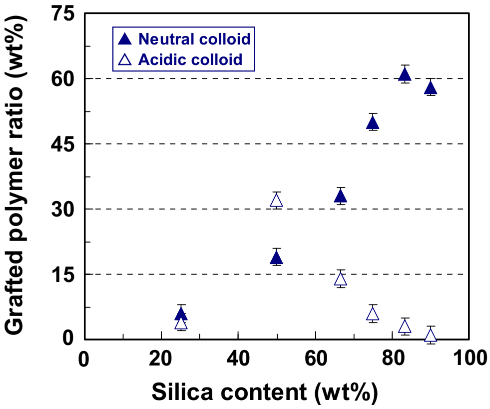


Fig. 7. GPR as a function of silica content in the hybrids.

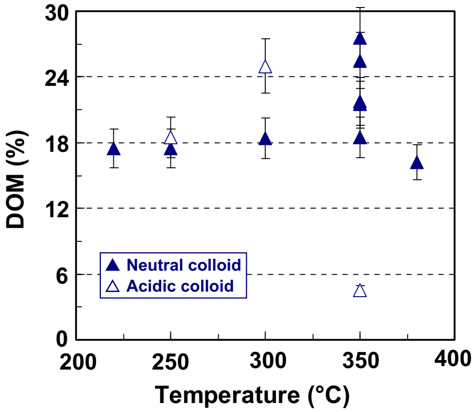


Fig. 8. The DOM as a function of reaction temperature for the hybrids with the silica content of 50 wt.%. The reaction time was 10 min.

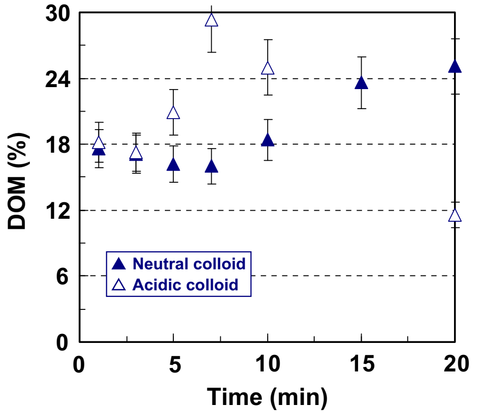


Fig. 9. The DOM as a function of reaction time for the hybrids with the silica content of 50 wt.%. The reaction temperature was 300 °C.

decreased at 350 °C. The cause of the decrease will be discussed in the next section.

As depicted in Fig. 8, the DOM of natural colloid-derived hybrids formed at 350 °C ranged between 19 and 28% while those at other temperatures did not scatter so largely. A potential cause for this large deviation at 350 °C is that this temperature is close to the supercritical temperature of the reaction medium. As the present reaction medium is a mixture of water and methanol evolved by hydrolysis of PTMS, the supercritical temperature is not 374 °C. Indeed, the estimated supercritical temperature in the present medium is around 350 °C [18]. It has been reported that the properties of water such as dielectric constant and ion product are drastically affected by a slight change in temperature and pressure near the supercritical condition [1]. The relatively large deviation in the DOM observed at this temperature may be attributable to a tiny deviation in the reaction conditions.

3.7. *The effect of reaction time on DOM*

To better understand the *in situ* hybridization mechanism, the time impact on DOM was also examined (Fig. 9). The DOM remained essentially unchanged until about 10 min and then gradually increased when a neutral colloid was used. The observed different time regime probably suggests that the hybridization reaction is a two-stage reaction. Details will be discussed in the next section. On the other hand, the DOM of the materials derived from the acidic colloid increased more rapidly until about 7 min and then started to decrease reaching a value as low as 12%. The decrease of DOM observed for the acidic colloid in Figs. 8 and 9 can be explained by degradation of the grafted polymer. The degradation should be due to a hydrolytic Si—C bond cleavage of phenyl groups yielding Si—OH groups. Although not shown here, benzene was detected from the soluble component of the hybridization product while an intensity of the characteristic absorption at 1430 cm^{-1} in the FT-IR spectrum assignable to a phenyl group significantly decreased. It is well known that Si—phenyl groups are hydrolytically unstable at elevated temperatures under an acidic condition [19]. The Si—OH groups thus formed undergo polycondensation with other Si—OH groups yielding Si—O—Si bonds. This implies that phenylsilsesquioxane units are converted to silica units by degradation process. Which takes place more readily at the longer reaction time and higher reaction temperatures under acidic conditions.

Table 3
Structural characterization of the insoluble hybrids obtained from reactions using neutral colloidal silica, PL-1.[a]

Batch #	Temp.[b]	Composition (mol.%)[c]					
		$T^{Ph,OR}$	T^{Ph}	Q^{OR}	Q	$[T^{Ph,OR}]/[T^{Ph,OR}+T^{Ph}]$	$[T^{Ph,OR}+T^{Ph}]/[Q^{OR}+Q]$
8	300	4	10	17	69	0.29	0.16
13	250	4	8	19	69	0.33	0.14
14	380	4	14	14	68	0.22	0.22
15	300	2	13	14	71	0.13	0.18

The abbreviations $T^{Ph,OR}T^{Ph}$, Q^{OR}, and Q denote Ph(RO)$SiO_{2/2}$, Ph$SiO_{3/2}$, (RO)$SiO_{3/2}$, and $SiO_{4/2}$ units (*R*: Me and H), respectively.

[a] Loaded [Silica]/[Polymer] weight ratio: 1:1. Heating time: 10 min except batch #15 which was 20 min.

[b] Temperature in °C.

[c] Calculated by the integral intensity of each resonance.

3.8. *Elucidation of the reaction mechanism via characterization of the soluble polymer*

We have discussed how the reaction conditions affect the hybridization reaction by characterizing the insoluble hybrid in the above sections. On the other hand, characterization of the soluble ungrafted polysiloxane would be helpful to better understand the mechanism of the present HTW method. FT-IR and ^{29}Si NMR analyses suggest that the ungrafted polysiloxanes are poly(phenylsilsesquioxane) with residual alkoxy and silanol groups. The structure is identical to that of the product derived from PTMS and water (without silica) by the present process. The molecular weight (Mw) of the soluble polysiloxane as a function of the reaction time was analyzed by GPC and is shown in Fig. 10 along with those derived from PTMS and water.

When the neutral colloid was used, the Mw of the ungrafted polymer increased as the reaction time increased. Taking the results shown in Figs 9 and 10 into account, the reaction under neutral condition is likely to take place as follows:

(1) The polymerization of PTMS yields grafted polysiloxanes even at a very early stage of the reaction until ca. 3 min. The Mw of the grafted polysiloxane does not seem to increase as the reaction time increases until around 10 min as shown by minimal change in DOM. This is probably because the propagation reaction is sterically hindered by silica. In this sense, this period can be regarded as a stage for silica's surface coverage by polysiloxane grafting. At the same time, the polymerization reaction of PTMS also takes place yielding ungrafted polysiloxanes whose Mw increases steadily as the reaction time increases.

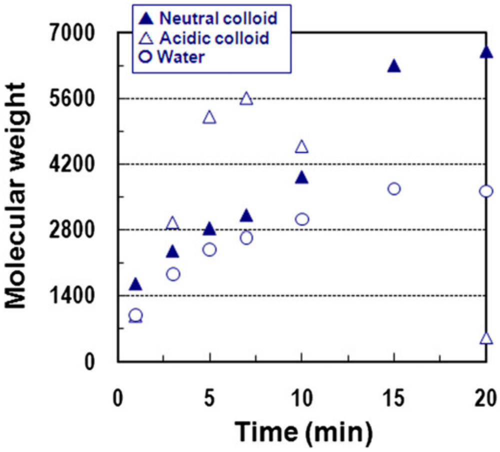


Fig. 10. The molecular weight of soluble polysiloxane as a function of reaction time at 300 °C.

(2) At the later stage beyond 10 min, the reaction may go into a different mode. DOM data showed that the Mw of the grafted polysiloxane increased with increasing reaction time. This period can be regarded as propagation stage of the grafted polysiloxanes. The Mw of ungrafted polysiloxane also increases at the same time.

The $[T^{\mathrm{Ph,OR}}]/[T^{\mathrm{Ph,OR}}+T]$ ratio for the ungrafted polysiloxane calculated by the ^{29}Si NMR analysis was 0.4, which is appreciably larger than 0.29 determined for the grafted polymer as shown in Table 3. This ratio decreases at higher degree of PTMS polymerization. These results suggest that the PTMS polymerization on a silica surface takes place in a manner different from that without silica. Furthermore, prolonged heating resulted in a significantly lower $T^{\mathrm{Ph,OR}}$ content as indicated by the $[T^{\mathrm{Ph,OR}}]/[T^{\mathrm{Ph,OR}}+T]$ ratio for Batch #15 in Table 3. The Mw increase of the ungrafted polysiloxane proved to accompany with the higher degree of polymerization of the grafted polysiloxane.

The Mw profile of the ungrafted polysiloxane from the hybridization reaction with the neutral colloid is close to that observed for polysiloxane derived from PTMS and water at the early stage of the reaction. However, a significant difference was observed between the two profiles at a later stage. A ^{29}Si NMR spectroscopic analysis of Batch #15 indicates that the soluble polysiloxane obtained by 20 min heating contains SiO_2 units in the structure although the content was very low. It strongly suggests that a small amount of silica unit was solubilized by high DOM resulting in discernible increase of the Mw for the soluble material.

The Mw profile for the ungrafted polysiloxane derived from the acidic colloid was different from that with the neutral colloid. The Mw decrease after 10 min heating can be attributed to the degradation of the polymer via acid-catalyzed Si–Ph bond cleavage as described in the previous section.

4. Conclusions

In situ hybridization between silica and polysiloxane was examined by a high temperature water technology using aqueous colloidal silica and PTMS as the starting materials. The synthetic process proved to be strongly pH dependent. Specifically, stability of the silica colloids and easiness of the PTMS polymerization are critical factors to control the hybridization. Because of hydrolytic degradation of Si–phenyl groups by heating at higher temperatures or long time under an acidic condition, the acidic colloid is not an appropriate silica source.

The hybridization reaction yields both insoluble and soluble polysiloxanes as the product. The former modifies the surface of silica (i.e., grafted polysiloxane) while the latter is an ungrafted polysiloxane. The DOM was determined through both TGA and solid state ^{29}Si NMR analyses and proved to be a very useful parameter for understanding the reaction mechanism. However, the DOM values obtained by the two methods were found to be different most likely due to the respective experimental uncertainty. The trend of the DOM values from the two methods, however, was found to be consistent under the present reaction conditions.

Finally, the reaction mechanism was elucidated by analyzing the DOM of the insoluble hybrid material and the Mw of the soluble polysiloxane. The hybridization reaction seems to be a two-stage reaction as suggested by the relatively constant DOM in the first 10 min followed by the gradual increase with an increasing reaction time. The first stage is believed to reflect the surface modification of silica with PTMS while the second stage represents propagation of the grafted polysiloxanes. The molecular weight of the soluble polysiloxane monotonously increased during the hybridization reaction. A study on the relationship between the DOM and dispersibility of the particles in a polysiloxane matrix is in progress.

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