JOURNAL OF MATERIALS SCIENCE **34** (1999) 6137–6141

Preparation and properties of borosilicate gels by the reaction of tetraacetoxysilane with boron tri-*n*-butoxide

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The preparation and properties of gels via borosiloxane polymers formed by the reaction of tetraacetoxysilane (TAS) with boron tri-*n*-butoxide (BTB) in tetrahydrofuran (THF) was investigated. The reaction formed polyborosiloxanes which underwent further condensation to give heterogeneous gels at room temperature and homogeneous gels with (TAS/BTB ≥ 2) or without (TAS/BTB $= 1$) cracks at 60 °C. The addition of ethanol to the reaction mixture formed homogeneous gels under milder conditions. In the presence of hydrochloric acid as a catalyst, transparent round gel plates of B_2O_3 contents up to 34 mol% were obtained by the reaction in the molar ratios of TAS/BTB = 9/2–1/2. Polyborosiloxanes of molecular weight around 1000 were found to be formed. It was found that the gels consisted of borosiloxanes incorporated with well cross-linked borosiloxane networks, which provided borosilicates containing B_2O_3 up to 30 mol% on heat treatment.

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1. Introduction

Several reports have been published on the preparation of SiO_2-B_2O_3 oxides by sol-gel method. In these works, borosilicate gels have been generally prepared by the reaction of boron trialkoxides with the siloxane oligomer formed by partial hydrolysis of tetraethoxysilane [1–10]. However, the preparation of borosilicate gels via polymer precursor has not been reported, with the exception of our previous works [11, 12].

Cohydrolysis of silicon and boron alkoxide is not preferable [3] to prepare the gels since hydrolysis of boron trialkoxide is faster and subsequent condensation with silicon alkoxide hardly take place, whereas partially hydrolyzed tetraalkoxysilane is allowed to react with boron trialkoxide even though the reactivity of boron trialkoxide is much lower than the other alkoxides of metals such as aluminum and titanium, which is realized from the results of the studies mentioned above. In addition to the low reactivity of boron and silicon alkoxide, the partial hydrolysis method is also encumbered by hydrolysis of borosiloxane bond with water formed from selfcondensation of the silicon oligomer.

Hetereofunctional condensation reactions, which are not accompanied by the formation of water, may provide a method for the preparation of homogeneous borosilicate gels, as reported for the reaction of boron trialkoxide with dialkyldiacetoxysilane [13] or diphenyldichlorosilane with boric acid [14]. Moreover, the method using borosiloxane polymers, as a precursor could be a way to obtain variously shaped borosilicates [11, 12] with different boron contents. As a continuation, the reactions of the borosilicate gels via precursor polymers have been investigated. In this work, we will report the preparation of borosilicate gels by the reaction of TAS with BTB under various conditions.

2. Experimental

2.1. Preparation of materials

Tetraacetoxysilane (TAS) [15] and boron tri-*n*-butoxide (BTB) [16] were synthesized according to known method. A 0.1 g/ml TAS-tetrahydrofuran (THF) solution was used to allow easy handing of TAS which is sensitive to hydrolysis. THF and ethanol were distilled after drying with conventional methods.

2.2. Preparation of borosilicate gels from TAS and BTB

All experiments were carried out under dry N_2 atmosphere. A certain amount (22–8.9 ml) of 0.1 g/ml

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TAS-THF solution and BTB (0.43–1.5 g) were mixed in the molar ratios TAS/BTB = 9/2–1/2 (10–50 mol % B_2O_3). The mixture was subjected to the following procedure: 1) After it was refluxed for 1–8 h, the resulting solution was transferred to a polyethylene beaker covered by a polyethylene film with 5 pinholes of ca. 1.0 mm in diameter, and aged at room temperature (Exp. no. 1) or at 60 °C (Exp. no. 2) in a desiccator equipped with a drying tube. 2) The mixture was refluxed for 2 h, followed by addition of 10 ml of ethanol, refluxing for another 2 h, and then similarly aging at room temperature (Exp. no. 3). 3) Dry HCl gas was introduced into the mixture at the ratio of 3.5 l/g of TAS for 80 min. The mixture was similarly aged at room temperature (Exp. no. 4), and round gel plates of ca. 35 mm in diameter and 3 mm in thickness was obtained in all experiments.

2.3. Heat treatment borosilicate gels and instruments

The gels were heat treated up to 1000 °C with a heating rate of 4 °C/h to prepare borosilicate oxides. IR spectra of gels and oxides were measured by KBr disk method using a Hitachi IR spectrophotometer, model 260-50. X-ray diffraction was measured before and after heat treatment using a Rigaku Denki equipment, model CN-2013. The chemical composition of gels was determined by inductively coupled plasma atomic emission spectroscopy using a SEIKO ICP-AES, model SPS-7000. Thermogravimetric and differential thermal analysis (TG-DTA) plots were recorded on a Rigaku Denki instrument, model TAS-100. ^{1}H-NMR spectra were recorded with a JEOL-JNM-PMX60 NMR spectrometer in chloroform-d or carbontetrachloride and a JEOL FX90Q NMR spectrometer in THF-chloroform-d.

3. Results

3.1. Preparation of borosilicate gels

The results on the preparation of gels from the homogeneous solutions obtained by the reaction of TAS with BTB under the different conditions are summarized in Table I. Aging the solutions at room temperature gave opaque gels (Exp. no. 1), whereas transparent gels of 10–20 mol % B_2O_3 with cracks and 33 mol % B_2O_3 without cracks were obtained when the solutions were aged at 60 °C (Exp. no. 2). In the region of 40–50 mol % B_2O_3, boric acid was deposited out on the surface of gels probably due to hydrolysis of BTB unreacted with water uptaken through drying tube, and thus these gels were transparent. In Exp. 3, on the other hand, the results are almost the same as in Exp. no. 2, but transparent gels were obtained by adding ethanol into the solution and refluxing, followed by aging at room temperature. Furthermore, it was found that hydrochloric acid could catalyze this reaction to provide transparent gels in all cases.

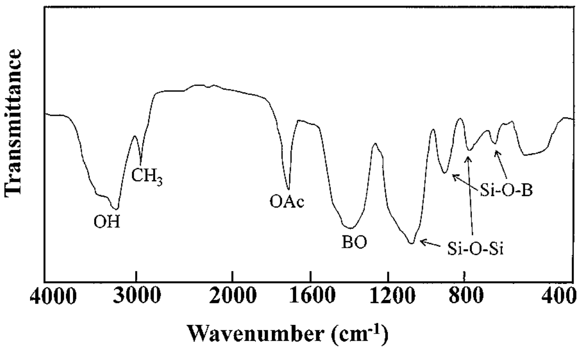


Figure 1 IR spectrum of polyborosiloxane reprecipitated with hexane.

On concentration of homogeneous solutions obtained from reaction of TAS with BTB in THF, heterogeneous and partly soluble (partially gelled) products were formed. Powdery precipitates were obtained by reprecipitation of the reaction mixtures with hexane. The IR spectrum of the precipitates (Fig. 1) shows the absorption peaks due to alkoxy and acetoxy groups, in addition to those due to B—O and Si—O—B bonds. The peaks due to OH and Si—O—Si bond are ascribed to hydrolysis of borosiloxane compound (as the spectrum was measured with KBr disk method). The signals due to *n*-butyl and acetoxy group are also observed in the ^{1}H-NMR spectrum of the precipitate (Fig. 2). The average molecular weight (M_n) of the precipitate was found to be ca. 1000 by GPC.

3.2. Properties of borosilicate gels

The results of the chemical composition by ICP-AES analysis of the gels are given in Table II. The difference between the calculated and observed B_2O_3 contents is due to incomplete condensation of BTB and TAS followed by partial cross-linkage of resulting poyborosiloxanes to provide opaque and heterogeneous

TABLE I Preparation of SiO_2-B_2O_3 gel plates from tetraacetoxysilane (TAS) and boron tributoxide (BTB)

			Molar ratio of TAS/BTB (B_2O_3 mol %)					
Exp. no.	Additive	Aging temp. (°C)	a 9/2(10)	b 17/6(15)	c 2(20)	d 1(33.3)	e 3/4(40)	f 1/2(50)
1	None	R.T.	−	−	−	−	−	−
2	None	60	+	+	+	++	−	−
3	EtOH	R.T.	+	+	+	++	−	−
4	HCl	R.T.	++	++	++	++	++	++

−: Opaque gels.
+: Homogeneous gels with cracks.
++: Homogeneous gels without cracks.

TABLE II Chemical composition of SiO_2-B_2O_3 gels, analyzed by ICP-AES

		B_2O_3 mol %					
Exp. no.	In feed	a 10	b 15	c 20	d 33.3	e 40	f 50
2		15.0	21.7	24.8	28.6	—	—
3	In gels	7.1	11.1	15.8	27.7	—	—
4		10.2	15.5	16.8	28.7	29.7	34.7

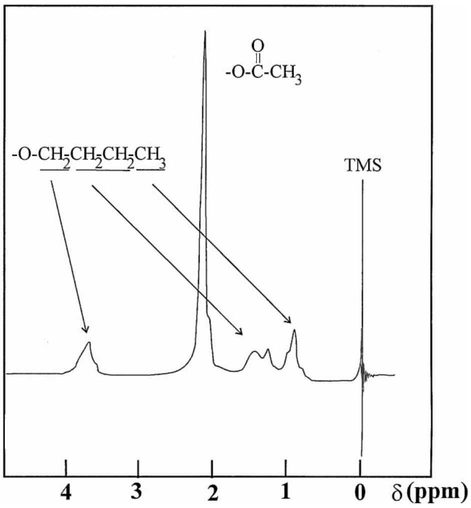


Figure 2 ^{1}H-NMR spectrum of polyborosiloxane reprecipitated with hexane.

gels. A reasonably good agreement was observed for the gels of B_2O_3 content below 15 mol % in Exp. nos. 3 and 4, but above 20 mol % significant differences are also detected.

Table III shows the results of the extraction of borosilicate gels with benzene and THF as a solvent. The chemical compositions before and after extraction are given together with the weight loss and degree of extraction. The residual gels after extraction show a marked increase of silicon and/or decrease of boron content as well as a large weight loss, especially in the gels of higher boron content. The extracts are the polymers with molecular weight of ca. 1000–10,000 with relatively high boron oxide content. Polyborosiloxanes are more soluble in THF than benzene.

DTA-TG curves of $80SiO_2$-$20B_2O_3$ gels (Fig. 3) show a total weight loss ca. 63% and the peaks due to evaporation of solvent and decomposition of organic groups are observed at 74 and 320 °C, respectively. On heat treatment, the gels of 10–33 mol % B_2O_3 (Exp. 4) turned black at ca. 300 °C and then white at the temperatures above 700 °C (10–15 mol %), 800 °C (20 mol %) and 1000 °C (33 mol %), depending on boron oxide content. Fig. 4 shows IR spectra of $67SiO_2$-$33B_2O_3$ gels heat-treated at various temperatures. The absorption patterns of the gels were almost same before and after heat treatment at 250 °C: 3400 (OH), 2900 (CH), 1450 (BO), 1100 and 800 (SiOSi), 930 and 670 (SiOB) cm^{-1}. Heat treatment of gels led to the increase in the peak intensity at 670 and 930 cm^{-1}, which is more clearly observed at above 500 °C. The peak intensity at 1450 cm^{-1}, on the other hand, decreases with broadening and shifts towards lower wavenumber shift. The increase in

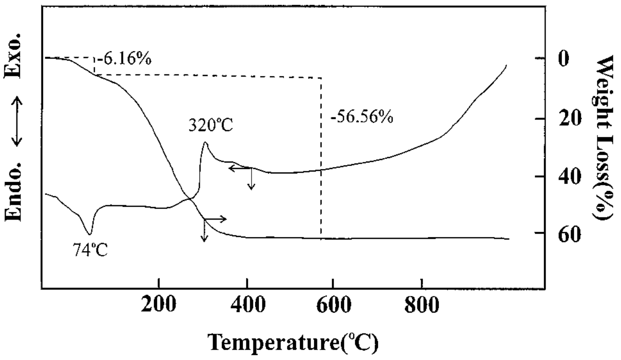


Figure 3 DTA and TG curves of gel (20 mol % B_2O_3).

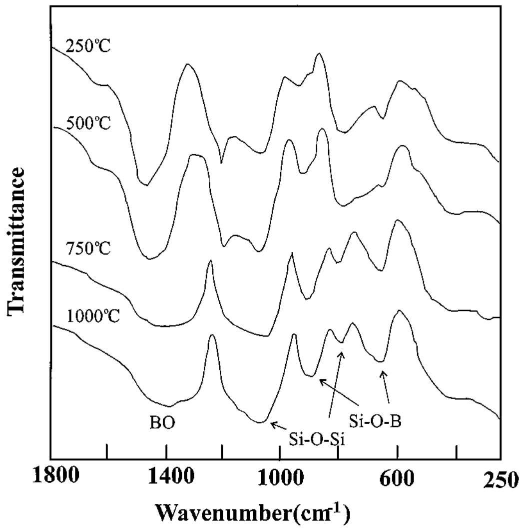


Figure 4 IR spectra of $67SiO_2$-$33B_2O_3$ gel on heat treatment.

TABLE III Composition of gels before and after extraction with organic solvents, analyzed by ICP-AES

		Chemical composition (mol %)						
		In feed		Before		After		
Exp. no.	Solvent	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	Weight loss[a] (%)
4-c	THF	80	20	83.6	16.8	98.1	1.9	61.4
4-c	C_6H_6	80	20	83.6	16.8	91.0	9.0	59.6
4-e	THF	50	50	65.3	34.7	96.7	3.3	85.9
4-e	C_6H_6	50	50	65.3	34.7	84.8	15.2	83.5

[a] Soluble extracts (polyborosiloxane).

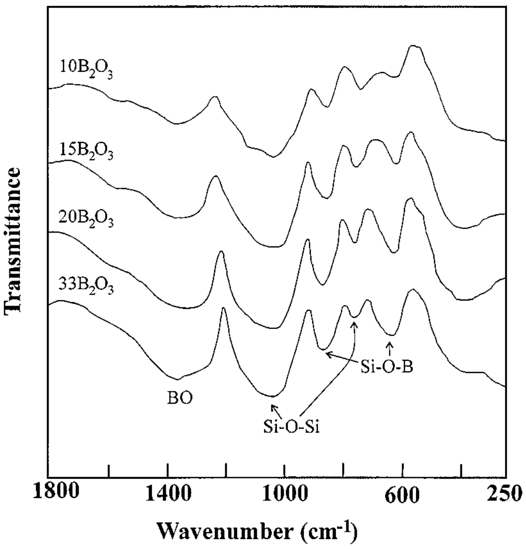


Figure 5 IR spectra of SiO_2-B_2O_3 gels heat treated at 1000 °C.

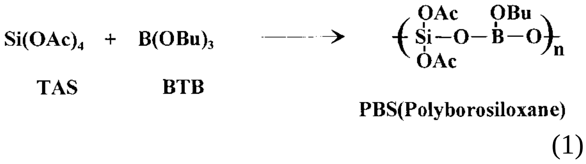
TABLE IV Chemical composition of SiO_2-B_2O_3 gel plates after heat treatment at 1000 °C, analyzed by ICP-AES

	Chemical composition (mol %)					
	In feed		Room temperature		1000 °C	
Exp. no.	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3
4-a	90.0	10.0	86.7	10.2	87.8	12.2
4-d	66.6	33.3	71.3	28.7	72.8	27.2
4-f	50.0	50.0	65.3	34.7	69.7	30.3

peak intensity at 670 and 930 cm^{-1} is also observed in the IR spectra (Fig. 5) of borosilicate gels with different boron oxide contents heat-treated at 1000 °C. The chemical composition of gels containing 13–34 mol % B_2O_3 after heat treatment at 1000 °C is summarized in Table IV. A decrease of B_2O_3 about 1–1.5 mol % except in the gels of 34 mol % B_2O_3 was detected. However, heat treatment of gels formed borosilicates whose boron oxide content is almost the same as those before heating. It was confirmed by X-ray analysis that gels are amorphous at 1000 °C regardless of composition.

4. Discussion

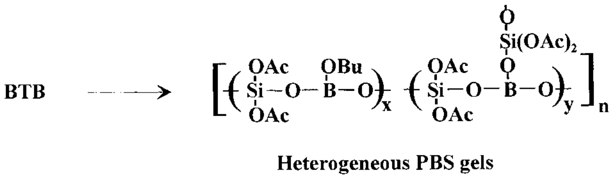
The results of the ^{1}H-NMR and IR spectra together with molecular weight measurement indicated that the poyborosiloxanes are formed according to the reaction represented in Equation 1.



$$\underset{\text{TAS}}{Si(OAc)_4} + \underset{\text{BTB}}{B(OBu)_3} \longrightarrow \underset{\text{PBS(Polyborosiloxane)}}{\left(\overset{OAc}{\underset{OAc}{Si}} - O - \overset{OBu}{B} - O \right)_n} \qquad (1)$$

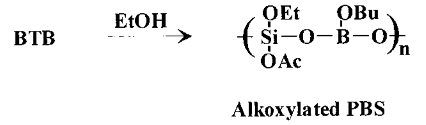
The condensation proceeds slowly in the absence of additives regardless of polyfunctional starting materials to form polyborosiloxane with low molecular weights (M_n) around 1000 by GPC. No appreciable increase in molecular weight as well as the amount of ester formed was observed either by refluxing or azeotropic distillation of the reaction mixtures for more than 8 h. On subsequent concentration of the mixture followed by aging at room temperature or 60 °C, the gels obtained were heterogeneous in every feed of B_2O_3 mol % (Exp. no. 1) or higher than 40 mol % (Exp. no. 2), as shown in Table I. In Exp. no. 3, on the other hand, the reaction gave homogeneous gels in feed of B_2O_3 less than 33.3 mol % under the milder condition (room temperature) compared with that in Exp. no. 2 (60 °C) when ethanol was added to the reaction mixture. In these experiments nos. 2 and 3, the B_2O_3 content of gels was inconsistent with that in every feed (Table II). Furthermore, homogeneous gel plates without cracks were obtained in every feed in the presence of hydrochloric acid as a catalyst, and additionally in feed less than 15%, the composition of gels was found to be in good agreement with that in feed.

The condensation reaction is represented in Equation 1 as it is reported [13, 17]. However, it appears to proceed slowly because no appreciable increase of molecular weight and the amount of ester formed are observed even by further heating. On concentration and/or further condensation, however, heterogeneous gels are formed probably because cross-linking between polyborosiloxanes competitively take place faster rather than condensation with the monomers (Equation 2),



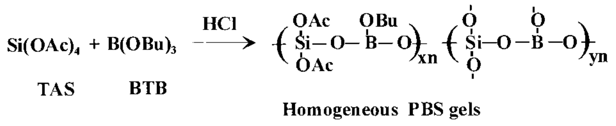
$$\text{BTB} \longrightarrow \underset{\text{Heterogeneous PBS gels}}{\left[\left(\overset{OAc}{\underset{OAc}{Si}} - O - \overset{OBu}{B} - O \right)_x \left(\overset{OAc}{\underset{OAc}{Si}} - O - \overset{\overset{Si(OAc)_2}{O}}{B} - O \right)_y \right]_n} \qquad (2)$$

resulting in the formation of gels including borosiloxanes or BTB (Exp. nos. 1 and 2). On adding ethanol, on the other hand, the acetoxy groups are substituted to form partially alkoxylated polyborosiloxanes with preferable functionality (Equation 3),



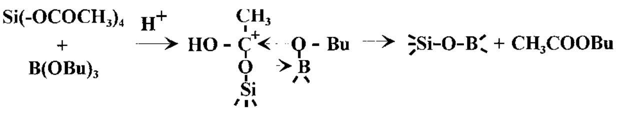
$$\text{BTB} \xrightarrow{EtOH} \underset{\text{Alkoxylated PBS}}{\left(\overset{OEt}{\underset{OAc}{Si}} - O - \overset{OBu}{B} - O \right)_n} \qquad (3)$$

which prevents local gelation by cross-linking and progress subsequent formation of homogeneous gels by controlled condensation (Equation 4),



$$\underset{\text{TAS}}{Si(OAc)_4} + \underset{\text{BTB}}{B(OBu)_3} \xrightarrow{HCl} \underset{\text{Homogeneous PBS gels}}{\left(\overset{OAc}{\underset{OAc}{Si}} - O - \overset{OBu}{B} - O \right)_{xn} \left(\overset{O}{\underset{O}{Si}} - O - \overset{O}{B} - O \right)_{yn}} \qquad (4)$$

although the condensation proceeds more slowly. Acid catalyzed condensation is followed by the mechanism schematically represented in Equation 5 [17]:



$$\begin{matrix} Si(\text{-}OCOCH_3)_4 \\ + \\ B(OBu)_3 \end{matrix} \xrightarrow{H^+} HO - \overset{CH_3}{\underset{\underset{Si}{O}}{C^+}} \lessdot O - Bu \longrightarrow {>}Si\text{-}O\text{-}B{<} + CH_3COOBu \qquad (5)$$

The carbonyl groups are protonated to allow nucleophillic attack of oxygen of BTB, resulting in the formation of borosiloxane bond. Condensation does not take place fast as well, and it is controlled not to provide heterogeneous gels. Even in the presence of additive and catalyst, the composition of polyborosiloxanes is not in agreement with that in feed except for the content of B_2O_3 less than 15%, possible due to a low reactivity of BTB and condensation of polyfunctional monomers.

Homogeneous gels were found to be composed of soluble polyborosiloxanes and borosiloxane networks by the extraction test: The extraction of gels provided polyborosiloxanes with molecular weights of 1000–10,000 as the extract of 60–85% and the residue, depending on the solvents and the reaction molar ratios (Table III). Therefore, polyborosiloxanes are incorporated with borosiloxane networks to form homogeneous gels.

Polyborosiloxanes showed an endothermic peak at 74 °C due to solvent evaporation and melting temperature with decomposition because of a weight loss just after melting (Fig. 3). All organic groups are removed at 320 °C to form borosilicate oxides, for no weight loss take place on further heating. No appreciable changes are observed in the composition of precursor and oxides formed, which supports that the boron component is bonded as the borosiloxane bond and consequently the linkages are well incorporated into oxide networks.

5. Conclusions

Reaction of TAS with BTB under specified conditions shows that:

1. Homogeneous polyborosiloxane gels of B_2O_3 content up to 34 mol % can be prepared via alkoxylation or proton activation.
2. The gels consist of soluble polyborosiloxanes well incorporated into cross-linked borosiloxane networks, which can be transformed to borosilicates upon heating.
3. This new method could provide highly condensed borosiloxanes capable of formation of borosilicate materials having controlled composition and variously shaped.

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Received 20 February 1998
and accepted 21 June 1999