Synthesis of Silica Gel Containing Dibutyltin Group from Sodium Metasilicate and Dibutyltin Compound

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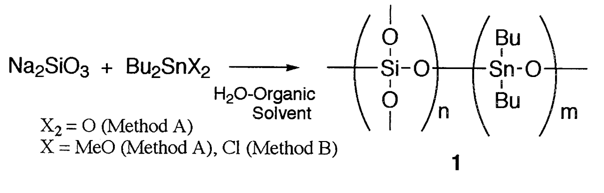
Silica gel **1** containing dibutyltin group was readily obtained from the reaction of sodium metasilicate and dibutyltin compounds. The obtained gel **1** was consisted of an almost equimolecular ratio of Si and Sn unit according to the initial feed ratio of the monomers. Dibutyltin groups in the gel **1** were readily removed by treatment with an aqueous inorganic acid.

In our preceding report, the incorporation of tributyltin group into polysiloxane is shown to be effective for protection from self-condensation of the polymeric and oligomeric silanols, which are generated from water glass.[1] The use of dialkyltin compounds instead of trialkyltin compounds for the reactions with polymeric or oligomeric silanol derivatives promises to afford another type of organotin derivatives of polysiloxane. They are thought to exhibit moderate reactivities at Si–O–Sn bond as presented in the reactions of organosilane and organotin analogue.[2] In addition, more regular sequences of organotin unit and siloxane unit in the copolymerized products are presumed compared to those in trialkyltin derivatives.[1] Such properties of the compounds having Si–O–Sn bond seem to be available for preparing various organosiloxanes derivatives and organofunctional silica gels.[3, 4] From the interests in the copolymerized product mentioned above and one kind of organofunctional siloxane derivatives, we have progressed the investigations on the copolymerization of sodium metasilicate (Na_2SiO_3)[5] with dialkyltin compounds such as dibutyltin oxide (Bu_2SnO), dibutyldimethoxytin [($Bu_2Sn(OMe)_2$], and dibutyltin dichloride (Bu_2SnCl_2).

In Method A, Bu_2SnO was employed for the reaction with Na_2SiO_3 to prepare the gel **1**. The reactions were carried out by simply mixing an equimolar amount of Na_2SiO_3 and Bu_2SnO in the mixed solvents of water and dichloromethane or benzene, in which the pH values of the water solution were adjusted from 2 to 6 with 3 N hydrochloric acid keeping the temperature below 10 °C. After the reaction mixture was stirred over night at room temperature, the precipitates formed were isolated by filtration and washed with water, methanol, and tetrahydrofurane. Then, the product **1** was dried under reduced pressure for 24 h at 60 °C. The yields of **1**, which were estimated on the basis of contents of Si in starting Na_2SiO_3 and **1**, varied in the range of 52% to 97% according to the reaction conditions as shown in Table 1. When the pH value of water layer was adjusted to ca. 4, the best yield of **1** was recorded (Run 2). Furthermore, $Bu_2Sn(OMe)_2$ was found to be usable for the reaction instead of Bu_2SnO in Method A. From this reaction, **1** was obtained in an analogous yield and the content of Sn in **1** was almost same to those in **1** from Bu_2SnO.

The preparation of **1** from the reaction of Bu_2SnCl_2 and Na_2SiO_3 was also examined in Method B. The reaction using an equimolar amount of Bu_2SnCl_2 and Na_2SiO_3 in the mixed solvent of water and benzene proceeded efficiently at room temperature to give **1** in 83% yield (Run 6). The obvious effects of tetrabutylammonium bromide (TBAB) as a phasetransfer catalyst on the yields of **1** was not observed in our case using Bu_2SnCl_2 (Run 7).[3]

The contents of Sn and Si in **1** were determined by gravimetric analysis in a similar manner to the preceding work.[1] The ratios of Sn/Si in **1** obtained by Method A were varied in the range of



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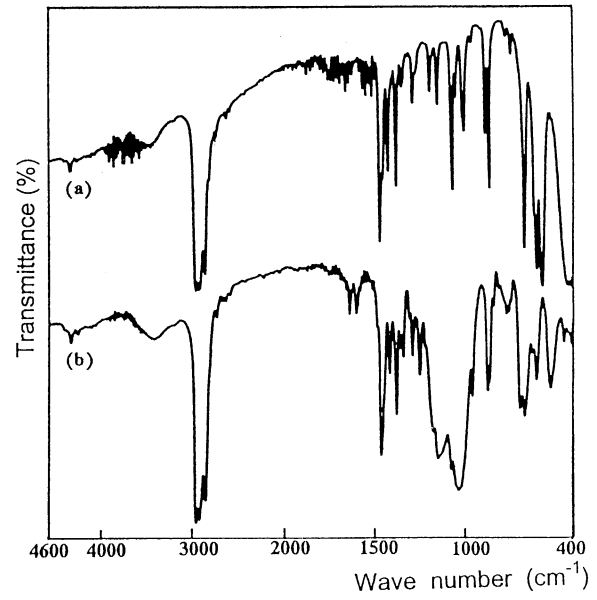

Figure 1. IR spectra of (a) dibutyltin oxide and (b) silica gel **1**.

Table 1. Preparation of silica gel **1** from sodium metasilicate (Na_2SiO_3) and dibutyltin compounds

	Reaction conditions[a]				Silica gel **1**	
Run	Dibutyltin compound	Organic solvent	Method[b]	pH	Yield[c] %	Molar Ratio of Si/Sn[d]
1	Bu_2SnO	CH_2Cl_2	A	2	63	1.0
2	Bu_2SnO	CH_2Cl_2	A	4	97	0.7
3	Bu_2SnO	CH_2Cl_2	A	6	91	0.8
4	Bu_2SnO	Benzene	A	6	52	1.4
5	$Bu_2Sn(OMe)_2$	Benzene	A	6	55	1.1
5	Bu_2SnCl_2	Benzene	B	—	83	1.1
6	Bu_2SnCl_2	CH_2Cl_2	B	—	69	1.2
7	Bu_2SnCl_2	CH_2Cl_2	B	—	70[e]	1.1

[a] An equimolar amount of Na_2SiO_3 and organotin compound were used for the reactions. [b] 3N Hydrochloric acid was used for adjusting pH value of water solution in Method A. [c] Calculated from the content of Si in Na_2SiO_3 and **1**. [d] The ratio was estimated from the results of gravimetric analysis. [e] The reaction was carriedout in the presence of tetrabutylammonium bromide (TBAB) as a phasetransfer catalyst.

0.7 to 1.4. On the other hand, in **1** prepared from the reactions using Bu_2SnCl_2 by Method B, the ratios varied in the narrower range of 1.0 to 1.2.

All the products **1** obtained by Method A and B showed analogous absorptions in the IR spectra as represented in Figure 1. Thus, several bands due to ν(C-H) were observed clearly at ca. 2900 cm^{-1} and the strong broad bands due to Si-O-Sn, Si-O-Si, and Sn-O-Sn bond were in the region from 960 to 1200 cm^{-1}. A weak broad band attributed to ν(OH) was observed in the region from 3100 to 3700 cm^{-1}. The absorptions assigened to Si–O–Sn bond of trimethylsiloxytrialkyltin were reported to be found in the region from 980 cm^{-1} to 1070 cm^{-1}.[6] In the spectra of **1**, this absorption seemed to be included in the strong broad absorptions at the region. The absrorption due to Si-O-Si bond in silica gel, which was obtained from Na_2SiO_3 by neutralizing with 3 N hydrochloric acid, was found around 1090 cm^{-1}. In the spectra of **1**, the corresponding absorption was found around 1060 cm^{-1}. However, the existence of Sn–O–Sn bonds in **1** was suggested by the observations of two characteristic absorption bands at 565 cm^{-1} and 595 cm^{-1}, which were detected in the spectra of Bu_2SnO.[7] These spectral data indicated that **1** is consisted of Si–O–Sn bonds, but Sn-O-Sn bonds also existed in **1** like a block copolymer.

The results of DTA-TG analysis of **1** were similar to those of the reported tributyltin derivatives, i.e., a sharp exothermic peak was observed at ca. 236 °C and two weak broad exothermic peaks at 340 °C and 370 °C.[1] The significant weight loss exhibited at the area of the former peak was thought to be caused by the elimination of tributyl groups on tin and agreed closely with the calculated value on the basis of contents of tin. In the DTA-TG traces of Bu_2SnO, four exothermic peaks at 208 °C, 239°C, 349 °C, and 369 °C were found. Except for the peak at 208 °C, other peaks were the same as those of **1**. This observation may support the speculation that the obtained gel **1** contained the sequences of Bu_2SnO.

In addition, the elimination of dibutyltin group to give silica gel was easily achieved by treating with diluted hydrochloric acid or nitric acid at room temperature. These results suggest that **1** shows moderate reactivities for further transformations to functionalized silica gels.

References and Notes

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