A Facile Preparation of Polysiloxane Containing Tributyltin Group as Efficient Protection Group

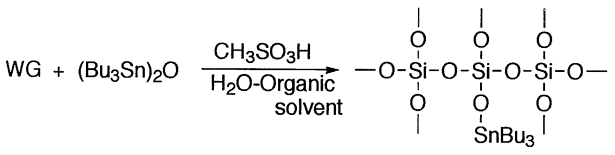
Takahisa Iida, Tomohiro Sekiya, Toshifumi Kageyama, Toshio Sugizaki, and Osamu Moriya*†
Department of Industrial Chemistry, Faculty of Engineering, Kanto Gakuin University, Mutsuura, Yokohama 236
†*Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239*

(Received August 30, 1996)

The polysiloxane having tributyltin groups, which showed a blocking effect from self-condensation to give silica gel, was prepared from the reaction of water glass and bis(tributyltin) oxide in the presence of methansulfonic acid. The molar ratios of Si/Sn in the obtained polysiloxanes were estimated by gravimetric analysis to be in the range of 2 to 3.

Synthetic procedures for the preparation of polymeric organosiloxanes, in which water glass (WG) and sodium silicate (Na_2SiO_3) are employed as the practical starting compounds, have been developed from the interests concerning useful hybrid materials.[1] The reported usage of the above silicate compounds to give functionalized polyorganosiloxanes generally consists of the two steps, i.e., transformation to oligomeric and/or monomeric silanols by neutralization of WG or Na_2SiO_3 and successive condensation with organic compounds such as alcohols or silyl derivatives. These processes are generally carried out in one-pot or step by step.[2] However, the intermediary silanols readily form silica gel by self-condensation. This means the difficulties to isolate such silanol intermediates and keep them until the appropriate time for desired reactions without gelation. On the other hand, tetraalkoxysilane, which is regarded as protected precursor of the monomeric silanol and soluble in common organic solvents, has been used recently for a variety of reactions including sol-gel process.[3] Similarly, protected polymeric or oligomeric silanols are thought to be useful intermediates for the syntheses of polyorganosiloxanes and silica gels functionalized by organic groups.

For a kind of the polysiloxane intermediate mentioned above, the polysiloxane protected by organotin groups seems to be an interesting candidate. Since, from the interpretations of the experimental facts reported in the chemistry of organotin compounds, the organotin protected polysiloxane is expected to be stable under neutral conditions, but shows moderate reactivities at Si-O-Sn bond.[4] On the basis of those considerations, we have started the investigations on synthetic applications of a variety of polysiloxanes containing organotin groups. In this report, we describe the facile procedure for preparations of tributyltin protected polysiloxane **1** from WG, which is regarded as a starting compound of the investigations.



1

At first, the reported reaction using tributyltin chloride (Bu_3SnCl) with a phase transfer catalyst, which successfully gave corresponding organotin derivative from Na_2SiO_3, was attempted.[5] However, this procedure was not effective to prepare the polymeric product **1** from WG (SiO_2, 28.7%; Na_2O, 9.4%). The desired product **1** was obtained by the modified procedure of Lentz, in which hexamethyldisiloxane was replaced to bis(tributyltin) oxide [$(Bu_3Sn)_2O$].[6] Thus, the reactions of WG and $(Bu_3Sn)_2O$ were carried out in the mixed solvents of water and a common organic solvent with an acid to control the pH value of water layer from 4 to 7 as shown in Table 1. The resulting polysiloxanes **1**, yields of which were based on the content of Si unit in starting WG and the product **1**, were isolated as precipitates insoluble in methanol. The precipitates **1** were dissolved into dichloromethane and reprecipitated from methanol for the analyses.[7]

The highest yield of **1** such as 84% was recorded in the reaction conducted under the following conditions; the initial molar ratio of $(Bu_3Sn)_2O/SiO_2$=1/1, pH=6 adjusted with methansulfonic acid, and in the mixed solvent of hexane-water (Run 1). The contents of tributyltin (Sn) and Si unit were estimated by gravimetric analysis.[8] The results of the analyses showed that the molar ratios of Si unit/Sn unit in **1** varied from 2 to 3 and were not changed essentially according to the feed ratios of the starting compounds as shown in the cases using half and double the molar quantity of $(Bu_3Sn)_2O$ to SiO_2 (Runs 4 and 5). These results suggest that less equimolar amount of tributyltin group to Si unit is enough to protect the polymeric silanol from self-condensation. Furthermore, it may be said that tributyltin group is enough bulky to prevent efficiently the access of each polymeric silanol molecule leading to gelation.

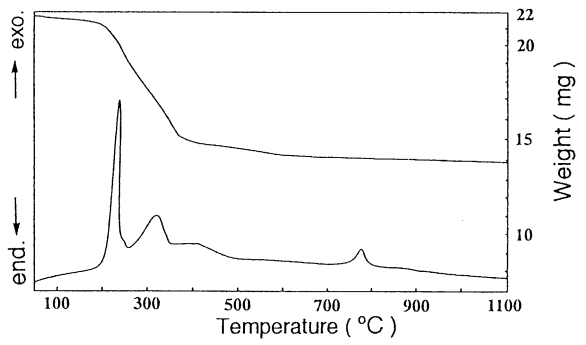


Figure 1. DTA-TG traces of tributylstannylated Polysiloxane **1** (21.75 mg, Run 2).

Table 1. Preparation of Tributylstannylated Polysiloxane **1** from WG and $(Bu_3Sn)_2O$

	Reaction conditions				Tributylstannylated polysiloxane **1**		
Run	Organic solvent	Acid	pH	Initial ratio of Si/Sn mol/mol	Yield[a] %	Ratio of Si/Sn[b] mol/mol	Molecular weight[c] Mn
1	Hexane	CH_3SO_3H	6	1	84	2.5	29000, 4800
2	Hexane	CH_3SO_3H	4	1	73	2.0	32000, 4600
3	Hexane	CH_3SO_3H	2	1	trace	—	—
4	Hexane	CH_3SO_3H	6	0.5	48	2.2	3500
5	Hexane	CH_3SO_3H	6	2	31	2.7	3800
6	Hexane	TosOH[d]	6	1	trace	—	—
7	Benzene	CH_3SO_3H	6	1	67	3.0	4000
8	CH_2Cl_2	CH_3SO_3H	6	1	(gel)	—	—
9	THF	CH_3SO_3H	6	1	trace	—	—
10	Hexane	HNO_3	6	1	(gel)	—	—
11	Hexane	HCl	6	1	(gel)	—	—

[a]Calculated from the content of Si in WG and Polysiloxane **1**. [b]The ratio was estimated from the results of gravimetric analysis. [c]Determined by GPC analyses based on polystyrene standard. [d]*p*-Toluene sulfonic acid monohydrate.

In the IR spectra of **1**, the strong and broad absorptions due to Si-O-Si and/or Si-O-Sn were observed around 1040 cm^{-1} and the absorptions assigned to methylene of tributyltin moiety were at 2900 cm^{-1}, respectively.[9] The DTA-TG traces, in which a heating rate was 10 °C/min in air, showed the characteristic exothermic point and the weight loss at ca. 245 °C (Figure 1). This thermal degradation seems to be attributed to the tributyl group of tin.

The molecular weight (Mn) of **1** found by GPC were in the region of 3500 to 32000.[10] The products **1** obtained in higher yields showed mainly two peaks at higher molecular weight region from 4000 to 30000. However, in the examples, in which lower yields of **1** were recorded, one peak corresponded to molecular weights from 3500 to 4000 was observed in the chromatograms of GPC analyses (Runs 4, 5, and 7).

The organic solvent using as a co-solvent obviously effected on the yields of **1**. From the reaction conducted in THF, only a trace of MeOH insoluble product was obtained (Run 9). Unsatisfactory result was also observed in the reaction using dichloromethane as a co-solvent, in which gel-like product was obtained mainly (Run 8). In the IR spectra of the gel, the absorptions around 2980 cm^{-1} due to methylene groups of tributyltin moiety were observed. This means that the incorporation of tributyltin moieties proceeded even in such gelation.

In addition, the elimination of tributyltin groups in the polymer **1** was examined. The treatment of **1** with diluted inorganic acids such as hydrochloric acid and nitric acid for several hours at room temperature in the mixed solvents of water and benzene gave silica gels. The yield of the resulting silica gel based on the contents of Si unit was over 75%. In the IR spectra of the resulting silica gels, no detectable absorptions due to butyl group was observed. The data of gravimetric analyses also supported this results.

The obtained polymers **1** were not soluble in methanol, ethanol, and acetonitrile, but soluble in hexane, benzene, chloroform, and dichloromethane. The efficiency of the protection group was demonstrated in the fact that **1** could be kept without gelation over three weeks in a solution of hexane (0.1 g/ml) at room temperature.

References and Notes

1 Y. Abe, in "*Muki Kobunshi I*," ed by M. Kajiwara and K.Murakami, Sangyo Tosyo, Tokyo (1992), Chap. 2, p. 45. H. Okamoto, *Kagaku Kogyo*, **1987**, 79.

2 Y. Abe, A. Kaijou, N. Shintani, Y. Nagao, and T. Misono, *J. Polym. Sci., Part A, Polym. Chem.*, **25**, 1671(1987). Y. Abe and T. Misono, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 565(1984). R. Currel and J. R. Parsonage, *Macromol. Sci.-Chem.*, A16(1), 141(1981). H. Inoue and S. Kohama, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 795(1981). J. Götz and C. R. Masson, *J. Chem. Soc., (A)*, 2683(1970).

3 S. Sakka, in "*Treatise on Materials science and Technology 22, Glass III*," ed. by M. Tomozawa and R. Doremus, Academic Press, New York(1982), p. 129.

4 R. Okawara, D. G. White, K. Fujitani, and H. Sato, *J. Am. Chem. Soc.*, **83**, 1342 (1961). S. Sakai, K. Ito, and Y. Ishii, *Yu Go Ka*, **28**, 1109(1970). M. Adachi, F. Lefebvre, and J. M. Basset, *Chem. Lett.*, **1996**, 221 and references therein.

5 S. Inagaki, E. Yamada, K. Okudaira, H. Okamoto, and J. Furukawa, *Kasenkoensyu*, **42**, 1(1985).

6 C. W. Lentz, *Inorg. Chem.*, **3**, 574(1964).

7 Tributylstannylated polysiloxane **1**: IR (KBr) 2900, 1100, 475 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.84 (9H, m), 1.10—1.26 (12H, br,m), 1.53 (6H, m); ^{13}C NMR ($CDCl_3$) δ 12.8, 16.6, 28.3, 29.6; ^{29}Si NMR ($CDCl_3$) δ –85— –110.

8 Gravimetric analyses were conducted as usual manner, i.e., the oxidation by nitric acid and treatment with hydrofluoric acid to determine the content of Si unit. The content of Sn was estimated from the weight of the residual ash regarded as SnO_2; A. Yoshida, *Bunseki*, **11**,876(1989).

9 The absroptions assigned to Si-O-Sn bond of organometalic analogues were found at 985 cm^{-1} and 1070 cm^{-1}; H. Schmidbaur, *Angew. Chem.*, **77**, 206(1965).

10 Gel permeation chromatography was measured by Shimazu7A HPLC (Shimazu Co. Ltd.): Column, GPC 802 and 804 (Shimazu); solvent, THF; flow rate, 1 ml / min.; temperature, 40 °C; detector, RI; Polystyrene standard.