Synthesis of polyorganosiloxane retaining SiO_4 framework from inosilicate mineral by trimethylsilylation

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A polyorganosiloxane retaining a SiO_4 tetrahedral framework has been synthesized by the reaction of an inosilicate mineral (*para*-wollastonite) with a trimethylsilylating reagent. The glassy product dissolved in a wide range of organic solvents but was insoluble in water. The analyses of the product by means of infra-red spectroscopy, X-ray powder diffraction and elemental analysis indicated that trimethylsilyl side groups were linked to the SiO_4 framework. The thermal stability of the product was determined by thermal analysis.

INTRODUCTION

Trimethylsilylation has been studied for the purpose of synthesizing volatile compounds from non-volatile materials. This reaction has also been applied to the study of silicate structures. Lentz[1] originally reported the preparation of the trimethylsilyl derivates from silicate minerals and also sodium silicate solutions whose derivatives were monomeric, low molecular weight compounds. On the other hand, a few workers have reported the direct synthesis of polyorganosiloxanes from silicate minerals with various silicate frameworks[2–5]. Currell *et al.*[2] applied this trimethylsilylation reaction for the preparation of polyorganosiloxanes from chlorite. However, the synthesis of polyorganosiloxanes from single chain silicates (pyroxene groups) has not been reported, except for one patent by Saunders and Cox[6]. Only Currell *et al.* have reported the partial trimethylsilylation of wollastonite and the product they obtained was insoluble in organic solvents.

The general trimethylsilylation reactions of silicates can be expressed by the following equations:

$$\equiv Si{-}O{-}M \xrightarrow{H^+} \equiv Si{-}O{-}H$$

$$\equiv Si{-}O{-}H \xrightarrow[\text{reagent}]{\text{Trimethylsilylating}} \equiv Si{-}O{-}Si(CH_3)_3$$

This paper describes the direct synthesis of a polyorganosiloxane retaining a SiO_4 main chain from the inosilicate mineral, *para*-wollastonite. The structure of the product is also discussed on the basis of its infra-red spectrum, X-ray powder diffraction pattern and elemental analytical data.

EXPERIMENTAL

Materials

Para-wollastonite (Hiba-gun, Hiroshima, Japan) was used in this study. The ground *para*-wollastonite was passed through a 325 mesh sieve. The X-ray powder diffraction pattern of the material was identical with the published data of *para*-wollastonite (ASTM 10-489), though the intensity was somewhat different.

Hexamethyl disiloxane (HMD) was obtained by the hydrolysis of chlorotrimethylsilane and distilled once (b.p. 100°–101°C). 2-Propanol and concentrated hydrochloric acid were reagent grade.

Trimethylsilylation

The *para*-wollastonite powder was added to the mixture of hexamethyl disiloxane, 2-propanol, water and concentrated hydrochloric acid. Quantities of reactants are given in *Table 1*. The reaction mixture was stirred vigorously for 48 h, at room temperature using a magnetic stirring bar.

After the reaction ceased, the lower aqueous layer was removed. The upper siloxane layer and insoluble solid were separated by centrifugation. The organic layer was evacuated by an aspirator to remove hexamethyl disiloxane and a product soluble in organic solvents was obtained. The insoluble product was washed with 2-propanol and dried.

Measurements

X-ray powder diffraction patterns were obtained with a Shimadzu VD-II diffractometer, using nickel-filtered CuKα radiation. Infra-red spectra were recorded using KBr discs or CCl_4 solutions with a Shimadzu IR-400 spectrometer. The molecular weight of the soluble product was determined by vapour pressure osmometry on a Hitachi–Perkin–Elmer 115 apparatus (solvent, benzene; reference, benzil; temperature, 40°C). Elemental analysis was carried out by a Yanagimoto MT-2. Thin layer chromatographic analysis was carried out according to the method of Hoebbel *et al.*[7]. Micro-differential thermal analysis (d.t.a.) curves were recorded on a Shimadzu DT-20B. Sample weight was 4 mg and α-Al_2O_3 was used as a reference material. The measurement was performed under an air atmosphere at a heating rate of 10°C/min.

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Table 1 Reaction conditions and the analysis of the products

	Reactants					Products						
						Soluble product				Insoluble product		
No.	*Para*-wollastonite (g)	HMD (ml)	2-Propanol (ml)	HCl (ml)	Water (ml)	Yield(g)	*MW*	H(%)	C(%)	Yield(g)	H(%)	C(%)
1	3	10	50	5	50	1.6	3100	6.9	25.0	0.8	5.2	17.7
2	3	10	0	5	50	0.4	7800	5.7	21.0	1.5	4.0	11.5
3	3	10	50	5	10	1.0	2500	7.0	26.0	1.4	5.8	17.8
4	2	20	50	5	50	1.7	3800	6.9	25.7	0.2	4.9	16.5

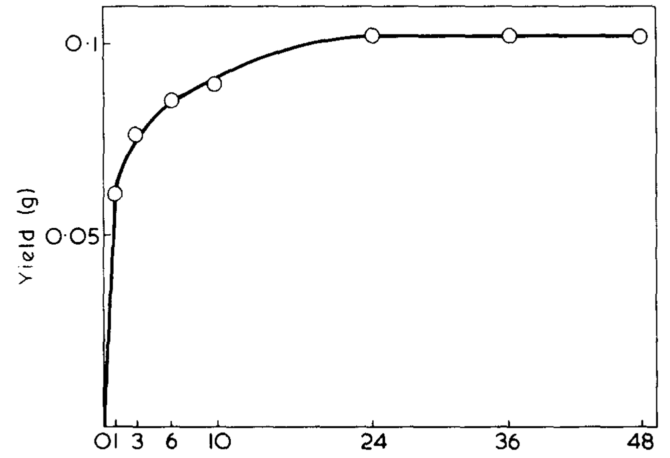


Figure 1 Yield of the soluble product as a function of reaction time

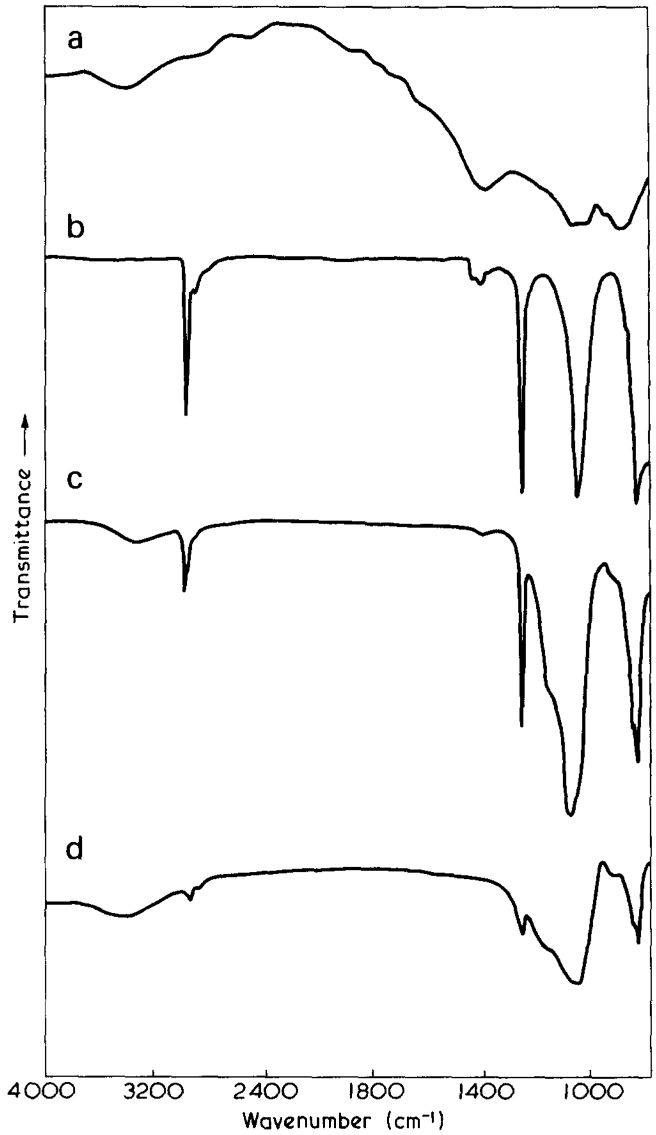


Figure 2 Infra-red spectra: (a) *para*-wollastonite; (b) hexamethyl disiloxane; (c) soluble product (no. 1); and (d) insoluble product (no. 1)

RESULTS AND DISCUSSION

The soluble products from the siloxane layers were colourless, glassy solids which dissolved in a wide range of organic solvents such as benzene, acetone, n-heptane and carbon tetrachloride. On the other hand, they were insoluble in water. The products insoluble in organic solvents were white powders and showed hydrophobic properties.

The yields and H and C contents of the products and molecular weights of soluble products are listed in *Table 1*. The amount of water affected the yield of the products (nos 1 and 3) and it was suggested that the amount of water influenced the solubility of *para*-wollastonite in the trimethylsilylation reaction system. In the case of the absence of 2-propanol (no. 2), the yield of the soluble product decreased. The molecular weight of the soluble product was higher and its C content was lower; this could be caused by the condensation of silicic acids. Though the role of 2-propanol in the trimethylsilylation of silicates has not been understood completely, it has been thought that 2-propanol influenced the mutual solubilities of the aqueous and organic layers and stabilized the silicic acids after leaching Ca in *para*-wollastonite by HCl[8]. The larger amount of the trimethylsilylating reagent led to a higher yield of the soluble product (No. 4). In the case of product no. 4, 1 ml of sample of the siloxane layer of the reaction mixture was withdrawn at given intervals of time during the reaction and products soluble in organic solvents were weighed after the evaporation of HMD under reduced pressure. As *Figure 1* shows, the yield of the soluble product increased with an increase in the reaction time and was constant after 24 h. *Figure 2* shows the infra-red spectra of the following: (a) the starting material (*para*-wollastonite), (b) hexamethyl disiloxane, (c) the product soluble in organic solvents (no. 1) and (d) the insoluble product (no. 1). Other products (nos 2–4) also showed similar patterns to those of the products of no. 1. The major bands in the spectrum of the soluble product (c) were due to CH (2960 cm^{-1}), CH$_3$ in Si(CH$_3$)$_3$ (1260 cm^{-1}) and Si–O–Si (1070–90 cm^{-1}), indicating the trimethylsilylation of silanol groups which appeared in the acid decomposition of the calcium silicate structure. The broad band around 3000–3700 cm^{-1} was thought to be due to hydrogen-bonded hydroxyl absorption. The presence of the hydroxyl groups in the soluble products suggested the steric hindrance of adjacent trimethylsilyl side groups.

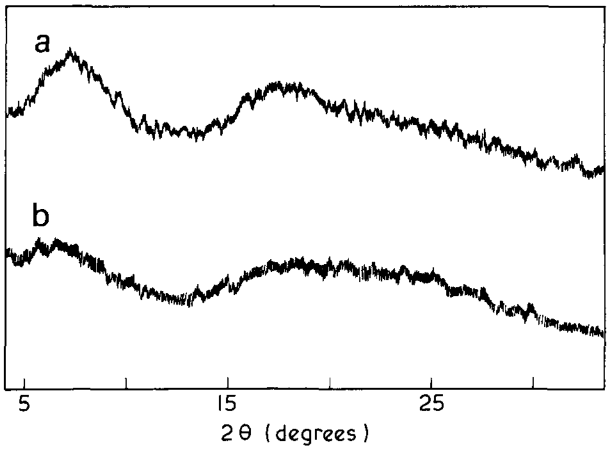


Figure 3 X-ray powder diffraction patterns: (a) soluble product (no. 1) and (b) insoluble product (no. 1)

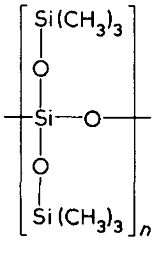
In agreement with the infra-red spectrum of the soluble product, the ratio of H/C calculated from H and C data in *Table 1* was 3.2–3.3, which was different from the value (H/C = 3) of the full substitution by trimethylsilyl groups.

The spectrum of the insoluble product (d) also showed the characteristic bands assigned to the trimethylsilyl groups. However, the intensity was weaker than that of the soluble product.

Thin layer chromatographic analysis of the soluble products obtained in this study indicated that the products contained a small amount of trimethylsilyl derivatives of low molecular weight silicic acids containing less than 4 silicon atoms.

X-ray powder diffraction patterns of the following were taken: (a) the product soluble in organic solvents (no. 1) and (b) the insoluble product (no. 1) and are given in *Figure 3*. The diffraction pattern of the insoluble product (b) indicated the decomposition of the silicate structure. The pattern of the soluble product (a) showed broad peaks at $2\theta = 7.2°$ (d = 12.3 Å) and 17°(d = 5.2 Å), which indicated the presence of repeating units.

The calculated H and C values from the idealized linear polymer retaining a SiO_4 unit as the main chain



$$\left[\begin{array}{c} Si(CH_3)_3 \\ | \\ O \\ | \\ -Si-O- \\ | \\ O \\ | \\ Si(CH_3)_3 \end{array}\right]_n$$

are H, 8.1% and C, 32.4%, respectively. The amount of carbon in the soluble products was lower than that of the linear poly[bis(trimethylsilyloxy)siloxane] (*Table 1*). This finding seemed to be due to the condensation of silanol groups and, because of this reaction, the simple linear organosilicate polymer could be obtained only with difficulty.

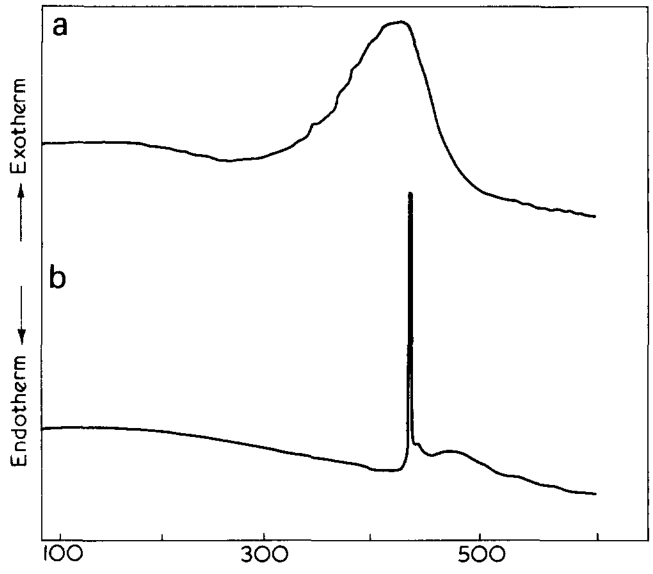


Figure 4 Micro-d.t.a. curves. A, soluble product (no. 4) and B, insoluble product (no. 4)

From these results, it was concluded that the product was a polyorganosiloxane containing a partly condensed SiO_4 framework (polyorganosilicate) and both trimethylsilyl $[(CH_3)_3Si–]$ and hydroxyl side groups were present.

Figure 4 shows the typical micro-d.t.a. curves of the soluble product (no. 4, curve A) and the insoluble product (no. 4, curve B). Curve A showed a broad exothermic peak (300°–500°C) due to the oxidation of organic groups. The strong, sharp exothermic peak at 430°C in curve B was attributed to the combustion of trimethylsilyl groups and similar thermal behaviour has been reported by Currell *et al.*[3]. The infra-red spectrum of the soluble product, heated to 600°C showed no absorption peaks due to organic groups. The detailed mechanism of thermal decomposition is now under investigation.

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