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Preparation and Pyrolysis of Polyphosphosilazane

Yusuke Mori, Ryoji Toyoda, Satoshi Kitaoka† and Yoshiyuki Sugahara*
Department of Applied Chemistry, School of Science and Engineering, Waseda University,
Ohkubo-3, Shinjuku-ku, Tokyo 169-8555, Japan
†Japan Fine Ceramics Center, Mutsuno-2, Atsuta-ku, Nagoya 456-8587, Japan

Polyphosphosilazane (POPHPS) has been synthesized through chemical modification of perhydropolysilazane (PHPS) with phosphonic acid dimethyl ester. The synthesized preceramic polymer contains three-coordinated phosphorus species possessing Si-O-P bonds, as shown by infrared and nuclear magnetic resonance spectroscopy. These spectroscopic analyses indicate that SiH_x groups in PHPS react with PH groups in phosphonic acid dimethyl ester. A possible mechanism could mainly involve a reaction between three-coordinated pyridinium salt $[OP(OCH_3)_2]^-[C_5H_5NH]^+$ and SiH_3 groups in PHPS with H_2 evolution. Thermogravimetry shows that the ceramic yield of POPHPS up to 900°C under Ar atmosphere is 88.7 mass%. X-ray diffraction analysis shows that an amorphous material is obtained after pyrolysis under N_2 atmosphere at 1000°C.

Key words: *Polysilazane, Preceramic Polymer, Silicon Phosphorus Oxynitride, Amorphous Materials*

1. Introduction

In recent years, silicon-based organometallic preceramic polymers have been widely applied for manufacturing high-performance ceramics such as Si_3N_4.[1-5] This chemical polymer-to-ceramics route offers a significant advantage for the preparation of ceramic coatings and fibers, whose preparation is impossible or difficult through conventional solid-state reactions. Furthermore, desired elements can be easily introduced into the preceramic polymers, and the chemical compositions of the resulting ceramic materials can therefore be controlled. This chemical route is consequently advantageous for producing homogeneous amorphous materials.[6]

Silicon oxynitride (Si-N-O materials) has excellent resistance to oxidation and thermal shock.[7,8] Phosphorus oxynitride (P-N-O materials), on the other hand, is well known for its chemical durability, and has a lower thermal expansion and higher glass-transition temperature than phosphate glasses.[9,10] Si-P-N-O composite materials are therefore expected to be candidates for excellent coating materials for high-temperature applications.

In this paper, we report that polyphosphosilazane (POPHPS) can be synthesized by a reaction of perhydropolysilazane (PHPS) with phosphonic acid dimethyl ester, and that an amorphous material can be obtained by pyrolysis of POPHPS under N_2 atmosphere at 1000°C. The preparation of POPHPS from PHPS and phosphonic acid dimethyl ester and the characterization of the product pyrolyzed at 1000°C under N_2 atmosphere are described.

2. Experimental Procedure

As a starting preceramic polymer, commercially-available perhydropolysilazane (PHPS, Clariant Japan, N-N310, average molecular mass of 974) was used as received. Phosphonic acid dimethyl ester [$H(O)P(OCH_3)_2$, Tokyo Kasei Kogyo] was used for chemical modification of PHPS. Pyridine (Kanto Chemical) and toluene (Kanto Chemical) were dehydrated before use. All the experiments were performed under protective nitrogen atmosphere.

PHPS in *p*-xylene (20 mass%) and phosphonic acid dimethyl ester (a molar ratio of Si/P=2.5) were dissolved into pyridine with stirring at 30°C. The resulting homogeneous solution was stirred at 30°C for 3h. Pyridine and *p*-xylene were then removed at 30-60°C under reduced pressure. The product was washed with toluene to give polyphosphosilazane (POPHPS) as a dark-brown viscous liquid.

POPHPS placed on a BN boat was pyrolyzed in an alumina tube under flowing nitrogen. The heating rate was 10°C/min from room temperature to 200°C and 5°C/min from 200°C to 1000°C. The temperature was maintained at 1000°C for 3h, and the pyrolyzed residue was cooled to room temperature.

The precursor was characterized by infrared (IR) spectroscopy (JASCO, FT/IR-460) as well as by ^1H, ^{29}Si, and ^{31}P nuclear magnetic resonance (NMR, JEOL, JNM-270X) spectroscopy in $CDCl_3$. The gaseous species evolved during the reaction between PHPS and phosphonic acid dimethyl ester was identified by gas chromatography (GC, Shimadzu, GC-8A). Thermogravimetry (TG, Perkin-Elmer, TGA7) was carried out at a heating rate of 10°C/min under flowing argon. The product pyrolyzed under N_2 atmosphere was examined by X-ray diffraction (XRD, Rigaku, Rint-2500) analysis using monochromated Cu Kα radiation.

3. Results and Discussion

3.1 Spectroscopic characterization of POPHPS

The IR spectra of PHPS, phosphonic acid dimethyl ester and POPHPS are shown in Fig. 1 (a), (b) and (c), respectively. The bands of PHPS are observed at 3380 cm^{-1} ($\nu_{N\text{-}H}$),[11] 2950-2900 cm^{-1} ($\nu_{C\text{-}H}$)[12] and 2160 cm^{-1} ($\nu_{Si\text{-}H}$).[11] In the IR spectrum of POPHPS obtained by the reaction of PHPS with phosphonic acid dimethyl ester [Fig. 1 (c)], the $\nu_{P\text{-}H}$ band, which is observed in the spectrum of phosphonic acid dimethyl ester at 2430 cm^{-1}, is not present. The $\nu_{Si\text{-}H}$ band at 2160 cm^{-1} decreases slightly in comparison with the spectrum of PHPS. The spectrum profile of the $\nu_{C\text{-}H}$ band at 2950-2900 cm^{-1} is, moreover, very similar to that of phosphonic acid dimethyl ester.

To investigate the reaction of PHPS and phosphonic acid dimethyl ester in more detail, the structure of POPHPS was analyzed using the NMR technique. The ^{1}H NMR spectra of PHPS, phosphonic acid dimethyl ester and POPHPS are shown in Fig. 2 (a), (b) and (c), respectively. The spectrum of PHPS [Fig. 2 (a)] exhibits four signals at 4.8, 4.3, 0.5-1.5 (broad) and 0.1-0.2 ppm, which are assigned to SiH/SiH$_2$, SiH$_3$, NH and Si(CH$_3$)$_3$ groups, respectively.[11, 12] The spectrum of POPHPS [Fig. 2 (c)] exhibits a new signal assigned to OCH$_3$ groups[13] at 3.5 ppm. The PH group signal, which is observed in the spectrum of phosphonic acid dimethyl ester at 5.4 ppm, is not observed. The relative intensities of the signal due to the SiH$_x$ groups at 4.8 and 4.3 ppm decrease slightly in comparison with the spectrum of PHPS. The signal due to the OCH$_3$ groups shifted from 3.7 ppm to 3.5 ppm after modification with phosphonic acid dimethyl ester.

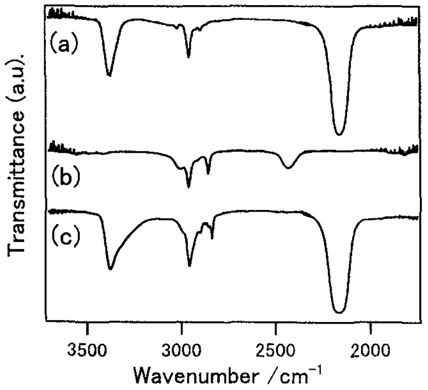


Fig. 1. IR spectra of (a) PHPS, (b) phosphonic acid dimethyl ester and (c) POPHPS.

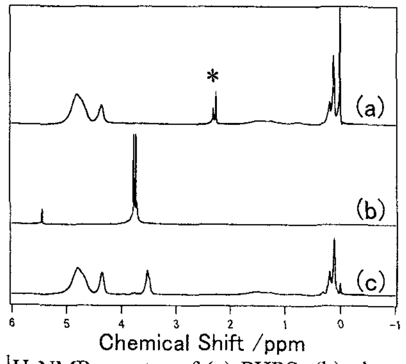


Fig. 2. ^{1}H NMR spectra of (a) PHPS, (b) phosphonic acid dimethyl ester and (c) POPHPS. (*: *p*-xylene)

The silicon environments were further investigated using ^{29}Si DEPT (distortion-less enhancement by polarization transfer)[14] NMR, and the results are shown in Fig. 3. The spectrum of PHPS [Fig. 3 (A)-(a)] exhibits three signals at -33, -35 and -49 ppm, which are assigned to H$_2$SiN$_2$, HSiN$_3$ and H$_3$SiN units, respectively.[15] In Fig. 3 (A)-(b) and (B)-(b), only the signals assigned to SiH$_2$ units are observed,[16] and the spectrum of POPHPS exhibits a new signal at -40 ppm [Fig. 3 (B)-(b)]. Since the substitution of a nitrogen atom with an oxygen atom in an Si(N,O)$_4$ tetrahedron leads to an upfield shift of the ^{29}Si NMR signal,[17] the 40-ppm signal could be assigned to H$_2$SiON units. (An H$_2$SiO$_2$ signal is expected to exhibit a larger upfield shift.) It is consequently possible that some Si-O bonds are introduced into POPHPS by chemical modification.

The ^{31}P NMR spectra of phosphonic acid dimethyl ester and POPHPS are shown in Fig. 4 (a) and (b), respectively. The spectrum of POPHPS [Fig. 4 (b)]

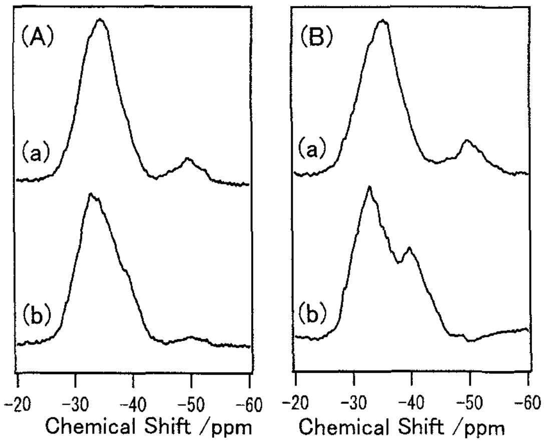


Fig. 3. ^{29}Si DEPT NMR spectra of (A) PHPS and (B) POPHPS. The θ_1 spectrum (a) exhibits the signals due to SiH, SiH$_2$ and SiH$_3$ units. The SiH$_2$ subspectrum (b) are generated by calculation of (1/2)(θ_1 -1.12 θ_2). [$\theta_1 = \pi/4$ and $\theta_2 = 3\pi/4$].

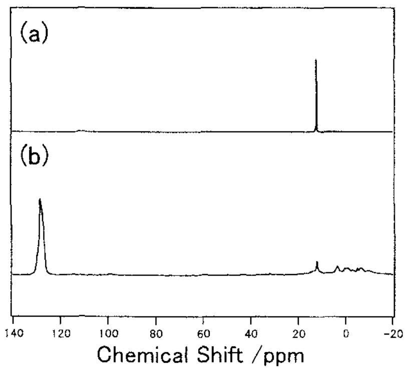


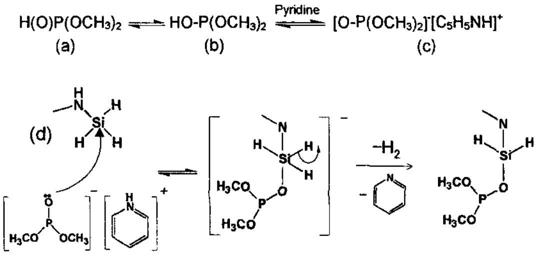
Fig. 4. ^{31}P NMR spectra of (a) phosphonic acid dimethyl ester and (b) POPHPS.

exhibits an intense broad signal at 128 ppm. Sum *et al.* reported that signals due to a $(MeO)_2POSi$ environment were observed at 127.3-128.3 ppm.[18] POPHPS appears to contain a similar three-coordinated phosphorus environment as a consequence.

3.2 Reaction mechanism and structure of POPHPS

The evolution of hydrogen during this reaction was observed using gas chromatography. The results of IR, ^1H, and GC indicate that the SiH_x groups react with the PH groups in phosphonic acid dimethyl ester with H_2 evolution. In addition, ^{29}Si DEPT NMR suggests the possible presence of the H_2SiON units, and ^{31}P NMR demonstrates that POPHPS contains the $(MeO)_2POSi$ environment.

The reaction mechanism can therefore be assumed to be as follows. Sum *et al.* revealed that four-coordinated phosphorus species isomerize to form three-coordinated phosphorus salt in the presence of a base such as NEt_3.[18] It is therefore assumed that phosphonic acid dimethyl ester (a) isomerizes to form a three-coordinated phosphorus salt (c) in the presence of pyridine as shown in Scheme 1. The assumed mechanism could mainly involve the reaction between the represented three-coordinated phosphorus salt (c) and the SiH_3 groups in PHPS (d) with H_2 evolution.[17] The nucleophile three-coordinated phosphorus salt (c) uses its lone-pair electrons on oxygen to attack the SiH_3 groups in PHPS (d). This leads to a transition state (e) with a partially formed Si-O-P bond and a partially broken Si-H bond. The departed hydride ion H^- attacks the pyridinium ion $[C_5H_5NH]^+$ to evolve H_2 and generate the $(MeO)_2POSi$ environment (f). A proposed POPHPS structure based on the above discussion is shown in Fig. 5. When the phosphonic acid dimethyl ester and pyridine were mixed, however, the solution did not afford any signal assignable to either (b) or (c) in a ^{31}P NMR spectrum, which is inconsistent with the proposed formation of either (b) or (c). It was reported that a signal assignable to the phosphorus salt could be clearly observed by ^{31}P NMR in the presence of stronger bases such as NaH.[19] It is therefore possible that a very small equilibrium concentration of the phosphorus salt (c) could be actively involved in the reaction in the presence of pyridine, which is a weaker base.



Scheme 1. The possible reaction between PHPS and phosphonic acid dimethyl ester.

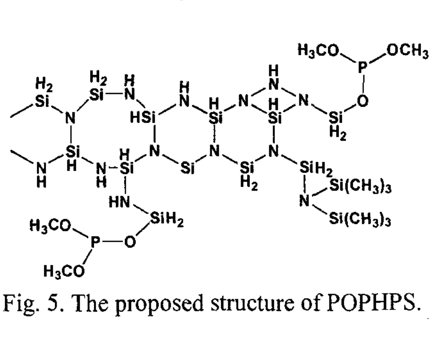


Fig. 5. The proposed structure of POPHPS.

3.3 Pyrolysis of POPHPS

The TG curves of PHPS and POPHPS are shown in Fig. 6 (a) and (b), respectively. The ceramic yield of PHPS up to 900°C under argon atmosphere is about 75 mass%. The mass loss of about 25 mass% is thought to correspond to the elimination of organic or organosilicon groups as gaseous species such as hydrocarbon, hydrogen, low molecular weight silazane compounds, or their fragments.[20] The product obtained by pyrolyzing POPHPS at 1000°C under argon atmosphere exhibits a ceramic yield of 88.7 mass%. It is therefore assumed that the mass loss would be suppressed by the cross-linking reactions, which possibly involve the OCH_3 groups.

The X-ray diffraction pattern of the product pyrolyzed at 1000°C under nitrogen atmosphere was very broad, as shown in Fig. 7. The product obtained by pyrolysis of POPHPS at 1000°C is therefore considered to be an amorphous material.

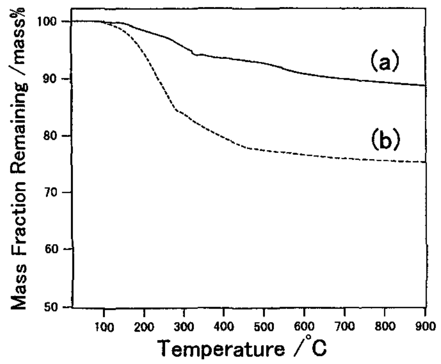


Fig. 6. TGA curves of (a) POPHPS and (b) PHPS.

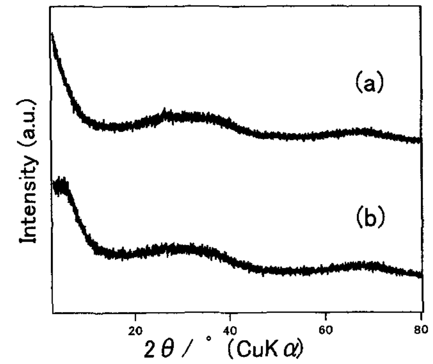


Fig. 7. XRD patterns of (a) PHPS-derived materials and (b) POPHPS-derived materials. (N_2 flow, pyrolyzed at 1000°C for 3h).

4. Conclusions

Polyphosphosilazane (POPHPS) has been synthesized from perhydropolysilazane (PHPS) and phosphonic acid dimethyl ester. Spectroscopic analyses suggest that the SiH_x groups in PHPS react with the PH groups in phosphonic acid dimethyl ester to generate the $(MeO)_2POSi$ environment in the structure of POPHPS. A possible mechanism involves the reaction between the three-coordinated pyridinium salt $[OP(OCH_3)_2]^-$ $[C_5H_5NH]^+$ and the SiH_3 groups in PHPS with H_2 evolution. The ceramic yield of POPHPS up to 900°C under Ar atmosphere is 88.7 mass%, as shown by TG analysis. An amorphous material is obtained by pyrolysis under N_2 atmosphere at 1000°C, as shown by XRD analysis. POPHPS can therefore be expected to be useful as a precursor for silicon-based materials which could exhibit excellent resistance to oxidation, thermal shock, and chemical durability.

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[16] In DEPT NMR, the $\pi/4$ spectra exhibit SiH, SiH_2 and SiH_3 signals in an upward direction. The $3\pi/4$ spectra, on the contrary, exhibit SiH and SiH_3 signals in an upward direction, and SiH_2 signals in a downward direction. The subspectra calculated of $(1/2)(\pi/4 -x\ 3\pi/4)$ consequently exhibit only SiH_2 signals. The parameter x is dependent on an NMR spectrometer.

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