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Organic−Inorganic Hybrid Material of Phenyl-Modified Polysilicophosphate Prepared through Nonaqueous Acid−Base Reaction

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An organic−inorganic hybrid material of phenylsilicophosphate was prepared through the solventless and catalyst-free nonaqueous acid−base reaction of orthophosphoric acid and phenyl-modified chlorosilane. The ^{31}P NMR results showed that the silicophosphate is constituted of an alternating $=(PO-O-Ph_2Si-O)_n-$ network, which is expected to be very homogeneous at an atomic level. It was found that the condensation took place through the nucleophilic addition of the phosphate ion to the organochlorosilane, that is, an S_N2 reaction mechanism. The electron-withdrawing property of the phenyl group attached to the central silicon, hence, forwarded the formation of the silicophosphate network.

1. Introduction

Organic−inorganic hybrid materials have attracted much attention because of their versatile combination of organic and inorganic building units. For example, the hybridization of thermally and mechanically stable inorganic components and optically functional organic components is very attractive for the development of materials for photonics application.[1]

The sol−gel method is usually utilized for preparing such hybrid materials because of the possible low-temperature processing to prevent the decomposition of the organic component. The sol−gel process is, however, sometimes hardly controllable because the hydrolysis and condensation reactions take place competitively, resulting in low reproducibility and the uncertain structure of the obtained materials. Recently, a solventless preparation of the organic−inorganic hybrid materials via a nonhydrolytic route has caught more attention to obtain a higher yield of the condensation reactions.[2−5] We also reported the preparation of organic−inorganic hybrid glasses through nonaqueous acid−base reactions by direct mixture of the starting materials.[6−9] It is expected that these materials are candidate materials for high-figure-of-merit nonlinear optical application because several kinds of optical centers including organic molecules, rare-earth ions, and metal nanoparticles can be simultaneously doped without the degradation of their functionalities. In addition, the hybrid materials with a thermosoftening property are expected to be substitute materials for the low-melting-point glasses presently available.

The glass network formation reaction of the acid−base reaction method is simply represented by the metathesis $M-OH + M'-Cl \rightarrow M-O-M' + HCl\uparrow$ (M and M′ are the glass network forming elements). Tin(II) methyl-modified silicophosphate glass could be obtained via nonaqueous acid−base reactions of orthophosphoric acid, methyl-modified chlorosilane, and tin(II) chloride, the softening temperature of which could be varied from room temperature to 100 °C by the preparation conditions and compositions. The material preparation via acid−base reaction can be carried out under solventless and catalyst-free conditions. A large bulk glass exceeding 5 cm in dimension could be obtained. The network formation reaction is driven only by the difference in the Lewis acidity and/or basicity of the starting materials. Therefore, homogeneity at the atomic level is realized. It was reported for the tin(II) methyl-modified silicophosphate glass that a considerable amount of P−OH remained in the matrix, and the fully condensed phosphate tetrahedral of the Q^3(3OSi) unit had never formed in the system due to the too low acid−base strength of the $H_3PO_4-Me_2SiCl_2$ pair.

In the present study, the organic−inorganic hybrid material of phenyl-modified polysilicophosphate was prepared through the acid−base reaction of H_3PO_4 and Ph_2SiCl_2. The reactivity is discussed on the basis of the inductive effect of organic functional groups (phenyl and methyl[9]) attached to silicon.

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Table 1. Compositions, Preparation Conditions, and Appearances of the Obtained Materials at Room Temperature

system	composition (molar ratio)	heat-treatment temperature/°C	appearance at room temperature
$H_3PO_4-Ph_2SiCl_2$	$H_3PO_4:Ph_2SiCl_2 = 1:x$	25 ($x = 1-2$)	viscous liquid
		100 ($x = 1.5$)	viscous liquid
		250 ($x = 1.5$)	glassy solid
$H_3PO_4-Ph_2SiCl_2-PhSiCl_3$	$H_3PO_4:Ph_2SiCl_2:PhSiCl_3 = 1:1:0.33$	250	glassy solid

The formation of the polysilicophosphate alternating copolymer was discussed, in comparison with the tin(II) methyl-modified silicophosphate previously reported, mainly by ^{31}P and ^{29}Si NMR spectroscopy, which gives us useful information on the local structure around atoms of interest.[10] The thermal and chemical properties of the obtained materials were investigated.

2. Experimental Section

Orthophosphoric acid, H_3PO_4 (MERCK, Germany), diphenyldichlorosilane, Ph_2SiCl_2 (Shin-Etsu Chemical Co., Ltd., Japan), and phenyltrichlorosilane, $PhSiCl_3$ (Shin-Etsu Chemical Co., Ltd., Japan), were used as starting materials. It should be pointed out that most of the commercially available phosphoric acids are supplied as a 75−89% aqueous solution. It is quite important to use anhydrous solid phosphoric acid as in the present study. All the samples were prepared under an atmosphere of N_2 gas (dew point <-60 °C) to expel the HCl gas evolved as a product of the acid−base reaction. The phenyl-modified silicophosphate was prepared from the $H_3PO_4-Ph_2SiCl_2(-PhSiCl_3)$ pair. All the compositions prepared in the present study are summarized in Table 1 with the heat-treatment temperature and the appearance. The scheme of the sample preparation is also shown in Figure 1. The mixture of H_3PO_4 and Ph_2SiCl_2 stirred at room temperature for 6 h was used for the evaluation of the acid−base reactivity by ^{31}P NMR spectroscopy. It was confirmed for the obtained viscous liquid that no further condensation took place at that temperature. To investigate the heat-treatment temperature dependence of the yield, we prepared samples with different heat-treatment temperatures of room temperature (25 °C), 100 °C, and 250 °C. When the heat-treatment temperature was less than ∼100 °C, the products were in a liquid phase even after being cooled to room temperature. The ternary $H_3PO_4-Ph_2SiCl_2-PhSiCl_3$ system was also prepared. The starting materials H_3PO_4, Ph_2SiCl_2, and $PhSiCl_3$ were mixed with stirring and then gradually heated to 250 °C in 6 h. The resultant homogeneous liquid was kept at 250 °C for 3 h and then cooled to ambient temperature, producing a transparent solid hybrid material.

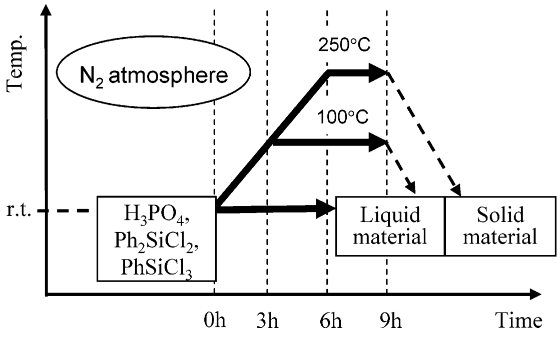

Figure 1. Preparation scheme of phenyl-modified silicophosphate from H_3PO_4, Ph_2SiCl_2, and $PhSiCl_3$.

The ^{31}P NMR and ^{29}Si NMR spectra were measured using a Chemagnetics CMX 400 NMR spectrometer. The chemical shift of ^{31}P was obtained relative to that of 85% H_3PO_4. ^{31}P static NMR measurements were performed for two kinds of liquid products which were heat-treated at 25 and 100 °C. ^{31}P MAS NMR spectra were obtained for the solid samples at a spinning rate of 12 kHz. The chemical shift of ^{29}Si NMR was obtained relative to that of tetramethyl silane using poly(dimethylsilane) as a secondary external reference (−34 ppm). ^{29}Si MAS NMR spectra were obtained at a spinning rate of 10 kHz.

The thermal properties of the solid samples were measured by differential scanning calorimetry, DSC (Diamond DSC instrument, Perkin-Elmer), at a heating rate of 10 °C/min and thermal mechanical analysis, TMA (Thermo plus TMA8310, Rigaku, Japan), at a heating rate of 10 °C/min.

Hydrolysis of the obtained hybrid materials was examined by the weight gain in saturated water vapor at 25 °C. The hybrid samples were prepared in a glass cup to maintain a constant surface area exposed to the surrounding atmosphere of 13.2 cm^2.

Ab initio molecular orbital calculations at the HF/6-31G* level were carried out for the $PO(OSi(C_6H_5)_2Cl_2)_3$ molecule to determine the stabilized molecular structure of the phenyl-modified silicophosphate using the Gaussian 98 program.[11] In the present paper, the stabilized structure is only shown in Figure 4. Further discussion on the other configurations and the electronic structure of the molecules will be reported elsewhere.

3. Results and Discussion

3.1. Acid−Base Reaction between a $H_3PO_4-Ph_2SiCl_2$ Pair. The acid−base reaction is driven by the Lewis acidity and/or basicity difference between the reactants. For example, in the case of the $H_3PO_4-Me_2SiCl_2$ pair, the main product of the phosphorus species was the so-called Q^2(2OSi,OH) unit, where m in $Q^m(m\text{OSi},(3-m)\text{OH})$ indicates the number of bridging oxygens per phosphorus atom.[8] Therefore, two of the three hydroxyl groups attached to the central phosphorus react with chlorosilane to form P−O−Si bonds in which the phosphorus assumes a Q^2(2OSi,OH) structure. Figure 2 shows the ^{31}P NMR spectra of liquid mixtures having the composition, in terms of molar ratio, H_3PO_4:$Ph_2SiCl_2 = 1:x$ ($x = 1-2$), where $x = 1.5$ is the stoichiometric composition, which were obtained by stirring H_3PO_4 and Ph_2SiCl_2 for 6 h at room temperature (25 °C). It was

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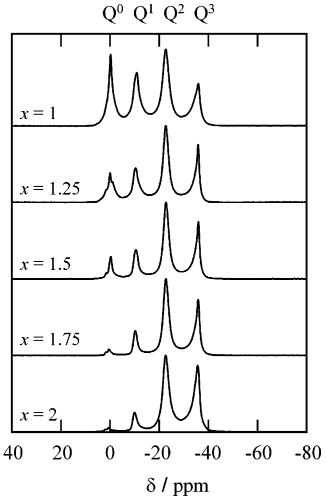

Figure 2. ^{31}P static NMR spectra of phenyl-modified silicophosphate prepared from a H_3PO_4 and Ph_2SiCl_2 pair at 25 °C for 6 h. The compositions of the starting materials are H_3PO_4:Ph_2SiCl_2 = 1:*x* (*x* = 1–2) in molar ratio. All samples are in the liquid state.

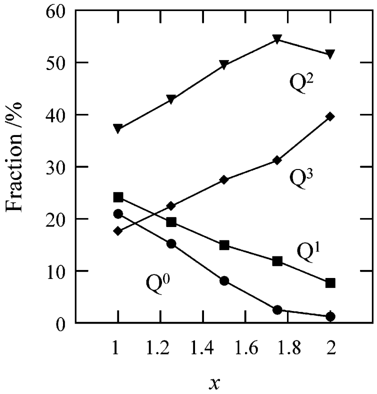

Figure 3. Fraction of each Q^m(*m*OSi,(3 − *m*)OH) species (*m* = 0–3) of the phenyl-modified silicophosphate with nominal compositions of H_3PO_4:Ph_2SiCl_2 = 1:*x* (*x* = 1–2) (6 h reaction at 25 °C).

confirmed by preliminary experiments that the obtained liquids were in an equilibrium state at that temperature. Over the whole range of composition, four distinct peaks were observed at −0.2, −10.6, −22.7, and −35.5 ppm, which are assigned to Q^0(3OH), Q^1(OSi,2OH), Q^2(2OSi,OH), and Q^3(3OSi), respectively. Figure 3 shows the compositional dependence of the fraction of each Q^m(*m*OSi,(3 − *m*)OH) unit in the H_3PO_4–Ph_2SiCl_2 system. It is clear that the main structure is the Q^2(2OSi,OH) unit in the whole composition. The residual Q^0(3OH) and Q^1(OSi,2OH) units remained in the matrix even in the compositional range of $x > 1.5$, where an excess amount of chlorosilane existed in the system. The fractions of the Q^0(3OH) and Q^1(OSi,2OH) units decrease and those of the Q^2(2OSi,OH) and Q^3(3OSi) units increase with increasing Ph_2SiCl_2. On the other hand, as reported in our previous paper,[9] the Q^3(3OSi) unit was not observed for the H_3PO_4–Me_2SiCl_2 system. The formation of Q^3(3OSi) corresponds to the higher reactivity of the H_3PO_4–Ph_2SiCl_2 acid–base pair than the H_3PO_4–Me_2SiCl_2 acid–base pair. The difference of reactivity of the acid–base pairs can be explained by taking into account of the different inductive effects of Ph and Me groups. The Me group is known as a weak electron-releasing substituent and the Ph group as an electron-withdrawing substituent. This inductive effect suggests that the reaction proceeds through the following S_N2-type reactions:[12]

Table 2. ^{31}P NMR Chemical Shifts of the Liquid Mixtures in the H_3PO_4–$R_nSiCl_{(4-n)}$ Systems (R = Me and Ph, *n* = 1 and 2)[a]

unit	chemical shift (ppm)				
	P–Me_2Si^1	P–Ph_2Si^2	P–$PhSi^3$	P–Ph_2PhSi^4	$P_2O_5{}^5$
Q^0(3OH)	0.0 ± 0.1	−0.2 ± 0.2	−0.2	0.2	
Q^1(OSi,2OH)	−10.4 ± 0.1	−10.6 ± 0.1	−12.0	−10.3	
Q^2(2Si,OH)	−21.1 ± 0.1	−22.7 ± 0.1	−28.7	−21.7	
Q^3(3OSi)	−31.0 ± 0.1	−35.5 ± 0.1	−40.2	−35.2 ± 0.8	−55

[a] The nominal compositions are (1) H_3PO_4:Me_2SiCl_2 = 1:1, (2) H_3PO_4:Ph_2SiCl_2 = 1:1, (3) H_3PO_4:$PhSiCl_3$ = 1:1, and (4) H_3PO_4:Ph_2SiCl_2:$PhSiCl_3$ = 1:1:0.33. Reference and preparation conditions (heat treatment temperature and duration): (1) ref 9, rt (room temperature), 3 h; (2) rt, 6 h; (3) rt, 6 h; (4) rt, 6 h; (5) ref 14, Q^3(3OP).

$$H_3PO_4 \leftrightarrows H_4PO_4{}^+ + H_2PO_4{}^- \text{ (autoprotolysis)} \qquad (1)$$

$$R_2SiCl_2 + H_2PO_4{}^- \rightarrow H_2O_3P{-}O{-}SiR_2Cl + Cl^- \qquad (2)$$

$$Cl^- + H_4PO_4{}^+ \rightarrow H_3PO_4 + HCl \qquad (3)$$

Phosphoric acid dissociates to produce phosphate ion in the rapid first step. The autoprotolysis constant, pK_{ap}, of H_3PO_4 was reported to be around 2, which gives rise to enough phosphate ion in the system.[13] The phosphate ion acts as a nucleophilic reagent to attack silicon of chlorosilane, resulting in the formation of a P–O–Si bond. Furthermore, by the repetition of (1)–(3), polycondensation proceeds. An electron-withdrawing substituent such as a Ph group should help to stabilize the negative charge on silicon in the transition states, causing the condensation reaction of the H_3PO_4–Ph_2SiCl_2 pair to increase.

The chemical shift of each unit observed for equimolar liquids of H_3PO_4 and Ph_2SiCl_2 (or $PhSiCl_3$) is summarized in Table 2, together with the previous results obtained for the H_3PO_4–Me_2SiCl_2 system. The chemical shift of Q^3(3OSi) in the H_3PO_4–Ph_2SiCl_2 system (−35.5 ppm) is observed at a smaller magnetic shield by ~20 ppm than that of P_2O_5,[14] indicating that, assuming the same structural configuration of the PO_4 tetrahedra, the partial charge on the oxygens connected to phosphorus in the H_3PO_4–Ph_2SiCl_2 system is smaller. Taking into account that the Pauling electronegativity values of P and Si are 2.1 and 1.8, respectively, Si–O bonding is expected to be more ionic than P–O bonding, resulting in an increase in the partial charge on oxygen by substitution of Si for P. This indicates that the P–O–Si bond is formed through an acid–base reaction. In addition, each Q^m(*m*OSi,(3 − *m*)OH) unit shows a sharp signal. These results indicate that one kind of structure unit corresponds to each signal. Therefore, it can be concluded that the alternating network of $=(PO{-}O{-}Ph_2Si{-}O)_n{-}$ is formed as a result of the nonaqueous acid–base reaction.

Figure 4 shows the molecular structure of Q^3(3OSi) in the H_3PO_4–Ph_2SiCl_2 system optimized by ab initio molecular

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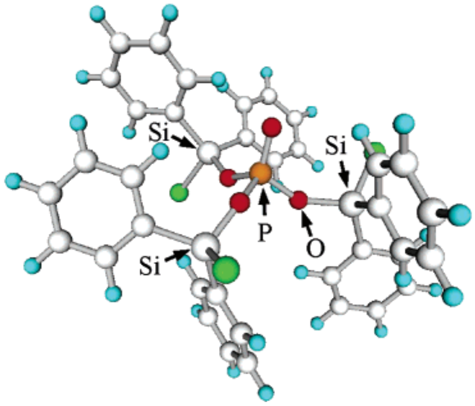

Figure 4. Molecular structure of $PO(OSi(C_6H_5)_2Cl_2)_3$, Q^3(3OSi), in the $H_3PO_4-Ph_2SiCl_2$ system optimized by ab initio molecular orbital calculation at the HF/6-31G* level.

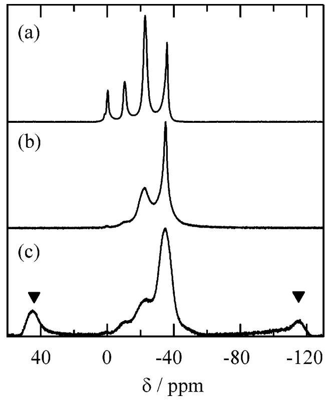

Figure 5. ^{31}P static NMR spectra of liquid samples of phenyl-modified silicophosphate heat-treated for 6 h at (a) 25 °C and (b) 100 °C. (c) ^{31}P MAS NMR spectrum of the hybrid solid sample of phenyl-modified silicophosphate heat-treated at 250 °C for 6 h with the nominal composition H_3PO_4:Ph_2SiCl_2 = 1:1.5. ▼ indicates the spinning sidebands.

Table 3. Fraction (%) of Q^m(mOSi,($3 - m$)OH) of the Mixture Having the Nominal Composition H_3PO_4:Ph_2SiCl_2 = 1:1.5 at Various Heat-Treatment Temperatures

	25 °C	100 °C	250 °C
Q^0(3OH)	8.1	0.0	0.0
Q^1(OSi,2OH)	15.0	0.1	9.1
Q^2(2OSi,OH)	49.4	50.0	22.8
Q^3(3OSi)	27.5	49.9	68.1

orbital calculation at the HF/6-31G* level.[15] We can see that the structure of Q^3(3OSi) is so crowded with six bulky phenyl groups that the formation of Q^3(3OSi) is inhibited to a considerable extent. Therefore, a steric hindrance effect of the bulky phenyl group in the S_N2 condensation reaction should be taken into account. Figure 5 shows the ^{31}P NMR spectra of the mixture of a nominal composition of H_3PO_4:Ph_2SiCl_2 = 1:1.5 heat-treated at (a) 25 °C, (b) 100 °C, and (c) 250 °C. All four peaks, Q^0(3OH)−Q^3(3OSi), are observed in the mixture obtained through the reaction at 25 °C. The fraction of each Q^m(mOSi,($3 - m$)OH) unit for the different heat-treatment temperatures is shown in Table 3. Raising the heat-treatment temperature to 100 and 250 °C drastically decreased Q^0(3OH) and Q^1(OSi,2OH) and increased Q^3(3OSi) to become predominant at 250 °C. The formation of Q^3(3OSi) is thus revealed to be thermally enhanced. This also supports the S_N2 mechanism of the condensation reaction.

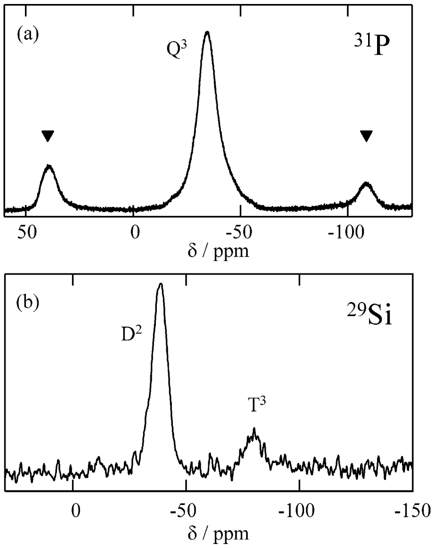

Figure 6. (a) ^{31}P MAS NMR and (b) ^{29}Si MAS NMR spectra of phenyl-modified silicophosphate with nominal composition of H_3PO_4:Ph_2SiCl_2:$PhSiCl_3$ = 1:1:0.33. ▼ indicates the spinning sidebands.

3.2. Complete Condensation in Organically Modified Polysilicophosphate Material. In the case of the $H_3PO_4-Ph_2SiCl_2$ system heat-treated at 250 °C, although a considerable amount of Q^3(3OSi) formed, a small amount of Q^1(OSi,2OH) and Q^2(2OSi,OH) still remained in the matrix, which is considered to be due to the large steric effect of the phenyl group and the insufficient electrophilicity of silicon for the formation of the Q^3(3OSi) unit. To scavenge the residual P−OH, the chemical composition was modified by incorporating $PhSiCl_3$ while the stoichiometry of the system was maintained. A lower steric hindrance and a more basic environment are expected for $PhSiCl_3$ than for Ph_2SiCl_2 because of the greater electron-withdrawing ability and smaller occupied volume of the chloride ion than the Ph group. Actually, the ^{31}P NMR chemical shift in the $H_3PO_4-PhSiCl_3$ system (see Table 2) is more negative than that in the $H_3PO_4-Ph_2SiCl_2$ system, indicating that the local environment of the central phosphorus is more basic. Figure 6 shows the ^{31}P MAS NMR and ^{29}Si MAS NMR spectra of the sample with a stoichiometric composition, in terms of molar ratio, of H_3PO_4:Ph_2SiCl_2:$PhSiCl_3$ = 1:1:0.33 heat-treated at 250 °C. The ^{31}P NMR spectrum consists of only one peak corresponding to the Q^3(3OSi) unit. In the ^{29}Si MAS NMR spectrum, two peaks (−38.3 ppm, −80.5 ppm) were observed. The peak at −38.3 ppm can be assigned to D^2(2OP,2Ph), which indicates that the silicon has two phenyl groups and two bridging oxygens. The peak at −80.5 ppm can be assigned to T^3(3OP,Ph), which indicates that the silicon has one phenyl group and three bridging oxygens.[16,17] The area ratio of the two peaks, area(D^2(2OP,2Ph))/area(T^3(3OP,Ph)) = 3.4, was almost comparable to the

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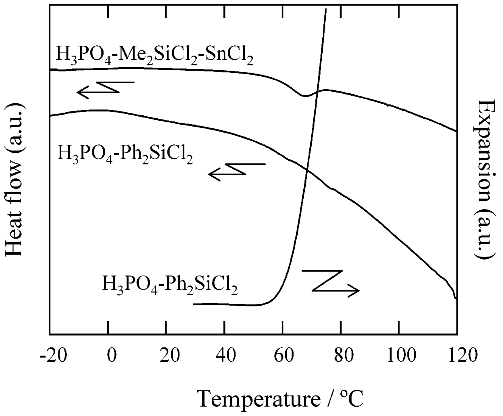

Figure 7. TMA curve of the hybrid sample of phenyl-modified silicophosphate and DSC curves of the hybrid samples of phenyl-modified silicophosphate and tin(II) methyl-modified silicophosphate.

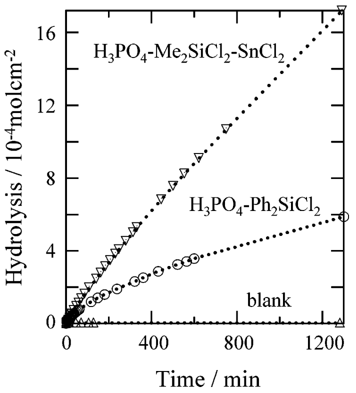

Figure 8. Time dependence of the weight gain of the hybrid samples of phenyl-modified silicophosphate and tin(II) methyl-modified silicophosphate in saturated water vapor at 25 °C.

nominal composition ratio of $Ph_2SiCl_2/PhSiCl_3 = 3.3$. No trace of the starting materials and the residual species D^0(2Ph,2Cl), D^1(OP,2Ph,Cl), T^0(Ph,3Cl), T^1(OP,Ph,2Cl), and T^2(2OP,Ph,Cl) was observed, indicating that the chlorosilane completely reacted with phosphoric acid. The ^{31}P and ^{29}Si MAS NMR spectra in the present study have revealed that the incorporation of $PhSiCl_3$ into the $H_3PO_4-Ph_2SiCl_2$ binary system can make the acid−base reaction complete. The improvement in the yield is ascribed not only to the electrophilic silicon of $PhSiCl_3$ but also to the lower steric hindrance of $PhSiCl_3$ than Ph_2SiCl_2.

3.3. Thermal and Chemical Properties of Phenyl-Modified Silicophosphate Hybrid Materials. Figure 7 shows the thermal properties of the phenyl-modified silicophosphate hybrid material obtained from the $H_3PO_4-Ph_2SiCl_2$ system as measured by DSC and TMA. The phenyl-modified silicophosphate hybrid material showed a sudden rise in the thermal expansion curve at 63 °C, which corresponds to the glass transition temperature, T_g. The coefficients of thermal expansion, CTEs, were estimated to be 5.0×10^{-5} and 3.7×10^{-2} K^{-1} below and above T_g, respectively. On the other hand, the DSC measurements showed that no endothermic step caused by the glass transition was observed for the phenyl-modified silicophosphate hybrid material. This indicates that the glass transition temperature of the present hybrid sample is distributed over a wide temperature range around the T_g observed in TMA. This may be due to the distribution of both the molecular weight and molecular configuration in the phenyl-modified silicophosphate materials. The DSC curve of the tin(II) methyl-modified silicophosphate hybrid glass obtained from the $H_3PO_4-Me_2SiCl_2-SnCl_2$ system, which has a distinct endothermic step around 60 °C, is also shown in Figure 7 for comparison. The molecular weight of the methyl system is less distributed and estimated around several hundred (∼400) determined by the end group determination method using NMR spectra.[9] Contrary to the methyl system, it was impossible to measure the molecular weight of phenyl-modified silicophosphate by the same method due to the fact that the fraction of the end group in the system is negligibly small. In other words, the silicophosphate network of phenyl-modified silicophosphate is well developed. In general, some organic polymers are characterized by a distribution of glass transition temperatures differing from those of inorganic glasses, not giving rise to a definite T_g by DSC measurements. We concluded that the thermal behavior of the phenyl-modified silicophosphate around the glass transition temperature seems to be rather polymer-material-like in contrast with the methyl-modified one.

The phenyl-modified silicophosphate hybrid material appeared to have much improved chemical durability compared with the tin(II) methyl-modified silicophosphate hybrid glass. The water vapor durability of the obtained hybrid material having the nominal composition $H_3PO_4:Ph_2SiCl_2 = 1:1.5$ was examined. When the silicophosphate network is subjected to hydrolysis, a weight gain due to the addition of water should be observed

$$Si-O-P + H_2O \rightarrow Si-OH + P-OH$$

A smaller weight gain corresponds to the higher water durability of the sample. The extent of hydrolysis per surface area is shown in Figure 8 together with that of tin(II) methyl-modified silicophosphate having the nominal composition $H_3PO_4:Me_2SiCl_2:SnCl_2 = 1:1:0.5$. It was found that the phenyl-modified silicophosphate hybrid sample exhibited a smaller hydrolysis rate at the surface layer than the tin(II) methyl-modified silicophosphate hybrid glass did. After 24 h, the degree of hydrolysis of the phenyl-modified silicophosphate hybrid sample became about one-third of that of the tin(II) methyl-modified silicophosphate hybrid glass. The phenyl-modified silicophosphate hybrid material retained transparency in an ambient atmosphere for more than one month, which is better than a typical ultraphosphate glass. On the other hand, tin(II) methyl-modified silicophosphate lost transparency within several minutes under the same conditions. In general, it is well-known that the ultraphosphate (Q^3(3OP) structure) has very low water durability because of the localization of the electron at the P=O double bond.[18,19] The hybrid material presented here also has an ultraphosphate-like structure. The difference between this hybrid material and the general ultraphosphate is that the hybrid materials have a network consisting of alternating $=(PO-O-Ph_2Si-O)_{n-}$. The hydrophobic nature of the phenyl groups attached to silicon next to phosphate is

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(18) Wazer, J. R. V.; Holst, K. A. *J. Am. Chem. Soc.* **1950**, *72*, 639−644.
(19) Wazer, J. R. V. *J. Am. Chem. Soc.* **1950**, *72*, 644−647.

considered to effectively prevent the water from attacking the active sites around the phosphate unit.

4. Conclusions

The organic−inorganic hybrid material phenyl-modified silicophosphate was prepared by a nonaqueous acid−base reaction. The hybrid material was found to have a unique structure which is characterized by an alternating $=(\mathrm{PO{-}O{-}Ph_2Si{-}O})_n-$ network. In the case of the H_3PO_4−Ph_2SiCl_2−$PhSiCl_3$ ternary system, almost all the phosphate and siloxane groups assume fully condensed structures. The chemical durability of the present hybrid material was rather better than those of the previous tin(II) methyl-modified silicophosphate hybrid glass and usual ultraphosphate glasses. The improved chemical durability is thought to come from the structure of the alternating $=(\mathrm{PO{-}O{-}Ph_2Si{-}O})_n-$ network. It is expected that the unique alternating copolymer structure creates a new material group and opens an application field for organically modified inorganic polymer chemistry.

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