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Articles

Hexagonal-Structured Polysiloxane Material Prepared by Sol−Gel Reaction of Aminoalkyltrialkoxysilane without Using Surfactants

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A higher-order nanostructured polysiloxane was prepared by the sol−gel reaction of 3-aminopropyltrimethoxysilane catalyzed by a strong acid such as hydrochloric acid or nitric acid. In the X-ray diffraction (XRD) profiles, this compound had three peaks: one prominent peak and two minor peaks. The *d*-value ratios of the three peaks were $1:{}^{1}/_{\sqrt{3}}:{}^{1}/_{2}$. This strongly indicates the formation of a hexagonal phase. The peaks shifted due to a change in the humidity and the resulting product was completely dispersed in water. In addition, the *d*-values of each peak of the anion-exchanged product changed while depending on the bulk of the counteranion. Such behaviors cannot be observed for hexagonal mesoporous silica. Therefore, we estimated that this hexagonal phase came from a stacking of rodlike polymer with Si−O−Si framework at the core and ammonium groups extruding outside. The transmission electron microscopy (TEM) images showed a stripe pattern, indicating that the rodlike polysiloxane had parallel stacking. The scanning electron microscopy (SEM) image showed that the aggregate of the polysiloxane lined up in a regular direction, suggesting that the nano-ordered rodlike structure influences the micro-ordered regular structure. This rodlike polysiloxane with a hexagonal phase belongs to a new type of higher-ordered material, based on siloxane bonds.

Introduction

Biological macromolecules such as proteins, nucleic acids, and polysaccharides are known to be controlled by not only their primary structures but also those of higher-ordered structures.[1] Supramolecular chemistry imitates such biomolecular systems, in an attempt to construct an architecture with the higher-ordered structure to render the higher functionality to the materials.[2] Therefore, the synthesis and control of the higher-ordered architecture for the synthetic macromolecules has been one of the important subjects in the field of supramolecular chemistry, for academic and application reasons.

So far, several organic synthetic macromolecules with higher-ordered structures have been developed using this supramolecular chemistry, e.g., inclusion complexes,[3] helical polymers,[4] noncovalent-bond-type dendrimers,[5] etc. The various interactions of organic macromolecules, e.g., hydrogen bond, hydrophobic interaction, and coordinated bond, are the driving force for the construction of higher-ordered structures. On the other hand, in the field of inorganic materials, several studies have been conducted on the preparation of higher-ordered materials. As one of the methods for the preparation of these higher-ordered materials, the hydrothermal synthesis of silica-based materials using

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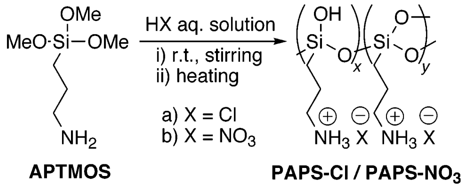
surfactants was reported.[6] Higher-ordered materials were also synthesized from layered silicates, kanemite, and surfactants under relatively mild conditions.[7] Porous silicas with regular structures have been formed by the calcination of these obtained materials to remove the surfactants, and the products are used as catalysts[8] and adsorbents.[9] Another method for preparing the inorganic higher-ordered materials is the hydrolysis and polycondensation (sol−gel reaction) of metal alkoxides, e.g., alkoxysilanes, utilizing self-assembly of the surfactants.[10,11] The surfactants forming micelles of various hypermorphs, such as hexagonal[10] and lamellar,[11] act as templates and allow the sol−gel reaction of alkoxysilanes to form a regular structure. Thus, the higher-ordered materials based on siloxane bonds, such as the silica and polysiloxane materials, have been synthesized only with the aid of the hydrophobic interaction of the surfactants[6,7,10,11] or long-chain alkyl groups in the monomers, which have the same role with the surfactants.[12] For the development of new functions and applications, the exploration of a novel synthetic method of higher-ordered materials based on siloxane bonds is considered important.

Recently, we found a new preparation method for a higher-order nanostructured polysiloxane material using a simple sol−gel method.[13] The synthesis was conducted by the sol−gel reaction of 3-aminopropyltrimethoxysilane (APTMOS) catalyzed by hydrochloric acid. This is the first-reported preparation of a higher-ordered material based on siloxane bonds without using surfactants or long-chain alkyl groups in the monomers. However, its detailed structure and formation mechanism have not yet been elucidated.

Scheme 1. Synthesis of Nanostructured Poly(3-aminopropyl)siloxane Complex Salts



In the present paper, we report the preparation of a higher-order nanostructured polysiloxane by the sol−gel reaction of APTMOS, and characterization of the resulting polysiloxane by X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Furthermore, to clarify the detailed structure, we examined the influence of humidity, its swelling behavior in water, ion-exchange reaction, and measured nitrogen adsorption−desorption isotherm. Consequently, we confirmed that the resulting rodlike polymer with Si−O−Si framework at the core was stacked to form a hexagonal phase. The present polysiloxane is a new type of hexagonal structured material based on siloxane bonds. In addition, we proposed the formation mechanism of this polysiloxane material. Emphasis was placed on the relationship between the formation mechanism of the polysiloxane with the hexagonal phase and the role of the counteranion.

Results and Discussion

Synthesis of Nanostructured Poly(3-aminopropyl)siloxane Complex Salts. When the hydrolysis and polycondensation of APTMOS were performed in the hydrochloric acid or nitric acid aqueous solution by heating (ca. 60−70 °C) in open systems until the solvent was distilled completely away, nanostructured polysiloxanes that contained alkylammonium groups—poly(3-aminopropyl)siloxane hydrochloride (PAPS−Cl) and poly(3-aminopropyl)siloxane nitrate (PAPS−NO$_3$)—were obtained (Scheme 1a,b).

XRD Measurement. For the XRD measurement, the films of the products on the glasses were obtained by drying the aqueous product solutions spread on flat glass substrates. Spectra a and b in Figure 1 show the XRD patterns of the films of products obtained using the acid catalysts: hydrochloric acid in spectrum a and nitric acid in spectrum b. These XRD profiles showed three peaks—one prominent peak and two minor peaks—with the *d*-value ratio of $1:{}^{1}/_{\sqrt{3}}:{}^{1}/_{2}$, strongly indicating that the nanostructures consist of a hexagonal phase, namely these three peaks can be assigned to the (100), (110), and (200) peaks. Support for this proposal is obtained by comparison with the diffraction pattern from randomly oriented polysiloxane powder samples (see spectra c and d in Figure 1). The (110) reflections of powdered samples are relatively stronger than those of the film samples. The reduction of the (110) reflection intensity for the film samples indicates that the *c*-axis of the hexagonal unit cell is oriented parallel to the

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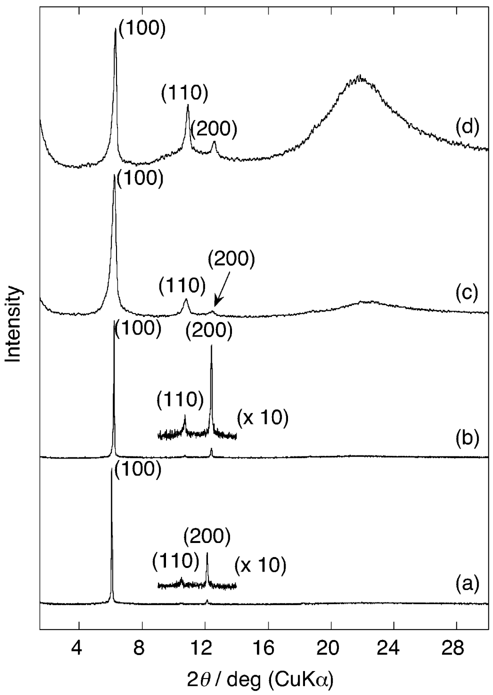


Figure 1. XRD patterns of the products: (a) film for PAPS−Cl, (b) film for PAPS−NO_3, (c) powdered PAPS−Cl, and (d) powdered PAPS−NO_3.

surface of the glass substrate. The broad peak centered at $2\theta = 22°-23°$ can be attributed to an irregular array of aminopropyl side chains. Generally, the XRD profiles of polysiloxanes with alkyl side chains show broad peaks at $2\theta \approx 20°-30°$.[12b] These XRD measurements revealed that the polysiloxanes with a hexagonal phase were formed using inorganic strong acids such as hydrochloric acid and nitric acid. However, we cannot determine, based on only these data, whether this hexagonal phase came from a mesoporous honeycomb structure or a stacking of a rodlike polymer with Si−O−Si framework at the core. The latter would be a new type of material, based on siloxane bonds. Therefore, we examined the influence of the humidity, swelling behavior in water, ion-exchange reaction, and measured nitrogen adsorption−desorption isotherm to elucidate the detailed structure.

Influence of Humidity and Swelling Behavior in Water. The XRD measurement of PAPS−Cl was performed while changing the humidity in the range of 8%−90% (Table 1). The three peaks—(100), (110), and (200)—shifted by changing the humidity; that is, the *d*-values increased for a high humidity and decreased for a low humidity. On the other hand, the *d*-value ratios of the three peaks did not change. These results indicate that the hexagonal phase was maintained even if the *d*-value changed by varying the amount of moisture. Such a behavior cannot be observed for hexagonal mesoporous silica (HMS). Therefore, we estimated that this hexagonal phase came from a stacking of rodlike polymer that consists of a Si−O−Si framework at the core and ammonium groups extruding outside.

Table 1. Influence of Humidity[a]

	d-value (nm)			*d*-value ratio[b]		
relative humidity (%)	(100)	(110)	(200)	(100)	(110)	(200)
8	1.286			1.000		
14	1.305	0.753		1.000	0.577	
20	1.326	0.764	0.668	1.000	0.576	0.504
30	1.365	0.792	0.685	1.000	0.580	0.502
40	1.393	0.804	0.696	1.000	0.577	0.500
50	1.415	0.817	0.708	1.000	0.577	0.500
60	1.441	0.837	0.722	1.000	0.581	0.501
70	1.469	0.850	0.734	1.000	0.579	0.500
80	1.499	0.875	0.749	1.000	0.584	0.500
90	1.538	0.895	0.773	1.000	0.582	0.503

[a] Retention time at each humidity was 2 h. [b] The theoretical ratio of hexagonal phase; (100) = 1, (110) = $1/\sqrt{3} = 0.577$, (200) = $1/2 = 0.5$.

Furthermore, to prove that this hexagonal phase came from the stacking of rodlike polymer, the swelling behavior in water was examined. Figure 2 shows the XRD patterns for the film of PAPS−Cl on glass after immersion in water for 30 s. No peak was observed before drying, indicating that many water molecules existed between the polymers and the polymers were completely separated (see spectrum a in Figure 2). With aging, peaks appeared, their positions shifted to higher 2θ values, and their intensities gradually increased (see spectra b−e in Figure 2). This behavior indicates that the rodlike polymer, completely dispersed in the water, gradually aggregated again and the hexagonal phase was constructed.

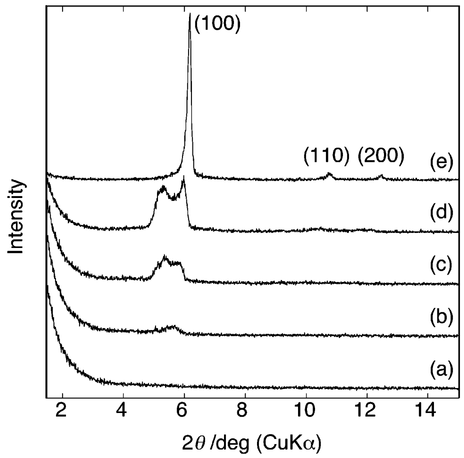
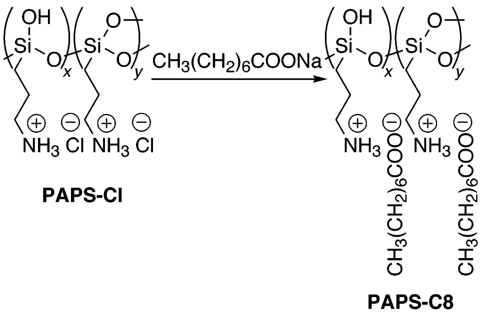


Figure 2. Evolution of the XRD profile starting from the PAPS−Cl fully dispersed in water: (a) start of aging, (b) after 8 min, (c) after 16 min, (d) after 24 min, and (e) after 32 min.

The behavior that *d*-values shifted or the structure collapsed by changing the amount of moisture would be evidence for the rodlike structure with alkylammonium groups around the polysiloxane core portion.

Ion-Exchange Behavior of PAPS−Cl. Because PAPS−Cl has ammonium groups around the polysiloxane core portion and Cl^- anions as counterions, an anion-exchange property can be expected. Therefore, we investigated the ion-exchange reaction with a fatty acid salt such as sodium *n*-octanoate (C8) (Scheme 2). By pouring the PAPS−Cl aqueous solution into an aqueous solution of sodium *n*-octanoate, precipitation immediately occurred. The obtained water-insoluble product, hereafter denoted as PAPS−C8, was characterized by infrared (IR) spectroscopy, carbon, hydrogen, and nitrogen (CHN) elemental analysis, and XRD. The IR spectrum of the product displayed strong absorptions at 1407 and 1555 cm^{-1} that were attributable to the carboxylate anion of the guest molecule in the product. The CHN elemental analysis data showed that the [guest]/[NH_3^+ in host] molar ratio for the product was

Scheme 2. Ion-Exchange Reaction of PAPS−Cl with Sodium *n*-Octanoate



ca. 1.0, indicating that the Cl^- in PAPS−Cl was completely substituted by the *n*-octanoate.

The XRD patterns of a film and a powder for PAPS−C8 are shown in Figure 3. The film of the product was obtained by drying an ethanol solution of product spread on a flat glass substrate. The XRD profile of the film sample showed peaks for a typical hexagonal phase, namely the *d*-value ratio is 1 (100):$^1/_{\sqrt{3}}$ (110):$^1/_2$ (200):$^1/_{\sqrt{7}}$ (210):$^1/_3$ (300), and the *d*-values of each peak of PAPS−C8 increase more than those of the original polysiloxane (PAPS−Cl; see spectrum a in Figure 1). This indicates that the diameter of the rodlike polysiloxane increased when the Cl^- anion as the counterion was exchanged into the bulky *n*-octanoate. The (110) peak of the powder sample is relatively stronger than that of the film sample (see spectrum b in Figure 3), as well as the original product (PAPS−Cl), indicating that the hexagonal unit of the film sample is orderly aligned to the surface of the glass substrate. From these results, we confirmed that the diameter of the rodlike polysiloxane was changed, according to the size of the counterion, while the hexagonal phase was maintained. Based on all the XRD results, it was suggested that the obtained polysiloxanes had a rodlike structure with a Si−O−Si framework at the core to form a hexagonal phase.

When the ion-exchange reaction was performed using the fatty acid salts with a longer alkyl chain (sodium *n*-decanoate, sodium *n*-dodecanoate, and sodium *n*-tetradecanoate), the peaks that are typical for the hexagonal phase were not obtained. We assumed that the interaction between the guest fatty acid salts with a longer alkyl chain was too strong to maintain the hexagonal phase. On the other hand, when the fatty acid salts with a shorter alkyl chain (sodium *n*-hexanoate and sodium *n*-butanoate) were used, the products did not form precipitates. Detailed studies on the ion-exchange reaction of PAPS−Cl with fatty acid salts are now in progress.

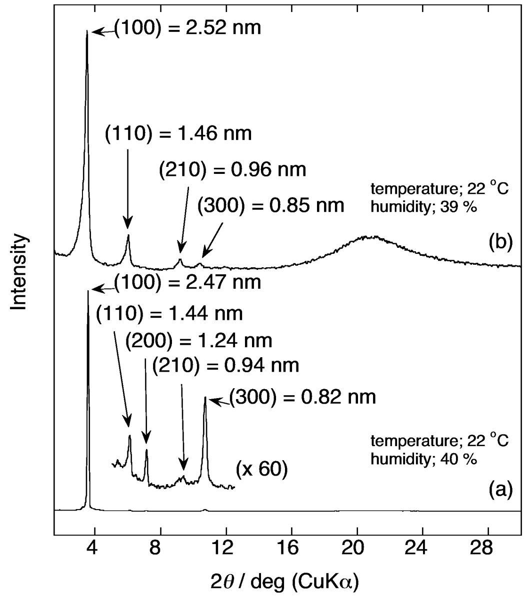


Figure 3. XRD patterns of PAPS−C8: (a) film sample and (b) powdered sample.

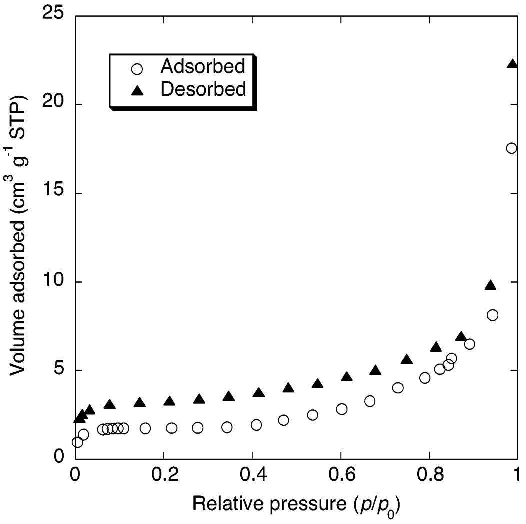


Figure 4. Nitrogen adsorption−desorption isotherm at 77 K of PAPS−Cl.

Nitrogen Adsorption−Desorption Isotherm Measurement. The nitrogen adsorption−desorption isotherm at 77 K of PAPS−Cl is shown in Figure 4. The Brunauer−Emmett−Teller (BET) surface area of PAPS−Cl was <6 m^2/g. This result indicates that the present polysiloxane (PAPS−Cl) was a dense structure. It is consistent with the XRD results described previously.

Electron Microscopic Analysis. The TEM images of PAPS−Cl and PAPS−NO_3 are shown in Figure 5, and a stripe pattern was observed. These patterns indicate that the rodlike polysiloxanes are stacked parallel. The periodic distance of these stripe patterns was ca. 0.95 nm. This value is different from the *d*-value measured by XRD (ca. 1.4 nm for a relative humidity of 40%−50%). TEM observation was conducted under high vacuum, and the specimens were heated by electron beam irradiation. Therefore, the moisture between rodlike polysiloxanes would completely disappear, leading to a decrease of the periodic distance. A preliminary XRD measurement at 220 °C showed that the peak shifted to ca. 1 nm. This result is consistent with the TEM observations.

The SEM image shows the aggregate, which lines up in a regular direction (Figure 6). This fact suggests that nano-ordered rodlike structure influences the micro-ordered regular structure. The appearance of the PAPS−Cl obtained by lyophilization seems to reflect this microstructure (Figure 7).

From the results described previously, it is estimated that the rodlike polysiloxane regularly aligns to form a hexagonal phase. In our previous report, we assumed that the product has a layered structure,[13] because the stripe patterns in the TEM images were interpreted to

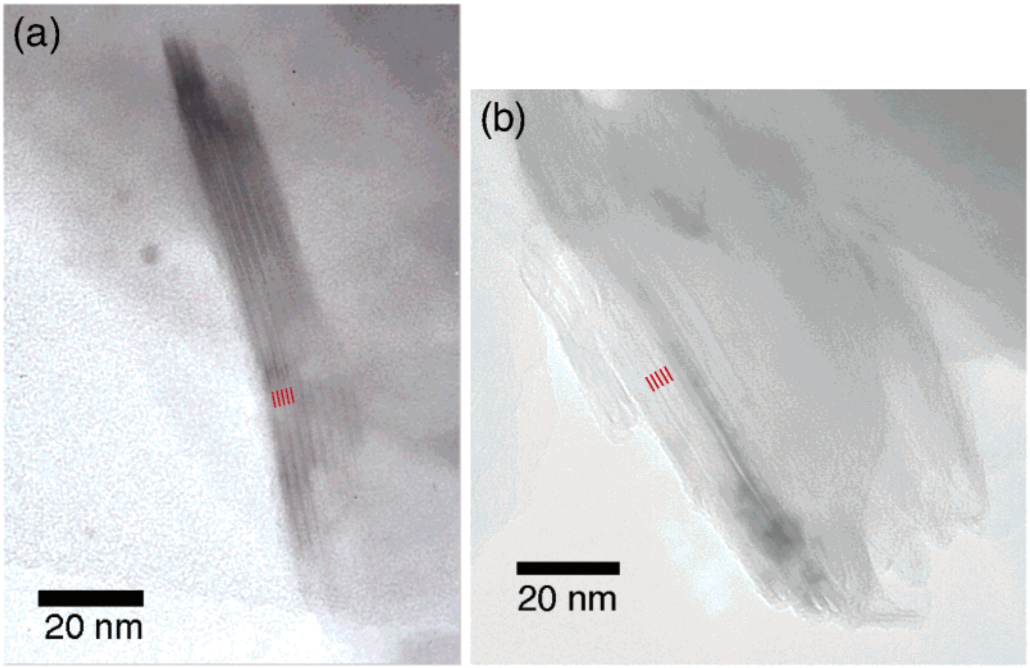


Figure 5. TEM images of (a) PAPS−Cl and (b) PAPS−NO_3.

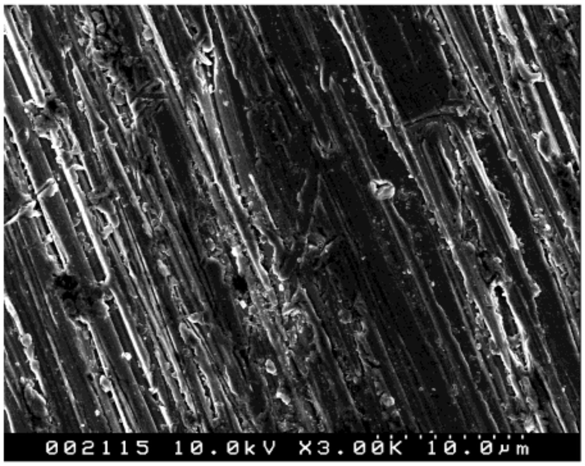


Figure 6. SEM image of PAPS−Cl.

Figure 7. Photograph of PAPS−Cl.

be the side view of the stacked layers.[14] Furthermore, this product showed the behavior of an ion-exchange reaction, which is typical for layered materials such as clay minerals, accompanied by a change in the *d*-value.[15] However, based on the present detailed characterization, particularly the XRD measurements, we concluded that the hexagonal phase is a more logical assignment.

Proposed Formation Mechanism of Rodlike Polysiloxane with the Hexagonal Phase. On the basis of the XRD measurement, we assumed that the present product had a hexagonal phase. The influence of humidity, swelling behavior in water, ion-exchange behavior, and nitrogen adsorption−desorption isotherm indicate that this hexagonal phase is due to the stacking of rodlike polysiloxane. Such a structure probably originates from the formation of the micelle in which ammonium groups extrude outside. Therefore, the formation of an ion complex is required because the ion complex has strong hydrophilicity. Based on these results, the mechanism for the formation of the structure with a hexagonal phase is proposed (Scheme 3). We assumed that the acid acted not only as a catalyst for hydrolysis, but also as a reagent for the formation of an ion complex with the amino groups. Rodlike micelles, which consisted of a hydrophilic ion complex site outside and an alkoxysilane and/or hydroxysilane site inside, would be organized in an aqueous solution, and then polycondensation might occur, leading to a one-dimensional rodlike polymer with a Si−O−Si framework at the core. Finally, this rodlike polymer would be stacked by drying to form the hexagonal phase. Here, we expected that this driving force for the formation of a rodlike micelle was not only a hydrophobic interaction utilized for the usual micelle formation but also self-

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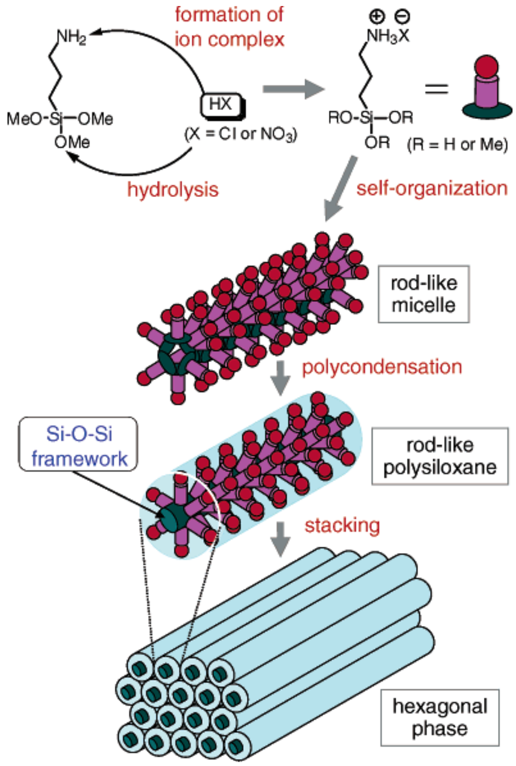
Scheme 3. Proposed Formation Mechanism of Rodlike Polysiloxane with Hexagonal Phase



organization of an ion complex, because the alkyl group (aminopropyl group) of APTMOS is too short to generate a strong hydrophobic interaction. The ion complex may be a key factor for formation of the structure.

Therefore, to examine the influence of an ion complex composed of an ammonium cation and a counteranion, a sol−gel reaction was performed by changing the amount of acid, and characterization was conducted via XRD and CHN elemental analysis. The XRD patterns of the films of the products obtained by using various amounts of nitric acid are shown in Figure 8. When the nitric acid existed in excess against APTMOS, the (100) peaks are very sharp, indicating a higher-ordered hexagonal phase (see spectra d−f in Figure 8). On the other hand, when the amounts of the nitric acids were less than those of the APTMOS, all the (100) peaks become broad (see spectra a and b in Figure 8). This indicates that a regular ordered structure is not formed for [acid]/[APTMOS] < 1. On the basis of the CHN elemental analysis data, the molar ratios of [NO_3^- as a counterion]/[NH_3^+ groups in polysiloxane] in the PAPS−NO_3 were calculated to be 0.99 (for spectrum f), 1.02 (for spectrum e), 1.01 (for spectrum d), 0.57 (for spectrum c), 0.60 (for spectrum b), and 0.15 (for spectrum a). These results reveal that complete coverage of the amino groups in the surface of the products with counteranions is necessary for the formation of the rodlike structure with the higher-ordered hexagonal phase.

Moreover, to investigate the influence of the counteranions on the construction of an ordered structure, we used an ion-exchange resin. An aqueous solution of PAPS−NO_3 with the perfect covering of counteranions (NO_3^-) was passed through a column of an anion-exchange resin treated with a NaOH aqueous solution.

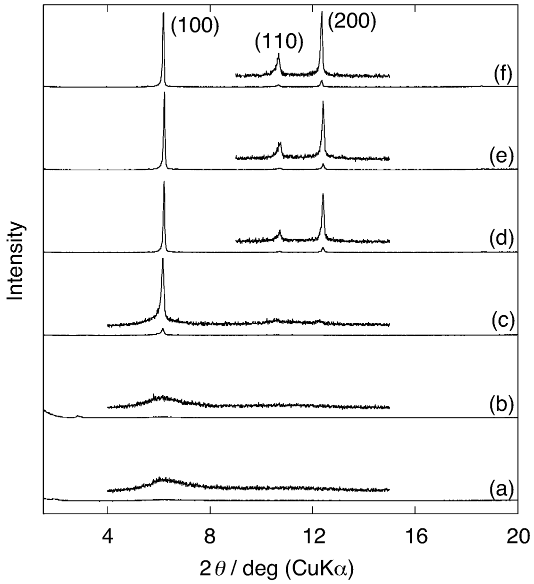


Figure 8. XRD patterns of the products obtained from various amounts of nitric acid as catalysts: feed ratios of [nitric acid]/[APTMOS] are (a) 0.50, (b) 0.75, (c) 1.00, (d) 1.25, (e) 1.50, and (f) 2.00. Amount of each product on glass substrate was ca. 10 mg/cm^2.

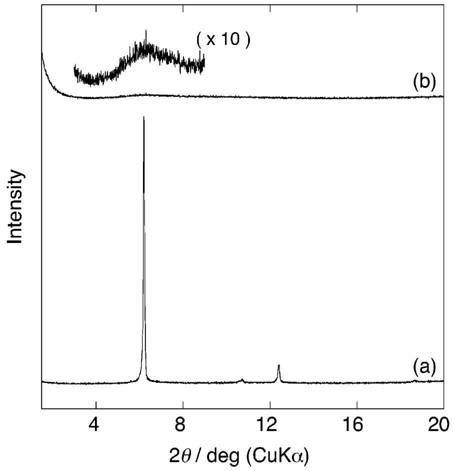


Figure 9. XRD patterns of (a) thin film for PAPS−NO_3 and (b) thin film for the product, which was treated PAPS−NO_3 with anion-exchange resin; the amount of each product on the glass substrate was ca. 10 mg/cm^2.

By this treatment, the counteranions of PAPS−NO_3 were converted to hydroxide (OH^-) ions from the nitrate (NO_3^-) ions. Free amino groups were formed when the water of the product aqueous solution was evaporated, which was confirmed by IR spectrometry (not shown) and CHN elemental analysis. As shown in spectrum b in Figure 9, the XRD pattern of the product after treatment with the anion-exchange resin clearly indicates the collapse of the ordered hexagonal phase. From these results, it can be concluded that the ion complex between the ammonium cation and counteranion is vital for the construction of a rodlike structure with a higher-ordered hexagonal phase.

Conclusions

We have synthesized a rodlike polysiloxane with a higher-ordered hexagonal phase by the sol−gel reaction of 3-aminopropyltrimethoxysilane (APTMOS) catalyzed by a strong acid such as hydrochloric acid or nitric acid without using surfactants. The present polysiloxane is a new type of higher-ordered material based on siloxane bonds; namely, a Si−O−Si framework exists at the core portion of the rodlike polymer forming the hexagonal phase. We clarified that ion complexes composed of ammonium groups around the polysiloxane core portion and counteranion are necessary for the construction of the rodlike structure with a hexagonal phase. We can expect numerous applications using the present polysiloxane, because this material has various characteristics, such as having many functional groups in the surface, anisotropy, and water solubility.

Experimental Section

Materials. All reagents and solvents were of reagent-grade quality, commercially purchased, and used without further purification.

Typical Procedure for the Preparation of PAPS−Cl. An 8.96 g (50 mmol) sample of 3-aminopropyltrimethoxysilane (APTMOS) was added to 150 mL of a hydrochloric acid aqueous solution (0.5 mol/L), and the reaction solution was stirred for 2 h at room temperature, followed by heating to 60°−70 °C in the open system until the solvent was completely distilled away. After the product was left overnight at 100 °C, it was dissolved in 300 mL of water and the product solution was lyophilized to yield ca. 7.31 g of needlelike white PAPS−Cl (yields of ca. 100%: the ideal chemical formula of PAPS−Cl [$Cl\cdot NH_3(CH_2)_3SiO_{1.5}$, (FW = 146.7)] was used).

Ion-Exchange Reaction of PAPS−Cl with Sodium *n*-Octanoate. A 0.147 g sample of PAPS−Cl was dissolved in 10 mL of water. The solution was poured into 10 mL of sodium *n*-octanoate aqueous solutions (0.1 mol/L) to precipitate the water-insoluble product. The precipitated products were collected by filtration, washed with water and then vacuum-dried at room temperature to yield ca. 0.050 g of white powdered PAPS−C8 (yields ca. 20%: the ideal chemical formula of PAPS−C8 [$CH_3(CH_2)_6COO\cdot NH_3(CH_2)_3SiO_{1.5}$, (FW = 254.4)] was used).

Preparation of PAPS with Free Amino Groups from PAPS−NO$_3$ Using Ion-Exchange Resin. A 0.50 g sample of PAPS−NO$_3$ was dissolved in 10 mL of water and the product solution was passed through a column of the anion-exchange resin (Amberlite IRA-900), which was prepared with a sodium hydroxide aqueous solution (1 N). Water from the product aqueous solution, after having passed through the column, was evaporated under reduced pressure using a rotary evaporator and then vacuum-dried at room temperature to yield ca. 0.30 g of PAPS (yields ca. 94%: the ideal chemical formula of PAPS [$NH_2(CH_2)_3SiO_{1.5}$, (FW = 110.2)] was used).

Measurements. XRD analysis of the products was conducted at a scanning speed of 2° 2θ/min, using a diffractometer (model RINT 1200, Rigaku Co., Ltd.) with nickel-filtered Cu Kα radiation (λ = 0.15418 nm). The nitrogen adsorption−desorption isotherms of the products were measured at 77 K on a Belsorp 28SA instrument (Bell Japan, Inc.). The TEM observations were performed on a JEOL model JEM 1010 electron microscope that was operating at an acceleration voltage of 100 kV. The SEM image was obtained using a Hitachi S-5000 scanning electron microscope. The IR transmittance spectra were recorded using a Perkin−Elmer 1600 FT-IR spectrometer. The CHN elemental analysis was conducted using a Perkin−Elmer 2400 II CHN element analyzer.

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