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Synthesis of rodlike polysiloxane with hexagonal phase by sol–gel reaction of organotrialkoxysilane monomer containing two amino groups

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Abstract

A higher-ordered polysiloxane was prepared by the sol–gel reaction of (3-(2-aminoethylamino)propyl)trimethoxysilane in a hydrochloric acid aqueous solution without using any surfactants. The X-ray diffraction profile of the resulting polysiloxane showed three peaks with the *d*-value ratio of $1:1/\sqrt{3}:1/2$, indicating that this polysiloxane has a hexagonal phase. The peaks shifted by changing the humidity. Therefore, we estimated that this hexagonal phase came from the stacking of a rodlike polymer with a Si–O–Si framework at the core and ammonium groups extruding outside. The TEM image of the polysiloxane showed a stripe pattern indicating an ordered arrangement. Because one repeating unit of the present polysiloxane has two ammonium groups, the ion-exchange capacity of this polysiloxane and viscosity of its aqueous solution were larger than those of the previous polysiloxane with single-ammonium group.

Keywords: Polymer materials; Polymer composite materials

1. Introduction

The self-organization of molecules to construct a higher-ordered architecture, i.e. supramolecular chemistry, has attracted increasing attention from a wide range of scientific interests [1,2]. The preparation of SiO-based materials, silicas and polysiloxanes, with higher-ordered structures is an extensively investigated area in materials chemistry due to their well-defined structure and unique properties. As one of the method for the preparation of these materials, the hydrothermal synthesis of silica-based materials using surfactants was reported [3,4]. Higher-ordered materials were also synthesized from layered silicates, kanemite, by the action of surfactants under relatively mild conditions [5,6]. The silica-based mesoporous materials have been formed by the calcination of these higher-ordered materials that removes the organic component such as the surfactants. Another method for preparing the SiO-based materials with higher-ordered structures is hydrolysis and polycondensation, i.e. a sol–gel reaction, of alkoxysilanes in the presence of the surfactants [7–19] and organoalkoxysilanes with long-chain alkyl groups which play the same role as the surfactants [20–25]. The surfactants and the long-chain alkyl groups forming micelles of various hypermorphs, such as hexagonal and lamellar, act as templates and allow the sol–gel reaction of alkoxysilanes to form a regular structure. Thus, the SiO-based materials with higher-ordered structures have been synthesized only with the aid of the hydrophobic interaction of the surfactants or long-chain alkyl groups in the monomer. For developing new functions and applications, the exploration of a novel SiO-based material with a higher-ordered structure is considered important.

Recently, we found a new methodology for the preparation of such a material, i.e. a synthetic method without using surfactants or long-chain alkyl groups in the monomers [26,27]. This new method was achieved by the sol–gel reaction of 3-aminopropyltrimethoxysilane

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(APTMOS) in hydrochloric acid or nitric acid aqueous solution. The obtained material is a new type of SiO-based material with a higher-ordered structure—a hexagonal phase. This material is not a hexagonal mesoporous-type silica, but the hexagonal phase is caused by the stacking of a rodlike polymer with a Si–O–Si framework at the core and ammonium groups extruding outside [27]. Due to its hydrophilic ammonium ions on the surface of each rod, it dissolves in water to form a clear solution. In addition, the hybridization of this polysiloxane with anionic organic molecules, e.g. sodium *n*-octanoate, could be achieved by ion-exchange reaction [27]. This reaction occurs in liquid phase because both materials—the rodlike polysiloxanes and the sodium *n*-octanoate—are soluble in water. Consequently, the hybrid material can be obtained immediately. Thus, this rodlike polysiloxane is expected as a prominent inorganic constituent for new higher-ordered inorganic–organic hybrid materials. For developing various new hybrid materials, preparation of the other types of rodlike polysiloxanes is necessary.

The present paper reports the synthesis of another cationic polysiloxane with a higher-ordered hexagonal phase by this polymerization technique utilizing the organization of an ion complex, for which an organotrialkoxysilane containing two amino groups, i.e. (3-(2-aminoethylamino)propyl)trimethoxysilane (AEAPTMOS), was used as a new monomer (Fig. 1). We also compared the property of the present polysiloxane (containing double-ammonium groups) with the previous one (containing single-ammonium group) [26,27].

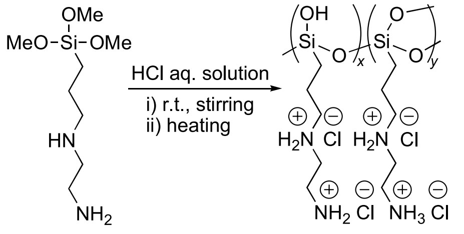
2. Experimental section

2.1. Materials

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

2.2. Typical procedure for preparation of poly(3-(2-aminoethylamino)propyl)siloxane hydrochloride (PAEAPS-Cl)

A 4.45 g (20 mmol) sample of (3-(2-aminoethylamino)-propyl)trimethoxysilane (AEAPTMOS) was added to 60 mL of a hydrochloric acid aqueous solution (1.0 mol/L), and then the reaction solution was stirred for 2 h at room temperature, followed by heating to 60–70 °C in an 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. 4.24 g of powdered white PAEAPS-Cl (yields ca. 94%: the ideal chemical formula of PAEAPS-Cl $[Cl_2 \cdot NH_3(CH_2)_2NH_2(CH_2)_3SiO_{1.5}$, (FW = 226.2)] was used).



AEAPTMOS **PAEAPS-Cl**

Fig. 1. Synthetic scheme for poly(3-(2-aminoethylamino)propyl)siloxane hydrochloride (PAEPS-Cl).

2.3. Ion-exchange reaction of PAEAPS-Cl with sodium *n*-octanoate

A 0.226 g sample of PAEAPS-Cl was dissolved in 20 mL of water. The solution was poured into 60 mL of a sodium *n*-octanoate aqueous solution (0.05 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. 0.355 g of white powdered PAEAPS-C8 (yields ca. 80%: the ideal chemical formula of PAEAPS-C8 $[(CH_3(CH_2)_6COO)_2 \cdot NH_3(CH_2)_2NH_2(CH_2)_3SiO_{1.5}$, (FW = 441.7)] was used); ^1H NMR (300 MHz, CD_3OD): δ 0.58–0.80 (br, H_a), 0.83–0.98 (t, H_1), 1.20–1.42 (m, H_2), 1.50–1.84 (m, H_3 and H_b), 2.12–2.29 (t, H_4), 2.60–3.21 (br, H_c).

2.4. Preparation of PAEAPS without counter ions using ion-exchange resin

A 0.20 g sample of PAEAPS-Cl was dissolved in 50 mL of water and this product solution was then passed through a column of the anion-exchange resin (Amberlite IRA-900), which was prepared with a sodium hydroxide aqueous solution (1 N). The obtained solution was lyophilized to yield ca. 0.05 g of PAEAPS without counter ions (yields ca. 37%: the ideal chemical formula of PAEAPS without counter ions $[NH_2(CH_2)_2NH(CH_2)_3SiO_{1.5}$, (FW = 153.3)] was used).

2.5. Measurements

The IR transmittance spectra were recorded using a Perkin–Elmer 1600 FT-IR spectrometer. The XRD measurements of the products were conducted at a scanning speed of $2\theta = 0.1°$/min using a RINT 1200 (Rigaku Co., Ltd) diffractometer with Ni-filtered Cu Kα radiation (λ = 0.15418 nm). The TEM observation was performed on a JEOL JEM-1010 electron microscope operating at an acceleration voltage of 100 kV. The nitrogen adsorption–desorption isotherms of the products were measured at 77 K on a Belsorp 28SA instrument (Bell Japan, Inc.). The ^1H NMR spectrum was recorded using a JEOL JNM-AL300 spectrometer. The CHN elemental analysis was conducted using a Perkin–Elmer 2400 II CHN element analyzer. The viscosities of the aqueous product solutions were measured by oscillational viscometer (CBC Materials Co., Ltd, Viscomate VM-10A).

3. Results and discussion

3.1. Synthesis of polyPAEPS-Cl

The hydrolysis and polycondensation of AEAPTMOS was carried out in a hydrochloric acid aqueous solution by heating (ca. 60–70 °C) in an open system until the solvent was completely distilled away. The resulting polysiloxane containing two ammonium groups in one repeating unit, PAEAPS-Cl, was characterized by the IR spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), and nitrogen adsorption–desorption isotherm measurement.

3.2. Characterization

The IR spectrum of the product showed conspicuous absorption bands due to the Si–O–Si bond at ca. 1150 cm^{-1}, those due to Si–OH at ca. 3440 and 1040 cm^{-1}, and those due to NH_3^+ at ca. 2980, 1620, and 1470 cm^{-1} (Fig. 2).

For the XRD measurement, the film of the product on the glass was obtained by drying the aqueous product solution spread on flat glass substrate. The XRD profile of the PAEAPS-Cl film 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 product has a hexagonal phase (Fig. 3). Therefore, these three peaks were assigned to the (100), (110) and (200) peaks, respectively. As shown in Table 1, the *d*-values of these three peaks were changed by varying 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). The SiO-based materials with the hexagonal phase reported so far are only mesoporous-type structures, which consist of an organic component at the core and a Si–O–Si framework at the outside [11–19,24,25]. However, the results from the humidity experiment indicated that the present material was hardly a mesoporous-type structure. Therefore, we assumed that this hexagonal phase came from the stacking of a rodlike polymer which consists of a Si–O–Si framework at the core and ammonium groups extruding outside.

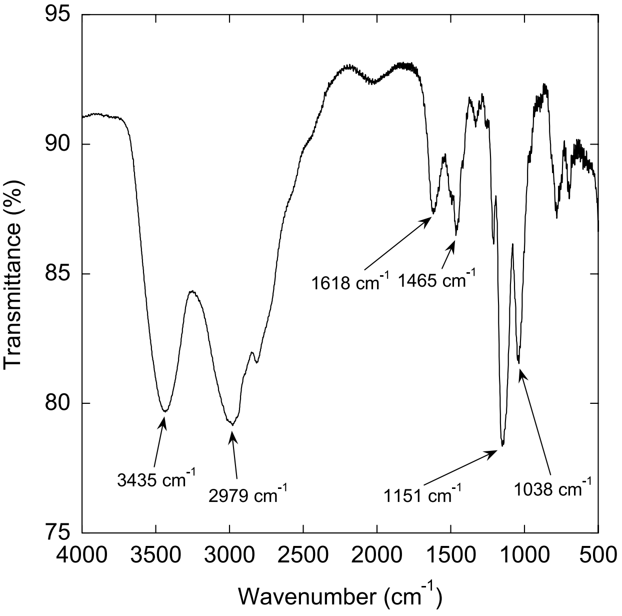


Fig. 2. IR spectrum of PAEAPS-Cl.

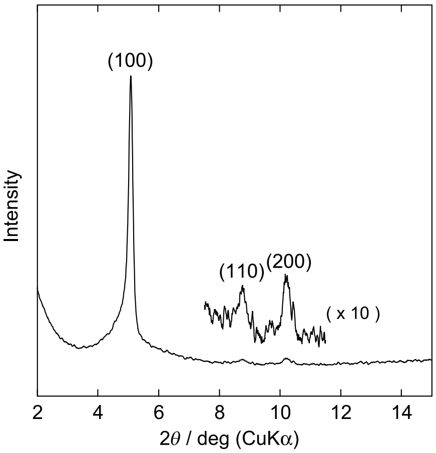


Fig. 3. XRD pattern of PAEAPS-Cl.

The TEM image of PAEAPS-Cl is shown in Fig. 4, and a stripe pattern was observed. This pattern indicates that the rodlike polysiloxanes are stacked parallel. The periodic distance of this stripe pattern was ca. 1.5 nm. This value is different from the *d*-value measured by XRD (ca. 1.8 nm for the relative humidity of 40–50%). The TEM observations

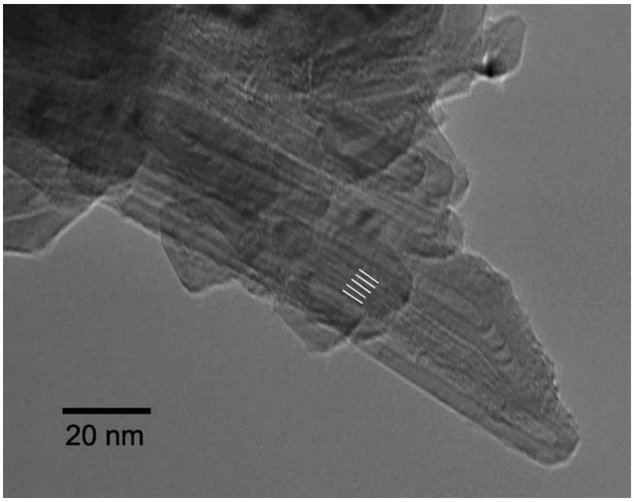


Fig. 4. TEM image of PAEAPS-Cl.

Table 1
Influence of humidity

Relative humidity (%)	*d*-value (nm)			*d*-value ratio[a]		
	(100)	(110)	(200)	(100)	(110)	(200)
7	1.582	0.914	0.793	1.000	0.578	0.501
14	1.632	0.945	0.813	1.000	0.579	0.498
20	1.682	0.971	0.837	1.000	0.577	0.498
30	1.738	1.006	0.867	1.000	0.579	0.499
40	1.795	1.037	0.892	1.000	0.578	0.497
50	1.851	1.071	0.927	1.000	0.578	0.501
60	1.928	1.120	0.966	1.000	0.581	0.501
70	1.998	1.155	0.991	1.000	0.578	0.496
80	2.058	1.195	1.032	1.000	0.581	0.502
90	2.148	–	–	1.000	–	–

Retention time of each humidity; 2 h.

[a] The theoretical ratio of hexagonal phase; (100) = 1, (110) = $1/\sqrt{3} = 0.577$, (200) = $1/2 = 0.5$.

were conducted in a high vacuum and the specimens were heated by electron beam irradiation. Therefore, the water molecules between the rodlike polysiloxanes would completely disappear leading to a decrease in the periodic distance. Such a behavior was also observed with the polysiloxane (PAPS-Cl and PAPS-NO_3) in our previous study [27].

The nitrogen adsorption–desorption isotherm at 77 K of PAEAPS-Cl is shown in Fig. 5. The Brunauer–Emmett–Teller (BET) surface area of PAEAPS-Cl was ca. 23 m^2/g. This result indicates that the present polysiloxane (PAEAPS-Cl) was a dense structure.

3.3. Ion-exchange reaction of PAEAPS-Cl with n-octanoate

Since PAEAPS-Cl has ammonium groups around the polysiloxane core part and chloride anions (Cl^-) as counter ions, an anion-exchange property is expected. In addition, an increase in the *d*-value is also expected when the Cl^- of PAEAPS-Cl is exchanged with a bulky fatty acid salt such as *n*-octanoate. Therefore, we investigated the ion-exchange reaction with sodium *n*-octanoate. By pouring the PAEAPS-Cl aqueous solution into an aqueous solution of sodium *n*-octanoate, precipitation immediately occurred. The obtained water-insoluble product, hereafter denoted as PAEAPS-C8, was characterized by ^1H NMR and XRD measurements. The ^1H NMR spectrum in CD_3OD of PAEAPS-C8 showed signals due to both the alkylammonium group in the side chain of the polysiloxane and *n*-octanoate as the counter ion (Fig. 6). Furthermore, the integrated ratio of the signals due to $-CH_2NH_2^+CH_2CH_2NH_3^+$ (signal H_c; 6H) of the polysiloxane to the signal due to $-CH_2COO^-$ (signal H_4; 2H) of *n*-octanoate was ca. 3:2. This indicates that one repeating unit of polysiloxane has two *n*-octanoates, i.e. the Cl^- in PAEAPS-Cl was substituted with the *n*-octanoate.

For the XRD measurement, the film of PAEAPS-C8 was obtained by drying its ethanol solution spread on a flat glass substrate. The XRD profile of the film of PAEAPS-C8 showed that the *d*-value of the diffraction peak at the lowest

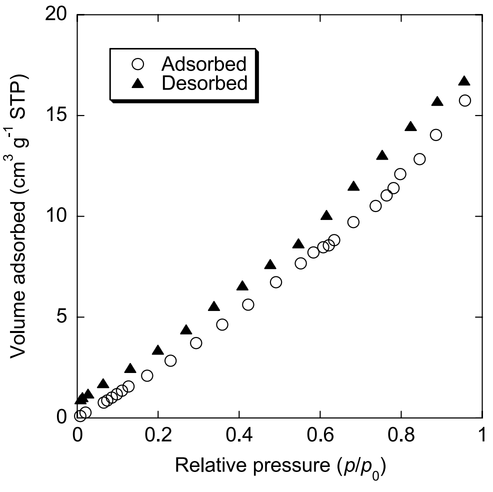


Fig. 5. Nitrogen adsorption–desorption isotherm at 77 K of PAEAPS-Cl.

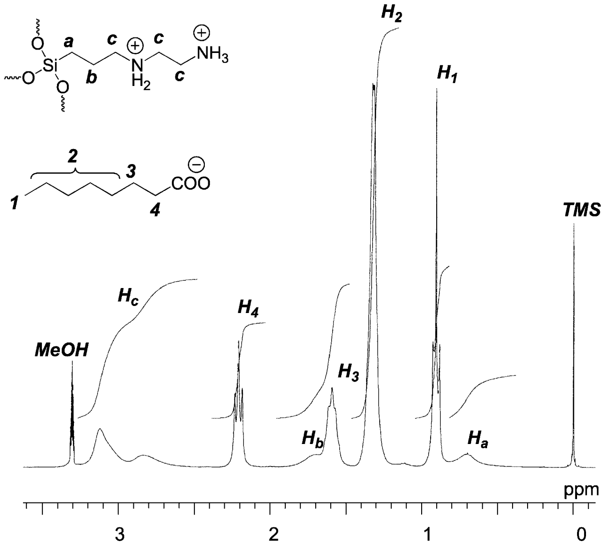


Fig. 6. ^1H NMR spectrum of PAEAPS-C8 in CD_3OD.

2θ angle (ca. 2.9 nm for relative humidity = 40–50%) increased more than that of the original polysiloxane; PAEAPS-Cl (ca. 1.8 nm for relative humidity = 40–50%) (Fig. 7). These results are consistent with the conclusion that the PAEAPS-Cl is a stacking material composed of rodlike polymers with $-NH_3^+Cl^-$ groups around the Si–O–Si core part. On the other hand, the minor peaks, (110) and (200) peaks, of PAEAPS-C8 could not be observed. Further, characterization of the PAEAPS-C8 structure is now in progress.

3.4. Influence of counter anions

To investigate the influence of the counter anions on the construction of an ordered structure, we used an ion-exchange resin. An aqueous solution of PAEAPS-Cl was passed through a column of an anion-exchange resin (OH^- type). By this treatment, the counter anions (Cl^-) of PAEAPS-Cl were converted into OH^-. The polysiloxane without counter ions was formed by lyophilization of the product solution, which was confirmed by IR spectrometry (not shown). As shown in Fig. 8, the XRD pattern of the product after treatment with the anion-exchange resin shows a broad diffraction peak. This indicates the collapse of the ordered hexagonal phase. This result reveals that complete coverage of the amino groups in the surface of the polysiloxane with a counter anion such as Cl^- is necessary for the formation of the rodlike structure with the higher-ordered hexagonal phase.

3.5. Proposed formation mechanism of rodlike polysiloxane with the hexagonal phase

Based on these results, the mechanism for the formation of the rodlike structure with a hexagonal phase was proposed. 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. Therefore, this rodlike polymer would consist of a Si–O–Si framework at the core and ammonium groups extruding outside. Finally, this rodlike polymer would be stacked by drying to form the hexagonal phase. The ion complex may be a key factor for the formation of the rodlike micelle which leads to a rodlike polymer with a hexagonal arrangement.

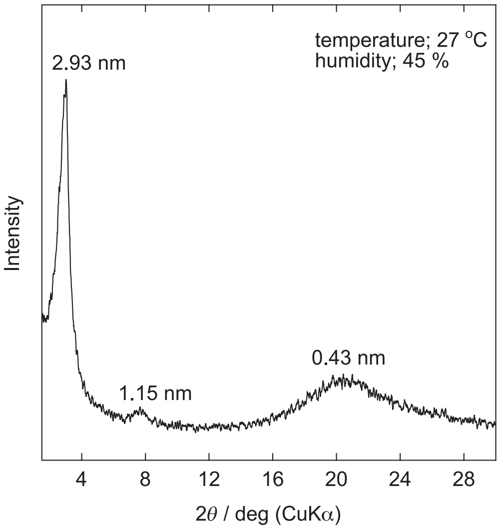


Fig. 7. XRD pattern of PAEAPS-C8.

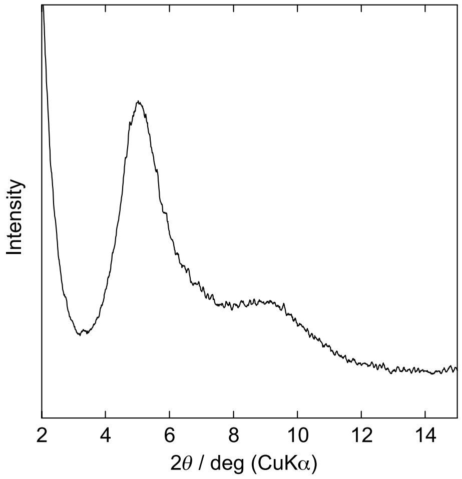


Fig. 8. XRD pattern of PAEAPS without a counter ion.

3.6. Comparison of properties between PAEAPS-Cl (containing double-ammonium groups) and PAPS-Cl (containing single-ammonium group) [27]

On the basis of CHN elemental analysis data, exchange amounts of *n*-octanoates in the PAEAPS-C8 and PAPS-C8 [27] were calculated as ca. 970 and 870 meq/100 g of the polysiloxanes (host materials), respectively; these theoretical values are 1290 and 900 meq, respectively. Because one repeating unit of PAEAPS-Cl has two ion-exchange sites, the ion-exchange capacity of PAEAPS-Cl increased more than that of PAPS-Cl.

To examine swelling behavior in water, the viscosity measurements were carried out. Time dependences of the viscosities for the aqueous product solutions (1 wt%) after adding water to the products are shown in Fig. 9. PAPS-Cl dissolved in water to give a clear solution in less than 5 min. On the other hand, thorough dispersion of PAEAPS-Cl in water took for 3–4 h, and the resulting solution was not still transparent. In addition, this PAEAPS-Cl suspension had higher viscosity (ca. 30 mPa s) compared with that of PAPS-Cl. It is probably because the interaction between rods of PAEAPS-Cl is stronger than that of PAPS-Cl due to the two ammonium groups in one repeating unit in

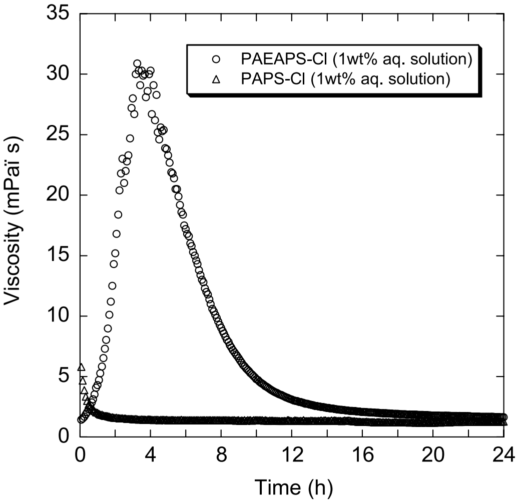


Fig. 9. Time dependences of the viscosities for the aqueous product solutions (1 wt%) after adding water to the products.

PAEAPS-Cl. With aging, the viscosity of the PAEAPS-Cl suspension gradually decreased and finally the solution became transparent. This is probably because the rod of PAEAPS-Cl, connected with each other, completely separated in water. Since the hexagonal phase recovered by drying the resulting transparent solution, the decrease in viscosity is not due to the decomposition of PAEAPS-Cl itself.

4. Conclusion

The rodlike polysiloxane with a hexagonal phase (PAEAPS-Cl) was prepared by the sol–gel reaction of an organotrialkoxysilane containing two amino groups (AEAPTMOS) in hydrochloric acid aqueous solution without using any surfactants. This rodlike structure consisted of a Si–O–Si framework at the core and ammonium groups extruding outside. We clarified that the ion complex composed of ammonium groups around the polysiloxane core part and counter ion such as Cl^- is necessary for the construction of the rodlike structure with a hexagonal phase. Because one repeating unit of PAEAPS-Cl has two ammonium groups, the ion-exchange capacity of PAEAPS-Cl and viscosity of its aqueous solution were larger than those of PAPS-Cl (containing single-ammonium group).

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