

Preparation and polymerization of pentaethoxydisiloxane

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Abstract

We previously reported the synthesis of pentaethoxydisiloxane (PEDS) by the oxidation of triethoxysilane (TES) with oxygen gas in the presence of a Rh catalyst. However, the isolate yield of PEDS was low (< 7%). Herein, we report a PEDS yield of 62% using a new synthetic method and the characterization of the PEDS polymer by nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy. The PEDS polymer was synthesized by hydrolysis–condensation of PEDS, and this polymer was composed of linear and branched chains and was the end group of the Q¹ unit.

Keywords : Hetero-disiloxane, Polymerization, NMR, FTIR

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1. Introduction

Pentaethoxydisiloxane (PEDS) is a heterosiloxane having a hydrido group and can be substituted by addition reaction with olefins¹⁾. We previously reported that PEDS was synthesized by the oxidation of triethoxysilane (TES) in the presence of Rh(PPh₃)₃Cl catalyst and activated molecular sieves with oxygen gas bubbling²⁾. This reaction proceeded via the formation of silanol (Si–OH) via the oxidation of the Si–H bond, followed by condensation between Si–OH and Si–OEt. However, this condensation reaction produces ethanol, and Si–OEt is formed by the reaction between Si–H and ethanol (Figure 1). Activated molecular sieves are necessary to remove ethanol.

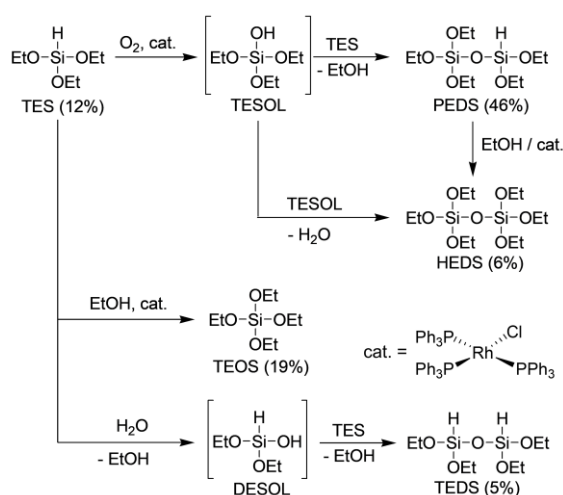


Figure 1 Scheme for oxidation of triethoxysilane. Numbers in parentheses indicate the GC area ratio.

We found that the side reactions could be suppressed when the adsorption rate of the molecular sieves was faster than the rate of ethoxylation³⁾. However, this reaction is an inefficient and inappropriate synthetic method for PEDS because the isolated yield of PEDS was 7%. According to the reaction mechanism, PEDS can be synthesized via the reaction of isolated triethoxysilanol (TESOL) with TES. Herein, we report a new synthetic method for PEDS. Moreover, we studied the PEDS polymerization and its structure, which could not be

polymerized due to insufficient amount of PEDS synthesized by the previous method.

2. Experimental section

2.1 Materials

Toluene and tetrahydrofuran (THF) were purified using standard methods and stored in activated molecular sieves. Triethoxysilane (TES), tetraethoxysilane (TEOS), chlorotrimethylsilane (TMSCl), and thionyl chloride (SOCl₂) were purchased from Tokyo Chemical Industry Co. Ltd. (Japan), and TES and TEOS were purified by distillation. Ammonium carbonate and *N,N*-dimethylformamide (DMF) were purchased from FUJIFILM Wako Pure Chemical Corporation (Japan). Water was purified using a PURELAB Flex 5 water purification system (ELGA, UK) with a resistivity of ~15 MΩ·cm.

2.2 Measurements

GC analysis was carried out on a GC-390 (GL Science, Japan) packed with an SE-30 capillary column (Agilent, USA) and a TCD detector. Helium was used as the carrier gas. The column temperature was programmed as follows: injection temperature at 250 °C, isothermal state at 80 °C for 2 min, then heating up to 200 °C at rate of 10 °C min⁻¹, followed by heating up to 280 °C at rate of 20 °C min⁻¹, and held at the final temperature of 280 °C for 2 min. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL Resonance JNM-ECP 300 spectrometer (JEOL, Japan; ¹H at 300 MHz, ¹³C at 75 MHz, and ²⁹Si at 60 MHz). Chemical shifts were reported in ppm relative to chloroform-*d* (CDCl₃) as the internal standard (for ¹H:7.26 ppm and ¹³C:77.16 ppm in residual chloroform) and tetramethylsilane as the internal standard (for ²⁹Si:0.00 ppm). For the ²⁹Si NMR spectra, Cr(acac)₃, as a paramagnetic relaxation agent, was added to the samples. Gel permeation chromatography (GPC) was performed

using an HPLC system (LC-6AD, Shimadzu, Japan) attached to a PLgel 5 μm Mixed-D column. THF was used as the eluent (1 mL min^{-1}). RID-10A was used as the detector at 40 $^{\circ}\text{C}$. The molecular weights were calculated based on polystyrene standards. Fourier-transform infrared (FTIR) spectra were recorded on an FT-IR spectrophotometer (FT/IR-6100, JASCO, Japan) using the neat method, in which the sample was sandwiched between two KBr crystal disks.

2.3 Preparation of triethoxysilanol (TESOL)

TESOL was prepared according to literatures ^{4,5}. TEOS (26 g, 0.13 mol) was added to a mixture of SOCl_2 (14.9 g, 0.13 mol) and DMF (0.13 mL), and then stirred for 4 h. Chlorotriethoxysilane was separated by distillation under reduced pressure (70–72 $^{\circ}\text{C}/36$ mmHg) and obtained as colorless liquid (yield 59%, GC purity 82%). A solution of chlorotriethoxysilane (9.9 g, 0.05 mol) and 100 mL THF was added, while stirring under an ice bath, to a suspension of water (4.5 g, 0.25 mol), $(\text{NH}_4)_2\text{CO}_3$ (28.5 g, 0.25 mol), and THF (250 mL). After stirring for 1 h, the precipitate was filtered, and the filtrate was dried over Na_2SO_4 . Thereafter, THF was evaporated in ice bath under reduced pressure, and TESOL was separated by distillation under reduced pressure (61 $^{\circ}\text{C}/1$ mmHg). TESOL was a colorless liquid (yield, 62%; GC purity, 82%), but TEOS was contaminated (12%).

2.4 Synthesis of PEDS

TESOL (1.1 g, 6.1 mmol) was added using a dropping funnel to a solution of TES (1.0 g, 6.1 mmol) and toluene (3 mL) and stirred at 100 $^{\circ}\text{C}$. After 4 hours, PEDS was isolated by distillation under reduced pressure (104 $^{\circ}\text{C}/11$ mmHg) to obtain

a colorless liquid (yield: 62%).

^1H NMR: $\delta = 1.24$ (t, $J = 7.0$ Hz, 9H, CH_3 in Q unit), 1.25 (t, $J = 6.9$ Hz, 6H, CH_3 in T unit), 3.86 (q, $J = 7.0$ Hz, 6H, CH_2 in Q unit), 3.87 (q, $J = 6.9$ Hz, 4H, CH_2 in T unit), 4.35 (s, 1H, Si-H). ^{13}C NMR: $\delta = 18.05$ (CH_3), 18.17 (CH_3), 58.27 (CH_2), 59.23 (CH_2). ^{29}Si NMR: $\delta = -67.7, -88.4$.

2.5 Polymerization of PEDS

PEDS (5.0 g, 17 mmol) and ethanol (25 mL) were placed in a 100 mL four-necked flask equipped with nitrogen inlet and outlet tubes and a mechanical stirrer. The mixture was stirred at 200 rpm and then cooled in an ice bath for 20 min. Thereafter, conc. HCl (aq) (0.28 mL), water (0.09 mL), and ethanol (5 mL) were added (HCl/PEDS=0.2, $\text{H}_2\text{O}/\text{PEDS}=1.0$). The resulting mixture was stirred for 10 min in an ice bath and then for 10 min at 22 ± 3 $^{\circ}\text{C}$. The hydrolysis–condensation reaction was carried out at 80 $^{\circ}\text{C}$ for 3 h under a nitrogen flow of 200 mL min^{-1} . The PEDS polymer was obtained as a colorless and viscous liquid (3.2 g). The average molecular weight (M_w) and polydispersity index were 24,000 and 6.8, respectively, as calculated by GPC.

2.6 Hydrolysis of PEDS followed by addition of TMSCl

PEDS (1.5 g, 5 mmol) was mixed in ethanol (7.5 mL) in an ice bath for 20 min. Then, conc. HCl (aq) (0.08 mL), water (0.03 mL), and ethanol (1.5 mL) were added (HCl/PEDS=0.2, $\text{H}_2\text{O}/\text{PEDS}=1.0$). The resulting mixture was stirred in an ice bath for 10 min, followed by the addition of TMSCl (0.64 mL). After stirring, the solvent was evaporated, and a colorless liquid was obtained.

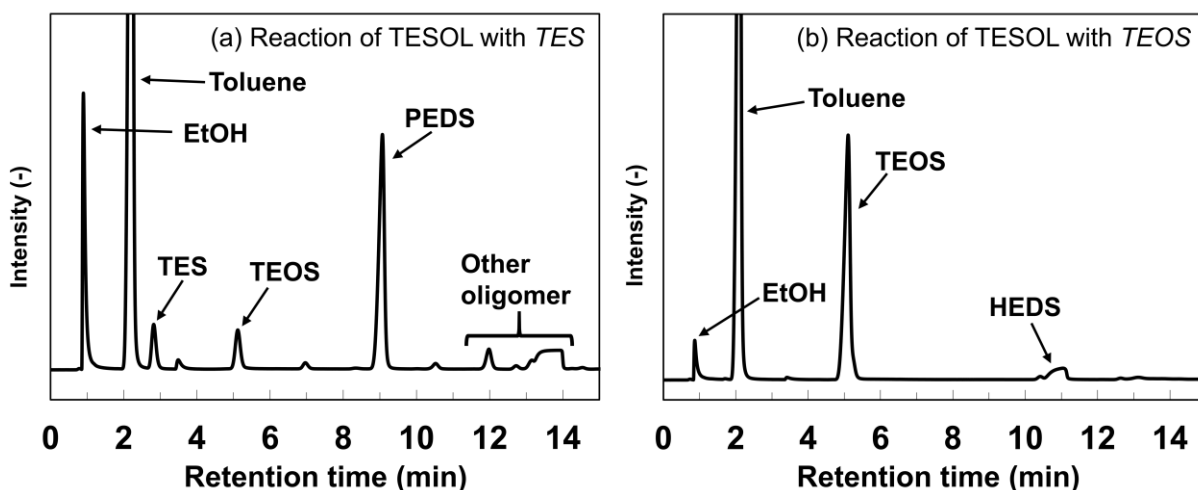


Figure 2 GC traces of the reaction solution of (a) TESOL with TES and (b) TESOL with TEOS at 100 °C for 4 h

3. Results and discussion

3.1 Synthesis of PEDS by the reaction of TESOL with TES

A GC chart of the TES and TESOL reaction solutions is shown in Figure 2a. TEOS was observed because TESOL was contaminated with TEOS; therefore, TES was not completely consumed. However, strong peaks corresponding to PEDS and ethanol were observed, indicating that the reaction between TESOL and TES proceeded under neutral conditions. In contrast, Figure 2b shows the GC chart of the reaction solution of TEOS with TESOL, and the intensities of ethanol and hexaethoxydisiloxane (HEDS) were very weak, indicating that little reaction occurred between TESOL and TEOS. TESOL could not be observed because it may have been adsorbed onto the SE-30 capillary column. As a result, TES is easily attacked by the silanol group and siloxane linkages can be formed even under neutral conditions because of the low steric hindrance of Si-H⁶.

3.2 Characterization of PEDS polymer

The PEDS polymer was prepared by the hydrolysis–condensation reaction of PEDS under nitrogen gas flow. Nitrogen gas was introduced to remove the hydrochloric acid catalyst and accelerate

the condensation reaction by evaporating the solvent^{5,7,8}. The ²⁹Si NMR spectra of PEDS and PEDS polymers are shown in Figure 3. PEDS displays two signals at –67.7 and –88.4 ppm due to T¹ unit (HSi(OEt)₂OSi(OEt)₃) and Q¹ unit (HSi(OEt)₂OSi(OEt)₃), respectively. PEDS polymer was confirmed by six obvious signals (–68.0, –77.2, –86.4, –88.9, –96.3, and –104 ppm) and four shoulder signals (–76.0, –84.6, –95.4, and –103 ppm). Because the cyclic form generally has a lower magnetic field than linear and branched chains⁹, the obvious signals were attributed to linear and branched chains, and shoulder signals were assigned to the cyclic form. However, the intensity of the shoulder signals was weak, indicating that only a small amount of cyclic form was present. The T¹ and Q¹ units of the PEDS polymer shifted to a slightly higher magnetic field than those of PEDS. This indicates that the T¹ and Q¹ units are the end groups of the PEDS polymer. The intensity of the T¹ unit was very weak; hence, the end group of the PEDS polymer was mainly the Q¹ unit. These attributes are summarized in Table 1.

The FTIR spectra of the PEDS and PEDS polymers are shown in Figure 4, and the absorption bands were attributed with reference to the literature^{10,11} and are summarized in Table 2. The position of νSi–H in the PEDS polymer shifted to a higher

wavenumber (from 2212 to 2240 cm^{-1}) than that in pristine PEDS, indicating that the condensation reaction proceeded^{12,13}.

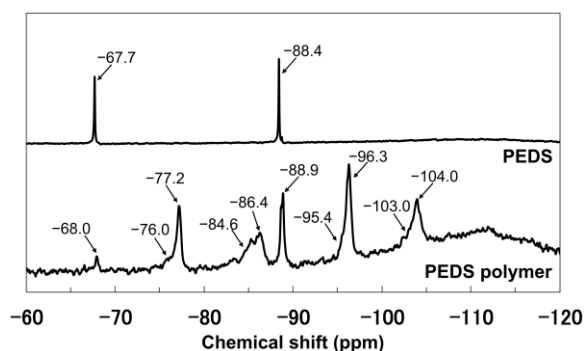


Figure 3 ^{29}Si NMR spectra of PEDS and PEDS polymer

Table 1 Assignment for ^{29}Si NMR spectra of PEDSs

PEDS	PEDS polymer	Assignment
-67.7	-68.0	T ¹
	-76.0	Cyclic T ²
	-77.2	Linear T ²
	-84.6	Cyclic T ³
	-86.4	Branched T ³
-88.4	-88.9	Q ¹
	-95.4	Cyclic Q ²
	-96.3	Linear Q ²
	-103.0	Cyclic Q ³
	-104.0	Branched Q ³

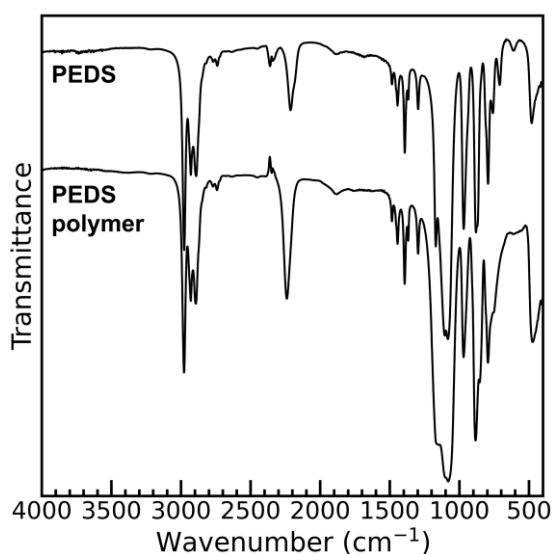


Figure 4 FTIR spectra of PEDS and PEDS polymer

Table 2 Assignment for FTIR spectra of PEDSs

PEDS	PEDS polymer	Assignment ^a
2979, 2931, 2890	2982, 2931, 2896	νCH_2 , νCH_3
2212	2240	$\nu\text{Si-H}$
1487–1296	1487–1296	δCH_2 , δCH_3
1170	1167	ρCH_3
	1150–1050	$\nu\text{Si-O-Si}$
1103, 1081	1103, 1081	$\nu\text{C-O}$
970	970	$\nu\text{C-C}$
882	885	$\omega\text{Si-H}$
	853	$\nu\text{Si-O-Si}$
796	793	$\nu\text{Si-O-Si}$
758	755	ρCH_2
710, 634, 612		
482	479	$\delta\text{Si-O-Si}$

^a ν : stretching, δ : scissoring, ω : wagging, ρ : rocking

The shape of $\nu\text{Si-O-Si}$ at 1150–1050 cm^{-1} indicated that the PEDS polymer was not comprised of ladder-like, cage-like, or strained cyclic structures^{14–16}, that is, the PEDS polymer was composed of linear, branched, and cyclic structures. However, the absorption band at ~ 550 cm^{-1} due to the cyclotetrasiloxane moiety¹⁷ was very weak. Thus, the structure of the PEDS polymer consists mainly of linear and branched chains, which is consistent with the ^{29}Si NMR results. From the results of ^{29}Si NMR and FTIR, the PEDS polymer was composed of mainly linear and branched chains and had an end group of Q¹ unit. Si-H can be modified by hydrosilylation¹, alkoxylation^{18–20}, hydroxylation²¹, and siloxylation^{22,23}; hence, PEDS polymers can be used as precursor polymers for many functional siloxane polymers and materials, such as mesoporous silica^{24–26}.

3.3 Hydrolysis of PEDS

To measure the initial stage of PEDS hydrolysis reaction, PEDS was hydrolyzed at ~ 0 $^\circ\text{C}$ for 10 min and silanol was capped with TMSCl. Figure 5 shows

the ^{29}Si NMR spectra of the hydrolysate. Two signals of the T^2 unit at ~ 75 ppm and two signals of the Q^2 unit at ~ 96 ppm were confirmed because the signals of trimethylsilyl-capped T^n and Q^n units appeared at a lower magnetic field than that of the condensation of T-T or T-Q ²⁷). The T^1 unit disappeared, and the Q^1 unit remained, indicating that the hydrolysis and condensation rates of the T^1 unit were faster than those of the Q^1 unit. The T unit is mainly transformed into the T^3 unit.

The signal pattern of the initial stage of hydrolysis of the PEDS differed from that of the PEDS polymer. We consider that the Si-O-Si network of the PEDS polymer was rearranged during the condensation reaction because Si-O-Si bonding is cleaved under acidic conditions ²⁸). Therefore, we believe that condensation reactions using formic acid can be used to obtain polymer-maintained PEDS backbones because formic acid can be easily transformed into formate compounds ^{29,30}). In the future, we will investigate this hypothesis by performing hydrolysis–condensation of PEDS using formic acid. The changes in the properties due to the polymer structure will also be investigated.

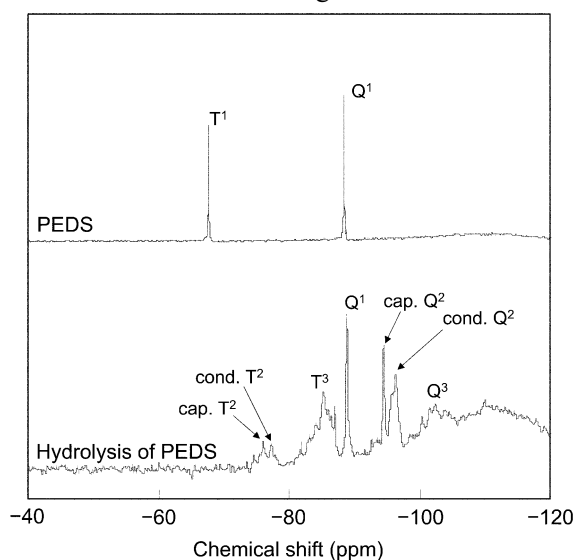


Figure 5 ^{29}Si NMR spectra of PEDS hydrolysis followed by addition of TMSCl . The “cap.” means capped with trimethylsilane, and the “cond.” means condensation between PEDSs.

4. Summary

We report a new method for the synthesis of PEDS via the reaction of TES with TESOL. In the previous method using the oxidation reaction of TES in the presence of the Rh catalyst, the isolated yield was 7%. In comparison, the isolated yield of PEDS by the new synthetic method was 62%, which was approximately nine times greater than that obtained by the previous method. The PEDS polymer was prepared by the hydrolysis–condensation reaction of PEDS under acidic conditions. This polymer is composed of both linear and branched chains. However, the PEDS backbone in this polymer is likely to be partially disintegrated, which is considered to perform a condensation reaction under acidic conditions. Therefore, it may be possible to synthesize polymers that retain the PEDS backbone by performing condensation reactions under neutral conditions.

Conflict of interest

The authors declare no competing interests.

CRedit authorship contribution statement

Iori Abe: Writing – original draft, visualization, investigation; **Yohei Sato:** Writing – original draft; **Ryohei Hayami:** Writing – original draft, visualization, investigation; **Kazuki Yamamoto:** Supervision; **Satoru Tsukada:** Supervision; **Takahiro Gunji:** Writing – review and editing, conceptualization, supervision.

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