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FULL PAPER

Facile preparation of a soluble polymer containing polyhedral oligomeric silsesquioxane units in its main chain

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A soluble polymer containing polyhedral oligomeric silsesquioxane (POSS) units in its main chain was successfully prepared in one-step by hydrolytic condensation of a mixture of two types of amino group-containing organotrialkoxysilanes using the aqueous trifluoromethanesulfonic acid (CF_3SO_3H) as a catalyst. In this CF_3SO_3H-catalysed synthesis, 3-(2-aminoethylamino)propyltrimethoxysilane and bis[3-(trimethoxysilyl)propyl]amine acted as a starting material of POSS and a cross-linker, respectively. The ^{29}Si NMR spectrum of the resulting POSS polymer only showed signals in the T^3 region. The IR spectrum of the hydrophobised POSS polymer indicated a single absorption peak at 1119 cm^{-1}, attributed to the Si–O–Si stretching absorption band, but no absorption peak at $ca.$ 3500 cm^{-1} for silanol groups. In addition, its weight-average molecular weight was 3.24 × 10^4. Overall, these results suggested the formation of a polymer composed of POSS units. The POSS polymer provided optically transparent films. This may result from the coexistence of POSS components bearing two different randomly distributed side-chain groups in the polymer, which suppresses crystallization. The POSS polymer exhibited 5% and 10% weight losses at 351 °C and 368 °C, respectively, indicative of its relatively high thermal stability.

Introduction

Siloxane-based materials known as silsesquioxanes (SQs; general formula: $[RSiO_{1.5}]_n$) adopt a wide range of structures, such as cage, open-cage, double-decker, ladder and random structures. In particular, polyhedral oligomeric SQ (POSS) compounds with well-defined cage-like structures have attracted much research attention for the development of organic–inorganic hybrid materials in academia and industry.[1–8] POSS compounds have been extensively used as inorganic fillers in polymer matrices, because in the presence of appropriate side-chain groups, they significantly improve the thermal and mechanical properties of the original polymers.[9] Conversely, their crystalline structures typically generate powders, hindering their sole application for useful materials. The development of POSS-containing polymeric materials is expected to solve this issue. Soluble polymeric materials containing POSS components in their side[10–15] or main chains[16–21] have exhibited excellent thermal and mechanical properties. In addition to these properties, some main chain-type POSS-containing polymers have displayed optical transparency. However, even though some of the polymeric POSS derivatives can be prepared as described above, multistep reactions and complicated isolations are required to prepare such polymers from the starting materials, *i.e.* trifunctional silane compounds, such as organotrialkoxysilanes or

organotrichlorosilanes. A few examples of soluble SQ-based polymeric materials such as ladder-like polySQs[22–37] have been produced, albeit with a limited number of side chains. Therefore, a facile preparation of soluble polySQs, such as main chain-type POSS-containing polymers, is highly desirable in SQ chemistry.

The hydrolytic condensation of 3-aminopropyltrimethoxysilane (APTMS) and 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS) using the aqueous superacid or strong acid have selectively and quantitatively produced cage-like oligoSQs (POSSs)[38,39] or rod-like (ladder-like) polySQs[24,26,28,34,37], respectively. In the hydrolytic condensation using the aqueous superacid trifluoromethanesulfonic acid (CF_3SO_3H) as a catalyst, amino group-containing POSS compounds have been prepared in higher yield within a shorter reaction time.[38,39] Plausible formation mechanism of POSS can be expected as follows. It is easy to occur the protonation of amino group of APTMS and AEAPTMS with a superacid CF_3SO_3H, because of dissociation of proton from the superacid. Consequently, charge repulsion occurred between these ammonium cation side-chains, resulting in the formation of the structure with long distance between the side-chain groups, that is cage-like structure (POSS). In the dilute aqueous solution of strong acids such as HCl and HNO_3, it is also expected that same behaviour occurs. However, in our synthetic method, aqueous solutions of APTMS and

AEAPTMS with acid catalysts were concentrated by heating in an open system. It is difficult to completely dissociate protons in high-concentrated aqueous solutions of strong acids. Therefore, the CF_3SO_3H-mediated formation of ammonium cations from APTMS or AEAPTMS is important in facilitating the preparation of these POSS compounds. Therefore, a method using a combination of amino group-containing organotrialkoxysilanes and superacid may be widely applicable for the synthesis of alkylammonium group-containing POSS derivatives.

In this study, we provide a new synthetic method of soluble polymer containing POSS units in its main chain, *i.e.* it was successfully prepared in one-step from organotrialkoxysilanes as starting materials. Here, the CF_3SO_3H-catalysed hydrolytic condensation of two organotrialkoxysilanes bearing different amino groups was investigated. This reaction involves AEAPTMS as a starting material of POSS and bis[3-(trimethoxysilyl)propyl]amine (BTMSPA) as a cross-linker, providing a main-chain POSS-based soluble polymer in one step.

Experimental

Materials

All reagents and solvents were commercially available and used without further purification.

Preparation of the POSS polymer

To a mixture of AEAPTMS (purity: 95%, 0.702 g, 3.00 mmol) and BTMSPA (purity: 90%, 0.190 g, 0.500 mmol), an aqueous CF_3SO_3H (0.5 mol L^{-1}, 32.5 mL, 16.25 mmol) was added with stirring at room temperature. The resulting solution was further stirred at room temperature for 2 h and heated to *ca.* 50 °C in an open system until the solvent evaporated completely (*ca.* 3 h). The crude product was maintained at 100 °C for *ca.* 2 h and an acetone/chloroform mixture (1:1 v/v, *ca.* 50 mL) was subsequently added at room temperature. The insoluble-part in this mixed solvent was isolated by filtration and washed with the acetone/chloroform mixture (*ca.* 100 mL) and chloroform (*ca.* 50 mL) to remove the excess CF_3SO_3H catalyst before being dried under reduced pressure at room temperature to yield the POSS polymer as a white powder (1.628 g; quantitative yield; the ideal chemical formulas of the repeating units of the AEAPTMS component [$SiO_{1.5}(CH_2)_3NH_2^+(CH_2)_2NH_3^+$ ($CF_3SO_3^-$)$_2$, FW = 453.4] and the BTMSPA component [$SiO_{1.5}(CH_2)_3NH_2^+(CH_2)_3SiO_{1.5}$ $CF_3SO_3^-$, FW = 353.4] (compositional ratio of AEAPTMS/BTMSPA components = 6.00) of this product were used for the determination). ^{1}H NMR (400 MHz, D$_2$O): δ 3.53–3.27 (br, NH$_3$CH_2CH_2NH$_2$– of the AEAPTMS component), δ 3.23–2.75 (br, –NH$_2$CH_2CH$_2$CH$_2$Si–), δ 2.10–1.48 (br, –NH$_2$CH$_2$CH_2CH$_2$Si–), δ 1.08–0.43 (br, –CH_2Si–). ^{29}Si NMR (80 MHz, dimethylsulfoxide (DMSO)-d_6): δ −66.5−−67.4 (T$_8$), δ −68.4−−69.2 (T$_{10}$).
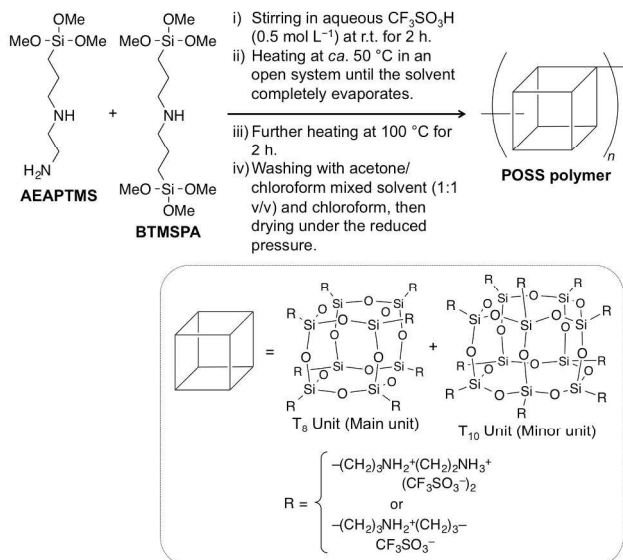
Preparation of the hydrophobic POSS polymer

Triethylamine (0.633 mL, 4.50 mmol) and the DMF solution (1.0 mL) of lauroyl chloride (0.700 g, 3.00 mmol) were successively added to N,N-dimethylformamide (DMF) solution (1.0 mL) of POSS polymer (0.446 g, 1.00 mmol unit) under vigorous stirring at room temperature. The mixture was stirred further for 10 min and 1.0 mol L^{-1} aqueous hydrochloric acid

(10.0 mL, 10.0 mmol) was added to this mixture. The solution was poured into acetone (*ca.* 200 mL), the precipitated product was isolated by filtration, successively washed with acetone (*ca.* 100 mL) and water (*ca.* 200 mL) and dried under reduced pressure at room temperature to yield the hydrophobic POSS polymer as a white powder (0.258 g; yield: *ca.* 61%; the ideal chemical formulas of the repeating units of the hydrophobic AEAPTMS component [$SiO_{1.5}(CH_2)_3N[CO(CH_2)_{10}CH_3](CH_2)_2NH[CO(CH_2)_{10}CH_3]$, FW = 517.9] and the hydrophobic BTMSPA component [$SiO_{1.5}(CH_2)_3N[CO(CH_2)_{10}CH_3](CH_2)_3SiO_{1.5}$, FW = 385.7] (compositional ratio of hydrophobic AEAPTMS/hydrophobic BTMSPA components = 3.41) of this product were used for the determination). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.84–2.80 (br, –(C=O)NHCH_2CH_2N(C=O)– of the AEAPTMS component and –(C=O)NCH_2CH$_2$CH$_2$Si–), δ 2.53–1.85 (br, –(C=O)CH_2–), δ 1.77–1.45 (br, –(C=O)NCH$_2$CH_2CH$_2$Si– and –(C=O)CH$_2$CH_2–), δ 1.39–1.05 (br, –CH_2–), δ 0.94–0.80 (br, CH_3–), δ 0.77–0.38 (br, –CH_2Si–). ^{29}Si NMR (80 MHz, DMSO-d_6): δ −66.1−−67.7 (T$_8$), δ −68.0−−69.4 (T$_{10}$).

Measurements

^{1}H and ^{29}Si NMR spectra were recorded using a JEOL ECX-400 spectrometer. IR spectra were recorded using a JASCO FT/IR-4200 spectrometer. Average molecular weights were determined by gel permeation chromatography (GPC) using polystyrene standards. These GPC analyses were performed using a HITACHI pump L-2130 and a HITACHI RI detector L-2490 on Shodex GPC KF-805L (bead size: 10 μm; measurable molecular weight range: 10^2 to 4 × 10^6) and KF-803L columns (bead size: 6 μm; measurable molecular weight range: 10^2 to 7 × 10^4). Chloroform was used as an eluent and was pumped through the system at a flow rate of 1.0 mL min^{-1} at 40 °C. UV–Vis spectra were recorded using a JASCO V-630 spectrophotometer. X-ray diffraction (XRD) measurements were performed at a scanning speed of $2\theta = 1.8°$ min^{-1} using an X'Pert Pro diffractometer (PANalytical) with Ni-filtered Cu Kα radiation (λ = 0.15418 nm). Thermogravimetric analysis (TGA) was conducted using an Exstar TG/DTA6200 apparatus (Seiko Instruments) at a heating rate of 10 °C min^{-1} up to 500 °C under nitrogen flow (250 mL min^{-1}). Decomposition temperatures T_{d5} and T_{d10} were determined for 5% and 10% weight losses, respectively. The differential scanning calorimetry (DSC) analyses were performed on an Exstar DSC6200 (Seiko Instruments). The sample was placed in an open aluminium pan and heated to 150 °C at a rate of 10 °C min^{-1} under a nitrogen flow (10 mL min^{-1}) and subsequently cooled from 150 °C to −100 °C at the same rate. The glass-transition temperature (T_g) values were determined as the onset of the third curves (from −100 °C to 150 °C at a rate of 10 °C min^{-1}) to eliminate the heat histories in the samples.

Scheme 1. Preparation of the POSS polymer by hydrolytic condensation of an AEAPTMS/BTMSPA mixture using aqueous CF$_3$SO$_3$H.

Results and discussion

Preparation and characterization of the POSS polymer

In the hydrolytic condensation, the AEAPTMS/BTMSPA mixture with feed molar ratio 6:1 was stirred in 0.5 mol L^{-1} aqueous CF$_3$SO$_3$H (CF$_3$SO$_3$H/amino group molar ratio = 2.5) at room temperature for 2 h. The resulting mixture was heated to dryness at *ca.* 50 °C in an open system (*ca.* 3 h). Next the residue was maintained at 100 °C for *ca.* 2 h, successively washed with an acetone/chloroform mixture and chloroform and dried under reduced pressure to give the POSS polymer in quantitative yield (Scheme 1). The polymer was soluble in 2-propanol, 1-propanol, acetone, ethanol, methanol, acetonitrile, DMF, DMSO and water. Incidentally, the product prepared from the AEAPTMS/BTMSPA mixture with feed molar ratio 3:1 was insoluble in any solvents including the aforementioned ones. On the other hand, the AEAPTMS/BTMSPA mixture with feed molar ratio 10:1 resulted in the preparation of a number of sole POSS compounds.

The ^{1}H NMR spectrum of the POSS polymer in D$_2$O only showed four signals attributable to its substituents. No signals were observed for the methoxy groups of AEAPTMS and BTMSPA (Fig. 1a), indicating that these starting materials were absent in the product. The average compositional ratio of AEAPTMS/BTMSPA components in the POSS polymer was estimated to be *ca.* 6.00:1.00 from the integrated ratio of the peaks **a** to **d, e** in the ^{1}H NMR spectrum (Fig. 1a).

^{29}Si NMR, IR and GPC measurements were performed to verify the formation of polymer composed of POSS units. The ^{29}Si NMR spectrum in DMSO-d_6 at 40 °C showed only two signals in the T^3 region, indicating the absence of silanol groups (Fig. 2a). The main signal at −66.5−−67.4 ppm and a minor peak at −68.4−−69.2 ppm were assigned to cage-like octamer (T$_8$) and cage-like decamer (T$_{10}$) units, respectively, because the signal for T$_{10}$ was found upfield (*ca.* 2 ppm) of that for T$_8$.[40] In addition, these chemical shifts were almost the same as those of AEAPTMS-derived POSS (AEAP-POSS; −66.9 ppm for T$_8$ and −68.9 ppm for T$_{10}$).[39] The integrated ratio of the signals due

to T$_8$ to T$_{10}$ units was estimated to be 0.76:0.24, providing a molar T$_8$/T$_{10}$ ratio of 0.80:0.20 (T$_8$/T$_{10}$= 0.76/8:0.24/10).
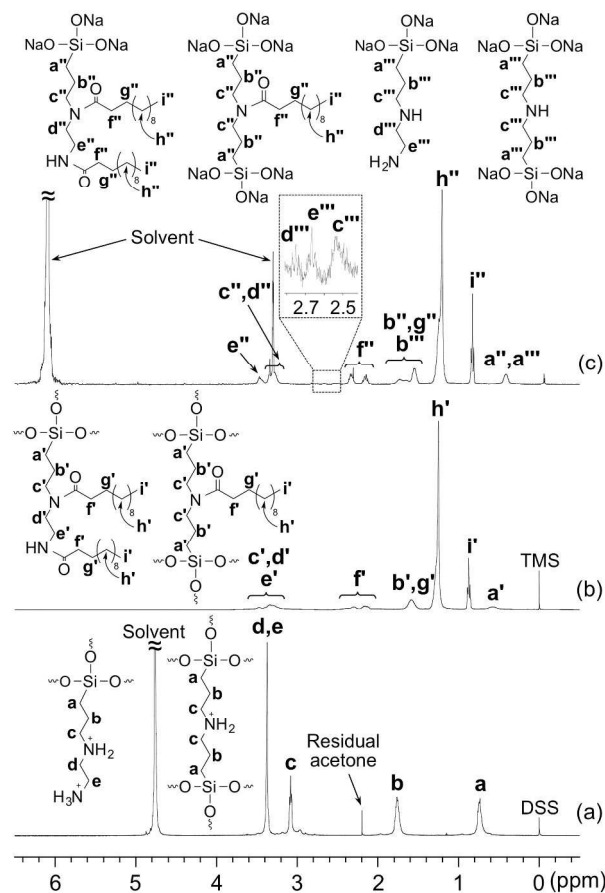
**Fig. 1** ^{1}H NMR spectra of (a) the POSS polymer in D$_2$O, (b) the hydrophobic POSS polymer in CDCl$_3$ and (c) the product obtained by hydrolysis of hydrophobic POSS polymer in a mixed solvent of CD$_3$OD/40%NaOD–D$_2$O (9:1 v/v). Chemical shifts were referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DDS) (δ 0.0), tetramethylsilane (TMS) (δ 0.0) and methanol (δ 3.3), respectively.
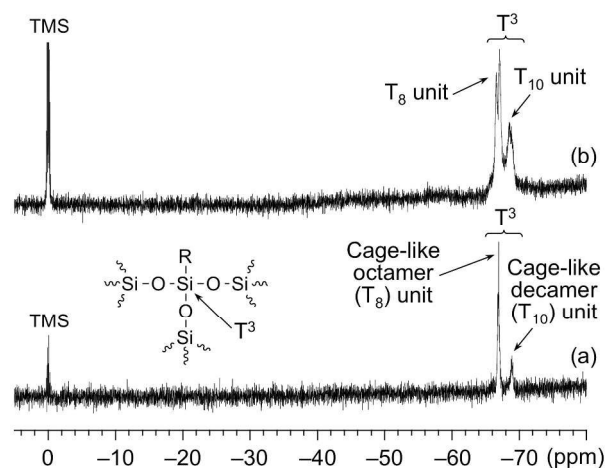
Fig. 2 ^{29}Si NMR spectra of (a) the POSS polymer in DMSO-d_6 and (b) the hydrophobic POSS polymer in CDCl$_3$. Chemical shifts were referenced to TMS (δ 0.0).

Furthermore, a POSS polymer bearing hydrophobic groups instead of $CF_3SO_3^-$ counter anions was prepared to visualise the Si–O–Si stretching absorption band by IR spectroscopy because this absorption overlapped with that corresponding to $CF_3SO_3^-$ (Fig. 3a). This hydrophobic POSS polymer was obtained by reaction of the POSS polymer with lauroyl chloride in DMF in the presence of triethylamine. It was soluble in toluene, diethyl ether, chloroform, THF and 1-butanol. Its ^1H NMR spectrum in $CDCl_3$ displayed signals assigned to lauroyl protons (Fig. 1b), indicating the introduction of covalently bound lauroyl groups into the POSS polymer. However, ^1H NMR peak broadening hindered the precise assessment of lauroyl functionalities, particularly the proportion of unreacted amino groups. To determine this proportion, the Si–O–Si main chains of the hydrophobic POSS polymer were hydrolysed using a mixed solvent of $CD_3OD/40\%NaOD-D_2O$ (9:1 v/v). The structure of the hydrolysis product was confirmed by ^1H NMR analysis of the reaction mixture. This spectrum showed signals corresponding to the methylene groups (**c′′′, d′′′, e′′′**, Fig. 1c) located near the amino groups at 2.4–2.8 ppm. The functionality of the lauroyl group was calculated to be 94% from the integrated ratio of the peaks **c′′′** to **a′′, a′′′**. The average compositional ratio of AEAPTMS/BTMSPA components in the hydrophobic POSS polymer (3.89), estimated from the integrated ratio of the peaks **a′′, a′′′** to **e′′′ + e′′** in the ^1H NMR spectrum (Fig. 1c), decreased compared with that of the POSS polymer (6.00). This may result from the loss of relatively low-molecular-weight POSS polymers containing a small number of BTMSPA cross-linkers during the acetone wash step of the polymer hydrophobisation.
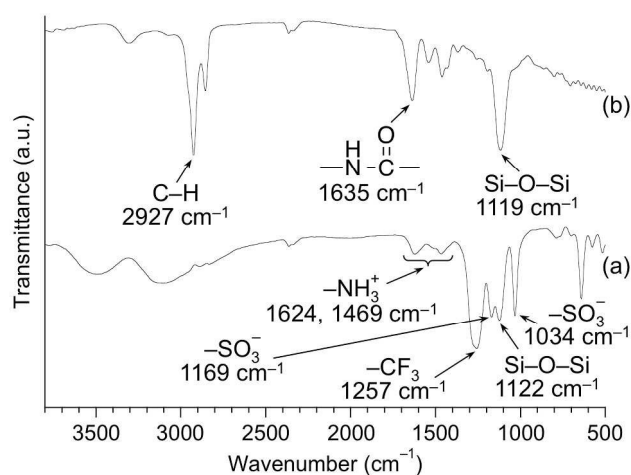

Fig. 3 IR spectra of (a) the POSS polymer and (b) the hydrophobic POSS polymer (KBr pellet).

The IR spectrum of the hydrophobic POSS polymer only showed a single absorption peak at 1119 cm^{-1} corresponding to Si–O–Si bonds (Fig. 3b). IR spectra of POSS derivatives usually show a single peak for Si–O–Si stretching because of their highly symmetrical structures.[41] In addition, this spectrum did not show any absorption peak for OH group at *ca.* 3500 cm^{-1}, indicating the absence of silanol groups in this polymer. Its ^{29}Si NMR spectrum in $CDCl_3$ at 40 °C exhibited a main signal assigned to T_8 units at -66.1–-67.7 ppm and a minor signal attributed to T_{10} units at -68.0–-69.4 ppm in the T^3 region, which is consistent with the absence of silanol groups.

Therefore, the POSS polymer retained its structure after reacting with lauroyl chloride. However, the integrated ratio of the signals for T_8 and T_{10} units in the hydrophobic POSS polymer was 0.63:0.37 ($T_8/T_{10} = 1.70$), which is lower than that of the POSS polymer ($T_8/T_{10} = 3.17$). A T_8 unit-rich polymer may present a lower average molecular weight than its T_{10} unit-rich equivalent, suggesting that this polymer was washed away by acetone during the POSS polymer hydrophobisation. Despite this change in the T_8/T_{10} unit ratio, ^{29}Si NMR and IR analyses demonstrate that the POSS polymer consisted of linked POSS T_8 and T_{10} units as main and minor components.

GPC measurements of the hydrophobic POSS polymer and AEAP-POSS, which was prepared from AEAP-POSS[39] under the same reaction conditions as the polymer hydrophobisation, were performed using chloroform as an eluent. The hydrophobic POSS polymer displayed a broad GPC peak at a higher molecular weight (Fig. 4a) than hydrophobic AEAP-POSS (Fig. 4b). Its weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) were estimated to be 3.24×10^4 and 2.24, respectively. These results indicate that the soluble polymeric material contained 9.7 POSS units on average in its main chain.
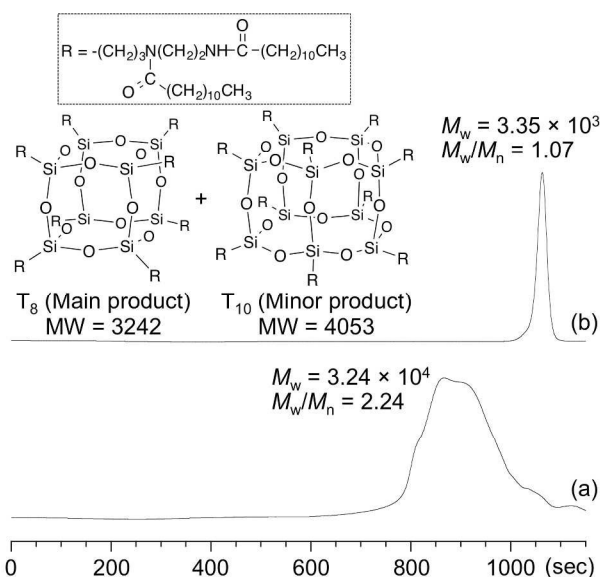

Fig. 4 GPC curves of (a) the hydrophobic POSS polymer and (b) the hydrophobic AEAP-POSS (eluent: chloroform, standard: polystyrene).

Film formation and optical properties

For UV–Vis and XRD measurements, POSS polymer and AEAP-POSS cast films were obtained by spreading and drying their corresponding aqueous solutions on flat glass substrates at room temperature.

Film transmittances were measured by UV–Vis spectroscopy. The UV–Vis spectrum of the POSS polymer film showed high transmittance in the visible wavelength region (Fig. 5a). A photograph of this film confirmed its transparency (Fig. 6a). In contrast, the UV–Vis spectrum of the AEAP-POSS film showed relatively low transmittance in the visible wavelength region (Fig. 5b), and a photograph of the film revealed its turbidity (Fig. 6b). These results show that the POSS polymer generates an optically transparent film.
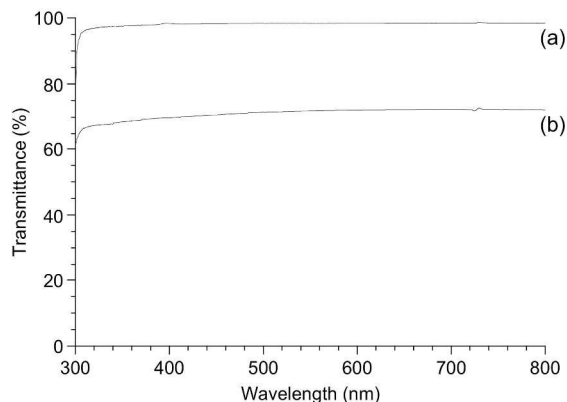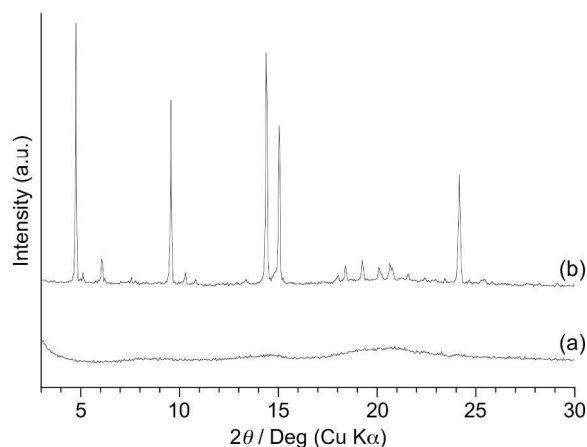
Fig. 5 UV–Vis spectra of (a) the POSS polymer film and (b) the AEAP-POSS film. The amount of each product on the glass was *ca.* 3.0 mg cm^{-2}.
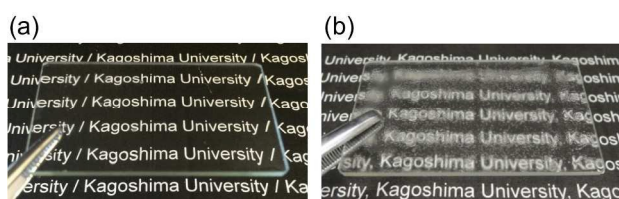
Fig. 6 Photographs of (a) the POSS polymer film and (b) the AEAP-POSS film. The amount of each product on the glass was *ca.* 3.0 mg cm^{-2}.

Common POSS compounds have rigid symmetrical cage-like structures, making regular arrays easy to construct. Indeed, the XRD pattern of the film cast from the AEAP-POSS solution contained many sharp diffraction peaks (Fig. 7b), consistent with a crystalline structure. Conversely, the POSS polymer film showed no diffraction peaks (Fig. 7a). This suggests that the polymer contained POSS components bearing two different randomly distributed side-chain groups, thus suppressing its crystallization. Because crystalline domains exhibiting similar sizes to the visible light wavelength may not exist in the POSS polymer film, an optically transparent film was obtained (Fig. 6a).


Fig. 7 XRD patterns of (a) the POSS polymer film and (b) the AEAP-POSS film. The amount of each product on the glass was *ca.* 3.0 mg cm^{-2}.

Thermal properties

Thermal stabilities of the POSS polymer and the hydrophobic POSS polymer were investigated by TGA. Thermograms of these polymers are shown in Fig. 8. T_{d5} (351 °C) and T_{d10} values (368 °C) were relatively high for the POSS polymer (Fig. 8). The values (T_{d5} = 263 °C and T_{d10} = 318 °C) were lower for the hydrophobic POSS polymer because of the presence of long alkyl side chains (Fig. 8) that were probably decomposed at relatively lower temperatures. In addition, DSC analyses of the POSS polymer and the hydrophobic POSS polymer were performed at a heating rate of 10 °C min^{-1}. The endothermic peaks assigned to the T_g for POSS polymer at 23 °C (Fig. 9a) and the T_m for hydrophobic POSS polymer at 18 °C (Fig. 9b) were observed, respectively.
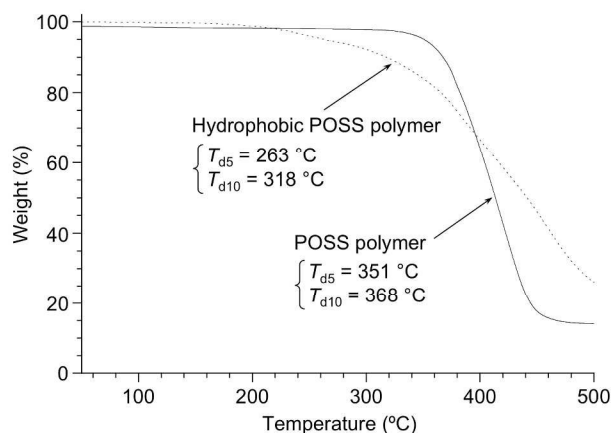
Fig. 8 TGA thermograms of the POSS polymer and the hydrophobic POSS polymer under nitrogen flow.
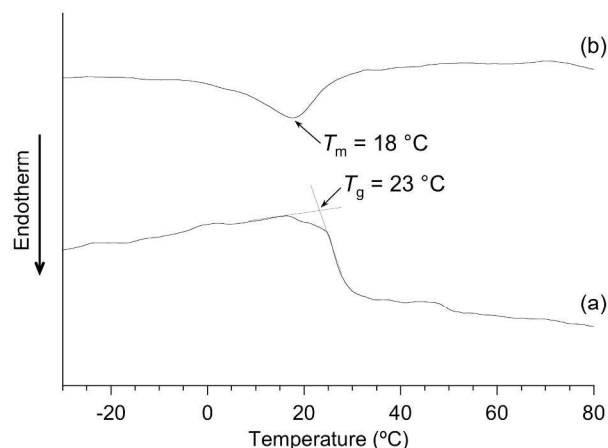
Fig. 9 DSC curves for (a) the POSS polymer and (b) the hydrophobic POSS polymer.

Conclusions

This study demonstrated that the one-step preparation of a soluble polymer containing POSS units in its main chain by hydrolytic condensation of a mixture of two amino group-containing organotrialkoxysilanes. This synthesis, catalysed by aqueous CF$_3$SO$_3$H, involved AEAPTMS as a starting material of POSS and BTMSPA as a cross-linker. The POSS polymer

produced an optically transparent film. Its structure contained POSS components bearing two different randomly distributed side-chain groups, thus suppressing its crystallization and resulting in the optically transparent film. In addition, the POSS polymer displayed relatively high thermal stability.

Notes and references

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