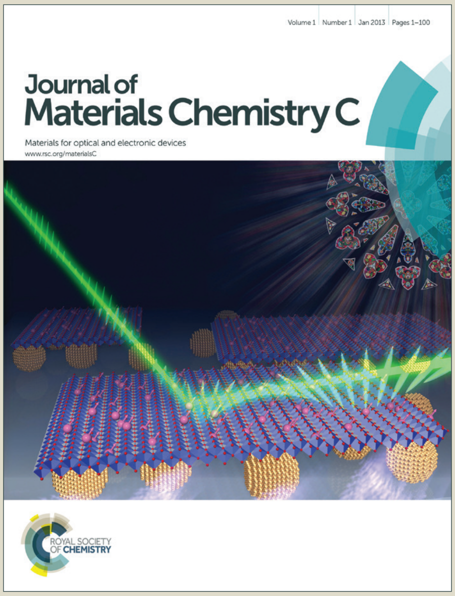
Journal of Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsC

Journal of Materials Chemistry C

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Full Paper

Preparation of low-crystalline POSS containing two types of alkylammonium groups and its optically transparent film

Takahiro Tokunaga,[a] Miki Shoiriki,[a] Tomonobu Mizumo[b] and Yoshiro Kaneko*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this study, a low-crystalline POSS containing two types of alkylammonium groups was successfully prepared by hydrolytic condensation of a mixture of two types of amino group-containing organotrialkoxysilanes, *i.e.* 3-(2-aminoethylamino)propyltrimethoxysilane and 3-aminopropyltrimethoxysilane, using aqueous trifluoromethanesulfonic acid as the catalyst and solvent. Due to the low molecular symmetry of the resulting POSS compound containing two different randomly distributed side-chain groups, its crystallization was suppressed, leading to the formation of an optically transparent film.

Introduction

Polyhedral oligomeric silsesquioxane (POSS) compounds with well-defined cage-like structures, which can be prepared by the hydrolytic condensation of trifunctional silane compounds, have attracted much attention in the research field of organic–inorganic hybrid materials from both academic and industrial viewpoints.[1–8] The POSS compounds are used extensively as inorganic fillers in polymer matrices. Such POSS fillers containing appropriate side-chain groups possess a superior ability to improve the thermomechanical properties of the original polymers.[9] In addition, the polymeric materials containing POSS components on side-chains[10–15] or the main-chain[16–19] can exhibit excellent thermal, mechanical and optical properties. POSS compounds are also used as direct cross-linking units with small organic molecules for the preparation of polymeric materials containing three-dimensional network structures.[20,21]

Even though some of the aforementioned polymer/POSS hybrids and polymeric POSS derivatives can form optically transparent films, it is difficult to prepare such films solely from POSS compounds due to their highly symmetrical and crystalline structures. Recently, Naka et al. reported that dumbbell- and star-shaped POSS derivatives obtained by linking a few POSS units formed optically transparent films,[22–24] because the reduced symmetry of the dumbbell- and star-shaped structures decreased their crystallinities.

Meanwhile, in the hydrolytic condensation of 3-aminopropyltrimethoxysilane (APTMOS) under acidic conditions, we found that cage-like oligosilsesquioxane (POSS)[25] and rod-like (ladder-like) polysilsesquioxanes[26–32] were selectively and quantitatively prepared by changing the type of acid catalyst employed. When the hydrolytic condensation of APTMOS was performed using an aqueous trifluoromethanesulfonic acid (CF_3SO_3H) as the catalyst and solvent, 3-aminopropyl POSS (AP-POSS) was prepared in higher yield (*ca.* 93%) with a shorter reaction time (*ca.* 5–6 h).[25] The formation of ammonium cations generated from APTMOS and the superacid CF_3SO_3H is important for the preparation of such POSS compounds. Therefore, it was assumed that this method using a superacid should be widely applicable for the preparation of alkylammonium group-containing POSS compounds using other types of amino group-containing organotrialkoxysilanes.

In this study, a low-crystalline POSS, which is hereafter denoted as Low-C POSS, containing two types of alkylammonium groups was successfully prepared by hydrolytic condensation of a mixture of the two types of amino group-containing organotrialkoxysilanes. Because the molecular symmetry of the resulting POSS compound with a random distribution of the two types of side-chain groups was low, its crystallization was suppressed. Consequently, a transparent film was obtained.

Experimental

Materials

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

Preparation of 3-(2-aminoethylamino)propyl POSS (AEAP-POSS)

To 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMOS; purity: 95%, 0.234 g, 1.0 mmol), an aqueous CF_3SO_3H (0.5 mol/L, 6.0 mL, 3.0 mmol) was added with stirring at room temperature. The resulting solution was further stirred at room temperature for 2 h, and then heated at *ca.* 50 °C in an open system until the solvent completely evaporated (*ca.* 2–3 h). Subsequently, the crude product was maintained at 100 °C for *ca.*

2 h, and then an acetone/chloroform mixed solvent (1:1 v/v, *ca*. 10 mL) was added at room temperature. The insoluble product was isolated by filtration, washed with this mixed solvent and chloroform, and then dried under reduced pressure at room temperature to yield 0.408 g of a white-powdered product (yield, *ca*. 90%; the ideal chemical formula of the repeating unit of this product $[SiO_{1.5}(CH_2)_3NH_2^+(CH_2)_2NH_3^+(CF_3SO_3^-)_2$, FW = 453.4] was used for the determination). This POSS compound is hereafter denoted as AEAP-POSS. ^{1}H NMR (400 MHz, D_2O): δ 3.38 (br, 4H, $NH_3\mathit{CH_2CH_2}NH_2$–), δ 3.09 (t, J = 7.33 Hz, 2H, –$NH_2\mathit{CH_2}$–), δ 1.77 (m, 2H, –$NH_2CH_2\mathit{CH_2}CH_2Si$–), δ 0.76 (t, J = 8.24 Hz, 2H, −$\mathit{CH_2}Si$−). The matrix-assisted laser desorption ionization-time of flight mass spectral (MALDI-TOF MS) analysis using 2,5-dihydroxybenzoic acid (DHB) as the matrix: Calcd for $[C_{40}H_{104}N_{16}O_{12}Si_8]$ assigned to octamer (T_8) 1224.6; found *m*/*z* 1225.7 $[M+H]^+$. Calcd for $[C_{50}H_{130}N_{20}O_{15}Si_{10}]$ assigned to decamer (T_{10}) 1530.8; found *m*/*z* 1531.8 $[M+H]^+$. ^{29}Si NMR (80 MHz, DMSO-d_6): δ −66.9 (T_8), δ −68.9 (T_{10}).

Preparation of Low-C POSS containing two types of alkylammonium groups

To a mixture of AEAPTMOS (purity: 95%, 0.234 g, 1.0 mmol) and APTMOS (purity: 96%, 0.187 g, 1.0 mmol), an aqueous CF_3SO_3H (0.5 mol/L, 15 mL, 7.5 mmol) was added with stirring at room temperature. The resulting solution was further stirred at room temperature for 2 h. The subsequent procedures were the same as those described above for the preparation of AEAP-POSS, and 0.652 g of a white-powdered product was obtained (yield, *ca*. 91%; the ideal chemical formulas of the repeating units of the AEAPTMOS component $[SiO_{1.5}(CH_2)_3NH_2^+(CH_2)_2NH_3^+(CF_3SO_3^-)_2$, FW = 453.4] and the APTMOS component $[SiO_{1.5}(CH_2)_3NH_3^+CF_3SO_3^-$, FW = 260.3] of this product were used for the determination). ^{1}H NMR (400 MHz, D_2O): δ 3.38 (br, 4H, $NH_3\mathit{CH_2CH_2}NH_2$− of the AEAPTMOS component), δ 3.10 (t, J = 7.33 Hz, 2H, –$NH_2\mathit{CH_2}CH_2CH_2Si$− of the AEAPTMOS component), δ 2.99 (t, J = 7.33 Hz, 2H, $NH_3\mathit{CH_2}$− of the APTMOS component), δ 1.76 (br, 2H, –$NH_2CH_2\mathit{CH_2}CH_2Si$− of the AEAPTMOS component and $NH_3CH_2\mathit{CH_2}CH_2Si$− of the APTMOS component), δ 0.77 (br, 2H, −$\mathit{CH_2}Si$− of the AEAPTMOS and APTMOS components). MALDI-TOF MS (DHB as a matrix): Calcd for $[C_{26}H_{69}N_9O_{12}Si_8]$ (ratio of the components of AEAPTMOS to APTMOS in T_8 = 1:7) 923.3; found *m*/*z* 924.6 $[M+H]^+$. Calcd for $[C_{28}H_{74}N_{10}O_{12}Si_8]$ (ratio of the components of AEAPTMOS to APTMOS in T_8 = 2:6) 966.4; found *m*/*z* 967.6 $[M+H]^+$. Calcd for $[C_{30}H_{79}N_{11}O_{12}Si_8]$ (ratio of the components of AEAPTMOS to APTMOS in T_8 = 3:5) 1009.4; found *m*/*z* 1010.7 $[M+H]^+$. Calcd for $[C_{32}H_{84}N_{12}O_{12}Si_8]$ (ratio of the components of AEAPTMOS to APTMOS in T_8 = 4:4) 1052.4; found *m*/*z* 1053.7 $[M+H]^+$. Calcd for $[C_{34}H_{89}N_{13}O_{12}Si_8]$ (ratio of the components of AEAPTMOS to APTMOS in T_8 = 5:3) 1095.5; found *m*/*z* 1096.7 $[M+H]^+$. Calcd for $[C_{36}H_{94}N_{14}O_{12}Si_8]$ (ratio of the components of AEAPTMOS to APTMOS in T_8 = 6:2) 1138.5; found *m*/*z* 1139.8 $[M+H]^+$. Calcd for $[C_{38}H_{99}N_{15}O_{12}Si_8]$ (ratio of the components of AEAPTMOS to APTMOS in T_8 = 7:1) 1181.6; found *m*/*z* 1182.8 $[M+H]^+$. Calcd for $[C_{36}H_{95}N_{13}O_{15}Si_{10}]$ (ratio of the components of AEAPTMOS to APTMOS in T_{10} = 3:7) 1229.5; found *m*/*z* 1230.7 $[M+H]^+$. Calcd for $[C_{38}H_{100}N_{14}O_{15}Si_{10}]$ (ratio of the components of AEAPTMOS to APTMOS in T_{10} = 4:6) 1272.5; found *m*/*z* 1273.6 $[M+H]^+$. Calcd for $[C_{40}H_{105}N_{15}O_{15}Si_{10}]$ (ratio of the components of AEAPTMOS to APTMOS in T_{10} = 5:5) 1315.6; found *m*/*z* 1316.7 $[M+H]^+$. Calcd for $[C_{42}H_{110}N_{16}O_{15}Si_{10}]$ (ratio of the components of AEAPTMOS to APTMOS in T_{10} = 6:4) 1358.6; found *m*/*z* 1359.6 $[M+H]^+$. Calcd for $[C_{44}H_{115}N_{17}O_{15}Si_{10}]$ (ratio of the components of AEAPTMOS to APTMOS in T_{10} = 7:3) 1401.6; found *m*/*z* 1402.7 $[M+H]^+$. ^{29}Si NMR (80 MHz, DMSO-d_6): δ −66.5 and −66.9 (T_8), δ −68.4 and −68.8 (T_{10}).

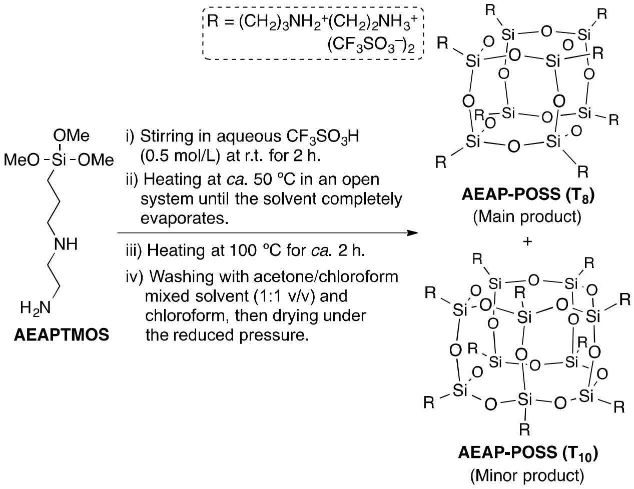
Measurements

The ^{1}H and ^{29}Si NMR spectra were recorded using a JEOL ECX-400 spectrometer. The IR spectra were recorded using a JASCO FT/IR-4200 spectrometer. The MALDI-TOF MS measurements were performed using a Shimadzu Voyager Biospectrometry Workstation Ver.5.1 with DHB as the matrix using the positive ion mode. The UV-Vis spectra were recorded using a JASCO V-630 spectrophotometer. The X-ray diffraction (XRD) measurements were performed at a scanning speed of 2θ = 1.8°/min using an X'Pert Pro diffractometer (PANalytical) with Ni-filtered Cu Kα radiation (= 0.15418 nm).

Results and discussion

Preparation and characterization of AEAP-POSS

Prior to attempting the preparation of Low-C POSS by hydrolytic condensation of a mixture of AEAPTMOS and APTMOS, it was first determined whether a POSS compound (AEAP-POSS) would be obtained when using only AEAPTMOS in an aqueous CF_3SO_3H, as was the case with AP-POSS.[25]



Scheme 1 Preparation of AEAP-POSS (T_8 and T_{10}) compounds by hydrolytic condensation of AEAPTMOS using an aqueous CF_3SO_3H as the catalyst and solvent.

The hydrolytic condensation of AEAPTMOS was performed under the following conditions: stirring of the reagent in a 0.5 mol/L aqueous CF_3SO_3H (CF_3SO_3H/AEAPTMOS, mol/mol = 3.0) at room temperature for 2 h. The resulting mixture was then heated at *ca*. 50 °C in an open system until the solvent completely evaporated (*ca*. 2–3 h). Next, the resulting crude product was continuously maintained at 100 °C for *ca*. 2 h, and then washed with an acetone/chloroform mixed solvent and chloroform at room temperature and dried under reduced pressure to obtain

AEAP-POSS in relatively higher yield (*ca.* 90%) with a shorter reaction time (*ca.* 6–7 h) (Scheme 1). The product was soluble in polar organic solvents, such as methanol, acetone and DMSO, as well as water.

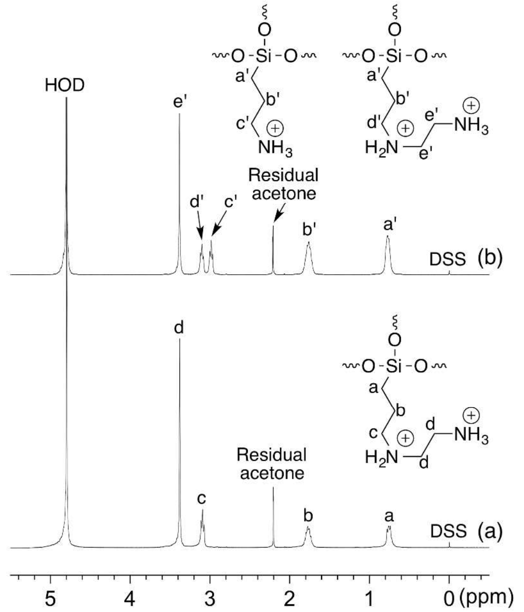


Fig. 1 ^{1}H NMR spectra of (a) AEAP-POSS and (b) Low-C POSS in D_2O. Chemical shifts were referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (δ 0.0).

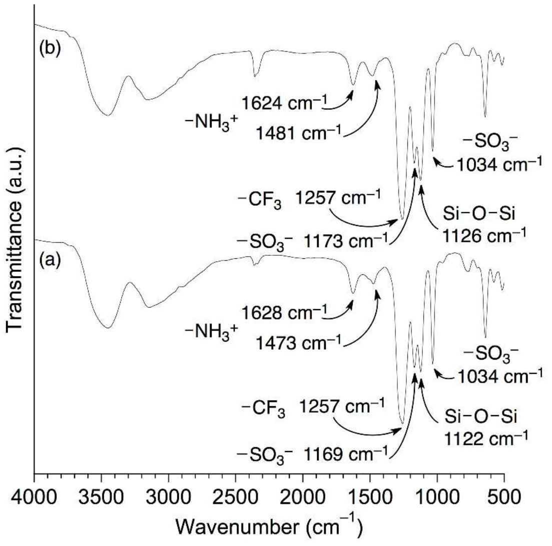


Fig. 2 IR spectra of (a) AEAP-POSS and (b) Low-C POSS in KBr pellets.

The complete consumption of AEAPTMOS and the structures of the substituent groups in the product were confirmed using ^{1}H NMR and IR analyses. The ^{1}H NMR spectrum of AEAP-POSS in D_2O showed only four signals assigned to the 3-(2-aminoethylamino)propyl groups (Fig. 1a), indicating that the AEAPTMOS reagent was not present in the product. The IR spectrum exhibited absorption at 1122 cm^{-1}, which was attributed to the Si−O−Si bonds (Fig. 2a), and confirmed that the hydrolytic condensation of AEAPTMOS went to completion to form the Si−O−Si bond framework. In addition, absorptions at 1628 and 1473 cm^{-1} (NH_3^+), 1257 cm^{-1} (CF_3), and 1169 and 1034 cm^{-1} (SO_3^-) were observed, indicating the presence of ammonium cations and trifluoromethanesulfonate anions in this product (Fig. 2a).

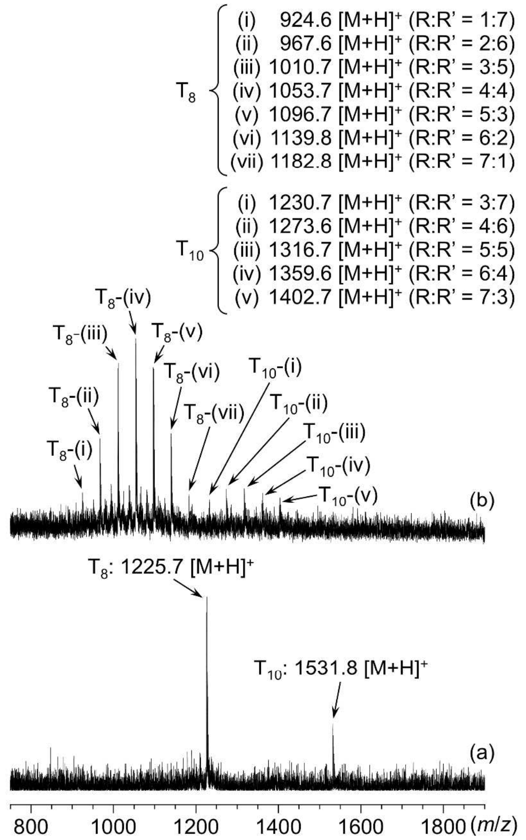


Fig. 3 MALDI-TOF MS spectra of (a) AEAP-POSS and (b) Low-C POSS.

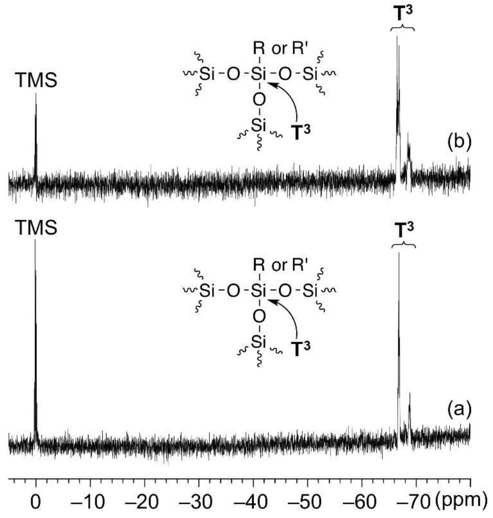


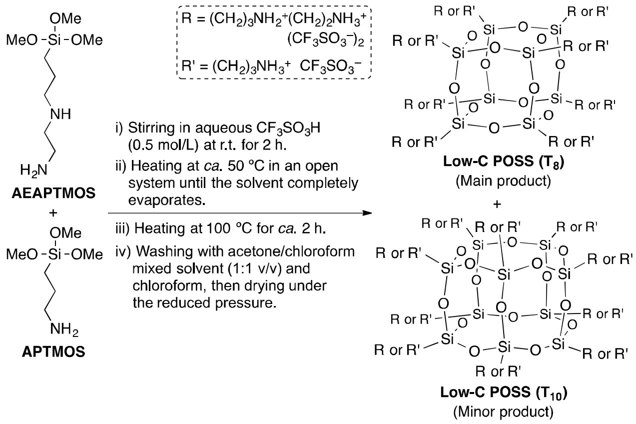
Fig. 4 ^{29}Si NMR spectra of (a) AEAP-POSS and (b) Low-C POSS in DMSO-d_6 at 40 °C. Chemical shifts were referenced to tetramethylsilane (TMS) (δ 0.0).

To confirm the structure of AEAP-POSS, MALDI-TOF MS and ^{29}Si NMR measurements were performed. In the MALDI-TOF MS spectrum of AEAP-POSS, two significant peaks were observed, which corresponded to the masses of cage-like octamer

(T_8) as a main product (*m/z* 1225.7 $[M+H]^+$) and cage-like decamer (T_{10}) as a minor product (*m/z* 1531.8 $[M+H]^+$) without the $CF_3SO_3^-$ counterions (Fig. 3a). Furthermore, the ^{29}Si NMR spectrum of AEAP-POSS in DMSO-d_6 at 40 °C showed two signals in the T^3 region at −66.9 ppm (a main signal) and at −68.9 ppm (a minor signal), indicating the absence of silanol groups (Fig. 4a). These signals are probably derived from T_8 and T_{10}, respectively, because it was reported that the signal due to T_{10} shifted to upfield (*ca.* 2 ppm) compared with that of T_8.[33] Because the integrated ratio of these signals was estimated to be 0.75:0.25, the molar ratio of T_8 to T_{10} was calculated to be 0.79:0.21 (= 0.75/8:0.25/10). Based on the MALDI-TOF MS and ^{29}Si NMR analyses, it was therefore concluded that AEAP-POSS possessed the structures of T_8 as a main product and T_{10} as a minor product, as shown in Scheme 1.

Preparation and characterization of Low-C POSS

In the present and previous[25] studies, the preparation of the alkylammonium group-containing POSS compounds, *i.e.* AEAP-POSS and AP-POSS, was achieved by the hydrolytic condensation of AEAPTMOS and APTMOS, respectively, using aqueous CF_3SO_3H as the catalyst and solvent. Therefore, the preparation of a POSS containing two types of alkylammonium groups (Low-C POSS) from a mixture of AEAPTMOS and APTMOS was investigated.



Scheme 2 Preparation of Low-C POSS (T_8 and T_{10}) compounds by hydrolytic condensation of a mixture of AEAPTMOS and APTMOS using an aqueous CF_3SO_3H as the catalyst and solvent.

It was found that Low-C POSS was obtained in higher yield (*ca.* 91%) with a shorter reaction time (*ca.* 7–8 h) when the hydrolytic condensation of a mixture of AEAPTMOS and APTMOS was performed using a 0.5 mol/L aqueous CF_3SO_3H (CF_3SO_3H/amino groups in AEAPTMOS and APTMOS, mol/mol = 2.5) under the same reaction conditions as described for the preparation of AEAP-POSS (Scheme 2). The resulting product was soluble in polar organic solvents, such as methanol, acetone and DMSO, as well as water. The complete consumption of AEAPTMOS and APTMOS and the structures of the substituent groups in the product were confirmed through ^1H NMR and IR analyses (Figs. 1b and 2b, respectively). The average compositional ratio of AEAPTMOS to APTMOS components in the product was estimated to be *ca.* 1:1 from the integrated ratio of the peaks **d'** to **c'** in the ^1H NMR spectrum (Fig. 1b).

The structure of Low-C POSS was further characterized based on MALDI-TOF MS and ^{29}Si NMR measurements. In the MALDI-TOF MS spectrum of Low-C POSS, several peaks were observed (Fig. 3b). These peaks corresponded to the masses of cage-like octamer (T_8) as main products for seven different AEAPTMOS (R) to APTMOS (R') component ratios (R:R' = 1:7, *m/z* 924.6 $[M+H]^+$; R:R' = 2:6, *m/z* 967.6 $[M+H]^+$; 3:5, *m/z* 1010.7 $[M+H]^+$; 4:4, *m/z* 1053.7 $[M+H]^+$; 5:3, *m/z* 1096.7 $[M+H]^+$; 6:2, *m/z* 1139.8 $[M+H]^+$; 7:1, *m/z* 1182.8 $[M+H]^+$) and cage-like decamer (T_{10}) as minor products for five different R to R' component ratios (R:R' = 3:7, *m/z* 1230.7 $[M+H]^+$; R:R' = 4:6, *m/z* 1273.6 $[M+H]^+$; 5:5, *m/z* 1316.7 $[M+H]^+$; 6:4, *m/z* 1359.6 $[M+H]^+$; 7:3, *m/z* 1402.7 $[M+H]^+$). In addition, the ^{29}Si NMR spectrum of Low-C POSS in DMSO-d_6 at 40 °C showed two signals in the T^3 region at −66.5 and −66.9 ppm (main signals, assigned to T_8) and at −68.4 and −68.9 ppm (minor signals, assigned to T_{10}), indicating the absence of silanol groups (Fig. 4b). The integrated ratio of the signals due to T_8 to T_{10} was estimated to be 0.74:0.26, indicating that the molar ratio of T_8 to T_{10} was 0.78:0.22 (= 0.74/8:0.26/10). Based on the MALDI-TOF MS and ^{29}Si NMR analyses, it was therefore concluded that Low-C POSS was a mixture composed of T_8 (a main product) and T_{10} (a minor product) with random distribution of the two types of side-chain alkylammonium groups.

Formation of films and their properties

For the UV-Vis and XRD measurements, the cast films of Low-C POSS, AEAP-POSS, AP-POSS and an equimolar AEAP-POSS/AP-POSS mixture were obtained by drying the corresponding aqueous solutions of these POSS compounds spread on flat glass substrates at room temperature.

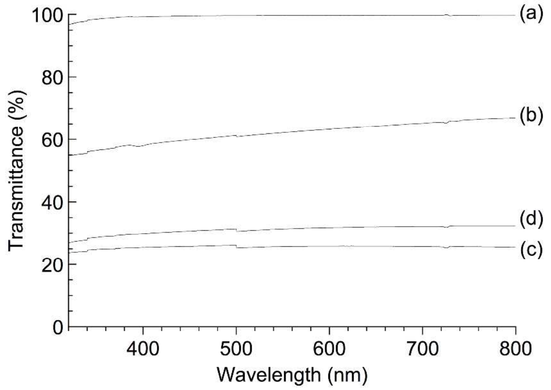


Fig. 5 UV-Vis spectra of films of (a) Low-C POSS, (b) AEAP-POSS, (c) AP-POSS and (d) an AEAP-POSS/AP-POSS mixture. The amount of each product on the glass was *ca.* 3.0 mg/cm^2.

The transmittances of the films were measured by UV-Vis spectroscopies. The UV-Vis spectrum of the Low-C POSS film showed high transmittance in the visible wavelength region (Fig. 5a). A photograph of this film also supported its transparency (Fig. 6a). On the other hand, the UV-Vis spectra of the AEAP-POSS and AP-POSS films indicated relatively low transmittances in the visible wavelength region (Figs. 5b and 5c, respectively), and photographs of these films revealed their turbidities (Figs. 6b and 6c, respectively). In addition, the film of the AEAP-POSS/AP-POSS mixture was turbid, which was confirmed in the UV-Vis spectrum (Fig. 5d) and by visual observation (Fig. 6d).

These results indicate that an optically transparent film can be obtained only by mixing two types of side-chain groups in a POSS compound at the elemental level, and not by mixing two types of POSS compounds at the molecular level.

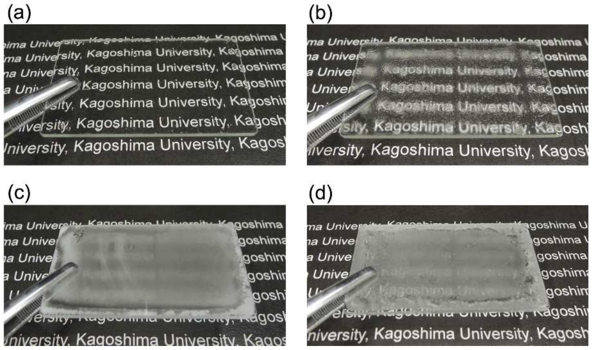


Fig. 6 Photographs of films of (a) Low-C POSS, (b) AEAP-POSS, (c) AP-POSS and (d) an AEAP-POSS/AP-POSS mixture. The amount of each product on the glass was *ca*. 3.0 mg/cm^2.

Because common POSS compounds have rigid symmetrical cage-like structures, it is easy to construct regular array structures. Indeed, the XRD patterns of the films formed from solutions of AEAP-POSS, AP-POSS and the AEAP-POSS/AP-POSS mixture contained many sharp diffraction peaks (Figs. 7b–d, respectively), indicating crystalline structures. On the other hand, that of the Low-C POSS film barely showed any diffraction peaks (Fig. 7a). This is because the molecular symmetry of the Low-C POSS compound with two different randomly distributed side-chain groups was low. Therefore, its crystallization was suppressed. Because crystalline domains with similar size to wavelength of visible light probably did not exist in the Low-C POSS film, an optically transparent film was obtained, as shown in Fig. 6a.

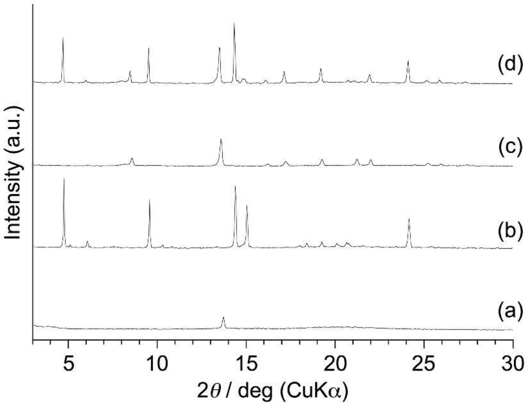


Fig. 7 XRD patterns of films of (a) Low-C POSS, (b) AEAP-POSS, (c) AP-POSS and (d) an AEAP-POSS/AP-POSS mixture. The amount of each product on the glass was *ca*. 3.0 mg/cm^2.

Conclusions

In this study, it was found that low-crystalline POSS (Low-C POSS) containing two types of alkylammonium groups could be prepared by hydrolytic condensation of a mixture of two types of amino group-containing organotrialkoxysilanes, *i.e.* AEAPTMOS and APTMOS, using the superacid CF_3SO_3H as the catalyst and solvent. Because the molecular symmetry of the resulting POSS compound containing two different randomly distributed side-chain groups was low, its crystallization was suppressed, resulting in the formation of an optically transparent film.

Acknowledgements

We wish to thank Prof. Y. Suda and Dr. M. Wakao of Graduate School of Science and Engineering, Kagoshima University (Japan) for support in MALDI-TOF MS measurements.

Notes and references

[a] *Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan. Fax: +81 99 285 7794; Tel: +81 99 285 7794; E-mail: ykaneko@eng.kagoshima-u.ac.jp*
[b] *Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan.*

1 R. H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, 1995, **95**, 1409.
2 D. A. Loy, B. M. Baugher, C. R. Baugher, D. A. Schneider and K. Rahimian, *Chem. Mater.*, 2000, **12**, 3624.
3 D. B. Cordes, P. D. Lickiss and F. Rataboul, *Chem. Rev.*, 2010, **110**, 2081.
4 R. M. Laine and M. F. Roll, *Macromolecules*, 2011, **44**, 1073.
5 S. W. Kuo and F. C. Chang, *Prog. Polym. Sci.*, 2011, **36**, 1649.
6 F. Wang, X. Lu and C. He, *J. Mater. Chem.*, 2011, **21**, 2775.
7 K. Tanaka and Y. Chujo, *J. Mater. Chem.*, 2012, **22**, 1733.
8 C. Samthong, R. M. Laine and A. Somwangthanaroj, *J. Appl. Polym. Sci.*, 2013, **128**, 3601.
9 K. Tanaka, S. Adachi and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 5690.
10 J. D. Lichtenhan, Y. A. Otonari and M. J. Carr, *Macromolecules*, 1995, **28**, 8435.
11 T. S. Haddad and J. D. Lichtenhan, *Macromolecules*, 1996, **29**, 7302.
12 A. Tsuchida, C. Bolln, F. G. Sernetz, H. Frey and R. Mülhaupt, *Macromolecules*, 1997, **30**, 2818.
13 A. Lee and J. D. Lichtenhan, *Macromolecules*, 1998, **31**, 4970.
14 P. T. Mather, H. G. Jeon, A. Romo-Uribe, T. S. Haddad and J. D. Lichtenhan, *Macromolecules*, 1999, **32**, 1194.
15 K. M. Kim and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 4035.
16 S. Wu, T. Hayakawa, R. Kikuchi, S. J. Grunzinger, M. Kakimoto and H. Oikawa, *Macromolecules*, 2007, **40**, 5698.
17 S. Wu, T. Hayakawa, M. Kakimoto and H. Oikawa, *Macromolecules*, 2008, **41**, 3481.
18 J. H. Jung and R. M. Laine, *Macromolecules*, 2011, **44**, 7263.
19 K. Wei, L. Wang and S. Zheng, *Polym. Chem.*, 2013, **4**, 1491.
20 C. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristov and A. L. Yee, *J. Am. Chem. Soc.*, 1998, **120**, 8380.
21 J. Choi, A. L. Yee and R. M. Laine, *Macromolecules*, 2004, **37**, 3267.
22 H. Araki and K. Naka, *Macromolecules*, 2011, **44**, 6039.
23 H. Araki and K. Naka, *Polym. J.*, 2012, **44**, 340.
24 H. Araki and K. Naka, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4170.
25 Y. Kaneko, M. Shoiriki and T. Mizumo, *J. Mater. Chem.*, 2012, **22**, 14475.
26 Y. Kaneko, N. Iyi, K. Kurashima, T. Matsumoto, T. Fujita and K. Kitamura, *Chem. Mater.*, 2004, **16**, 3417.
27 Y. Kaneko, N. Iyi, T. Matsumoto and K. Kitamura, *Polymer*, 2005, **46**, 1828.
28 Y. Kaneko and N. Iyi, *Z. Kristallogr.*, 2007, **222**, 656.
29 Y. Kaneko and N. Iyi, *J. Mater. Chem.*, 2009, **19**, 7106.
30 Y. Kaneko and N. Iyi, *Kobunshi Ronbunshu*, 2010, **67**, 280.
31 Y. Kaneko, H. Toyodome and H. Sato, *J. Mater. Chem.*, 2011, **21**, 16638.
32 Y. Kaneko, H. Toyodome, M. Shoiriki and N. Iyi, *Int. J. Polym. Sci.*, 2012, 684278.

33 V. Ervithayasuporn, X. Wang and Y. Kawakami, *Chem. Commun.*, 2009, 5130.