



Intermolecular interaction of supramolecular organic–inorganic hybrid composites of sulfonated polystyrene and oligomeric silsesquioxane possessing pyridyl groups

Mitsuhiro Shibata*, Ryosuke Horie, Wataru Yoneta

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan

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ABSTRACT

Supramolecular organic–inorganic hybrid composites of pyridyl groups-possessing oligomeric silsesquioxane (PyOSS) synthesized by the reaction of 2-(2-pyridylethyl)trimethoxysilane and trimethoxyphenylsilane in the molar ratio of 3/5 with 1,3-propanedisulfonic acid (PDS), 1,5-naphthalenedisulfonic acid (NDS), and poly(4-styrenesulfonic acid) (PSS) were prepared by solution casting method at SO_3H /pyridine 1/1. From the FT-IR analysis, the formation of pyridinium cation moiety was confirmed for PDS/PyOSS and NDS/PyOSS, while it could not be elucidated for PSS/PyOSS. As a result of XPS analysis of the newly prepared hybrid composites of PyOSS and sulfonated polystyrenes (SPSx's) with different degrees of sulfonation ($x = 3, 8, 23\%$), the formation of pyridinium ion structure was confirmed for SPS23/PyOSS, and the ionic interaction gradually changed to hydrogen-bonding interaction with decreasing degree of sulfonation of SPSx. Although the glass transition temperature of SPSx moiety was little affected by the addition of PyOSS, the glass transition itself was gradually weakened and was not detected for SPS23/PyOSS.

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1. Introduction

Silsesquioxanes with the general molecular formula $(\text{RSiO}_{3/2})_n$ are a class of inorganic compounds that exist in a variety of structures such as random, ladder, cage (polyhedral), and partial cage structures [1]. Among their silsesquioxanes, polyhedral oligomeric silsesquioxane (POSS) compounds are of particular interest since they possess an octahedral cage-like structure [2–4]. The POSS substituted with multiple reactive groups are useful molecular nanobuilding blocks in the formation of organic–inorganic hybrid networks. Functional groups such as epoxy [5–14], amine [15–18], vinyl [19–22], and methacryl [23–26] have been successfully incorporated into POSS structures and used for the preparation of the hybrid nanocomposites. Numerous POSS derivatives are nowadays commercially available. However, they are very expensive reagents, and further modification by some reactions and subsequent purification are generally difficult. Recently, Zhao et al. reported a convenient preparation method of aminopropyl/phenylsilsesquioxane containing the structures other than POSS by the

reaction of aminopropyltriethoxysilane and triethoxyphenylsilane in the presence of tetramethylammonium hydroxide (TMAOH) [27]. We had also reported a facile synthesis of methacryl-substituted polysilsesquioxane from 3-(trimethoxysilyl)propyl methacrylate by use of TMAOH and its application to the preparation of hybrid network polymers [28–30].

On the other hand, the formation of supramolecular polymer network by use of non-covalent interactions such as hydrogen-bonding and Coulombic interactions between multifunctional monomers, oligomers, and polymers has received increasing attention in recent years [31–46]. There have been many literatures regarding the supramolecular polymer networks by use of the hydrogen-bonding interaction such as the combination of carboxylic acid/pyridyl or imidazolyl group [32,33,37], maleimide/melamine [34], and ureido-pyrimidone units [35]. Regarding the supramolecular polymer networks based on ionic interaction, ionomers and polyion complexes such as poly(4-vinylpyridine) (P4VP)/poly(styrenesulfonic acid) (PSS), poly(styrene-co-styrenesulfonic acid)/poly(styrene-co-(4-vinylpyridine)), P4VP/poly(acrylic acid) etc. [38–44] are reported in the literatures. Also, we had already reported the supramolecular polymer network based on the ionic interaction between P4VP and disulfonic acid compounds [45]. Regarding supramolecular organic–inorganic hybrid composites, Chujo et al.

* Correspondence author. Tel.: +81 47 478 0423; fax: +81 47 478 0439.

E-mail address: shibata@sky.it-chiba.ac.jp (M. Shibata).

recently reported poly(vinyl chloride)/octaphenylethyl POSS hybrid composites based on CH/ π interaction [46]. To the best of our knowledge, there has been no report on the supramolecular organic–inorganic hybrid nanocomposite by use of ionic interaction between multifunctional POSS and organic compound.

The present paper describes the molecular interaction and thermal properties of supramolecular organic–inorganic hybrid composites based on polysulfonated compounds and pyridyl groups-substituted oligomeric silsesquioxane (PyOSS) prepared via one-pot reaction. Especially, our attention is focused on the intermolecular interaction between PyOSS and sulfonated polystyrenes with different degree of sulfonation.

2. Experimental part

2.1. Materials

1,5-Naphthalenedisulfonic acid (NDS) tetrahydrate, 1,3-propanedisulfonic acid (PDS) 50–60 wt% in water, and 1,2-dichloroethane were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). The polystyrene (PSt) used in this study is general purpose polystyrene, G9504 (weight-average molecular weight: ca. 400,000) supplied from PS Japan Corporation (Tokyo, Japan). Acetic anhydride ($d = 1.08$ g/mL) and sulfuric acid (96%, 1.840 g/mL, 25 °C) were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Poly(4-styrenesulfonic acid) (PSS) 18 wt% in water, trimethoxyphenylsilane (TMPS, 1.062 g/mL, 25 °C), 10 wt% TMAOH ($d = 1.006$ g/mL, 25 °C) in water were supplied from Sigma–Aldrich Japan Corp. (Tokyo, Japan). 2-(2-Pyridylethyl)trimethoxysilane (PETMS, $d = 1.06$ g/mL, 20 °C) was purchased from Gelest Inc. (Morrisville, PA). The structures of PDS, NDS, PSS, PETMS, and TMPS are shown in Fig. 1 and Fig. 2.

2.2. Preparation of PyOSS

Synthetic scheme of PyOSS is shown in Fig. 2. A mixture of methanol (75 mL), ion-exchanged water (25 mL), and 10 wt% tetramethylammonium hydroxide aqueous solution (10.0 mL, 11.0 mmol) were stirred in a 250 mL flask. A mixture of PETMS (5.00 mL, 23.3 mmol) and TMPS (7.20 mL, 38.6 mmol) was added to the above solution at room temperature. The mixture was stirred for 24 h, and further kept at room temperature for 24 h. The formed precipitate

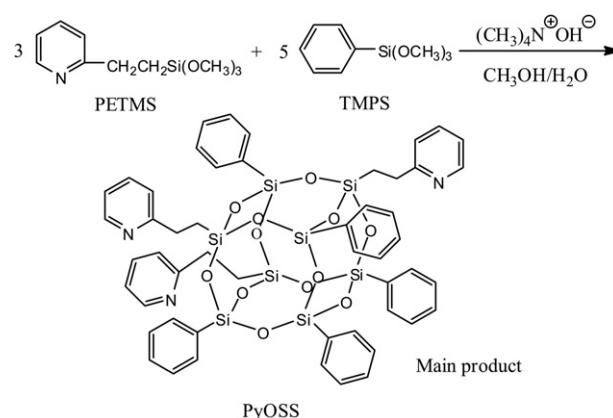


Fig. 2. Synthetic scheme of PyOSS.

was collected by decantation of most clear supernatant, washed by vacuum filtration with methanol/ion-exchanged water (3/1 by volume), and then washed again with methanol. The rinsed powder was dried under vacuum for 24 h at 50 °C to give PyOSS (7.50 g) of as a white powder in 86% yield. The ratio of pyridylethyl/phenyl groups measured by ^1H NMR for PyOSS was 3.2/4.8, although the feed molar ratio of PETMS/TMPS was 3.0/5.0. Theoretical average molecular weight (1126.5) of the T^3_8 cubic polyhedral oligomeric silsesquioxane with 3.2/4.8 pyridylethyl/phenyl groups ($\text{C}_{51.2}\text{H}_{49.6}\text{N}_{3.2}\text{Si}_8\text{O}_{12}$; 1126.5) was used for the calculation of feed amount on the preparation of hybrid composites.

2.3. Preparation of sulfonated polystyrenes

A typical synthetic procedure of sulfonated polystyrene (SPSx) with the degree of sulfonation (x) of ca. 8% (SPS8) is as follows [47]: To a solution of PSt (10.4 g, phenyl group: 100 mmol) in 1,2-dichloroethane (49 mL) was added the acetyl sulfate solution (10.0 mL) prepared *in situ* by the reaction of acetic anhydride (1.5 mL, 16 mmol) and sulfuric acid (0.56 mL, 10 mmol) in 1,2-dichloroethane (7.9 mL) at 0 °C. After stirring for 1 h at 50 °C, the reaction mixture was poured into methanol (300 mL). The formed precipitate was filtered, washed with water several times and then with methanol, and vacuum-dried at 110 °C for 3 days to give sulfonated polystyrene (9.5 g) with the degree of sulfonation of 7.75% (SPS8) as a white powder in 85% yield. The sulfonated polystyrenes with the degree of sulfonation of 3.12 and 23.2% (SPS3 and SPS23) were prepared in a similar manner to the synthesis of SPS8

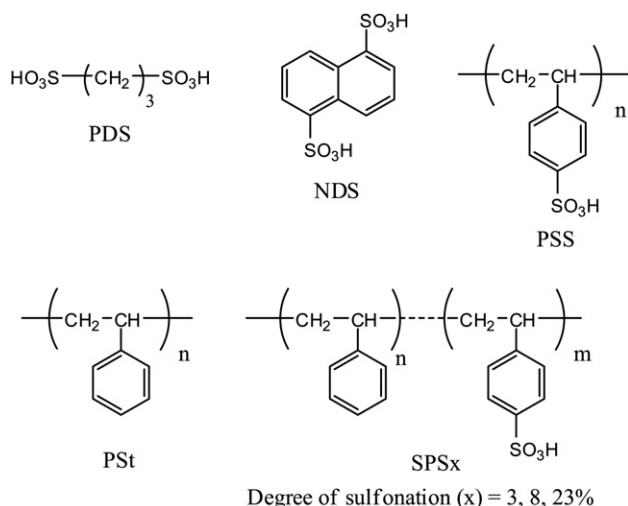


Fig. 1. Structures of PDS, NDS, PSS, PSt, and SPSx.

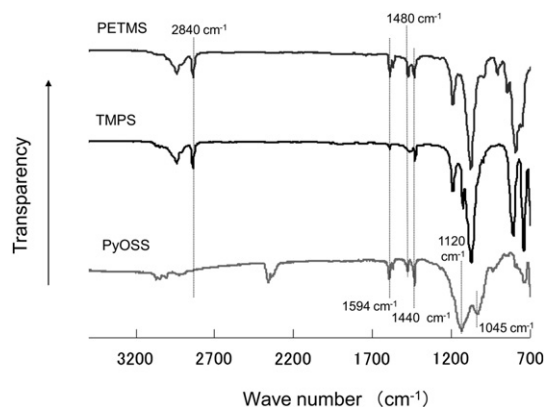


Fig. 3. FT-IR spectra of PETMS, TMPS, and PyOSS.

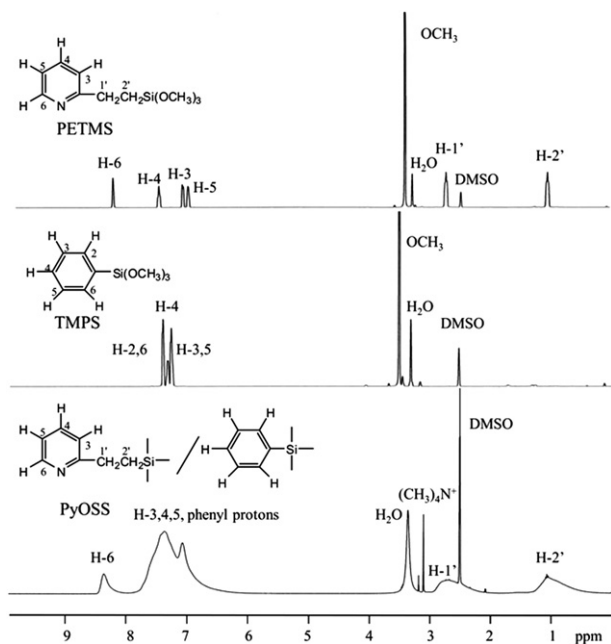


Fig. 4. ^1H NMR spectra of PETMS, TMPS, and PyOSS in $\text{DMSO}-d_6$.

except using 5.0 mL and 25.0 mL of acetyl sulfate solution, respectively. The degree of sulfonation of SPSx was measured by the titration of a tetrahydrofuran (THF) solution of SPSx with 0.1 N KOH in methanol using Phenolphthalein. The degree of sulfonation of PSt and PSS is 0% and 100%, respectively.

2.4. Preparation of PDS/PyOSS, NDS/PyOSS, PSS/PyOSS hybrid composites

A typical synthetic procedure of PDS/PyOSS is as follows: To a mixture of PDS 55% in water (0.408 g, SO_3H :2.20 mmol) and

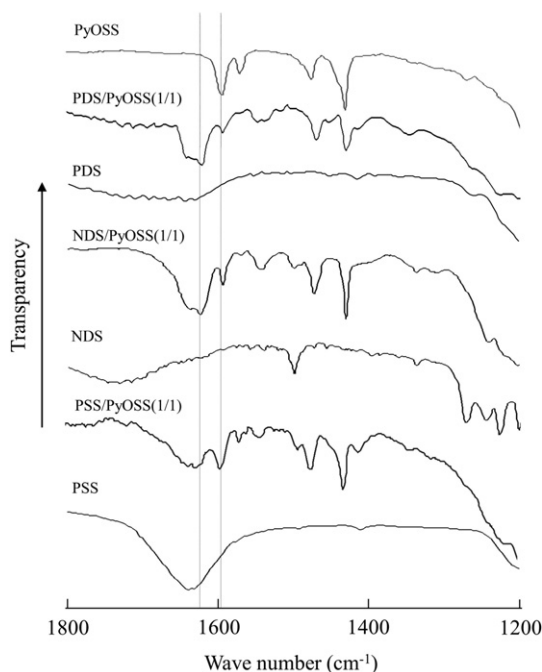


Fig. 5. FT-IR spectra of PDS/PyOSS(1/1), NDS/PyOSS(1/1), PSS/PyOSS(1/1), and their single components.

Table 1

Thermal properties of PDS/PyOSS, NDS/PyOSS, and PSS/PyOSS hybrid composites with the molar ratio of SO_3H /pyridine 1/1.

Sample	SiO content (wt%)	T_m^b ($^{\circ}\text{C}$)	T_d^d ($^{\circ}\text{C}$)
PDS ^a	0	125.6	256.4
PDS/PyOSS	28.6	ND	373.9
NDS	0	168.9	206.0
NDS/PyOSS	26.3	ND	368.4
PSS ^a	0	ND ^c	328.1
PSS/PyOSS	24.3	ND ^c	420.1
PyOSS	37.0	ND ^c	388.6

^a The samples for the thermal analyses were prepared by drying aqueous PDS and PSS solutions at 180 $^{\circ}\text{C}$ for 1 h.

^b The T_m measured by DSC.

^c T_g was not also detected.

^d The temperature at 5% weight loss measured by TGA at a heating rate of 20 $^{\circ}\text{C}/\text{min}$.

THF/water (13.5 mL/1.5 mL) was added a solution of PyOSS (0.774 g, pyridine: 2.20 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 24 h, poured onto a Petri dish, and then dried at 70 $^{\circ}\text{C}$ for 1 day, 100 $^{\circ}\text{C}$ for 3 h, and finally 140 $^{\circ}\text{C}$ for 1 h to give a PDS/PyOSS hybrid composite with SO_3H /pyridine 1/1 (PDS/PyOSS(1/1)) as a brittle pale brown flake.

In a similar manner to the preparation of PDS/PyOSS(1/1) except for the use of 0.396 g (SO_3H :2.20 mmol) and 2.25 g (SO_3H :2.20 mmol) of NDS tetrahydrate and PSS 18 wt% in water, respectively, NDS/PyOSS(1/1) and PSS/PyOSS(1/1) were prepared as pale brown solid.

2.5. Preparation of SPSx/PyOSS hybrid composites

A typical synthetic procedure of SPS8/PyOSS is as follows: To a solution of SPS8 (3.13 g, SO_3H :2.20 mmol) in THF (30 mL) was added a solution of PyOSS (0.774 g, Pyridine: 2.20 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 24 h, poured onto a Petri dish, and then dried at 70 $^{\circ}\text{C}$ for 1 day, 100 $^{\circ}\text{C}$ for 3 h, and finally 140 $^{\circ}\text{C}$ for 1 h to give a SPS8/PyOSS hybrid composite with SO_3H /pyridine 1/1 (SPS8/PyOSS(1/1)) as a pale brown film.

In a similar manner to the preparation of SPS8/PyOSS(1/1) except for the use of 7.51 g (SO_3H :2.20 mmol) and 1.164 g (SO_3H :2.20 mmol)

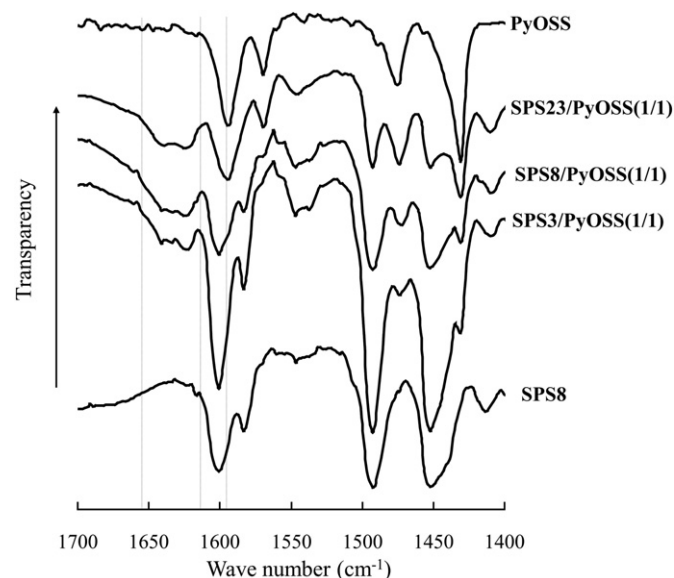


Fig. 6. FT-IR spectra of SPSx/PyOSS(1/1), PyOSS, and SPS8.

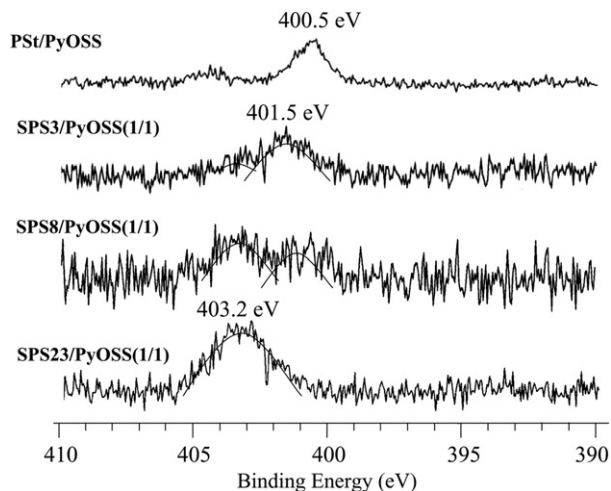


Fig. 7. N 1s spectra of PSt/PyOSS and SPSx/PyOSS(1/1) ($x = 3, 8$, and 23).

of SPS3 and SPS23, respectively, SPS3/PyOSS(1/1) and SPS23/PyOSS(1/1) were prepared as pale brown films. The SPSx/PyOSS hybrid composites with the molar ratios of SO_3H /pyridine 2/1 and 3/1 (SPSx/PyOSS(2/1) and SPSx/PyOSS(3/1)) were also prepared. As a comparison, the PSt/PyOSS composite film with SiO content 7.34 wt% was similarly prepared from a solution of PSt (3.13 g) in THF (30 mL) and a solution of PyOSS (0.774 g) in THF (10 mL).

2.6. Measurements

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AV-400 (400 MHz) using $\text{DMSO}-d_6$ as a solvent. FT-IR spectra were measured on a FT-IR 8100 spectrometer (Shimadzu Co. Ltd., Japan) by KBr or ATR method. Gel permeation chromatography (GPC) of PyOSS was carried out at 40°C on a Shimadzu LC-10A series apparatus equipped with two PLgel $5\ \mu\text{m}$ Mixed-D GPC columns (Polymer Laboratories Ltd., the linear range of molecular weight: 200–400,000) and a refractive index detector. THF was used as an eluent at a flow rate of 0.5 mL/min. Polystyrene standards with a narrow distribution of molecular weight (M_w : 580–377,400) were used for molecular weight calibration. The

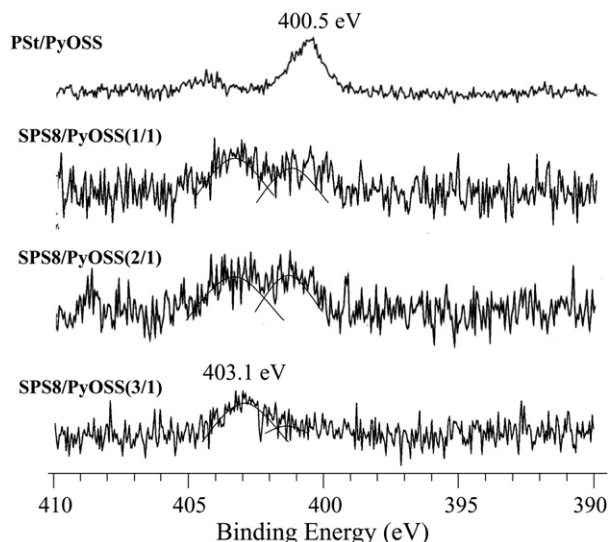


Fig. 8. N 1s spectra of PSt/PyOSS and SPS8/PyOSS(1/1, 2/1, and 3/1).

differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer Diamond DSC in a nitrogen atmosphere. In order to eliminate a thermal history of the samples, the samples were heated to 180°C at a rate of $20^\circ\text{C}/\text{min}$, held at the temperature for 3 min, and then cooled to 25°C at a rate of $20^\circ\text{C}/\text{min}$. After held at 25°C for 2 min, the second heating scan was monitored at a heating rate of $20^\circ\text{C}/\text{min}$ for determining glass transition temperature (T_g) and melting temperature (T_m). Thermal degradation temperature (T_d) at 5% weight loss was measured on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. The XPS measurements were carried out on a photoelectron spectrometer (JEOL Ltd., JPS-90SX) using $\text{Mg K}\alpha$ radiation at 10 kV and 10 mA. Solubility of the composites was tested after a mixture of composite (10 mg) and solvent (0.5 mL) was treated with supersonic waves for 5 min, and then allowed to stand for 24 h at room temperature.

3. Results and discussion

3.1. Characterization of PyOSS

The reaction of PETMS/TMPS (molar ratio: 3/5) in the presence of TMAOH in methanol/water gave PyOSS, as was shown in Fig. 2. Fig. 3 shows FT-IR spectrum of the obtained PyOSS. The absorption peak at $2840\ \text{cm}^{-1}$ ascribed to the C–H stretching vibration of methoxy group is observed for TMPS and PETMS. In case of PyOSS, the corresponding peak at around $2840\ \text{cm}^{-1}$ was very weak and a broad absorption peak based on hydroxyl group was not observed in the region from 3200 to $3500\ \text{cm}^{-1}$, suggesting the completion of the hydrolysis and condensation of trimethoxysilyl groups of PETMS and TMPS. The absorption peaks at 1594 – $1440\ \text{cm}^{-1}$ based on the framework vibrations of pyridine ring and benzene ring for PETMS and TMPS, respectively are observed for PyOSS, suggesting that PyOSS possesses both pyridyl and phenyl groups. PyOSS showed the absorption peaks at 1120 and $1045\ \text{cm}^{-1}$ ascribed to the symmetric and asymmetric Si–O–Si stretching vibrations. Brown et al. reported that caged POSS's give only one Si–O–Si band at 1120 – $1130\ \text{cm}^{-1}$, while polysilsesquioxanes containing open cages and perhaps some ladder structure exhibits two band at 1135 – 1150 and 1045 – $1060\ \text{cm}^{-1}$ [48]. These results suggest that PyOSS has mainly caged POSS structure, and that incomplete cages and some ladder structures are also contained as minor components.

Fig. 4 shows the ^1H NMR spectrum of the obtained PyOSS in $\text{DMSO}-d_6$. The ^1H signal of methoxy group observed for PETMS and TMPS at 3.34 and 3.40 ppm, respectively disappeared for PyOSS, suggesting the completion of condensation reaction. The ^1H signal of H-6 of pyridyl group was observed at 8.35 ppm (bs), and the other protons (H-3,4,5) of pyridyl group and phenyl protons were observed at 7.8–6.8 ppm (bm). From the integral values of their proton signals, the ratio of pyridylethyl/phenyl groups of PyOSS was evaluated to be 3.2/4.8 on the assumption that PyOSS is octa-substituted T^3_8 cubic POSS. The broadening of the proton signals of PyOSS should be related to the fact that PyOSS is a mixture of the compounds with different numbers and positions of pyridylethyl and phenyl groups. The number and weight average molecular weights (M_n and M_w) of PyOSS relative to polystyrene standards were 900 and 1400, respectively. Their values were reasonable considering theoretical average molecular weight (1126.5) of the T^3_8 cubic POSS with the pyridylethyl/phenyl ratio of 3.2/4.8.

3.2. Characterization and thermal properties of the hybrid composites of PDS, NDS, and PSS with PyOSS

Fig. 5 shows the FT-IR spectra of the hybrid composites of PDS, NDS, and PSS with PyOSS at SO_3H /pyridine 1/1 as compared with the

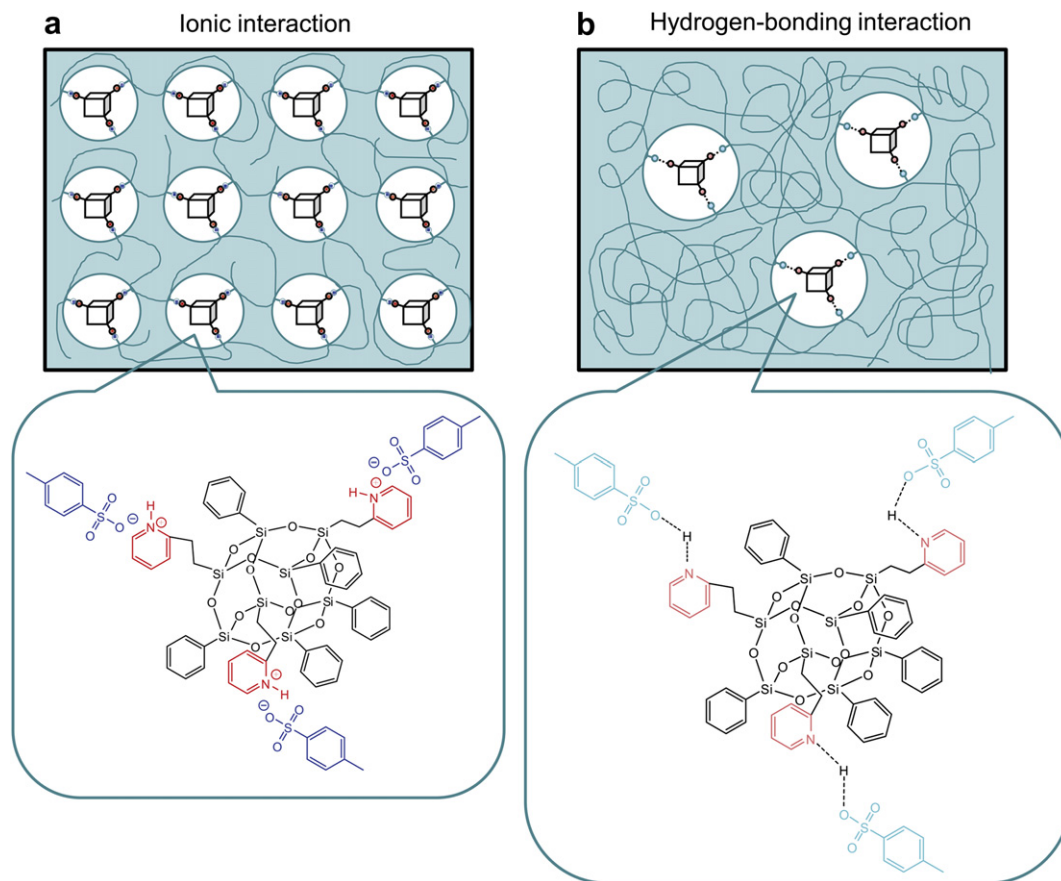


Fig. 9. Illustration of (a) ionic interaction of SPSx/PyOSS(1/1) with a high degree of sulfonation and (b) hydrogen-bonding interaction of SPSx/PyOSS(1/1) with a low degree of sulfonation.

corresponding single components. The absorption peak at 1594 cm^{-1} for PyOSS is attributed to the framework stretching of the pyridine and benzene ring. The PDS/PyOSS(1/1) and NDS/PyOSS(1/1) hybrid composites exhibited strong absorption peaks at around $1626\text{--}1650\text{ cm}^{-1}$ related to the framework stretching of pyridinium ring, which are not appeared for PDS, NDS, and PyOSS, suggesting that pyridine rings of PyOSS are protonated by the action of the sulfonic acids (PDS and NDS). We had already reported a similar change of pyridine ring-based absorption peak of poly(4-vinylpyridine) for the ionic complexes with PDS or NDS [45]. A broad absorption peak related to a harmonic overtone of the out-of-plane C–H bending vibration of *p*-disubstituted aromatics was observed for PSS itself at around 1650 cm^{-1} . Therefore, the formation of

pyridinium moiety for PSS/PyOSS(1/1) could not be confirmed by FT-IR analysis because of the overlapping of the absorption peaks at around 1650 cm^{-1} . Although all the single components (PDS, NDS, PSS, PyOSS) were soluble in *N,N*-dimethylformamide (DMF), none of the hybrid composites with PyOSS dissolved completely in DMF, indicating the presence of intermolecular interaction.

Table 1 summarizes T_m measured by DSC and T_d at 5% weight loss measured by TGA for the hybrid composites of PDS, NDS, and PSS with PyOSS. Although the dried PDS and NDS samples showed T_m at

Table 2
Thermal properties of PSt, SPSx and SPSx/PyOSS.

Sample	Molar ratio of SO ₃ H/Py	PyOSS content (wt%)	SiO content (wt%)	T_g^a (°C)	T_d^b (°C)
PSt	—	0	0	104.0	424.8
PSt/PyOSS	—	19.8	7.3	102.1	434.7
SPS3	—	0	0	112.2	404.7
SPS3/PyOSS	1/1	9.3	3.5	112.2	415.0
	2/1	4.9	1.8	107.5	404.1
	3/1	3.3	1.2	108.4	409.3
SPS8	—	0	0	117.9	413.8
SPS8/PyOSS	1/1	19.8	7.3	118 ^c	417.5
	2/1	11.1	4.1	115.1	416.3
	3/1	7.6	2.8	116.0	415.1
SPS23	—	0	0	150.0	363.0
SPS23/PyOSS	1/1	39.9	14.7	ND	392.9

^a The T_g measured by DSC.

^b The temperature at 5% weight loss measured by TGA at a heating rate of $20^\circ\text{C}/\text{min}$.

^c Approximate T_g value is shown because a clear glass transition was not observed.

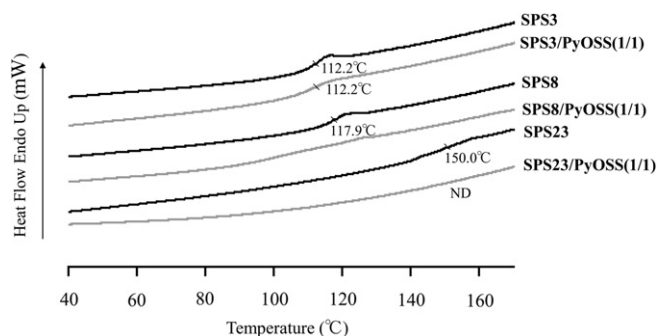


Fig. 10. The second heating DSC thermograms of SPSx and SPSx/PyOSS(1/1) ($x = 3, 8$, and 23).

125.6 and 168.9 °C, respectively, T_m was not detected for PDS/PyOSS (1/1) and NDS/PyOSS(1/1), indicating the absence of free PDS and NDS. The PSS showed neither T_m nor T_g because of a strong hydrogen-bonding interaction of sulfonic acid groups. Also, neither T_m nor T_g was observed for PSS/PyOSS(1/1). The T_d 's of PDS/PyOSS (1/1) and NDS/PyOSS(1/1) were higher than those of PDS and NDS, while a little lower than that of PyOSS. On the other hand, PSS/PyOSS (1/1) showed a higher T_d than PSS and PyOSS. This result is related to a high crosslinking density by the ionic interaction for PSS/PyOSS.

3.3. Characterization of the hybrid composites of SPSx and PyOSS

Fig. 6 shows FT-IR spectra of SPSx/PyOSS(1/1) hybrid composites as compared with PyOSS and SPS8. Although PSS had a weak absorption peak at 1650 cm^{-1} , SPS8 did not show a clear absorption peak in the region from 1630 to 1670 cm^{-1} . In a similar manner, SPS23 and SPS3 showed no clear absorption peak in the same region, although their spectra are not shown in the figure. The SPSx's ($x = 3, 8$, and 23)/PyOSS(1/1) hybrid composites showed new absorption peaks at around 1615–1660 cm^{-1} , suggesting that there is ionic bonding interaction between SPSx's and PyOSS. Similar trend on IR spectra had been reported for the polyion complex of poly(styrene-co-styrenesulfonic acid) and poly(styrene-co-4-vinylpyridine) [41,44]. It is also known that the framework stretching of pyridine ring around 1594 cm^{-1} shifts to a little higher wave-number when the pyridine nitrogen is involved in hydrogen-bonding interaction [40]. However, SPSx itself has an absorption band at around 1600 cm^{-1} due to the framework stretching of benzene ring. Therefore, we could not evaluate the presence of the hydrogen-bonding interaction of SPSx/PyOSS by FT-IR analysis. The reaction mixture of SPSx and PyOSS in THF was homogeneous solution, which was casted and dried to afford SPSx/PyOSS film. The isolated SPSx/PyOSS films did not completely dissolve in THF. The obtained SPS3/PyOSS(1/1) with SiO content 3.5 wt% was transparent, while SPS8/PyOSS(1/1) and SPS23/PyOSS(1/1) films with SiO content 7.3 and 14.7 wt%, respectively were somewhat translucent. This result indicates that some aggregation of PyOSS molecules occurs for SPS8/PyOSS(1/1) and SPS23/PyOSS(1/1).

In order to clarify the molecular interaction between SPSx and PyOSS, the measurements of XPS of the SPSx/PyOSS film samples were performed. Fig. 7 shows N1s spectra of SPSx/PyOSS(1/1) ($x = 3, 8$, and 23) hybrid composites. As a comparison, the XPS spectrum of PSt/PyOSS composite film with SiO content 7.3% is shown in the figure. The PSt/PyOSS without a specific interaction showed a pyridine N 1s peak at 400.5 eV. The XPS spectra of SPS3/PyOSS and SPS8/PyOSS do show the existence of both ionic and hydrogen-bonding interactions in SPS3/PyOSS and SPS8/PyOSS. The two spectra can be curve-fitted with two peaks, one at 403.2 eV for pyridinium nitrogen and the other at 401.5 eV for hydrogen-bonded nitrogen. Hydrogen-bonding is predominant in SPS3/PyOSS whereas ionic interaction is more important in SPS8/PyOSS. For SPS23/PyOSS, the single peak at 403.2 eV clearly shows that the interaction is ionic exclusively. Zhou et al. reported a similar trend on the pyridine/pyridinium N 1s peaks for the complexes of PV4P and poly(acrylic acid) or poly(methacrylic acid) [40]. Also, our group reported the similar trend for the complexes of P4VP and PDS or NDS [45]. When SO_3H /pyridine ratio was increased for PSS8/PyOSS from 1/1 to 3/1, the broad peaks containing both ionic and hydrogen-bonding interaction changed to a peak at 403.1 eV due to the formation of pyridinium ion structure (Fig. 8). From these observations, the illustrations shown in Fig. 9 are proposed for the correlation among degree of sulfonation, molecular interaction and morphologies of SPSx/PyOSS(1/1). The PyOSS content in SPS23/PyOSS(1/1) with ionic interaction and SPS3/PyOSS with hydrogen-bonding interaction are 39.9 and 9.3 wt%, respectively. Lower the degree of sulfonation of SPSx is, longer the length between

the sulfonic acids is. Therefore, short range—ionic interaction of three pyridyl groups of PyOSS molecule and three sulfonic acid groups of SPS23 is possible for a small cavity of SPS23/PyOSS. On the other hand, long-range hydrogen-bonding interaction between the pyridyl and sulfonic acids groups is favored for a larger cavity of SPS3/PyOSS.

3.4. Thermal properties of the hybrid composites of SPSx and PyOSS

Fig. 10 shows the second heating DSC thermograms of SPSx and SPSx/PyOSS(1/1). The T_g of SPSx increased with increasing degree of sulfonation (x), because of hydrogen-bonding interaction between sulfonic acid groups. In case of PSS which corresponds to SPS100, glass transition was not detected. However, the incorporation of PyOSS into SPSx did not result in an increase of T_g . The T_g of SPS3/PyOSS(1/1) was almost the same value as that of SPS3. The glass transition became gradually obscure with increasing degree of sulfonation, and T_g was not detected as a clear transition point for SPS23/PyOSS(1/1). Table 2 summarizes the T_g and T_d for all the SPSx/PyOSS hybrid composites. Even if the SO_3H /pyridine ratio was changed for the hybrid composites, the T_g was not increased. These results are attributed to large free volume of POSS moiety and long distance between the crosslinking points. All the SPSx/PyOSS hybrid composites showed a higher T_d than the corresponding SPSx. The extent of an increase of T_d became bigger with increasing PyOSS content of the composites. Similar trends for T_g and T_d were reported for the covalent bond-type hybrid polymer networks formed by the curing reactions of octaglycidyl dimethylsiloxyl-POSS and diaminodiphenylmethane [15] and diglycidyl ether of bisphenol A and octaaminophenyl-POSS [16].

4. Conclusions

Supramolecular organic–inorganic hybrid composites of various sulfonic acids such as PDS, NDS, PSS, and SPSx with PyOSS were prepared and their molecular interactions and thermal properties were investigated. From the FT-IR analysis, the formation of pyridinium cation moiety was confirmed for PDS/PyOSS(1/1) and NDS/PyOSS(1/1), while it could not be elucidated for PSS/PyOSS (1/1). As a result of XPS analysis of SPSx/PyOSS films, the formation of pyridinium ion structure was confirmed for SPS23/PyOSS, and the ionic interaction gradually changed to hydrogen-bonding interaction with decreasing degree of sulfonation of SPSx. Although T_g of SPSx moiety was little affected by the incorporation of PyOSS, the glass transition itself was gradually weakened and was not detected for SPS23/PyOSS. The 5% weight loss temperatures of all the sulfonic acid/PyOSS composites were higher than those of the corresponding sulfonic acids.

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