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Polymer hybrids of functionalized silsesquioxanes and organic polymers utilizing the sol–gel reaction of tetramethoxysilane

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Abstract

The ternary polymer hybrids were prepared by organic polymers such as poly(2-methyl-2-oxazoline) (POZO) or poly(*N*-vinylpyrrolidone) (PVP) and aminopropylsilsesquioxane (Cube-aminopropyl) utilizing the sol–gel reaction of tetramethoxysilane (TMOS). The prepared polymer hybrids were characterized by IR, thermogravimetric analysis (TGA), X-ray diffraction (XRD), ^{1}H NMR, scanning electron microscopy (SEM), etc. In this hybrid system, hydrogen-bonding interactions played a critical role in the formation of the transparent polymer hybrids. Polymer hybrids using POZO showed high transparency and homogeneity in a wide range of the feed ratios of POZO to Cube-aminopropyl. On the other hand, in case of polymer hybrids using PVP, higher Cube-aminopropyl ratio brought about the phase separation, indicating the aggregation of the Cube-aminopropyl itself. The homogeneity of ternary polymer hybrids was found to be closely dependent on the difference between strength of hydrogen bonding interaction of polymer and residual silanol groups of silica gel and strength of that of polymer and Cube-aminopropyl. It is also observed that initial decomposition temperature of polymer hybrids was increased with increasing the Cube-aminopropyl ratio. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ternary polymer hybrids; Hydrogen bonding interaction; Polyhedral oligomeric silsesquioxanes (POSS)

1. Introduction

Organic–inorganic hybrid materials made by the sol–gel reaction have been studied so far because of the advantages of the sol–gel technique such as the reaction condition of ambient temperature and high uniformity of organic parts in the silica matrix [1–3]. The hybrid materials obtained by the combination of organic polymers and inorganic materials using the sol–gel reaction provide high thermal stability [4] and good mechanical strength [5,6] such as the large values of the ultimate strength and the rupture energy to the organic polymers and show high transparency for development of optical materials [7,8] as well as contact lenses [9]. These organic–inorganic hybrid materials could be prepared by various methods, depending on what kind of interaction is employed between organic polymers and inorganic elements or how organic moieties are introduced to the organic phases. For instance, the utilization of physical interaction or covalent bonds between two phases is one of the effective methods to obtain homogeneous hybrid materials. An in situ polymerization, which is simultaneous polymerization of both organic monomer and inorganic precursor, is another important method to prepare composite materials without any physical or chemical interactions. In our group, various structures of organic–inorganic hybrids have been prepared so far utilizing physical interaction such as hydrogen bonding [10,11], aromatic [12], and ionic interaction [13] between organic polymers and silica gel or an in situ polymerization of the monomer in sol–gel reaction mixture [14]. Also, using polyhedral oligomeric silsesquioxanes (POSS) having hybrid chemical compositions with well-defined cage structures, various liquid crystalline (LC) hybrid materials have been studied. Such examples are LC silsesquioxanes having various mesogenic moieties [15] and LC organic–inorganic hybrid polymers using functionalized silsesquioxanes [16]. The obtained LC hybrid materials using silsesquioxanes showed very wide temperature range of LC phase and high thermal stability. Thus, POSS-based hybrids may offer potential for preparing thermoplastic hybrid materials having remarkable mechanical properties.

Here, we present the first preparation of ternary polymer hybrids having organic polymer and POSS by utilizing the sol–gel reaction of tetramethoxysilane (TMOS). Organic polymers such as poly(2-methyl-2-oxazoline) (POZO) or poly(*N*-vinylpyrrolidone) (PVP) have been incorporated homogeneously into silica gel by hydrogen bonding

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interaction as previously published in our group [10,11]. It was also reported that the homogeneous hybrid materials could be prepared by combining functionalized POSS and polar organic polymers [17,18]. These hybrid films based on POSS could be dissolved in solvent and cast again without any separation. In this connection, we became interested in ternary polymer hybrids system including organic polymer and POSS with silica gel which make it possible to form single phase organic–inorganic polymer hybrids with each other. It is of interest to investigate the effect of strength of the interactions on dispersity of organic polymer and aminopropylsilsesquioxane (Cube-aminopropyl) in the silica matrix and the effect of Cube-aminopropyl on the homogeneity and properties of polymer hybrids.

2. Experimental section

2.1. General procedure

^{1}H NMR spectra were recorded using a 270 MHz JEOL-JNM-GX270 NMR spectrometer. FT-IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer. The thermal behavior was examined by thermogravimetric analysis (TGA) (TG/DTA6200, Seiko Instruments) under nitrogen. The morphologies of polymer hybrids were observed by scanning electron microscopy (SEM) (JEOL JSM-5310/LV). The crystallinities of Cube-aminopropyl and polymer hybrids were determined by X-ray diffraction (XRD) (Perkin Elmer system 2000).

2.2. Materials

TMOS (TCI: Tokyo Chemical Industry Co., Ltd) was used after distillation under nitrogen. Methanol was distilled with sodium under nitrogen. 2-Methyl-2-oxazoline (Aldrich) was distilled over potassium hydroxide and stored under nitrogen. Methyl *p*-toluenesulfonate was distilled under reduced pressure. Aminopropyltriethoxysilane (Aldrich), PVP (TCI), and 0.1 M HCl (Wako Pure Chemical Industries) are commercially available and were used as received.

2.3. Synthesis of aminopropylsilsesquioxane (Cube-aminopropyl) (*1*)

Cube-aminopropyl was prepared by aminopropyltriethoxysilane using the detailed experimental procedure described in a previous literature [19].

2.4. Synthesis of organic polymers (POZO and PVP)

POZO ($M_n = 6300$, $M_w = 10,300$, $M_w/M_n = 1.64$, polystyrene standard; eluent, DMF) (**2**) was prepared by the ring opening polymerization of 2-methyl-2-oxazoline initiated by methyl *p*-toluenesulfonate (MeOTs) [20,21]. PVP (average $M_w = 630,000$) was used as supplied.

2.5. Preparation of ternary polymer hybrids having organic polymers and POSS in the silica matrix

Prescribed amounts of polymer (PVP or POZO) and Cube-aminopropyl were dissolved in methanol and stirred for 30 min. To the solution was added TMOS and 0.1 M aqueous HCl as a catalyst for sol–gel reaction. The weight of polymer was fixed at 0.2 g. The weight of Cube-aminopropyl was varied to that of polymer (1/1, 1/2, 1/4, 1/8). The weight of TMOS was fixed five times to that of polymer and 4 mol equivalents of aqueous HCl to TMOS was added. The resulting mixture was stirred at room temperature for 1 h in a sealed bottle. Then, the mixture was placed in a container covered with a paper towel and left in air to evaporate the solvent. After the complete removal of the solvent, polymer hybrids were obtained as a glassy material.

2.6. Soxhlet extraction of polymer hybrids

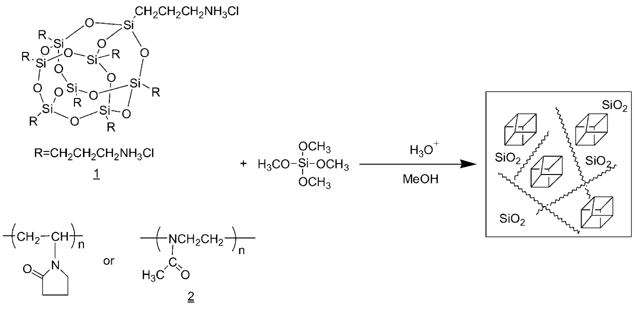
The powders of polymer hybrids were put in a cellulose timber and extracted with methanol using a Soxhlet apparatus for 5 days. The extract was evaporated and then measured by ^{1}H NMR.

2.7. X-ray diffraction measurement of polymer hybrids

All the measurements were made in $\theta/2\theta$ mode at room temperature. The 2θ scan data were collected at 0.02° interval and the scan speed was $2°\ (2\theta)\ \mathrm{min}^{-1}$.

3. Results and discussion

Cube-aminopropyl (**1**) was synthesized by the hydrolytic condensation reaction of aminopropyltriethoxysilane in acidic aqueous methanol. The only one sharp symmetrical peak (−66.5) in ^{29}Si NMR and characteristic peaks (0.72, 1.72, 2.76, and 8.2 ppm) in ^{1}H NMR spectra indicated the POSS having cage-like structure with aminopropyl groups as the donor group of hydrogen bonding interaction was synthesized. The homogeneous single phase polymer hybrids were prepared by the obtained Cube-aminopropyl and various organic polymers such as PVP, POZO, poly(vinyl alcohol) (PVA), or poly(*N,N*-dimethylacrylamide) (PDMAAm) using hydrogen bonding interaction [18]. They were optically transparent and showed reversible film-forming property and higher elastic modulus and ultimate elongation than those of polymer. In this study, ternary polymer hybrids were prepared by mixing both Cube-aminopropyl and organic polymer simultaneously in a methanol solution of TMOS with acid catalyst (Scheme 1). Tables 1 and 2 describe the results of preparation of ternary polymer hybrids with POZO and PVP, respectively. As shown in Table 1, in case of polymer hybrids from POZO, the transparent and homogeneous polymer hybrids could be obtained without any influence of Cube-aminopropyl ratio to POZO. On the other hand, in case of polymer hybrids



Scheme 1.

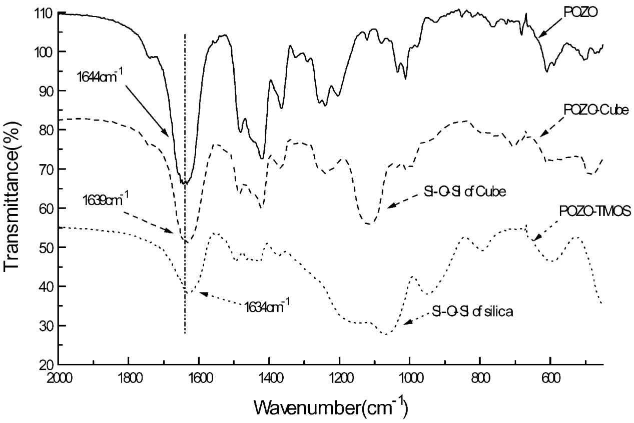


Fig. 1. FT-IR spectra of ternary polymer hybrids from POZO.

from PVP (Table 2), higher Cube-aminopropyl ratio to PVP brought about the phase separation. This result may be ascribed to the unbalanced surroundings derived from difference between hydrogen bonding strength of polymer and residual silanol groups of silica gel and that of polymer and Cube-aminopropyl. The intensity of hydrogen bonding interaction was confirmed to measure the shift degrees of amide carbonyl peaks of polymer induced by the formation of hydrogen bonding interaction by FT-IR. Fig. 1 shows IR spectra of polymer hybrids from POZO. The intensity of hydrogen bonding interaction ($10\,\mathrm{cm}^{-1}$) between POZO and residual silanol groups of silica gel was similar to that ($5-10\,\mathrm{cm}^{-1}$) between POZO and Cube-aminopropyl. As shown in Fig. 2, the intensity of hydrogen bonding interaction ($24\,\mathrm{cm}^{-1}$) between PVP and residual silanol groups of silica gel was much more stronger than that ($5-10\,\mathrm{cm}^{-1}$) between PVP and Cube-aminopropyl. This unbalanced hydrogen bonding interactions result in single phase polymer hybrids of PVP and silica gel which cause the aggregation of Cube-aminopropyl having weak hydrogen bonding strength in ternary systems. The morphologies of polymer hybrids were observed by SEM measurement. Polymer hybrids using PVP showed the white domains of aggregation of Cube-aminopropyl (1–2 μm) as shown in Fig. 3(a). On the other hand, in case of polymer hybrids using POZO (Fig. 3(b)), no phase separation could be observed. That is, POZO and Cube-aminopropyl were homogeneously and uniformly dispersed in the silica matrix at a molecular level. Another attempt for homogeneity was made to estimate the crystallinity of polymer hybrids by the powder XRD measurements. For polymer hybrids using POZO (Fig. 4(a)), the diffraction patterns are featureless, showing only broad amorphous halos ($2\theta = 20$–30) derived from homogeneously amorphous silica matrix. This result indicates that the complete and homogeneous mixing of POZO and Cube-aminopropyl and inorganic phase caused

Table 1
Preparation of ternary polymer hybrids from POZO (methanol was used as a solvent)

Run	Materials (g)	TMOS (g)	HCl (0.1 M) (ml)	Appearance[a]
1	POZO (0.2 g)	1	0.47	Transparent
2	POZO (0.2 g)Cube (0.1 g)	–	–	Transparent
3	POZO (0.2 g), Cube (0.2 g)	1	0.47	Transparent
4	POZO (0.2 g), Cube (0.1 g)	1	0.47	Transparent
5	POZO (0.2 g), Cube (0.05 g)	1	0.47	Transparent
6	POZO (0.2 g), Cube (0.025 g)	1	0.47	Transparent

[a] Homogeneity was observed optically.

Table 2
Preparation of ternary polymer hybrids from PVP (methanol was used as a solvent)

Run	Materials (g)	TMOS (g)	HCl (0.1 M) (ml)	Appearance[a]
1	PVP (0.2 g)	1	0.47	Transparent
2	PVP (0.2 g), Cube (0.1 g)	–	–	Transparent
3	PVP (0.2 g), Cube (0.2 g)	1	0.47	Turbid
4	PVP (0.2 g), Cube (0.1 g)	1	0.47	Turbid
5	PVP (0.2 g), Cube (0.05 g)	1	0.47	Turbid
6	PVP (0.2 g), Cube (0.025 g)	1	0.47	Transparent

[a] Homogeneity was observed optically.

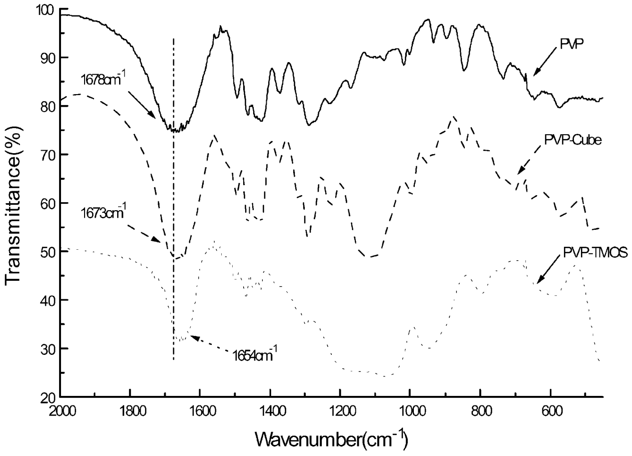


Fig. 2. FT-IR spectra of ternary polymer hybrids from PVP.

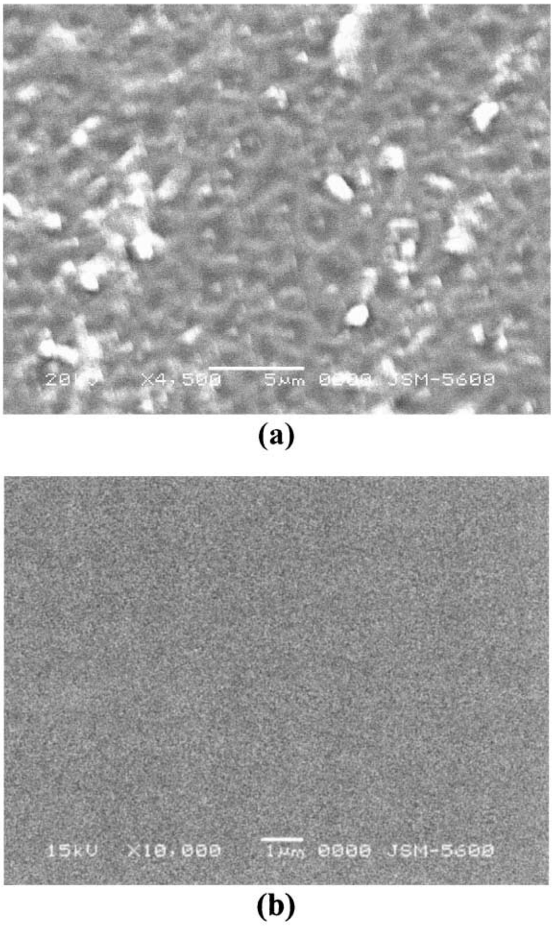


Fig. 3. SEM images of polymer hybrids from Cube-aminopropyl. (a) PVP/Cube-aminoprpopyl/TMOS = 0.2 g/0.1 g/1.0 g; (b) POZO/Cube-aminopropyl/TMOS = 0.2 g/0.1 g/1.0 g.

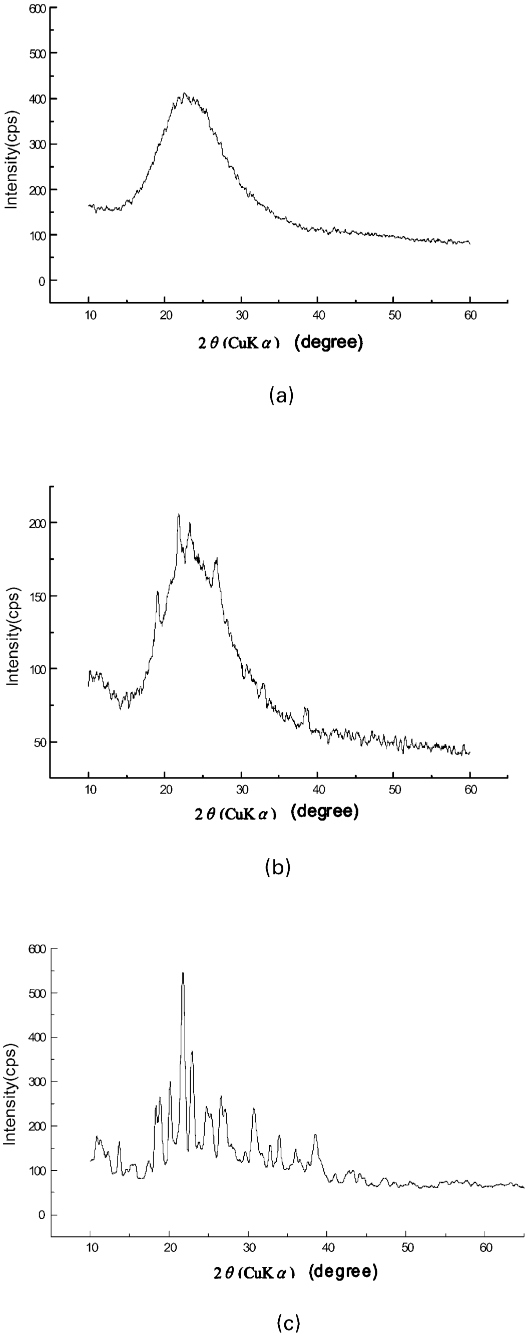


Fig. 4. XRD patterns of ternary polymer hybrids. (a) POZO/Cube-aminopropyl/TMOS = 0.2 g/0.1 g/1.0 g; (b) PVP/Cube-aminopropyl/TMOS = 0.2 g/0.1 g/1.0 g; (c) only Cube-aminopropyl.

by balanced hydrogen bonding interactions in ternary systems results in the disappearance of the crystallinity of Cube-aminopropyl. However, polymer hybrids using PVP (Fig. 4(b)) showed distinctive reflections indicative of crystallinity of Cube-aminopropyl which is shown in Fig. 4(c) in amorphous halo peaks. This means that Cube-aminopropyl is not uniformly dispersed and aggregated a little bit in silica matrix. The effect of different strength of hydrogen bonding interactions in ternary polymer hybrids was estimated by solvent extraction experiments. The obtained polymer hybrids were crushed into powders, which were extracted with CH_3OH. Fig. 5 shows ^1H NMR spectra of the extracts of polymer hybrids after the solvent extraction. In case of polymer hybrids using POZO, almost

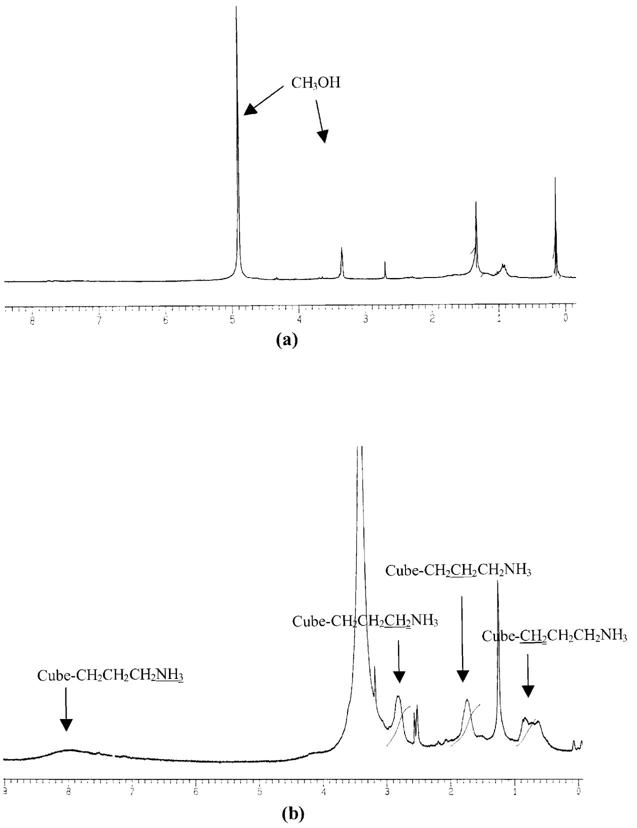


Fig. 5. ^{1}H-NMR spectra of ternary polymer hybrids from POZO: (a) in CD$_3$OD and from PVP; (b) in DMSO-d$_6$ after solvent extraction.

no extraction occurred, which is resulted from the high homogeneity of Cube-aminopropyl and POZO in silica gel by balanced hydrogen bonding interactions. On the other hand, the extracts of polymer hybrids using PVP showed only peaks of Cube-aminopropyl. This could be due to the aggregation of Cube-aminopropyl by non-homogeneity of Cube-aminopropyl and PVP in silica gel derived from unbalance and difference between hydrogen bonding strength of PVP and residual silanol groups of silica gel and that of PVP and Cube-aminopropyl. In other words, transparent and homogeneous ternary polymer hybrids having semi-interpenetrating polymer network (semi-IPN) structure by balanced hydrogen bonding interactions show higher resistance toward solvent extraction. The thermal stabilities of ternary polymer hybrids were observed by TGA thermograms as shown in Fig. 6. The temperature of 10% decomposition of polymer hybrids was increased with increasing the weight of Cube-aminopropyl. This is a measure of the effect of inorganic POSS unit behaving as a hard, compact component on polymer hybrids thermal properties. In addition, the obtained polymer hybrids have higher thermal stability compared to that of the polymer itself.

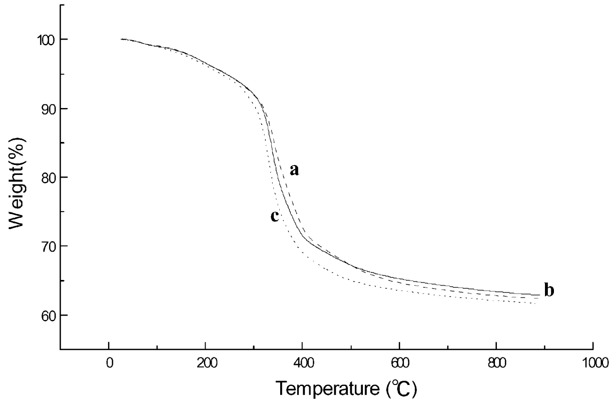


Fig. 6. TGA thermograms of ternary polymer hybrids from POZO with a heating rate of 10 °C min^{-1}: (a) POZO/Cube-aminopropyl/TMOS = 0.2 g/0.1 g/1.0 g; (b) POZO/Cube-aminopropyl/TMOS = 0.2 g/0.05 g/1.0 g; (c) POZO/Cube-aminopropyl/TMOS = 0.2 g/0.025 g/1.0 g.

4. Conclusion

The ternary polymer hybrids having Cube-aminopropyl by the sol–gel reaction of TMOS were prepared with varying a range of the feed ratios of polymer to Cube-aminopropyl and examined by SEM, FT-IR, SEM, TGA, XRD, etc. The balance of intensity of hydrogen bonding interactions between each of the elements strongly influences the high homogeneity of the ternary polymer hybrids. The ternary polymer hybrids from POZO obtained by the balanced hydrogen bonding interactions have higher solvent-resistance property compared to those from PVP. The ternary polymer hybrids were also found to have high thermal stability due to the rigid silica matrix as well as the hard and compact inorganic silica-like core of POSS.

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