POSS related polymer nanocomposites

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This review describes the syntheses of polyhedral oligomeric silsesquioxane (T\textsubscript{8}-POSS) compounds, the miscibility of POSS derivatives and polymers, the preparation of both multifunctional and monofunctional monomers and polymers containing POSS including styryl-POSS, methacrylate-POSS, norbornyl–POSS, vinyl-POSS, epoxy–POSS, phenolic–POSS, benzoxazine–POSS, amine-POSS, and hydroxyl-POSS. The thermal, dynamic mechanical, electrical, and surface properties of POSS-related polymeric nanocomposites prepared from both monofunctional and multifunctional POSS monomers are discussed. In addition, we describe the applications of several high-performance POSS nanocomposites in such systems as light emitting diodes, liquid crystals, photoresist materials, low-dielectric constant materials, self-assembled block copolymers, and nanoparticles.

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**Nomenclature**

AFM atomic force microscopy

AM-POSS aminopropylisobutyl POSS

ATRP atom transfer radical polymerization

iBu-POSS isobutyl-POSS

CD cycloexctrians

Cp-POSS cyclopentyl-POSS

Cy-POSS cyclohexyl-POSS

DDM 4,4'-diamidodiphenyl methane

DAS 4,4'-diamidodiphenyl sulfone

DMA dynamic mechanical analysis

DSC differential scanning calorimetry

DOP dioctyl phthalate

DGEBA diglycidyl ether bisphenol A

IR infrared spectroscopy

LiClO₄ lithium perchlorate

OMAIBu–POSS methacrylo isobutyl-POSS

NMR nuclear magnetic resonance

MALDI–TOF matrix-assisted laser desorption ionization-time of flight

OA-POSS octakis[dimethyl(4-acetoxyphenethyl)siloxy]-POSS

OAM-POSS octa[(aminopropyl)-POSS

OAP-POSS octakis[(aminophenyl)-POSS

OIBu-POSS octaisobutyl-POSS

ODA 4,4'-diaminodiphenyl ether

ODADS 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid

OEC-POSS octaepoxy cyclohexyl dimethylsilyl-POSS

OF-POSS octakis[(dimethylsiloxyhexafluoropropyl ether)-POSS

OG-POSS octaglycidyl dimethylsilyl-POSS

OH-POSS octakis[3-hydroxypropyldimethylsilyl]-POSS

OMA-POSS octamethacryl-POSS

OM-POSS octa-methyl-POSS

OP-POSS octakis[dimethyl(4-hydroxyphenethyl)siloxy]-POSS

OV-POSS octa-vinyl POSS

OPE-POSS octa-phenethyl-POSS

OS-POSS octakis[dimethyl(phenethyl)siloxy]-POSS

PA polyamide

PAA poly(amic acid)

PAMAM poly(amideamine)

PAS poly(acetoxy styrene)

PBD poly(butadiene)

PBLG poly(γ-benzyl-L-glutamate)

PBT poly(ethylene terephthalate)

PC poly(carbonate)

PCL poly(ε-caprolactone)

PDIB-POSS 1,2-propanediol isobutyl-POSS

PE poly(ethylene)

PEEK poly(ether ether ketone)

PEI poly(ethylene-imine)

PET poly(ethylene terephthalate)

PLGA poly(lactide-co-glycolide)

POSS polyhedral oligomeric silsesquioxane

PP poly(propylene)

PPO poly(dimethyl phenylene oxide)

PP-g-MA PP-grafted maleic anhydride

PS poly(styrene)

PSMA poly(styrene-co-maleic anhydride)
1. Introduction

Relative to metals and ceramics, polymeric materials generally have lower moduli and strength. One way to effectively improve the mechanical properties of polymers is to reinforce them with nano-sized inorganic particles (defined herein as having at least one dimension in the range 1–100 nm). Using this approach, the polymer properties can be efficiently improved while maintaining its inherently low density and high ductility. Improvements in mechanical properties are often found even at relatively low filler content. The nanofillers may have spherical (metal or semi-conductive nanoparticles (NPs)), layered (clay), or fibrous (nanofibers and carbon nanotubes) shapes. Such polymer nanocomposites are diverse and versatile functional materials, with applications in systems ranging from electronic devices to biosensors and catalysts. The field of polymer nanocomposite materials has attracted great attention from polymer scientists and engineers in recent years. The simple premise involves using building blocks of nanosize dimensions to create new polymeric materials exhibiting improved physical properties.

Silsesquioxanes are nanostructures having the empirical formula RSiO$_{1.5}$, where R is a hydrogen atom or an organic functional group such as an alkyl, alkyene, acrylate, hydroxyl, or epoxide unit. Based on images in the first review of POSS polymers and resins published by the Pittman group, Fig. 1 illustrates that silsesquioxanes can be formed as random, ladder, cage, or partial cage structures [1,2]. Scott [3] discovered the first oligomeric organosilsesquioxane, (CH$_3$SiO$_{1.5}$)$_n$, along with other volatile compounds through the thermolysis of polymeric products prepared from co-hydrolysis of methyl trichlorosilane and dimethyl chlorosilane.

Although silsesquioxane chemistry has been studied for more than half a century, interest in this field has increased dramatically in recent years. Baney et al. [4] reviewed the preparation, properties, structures, and applications of silsesquioxanes, especially those of ladder-like polysilsesquioxanes (Fig. 1(b)). More recently, attention has been concentrated on silsesquioxanes possessing the specific cage structures displayed in Figs. 1(c)–(f). These polyhedral oligomeric silsesquioxanes are commonly referred to by the acronym "POSS". Derivatives of POSS are true hybrid inorganic/organic chemical composites that possess an inner inorganic silicon and oxygen core (SiO$_{1.5}$)$_n$ and external organic substituents that can feature a range of polar or nonpolar functional groups. POSS nanostructures having diameters ranging from 1 to 3 nm can be considered as the smallest possible particles of silica, i.e., molecular silica. Unlike most silicones or fillers, POSS molecules contain organic substituents on their outer surfaces, making them compatible or miscible with most polymers. In addition, these functional groups can be specifically designed as either non-reactive (e.g., for polymer blending) or reactive (for copolymerization). POSS derivatives can be prepared with one or more covalently bonded reactive functionalities suitable for polymerization, grafting, blending, or other transformations. Unlike traditional organic compounds, POSS derivatives are nonvolatile, odorless and environmentally friendly materials. The incorporation of POSS moieties into a polymeric material can dramatically improve its mechanical properties (e.g., strength, modulus, rigidity) as well as reduce its flammability, heat evolution, and viscosity during processing. These enhancements apply to a wide range of commercial thermoplastic polymers, high-performance thermoplastic polymers, and thermosetting polymers [1,2]. It is especially convenient to incorporate POSS moieties into polymers through simple blending or copolymerization. In addition, when POSS monomers are soluble in monomer mixtures, they can be incorporated as true molecular dispersions in the resulting polymer matrix. The macrophase separation that usually occurs through the aggregation of POSS units can be avoided through copolymerization (i.e., covalent bond formation between the POSS units and the polymers)-a significant advantage over the traditional filler technologies. POSS nanostructures also have significant promise for use in catalyst supports and biomedical applications, such as scaffolds for drug delivery, imaging reagents, and combinatorial drug development [5,6].

In this review, we describe methods for synthesizing POSS compounds and preparing monomers and polymers containing POSS derivatives. We discuss both mono- and multifunctional POSS monomers that have been used to develop thermoplastic and thermosetting polymers. In addition, we compare the miscibility, phase behavior, thermal, dynamic mechanical, electrical, and surface properties of polymers containing POSS units.

2. General approaches in the syntheses of polyhedral oligomeric silsesquioxanes

POSS derivatives featuring Si–O linkages in the form of a cage present a silicon atom at each vertex, with substituents coordinating around the tetrahedral silicon vertices. The nature of the exo cage substituents in such compounds determines the mechanical, thermal, and other physical properties. The number of RSiO$_3$ units determines the shape of the frame, which is uniquely unstrained for 6–12 units. Voronkov et al. [7] have reviewed the known methods of synthesizing POSS compounds. Many substituents appended to the silicon/oxygen cages (SiO$_{1.5}$)$_n$ (where R is an organic or inorganic group) allow the poly-

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**Abbreviations**

- PU: polyurethane
- PVC: poly(vinyl chloride)
- PVP: poly(vinyl pyrrolidone)
- P4VP: poly(4-vinyl pyridine)
- PVPn: poly(vinyl phenol)
- Q$_8$M$_8$$^H$: octakis(dimethylsiloxy)silsesquioxane
- SAXS: small-angle X-ray scattering
- SEM: scanning electron microscopy
- SH-POSS: mercaptopropyl-isobutyl-POSS
- TEM: transmission electron microscopy
- TGA: thermal gravity analysis
- WAXD: wide-angle X-ray diffraction

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**References**

merization of POSS units or the copolymerization of specific POSS derivatives with other monomers.

2.1. Monofunctional POSS

Monofunctional POSS derivatives are among the most useful compounds for polymerization or copolymerization with other monomers. Fig. 2 summarizes the three general approaches to synthesize monofunctional POSS derivatives of the form \( R'R_Si_8O_{12} \) [10].

**Route I. Cohydrolysis of trifunctional organo- or hydrosilanes:** Polycondensation of monomers is the classical method of synthesizing silsesquioxanes [8–10]. When this reaction is performed in the presence of monomers possessing various R groups, mixtures of heterosubstituted compounds are obtained, including the desired monosubstituted products (ca. 48% overall yield).

**Route II. Substitution reactions with retention of the siloxane cage:** Fig. 2 presents a selection of substitution reactions using octahydro-silsesquioxanes as the starting materials (IIa–c) that have been applied successfully to prepare monosubstituted silsesquioxanes [11–13]. By adjusting the ratio of the reactants, it is possible to obtain a considerable yield (18.6–43.6%) of the desired monosubstituted product.

**Route III. Corner-capping reactions:** Feher and coworkers [14–17] developed this approach starting from incompletely condensed \( R_Si_7O_9(OH)_{3} \) molecules \( (T_7) \). The three silanol groups are very reactive toward \( R'SiCl_3 \), giving the fully condensed products. Variation of the R' group on the silane enables the syntheses of a variety of monofunctionalized siloxane cages [18]. Subsequent transformations can be performed until the desired functionality is obtained. Moreover, incompletely condensed silsesquioxanes offer a route for the generation of hetero- and metalla-siloxanes, in which a hetero main group or a transition metal element is introduced into the Si–O framework [19–21].

2.2. Multifunctional POSS

POSS \( (RSiO_{1.5})_n \) derivatives have values of \( n \) of 4, 6, 8, 10, or 12, with the R groups being hydrogen, alkyl, aryl, or inorganic units. Unique POSS structures \( (R=H) \) can be formed through the hydrolysis and condensation of trialkoxysilanes \( [HSi(OR)_3] \) or trichlorosilanes \( (HSiCl_3) \) [7]. The hydrolysis of trimethoxysilane in a cyclohexane/acetic acid mixtures in the presence of concentrated hydrochloric acid provides the octamer in low yield (13%) [22]. Another synthetic approach to generate multifunctional POSS derivatives is the functionalization of preformed POSS cages; e.g., through Pt-catalyzed hydrosilylation of alkenes or alkynes with \( (HSiO_{1.5})_8 \) and octakis(dimethylsiloxy)silsesquioxane \( ((HMe_2SiOSiO_{1.5})_8, Q_8M_8H) \) cages (Fig. 3) [23–25].

3. Hydrogen bonding and miscibility behavior of polymer/POSS nanocomposites

3.1. Hydrogen bonding interactions between polymers and POSS

Most inorganic silicas or ceramics are immiscible in most organic polymer systems because of poor specific interactions within these organic/inorganic hybrids and the negligibly small combined entropy contribution to the free energy of mixing. Specific intermolecular interactions are generally required to enhance the miscibility of polymers and inorganic particles. Such interactions include hydrogen bonding, dipole–dipole interactions and acid/base complexation [26]. Determining the types and strengths of the interactions between the POSS derivatives and polymers is an important challenge. For convenience, our group has prepared a phenolic/POSS hybrid from a mixture of phenolic resin and an octaisobutyl-POSS
Fig. 2. Three general ways to synthesize monosubstituted octasilasquioxane.

(OiBu-POSS) to investigate the miscibility, specific interactions, and microstructural behavior [27]. The nature of the hydrogen bonding sites in the phenolic/POSS hybrid was investigated, using 2D-IR correlation spectroscopy [28,29]. Fig. 4 presents the synchronous and asynchronous 2D correlation maps in the range from 1000 to 1250 cm\(^{-1}\) [27]. The absorption bands of the OiBu-POSS derivative at 1100 and 1223 cm\(^{-1}\) correspond to siloxane Si–O–Si and Si–C stretching vibrations, respectively, and the peak at 1223 cm\(^{-1}\) is due to the phenyl–OH stretching vibration of the phenolic. Two positive cross-peaks in the synchronous 2D map in Fig. 4(a) indicate the existence of hydrogen bonds between the siloxane group of the POSS derivative (1100 cm\(^{-1}\)) and the phenyl–OH group (1223 cm\(^{-1}\)).

Fig. 3. An example of the synthesis of a multifunctional POSS, (octakis[dimethyl(phenethyl)siloxy] silsesquioxane, OS-POSS).
of the phenolic. In the asynchronous 2D correlation map in Fig. 4(b), the 1100 cm$^{-1}$ absorption splits into two separate bands located at ca. 1105 and 1160 cm$^{-1}$ for the POSS units, suggesting two different types of siloxane (Si–O–Si) sites in the POSS cage. One (at higher wavenumber) undergoes hydrogen bonding with the OH groups of the phenolic, while the other (at lower wavenumber) is free. The positive crosspeaks at 1105 and 1220 cm$^{-1}$ also reveals the presence of hydrogen bonding between the siloxane (Si–O–Si) groups of the POSS and the phenyl–OH groups of the phenolic resin.

3.2. Miscibility between polymers and POSS derivatives

Painter and Coleman [26] suggested that adding an additional term to the simple Flory–Huggins expression to account for the free energy of hydrogen bond formation upon mixing two polymers, as formulated in Eq. (1):

$$\frac{\Delta G_m}{RT} = \frac{\phi_A}{M_A} \ln \phi_A + \frac{\phi_B}{M_B} \ln \phi_B + \phi_A \phi_B \chi_{AB} + \Delta G_H \frac{RT}{RT}$$

(1)

where $\Delta G_H$ denotes the free energy change contributed by the hydrogen bonding between the two components. The combinatorial entropy expressed in the first two logarithmic terms contributes a very small, but nonetheless favorable, amount to the free energy of mixing. $\phi_A$ and $\phi_B$ are the volume fractions of polymers A and B in the blend, respectively, and $M_A$ and $M_B$ are the corresponding degrees of polymerization. According to the Painter–Coleman association model (PCAM) [30,31], the equilibrium constant for the association of a non carbonyl group component with a hydrogen bond-donating component can be calculated using the classical Coggeshall and Saier (C&S) equation (2) [32]:

$$K_a = \frac{1 - f_m^{\text{OH}}}{f_m^{\text{OH}}(C_A - (1 - f_m^{\text{OH}})C_B)}$$

(2)

where $C_A$ and $C_B$ are the concentrations (in mol L$^{-1}$) of OiBu-POSS and 2,4-dimethylphenol (a model compound for phenolic) and $f_m^{\text{OH}}$ is the fraction of free hydroxyl group of 2,4-dimethylphenol. Fig. 5 displays the OH group absorption of 2,4-dimethylphenol in cyclohexane solutions containing various concentrations of OiBu-POSS.

![Fig. 5. FT-IR spectra of 2,4-dimethylphenol (xylene) with various OiBu-POSS concentrations.](Fig. 5. FT-IR spectra of 2,4-dimethylphenol (xylene) with various OiBu-POSS concentrations. Reprinted with permission from Ref. [27]. Copyright 2004, Wiley-VCH, Germany.)
the intensity of the free OH absorption at 3620 cm$^{-1}$ decreases upon increasing the OiBu-POSS content. The absolute intensity of the free OH group at 3620 cm$^{-1}$ is an indication of the content of free OH groups in the mixture [33,34]. The value of $K_A$ of 38.67 was obtained by using C&S equation. The equilibrium constant for self-association of the Novalic type phenolic resin is 52.3 [33]. Since the equilibrium constant for the association between phenolic/OiBu-POSS is smaller than that for the self-association of pure phenolic, the phenolic/OiBu-POSS hybrid should be partially miscible or immiscible. For this reason, functionalization of POSS derivatives with pendant hydrogen bond-acceptor groups should improve their miscibility with phenolic resin. Functionalization of Q$_8$M$_8$H can be achieved through hydrolysisylation of its Si–H groups with acetoxystyrene [35] in the presence of a Pt catalyst to form octakis(dimethyl(4-acetoxy phenethyl)siloxy)silsesquioxane [OA-POSS; Fig. 6(b)].

Fig. 7 presents scaled room temperature IR spectra of pure phenolic and various phenolic/OA-POSS nanocomposites [35]. Fig. 7a reveals that the intensity of the free OH absorption (3525 cm$^{-1}$) decreases gradually as the OA-POSS content of the blend is increased from 5 to 90 wt%. The band for the hydrogen-bonded OH units in the phenolic shifted to higher frequency (toward 3465 cm$^{-1}$) upon increasing the OA-POSS content. This change is due to the switch from hydroxyl–hydroxyl interactions to the formation of hydroxyl–carbonyl and/or hydroxyl–siloxane hydrogen bonds. Fig. 7b displays the room temperature IR spectra (1680–1820 cm$^{-1}$) of various phenolic/OA-POSS blend composites. The C=O stretching frequency is split into bands at 1763 and 1735 cm$^{-1}$, corresponding to free and hydrogen-bonded C=O groups, respectively [36–39]. Fig. 8 indicates that the experimental values of $K_A$ are generally lower than the predicted values when using the value of $K_A$ of 64.6 obtained from the phenolic/PAS blends [34]. This result reveals that the OH groups of phenolic interact with the C=O groups of the ace- toxystyrene units as well as the siloxane groups of the POSS core. The equilibrium constants $K_A$ for the association of phenolic/OA-POSS and the phenolic/PAS blend blends are 26.0 and 64.6. Therefore, the value of $K_A$ for the interaction between the OH group of phenolic and the siloxane groups of the POSS derivative is equal to 38.6 (i.e., $64.6 - 26.0 = 38.6$), consistent with the value reported based on the classical C&S methodology [32]. Our group also synthesized a new POSS derivative containing eight phenol groups (octakis(dimethyl(4-hydroxyphenethyl)siloxy)silsesquioxane, OP-POSS, Fig. 6 (b)) and copolymerized it with phenol and formaldehyde to form covalently linked novolac-type phenolic/OP-POSS nanocomposites that exhibited higher thermal stabilities and lower surface energies [40]. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the phenolic/OP-POSS nanocomposites at various weight ratios revealed that each of these hybrids possessed essentially a single value of $T_g$, suggesting that they each featured a single phase [40]. The values of $T_g$ of these nanocomposites were significantly enhanced after incorporation of OP-POSS units, presumably because of the restricted motion of the polymer chains caused by physical crosslinking through hydrogen bonds with the evenly distributed POSS units within the phenolic matrix.

In addition, our group has synthesized three amorphous POSS derivatives: OS-POSS (Fig. 3), OA-POSS and OP-POSS (Fig. 6). Fig. 9 displays MALDI-TOF mass spectra of these compounds. Monodisperse mass distributions of the sodiated molecular ions appear at 1873 g/mol for [OS-POSS + Na]$^+$, 2337 g/mol for [OA-POSS + Na]$^+$, and 2001 g/mol for [OP-POSS + Na]$^+$, the good agreement between the experimental and calculated molecular masses confirms the well-defined structures of OS-POSS,
OA-POSS, and OP-POSS [25]. Blending OS-POSS, and OP-POSS with polystyrene PS, PAS, or P4VP facilitated investigation of the effects of intermolecular interactions on the dispersion of these POSS derivatives in the polymer matrices [hydrophobic interactions between aromatic rings (OS-POSS/PS), dipole–dipole interactions between ester groups (OA-POSS/PAS), and hydrogen bonding between phenol and pyridine units (OP-POSS/P4VP)]. Fig. 10 displays transmission electron microscopy (TEM) images and schematic representations of the microstructures of these POSS-based polymer nanocomposites [25].

Our octakis-functionalized amorphous POSS derivatives were dispersed through physical intermolecular interactions between their outer organic units and the organic polymer matrices. Thus, the size and distribution of the POSS aggregates depend strongly on the type and strength of the intermolecular interactions. Clearly, the weak aromatic hydrophobic interactions between OS-POSS and

![Fig. 7. IR spectra for phenolic/AS-POSS blends: (a) hydroxyl and (b) carbonyl. Reprinted with permission from Ref. [35]. Copyright 2006, Wiley-VCH, Germany.](image)

![Fig. 8. Fraction of hydrogen-bonded carbonyl groups versus phenolic contents. Reprinted with permission from Ref. [27]. Copyright 2006, Wiley-VCH, Germany.](image)

![Fig. 9. MALDI-TOF mass spectra of (a) octakis[dimethyl(phenethyl)siloxy] silsesquioxane, (OS-POSS), (b) octakis[dimethyl(4-acetoxy phenethyl)siloxy]-POSS (OA-POSS) and octakis[dimethyl(4-hydroxyphenethyl)siloxy]-POSS (OP-POSS). Reprinted with permission from Ref. [25]. Copyright 2008, Elsevier Science Ltd., UK.](image)
POSS feedstocks functionalized with various reactive organic groups can be incorporated into virtually any existing polymer system through grafting, copolymerization or blending. The incorporation of POSS nanocluster cages into a polymeric material can result in dramatic improvements in the polymer’s properties including greater temperature and oxidation resistance, surface hardening, and reduction in flammability. Therefore, research in POSS-related polymers and copolymers has accelerated in recent years. Depending on the number of POSS functional groups, various architectures of polymer/POSS nanocomposites can be obtained (Fig. 11) [41]. Some representative systems are discussed below.

4. POSS-containing polymers and copolymers

4.1. Polyolefin/POSS and norbornyl/POSS copolymers

4.1.1. Polyethylene and norbornyl/POSS copolymers

A number of interesting design strategies for the preparation of polyolefin/POSS hybrid materials have evolved over the past decade [42–50]. Coughlin and coworkers [42] synthesized PE hybrid containing POSS through ring-opening metathesis copolymerization (Fig. 12). From studies of nanostructured PE-POSS copolymers through controlled crystallization and aggregation, they found that two distinctly different crystallizing components were present in these copolymers and the final structure depended on the respective crystallization kinetics under different crystallization conditions [42]. Fig. 13 presents TEM micrographs of polybutadine-POSS (PBD-POSS) random copolymers with POSS contents of 12 and 43 wt% [51]. In Fig. 13(a), POSS aggregates are clearly observed as short randomly oriented lamellae having lateral dimensions of ca. 50 nm. The thickness of the lamellae ca. 3–5 nm, roughly corresponds to twice the diameter of a POSS NP. Increasing the incorporation ratio of POSS to 43 wt% resulted in the formation of continuous lamellae having lateral lengths on the order of microns (Fig. 13(c)). The irregular lamellar spacing observed in this image possibly arose from a combination of both twisting of the POSS lamella and the random nature of the copolymers. The morphology bears similarity to the lamellar morphology formed by precise diblock copolymers [51]. Furthermore, Coughlin and coworkers [42,52] and Mather et al. [53] reported polyolefin copolymers containing norbornyl–POSS macromonomers. Polyolefin-POSS copolymers incorporating norbornylene–POSS macromonomer have been prepared using a metalloocene/methyl aluminoxane (MAO) co-catalyst system [52]. Using a Pd-diimine catalyst, Ye and
coworkers [54] synthesized hyperbranched PE containing covalently tethered POSS NPs through chain-walking ethylene copolymerization with a POSS macromonomer bearing a polar acryloisobutyl-POSS unit. The covalent incorporation of the high-mass POSS NPs significantly reduced the intrinsic viscosity of the copolymers relative to the pure PE of the same molecular weight, owing to the highly compact spherical cage structure of the POSS NPs. Thermal studies confirm that the incorporation of POSS units significantly enhanced the thermal oxidative stability of the polymers in air, with the value of $T_g$ of the copolymer increasing upon increasing the POSS contents.
Joshi et al. [47] used a melt mixture route to prepare high-density PE/octamethyl-POSS (OM-POSS) nanocomposites. The rheological results revealed that, at lower filler contents (0.25–0.5 wt%) the POSS particles acted as a lubricant to reduce the complex viscosity of the nanocomposites. At higher POSS concentrations, the viscosities of the nanocomposites increased. The POSS derivatives remained miscible with HDPE at lower concentrations and lower temperatures, but they tended to aggregate at higher concentrations and higher temperatures. From studies of non-isothermal crystallization of the HDPE/OM-POSS nanocomposites using the Kissinger method [49], they also found that the presence of the POSS units did not have any significant effect on the activation energy for the transport of the polymer segments to the growing surface. They observed that only those POSS units dispersed at the molecular level could act as nucleating agents while the POSS nanocrystals did not affect the crystallization process.

4.1.2. Polypropylene/POSS nanocomposites

Zhang et al. [55] prepared polypropylene-POSS nanocomposites using a C2 symmetric ansa-metallocene catalyst in conjunction with a modified MAO. Their PP/POSS copolymers exhibited improved thermal stabilities with higher degradation temperature and char yields, revealing that inclusion of the inorganic POSS NPs made the organic polymer matrix more thermally robust. Hsiao and coworkers [56] used DSC to investigate a series of isotactic polypropylene (iPP) melt-blended with nanostructured OM-POSS molecules to study the quiescent melt crystallization behavior and shear-induced crystallization behavior. They observed that the addition of OM-POSS molecules increased the crystallization rate of iPP under both isothermal and non-isothermal conditions, implying that POSS crystals acted as nucleating agents, a finding that is similar to that with PE systems. Tabuani and coworkers [57–61] reported the influence of the POSS substituent on the morphological and thermal characteristics of melt-blended PP/POSS composites [57–61]. By varying the amount of filler, they investigated the effects of three different alkyl substituents (R= ethyl, isobutyl, iso-octyl) in the POSS structure on the morphological characteristics, crystallization and melting behavior of PP/POSS composites. They found that the lengths of the alkyl groups of the POSS molecules played a fundamental role affecting the degrees of dispersion and interactions with the PP matrix during the cooling process from the melt.
Two metal-POSS (M-POSS) systems, Ti(IV)- and Al(III)-isobutyl-POSS were blended with PP to study the morphological, crystallization, and thermal behavior of these M-POSS/PP composites [61]. Ti- and Al-POSS had different effects on the thermoxidative behavior of the polypropylene matrix in the M-POSS/PP composites, revealing the clear specificity of the metal center on the PP degradation pathway. In particular, Ti-POSS significantly stabilized PP when heated in air, whereas Al-POSS had only limited effects. Moreover, Ti-POSS affected the crystallization of PP, driving the crystallization process along specific crystallographic directions.

Fina et al. [62] reported the maleic anhydride-grafted polypropylene (PP-g-MA)/POSS hybrids prepared through grafting of aminoethylaminopropyl heptaisobutyl POSS (AM-POSS) in a one-step reactive blending process (Fig. 14). Morphological analyses revealed the dispersion of POSS units on the nanoscale because of the high chemical reactivity between POSS and PP-gMA. The presence of grafted POSS moieties improved the thermoxidative stability of PP-g-MA, in terms of delaying mass loss during thermal degradation under air, relative to pure PP-g-MA and PP-g-MA containing comparable amount of the non-reactive OiBu-POSS.

Chen and coworkers [63,64] studied the isothermal crystallization kinetics and morphological development of iPP blended with small loadings of OM-POSS. The predominantly nanocrystalline POSS acted as an effective nucleating agent to promote the nucleation rate of iPP. In contrast, the minor amount of those slightly miscible and dispersed POSS molecules retarded the nucleation and growth rates of iPP in the remaining bulk region. Zhou et al. [65–68] studied the crystallization behavior of PP/octavinyl-POSS (OV-POSS) prepared using two different processing methods: reactive blending and physical blending. Crystallization in the PP/POSS composites was strongly influenced by the processing method. POSS particles can act as effective nucleating agents to accelerate the crystallization of PP. The crystallization rate increased more dramatically for the reactive blending composite because of the stronger nucleating effect of PP-grafted POSS. The surface energy of chain folding of the physical-blend and reactive-blend composites changed from 156.5 mJ/m² for pure PP to 81.2 and 24.5 mJ/m², respectively [62].

Misra et al. [69] used melt blending to study the surface energy and mechanical behavior of PP/OiBu-POSS nanocomposites. Incorporation of 10% POSS resulted in a 3% reduction in the surface energy (to 24 mN/m), and a 27% increase in the water contact angle (to 99'). The increased water contact angle reveals the hydrophobic nature of the PP/POSS nanocomposite surface. The observed increases in surface hydrophobicity by increasing POSS concentration can be related to surface roughness through AFM roughness analysis [69]. Tang and Lewin [70] studied the migration and surface modification of PP/POSS nanocomposites by annealing the melt and by heating the solid blend in a microwave oven. Their static contact angle measurements revealed very high hydrophobicity as well as low surface free energy of the surface of the annealed sample, close to Teflon or pristine POSS. The migration of POSS was due to its lower surface tension and lower cohesive energy with the matrix chains relative to the cohesion energy between polymer chains, and the density and temperature fluctuations of the matrix chains upon relaxation repulse. As a result, the POSS units were propelled to the surfaces [70].

4.1.3. Other polyolefin POSS nanocomposites

Cohen and coworkers [71,72] found that octamethacryl-POSS (OMA-POSS) has the ability to plasticize PVC better than organic plasticizers such as dioctyl phthalate (DOP). They found that the value of $T_g$ of ternary blends of PVC/POSS/DOP could be reduced to near room temperature. Zheng et al. [73] reported that the inclusions of octaglycidyl dimethylsilyl POSS (OG-POSS) into PEI resulted in higher values of $T_g$ and enhanced thermal stabilities relative to those of pure PEI. In addition, PEI containing hepta(3,3,3-trifluoropropyl) glycidylether-propyl POSS exhibited typical amphiphilicity as evidenced by increased surface hydrophobicity.

4.2. Polystyrene/POSS nanocomposites

Linear thermoplastic hybrid materials containing an organic PS backbone and large inorganic silsesquioxane
groups pendent to the polymer backbone have been prepared through free radical copolymerization [Fig. 15] [74]. The pendent inorganic groups drastically modify the thermal properties of the PS, interchain and/or intrachain POSS–POSS interactions affect the solubility and thermal properties. Haddad and coworkers [75] reported the viscoelastic behavior of poly(4-methylstyrene) (P4MS)-POSS nanocomposites in which the POSS units possessed various R groups such as cyclopentyl (Cp) and cyclohexyl (Cy) moieties. Rheological measurements revealed that the polymer dynamics were profoundly affected by the POSS contents. In addition, the glass transition and decomposition temperatures increased upon increasing POSS content. Mather and coworkers [76] reported the linear viscoelastic properties of PS-iBu-POSS nanocomposites. Fig. 16(a) shows a TEM image of PS-POSS incorporating 6 wt% iBu-POSS where the domain size ranging from 1.5 to 3 nm was close to the dimensions of a single POSS molecule [76]. Further increase in the iBu-POSS concentration led to an increase in the dispersed particle density (Fig. 16(b)), whereas the particle size remained nearly unchanged, indicating that the iBu-POSS groups grafted on the PS chain were well dispersed in the PS matrix almost at the molecular level. iBu-POSS was found to have a plasticizer-like effect, yielding a monotonic decrease in \( T_g \) upon increasing the iBu-POSS contents.

Mather and coworkers [77] also studied the linear viscoelastic behavior of PS-POSS nanocomposites featuring three different functional groups: i-Bu, Cp, and Cy. The \( T_g \) was strongly dependent on the POSS vertex group, i-Bu played a plasticizer-like role while Cp and Cy enhanced \( T_g \). The rubbery plateau modulus decreased upon increasing the POSS contents which was also strongly dependent on the nature of vertex groups following the order i-Bu-POSS > Cp-POSS > Cy-POSS. They reported two distinct effects of POSS incorporation: influencing the microscopic topology of the polymer chains and the intermolecular interaction between PS and POSS.

Patel et al. [78] performed molecular dynamic simulations of PS-POSS nanocomposites featuring various R groups to identify the origin of the property changes imparted upon the chemical incorporations of POSS. When the POSS substituents were phenyl groups, the increase in
the \( T_g \) of the PS-POSS copolymer was significantly greater than that of alkyl groups. Such R group compatibility allows massive pendant POSS moieties to exert larger restrictions on segmental motion. When the R groups are alkyl functions, they are less compatible with the PS phenyl rings and pack less efficiently [78]. Monticelli et al. [79] reported the preparation of PSMA through one-step reactive blending with AM-POSS, similar to the PP-g-MA/POSS system described above [62]. The grafted POSS had no significant influence on the thermal and mechanical properties because of the competing effects of (i) the molecular constraints imparted by the presence of the bulky POSS cages and (ii) the increase in the free volume.

Couglin and coworkers [80] reported a synthetic protocol for preparing well-defined POSS-PS hemi-telechelic hybrids through anionic living polymerization. These model systems provided the opportunity to experimentally probe the ordering or aggregation behavior of inorganic NPs within polymeric matrices. Zheng et al. [81] employed a reversible addition-fragmentation transfer (RAFT) agent to prepare by AM-POSS. The POSS-containing RAFT agent was successively applied to the RAFT polymerization of styrene, producing the organic/inorganic hybrid homopolymer and block copolymers. The thermal properties of the hybrid PS derivatives were effectively enhanced by the presence of POSS molecules. Liu and coworkers [82] used a combination of atom transfer radical polymerization (ATRP) and click chemistry techniques to synthesize a quadrifoil-shaped star-cyclic PS derivative containing a POSS core, a new chain topology for nonlinearly shaped polymers. Ning et al. [83] reported PS/octa-phenethyl-POSS (OPE-POSS) nanocomposites prepared through simple solution blending, homogeneous transparent films were obtained at POSS contents from 0 to 40 wt% POSS as a result of interactions between the phenyl groups of POSS and PS. Rotello and coworkers [84] reported that multiple hydrogen bonding interactions in the POSS-DAP POSS–POSS crystalline packing. Couglin and coworkers [85] developed a synthetic route for preparing syndiotactic PS (sPS)/POSS copolymers. Copolymerizations of styrene and POSS afforded a novel nanocomposite of sPS and POSS [86].

The rate of copolymerization was much slower than that of radical polymerization, presumably because of a coordination polymerization mechanism.

Our group has used free radical polymerization to synthesize a series of poly(acetoxyisobutylstyrylPOSS) (PAS-POSS) hybrid systems mainly [87,88]. At lower POSS contents, the POSS moieties mainly played a diluent role by reducing the degree of PAS self-interaction. At higher POSS contents in these hybrids, interactions between the siloxane units of the POSS moieties and the dipolar carbonyl groups of the PAS became dominant, resulting in of \( T_g \). In addition, nanoscale physical aggregation of POSS was also partially responsible for these effects. Xu and coworkers [89,90] reported a series of network formed from PAS (or PS)/OV-POSS hybrid nanocomposites that had been prepared through free radical polymerization. Similar PAS networks were also formed from linear pendant POSS in a PAS matrix [87,88].

Fig. 17. The multiple hydrogen bonding interaction between POSS-DAP and PS random copolymers.

### 4.3. Poly(acrylate)/POSS copolymers

Poly(methyl methacrylate) (PMMA) is a transparent polymeric material possessing many desirable properties including light weight, high light transmittance, chemical resistance, colorlessness, resistance to weathering, corrosion, and good insulating properties [91–94]. Methacrylate-substituted POSS macromers can be prepared containing one polymerizable functional group (Fig. 18) [95–100]. The resultant materials are generally transparent and brittle because the incorporation of the POSS group into linear polymers tends to prevent or reduce the segmental segregation or mobility. In general, glass transition and decomposition temperatures increase upon increasing the POSS contents. Kopesky et al. [96] reported PMMA containing both tethered and untethered POSS units, the presence of tethered-POSS in the entangled copolymers decreased the plateau modulus relative to that of the pure PMMA homopolymer. The untethered-POSS units induced a significant increase in the zero-shear viscosity due to the associations between the POSS moieties. Chen and coworkers [101] used living metallocene polymerization to prepare an interesting stereoregular methacrylate-POSS hybrid polymer possessing a high value of \( T_m \) (ca. 213 °C). Laine and coworkers [102] used the “core-first” method and ATRP to synthesize a star PMMA from an octafunctional silsesquioxane cube. PMMA polymers featuring chain-end-tethered POSS moieties have been widely reported [103–107]. For example, Fukuda and coworkers [103,104] used an incompletely condensed POSS derivative possessing a highly reactive trisodium silanolate group to synthesize several initiators for ATRP, thereby obtaining tadpole-shaped polymeric hybrids with a POSS unit.
Fig. 18. Synthesis of PMMA–POSS copolymers.

Fig. 19. Synthesis of fluorinated POSS initiator for ATRP.

Fig. 20. Surface-initiated ATRP of MAiBu-POSS monomer to form poly(MAiBu-POSS) on Si wafer.
Fig. 21. Reaction scheme to prepare PEO-octafuctionalized silsesquioxanes.

at the end of the polymer chain (Fig. 19). Our group has used ATRP to synthesize PMMA hybrids having controllable molecular weights with a chain-end-tethered POSS moiety [105]. Similar structures have been reported by Kotal et al. [106] (thiol-mediated radical polymerization) and Liu et al. [107] (ATRP polymerization). Blending both PMMA-POSS and PMMA with phenolic resin revealed that the POSS terminus affected the thermal properties, miscibility behavior, and hydrogen bonding interactions [105]. Further investigation of specific association between the terminal siloxane units of the POSS moieties and the OH groups of the phenolic revealed an interesting screening effect [31] in these phenolic and low-molecular-weight PMMA-POSS blends (for PMMA molecular weight below its entanglement value) [105] that tends to significantly decrease the hydrogen bond formation of the hydroxyl-carbonyl inter-association. Chen et al. [108] reported the polymerization of a methacrylo isobutyl-POSS (MAiBu-POSS) monomer from a self-assembled monolayer of ATRP initiators covalently immobilized on Si wafers (Fig. 20). This simple and effective approach allows the preparation of well-defined POSS-containing polymer films from flat surfaces.

Network structures featuring pendent POSS groups have been synthesized using free radical polymerization [109–118]. The presence of POSS units in these systems did not increase $T_g$ or improve the mechanical properties, it actually caused decreases in $T_g$ and elastic moduli in both glassy and rubbery states. For example, Galy and coworkers [98] reported a dimethacrylate-based network with a multifunctional methacrylate-POSS (OMA-POSS) that exhibited improved miscibility with the dimethacrylate monomer and better dispersion in the network structure than did the corresponding monofunctional methacrylate-POSS. The rubbery modulus increased upon increasing the POSS contents, but the $T_g$ remained constant. Yang and coworkers [112] used free radical polymerization or solution blending to prepare a series of network hybrids of PMMA with OV-POSS. The increase in $T_g$ strongly correlated with the degree of dipole–dipole interaction between the carbonyl groups of PMMA and POSS. The thermal stability was enhanced upon increasing the POSS content, mainly due to the uniform dispersion of the nanoscale inorganic POSS at the molecular level.

4.4. Poly(ethylene oxide)/POSS nanocomposites

Poly(ethylene oxide) (PEO) is used as an important polymeric electrolyte in lithium ion batteries because of its ability to solvate lithium ions [119–121]. One approach to increase the room temperature (RT) conductivity of PEO-based polymer electrolytes is to attach short-chain PEO (i) oligomers as side chains to form “comb-shaped” or “hairy rod”-like polymeric structures, or (ii) as “arms” from inorganic scaffolds. The grafting of oligomeric PEO chains onto Q8M8H to produce PEO-functionalized silsesquioxanes has been widely reported (Fig. 21) [122–128]. The grafting of PEO onto POSS results in a chain-length-dependent increase in $T_g$ and suppression of crystallization because these dendrimers or star polymers feature high ratio of chain ends. In addition, PEO grafted with POSS have a lower melt viscosity and greater free volume than those of the linear PEO polymers having a similar molecular weight. Since these PEO-POSS hybrids do not crystallize and have relatively lower $T_g$ than the corresponding PEO chains, they have potential to be used as low temperature solvents in lithium ion batteries. Wunder and coworkers [125] reported a strong self-supporting film prepared from 10% methyl cellulose and 90% PEO-POSS/LiClO4 that possessed an RT conductivity of $10^{-5}$ S/cm [125,126];
higher conductivity of $10^{-4}$ S/cm was obtained from a PEO
- POSS/LiN(CF₃CF₂SO₂)₂ hybrid.

Huang et al. [124] reported that similar to the linear PEO
homopolymer, the star PEO formed inclusion complexes
(ICs) with α- and γ-cyclodextrin (CD), but not with β-CD.
CDs are among the most popular host molecules employed
to construct molecular assemblies; they are cyclic oligosac-
charides comprising six (α), seven (β), or eight (γ) glucose
units linked through 1,4-α-glucosidic bonds [129,130]. A
channel-type structure was found in the ICs, but the seg-
ments of PEO arms near the POSS cores were not covered
by CD units [123]. Zheng et al. [131] reported an IC formed
from N₃-POSS and a dialkene-terminated PEO with CD
units. TGA analyses showed that the organic/inorganic
hybrid polyrotaxanes exhibited enhanced thermal stability
relative to that of polypropylorotaxaine. They also reported
an interpenetrating polymer network (IPN) prepared via
in situ crosslinking between OG-POSS and bisphenol A in
the presence of PEO. FTIR spectroscopic analysis showed
the presence of hydrogen bonding between the hydroxyl
group of POSS and the ether groups of PEO. TGA revealed
that the thermal stability of the IPNs was dependent on the
mass ratios of the POSS network to PEO [132].

Our group has investigated the effects of three dif-
ferent octuply functionalized POSS derivatives (OS-POSS,
OA-POSS and OP-POSS) in PEO matrix nanocomposites
[133]. The intermolecular interactions between these POSS
derivatives and the PEO segments have a great effect on the
thermal properties and miscibility behavior of their respec-
tive blends. The strongest hydrogen bonding interaction
occurred between OP-POSS and PEO, as a result, its blend
displayed superior thermal properties. The addition of an
amorphous hydrogen-bonding POSS nanoparticle into PEO
tends to depress the rates of crystallization and spherulite
growth, the OP-POSS/PEO showed greater influence than
OA-POSS/PEO, consistent with the relative intermolecular
hydrogen bonding strengths.

Well-defined amphiphilic telechelic polymers incorpo-
rating POSS have been synthesized through direct urethane
linkage between the OH end groups of a poly(ethylene gly-
col) (PEG) homopolymer and the monoisocyanate groups of
a POSS macromer [134–136]. These amphiphilic telechelics
exhibited a relatively narrow and unimodal molecular
weight distribution ($M_w/M_n$ < 1.1), with close to 2.0 end
groups per PEG chain [134]. The crystallinity of the PEO
segments in the amphiphilic telechelics decreased dramat-
ically upon increasing the POSS content to 40.7%, becoming
amorphous at values beyond ca. 50%.

4.5. Polyester/POSS nanocomposites

4.5.1. PCL/POSS nanocomposites

Our group has synthesized a series of the
organic/inorganic hybrid star PCLs through coordinated
ring-opening polymerization of $\varepsilon$-caprolactone using
octakis(3-hydroxypropyl) POSS (OH-POSS)
as the initiator [137]. Similar to the linear PCL analogues
reported previously, these star PCLs formed ICs with α-
and γ-CD, but not with β-CD [137]. The stoichiometries
of all of the ICs with α- and γ-CD were greater than those
of the corresponding CD/linear PCL ICs because of steric
hindrance around the bulky POSS core (i.e., some of the
$\varepsilon$-caprolactone units near the core were unable to form
ICs: Fig. 22) [137]. Another possible structure for the
γ-CD/star PCL ICs would have two PCL chains simultane-
ously included within a single γ-CD channel. The inclusion
of arms from two different star PCLs within the same
γ-CD might occur as a result of unequal splaying of each
arm of the star polymer. As a result, a gel-like physically
crosslinked structure was formed. Zheng and coworkers
[138] reported another approach for the preparation of
octakis(3-hydroxypropyl)-POSS using an octafunctional
initiator for the synthesis of eight-armed star-shaped
PCLs. Organic/inorganic star PCLs possessing various
degrees of polymerization have been synthesized through ring opening polymerization catalyzed by stannous(II) octanoate [Sn(Oct)\(_2\)]\[138\].

Our group has prepared a mono-POSS-end-capped PCL through ring-opening polymerization from hydroxyethylisobutyl-POSS (mono-OH-POSS; Fig. 23)\[139\]. Similar chemical structures have been prepared by other researchers using the ring-opening polymerization of caprolactone monomer\[140–142\]. From a study of the melting and crystallization behavior of POSS-end-capped PCL, Zheng and coworker\[140\] found enhanced equilibrium melting temperatures relative to that of the pure linear PCL. Both the overall crystallization and spherulitic growth rates of the POSS-end-capped PCL increased with the increase of POSS contents.

Our group has also reported that mono-POSS-end-capped PCL can form ICs with \(\alpha\)- and \(\gamma\)-CDs, but not with \(\beta\)-CD. The PCL chain becomes included within the channel provided by the CDs to form a columnar crystalline structure\[139\]. A similar result was reported by Zheng and coworker\[143\], who found that the POSS-terminated PCL forms a channel-type crystalline structure with \(\alpha\)-CD\[143\]. In addition, this POSS end-capped PCL, prepared through in situ polymerization with epoxy monomer, can obtain organic–inorganic hybrid nanocomposites after thermal curing\[144\].

Lee et al.\[142\] reported the preparation of double networks featuring the superposition of a covalent network with a physical network derived from a well-defined crystalline phase of strongly hydrophobic POSS moieties. Each covalent network chain features PCL or PLGA tethers on a single POSS moiety as a difunctional initiator for PCL or PLGA ring-opening polymerization. Inoue and coworkers\[145\] reported a PCL doubly end-capped with fullerene and POSS units. The aggregation of the fullerene moieties had much larger confinement effect on the crystallization of PCL than that of POSS. The successful incorporation of two nanosized objects into a PCL matrix may result in systems that display multi-functional properties\[145\].

4.5.2. Other polyester/POSS nanocomposites

Hana et al.\[146\] prepared bacterial poly(3-hydroxyalkanoate-co-3-hydroxyalkenoate), (PHAED/POSS) nanocomposites through free radical addition reactions of mercaptopropyl-isobutyl-POSS (SH-POSS) to the side-chain double bonds of the polymer. The appearance of the POSS-based PHAE changed from non-sticky and elastic to brittle and glass-like upon increasing the POSS contents; this system has potential application because it can be classified as non-toxic and suitable for food contact. In addition, PC/OPE-POSS nanocomposites have been produced through melting or solution blending\[147–149\]. Since PC/POSS nanocomposites can be classified as polymer chains containing non-bonded POSS moieties, the substituent groups of the POSS units play an important role determining the miscibility of PC and POSS. Yoon et al.\[150\] prepared the PET/POSS nanocomposites through melt blending and in situ polymerization method. PET/POSS composites prepared through melting blending with small amounts of POSS resulted in phase separation and poor mechanical properties. To obtain a homogeneous phase of the blend, they employed in situ polymerization using the reaction between the epoxy groups of a triepoxy-POSS derivative and the hydroxyl end groups of PET and resulted in improved bulk mechanical properties when compared with pure PET\[150\]. Zhou et al.\[151\] used a similar method to prepare PBT/POSS nanocomposite through reactions between the epoxy groups of POSS (octakis(epoxycyclohexyldimethylsilyl)-POSS, OEC-POSS) and the hydroxyl groups of PBT within a twin-screw extruder. The melt flow index of PBT decreased, while the elongation at break and tensile strength increased, after the addition of OEC-POSS. Kim et al.\[152\] used in situ polymerization to prepare poly(trimethylene terephthalate) (PTT)/POSS nanocomposites by incorporating 1,2-propanediolisobutyl-POSS (PDB-POSS) with PTT monomer (dimethyl terephthalate (DMT) and 1,3-propanediol (PDO)). Increasing the POSS content caused the resultant PTT blends to exhibit decreased glass transition, cold crystallization and melting temperatures.
In addition, the initial modulus, breaking strength, and elongation at break all decreased upon increasing the POSS content.

4.6. Polyamide/POSS nanocomposites

4.6.1. Nylon/POSS nanocomposites

Ricco and coworkers [153,154] prepared polyamide 6/POSS nanocomposites through two different in situ polymerization mechanisms (hydrolytic and anionic) from 3-caprolactam (CL) in presence of AM-POSS. These Nylon 6/POSS nanocomposites featured a modified version of the polymeric crystal structure of Nylon 6, exhibiting decreases in their crystallinity and \( T_g \). In addition, the octaepoxycyclohexyldimethylsilyl-POSS (OEC-POSS) has been used as a reactive compatibilizer in PPO/PA6 blends via melt-mixing [155]. The morphology of the composites transformed from a droplet/matrix to a co-continuous morphology upon increasing the OEC-POSS content from 2 to 4 phr. The PPO/PA6/POSS composites with a co-continuous morphology had better mechanical properties than those having the droplet/matrix morphology. Yu et al. [156] prepared Nylon 1010/POSS composites through melt blending with OV-POSS and OEC-POSS; these Nylon 1010/POSS composites exhibited higher decomposition temperatures and char yields. Wan et al. [157] prepared polyamide 12 (PA12)/POSS composites through melt blending and found that the presence of trisilanolphenyl-POSS did not affect the crystalline structure of PA12, but it did enhance its tensile strength and thermal stability.

4.6.2. PNIPAM/POSS nanocomposites

Poly(N-isopropyl acrylamide) (PNIPAM) undergoes a sharp coil–globule transition in water at 32 \(^\circ\)C, changing from a hydrophilic state below this temperature to a hydrophobic state above it [158–160]. The lower critical solution temperature (LCST) corresponds to the region in the phase diagram where the enthalpic contribution of water hydrogen-bonded to the polymer chain is less than the entropic gain of the system as a whole, it is largely dependent on the hydrogen-bonding capabilities of the constituent monomer units. Zheng and coworkers [161] reported that PNIPAM/POSS nanocomposites prepared through the chemical reaction between the N–H group of PNIPAM and the epoxy group of octa[propylglycidyl ether]-POSS swelled in water and exhibited the characteristics of hydrogels. These POSS-containing hybrid hydrogels showed substantially faster swelling, de-swelling and re-swelling response rates than a control organic gel featuring a comparable degree of crosslinking. They also incorporated the POSS-end-capped PEO into the cross-linked PNIPAM to form a physically interpenetrating polymer network structure [162]. Acrylic-POSS, NIPAM monomer and \( N,N \)-methylenebisacrylamide have been used to prepare POSS-containing PNIPAM cross-linked networks [163]. These nanocomposite hydrogels displayed significantly faster response rates than those of the pure PNIPAM hydrogel in terms of swelling, de-swelling, and re-swelling. Zhang et al. [164] used the POSS-containing RAFT agent in the RAFT polymerization of NIPAM to form a POSS-end-capped PNIPAM hybrid, which assembled into well-defined core/shell nanostructured micelles in solvents, with the average diameter of the micelles increasing upon increasing the molecular weight of PNIPAM.

4.6.3. PVP/POSS nanocomposites

Eshel et al. [165] reported that the presence of small amounts of POSS within PVP hydrogels enhanced the storage modulus and the swelling ability relative to those for the pure PVP hydrogels. Due to its large surface area, only relatively small amounts of POSS was needed to cause significant changes. Our group prepared PVP/POSS nanocomposites with isobutyl-POSS (pendant type) through one-step free radical copolymerization. \( T_g \) of the PVP/POSS hybrid was influenced by three main factors: (1) the diluent role of the POSS units to reduce the self-association of the PVP; (2) strong interactions between the POSS siloxane and the PVP carbonyl groups; and (3) physical aggregation of the nanosized POSS units [166]. At a relatively low POSS content, the role as a diluent dominated and resulted in decreasing \( T_g \). At a relatively high POSS content, the latter two factors dominated and resulted in increasing \( T_g \) for the PVP/POSS hybrid. Xu and coworkers [167] studied PVP/POSS networks containing OV-POSS with the POSS units in a junction structure, the change in \( T_g \) was primarily due to the effect of the crosslinking structure. Furthermore, a series of poly(vinylphenol-co-vinylpyrrolidone-co-isobutylstyryl-POSS) (PVPh-co-PVP-co-POSS) hybrid polymers incorporating various POSS contents have
been prepared through free radical copolymerization of acetoxy styrene, vinylpyrrolidone, and POSS, followed by selective removal of the acetyl protecting group (Fig. 24) [168,169]. The \( T_g \) of the PVPh–PVP–POSS hybrid increased substantially upon incorporating the POSS moieties [169]. The presence of the physically crosslinked (hydrogen bonded) POSS units in these hybrid polymers restricted the polymer chain motion, resulting in extremely high \( T_g \). We also discussed the miscibility behavior and interaction mechanism of poly(methyl methacrylate-co-vinylpyrrolidone) (PMMA-co-PVP) with OP-POSS [170–172]. The VP units in PMMA acted as physical crosslinking points to increase the \( T_g \) of the PMMA-co-PVP copolymer; each of their DSC traces featured only a single glass transition temperature. Moreover, intermolecular hydrogen bonding became stronger than intramolecular hydrogen bonding after copolymerization with the VP, because the hydroxyl group preferred to interact with the VP segments. Furthermore, the presence of OP-POSS units in LiClO\(_4\)/OP-POSS/MMA61 ternary blends leads to enhance the ionic conductivity [171,172].

4.6.4. Other polyamide/POSS nanocomposites

Liu et al. [173] prepared POSS-tethered aromatic polyamide nanocomposites through Michael addition between maleimide-containing polyamides and AM-POSS. These polyamide-POSS nanocomposites showed good homogeneity and higher storage and Young’s modulus, but slightly decreased their \( T_g \)s and significantly lowered dielectric constants. Through the reaction between NCO-POSS and NH\(_2\)-PAMAM, Dvornic et al. [174] prepared a core/shell system featuring a PAMAM dendrimer core and a POSS shell. Hybrid star-shaped polyoxazolines (POZ) with POSS cores have been prepared through ring-opening polymerization of 2-methyl-2-oxazoline using various octafuctional POSS derivatives as initiators [175,176]. The core-first method, using an active multifunctional core to initiate growth of polymer chains, allowed the synthesis of hybrid POSS-core star-shaped POZ. The thermal stability of this star shaped POZ/POSS nanocomposite was greater than that of the corresponding pure linear POZ. They also reported the preparation of POSS-end-capped POZ nanocomposites by ring-opening polymerization of 2-methyl-2-oxazoline initiated by a functionalized POSS derivative.

Similar to polyamide chains, the peptide chains possess distinct secondary structures that influence the well-defined tertiary structures of proteins. Poly\(\gamma\)-benzyl-\(\gamma\)-glutamate) (PBLG) is a synthetic polypeptide that forms \(\alpha\)-helix and \(\beta\)-sheet secondary structures that are stabilized through intramolecular and intermolecular hydrogen bonds, respectively [177]. The \(\alpha\)-helical form of PBLG exists as a rigid-rod structure in the solid state and in solution, providing PBLG with its unique bulk and solution properties, including thermotropic liquid crystalline ordering and thermo-reversible gelation [178–180]. POSS–PBLG helical polypeptide copolymers are macromolecular self-assembling building blocks that have been synthesized through ring-opening polymerization of \(\gamma\)-benzyl-\(\gamma\)-glutamate N-carboxyanhydride (\(\gamma\)-Bn-Glu NCA) using AM-POSS as a macroinitiator (Fig. 25) [181].

The incorporation of POSS units at the chain ends of PBLG moieties has two important effects: (i) allowing intramolecular hydrogen bonding between the POSS and PBLG units to enhance the latter’s \(\alpha\)-helical conformations in the solid state and (ii) preventing the aggregation of nanoribbons through the POSS blocks’ protrusion from the ribbons, leading to the formation of clear gels in solution. 2D IR correlation spectroscopy has been used to detect the presence of intramolecular hydrogen bonds between the POSS and PBLG units. Fig. 26(a) presents the synchronous 2D correlation map (from 800 to 2000 cm\(^{-1}\)) for the POSS–PBLG\(_{18}\) sample; the bands at 1730, 1655, and 1550 cm\(^{-1}\) correspond to the C=O, amide I, and amide II bands of the PBLG unit, respectively [181]. The band at 1087 cm\(^{-1}\) represents Si–O–Si stretching of the POSS cage. These four absorptions exhibit many positive auto and cross peaks. A new auto-peak appeared at 1150 cm\(^{-1}\) for the copolymer, indicating that hydrogen bonding occurred between the amide and carbonyl groups of the PBLG unit and the siloxane groups of the POSS moiety. In contrast, the corresponding asynchronous 2D correlation map (Fig. 26b) does not show any such auto or cross peaks over the same wavenumber range. Thus, the incorporation of a POSS moiety at the PBLG chain end leads to intramolecular hydrogen bonding between the POSS and PBLG units, such that the latter units form \(\alpha\)-helices in the solid state.

Fig. 27(a) and (b) presents TEM images of fibrous structures formed from pure PBLG\(_{53}\) and from the POSS–PBLG\(_{56}\) copolymer. The turbid gel formed by the pure PBLG\(_{53}\) featured a disordered and irregular fiber aggregation width.
ranging from 500 to 1000 nm (Fig. 27(a)) [181]. Strong dipolar \( \pi-\pi \) interactions between the phenyl groups and PBLG rods stabilized the micro-fibers that were intertwined into an irregular 3D network structure. In contrast, the clear gels of the POSS–PBLG\(_{56}\) copolymer featured bundles of ordered fibers, with the fiber units having a width of ca. 10 nm. AFM experiment revealed the fibers’ lateral dimensions and height profile (Fig. 27(c)). In the AFM height profile, these fiber units possessed an average height of ca. 2 nm and a lateral dimension of ca. 25 nm, implying that the fibrous structure were not cylindrical, but rather had a ribbon- or tape-like morphology formed by stacking of the POSS–PBLG copolymer chains, which contained PBLG helices (diameter: ca. 1.5 nm). SAXS measurements of the dried toluene gels of POSS–PBLG\(_{56}\) suggested an individual fiber width of 11.8 nm, consistent with the TEM
and AFM results. Observation of such a lateral dimension of the fiber through SAXS was not possible for the pure PBLG_{53} gels because of the lack of order in their fibers. WAXD (Fig. 27(e)) profiles of the dried POSS–PBLG_{56} gels showed three diffraction peaks at 3.6, 1.6 and 0.54 nm, corresponding to the distance between two neighboring POSS blocks, the distance between the α-helices of the PBLG units, and the pitch length of the α-helix, respectively. The POSS–PBLG copolymer can self-assemble in an anti-parallel manner to minimize steric hindrance between the POSS blocks, thereby forming an unfavorable orientation of the PBLG helical dipole moment in the nanoribbon structure (Fig. 27(f)) where the long axis of the PBLG helix is parallel to the plane of the ribbon. In an anti-parallel stacking mode, the distance between two neighboring POSS blocks is ca. 3.7 nm, a situation that cannot accommodate the bulky POSS units in the planar nanoribbon structures without changing the morphology. The POSS block protrudes outside of the ribbon due to high solubility in toluene, suppressing aggregation between the nanoribbons and forming clear gels.

4.7. Polyimide/POSS nanocomposites

Polyimides (PIs) are widely used in the microelectronics industry because of their excellent tensile strengths and modulus, good thermal stabilities and dielectric properties, and high resistance to organic solvents. Two routes are commonly employed to incorporate POSS units into a PI matrix. One method to achieve PI–POSS nanocomposites is to use a POSS derivative possessing eight functional groups (e.g., epoxy or amino groups) to serve as a crosslinking agent. Laine and coworkers [182] described the nitration of octa-phenyl POSS and subsequently produced octakis(aminophenyl)-POSS (OAP-POSS) through Pd/C-catalyzed hydrogenation (Fig. 28). OAP-POSS was then employed in conjunction with dianhydrides to prepare extremely thermally resistant cross-linked PI networks [182]. He et al. [183] and our group [184] have both demonstrated that polyamic acid (PAA), a PI prepolymer, can react with OG-POSS (Fig. 29). Using these approaches, the dielectric constants of the PI nanocomposites can be reduced, and their thermal properties modified, upon increasing the POSS content. Excess 4,4′-oxydianiline diamine (ODA) was reacted initially with 4,4′-carbonyldiphthalic anhydride (BTDA) and then the terminal amino groups of the PAA were reacted with OG-POSS. By varying the equivalent ratio of ODA and using PAAs of various molecular weights, nanocomposites possessing various morphologies have been obtained. The decrease in the dielectric constant of the PI–POSS hybrids results from nano-void volume of the POSS cores and from the free volume increase resulting from the presence of the rigid and large POSS units inducing a loose PI network [184]. He and coworkers [185] also reported the use of OH-POSS for the preparation of PI/POSS nanocomposites; high-performance low-k PI nanocomposites were obtained when PAA was cured with OH-POSS.

Our group has used a hybrid star PEO-POSS template to prepare nanoporous PI films (Fig. 21) [129]. These nanoporous foams were generated by blending PI as the major phase with a minor phase consisting of the thermally labile PEO-POSS NPs. During oxidative thermolysis, these labile PEO-POSS NPs released small molecules as byproducts diffusing out of the matrix, thereby leaving voids within the polymer matrix. Fig. 30 illustrates the storage modulus and tan δ for pure and porous PIs containing 5 wt% PEO-POSS [129]. The pure PI has a modulus of ca. 2000 MPa at room temperature and a single \( T_g \) at 370 °C.
In the case of the porous PI, two relaxations appear at ca. 360 and 385 °C, based on the tan δ peaks. The relaxation at 360 °C is a typical microphase separation for a porous PI undergoing a sudden decrease in storage modulus. This transition (370 °C for the homopolymer) arose from the finite solubility of the PEO-POSS NPs in the matrix and from the microphase separation of the foams after curing. The overall modulus of the porous PI was lower than that of the pure PI due to its foam structure. At higher temperatures (>370 °C), these foams collapsed and the porous structure no longer existed. The higher value of \( T_g \) of the nanoporous system (385 °C, based on the maximum of the tan δ peak) was probably due to the content of residual silica produced by PEO-POSS in the solid matrix. The resulting storage modulus and softening temperature decreased slightly with increasing content of nanofoam in the PI matrix. After post-curing, however, the foam structure collapsed and the storage modulus increased upon increasing the PEO-POSS content; in addition, the relaxation effect through the microphase separation of the nanofoams disappeared. The increased modulus in this nanocomposite may have arisen from (i) the SiO₂ particles derived from the PEO-POSS being distributed evenly within the polymer matrix or (ii) the presence of physical bonds (e.g., hydrogen bonding) between the PI units and these rigid silica particles, hindering the mobility of the polymer chains and resulting in higher-than-expected values for the modulus and \( T_g \). A significant reduction in dielectric constant (\( k \), from 3.25 to 2.25) occurred for the porous PI hybrid films having pore sizes in the range from 10 to 40 nm.

The second common method for the preparation of PI/POSS derivatives featuring low dielectric constants and good thermal properties was accomplished by blending the PI precursor with a fluorinated POSS derivative (OF-POSS)[186,187]. The low polarizability of OF makes it compatible with PI matrices; therefore, it can improve the component dispersion and increase the free volume of the resulting composites, both of which are responsible for the observed lower dielectric constants of PI-OF nanocomposites. Yeh and coworkers[186] reported a high-performance and low-\( k \) PI nanocomposite from PAA cured with octakis(dimethylsiloxymethylene)propylglycidyl ether)-POSS (OFG-POSS)[185,187]. This reactive POSS isomer has an average of four epoxy groups and four fluoro groups on the POSS cage; its epoxy group reacted with PAA to form a PI/POSS nanocomposite featuring a network framework (Fig. 31). The resulting PI/OFG-POSS nanocomposite had a high crosslinking density, high porosity, high hydrophobicity, and low polarizability.

A third method for the simultaneous and convenient production of high-performance PI with a low dielectric constant involves the introduction of an octa-acrylated POSS into a PI matrix to form PI semi-interpenetrating polymer network (semi-IPN) nanocomposites[186]. Analyses using DSC and FTIR spectroscopy revealed that the self-curing of methacrylated-POSS and the imidization of PAA occurred simultaneously. The semi-IPN structures of the [PI/POSS] nanocomposites featured aggregated POSS NPs (average size: ca. 50–60 nm) uniformly embedded within the matrix. At high POSS contents, the PI/POSS nanocomposites featuring interconnected POSS particles were highly crosslinked and, therefore, exhibited enhanced...
glass transition temperatures. The high porosity of the PI/POSS nanocomposites resulting from the nanometer-scale porous structure of POSS markedly reduced the dielectric constant of PI. Similar methods have been employed by Chen and coworkers [188,189] to prepare the low dielectric-constant nanocomposites of PIs with grafted methacrylate side chains containing POSS units prepared through thermally initiated free-radical graft copolymerization of MA-POSS with ozone-preactivated PAA, followed by thermal imidization.

Wei and coworkers [190–192] reported the grafting of a POSS derivative to PI-tethered POSS nanocomposites possessing well-defined architectures. Relative to pure PI, these types of POSS nanocomposites have both lower and tunable dielectric constants, and controllable mechanical properties. The presence of these tethered POSS molecules in the amorphous PI resulted in a nanoporous crystalline structure and also in an additional ordered architecture through microphase separation. Using this approach, the dielectric constant of the film can be tuned by controlling the amount of added POSS [189,190]. Wright et al. [193] reported a series of end-capped and hydroxymethyl-functionalized PIs covalently attached to the AM-POSS polymer backbone; POSS loadings as high as 36 wt% could be obtained while maintaining excellent processability and optical clarity of resulting films. Seckin et al. [194] reported a similar method using octakis(aminopropyl)-POSS (OAM-POSS) for the molecular-level design of low dielectric-constant PI materials for use in the manufacture of integrated circuits. The presence of OAM-POSS units restricts chain rotation through multiple-point attachment to the PI backbone, thereby creating additional free volume in the film to lower its dielectric constant. A process for synthesizing POSS–PI star nanocomposites has been reported [194] involving the formation of a porous-type POSS derivative and subsequent reaction with a PI precursor. Appropriate insertion of POSS units into a PI backbone can reduce its dielectric constant and also improve its mechanical and thermal properties. Wu and coworkers [195,196] reported a new method for preparing main chain PI–POSS hybrids from a double-decker shaped silsesquioxane diamine and various tetracaboxylic dihydrides; these hybrids possessed good thermal stability, improved mechanical properties and low-dielectric constants.

4.8. Polyurethane/POSS nanocomposites

Hsiao and coworkers [197] prepared polyurethane (PU)/POSS nanocomposites through the reactions of POSS derivative featuring one corner group substituted by either a hydridomethylsiloxo group (hydrido-POSS) or a 3-(allyl bisphenol-A) propyldimethylsiloxo groups (BPA-POSS). BPA-POSS compound is a diol used as a chain extender in PU synthesis. Turri and coworkers [198,199] synthesized a linear PU/POSS nanocomposite through a diol-functionalized POSS macromer; this nanocomposite exhibited significantly enhanced surface hydrophobicity and decreased surface energy relative to that of PU. These approaches have opened up new pathways for the development of high-performance nanostructured waterborne coatings. Mather and coworkers [200] prepared a PU system using an organic biodegradable PDLA soft block and an
inorganic diol-POSS hard block. Pielichowski and coworker [201] synthesized PU/POSS nanocomposites using MDI with polytetramethylene glycol, 1,4-butanediol, and diol-POSS; TGA revealed that the highest thermal stability occurred at POSS contents of 4 and 6 wt%. Neumann et al. [202] synthesized a POSS macromer with eight reactive isocyanate groups ((NCO)₈-POSS) through hydrosilylation of m-isopropenyl-R,R-dimethylbenzyl isocyanate (m-TMI) with Si–H bonds of Q₈M₈H and resulted in quantitative yield only the α-addition product without any competing reaction of the isocyanate group (Fig. 32). This macromer has also been used to synthesize the first cross-linked PU featuring discrete POSS molecules dispersed within the polymer matrix [204]. He and coworkers [203] subjected the same (NCO)₈-POSS macromer to polyaddition reactions with (OH)₈-POSS; resulting hybrid films were relatively transparent. The incorporation of octafunctional POSS in PU films resulted in higher thermal stability and crosslink density. Nanda et al. [204] prepared aqueous PU dispersions with functionalized POSS through homogeneous solution polymerization. The use of acetone as the initial polymerization solvent allowed the facile incorporation of both diamine- and diol-functional POSS monomers. The storage modulus, glass transition temperature, complex viscosity, and surface hydrophobicity all increased upon increasing the POSS content, due to incorporation of the POSS moieties into the PU hard segment domains. They also discussed the viscoelastic behavior of PU-urea film prepared by varying the functionalized diamino-POSS contents and found significant increases in the melt viscosity and zero shear viscosity resulted from the reaction between diamino-POSS and the hard segment of PU [205,206].

4.9. Phenolic/POSS nanocomposites

Our group has investigated phenolic/POSS nanocomposites, as described in Section 3, concerning the miscibility of phenolic resin with different functionalized POSS derivatives. Zhang et al. [207] also prepared a resole phenolic resin with trisilanophenyl-POSS nanocomposites through solution blending, where the thermal stability increased with the increase of POSS loading while the Tₘ of the nanocomposite was only slightly affected by the loading of POSS. Zhang et al. [208] used the OAP-POSS as a cross-linking agent for the phenolic resin because the OAP-POSS can form both covalent and hydrogen bonds with phenolic resin and POSS NPs. The storage modulus in both glassy and rubbery regions, the thermal stability and Tₘ of the POSS composites were improved in the presence of 1 wt% OAP-POSS. Zheng and coworkers [209] also used OG-POSS as a cross-linking agent for phenolic resin; Tₘ and thermal stability of the phenolic/POSS nanocomposites both increased upon increasing the POSS content. These phenolic/POSS nanocomposites also displayed significantly enhanced surface hydrophobicity as well as reduction in surface free energy which is consistent with our group’s previous findings [40].
4.10. Epoxy/POSS nanocomposites

Monofunctional POSS–epoxies have been incorporated into the backbones of epoxy resins to improve their thermal properties [210–217]. Multifunctional epoxy-substituted POSS monomers have been incorporated into an epoxy resin network composed of di- and tetra-functionalized epoxies. The presence of POSS units can increase the glass transition temperature of epoxy resin because the nanoscopic sizes and masses of the POSS cages enhance their ability to hinder the segmental motion of molecular chains and network junctions [218–239].

4.10.1. Multifunctional epoxy–POSS nanocomposites

Laine et al. prepared an epoxy–POSS macromer through the reaction of Q8M8H with 4 or 8 equiv of allyl glycidyl ether using Karstedt's catalyst [Pt(dvs)] (Fig. 33) [220]. The epoxy nanocomposites were prepared by reacting OG-POSS with 4,4′-diaminodiphenylmethane (DDM) at various compositional ratios.

DMA results and model reaction studies suggested that the maximum cross-linking density would be obtained at an NH2-to-epoxy ratio (N) of 0.5, with the mechanical properties maximized at a value of N of 1.0 [219]. Mather and coworkers [220] reacted OG-POSS with 4,4′-diaminodiphenyl sulfone (DDS) to study the relationship between the thermal and rheological properties and the nanoscopic deformation property and, thereby, determine the toughening mechanism. DMA analysis showed that increasing the DDS concentration increased the storage modulus in both the glassy and rubbery states due to the increased crosslink density. The main toughening mechanism in the epoxy/POSS was void formation at nanoscale, possibly templated by limited POSS aggregation. He and coworkers [225] also reported the thermomechanical properties of OG–POSS modified epoxy resins. Lee et al. [226] reported the epoxy resin reacting with OG-POSS and DDM to form epoxy/POSS nanocomposites. DSC and DMA analyses showed that the $T_g$ remained almost unchanged at POSS concentration (<30 wt%), whereas the nanocomposites containing POSS at greater than 40 wt% displayed values of $T_g$ lower than that of the control epoxy. Xiao et al. [230] studied epoxy resin prepared from OG-POSS cured with 4,4-methylenebis(cyclohexylamine) and...
FTIR spectroscopy revealed that the curing reactions of epoxy–POSS are more difficult than those of diglycidyl ether bisphenol A (DGEBA) resin because of steric hindrance. The resulting POSS composites did not exhibit glass transition behavior because of motion of the tethers between the POSS cores. Bian et al. [232] investigated the segmental dynamics in OG-POSS/poly(propylene oxide) nanocomposites. Pure poly(propylene oxide) exhibited two relaxation processes (normal and segmental modes). The OG-POSS undergoes a segmental process at lower frequency and a local relaxation at higher frequency. Teo et al. [233] prepared epoxy/POSS nanocomposites through copolymerization of OG-POSS, tetraglycidyl-4,4′-diaminodiphenyl methane (TGDDM), and hexahydrophthalic anhydride (HHPA). Kinetic studies revealed that the rate of curing of OG/HHPA was significantly higher than that for TGDDM/HHPA. By introducing 5 mol% OG-POSS into the networks, the hybrid underwent a large jump of 20 °C in its $T_g$ and a slight improvement in $T_g$ and storage modulus, compared with that of TGDDM/HHPA. Rico et al. [234] reported epoxy/OG-POSS nanocomposites in which OG-POSS was used to partially replace the DGEBA resin while the curing agent was the aromatic diamine, 4,4-(1,3-phenylenediisopropylidene) bisaniline. They used three different methods, the differential of Kissinger, the integral of Flynn–Wall–Ozawa, and the phenomenological model of Kamal to obtain the kinetic parameters of the curing reaction. The presence of POSS accelerated the rate of opening of the glycidyl epoxy rings of DGEBA. The behavior of the mixture during the curing process could be explained in terms of an autocatalytic model, corrected for the contribution of the diffusion of the molecules during the course of the reaction. Our group has also reported a new nanomaterial based on OG-POSS and meta-phenylenediamine (mPDA) [240]. The activation energy in curing the OG-POSS/mPDA system was higher than that of the DGEBA/mPDA system, as determined using both the Kissinger and Flynn–Wall–Ozawa methods. In an isothermal kinetic study based on an autocatalytic system, the activation energy for the curing of OG-POSS/mPDA was also higher than that of the DGEBA/mPDA system [240]. The $T_g$ of the cured OG-POSS/mPDA product was significantly higher than that of the DGEBA/mPDA material because the POSS cages effectively hindered the motion.
of the network junctions. The cured OG-POSS/mPDA product possessed inherently higher thermal stability than that of the cured DGEBA/mPDA product, as evidenced by the higher maximum decomposition temperature and the higher char yield of the former system. The dielectric constant of the OG-POSS/mPDA material \( (k = 2.31) \) was substantially lower than that of the DGEBA/mPDA system \( (k = 3.51) \) because of the presence of the nanoporous POSS cubes in the epoxy matrix [240]. Our group has also prepared epoxy/POSS nanocomposites from OG-POSS and the small-molecule curing agents of diethylphosphite (DEP) and dicyandiamide (DICY), the nanocomposites possessing high OG-POSS contents exhibited good thermal stability, lower flammability, and high storage modulus [239]. We observed a disordered POSS aggregation structure in the DGEBA/OG-POSS nanocomposites, with an average particle size of 30–50 nm through photopolymerization; all of these nanocomposites exhibited enhanced storage modulus in the rubbery state due to the nano-reinforcement effect of the POSS cages and the additional degree of crosslinking formed through reactions between the DGEBA and OG-POSS units [241].

Fig. 37. Molecular structure of MEH-PPV-POSS and PFO-POSS.

4.10.2. Multifunctional NH₂-POSS and OH-POSS nanocomposites

Zheng and coworkers [244] reported epoxy/POSS nanocomposites based on DGEBA and DDM in the presence of two POSS monomers containing aminophenyl and nitrophenyl groups. The morphologies of the resulted
hybrids were dependent on the type of functional group in the POSS monomer. The OAP-POSS containing epoxy/POSS nanocomposites exhibited homogeneous morphologies. In contrast, phase separation induced by polymerization occurred in the hybrids containing octakis(nitrophenyl)-POSS, with spherical particles of the POSS-rich phase (average diameter: 0.5 mm) dispersed within the continuous epoxy matrix. They also prepared octamaleimidophenyl-POSS via the imidization reaction between octamaleimidophenyl-POSS and maleic anhydride [245]. Epoxy/POSS nanocomposites were obtained after in situ polymerization of DGEBA, DDM, and octamaleimidophenyl-POSS. The \( T_g \) of the epoxy/POSS nanocomposites increased with the increase of POSS content. Cho et al. [246] also reported a similar nanocomposite structure. Zhang and coworkers [247–249] prepared epoxy/POSS derivatives from DGEBA and OAM-POSS, the incorporation of POSS into the epoxy resin improved the thermal stabilities of the epoxy significantly. The average activation energies of thermodegradation of the epoxy/POSS nanocomposites were calculated using the integral method by Flynn–Wall–Ozawa \( (E = 105.01 \text{ kJ/mol}) \) and the Coats-Redfern method \( (E = 113.07 \text{ kJ/mol}) \) [247].

The curing of the epoxy/OAM-POSS hybrid resin system using DDS as a curing agent, the reactivity of the epoxy/POSS system was slightly lower than that of the pure epoxy resin based on the Kissinger and Flynn–Wall–Ozawa methods [249]. Pellice et al. [250] reported epoxy/POSS nanocomposites through the reactions of OH-POSS with DGEBA in the presence of benzylidimethylamine. The elastic modulus and the yield stress both increased with the increase of POSS contents as a result of the increase in cohesive energy density caused by hydrogen bonding of the hydroxyl groups.

### 4.10.3. Monofunctional epoxy–POSS and NH\(_2\)-POSS nanocomposites

Lee et al. [210] reacted DGEBA epoxy resin with monofunctional-epoxy–POSS and subsequently cured the system to obtain transparent nanoreinforced polymer
networks. The $T_g$ increased and broadened upon increasing the content of monofunctional epoxy–POSS. The increase in $T_g$ occurred without increasing the degree of crosslinking within the network by DMA analyses. This phenomenon might have been due to the nanoscopic size of these POSS cages and their ability to hinder the motion of the molecular chains and network junctions [210,211]. Such epoxy/POSS nanocomposites could be used for electronic packing applications [217]. The flexural and thermal properties improved upon the addition of 1 or 2 vol.% of the mono-functional epoxy–POSS. Li et al. [212] also incorporated the monofunctional–epoxy–POSS into epoxy network and obtained good dispersion even at POSS content as high as 25 wt%. When blending epoxy with the prepolymer of the ladderlike polyphenylsilsesquioxane (PPSQ), the resulting epoxy/PPSQ blends displayed good miscibility only at low PPSQ contents (<10 wt%). Phase separation was clearly observed when the PPSQ content was 15 wt%. Abad et al. [213] reported the epoxy/POSS nanocomposites prepared via incorporation of monofunctional–epoxy–POSS into an epoxy network following a two-stage process. In the first stage, the POSS–epoxy was reacted with an aromatic diamine and the precursor was then reacted with a stoichiometric amount of DGEBA in the second step to generate the organic/inorganic hybrid materials. The higher $T_g$ observed for the POSS-modified epoxy might have been associated with the hindering of the polymer chain motions caused by covalent bonding to the POSS clusters. Phase separation may occur if the POSS bearing organic groups are incompatible with the epoxy network. Barral et al. [214] performed TGA analyses to determine the thermodegradation behavior of DGEBA/DDM and monofunctional epoxy–POSS. The activation energies of decomposition of this system determined using the Flynn–Wall–Ozawa ($E = 88.9$ kJ/mol) and Coats-Redfern ($E = 85.2$ kJ/mol) methods were comparable. Williams and coworkers [213] investigated the influence of prereaction on the aggregation-state crystallinity of the POSS domains using monofunctional epoxy–POSS containing either seven isobutyl or phenyl groups. When the monofunctional POSS is used as a modifier of the polymer networks, phase separation may occur either in the initial mixing stage or in the course of polymerization. The nature of the inert organic group and the pre-reaction of the epoxy functionality have significant effects on the morphologies generated, the crystallinity of the segregated POSS domains, and the amount of residual POSS in the polymer network. Liu et al. [218] used a two-step method to prepare an epoxy/POSS composite containing 50 wt% POSS resulting in good homogeneity. The AM-POSS was first reacted with DGEBA to form an epoxy POSS precursor and then the system was cured using a curing agent (e.g., DICY or DEP). The use of small-molecule curing agents efficiently inhibited macrophase separation and enhanced the thermal properties of the hybrid materials.

### 4.10.4. Other epoxy/POSS systems

Zheng et al. [251] synthesized hepta(3,3,3-trifluoropropyl)-POSS end-capped PEO through hydrosilylation of allyl-terminated PEO with hepta(3,3,3-trifluoropropyl)hydrosilsesquioxane and then incorporated it into epoxy resin to form epoxy/POSS nanocomposites. Contact angle measurements of the epoxy/POSS nanocomposites revealed significant enhancement in surface hydrophobicity as well as reduced surface free energy. Both AFM and XPS provided evidence for high levels of POSS moieties on the surface of the epoxy resin. Zheng and coworkers [252] reported similar results after changing the PEO to PCL. The epoxy resin featured a variety of nanostructures depending on the concentration of the POSS end-capped PCL. The formation of epoxy/PCL-POSS nanostructure was interpreted in terms of the component miscibility and the mechanism of self-assembly [144].

Lee et al. [253] studied the influence of incompletely condensed phenyl-trisilanol POSS on the thermomechanical properties of epoxy/POSS nanocomposites. The $T_g$ of the resulting epoxy/POSS nanocomposites increased after incorporation of even small amounts of POSS-triol, consistent with the observed increase in the rubbery plateau modulus resulting from the increased crosslinking density. Zheng and coworkers [254] also incorporated this incompletely condensed POSS derivative into epoxy networks, with POSS contents of up to 30 wt%. The phase-separated component exhibited higher $T_g$ than did the nanocomposite, while the nanocomposite displayed higher storage modulus of the glassy state based on DMA analyses.

![Fig. 40. Synthesis of POSS with eight bent-core liquid crystal](image-url)
Fig. 41. Synthetic routes of POSS-containing photosensitive copolymers.

4.11. Polybenzoxazine/POSS nanocomposites

1,3-Benzoxazines are intriguing heterocyclic compounds that have attracted considerable attention for their use as cyclic monomers. These benzoxazine monomers are readily synthesized through the reaction of primary amines with phenol and formaldehyde. These monomers can be polymerized through ring-opening polymerization in the absence of a catalyst, without releasing any byproducts [255,256]. Wang et al. [257] reported that the strong intramolecular hydrogen bonds within polybenzoxazines (PBZs) make them a new class of non-fluorine/non-silicon low-surface-free-energy polymeric materials, which have wide-ranging applications as superhydrophobic surfaces [258,259], in lithographic patterning [260], and as mold-release materials in nanoimprint technology [261]. To improve the performance of PBZs, polymerizable alkynyl and allyl side groups have been introduced into the benzoxazine monomers. Another approach to improve the stability of PBZs is by blending with other polymers [262], such as PU and epoxy resin, or with inorganic silica-based materials, such as clay [263] and POSS [264–269]. Our group has synthesized a novel benzoxazine containing POSS monomer (BZ-POSS) through two routes (Fig. 35): (i) hydrosilylation of a vinyl-terminated benzoxazine with a hydrosilane-functionalized POSS derivative (H-POSS) and (ii) the reaction of a primary amine-containing POSS (AM-POSS) with phenol and formaldehyde [266]. The BZ-POSS monomer was then copolymerized with other benzoxazine monomers through ring-opening polymerization under conditions similar to those used to polymerize pure benzoxazines. The thermal properties of these POSS-containing organic/inorganic PBZ nanocomposites were improved relative to those of the pure PBZ. Our group has also blended a vinyl-terminated benzoxazine (VBa) with H-POSS through ring-opening polymerization [265]. For comparison, we also treated VBa with POSS derivative lacking the hydrosilane group (OiBu-POSS). The glass transition temperature of the PVBa-POSS copolymer increased from 307 to 333 °C. The degradation temperature under N₂ also increased and the char yield was greater than 40 wt% at 600 °C, thus, modifying PBZ through the incorporation of POSS improved the thermal stabilities of these composite materials. We further prepared PBZ/POSS nanocomposites using a reactive multifunctional benzoxazine POSS (OBZ-POSS) and benzoxazine monomers at various compositional ratios [266]. We synthesized the OBZ-POSS curing agent containing eight organic benzoxazine ethers through hydrosilylation of VB-a with Ψ₈M₈H using a Pt complex catalyst. Incorporation of the silsesquioxane core into the PBZ matrix significantly hindered the mobility of the polymer chains and enhanced the thermal stability of these hybrid materials. We also prepared poly(VB-a)/POSS hybrids through hydrosilylation of VB-a hydrosilylation with POSS, followed by thermal curing of the benzoxazine monomer to form poly(VB-a)/POSS hybrid nanocomposites. FTIR spectra indicated that not all of the Si–H groups had reacted with VB-a, presumably due to the steric bulk of the POSS cages. The addition of POSS to the poly(VB-a) network greatly increased the crosslinking density and improved the thermal properties [266].

Yu and coworkers [267] reported the reaction between OAP-POSS with 2,2(1,3-phenylene)-bis(4,5-dihydrooxazoles) (PBO) at various temperatures. They used OAP-POSS to modify benzoxazine in the presence of PBO. When only a small amount of OAP-POSS was incorporated into the system, both T₉ and Tₐ of the resulting PBZ/POSS nanocomposites were substantially enhanced relative to those of the pure PBZ and PBZ-PBO resins, while the storage modulus was still maintained at higher temperatures. They prepared a multi-benzoxazinyl functionalized POSS derivative (OBZ-POSS) from OAP-POSS, p-cresol, and para-formaldehyde; BZ monomer and OBZ-POSS were copolymerized through ring-opening copolymerization [267]. DMA and TGA analyses showed that the thermal stability, cross-linking densities, and flame retardance of the PBZ/POSS nanocomposites all increased with the increase of OBZ-POSS contents. Yu and coworkers [268]...
also reported PBZ formed from the incomplete functionalized trisilanol-POSS, the thermal stability of the composite was greatly enhanced after the incorporation of the POSS units.

Zheng and coworker [269] prepared PBZ/POSS nanocomposites based on OG-POSS in which the crosslinking reactions divided into two steps: (1) ring-opening polymerization of benzoxazine and (2) reaction between the in situ formed phenolic hydroxyls of PBZ and the epoxide groups of OG-POSS. DSC and DMA analyses showed that the PBZ/POSS nanocomposites exhibited higher \( T_g \) than that of the pure PBZ. In the glassy state, the storage modulus increased when the nanocomposites contained less than 30 wt% of POSS. We also combined the advantageous properties of allyl-functionalized benzoxazine and POSS nanocomposites to improve both the thermal and mechanical properties of the resulting PBZ matrix [270]. We synthesized a multifunctional POSS bearing eight vinyl-terminated benzoxazine groups (VBa-POSS) through the reaction of OP-POSS with formaldehyde and allyl amine (Fig. 36) [270] and then copolymerized it with VBa benzoxazine monomers through ring opening polymerization. Since these PBZ/POSS hybrid materials incorporated large numbers of POSS units into their PBZs, they exhibited notably improved thermal and mechanical properties. We observed a gradual increase in the decomposition temperature of the PBZ/POSS nanocomposites upon increasing the VBa-POSS content. The char yield, another indicator of thermal stability, also increased upon increasing the POSS content in these hybrid materials. We also prepared a new class of polybenzoxazine–POSS network nanocomposites by reacting the multifunctional benzoxazine POSS (OBZ-POSS), which was synthesized from octa-azido functionalized POSS (OVBN3-POSS) with 3,4-dihydro-3-(prop-2-ynyl)-2H-benzoxazine (P-pa) via a click reaction [271]. Incorporation of the silsesquioxane core into the PBZ matrix significantly hindered the mobility of the polymer chains and thus enhanced the thermal stability of these hybrid materials.

5. POSS-containing functional materials

5.1. Polymer light emitting diodes (PLEDs) incorporating POSS hybrid polymers

Heeger and coworkers [272,273] reported the incorporation of POSS moieties into conjugated polymers by synthesizing semiconducting polymers, POSS-anchored poly(2-methoxy-5-(ethoxyloxy)-1,4-phenylenevinylene) (MEH-PPV-POSS) and POSS-anchored poly(9,9-dihexylfluorenyl-2,7-diyl) (PFO-POSS) (Fig. 37). Relative to the corresponding parent polymer, these POSS-anchored semiconducting polymers exhibited higher brightnesses and external quantum efficiency. It has been suggested that the presence of POSS reduces the formation of aggregates and/or excimers or lowers the concentration of conjugated defects. Shim and coworkers [274–277] prepared POSS-substituted polyfluorene polymers and found that the incorporation of POSS units inhibited interchain interactions and fluorenone formation, thereby leading to a reduction in undesired emission (>500 nm) of the poly(dialkylfluorene)s and improved thermal stability.
of the PFOPOSS systems. Devices incorporating PFOPOSS hybrids as emitting layers have exhibited very stable blue light emissions and high performance [277].

Hsu and coworkers [278] and Wei and coworkers [279,280] reported asymmetric conjugated polymers featuring POSS units attached to their side chains. An electroluminescent (EL) device prepared from MEH-PPV emitted a strong peak at 590 nm and a vibronic signal in the range 610–620 nm [278]. The introduction of bulky siloxane units into the PPV side chains presumably increased the interchain distance, thereby retarding interchain interactions and reducing the degree of exciton migration to defect sites.

A star-like polyfluorene derivative, PFO-SQ, has been synthesized through the Ni(0)-catalyzed reaction of octa(2-(4-bromophenyl)ethyl)silsesquioxane (OBPE-SQ) and polydioctylfluoroene (PFO) [281]. The incorporation of the silsesquioxane core into the polyfluorene significantly reduced the degree of aggregation and enhanced the thermal stability. The incorporation of inorganic silsesquioxane cores into polyfluorenes is a new method for preparing organic light-emitting diodes with improved thermal and optoelectronic characteristics [281]. Our group reported a POSS-based blue-light electroluminescent NP, octakis[N-(9-ethyl-9H-carbazol-3-yl)undecanamide-11-dimethylsiloxy]silsesquioxane (POSS-C11-Cz), possessing eight carbazole chromophore arms, that was synthesized through hydrosilylation of the terminal olefin with octakis(dimethylsiloxy)silsesquioxane (Fig. 38) [282]. The optical and photoluminescence (PL) spectra of POSS-C11-Cz in solution and in the solid state indicated reduced levels of aggregation and excimer formation because interchain interactions were prohibited in the presence of the bulky POSS cores. Moreover, PL spectra of the POSS-C11-Cz (3 wt%)/polyfluorene (97 wt%) blend revealed that its color was stable after heating at 200 °C for 5 h; in contrast, the pure polyfluorene exhibited a significant green emission at 530 nm after such treatment.

5.2. Liquid crystal polymers (LCPs) incorporating POSS hybrid polymers

With the goal of developing diverse building blocks for nanocomposite materials, Laine and coworkers [283] synthesized liquid crystalline materials by appending mesogenic groups to cubic silsesquioxane cores via hydrosilylation of allyloxy-functionalized mesogens with Q₈M₈H. Fig. 39 indicates that hydrosilylation led to each cube to possess an average of five appended LC groups. Despite the structural irregularity, three of the four penta-LC-cube derivatives exhibited LC transitions, with a tendency to form the SmA phase. One interesting observation was the redistribution of the diffuse liquid-like scattered intensity at 11–12 Å in the smectic phase upon alignment. These results provide the basis for future work on producing LC cubes as potential precursors to LC-ordered organic/inorganic nanocomposites. Although, the LC transition temperatures were reduced somewhat, they remained above those considered useful for biologically important applications [283]. Chujo and coworkers [284] reported the preparation of a POSS macromonomer through radical copolymerization and LC hybrid copolymers incorporating various proportions of the synthesized LC monomer; the thermal stability of the hybrid polymers increased upon increasing the ratio of POSS moieties. Zhou and coworkers [285] prepared bent-core liquid crystals with different numbers of bent-core mesogens end-capped onto POSS cores through hydrosilylation (Fig. 40). A two-bilayer SmCAPA phase was observed when eight bent-core mesogens were end-attached to POSS. Monolayer SmCPA phases were obtained upon increasing the content or the size of the siloxane core.

5.3. Lithographic applications of POSS-containing photoresists

Several POSS-based photoresists have been reported including positive-tone systems. Wu and coworkers [286,287] reported that the incorporation of POSS units in methacrylate-based chemically amplified photoresists influenced their reactive ion etching (RIE) behavior. Whereas polymers incorporating low POSS concentrations exhibited little improvements in their RIE resistances, the presence of 20.5 wt% of POSS monomer in a methacrylate-based resist significantly improved the RIE resistance in O₂ plasma. High-resolution TEM revealed that the improved RIE resistance was due to the formation of rectangular
crystallite-constituting networks of the silica cages uniformly distributed within the polymer matrix [286, 287]. Gonsalves and coworkers [288, 289] characterized a series of POSS-containing positive-tone photoresists for use in both extreme ultraviolet lithography (EUVL) and electron beam lithography. These photoresist systems exhibited the ideal combination of enhanced etch resistance and enhanced sensitivity required to satisfy both low- and high-voltage patterning applications. The photoresist sensitivity was enhanced after the direct incorporation of a photoacid-
Fig. 45. TEM images of (a) pure PCL-b-P4VP diblock copolymer, stained by I₂ (b) pyridine/OH = 4/1, (c) pyridine/OH = 2/1, and (d) pyridine/OH = 4/3 without staining. P4VP domain appears as dark region and the PCL domain as bright region in the micrographs.

5.4. Low-k applications of POSS-containing materials

To decrease the dielectric constants of polymers, several research groups [297–301] have explored the possibility of incorporating various nanoforms into polymer matrices to take advantage of the low dielectric constant of air \((k = 1)\). There are two typical routes employed for preparing materials with low dielectric constants: (i) nanopore formation through decomposition (e.g., thermal decomposition, photodegradation with UV irradiation, or solvent etching) of a dispersed phase within a material matrix and (ii) incorporation of a low-\(k\) moieties (e.g., fluorinated...
units, supercritical fluids, or low-k particles) within a material matrix. Recently, several low dielectric constant materials have been prepared through dispersion of POSS-containing molecules into polymer matrices. Our group has prepared some POSS-containing low-k materials using both of the methods mentioned above, taking advantage of hydrogen bonding interactions between the POSS moieties and the OH groups of the matrix to achieve homogenous nanocomposites [128,301], in which the POSS moieties not only served as low-k materials but also contributed to the improved thermal and mechanical properties.

For the molecular-level design of low-k materials, Seckin et al. [194] studied star PIs incorporating OAM-POSS through in situ curing of PAA macromolecules. The presence of OAM-POSS, which imparted restricted rotation by multiple point attachment to the PI backbone, introduces free volume into the films, thereby lowering their dielectric constants. The process for synthesizing the POSS-PI star nanocomposites involved two steps: forming the porous-type POSS and then reacting it with the PI precursor. The POSS-containing PIs exhibited a number of desirable properties including low-water absorption and high thermal stability. Thus, insertion of POSS units into a PI backbone can reduce a material’s dielectric constant while also improving its mechanical and thermal properties. Xu and coworker [302] prepared four novel organic/inorganic network hybrids via hydrosilylation of dienes with octahydridosilsesquioxanes (H₈-POSS). All of their POSS hybrid films exhibited high thermal stability and low dielectric constants. Interestingly, these properties were tunable by adjusting the length and structure of the linking chain between the POSS cages. Liu et al. [303] prepared ultralow k (k = 1.47) POSS nanocomposites from two liquid monomers using a spinning-on process; their low dielectric constants were attributed to the formation of lamellar POSS structures.

5.5. Self-assembly behavior of POSS-containing block copolymer materials

Self-organizing materials allow the development of “bottom-up” method, a relatively simple and low-cost process for fabrication of large-area periodic nanostructures from diblock copolymers or other materials (e.g., low molecular weight compounds) by controlling their self-assembly [304–306]. Pyun and Matyjaszewski and coworkers [307,308] used ATRP to synthesize an MA-POSS homopolymer and block copolymers from a cyclopentyl-substituted POSS monomer. They employed ATRP to prepare the block copolymer from MA-POSS and n-butyl acrylate, with 4-methylphenyl 2-bromoisobutyrate as the initiator and CuCl/PMDETA as the catalyst (Fig. 43) [307,308]. TEM characterization of the triblock copolymer thin film P(MA-POSS)₁₀-b-PBA₂₀₁-b-P(MA-POSS)₁₀ revealed the formation of PBA cylinders in a P(MA-POSS) matrix.

Liu and coworker [309] also prepared a well-defined diblock copolymer based on POSS through ATRP with POSS/MMMA-Cl as a macro-initiator; their AB diblock copolymer based on POSS formed tadpole-shaped structures, with the inorganic head of the POSS units and an organic tail of polymer. Lee and coworkers [310–312] used hydrosilylation to prepare an organic/inorganic triblock copolymer of SBS containing grafted POSS. Their POSS derivative was designed to contain a single silane functional group for grafting onto 1,2-butadiene units in the PB soft block. Since these POSS moieties were dispersed on the molecular scale, the SBS copolymer gradually lost its long-range ordering upon increasing the POSS content. SAXS analysis showed that the scattering of the cylindrical structure became diffuse with the lamellar structure and transformed into a perforated layer morphology. Zhu and coworkers [313] reported the self-assembly of a PEO-b-
PE-POSS triblock copolymer, in which the POSS molecules crystallized prior to crystallization of PE, forming a well-defined lamellar structure. Hirai and coworkers [314, 315] prepared two kinds of POSS-containing block copolymers, PMMA-\(b\)-PMAPPOSS and PS-\(b\)-PMAPPOSS, through anionic living polymerization. These two kinds of diblock copolymers formed various self-assembled structures including spherical, cylindrical, and lamellar morphologies (Fig. 44) [315]. When applied in lithography processes, these diblock copolymers possessed narrow polydispersity and resulted in well-defined morphologies [316]. Using a POSS-PEO macroinitiator for the ATRP of styrene, Zhang et al. [317] synthesized PS-\(b\)-PEO diblock copolymer featuring a POSS moiety at the junction of the diblock copolymer between the two blocks. Self-assembly of this block copolymer led to the formation of vesicles in aqueous solution. Cheng and coworkers [318] used silyl-hydrid functionalized 1,1-diphenylethylene derivative (DPE-SiH) as an intermediate for the anionic synthesis of in-chain-functionalized polymers, where the reactive Si–H bond of the POSS cage at the junction was used for the preparation of PS-\(b\)-PDMS diblock copolymers.

Our group has reported the variation of self-assembled morphologies of the immiscible PCL-\(b\)-P4VP diblock copolymer upon increasing the OP-POSS content through competitive hydrogen bonding interactions [319]. TEM images revealed highly long-range ordered morphologies such as cylinder or sphere structures at relatively low OP-POSS contents and shifted to short-range ordered or even disordered structures at higher OP-POSS contents (Fig. 45) [319]. Fig. 46 presents a plot of the morphological transformations occurred upon increasing the OP-POSS content [319]. A long-range ordered nanostructure existed in PCL-\(b\)-P4VP/OP-POSS at lower OP-POSS contents pyridine/OH = 4/1 (lamellae structure), pyridine/OH = 2/1 (cylinder structure), short-range order nanostructure existed at relatively higher OP-POSS contents (pyridine/OH = 4/3 to 1/1), and the disorder structure existed at the highest OP-POSS content (pyridine/OH = 1/2). We also reported a series of star block copolymers through nitroxide-mediated radical polymerization (NMRP) from POSS NPs through core-first polymerization [320]. We first incorporated \(N\)-alkoxymine groups onto the eight corners of a POSS cube through quanti-
tative hydrosilylation of 1-((allyloxy)-1-phenylethoxy)-2,2,6,6-tetramethylpiperidine (allyl-TEMPO) with Q8M8H using Karstedt’s agent as the catalyst. We then used the octakis(-N-alkoxyamines)-POSS (OT-POSS) as a platform to synthesize star (PS)8-POSS homopolymers and the diblock copolymers (PS-b-P4VP)8-POSS and (PS-b-PAS)8-POSS through NMRP. Subsequent selective hydrolysis of the acetyl protective groups of (PS-b-PAS)8-POSS led to the formation of (PS-b-PVPh)8-POSS, featuring strongly hydrogen bonding groups (Fig. 47) [320].

5.6. Nanoparticle with POSS-containing materials

5.6.1. POSS modified clay nanocomposites

Nanoclay-filled polymeric systems offer the prospect of great improving many of the physical properties of polymers. Montmorillonite (MMT), an aluminosilicate mineral featuring sodium counterions between its layers, is the most commonly used clay. The space between these clay layers is referred to as the clay gallery for these purposes. To make this inorganic clay compatible with organic polymers, the sodium counterions are usually ion-exchanged with an organic ammonium or phosphonium salt to convert the material into hydrophobic ammonium- or phosphonium-treated clays. Alkyl ammonium salts of low molecular weight are thermally unstable; therefore, their use greatly limits the processing of such materials, especially at elevated temperatures.

Our group first reported that ammonia-POSS could be used as a surfactant to modify the clay gallery. The major reason for choosing POSS molecules in this role is their thermal stability up to 300 °C, higher than the thermal degradation temperatures of most organic molecules. POSS derivatives containing amino functional groups can function as surfactants for the treatment of clay; enhanced thermal stability of the resulting nanocomposites can be
expected. When the POSS surfactant was inserted between the galleries of the clay, the d spacing increased from 1.26 nm for the pristine clay to 1.61 nm, indicating that the POSS surfactant was indeed intercalated into the galleries of the clay. The POSS surfactant-intercalated clay composite (POSS/clay; Fig. 48) exhibited only one diffraction peak, no peak was detected from the aggregation of POSS [321]. Cariniato et al. [322] also reported the intercalation of bifunctional protonated titanium-containing aminopropyl isobutyl POSS (Ti-NH$_3$-POSS) within the interlayer space of a synthetic sodium saponite. The embedding of Ti-NH$_3$-POSS into this clay led to significant stabilization of the resulting hybrids. Our group has compared the effects of different chain lengths of NH$_2$-POSS as intercalated agents for organically modified clays [323,324]. For the NH$_2$-POSS/clay and C$_{20}$-POSS/clay, the value of 2$\theta$ shifted from 6.92$^\circ$ (1.28 nm) to 5.51$^\circ$ (1.61 nm) and 2.33$^\circ$ (3.80 nm), respectively, after ion exchange, indicating that the basal spacing was expanded as the sodium cations in the interlayer galleries were replaced by the intercalated agents of NH$_2$-POSS and C$_{20}$-POSS [323]. The increase basal spacings indicate that the clay can be efficiently intercalated by NH$_2$-POSS and C$_{20}$-POSS. The d-spacing of the C$_{20}$-POSS-modified clay was substantially greater than that of the NH$_2$-POSS modified clay, nevertheless, the NH$_2$-POSS clay was relatively more stable than the C$_{20}$-POSS-modified clay because long alkyl chains are inherently thermally unstable.

Zheng and coworkers [325] prepared the octakis(ammonium chloride) salt of OAPS-POSS as an intercalating agent to modify MMT. X-ray diffraction data indicated that MMT was successfully intercalated by this ammonium salt of OAPS-POSS: the basal spacing of the MMT galleries was expanded from 1.3 to 1.7 nm. TEM imaging indicated a random dispersion of intercalated/exfoliated aggregates in the epoxy matrix. TGA analysis showed that the incorporation of POSS-MMT into epoxy networks improved thermal stability; the char residue increased with increasing the concentration of POSS-MMT. Fox et al. [326] reported a POSS-imidazolium surfactant for use as an organic modifier for MMT and observed that the self-assembled crystalline POSS domains were present in the clay interlayer. The d-spacing of the exchanged clay was ca. 3.6 nm, sufficiently high to accommodate the bilayer structure of the POSS and the POSS/clay exhibited higher thermal stability than that of typical ammonium-exchanged MMT. Wan et al. [327] also reported an NH$_2$-POSS modified MMT that exhibited a large interlayer distance and large specific surface area. Their POSS-MMT hybrid was used as a catalyst support to initiate the ring-opening polymerization of cyclic butylenes terephthalate oligomer. TEM and XRD revealed an exfoliated structure, with no diffraction peaks detected through XRD analysis. The tensile properties of the resultant PBT/POSS-MMT composites were highly improved relative to those of the pristine PBT due to the homogeneous dispersion of POSS-MMT in the PBT matrix.

5.6.2. POSS modified gold nanoparticles

Self-assembly of NPs with controlled organization of NPs into ordered or hierarchical structures offers potential applications in optoelectronics, sensing, imaging, and biomedical applications. Schmid et al. [328] used 3-mercaptopropylcyclopentyl-POSS (SH-POSS) to quantitatively exchange the PPh$_3$ ligands in (PPh$_3$)$_{12}$Au$_{55}$Cl$_6$ in an attempt to obtain POSS-Au NPs stabilized through Au–S bonds. However, they obtained amorphous structures, demonstrating the dramatic influence of this POSS ligand on the cluster properties. Naka and coworkers [329] and Rotello and coworkers [330–332] prepared POSS-Au hybrid
Fig. 51. TEM images of Au-POSS nanoparticles in a PnBMA homopolymer matrix (a) and PnBMA-r-PiBPPMA copolymer matrix (b). Reprinted with permission from Ref. [335]. Copyright 2009, Wiley-VCH, Germany.

NPs stabilized through electrostatic interaction with the HCl salts of OAPS-POSS or through hydrogen bonding with diaminopyridine-monofunctionalized octasilsesquioxane [330]. Such strong intermolecular interactions (i.e., electrostatic and hydrogen bonding interactions) suppressed the thin-film-forming characteristic of POSS during crystallization. Using this strategy, both the chemical and physical nature of the surface could be controlled through deposition of POSS-based surface modification agents. Rotello et al. [332] also used carboxylic acid-functionalized, mixed monolayer-protected Au clusters in conjunction with quaternary trimethylammonium-functionalized POSS units to produce well-ordered aggregates. TEM and SAXS analyses showed an increase in the average interparticle spacing upon self-assembly with POSS. This increase in spacing influenced the surface plasmon resonance band of the larger 6.8 nm Au NPs, as determined using UV–vis spectroscopy. Naka and coworkers [329] prepared microporous nanocomposites of Pd and Au NPs by taking advantage of the electrostatic attraction between oppositely charged Au NPs coated with carboxylate groups (Au-COO⁻) and spherical aggregates of Pd NPs (Pd-NH₃⁺), having a mean diameter of 20 nm and stabilized and cross-linked by OAPS-POSS (POSS-NH₃⁺) [329]. Amide bonds were formed between the reactive ion couples to generate more stable nanocomposites with improved chemical and physical properties. They exhibited excellent catalytic properties because of their large surface areas and the synergistic effects of the Pd and Au NPs. They also prepared a colloidal form of PdNPs@AuNPs by stirring the aggregates of Pd NPs protected by POSS-NH₃⁺ with the colloidal Au NPs at room temperature [333].

Our group has used SH-POSS as a protective group for the preparation of POSS-protected Au NPs (POSS-Au NPs) as shown in Fig. 49 [334]. The organic/inorganic hybrid SH-POSS NPs exhibited an interesting platelike morphology arising from steric hindrance between the isobutyl groups of SH-POSS. Fig. 50(a) shows an optical microscopy (OM) image of the Au-POSS aggregates, displaying red ferny-like structures on the order of a few micrometers. Fig. 50(b) displays a TEM image of the Au NPs dispersed within the ferny-like structure; these aggregates comprised individual Au NPs surrounded by SH-POSS units. The upper-right hand inset to Fig. 50(b) shows the selected-area electron diffraction (SAED) pattern of the Au NPs, revealing a face-centered cubic (FCC) structure corresponding to the (1 1 1), (2 0 0) and (2 2 0) Au crystalline facets, while many small particles have independent orientations. The TEM image of the POSS-functionalized Au NPs in Fig. 50(c) displays that the average diameter of the Au cores, calculated from Fig. 50(c), was ca. 5 nm. These Au-POSS NPs formed partial aggregated upon blending with poly(n-butyl methacrylate) (PnBMA) homopolymer, due to poor miscibility between Au-POSS and PnBMA polymer matrix [335]. The incorporation of POSS moieties into the PnBMA main chain to form a random copolymer matrix resulted in well-dispersed Au NPs because the POSS–POSS interactions enhanced the miscibility of the Au NPs in the
References


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