Developments of polyhedral oligomeric silsesquioxanes (POSS), POSS nanocomposites and their applications: A review

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This review presents a brief account of recent developments in synthesis and properties of organic-inorganic hybrids using polyhedral oligomeric silsesquioxanes (POSS) nanoparticle, and applications of POSS monomers and nanocomposites. Thermal, rheology and mechanical properties of polyimides, epoxy polymers, polymethymethacrylate, polyurethanes, and various other polymer nanocomposites are discussed.

Keywords: Nanocomposites, Polyhedral oligomeric silsesquioxanes, Thermal and mechanical properties

Introduction

A variety of physical property enhancements (processability, toughness, thermal and oxidative stability) are expected to result from incorporation of an inorganic component into an organic polymer matrix. Many organic-inorganic hybrid materials have shown dramatic improvement in macroscopic properties compared with their nonhybrid counterparts[1-6]. Hybrid organic-inorganic materials based on incorporation of polyoctahedral oligomeric silsesquioxanes (POSS) into polymeric matrices have received a considerable attention[7-13]. Silsesquioxanes (Fig. 1)[14], which consist of a rigid, crystalline silica-like core that is perfectly defined spatially (0.5-0.7 nm), have general formula $(RSiO_{1.5})_a(H_2O)_{0.5b}$, where R is a hydrogen atom or an organic group and a and b are integer numbers ($a = 1$, 2, 3, ...; $b = 0, 1, 2, 3, ...$), with $a + b = 2n$, where n is an integer ($n = 1, 2, 3, ...$) and $b = a + 2$. Of several structures of silsesquioxanes (random, ladder and cage), cage structures contain 8 silicon atoms placed at cube vertices. Cubic structural compounds (completely and incompletely condensed silsesquioxanes) are commonly illustrated as T_6, T_7, T_8, T_{10}, and T_{12}, based on the number of silicon atoms present in cubic structure (Fig. 2). In early 1900s, Kipping[15] found that polycondensation of siliconic acids invariably leads to

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extremely complex mixtures of silsesquioxanes. Later in 1946, POSS were isolated along with other volatile compounds through thermolysis of polymeric products obtained from methyltrichlorosilane and dimethylchlorosilane cohydrolysis[16]. A variety of POSS nanostructured chemicals contain one or more covalently bonded reactive functionalities that are suitable for polymerization, grafting, surface bonding, or other transformations[17-18]. Incorporation of nanosized POSS macromers into polymers has produced significant improvement in thermal and oxidative resistance as well as reduction in flammability of several POSS-based polymers; these systems then being suitable candidates in high-temperature and fire-resistant applications[19-21]. POSS compounds can be incorporated into polymers by blending, copolymerization or grafting[22-29]. POSS-polymer blends create interesting materials, but occurring of microphase separation may decrease possible advantages connected with nanoscale incorporation[30]. Organic polymers can be reinforced with POSS by attaching single or multiple polymerizable groups to POSS cage.

In catalysis chemistry, metallosilsesquioxanes are receiving considerable interest[31,32]. Incompletely condensed silsesquioxanes [cyclopentylsilanetriol $Cy_7Si_7O_9(OH)_3$] share structural similarities with β-cristobalite and β-tridymite and are thus quite realistic models for silanol sites on silica surfaces[33,34]. Incompletely-condensed silsesquioxane frameworks have attracted attention as models for silica[35,36], as ligands in
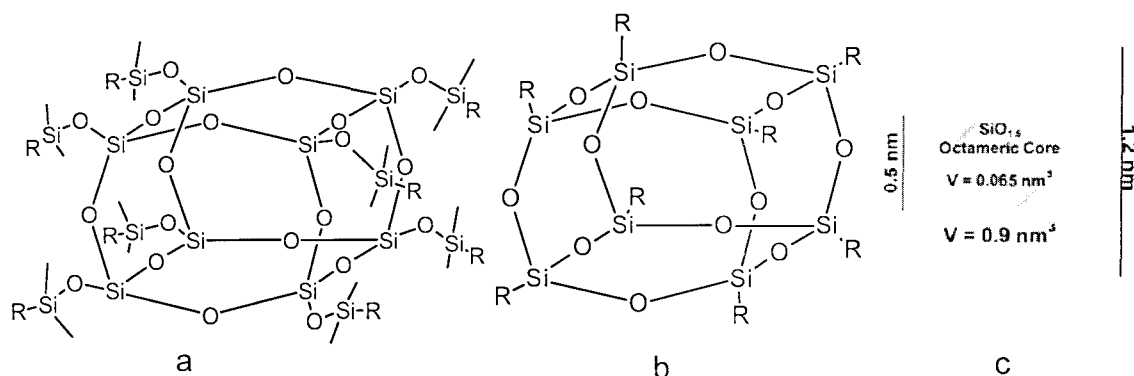
Fig. 1—Silsesquioxanes: (a) Q8 (Q = $SiO_{2/2}$), R =H, vinyl, epoxy, methacrylate, etc.; (b) R_8T_8 (T = R-$SiO_{3/2}$), R = alkyl, alkene, acetylene, acrylate; (c) Typical sizes/volumes[14]

homogeneous models for aluminosilicates[37,38] and silica supported catalysts[39,40], and as building blocks for network solids[41,42].

Methodologies adopted for Functionalization of POSS Monomer

New chemical reagents and nanocomposites (NCs) have been developed using POSS molecule. Polyhedral silsesquioxanes are prepared from monomers of $XSiY_3$ type, where X is a chemically stable substituent (CH_3, phenyl, or vinyl), and Y is a highly reactive substituent (Cl, OH, or OR). Thus, using $XSiY_3$-type, POSS can form linear, cyclic, or polycyclic siloxanes as

$$nXSiY_3 + 1.5nH_2O \longrightarrow (XSiO_{1.5})n + 3nHY \quad ...(1)$$

Octahydridosilsesquioxane[43-45] (T_8H), results from hydrolysis condensation of $HSiCl_3$ with very low yield of products [T_8H (15-20%) and $T_{10}H$ (5-10%) cubes]. Kudo et al[46] explored on synthesis of POSS and entire reaction scheme (Fig. 3). Reaction rate, degree of oligomerization, and yield of polyhedral compounds formed depend strongly on following factors[47]: i) Concentration of initial monomer in solution is an important variable; ii) Nature of solvent; iii) Identity of substituent X in initial monomer; iv) Nature of functional groups Y in monomer; v) Type of catalyst; vi) Reaction temperature; vii) Rate of water addition; and viii) Solubility of polyhedral oligomers formed. Using these conditions, octameric silicate anion systems were developed from hydrolysis and polycondensation of tetraalkoxysilane in presence of tetramethylammonium (TMA) ions [$N^+(CH_3)_4$] under appropriate conditions, which yield double four membered ring silicate anion ($Si_8O_{20}^{8-}$) selectively. Hasegawa et al[48,49]

extended concept of Hoebbel et al[50] and identified a high-yield route to obtain POSS cubes with hydride and vinyl functional groups by silylation of silicate anion ($Si_8O_{20}^8$) solution (Scheme 1).

Cubes with vinyl and Si-H groups permit selective attachment of numerous moieties to cubes through Pt-catalysed hydrosilylation (PCH).Octa (dimethylsilyloxy) silsesquioxane (Q_8M_8H) and octa (hydrido) silsesquioxane (T_8H) cubes can be modified into various octafunctionalized macromonomers by hydrosilylation reaction between terminal Si-H groups on POSS cube with an unsaturated carbon double bond in presence of a Pt catalyst (Scheme 2). A series of polyethylene glycol (PEG) substituted octa silsesquioxanes[51] prepared by PCH of unsaturated PEG with Q_8M_8H, T_8H and thermal effect of organic peripherals attached on vertices of POSS were studied. Another example of hydroxyl terminated POSS is reported[52] through PCH of Q_8M_8H with allyl alcohol. Controlling catalyst concentration and choosing appropriate solvent undergo 100% C-silylation rather than O-silylation of –OH group of allyl alcohol. Matisons et al[53] reported preparation of octaisocyanato substituted silsesquioxane by hydrosilylation of Q_8M_8H with m-isopropenyl-α-α'-dimethylbenzyl isocyanate in THF medium using Karstedt's catalyst, and proved that isocyanate functionalised POSS macromer was suitable nanocrosslinker for preparation of organic-inorganic hybrid polyurethane. A simple two-step synthetic methodology was developed for octaphenol-POSS through PCH of 4-acetoxystyrene with Q_8M_8H and subsequent hydrolysis of acetoxy units[54]. Ogunniyi et al[55] reported synthesis of etheric chlorine-terminated silsesquioxane using 2-chloroethyl vinylether
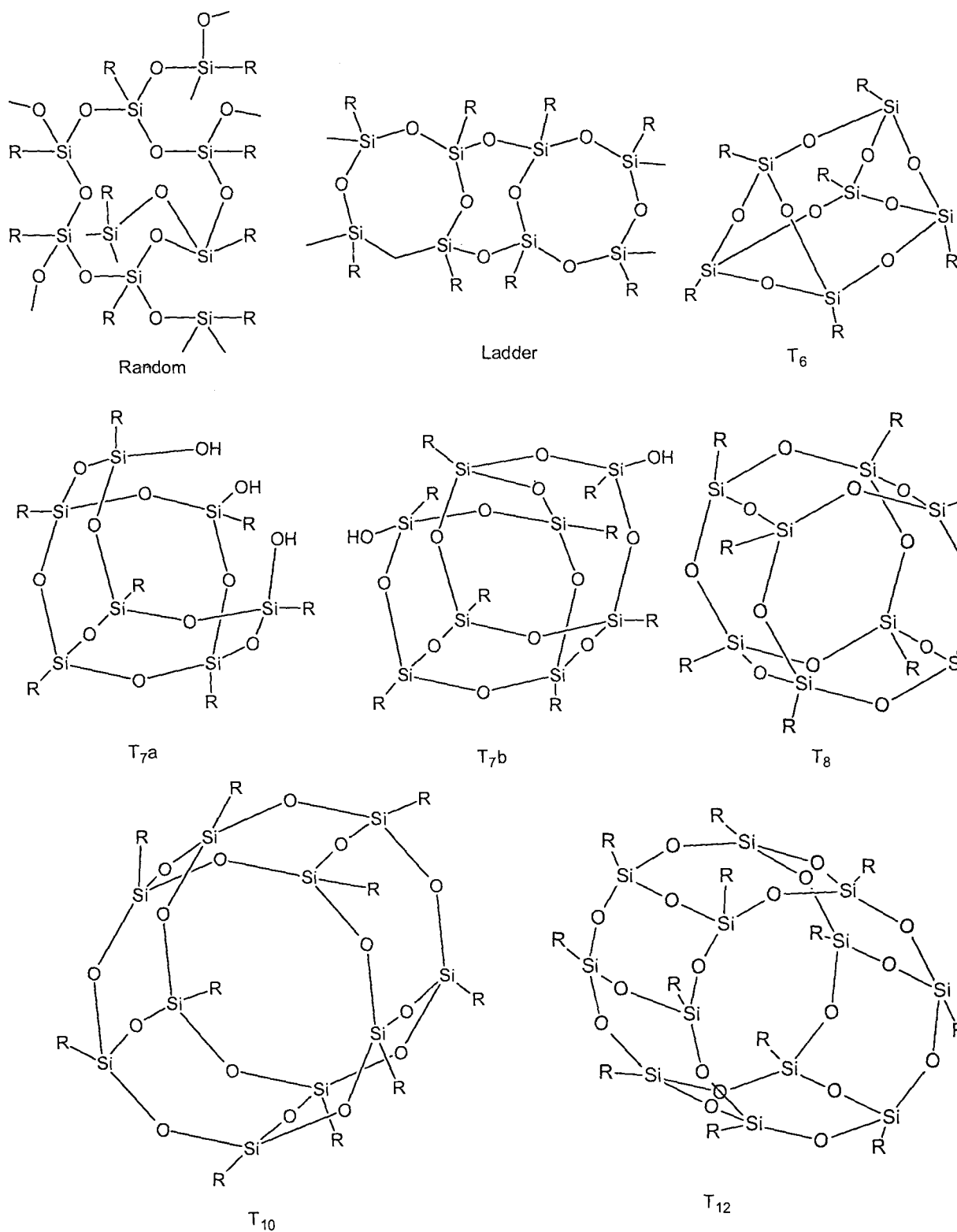
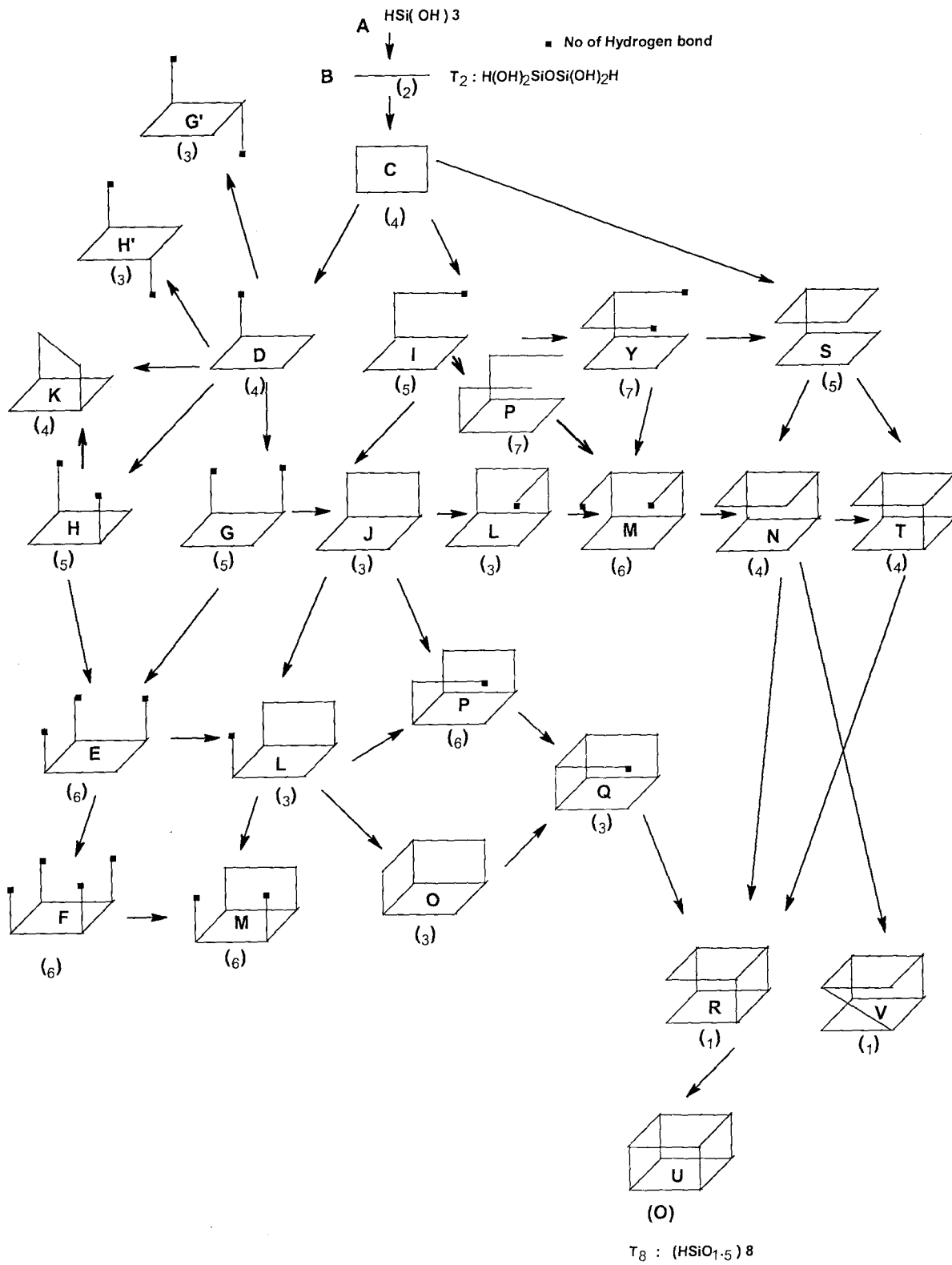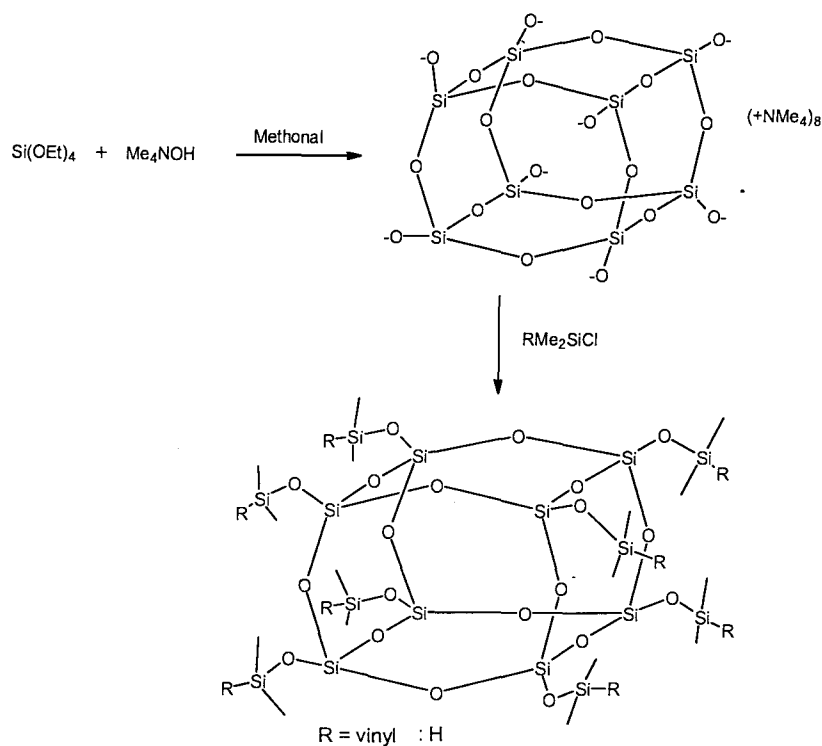Fig. 2—Chemical structures of different types of silsesquioxanes

Fig. 3—Schematic representation of all processes from silanol (A, HSi(OH)$_3$) to T$_8$(U)

Si(OEt)$_4$ +   Me$_4$NOH $\xrightarrow{\text{Methonal}}$ (+NMe$_4$)$_8$

RMe$_2$SiCl

R = vinyl : H

Scheme 1—Synthesis of vinyl and hydride functionalised silsesquioxanes

with T$_8$H through PCH. Various epoxy functionalized POSS [Octakis(dimethylsiloxypropyl glycidylether) silsesquioxane, Octa(ethylcyclohexylepoxide dimethylsiloxy)silsesquioxane and octakis(dimethylsiloxy hexafluoropropyl glycidyl)silsesquioxane] were successfully synthesized through PCH by reacting Q$_8$M$_8$H with allyl glycidyl ether (AGE), 4-vinyl-1,2-cyclohexene epoxide and allyl-1,1,2,3,3,3-hexafluoropropyl ether respectively[56,57].

Octakis(dimethylsiloxypropyl aminobenzoate) silsesquioxane have been successfully prepared by reacting Q$_8$M$_8$H with allyl-4-aminobenzoate through PCH reaction[58]. Stradiotto *et al*[59] reported synthesis of octacyanosilsesquioxane by reacting acetonitrile with Q$_8$M$_8$H in presence of toluene medium. Various other functional groups such as silanes and a-olefins substituted POSS through PCH reactions also reported[60]. If stoichiometry is correctly controlled, PCH also offers a good method for synthesis of mono-, di- and poly-substituted silsesquioxanes[61].

Brown *et al*[62] extensively studied synthesis of another type of POSS, octaphenyl silsesquioxane (OPS) and various other side products formation during hydrolysis

and polycondensation of phenyl trichlorosilane in acetone medium. Laine *et al*[63-65] successfully explored various reactive functional groups (amine, iodo- and bromo-) on phenyl ring of OPS (Scheme 3). Laine *et al*[63] successfully nitrated OPS using fuming nitric acid. Octa(aminophenyl)silsesquioxane (OAPS) was prepared in two steps by nitration of OPS in fuming nitric acid to form octa-(nitrophenyl)silsesquioxane (ONPS) followed by mild reduction of ONPS using formic acid and triethylamine in presence of Pd/C catalyst, resulting in quantitative conversion with equal quantities of *m*- and *p*- nitro substituted in each phenyl ring. One step ahead of nitration of OPS, poly(bromooctaphenyl silsesquioxane)s (Br*x*OPS) was synthesised via bromination with Br$_2$/Fe in dichloromethane[64]. Iodo-substituted OPS by iodination using iodinemonochloride (ICl) at -40°C gave highly crystalline, octaiodinated OPS, which shows 93% selectivity for *p*- substitution, in 30-40% overall yield[65]. Feher *et al*[66] established a direct synthetic strategy for amine functionalized POSS through hydrolytic condensation of aminopropyltriethoxysilane in MeOH and conc. HCl, but product obtained under these conditions is aminehydrochloride salt. Octa
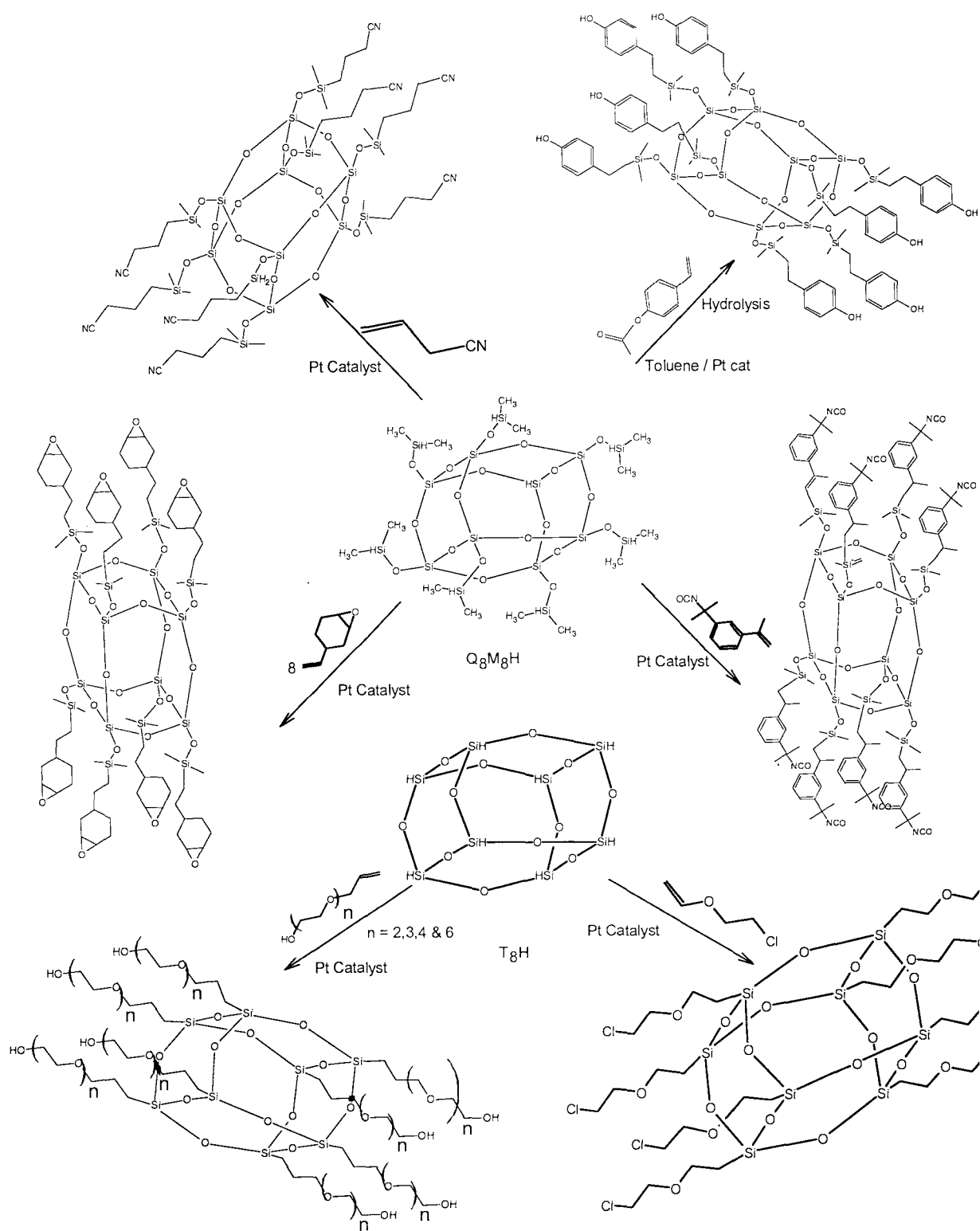
Scheme 2: — Synthesis and structures of octafunctional POSS macromonomers through hydrosilylation reaction
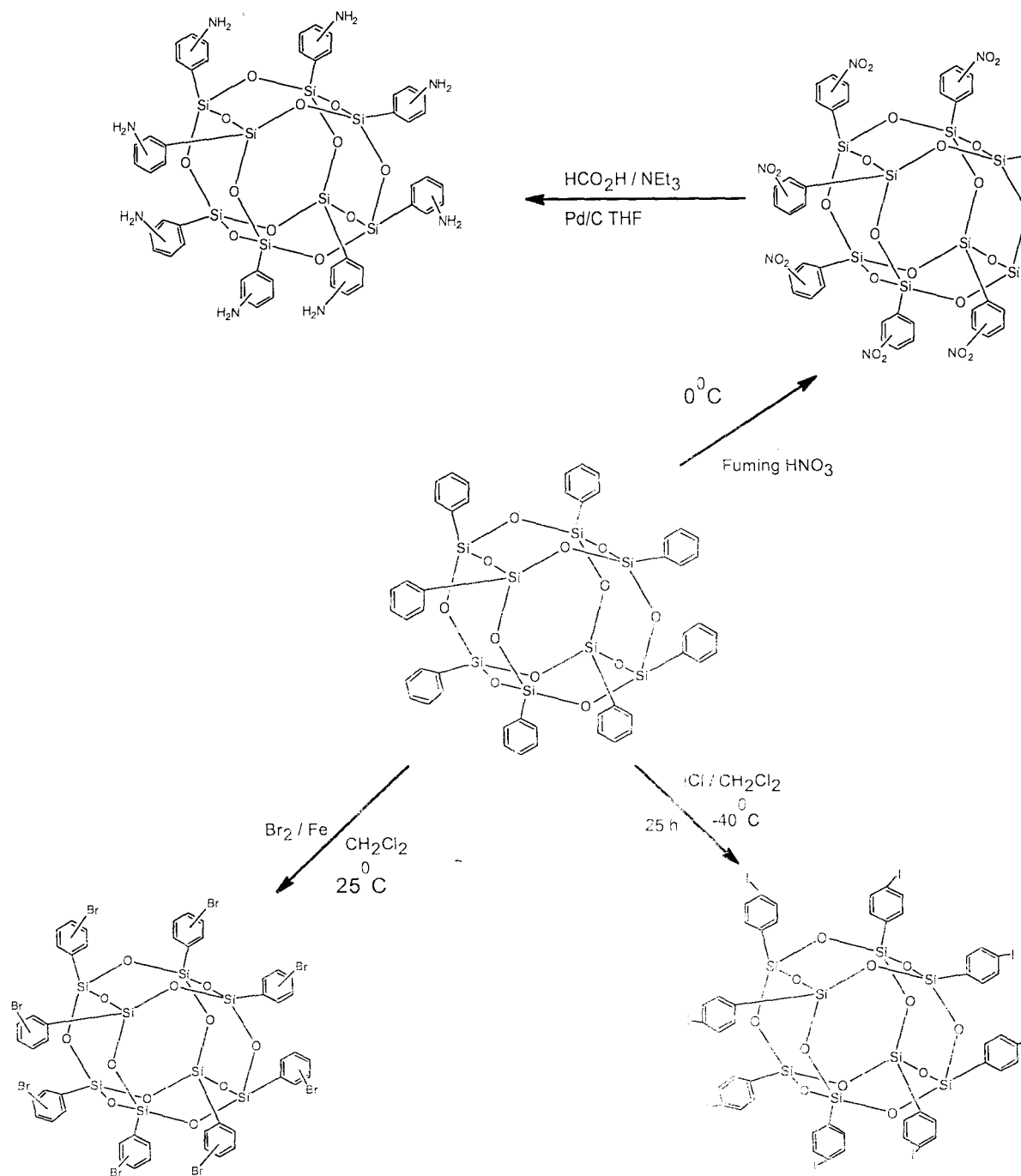
Scheme 3—Synthesis and structures of octafunctional POSS macromonomers containing nitro, amine, bromine and iodine groups

(aminehydrochloride) silsesquioxane is highly soluble in water and poorly soluble or insoluble in most of organic solvents and is somewhat hygroscopic. To make stable POSS amine, aliphatic amine of POSS using methacrylol chloride gave methacrylic acid groups that could be used as nanoconstruction sites for nanohybrids.

Silsesquioxane bearing various other functional groups[67-70] (esters, norborenyl, choloro- and chloroammoniumpropyl) have been developed. Concentration and type of initial monomer groups alter
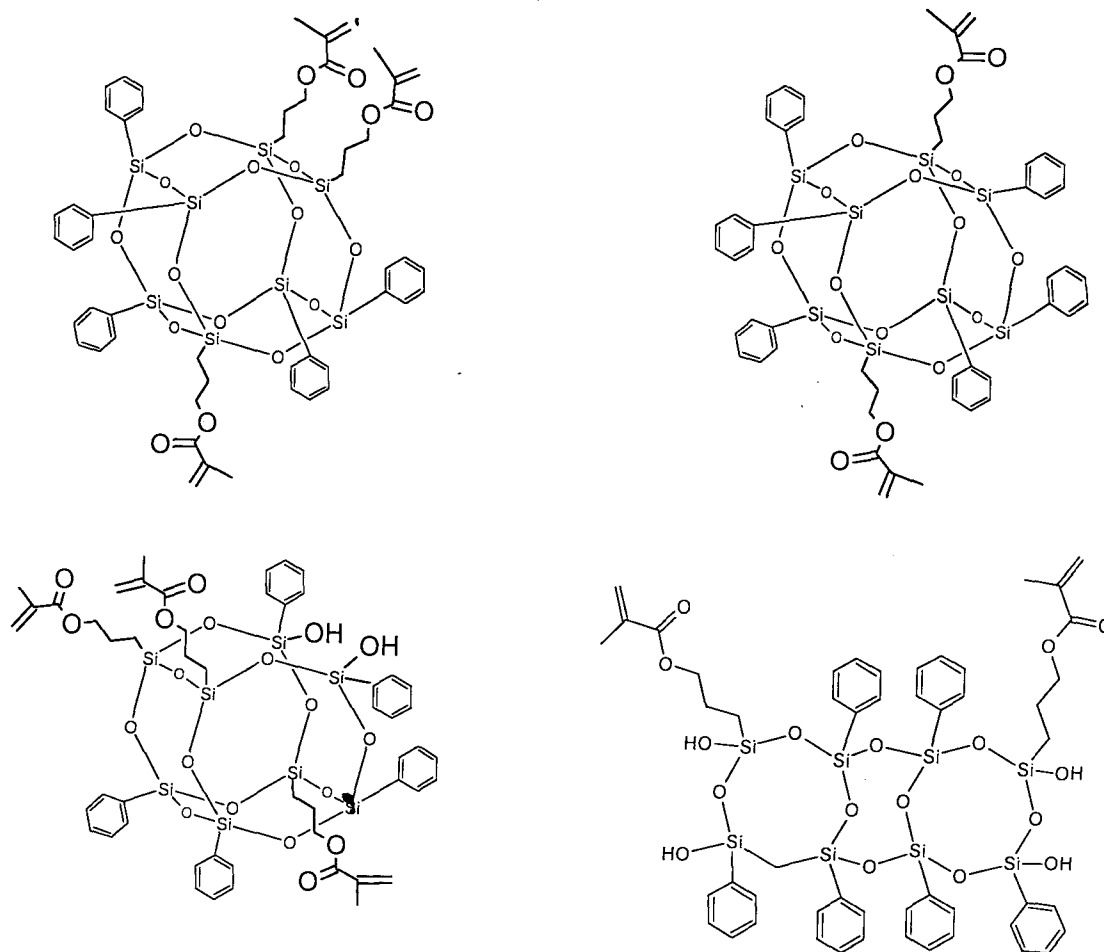
Scheme 4—Structures of mixed octafunctional POSS macromonomers

cubic structure by changing feed composition[71] of phenyltrimethoxysilane(PTMS) and 3- (methacryloxy) propyltrimethoxysilane(MPTMS). Four different molar ratios of monomers PTMS/MPTMS were co-condensed in presence of formic acid to yield four different types of POSS with various functional group ratios (Scheme 4).

Among POSS monomers, mono- functionalised silsesquioxane is a suitable monomer for synthesis of linear thermoplastic NCs. Corner capping reaction yields a closed cube with 7 corners of inert groups (cyclopentyl or cyclohexyl) and remaining one vertices possesses highly reactive functional groups (hydride, chloride, hydroxide, nitrile, amine, isocyanate, styryl, olefin, acrylic, epoxide, norbornyl, bisphenol, acid chloride, alcohol, and

acid) (Scheme 5)[72]. Lichtenhan et al[73] synthesized mono norborenyl substituted cyclopentyl siloxane through corner capping reaction of cylopentylsilanetriol $Cy_7Si_7O_9(OH)_3$ with trichloronorborenyl silane. Haddad et al[74] derived monostyryl functionalised POSS through corner caping reaction using trichlorosilane styrene in presence of THF medium. Aminopropyl substituted POSS was synthesised by reacting aminopropyl triethoxysiloxane with $Cy_7Si_7O_9(OH)_3$[75]. Zheng et al[76] synthesised hydroxylpropyl corner capped phenylsilanetriol. 2-(Trichlorosilyl)ethyl acetate was end capped on iso-butyl-POSS and acetate was hydrolysed to yield hydroxyl functionalised POSS[77]. A POSS framework with two anilino pendant groups was prepared in good yield using $diexo$-$(c$-$C_5H_9)_8Si_8O_9(OH)_2$ followed by adopting various synthetic procedures (Scheme 6)[78].

R-SiCl$_3$ $\xrightarrow{\text{H}_2\text{O}}$

R = Cyclopentyl, Cyclohexyl
      Isobutyl, Phenyl

Cl$_3$SiR'

NEt$_3$

R' = hydride
      chloride
      hydroxide
      nitriles
      amines
      isocynates
      styryls
      olefins
      acrylics
      epoxides
      norbornyls
      bisphenols
      acid chlorides
      alcohols
      acids

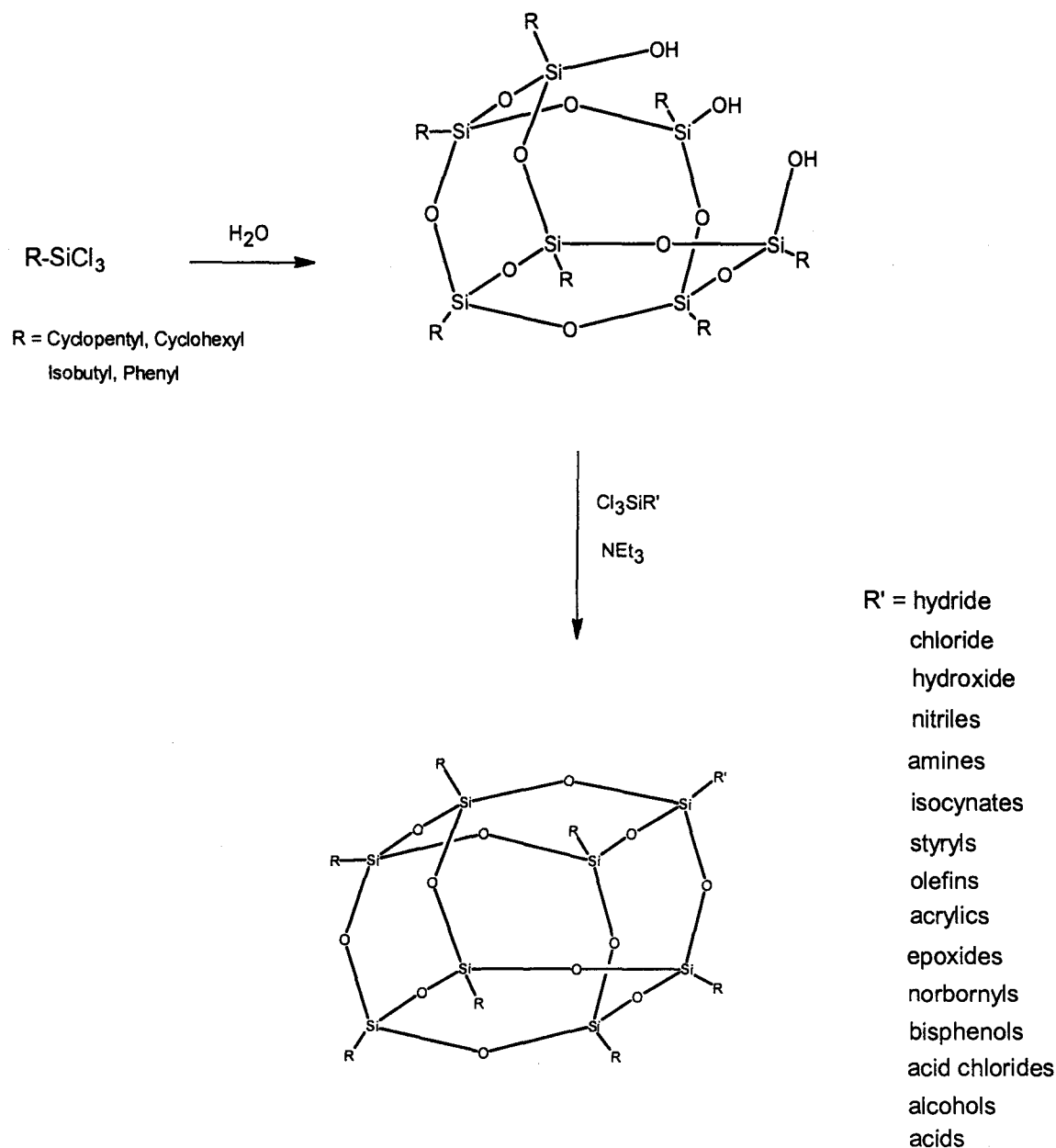Scheme 5—Synthesis and structures of monofunctional POSS macromonomers

Hybrid Nanocomposites from Completely Condensed Silsesquioxane Monomers

POSS/Polyimide Hybrid Nanocomposites (NCs)

Laine *et al*[63] synthesized OAPS as a robust nanosized building block for construction of materials with nanometer control between organic and inorganic components. A three-dimensional polyimide[63] was synthesized by using OAPS with pyromellitic dianhydride (PMDA) in NMP and DMF solutions (Scheme 7). Polyimide NCs show thermal stabilities >500°C (5% mass loss temperature) and char yields >75% even at 600°C. Resulting materials are completely amorphous, and extreme rigidity of organic tethers linking cube vertices prevents long-range order occurring during curing reaction[79,80].

R = C₆H₅

HBF₄ OMe₂

BF₃ OEt₂

76 %

H⁺ / MeOH
59%
two steps
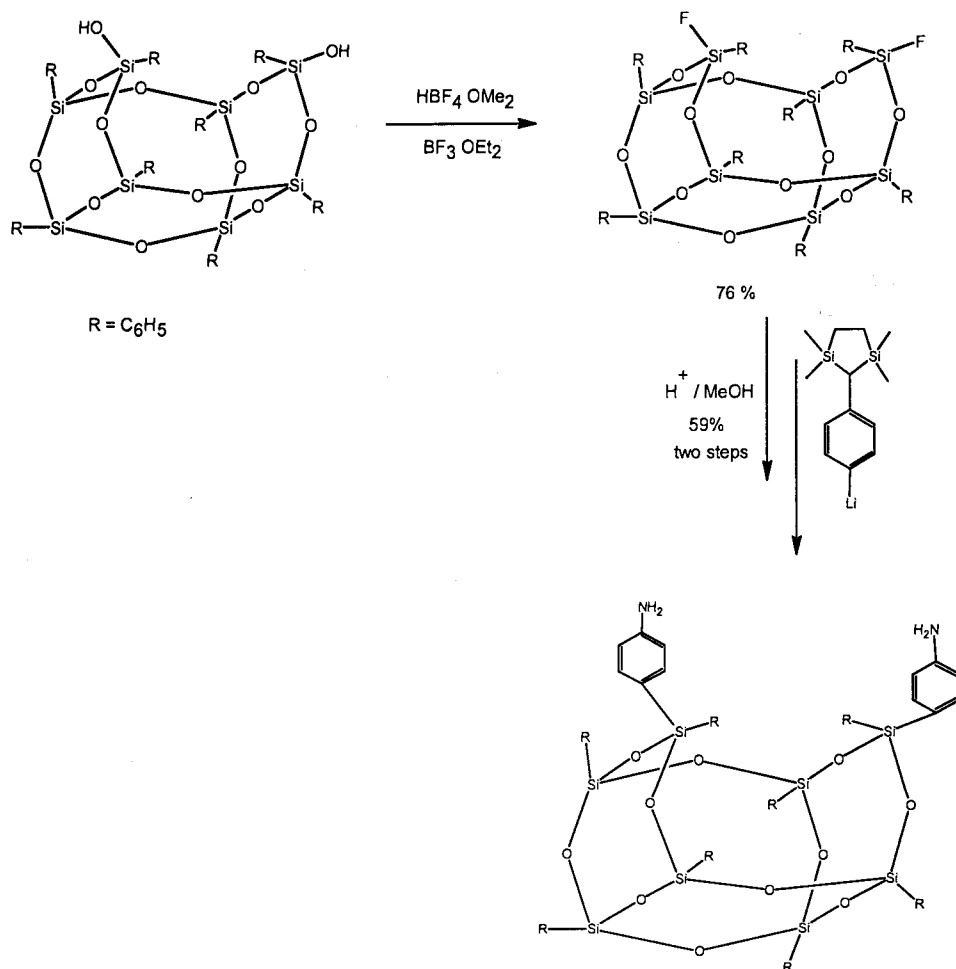
Scheme 6—Synthesis of diamine functionalised POSS macromonomer

Polyimide-POSS NCs[81,82] were prepared by reacting OAPS with polyamic acid (PAA) solution for low dielectric properties and improved thermo-mechanical properties. Zheng et al[83] synthesized octamaleimidophenyl/POSS (OmipPOSS) NCs via imidization reaction between OAPS and maleic anhydride. Thermosetting hybrids containing OAPS (10 wt%) were obtained via in situ polymerization of diglycidylether-bisphenol A (DGEBA) and 4,4'-diaminodiphenylmethane (DDM) in presence of OAPS. OmipPOSS NCs containing 2.5 and 5 wt% of OmipPOSS displayed enhanced glass transition temperatures (Tg's) (178 and 174°C) compared with control, epoxy resin (172°C). On the other hand, hybrids containing 7.5 and 10 wt% of OmipPOSS have lower Tg's than control epoxy. Enhancement in glass transition temperatures is due to nanoreinforcement effect of POSS on polymer matrix.

At very high percentage (7.5 and 10 wt%), restriction of rigid POSS was lost and bulky groups behaved like plascticizer. Alagar et al[84] showed improved thermomechanical properties of OmipPOSS NCs.

Polyimide NCs are also obtained by reacting amine terminated PAA, with POSS containing epoxy pendant groups (instead of OAPS). In NC, network linkages between POSS cube and polyimide molecules primarily arise from curing reaction between terminal amine groups of PAA and epoxy groups of POSS cube[85]. Epoxy POSS incorporated NCs show high rubbery state region and with high tensile modulus 1045.6 Mpa at 400°C, which is 23 times greater from conventional epoxy polyimide composites. Very low dielectric values (dielectric constant=2.30) of polyimide-POSS was reported by synthesizing mixed glycidyl epoxy and fluorinated epoxy functionalised POSS[86]. Polyimide's with low dielectric
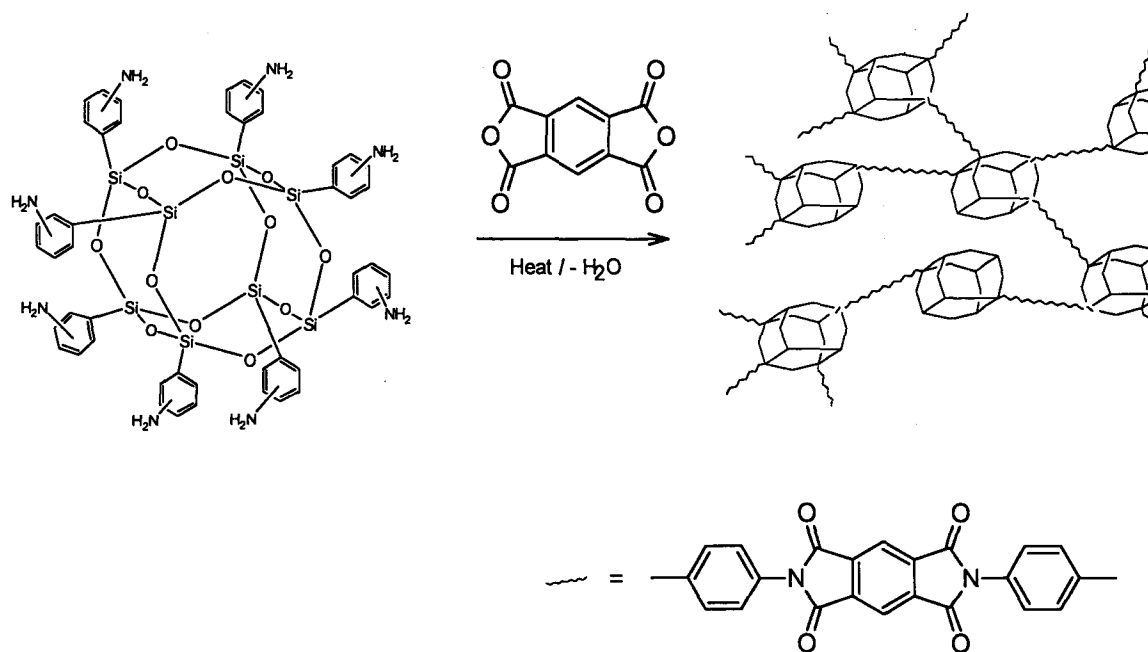
Scheme 7—Synthesis of polyimide/POSS nanocomposites

constants (K=2.65) (Pure PI, K=3.22), are obtained by the use of aliphatic amine POSS, but, thermal stabilities of NCs became poor due to weak aliphatic groups of POSS molecules[87].

Wei *et al*[88] reported about linear polyimide by reacting diamine functionalised POSS with dianhydrides. But, NCs obtained using these diamine functionalized POSS shows lower thermal properties than that of pure polyimide due to degradation of cyclopentyl groups present in 7 corners of POSS molecules (at 400°C). In-plane coefficient of thermal expansion of POSS/polyimide NCs increases with POSS amount as a result of increase in free volume in polyimide due to POSS molecules. Self-assembly architecture was observed for polymer chain at 10% loading of POSS molecule. As POSS amount increases to 10 mol %, decrease in Young's modulus, maximum stress and elongation become more apparent (10%). But, dielectric constant of NCs got lowered and this could be tuned by varying mole ratio of POSS content. Oikawa *et al*[89] synthesized polyimide NCs using double-decker-shaped POSS molecule (Scheme 8). In first step, double-decker-shaped silsesquioxane containing aromatic tetracarboxylic dianhydride (DDSQDA) end groups were synthesized. This dianhydride is derived from DDSQ-diamine by functional group conversion method. POSS-Polyimide (POSS-PI) exhibits good thermal stability up to 500°C and POSS molecule in main chain (POSS-PI)

having high molecular weights (up to $?_{inh}$=0.61 dL/g) and particularly, fluorinated POSS-PI shows good combined characteristics, including low dielectric constant (K=2.43) with good mechanical properties (tensile strengths, 72.3 MPa; initial modulus, 1.8 GPa; and elongation at breakage, 8.0-15.9%), excellent optical properties, and is organosoluble as a good candidate for microelectronic applications.

Poly(methyl methacrylate) (PMMA)-POSS grafted polyimides were synthesized by thermally initiated free-radical graft copolymerization of methacrylcyclopentyl-POSS (MA-POSS) with ozone-preactivated PAA, followed by thermal imidization to achieve material with low dielectric values. Dielectric constant of film can be tuned by varying molar ratio of grafted MA-POSS side chains in copolymer[90]. Brunsvold *et al*[91] grafted silsesquioxane through a two-step chemical process. (3-Aminopropyl)(hepta-*iso*-butyl) POSS was covalently attached to polyimide backbone containing reactive acid chlorides. Polyimide/POSS NCs could be developed by crosslinking amine functionalsied trialkoxysilane precursor with dianhyrdides[92-95].

POSS/Epoxy Hybrid Nanocomposites (NCs)

Reactivity of mono- and multi-functional POSS-epoxy monomers and their effect on the formation of epoxy-amine networks containing POSS as a pendant unit or as
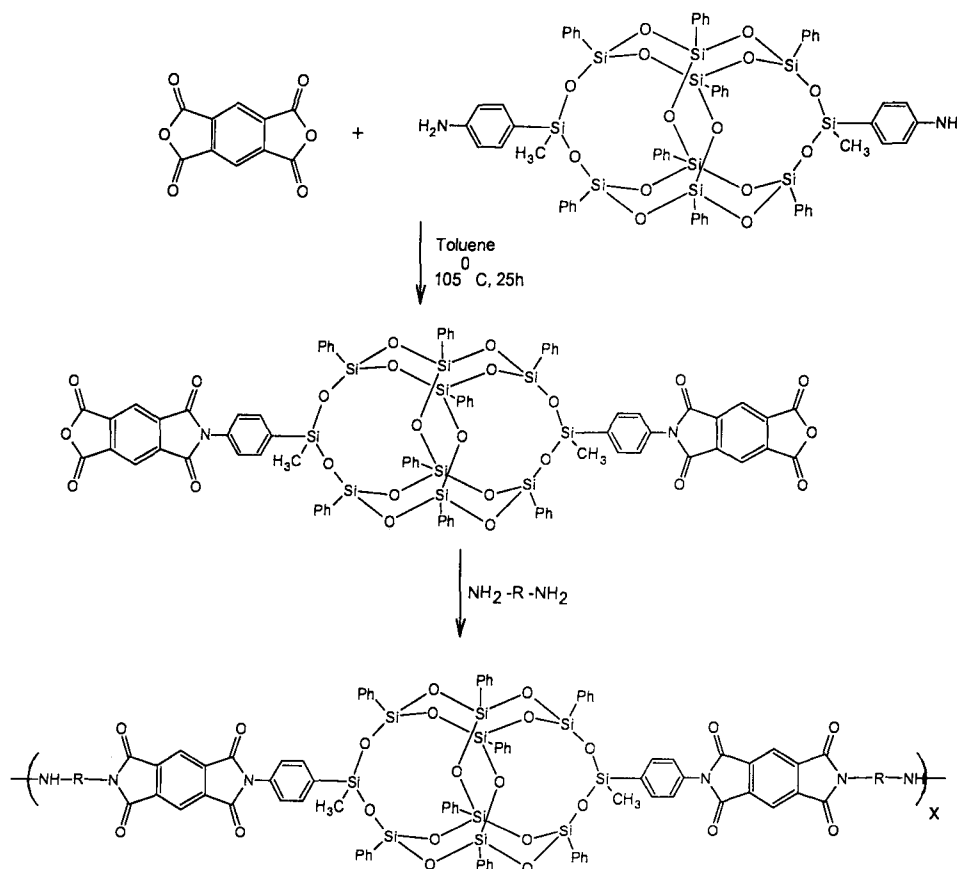
Scheme 8—Synthesis of polyimide/POSS nanocomposites containing double-decker shaped silsesquioxanes

junctions was evaluated[96]. POSS epoxy monomers are less reactive towards amines than DGEBA, may be due to sterical crowding around epoxy groups caused by inert POSS substituents and also due to reduced epoxy group's mobility. Epoxy POSS could be chemically or photochemically cured to give hard, scratch- and solvent-resistant materials containing up to 65% masked silica[97]. Epoxy NCs with completely defined organic/inorganic phases were prepared by reacting octakis(glycidyldimethylsiloxy)octasilsesquioxane(OG) with DDM at various compositions to alter thermomechanical properties[98] (Scheme 9). From resulting material, moduli and fracture toughness of NCs were found less than those of organic resins. Choice of short-chain, polyfunctional epoxies[99] combined with nontraditional resin stoichiometries is a possible way to control epoxy resin co-effiecient of thermal expansions over an order of magnitude. An additional advantage is that epoxy-POSS resin has a low viscosity of about 350 CPs at room temperature, making it suitable for composite

processing techniques and thermomechanical stabilities are better than that of standard Ciba epoxy resins[100, 101].

Chen et al[102] investigated epoxy NCs using octa(2,3-epoxypropyl)silsesquioxane (OE) with diamines of 4,4'-methylenedianiline (DDM) and 5-trifluoromethyl-1,3-phenylenediamine (FPA). Resultant fluorinated epoxy NCs show Tg of 170°C, which was higher than diglycidyl ether of bisphenyl A (DGEBA)/DDM at the same stoichiometric ratio. It also possesses excellent thermal, mechanical, and dielectric characteristics with high storage modulus of 1.8 GPa (30°C) and 0.3 GPa (250°C), low coefficient of thermal expansion of 86 μm/m°C, and dielectric constant of 2.19. Polybenzoxazine(PBA)-epoxy/POSS nanocomposites (40 wt% of POSS) was obtained through intercomponent reaction between phenolic hydroxyls of PBA and epoxide groups of epoxyPOSS[103]. Introduction of POSS, thermal stability of polymer matrix and oxidation resistance of materials were significantly enhanced. Nanoscale dispersion of POSS in NCs (<30 wt% POSS) displayed higher storage

Epoxy-polymer
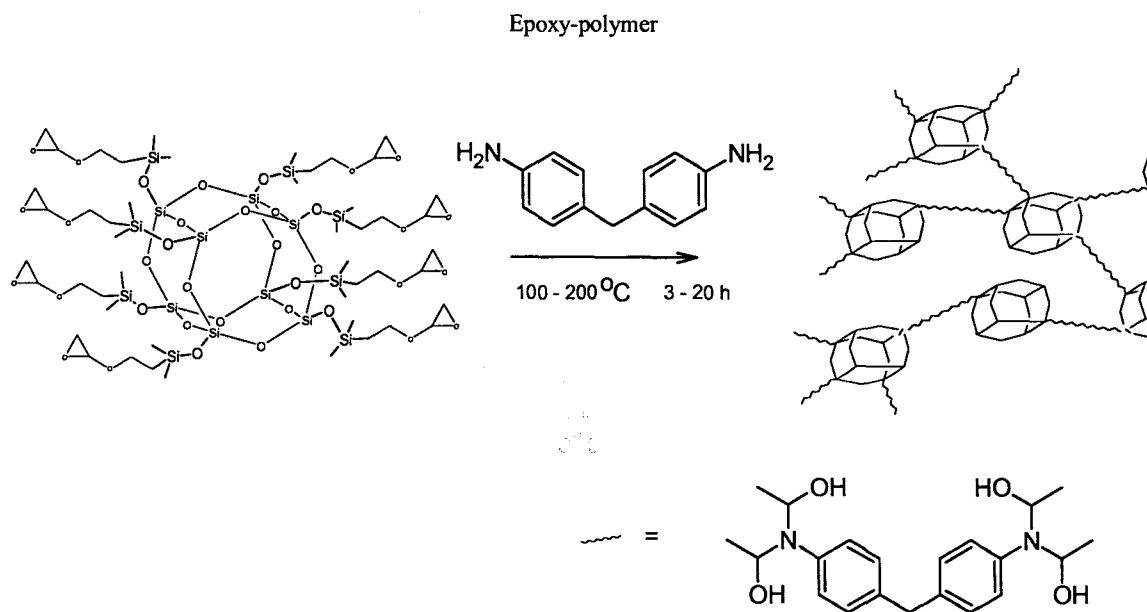
Scheme 9—Synthesis of epoxy/POSS nanocomposites

moduli in glassy state than control PBA. But, storage moduli for NCs (> 30 wt% POSS) are lower than that of control PBA, and this could be responsible for porosity of NCs. Enhanced thermal properties and good homogeneity of epoxy/POSS NCs was obtained by reaction of DGEBA with monoalkylamine functional POSS and microphase separation of material could be controlled by small molecule curing agents[104]. POSS monomers containing 8 aliphatic amine groups on vertices were first incorportated into DGEBA[105]. Improved thermal stability was achieved on increasing chain length of diamine with diepoxy hexavinyl POSS[106]. Life time of epoxy NCs at different temperatures was predicted using kinetic parameter, based on thermal degradation of NCs[107]. Lu *et al*[108] also investigated thermal properties and curing kinetics of epoxy/POSS hybrid networks.

Poly(methacrylate)/ POSS Hybrid Nanocomposites (NCs)

Matisons *et al*[109] reported various methyl methacrylate functionalised POSS macromonomers with different PEG chain lengths and then polymerized with methyl methacrylate to produce a series of hybrid materials. Although POSS is a bulky and multifunctional crosslinker, glass transition temperature increase with an increase in POSS concentration. In some instances, group bulkiness created a free volume and chain separation, which led to a reduction in glass transition temperature. Incorporation of POSS always increases thermal stability. By applying

ATRP method[110], PMMA-POSS hybrid NCs were prepared and their thermal properties were investigated. Hybrids were obtained by use of octafunctional octakis(3-hydroxypropyldimethylsiloxy)octasilsesquioxane (OHPS) and OAPS nano-cages as ATRP initiators. No significant improvement was observed in thermal stability of NCs as compared with linear PMMA. Mandal *et al*[111] developed an efficient and versatile method for synthesis of POSS-polymethacrylate hybrids (Scheme 10), such as POSS-poly(methyl methacrylate) (POSS-PMMA), POSS-poly(ethyl methacrylate) (POSS-PEMA), and POSS-poly(benzyl methacrylate) (POSS-PBzMA) of controllable molecular weights and low polydispersities by thiol-mediated radical polymerization at elevated temperature (100°C). POSS content in these hybrid materials could be varied, by tuning reactant concentrations and degree of polymerization of grafted polymethacrylate chains. Wu *et al*[112] studied surface properties of poly(methyl methacrylate-co-*n*-butyl acrylate-co-cyclopentylstyryl polyhedral oligomeric silsesquioxane) [poly(MMA-co- BA-co-styryl-POSS)] terpolymers and found that incorporation of styryl-POSS into polymer resulted in increasing interactions between polymer and solvent, dispersive component of surface free energy of polymer and acidity of surfaces of polymers. Toughness property[113] of PMMA using POSS nanocages at loadings between 0 and 15 wt% was investigated using Cyclohexyl-POSS, methacryl-POSS
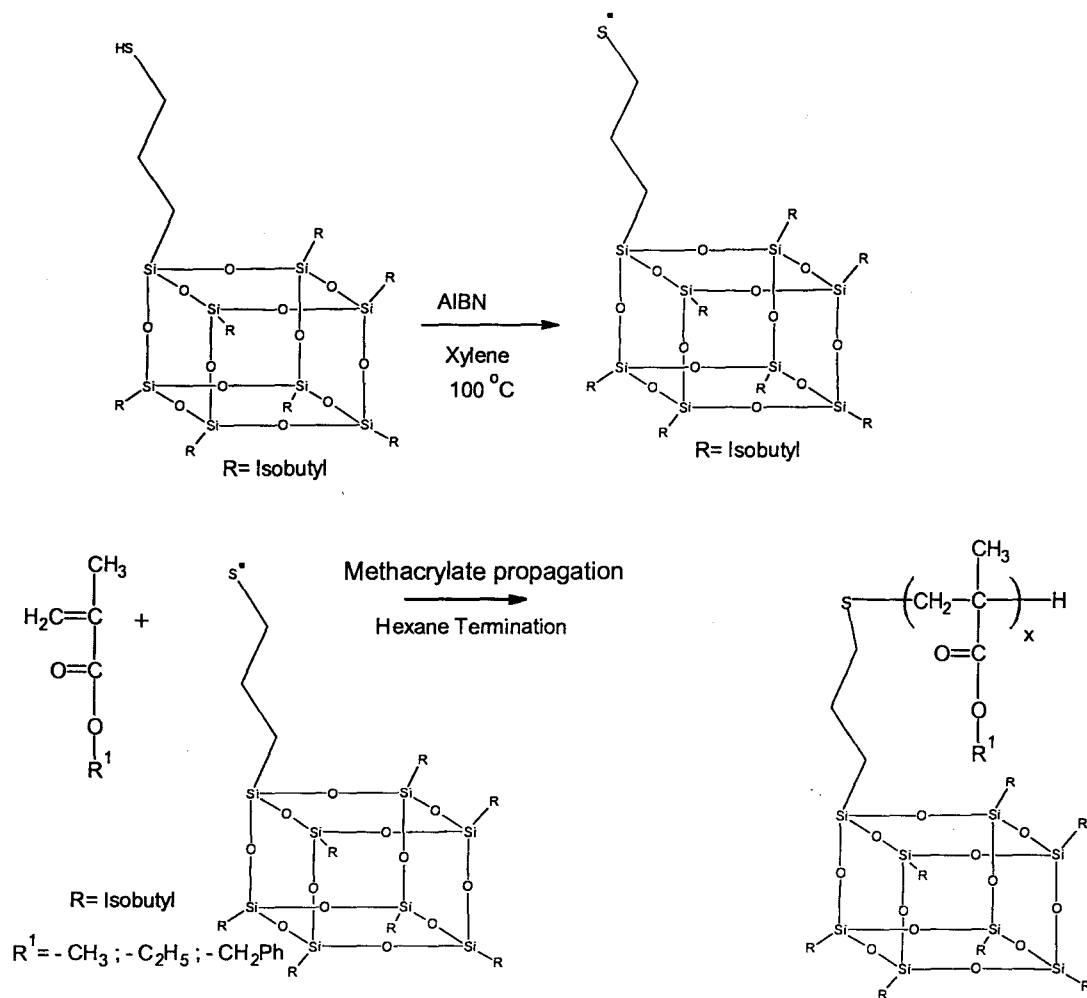
Scheme 10—Synthesis of thiol mediated polymethacrylate/POSS nanocomposites

and trisilanol-phenyl-POSS. Binary blends of POSS and PMMA were able to improve impact toughness of PMMA. In order to toughen PMMA with rigid fillers, weakly adhering particles (size, 100 nm) are required. Li et al[114] synthesized a soluble poly(MMA-co-octavinyl-POSS) hybrid by common free radical polymerization and resulting hybrid NCs show higher Tg and better thermal property than parent PMMA homopolymer. Tg improvement results from dual contributions of motion hindrance of PMMA chain imposed by nanometer POSS cores and dipole-dipole interaction between PMMA chains and POSS cores. Thermal stability enhancement is mainly attributed to incorporation of nanoscale inorganic POSS uniformly dispersed at molecular level. Silverstein et al[115] reported that degree of polymerization increased with increase in POSS content for linear PMMA-POSS NCs and shows a relatively low PDI than conventional PMMA.

Gerard et al[116] synthesized polymer networks either as linear chains or as cross linked PMMA-POSS NCs. POSS-POSS interaction was found to be main parameter governing network morphology. However, dynamic mechanical properties remain nearly at the same level as neat matrix. Multifunctional POSS shows a higher miscibility with dimethacrylate monomer and disperses very well in cured network. Molecular dynamic simulation studies were carried out for PMMA-POSS NCs[117].

Norborenyl/POSS Hybrid Nanocomposites (NCs)

Mono- and tri- functionalized norbornenyl-POSS are copolymerized with dicyclopentadiene(DCPD). POSS loading[118] slightly decreases thermal oxidative resistance of copolymer before primary decomposition temperature of PDCPD network due to lower thermal stability of POSS. Modulus and yield stress, compression, and

R=Cyclopentyl
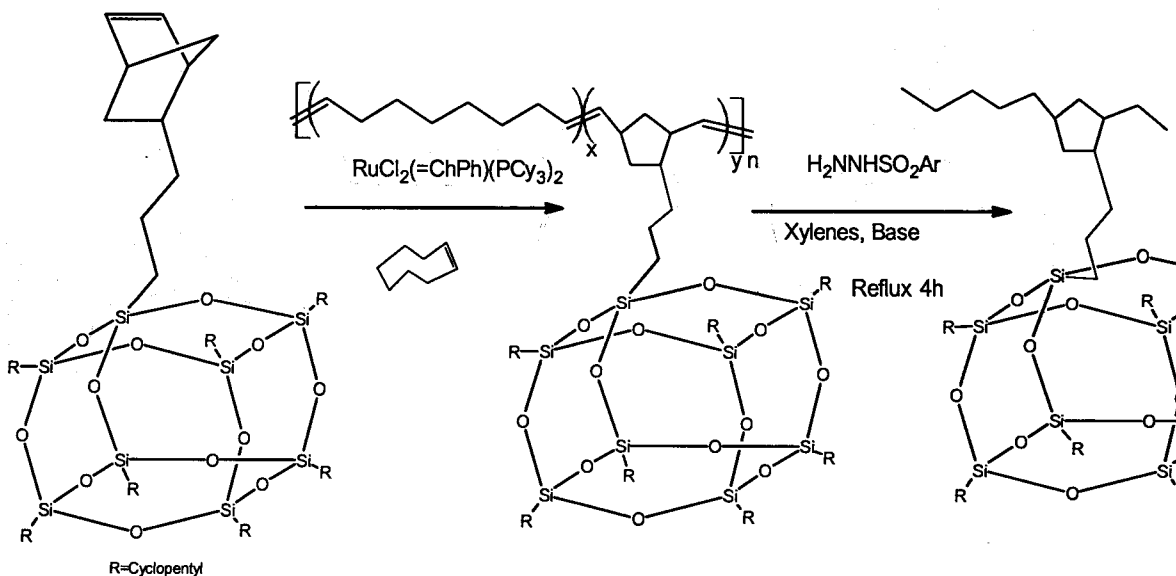
Scheme 11—Synthesis of norbornene block polyethylene-POSS random copolymers

fracture toughness of copolymers decrease with POSS loading, irrespective of cross link density. For mono-functionalized POSS, decrease in toughness is in agreement with loss of irreversible damage occurring during fracture. Microstructural and mechanical relaxation investigation was carried out for norbornene/POSS-norbornene hybrid polymers[119]. POSS copolymerization enhances a-relaxation temperature, T_a in proportion to the weight fraction of POSS-norbornenyl comonomer. However, magnitude of this dependence is larger for POSS-norbornenyl comonomer possessing cyclohexyl corner groups (CyPOSS) than for copolymer with cyclopentyl corner groups (CpPOSS). Norbornene block polyethylene-POSS random copolymers[73] (Scheme 11) were obtained by ring-opening metathesis copolymerizations of cyclooctene and POSS monomer 1-[2-(5-norbornen-2-yl)ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo [9.5.1.13,9.15,15.17,13] octasiloxane (POSS– norbornylene) using Grubbs's catalyst, followed by reduction of double bonds in the copolymers. Polyethylene–POSS copolymers showed a 70°C improvement, relative to a polyethylene control sample of similar molecular weight. Kwon *et al*[120] reported synthesis of POSS-containing block copolymers for the first time via living ring-opening metathesis polymerization.

Polyurethane(PU)/POSS Hybrid Nanocomposites (NCs)

Linear PU/POSS NCs[121] were obtained through bisphenol functionalised POSS (Scheme 12).

Polyurethane networks[122] with POSS were obtained by reacting OAPS with isocyanate terminated polyurethane prepolymer. Thermal stability of hybrid polyurethanes is more than conventional PU elastomer due to nanoscale reinforcement effect of POSS on polyurethane networks. In glassy state (-75 to -25°C), all POSS-containing hybrids are significantly higher than that of control PU even at 2 wt% of POSS incorporation. PU-POSS networks have been synthesized by taking epoxy-POSS monomer[123]. Thermal and mechanical properties show similar trend to that of PU-POSS networks prepared using OAPS macromonomer. Contact angle measurements showed that organic-inorganic NCs displayed a significant enhancement in surface hydrophobicity, as well as reduction in surface free energy. Improvement in surface properties was ascribed to the presence of POSS moiety in place of polar component of polyurethane. Wu *et al*[124] studied thermal and rheology properties of hybrid polyester-POSS resins and PU-POSS using 1-(2,3-propanediol)propoxy-3,5,7,9,11,13,15-isobutylpentacyclo-POSS diol cured with isophorone diisocyanate (IPDI) trimer. Pure polyester resin displayed Newtonian flow behaviour, but all resins with POSS presented a first shear-thinning branch.

POSS/Polystyrene Hybrid Nanocomposites (NCs)

Polystyrene-POSS NCs (Scheme 13) were obtained by free radical polymerization using AIBN-initiator[74]. Both homopolymers and copolymers with varying proportions of POSS content modifies thermal properties
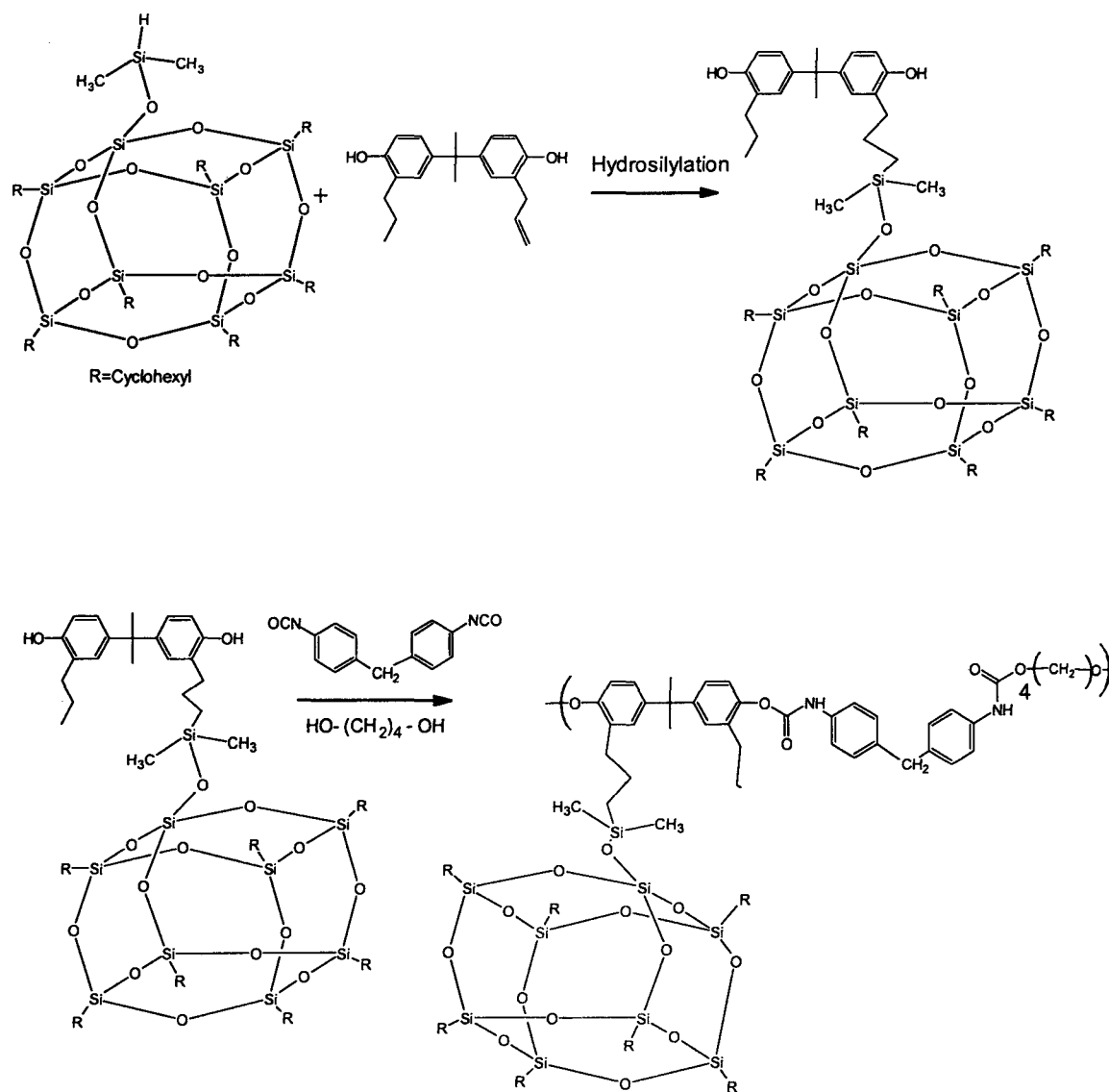
Scheme 12—Synthesis of polyurethane/POSS linear copolymer

drastically and allows for tailoring polymer softening temperature (> 200°C range). Thermal stability, compared with polystyrene modified with pendent C_{60} fullerenes (diam 7.07 Å), shows a Tg of 166°C for an approx. 11 mol% C_{60} incorporation. This is comparable to Tg's seen in 9 mol% polystyrene-POSS copolymers. A series of hybrid organic/inorganic triblock copolymers[125,126] of polystyrene-butadiene-polystyrene (SBS) grafted with POSS molecules with different chemical constituents groups (phenyl, cyclopentyl, cyclohexyl and cyclohexenyl) in POSS cube have been investigated and observed that POSS with phenyl moiety, when grafted to polybutadiene (PB) phase, appears to show favourable interaction with polystyrene (PS) phase and Ph-POSS plasticizes SBS.

Dramatic improvement in thermal properties of NCs were observed for poly(styrene-co-octavinyl-polyhedral oligomeric silsesquioxane) (PS-POSS) organic-inorganic hybrid NCs containing various percent of POSS prepared via one-step free radical polymerization[127]. Ferrocene metal bonded polystyrene-POSS NCs[128] were synthesized and exhibit paramagnetic properties with a remnant magnetization of 0.035 emu/g and indicated that polystyrene-POSS shows ideal soft magnetic properties.

## Nanocomposites (NCs) based on Incomplete Silsesquioxanes

Heptameric siloxanes with partially formed cages containing 2 or 3 residual silicon hydroxyl functional
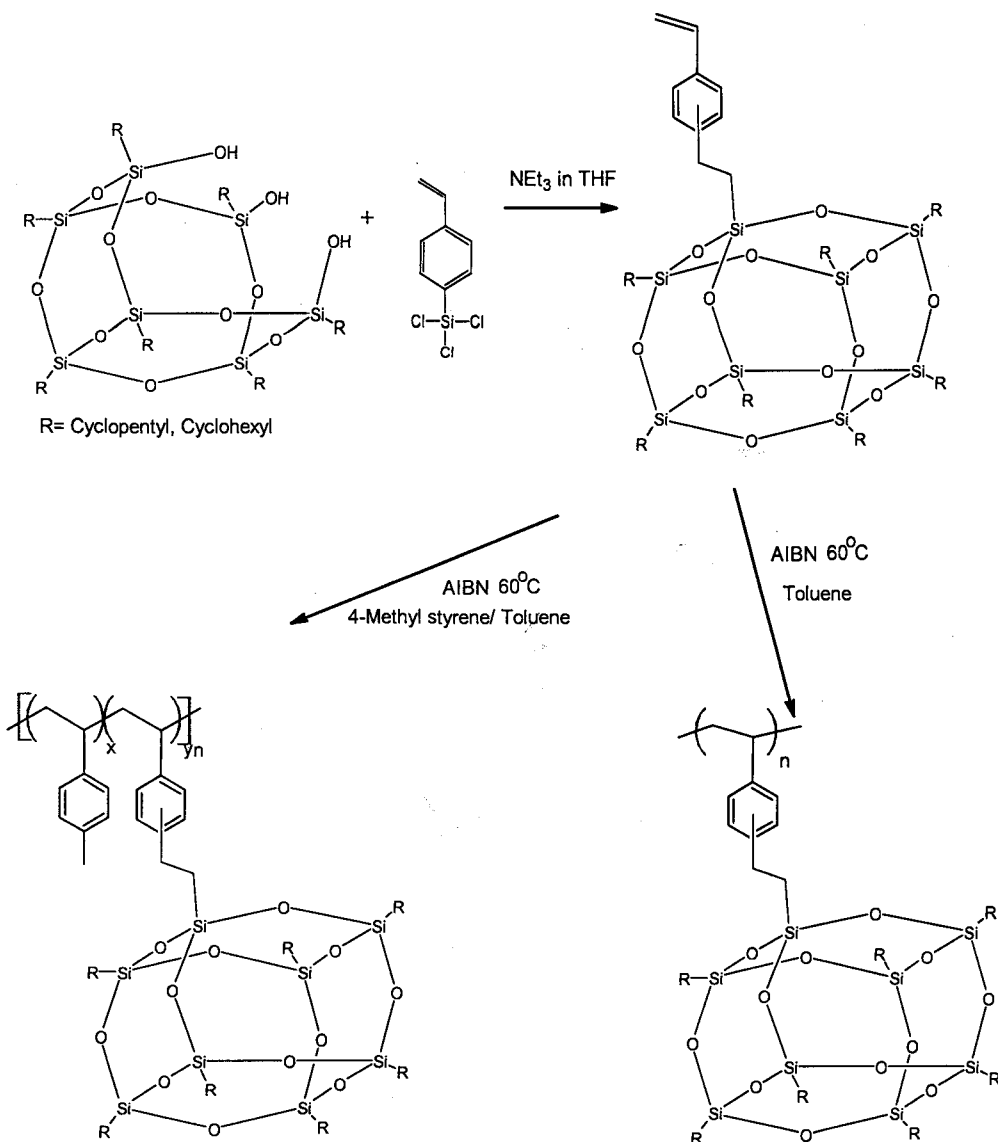
Scheme 13—Synthesis of polystyrene/POSS nanocomposites

groups, obtained through hydrolysis/condensation of alkyl-or aryl trichlorosilanes, are called as incomplete silsesquioxane. Feher *et al*[129,130] synthesized partial cage silsesquioxane from hydrolytic cleavage of completely condensed POSS. A variety of NCs were obtained through reactive silicon hydroxyl functional groups(-SiOH) (Scheme 14). Pittman *et al*[131] reported effect of partially caged trisilanol phenyl POSS on thermal and mechanical properties of cyanate-ester NCs and suggested that three-hydroxyl groups in POSS aid solubility into cyanate-ester resin and also reacts with cyanate ester resins at high temperatures to aid dispersion. Storage moduli (E) is higher than those of pure cyanate ester over entire

temperature range of 35-350°C. Continued curing leads to aggregation of POSS, which is bound to resin molecules and aggregation process depends on concentration of POSS. There is a formation of Si-O-Si bonds from silanol groups of POSS also occurring, both intramolecularly and intermolecularly at 250-300°C. Latter could create dimers or trimers of POSS when there is enough freedom of motion or when molecules of POSS are in close proximity. Storage modulus for 1, 3, 5 and 10 wt% POSS are greater than that of pure resin composites except when 15 wt% of POSS was present. Also, Tg of 1, 3, and 5 wt% POSS composites, flexural strength and flexural modulus are higher than that of neat cyanate ester composites.
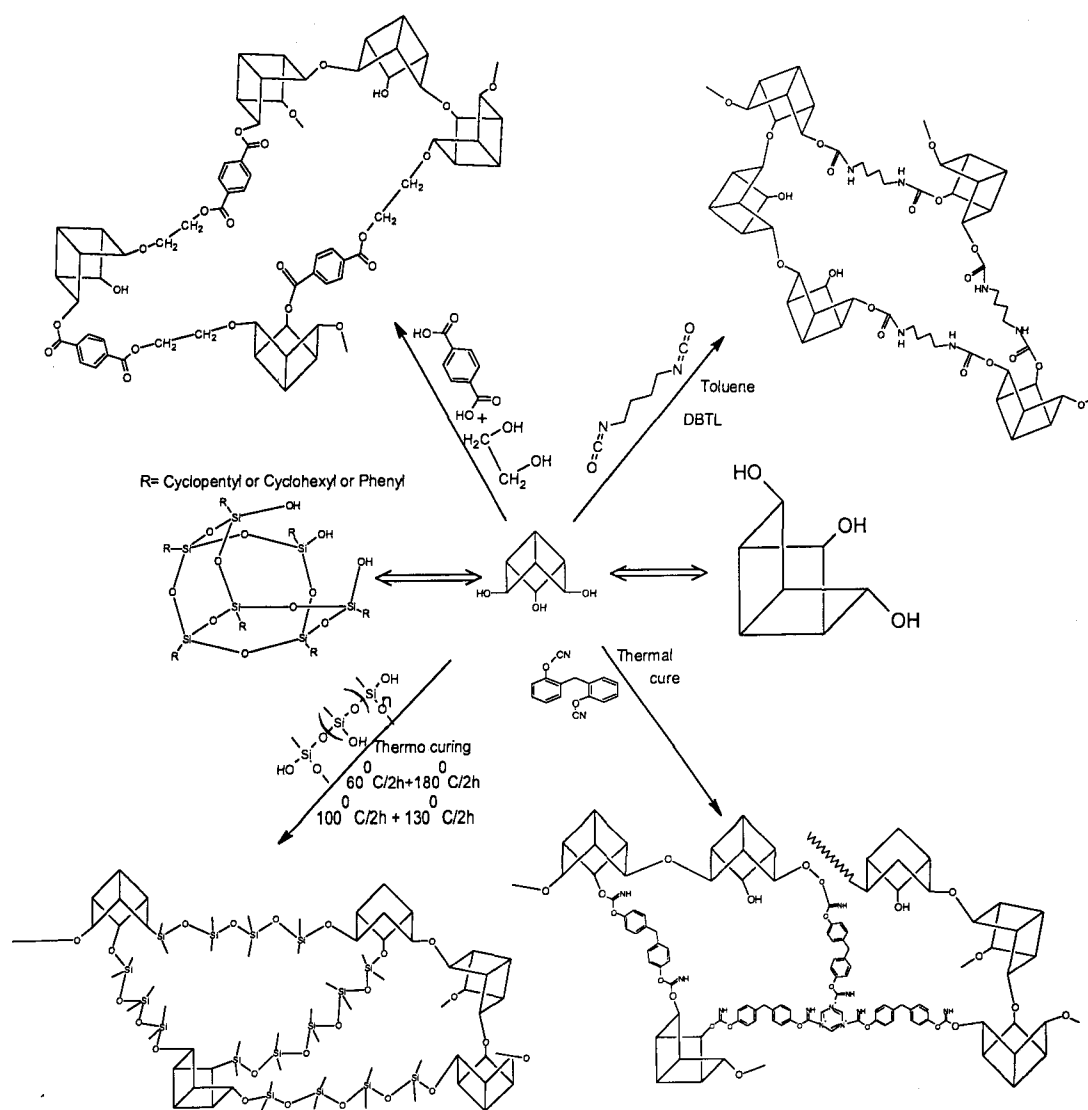
Scheme 14—Synthesis and structures of polyester, polyurethane, polydimethylsiloxane and cyanate ester
nanocomposites using partially caged silsesquioxanes

Choudhury et al[132] reported synthesis of transparent hybrid polyurethane using partially caged POSS for thin film coating. Partially caged POSS components retain their partial cage structure after curing and impart high glass transition temperature and high thermal stability to product as compared to conventional polyurethanes, which is essential in their application as weatherable coatings. Application of hybrid as a coating resulted in formation of a homogeneous ⌒ne-phase lamellar coating with excellent coverage of substrate. Similarly, prevention of discoloration of poly(ethylene terephthalate) (PET) during melt processing, by usage of trisilanolisobutyl-POSS have been reported[133]. Thermal studies displayed that partially caged POSS increases thermooxidative stability with increase in shear storage modulus, indicating

better melt elasticity and a broader window of processability of material for commercial applications. Synthesis of polyurethane NCs based on completely and incomplete condensed silsquioxanes have been reported and effect of dual cage structure on thermal, mechanical and morphological properties was evaluated[134]. Completely condensed silsesquioxane decreases thermal and mechanical properties of NCs with increase in POSS aggregation of PU matrix.

Influence of trisilanol phenyl-POSS on thermo-mechanical properties and curing of epoxy-amine networks were investigated[135]. Phenyl-trisilanol polyhedral silsesquioxane is highly soluble in DGEBA epoxy resin and addition of POSS-triol improves cross-linking reaction of epoxy-amine networks. Methyl silicone resin/POSS

composites with various proportions of POSS monomer using trisilanolisobutyl-POSS were synthesized[136,137]. Thermal stability of methyl silicone resin greatly improved by introduction of POSS cages. Segmental motion of PDMS chain was retarded by large mass and steric hinderance of bulky POSS. Organic-inorganic hybrid composites evolved via *in situ* polymerization of DGEBA in presence of trisilanolphenyl-POSS[138]. Phase separation of trisilanolphenyl-POSS induced by reaction occurred, and heterogeneous morphology was obtained for hybrid composites. Spherical POSS-triol particle aggregates (diam, 0.3-0.5 μm) were dispersed in continuous epoxy matrices. Phase separated NCs show very high Tg's and with high storage modulus in glassy states. Dissolving trisilanolphenyl-POSS and phenolic resin into THF, followed by solvent removal and curing prepared phenolic-POSS NCs. Both nano- and micro-sized POSS filler aggregates and particles were heterogeneously dispersed in cured matrix[139]. POSS silanol/phenolic hydroxyl hydrogen bonding increases compatibility, which is beneficial for POSS dispersion in matrix that does not prevent phase separation. Thermal stability and Tg of NCs is only slightly affected by loading of POSS.

Various Other POSS Nanocomposites (NCs)

Crosslinked polysiloxanes were directly synthesized by anionic ring-opening copolymerization of octaisobutyl-POSS as a multifunctional monomer with octamethylcyclotetrasiloxane (D4) using base catalysts [potassium hydroxide (KOH) or tetramethylammonium hydroxide (Me_4NOH) siloxanolate], indicating that crosslinked polysiloxanes exhibit distinct Tg and excellent thermal stability[140]. Synthesis of liquid crystal POSS and specific problems connected with the nature of silsesquioxane cage, and special properties that their geometry imparts to their mesogenic behaviour of liquid-crystal polyhedral silsesquioxane materials have been described[141]. Synthesis of these materials is based on a silsesquioxane cage modification process, starting with a suitably functionalized cage, to which mesogens are attached[142]. Many systems are obtained based on hydrosilylation reaction of hydrido-silsesquioxanes and mesogenic groups[143]. Richardson *et al*[144] reported a hexadecamer, first-generation, octasilsesquioxane liquid-crystalline dendrimers.

POSS-POSS nanohybrids were synthesized by hydrosilylatively copolymerized with stoichiometric amounts of octavinylsilsesquioxanes, with T_8H and Q_8M_8H in toluene using Pt catalyst[145]. POSS cubes with longer spacer groups are more reactive than those with no spacer groups. Pores within POSS cube interiors (diam, 0.3 nm), and pores between cubes (diam, 1-50 nm) were determined according to nitrogen absorption, positron annihilation lifetime spectroscopy (PALS), and small angle X-ray scattering (SAXS) data. Benzoxazine/POSS hybrids were synthesized by using octafunctional cubic silsesquioxane (MBZ-POSS) with 8 organic benzoxazine tethers as a curing agent[146-148]. In benzoxazine/POSS hybrids, POSS aggregates occur in larger scale at higher POSS contents and reason for heterogeneous phase separation may be from less compatibility of inorganic silsesquioxane core with organic benzoxazine species. During formation of polybenzoxazine/POSS hybrids, POSS particles were separated from polybenzoxazine rich region, leading to POSS rich domains (50-1000 nm). Zheng *et al*[103] OG was used to prepare polybenzoxazine(PBA)/POSS NCs. Crosslinking reactions involved during formation of polybenzoxazine(PBA)/POSS NCs can be divided into two types: 1) Ring-opening polymerization of benzoxazine; and 2) Subsequent reaction between *in situ* formed phenolic hydroxyls of PBA and epoxy groups of OG. Other polybenzoxazine/POSS NCs obtained by reaction of OAPS and 2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles) (PBO) are reported[149]. Dynamic mechanical analyses indicated that NCs exhibited higher Tg values than pristine PBZ and PBZ-PBO resins. Storage modulus of NCs was maintained at higher temperatures even with a small amount of OAPS incorporated into composite systems. Thermal stability of hybrid was also improved by inclusion of OAPS. Crosslinked poly(4-vinylpyridine)/POSS NCs were obtained by the reaction of epoxy group of OG with pyridine ring of poly(4-vinylpyridine)[150].

Amphiphilic silsesquioxane derivative, 1-(1,ω-propylenemethoxy)oligo(ethyleneoxide)-3,5,7,9,11,13,15-heptahydridopentacyclo [9.5.13,9.15,15.17,13] octasiloxane has been prepared by reacting T_8H and allyl functional oligo(ethyleneoxide) (*M*n =750g/mol) through PCH[151]. Associative behaviour of new amphiphilic telechelics containing POSS as an end-group of PEG of varying chain length were investigated using capillary viscometry. Viscosities were strongly affected by solvent composition in THF/water mixtures[152].

POSS modification increases storage modulus and Young's modulus of polyamides, slightly decreases their Tg from 312° to 305°C, and significantly lowered their dielectric constants from 4.45 to 3.35[153]. Supramolecular inclusion complexation (ICs) of POSS-capped

polycaprolatone (PCL) with α-and γ-cyclodextrins (CL) were derived.[76,77,154] Crystallization kinetics of silsesquioxane based hybrid star, poly(3-caprolactone) was investigated by synthesising a series of silsesquioxane based hybrid star poly(3-caprolactone) having different arm lengths through ring-opening polymerisation of 3-caprolactone[155].

Poly(alkyl silsesquioxane), PASSQ, copolymers consisting of various chemically linked alkyl units over methyl group as a pore forming moiety, and 1,2- bis-trimethoxysilylethane (BTMSE), were synthesized and their thermo-mechanical and optical properties were investigated[156]. Higher alkyl groups in PASSQ were composed and thereby lower refractive indices were achieved from 1.45 to 1.27 due to formation of nanopores in film. Modulus for BTMSE based PASSQ films were significantly higher than 3.8 GPa of typical thin film of poly(methyl silsesquioxane). Smith et al[157] synthesized and characterized PFCB aryl ether copolymers and multiblock copolymers with pendant cyclobutyl and iso-butyl-functionalized POSS cages. Synthesis of POSS aryl trifluorovinyl ether (TFVE) monomers was accomplished by condensation of commercial monosilanolalkyl-POSS with a TFVE-functionalized chlorosilane. POSS/PFCB aryl ether copolymers demonstrated excellent solution processability, producing optically transparent and flexible films. Incorporation of POSS showed no change in thermal stability as compared to PFCB aryl ether homopolymer.

Blends of POSS Nanocomposites (NCs)

Polysiloxane composites containing POSS were prepared by melt blending. Crosslinking polysiloxane caused changes in POSS solubility that enhanced phase separation. But crosslinks caused constraints, which decreased domain sizes of precipitated phases[158]. Octamethyl-POSS-HDPE NCs were prepared by melt mixing route. Joshi et al[159] observed that POSS does not interfere with crystallization of HDPE. At low concentrations (0.25-0.5 wt%), POSS particles act as lubricants, lead to decrease in complex viscosity as compared to neat HDPE, show significantly high storage modulus and also enhanced thermomechanical properties than HDPE.

Composites of poly(methyl vinylsiloxane) with POSS were prepared by melt blending showing that highly crystalline POSS macromers could undergo condensation reactions at 230°C in air, leading to partially amorphous structures. Also, POSS crystals apparently dissolved in polysiloxane at high temperatures and POSS crystals with hexahedral or flake-like structures recrystallized out upon cooling. Both crystallites and POSS molecules co-existed in these blends, with the amount of dispersed molecular POSS being increased at higher temperatures. POSS molecules exhibited some physical interactions with free polysiloxane chains that are not crosslinked. But, crosslinking induced phase separation. In curing process, POSS molecules could react with polysiloxane, resulting in decreases in crosslink density. Original POSS crystals could also be dissolved in polysiloxane during initial curing stages, but recrystallization upon cooling gave regenerated crystals that were roughly spherical[160]. Thermal properties and morphological development of isothermally crystallized isotactic polypropylene (IPP) blended with nanostructured POSS molecules at very small loading of POSS were studied[161].

Maitra et al[162] grafted various oligomeric PEO with different chain lengths (n=2,4,8,12) onto Q_8M_8H, and reported that silica surface affect thermal behaviour of oligomeric PEOs. Most dramatic effect was observed for PEO(n=4), where originally crystalline material became completely amorphous; 4 PEO repeat units were insufficient for crystallization to occur at surface and PEO oligomers crystallized with increasing side chain length. Maxima in ion conductivity observed for PEO chain lengths (n=4 and 8) have been attributed to the absence of crystallinity as well as enhanced mobility of short side chains in comblike polymers. Mya et al[163] discussed crystallization behaviour of star-shaped poly(ethylene oxide) with cubic silsesquioxane (CSSQ).

Bridged Polysilsesquioxanes

Bridged polysilsesquioxanes (BSSs) represent class of highly crosslinked hybrid organic-inorganic polymers, which are derived from hydrolytic polycondensation of organo-bridged silsesquioxane precursors having general molecular formula $(RO)_3$-Si-R'-Si-$(OR)_3$, where R and R' are organic groups[164,165]. BSSs, prepared by sol-gel polymerization of organo-bridged trialkoxysilane precursor, are network polymers, in which basic building block contains two silicons directly attached to a hydrocarbon bridging group. Remaining three bonds to each silicon are siloxane linkages. By connecting two or more silsesquioxane groups to R', a material with as many as six siloxane linkages (Si-O-Si) per monomer unit can be prepared, as opposed to just four in tetraalkoxy silanes. By introducing hydrocarbon spacers into siloxane network, properties (hydrophobicity, surface area, pore size, UV-visible absorption, and fluorescence) can be

significantly modified[166,167]. These materials allow to have properties (porosity, permeability, permselectivity, chemical functionality, and chemical, mechanical, and thermal stability) to be fine-tuned because of vast variety of synthetically available monomers[164,165,168,169]. Honma *et al*[170,171] synthesized a protonic conductive polysilsesquioxane membrane containing PEG, polypropylene oxide and polytetramethylene oxide bridging groups functionalized with isocyanotopropyltriethoxysilane and condensed in presence of phosphotungstic acid or monododecyl phosphate. Khiterer *et al*[172] reported BSSs containing covalently bound sulfonic acid group materials that were utilized to prepare mechanically stable gel membranes for fuel cell application. BSS molecules are utilized as precursors for synthesis of periodic mesoporous organosilicas (PMOs) or bifunctional PMOs. New methodology was adopted for preparation of PMOs films by adopting evaporation-induced self assembly procedure to obtain spherical NPs from initially developed basic aqueous medium precipitation procedure[173].

Surfactant-directed self-assembly[174,175] and self-directed assembly[176,177] methods have been successfully developed for fabrication of BSSs with well-organized structure. Self-directed assembly that takes advantage of weak interactions, such as H bonding, p-p, and/or hydrophobic interactions between bridging groups (R'), provides a very easy method for fabricating hierarchical structure. By judicious choice of organic substructure (R') in precursor, new intrinsic nanomaterials including both the nature of molecules and their collective properties within aggregate will be realized[178]. All mesoporous organosilicas contain aliphatic organic groups with relatively short chains (ethane or ethylene) or aromatic (arylene, thiophene and biphenylene) moieties[174,179-182]. A very few reports are available for amines and thiols incorporated PMOs[183].

Applications

Poly(carbonate-urea)urethane (PCU)/(POSS) NCs were potentially used in cardiovascular bypass grafts and microvascular component of artificial capillary beds. POSS NCs possess greater thromboresistance than polytetrafluoroethylene and poly(carbonate-urethane), making it an ideal material for construction of both bypass grafts and microvessels[184,185]. Kaneshiro *et al*[186] reported that L-lysine dendrimers with an octa(3-aminopropyl)silsesquioxane core (OAS) with 4th generation is a suitable candidate for controlled *in vitro* gene delivery and transfection in human breast carcinoma cells (MDAMB- 231 cells). Preliminary toxicity evaluation predicted that L-lysine dendrimers is an excellent biocompatibile NC. POSS monomer (POSS-MA) was used as a novel dental restorative composites to place commonly used dental base monomer 2,2'-bis-[4-(methacryloxypropoxy)- phenyl]-propane (Bis-GMA)[187]. Amino functionalized silsesquioxane provide curl retention for hair[188].

Polyfluorenes/POSS NC shows maximum luminescence intensity and quantum efficiency, which is almost twice as good as those of PFO EL device, and is an excellent material for optoelectronic applications[189]. Introduction of POSS moieties into PPVs improves EL properties of PPV derivatives. Improvement in EL properties of POSS incorporate PPV is due to formation of suitable insulation domains of POSS moieties in conjugated polymer matrices, resulting in a balance of charge carriers of electrons and holes[190]. Castaldo *et al*[191] presented polymeric NC sensors, based on a POSS by selecting proper matrix such as poly [(propylmethacryl-heptaisobutyl- POSS)-co-(n-butylmethacrylate)] and a suitable choice of other external home-made fillers (graphite, copper, silicon, zinc and their alloys). Hybrids could be used in sensing of both polar and apolar analytes. Sulfonic acid containing bridged POSS hybrid materials is used as proton-exchange membranes for fuel cell applications and electrolyte materials are suitable materials for automotive industry[172].

Polyphenylsilsesquioxane is used as interlayer dielectrics and protective coatings films for semi conductor devices, liquid crystal display elements, magnetic recording media and optical fiber coating[187]. Polymethyl silsesquioxane is used as an additive material in cosmetics, polypropylene films and methacrylic resins. Polymethyl silsesquioxane with epoxy containing siloxanes adheres well to rubber and plastics and could be used to provide nonsticking, water repellant and abrasion resistant films on paper, rubber, plastics and metals[187]. Poly(aminopropyl silsesquixane) and specific carbonyl compounds of silsesquioxane acts as an antitumour agent[187]. Silsesquioxane films, particularly OAPS/imide and OAPS/ epoxide films, provide excellent O_2 barrier properties, and is an ideal candidate for packaging applications[192]. In PVC, POSS behaves as a plastizecer like dioctyl phthalate (DOP) and could be used as a plastizicer[193]. Metal containing POSS cages (gallium-containing cage silsesquioxanes and aluminosilsesquioxane)[194,195] have been synthesized, for the use of silicasupported metal catalysts.

Conclusions

Each specific POSS can behave differently in a specific resin attributed to size of POSS cage, nature of organic periphery, number of reactive functionalities, and concentration and solubility of POSS in the resin. These factors determine whether POSS is incorporated as isolated and uniformly dispersed molecules, unreacted and phase separated particles, or matrix-bound aggregates. Different morophologies affect physical and mechanical properties of final material. There has been enormous growing application for POSS NCs. POSS monomers and some copolymers of POSS are commercially available in Hybrid Plastics Company (http://www.hybridplastics.com/), Fountain Valley, CA.

Acknowledgements

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