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Introduction of Organosilicon Materials

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1.1 Introduction

The chemistry of organosilicon polymers has reached a high level of maturity during the past century, which established a fundamental basis for their application in materials science. Because of their inorganic–organic chemical compositions, the unique dual nature of organosilicon polymers makes them an important bridge between inorganic and organic polymers and contributes to an interesting combination of properties [1–3]. According to the structural differences in the backbone, organosilicon polymers can be mainly divided into polysiloxanes (Si–O), polysilsesquioxanes (Si–O), polysilanes (Si–Si), polycarbosilanes (Si–C), and polysilazanes (Si–N) [4]. Compared to carbon, the size and electronegativity of silicon significantly affect the structural properties of the bond and endow polymeric organosilicon with unique features [5]. Polysiloxane-based materials are attractive because of their high backbone flexibility, low glass transition temperatures, good thermal and oxidative stability, high gas permeability, excellent dielectric properties, and biocompatibility [6]. Polysilsesquioxane-based materials, mostly referred to as polyhedral oligomeric silsesquioxane (POSS)-based materials, demonstrate improved mechanical and thermal properties, oxidation resistance, gas permeability, reduced flammability, and antibiofouling and antibacterial properties [7]. Polysilane-based materials are characteristic of fantastic optical and electronic properties owing to delocalization of σ-electrons and conjugation along the σ-bonds of backbone [8]. Polycarbosilane-based materials can exhibit excellent thermal stability at relatively low temperature and pyrolytic properties at high temperature as well as high mechanical strength and ultralow

dielectric constant [9]. Polysilazane-based materials are best known not only for pyrrolytic properties but also for possessing some similar or preferable properties relevant to polysiloxane-based materials as a result of their isoelectronic molecular structure, such as thermal stability, low fire hazard, high mechanical resistance, and high surface energy [3].

In recent years, considerable attention has been drawn to the research of novel silicon-containing hybrid copolymers for further expansion and improvement of materials possessing specific useful properties [10]. Thanks to the fast development of polymer science, a variety of such copolymers with well-defined architectures as well as elements of selectivity and self-assembly has been reported [6, 7]. Distinguishing from pure organosilicon materials, the properties of hybrid materials include not only the sum of the individual contributions of their components but also the strong synergy created by extensive hybrid interfaces [11]. For the preparation of silicon-containing copolymers, a very popular and simple strategy is to synthesize organosilicon oligomers/polymers with reactive functionally terminated groups first by different approaches, which will be discussed in detail later. As preformed segmental components, they can go on to copolymerize with a wide range of (i) monomers via step growth [12], anionic [13], ring-opening [14], or living free radical polymerization [15, 16] or (ii) polymer blocks via coupling reaction such as click chemistry [17] and hydrosilylation [18], constructing well-defined architectures such as block [19], graft [20], and star-like [21] copolymers. The significant advantages of the silicon-containing copolymers are their flexible chemistry, which manifests as a wide selection of substituents on the silicon atom of the backbone, controlled molecular weight of copolymers, and tailor-designed backbone composition, implementing the facile tunability of specific material properties [6].

Organosilicon polymers with versatile properties hold great interest for a wide range of potential applications including biomaterials [22], functional coatings [23], electronic and photic devices [24], catalysts [25], ceramics [26], membranes [27], additives, and modifiers [28]. More details on this topic will be discussed later. There is no doubt that their integration with organic polymers can further enlarge the compatibility for an expansion in breadth as well as in depth of utilitarian scope. A myriad of literature has proved the emergence of quite a few new applications such as nanostructured self-assemblies [29], shape memory materials [30], and 3D printing devices [31], which will be discussed in detail in Chapters 4, 5, and 10 respectively.

1.2 Synthesis of Polymeric Organosilicon Materials

The synthetic strategies for polymeric organosilicon have been diverse and mature with the development over the past century [1–3]. Because of the presence of silica in nature, the monomers for polymeric organosilicon are obtained upon a synthetic route. Silanes have the general formula $R_{4-n}SiX_n$, where X is the reactive groups having Cl, –OR, –OOCR, and $–NR_2$ as the most fundamental precursors for organosilicon polymerization. They can be produced by (i) direct reaction of an organic compound with silicon at elevated temperature;

(ii) chlorination of silicon and a subsequent substitution reaction by organic groups with organometallic reagents such as organolithium compounds, Grignard reagents, and organic zinc compounds; or (iii) transformation of silicon into silyl hydrides and a subsequent addition to multiple bonds in a hydrosilylation process [32]. Notably, hydrosilylation is a characteristic reaction in organosilicon chemistry and has been utilized as a prevailing approach to binding organic groups and silicon moieties [33]. Starting from functional silanes, methods for different kinds of polymeric organosilicon will be discussed in this section. In view that there are considerably more research directed toward polysiloxanes and polysilsesquioxanes (especially POSS), these two classes are emphasized, although others also receive a lot of attention from organosilicon chemists. In addition, given that this book focuses on the utilization of polymeric organosilicon in copolymers, methods bringing functionalization of chain ends will be highlighted.

1.2.1 Polysiloxanes

Polysiloxanes having the general formula $(-R_2Si-O-)_n$, also termed as silicone polymers or polyorganosiloxanes, are composed of a backbone with alternate silicon and oxygen atoms while two organic substituents are linked to each silicon atom. The general route to polysiloxanes from monomers consists of two steps: (i) hydrolytic polycondensation of the bifunctional silane precursors resulting in a mixture of linear and cyclic oligomers and (ii) transformation of the oligomers into high-molecular-weight polymers either by polycondensation of the short-chain linear oligomers or by ring-opening polymerization of the cyclic oligomers. Such process is mostly based on dimethyldichlorosilane (DDS) and puts out polydimethylsiloxane (PDMS), which are the best-known silicone polymers [34].

As for polycondensation routes, linear oligomers with silanol end group are reactive toward a wide range of silyl-functional groups such as –SiH, –SiCl, –SiOR, –SiOOCR, and –SiNR$_2$ and hence can be polymerized via either homofunctional or heterofunctional condensation when the resultant polymers are conferred with the potential of terminal functionalization. However, the application of polycondensation routes in academic and industry is limited for issues such as size dependence and side reactions [3]. In contrast, ring-opening polymerization of cyclic oligomers permits the synthesis of high-molecular-weight polysiloxanes with better selectivity and precision, playing an important role in the preparation of reactive functionally terminated silicone oligomers including monofunctional silicone oligomers and α,ω-reactive difunctionally terminated (telechelic) silicone oligomers, which are very critical starting materials for a wide range of silicone copolymers [35].

The monofunctional silicone oligomers are mostly synthesized through anionic polymerization of hexamethylcyclotrisiloxane (D$_3$) initiated by lithium silanolate in the presence of an activator such as tetrahydrofuran (THF) or diglyme (Figure 1.1), and the functional group is introduced during the deactivation of the silanolate ion using a functional chlorosilane [10]. The preparation of telechelic silicone oligomers, which are more commonly used in
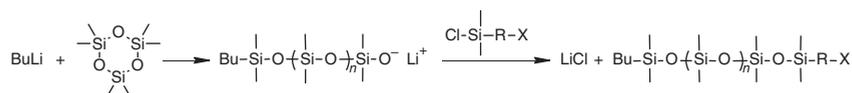
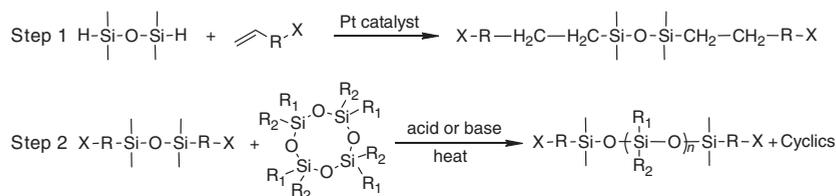**Figure 1.1** Synthetic scheme for monofunctional silicone oligomers.

Figure 1.2 Synthetic scheme for telechelic silicone oligomers.

copolymerization, generally adopts acid- or base-catalyzed ring-chain equili-bration or redistribution reactions, as shown in Figure 1.2. Based on the nature and the reactivity of the functional end groups, strong acids such as sulfuric acid, trichloroacetic acid, and sulfonic acid or strong bases such as sodium hydroxide, potassium hydroxide, and quaternary ammonium hydroxide can be selected as catalysts. With proper temperature ranging from 50 to 100 °C, the polymerization leads to a complex equilibria between cyclic and open-chain populations, and the yield is dependent on the initial concentration of mono-mer as well as the size and polarity of organic substituents at silicon atoms [36]. The introduction of end blockers in the initiation of the ring-opening polym-erization (ROP) routes is also significant to both the precise control over poly-mer molecular weight and the functionalization of chain ends. The end blockers can be classified as (i) siloxane oligomers with reactive functional groups (X) such as chlorine, hydroxy, and alkoxy directly attached to the terminal silicon atoms (Si–X termination) and (ii) siloxane oligomers with a short hydrocarbon bridges (R) between them (Si–R–X termination), but actually, the latter kind turns out to be preferable for copolymerization. Si–X end blockers can simply be obtained by hydrolysis of bifunctional silanes, whereas Si–R–X end blockers need another step of hydrosilylation reaction between Si–H-terminated sili-cone oligomers and vinyl or allyl terminated functional organic reagents. Although Si–X end blockers have higher reactivities for subsequent copolym-erization compared to their Si–R–X counterparts, the formation of Si–O–C linkages between polysiloxanes and organic segments are so susceptible to hydrolysis under acidic or basic conditions as to become an unignorable disad-vantage, while the insertion of hydrocarbon bridges (R) to be Si–R–X end blockers can effectively avoid this problem [6]. By the use of various cyclic oli-gomers such as octamethylcyclotetrasiloxane (D_4) [37], diphenylsiloxane [38], methylphenylsiloxane [39], and methyltrifluoropropylsiloxane [40], polysilox-anes terminated with functional groups have been widely reported, which are great candidates for the preparation of silicone-containing hybrid copolymers

and hold unlimited potential for extensive applications. A thorough discussion about this topic is available in Chapter 2.

1.2.2 Polysilsesquioxanes

Polysilsesquioxanes have a structure with empirical formula $RSiO_{3/2}$, where R can be a hydrogen atom or an organic moiety and are generally prepared by precursors of formula $RSiX_3$ via hydrolysis and subsequent polycondensation, where X is a group, such as chlorine and alkoxy, prone to hydrolysis in the presence of acid or base catalysts and R is a hydrolytically stable organic moiety [1]. A combination of multiple factors including types of substituents at silicon atoms, concentration of initial monomers and water, catalyst, temperature, and solvent will determine the structures of the resultant polymeric silsesquioxanes varying from oligomeric cages to ordered ladder structures to three-dimensional network, as shown in Figure 1.3, and a great concentration has been cast on the area of corresponding polysilsesquioxanes [29, 41, 42]. Besides, rapid growth has also been witnessed for bridged polysilsesquioxanes, whose silicon atoms are linked by their organic moiety additionally. The main difference of bridged polysilsesquioxanes from others lies at the precursors, which possess more than one functional moiety $-Si(OR)_3$ and are thus active for sol–gel processing to construct more attractive Si–O–Si networks [43]. Among all these structure, cage-like POSS is the hottest compound for investigation. POSS of formula $(RSiO_{1.5})_n$, where n is an even integer larger than 4 and R is an active or inert organic group, is considered as the smallest silica particle with a definite nanostructure that can
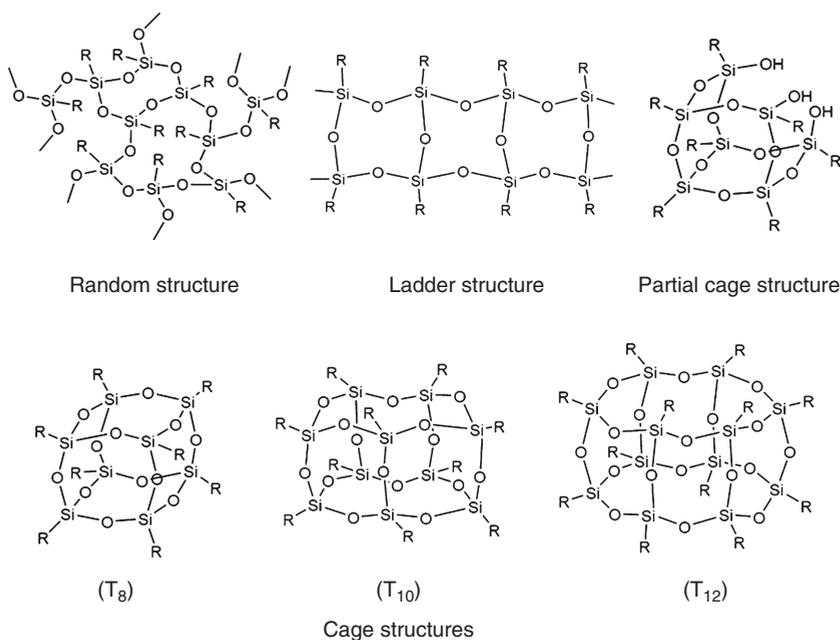

Random structure   Ladder structure   Partial cage structure

(T_8) (T_{10}) (T_{12})

Cage structures

Figure 1.3 Various structures of polysilsesquioxanes.

be incorporated into polymer matrices to fabricate a wide range of novel hybrid materials with promising properties [44].

As a result of the stability of the Si_4O_4 ring structure, the spontaneous formation of T_8 POSS is preferential over other cubic species such as T_{10} and T_{12} and offers them a huge advantage in the synthesis to achieve functional T_8 POSS molecules by flexible approaches (Figure 1.4). Thus, in the past few decades, tremendous efforts have been devoted to the development of octasilsesquioxane (T_8 POSS). Quite a number of T_8 POSS species have been successfully prepared from hydrolysis and condensation reactions of trifunctional chlorosilanes or alkoxysilanes. Together with the substitution of functional groups at one or more of the corner silicon atoms or the modification of functional groups, an abundant source of T_8 POSS derivatives from the existing T_8 core are provided. In most cases, T_8 POSS molecules bear one reactive group for further modification, grafting or polymerization and seven unreactive groups for stability, solubility, and compatibility known as monofunctional POSS (T_8R_7R'), or eight reactive groups of the same kind named as octafunctional POSS (T_8R_8). Meanwhile, compounds such as $T_8R_6R'_2$, $T_8R_6R'R''$, $T_8R_5R'_3$, and $T_8R_4R'_4$ obtained by chemical modification have also come into notice in recent years, largely expanding the catalog of POSS molecules. However, it is noteworthy that the synthetic routes toward POSS directly from trifunctional chlorosilanes or alkoxysilanes actually produce a mixture of products and often leads to long reaction time and low yield as inherent downsides. Thus, optimization of reaction conditions is still an interesting point of research. Besides, the issue of stability of the POSS core in the process of organic modification, that is, the cleavage
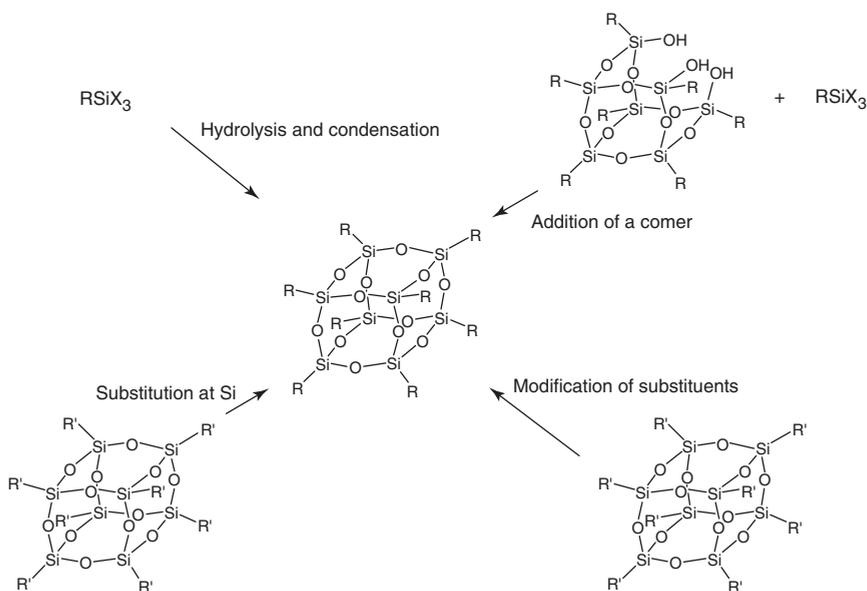
Figure 1.4 Synthetic schemes for functional POSS. Source: Cordes et al. 2010 [45]. Reproduced with permission of American Chemical Society.

of Si—O bonds, will also cause some problems. Instead, the simplicity of corner-capping reactions makes them a preferred method for the functionalization of POSS, especially monofunctional POSS. In this approach, corner-truncated cube species $R_7Si_7O_9(OH)_3$ (T_7) are firstly synthesized by incomplete condensation of trifunctional organosilanes or hydrolytic removal of one silicon atom from a stable T_8 POSS molecule, succeeded by addition of a capping agent such as chlorosilane or alkoxysilane to T_7 where a variety of novel T_8 POSS molecules are produced [45, 46].

Based on functionalized POSS molecules, well-defined POSS-containing hybrid polymers with different architectures including telechelic polymers, block copolymers, and star-shaped polymers can be developed by advanced polymer synthetic approaches such as anionic polymerization, living radical polymerization, and click chemistry, where POSS molecules function as monomers, ROP initiators, atom transfer radical polymerization (ATRP) initiators, reversible addition fragmentation chain transfer (RAFT) agents, or are directly used to couple with the end group of polymer chains [7]. Chapter 3 will give a discussion in depth about this topic.

1.2.3 Other Polymeric Organosilicon Materials

Except for polysiloxanes and polysilsesquioxanes, a relatively new class of polymeric organosilicon materials such as polysilanes, polycarbosilanes, and polysilazanes also open many interesting possibilities for hybrid materials.

Polysilanes are composed of a backbone of catenating silicon atoms, which typically bear two organic side chains each. The most commonly used method to prepare polysilanes is Wurtz-type reductive coupling of dichlorodiorganosilanes under the catalysis of alkali metals, as shown in Figure 1.5. As the reactions are carried out at a high temperature and strongly reducing environment so that the functional substituents at silicon atoms are limited to alkyl, aryl, and fluoroalkyl groups or those are well protected that can withstand such conditions, post-polymerization functionalization is required. Meanwhile, factors such as temperature, solvent, and reductant have significant impact on the reaction as well. It is interesting that in many cases, especially when the side chains lack
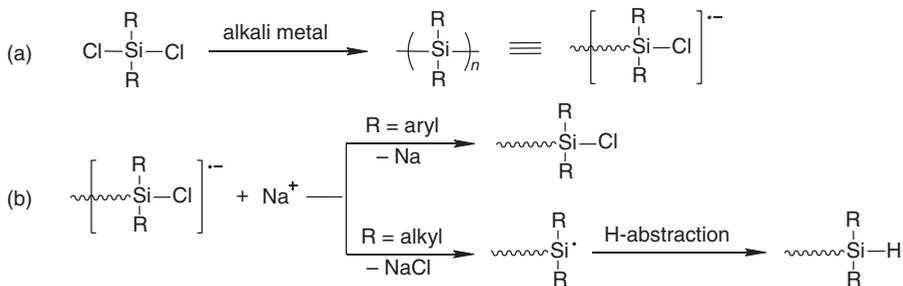
Figure 1.5 (a) Synthesis of polysilanes via Wurtz-type reductive coupling polymerization and (b) side chain-dependent termination.

radical-stabilizing substituents, hydrogen-terminated chains are obtained with the hydrogen atom extracted from a solvent such as toluene or xylene, offering great possibilities of functionalizing polysilane chain ends for further copolymerization with organic polymers [47]. In addition, given the disadvantages of Wurtz-type reductive-coupling reaction such as polymodality and poor molecular weight distributions resulting from end-biting and back-biting of polysilane chains, alternative approaches including ring-opening polymerization of cyclotetrasilanes [48], catalytic disproportionation of alkoxydisilanes [49], anionic polymerization of masked disilenes [50], and dehydrocoupling polymerization of primary silanes ($RSiH_3$) catalyzed by transition metal [51] are also available to prepare polysilanes.

Polycarbosilanes usually refer to a class of polymers characterized as difunctional organic groups in the backbone to bridge the silicon atoms, which are conventionally converted by polysilanes explicitly or implicitly upon thermolysis, namely Yajima strategy. Besides, more direct routes to prepare polycarbosilanes without polysilane intermediates have been developed, too. One of the approaches undergoing intensive investigation is ring-opening polymerization. Structures such as 1,3-disilacyclobutane, 1-silacyclopent-3-ene, 3,4-benzosilacyclopentene, silacyclobutane, 2,3-benzosilacyclobutene, and silicon-bridged ferrocenophanes can be premodified with required organic substitutions on silicon atoms and then act as a variety of monomers for corresponding polycarbosilanes in the presence of an appropriate catalyst, as shown in Figure 1.6 [52]. Another method involving coupling reaction between halogen atoms and metal atoms is also commonly used. In early years, such polycarbosilanes are derived from chlorosilanes together with alkyl halides or solely chlorosilanes bearing alkyl chloride substituents on silicon atoms via Wurtz–Fittig coupling with sodium or potassium, while in recent years, the use of Grignard and organolithium reagents has come into mainstream gradually [3]. Moreover, various reactions including dehydropolycondensation coupling of hydrogenosilanes [53] and hydrosilylation of hydrogen silanes with alkenes and alkynes or vinylhydrogenosilanes alone [54] have been reported for the elaboration of polycarbosilanes, too.

Meanwhile, cyclolinear polycarbosilanes have attracted some attention as an emerging group of organosilicon polymers with novel beads-on-a-string structure. They are mostly prepared from 1,3-disilacyclobutane with alkylene or
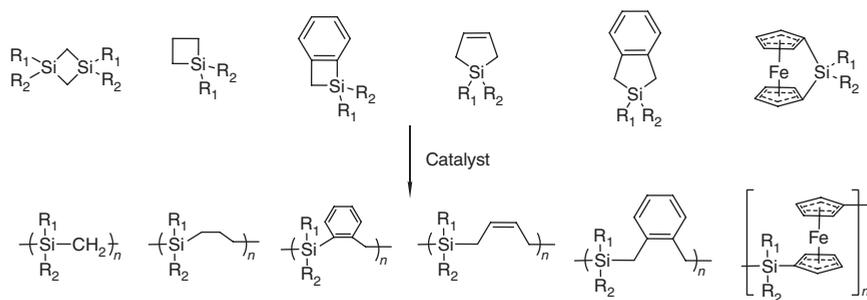

Figure 1.6 Various monomers for ROP of polycarbosilanes.

halogen groups, which are reactive for acyclic diene metathesis polymerization (ADMET) or Grignard coupling reactions, respectively, and polymerized into polymeric organosilicon materials with a general formula as $\{-[RSi(CH_2)_2SiR]-Y-\}_n$, where R and Y can be different organic groups such as alkyl and aryl. Interestingly, as 1,3-disilacyclobutane derivatives have proved to be useful monomers for conventional linear polycarbosilanes, the strained rings in the backbone of such cyclolinear polymers are naturally latent cross-linking sites that can form network polycarbosilanes under suitable conditions [9].

Polysilazanes, as an analog to polysiloxanes, whose oxygen atoms in the main chain are replaced by nitrogen atoms, are also an unneglectable part of organosilicon polymers, although their preparative methods are less well explored. There are mainly two classes of routes to polysilazanes: one is polycondensation of functional silanes and amines and the other is ionic ring-opening polymerization of cyclosilazanes (Figure 1.7). Ammonolysis or aminolysis reactions of dihalogenosilanes with ammonia or amine are the most commonly used methods in the former case. However, these reactions usually yield a complex mixture of linear and cyclic oligomers, and thus some chemists have turned to the latter routes for better control of the polymerization nowadays. Cyclodisilazanes, cyclotrisilazanes, and cyclotetrasilazanes synthesized from amine and dichlorosilane have exhibited potential for ionic ring-opening polymerization in a similar mechanism to polysiloxanes. Yet, the effect of steric hindrance resulting from nitrogen substituent of cyclosilazanes is an extra factor that needs to be taken care of, which may reduce the accessibility of silicon atoms and decrease the polymerizability [55].

This section only offers a primary summary for the synthetic strategies of several representative kinds of organosilicon polymers. Beyond that, novel structures such as hyperbranched polymers [56], dendrimers [57], and conjugated organosilicon [58] are also remarkable while several literature studies specializing in this topic are already available for extensive reading.
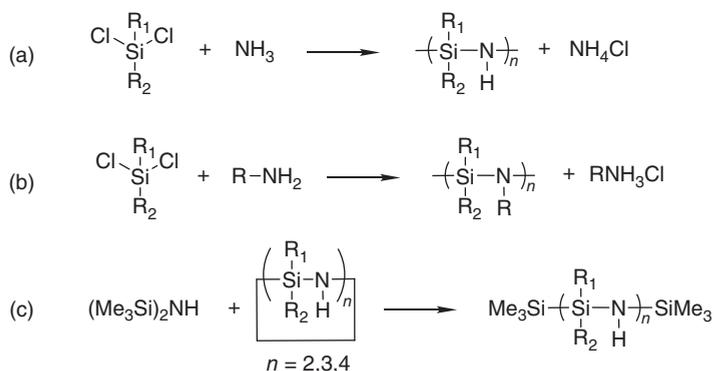
Figure 1.7 Synthetic schemes for polysilazanes including polycondensation of dichlorosilanes with (a) ammonia or (b) amino, and (c) ring-opening polymerization of cyclosilazanes.
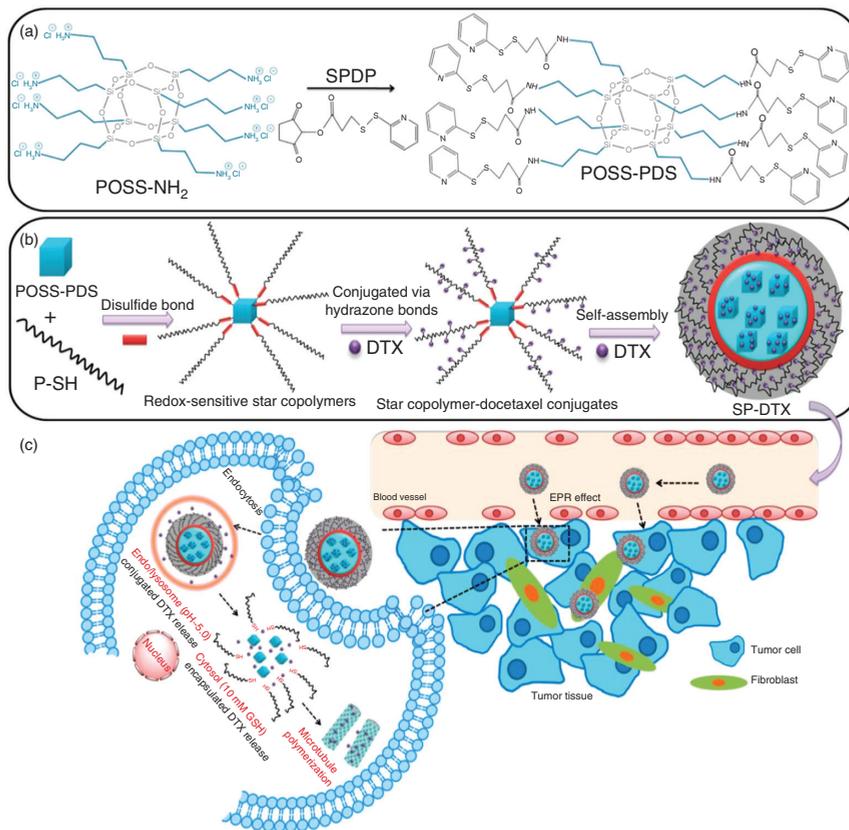
1.3 Applications

The evolution of synthesis established a foundation for the extensive applications of various polymeric organosilicon materials, and the characteristic composition of main chain gives each kind of polymers their own unique properties as mentioned earlier and make them advantageous in very different fields. Owning to the excellent photophysical and electronic properties, polysilanes have been mainly investigated as optoelectronic materials such as photoresists [59], photoinitiators [60], photoconductor [61], nonlinear optical materials [62], and materials for organic electroluminescent devices [63]. Meanwhile, considerable progress has been achieved for polycarbosilanes and polysilazanes as ceramic precursors on the basis of their pyrolytic properties, which can potentially generate high-performance nonoxide ceramics known as silicon carbide (SiC) and nitride (Si_3N_4) [64]. Moreover, the maturity and facility of the preparative methods for Si–O–Si-based organosilicon materials, including polysiloxanes and polysilsesquioxanes, have significantly promoted the understanding of their structure–property relationships and further contributed to the prosperity of applications [3]. With regard to polysiloxanes, more commonly known as silicone and referring to PDMS in most cases, with good thermal and oxidative stability as well other useful properties, they have become the earliest materials gaining widespread commercial applications such as elastomers [65], sealants [66], lubricants [67], surfactants [68], coatings [23], thermal and electrical insulation materials [69], and biomedical devices [70]. As for polysilsesquioxanes, distinguished by their nanostructure, rigidity, and thermal stability, a lot of research has been devoted to the incorporation of POSS moieties into polymers by blending or copolymerization to create polymer nanocomposite with reinforced properties, promising to be applied in nanomedicine [71], catalysts [72], electronic devices [73], military and aerospace fields [74], etc. In view that there is a myriad of applications for the latter two kinds of organosilicon hybrid materials, this section will introduce three hot fields specifically, i.e. biomaterials, optical and electronic materials, and surface modification.

1.3.1 Biomaterials

Both PDMS and POSS exhibit physiological inertness, low toxicity, good thermal and oxidative stability, excellent mechanical and viscoelastic properties, and high gas permeability provided by Si—O bond in the structure, which makes them suitable for biomedical application. PDMS is a potential candidate for implantable biomedical devices including blood pumps, cardiac pacemaker leads, mammary prostheses, replacement esophagus, maxillofacial reconstruction, finger joints, contact lenses, and catheters [70]. For example, Hao et al. prepared a kind of macromonomers from octamethylcyclotetrasiloxane (D_4) and 2,4,6,8-tetramethylcyclotetrasiloxane (D_4H) via ring-opening polymerization and subsequent hydrosilylation of Si–H with allyl methacrylate, which were injectable and curable under irradiation of blue light in the presence of a photoinitiator to form a soft gel *in situ* within five minutes, which is promising to be used as intraocular lens in human eyes in the place of hardened natural lens for

restoring eyes' ability [75]. Simmons et al. developed a kind of drug-eluting stents loaded with dexamethasone acetate (DexA) from PDMS-based polyurethane, which consisted of hard segments of 4,4′-methylenediphenyl diisocyanate (MDI) and 1,4-butanediol (BDO) and mixed soft segments of PDMS and polyhexamethylene (PHMO) in the ratio of 80 : 20. The materials demonstrated excellent long-term biostability and may be used as a delivery vehicle of therapeutic agents for drug-controlled release *in vivo* [76]. Besides, soft lithography using PDMS allows one to fabricate complex microfluidic devices easily [77]. Together with optical transparent properties suitable for detection, PDMS-based microfluidic devices hold great interest in lab-on-a-chip (LOC) systems for biochemical analysis and point-of-care (POC) disease diagnosis. Li et al. attempted to combine the high performance in the flow control for PDMS-based microfluidic devices and the ease of immobilizing biosensors on a chip for paper-based microfluidic devices and reported a versatile and cost-effective PDMS/paper hybrid microfluidic device integrated with loop-mediated isothermal amplification (LAMP) reaction to achieve rapid, sensitive, and instrument-free detection of meningitis-causing bacteria [78].

Even more effort has been focused on POSS as it has been considered as a next-generation material in several biological fields [79]. For example, Huang et al. developed a kind of POSS-based nanomedicine with pH and reduction dual responsiveness, as shown in Figure 1.8. Amphiphilic star-shaped polymers were synthesized by grafting semitelechelic *N*-(2-hydroxypropyl) methacrylamide (HPMA) copolymers to a POSS rigid core through reductively degradable disulfide bond. The hydrophobic drug docetaxel (DTX) was either attached to the grafts by pH-sensitive hydrazone bonds or encapsulated into the POSS core, ensuring high drug loading capacity. The final conjugates could self-assemble into nanoparticles and release DTX under acidic lysosomal and reducing cytoplasmic environments, which are usually generated by tumor tissues and thus open the possibility of an efficient approach to transport hydrophobic drugs for cancer therapy [80]. Except for drug delivery, gene delivery has also become a hot topic for emerging gene therapy. Star-shaped block polymers with a cationic poly(2-dimethylamino) ethyl methacrylate (PDMAEMA) shell and a zwitterionic poly[*N*-(3(methacryloylamino) propyl)-*N,N*-dimethyl-*N*-(3-sulfopropyl) ammonium hydroxide] (PMPDSAH) corona grafting from a POSS-cored initiator through atomic transfer radical copolymerization were reported by Liu et al. The copolymers could self-assemble into core-shell-corona micelles in aqueous solutions, during which anticancer drug doxorubicin (DOX) and tumor-suppressing gene *p53* were encapsulated benefitting from the strong DNA condensation ability of PDMAEMA and the hydrophobicity of POSS. Meanwhile, the micelles were stabilized by antifouling PMPDSAH in serum environment, which could restrain the production of polymer-specific antibodies and thus prolong their retention time *in vivo*. The micelles showed good drug and gene loading capacity, high gene transfection efficiency, reduced bovine serum albumin (BSA) protein absorption *in vitro*, and result in high tumor cell apoptosis in mice model, which were promising to be used for further clinical applications [81]. As we can see, the self-assembly of POSS into ordered nanostructures plays a significant role in their applications, and this topic will be discussed with a full

Figure 1.8 Application of POSS in drug delivery. (a) Synthesis procedure of octa-functional POSS. (b) Fabrication of drug-loaded POSS nanoparticles. (c) Illustration of tumor accumulation and intracellular trafficking pathway of POSS nanoparticles. Source: Yang et al. 2016 [80]. Reproduced with permission of American Chemical Society.

illustration in Chapter 4. In addition, Chen et al. used amino-modified POSS to link on the surface of upconversion nanoparticles (UCNPs) via simple addition reaction and achieve a transfer from hydrophobicity to hydrophilicity for UCNPs while their high-size monodispersity was well preserved. Thanks to the low cytotoxicity and excellent biocompatibility of POSS, the POSS–UCNPs displayed good performance for both *in vitro* cell imaging and *in vivo* small animal imaging [82]. Besides, Lu et al. prepared a series of POSS–polyethylene glycol (PEG) hybrid hydrogels by covalently grafting POSS into tetra-arm PEG and further cross-linked by matrix metalloproteinase (MMP)-degradable peptide both via Michael-type addition reaction between thiol group and maleimide group. Such biodegradable hydrogels gained higher mechanical properties, lower equilibrium swelling ratio, and tunable degradation rate because of the incorporation of POSS, having the potential to be used as a tissue-engineering scaffold [83].

1.3.2 Optical and Electronic Materials

Modifications of side or end groups of polysiloxanes and POSS vertex groups are extensively explored in order to give access to new applications. Their derivatives with unique optical or electronic properties are just a manifestation. Polysiloxanes bearing liquid crystalline groups via hydrosilylation is mostly an important family of polysiloxanes. Among them, liquid crystalline elastomers (LCEs) have attracted significant attention because of their reversible anisotropic dimensional shape responses to applied stimuli, which can dramatically impact the microscopic orders or molecular structures of uniaxially aligned liquid crystal mesogens and further change the macroscopic shapes of the whole LCE materials, opening the prospect for applications such as actuators and sensors [84]. For example, Yang et al. reported multistimuli-responsive LCE composite films prepared from a mixture of poly(methylhydrosiloxane) (PMHS), vinyl-terminated side-on azobenzene-containing mesogen A44 V6, vinyl-terminated side-on mesogen V444, cross-linker 11UB, Pt catalyst, and single-walled carbon nanotubes (SWCNTs). The composites integrated the thermal-induced liquid crystal (LC)-to-isotropic phase transition effect of liquid crystalline, trans–cis tautomerization effect of azobenzene and photothermal effect of SWCNTs and could perform a fully reversible shrinking/expanding response toward heat or near-infrared (NIR) light stimulus, and a fully reversible bending behavior under ultraviolet (UV) irradiation, holding potential for applications of control devices, logic gate devices, etc. [85]

POSS are widely explored in their applications for photoluminescence (PL) and electroluminescence (EL) devices [7]. For example, Wang et al. developed a novel kind of eight tetraphenylethene (TPE)-modified POSS through amide condensation reaction, which was endowed with the effect of aggregation-induced emission (AIE), as shown in Figure 1.9. Their studies indicated that POSS core had superstrong self-assembly properties by organic modification and could form different morphologies in different solvents and concentrations through hydrogen bond interaction. Compared with TPE–NH$_2$, POSS–TPE exhibited enhancement in aggregate emission, monomer emission, and quantum yields in the aggregate state. With appropriate selection of solvent and concentration, the monomer emission was quenched while the aggregate emission was enhanced as a result of the aggregation-induced restriction of intramolecular rotation in combination with the increasing π–π stacking interactions of TPE units. Because of strong noncovalent interaction forces between POSS–TPE and aromatic molecules, fast detection of methamphetamine and ketamine was performed successfully by quenching aggregate emission, suggesting that POSS–TPE was hopeful in the application of a new AIE chemosensor [86]. Cheng et al. studied a POSS derivative containing eight π-conjugated chromophores 3,6-dipyrenylcarbazole (DPCz) obtained via hydrosilylation reaction as electroluminescence materials for nondoped blue organic light-emitting diode (OLED) devices. POSS–DPCz displayed a sterically bulky three-dimensional structure, which could effectively inhibit the crystallization behavior of emissive units DPCz and restrict the motion of structural perturbation, conductive to enhance the color
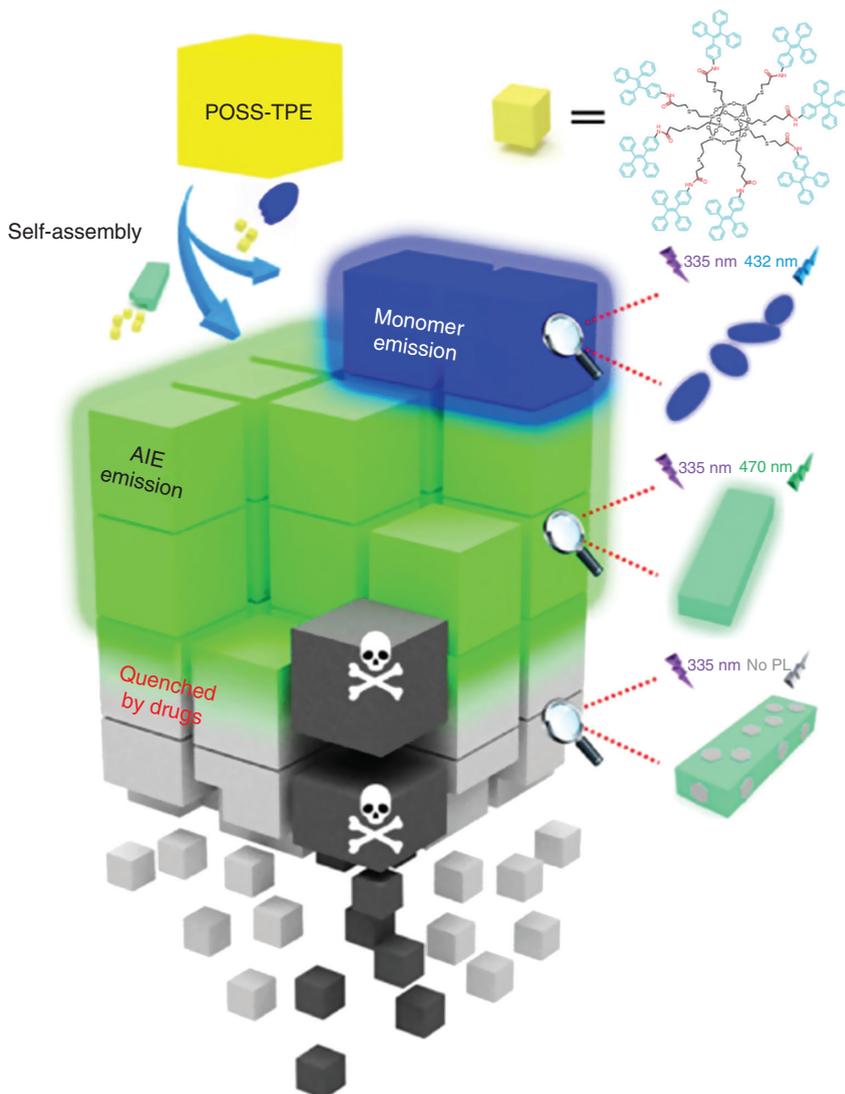
Figure 1.9 Application of POSS for photoluminescence. Source: An et al. [86].

purity and stability, emission quantum yield, and thermal stability of the materials. As a result, the luminous efficiency and maximum brightness of the POSS–DPCz device are almost two times higher than that of the control DPCz-based device, proving it to be a possible route to fabricate practical OLED devices with improved optoelectronic performance [87]. Moreover, POSS are also available for the application in proton exchange membranes (PEMs) of fuel cells. Gong et al. incorporated double-decker silsesquioxane (DDSQ), a difunctional POSS unit, into the backbone of linear sulfonated polyimides (SPIs) with advantages such as enhanced oxidative and hydrolytic stabilities, low swelling ratio combined with high water uptake, adequate thermal stability and mechanical properties,

and low methanol permeability over SPI alone. Meanwhile, compared with other POSS hybrid membranes fabricated by direct blending or cross-linking methods, POSS in the SPI main chain show more uniform dispersion and increase the confined bound water molecules within the formation of continuous proton transformation channels, thereby increasing proton conductivity [88]. Besides, POSS have been loaded in some LC media to optimize the electro-optical (E-O) performance of LC systems. For example, POSS is considered as one of the promising candidates for the formation of vertical alignment (VA) of LC because of some new E-O properties such as memory effect, frequency modulation response, and low driving voltage. Jeong et al. synthesized a cyanobiphenyl monosubstituted POSS giant molecule connected by a flexible alkyl chain, called POSS–CBP$_1$, to improve the compatibility and interaction of POSS with LC media. POSS–CBP$_1$ showed an excellent dispersion in nematic (N) LC media and could gradually diffuse onto the glass substrate. Owing that the interaction between POSS and substrate was much higher than that between cyanobiphenyl moieties and substrate, the molecular orientation of POSS–CBP$_1$ was perpendicular to the surface and formed homeotropic alignment, which should lead to a clear dark state in the absence of an electric field and was proved by polarized optical microscopy (POM) images. Also, the interaction between POSS–CBP$_1$ and substrate was strong enough for the VA of LC to remain stable under thermal fluctuations, making such materials potential for electro-optical applications, e.g. LC displays (LCD) [89]. POSS-based high-performance organic optoelectronic materials have been recognized as the most promising materials in both academic research and industry applications, and Chapter 8 will delve into this topic.

1.3.3 Surface Modification

The versatile properties of PDMS- and POSS-based materials including excellent mechanical properties, thermal stability, oxidation resistance, reduced flammability, hydrophobicity, low surface energy, and so forth provide them broad possibilities in the application of surface modification of materials and tremendous endeavor has been devoted to achieve accomplishing various functions such as anticorrosion, antifouling, self-cleaning, flame resistance, antireflection, anti-icing, and antifogging [23, 90].

Metal corrosion is a challenging problem in the twenty-first century as most common applications in everyday human life are virtually based on metals. PDMS is an important category of anticorrosion coatings for pure and alloyed metals such as magnesium, aluminum, iron, and copper because of its hydrophobicity, chemical inertness, easy modification and processing, and environmental friendliness. For example, Guo et al. fabricated PDMS–titania (TiO$_2$) nanocomposite coating prepared from a mixture of hydroxyl-terminated PDMS, TiO$_2$ nanoparticles, curing agent tetraethoxysilane (TEOS), and catalyst dibutyltin dilaurate (DBTDL) via spin-coating method on aluminum alloys AA 2024. The good hydrophobicity and structure compactness of PDMS could delay the rate of penetration of water and corrosive ions into the substrate and obstruct the flow of the current to protect the metal, while the incorporation of TiO$_2$ nanoparticles

could produce a micro–nano rough structure with a larger amount of air to block the entry of water, which compensated the negative effect caused by some existing microspores and microcracks in the organic coatings and improved the durability of corrosion resistance. The results demonstrated that the coating still had a protective effect on the metal after 40 days of immersion [91]. As a class of nanoparticles, the reinforced effect of POSS was investigated by Minaee et al. in the system of polypyrrole (PPy)/POSS nanocomposite coating on a copper substrate prepared via cyclic voltammetry technique. Compared to uncoated Cu and PPy/Cu, the corrosion potential for PPy/POSS/Cu was more positive and the corrosion rate of PPy/POSS-coated Cu was lower, indicating the effective protection against copper corrosion of PPy/POSS coatings [92].

Marine biofouling formed by settlement and accumulation of microorganisms, plants, and animals on surfaces immersed in seawater is a vexing issue. The low surface energy and elastic modulus of PDMS minimize adhesion strength for fouling organisms and make them promising to be applied as antifouling coatings. For example, Zhang et al. reported a kind of PDMS-based polyurea (PDMS-PUa) synthesized from α,ω-aminopropyl-terminated PDMS and isophorone diisocyanate (IPDI), which could be reversibly cross-linked because of strong hydrogen bond interaction. In addition, antifoulant 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) was introduced into PDMS-PUa with controlled release behavior to improve the antifouling and fouling release performance because PDMS was not effective under static conditions. The resultant coatings exhibited persistent antifouling and fouling release ability for more than six months as well as excellent self-repairing, enhanced mechanical properties, and good adhesion to substrates [93]. Likewise, POSS can be utilized as antifouling materials taking advantage of their superhydrophobicity and have been increasingly investigated as potential water- or oil-repellent coatings. For example, Sun et al. deposited branched poly(ethylenimine) (PEI), silver nanoparticles (AgNPs), and fluorinated decyl POSS (F-POSS) onto cotton fabrics in turn through a simple solution-dipping method and successfully construct a novel kind of colored cotton fabrics with multiple functions. AgNPs could act as a safe dye for cotton fabrics with antibacterial properties while F-POSS could autonomously migrate to fabric surface because of low surface energy and confer superhydrophobicity for self-cleaning properties. As results showed, even damaged by plasma etching and inverted to superhydrophilic surface, such fabrics could quickly restore superhydrophobicity through rearrangement of embedded F-POSS molecules, improving the durability of cotton fabrics [94].

Flame resistance is an important feature required by materials in quite a lot of practical applications for fire safety. There have been numerous investigations focusing on the use of PDMS as a flame retardant as it can migrate to the material surface and produce a silicaceous char layer during combustion to effectively reduce the flammability of materials. For example, Dong et al. developed a novel kind of flame retardant coupling PDMS with other flame-retardant elements such as nitrogen, sulfur, and iodine, where part of methyl groups of PDMS were substituted by iodine butyl or sulfonate amino groups. The obtained

copolymer, known as (IB-N-SA) PDMS, could combine to cotton fabrics with covalent bond because of the activity group and accomplish double functions as flame retardancy and water repellence [95]. Because of the good heat resistance and thermal oxidative stability of POSS, polymer-POSS nanocomposites with improvement in fire retardance and enhancement in mechanical properties have attracted great attention. For example, Chen et al. grafted octaminopropyl POSS (oapPOSS) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) to the framework of graphene oxide (GO) through reaction of the active functional groups to develop a novel flame retardant, as shown in Figure 1.10, which was then incorporated into polypropylene (PP) matrix to prepare the flame-retarded PP nanocomposites. By the synergistic effects of three components including the barrier property of graphene sheets to prevent heat and volatile transfer, the rigid shield provided by Si–O–Si structure to improve the thermal oxidative stability, the generation of inert gas from amino group in POSS to dilute the combustible volatiles, and the catalysis of phosphorus in DOPO to promote the char formation, the flame retardancy of the PP matrix was significantly enhanced [96].

The modification and functionalization of materials with the assistance of PDMS or POSS and their derivatives to meet the requirements of applications have been a hotspot in research. A comprehensive introduction is given in Chapters 6–8.
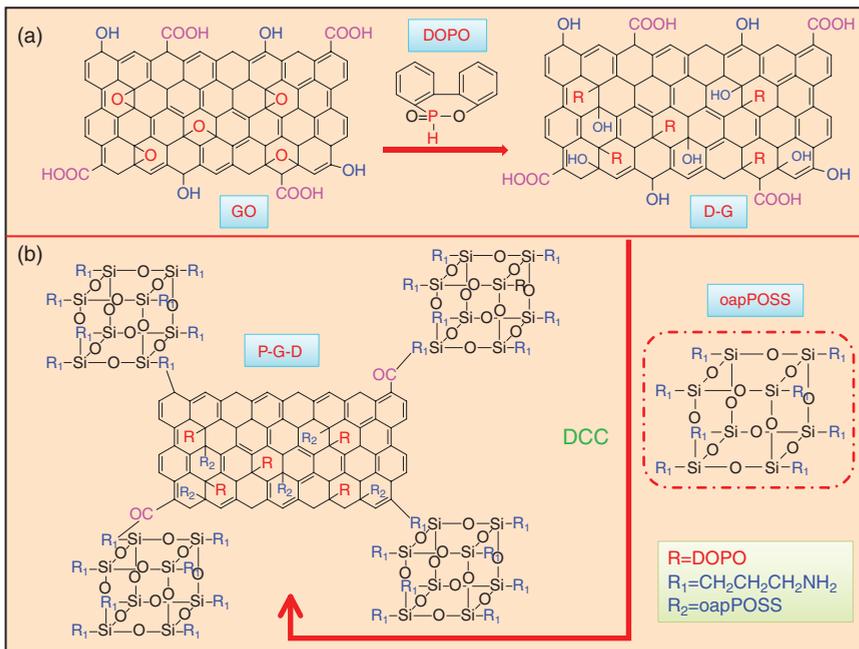
Figure 1.10 Application of POSS as flame retardant. Modification of (a) DOPO and (b) oapPOSS onto GO in turn. (DCC: N, N-dicyclohexylcarbodiimide). Source: Yuan et al. [96].

1.4   Conclusion and Outlook

The great progress of organosilicon polymer chemistry over the past few decades provides diverse synthetic approaches to produce a variety of organosilicon polymers with controlled architectures, unique properties, and broad application prospects. In particular, because of the ease of synthesis and modification of PDMS and POSS, much effort has been devoted to the investigation of polymers based on these two classes of organosilicon. Meanwhile, although there has been relatively less literature for other classes of organosilicon such as polycarbosilanes, polysilazanes, and polysilanes so far, they also hold the interest of many researchers and are considered to be materials of the future.

Nowadays, organosilicon-based materials are used almost everywhere in our life, while the high demand also becomes a powerful driving force for the perfection and expansion of organosilicon polymers in the field of fundamental research. With the advancement of polymer chemistry, silicon-containing hybrid copolymers based on reactive functionally terminated silicon-containing moieties have gained more and more attention in recent years for the intriguing combination of material properties from novel polymeric organosilicon and conventional organic polymer segments, which possess some incomparable advantages over pure organosilicon materials and open up the possibility for new applications. As this book exactly aims to offer a comprehensive and systematic overview of the latest developments in functional hybrid silicon copolymers, we hope the brief introduction of the synthesis, structure, and properties for polymeric organosilicon in this chapter can help to offer a better understanding for the design and preparation of novel silicon-containing hybrid copolymers in the following chapters.

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