

Chapter 2

Organic–Inorganic Polymer Hybrids: Synthetic Strategies and Applications

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Abstract Hybrid materials generated via the combination of functional polymers with inorganic nanostructured compounds, with the latter exhibiting size-dependent physical and chemical properties, have become a major area of research and technological development owing to the remarkable properties and multifunctionalities deriving from their nanocomposite/nanohybrid structure. In this chapter, the different fabrication routes for generating organic–inorganic polymer hybrid materials are discussed. Those include blending processes, sol–gel methods, emulsion polymerization and photopolymerization, metallosupramolecular and coordination approaches, intercalation, microwave-assisted and electrochemical synthesis, synthetic routes based on surface grafting, and finally self-assembly and block copolymer-mediated synthetic strategies. The existing versatility in materials’ design in organic–inorganic polymer hybrids, in respect to the structural, compositional, and architectural characteristics, creates new prospects for many applications in very diverse areas. In the second section of this chapter, the applicability of organic–inorganic polymer hybrids in various fields including biomedicine, sensing, environmental remediation, energy, construction, automotive and coating technologies, catalysis, and optoelectronics is reviewed.

2.1 Introduction

The modern society is facing a number of challenges related to health, sustainability, and environmental protection. Inevitably, the necessity of designing and developing new functional materials that could improve the quality of life and lead to the development of advanced technologies is of paramount importance.

During the past decades, polymer science has strongly been entering the field of organic–inorganic hybrids, aiming to combine the properties of polymers with those of inorganic components. The former include ease of processing, lightweight, flexibility, extremely high versatility in materials’ design in regard to the structural

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and architectural characteristics and consequently in materials' properties. Inorganic materials exhibit superior thermal and mechanical behavior as well as unique optical, electrical, catalytic, and magnetic properties, especially when those are characterized by nanoscale (10^{-9} m) dimensions.

The tremendous increase in the number of publications, reports, and patents appearing during the past years on the design, synthesis, properties, and applications of organic–inorganic polymer hybrids demonstrates the high interest of the scientific community and of the industrial sector toward this rapidly emerging field, as shown by the number of publications from 2000 onwards on “polymer hybrids” and “polymer composites” (Source: Web of Science, June 2014) exceeding 85,000.

The advancements in the synthetic methods employed for developing such materials as well as in the characterization techniques and computational tools have enabled the fine-tuning of the materials' structural and compositional characteristics resulting—in many cases in a predictable manner—in the desirable behavior, property, or response.

Organic–inorganic polymer hybrids based on combinations of polymers, with metals, ceramics, or both, have been prepared by a variety of synthetic methods and have been exploited in different applications. The use of an appropriate polymer coating provides solubility and high colloidal stability of the inorganic nanocomponents in organic or aqueous solvents, thus facilitating their low-temperature, low-cost processing, whereas it enables their applicability in certain areas requiring the use of nanoparticles with long-term colloidal stability in solution (e.g., magnetic nanoparticles destined for use as contrast enhancement agents in magnetic resonance imaging (MRI) or ceramic-based nanocontainers employed as drug delivery systems). Most importantly, the flexibility in materials' design and the high versatility in existing synthetic methodologies that can be employed for the preparation of a targeted polymer-based hybrid system enables the development of novel multifunctional materials with new characteristics and functions that derive from the combination of the properties of the organic and the inorganic components, as well as from additional synergistic effects that allow the tailoring and fine-tuning of the materials' properties.

The present chapter aims in providing a general overview of the different synthetic methods developed toward the preparation of organic–inorganic polymer-based nanohybrids/nanocomposites and of their applications in various fields including biomedicine, sensing, energy, catalysis, optoelectronics, environmental remediation, and finally in construction, automotive, and coating technologies.

2.2 Synthetic Strategies for the Preparation of Organic–Inorganic Polymer Hybrids

Numerous experimental methodologies have been developed for synthesizing polymer–inorganic hybrids. In this section, the different synthetic approaches used toward this purpose are reviewed (Luan et al. 2012; Jeon and Baek 2010). First, blending methods are discussed, followed by the sol–gel synthetic approach that

has been used for the synthesis of polymer–metal oxide nanocomposites focusing mostly on polymer–silica systems. Subsequently, emulsion polymerization is presented with particular emphasis in miniemulsion processes that have been proved to be highly promising and effective in the preparation of polymer-based hybrid materials. Other synthetic strategies are also briefly discussed such as metallosupramolecular polymerization, photopolymerization, intercalation, electrochemical synthesis, and microwave irradiation. The surface grafting methods are presented in more detail including the “grafting from,” “grafting to,” and the “grafting through” approaches. Finally, self-assembly techniques and block copolymer-mediated synthetic methods are discussed.

2.2.1 Blending

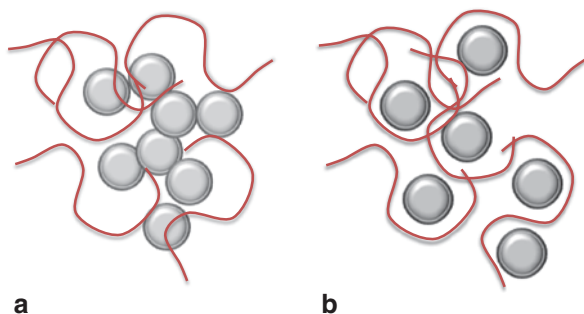
2.2.1.1 Solution and Melt Blending

One of the simplest methods for producing polymer–inorganic nanocomposites is solution blending. In this method, a polymer solution is generated first by dissolving the polymeric material in a good solvent followed by the introduction of the inorganic nanoparticulates. The dispersion of the latter is accomplished via mechanical stirring or ultrasonication. The resulting polymer-based nanocomposites can then be easily processed to generate solid-state nanocomposites upon solvent evaporation. Although this method for preparing polymer-based hybrids is simple and of low cost, it suffers from nanoparticle aggregation due to the strong tendency of the inorganic nanoparticles to agglomerate so as to reduce their surface energy. Such nanoparticle agglomeration phenomena lead to materials characterized with high inhomogeneity and inferior physical, chemical, and mechanical properties compared to their counterparts, resulting from the ineffective mixing of the organic and the inorganic components.

For this reason, and to ensure good intermixing between materials with different cohesion energies, the inorganic nanoparticles are usually introduced in the polymer solution after being functionalized with either organic molecules or macromolecules to ensure good solubility and mixing at a molecular level with the polymer matrix as schematically depicted in Fig. 2.1.

Melt blending does not require the use of organic solvents, thus rendering it more environmentally friendly compared to the solution blending method. Moreover, it is performed under similar processing conditions as those commonly used for the parent polymers, i.e., thermal treatment and shearing at temperatures above the polymer-softening point. During this process, the polymer is present in its melt state when mixed with the inorganic nanofillers. Melt blending has been commonly introduced in the synthesis of polymer-based nanocomposites. Many examples describe the synthesis of polymer–silica systems by using the melt-blending technique, but there are also numerous literature reports describing the fabrication of polymer-based hybrids in which the polymers are combined with different types of

Fig. 2.1 Polymer–inorganic nanocomposite material in which **a** nanoparticle agglomeration takes place and **b** nanoparticles are well dispersed within the polymer matrix



inorganic nanoparticles including nanoclays (Albdiry et al. 2013), silica (Lai et al. 2013; Reddy and Das 2005), metal nanoparticles (MNP) (Xia et al. 2006), semiconducting quantum dots (QD), (Minhao Wong et al. 2012) and Al_2O_3 nanoparticles (Psarras et al. 2011) to mention only a few.

2.2.1.2 Powder Blending

Solid-state powder processing has been also used for the synthesis of polymer–inorganic hybrids. The use of solid-state processes is advantageous from the aspect that they do not require any solvents (i.e., environmental issues arising from solvent removal and disposal do not exist) or polymer heat treatment, and they overcome the processing problems associated with the high nanoparticle loading, observed in the case of solution and in particular in the case of melt processing due to the tremendous increase in the viscosity of the melt rendering the whole process infeasible. Moreover, polymers with poor solubility in organic solvents or with high melting temperatures cannot be co-processed with inorganic nanoparticles using the aforementioned techniques to obtain polymer–inorganic hybrid materials.

High-energy ball milling (HEBM; Castrillo et al. 2007) has been used for synthesizing polymer–inorganic hybrid materials. During the HEBM process, a series of energy-transfer events takes place promoting intermixing between polymers and inorganic nanoparticles. Existing agglomerates of the filler particles break up into smaller (nano) particles during the process resulting in their homogeneous dispersion inside the polymer matrix. This in turn leads to a composite material where the properties of the individual components are retained, whereas depending on the degree of interaction between the filler particles and the polymer matrix, new properties may arise due to synergistic interfacial effects.

Polymers have been combined with silica (Olmos et al. 2012; Pantaleon and Gonzalez-Benito 2010; Gonzalez-Benito and Gonzalez-Gaitano 2008), barium titanate (Olmos et al. 2013; Serra-Gomez et al. 2012), TiO_2 (Ouyang et al. 2012), nano-clay minerals (Vertuccio et al. 2009; Mangiacapra et al. 2006), magnetoresponsive MNP (Giri 1997; Bao and Jiang 2005; Zhu et al. 2006; 2008), and nickel-ferrite nanopowder (Azhdar et al. 2008) employing cryogenic HEBM.

As in the case of melt and solution blending, the mixing efficacy between polymers and inorganics can be further assisted by functionalization of the inorganic surface with organic (macro) molecules.

2.2.2 Sol–Gel Synthesis

The synthesis of polymer-based organic–inorganic hybrids by the so-called sol–gel method dates back more than two decades. Nevertheless, this is still a highly emerging field since newly developed sol–gel synthetic approaches result in the generation of advanced polymer-based hybrid materials enabling at the same time structural and configurational control (Pandey and Mishra 2011). Such materials combining organic polymers with inorganic solids at the nanoscale, exhibiting properties not only of their counterparts but also new ones arising by the hybridization process, are highly promising in optical, mechanical, biological, electrical, catalytic, and other applications (Ogoshi and Chujo 2005).

2.2.2.1 Basics of the Sol–Gel Method

The sol–gel method makes use of metal alkoxides that undergo two stepwise reactions: hydrolysis and condensation. These reactions result in the generation of an inorganic network. A general reaction scheme of the sol–gel process is provided in Fig. 2.2.

The incorporation of organic macromolecules within the inorganic network generated via sol–gel including silica, alumina, titania, germania, and vanadia is feasible due to the mild reaction conditions employed (Chujo and Saegusa 1992; Zou et al. 2008; Mark 1996). As a consequence, numerous organic (polymer)–inorganic (metal oxide) hybrids have been prepared by this method. However, most studies describe the synthesis of silica-based polymer hybrids due to the well-known chemistry of silica, the high stability of the Si–O bond, as well as the availability of the starting materials, whereas the high reactivity of other metal oxides in sol–gel processes results in aggregation phenomena and inhomogeneity issues.

A principal requirement for obtaining materials characterized by high homogeneity and transparency, is the molecular- or nanodispersion of the organic counterpart within the inorganic matrix. This is realized via the development of specific interactions between the organic and the inorganic elements that can be either physical or chemical bonding. Depending on the type of interactions developed, the polymer-based hybrids prepared by the sol–gel approach can be divided into two classes as schematically presented in Fig. 2.3.

Class I includes the systems where only physical interactions take place between the organic and the inorganic components, including hydrogen bonding, ionic, aromatic (π – π interactions), etc. In this case, both the polymer and the starting inorganic “monomer” must possess specific functionalities that would enable the devel-

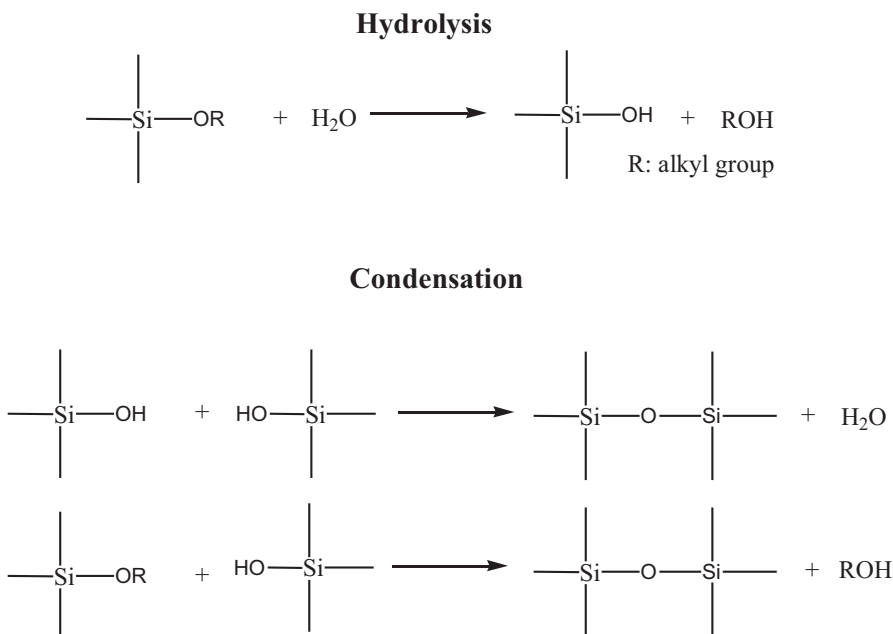
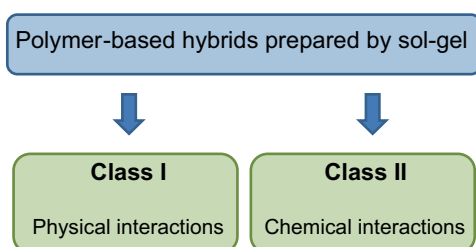


Fig. 2.2 The sol–gel reaction process involving hydrolysis and subsequent condensation steps

opment of such interactions. For example, polymers possessing H-bonding functionalities, including polyamides (Sarwar et al. 2009), polyurethanes (Zhang et al. 2011a), polycarbonates (Lionti et al. 2013), as well as biopolymers (Coradin et al. 2006), have been successfully employed in the synthesis of *Class I* polymer-based hybrids by sol–gel. Similarly, the inorganic precursors can be selected so as to promote such interactions with the polymer chain. For example, the incorporation of silicate monomers containing aromatic moieties facilitate the generation of homogeneous polymer–silica hybrids with polymers containing aromatic groups (Tamaki et al. 1998). In contrast, when the inorganic precursors used lack such moieties, the resulting hybrid materials are characterized by insufficient homogeneity due to the immiscibility, and consequently phase separation between the organic and inorganic components occurs.

Fig. 2.3 Classification of polymer-based hybrids prepared by the sol–gel approach in *Class I* and *Class II* materials



In *Class II*, the different phases are strongly held together by chemical bonding. Different synthetic approaches were used toward this purpose with the most popular ones being the use of alkoxy silane ($-\text{Si}(\text{OR})_3$)-functionalized polymers (Huang et al. 2004; Sardon et al. 2010; McDowell et al. 2010) and of telechelic (possessing two identical reactive end groups) polymers with functional moieties that enable co-condensation reactions to take place (Julián et al. 2004; Uilk et al. 2003; Chujo et al. 1993).

Alternatively, for achieving miscibility between noncompatible polymer–metal oxide systems, different strategies have been used including the incorporation of compatibilizers. These are usually macromolecules exhibiting good miscibility properties with both, the inorganic metal oxide network and the polymer that is incompatible with the inorganic counterpart. Alternatively, macrocycles assisting the dispersion of polymer chains via the host–guest interactions developed between the polymer and the hydrophobic cavity of the macrocycle have been employed (Ogoshi and Chujo 2005).

2.2.2.2 In Situ Preparation of Polymer-Based Hybrids via Sol–Gel

(i) H_2O -catalyzed sol–gel/polymerization

The use of a monomeric unit combining an organic polymerizable group with a metal alkoxide moiety, allows for the simultaneous formation of the polymer chain, and of the inorganic network (Fig. 2.4). Depending on the type of the polymerizable group employed, different polymerization methods have been used for the in-situ formation of polymer–metal oxide hybrids including ring-opening polymerization (ROP) and free-radical polymerization (Ogoshi and Chujo 2005).

(ii) Nonhydrolytic sol–gel/polymerization

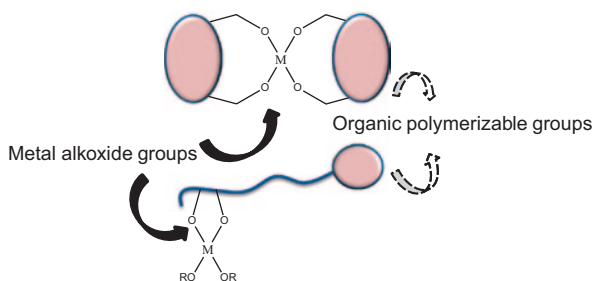


Fig. 2.4 Two different structures of hybrid “monomers” containing both metal oxide and organic polymerizable moieties, employed for the in-situ preparation of polymer–metal oxide hybrid materials by H_2O -catalysed sol–gel polymerization. The *dashed white* arrows show the organic polymerizable groups (e.g., vinyl monomers or monomers susceptible to ROP), whereas the *black* arrows point to the metal–alkoxide moieties employed for the generation of the inorganic gel.

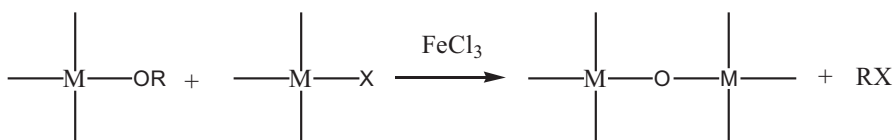


Fig. 2.5 General reaction scheme of the NHSG process. *NHSG* stands for nonhydrolytic sol-gel

In 2001, the first report appeared describing the sol-gel synthesis of a polymer-metal oxide network, obtained in the absence of solvents (i.e., the organic monomer was polymerized in the bulk simultaneously with the formation of the inorganic metal oxide network), and without the necessity of using water as a catalyst (Hay and Raval 2001). This synthetic approach involves a ligand exchange reaction that takes place in the presence of metal halides (e.g., FeCl_3) or organic molecules with oxygen donor moieties such as an alcohol, ether, etc., as seen in Fig. 2.5.

For example, nonhydrolytic sol-gel (NHSG) has been used for synthesizing silica-dimethylsiloxane hybrids where the NHSG synthesis of silica took place simultaneously with the ROP of hexamethylcyclotrisiloxane in the presence of FeCl_3 introduced as a catalyst (Apperley et al. 2002). In other cases, the NHSG process is used to prepare the colloidal metal oxide first, which is then mixed with preformed polymer chains to yield the desired nanocomposite (Song et al. 2008). Alternatively, the polymer/metal oxide nanocomposites are prepared by an in situ formation of the metal oxide through NHSG, starting from a mixture of the corresponding metal oxide precursor, an oxygen donor, and preformed polymer chains (Morselli et al. 2011).

(iii) The interpenetrating polymer network approach

The interpenetrating polymer network (IPN) process involves the simultaneous cross-linking processes of the organic and the inorganic components resulting in the formation of an interpenetrated organic-inorganic hybrid network structure as schematically depicted in Fig. 2.6 (Wen and Wilkes 1996).

Thermo-reversible IPN polymer hybrids consisting of organic polymer chains and silica gel were prepared by acid-catalyzed sol-gel reaction of tetramethoxysilane (TEOS) to generate the silica network. The reaction took place in the presence

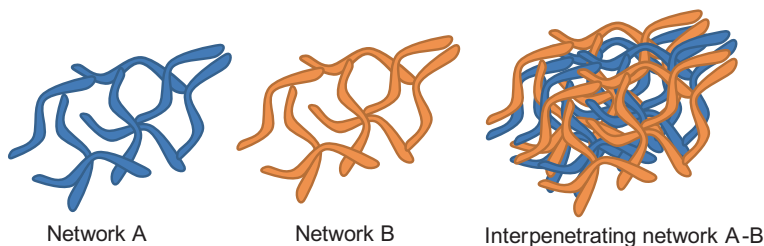


Fig. 2.6 Schematic presentation of an interpenetrating network consisting of two different networks (*Network A* inorganic; *Network B* organic) strongly interpenetrating each other

of poly(oxazoline) polymers bearing maleimide and furan groups that reacted together via a Diels–Alder reaction process to generate the organic network (Imai et al. 2000). In another example, bipyridyl-containing polystyrene and poly(ethylene oxide) led to network formation in the presence of a ruthenium salt. This coordination cross-linking process was carried out simultaneously with the generation of silica gel via a sol–gel process starting from TEOS (Tomoki et al. 2001).

2.2.2.3 Structurally Defined Polymer-Based Hybrids by Sol–Gel

To date, there is considerable attention on the development of new synthetic routes that enable the fabrication of polymer–metal oxide hybrid materials with controlled particle size, morphology, and porosity. After the first report back in 1992 on the synthesis of mesoporous silica (MCM41) by following a surfactant-templating procedure (Beck et al. 1992), the main focus has been on the development of mesoporous metal oxides exhibiting ordered structures at the 1–50-nm scale (Gu and Schueth 2014; Soler-Illia and Azzaroni 2011) using different types of surfactants (Antonietti 2001; Palmqvist 2003; Holmberg et al. 2005; El-Safty 2011), block copolymers (Soler-Illia et al. 2003; Deng et al. 2013; Orilall and Wiesner 2011), surfactant/block copolymer mixtures (Hellweg 2011; Ma et al. 2003), and macromolecular dendrimers (Tsiourvas et al. 2013) as structure-directing mediators.

The different pathways developed so far for producing mesoporous materials are presented schematically in Fig. 2.7. Those involve the direct precipitation, the true liquid-crystal templating (TLCT), the evaporation-induced self-assembly (EISA) and exotemplating routes (Soler-Illia and Azzaroni 2011). Briefly, the precipitation process involves the assembly of the inorganic precursors and the organic template occurring via hydrolysis/condensation of the inorganic precursors followed by template removal, resulting in the desired mesoporous material. In the TLCT templating, a liquid crystalline mesophase is generated first, followed by infiltration of the inorganic precursor within this mesophase, and subsequent creation of the inorganic network around the liquid crystalline nanodomains. A popular, solution-based route to synthesize oriented mesoporous metal oxide materials is based on the combination of sol–gel chemistry and dip or spin coating, using organic templating agents such as low molecular weight surfactants or amphiphilic block copolymers (ABCs). This method is called EISA (Brinker 2004).

The periodic structure, porosity, and degree of orientation of the resulting mesoporous films depend strongly on the template used. Triblock copolymers of the Pluronic family (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), PEO–PPO–PEO), or polyethylene oxide-based surfactants, such as the Brij family ($\text{CH}_3-(\text{CH}_2)_{10-16}-(\text{O}-\text{C}_2\text{H}_4)_{1-25}-\text{OH}$), have been found particularly useful as templates in EISA processes (Liu 2009; Chu et al. 2014; Herregods et al. 2013; Ma et al. 2010; Henderson et al. 2006) by acting as structure-directing agents. In such processes, the inorganic precursors are mixed together with the organic amphiphile in solution.

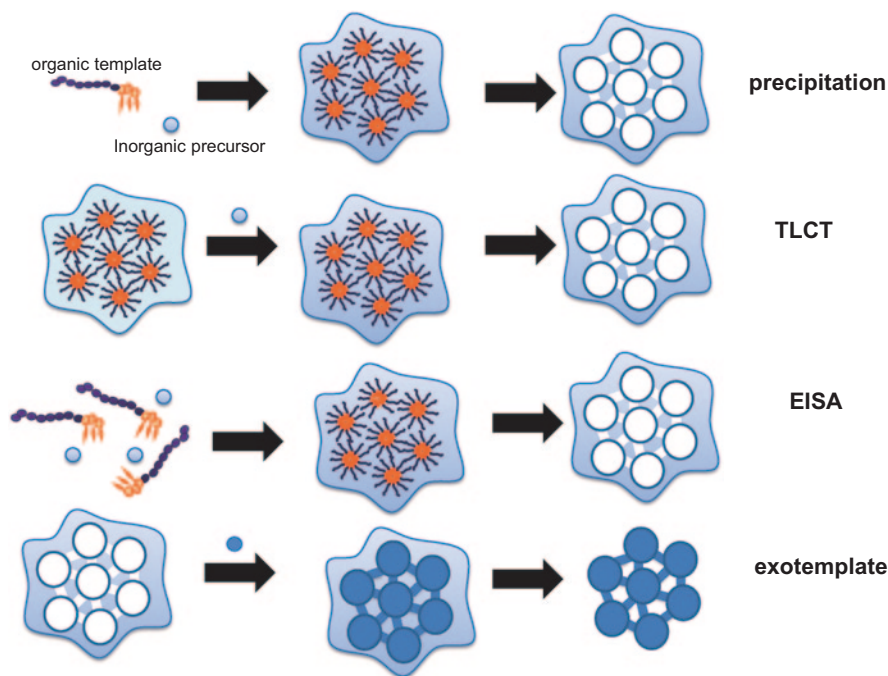


Fig. 2.7 Synthetic pathways leading to the generation of mesoporous inorganic materials: The direct precipitation, the true liquid crystal templating (*TLCT*), the evaporation-induced self-assembly (*EISA*), and the exotemplating route

This is followed by solvent evaporation resulting in an increase in solution concentration of the templating reagent that eventually exceeds the critical micellar concentration (*cmc*) resulting in its self-assembly into spherical, cylindrical, or lamellae nanostructures. Subsequently, the inorganic material solidifies around the organic self-assembled nanomorphologies resulting in well-ordered mesoporous hybrids. Upon calcination at higher temperatures, the organic structure-directing reagents can be removed resulting in the generation of well-ordered inorganic nanostructures. Finally, in the exotemplating route, a hard mesoporous matrix is used as a template. In this template, the desired inorganic precursors are loaded via infiltration, followed by gelation, and subsequent removal of the exotemplate. The structural characteristics of the final product imitate the structure of the initial mesoporous template in a “complementary” manner.

Different synthetic strategies have been proposed for the development of polymer-based mesoporous hybrids. These include (a) polymerization (chemical, electrochemical) of monomeric species incorporated within the pores of the mesoporous template either from the liquid or from the gaseous phase, (b) infiltration of preformed polymers inside the pores of the template, (c) in situ growth of macromolecules with linear or dendronized architectures and (d) use of structure-directing agents with polymerizable functionalities.

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