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Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale

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Abstract

Hybrid inorganic–organic materials are promising systems for a variety of applications due to their extraordinary properties based on the combination of the different building blocks. The combination of nanoscale inorganic moieties with organic polymers has a high potential for future applications and has therefore attracted a lot of attention during the last years. Since there are countless different combinations of the two moieties, there are also a large number of methodologies to combine them in one material. This review is written with the intention to give an overview of principal concepts of the preparation of such materials for different applications. It focuses on the chemical aspects of the incorporation of inorganic building blocks such as silica networks, porous materials, metals, etc. into an organic polymeric matrix. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hybrid materials; Nanocomposites; Polymers; Nanoparticles

Contents

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1. Introduction

Inorganic–organic composite materials are increasingly important due to their extraordinary properties, which arise from the synergism between the properties of the components. There are several routes to these materials, but probably the most prominent one is the incorporation of inorganic building blocks in organic polymers. These materials have gained much interest due to the remarkable change in properties such as mechanical [1], thermal [2–5], electrical [6], and magnetic [7] compared to pure organic polymers. The most commonly employed preparation procedures for these materials are the use of the sol–gel process for the formation of the inorganic network, the incorporation of preformed dense inorganic structures, such as clusters and particles, and the formation of hybrids using porous or layered inorganic materials either by interpenetration of the organic polymers into the voids, or by exfoliation of the inorganic material. The unique properties of these materials, such as their high optical transparency, as well as the lack of data on structure–property relationships at a nanoscale, has led to emerging research in this area. Most of the efforts are based on well-known macro- or microcomposites between inorganic moieties and organic polymers, and expand ideas from this microcosmos to a new class of materials, called nanocomposites [8]. Expressions like 'nanoparticles' and 'nanocomposites' seem to be very trendy, and are often misused in the literature for systems which do not properly fall under the label 'nano' in the sense of advertising. Aside from the inappropriate use of the term nano, there is a strong need to understand the mechanism of the formation of such materials. Important aspects of the chemistry involved in the formation of these systems are the uniformity, phase continuity, domain sizes and the molecular mixing at the phase boundaries, which all have a direct influence on optical, physical, and mechanical properties [9]. Owing to numerous papers published on polymer organic–inorganic composite materials, it is impossible to completely review this field. Therefore, this review will focus on the most common principal concepts used to incorporate inorganic systems in the submicron range (up to a few hundreds of nanometers) into an organic polymeric matrix, and the resulting properties of such materials. The reader is referred to the literature cited for a more detailed description.

While the incorporation of microscale and larger inorganic fillers into organic polymers is scientifically well explored, the decrease in size of the inorganic component into the nano dimension, and the simultaneous increase of the interfacial area, results in new extraordinary materials properties which require further investigations. Additionally, the properties of the composite materials depend on the morphology of the phases, which has to be controlled over several length scales. Therefore, the development of such materials is a 'land of multidisciplinarity' [10], where chemists, physicists, material scientists and engineers have to work closely together.

From a chemical point of view, one can distinguish between several ways to incorporate inorganic systems in organic polymers depending on the interactions between the moieties: materials with strong (covalent, coordination, ionic): weak (van-der-Waals, hydrogen-bonds, hydrophilic–hydrophobic balance); or without chemical interactions between the two components (Fig. 1) [10,11]. A critical challenge in the design of these hybrid inorganic–organic systems is a control of the mixing between the two dissimilar phases. Several chemical approaches that may be applied to overcome this problem will be described in this review.

2. Interpenetrating networks

The formation of interpenetrating networks (IPNs) between inorganic and organic moieties is carried out either by a sequential two-step process, wherein a secondary network is formed in a primary one, or by the simultaneous formation of the two networks. The resulting materials are microscopically phase separated, but macroscopically uniform [12]. Examples of the two-step process include the creation of an organic polymer penetrating into the pores of an inorganic porous material, such as a zeolite or mesoporous amorphous materials, or between the sheets of a layered lattice, such as a clay mineral. In these cases the inorganic moiety is a rigid, preformed natural or synthetic host matrix, with a regular pore or channel structure in the nanoscale. In another process, an inorganic (crosslinked) moiety is formed by a polycondensation reaction, and interpenetrates during this process into an organic polymer. Difficulties of such an approach are potential incompatibilities between the moieties, leading to phase separation, and the challenge to find reactions for the formation of the second network which can be carried out in the presence of the first one. A major problem arises from the different stabilities of the materials. While inorganic systems are thermally quite stable and are often formed at high temperature, most organic polymers have an upper temperature limit of around 250 °C. Therefore, the synthesis of hybrid systems requires a strategy wherein the formation of the components is well-suited to each, e.g. the use of a low-temperature formation procedure. Hence, classical high temperature solid-state reactions for the preparation of the

Nomenclature

AA	acrylamide
An	aniline
ATRP	atom transfer radical polymerization
BA	*n*-butyl acrylate
bpy	2,2′-bipyridine
DMAA	*N*,*N*-dimethylacrylamide
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
EA	ethyl acrylate
EO	ethylene oxide
GLYMO	3-glycidoxypropyltrimethoxysilane
HEA	2-hydroxyethyl acrylate
HEMA	2-hydroxyethyl methacrylate
IPN	interpenetrating network
MA	methyl acrylate
MAc	methacrylic acid
MEMO	3-methacryloxypropyltrimethoxysilane
MMA	methyl methacrylate
2MO*x*	2-methyl-2-oxazoline
NVP	*N*-vinylpyrrolidone
PDMS	polydimethylsiloxane
PTA	phenyleneterephthalamide
PV	*p*-phenylenevinylene
Py	pyrrole
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
SEM	scanning electron microscopy
St	styrene
TEOS	tetraethoxysilane
TEM	transmission electron microscopy
TFEA	2,2,2-trifluoroethyl acrylate
TMO	tetramethylene oxide
TMOS	tetramethoxysilane
Tp	thiophene
VA	vinyl alcohol
VAc	vinylacetate
VE	vinylether
2VP	2-vinylpyridine
4VP	4-vinylpyridine
4VPh	4-vinylphenol

inorganic component must fail due to the limited thermal stability of the organic polymers. For this reason milder reactions have to be applied for the formation of the inorganic network. An ideal procedure for the generation of such hybrid materials is the sol–gel process [13]. This process starts with molecular precursors at ambient temperatures, forming metal oxide frameworks by hydrolysis and condensation reactions (Scheme 1). The morphologies and properties of the resulting materials are controlled by the reaction conditions and the precursors used. Typical sol–gel processing variables leading to different morphologies of the materials are the water to alkoxy and catalyst to alkoxy ratios, and the type of solvent and catalyst used. For example, whereas optically transparent silicate/polymer hybrid materials are often obtained in an acid catalyzed sol–gel process, nucleophilic catalysts such as fluorides or hydroxides give opaque materials due to a more particulate inorganic phase [14]. The most prominent inorganic material formed by the sol–gel method is unmodified or modified SiO_2, using precursors of the type $Si(OR)_4$ for unmodified networks or $R'_nSi(OR)_{4-n}$ for modified networks. Contrary to other metal alkoxides, the C–Si bond is stable with respect to hydrolysis, and therefore a variety of modifications can be directly and durably incorporated into the SiO_2 network. The organic groups introduced into the sol–gel precursor can fulfill two functions: (i) modification of the inorganic network, resulting in improved compatibility between the two phases, and/or (ii) the formation of a strong linkage between the organic and the inorganic phase via covalent bonds. Furthermore, the process may be extended to metal oxide networks using various metal alkoxide precursors [15]. Although silicon alkoxides are probably most studied, other metals often used include tin, titanium, zirconium, cerium, and aluminum. As the M–C bond is not hydrolytically stable, the incorporation of functional groups requires another methodology, for example, via the coordination of multidentate functional ligands, which show a higher stability towards substitution reactions. Frequently used strategies for the formation of IPN hybrid materials applying the sol–gel approach are: (i) mixing of the precursor for the sol–gel process with the organic polymer followed by an inorganic polycondensation reaction, (ii) polymerization of an organic monomer in the inorganic gel, (iii) simultaneous formation of the inorganic and organic network, and (iv) dual network materials in which the molecular precursors for the formation of the two networks are covalently linked to each other (telechelics, etc.). The amount of incorporated inorganic moiety can be varied over a wide range. In addition to the sol–gel processing parameters, the morphology of the hybrid materials obtained by the interpenetration of polymers and inorganic moieties is dependent on polymer variables such as the molecular weight, the presence and extent of polymer functionality and shape, and the solubility of the polymer in the sol solution. Therefore, possibilities for synthesizing this type of material are immense, and only a small selection can be presented here.

2.1. Sol–gel process in presence of preformed polymer

A typical application area for hybrid materials are optical systems that require homogeneous and transparent materials which cannot be obtained from mixtures that are already macroscopically phase separated. This is often the case if hydrophobic polymers are mixed with sol–gel solutions. Therefore, organic polymers with functional groups that

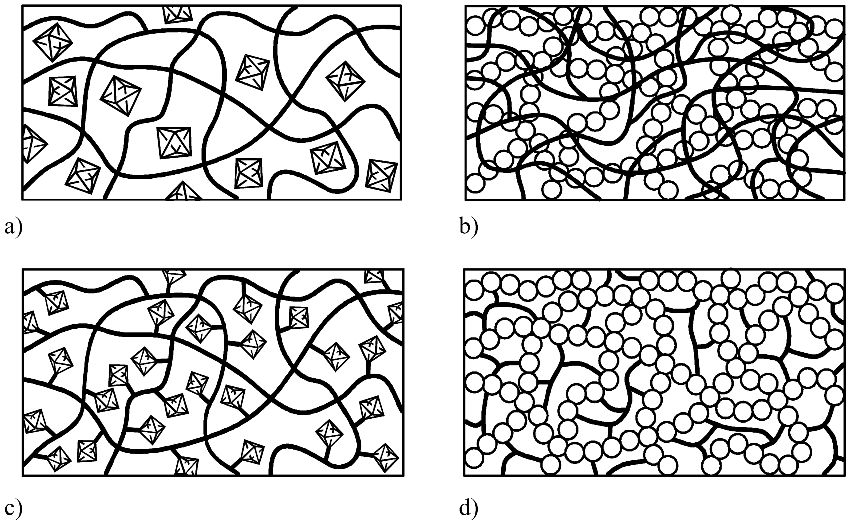
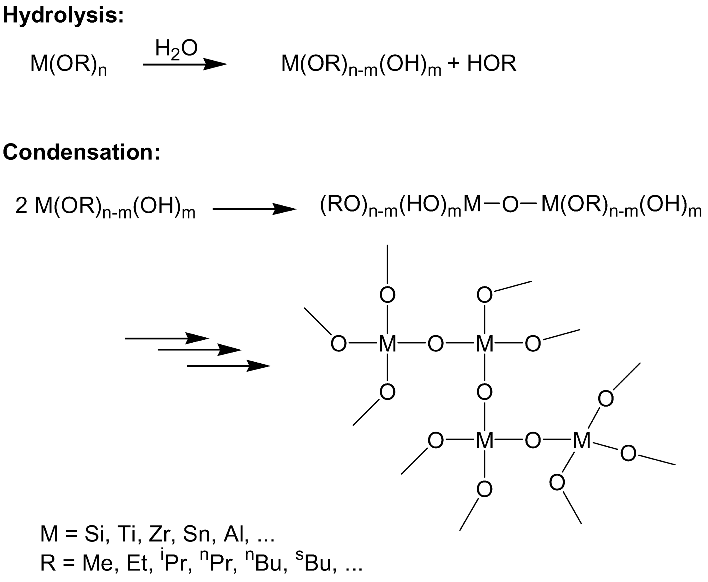


Fig. 1. Different kinds of inorganic–organic composite materials. (a) embedding of the inorganic moiety into the organic polymer, (b) interpenetrating networks (IPNs); with chemical bonds: (c) incorporation of inorganic groups by bonding to the polymer backbone, and (d) dual inorganic–organic hybrid polymer.

have specific interactions with compounds created in the sol–gel process, e.g. hydrogen bonding to residual silanol groups on the formed silica, have to be chosen. A broad variety of organic polymers with hydrogen bonding ability such as poly(2MOx), poly(VP), poly(DMAA), poly(VA), poly(MMA), poly(VAc), polyamides, polyethersulfones [16], polymeric perfluoroalkylsulfonates (Nafion) [17–20], and hydroxy end-capped polysiloxanes were incorporated into sol–gel reaction mixtures [21–28]. Due to the interactions between the polymer and the silanol groups generated during the sol–gel process, a macrophase separation is avoided, and the resulting materials have a high degree of homogeneity and optical transparency. However, this property is dependent on the reaction conditions of the sol–gel process, e.g. the pH value. Similar interactions are observed when poly(oxypropylene) is used in the formation of epoxide–amine networks reinforced by SiO_2. The resulting materials show strong structural differences depending on whether a one step or a two-step procedure was used to form the IPNs [29–31].

While in most of the studies, tetraalkoxysilanes were used as precursors for the inorganic network, trialkoxysilanes with an organic functionality have also been employed. Often the organic group has a significant



Scheme 1.

influence on the resulting material. In a hybrid material formed from poly(VAc) and phenyltriethoxysilane it was observed that the glass transition temperature (T_g) of the polymer increases in a similar way as it does with TEOS as precursor. However, a mechanical reinforcement of the polymer has not been observed [32]. This behavior probably has its origin in the different extend of network formation with the two silicate precursors. In the case of tetraalkoxysilane, depending on the reaction conditions, a highly crosslinked silica network can be formed, while in the case of trialkoxysilanes a lower degree of crosslinking is usually observed. Additionally, the functionality of the trialkoxysilane can be used for the formation of a covalent linkage between the polymer and the silica species. For example, aminophenyltrimethoxysilane was used as a compatibilizer which reacts with the phthaloyl chloride end-capped polyamide [27,33]. In another study, the interfacial bonding between the phases of hydroxypolybenzoxazole and sulfopolybenzobisthiazole polymers and the silica, is improved by the use of isocyanatopropyltriethoxysilane and *N*,*N*-diethylaminopropyltrimethoxysilane, respectively [34].

Inorganic polymers such as polyphosphazenes modified with methoxyethoxyethoxy side groups also show hydrogen bonding to the silicate species. Optically transparent composite films with titania, zirconia and alumina were formed with these inorganic polymers as well as with purely organic macromolecules [35,36].

If the time of the sol–gel network formation is fast enough, a macroscopic phase separation is avoided. This was proved applying the very fast non-aqueous sol–gel process where formic acid is used together with silicon alkoxides. In this process the water necessary for the condensation of the silicate species is produced by an esterification reaction of the alcohols released by the silica precursor and formic acid. In these systems, a TEOS/poly(MMA) hybrid can be obtained in 15 min compared to 200 h using the usually employed systems [37]. Another way to enhance the homogeneity of the hybrid materials is the use of polymeric compatibilizers such as copolymers of poly(St) and poly(4VPh) which help to reduce the interfacial tension in incompatible systems [38]. Applying this method the particle size of the silicate species can be significantly reduced leading to a better adhesion between the organic polymer and the inorganic moieties.

The sol–gel process can be employed using a variety of different inorganic precursors, therefore the inorganic part of the hybrid material is not limited to SiO_2. Examples are composites of poly(BA), PDMS or poly(PTA) with titania/silica or pure titania species [39–43]. Composite materials with inorganic species such as zirconia or mixed silica–titania or silica–alumina have been produced using Nafion as the polymer component [44,45].

It is important to mention that the parameters employed for the sol–gel process have a crucial influence on the morphology of the inorganic species in the resulting material which directly influences its properties [46].

2.2. Polymerization in sol–gel networks

Similar to the mixing of preformed organic polymers with the precursors for the sol–gel process, a mixing between silica and the monomers of an organic polymer is problematic if no attracting interactions between the two phases exist.

The high porosity of a silica network formed by the sol–gel process can be used for an impregnation of the material with polymers as well as with monomers, which can be polymerized in situ. With such a technique, poly(MMA)/silica hybrids were prepared, and it was shown that the mechanical properties of the pure silica species can be improved significantly depending on the amount of poly(MMA) included and by the addition of a coupling agent such as methacryloxytrimethoxysilane [47].

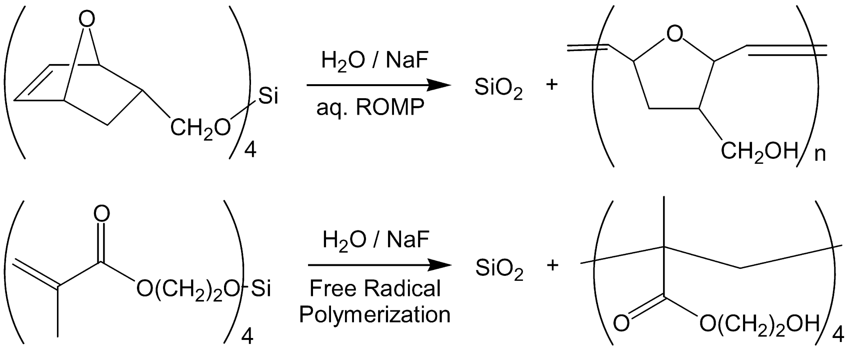
Swelling of sol–gel derived crosslinked poly(TMO) silica hybrids in various monomers such as cyclohexyl methacrylate, VP or Mac, and polymerization with ^{60}Co gamma radiation resulted in transparent hydrogels. These materials revealed significant changes in the mechanical and dynamic mechanical properties, such as the elastic modulus, which increased in some cases by several magnitudes, compared to the precursor systems [48,49].

Contrary to the polymerization in sol–gel networks, the infiltration of preformed polymers into these networks is rare due to the difficulties connected with the slow diffusion of organic polymer chains into the porous inorganic network structure. As a result the infiltration of the monomer and an in situ polymerization is preferred.

2.3. Simultaneous formation of interpenetrating networks

The simultaneous formation of two networks can result in the most homogeneous type of materials. Applying this method towards hybrid materials three processes are in competition: (i) the kinetics of the hydrolysis and condensation forming the inorganic phase, (ii) the kinetics of the polymerization of the organic phase, and (iii) the thermodynamics of the phase separation between the two phases. If the kinetics of the two network-forming processes are tailored in such a way that they occur simultaneously and rapidly enough, phase separation can be avoided or minimized, thus producing a homogeneous material. Additional parameters such as attractive interactions between surface hydroxy groups of the sol–gel products and the organic monomer, for instance, hydrogen bonds, or the correct adjustment of the hydrolysis conditions can be used to avoid phase separation.

The formation of homogeneous and optical transparent hybrid materials by the bulk free radical polymerization of HEMA, simultaneously with the sol–gel reaction of TEOS as precursor is an example in using the advantage of an attracting interaction [50,51]. The resulting materials were characterized by DSC, SEM, TEM, SAXS, and DMA measurements. From these measurements, it was concluded that the two systems form a bicontinuous, truly interpenetrating material. Additionally, SAXS, SANS, and TEM



Scheme 2.

studies on a HEA/TEOS system revealed that there is a dramatic change in the micromorphologies if the relative rates of the two polymerization processes are changed in such a way that when the sol–gel polymerization is faster the phases are more finely dispersed. If covalent bonds were introduced between the two phases, the homogeneity of the material was further improved [52].

Polyimide–silica gel hybrids have been prepared by the simultaneous formation of polyimides and a silica network formed in a sol–gel process. The hydrolysis and condensation of TMOS was carried out in a solution of *N*,*N*-dimethylacetamide (DMAc) containing 5% LiCl, $CaCl_2$ or $ZnCl_2$, and a polyimide intermediate. Films were cast from the resulting mixtures and the solvent was gradually evaporated. The results of this procedure were clear, transparent, pale yellow or amber-colored hybrid films in which the salts were dispersed at the molecular level. Pyrolysis of the composites at 600 °C gave mesoporous silica [53]. Thermoresponsive composites were obtained from the in situ polymerization of *N*-isopropylacrylamide, methylenebisacrylamide, and TMOS. The resulting hybrid materials showed a swelling behavior typical of interpenetrating polymer network structures. The polymer hybrid materials swelled in water, and the degree of swelling decreased continuously with increasing temperature. The cleavage of interactions of the poly(*N*-isopropylacrylamide) chains was observed as an endothermic peak in the DSC plot [54].

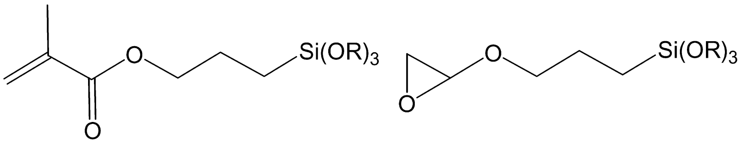
Besides the use of monomers with strong interactions to the sol–gel network forming species, hydrophobic systems such as poly(St) can also be homogeneously incorporated into such materials by tuning reaction conditions such as the sol–gel catalyst concentration [55,56]. Another method of inducing attractive interactions between the organic polymer and the sol–gel derived SiO_2 species is the incorporation of organic groups in the SiO_2 network using trialkoxysilanes. Even $\pi-\pi$ interactions between poly(St) and phenyltrialkoxysilanes seem to improve the positive interactions [57].

Non-shrinking nanocomposites have been produced via different approach [58–61]. Silicon alkoxides possessing polymerizable alkoxy groups have been synthesized. The alkoxy groups were liberated during the sol–gel processing as the corresponding alcohol (Scheme 2). Aqueous ring-opening metathesis polymerization (ROMP) [62] as well as free radical polymerization were used for the organic polymerization reaction.

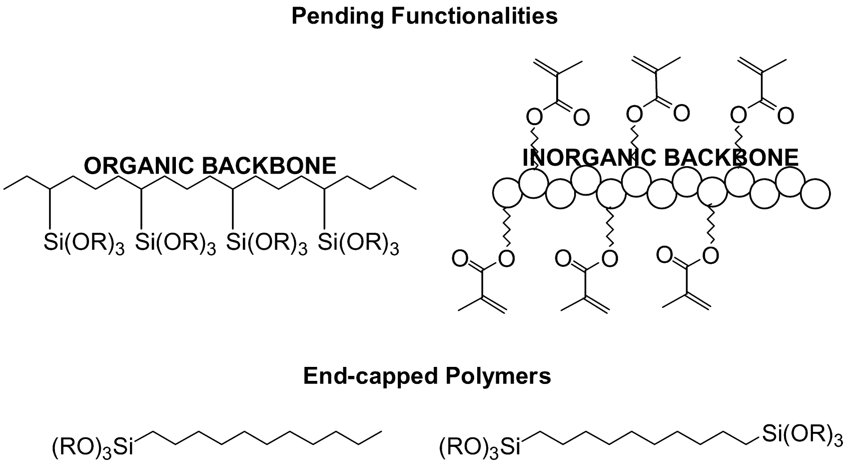
2.4. Dual network precursors

The network forming functionalities can also be covalently connected to each other. This is realized in two different ways: (i) functional groups for the organic and inorganic polymerization/polycondensation process are incorporated in one molecule or (ii) functional groups for the second polymer are incorporated in a preformed polymer of the other type. Typical examples for bifunctional precursors are the commercially available molecules GLYMO or MEMO (Scheme 3). These systems allow either a simultaneous or a sequential formation of two networks. Furthermore, a preformed network or polymer—either inorganic or organic—can be functionalized with pending functional groups capable of forming the second network. Another possibility of forming such materials is the preparation of organic polymers, which were initiated or quenched by a species that allow the incorporation into sol–gel networks (end-capped polymers) (Scheme 4).

Triethoxysilyl mono- and di-terminated polyoxazolines were prepared by quenching the polyoxazolines either by amine functionalized trialkoxysilanes or by unsaturated amines, which were then subjected to hydrosilation with



Scheme 3.



Scheme 4.

trialkoxysilanes. These triethoxysilyl-terminated polyoxazolines were either used to surface-modify silica gels, or for acid-catalyzed sol–gel reactions [63–66].

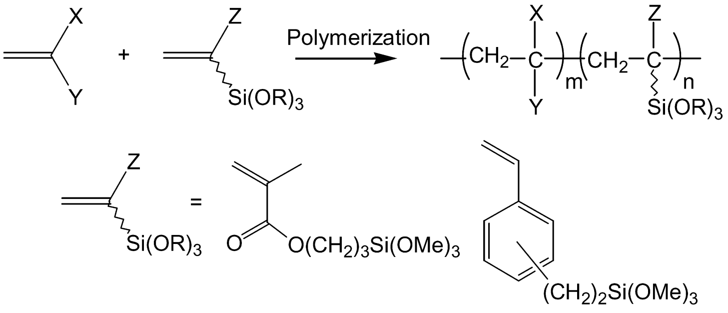
Unsaturated monomers such as MEMO or styrylethyltrimethoxysilane have been homo- or copolymerized with methyl methacrylate [67–73], styrene [69,74–76] or acrylonitrile [77] (Scheme 5). The functionalized polymer chains were hydrolyzed and cocondensed with TEOS and/or other precursors for the formation of the inorganic network via an acid-catalyzed sol–gel route. The lack of well-defined glass-transition temperatures for the polymers in the silica matrix revealed that the polymer chains were uniformly distributed in the materials. Accordingly, the poly(MMA)–SiO_2 as well as the poly(St)–SiO_2 hybrid materials had an excellent optical transparency.

The sol–gel process of transition metals such as titanium, zirconium, or vanadium is very fast compared to that of silicon, and therefore a better control over the polycondensation is required to obtain homogeneous composite materials in a simultaneous inorganic and organic polymerization reaction. This can be achieved via a partial substitution of alkoxides groups in the precursors by stronger complexing ligands such as bidentate systems. As dual network forming precursors they also have to contain a functional group which is able to react in an organic polymerization, for example, a ligand such as acetoacetoxyethyl methacrylate. This method was used in the copolymerization of methacrylate with titanium, zirconium, or vanadium precursors resulting in hybrid organic–inorganic copolymers intimately interpenetrated on a nanometer scale [78–80].

3. Incorporation of metals and metal complexes in polymers by coordination interactions

Although the inclusion of metals in polymers occurs usually on the molecular scale and therefore these systems are not covered by this review, this section was added for the completeness of this paper. Furthermore, based on the long lasting investigations of such systems, they can be helpful to understand the mechanisms, e.g. nucleation in a polymeric matrix, of other inorganic–organic hybrid species and they are potential precursors for metal cluster containing polymers.

Methods for the inclusion of metals in organic polymers are the: (i) polymerization and copolymerization of metal-coordinating monomers, (ii) coordination of metals to preformed polymers, (iii) direct incorporation of the metal into the polymer chain, (iv) incorporation of the metal into



Scheme 5.

plasma polymers, and (v) mechanochemical synthesis [81]. Although all of these techniques lead to polymeric products with metal inclusion, the latter two are only discussed for completeness, and the interested reader is referred to other reviews in this field [81,82]. Consequently, the area of so-called metal centered macromolecules, which has been a new subject in research in recent years, will be reviewed here.

3.1. Coordination of metals to the polymer backbone

The major interactions that can be used for the incorporation of metals in polymers are the use of functional groups to form coordination compounds. All types of interactions suitable to form a metal complex can be applied. Due to their Lewis basicity poly(vinyl pyridines) [83], poly(vinyl amines) [84] or poly(L-histidine) [85], as homo- or copolymers, have a high affinity to coordinate metal ions such as Zn [83], Ni [86], Co, Ru [87], Pd [88], or lanthanides [89], which were incorporated as salts. The so-called coordination crosslinking takes place if the polymer coordination sites displace the ligands of the metal salt or complex. Examples include the replacement of the acetonitrile ligands in bis(acetonitrile)dichloropalladium, or coordinated water molecules in cobalt salts by π-bonds in the polymer backbone. The incorporation of such metals leads to drastical changes in the properties of the polymers such as an increasing T_g [84].

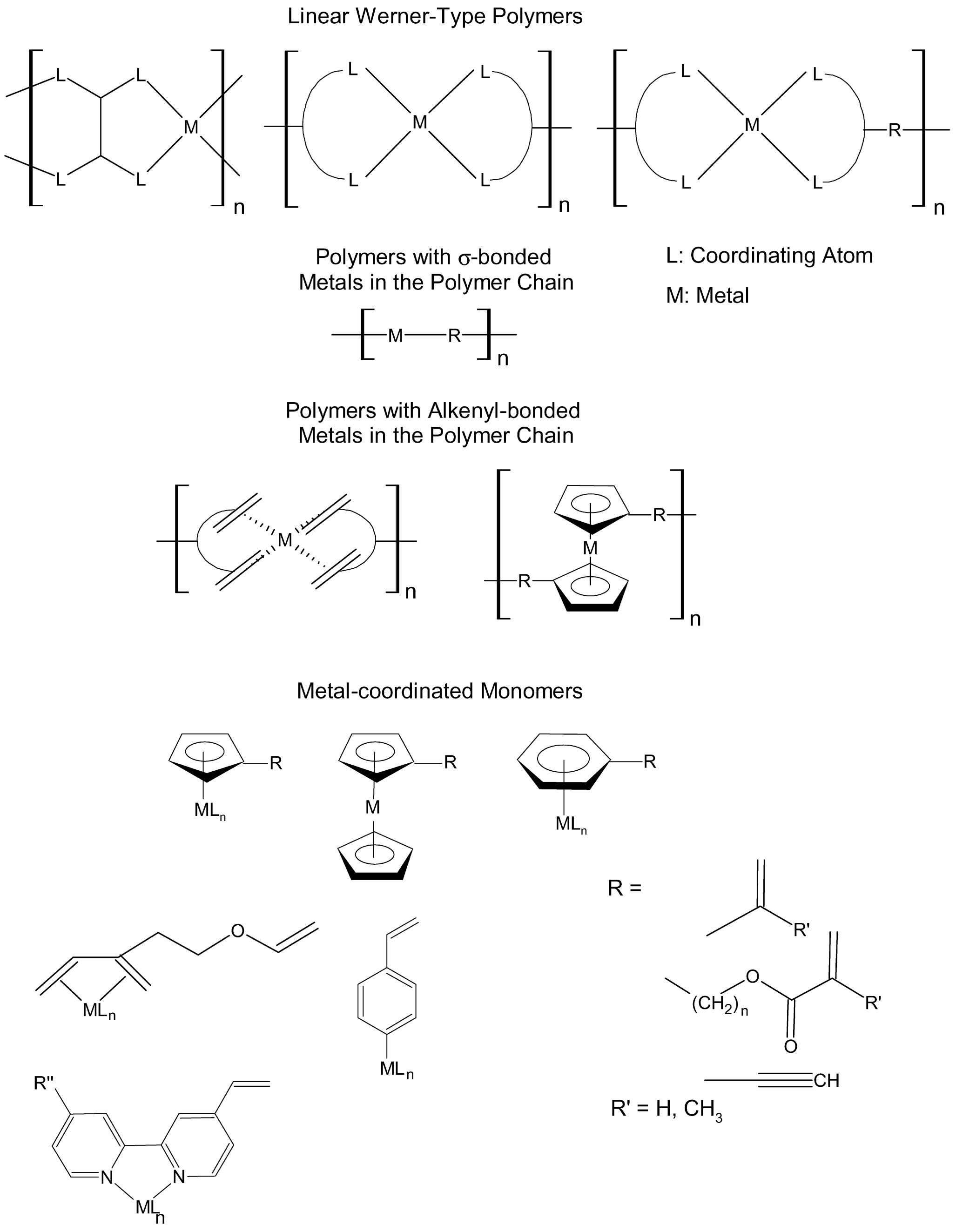
Palladium salts incorporated into a polyolefin containing unsaturated side groups such as polybutadiene or polyisoprene can cause crosslinking between the polymer chains by palladium catalyzed Heck-type reactions. This methodology used to obtain crosslinked polymeric systems is called ‘reactive blending’ [88,90,91]. The swelling behavior of such crosslinked systems is dependent on the salt concentration and decreases with increasing palladium content. The mechanical and thermal properties of the resulting polymer blends such as an enhanced stress–strain behavior, an increase in Young’s modulus as well as an increase of T_g up to 100 °C depending on the $PdCl_2$ content [92], and the annealing process is significantly influenced by the Pd content [93]. In addition to the formation of crosslinked systems, transition metal additives can also help to compatibilize polymeric mixtures which would otherwise exhibit phase separation [87,90,91,94,95].

3.2. Metal-coordinated monomers

A useful way to incorporate metals into polymers is the use of metal-coordinating monomers in the polymerization reaction. Polymerization and copolymerization of such compounds has already attracted much interest in the literature [81,96–101]. Many of the metal-containing polymers have only short chains, possess very poorly defined structures, and/or are often insoluble in common organic solvents as a result of intermolecular forces between single chains or crosslinking by bridging coordination sites. In the past, this often led to a poor characterization of these interesting materials. In principal two different polymer systems can be distinguished: those in which the metal is part of the polymer chain and others in which the metal is coordinated to pendent groups. There are a huge number of possibilities using combinations of different ligands and metals, as a result this review will give only a short overview of possible monomers which have already been discussed in the literature. In Scheme 6 possibilities for polymers with metals in the chain and a selection of potential metal-coordinated monomers used in polymerization reactions is shown. References for these systems can be found in the cited reviews.

3.3. Metal-centered polymers

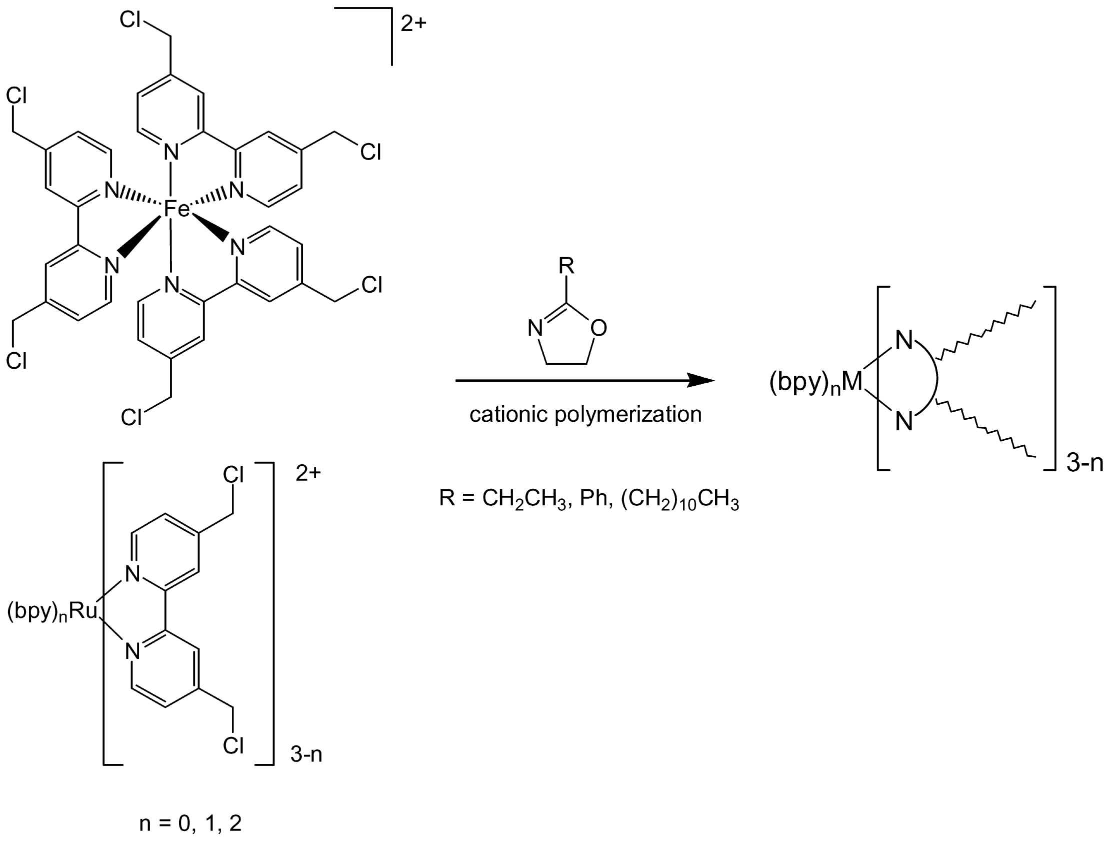
In recent years, a new type of metal-centered polymeric systems was developed, the so-called metal core macromolecules. In this approach, a metal is coordinated with ligands that include functional groups that are able to initiate a polymerization reaction, or that can be transformed to have such a functionality [102–105]. Fe(II) and Ru(II) complexes, with one to three (4,4′-halomethyl)-2,2′-bipyridine (bpy) ligands, have been used to initiate living cationic oxazoline polymerizations (Scheme 7) [102,104,105]. The polymerizations yielded hybrid systems with molecular weights from 1600 to 4600 and low polydispersities. The obtained polymers revealed the same UV/VIS absorptions as the initiators indicating that the polymers were still coordinated to the metal via the initiating ligands. Disassembly of the metal core has been achieved under various conditions. For example, treatment of the iron complex with aqueous K_2CO_3 yielded a colorless solution with concomitant precipitation of an iron oxide/hydroxide. The original violet color of $[Fe(bpy)_3]^{2+}$ was shown to be restored by treatment of the solution with $(NH_4)_2Fe(SO_4)_2$, which revealed that the bpy terminated polymers reassemble around the iron center. By using different oxazoline monomers, i.e. 2-ethyl-, 2-undecyl- or 2-phenyl-2-oxazoline, amphiphilic metal-centered six-arm star block copolymers have been prepared [104]. A similar approach was used to prepare 6,6′-bisfunctional 2,2′-bipyridine copper complexes as initiators for the living cationic polymerization of 2-ethyl-2-oxazoline [106]. Block copolymers with poly(2-phenyl-2-oxazoline) as the second block were also synthesized by the same method. This study was extended to (5-bromomethyl-5′-methyl)-2,2′-bipyridine as a ligand for Co(II), Fe(II) and Ru(II) to form initiators for living cationic polymerization of 2-oxazolines [107]. Ru(II) complexes bearing one to three chloromethyl functionalized bpy ligands have been used as ATRP-initiators in styrene polymerizations producing Ru(II) core complexes with two, four, and six arms [103,108].



Scheme 6.

4. Intercalation in 2D layered materials

Considerable interest has concentrated in the last decades on the insertion of polymers into host lattices due to the unique properties of the resulting materials. Composites from inorganic layered lattices with polymers have been known for quite a long time and this review can only introduce this very broad research field. Readers who are more interested are referred to more detailed reviews and references therein [109–114]. Classically inorganic 2D mineral lattices have been used as fillers. They were incorporated into polymers to improve the bulk properties such as shrinkage on molding, stiffness, heat resistance, and flammability, decrease of electrical conductivity, or permeability for gases such as oxygen or water vapor [115, 116]. In recent years these classical applications expanded



Scheme 7.

based on special properties, e.g. the higher degree of ordering of the polymers between the layers, or optical, mechanical, and electronic properties, in the region of sophisticated ‘high-tech’ materials with possible applications in lots of different areas.

There are several procedures to incorporate inorganic layered 2D materials finely dispersed into a polymer matrix. In principal these can be distinguished using the following classification: (i) intercalated hybrids in which one or more molecular layers of polymer chains are inserted between the sheets or galleries of the inorganic host, (ii) delaminated hybrids in which the layers are exfoliated (or delaminated) and homogeneously dispersed in a polymer matrix, or (iii) systems between the two extremes (Scheme 8) [109,111]. Contrary to intercalated systems the exfoliated hybrids only contain a small weight percentage of host layers with no structural order. To obtain polymer systems reinforced by single sheets from mineral clays, the reaggregation of the layers in the polymer matrix has to be prevented.

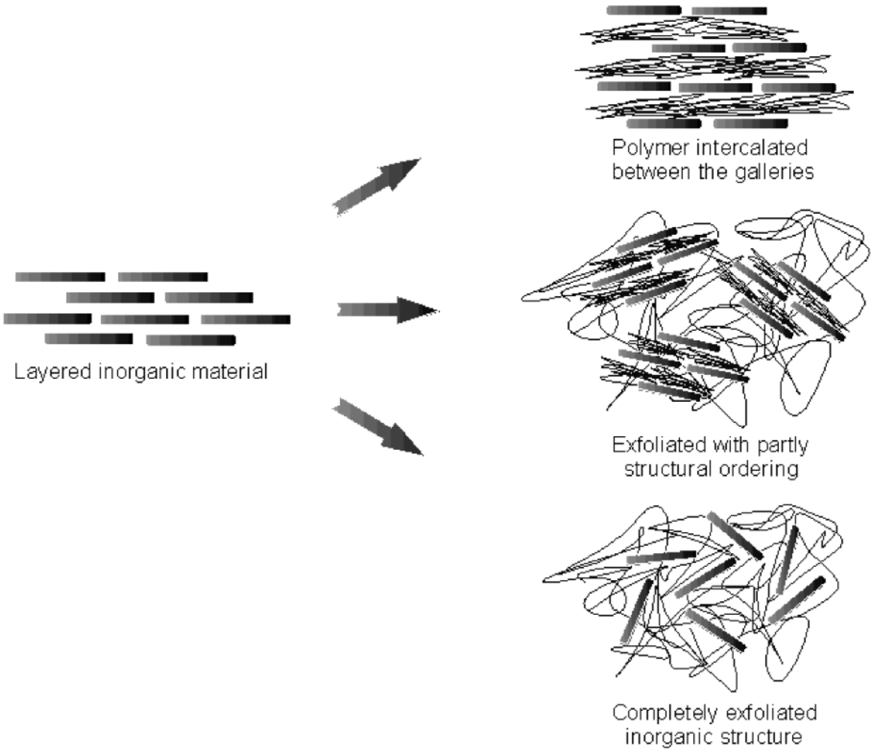
Principally, three methods for the formation of polymer–clay nanocomposites can be used.

(i) Intercalation of monomers followed by in situ polymerization.
(ii) Direct intercalation of polymer chains from solution.
(iii) Polymer melt intercalation.

Each of these methods has its advantages and disadvantages, for example, the in situ polymerization only works with suitable monomers, or the intercalation of polymer chains has a quite slow kinetics originating from diffusion phenomena.

For the in situ polymerization, one can take advantage of the oxidizing properties of some of the host lattices to induce polymerization of suitable monomers. For example, conjugated polymers such as poly(An), poly(Py), or poly(Tp) were formed within the galleries of vanadium oxide, molybdenum trioxide, tantalum sulfide, or vanadyl phosphate [117–120]. The resulting materials are intercalated systems in which the polymers are located between the layers. If the oxidation potential of the host itself is not high enough molecular oxygen in the presence of redox active host ions (e.g. Fe^{3+}, Cu^{2+}) can be used for the oxidative polymerization process. This method has been termed ‘redox-intercalative polymerization’.

Solution methods (either in situ polymerization or solution intercalation) often require an exchange of the metal cations, which could be located between the crystalline layers, by organic cations such as alkylammonium



Scheme 8.

cations. These cations lower the surface energy of the inorganic host and improve the wetting characteristic of the materials with regard to the polymer. Additionally functional groups, which allow a chemical reaction with monomers, oligomers, or polymers and hence, improve the adhesion between the inorganic phase and the polymer matrix, can be introduced using the corresponding organic cation. Applying these methods, composite materials such as Nylon hybrids [121–123], epoxy resin materials [124, 125], or in situ poly(MMA) [126], and poly(caprolactone) [127] polymerized systems have been produced with ion-exchanged clays. Interactions of functional groups in monomers such as maleic anhydride [128], or epoxy resins [129] with the ionic surface of the clay galleries can support the swelling of the clay and the polymerization of the monomers can proceed between the galleries. Ionic initiators for nitroxyl-mediated living free radical polymerizations were intercalated in the galleries of montmorillonite, followed by a polymerization of styrene. The resulting nanocomposite contained the silicate randomly dispersed spatially and directionally in the polystyrene matrix. The polymer was desorbed from the silicate and analyzed. The resulting molecular weight and molecular weight distribution showed that a well-controlled polymerization occurred between the layers [130]. Even polyolefins, such as polyethylene, have been polymerized in situ between the layers of a fluorohectorite using a cationic palladium catalyst [131]. Many of the in situ polymerization techniques subsequently completely separate the layers from each other and/or form the hybrid matrix material with homogeneously distributed platelets.

The incorporation of preformed polymeric chains from solution between the sheets of the minerals may also result in intercalated composite materials. If this procedure is applied, the polymer has to be soluble in a solvent which can fill the space between the layers. In most of the cases, a polar solvent is required which helps to swell the clay and, in some cases, leads already to a total exfoliation resulting in solvent dispersed single-sheet colloids. Additives such as long-chain alkyl amine or ammonium salts can also be used to separate the layers. Poly(EO) of molecular weight 10^5 has been intercalated between the galleries of montmorillonite using polymer solutions in H_2O, MeOH, or acetonitrile [132]. This study showed that the nature of the solvent is crucial to facilitate the insertion of organic materials between the layers. Based on the different polarity of the solvents, a different degree of swelling is reached and thus an easier incorporation of the high molecular weight macromolecules. Water-soluble polymers such as polydiallylamine [133], poly(NVP) and poly(4VP) [134] have been intercalated into the layers of different inorganic materials. Generally, surfactants, such as amphiphilic block copolymers, can also be used to support the swelling of the layered material and additionally serve as compatibilizers between the hydrophilic surface and hydrophobic polymers. Employing this universal approach, it is possible to combine nearly any kind of inorganic material with any kind of polymeric material by tailoring the compatibilizing macromolecule in the correct way. For example, block combinations such as poly(EO)-*b*-poly(St), poly(EO)-*b*-poly(MMA), poly(MMA)-*b*-poly(MAc), or poly(St)-*b*-poly(2VP) have been used as compatibilizing agents in the formation of composite poly(St) and poly(MMA) materials [135,136].

Another possibility to introduce an otherwise incompatible polymer into the layered inorganic material is the functionalization of the polymer with groups that allow an easy incorporation of the polymer followed by a post-treatment to remove the functionalization. Poly(PV) has been integrated in MoO_3 using poly(*p*-xylene-α-dimethylsulfonium) chloride as precursor which can easily be intercalated followed by heat treatment to convert the precursor into the final polymer [137]. Polypropylene was intercalated into montmorillonite using either functionalized random or diblock copolymers and common organo-modified layered systems, or by using neat/unmodified polypropylene and a semi-fluorinated organic modification for the silicates [138].

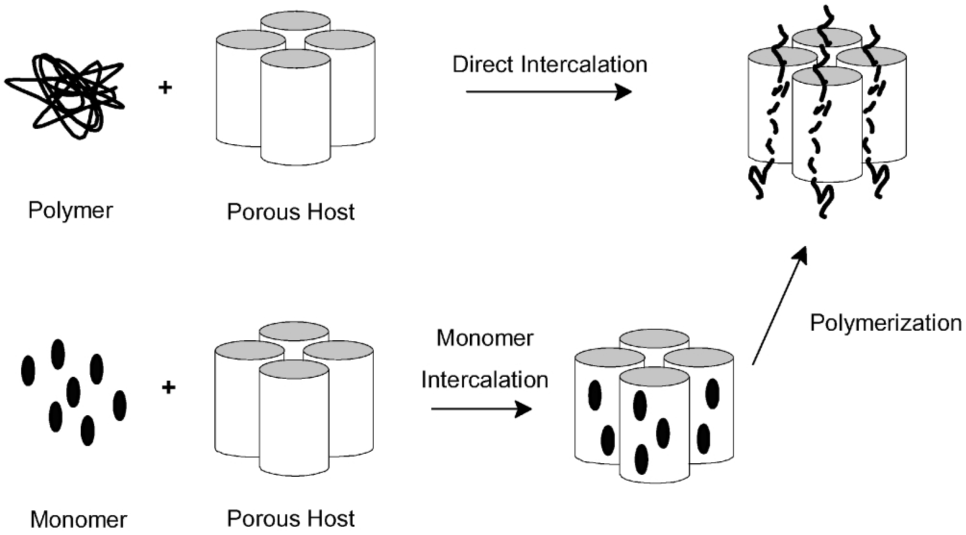
Especially with respect to environmental issues, the direct melt intercalation into layered host lattices is the preferred process for the formation of hybrid materials. This process is based on the heating of a mixture of the polymer and the layered system above the T_g, or the melting temperature (T_m) of the polymer, and the diffusion of the polymer between the galleries of the layers. With such a method, poly(EO) [139] was incorporated in different host lattices. The process was enhanced again using long-chain alkyl ammonium ions, which were preintercalated into the inorganic material. Even unpolar polymers such as poly(St) have been intercalated into montmorillonite by melt intercalation [140]. The poly(St) was afterwards deintercalated by suspending the hybrid in toluene.

5. Intercalation in 3D frameworks: zeolites, molecular sieves and M41S-materials

Zeolites are crystalline aluminosilicates with well-defined pores smaller than 2 nm. There are a variety of naturally occurring as well as synthetic zeolites. Zeolites have attracted much interest as catalysts and adsorbents due to their thermal stability and intraporous acidity. Molecular sieves are also crystalline framework materials, but of a non-aluminosilicate nature. M41S-materials belong to the class of mesoporous three-dimensional (3D) solids with ordered porosity in the pore size range 2–10 nm. Due to their special properties, such as the controllable pore size, there is a plethora of possible applications of these materials [141,142]. All these porous inorganic solids are excellent hosts for intercalation reactions because they contain well-defined empty pores and channels. A unique feature of these materials is their ability to discriminate between shapes and sizes of molecules. Therefore, the design of new materials requires a match of the features of the guest with those of the host. Contrary to the layered materials, which are able to delaminate completely if the forces produced by the intercalated polymers overcome the attracting energy of the single layers, this is not possible in the case of the stable 3D framework structures. The obtained composites can be viewed as host–guest hybrid materials. There are two possible routes towards this kind of hybrid material: (i) direct threading of preformed polymer through the host channels (soluble and melting polymers) which is usually limited by the size, conformation, and diffusion behavior of the polymers, and (ii) the in situ polymerization in the pores and channels of the hosts (Scheme 9).

Hybrid inorganic–organic materials from zeolite 13X, and crosslinked or linear poly(St) and poly(EA) were prepared. It was shown that two different composites were formed, the so-called ‘pseudo-interpenetrating polymer networks’ (PIPNs) and full IPN. The PIPNs were formed when no crosslinking compound such as ethylene glycol dimethacrylate was added, while IPNs were formed in the presence of these species [143]. An easy way to distinguish between the two types of hybrid materials is the extraction with suitable solvents. While the polymer chains could be partially or completely removed from the PIPNs, this was not possible in the case of IPNs. From the results of different characterization methods, such as SEM, SAXS, DSC and solid-state ^{13}C NMR, it was concluded that some of the poly(St) chains are incorporated within the internal 3D channels of the zeolite particles [144,145]. The DSC studies revealed that poly(St) incorporated in the channels of the zeolite 13X did not show a bulk T_g which is consistent with studies of poly(St) intercalated into layered silicates [146]. This observation is traced back to a possibly more extended, one dimensionally oriented polymer chain conformation which does not exhibit a bulk T_g. A surface-mediated cationic polymerization technique was applied for the formation of poly(PVE)–HY–zeolite hybrid materials containing polyenylium sequences [147]. The zeolite polymer hybrids had similar properties than the clay polymer hybrids. For example, the conductivity of a polyethyleneoxide/$LiBF_4$ system was increased by two orders of magnitude through inclusion in a zeolite [148].

Special properties of zeolites such as their active sites in their cavities or the ability to entrap molecules of the right size in their channels and pores can be used to form materials which cannot be prepared from other porous solids. The active sites often play a major role in catalytic processes for which zeolites are well known. This particular property can be utilized in the synthesis of hybrid materials when employing acid catalyzed polymerizations, such as the acetylene polymerization with H-ZSM-5 zeolite [149]. Organic chromophores have been trapped in zeolite cages and afterwards embedded in a polymethacrylate matrix



Scheme 9.

[150]. To obtain high optical transparency the refractive index of the polymer was adjusted to those of the zeolite.

The active protons of HY zeolites were used for cationic polymerizations of several vinyl monomers inside the pores. In porous materials where no such protons are present, such as MCM-41, arylmethylium was incorporated. Utilizing this method the synthesis of well-defined poly(vinyl ethers) or poly(vinylcarbazole) under conditions of constricted geometry can be achieved [151].

Poly(PV) was incorporated in the most prominent and most studied mesoporous silica material MCM-41 by an in situ polymerization of xylene bis(tetrahydrothiophenium chloride). The polymerization was most likely initiated by deprotonated surface hydroxy groups and took place in the pores of the material. The obtained powder showed the typical luminescence behavior of PPV. The advantage of the resulting material is that the quenching of photoluminescence, which is based on interchain interactions of the polymer chains, is decreased [152]. A cationic polymerization of cyclohexyl vinyl ether (CHVE) was achieved using triphenylmethylium or bis(4-methoxyphenyl)methylium silanolate ion pairs, as well as mobile acidic silanols as initiators. Depending on the initiation mechanism, different structures of the polymer were obtained in the channels of the material [153]. For a better adhesion between the pore walls and the incorporated polymer, the pore wall of the MCM was functionalized with methacrylate groups during the synthesis of the silicate material. Different characterization methods showed that the methacrylate groups are readily and completely accessible. Adsorbed MMA was polymerized in the pores resulting in an inorganic–organic hybrid material [154].

Porous inorganic structures can serve as templates for well-defined conducting structures of nanometer dimensions such as ‘molecular- or nano-wires’. Therefore, different types of conducting polymers have been prepared in the host channels of these inorganic materials. Poly(An) was synthesized in the channels of mordenite, MCM-41 and zeolite Y [155–157]. The monomer was intercalated from solutions or vapor phase adsorption followed by oxidative polymerization in the presence of Cu(II), Fe(III), or persulfate. A similar approach was used to incorporate and polymerize acrylonitrile in the channels of MCM-41. Pyrolysis of the intrachannel polyacrylonitrile results in the formation of encapsulated of graphite-type carbon wires [158].

Poly(Py) and poly(Tp) have also been successfully included in the channels of different porous hosts [159, 160]. The conductivity of the obtained polymer filaments in the host was studied by contactless microwave absorption.

6. Incorporation of inorganic particles and clusters

Physical mixtures of organic polymers and preformed inorganic particles may lead to separation in discrete phases, resulting in poor mechanical, optical, electrical, etc. properties. In addition, particle agglomeration tends to weaken mechanical or optical properties of the resulting materials. The latter problem especially is observed in a variety of hybrid systems in which clusters and particles are involved. Unmodified inorganic particles tend to aggregate in the polymer matrix independent of the kind of material and the size. To avoid these drawbacks different methods can be applied, for example, the use of functional polymers [161] which interact with the surface of the particles, or surface modification of the particles to change their character.

6.1. Incorporation of unmodified particles

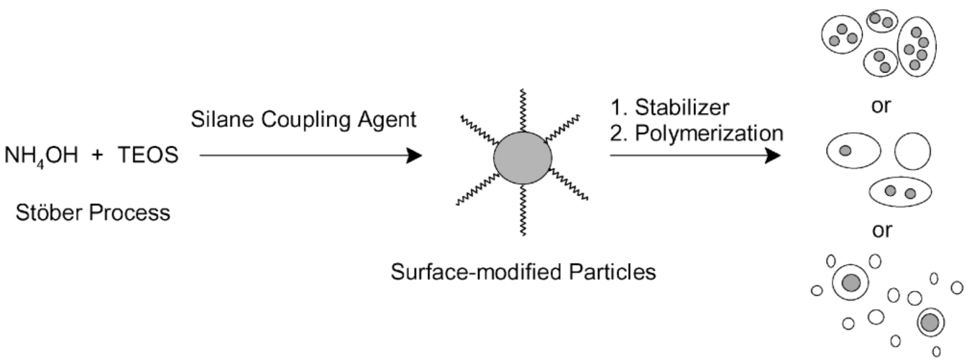
Nanocomposites based on nanosized inorganic particles and clusters are an emerging field of research activity due to the interesting properties of the particles, such as their behavior as quantum dots or their possible super-para and super-ferromagnetism, in combination with the other properties of the materials including, for example, their optical transparency. Another advantage of such hybrid composites of particles in an organic polymer matrix is the possible protection of systems that are sensitive towards environmental conditions (oxygen, humidity, etc.) by coverage with a protecting polymeric skin or inclusion in a polymeric matrix [7]. Furthermore, the content of the inorganic moiety can be gradually changed in the polymeric matrix. Ordering in such systems also plays a role, from highly ordered superlattices to so-called stochastic mixtures where the particles are randomly dispersed. Therefore, the possibilities for these materials cover a wide range of applications with many yet unknown future perspectives [82].

In principle, there are five possibilities to overcome the phase separation in hybrid particulate systems: the use of a polymer which interacts (van-der-Waals, dipolar, hydrogen bonds, etc.) with the particles; the covalent attachment of an inert organic layer on the surface of the particle core that serves as a compatibilizer at the particle/polymer interface; the encapsulation of the particles by special polymerization techniques such as emulsion polymerization; the attachment of functional groups which allow a covalent linkage with the polymer; or the attachment of initiation groups for grafting of polymer chains from the particle surface.

6.2. Encapsulation of particles in a polymer shell

Encapsulation of small inorganic particles by a polymer layer, so-called core–shell particles, can be carried out applying an emulsion polymerization process. Polymerization occurs primarily at the surface of unmodified particles due to the adsorption of the monomer on the surface, followed by polymerization in the adsorbed layer [162–164]. The formation of an initial hydrophobic layer on the surface of the particles seems to be crucial for the formation of the polymer shell. Methods for the introduction of such a layer include the use of non-ionic surfactants, amphiphilic block copolymers, etc. Furthermore, these surface-active molecules fulfill another task: they avoid agglomeration of the particles. The concentration of such compatibilizing molecules in solution needs to be tuned carefully because a latex formation in free micelles in the emulsion can be observed at higher concentrations. Additionally these molecules are usually only weakly bonded to the surface and can therefore desorb easily. Hence, the covalent attachment of organic groups, which potentially can interact in the polymerization reaction, is used for surface modification [165–170]. Using a one-pot process, nanosized, surface-modified silica particles encapsulated with a polymeric layer have been formed (Scheme 10). Depending on the reaction conditions like stabilizer concentration, different products were obtained, e.g. those in which a few particles were encapsulated in a polymer shell and those where only single shell particles were formed. Additionally, pure polymer latex particles can also be formed in the emulsion.

Not only the nanosized particles themselves are interesting systems, but also materials formed by their assembly. The formation of so-called colloidal crystals is a challenge because the self-organization is strongly dependent on the size distribution that influences the formation of the packing pattern, as well as on the surface functionality influencing the interactions between the particles [171]. The resulting materials can have feature sizes of the wavelength of electrons, photons, or both, and they are interesting materials for optics, electronics (photonic crystals, quantum dot or dielectrical lattices), or chemical sensing [172]. 3-(Trimethoxysilyl)propyl coated silica particles were prepared by the Stöber method [173,174] followed by a surface-modification [175]. These particles were self-assembled in a film and UV copolymerized with different monomers such as MA, MMA, HEMA, and TFEA. The systems were able to selectively filter light with a bandwidth less than 20 nm [176].



Scheme 10.

6.3. In situ growth of inorganic particles in a polymer matrix

The thermal decomposition of volatile metal compounds in a polymer matrix leads to the formation of zero valent metal particles, or particles of their oxides dispersed in the polymer. Stable homogeneous dispersions of a variety of metals have been obtained by this approach. For the formation of homogeneous dispersions, it is important to have some kind of interaction between the metal complex and the polymer matrix. This is achieved either by the direct coordination of the metal complex to amino or hydroxyl groups, etc. in the polymer, or by the substitution of a labile ligand in the metal complex with unsaturated groups in the polymer (poly(St), polybutadiene, etc.) during the thermal decomposition of the complex. Probably the best-studied metal polymer composites obtained by this thermal decomposition route are cobalt and iron carbonyls in the presence of polymers such as polybutadiene, poly(St), polypropylene, different block copolymers, etc. [177–179]. The size of the metal nanoparticles formed in the polymer matrix depends on the reaction conditions, for example, the thermolysis temperature or the solvent. Additionally, the number of polar groups on the polymer backbone seems to be important for the particle size; the more polar the groups, the smaller the particles [82]. Instead of the metal carbonyls other organometallic species can also be used as precursors for the metal species in the composite materials.

Another method to obtain polymer-immobilized nanoparticles is the reduction of metal salts from solutions or suspensions in the presence of a polymer, or of mononuclear metal complexes bonded to the polymer. This method was used in the production of composites containing Pd and Au nanoparticles in a synthetic rubber film [180]. The reduction can be carried out by agents such as hydroquinone, *p*-phenylenediamine, pyrogallol, hydrogen, etc. [82]. Electrochemical methods [82], radiation-induced or photochemical reduction are sometimes preferred to hydrogen reduction [181]. The polymer metal interaction is an important parameter in all these syntheses especially for the size and size distribution of the metal particles as well as for their dispersion. The polymer often plays the role of a ligand which helps to avoid the association of complexes and therefore limits the size of the formed particles. Furthermore, the interaction between the polymer and the metal particles stabilizes the latter and helps to prevent their oxidation.

Iron oxide nanoparticles were incorporated in a poly(An) matrix adding iron salts to the polymer and subsequently changing the pH to alkaline conditions by adding a base. The obtained materials showed ferromagnetism [182,183].

A quite new method for the in situ generation of particles in polymers is the use of specific structures formed by the macromolecules, for example, the use of supramolecular arrangements of block copolymers that form micellar ‘nanoreactors’ or the application of particular shaped macromolecules such as dendrimers.

Gold nanoparticles were formed within the microdomains of a poly(St)-*b*-poly(2VP) diblock copolymer in the presence of additional Py. The polymerization of Py was effected by $HAuCl_4$, which simultaneously generated Au nanoparticles [184]. Thus, Au-poly(Py) nanocomposite core–shell particles were formed which was confirmed by TEM measurements.

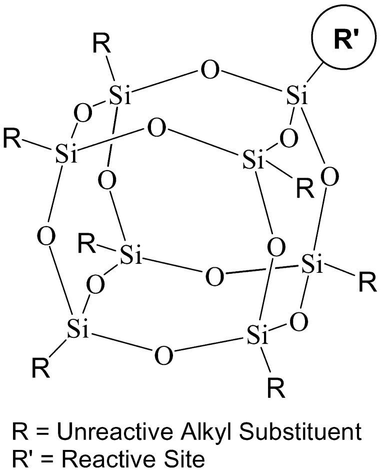
Crosslinked polymer matrices were used for the in situ growth of magnetic γ-Fe_2O_3 nanoparticles. The resulting nanocomposites were transparent due to the small metal oxide particle size, and the magnetization of the nanocomposite was greater by more than an order of magnitude than those of the strongest room-temperature transparent magnets [185,186].

One of the challenges in nanochemistry is the production of specific nanoscale objects in unlimited quantities. This is due to the fact that control of the critical nanorange length means control of new macroscopic properties. Dendrimers as monodisperse macromolecules can fulfill the demands of precursors for such materials. Dendritic molecules are formed by connectors and branching units built around a small molecule or a linear polymer (core) which leads to a spherical or rod-like macromolecule. Based on the high level of synthetic control, these systems are well defined in their molecular weights as well as in their functionalities. For example, depending on the final step of the synthesis the interior and exterior can be very different, e.g. hydrophilic and hydrophobic. These special properties make dendrimers ideal systems for hosts in the formation of nanoparticles. In a typical process of the formation of metal nanoparticles metal ions are preorganized by the dendrimer molecule and subsequently immobilized in or on the macromolecule. Size, shape, size distribution, and surface functionality of the metal nanoparticles are determined by the dendritic template as well as by the chemistry of the preorganization and immobilization process. Mesoscopically ordered hybrid materials were formed using functional dendrimers and the titanium oxo cluster $[Ti_{16}O_{16}(OEt)_{32}]$ as nano building blocks. The two components were crosslinked through covalent bonds formed by nucleophilic reactions between the functional tips of the dendrimers and the titanium centers of the clusters [187].

6.4. Surface-modification with polymerizable groups

Research in this area spans the modification of commonly used inorganic fillers or particles, up to the recent commercial availability of a variety of polyhedral oligomeric silsesquioxanes (POSS), $R_8Si_8O_{12}$ nanoclusters (Scheme 11).

There are two principle possibilities to functionalize the inorganic species with organic groups: (i) grafting functional organic groups onto the surface of preformed clusters or particles, and (ii) in situ functionalization of the clusters or particles during their formation. The advantage of the first method is that the inorganic particles can be

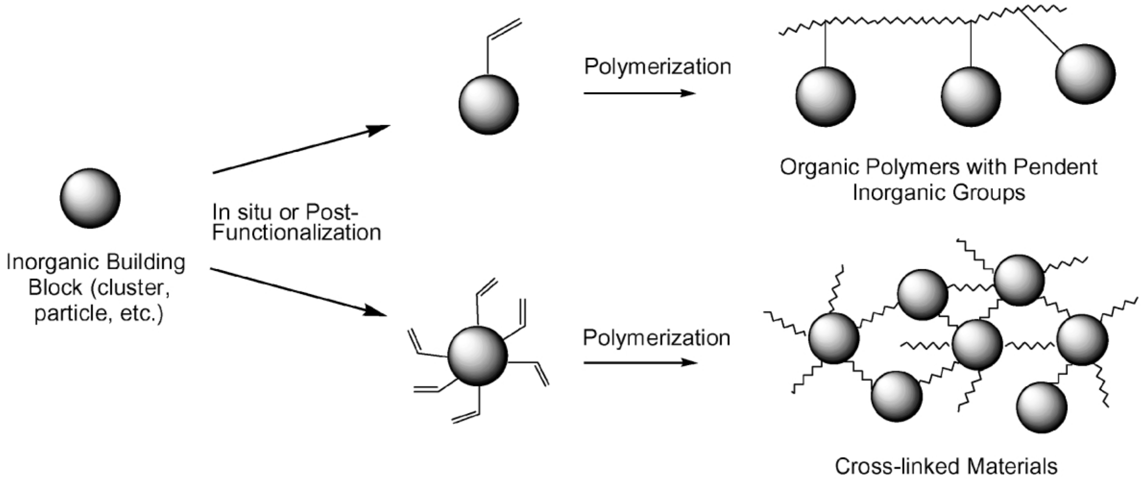


Scheme 11.

prepared by well-established techniques. However, for a covalent modification of the surface reactive groups, such as hydroxy groups or coordination centers, must be available. Sometimes, especially in the case of clusters, the modification by organic moieties may require a rearrangement of the surface groups. Another possibility for surface-modification is the attachment of organic groups by ionic interactions. In the 'in situ-functionalization' method, the particles are formed in the presence of functional molecules, which serve to cap their surface. An additional parameter which has an important influence on the properties of the final hybrid materials is the number of reactive functional groups available on the surface. If only one group is present, the particulate systems can be used as monomers to form linear polymers; more than one functionality leads to crosslinked systems (Scheme 12) [188,189].

Metal oxide clusters. Although there are many organometallic clusters with potential polymerizable ligands such as acrylate, vinylpyridine, vinylimidazole, acrylonitrile, etc. they were only rarely used as monomers in polymerization processes [82]. In these polymerizations the interaction of the polymerizing species with additional ligands coordinated to the metal was often observed which led to difficult to characterize materials. Metal oxide clusters have recently been investigated due to their interesting optical, electronic, and magnetic properties. The heterotungstate cluster $K_4[SiW_{11}O_{39}]$ was derivatized by reaction with various trichloro- or triethoxysilanes $RSiX_3$ ($X = Cl$ or OEt) containing polymerizable groups R (R = allyl, vinyl, styryl, or methacrylate) [190,191]. Two functional groups per cluster unit were thus introduced, and the obtained anionic clusters had the composition $[SiW_{11}O_{39}(OSi_2R_2)]^{4-}$. The polymerizable groups bonded to the surface were used for crosslinking the clusters by free radical polymerization in solution (without the addition of organic monomers). Their reactivity was found to be similar to that of the corresponding silanes and increased in the order R = vinyl (polymerization yield 5% in DMF) ≪ allyl (20%) < methacryl (65–70%) < styryl (100%). The hydrodynamic radius of the obtained inorganic–organic hybrid polymers varied between 5 and 120 nm, but did not always correspond to the polymerization yields. ^{29}Si NMR, UV spectroscopic investigation, and cyclic voltammetry studies showed that the structural integrity of the clusters was preserved upon polymerization and that the clusters retained their typical redox and optical properties in the polymers.

This work was extended by similarly functionalized polyoxotungstate cluster for the crosslinking of organic polymer chains. The cluster $[\gamma\text{-}SiW_{10}O_{36}(OSi_2R_2)]^{4-}$ ($R = [CH_2{=}CMe{-}C(O)OCH_2CH_2CH_2]$) was obtained by reaction of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with MEMO [192]. Functionalization via both covalent and ionic interactions was achieved by additionally employing the quaternary, methacrylate-substituted ammonium counter-ion $[CH_2{=}CMe{-}C(O)OCH_2CH_2CH_2NMe_3]^+$. These clusters were copolymerized in



Scheme 12.

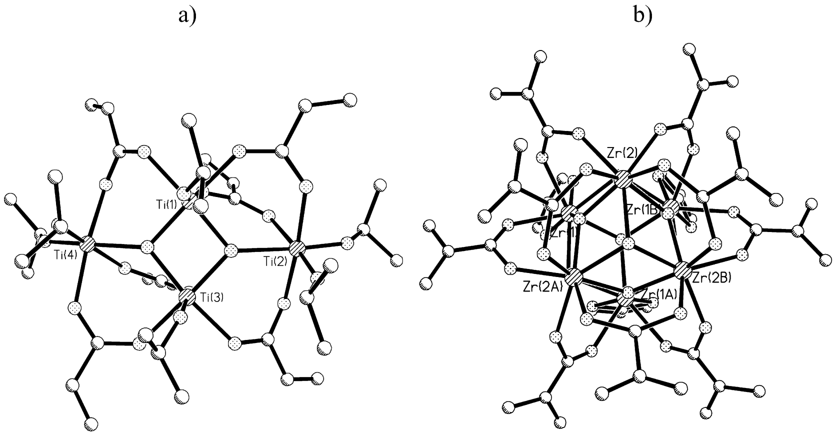


Fig. 2. Surface-modified oxometallate compounds with (a) titanium or (b) zirconium as metal, and acrylate or methacrylate as polymerizable group at the surface. These systems were used as crosslinking agents in polymerization reactions.

acetonitrile with ethyl methacrylate in different ratios (1:10 to 1:50), and swollen gels were obtained. The degree of swelling increased with an increasing comonomer to cluster ratio, i.e. dependent on the crosslinking density. Spectroscopic investigations again proved that the polyoxotungstate was incorporated in the material without a structural change.

Oxo-hydroxo stannate clusters as building blocks for hybrid materials were formed using the cationic cluster $[(BuSn)_{12}O_{14}(OH)_6]^{2+}(OH^-)_2$. Functional organic groups were obtained by exchange of the hydroxide counter-ions against methacrylate anions [193,194]. The methacrylate anions not only interact with the cluster cation by Coulomb interactions, but also by hydrogen bonding to the hydroxy groups capping the cluster surface. Homopolymerization of the functional clusters by free radical polymerization failed, probably due to sterical hindrance between the macrocations. Free radical copolymerization with MMA in THF (1:13 to 1:52 ratio) resulted in soluble inorganic–organic hybrid polymers.

A different approach for the functionalization of oxoclusters is the in situ modification during their formation. This was mainly investigated for the preparation of organically substituted oxotitanium and oxozirconium clusters [195–199]. When titanium or zirconium alkoxides $M(OR)_4$ (M = Ti, Zr), or mixtures of both, were allowed to react with a defined excess of acrylic or methacrylic acid, crystalline clusters of the general composition $M_xO_y(OH/OR)_z(OOCR)_w$ of differing size and shape were obtained (Fig. 2). There are a variety of structurally characterized examples with different morphologies. Copolymerization of these clusters with MMA or MAc in ratios between 1:50 and 1:200 resulted in polymers in which the polymer chains were efficiently crosslinked by the oxometallate clusters [200–203]. Glassy, insoluble materials were typically obtained upon copolymerization with MMA, and insoluble powders with MAc. The specific surface area of the doped poly(MAc) depended on the amount of incorporated cluster and increased with an increasing cluster proportion. The cluster crosslinked poly(MMA) was insoluble in common organic solvents, but swellable. The solvent uptake upon swelling increased with an increasing comonomer to cluster ratio. The thermal stability of poly(MAc) and poly(MMA) was improved by the cluster crosslinking, and the thermal depolymerization observed in the undoped polymers was inhibited.

Doping or crosslinking of organic polymers with tungsten, tin, zirconium or titanium oxide clusters can be considered an extension of the so-called POSS reinforced polymers, in which silicon oxide clusters are incorporated into organic polymers. Variation of the inorganic building blocks by using transition metal oxide clusters could possibly widen the range of properties of these inorganic–organic hybrid polymers.

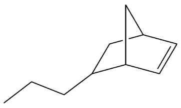
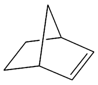
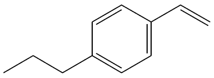
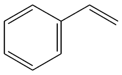
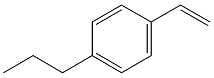
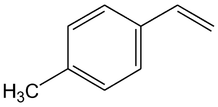
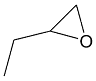
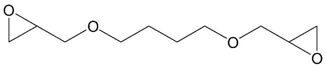
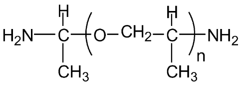
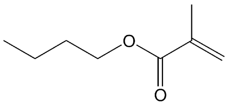
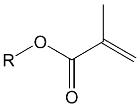
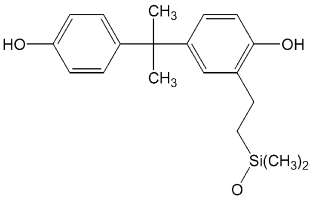
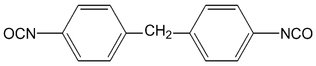
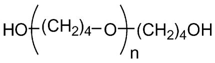
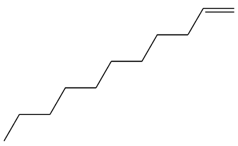
Silsesquioxanes cubes. Probably, the most prominent representatives of cluster-like inorganic components are the silsesquioxane cubes. These systems are obtained as mono- or octafunctionalized systems.

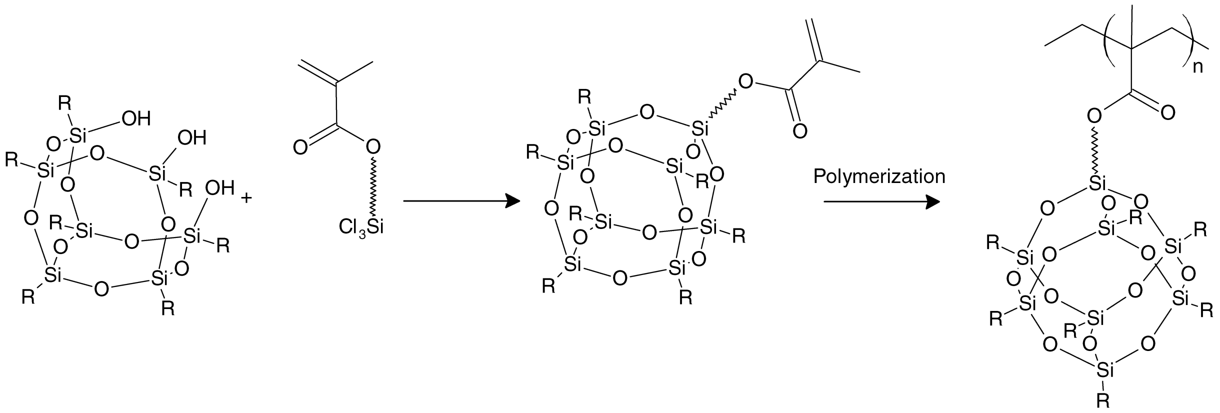
Octafunctionalized cages such as the anionic oxy-functionalized system $(SiO_{2.5})_8^{8-}$ or the octahydrido species $(HSiO_{1.5})_8$ are obtained in reasonable yields and have been used as precursors for multifunctionalized crosslinking agents. Functionalization of the $(SiO_{2.5})_8^{8-}$ cube is carried out by quenching the anionic silsesquioxane with $ClSiMe_2H$ and further hydrosilation. The octahydrido compound can be prepared by slow hydrolysis of $HSiCl_3$ and functionalized by hydrosilation. The Pt-catalyzed hydrosilation of $(HSiO_{1.5})_8$ and $(H(CH_3)_2SiOSiO_{1.5})_8$ with propargyl methacrylate occurred specifically at the propargyl site retaining the methacrylate functionality for subsequent polymerization [204]. The silsesquioxane cubes were hydrosilated with allyl glycidyl ether in a similar way [205]. A different approach to such crosslinking species is the epoxidation of vinyl-substituted cubic polyhedral silsesquioxanes with *m*-chloroperoxybenzoic acid which can be directed to a partial, or full epoxidation of the vinyl groups [206]. The crosslinking components received from this reaction are soluble in organic solvents, e.g. THF, toluene, hexane and CH_2Cl_2, and were used in thermal and photochemical polymerizations to give hard, abrasion resistant, insoluble composites containing up to 65 wt% silica.

In recent years, POSS inorganic–organic hybrid polymers have been developed up to a commercial scale. The chemistry of these systems is based on the design of well-defined inorganic oligomers with only a single polymerization or initiation site per cluster. Each of these clusters has an inorganic silica-like core and is surrounded by eight organic groups, seven of which are inert towards polymerization and only one is active. Polymerization at this single site results in a linear polymer with pendent inorganic clusters of approximately 1.5 nm diameter. The unique property of such materials is that there is no crosslinking and the pending linear polymeric structure allows for an easier processing and characterization of these systems by conventional analytical methods compared to, for example, IPNs. The modifications of polymers with these inorganic building blocks have an influence on the thermal, oxidative and dimensional stability of the linear polymer chains [207]. Different polymer backbones have been synthesized using a variety of different substitution patterns at the silica cage (Table 1).

Methacrylic-substituted POSS monomers were synthesized by corner capping the trisilanol cages $R_7Si_7O_9(OH)_3$ ($R = c\text{-}C_6H_{11}$, $c\text{-}C_5H_9$) with methacrylate containing trichlorosilanes (Scheme 13) [208]. Homo- and copolymers of these systems reveal no thermal transitions below their decomposition temperature of

Table 1
Different POSS compounds ($R'R_7Si_8O_{12}$) as monomers for copolymerizations

R'	Polymerization	Comonomers	Reference
	ROMP		[212]
	Free radical polymerization		[209]
	Free radical polymerization		[210]
	Epoxy resin formation	 	[207]
	ATRP	 R = Me, ^{n}Bu	[213]
	Polyurethane synthesis	 	[211]
	Ziegler–Natta	Ethene, propene	[215]



Scheme 13.

388 °C. Styrylethyl-substituted systems were homo- and copolymerized with styrene via a free radical polymerization initiated by AIBN [209]. A reactivity change of the POSS macromers compared to styrene was not observed. Generally, POSS inclusion changes the thermal properties of the obtained polymers drastically towards thermally more robust systems, and the T_g is efficiently enhanced upon copolymerization with the associated POSS monomer. Rheological measurements revealed that an increasing proportion of POSS also affects the polymer dynamics [210]. A high-temperature rubbery plateau developed at higher concentrations of POSS, this has also been explained by interchain interactions between the pendent inorganic groups on the polymer backbone. The tensile modulus of POSS reinforced polyurethanes was greatly increased by the pendent inorganic molecules [211]. Morphological studies by X-ray analysis on randomly copolymerized norbornene–POSS systems revealed that at higher concentration of cyclopentyl-substituted systems more ordered regions, probably caused by agglomerating POSS cages, were present [212]. Homopolymers, diblock-, and branched triblock copolymers with quite low polydispersities were obtained from ATRP of methacrylate-substituted POSS systems with methyl methacrylate and *n*-butyl acrylate [213]. In addition substituted POSS was also used as an initiator for ATRP [214]. Moreover, hybrid materials of mono-functionalized POSS systems were obtained by homo- or copolymerization via Ziegler–Natta polymerization with olefins [215]. Besides the non-crosslinked materials, epoxy resins with terminating POSS systems were produced, and their thermal and mechanical properties were investigated [207].

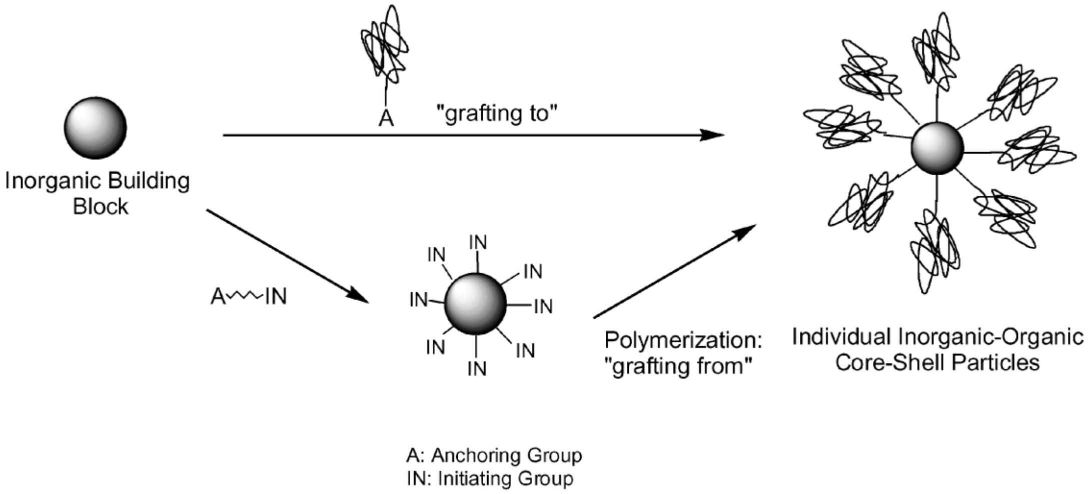
The POSS cages with one reactive substituent have seven inactive substituents to increase the solubility, usually cyclohexyl and cyclopentyl groups. These substituents lead to remarkable properties of the silica cages. For example, the cyclohexyl-substituted system is twice as soluble as the cyclopentyl-substituted cage [209]. Furthermore, a change of the size of substituents from cyclopentyl to cyclohexyl also affects the T_g in such a way that with the same amount of POSS, the cyclopentyl-substituted polymer has a much larger T_g than the cyclohexyl-substituted macromolecule. These solubility differences are believed to be based on the lattice energy in the crystalline solid.

The systems discussed are representative examples of a larger number of related studies, in which substituted POSS have been applied as monomers to produce various polymers with pendant POSS substituents. The common feature of all systems is that several polymer properties are promoted by the incorporation of POSS. Among other properties, higher degradation and glass transition temperatures, reduced flammability, reduced viscosity, and higher oxidation resistance are observed.

6.5. Surface-modification with initiating groups

Initiating groups attached to the inorganic core allow the grafting of polymers *from* the surface of the inorganic moiety. This approach has advantages over the more often used 'grafting to' technique where end-functionalized polymers are grafted *to* the surface of inorganic particles, i.e. leading to restrictions in the surface coverage. The 'grafting from' approach leads to particle-like structures, which can be tailored by the size and functionality of the inorganic core and/or the polymer shell. In principle, this approach can be used for all kinds of inorganic cores (Scheme 14). In every case, a key step is the attachment of initiating groups onto the particle surface. The methods described before used to attach the functional groups by ionic or covalent bonds can be applied again. In most of the work done in this area, polymers were grafted from nanometer- and micrometer-sized silica particles [216–219].

Free radical polymerizations. Diazo groups capable of initiating free radical polymerization were attached to the surface of pyrogenic amorphous silica (Aerosil™) using a multistep synthesis [216]. The silica surface showed a diazo



Scheme 14.

group overage from 0.03 up to 0.1 diazo groups per 100 Å^2. This means that only every 30th hydroxy group had reacted. Poly(St) was grafted from the thus modified surface. It should be noted that in free radical polymerizations with the described macroinitiators, polymerization also occurs in the solution because the surface-attached initiator decomposes into two radicals from which one initiates polymerization in solution. A linear dependence between the monomer and initiator concentration and the polymer coverage was observed. Termination of the grafting chains occurred due to the lack of initiating radicals or sterical hindrance at the surface. The molecular weight of the polymers cleaved from the surface by HF treatment were up to 1.46×10^6, while those of the homopolymers formed in the solution simultaneously were up to 1.75×10^6.

In more recent studies, silane-coupling agents such as alkoxysilanes [219–221] or chlorosilanes [217,218] have been used to modify the surface of silica particles. For example, 4,4′-azobis(4-cyanopentanoic acid) was immobilized on the surface of pyrogenic silica via amide bonds through attached aminophenyltrimethoxysilane. The concentration of diazo groups at the surface reached 0.2 mmol/g. DSC measurements proved that the stability of the initiator decreased upon immobilization. Poly(MMA) with a molecular weight of up to 8.7×10^5 was grafted from the surface. The polymerization was highly affected by the Trommsdorff effect [222] which was also made responsible for the higher molecular weights of the grafted polymer compared to the homopolymer.

Polyesters were grafted from various ultrafine inorganic particles such as silica, titania and ferrite by anionic ring opening copolymerization of epoxides and cyclic acid anhydrides [221]. The silica, titania and ferrite particles had sizes of 16, 120 and 15 nm, respectively, and surface hydroxy group concentrations of 1.37, 0.77 and 0.55 mmol/g. The initiating group was a potassium carboxylate, which was attached to the surface by a series of modifications. The amount of initiating groups on the surface of the silica, titanium oxide and ferrite particles was 1.92, 0.94 and 0.62 mmol/g, respectively. The used organic monomers were styrene oxide, chloromethyloxirane, gylcidyl methacrylate, gylcidyl phenyl ether, phthalic anhydride, succinic anhydride, and maleic anhydride.

Surface anchored peroxide initiators were used for the grafting of methyl methacrylate [221]. This type of initiator was attached to the surface by treatment of silica particles with thionyl chloride to obtain surface Si–Cl groups, which were then reacted with *tert*-butyl hydroperoxide or diisopropylbenzene hydroperoxide to form the initiating groups. Depending on the type of peroxide, the concentration of initiators on the surface was 0.08 mmol/g for *tert*-butyl peroxide and 0.29 mmol/g for diisopropylbenzene peroxide. Both peroxide groups were able to initiate the polymerization and led to the grafting of poly(MMA).

The study of the kinetics and mechanism of an azo-initiated free radical styrene polymerization from modified silica particles was part of more detailed studies for the grafting of polymers from surfaces [218]. In these studies initiators with a cleavable ester group were attached to the surface. After the polymerization, the ester group was catalytically cleaved. The differences between the obtained poly(St) homopolymer and the polymers obtained by polymerization in solution were mainly due to differences in the termination reactions. It was found that although the initiator efficiency of surface-attached initiator is slightly decreased, it still allows the formation of high molecular weight polymer with high graft density.

ATRP. Contrary to free radical polymerizations, where as discussed earlier, polymerization also occurs in the solution, this is not the case for controlled radical polymerization, such as transition metal-mediated ATRP. With this technique poly(AA) was polymerized from silica

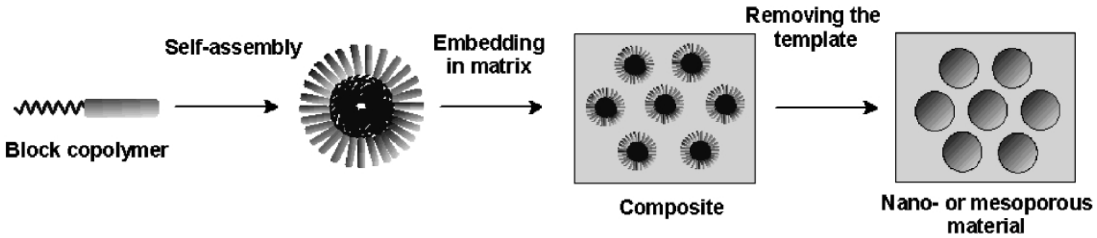


Fig. 3. Schematic representation of the formation of structured nano- or mesoporous materials by a self-assembly process of block copolymers.

particles for chromatographic applications [217]. [2-(*m*/*p*-Chloromethylphenyl)ethyl]trichlorosilane was attached to the surface of a silica gel with a particle diameter of 5 μm and a pore size of 86 nm. A dense 5.1 μmol/m^2 monolayer of the initiator was thus created. The film thickness of the grafted poly(AA) was calculated to be 10 pm and therefore would reduce the average pore size of the silica gel but not block the pores. The modified silica was used as a solid phase in size-exclusion chromatography and revealed a very good separation behavior for a mixture of the four proteins thyroglobulin, ovalbumin, ribonuclease A and aprotinin. The elution times were much faster than with a commercially available silica-based stationary phase.

In another study, silica spheres with a diameter of 70 nm were produced by the Stöber process and modified by reaction with the silane coupling agent [2-(4-chloromethylphenyl)ethyl]dimethylethoxysilane [219]. A surface concentration of the initiator of 0.14 mmol/g was thus achieved. The obtained particles were used as macroinitiators for ATRP of styrene. In a similar approach (11$'$-chlorodimethylsilylundecyl)-2-chloro-2-phenylacetate was covalently attached to the surface of commercially available silica particles and ATRP grafting of styrene from the surface was achieved. The grafted polymers were detached from the solid particles for analysis. After polymerization of a first generation of grafts and work-up of the hybrid particles, the chain ends of the grafts were still active to initiate a second monomer feed [223]. Furthermore, gold nanoparticles were modified with thiole-functionalized initiators for ATRP and BA was polymerized from the surface [224].

7. Nanoengineering of composite materials

An important area with respect to potential applications of nanocomposite materials is the ability to design these materials in the nanoscale. The formation of hierarchically well-ordered materials from the micro- to the nanoscale is especially important for many possible applications. The specific role of the polymer, for example, in structure-direction, is based on their properties, e.g. phase behavior, which are often not available in the same broadness with other templates.

Probably, the most prominent example is the formation of nano- and mesostructured materials applying the self-assembly process of block copolymers. A milestone in the formation of such materials was the discovery that in addition to single molecules molecular assemblies, found, for example, in liquid crystals, can be used for templating inorganic matrices [225]. This supramolecular self-assembly relies on the ability of molecules such as surfactants to self-assemble into micellar structures that, when concentrated, undergo a second stage of self-organization resulting in liquid crystalline mesophases. Molecular inorganic species can cooperatively assemble with these structure-directing agents (templates) to form the mesoscopically ordered inorganic backbone of the final material (Fig. 3). Usually the intention of this preparation route is the formation of porous, molecular sieve-like materials, which can be obtained from the nanocomposites by removal of the polymer template. In addition to the classical ionic surfactants used, the application of block copolymers as templates in block-selective solvents is an emerging field in materials chemistry. The polymeric approach allows for the extension of the size of the organized domains into larger scale features, and the possibility to reach morphologies which cannot easily be obtained with usual surfactants [226, 227]. A plethora of different polymers have already been used as structure-directing media and therefore only a short list of examples is given here: polybutadiene-*b*-poly(vinylpyridinium) [226]; anionic poly(ethylethylene)-*b*-polystyrenesulfonate [226]; poly(butadiene-*b*-ethylene oxide) [228]; ABC triblocks [229]; commercially available PEO-based systems [230–233]. Besides block copolymers hyperbranched macromolecules also showed a structure-directing ability [234].

The formation of the inorganic network is based, in most of the cases, on the sol–gel process already discussed. The resulting porous materials attract interests, for example, for their potential application as ultralow dielectric materials for advanced microelectronic devices [234,235].

Most of the above-mentioned structured materials are based on a silicate inorganic network, however, other metal oxides were also the source of the inorganic framework. Organically modified aluminosilicate mesostructures were synthesized from (3-glycidyloxypropyl)trimethoxysilane and aluminum-*sec*-butoxide with the use of isoprene–ethylene oxide block copolymers as the structure-directing molecules [236–239].

Another approach to design the morphology on the nano- or mesoscale is the use of a 3D self-assembly of nanoparticles for the formation of ordered materials in such a way that the voids between the lattice were filled with a material forming a rigid network. Two approaches can be applied: (i) either the template is of organic nature and the network formation occurs by inorganic processes, or (ii) the templates are inorganic spheres and a polymer forms the network. For the first approach mainly latex colloids, such as crosslinked polystyrene, are used and the voids between the nanospheres are filled with inorganic material precursors. These materials have recently attracted much interest due to their potential application as optical waveguides [240].

A different method of preparing ordered composites is the use of artificial 3D periodic opal lattices with silica spheres smaller than 300 nm. These systems were infiltrated with monomers, which were crosslinked in the voids, or preformed polymers. From this periodic composite structure, the silica opal was etched out and so-called inverse polymer opals were formed. In this approach polymers such as ferroelectric vinylidene fluoride–trifluoroethylene copolymers [241], poly(3-alkylthiophene) [242], or bisphenol A-epichlorohydrin copolymer epoxy resin were used [243]. Furthermore, monomers can also be polymerized in the voids, for example (*p*-xylenebis(tetrahydrothiophenium chloride)), was polymerized in situ [244].

8. Applications

The possible applications of the described materials are manifold and the future of these materials appears bright. Especially, the tremendous possibilities of different combinations in nanocomposites between inorganic and organic species, allow properties which cannot be obtained by traditional composite materials. In this review only a limited amount of applications can be exemplary introduced. The examples follow the specific properties of the nanocomposites.

Optical transparency. Although many of the features of inorganic and organic polymeric moieties that are important for optical issues such as the refractive index are very different, the resulting material can often be prepared to be optically transparent. This is based on the small length scale over which phase separation may exist.

In order to implement optoelectronic or photonic properties into devices, the materials have to fulfill high optical quality demands and have to be stable over a long period. Furthermore, the control of the refractive index as well as the thickness and, therefore, the processibility of the materials are important. Due to its low optical losses (high optical quality), silica glass and composites made from it seem to be very useful for these devices [245,246]. For example, photoconducting composites were prepared by the incorporation of cadmium sulfide particles in a polyvinylcarbazole matrix. The resulting materials allowed the tuning of the band-gap of the sensitizing nanocrystals so that their spectral response was adjusted to suit a particular wavelength of operation [247,248].

The already mentioned low optical loss of silica-based composite materials, the ability to tune light scattering, and depending on the composition of the low reflectivity, makes such hybrid materials possible candidates as glues between waveguide optical fiber interfaces. Therefore, they have potential applications in optical interconnection devices used in telecommunication networks. However, the problem in such cases is the volume shrinkage. New composite inorganic–organic materials based on a silica and a crosslinked polymer phase resulted in low volume shrinkage during network formation [249].

Mechanical and thermal properties. The enhancement of mechanical and thermal properties of polymers by the inclusion of inorganic moieties, especially in the form of nanocomposites, offers the possibility for these materials to substitute classical compounds based on metals or on traditional composites in the transportation industry. This is especially interesting due to environmental issues and the demand for lightweight materials resulting in a better fuel economy [250].

Scratch-resistance or barrier property inorganic–organic coatings were developed by a polymer/sol–gel approach [37,251]. For example, UV curable systems were obtained by the cocondensation of 3-(*N*-styrylmethyl-2-aminoethylamino)-propyltrimethoxysilane hydrochloride and varying amounts of TMOS using 1-hydroxycyclohexylphenylketone as photoinitiator (Fig. 4). Thermally curable compositions consisted of TMOS, GLYMO, 3-aminopropyltriethoxysilane, aluminum-*sec*-butoxide, and zirconium-*n*-propoxide. A study of these systems revealed that the oxygen permeability decreased with increasing density of the inorganic moiety as well as with the organic network, which was varied through the ratios of the precursors [251].

Alteration of optical properties. Third order non-linear optical (NLO) materials were obtained by composites based on sol–gel processed inorganic oxide/conjugated polymers. Organic polymers with π-electron conjugation are an important class of potentially useful NLO-materials due to their large non-resonant third-order non-linearity with fast response time. However, pure PPV films exhibit relatively high optical losses, while silica has a low optical loss, its non-linear susceptibility is very low. Therefore, a combination of both systems leads to new materials with superior NLO properties [252].

Nanocomposite-based devices for electronic and optoelectronic applications include light-emitting diodes, photodiodes, solar cells, gas sensors and field effect transistors. While most of these devices can also be produced as fully organic polymer-based systems, the composites with inorganic moieties have important advantages such as the improvement of long-term stability, the improvement of

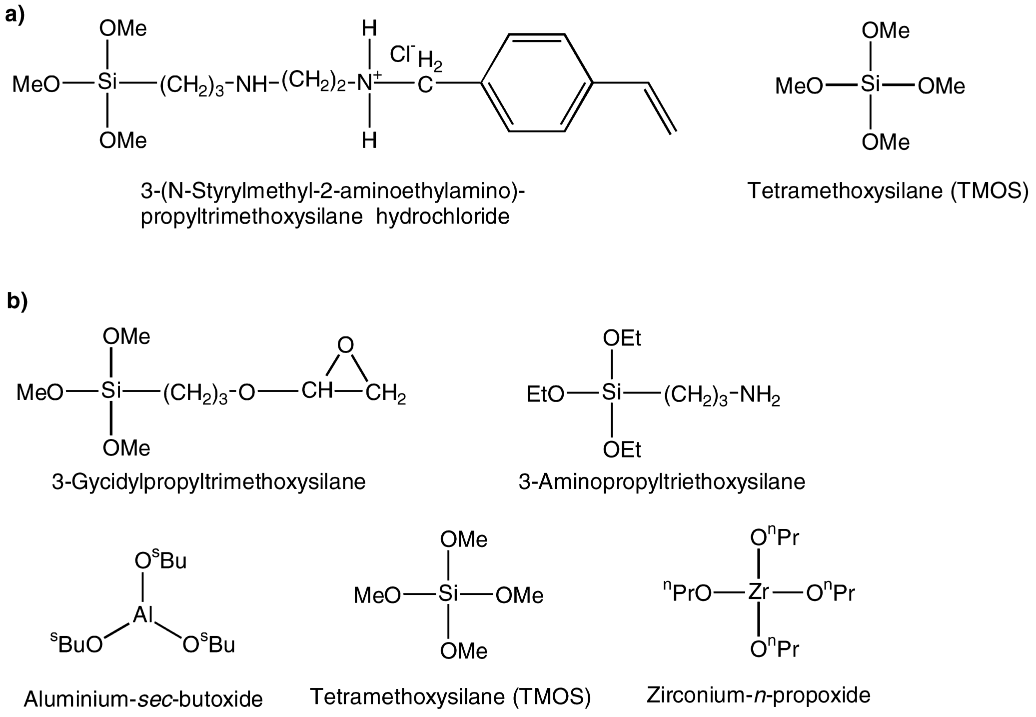


Fig. 4. Composition of (a) UV curable and (b) thermally curable inorganic–organic hybrids for application as oxygen barrier coatings.

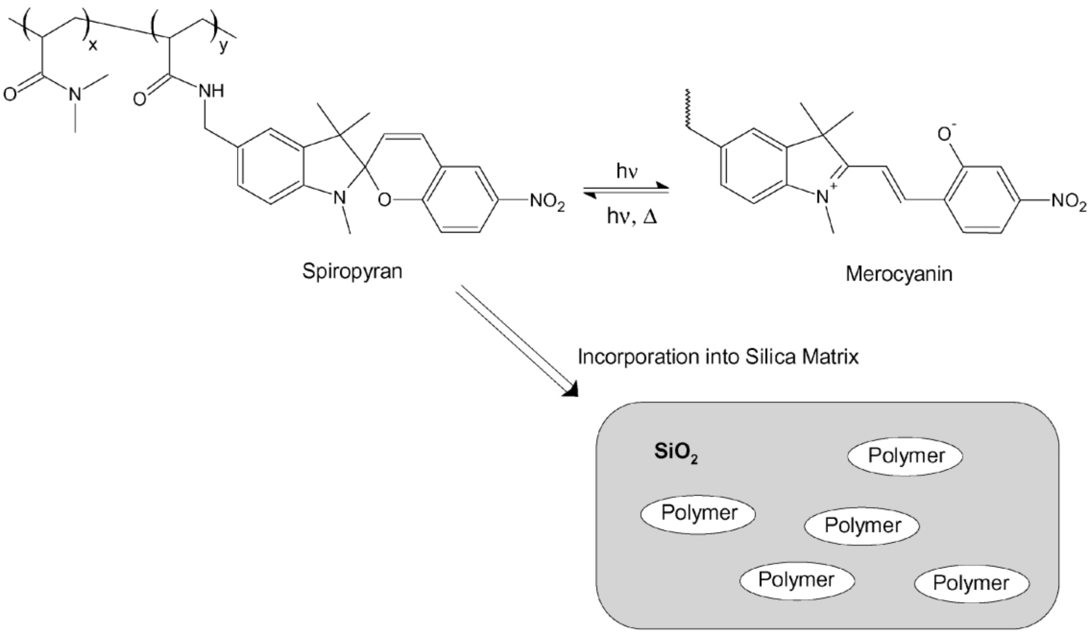
electronic properties by doping with functionalized particles, and the tailoring of the band gap by changing the size of the particles [253].

Switchable inorganic–organic hybrid materials have been formed by the incorporation of switchable species into a polymer/sol–gel mixture. For example, azobenzene-modified poly(2MOx) was synthesized and incorporated in a silica sol–gel network. The photochemical induced *trans–cis* isomerization of the azobenzene chromophores in the polymer hybrid was confirmed by absorption spectra [254]. A reverse photochromism was also observed in a spiropyran-modified poly(*N*,*N*-dimethylacrylamide) embedded in a silica matrix. Based on the solvatochromic behavior of the chromophore, which is different in a pure silica matrix than in a polymer matrix, it was concluded that the spyropyran is surrounded solely by the organic polymer (Scheme 15) [255].

Chemical sensors. A composite from poly(Py) derivatives and tin dioxide gave reversible changes in electrical resistance at room temperature when exposed to a variety of different organic vapors, such as esters, alcohols, and ketones. The sensitivity of this device was in the range of existing sensors based on ceramic materials or pure polymer films [256].

Self-organization. Colloidal crystals, which can be used in different optical applications, were produced by the modification of monodisperse, charged, nanometer-sized colloidal silica particles with MEMO in methyl acrylate. These dispersions can be photopolymerized and the resulting composites show Bragg diffraction which is an indication of 3D ordering in the resulting material. The diffraction wavelength is tuned by varying the d-spacing of the crystal lattice and the Bragg angle [176,257,258].

Conducting properties. Composite electrolyte materials for applications such as solid-state lithium batteries or supercapacitors have been produced using organic–inorganic polymeric systems formed by the mixture of organic polymers and inorganic moieties prepared by the sol–gel techniques. In these systems at least one of the network forming species should contain components that allow an interaction to the conducting ions. This is often realized using organic polymers which allow an interaction with the ions such as poly(EO) [259–261]. Another method towards these materials is the cocondensation of alkyl-sulfone functionalized alkoxysilanes with reactive polymerizable alkoxysilanes such as MEMO and GLYMO and UV, or thermal induced polymerization of the functional groups. The resulting materials were optically transparent, water stable, proton conducting membranes in which the proton conducting ability was dependent on the content of $-SO_3H$ groups and coordinated water [262,263]. Proton conducting composites were also obtained by the formation of IPNs from silicon alkoxide end-capped poly(EO), phenyltriethoxysilane using monododecylphosphate or phosphotungstic acid to induce the proton conductivity [264]. The application of hybrid composites is interesting for these systems due to their membrane stability at high temperatures compared to pure organic systems.



Scheme 15.

The combination of conducting polymers with inorganic species is another example for nanocomposites with a potentially important application. A variety of combinations have already been tested and especially poly(An) and poly(Py) show an interesting potential in combination with iron oxides, barium titanate, platinum, and tungsten oxide for magnetical, energy storage, catalytic, and electrochromic devices, respectively [265].

9. Summary

The incorporation of nanoscale inorganic species in organic polymers offers the possibility of the formation of a plethora of novel materials with a high potential for new application. For optimal control of the properties of these new materials, it is highly important to tailor the formation process from the point of view of the final product. For example, the formation of highly optical transparent material requires another process other than that of a system with good thermal and mechanical properties. At the present time, this very interdisciplinary scientific area is open for new ideas from all disciplines and therefore a promising future can be foreseen.

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