Invited Review

Inorganic Clusters in Organic Polymers and the Use of Polyfunctional Inorganic Compounds as Polymerization Initiators

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Summary. Silicon oxide or metal oxide clusters or small particles with polymerizable organic groups covalently bonded to their surface can be copolymerized with organic monomers by various polymerization techniques. Whereas the preparation and properties of the polymers reinforced by $R_8Si_8O_{12}$ have already been well investigated, analogous materials with incorporated transition metal oxide clusters are only beginning to show their potential as an interesting new class of inorganic-organic hybrid polymers. In the second part of the article, approaches are reviewed in which the inorganic building block serves as an initiator for polymerization reactions. This results in materials in which the organic polymer is grafted from an inorganic core. Most work has been done with surface-modified silica particles. Free radical polymerizations and atom transfer radical polymerizations with macroinitiators are summarized. The latter method results in polymeric particles in which an inorganic core is surrounded by an organic polymer shell. A new approach is the use of polyfunctional inorganic molecules or molecular clusters as initiators.

Keywords. Inorganic-organic hybrid materials; Nanostructures; Clusters; Polymerizations.

Introduction

The development of new materials for the technological demands of the 21st century is a major goal of materials science. The 'classical' materials have often reached their limits, especially in areas such as microelectronics, optics, sensor technology, catalysis, ceramics, *etc*. Therefore, new materials with tunable properties are needed. A class of materials which could meet this requirement are hybrid materials, especially those in which inorganic and organic components are combined. These systems merge, to some extent, the properties of the two components on a molecular scale and therefore allow a deliberate tailoring of properties between purely inorganic and purely organic materials. A special challenge of increasing importance is to tailor not only the composition of such materials, but also their structures, especially in the nanometer range. This allows for making use of the physical phenomena associated with this length scale. The goal is reached by the deliberate

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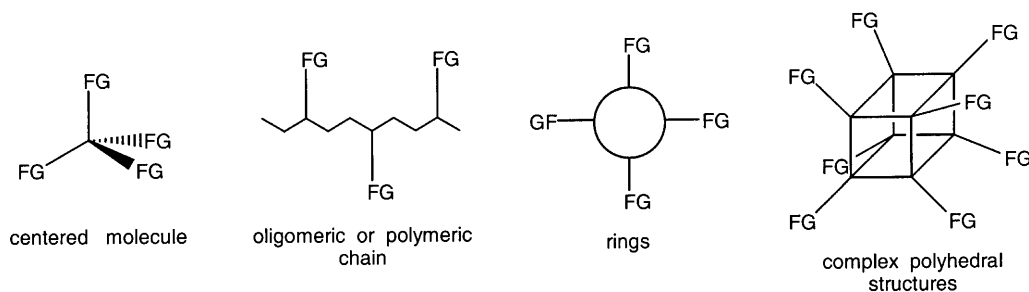
Scheme 1. Potential multifunctional building blocks for inorganic/organic hybrid polymers (FG = polymerizable or initiating functional group)

arrangement of structurally well-defined inorganic or organic macromolecules as building blocks.

In principle, two kinds of inorganic/organic hybrid materials can be distinguished: those with or without strong covalent or ionic bonds between the organic and the inorganic components. Compared to materials in which the organic component is just entrapped in an inorganic host, or vice versa, bonding between the two components overcomes problems of macro- or micro-phase separation, leaching, etc. This article only reviews a special sub-class of these materials – those in which functional organic groups attached to the core of an inorganic precursor allow the formation of covalent bonds to an organic polymer. In Scheme 1 such precursors are
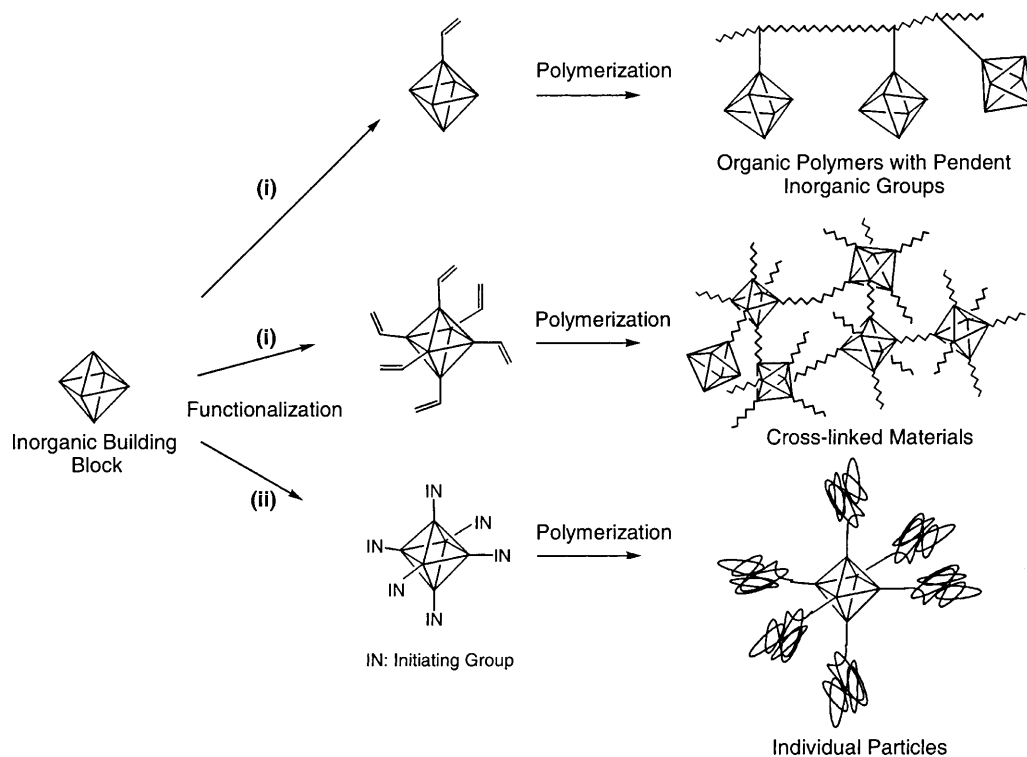
Scheme 2

arranged according to the structure of the inorganic building blocks (FG = functional organic group). We concentrate on two aspects: the use of pre-formed clusters as the inorganic component (right hand side of Scheme 1), and the use of polyfunctional inorganic entities as initiators for organic polymerization reactions.

The inorganic building blocks can be used in two different ways (Scheme 2): (*i*) as monomers if they are substituted with one or more polymerizable groups, or (*ii*) as initiator for polymerization reactions. The first approach allows the preparation of either linear polymers with pendent functionalities at the polymeric chain or cross-linked materials, whereas the second approach results in materials where the organic polymer is grafted from an inorganic core.

Organic Polymers Reinforced by Covalently Bonded Inorganic Clusters

Research in this area was promoted by the recent commercial availability of a variety of polyhedral oligomeric silsesquioxanes (POSS), $R_8Si_8O_{12}$ (see below). These compounds were incorporated in various organic polymers by covalent attachment to the polymer chain and showed some interesting improvements of the thermal and mechanical properties of the parent polymer. Extending this field to other inorganic clusters could allow the variation of materials properties in a wider range and, additionally, the introduction of properties typical of the inorganic component such as thermal or electronic conductivity, sensing, *etc*. Very promising dopants in this respect are oxometallate clusters which have interesting properties in several areas of materials science [1–6]. Such clusters have diameters in the range of a few nanometers and can therefore be considered structurally well-defined (*i.e.* monodispersed) nanoparticles.

In principle, there are two possibilities to functionalize metal oxide nanoclusters by organic groups: (*i*) grafting functional organic groups onto the surface of pre-formed oxometallate clusters, and (*ii*) *in situ* functionalization of the clusters during their formation. The advantage of the first method is that the cluster cores can be prepared by well-established techniques. However, for a covalent modification of the cluster surface, reactive groups, such as OH groups, must be available, and sometimes the modification by organic groups may require a rearrangement of the cluster to accommodate multidentate ligands. Since such clusters are very stable, their rearrangement is generally not thermodynamically favoured, and therefore the substitution of the cluster surface by organic groups may be difficult to achieve. The attachment of organic groups by ionic interactions is also possible. In this case, the charge on the cluster should be spatially located, because delocalized charges result in weak interactions which can be broken during further reactions. In the *in situ* functionalization method, the oxo-clusters are formed in the presence of functional molecules which serve to cap the cluster surface. The incorporation of the organic groups on the cluster surface is controlled by the chemical reactions by which the cluster is formed. The advantage is that the process is based on a self-assembly of the inorganic and organic units.

Metal oxide clusters

The first method was used by *Judeinstein* to derivatize $K_8[SiW_{11}O_{39}]$ by reaction with various trichloro- or triethoxysilanes $RSiX_3$ (X = Cl or OEt) containing
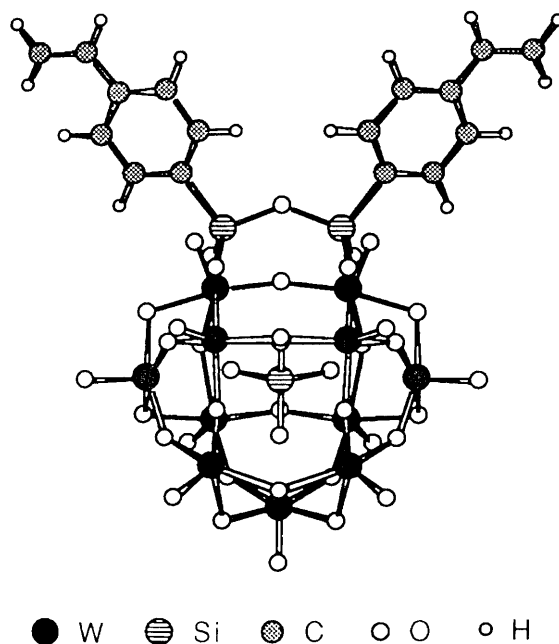
Fig. 1. Structure of $[SiW_{11}O_{39}(OSi_2(C_6H_4CH=CH_2)_2)]^{4-}$ (reprinted by permission of the American Chemical Society from Ref. [7])

polymerizable groups R ($R =$ allyl, vinyl, styryl, 3-methacryloxypropyl) [7, 8]. 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 styryl derivative is shown in Fig. 1. The polymerizable groups bound to the cluster surface were used for cross-linking 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*) $\ll$ allyl (20%) $<$ methacryl (65–70%) $<$ styryl (100%). The hydrodynamic radius of the obtained inorganic-organic hybrid polymers varied between 5–120 nm, but did not always correspond to the polymerization yields. From SAXS data it was concluded that hybrid polymers with different spatial repetitions of the clusters and structures (linear or branched and compact) were probably obtained depending on the polymerization conditions. ^{29}Si NMR and UV spectroscopic investigations as well as 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. For example, transparent films deposited from polymer solutions on different substrates turned blue upon UV irradiation or electrochemical reduction.

This work was extended by *Mayer et al.* who used another, similarly functionalized polyoxotungstate cluster for the cross-linking of organic polymer chains. The cluster $[\gamma\text{-}SiW_{10}O_{36}(OSi_2R_2)]^{4-}$ ($R = CH_2 = CMeC(O)OCH_2CH_2CH_2$) was obtained by reaction of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with methacryloxypropyltrialkoxysilanes (Eq. (1)) [9]. Functionalization by both covalent and ionic interactions was achieved by additionally employing the quaternary methacrylate-substituted
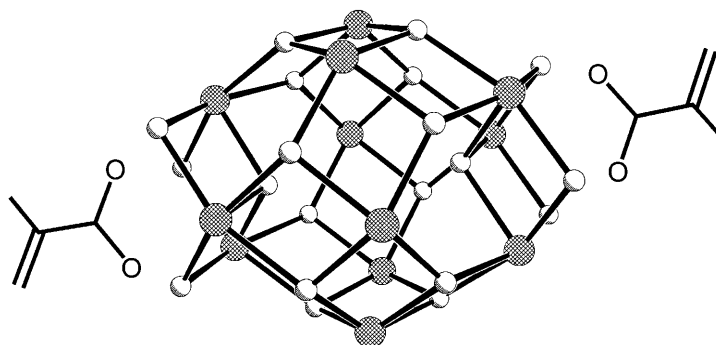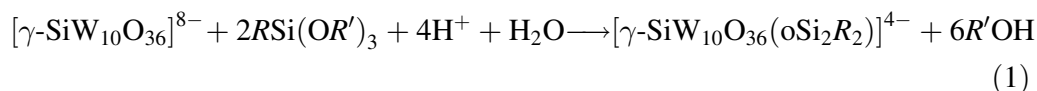
Fig. 2. Core of the cluster $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ together with the methacrylate anions; only the tin (checkered spheres) and oxygen (plain spheres) atoms of the cluster are shown for clarity

ammonium counterion $CH_2{=}CMeC(O)OCH_2CH_2CH_2N^+Me_3$. These clusters were copolymerized in acetonitrile with ethyl methacrylate in different ratios (1:10 to 1:50), and swollen gels were obtained. The swelling index increased with increasing comonomer-to-cluster ratio, *i.e.* dependent on the cross-linking density. Spectroscopic investigations again proved that the polyoxotungstate was incorporated in the material without a structural change.

$$[\gamma\text{-}SiW_{10}O_{36}]^{8-} + 2RSi(OR')_3 + 4H^+ + H_2O \longrightarrow [\gamma\text{-}SiW_{10}O_{36}(oSi_2R_2)]^{4-} + 6R'OH \tag{1}$$

Ribot et al. used the approach to functionalize pre-formed clusters to prepare hybrid materials based on oxo-hydroxo stannate clusters [10, 11]. The cationic cluster $[(BuSn)_{12}O_{14}(OH)_6]^{2+}(OH^-)_2$ (Fig. 2) was obtained by hydrolysis of $BuSn(O^iPr)_3$. The introduction of functional organic groups was achieved by exchange of the hydroxide counterions against methacrylate anions (Eq. (2)). The methacrylate anions not only interact with the cluster cation by *Coulomb* interactions, but also by hydrogen bonds to the OH 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 methyl methacrylate (*MMA*) in *THF* (1:13 to 1:52) resulted in soluble organic-inorganic hybrid polymers. The yield of the polymer fraction precipitated by dropping the polymer solution into diethyl ether, and the mean molecular mass of the precipitated polymer (determined by GPC) decreased with increasing *MMA*/ cluster ratio. These findings indicate the absence of a substantial cross-linking by the clusters. At high cluster proportions, the polymerization is partly inhibited toward propagation by the difunctional cluster comonomer. The amount of cluster incorporated in the polymeric product was always lower than in the feed, indicating a lower reactivity of the cluster with respect to the *MMA* comonomer.

$$[(BuSn)_{12}O_{14}(OH)_6](OH)_2 + 2CH_2{=}CMeC(O)OH \xrightarrow[-2H_2O]{}$$
$$[(BuSn)_{12}O_{14}(OH)_6](CH_2{=}CMeC(O)O)_2 \tag{2}$$
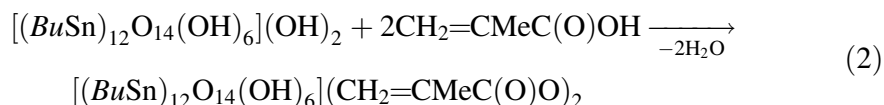
A different approach for the functionalization of oxo-clusters is the *in situ* modification during their formation used by *Kickelbick et al.* for the preparation of

organically substituted oxotitanium and oxozirconium clusters [12–15]. 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 are obtained. Structurally characterized examples include the zirconium clusters $Zr_6(OH)_4O_4(OMc)_{12}$ ($OMc =$ methacrylate), $Zr_4O_2(OMc)_{12}$, [12], and $[Zr_3O(OBu)_5(OMc)_5]_2$ [17], the titanium clusters $Ti_6O_4(OEt)_8(OMc)_8$ [16], $Ti_4O_2(O^iPr)_6(OOCR)_6$ ($OOCR = OMc$ or $OAcr$, $OAcr =$ acrylate) [17] and $Ti_9O_8(OPr)_4(OMc)_{16}$ [13], and the mixed-metal clusters $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$, $Zr_6Ti_2O_6(OMc)_{20}$, $Zr_4Ti_2O_4(OBu)_2(OMc)_{14}$, and $Zr_2Ti_4O_4(OBu)_6(OMc)_{10}$ [17]. In the first step of the reaction, one or more alkoxide ligands are substituted by carboxylate groups. The thus liberated alcohol then undergoes an esterification reaction. The water produced together with the ester serves to hydrolyze the remaining alkoxide groups and acts as the source of oxide or hydroxide groups in the clusters. The very slow production of water allows a very controlled growth of the carboxylate-substituted oxometallate clusters.

The molecular structures of the clusters $Zr_6(OH)_4O_4(OMc)_{12}$, $Zr_4O_2(OMc)_{12}$, $Ti_6O_4(OEt)_8(OMc)_8$, and $Ti_4O_2(O^iPr)_6(OAcr)_6$ are shown in Fig. 3 as examples. The plots below the ball-and-stick models show the linkage of the coordination polyhedra (only the metal and oxygen atoms are shown in these representations) and that the double bonds of the (meth)acrylate ligands are fully accessible for chemical reactions.

Copolymerization of the clusters shown in Fig. 3 with methyl methacrylate (*MMA*) or methacrylic acid (*MA*) in ratios between 1:50 and 1:200 resulted in polymers in which the polymer chains are efficiently cross-linked by the oxometallate clusters [18–21]. Glassy, insoluble materials were typically obtained upon copolymerization with *MMA*, and insoluble powders with *MA*. The specific surface area of the doped *PMA* depended on the amount of cluster incorporated and increased with an increasing cluster proportion. The cluster cross-linked *PMMA* was insoluble in common organic solvents but swelled. The solvent uptake upon swelling increased with an increasing comonomer-to-cluster ratio. The thermal stability of *PMA* and *PMMA* was improved by the cluster cross-linking, and the thermal depolymerization observed in the undoped polymers was inhibited. The impedance spectra of *PMMA* doped with various proportions of $Zr_4O_2(OMc)_{12}$ showed that the capacitance of the polymers decreases with an increasing proportion of the cluster. The polymer doped with 2 mol% of $Zr_4O_2(OMc)_{12}$ showed an increase in conductivity to $0.9 \cdot 10^{-6}$ S $\cdot$ cm^{-1} at 74°C [21].

Doping or cross-linking of organic polymers with the tungsten, tin, zirconium, or titanium oxide clusters mentioned can be considered an extension of the so-called POSS (polyhedral oligomeric silsesquioxane) 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 considerably.

Polyhedral oligomeric silsesquioxanes (POSS)

Much progress has recently been achieved in the area of POSS-reinforced polymers with a variety of different organic polymers. The most often used type of POSS is
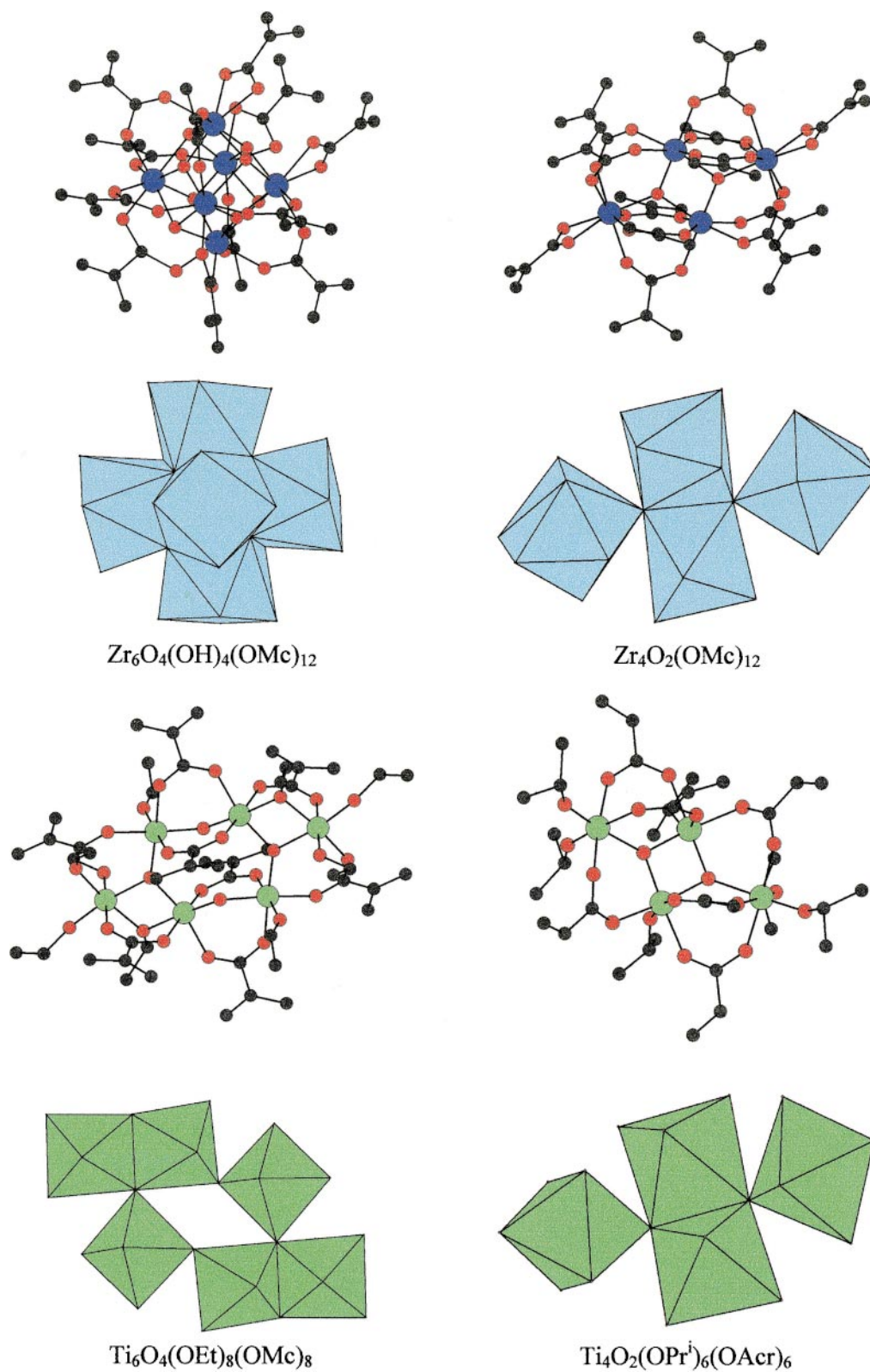
Fig. 3. Molecular structures of the clusters $Zr_6(OH)_4O_4(OMc)_{12}$, $Zr_4O_2(OMc)_{12}$, $Ti_6O_4(OEt)_8(OMc)_8$, and $Ti_4O_2(O^iPr)_6(OAcr)_6$ (reprinted by permission of Wiley-VCH from Ref. [21])
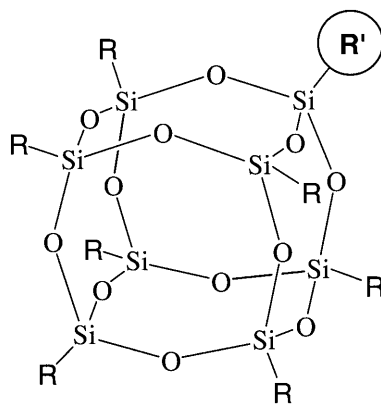
Fig. 4. Structure of the polyhedral oligomeric silsesquioxanes (POSS) $R_8Si_8O_{12}$; if POSS is used as a monomer in polymerization reactions, $R \neq R'$ (R': polymerizable group, R: substituents increasing the solubility)

$R_8Si_8O_{12}$ (Fig. 4). The organic groups bonded to the silicon atoms can be the same or may be different. The most frequently employed variety is $R'R_7Si_8O_{12}$ where only one group (R') is polymerizable, whereas the other groups serve to improve the solubility in orgaic solvents. These monomers are used in the preparation of linear polymers with nanosize inorganic clusters pendent on an organic backbone. Compared to the cross-linked materials, these polymers are easier to process, and their properties are easier to control.

Haddad et al. used $R'R_7Si_8O_{12}$ ($R' = $ styrylethyl, $R = $ cyclohexyl or cyclopentyl) to synthesize homo- and copolymers with 4-methylstyrene as comonomer by free radical polymerization [22]. Despite the bulkiness of the siloxane cube, the reactivity of the POSS macromer and 4-methylstyrene is approximately the same. The degree of polymerization (between 100 and 400) also confirmed that even in POSS homopolymers reasonable degrees of polymerization were obtained despite the sterical demand of the inorganic substitutent. It was shown that the cycloalkyl substituents at POSS influence the properties of the polymers. The change of the thermal properties was significantly larger for $R = $ cyclopentyl than for $R = $ cyclohexyl, which was attributed to POSS-POSS interchain interactions. Rheological measurements revealed that the polymer dynamics is also affected by an increasing proportion of POSS [23]. A high-temperature rubbery plateau developed at higher concentrations of POSS which was also explained by interchain interactions between the pendent inorganic groups on the polymer backbone.

A norbornyl-functionalized POSS macromer was polymerized by ring-opening metathesis polymerization (ROMP), and polynorbornene-POSS copolymers with up to 50 wt% POSS have been prepared [24]. An increase in the POSS content resulted in an increase in T_g, but had nearly no effect on the thermal stability. The cycloalkyl substitutents at the silicon atoms had a similar effect on T_g as in the POSS/styryl polymers. Dynamic mechanical analysis (DMA) revealed that the temperature corresponding to the α-transition (T_α) increased with increasing POSS macromer content in the copolymers. DMA also showed that this dependence is larger for cyclohexyl-substituted POSS comonomers than for the cyclopentyl derivatives. In

contrast, the β-relaxation is independent of the POSS weight fraction. The activation energy for the β-relaxation seems to have its source in the motion of the cycloalkyl substituents. Wide angle X-ray scattering (WAXS) analysis showed that the cyclohexyl-substituted POSS preserves the amorphous character of the norbornene polymer, whereas the cyclopentyl-substituted system exhibits some additional ordering due to POSS aggregation. In summary, it is obvious that not only the siloxane core but also the substituents are important for the thermal and mechanical behavior of these hybrid materials.

The discussed examples represent 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 upgraded by the incorporation of POSS. Among other properties, higher degradation and glass transition temperatures, reduced flammability, reduced viscosity, and higher oxidation resistance have been observed.

Different polymer morphologies than those described before were produced by *Matyjaszewski et al.* with methacrylate substituted POSS [25–27]. They prepared homo, random, and block copolymers as thermoplastic elastomers from methacryloyl- and styryl-substituted POSS macromers by atom transfer radical polymerization (ATRP). Star block and ABA triblock copolymers were synthesized with poly-(methyl methacrylate – POSS) as the hard block and poly-(butyl acrylate) as the soft block. The obtained polymers showed rather low polydispersities typical for controlled radical polymerization methods. For the synthesis of the triblock copolymers, the macroinitiator was prepared by an ATRP reaction of butyl acrylate using 2,6-dibromoheptanedioate as initiator. The chain extension was carried out with methylacrylate-substituted POSS as the monomer. The star block copolymer was similarly synthesized using 1,1,1-*tris*-(4-(2-bromoisobutyryloxy)-phenyl)-ethane as the initiator.

Inorganic Moieties as Initiators

Initiating groups attached to the inorganic core allow the grafting of polymers from their 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. The 'grafting to' method has restrictions, for example, in the surface coverage, whereas 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 2). In any case, a key step is the attachment of initiating groups onto the particle surface. The methods described before to attach the functional groups by ionic or covalent bonds can be used again. In most of the work done in this area, polymers were grafted from nanometer- and micrometer-sized silica particles [28–31].

Free radical polymerizations

Laible et al. used a multistep synthesis to modify the surface of pyrogenic amorphous silica (Aerosil[TM]) with diazo groups capable of initiating the free-radical
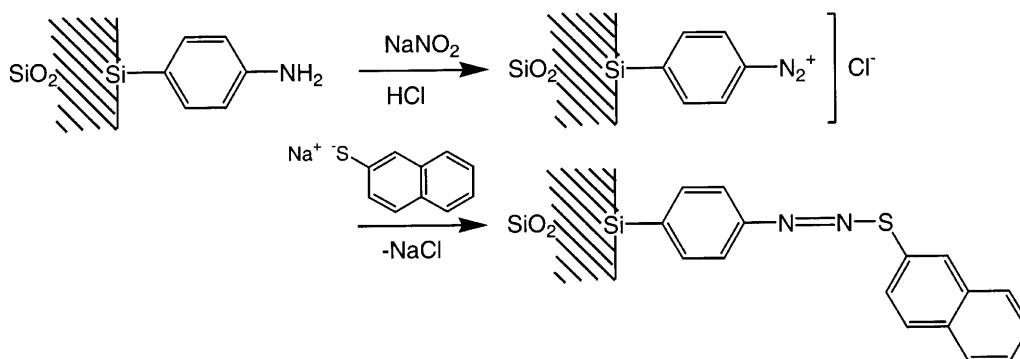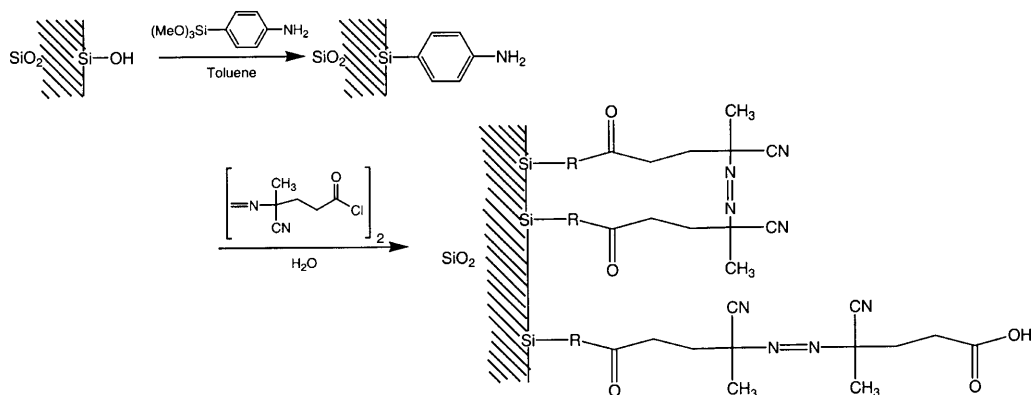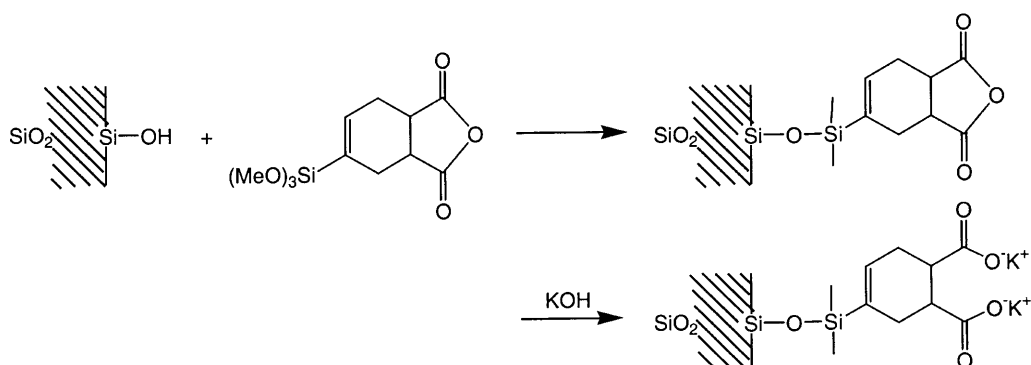
Scheme 3

polymerization of styrene [28]. The surface Si–OH groups were first converted to Si–Cl groups followed by phenylation and nitration of the phenyl substituents and reduction of the $C_6H_4NO_2$ substituents to $C_6H_4NH_2$. The diazo groups at the silica surface were eventually obtained as shown in Scheme 3 with a coverage of up to 0.03 to 0.1 diazo groups per $100\,\text{Å}^2$. This means that only every thirtieth OH-group had been transformed. Polystyrene 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 due to the fact that the surface-attached initiator decomposes into two radicals, one of which initiates polymerization in the solution. An increase in polymerization temperature caused an increase in polymer coverage on the particles, and the limiting coverage was reached earlier. The temperature dependence of the homopolymer in solution was similar to that of the grafted polymer. A linear dependence between 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 weights of the polymers cleaved from the surface by HF treatment ranged up to 1.46×10^6, whereas those of the homopolymers formed in the solution simultaneously reached values of about 1.75×10^6.

In more recent studies, silane coupling agents like alkoxysilanes [31–33] or chlorosilanes [29, 30] have been used to modify the surface of silica particles. *Boven et al.* attached aminophenyltrimethoxysilane to pyrogenic silica and immobilized 4,4′-azo-*bis*-(4-cyanopentanoic acid) *via* the formation of amide bonds (Scheme 4). The concentration of diazo groups at the surface reached 0.2 mmol/g. Due to the bidentate nature of the diazo compound, the two attachment modes shown in Scheme 4 are possible. The identity of the initiators at the surface was checked by DRIFT spectroscopy. DSC measurements proved that the stability of the initiator decreased upon immobilization. Poly-(methyl methacrylate) with molecular weights up to 8.7×10^5 was grafted from the surface. The polymerization was highly affected by the *Trommsdorff* effect [34] which was also made responsible for the higher molecular weights of the grafted compared to the homopolymer.

Tsubokawa et al. grafted polyesters from various ultrafine inorganic particles such as silica, titania, and ferrite by anionic ring opening copolymerization of epoxides and cyclic acid anhydrides [33]. The silica, titania, and ferrite particles had
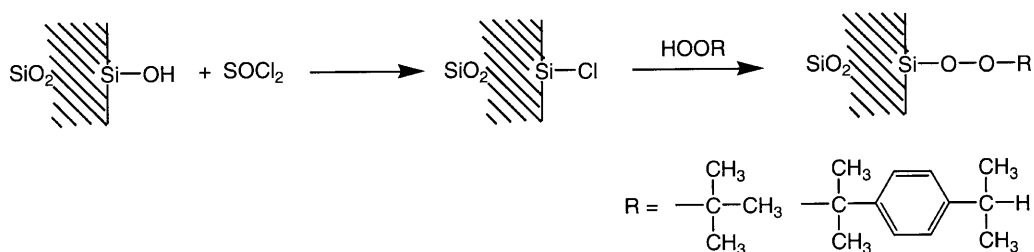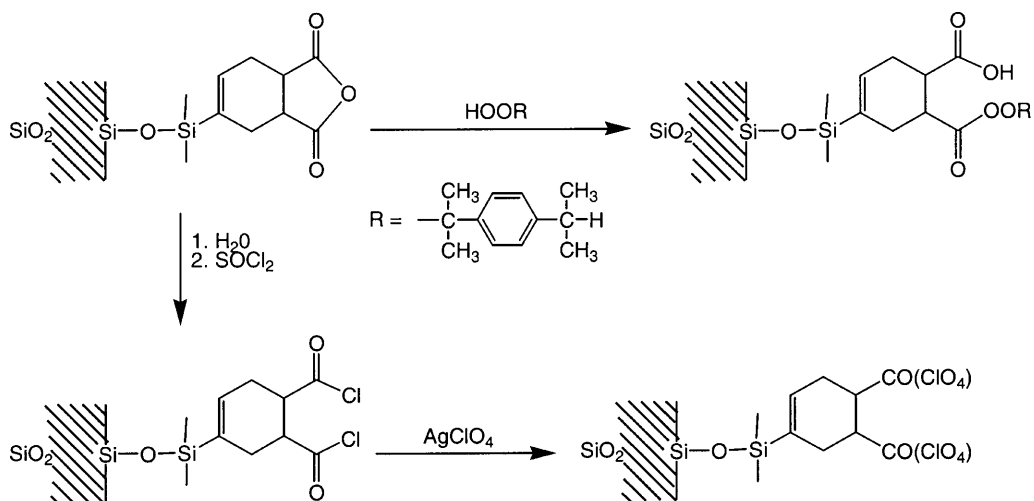
Scheme 4

Scheme 5

sizes of 16, 120, and 15 nm and surface OH 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 the reaction sequence shown in Scheme 5. The amount of initiating groups on the surface of the silica, titania, and ferrite particles was 1.92, 0.94, and 0.62 mmol/g. The organic monomers used were styrene oxide, chloromethyloxirane, glycidyl methacrylate, glycidyl phenyl ether, phthalic anhydride, succinic anhydride, and maleic anhydride. The dispersions of the polymer-modified particles in chloroform were stable over one month with a high particle content, whereas the unmodified particles precipitated completely within two days.

Tsubokawa et al. also investigated the grafting of methyl methacrylate initiated by surface anchored peroxide initiators [35]. 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 (Scheme 6). 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-(methyl methacrylate); the modified particles gave stable dispersions in *THF*. In
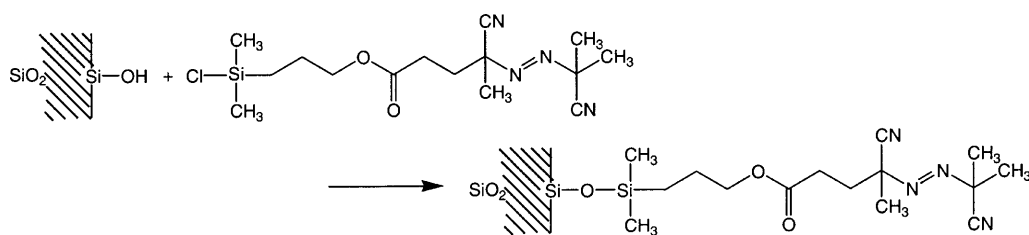
Scheme 6

Scheme 7

another paper, *Tsubokawa et al.* compared two different initiating mechanisms of the graft polymerization of styrene from silica particles, *i.e.* radical graft polymerization initiated by peroxy esters and cationic polymerization initiated by acylium perchlorate groups [36]. The initiating groups were again attached to the surface using 4-trimethoxysilyltetrahydrophthalic anhydride and opening of the anhydride as shown in Scheme 7. After the polymerization, the polystyrene was cleaved from the surface by treatment of the particles with aqueous alkaline solutions. The molecular weights of polystyrenes obtained by radical graft polymerization were much larger than those of polymers prepared by the cationic graft polymerization. However, the number of grafted polystyrene chains in the radical polymerization was much smaller than that in the cationic polymerization. The dispersibility of polystyrene grafted silica was not only influenced by the length but also by the number of grafted chains.

Rühe et al. studied the kinetics and mechanism of an azo-initiated free radical styrene polymerization from modified silica particles [30]. The diazo-derivatized silica shown in Scheme 8 was used as an initiator. After the polymerization, the ester group was catalytically cleaved. The differences between the obtained polystyrene homopolymer and the polymers obtained by polymerization in solution were mainly due to differences in the termination reactions. For example, when termination of
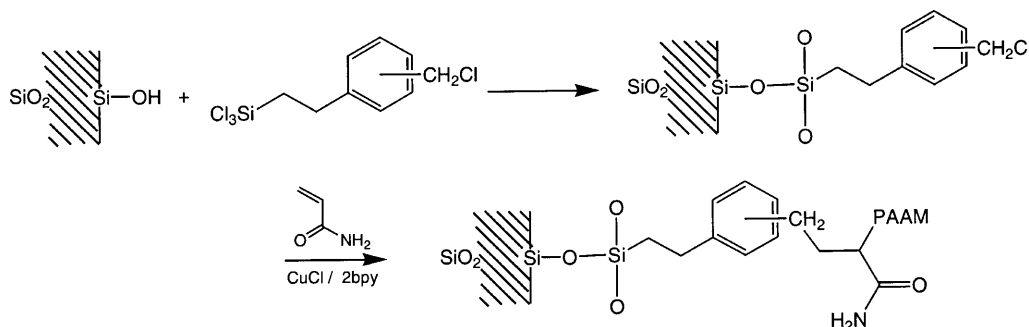
Scheme 8

surface attached polymers by free chains in the solution becomes a major pathway of termination, the rate of termination decreases with increasing graft density, because the free chains have to diffuse against a concentration gradient into the film. An additional difference between surface polymerization and solution polymerization was that all transfer reactions to solvent, monomer, or transfer agent in the case of the first one led to a termination of the surface attached chains and the film growth stopped, whereas in solution the active center was only transferred and a new polymer chain started. Although the initiator efficiency of surface-attached initiator is slightly decreased, it still allows the formation of high molecular weight polymers with high graft density.

Atom transfer radical polymerization

Contrary to free radical polymerizations, where polymerization also occurs in the solution as discussed above, this is not the case for controlled radical polymerizations such as transition metal-mediated atom transfer radical polymerization [37, 38]. *Wirth et al.* used this method to polymerize polyacrylamide from silica [29]. (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 polyacrylamide was calculated to be 10 pm and therefore reduced 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,

Scheme 9

and aprotinin. The elution times were much faster than with a commercially available silica-based stationary phase.

Patten et al. also used ATRP to generate polymer-modified silica particles [31]. 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. 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. The polymerization was followed by dynamic light scattering and GPC measurements of the polymers after cleavage from the surface. The molecular weight distributions of the polymers remained narrow. TEM micrographs revealed that at higher polymer conversions the hybrid nanoparticles agglomerate upon evaporation of the solvent to form domains. The distance between the nanoparticles within these domains increased from 10 to 40 nm depending on the molar mass of the grafted polystyrene chains. When silica particles with narrow size distributions (< 10%) were used, the agglomerated domains of the hybrid particles in a film were packed into hexagonal arrays.

The previous examples showed the formation of particles in the micro- and upper nanometer scale. Smaller length scales for the inorganic moiety were achieved when molecules or molecular clusters were used as initiators. Only a few examples of such systems are known until today.

Metal core macromolecules

Fraser et al. used various metal compounds as polymerization initiators [39, 40]. The authors called the resulting materials metal core macromolecules (MCMs). Fe(II) and Ru(II) complexes with one to three (4,4′-halomethyl)-2,2′-bipyridine (*bpy*) ligands were used to initiate living cationic oxazoline polymerizations (Scheme 10) [39, 41, 42]. The polymerizations yielded hybrid systems with molecular weights from 1600 to 4600 and polydispersities < 1. The obtained polymers revealed the same UV/Vis absorptions as the initiators, indicating that the polymers are still coordinated to the metal *via* the initiating ligands. Possible applications of these systems are sensors which response to environmentally relevant compounds that are able to diffuse through the polymer layer and destroy the metal core. The disassembly of the hybrid materials was 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 restored by treatment of the solution with $(NH_4)_2Fe(SO_4)_2$, which shows that the *bpy* terminated polymers reassemble around the iron center. Films of the Fe containing polymer underwent a partly reversible thermal bleaching when heated to ∼210°C. This observation is probably based on a disassembly of the coordination compound. By using different oxazoline monomers, *i.e.* 2-ethyl-, 2-undecyl-, or 2-phenyl-2-oxazoline, amphiphilic metal-centered six-arm star block copolymers were prepared [41].

Schubert et al. used a similar approach to prepare 6,6′-bisfunctional 2,2′-bipyridine copper complexes as initiators for the living cationic polymerization of 2-ethyl-2-oxazoline [43]. Polymers with low molecular weight distributions were again obtained. It was proven by UV/Vis spectroscopy that the Cu(I) complex was
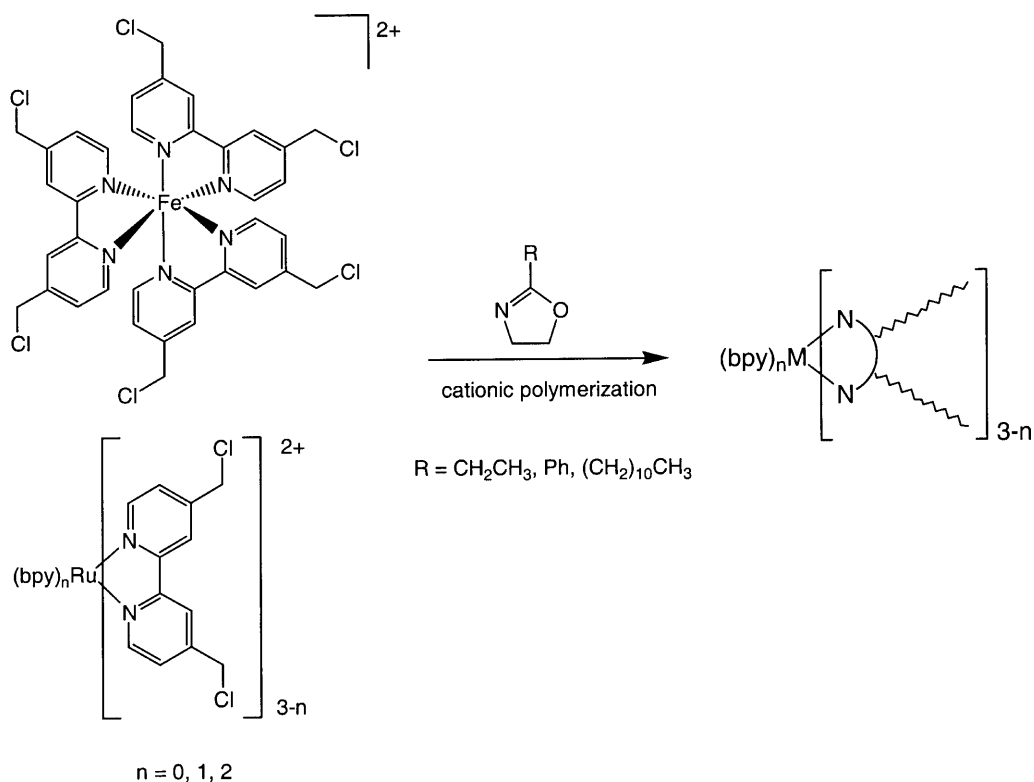
Scheme 10

retained in the polymer. The copper atom was removed from the star polymer by treatment with a K_2CO_3 aqueous solution. Block copolymers with poly-(2-phenyl-2-oxazoline) as the second block were 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 [44].

Ru(II) complexes bearing one to three chloromethyl functionalized *bpy* ligands were used as ATRP initiators in styrene polymerizations producing Ru(II) core complexes with two, four, and six arms [40, 45]. The initiator complexes were used for ATRP of styrene at 110°C. The Ru(II) core polymers were precipitated with methanol as pale orange solids. The obtained polymers had molecular weights of up to 1.4×10^5 and polydispersities < 1.4. Electronic adsorption spectra showed the typical ligand charge-transfer bands for $[Ru(bpy)_3]^{2+}$ chromophores. As powders or as films, the metal polymers are luminescent with an emission maximum at ∼609 nm.

Surface modified particles and polyfunctional metal complexes are the two extremes in terms of the size of the initiator. Clusters are between these two length scales. We have already discussed above the use of functionalized inorganic clusters as monomers or cross-linking agents. In a similar way, initiating groups can also be attached to a cluster surface. We obtained clusters suitable as initiators for ATRP reaction by the *in situ* modification of clusters described above, *i.e.* by reaction
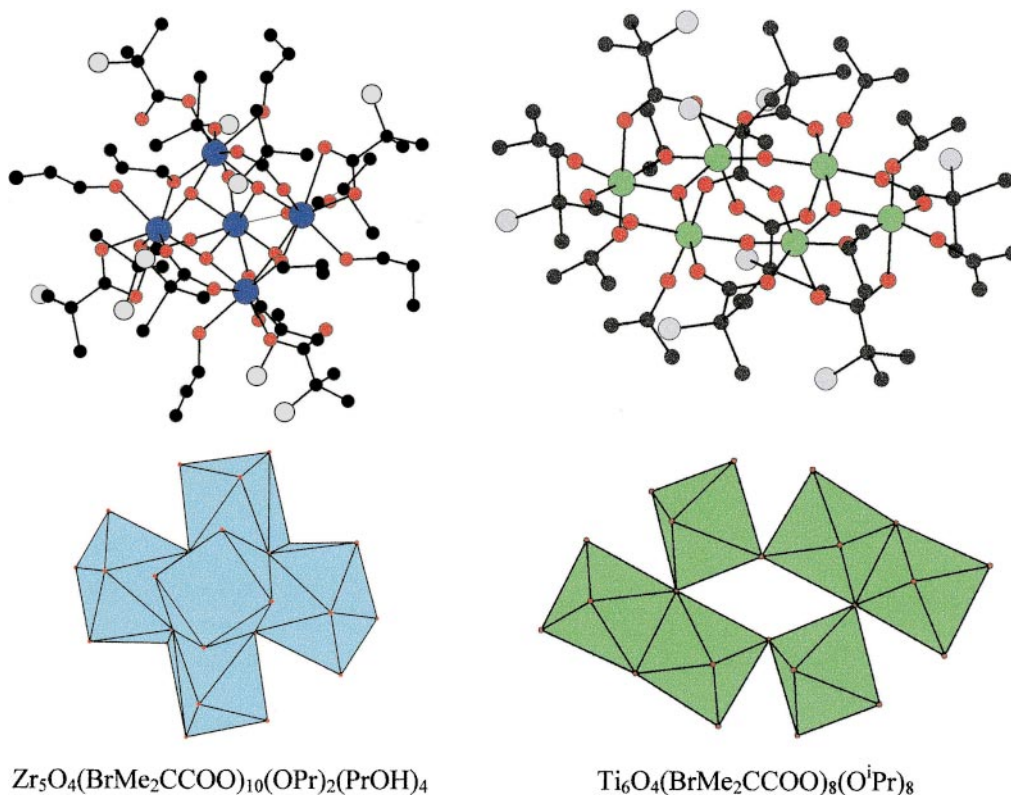
$Zr_5O_4(BrMe_2CCOO)_{10}(OPr)_2(PrOH)_4$ $Ti_6O_4(BrMe_2CCOO)_8(O^iPr)_8$

Fig. 5. Structure of the clusters $Zr_5O_4(BrMe_2CCOO)_{10}(OPr)_2(PrOH)_4$ and $Ti_6O_4(BrMe_2CCOO)_8$-$(O^iPr)_8$

of $M(OR)_4$ ($M =$ Ti, Zr) with 2-bromoisobutyric acid [46]. The cluster $Ti_6O_4(BrMe_2CCOO)_8(O^iPr)_8$ was obtained from a 1:1 mixture of $Ti(O^iPr)_4$ and the acid and $Zr_5O_4(BrMe_2CCOO)_{10}(OPr)_2(PrOH)_4$ from a 1:4 mixture of $Zr(O^nPr)_4$ and the acid (Fig. 5). The Ti cluster bears 8, the Zr-cluster 10 potential initiation sites for polymerization reactions. Polymerizations using these initiators are currently under investigation. The hybrid polymers obtained with the cluster initiators promise a good processibility due to the lack of cross-linking and potential applications as materials for optical applications such as high refractive index materials.

Conclusions

The examples discussed in this review article demonstrate that there are two promising possibilities to incorporate inorganic moieties into an organic polymer by a covalent linkage: the polymerization of appropriately substituted compounds with organic comonomers and the use of inorganic structures to initiate atom transfer radical polymerizations. The doped polymers constitute a new class of (hybrid) polymers. The first approach leads, depending on the number of functional groups, either to cross-linked systems (in the case of multifunctional inorganic precursors) or to linear polymers (if the inorganic precursor carries only one polymerizable group).

Both approaches allow the inorganic moiety to be incorporated into a polymer matrix under retention of their typical properties. The incorporation of the inorganic structures has severe consequences on the physical properties of the parent polymers. The microstructure of the materials is not always homogeneous, as interactions between the inorganic moieties are sometimes observed which can lead to additional mechanical effects.

When inorganic moieties are used as initiators for controlled as well as uncontrolled polymerization reactions, hybrid core-shell particles with an inorganic core and a polymeric shell are obtained. The diameter of the inorganic core can be modified from several nanometers into the micrometer range. Silica was used in the majority of the studies so far after grafting the initiating groups to the particle surface *via* the surface silanol groups. The polymer shell results in a change in the properties of the particles. For example, stable dispersions in organic solvents can be prepared, or regular mesostructures by self-assembly. On the lower length scale, appropriately substituted coordination compounds can be used as initiators. The obtained polymeric systems still show the typical features of the coordination compound *e.g.* UV absorption. The metal center can be reversibly released from the polymer by chemical treatments. Metal oxide clusters substituted by initiating groups are a promising a new kind of initiator for controlled radical polymerization.

Acknowledgments

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