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Polymers Reinforced by Covalently Bonded Inorganic Clusters

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Organically modified transition-metal oxide clusters (OMTOCs) are structurally well-defined nanosized building blocks for the preparation of a new type of inorganic−organic hybrid materials. There are two principal methods to synthesize OMTOCs with polymerizable organic groups attached to their surface: the groups can either be grafted to a preformed cluster ("surface modification" method) or introduced during the cluster synthesis ("in situ" method). The advantages and disadvantages of both methods are discussed. OMTOCs with polymerizable surface groups can be polymerized with or without an organic copolymer to yield polymers which are—in most cases—highly cross-linked by the inorganic constituents. The structural integrity and the properties of the clusters are retained upon incorporation into the polymers. Because there are hitherto only a few examples of cluster-reinforced polymers, restricted to tungsten, tin, titanium, and zirconium oxide clusters, the article reviews the early stages of an interesting new approach to inorganic−organic hybrid polymers and highlights possibilities for future materials syntheses.

Introduction

The basic idea behind the development of inorganic−organic hybrid materials is the combination of inorganic and organic moieties on a molecular scale to achieve a synergetic combination of the properties typical of each of the constituents. Modification of the kind and proportions of the organic and inorganic constituents allows, in principle, a deliberate tailoring of properties between purely inorganic and purely organic materials.

One class of inorganic−organic hybrid materials are those in which the organic component is just entrapped in an inorganic host or vice versa. Examples include inorganic−organic hybrid polymers with interpenetrating but otherwise nonconnected networks, polymers filled with inorganic (nano)particles, or layered inorganic compounds intercalated by organic polymers. In the second class of inorganic−organic hybrid materials, the constituents are connected with each other by strong covalent or ionic bonds. Although the preparation of these materials usually requires some effort to establish the chemical link, for example, the development of special precursors, the bonding between the two components overcomes problems of macro- or microphase separation or leaching and allows materials development strategies similar to those for block copolymers in organic polymer chemistry.

The most versatile method for the preparation of inorganic−organic hybrid materials is sol−gel processing, which allows the formation of the inorganic entities starting from molecular precursors. The focus of this article is on covalently bonded inorganic−organic hybrid materials composed of extended inorganic and organic structures (rather than inorganic materials with pending organic groups). There are three approaches to prepare such hybrid polymers by sol−gel processing:

1. Formation from compounds of the type $[(RO)_nM]_xY$, in which Y is an organic group or polymer chain linking two ($x = 2$) or more ($x > 2$) metal alkoxide units $[M(OR)_n]$. The structure of the preformed organic building block (Y) is retained in the final material. For example, organic groups of variable length (e.g., saturated or unsaturated hydrocarbon chains or polyaryls) substituted with $Si(OR)_3$ groups at both ends or polymers with grafted $Si(OR)_3$ groups were used.[1]

2. Formation from functionalized inorganic building blocks. Here, the preformed inorganic structures are cross-linked by polymerization reactions of the organic functions.[2]

3. Formation from bifunctional molecular precursors $(RO)_nM{-}X{-}A$ bearing an inorganic $(RO)_nM$ and an organic functionality (A).[3] The latter must be capable of undergoing polymerization or cross-linking reactions. Usually, these precursors are reacted first with water. After sol−gel processing, that is, formation of the inorganic network, the organic groups A are polymerized or cross-linked to form extended organic structures. Although the order of forming both networks is the same as that in the second approach, there is a procedural difference, as the inorganic building blocks are formed in situ and usually have no defined nanostructures.

For the development of inorganic−organic hybrid polymers, the third approach is most often used. The majority of materials is based on polysiloxane backbones, and therefore these materials can be considered prototypes with regard to the extension to other inorganic components. A special challenge of increasing importance is to tailor not only the composition of hybrid materials but also their structural features, especially in the lower nanometer range. This goal is more easily reached by the first two approaches, that is, the use of

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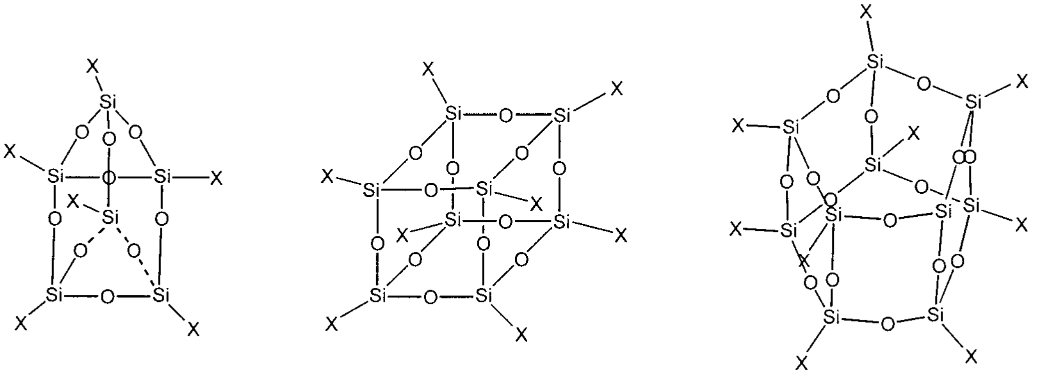

Figure 1. Molecular structures of $(XSiO_{1.5})_n$ cages for $n = 6, 8, 10$ (X = R, H, OH, etc.).

structurally well-defined inorganic or organic building blocks and their deliberate mutual arrangement. The inorganic counterpart of grafting $Si(OR)_3$ groups to organic polymers (one variation of the first approach) is to graft reactive organic groups onto the surface of inorganic particles such as silica (one variation of the second approach). This is done to achieve a strong interaction between filler particles and their polymer surrounding. However, the inorganic particles that can thus be incorporated into organic polymers are rather large (upper nanometers to micrometers) and usually have some size distribution. Particularly if one wants to make use of the physical phenomena associated with the lower nanometer scale, smaller and structurally better defined inorganic particles must be used. This leads to clusters as the inorganic units, which have a defined stoichiometry, size, and shape. The use of structurally well-defined clusters as inorganic building blocks for the synthesis of inorganic−organic materials is the topic of this article.

Only one cluster type was already investigated in some detail as a constituent of inorganic−organic hybrid materials, the polyhedral oligomeric silsesquioxanes, $[RSiO_{3/2}]_n$ (POSS), or spherosilicates, $[ROSiO_{3/2}]_n$.[4] Representative examples are shown in Figure 1. The most often used silicate cage is the cubic octamer, $R_8Si_8O_{12}$ or $(RO)_8Si_8O_{12}$. The groups R can be used for cross-linking or polymerization reactions by which the silicate cages are incorporated into hybrid polymers. For example, catalytic hydrosilylation reactions between the octa-functional $(alkenyl\text{-}SiR_2O)_8Si_8O_{12}$ and $(HSiR_2O)_8Si_8O_{12}$ or $H_8Si_8O_{12}$ gave microporous solids.[5] True hybrid polymers (with organic groups connecting the silicate cages) were prepared by radical polymerization of $(R-SiMe_2O)_8Si_8O_{12}$ (for example, R = vinyl, epoxy, $CH{=}CHCH_2OC(O)CMe{=}CH_2$) or $R_8Si_8O_{12}$ (for example, R = $(CH_2)_3OCH_2$−epoxy).[6]

Recently, a new type of POSS-based hybrid polymer has gained much interest in which POSS molecules are just appended to thermoplastic resins, such as polyolefins, polyepoxides, or polyurethanes.[7,8] The development of these materials was made possible by the straightforward synthesis of monofunctional derivatives of the type $R'R_7Si_8O_{12}$ in which only the group R′ is polymerizable. The hybrid polymers are prepared by using $R'R_7Si_8O_{12}$ as comonomers in polymerization reactions. The common feature of the obtained materials is that several polymer properties are upgraded by the incorporation of POSS. For example, degradation and glass transition temperatures are increased, flammability and viscosity are reduced, and the oxidation resistance becomes higher.

In this article, POSS-derived hybrid polymers will not be reviewed. This has been done elsewhere.[4,7] The focus is instead on polymers with transition-metal oxide clusters as the inorganic component, although comparisons to POSS systems will occasionally be made. The interesting properties of POSS-reinforced polymers have widened the view on what is conceivable with other inorganic clusters, considering the wealth of such compounds in terms of composition, structures, and properties. Apart from the property enhancements observed for POSS-reinforced polymers, interesting catalytic, magnetic, or electric properties can be *additionally* expected if transition-metal-based clusters are employed. The development of the corresponding hybrid materials is in the very beginning. This is mainly due to the lack of suitable organically modified transition-metal oxide clusters (OMTOC) as the transition-metal equivalents to the POSS. The first part of this review therefore deals with methods of how such cluster precursors can be prepared or suitably modified, before attention is drawn to what is already known about OMTOC-reinforced polymers. Because there are hitherto only a few examples, this article not only reviews the early stages of a potentially interesting development but also highlights possibilities for future materials syntheses. It should be pointed out that the general aspects discussed for OMTOCs should be also applicable for other inorganic clusters, for example, sulfide clusters capped by organic groups.[9] A recent example is the preparation of boron carbide ceramics from polyolefins with pendent borane clusters.[10]

Synthesis of Organically Modified Transition-Metal Oxide Clusters (OMTOC)

A key issue of all preparation methods is the stable attachment of suitable organic groups to the metal atoms at the surface of the clusters. The problem is related to the organic modification of transition-metal alkoxides for sol−gel processing.[3,11] Linkage of organic groups is not possible via metal−carbon bonds because these bonds—unlike silicon−carbon bonds—are hydrolytically unstable. It can be achieved, however, via bi- or multidentate (chelating or bridging) groups, such as carboxylates, sulfonates, phosphonates, β-diketonates, and so forth. These groups may carry organic functionalities, such as polymerizable double bonds.

There are two strategies for the preparation of organically modified transition-metal oxide clusters, that is, for the introduction of the multidentate groups. The groups can either be grafted to a preformed cluster ("surface modification" method) or be introduced during the cluster synthesis ("in situ" method). The advantages and disadvantages of both methods will be discussed subsequently. The discussion is restricted to clusters bearing functional organic groups that allow incorporation of the clusters into organic polymers by covalent or ionic bonds.

Surface Modification of Preformed Metal Oxide Clusters. A huge variety of neutral or (mostly) charged metal oxide clusters is known, and there are established routes for their preparation. For the attachment of organic groups at the cluster surface, reactive groups must be available, such as OH, Cl, or OR groups. A principal problem is the simultaneous balancing of charges and coordination numbers upon substitution. If one assumes that the metal atoms in a cluster are coordinatively saturated, then the substitution of monoanionic, *mono*dentate OH, Cl, or OR groups by the above-mentioned monoanionic, *bi*dentate groups would require a rearrangement of the cluster to make additional coordination sites available. Alternatively, bridging groups may change their coordination mode (e.g., bridging OR or OH to terminal, μ_3 oxygens to μ_2 oxygens, etc.) to open vacant coordination sites. Because most of the clusters are very stable, such rearrangements will be rare. One of the few examples is the conversion of $Ti_7O_4(OEt)_{20}$ ($=Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_8(\mu_1\text{-}OEt)_{12}$) to $Ti_6O_4(OEt)_{14}(benzoate)_2$ ($=Ti_6(\mu_4\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OEt)_6(\mu_1\text{-}OEt)_8(\mu_2\text{-}benzoate)_2$) upon reaction with acetic benzoic acid.[12]

Because of the need to balance charges and coordination numbers simultaneously, the substitution of the cluster surface by organic groups is only possible without major difficulties if both the number of coordination sites occupied by the entering ligands and their charges are the same as that of the leaving groups. This is illustrated in the following examples.

Manganese oxide clusters of the general composition $Mn_{12}O_{12}(OOCR)_{16}$ (R = alkyl, aryl), which have very interesting magnetic properties, are prepared from manganese acetate, the corresponding acid and $KMnO_4$. The strongly oxidizing conditions during the synthesis do not allow the incorporation of unsaturated groups. The preparation of acrylate-substituted clusters—with a high degree of substitution (n)—was achieved by reaction of the acetate derivative with acrylic acid (eq 1).[13] Because the acetate ligands are substituted by another carboxylate, the charge/coordination number balance is not affected.

$$Mn_{12}O_{12}(OOC-CH_3)_{16} + nCH_2{=}CH-COOH \rightarrow Mn_{12}O_{12}(OOC-CH_3)_{16-n}(OOC-CH{=}CH_2)_n + nCH_3-COOH \quad (1)$$

The heterotungstate cluster $[SiW_{11}O_{39}]^{8-}$ was derivatized by reaction with various organotrichloro- or organotriethoxysilanes $RSiX_3$ (X = Cl or OR′) with polymerizable groups R (R = allyl, vinyl, styryl, or 3-methacryloxypropyl, $[(CH_2)_3OC(O)CMe{=}CH_2]$).[14] The obtained anionic clusters have the composition $[SiW_{11}O_{35}(O_5Si_2R_2)]^{4-}$ (eq 2); that is, two functional organic substituents per cluster unit were introduced.

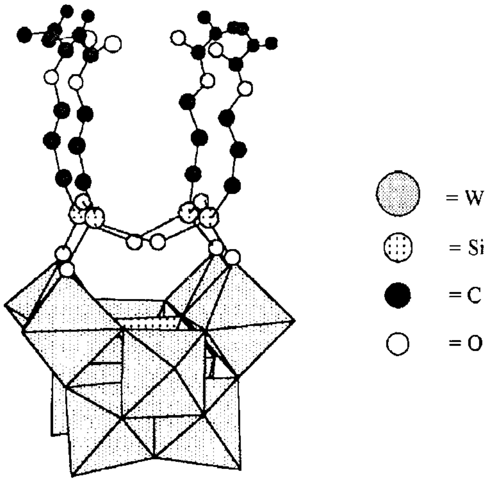

Figure 2. Molecular structure of the polyanion $[\gamma\text{-}SiW_{10}O_{36}(O_4Si_4R_4)]^{4-}$ (R = $(CH_2)_3OC(O)CMe{=}CH_2$) (reproduction from ref 28 with permission from Wiley-VCH).

$$[SiW_{11}O_{39}]^{8-} + RSiX_3 + H_2O \rightarrow [SiW_{11}O_{35}(O_5Si_2R_2)]^{4-} + 6X^- + 2H^+ \quad (2)$$

The clusters $[\gamma\text{-}SiW_{10}O_{32}(O_5Si_2R_2)]^{4-}$ and $[\gamma\text{-}SiW_{10}O_{32}(O_8Si_4R_4)]^{4-}$ (R = vinyl or 3-methacryloxypropyl) were similarly obtained by reaction of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with the corresponding $RSi(OR')_3$.[15] Depending on the synthesis conditions, either the disiloxane or the tetrasiloxane derivative (Figure 2) was formed.

The unsaturated organic groups are attached to the cluster core via W−O−Si−C linkages. In a formal sense, four surface $-O^-$ groups are replaced by the bridging $[R_2Si_2O_5]^{4-}$ or $[R_4Si_4O_8]^{4-}$ unit, respectively. Both the overall charge of the ligands and the number of occupied coordination sites are thus preserved, and no rearrangement of the clusters is necessary to accommodate the organosiloxyl groups.

The attachment of organic groups by ionic interactions is also possible. Additional functionalization of $[\gamma\text{-}SiW_{10}O_{32}(O_5Si_2R_2)]^{4-}$ by interactions with the counterion was achieved by employing the quaternary, methacrylate-substituted ammonium ion $[CH_2{=}CMe-C(O)OCH_2CH_2CH_2NMe_3]^+$.[16]

An electrostatic interaction between a metal oxide cluster and a polymerizable group was chosen to derivatize $[Bu_{12}Sn_{12}O_{14}(OH)_6](OH)_2$, which is formed upon hydrolysis of $BuSn(OPr)_3$. The two hydroxide counterions can be exchanged by reaction with methacrylic acid to give $[Bu_{12}Sn_{12}O_{14}(OH)_6](OMc)_2$.[17]

In Situ Modification. In this method, the oxoclusters 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 building blocks. This may be illustrated by the following example.[18] When $Zr(O^nPr)_4$ is reacted with an excess of methacrylic acid ($CH_2{=}C(Me)COOH{=}McOH$), the cluster $Zr_6(OH)_4O_4(OMc)_{12}$ (Figure 3) is formed quantitatively, in which chelating and bridging methacrylate ligands cover the cluster surface. The cluster has a roughly spherical shape and a diameter of about 1 nm. Although the mechanism of the reaction has not been

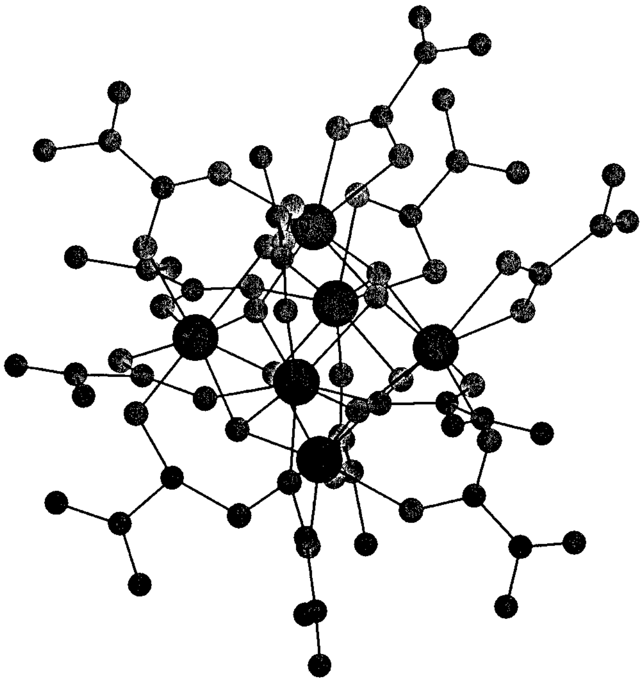

Figure 3. Molecular structure of the cluster $Zr_6(OH)_4O_4$(methacrylate)$_{12}$ (reproduction from ref 31a with permission from Wiley-VCH).

elucidated, the following sequence of reactions appears reasonable. In the first step of the reaction, two alkoxide ligands are substituted by carboxylate groups (eq 3). The thus liberated alcohol then undergoes an esterification reaction (eq 4). The water produced together with the ester serves to hydrolyze the remaining alkoxide groups (eq 5) 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 oxometalate clusters.

$$Zr(OPr)_4 + 2McOH \rightarrow Zr(OMc)_2(OPr)_2 + 2PrOH \quad (3)$$

$$PrOH + McOH \rightarrow McOPr + H_2O \quad (4)$$

$$6Zr(OMc)_2(OPr)_2 + 8H_2O \rightarrow Zr_6(OH)_4O_4(OMc)_{12} + 12PrOH \quad (5)$$

The cluster $Zr_6(OH)_4O_4(OMc)_{12}$ is a transition-metal analogue of POSS. Both types of compounds are formed by controlled hydrolysis of organically substituted alkoxide precursors ($Zr(OMc)_2(OPr)_2$ or $RSi(OR')_3$, respectively) and can be considered nanosized oxide particles, the surface of which is covered by organic groups. The resemblance with the parent oxide is even greater in the case of the zirconium cluster because the structure of the cluster core is analogous to the basic structural unit of tetragonal zirconia. An important difference—resulting from the differences in the structural chemistry of Si and Zr—is, of course, the kind and linkage of the coordination polyhedra (corner-sharing tetrahedra in POSS, edge-sharing square antiprisms in $Zr_6(OH)_4O_4(OMc)_{12}$).

By varying the $Zr(OR)_4$/methacrylic acid ratio and the kind of OR groups, clusters with a different size and shape and a different degree of substitution can be obtained. Starting from zirconium and titanium alkoxides, the zirconium clusters $Zr_4O_2(OMc)_{12}$[17] and $[Zr_3O(OBu)_5(OMc)_5]_2$[19] and the titanium clusters $Ti_6O_4(OEt)_8(OMc)_8$,[20] $Ti_4O_2(OPr^i)_6(OMc)_6$,[18] and $Ti_9O_8(OPr)_4(OMc)_{16}$[21] were also obtained and structurally characterized. Particularly interesting are the Ti/Zr mixed-metal clusters $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$, $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$, $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$, and $Ti_2Zr_6O_6(OMc)_{20}$ because of their rodlike shape of variable length (1.2−1.8 nm [distance between the most distant oxygen atoms], diameters ≈ 0.65 nm) (Figure 4) and because they are good examples to illustrate how charges and coordination numbers are balanced in a self-limiting process during the growth of the clusters.[22]

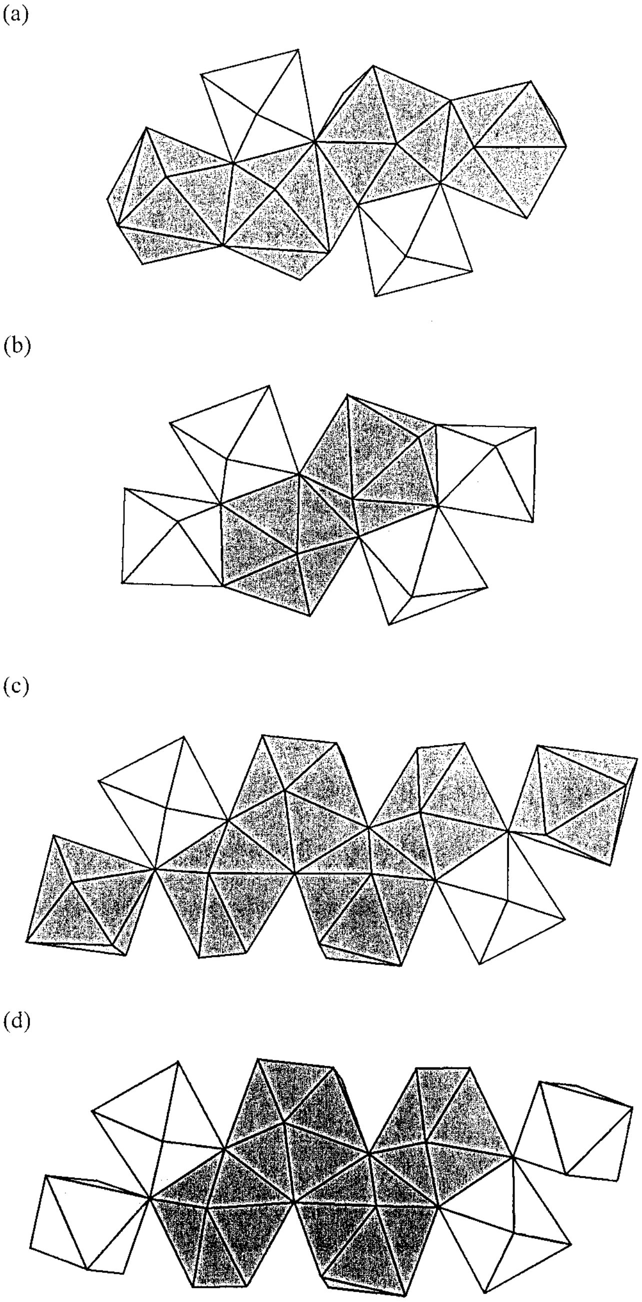

Figure 4. Core of connected polyhedra of the mixed-metal clusters (a) $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$, (b) $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$, (c) $Ti_2Zr_6O_6(OMc)_{20}$, and (d) $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ (reproduction from ref 22 with permission from Wiley-VCH).

In the clusters with the $M_6O_4^{16+}$ core (each of the oxide ions of the cluster core is μ_3), the monoanionic ligands have to balance the 16 positive charges, but a different number of coordination sites, due to the different coordination numbers of Ti and Zr (6 per Ti, 8 per Zr). Thus, the $Ti_2Zr_4O_4$ core in $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ has 32 vacant coordination sites, while the $Ti_4Zr_2O_4$ core in $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ has only 28. Because each of the methacrylate ligands is bidentate (bridging or chelating), both butoxy groups in $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ need to be bridging (μ_2). The same calculation shows that two of the butoxy groups in $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ must be bridging while the remaining four are terminal. This prediction was verified by the X-ray structure analyses. In the clusters with the $M_8O_6^{20+}$ core, the 20 monoanionic ligands have to occupy 38 coordination sites in $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ and 40 in $Ti_2Zr_6O_6(OMc)_{20}$ (two zirconium atoms are only 7-coordinate). Thus, the 4 butoxy groups of $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ must be terminal. In $Ti_2Zr_6O_6(OMc)_{20}$, the methacrylate ligands occupy all coordination sites, and therefore no monodentate ligands are required.

The cluster $Ti_3O_2(O^iPr)_5(HO^iPr)(OCMe{=}CH_2)_3$, which contains polymerizable enolate ligands, was obtained by reaction of $Ti(O^iPr)_4$ with acetone.[23] As in the reactions with carboxylic acids, the μ_3-oxide groups are formed by a nonhydrolytic process, in this case probably by an aldol condensation.

A zirconium cluster with another polymerizable ligand was prepared by hydrolysis of a solution of $Zr(OPr)_4$ and 0.6 equiv of allylacetoacetone.[24] Because the Zr/allylacetoacetate ratio in the obtained cluster $Zr_{10}O_6(OH)_4(OPr)_{18}$(allylacetoacetate)$_6$ is the same as that employed in the starting solution, it can be assumed that part of the zirconium alkoxide is first substituted by allylacetoacetone, and the resulting $Zr(OPr)_4$/ $Zr(OPr)_3$(allylacetoacetate) mixture is then cohydrolyzed.

It should be pointed out that the $Zr(OR)_4$/methacrylic acid combination is often employed—together with organotrialkoxysilanes, mostly (methacryloxypropyl)-trialkoxysilanes—as a component for the preparation of inorganic−organic hybrid materials by sol−gel processing.[25] Inorganic−organic hybrid polymers with oxozirconium components were also made from $Zr(OR)_4$ modified by the polymerizable β-diketonate 2-(methacryloyl)oxyethylacetoacetate.[26] The inorganic structures formed from these precursor mixtures have not been investigated but may be related to the clusters described before, although they have probably polydisperse size distributions.

The "in situ" modification method is certainly not restricted to titanium and zirconium clusters, although only one example is known for other transition metals. The cluster $Nb_4O_4(O^iPr)_8(OMc)_4$ was obtained by in situ hydrolysis from $Nb(O^iPr)_5$ and methacrylic acid as discussed above.[27]

Synthesis and Properties of the Cluster-Reinforced Polymers

All the clusters discussed in the previous section contain polymerizable double bonds. In this section, the properties of the materials obtained by free radical polymerization of the clusters—either with or without organic monomers—will be discussed. A general observation is that the structural integrity of the clusters is preserved upon polymerization. Clusters with functional groups that allow other polymerization techniques, such as epoxide or controlled radical polymerizations or polyaddition reactions, have not yet been investigated but offer tremendous possibilities for materials syntheses. [2]

Heterotungstates. The reactivity of $[SiW_{11}O_{34}(O_5Si_2R_2)]^{4-}$ (R = polymerizable group) in free radical solution polymerizations was found to be similar to that of the corresponding silanes ($RSi(OR')_3$) and increased in the order R = vinyl (polymerization yield 5% in DMF) ≪ allyl (20%) < methacryl (65−70%) < styryl (100%).[13] The polymerization yield was greatly influenced by the kind of solvent. The hydrodynamic radius of the obtained homopolymers—determined by quasi-elastic light-scattering techniques—varied in the range 5−120 nm, but did not always correspond to the polymerization yields. From SAXS data it was concluded that hybrid polymers with different structures (linear or branched) and spatial repetitions of the clusters were probably obtained, depending on the polymerization conditions. UV spectroscopic and cyclic voltammetry studies showed that the clusters retain their typical redox and optical properties in the polymers. For example, transparent films of 0.3−1 μm, deposited from polymer solutions on different substrates, turned blue upon UV irradiation or electrochemical reduction.

The cluster $[\gamma\text{-}SiW_{10}O_{32}(O_5Si_2R_2)]^{4-}$ (R = $CH_2{=}CMe{-}C(O)OCH_2CH_2CH_2$) was copolymerized with ethyl methacrylate (EMA) in acetonitrile in different molar ratios (1:10 to 1:50), and swollen gels were obtained.[16] When the polymerizations were carried out in the presence of the unfunctionalized cluster $[\gamma\text{-}SiW_{10}O_{32}(O_5Si_2Ph_2)]^{4-}$ (phenyl substituent instead of the methacryloxypropyl group), no gel was formed. This shows that the clusters act as cross-linkers. The swelling index (weight of solvent that the dry material can adsorb) of the cluster-doped polymers increased with an increasing EMA/cluster ratio, that is, it depended on the cross-linking density. The cross-linking density was larger for $[CH_2{=}CMe\text{-}C(O)OCH_2CH_2CH_2NMe_3]^+$ than for K^+ as the counterion, as expected. An interesting solvent influence was observed. The largest swelling indices were observed for solvents in which both the polyoxometalate and the undoped polymer are soluble. This observation shows that the polyoxometalate contributes significantly to the swelling properties of the gel. Although the molar concentration of the polyoxometalate is low with respect to EMA, its weight fraction in the gel is high. Thus, when it is insoluble, less solvent can be regained by the gel.

Swellable gels were also obtained by radical polymerization of acrylamide with 2−10 mol % of $[\gamma\text{-}SiW_{10}O_{32}(O_8Si_4R_4)]^{4-}$.[28] When the polymerization was carried out in the presence of 0.25−18 vol % of citrate-stabilized magnetic γ-Fe_2O_3 nanoparticles (6−14 nm), magnetic gels were obtained. The magnetization curve of the ferrogels was the same as that of aqueous suspensions of the γ-Fe_2O_3 particles. The structure and the swelling behavior of the cluster-cross-linked polyacrylamide network was not changed by the incorporation of the particles. It was shown that the mobility of the Fe_2O_3 particles in the polymer network and their leaching out of the swollen gels depend both on the particle size and on the proportion of the heterotungstate cluster used for cross-linking. The latter determines the mesh size of the polymer network. When the mesh size to particle

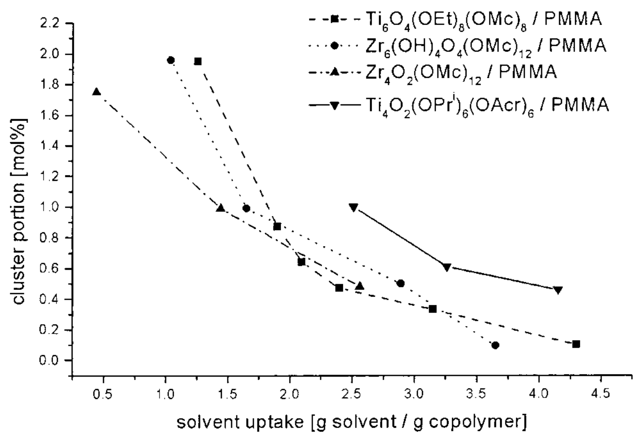

Figure 5. Swelling behavior of PMMA cross-linked by oxozirconium or oxotitanium clusters.

size ratio becomes larger, the mobility of the particles increases, and they are more easily liberated from the network during swelling.

Tin Oxide Clusters. Homopolymerization of $[(BuSn)_{12}O_{14}(OH)_6](OMc)_2$ by free radical polymerization failed, probably because of steric hindrance between the macrocations. However, copolymerization with methyl methacrylate (MMA) in THF (1:13 to 1:52 ratio) resulted in soluble organic–inorganic hybrid polymers.[17] 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 when the MMA/cluster ratio was decreased. 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 that in the feed, which indicates that the cluster has a lower reactivity than the MMA comonomer.

Another type of hybrid polymer was obtained by reacting $[(BuSn)_{12}O_{14}(OH)_6](OH)_2$ with dicarboxylic acids, such as adipinic acid or *p*-terephthalic acid.[29] As soon as the dicarboxylic acids were added to the cluster solution, polymeric precipitates were obtained. In the insoluble polymers, the $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ units are linked together through electrostatic interactions with the $^{-}OOC{-}R{-}COO^{-}$ counteranions. The structure was described to be “rosary-like”, with alternating cluster and dicarboxylate units.

Oxotitanium and Oxozirconium Clusters. Rigid foams were prepared by w/o emulsion copolymerization of styrene and $Ti_3O_2(O^iPr)_5(HO^iPr)(OCMe{=}CH_2)_3$ as cross-linker.[23] However, there was no special advantage in using the cluster compared to monomeric titanium compounds $Ti(OR)_2(PL)_2$ or $Ti(OR)_3PL$ (PL = polymerizable ligand, such as 2-(methacryloyl)oxyethylacetoacetate, oleate, or geraniolate).

Polymerization of the clusters $Zr_6(OH)_4O_4(OMc)_{12}$, $Zr_4O_2(OMc)_{12}$, $Ti_4O_2(OPr^i)_6(OAcr)_6$ (OAcr = acrylate), and $Ti_6O_4(OEt)_8(OMc)_8$ with MMA or methacrylic acid (MA) as comonomers (1:50–1:200 molar ratio) in benzene or toluene resulted in polymers in which the polymer chains are efficiently cross-linked by the oxometalate clusters.[30–32] Glassy materials with no measurable surface area were typically obtained upon copolymerization with MMA. They are transparent when the cluster proportion is low (<2 mol %) but become opaque or whitish when the cluster proportion is increased. The glass transition temperature (T_g) of PMMA (105 °C) increased to 127.5 °C when the polymer was cross-linked by 0.3 mol % $Ti_6O_4(OEt)_8(OMc)_8$.[32] Contrary to undoped PMMA, the cluster-cross-linked polymers are insoluble but swell in organic solvents. The solvent uptake upon swelling increases with an increasing proportion of the clusters in the polymer and also depends—to some extent—on the kind of cluster (Figure 5).[30]

Different polymer morphologies can be obtained when the solvent is changed. When MMA was copolymerized with 1 mol % $Zr_6(OH)_4O_4(OMc)_{12}$ or $Ti_6O_4(OEt)_8(OMc)_8$ in the absence of a solvent or in benzene solution, hard transparent glasses were obtained. However, the polymer structure of the two glasses must be somewhat different because the polymer prepared without solvent swells less and takes up only half the amount of ethyl acetate compared to the polymer prepared in benzene

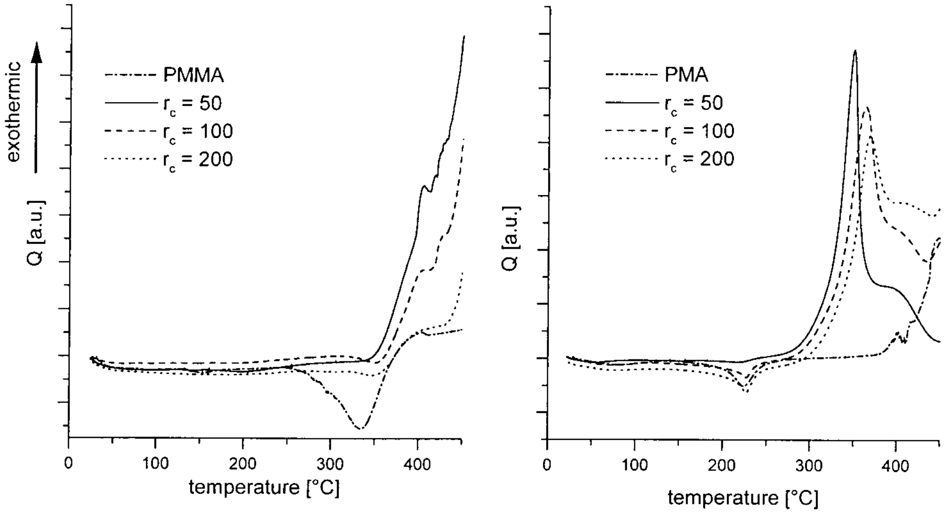

Figure 6. Thermal behavior of cluster-cross-linked PMMA (left, cross-linked by $Zr_6(OH)_4O_4(methacrylate)_{12}$) and PMA (right, cross-linked by $Ti_6O_4(OEt)_8(OMc)_8$). r_c is the organic monomer to cluster molar ratio (reproduction from ref 30c with permission from the Materials Research Society).

solution. Polymerization in heptane/benzene (1:1) resulted in a colorless powder with a specific surface area of 3.2 m^2/g.[30c]

Copolymerization of the clusters with MA resulted in insoluble powders, the specific surface area of which depended on the cluster proportion. For example, the BET surface area of PMA cross-linked by the cluster $Ti_6O_4(OEt)_8(OMc)_8$ increased from 12 to 200 m^2/g when the cluster proportion was increased from 0.3 to 2 mol %.

The thermal stability of PMA and PMMA is improved by the cluster cross-linking. Undoped PMMA and PMA depolymerize above 330 and 230 °C, respectively. Figure 6 shows two examples. Depolymerization of PMMA is strongly reduced by cross-linking with 0.5−1 mol % $Zr_6(OH)_4O_4(OMc)_{12}$ and suppressed with 2 mol % cluster (Figure 6, left). The same features were observed for cluster-doped PMA (Figure 6, right). At higher temperatures, the polymers are oxidatively degraded in air.[30,32]

The improvement of mechanical properties by incorporation of clusters was shown for a polymer obtained from bis[(methacryloyloxy)propoxycarbonylethyl)](3-triethoxysilyl)propylamin, $(EtO)_3Si(CH_2)_3N[CH_2CH_2C(O)OCHMeCH_2OC(O)CMe{=}CH_2]_2$. After sol−gel processing of this alkoxysilane, followed by evaporation of all volatile compounds and photochemical polymerization of the organic groups, a glassy polymer was obtained with a flexural strength of 46 MPa and a flexural modulus of 1230 MPa. After storage in water for 7 d, these values decreased to 31 and 1000 MPa, respectively. When polymerization was carried out in the presence of 10 wt % of $Zr_4O_2(OMc)_{12}$, the flexural strength was about the same (47 MPa), but the flexural modulus was increased to 1900 MPa. A second major improvement was that the cluster-cross-linked polymers did not loose their flexibility upon water storage. After storage in water for 7 d, a flexural strength of 52 MPa and a flexural modulus of 1920 MPa were measured.[33]

The impedance spectra of PMMA doped with various proportions of $Zr_4O_2(OMc)_{12}$ showed that the electrical properties of the hybrid materials are affected by the cluster proportion.[31] The electrical response is equivalent to a circuit with a resistance parallel to the capacitance. With low cluster proportions, the dielectric properties of the material are close to those of undoped PMMA. For PMMA doped with 0.5% or 1% $Zr_4O_2(OMc)_{12}$ very high resistances were measured, thus indicating that both these polymers are characterized by excellent dielectric properties The conductivity of the polymer doped with 2 mol % $Zr_4O_2(OMc)_{12}$ at 74 °C (0.9×10^{-6} $S \cdot cm^{-1}$) was by a factor of 10 higher than the conductivity of the same material at 18.8 °C. This was attributed to the larger concentration of zirconium charge carriers.

Conclusions

With the development of preparative methods for metal oxide clusters having reactive organic groups on their surface, the development of an interesting new type of inorganic−organic hybrid polymers becomes possible. These materials are characterized by the presence of structurally well-defined nanosized inorganic objects that are incorporated in the organic polymers via covalent bonds. In all cases known until present, the integrity and the typical properties of the clusters are preserved upon copolymerization with organic monomers. Because most known clusters are multiply substituted by reactive organic groups, highly cross-linked polymers were mostly obtained. One objective of future research therefore should be the control of the cross-linking sites per cluster.

The development of hybrid materials by this approach is in a rather early stage. However, the currently available results show that there is a high potential for future developments toward novel-nanocomposite materials. The prefabrication of the inorganic nano-objects allows the tailoring of specific properties.

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