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Inorganic-Organic Hybrid Polymers Based on Surface-Modified Metal Oxide Clusters

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Summary: Transition metal oxide clusters with unsaturated carboxylate ligands bonded to their surface were polymerized in the presence of organic co-monomers by various polymerization techniques to form cluster-reinforced polymers. The properties of the cluster-crosslinked hybrid polymers are distinctly different to those of the parent polymers and originate from both crosslinking and filler effects. Variation of the cluster proportion, the kind of employed cluster, the ratio of functional and non-functional capping ligands and the polymerization conditions allows modifying the materials properties of the hybrid materials. The most important changes in materials properties compared with the cluster-free polymers relate to the swelling behavior, thermal stability and mechanical properties. Furthermore, cluster-specific properties can be introduced into the polymers, such as magnetic properties.

Keywords: inorganic-organic hybrid materials; magnetic polymers; metal oxo clusters; swelling; tensile strength; thermal stability

Introduction

Sol-gel derived hybrid polymers, i.e. materials with a polymeric structure formed from both inorganic and organic units, are commonly prepared from small molecular compounds. A typical example is the often used methacrylate-substituted trialkoxysilane $(RO)_3SiCH_2CH_2CH_2OC(O)C(Me)=CH_2$ which, optionally in combination with other (semi-)metal alkoxides and/or organic monomers, gives rise to networks with both organic and inorganic substructures. Structural control in such systems, especially the size and dispersion of the inorganic constituents in the organic polymer, is often difficult. A different approach is therefore to use pre-formed molecular clusters to introduce the inorganic structures in the hybrid polymer.[1,2] In order to connect the clusters to the organic polymer by chemical bonds, the employed clusters must be equipped with functional organic groups at their surface. In a typical procedure, a mixture of the functionalized clusters and organic co-monomers is subjected to polymerization reactions by which the cluster-reinforced hybrid polymers are formed.

Compared to functionalized (nano-)particles, the use of clusters has several advantages:

- Each cluster in a given sample has, by nature, the same composition, size and shape. Neverthelesee can clusters of varying composition, size and shape be prepared.
- Clusters are big molecules, i.e. they can be dissolved in organic solvents, purified, etc., and can be characterized by the analytical tools of molecular chemistry.
- Due to their molecular nature, surface modification is straightforward and can be monitored by standard analytical methods.
- In most clusters, all metal atoms are surface atoms, i.e. clusters can be regarded as nanoparticles without "inner" atoms.

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This results in the highest possible interface and interphase in the hybrid polymers.

The main reasons why the clusters should be attached to the polymer chains by chemical bonds are to make use of crosslinking effects and to control dispersion of the clusters in the hybrid polymer.

A sub-class of such materials that already aroused some interest and resulted in various applications because of their interesting property profiles is the so-called POSS-reinforced polymers.[3] The employed cage compounds ("clusters") in this particular case are polyhedral oligomeric silsesquioxanes, $[RSiO_{3/2}]_n$, or spherosilicates, $[ROSiO_{3/2}]_n$, mostly the octameric derivatives ($n = 8$) with a cubic cluster core of silicon atoms bridged by the oxygen atoms. One functional or non-functional organic group R is attached to each silicon atom and thus provides an organic shell to the silicon oxide cluster core. Depending on the number of polymerizable groups per cluster, the POSS units can be pending (one polymerizable group) to highly crosslinking, and various types of organic polymers have been reinforced by POSS.

Looking at such materials from an inorganic point of view, the range of properties and potential applications could be dramatically broadened, if not only the organic base polymer but also the inorganic cluster is varied.

Preparation of the Clusters

The first step to do so is to provide suitable clusters capped by functional organic groups. Preparative routes for such clusters have been discussed in detail elsewhere.[1] The two principal routes are the synthesis of the clusters in the presence of the (functional) capping ligands or the post-synthesis modification of surface groups. Our work is focussed on carboxylate-substituted metal oxo clusters, which are easily obtained by either method and functionalized by employing functional carboxylic acids. Representative examples are shown in Figure 1. Two cluster features can be varied:

- Composition, size and shape of the cluster core. For example, we have prepared a great variety of carboxylate-substituted metal oxo clusters by reacting metal

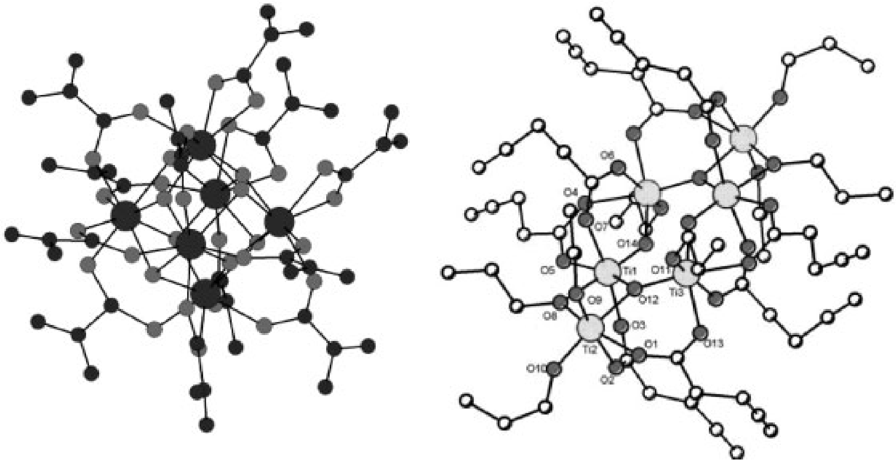

Figure 1.
Left: $Zr_6O_4(OH)_4$(methacrylate)$_{12}$ for free-radical polymerization[9]; right: $Ti_6O_4(OPr)_8(OOCCH_2CH_2C{\equiv}CH)_8$ for click reactions.[6]

alkoxides with the corresponding carboxylic acids.

- The organic functionality and thus the polymerization method to be used. Carboxylate-substituted metal oxo clusters with the following functionalities have been prepared until present: (meth)-acrylate derivatives for free radical polymerization,[4] norbornene-2-carboxylate derivatives for ring-opening metathesis polymerization,[5] 4-pentynoate derivatives for click reactions,[6] 2-bromo-*iso*-butyrate derivatives as initiator for atoms-transfer radical polymerization[7] and 3-mercaptopropionate derivatives for thiol-ene reactions.[8]

Another option for varying the functionality of the cluster surface is the variation of the functional/non-functional ligand ratio. Carboxylate ligands can be exchanged against other carboxylates present in solution. This allows variation of the capping ligands by (partial) exchange. For example, when the cluster $Zr_6O_4(OH)_4(OMc)_{12}$ (OMc = methacrylate) was reacted with propionic acid, part of the methacrylate ligands was exchanged, and $Zr_6O_4(OH)_4(OMc)_7(propionate)_5$ was obtained with retention of the cluster core (complete exchange is possible with an excess of propionic acids).[10] Partial exchange allows varying the proportion of reactive groups on the cluster surface and thus the crosslinking density during polymerization, although we have not yet utilized this option of varying the properties of the hybrid polymers.

Preparation and Structure of Cluster-Reinforced Polymers

In the remainder of this article, some hybrid materials will be discussed which were obtained by free radical polymerization of (meth)acrylat-substituted metal oxo clusters with organic co-monomers. In a typical protocol, the clusters were dissolved in an excess of the styrene or methyl methacrylate and then thermally polymerized in the presence of a radical initiator. The materials discussed below contain cluster proportions of about 1–2 mol% because the typical solubility of the clusters in the monomers is in this range. Solution polymerization, with higher cluster proportions, is also possible, with the problem of solvent removal from the obtained hybrid polymers. The clusters can even be polymerized in the absence of organic monomers. However, this results in intractable, hard solids. It should be pointed out that 1 mol% of cluster corresponds to different wt% of metal oxide, depending on the type of used cluster. For example, 1 mol% of cluster is equivalent to 4.3 wt% of ZrO_2 for $Zr_4O_2(OMc)_{12}$ and 6.3 wt% for $Zr_6O_4(OH)_4(OMc)_{12}$, 1 mol% of $Hf_4O_2(OMc)_{12}$ corresponds to 7.2 wt% of HfO_2.

Before turning to materials properties, an important issue is the dispersion of the clusters in the polymers. A very suitable method for studying the cluster distribution is small-angle X-ray scattering (SAXS), because the inter-cluster distance is 1–5 nm and the electron density difference between the organic and inorganic entities is large. For a random dispersion of the clusters, a single maximum is expected which shifts to lower scattering vectors (larger average cluster-cluster distance) when the cluster proportion of the cluster is decreased. We observed a random dispersion in several cases, such as poly(methyl methacrylate) (PMMA) crosslinked by $Zr_6(OH)_4O_4(OMc)_{12}$, $Zr_4O_2(OMc)_{12}$ or $Ti_6O_4(OPr)_8(acrylate)_8$, polystyrene (PS) crosslinked by $Ta_4O_4(OEt)_8(OMc)_4$, or poly(ethyl acrylate) crosslinked by $Mn_{12}O_{12}(acrylate)_{16}$. However, we also observed cases where the SAXS data indicate some clustering of the clusters, either because two maxima are observed or because a single maximum does not shift upon varying the cluster proportion.[11]

We investigated the latter case recently in some detail for PS crosslinked by $Zr_6O_4(OH)_4(OMc)_{12}$, where only one maximum in the SAXS curves, at about $q = 3.7\ nm^{-1}$, was observed.[4] This maximum did not shift significantly when the cluster proportion in the polymer was

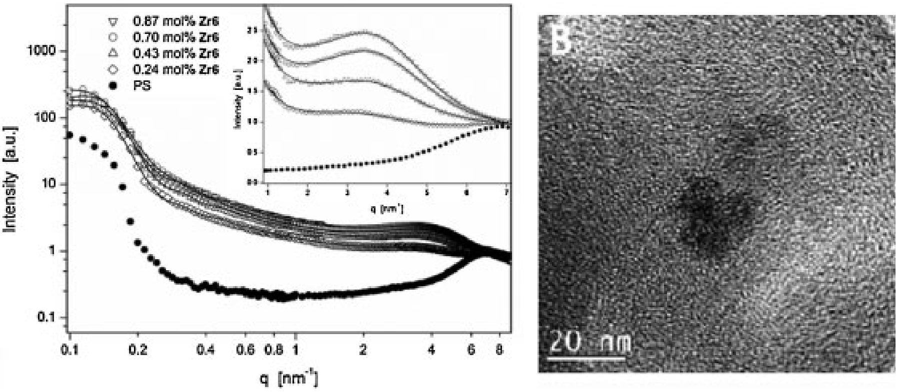

Figure 2.

Left: SAXS curves of PS doped with $Zr_6O_4(OH)_4(OMc)_{12}$ (**Zr6**) after background correction and normalization. The solid lines are fits according to the Beaucage model as described in the text. Right: TEM micrograph of PS doped with 0.24 mol% of **Zr6**. Reproduced by permission of Wiley-Interscience from Ref. 4.

varied between 0.24 and 0.87 mol% (Figure 2). The cluster-cluster distance calculated from the maximum was 1.7–1.8 nm, which was significantly less than the calculated average distances assuming that the clusters are randomly distributed in the hybrid polymers. A more detailed interpretation of the SAXS data with the Beaucage model, which describes the scattering from complex systems containing multiple structural features, resulted in a structural model of randomly distributed cluster aggregates of different size ("clusters of clusters"), where only the packing density of the aggregates increased with increasing cluster proportion, but no phase separation or specific size or distance of aggregates was found within the observed *q* range. This was confirmed by electron microscopy where randomly distributed small (~5 nm) and big (~100 nm) aggregates were observed.[4] Bigger aggregates were not present and can be excluded because the samples are macroscopically transparent.

The following experiment is in line with these observations: When the crosslinking cluster is chemically destroyed, the molecular mass distribution of the resulting purely organic polymer should allow conclusions on the lengths of the polymer chains connecting the clusters in the hybrid polymer. Most of the metal oxo clusters used in our work cannot be selectively degraded. However, we found one example, where this is the case. When Zr_4O_2(methacrylate)$_{12}$ is treated with acetylacetone, the mono-nuclear complex Zr(acac)$_2$(methacrylate)$_2$ is formed.[12] When the same experiment was done with PS or PMMA crosslinked with Zr_4O_2(methacrylate)$_{12}$, the cluster was degraded and all Zr was extracted from the polymer. Analysis of the resulting Zr-free polymer gave M_n of $7.1 \cdot 10^5$ for PMMA and $1.0 \cdot 10^5$ for PS. However, the polydispersities were very high, *viz.* 8.8 and 4.4, respectively.[13] This shows that the clusters are connected by organic cords of strongly varying lengths.

Materials Properties of the Hybrid Polymers

Cluster-crosslinked PMMA or PS is no longer soluble in organic solvents, but swells instead, as expected for crosslinked polymers. Swelling clearly depends on the polymer/cluster ratio: the degree of swelling decreases with an increasing cluster proportion. However, the swelling also depends on the cluster type, as shown in Figure 3, and does not correlate with the

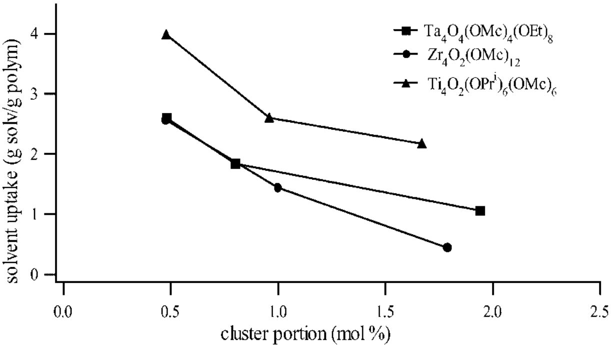

Figure 3.
Swelling of PMMA crosslinked by the tetranuclear clusters $Ta_4O_4(OEt)_8(OMc)_4$, $Ti_4O_2(OiPr)_6(OMc)_6$ or $Zr_4O_2(OMc)_{12}$ in ethyl acetate for 3 d at room temperature. Reproduced by permission of the Materials Research Society from Ref. 14.

number of polymerizable groups per cluster unit.[14] The origin of this effect is currently unknown.

One of the most important features of the cluster-based hybrid polymers is their higher thermal stability compared with the undoped polymers. The thermal stability of PS or PMMA is increased by small proportions of clusters, but also depends on the polymerization conditions. PMMA crosslinked by small cluster proportions does not burn when ignited, because unzipping of the polymer is apparently suppressed. When the polymerization conditions for PS or PMMA, crosslinked by 0.5 mol% of $Zr_6O_4(OH)_4(OMc)_{12}$, were optimized by applying a step polymerization protocol, the onset of thermal decomposition was increased by ca. 50° for PS and ca. 110° for PMMA. The increase in thermal stability correlated with a higher char yield.[15] A purely inorganic residue, the mass of which corresponds to the proportion of the employed cluster, is obtained when the organic moieties of hybrid polymers are completely pyrolyzed in air.

However, the increased thermal stability is not necessarily caused by the crosslinking. This was shown by the following experiment.[16] Two types of cluster-doped hybrid polymers were prepared by free radical polymerization of styrene under the same conditions: (i) First, clusters with *polymerizable* methacrylate ligands were used, such as $Zr_6O_4(OH)_4(OMc)_{12}$ or $Zr_{12}O_8(OH)_8(OOCMe)_{16}(OMc)_8$. In this case, the gel times were short, and transparent materials were obtained which swelled in toluene, as expected for crosslinked polymers. (ii) Second, the use of clusters with *non-polymerizable* ligands, such as $Zr_6O_4(OH)_4(OOC\text{-norbornenyl})_{12}$ or $Zr_{12}O_8(OH)_8(\text{acetate})_{24}$, resulted in 2–3 times longer gel times and turbid polymers which were soluble in toluene. In this case the clusters clearly were only nanofillers. However, the onset temperatures of thermal decomposition and the glass transition temperatures of both series of cluster-containing polymers were nearly the same and were higher than that of neat PS, independent of whether the clusters were crosslinking or blended into the polymer. This shows that the improved thermal stability is mainly due to the filler effect of the clusters rather than to their participation in network formation. Crosslinking provides extra benefits, such as rendering the hybrid polymers insoluble.

The step polymerization protocol mentioned above allowed preparing bubble- and crack-free bulk samples of $Zr_6O_4(OH)_4(OMc)_{12}$-crosslinked PS on a 30 g scale (0.24–0.87 mol% cluster proportion) with dimensions required for mechanical testing.[4] The dynamic mechanical response of the hybrid polymers was characteristic for thermoplastic materials. Storage moduli (E′) at room temperature were slightly higher than that of neat PS. The increase in E′ was much more pronounced above T_g. because of the crosslinking and the nanofilling contribution of the clusters. Crosslinking with different proportions of the cluster did not change the linear thermal expansion coefficient α in the glassy state. This behavior is also found for polystyrene crosslinked by organic groups. Above T_g, the hybrid polymers became rubber-like, and the properties were determined by the network structure. Thus, α decreased with increasing cluster proportion above T_g.

Judged from the stress-strain curves, the materials became more brittle with increasing cluster proportion although the elastic properties were still governed by the PS matrix. This is as expected for hybrid materials with small proportions of the inorganic component. The changes in the tensile moduli with increasing crosslinking were not pronounced which is commonly observed for thermosetting resins in the glassy state. However, the tensile strength was significantly improved and exhibited a distinct positive correlation with increasing network density (Figure 4). The polymer network densities correlate with the cluster proportion.

Microhardness measurements revealed no significant changes of indentation moduli and of indentation hardness when PS was doped with $Zr_6O_4(OH)_4(OMc)_{12}$, although the scratch resistance was improved with increasing cluster proportion. An increase of craze initiation stress was found with increasing cluster proportion, as determined by ball indentation experiments (Figure 5). In scratch tests with constant load, a reduction of pile-up and a stronger recovery was observed for the hybrid materials compared to undoped PS. Scratch tests with a constant increase of load showed an increase of the critical load for crack opening during scratching.[17]

In addition to nanofiller and crosslinking effects, the clusters can add an additional quality to the hybrid polymers, *viz.* properties that are inherent to the cluster itself. A first example is poly(ethyl acrylate) crosslinked by the magnetic cluster $Mn_{12}O_{12}(acrylate)_{16}$.[18] Mn_{12} clusters of general composition $Mn_{12}O_{12}(OOCR)_{16}$ are one of the best examples of molecular magnets. The acetate-substituted cluster has a high total spin of $S = 10$ and is superparamagnetic at low temperatures with an energy barrier in the range 70 K. Ac susceptibility measurements showed that the magnetic properties are

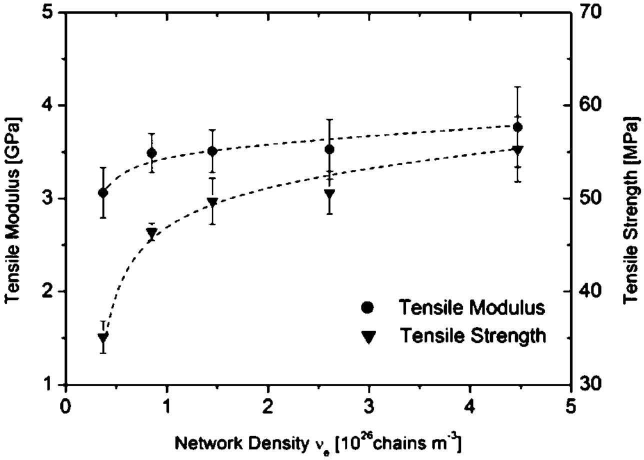

Figure 4.
Tensile modulus and tensile strength *vs.* network density. Reproduced by permission of Wiley-Interscience from Ref. 4.

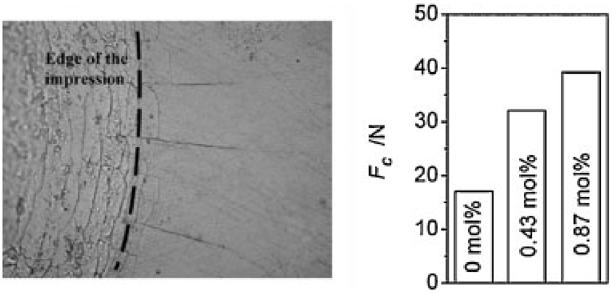

Figure 5.
Left: Development of radial crazes at the edge of an impression. Right: dependence of the critical load for craze initiation on the cluster proportion. Reproduced by permission of Springer Wien from Ref. 17.

retained in the hybrid polymer obtained by co-polymerization with $Mn_{12}O_{12}(acrylate)_{16}$. A superparamagnet-like behavior was observed with a relaxation following an Arrhenius law with $\tau_0 = 4–8 \cdot 10^{-8}$ s and an energy barrier in the range 45–65 K. The observed weak intercluster antiferromagnetic interaction is similar to that in crystals of the molecular cluster. The polymerization of the magnetic clusters in the presence of organic monomers thus allows preparing magnetic materials that can be processed like typical organic polymers but retain the properties of the molecular magnets. Furthermore, the inter-cluster distance can easily be controlled by the cluster/monomer ratio in the starting mixture.

Conclusions

A new type of hybrid polymer is obtained when clusters capped by polymerizable organic groups are co-polymerized with organic monomers. These hybrid polymers exhibit properties different to the parent polymers. The property changes are brought about by the clusters as multifunctional crosslinkers as well as inorganic (nano-)fillers. The interplay of these effects and their individual contribution to the macroscopic properties renders a general discussion and prediction of the materials properties difficult. While an individual property change may also be feasible with other crosslinkers or fillers, the combination of different property changes renders this class of hybrid polymers attractive. The materials properties not only depend on the polymerization conditions and the cluster proportion, but also on the kind of employed cluster. A nearly unexploited option is to incorporate clusters with intrinsic physical properties in the polymers, such as clusters with special magnetic or optical properties.

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