**EXAFS Investigations on Nanocomposites Composed of Surface-Modified Hafnium Oxo Clusters and Organic Polymers**

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Inorganic-organic hybrid materials have gained an enormous interest in the last decades due to their chemical, physical and mechanical properties which can be used for various technical applications. Recently a new type of inorganic-organic polymer was developed by copolymerizing unsaturated organic monomers with transition metal oxide clusters containing polymerizable organic ligands [1]. We showed in an earlier work that it is possible to prepare oxo clusters of the elements zirconium and titanium and to incorporate them in a variety of polymers [2]. By using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy we were able to detect that the cluster core was retained in these composites. The properties of the hybrid polymers depend on the cluster to monomer ratio (i.e. crosslinking density) and the nature of the incorporated cluster [3]. Therefore several new clusters were synthesized and copolymerized with various monomers in different molar ratios. In this study, EXAFS measurements at the Hf LIII-edge were carried out at beamline X1.1 on a hafnium oxo-cluster (HfO₆(OMc)₁₂, Figure 1) and its hybrid polymers in poly(methyl methacrylate) (PMMA) in order to determine whether the cluster core remains stable in these polymers. The hafnium(IV) cluster was prepared by reaction of hafnium(IV) n-butoxide (Hf(O’Bu)₄) with methacrylic acid (HOMc) [4]. The investigated hybrid polymers were obtained by free radical polymerisation of the cluster and the monomer units (methyl methacrylate) in cluster to monomer ratios of 1:50, 1:100 and 1:200. The EXAFS spectra were analysed with the program packages described in literature [5,6]. The program Autobk 2.61 was used for background removal, the EXCURV92 module [7] of CERIUS² was used for curve fitting of the EXAFS function.

**Figure 1:** Experimental (solid line) and calculated (dotted line) \(k^{3}\chi(k)\) functions (a,c) and their Fourier transforms (b,d) of the Hf₇-cluster in PMMA ratio 1:50 (top) and 1:200 (bottom), measured at the Hf LIII-edge. Picture on the right: Molecular structure of the cluster Hf₆O₆(OMc)₁₂ according to single crystal XRD [4].
The results of the EXAFS analysis are shown in Table 1. The structural parameters of the pure cluster determined by EXAFS are in agreement with those found from the single crystal XRD [4], even if the second Hf-Hf distance was found to be 0.19 Å shorter than expected. This phenomenon was already described for the analogous zirconium cluster Zr₄O₂(OMc)₁₂ [8]. For the analysis of the EXAFS data of the hybrid materials (shown in Figure 1), the coordination numbers were fixed to the values of the crystalline cluster. From the EXAFS data of the Hf₄-cluster in PMMA 1:50 it can be concluded that the structure of the cluster core is still present in the polymer matrix, whereas in the cases of the polymers with cluster to monomer ratios 1:100 and 1:200 a partial degradation into dimers or higher aggregates must be assumed from the decrease of the hafnium signal at 3.46 Å. To quantify this degradation, the coordination number of the second hafnium shell was iterated in the cases of cluster to monomer ratios 1:100 and 1:200 by setting the Debye-Waller factor to a value of 0.055 Å (known from the Hf₄-cluster in PMMA, ratio: 1:50).

References