

# Tantalum oxide nanomers for optical applications

B. Braune<sup>a</sup>, P. Müller<sup>a</sup>, H. Schmidt<sup>a</sup>

<sup>a</sup>Institut für Neue Materialien GmbH, im Stadtwald, D 66123 Saarbrücken

## ABSTRACT

The synthesis of transparent nanomers by the incorporation of nanoscaled tantalum oxide into an organic-inorganic composite matrix and their subsequent characterization are presented. The matrix materials used consist of a mixture of organically functionalized silanes and polymerizable monomers. The mixture does not exhibit phase separation, even down to the lowest nanometer scale, as revealed by SAXS measurements. The addition of nanoscaled Ta<sub>2</sub>O<sub>5</sub> particles (mean particle diameter: 4 nm as determined by photon correlation spectroscopy) aims to increase the refractive index of the nanomers. The preparation of the oxide sol and the optimization of the synthesis with respect to compatibility with the matrix material, thereby avoiding agglomeration effects, is described. After incorporation of the particles in the monomer mixture, a photopolymerization step, followed by curing with a temperature program up to 90 °C, led to colourless and transparent monoliths.

The volume shrinkage, caused by polymerization, decreases from 8.2 % for the unfilled matrix material to 5.8 % for a nanomer containing 30 wt. % tantalum oxide. The shrinkage decreases linearly with increasing filler content of tantalum oxide. The increase in refractive index is about  $7.4 \times 10^{-4}$  per wt. % oxide (measured at a wavelength of 546.1 nm). The colouration of the monoliths is expressed as yellowness index G according to DIN 6167. Colour values attained for nanomers with up to 15 wt. % tantalum oxide are comparable to values for commercial optical polymer materials. Nanomers containing 15 wt. % tantalum oxide show transparency losses at a wavelength of 850 nm below 0.1 dB/cm.

**Keywords:** nanomer, organic-inorganic composite, yellowness index, tantalum oxide

## 1. INTRODUCTION

In the past years the rapid evolution of sol - gel technology has led to organic - inorganic composite materials with properties that are of particular interest for applications in optics or optoelectronics. In 1984, Schmidt and Philipp<sup>1</sup> had obtained a composite material with adjustable refractive index  $n_D$  from 1.5 to 1.7 suitable for contact lenses, by cocondensation of epoxy and methacrylic substituted silanes with titanium alkoxides. The curing of the mixtures was carried out at 100 °C. In a similar way, Wang and Wilkes<sup>2</sup> have produced films by cocondensation of titanium isopropoxide and triethoxysilane capped poly(arylene ether ketone) (PEK) or poly(arylene ether sulfone) (PSF). Refractive indices,  $n_D$ , from 1.60 to 1.75, depending on the titanium content, were measured on films cured at 200 °C.

Another field of application for sol-gel derived materials are solid state lasers. A number of laser dyes have been successfully incorporated into so called „ORMOSIL“ (=ORganically MOdified SILane) - matrices, firstly described by Scholze et al.<sup>3</sup>, the organic modifier being methacrylic or epoxy groups<sup>4,5</sup>. Reisfeld, Brusilowski et al.<sup>6</sup> synthesised a solid state laser by incorporation of the laser dye BASF 241 (a perylene derivative) in a matrix of MMA - impregnated silica-gel. Organic - inorganic composite materials may also be used for waveguide applications. S. Motakef et al.<sup>7</sup> have synthesised a variety of composite materials by cocondensation of tetraethylorthosilicate (TEOS), N-triethoxysilylpropyl - O -polyethyleneoxide - urethane and metal alkoxides of titanium, germanium, zirconium, tantalum, zinc and lead, calling these composites „polycerams“. The optical loss of the materials measured at a wavelength of 632.8 nm ranges from < 0.25 dB/cm to 3.27 dB/cm. Yoshida and Prasad<sup>8</sup> have found optical propagation losses from 0.2 dB/cm to 0.62 dB/cm for slab waveguides made by spin-coating and hardening of a film containing titaniumacetocomplexes, prehydrolyzed TEOS and polyvinylpyrrolidone (PVP) at 200 °C. A linear relationship was found for the refractive index of the films in dependence on the titania concentration (wt. %).

A common feature of the above reported investigations is the mixing of the components on a molecular scale (except<sup>5</sup>) to avoid phase separation and therefore undesirable light scattering effects. However, the existence of a nanoparticulate phase would make it possible to employ the solid state properties of the nanoparticles for achieving special properties such as

increased scratch resistance or tailoring the refractive index for example. To ensure transparency of the nanocomposites, the particle size has to be small enough to minimise light scattering from the particles, which may cause opacity of the material. Depending on the refractive index difference between the particles and the matrix as well as on the particle concentration<sup>9</sup>, the upper limit for the particle size  $D$  is  $D \leq \lambda/20$ .

A new coating material for transparent polymers was reported by Kasemann, Schmidt and Wintrich<sup>10</sup>. A cocondensation product of TEOS and 3-glycidyoxypropyltrimethoxysilane (GPTS) was loaded with boehmite ( $\text{AlO}(\text{OH})$ ) having a particle size smaller than 50 nm. The scratch resistance and hardness of the spin-coated films, thermally cured at 100 °C, was found to be substantially improved compared to systems without phase separation. The synthesis of a composite („nanomer”) of 3-methacryloxypropyltrimethoxysilane (MPTS), tetraethyleneglycoldimethacrylate (TEGDMA) and zirconium oxide nanoparticles, with a particle size of 5 nm to 8 nm, was reported by Oliveira et al.<sup>11,12</sup>. The zirconium oxide nanoparticles were formed in the matrix during synthesis using methacrylic acid as complexing agent. Via the migration of the nanoparticles in an applied electric field a radial gradient in the refractive index ( $r$ -GRIN) of 0.07 over a distance of 5 mm was achieved.

A tailoring of the refractive index of an organic-inorganic composite material can be achieved by the incorporation of high refractive index nanoparticles. Since transparency losses of nanomers, due to light scattering, depend not only on the size of the high refractive index particles but on their concentration as well, it is necessary to keep the particle concentration as low as possible, employing particles having highest possible refractive indices. In a first approach<sup>16</sup>, sol-gel derived nanosized titania ( $\text{TiO}_2$ ) was chosen as refractive index modifier since the refractive index of the crystalline titania is higher compared to the refractive index of crystalline  $\text{ZrO}_2$  ( $n=2,5$  at 500 nm for Anatase  $\text{TiO}_2$  compared to  $n=2,15$  at 500 nm for  $\text{ZrO}_2$ <sup>13</sup>). Due to the catalytic activity of  $\text{TiO}_2$ , a degeneration of the matrix leading to strong yellowing of the composites was unavoidable; a coloration however limits the application of the nanomers to fixed wavelength regimes and should be avoided. This effect was reported for polyethylene films containing nanosized  $\text{TiO}_2$ <sup>14</sup>. The reduction of the catalytic activities of  $\text{TiO}_2$  is achieved by a particle modification, leading to a  $\text{SiO}_2$ - or a  $\text{Al}_2\text{O}_3$ - film on the particle surface, which acts as a spacer between particle and matrix<sup>15</sup>. A surface modification of the sol-gel derived  $\text{TiO}_2$  by the use of silanes and/or aluminium alkoxides was carried out in order to suppress yellowing of the nanomers; however colourlessness could not be achieved<sup>16</sup>. For tantalum oxide, a bulk refractive index of 2.03-2.8, dependent on the crystalline modification, in combination with the absence of absorption at wavelengths greater than 325 nm was reported<sup>17,18</sup>. Furthermore, there is no evidence for a catalytic activity of tantalum oxide particles. Moreover, the use of conventional colourless photoinitiators is possible for tantalum oxide, unlike to titania, showing strong absorption for wavelengths smaller than 390 nm. The photoinitiation of the radicalic polymerisation facilitates the synthesis of the nanomers and reduces the overall reaction time. The synthesis of sol-gel derived tantalum(V)oxide films as antireflecting coating for high power laser applications and as proton conducting film was reported by several authors<sup>17-19</sup>. The authors conducted the hydrolysis of tantalum(V)ethoxide in ethanol using different stabilising agents such as acetic acid, HCl,  $\text{HNO}_3$ , tetramethylammonium hydroxide (TMAH) and triethylamine (TEA). A molar ratio [stabiliser]/[Ta] of 0.2 to about 7 for the organic acids and 0.1 to 0.3 for the inorganic acids and basic stabilisers was reported for various ratios  $[\text{H}_2\text{O}]/[\text{Ta}]$  from 4 to 200. The refractive indices of the films however did not exceed  $n=1.78$  (at 500 nm) up to curing temperatures of 150 °C.

The aim of the investigations presented here was to employ tantalum oxide as a substitute for titania as refractive index modifier. Unlike as in the case of  $\text{TiO}_2$ , the use of tantalum oxide was supposed to lead to colourless nanomers because of the features of tantalum oxide described above. For this reason the particle synthesis was carried out with different solvents and stabilisers, as well as conducting experiments with different surface modifiers. Furthermore, the influence of the particle loading on the optical properties like refractive index or Abbe number, was investigated.

## 2. EXPERIMENTAL

**Particle synthesis:** For the particle synthesis tantalum(V)ethoxide of 99.9 % purity (ABCR) was used without further purification. Hydrolysis and condensation reactions were carried out in 3 different solvents: Ethanol, 1-propanol and n-butanol. HCl,  $\text{HNO}_3$ , formic acid and methacrylic acid were employed as stabilising agents so each acid was combined with each of the solvents mentioned above. Each of the 12 experiments were conducted in the following way: alcohol, acid and water were homogenised by vigorous stirring for 30 minutes, followed by the slow addition of calculated amounts of tantalum(V)ethoxide under stirring. The molar ratio [water]/[Ta] was 6 and the molar ratio [acid]/[Ta] was 1.3 for each synthesis. The molar ratio [Ta]/[solvent] was kept at 0.13 mole/l. The sols were stirred for 24 hours before being used in the nanomer synthesis. In order to improve the dispersion of the particles in a matrix and to stabilise the particles sterically, the

tantalum oxide particles were surface modified using 3-methacryloxypropyltrimethoxysilane (MPTS) and diphenyldimethoxysilane (DPDMS). The surface modification was carried out as follows: one mole of the silane per mole Ta-precursor was mixed with the solvent in a volume ratio of silane/solvent of 1:50. After stirring this mixture was added to the particulate sol and refluxed for 1 h. Hydrolysis and condensation reaction of the silane was carried out by addition of 0.1 N HCl in a ratio 1.5 mole water per mole MPTS or 1 mole water per mole DPDMS after refluxing of the mixture. After 60 minutes stirring, the solvent and the residual water were removed from the sol by vacuum distillation. In every synthesis a viscous and colourless liquid was obtained, which was added to the matrix monomers.

**Synthesis of the nanomers:** Two different organic - inorganic host matrices for the incorporation of the nanoscaled particles were employed: (A) MPTS/tetraethyleneglycoldimethacrylate (TEGDMA) in a molar ratio 1:1 as a model for a system with high silane content. The second matrix material (B) was composed of MPTS/DPDMS/TEGDMA/2,2-Bis[4(2'-methacryloyl-oxy-2'-hydroxy)propoxyphenyl]propane (BIS-GMA) in a molar ratio 18:12:50:20 as an example for a matrix material containing high amounts of organic monomers, especially aromatic groups, leading to an increase in refractive index of the matrix material. This particular composition was chosen because of its high transparency and the relatively high refractive index ( $n=1.54$  at 500 nm). The silanes used were subjected to hydrolysis and condensation before adding them to the organic monomers. These processes have been carried out by adding 0.1 N HCl to the silane or silane mixture in a molar ratio  $[\text{Si}]/[\text{H}_2\text{O}]$  of 1:1.5 for MPTS and 1:1 for DPDMS. The silane/water mixture was stirred for 24 hours at 40 °C, followed by removal of the residual solvent at 40 °C under reduced pressure. The viscous liquids obtained were added to the organic monomer followed by vigorous stirring in order to obtain a homogenous mixture. Darocure 1173 (CIBA-GEIGY) in a molar ratio  $[\text{initiator}]:[\text{C}=\text{C}]$  of 0.004:1 was added as a photoinitiator and INP-75-A1 (Peroxid Chemie GmbH) in a molar ratio  $[\text{initiator}]:[\text{C}=\text{C}]$  of 0.002:1 was employed for thermal curing. After degassing for 30 minutes under reduced pressure the first polymerisation step was performed by UV light exposure using a BELTRON UV curing unit followed by thermal polymerisation at 90 °C for 12 hours. The polymerization reactions were conducted in Teflon moulds having volumes between 4 ml and 150 ml.

**Optical properties:** Measurement of the particle size was carried out by photon correlation spectroscopy (PCS) using a ALV/SP-125 Laser Goniometer (ALV-Laser Vertriebsgesellschaft mbH) (laser wavelength: 632,8 nm). The refractive index of the nanomers was measured using a Pulfrich refractometer (Carl Zeiss, Jena). The coloration of the nanomers was calculated from transmission spectra and was expressed as yellowness index G according to DIN 6167. G is calculated using the X, Y and Z values for the 1931 CIE standard observer (2 ° observer) and standard illumination  $D_{65}$  according to equation (1).

$$G = \frac{a \times X - b \times Z}{Y} \quad (1)$$

a,b: constant values; for  $D_{65}$  and 2 ° observer:  $a= 1.298$ ,  $b= 1.133$

**Density of liquid and solid nanomers:** Density measurements on reaction mixtures before polymerisation have been carried out using a pycnometer having a volume of 10.17 ml at 20 °C. The pycnometer with the liquid was kept in a thermostatted water bath at 20 °C ( $\pm 0.1$  °C) for 60 minutes before weighing. The density of the nanomers was measured in water according to the Archimedes bouyancy method.

**Small angle X - ray scattering (SAXS):** Small angle X - ray measurements were carried out on a PAAR type KKK Kratky camera with position sensitive detector. For this purpose thin slices were cut from the nanomers with a thickness ranging from 300  $\mu\text{m}$  to 1000  $\mu\text{m}$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. Transparency and coloration of the nanomers

The synthesis of nanomers containing tantalum oxide aims at the generation of a material with scaleable refractive index and Abbe number for optical applications. The occurrence of coloration, that means transparency losses for special wavelengths, would restrict the field of application and must be as low as possible. Regarding this fact, the first criterion for the suitability of a tantalum oxide particle synthesis for the generation of nanomers is, that the nanomers containing these

particles are colourless. Former investigations showed that the synthesis parameters for the particle generation (e.g. employed solvent and stabiliser), as well as the applied coating of the particles, strongly influence the coloration of the tantalum oxide nanomers<sup>20</sup>. In order to have a tool for the quantitative evaluation of differences in coloration for nanomers containing particles from different synthesis routes, the yellowness index G according to DIN 6167 with samples having a thickness of 1.3 mm was used. Monoliths showing opacity, coming from insufficient dispersion of the particles, were examined visually since an accurate measurement of the yellowness index was impossible.

Incorporation of particles from all syntheses in matrix (A) at 5 wt. % tantalum oxide led to yellow nanomers ( $G > 5$ ) except for two cases, where a reduced coloration was detectable: A synthesis based on ethanol as solvent and HCl as stabilising agent ( $G = 2.3$ ) and a butanol based synthesis also with HCl as stabiliser ( $G = 2.9$ ).

At 5 wt. % particle loading in matrix (B) only the incorporation of particles from the butanol based synthesis led to nearly colourless nanomers. But the incorporation of higher amounts of tantalum oxide led to a yellowing again for every particle/matrix combination. Since the dispersion of the particles without additional coating is poor in matrix (B), the synthesised monoliths showed strong light scattering, avoiding the exact measurement of the yellowness indices.

A suppression of the coloration, accompanied by prevention of scattering (agglomeration), was attained by employing a coating with MPTS to the particles. Even a particle loading of 15 wt. % of MPTS-coated tantalum oxide from the butanol based synthesis in matrix (B) led to a yellowness index of 1.46. This value is comparable to a G value of 0.55 for CR39 (Poly-diethyleneglycol-(bisallylcarbonat)), a commercially available eye-glass polymer which is described as colourless by the manufacturer. It is remarkable, that the change of the modifying agent from MPTS to DPDMS, employed in the same molar amount, resulted in an increased yellowness of the nanomers as well as in an increased agglomeration tendency of the nanoparticles (monoliths were slightly opaque).

The conclusions that can be drawn from these measurements is that the choice of the solvent during particle synthesis has a strong influence on the coloration of the nanomers synthesised. At particle loadings greater than 5 wt. % a surface modification is necessary in order to avoid yellowing. The employed silanes (MPTS or DPDMS) for the modification are reacting with the OH-groups of the particle surface, giving an (organically modified) silica layer. The decreased yellowness index of the nanomers when employing coated tantalum oxide particles should be in relation with a reduced particle-matrix interaction, avoiding direct contact of organic material with the particles. The choice of the surface modifier also affects the coloration, as can be seen in the case of nanomers containing MPTS and DPDMS modified particles from the butanol based synthesis in matrix (B). The lower coating efficiency of the DPDMS, when compared with the MPTS is indicated by higher values for the yellowness index and reduced agglomeration stability of the particles. This may be caused by the difference in molecular dimensions of the silanes. DPDMS is sterically more hindered due to the two phenyl groups per silane molecule, resulting in a coating with higher porosity. Moreover DPDMS may react slower with the particle surface in a hydrolysis and condensation reaction as MPTS, leaving areas of the particle surfaces unmodified. However, further investigations have to be carried out in order to obtain a more detailed view on the involved mechanisms.

As another result of the coloration measurements only particles from the butanol based synthesis were used for further investigations and the coating of the particles, when applied, was done with MPTS.

The crucial parameter for the synthesis of transparent nanomers is the dispersion of the particles within the matrix; particle agglomeration leads to opacity of the nanomer and must therefore be avoided. Agglomeration can be caused by a non-matching of the chemical groups on the particle surface with the intrinsic chemical groups in the matrix material. As an example, hydrophilic particles will agglomerate in a hydrophobic matrix, similar to an emulsion. Incorporation of particles from the butanol based synthesis in matrix (A) led to only slight opacity, whereas the incorporation of particles from the same synthesis in matrix (B) led to severe opacity which may be explained as follows: Sol - gel derived tantalum oxide is always associated to water in the form  $Ta_2O_5 \cdot n H_2O$ <sup>21</sup> and the tendency to phase separation between the hydrophilic particles and the matrix will increase with increasing hydrophobicity of the matrix. Due to the reduced content of hydrophilic groups in matrix (B), when compared with matrix (A), the mismatch in hydrophilic-hydrophobic balance between particles and matrix is also increased when employing matrix (B), leading to a difference in dispersion behaviour of nanoscaled tantalum oxide. A surface modification of the particles with MPTS from the butanol based synthesis however led to transparent nanomers exhibiting no opacity. Unlike to these results the employment of DPDMS as coating agent is unsatisfactory, probably due to the same reasons already discussed for the differences in the coloration behaviour.

### 3.2. Small angle x-ray scattering on tantalum oxide nanocomposite

Deducing from the high transparency of the nanomers containing MPTS-surface modified tantalum oxide in matrix (B), it can be concluded that the surface modification leads to a better dispersion of the particles. In order to confirm this assumption, small angle X - ray scattering was conducted on a nanomer system with 15 wt. % tantalum oxide particles (MPTS modified) from the butanol based synthesis dispersed in matrix (B). Moreover SAXS measurements can be used to acquire information about the particle size in the composite and therefore about the hydrolytic stability of the particles during the nanomer synthesis. It is important to verify that the transparency of the nanomers containing surface modified tantalum oxide is not caused by a disintegration of the tantalum oxide particles during the nanomer synthesis down to a molecular scale. The system described here can be investigated very well by SAXS measurements because of the great difference in the scattering power between carbon and silicon on the one hand and tantalum on the other hand. In addition, SAXS measurements allow a representative volume of the sample to be analysed, giving an increased certainty as compared to electron microscopic methods. As a reference, a measurement was carried out on the same matrix material without incorporated tantalum oxide, in order to correct the intensity for the background scattering of the matrix. The plot of the intensity,  $I$ , vs scattering vector  $q$  of the tantalum oxide nanocomposite is shown in fig. 1.

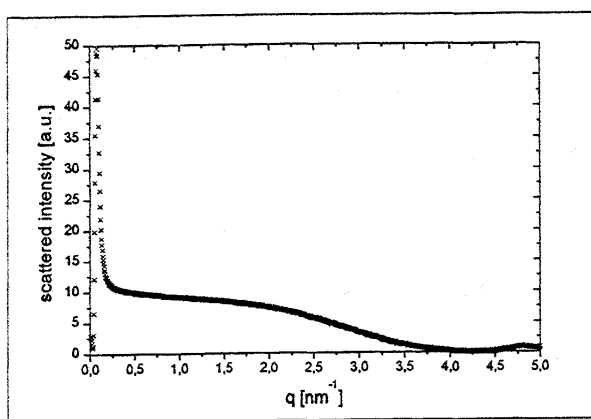


Figure 1: scattered intensity vs. scattering vector  $q$  for a nanomer containing 15 wt. % tantalum oxide (MPTS modified) from butanol based synthesis in matrix (B). Scattering intensity is corrected for the background scattering of the matrix.

A broad shoulder is present around  $q = 2 \text{ nm}^{-1}$ , which can be assigned to a particle distance distribution with a maximum at 3 nm. The high scattering intensity at  $q$  values smaller than  $0.25$  indicates the occurrence of agglomerates. Since no significant transparency losses are observable by UV-VIS spectroscopy, the agglomerates have a small size or occur in minor accounts. For  $q$  values higher than  $3.0$  the scattered intensity is decreasing, being zero at  $4 \text{ nm}^{-1}$ . Using the relation  $r(\text{radius}) \equiv \pi / q$  it can be concluded that no particles of a size smaller than about 3 nm are present. A Guinier - plot  $\ln(I)$  vs  $q^2$  was calculated from the slope of the graph between  $q = 0.03 \text{ nm}^{-1}$  and  $q = 0.09 \text{ nm}^{-1}$  in order to calculate the radii of the tantalum oxide nanoparticles: The result is shown in fig. 2.

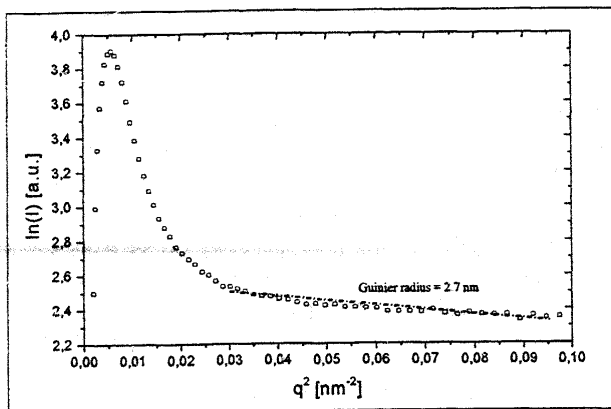


Figure 2 : determination of the tantalum oxide particle size from an  $\ln(I)$  vs.  $q^2$  - plot for a nanomer containing 15 wt. % tantalum oxide (MPTS modified) from butanol based synthesis in matrix (B).

From the linear region in the  $\ln(I)$  vs.  $q^2$  - plot a particle size of 5.4 nm (Guinier radius = 2.7 nm  $\pm$  0.5 nm) could be calculated. In the same way a Guinier radius of 17.5 nm was calculated for the agglomerates mentioned above. PCS measurements carried out on sols aged for 24 hours gave a medium particle size of 4 nm. The difference to the particle size calculated by SAXS measurements may be due to the surface modification process of the particles. The conclusion which can be drawn from the SAXS measurements is that the surface modification leads to a good dispersion of the tantalum oxide particles in the matrix as can be seen by the occurrence of a shoulder at about  $2 \text{ nm}^{-1}$  in the  $I$  vs.  $q$  plot, indicating a distribution of particle distances with an average value of 3 nm.

### 3.3. Refractive index and Abbe number of the nanomers

Refractive index and Abbe number are essential parameters for materials used in optical applications, since they determine the dimensions of optical elements. In waveguide applications for example the difference between the refractive index of the waveguide and the surrounding material has to be at least 0.1 in order to fulfil the requirement of total reflection of the light beam on the waveguide walls. In order to determine the influence of the tantalum oxide content on the refractive index and the Abbe number of the nanomers, tantalum oxide particles from the butanol based synthesis already described above were incorporated in matrix (A) without further surface modification, which was not applied on the particles since the amount of silane needed for the surface modification would exceed the overall amount of silane in the composition of the matrix for particle loadings greater than 30 wt. %. The results are shown in fig. 3.

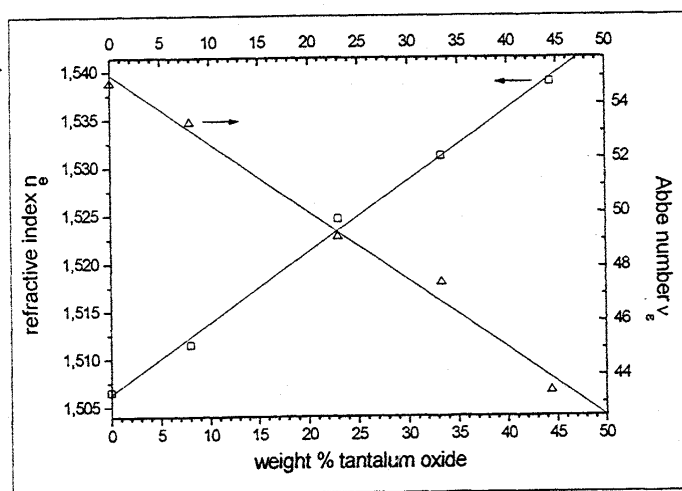


Figure 3: refractive index and Abbe number of nanomers containing particles from the butanol based synthesis without surface modification in matrix (A).

There is a linear relationship between the particle loading and the refractive index as well as with the Abbe number of the nanomers. From the diagram an increase in refractive index of  $7.4 \times 10^{-4}$  per wt. % tantalum oxide was calculated. At tantalum oxide contents higher than 10 wt. % a yellowing of the nanomers could be observed, which may be due to the lack of surface modification of the particles. All nanomers containing tantalum oxide without a surface modification in matrix (A) are slightly opaque, a fact which was attributed to particle agglomeration.

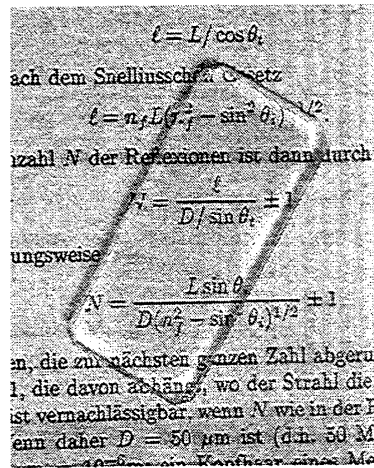
### 3.4. Optical losses of the nanomers

Optical losses in the visible wavelength regime or at fixed wavelengths due to absorption and/or light scattering should be as low as possible in order not to restrict the field of application for the nanomers. Especially for waveguide applications optical losses have to be avoided. Bulks from nanomers containing MPTS modified particles from the butanol based synthesis in matrix (B) were investigated by UV-VIS spectroscopy in order to calculate the optical losses at a wavelength of 850 nm, a common wavelength for waveguide applications (table 1). The losses were calculated taking into account the thickness of the nanomer (1.3 mm) and the reflectance (using the Fresnel equation<sup>22</sup>) at this wavelength. The calculation of losses makes it easier to compare the transparency of a nanomer with the transparency of materials described in literature.

**Table 1: Optical losses of nanomers dependent on the tantalum oxide content for MPTS surface modified particles from the butanol based synthesis in matrix (B) at a wavelength of 850 nm.**

wt. % tantalum oxide	optical loss in dB / cm
0	<0.1
15	0.1
30	0.4

Low values are obtained for the optical losses compared to composite materials presented by other authors (< 0.25 dB/cm in<sup>7</sup>, 1.4 dB/cm in<sup>8</sup>). These results are in correspondence with the results from PCS and SAXS measurements revealing particle diameters for the tantalum oxide in the range of 5 nm, thereby minimising transparency losses caused by light scattering. A photograph of a transparent nanomer containing 15 wt. % MPTS modified tantalum oxide particles from the butanol based synthesis in matrix (B), having a thickness of 5 mm, is presented in fig. 4.



**Figure 4: photograph of a nanomer (thickness 5 mm) containing 15 wt. % tantalum oxide (MPTS - modified) from the butanol based synthesis in matrix (B).**

### 3.5. Volume shrinkage at polymerisation

In the course of free radical polymerisation reaction of double bonds a volume reduction occurs due to a decreased distance of the resulting C-C-single bond when compared with the initial van-der-Waals distance of two distinct monomer molecules. Since the shrinkage may cause stress or cracks in the material or separation of components in systems such as channel waveguides, it is desirable to minimise the shrinkage. The nanomers offer the possibility of reducing the polymerisation shrinkage due to the presence of non-polymerisable ceramic particles. The volume shrinkage during polymerisation was calculated from the specific gravities of the liquid mixtures and the corresponding nanomers. These investigations were conducted with MPTS modified tantalum oxide particles from the butanol based synthesis dispersed in different amounts in matrix (B) as is shown in fig. 5.

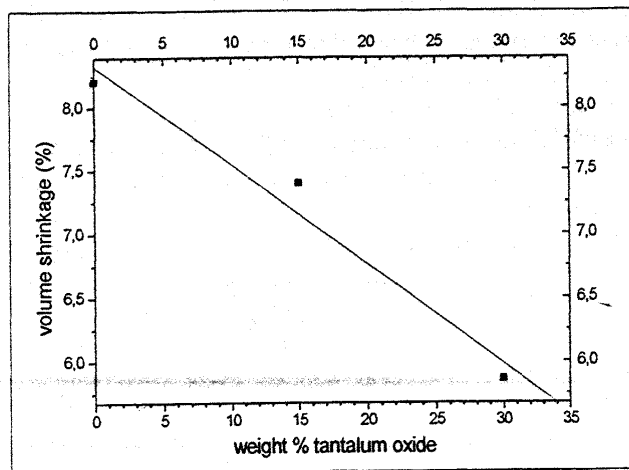


Figure 5: relationship between volume shrinkage and tantalum oxide particle loading of a nanomer consisting of particles from butanol - based synthesis incorporated in matrix (B).

Compared to the majority of pure organic monomers, exhibiting a shrinkage of  $\geq 10\%$ , the values obtained for the nanomers are significantly lower. Even the matrix material itself has a shrinkage of only 8.5%, caused by the inorganic network built up by the employed silanes, reducing the molar amount of double bonds. This enables to produce relatively stress-free monoliths with low birefringence.

#### 4. SUMMARY

Tantalum oxide synthesis was carried out by variation of the solvent and the stabilising agent. By the incorporation of tantalum oxide particles from these syntheses in two different types of organic - inorganic matrices it was found that the coloration of the nanomers is not only dependent on the sol synthesis parameters (such as the employed solvent or stabiliser) but on the surface modification as well. Moreover, the surface modification improves the dispersion of the particles in the matrix, as was shown by SAXS measurement. The refractive index was tailorable by the tantalum oxide content, an important feature for employing these nanomers as materials in optics. In addition an excellent transparency and the absence of light scattering of the nanomers up to high tantalum oxide contents, verifying the small tantalum particle size (particle diameter in the range of 5 nm), emphasises the potential for optical applications. With respect to the low volume shrinkage of the presented nanomers the production of stressfree and crackfree bulk materials is easily achievable.

#### 5. CONCLUSIONS

A new material for optical applications is presented, using simple fabrication techniques, known from the polymer production. Tailorable optical properties like refractive index or Abbe number by achieving high transparency are attractive features of tantalum oxide nanomers. The possibility of using these nanomers as a substitute for organic polymers in optical applications such as waveguide materials is clearly visible.

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