Synthesis and Properties of Transparent ZrO_2 Containing SiO_2 Polymethacrylate Polymers

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Abstract

The synthesis of zirconia modified polymerized methacryloxypropylsilane as a new material with a potential for optical application has been investigated. The material is synthesized by copolymerizing 3-methacryloxypropyl trimethoxysilane and zirconium propylate chelated by methacrylic acid. The methacrylic acid serves as a complexing agent and participates in the polymerization process in order to incorporate the zirconia homogeneously into the polymer. Transparent bulk materials have been prepared by this process.

1. Introduction

The properties of ORMOCERs prepared by the sol-gel process[1] can be varied in a wide range by composition and processing conditions. Materials with a high refractive index thereby generally require the incorporation of inorganic components like ZrO_2 or TiO_2 as inorganic network formers[2]. But due to the high reactivity of zirconium- and titanium alkoxides, the addition of water for hydrolysis must be carried out very carefully. In order to improve the processing properties of these metalalkoxides chemical modification with ß-dicarbonyl compounds or carboxylic acids is often used[3]. In general, complexing ligands can be used to control hydrolysis and condensation[3,4]; but this does not necessarily lead to a molecular distribution of the metal oxide within the polymeric matrix, as to be concluded from[4]. For the molecular scale fixation of metal oxides within the matrix the use of polymerisable complex formers seems to be a suitable route as shown in[5]. In this case, ß-diketonates with polymerisable ligands were used. For $Zr(OPr^n)_4$, the complexation with methacrylic acid was investigated. Mechanical properties of ZrO_2 containing polymers have been reported[6,7]. In this paper, the preparation of bulk materials with respect to optical applications is investigated. Therefore, a three component system prepared from $Zr(OPr^n)_4$, methacrylic acid, and 3-methacryloxypropyl trimethoxysilane was investigated. Therefore a synthesis route in order to achieve homogeneous monoliths had to be developed. Therefore, hydrolysis and condensation of the silane as well as of the complexed zirconia precursor was investigated, too.

2. Experimental

Hydrolysis of 3-methacryloxypropyl trimethoxysilane was investigated
with 0.15 - 0.3 mole H_2O/mole silane. Thereby a pH of 5.5 was adjusted
by bubbling through the reaction mixture CO_2. Due to the immiscibility
with water, the mixture is diphasic and was stirred for 16 hrs in order
to obtain a homogeneous solution. The residual water content after this
time was determined by Karl Fischer titration. For the preparation of
a ZrO_2 containing polymethacryloxypropyl siloxane, one mole of the si-
lane was prehydrolysed with 1.5 mole water as described before. The
prehydrolysed clear solution was cooled down with an ice bath to 0°C
and 0.2 mole zirconium propoxide and 0.2 mole methacrylic acid were
added. After 30 minutes, additional 0.4 mole water was added. For poly-
merization a photoinitiator (IRGACURE 164, Ciba Geigy company 5 wt.%)
was added and methanol and propanol were removed by vacuum treatment.
The remaining highly viscous liquid was poured into plastic tubes (4 mm
in diameter, 50 mm in length) and exposed to UV irradiation for 3
minutes.

3. Results and Discussion

3.1 Reactions of 3-methacryloxypropyl Trimethoxysilane (MPT)

The investigation of the hydrolysis reaction of MPT was carried out
since previous experiments had shown a strong dependance of the drying
behavior of the UV cured rods on the amount of the water addition to
the silane. CO_2 was used as a slightly acid catalyst because it can be
easily removed from the reaction mixture. Independent of the added
amount of H_2O, the concentration of the residual H_2O remained constant
after 16 hrs. In Fig. 1 the concentration of the residual water in the
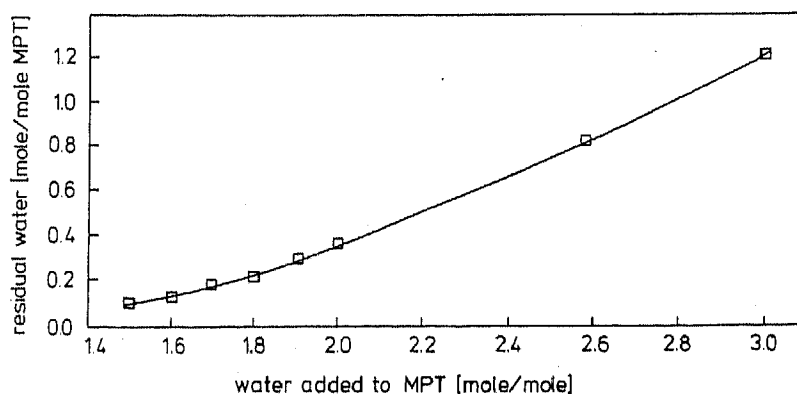reaction mixture is shown as a function of the added water.

Figure 1: Residual water content as a function of water added to MPT
after a reaction time of 16 hrs; pH: 5.5

As one can clearly see, only with initial concentrations of <1.5 mole

H_2O the H_2O content of the reaction mixture becomes very low ($\leq$ 0.1 mole). The following UV curing experiments showed that only with low H_2O contents monoliths could be obtained. For the monoliths preparation, 1.5 mole H_2O were chosen as standard preparation conditions.

3.2 Complex Formation

The formation of the $Zr(OR)_4$ methacrylic acid complex is described elsewhere[7].

$$Zr(OPr^n)_4 + CH_2{=}C(CH_3)COOH \longrightarrow Zr(OPr^n)_3(OOC(CH_3)C{=}CH_2 + Pr^nOH \tag{1}$$
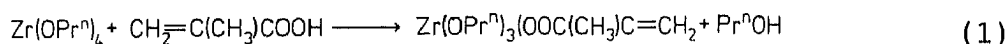
As shown by IR spectroscopy, a bidental chelate complex is formed by substituting one OR group of $Zr(OR)_4$. The reaction of this complex with various concentrations of H_2O was investigated by Karl Fischer titration. The results show that only 1.5 mole H_2O per mole complex are consumed and a stable sol with very fine particle sizes (3-10 nm, determined by dynamic light scattering) is obtained. From this sol, a crystalline material can be received by evaporating the solvents. The crystallized phase can be redissolved in ethanol and purified by this method: the slightly yellow colour, as a result of the complex formation, disappears. The redissolved complex can be used for monolith preparation as an alternative way.

3.3 Preparation of Monoliths

Monoliths were prepared from a solvent-free sol of prehydrolysed 3-methacryloxypropyl trimethoxysilane and the modified zirconium propoxide. Solidification takes place by copolymerization of the methacrylate groups as well as by condensation of hydroxyl and alkoxyl groups. Therefore the formation of an inorganic/organic network as shown in Fig. 2 can be assumed.
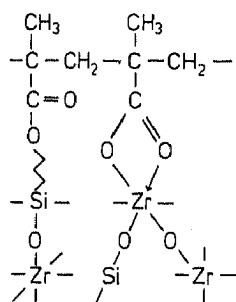

Figure 2: Network model of the transparent monoliths

The polymerisation step was followed by IR spectroscopy. The IR

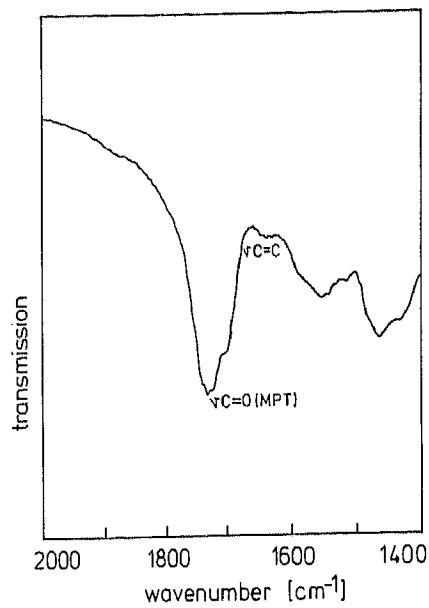spectroscopy of a polymerised sample is shown in Fig. 3.

Figure 3: IR-spectrum of the polymerised monolith

As one can see, the C=C double bond at 1640 cm^{-1} has almost disappeared showing a high polymerization yield. The effect of excess water in the reaction mixture leads, as already indicated, to a disaggregation of the rod. There is no clear explanation for this effect, but one reason might be that condensation is leading to a brittle material before polymerisation takes place; enhanced polymerisation then can cause internal stresses finally leading to cracking.

The results show that due to the chemical modification, the zirconia can be incorporated into the inorganic/organic network on a very small scale. Therefore a homogeneous distribution of the zirconium compound can be assumed which was proved by TEM micrographs (Fig. 4). Upto a magnification of 10^6 no phase separation could be detected. The dash spots do not indicate phase separation but are caused by elementary carbon from the sample preparation.
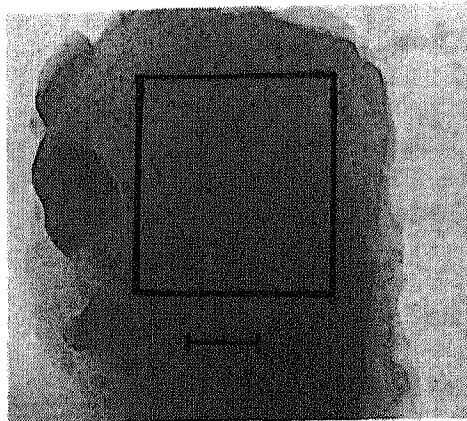

Figure 4: TEM micrograph of a monolith; the bar refers to 80 nm; the square indicates an area with only a few carbon spots.

Monoliths, 4 mm in diameter and 50 mm in lenght, exhibit an average fracture strength of 79 MPa, which is surprisingly high. The optical transparency of the material was measured by UV/VIS-spectroscopy (Fig. 5).
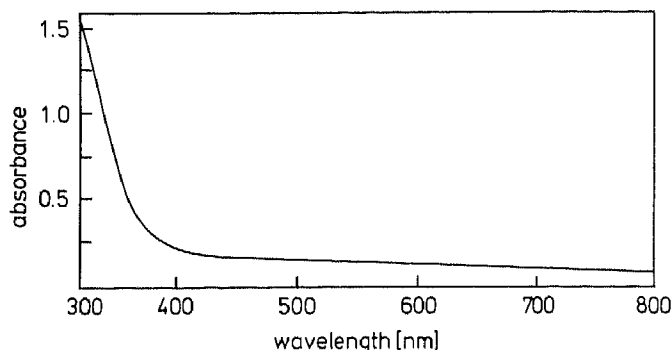

Figure 5: UV/VIS-spectrum of a monolith

Due to the pale yellow colour of the material, the absorption increases below 350 nm. This result can be attributed to impurities, e.g. of transition metal complexes with higher extinction coefficiency (Fe^{3+}), because the zirconium alkoxide was stored in iron containers and used without further purification. As already shown, the colour can be removed by purifying the zirconium complex.

A value of 1.51 was determined for the refractive index. This result might be due to the low zirconia content of only 17 mole%. Therefore, further experiments have to be carried out in order to increase the zirconia content as well as the refractive index. The high mechanical strength combined with the good optical transparency of this type of material show an interesting potential for optical applications, especially because further optimization and variations of composition are possible in a wide range.

4. Acknowledgement

5. References

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