Kinetic investigations on TiO$_2$ nanoparticles as photo initiators for UV-polymerization in acrylic matrices

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Abstract

TiO$_2$ nanoparticles of anatase, useful as photosensitive initiators to induce free radical polymerization in acrylic monomers have been prepared by chemical synthesis. Appropriate surface modification of TiO$_2$ has been achieved in order to compatibilize the particles with the acrylic monomers to obtain an almost homogeneous distribution down to the primary particle size. The surface modification has been additionally fine tuned in such a way, that an efficient transfer of the electrons generated on TiO$_2$ during UV-exposure could be achieved towards the monomer mixture in order to start the polymerization reaction. The formation of the anatase modification could be confirmed by XRD. Particle sizes were determined by UPA, which showed a distribution between 1-10 nm depending on the preparation method used. Transmission electron microscopy carried out with the UV-polymerized coating layers proved the homogeneous distribution of the anatase nanoparticles. Kinetic investigations on the photo-polymerization behavior have been accomplished by photo-DSC and Raman spectroscopy. Curing time was determined in dependence of the materials composition.

Introduction

Two effects of TiO$_2$ are commonly known; first the high refracting index and the associated effect of light scattering [1] and second the degradation effect on polymer matrices [2; 3].

Besides the two mentioned effects of TiO$_2$ in polymer mixtures a third effect can be taken into account. Several authors describe the possibility that TiO$_2$ may catalyze the photo polymerization of acrylic monomers. But they come to different results concerning the accelerating or non-accelerating properties of TiO$_2$ for the polymerization process of acrylate monomers. Damm et al. describe acrylate polymerization with pure TiO$_2$ [4]. Samples of TiO$_2$ having different BET surface areas and different numbers of primary crystallites per secondary particle were prepared by annealing amorphous TiO$_2$ at different temperatures. Amorphous TiO$_2$ was not able to initiate the polymerization of the trisacrylate used. The maximum polymerization rate as well as the monomer conversion after an illumination time of 120 s increased with increasing number of primary crystallites per agglomerate. Damm et al. as well applied doped TiO$_2$ [5; 6]. The polymerization rate slightly increased with increasing Fe^{3+} content of the TiO$_2$ in the concentration range from 0.1 to 1 mol % Fe^{3+}. Maximum polymerization rate was observed for 1 mol % Fe^{3+} followed by decreasing rates at even higher Fe^{3+} contents. A TiO$_2$ sample containing 10 mol% Fe^{3+} did not show any photocatalytic activity [5]. Also nitrogen and carbon doped titania powders initiated acrylate polymerization upon UV excitation. The polymerization rate constants were similar for titania or N-doped titania but about two times larger for the

C-doped materials [6]. Ni et al. pointed out the pH-dependence of the photo catalytic effect of TiO_2 [7]. The results from ESR spin-trapping analysis at various pH conditions suggested that trapping holes by OH^- act as competitive ways towards OH radicals. With the aid of these results, pH-dependence of the initiation quantum efficiency was correlated to the influence of pH on the initiating species. Assuming that the photogenerated holes have higher initiation efficiency than OH radicals, the observed pH dependence of polymerization rate was reasonably interpreted. Li et al. examined different monomers with TiO_2 and found accelerating and decelerating properties depending on the used monomers [8]. TiO_2 nanoparticles were first milled into butyl acetate or trimethylolpropane triacrylate (TMPTA) to obtain TSB (Nano TiO_2-slurry in butyl-acetate) and TST (Nano TiO_2-slurry in trimethylolpropanetriacrylate) slurries, then embedded into epoxy acrylate to obtain UV-curable coatings. It was found that TST-based coatings had a decreasing but TSB-based coatings had an increasing UV curing rate in comparison to the pristine epoxy acrylate. They also made kinetic investigations using IR-spectroscopy [9]. Here epoxy acrylate/TiO_2 nanocomposites showed decreasing photopolymerization rates in comparison with pure epoxy acrylate. The photopolymerization rate of the nanocomposite could also be influenced by initiator types, oxygen content, film thickness, irradiation intensity, dispersing media of TiO_2 slurry, and of course by the properties of the used monomers.

Semiconducting TiO_2 is a potential candidate for the UV-curing of monomers [10; 11; 12], as it is well known that by UV-excitation a valence hole and a conduction electron can be created in the solid. Such a transition only takes place if the energy of the irradiated wavelength is equal or higher than the band gap of the used photo catalyst. TiO_2, in its modification anatase, has a band gap of 3.289 e V. With respect to nanoparticles acting as polymerization initiators there is already a patent which describes this feature for the thermal and/or photochemical polymerization of species which have at least one polymerisable carbon-carbon multiple bond and/or at least one ring which contains carbon and which is accessible to ring-opening polymerization [13].

In the present investigation it was of interest to use the anatase modification because of its better performance in quantum efficiency and stabilization of charge carriers [14]. In addition a particle size range of about 10 nm has been chosen for the investigations. In this size range for TiO_2 a quantum size effect leading to a blue shift of absorption is expected [15].

The special advantage of using a solid state catalyst for UV-polymerization is that the catalytic function of the particles is sustained when particular conditions are fulfilled. It has to be assured that redox reactions $Ti^{4+} \rightarrow Ti^{3+} \rightarrow Ti^{4+}$ are possible. In contrast to this organic molecular initiators are destroyed during the UV irradiation to form radicals

that initiate the polymerization process. Molecular fragments are able to migrate through the polymer matrix which might lead to some contamination problems e. g. if the food package sector is focused. Nanoparticles are assumed to be linked to the polymer matrix thus avoiding migration problems.

Results and discussion

For the basic investigations of free radical photo-polymerization behavior of reactive monomer mixtures in presence of inorganic nanoparticulate photo-initiators a combination of acrylate monomers and titania nanoparticles in the anatase modification have been chosen. Acrylates offer the possibility to provide a wide variability of different monomers having different polarity and polymerization speed which might be important to select a suitable test system. Anatase type titania has been preferred because sufficient quantum yield could be expected. Before starting the formation of nano-dispersions consisting of liquid acrylates and titania nanoparticles, suitable and reproducible synthesis conditions have been worked out concerning the fabrication of anatase nanoparticles with controlled particle size in the lower nano-size range and appropriate surface modification providing compatibility to the acrylate matrix selected.

Ex situ synthesized TiO_2-nanoparticles coated with 1-propanol crystallize in the favored anatase modification (Figure 1).

The diffraction pattern proves the formation of the anatase modification of
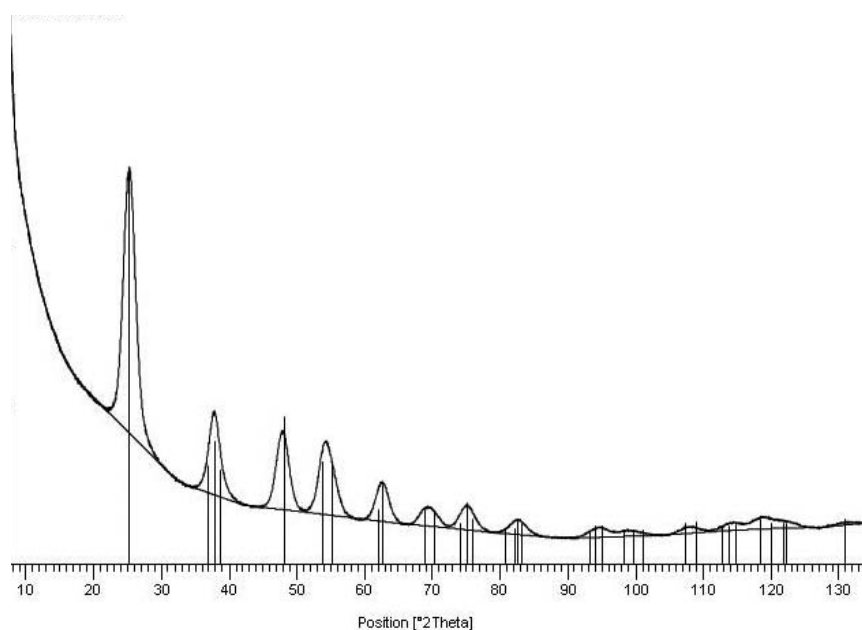

Figure 1: XRD-spectrum of TiO_2-nano-particles coated with 1-propanol (= TiO_2-1P); vertical lines show the theoretically calculated intensities of the anatase modification. The calculated particle size from the halfwidth of the signals was 4.9 nm.

titania. Particle size was calculated by the Debye-Scherrer equation to be about 5 nm. This should correspond to the primary particle size.

The particle size of TiO_2-1P particles was also investigated by TEM (s. Figure 2) and dynamic light scattering measurements (s. Figure 3) in order to compare it with the particle size from XRD. TEM gave similar values of 5 nm, corresponding to the primary particle size calculated from XRD. In the TEM also agglomerates of about 8 nm can be observed. UPA gave values between about 6 to 11 nm. The slightly higher value of UPA is caused by the different measuring methods. TEM and XRD usually show a number average of the particle size radius whereas UPA results correspond more to

a volume average because the first measure is the coefficient of diffusion which is calculated according to Stokes' equation which contains the hydrodynamic radius (Stokes radius) that includes the solvent-covering of the particles. The particle size d_{10} means that 10 % of the volume of all the particles have a size of 5.8(3) nm and less. This value corresponds well to the primary particle size calculated from XRD. The d_{90}-value shows that 90 % of the volume consist of very small agglomerates having a size of about 10.8 nm.

Kinetic investigations were done by photo-DSC measurements in combination with IR- and Raman-spectroscopy. In order to obtain comparable results all UV-curings were done with the Hg-Xe-lamp of the photo-DSC device. It provides an UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample. Photo-DSC data obtained during UV-curing of DTMPTA (di(trimethylolpropane) tetraacrylate) with different amounts of TiO_2-1P are shown in Figure 4.
DTMPTA without any nanoparticles (full line) already shows a curing behavior. The maximum conversion takes place 80 s after the start of UV-irradiation, but even after 1200 s there is still a remaining heat flow indicating a slow reaction. DTMPTA with 1 % of TiO_2-1P (dashed line) shows a faster reaction time. The maximum of conversion appears 23 s after the irradiation starts and the total conversion is finished after about 300 s which is indicated by the horizontal baseline. With 2.5 % of TiO_2-1P (dotted line) the main conversion time after 23 s is still observed but a second heat flow peak appears after about 200 s, pointing to a second reaction. Also the reaction is finished after about 300 s. In the case of 5.0 % TiO_2-1P (dash-dotted line) no reaction at all is observed, indicating that the UV absorbents properties of the titania become dominant over the electron transfer which could start polymerization.

For the investigation of the double-bonding conversion Raman-spectroscopy has been applied. The C=C double bond conversation is followed in spectra normalized on the C=O carbonyl signal as internal standard in acrylate systems.
Figure 5 shows Raman spectra of DTMPTA with 0 and 5 % TiO_2-1P uncured and DTMPTA with 5 % TiO_2-1P after curing in the photo-DSC-device. The spectra are scaled on the C=O band at 1723 cm^{-1}, which is not changing during polymerization reaction.
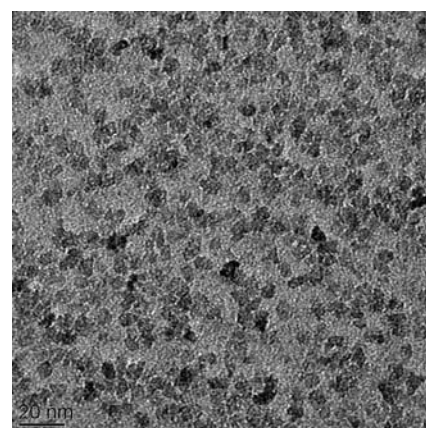

Figure 2: TEM-micrograph of TiO_2-nano-particles coated with 1-propanol (= TiO_2-1P); measured average particle size = 4-8 nm.
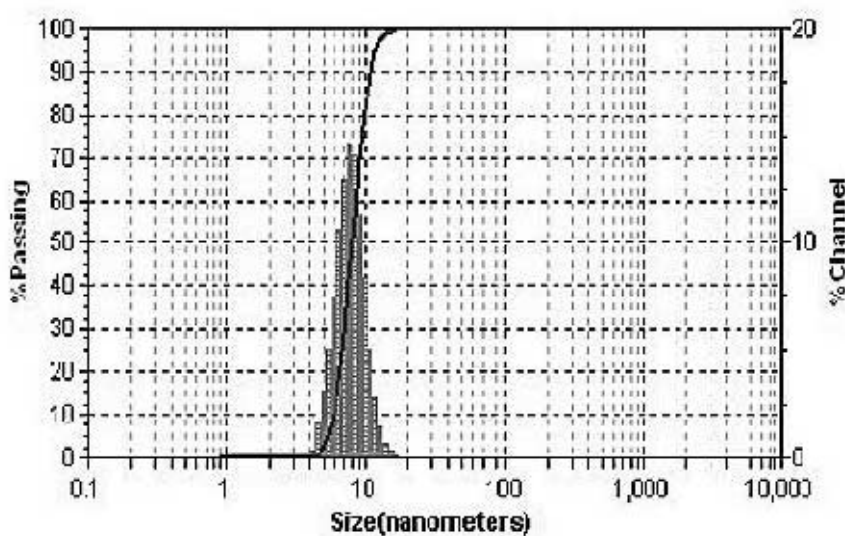

Figure 3: UPA-measurement of TiO_2-nano-particles coated with 1-propanole (= TiO_2-1P) in toluene; volume distribution; loading index 0.048; d_{10} = 5.84 nm; d_{50} = 8.00 nm; d_{90} = 10.80 nm; M_{Volume} = 8.21 nm; $M_{Nummber}$ = 6.96 nm; $M_{Average}$ = 7.76 nm.

14

In the spectra there are three different vibrational absorptions proving a bidental chelating TiO_2-COO complex: 1600 cm^{-1}, 1499 cm^{-1} and 1161 cm^{-1}. They only occur in samples with TiO_2-1P being present, no matter whether the samples are cured or not. The diagram also shows that C=C double-bondings decrease whereas CH_2 bondings are formed. This is a hint proposing a polymerization process.

To take a closer look to the polymerization process, mixtures of DTMPTA with various amounts of TiO_2-1P have been compared. In Figure 6 the Raman spectra clearly show that there is a dependence between the amount of TiO_2-nanoparticles and the conversion rate of the C=C double bonds of acrylate DTMPTA.

Increasing TiO_2-1P content in the mixture leads to a decrease of C=C double bonds. Combining the results of DSC-measurement and Raman-spectroscopy a complex relationship has to be taken into account. Obviously, the total reaction conversion passes through a maximum of speed when using 1 % TiO_2-1P in the mixture. Responsible for that could be three different effects: First, TiO_2-nanoparticles catalyze the polymerization of double-bondings like those in acrylates; second, TiO_2 is known to work as a UV-absorber which inhibits photo chemical reactions.

A third reaction possibility is the degradation of the monomer and / or polymer in form of an ester cleavage that had to lead to carbonic acid fragments. These fragments could not be verified, neither by NMR nor by IR. The second effect of
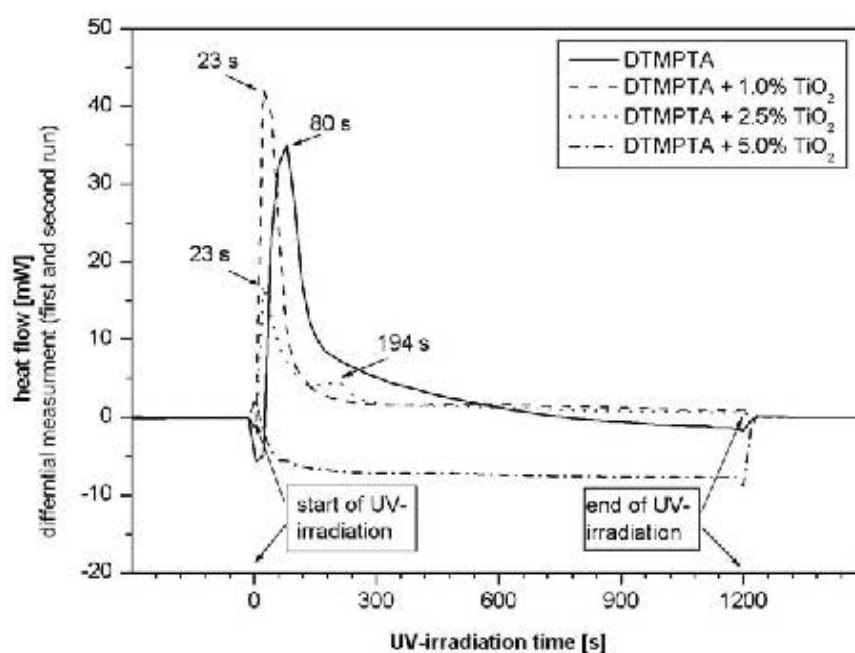

Figure 4: Photo-DSC-measurement of di(trimethylolpropane) tetraacrylate (=DTMPTA) with different amounts (0, 1, 2.5, 5 %) of TiO_2-nano-particles coated with 1-propanole (= TiO_2-1P). Diagram shows spectra after subtraction of the heat flow baseline of the UV-lamp. UV-irradiation initiates 5 min after the start of the run (point 0); it ends 25 min after the start of the run (point 1200) => irradiation time 20 min. Measurement under N_2-flow at a constant temperature of 25 °C. UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample.

inhibiting C=C double bonding conversion may be seen in Figure 6. The first effect of catalyzing the reaction, e. g. to speed up the polymerization process can be pointed out with photo DSC measurement as we see in Figure 4. With 1 % and 2.5 % of TiO_2-1P in DTMPTA the process starts earlier than without a catalyst, but in total the conversion rate decreased as the UV absorbing properties prevailed over the catalytic ones.

All samples showed a change in color during irradiation. The samples switched from transparent yellow (Ti^{4+} from TiO_2-COO complex) to dark blue which is due to the formation of Ti^{3+}. By UV-irradi-

ation an electron–hole–pair formation takes place. The hole can be filled by an electron coming from the acrylate matrix. This transfer produces a Ti^{3+} and an acrylate radical, which now may polymerize. In order to get the catalyst (Ti^{4+}) back, the Ti^{3+} must formally be oxidized either by diffusing oxygen from the top of the surface or by another oxidizing agent. By storing the samples under normal atmosphere, the blue color again turned transparent, which supports the idea of reversible change between Ti^{4+} and Ti^{3+} and of oxygen-diffusion. If the amount of TiO_2-1P rises to an amount of 5 % in the mixture the color turned to a very dark blue but the complete polymerization process is hindered by absorption due to the general UV-protecting properties of TiO_2.

For this reason the finding that the mechanism of photo-catalytic polymerization only works satisfactorily in thin layers could be supported, where the oxygen might diffuse through the coating layer or in mixtures with a low amount of particles where enough UV-light might be transmitted through the monomer matrix. Curing of acrylate mixtures containing more than 2.5 % TiO_2 might be possible by using a UV source with higher radiation output.
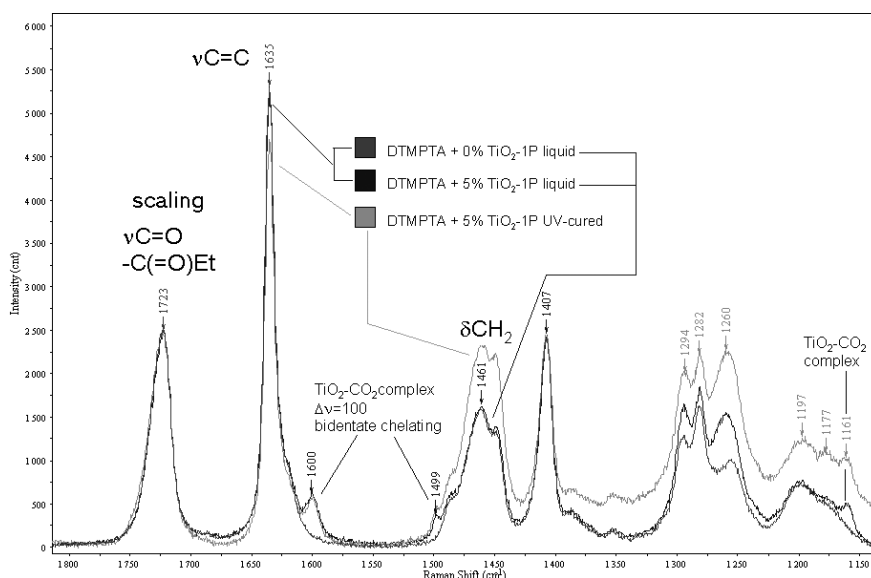

Figure 5: Raman-spectra of di(trimethylolpropane) tetraacrylate (=DTMPTA) with different amounts of TiO_2-nanoparticles coated with 1-propanole (= TiO_2-1P) (0 %, 5 %) before and after UV-curing. The spectra are normalized on the C=O band at 1723 cm⁻¹. UV-source for curing: Hg-Xe-lamp LC 5 L8222-01 without filter from DSC-device. UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample. Curing time : 20 min.
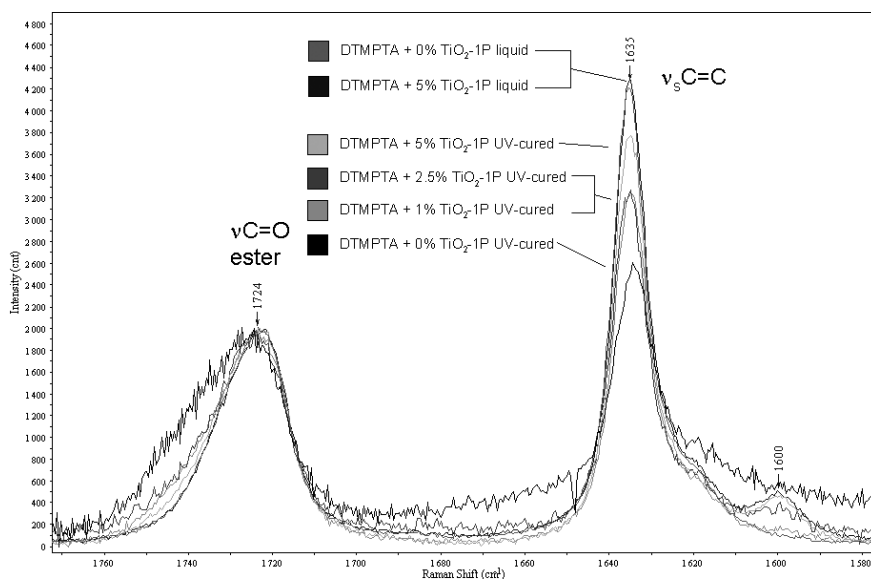

Figure 6: Raman spectra of di(trimethylolpropane) tetraacrylate (= DTMPTA) with various amounts of TiO_2-nanoparticles coated with 1-propanole (= TiO_2-1P) (0, 1, 2.5 and 5 %) before curing (liquid) and after UV-curing in the photo-DSC device. UV-source for curing: Hg-Xe-lamp LC 5 L8222-01 without filter from DSC-device. UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample. Curing time : 20 min.

Conclusion

TiO$_2$-nanoparticles can be synthesized *ex situ* using common precursors like titanium tetraisopropoxide in the solvent 1-pentanol that simultaneously works as a surface modifier. Homogeneous distribution of the particles in acrylates can be achieved. This leads to particles in the low nano-size range (1-11 nm). Raman measurements showed that TiO$_2$ is linked to the acrylic matrix by complexation of Ti by the carboxylic groups of the acrylates. It can be assumed that there is no unwanted migration process in the final polymer. This statement has to be an object of further investigations.

Looking at the polymerization process different effects during the UV-irradiation of the mixtures of acrylate with TiO$_2$-nano-particles have been observed. It could be shown that three influences may have to be taken into account in order to judge the catalytic performance of TiO$_2$. The accelerating catalytic effect of TiO$_2$-1P is superposed by the UV-absorbing effect of TiO$_2$ that leads to a decrease of the total conversion rate for filler contents higher than 2.5 %. This was shown by comparing measurements in photo-DSC and Raman-spectrometry. In the present case the degradation of monomer and/or polymer, a third possible effect, could be ruled out neither by Raman nor by photo-DSC. The implication of these findings is that TiO$_2$ can only be used in low concentrations and for thin films.

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