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Acylstannanes - A New Generation of Cleavable and Highly Reactive Photoinitiators for Curing at Wavelengths Above 500 nm with Excellent Photobleaching Behavior

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Abstract: Within this work, a novel acylstannane-based photoinitiator (PI) is presented. Tetrakis(2,4,6-trimethylbenzoyl)stannane (1) reveals outstanding properties, compared to state of the art acylgermane-based initiators. Most importantly the initiator shows absorption up to 550 nm, which allows higher penetration depths, especially in highly filled photopolymers. Besides that, 1 shows extremely high photoinitiating activity towards (meth)acrylic double bonds, as well as very fast photobleaching. Furthermore, unlike many organotin compounds, 1 shows surprisingly low cytotoxicity.

Visible light-induced photopolymerization has a wide field of application, such as printing inks and different kinds of coatings. Recently, its scope was further expanded by more advanced techniques like dental curing^[1] or lithography-based ceramic manufacturing.^[2] This evolution was facilitated by the development of highly reactive acylgermane-initiators,^[3] such as bis(4-methoxybenzoyl)diethylgermane (Ivocerin[®], 2). These photoinitiators are used to initiate radical polymerization of a large variety of monomers upon radiation in the visible range with wavelengths up to 490 nm. A working Type I system, which can be cleaved using radiation with wavelengths above 500 nm and in addition to that shows sufficient photobleaching has not been previously reported. To achieve a bathochromic shift of the $n\pi^*$ absorption band and therefore go from classical UV Type I photoinitiators (e.g. hydroxyalkylphenones) to systems working under visible light irradiation, a heteroatom has to be introduced next to the benzoyl chromophore (e.g. acylphosphine oxides,^[4] acylsilanes,^[5] acylgermanes^[3]). The absorption band of the $n\pi^*$



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absorption is shifted to longer wavelengths due to orbital interactions of the empty d orbitals of the heteroatom with the π^* orbital of the carbonyl group.^[6] Within this communication, we report the synthesis of tetrakis(2,4,6-trimethylbenzoyl)stannane (1) and more importantly we demonstrate its suitability as photoinitiating species in visible light free radical polymerization, which is in line with a recent patent publication.^[7] We show, that 1 could be the first of a new, promising generation of photoinitiators.

The new photoinitiator **1** was synthesized based on procedures known from the analogue Si- and Ge-compounds (Scheme 1).^[5, 8] Using the method of Marschner,^[8b] tris(trimethylsilyl)stannyl potassium could be obtained reacting tetrakis(trimethylsilyl)stannane with potassium *tert*. butoxide. The potassium species was then further reacted with 4 eq. of 2,4,6-trimethylbenzoyl fluoride to achieve the desired product **1** in high purity (58% yield).



Scheme 1. Synthesis of tetrakis(2,4,6-trimethylbenzoyl)stannane (1)

Tetrakis(2,4,6-trimethylbenzoyl)stannane (1) was then investigated regarding to its photochemical properties. For that purpose, the commercial state of the art initiator lvocerin[®] (2), tetrakis(2-methylbenzoyl)germane (3) as well as Irgacure[®] 784^[9] (4) were used as reference compounds for comparison (Scheme 2).



Scheme 2. Reference systems: Ivocerin® (2), tetrakis(2-methylbenzoyl)germane (3) and Irgacure® 784 (4)

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Figure 1. a) UV-VIS spectra for compounds 1, 2, 3 and 4 and b) enlarged tailouts of $n\pi^*$ transition bands

UV-VIS spectroscopy (c = 1 x 10^{-3} mol L⁻¹ of 1, 2, 3 and 4 in acetonitrile) showed, that the $n\pi^*$ absorption band lies within the visible range for all 3 compounds (Figure 1). However, for the tinbased compound 1 the absorption band tails out at particularly high wavelengths. It reaches out to ~550 nm, which is, when compared to 2 (~480 nm) and 3 (~500 nm), a bathochromic shift of at least 50 nm. This is probably caused by the orbital interactions of the Sn d orbitals with the π^* orbitals of the carbonyl group. This specific long wavelength absorption makes 1 unique in terms of classical Type I photoinitiators.

The analysis of the formation of the reactive excited triplet state T^1 for compounds **1**, **2**, **3** and **4** and the calculated UV-VIS spectra are shown below (Figure 2). The calculated spectra (acetonitrile) are in good agreement with the experimental ones, though the appearing bands are slightly shifted to shorter

wavelengths for compounds 1, 2 and 3. After the absorption of photons with a wavelength of 460 nm (2.70 eV), the first excited singlet state S¹ will be populated. The effective population of S¹ should proceed more effectively for PIs 1 and 4 due to larger S^{0} - S^{1} transition energies than for compounds 2 and 3. Furthermore, due to the fact, that the absorption bands of titanocene 4 are considerably red shifted compared to the ones of the other PIs, the population of S¹ is also possible by excitation with 522 nm (2.38 eV). After intersystem crossing (ISC) the triplet state T1* will be formed. This T1* state undergoes further relaxation through adjustment of the molecular structure to the changes of electron distributions upon excitation. The calculations show, that for compounds 1, 2 and 3 the first excited states S¹ and T¹ are formed mostly through excitations of oxygen n electrons into the π^* orbital localized on the carbonyl double bond. These n and π* electrons are oriented perpendicular to each other resulting in the low oscillator strength of the S⁰-S¹ transition. In the case of compound 4 an even lower energy of the S⁰-S¹ transition can be found due to excitation of π electrons from the aromatic ring into the titanium d orbital. In the cases of compounds 2, 3 and 4 the energy of triplet relaxation is sufficient to undergo exergonic bond scission reactions leading to the formation of reactive radicals, which could initiate polymerizations. Moreover, for the new acylstannane 1 the unrelaxed triplet T1* undergoes Sn-C bond scission already during triplet optimization, indicating a very effective formation of reactive species.

For many applications of photopolymerization in the visible range, the final material should not show any coloration after curing. Due to the photocleavage of the Sn-CO bonds,



Figure 2. Calculated UV-VIS spectra and Jablonski energy scheme of the population of the reactive triplet by excitation with 460 nm and 522 nm of (a) acylstannane 1, (b) Ivocerin® 2, (c) tetrakis(2-methylbenzoyl)germane 3 and (d) titanocene 4 by two-photon excitation of studied TPA PIs (calculated in acetonitrile at the TDM06-D3/LACVP(d,p)/PBE level of theory); f-oscillator strength

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Figure 3. Steady state photolysis of PIs in acetonitrile ($c_0 = 1 \times 10^{-3} \text{ mol } \text{L}^{-1}$) under argon with 460 nm LED for (a) acylstannane 1, (b) Ivocerin[®] 2, (c) tetrakis(2-methylbenzoyl)germane 3 and (d) titanocene 4

acylstannanes are expected to show fast photobleaching, as acylgermanes do as well. To investigate the photobleaching behavior of 1, steady state photolysis was carried out. The results were then compared to those of 2, 3 and 4. Each PI was dissolved in acetonitrile ($c_0 = 1 \times 10^{-3} \text{ mol } \text{L}^{-1}$) and the solutions were then irradiated with a LED (460 nm). Samples were taken in defined intervals and UV-VIS spectra were recorded (Figure 3). As the achieved data show, 1 showed very fast photobleaching. After 3 minutes, the $n\pi^*$ transition band of **1** had disappeared. For **2** and 3, substantially longer radiation times (15 minutes) were needed to reach the same point. Compound 4 showed fast photobleaching in solution as well, however its photoproducts show absorption up to 650 nm. From the photolysis experiments, the rate of photoinitiator decomposition R_d as well as the quantum yield of decomposition Φ_d were calculated for PIs 1-4 ($\Phi_d = 0.90$ for acylstannane 1) and arranged within a table in the supporting information of this article.

To explore the photoinitiating activity of **1**, photo-DSC experiments were carried out in dimethacrylates as well as in diacrylate formulations. This technique can be used to determine the time until heat flow maximum is reached (t_{max}) and the overall double bond conversion (DBC) as well as parameters like the time until 95% of the overall heat flow is reached (t_{95}) and the rate of polymerization (R_p). Curing was carried out using two different LEDs (460 and 522 nm). The light intensities were 1 W cm⁻² (460 nm) and 0.42 W cm⁻² (522 nm). The prepared formulations contained 0.1wt% of **1** either in a 1:1 mixture of urethane dimethacrylate (UDMA) and decanediol dimethacrylate (D₃MA) or in hexanediol diacrylate (HDDA). As stabilizer, 500 ppm of butylated hydroxytoluene (BHT) were added. For comparison, formulations of **2** (2 times the equimolar amount of **1** used), **3**



Figure 4. Photo-DSC conversion curves for PIs 1-4 in methacrylates using (a) a 460 nm LED and (b) a 522 nm LED as well as in HDDA using (c) a 460 nm LED and (d) a 522 nm LED

(equimolar amount of 1 used) and 4 (2 times the equimolar amount of 1 used) in the same monomers were prepared as well. The amounts of PI used were those related to the amount of cleavable groups present in the structures. The conversion curves for the experiments with the 460 nm LED show (Figure 4a,c), that the activity of tetrakis(2,4,6-trimethylbenzoyl)stannane (1) to initiate free radical polymerization is extremely high in both monomer systems. Looking at the achieved results, the values are within the range of the reference compounds 2 and 3. As expected, 4 does not show high initiating activity upon curing at 460 nm. However, the experiments using the 522 nm LED showed, that at that wavelength the acylstannane 1 still shows high reactivity, while for 2 and 3 no photopolymerization occurred (Figure 4b,c). Comparing the achieved results of 1 with those of 4, the reactivities of 1 and 4 are guite similar, however, in HDDA the acylstannane 1 shows a higher final DBC. For PI 1 the lower conversions reached upon irradiation with 522 nm compared to those achieved upon irradiation with 460 nm can on one hand be explained by the lower light intensity and the lower extinction coefficient of 1 at 522 nm. Furthermore, it can be assumed, that upon irradiation with 522 nm only for the tetrakis- (and maybe the subsequently formed trisacyl) species the $n\pi^*$ absorption tailout is sufficient to cause cleavage during polymerization. The remaining bis- and monoacyl species may not further cleave at 522 nm, which is also indicated by slightly yellow coloration of the polymeric samples (compared to colorless for 460 nm) directly after curing. The collected values for $t_{\text{max}},$ DBC, t_{95} and R_{p} of all experiments are given within the supporting information of this article.

To demonstrate the potential advantages of **1** in industrial applications such as additive manufacturing, penetration depth

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Figure 5. Setup used for curing depth (a, b) and green laser curing experiments (c) $% \left({{\mathbf{x}}_{b}^{\prime }}\right) =\left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) =\left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) =\left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right) =\left({{\mathbf{x}}_{b}^{\prime }}\right) \left({{\mathbf{x}}_{b}^{\prime }}\right)$



Figure 6. Curing depth experiments: Resulting polymer after curing of formulation containing (a) 0.1wt% of acylstannane **1** and 50wt% of ZrO₂ in HDDA with a 522 nm LED and (b) a formulation containing 0.1wt% of Ivocerin[®] **2** and 50wt% of ZrO₂ in HDDA with a 460 nm LED at the same light intensity



Figure 7. Green laser curing experiments in UDMA:D₃MA (1:1): a) variation of PI concentration (0.01 - 0.1wt% of 1, 10wt% of filler); b) variation of filler content (0 - 70wt% of filler, 0.1wt% of 1); c) variation of curing time (60 - 500 s, 0.1wt% of 1, 50wt% of filler); d) variation of curing time (60 - 500 s, 0.1wt% of 4, 50wt% of filler)

experiments were carried out. Especially in recently developed processes like lithography-based ceramic manufacturing^[2] this is of great importance. The big advantage of using light with longer wavelengths is the potentially higher penetration depth of the light into the material, which should lead to higher curing depths as well. To investigate this subject, a cylindrical mold was placed on a glass plate and filled with a formulation containing hexanediol diacrylate (HDDA), 50wt% of inorganic filler (ZrO₂, Lithoz GmbH) either 0.1wt% as well as of tetrakis(2.4.6trimethylbenzoyl)stannane (1) or Ivocerin® (2). As stabilizer, 500 ppm of butylated hydroxytoluene (BHT) were added. The setup is shown below (Figure 5a,b). The formulations were then cured for 240 s each and the resulting curing depths were then measured from the obtained polymeric samples. In the case of Ivocerin[®] (2) a 460 nm LED was used for curing, however, for the sample containing tetrakis(2,4,6-trimethylbenzoyl)stannane (1) a 522 nm LED was utilized. The light intensities were adjusted to be 33.5 mW cm⁻² behind the glass plate for both light sources. After curing the samples were taken out from the mold and unreacted formulation was washed away. The height of the resulting polymeric samples (Figure 6) was then measured at the centre. The sample, which contained 1 and was polymerized using the 522 nm LED showed a much higher curing depth (more than double), proving the higher penetration depth and demonstrating potential advantages of the acylstannane 1 in many applications.

To further test the novel photoinitiator 1 on its ability to initiate polymerization particularly at wavelengths above 500 nm, experiments using a green laser (532 nm) were carried out. A similar setup to the one shown above (Figure 5c) was used, except in this case the LEDs were replaced by a commercial green laser pointer. A large amount of samples was polymerized using this setup, varying the PI concentration, the filler content (Schott[®] dental glass) as well as the curing time (Figure 7a-d). The samples containing 1 show remarkable results. The absorption of tetrakis(2,4,6-trimethylbenzoyl)stannane (1) at 532 nm is still high enough to cause cleavage upon radiation at this wavelength. Even formulations with high filler contents (up to 70%) could be polymerized using the given setup. Furthermore, the PI concentration could be lowered significantly, but still giving satisfying results. The studies regarding the curing time further showed, that with higher curing times, the achieved curing depth could be increased (Figure 7c,d). Although with formulations containing Irgacure® 784 (4) slightly higher curing depths could be achieved, the samples containing the acylstannane 1 revealed very fast photobleaching in the crosslinked polymer (Figure 7a-c), which is desired in many industrial applications such as e.g. dental materials. The samples containing titanocene 4 did not show any photobleaching (Figure 7d). The collected values for all green laser curing experiments are given within the supporting information of this article.

Since many organotin compounds show considerable cytotoxicity, cytocompatibility evaluation was carried out for the photoinitiators 1-4. For cytocompatibility testing, L929-mCherry cells were exposed to different concentrations of initiators 1-4 and therefore incubated with different dilutions of PI in dimethylsulfoxide (DMSO; 0.1, 0.05, 0.025, 0.0125, 0.00625 and 0.003125 mM). Besides the evaluation of the cytotoxicity of the photoinitiator itself, also the cytocompatibility of the photolysis products upon exposure to UV light (365 nm, 10 min) was examined. For PI concentrations of 0.1 mM, the corresponding amount of DMSO present (1%) is high enough to cause severe cell death (cf. Supporting Information). However, at a PI concentration of 0.05 mM cell survival in the DMSO control lies at around 80%. At that concentration for all four initiators the metabolic activity of the cells, (irradiated and not irradiated with UV) is decreased drastically to less than 60%, where the cells exposed to the acylstannane 1 showed the highest survival rate. At PI concentrations of 0.025 mM only the cells exposed to

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initiators 1 and 4 showed high metabolic activities at around 80%, however, the acylgermane 3 only showed 36% (no UV irradiation). For the UV illuminated samples at the same concentration, the metabolic activity was above 65% for all initiators (70% for acylstannane 1). At lower concentrations the metabolic activity of the cells in almost all samples was higher than 80%. The only exception was the cells exposed to 0.0125 mM of initiator 3 (no UV curing), for which the metabolic activity was decreased to 70%. Summarizing the results, the new Sn-based initiator 1 surprisingly showed higher cytocompatibility than the structurally similar germanium compound 3 and the obtained values generally lie in the same range as the ones achieved for compounds 2 and 4. Furthermore, the photolysis products of 1 (upon radiation with UV) reveal high cytocompatibility as well. All cytocompatibility data including cell microscopy are given within the supporting information of this article.

In conclusion, a novel stannane-based photoinitiator for radical polymerizations in the visible range, particularly at wavelengths above 500 nm was presented. It showed high reactivity compared to current state of the art PIs in methacrylateand acrylate formulations. Unlike known germane-based compounds, tetrakis(2,4,6-trimethylbenzoyl)stannane (1) was able to initiate polymerization upon green light radiation (522 nm LED, 532 nm laser) leading to higher curing depths in filled systems, which is desirable for many industrial applications. The acylstannane **1** further showed very fast photobleaching in solution as well as within the polymer network. In contrast to many organotin compounds, compound **1** and its photoproducts showed surprisingly low cytotoxicity, especially when compared to similar germanium compounds.

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Keywords: Photoinitiator • Long wavelength • Photopolymerization • Visible light • Photobleaching

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