Towards a Quantitative Description of Radical Photoinitiator Structure-Reactivity Correlations

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ABSTRACT: The fundamental influence of the structure and substitution of radical photoinitiators was investigated via a trifold combination of pulsed-laser polymerization with subsequent electrospray-ionization mass spectrometry (PLP-ESI-MS), femtosecond transient absorption (fs-TA) spectroscopy, and quantum chemistry. For the first time, a library of benzoin-derived photoinitiators with varied substitution patterns was synthesized. In the PLP-ESI-MS study, different photoinitiators were compared pairwise in so-called cocktail experiments, enabling the direct comparison of their initiation efficiency. In the fs-TA experiments, the transient response was observed after UV excitation in the visible spectral region, allowing for a description of excited state dynamics, which was analyzed with the aid of TD-DFT calculations. Ab initio calculations were undertaken to determine the reactivity of the radical fragments generated from these photoinitiators and to quantify the influence of various substituents on the rate of addition to monomer. In summary, the influence of the substituent on the initiation efficiency, intersystem crossing (ISC) behavior, excited state dynamics, and the extinction coefficients were analyzed. Hence, relaxation pathways and reaction mechanisms were optimized to explain disparate initiation efficiencies of a wide range of newly designed photoinitiators with varying substitution patterns. The strongly divergent absorptivities of the different photoinitiators and their corresponding initiation efficiencies underline that the absorptivity of a molecule is by no means an unequivocal measure for its reactivity when excited at a specific wavelength. In fact, the most efficient initiators are governed by one $n\pi^*$ singlet state with a very low extinction coefficient at the excitation wavelength and one or two triplet states with $n\pi^*$ character.

Introduction

Radical photoinitiators play a fundamental role in key polymer applications in academia as well as in industrial research, spanning from coatings, adhesives, varnishes, to dental and cosmetic applications.^{1,2} Thus, the initiation process of the photoinduced polymerization reaction is of crucial importance for the chemical nature of the final product as well as for the rate at which the polymerization is initiated. Although light usually plays a role solely in the very first step of a polymerization, a closer look into the fate of an initiator molecule upon irradiation gives valuable information on how and with which propensity an initiating fragment is incorporated into a polymer

chain, i.e., how it is actually able to initiate a polymerization.³ A tremendous number of different photoinitiator systems for light-induced free radical polymerization (FRP) have been reported over the past decades. However, to the best of our knowledge, no fundamental studies addressing the specific structure-reactivity correlation of a photoinitiator have been reported to date. Thus, the design of new photoinitiators has been based on trial and error experimentation. The differentiation into type I (radical formation after α -cleavage of the excited molecule) and type II photoinitiators (radical formation after H-abstraction from a second molecule) categorizes the radical formation pathway. For type I photoinitiators, such as acetophenones,^{3,4} hydroxyalkyl phenones,^{5,6} acyl-

germanes,^{7,8} acylphosphines,⁹ or benzoin^{3,10} and its derivatives, radical formation is based on a unimolecular process. They usually exhibit an ultrafast intersystem crossing (ISC) upon irradiation with UV light from a singlet to a triplet state and subsequently undergo α -cleavage, forming two radical fragments, at least one of which is capable of initiating a polymerization reaction. The performance of photoinitiators strongly depends on the employed system and the targeted product properties. The comparison of photoinitiators is possible in manifold ways, for instance based on their polymerization rate,¹¹⁻¹⁵ their UV-Vis absorbance,¹²⁻¹⁴ or their final monomer conversion in particular applications. Therefore, a series of techniques has been employed in order to evaluate the photochemical properties of photoinitiator systems, such as the IR spectroscopic evaluation in real time,¹¹⁻¹⁴ steady-state photolysis^{12,14} or photo-differential scanning calorimetry (photo-DSC).¹⁶ A focus not only on the photochemical behaviour of photoinitiators, but on the mechanistic aspects of radical formation has been provided by time-resolved laser flash spectroscopy with detection via UV-Vis, IR, and EPR for the investigation of the photochemistry and -physics of a series of photoinitiators, carried out by Gescheidt and co-workers.⁵ The initiating species can thereby be pursued by EPR spectrometry,¹²⁻¹⁴ and possible side products can be detected by photochemically induced dynamic nuclear polarization (CIDNP).⁷ As pointed out in our previous studies^{3,17} electrospray-ionization mass spectrometry coupled with pulsed-laser polymerization (ESI-MS-PLP) combined with femtosecond pump-probe spectroscopy serves as a powerful tool for quantitative photoinitiator comparison. In this way, specific photoinitiator fragments can be compared in their initiation ability, resulting in so-called initiation efficiency ratios that can be determined for different photoinitiator couples, for instance for benzoin and 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MMMP), two widely used photoinitiators, or benzoin and 4-methyl benzoin (4MB).³

Typically, chemists tend to refer to the absorptivity of a photoreactive molecule at a certain wavelength in order to determine its reactivity and / or efficiency. In simple terms, a molecule with a high extinction coefficient absorbs more photons than a molecule with a lower extinction coefficient. Consequently, the molecule with the higher extinction coefficient should be excited with a higher probability and, for in-

stance, perform a bond cleavage at higher yield compared to molecules with lower extinction coefficients. Therefore, a frequent conclusion is that a good photoinitiator is characterized by a high absorptivity at the employed wavelength. Herein, we will show that this approach is at best questionable. The main reasons are that the absorption of a photon can entail a multitude of different processes, whereof the bond cleavage is only one of several possible pathways. After the absorption of a photon the photoinitiator molecule is promoted into an electronically excited state. From this state the molecule can perform a series of deactivation processes that can be chemical in nature or involve energy loss via radiative (luminescence) or nonradiative pathways (internal conversion, IC, and ISC). Hence, a competition among several processes exists. Finally, the reactivity of the photoinitiator radical itself is still of high importance. A multitude of formed radicals cannot be efficient if they are not sufficiently reactive to add to a monomer double bond. Thus, for the comparison of photoinitiators it is of high importance to keep in mind that disparate initiator performances can be due to different rates of radical production as well as different radical reactivities.^{3,18} In the present study a route towards a quantitative analysis is suggested when searching for efficient photoinitiators. Aiming at an instruction for a "tailor-made" photoinitiator fulfilling specific requirements and demands, the influence of substitution is investigated in the light of the Hammett relation.¹⁹ It will be shown that this aspect requires detailed knowledge of the nature of the molecules' electronic states. Based on the commonly employed photoinitiator benzoin, we synthesized a library of benzoin-like photoinitiators with varied substitution patterns. The photoinitiators of the library were, amongst others, chosen due to their red shift in the absorption behaviour compared to benzoin. As will be demonstrated, a stronger red shift does not necessarily result in a better initiation efficiency in comparison to benzoin. Indeed the opposite is often the case. For a quantitative comparison of the selected photoinitiators, pulsed-laser polymerization combined with electrospray-ionization mass spectrometry (PLP-ESI-MS) served as the comparative tool, investigating two photoinitiators, respectively, in a so-called cocktail experiment. Additionally, femtosecond-transient absorption (fs-TA) experiments were applied to monitor the transient response of the photoinitiators after UV excitation in the visible spectral region, allowing for an elucidation of the excited state dynamics. Quantum chemical calculations were used to determine (i) the location and character of excited electronic states and (ii) the rate coefficients for the addition of photoinitiator radical fragments to methyl methacrylate (MMA). Finally, results from the three different viewpoints are summarized to provide insight into the structure-reactivity relationships of photoinitiators.

Figure 1. Overview of the analyzed photoinitiators with varied substitution (left side) and their corresponding extinction coefficients in the UV-Vis region, respectively (right side). For clarity reasons the axis for the extinction coefficient of the photoinitiator NMe₂Bz is situated on the right side. Bottom: Table with the extinction coefficients for the analyzed photoinitiators at 351 nm. ^aAt 351 nm excitation wavelength.

Results

Building on our previous investigation of benzoin and its characteristic excitation behaviour,³ one of the aims of the present work was to enhance its efficiency. To this end, we selected substituents designed to increase the absorptivity in the UV-Vis region and thus, enhance the initiation efficiency of the benzoin derivative. For the prediction of the absorptivity, Hammett parameters can be taken into account. They enable the gradual increase of the extinction coefficient for the desired excitation wavelength (i.e., at 351 nm), as shown in the further course of this study. Thus, a library of photoinitiators (see **Figure 1**, left side) was synthesized, based on the molecular structure of benzoin, but with varying substitution patterns. Electron donating groups, such as methyl and dimethylamine, and electron withdrawing groups, such as fluorine, were incorporated into the benzoin structure. Substitutions were made at the aromatic ring: alongside the carbonyl group and alongside the hydroxyl group. In addition to benzoin derivatives, the photoinitiator library contains benzil and its substituted derivative difluorobenzil (DFB). Every substitution in a molecule causes a change in its electronic structure, associated with a change in its reactivity. The actual effect of the substitution on the photoinitiator reactivity and excited state dynamics is analyzed and interpreted.

UV-Vis Spectroscopic Evaluation of Photoinitiators

As noted in the introduction, the initiation efficiency of a photoinitiator is frequently linked to its absorptivity. In general, a high extinction coefficient at the employed wavelength can be beneficial for the reactivity of a photoinitiator. However,

our experiments show that a strong absorptivity is not mandatory for an efficient photoinitiator. The photoinitiators of the library depicted in **Figure 1** were, amongst others, chosen due to their red shifted absorption compared to benzoin. We demonstrate that photoinitiators with a stronger red shift showed a poorer performance and a lower initiation efficiency in comparison to benzoin. UV-Vis spectrometry of the employed photoinitiators shows large differences between the benzoin derivatives. Benzoin itself, a well-known photoinitiator, shows a very low extinction coefficient (64 L·mol⁻¹·cm⁻¹ at 351 nm excitation wavelength) compared to its derivatives, most of which are not known to act as photoinitiators (see **Figure 1**). The fluorine-substituted benzoin derivatives FBz, FBz Iso, and F₂Bz show similar extinction coefficients (60 L·mol⁻¹·cm⁻¹, 66 L·mol⁻¹·cm⁻¹, and 63 L·mol⁻¹·cm⁻¹ at 351 nm). The extinction coefficients of benzil and DFB are comparable to those of FBz and F₂Bz. The dimethylamine-substituted derivative NMe₂Bz Iso and the corresponding fluorine-carrying FNMe₂Bz show a similar absorption behaviour, regarding the extinction coefficient (1812 L·mol⁻¹·cm⁻¹ at 351 nm for NMe₂Bz Iso and 1950 L·mol⁻¹·cm⁻¹ for FNMe₂Bz) as well as the absorption pattern. The dimethylamine-substituted derivative NMe₂Bz shows a particularly increased extinction coefficient (23400 L·mol⁻¹·cm⁻¹ at 351 nm) and a different absorption pattern compared to all other analysed photoinitiators.

Initiation Efficiencies seen from PLP-ESI-MS

In the PLP-ESI-MS study, the various photoinitiators were compared pairwise in so-called cocktail

Scheme 1. Pathway of radical formation and the main disproportionation products for both radical fragments using the example of benzoin (Bz) as a typical photoinitiator. The combination products are omitted for clarity reasons.

experiments, enabling the direct comparison of their initiation efficiency. In a PLP experiment, the laser beam hits the sample containing photoinitiators in various ratios and monomer. Excitation of the photoinitiator leads to the generation of radicals that can initiate a free radical polymerization (FRP) of the monomer. The termination processes of an FRP are disproportionation and combination, as illustrated in **Scheme 1**. The nature of the monomer determines the ratio of disproportionation to combination products. In the case of methacrylates, the disproportionation products are superior in number, however combination products can still be found. Since the occurrence of two initiator fragments that act as chain ends provides no information on which fragment initiated the propagation, a mass spectrometric analysis of combination products gives no insight into the initiation process. The information on which fragment of the employed photoinitiator served as the initiating radical, i.e., how the propagation of a polymer chain was initiated, is retained in the disproportionation products. Additionally, when at least two photoinitiators are employed, the disproportionation products provide information on which specific radical fragment performs better. In a mass spectrum, disproportionation peaks appear in pairs with a mass difference of 2 amu. In this study the disproportionation peaks are labelled “X=” or “XH” – where “X” defines the chemical nature of the α -position of the polymer chain, i.e., the fragment that initiated the propagation (for instance B, FB, or MB) – while “=” and “H” imply the nature of the ω -end of the chain, depending on the role of the end group in the H-abstraction during the disproportionation process. The quantitative comparison of the initiation efficiency of several photoinitiators towards MMA in PLP was carried out employing a method evaluating the peak heights Δh of the polymer signals in each repeating unit (illustrated in **Figure 2**). The two disproportionation structures – bearing a double bond or no double bond at the chain end (for instance B= or BH) – form a peak cluster (see **Figure 2**). The first peak of such a cluster shows no isobaric overlap with the other product peaks and is thus selected for the comparison. As already described in our earlier publications the relative peak heights are employed for the determination of a mole fraction $F^X(i)$ of a disproportionation product with the end group X, originating from the initiating fragment.^{3,10,17,20-22} Thus, the relative number of macromolecular chains initiated by the aforementioned fragment X is directly correlated with $F^X(i)$. If the assumption is valid that the propagation of the monomer radical is not affected by the initiating fragment (at least not for $DP_n > 2$), the end group X is equally distributed over all chain lengths. The $F^X(i)$ values for a certain fragment X can be plotted versus the degree of polymerization, DP_n (refer to **Figure S1**), in order to illustrate the distribution of X over all chains detected in the ESI-MS. A chain length-independent ionization process can be assumed if the aforementioned plot exhibits a constant gradient close to

zero (as seen in **Figure S1**). In this case the polymer chain length has no influence on its ionization ability. However, in order to compensate a potentially mass biased ESI-process, the mass bias-free ratio $G_{m/z,0}$ of two disproportionation products is obtained, employing an established method described in our earlier mass spectrometric studies.^{3,10,17,20,21}

Figure 2. ESI-MS spectrum of pMMA initiated by a mixture of Benzoin / FBz in the ratio 1 / 1, showing the disproportionation peaks B= and FB=. The peak heights $\Delta h^D_{B=}$ and $\Delta h^D_{FB=}$, employed for the determination of the initiation efficiencies, are exemplarily shown.

The approach utilized here is equivalent to our previous studies, for instance in the case of the quantitative comparison of MMMP, benzoin, and 4MB³ or the mesitoyl and benzoyl fragment.¹⁰ For the quantitative comparison of the initiation efficiency of photoinitiators, PLP experiments with different molar ratios of the respective species have to be carried out. Subsequently, $G_{m/z,0}$ of each repeating unit is plotted against the varied molar

Table 1. Overview of the initiators compared via PLP-ESI-MS, their corresponding initiation efficiency ratios, and the initiation efficiency ratios normalized with respect to the extinction coefficients at 351 nm.

Compared fragments (initiators)		Initiation efficiencies PLP-ESI-MS	Initiation efficiencies normalized to ϵ^b
B (Benzoin)	MB (4MB)	1 : 0.86 ^c	1 : 1.06
B (Benzoin)	FB (FBz)	1 : 0.75	1 : 0.80
MB (4MB)	B (FBz Iso)	1 : 2.44	1 : 2.92

FB (FBz)	B (FBz Iso)	1 : 1.10	1 : 1.00
B (Benzoin)	FB (F ₂ Bz)	1 : 1.09	1 : 1.11
BNMe₂ (NMe ₂ Bz)	B (Benzoin)	n.d. ^a	
B (NMe ₂ Bz Iso)	MB (4MB)	n.d. ^a	
B (Benzoin)	FB (FNMe ₂ Bz)	n.d. ^a	
B (Benzil)	FB (DFB)	1 : 1.67	1 : 1.78

photoinitiator ratios in the initial polymerization mixture, exhibiting a linear trend (see **Figure S2**). The ratio at which $G_{m/z,0} = 1$ is the initiator ratio that is necessary to achieve an equal initiation ability of the compared fragments and that is consequently the quantitative initiation efficiency ratio between these fragments. The resulting initiator efficiency ratios are provided in **Table 1**, alongside the same values normalized against the extinction coefficients at 351 nm, and the results are discussed below.

Femtosecond Pump-Probe Spectroscopy

In order to gain deeper insight into the relevant processes within the excited states of a photoinitiator, pump-probe experiments were performed. Transient absorption (TA) profiles of the photoinitiators shown in **Figure 1** were recorded using MIB as the solvent that is structurally similar to the monomer MMA. All initiators were excited at 351 nm, the same wavelength as employed in the PLP experiments. The photoinitiator is excited into a specific electronic state by the pump pulse and the evolution of the excited states' population of the samples was probed at several wavelengths in the range of 500 to 600 nm. Due to the low extinction coefficients for some of the initiators and the resulting low amplitudes (< 1 mOD) under excitation at 351 nm, no transient absorption spectra were recorded with a white-light continuum.

In the further course of this study, the results of the pump-probe experiments are presented in separated groups consisting of structurally similar photoinitiators. The transient spectra of all samples probed at 500 nm are shown in **Figure 3 – 5** and discussed below. Some of the photoinitiators possess a manifold of higher singlet and triplet states leading to a superposition of different processes after UV excitation, whereby entanglement of the dynamics to specific electronic states is somewhat difficult. As in our previous study,¹⁷ we found out that a useful comparison was nevertheless possible by probing at 500 nm, where the number of superimposed excited states seems to be at a minimum. The results for further probe wavelengths can be found in the supporting information. All pump-probe experiments were evaluated by fitting with triexponential functions in order to obtain time constants τ_i and their related amplitudes A_i (see **Table S2-S4**).¹⁷ Furthermore, it is important to note that the obtained transients for the different photoinitiators vary remarkably in their behavior on a short timescale. Usually, the time constant τ_1 represents a combination of IC and ISC. The time constant τ_2 reflects different triplet dynamics including radical formation, depending on the present relative position and number of states as well as their characters. At this state of analysis, a more detailed assignment is not possible, yet also not necessary for the interpretation within the scope of the current work, this also includes τ_3 .

Initiation Efficiencies seen from Theoretical Calculations

In order to assess the transient data and gain a better understanding of the dynamical processes taking place, it is necessary to have a general idea of the electronic state properties of all investigated photoinitiators. Since photoinitiators of type I are evaluated in this study, radical formation obviously arises from triplet states and therefore the preceding step of relaxation via ISC from an excited singlet state is the initial and determining process for efficient initiation. In this context it can be helpful to consider the magnitude of the energy gap between originating singlet state and underlying triplet states. As is already known from earlier studies of benzoin and 4MB¹⁷ and predicted by the El-Sayed selection rules²³ the character of singlet states and maybe also of the triplet states is important in determining the efficiency of a photoinitiator. Therefore a closer look of the involved orbitals is essential and useful. Another important factor that influences photoinitiator efficiency is the reactivity of the radical fragments generated from bond scission. If these radical fragments are not sufficiently reactive, then the photoinitiator will be unable to effectively initiate FRP. Photo-induced homolysis of benzoin and its derivatives produces two characteristically different radical fragments that have quite distinct reactivity. Acyl radicals, like most other sp² type radicals, are unstable and highly reactive species. Because of their electronic structure, acyl radicals are not as effectively stabilized by adjacent substituents as sp³ type radicals. Benzoin derived acyl radicals are relatively localized and so varying the para-substituent of the adjacent phenyl would alter their reactivity mainly through inductive effects. In contrast, hydroxybenzyl radicals are significantly more stable and much less reactive sp³ type radicals. These radicals are stabilized by conjugative interactions with the adjacent

Table 2. Theoretically calculated barriers (kJ·mol⁻¹) and rate coefficients ($\times 10^4$ L·mol⁻¹·s⁻¹) for the addition of photoinitiator radical fragments to MMA, in bulk at -5 °C.

Radical fragment	$\Delta G^\ddagger_{\text{gas}}$	k_{gas}	$\Delta G^\ddagger_{\text{sol}}$	k_{sol}
FB	48.8	7.7	40.3	16
B	51.6	2.2	42.4	6.3
MB	51.8	2.0	42.8	5.1
BNMe ₂	51.7	2.1	43.2	4.2
BnNMe ₂	46.7	20.0	50.8	0.14
Bn	49.9	4.8	55.0	0.02
BnF	49.5	5.6	56.5	0.01

*Note: rate coefficients have been corrected (by a factor of 2) for reaction path degeneracy.

phenyl and hydroxyl groups and are thus significantly less reactive. The reactivity of these radicals should also be more sensitive to variations in the para-substituent, as this substituent forms part of the aromatic π system that stabilizes the radical (mesomerically).

To assess the reactivity of the initiator derived radicals toward MMA, rate coefficients were calculated using high-level ab initio molecular orbital theory calculations (**Table 2**). For the radical fragments investigated in this study, the following

order of reactivity for addition to MMA was obtained; $\text{FB} > \text{B} > \text{MB} > \text{BNMe}_2 \gg \text{BnNMe}_2 > \text{Bn} > \text{BnF}$. Interestingly, incorporating an electron donating para substituent (NMe_2) slightly lowers the reactivity of acyl type radicals to monomer while it significantly increases the reactivity of hydroxybenzyl radicals. Likewise, incorporating an electron withdrawing para substituent (F) increases the reactivity of acyl radicals but it significantly decreases the reactivity of hydroxybenzyl radicals. If it is assumed that polar-effects favor the addition of radicals with well-defined electrophilic or nucleophilic character, these divergent substituent effects can be rationalized by considering the polar characteristics of the corresponding radical species. The hydroxybenzyl radical is relatively nucleophilic and incorporating an electron donating substituent in the para position will further increase this nucleophilic character. In contrast, acyl radicals because of their sp^2 structure, are very electrophilic and incorporating an electron withdrawing para substituent will further increase this electrophilic character through inductive effects. As anticipated a greater effect is observed moving from $\text{R} = \text{F}$ to $\text{R} = \text{NMe}_2$ in hydroxybenzyl type radicals (factor of 10 increase k_{add}) compared with acyl systems (factor of 5 decrease in k_{add}). For further details refer to the supporting information.

Discussion

Analysis of the Photoinitiators

In the following, a detailed discussion of the behavior of the photoinitiators is provided. The initiators are simultaneously examined from the three previously described perspectives: via PLP-ESI-MS, femtosecond spectroscopy, and theoretical calculations.

FBz, FBz Iso, and F_2Bz

Halogen substituents in organic compounds generally exert inductive (-I) as well as mesomeric effects (+M), based on their electronegativity and free electrons. This dual effect

makes them an interesting group of substituents for photoinitiators. Fluorine, as the most electronegative element, takes on a special position. Three fluorine-substituted benzoin derivatives, once in para-position of the benzoyl group (FBz), once in para-position of the hydroxyl-carrying aromatic ring (FBz Iso), and once at both para-positions (F_2Bz) were investigated. FBz was compared to benzoin via PLP-ESI-MS. Thereby, the comparable polymer output of both initiators in PLP is beneficial. In a direct comparison an initiation efficiency ratio of $0.75 / 1$ for the fragments FB / B was determined, related to the fluorine-substituted benzoyl fragment (FB) compared to the benzoyl fragment (B). Thus, FBz shows a lower initiation efficiency than benzoin. FBz Iso, the regioisomer of FBz, was compared to 4MB. A mass spectrometric comparison of FBz Iso to benzoin cannot be performed due to their identical benzoyl fragments. However, since the initiation efficiency ratio between benzoin and 4MB ($\text{B} / \text{MB} = 1 / 0.86$) has been determined in a previous study,³ the para-methyl substituted benzoyl fragments from various photoinitiator structures. Thus, FBz Iso proved to be an excellent photoinitiator with an initiation efficiency ratio of $\text{B} / \text{MB} = 2.44 / 1$ for the benzoyl fragment (B) derived from FBz Iso compared to the methyl benzoyl (MB) of 4MB. Interestingly, no polymer initiated by the para-fluorine substituted fragment of FBz Iso (BnF) was found in the ESI-MS (this can be explained by the particularly low rate coefficient of BnF for the addition to MMA). The comparison of FBz to FBz Iso resulted in an initiation efficiency ratio of $\text{FB} / \text{B} = 1 / 1.1$, assigning a better initiator performance for FBz Iso. F_2Bz , the benzoin derivative with fluorine substitution at both para-positions, showed a higher initiation efficiency compared to benzoin: $\text{FB} / \text{B} = 1.1 / 1$. Thus, fluorine-substitution at the non-initiating hydroxy fragment shows a positive impact on the initiation efficiency. However, the fluorine-substitution at the initiating benzoyl fragment, next to the non-initiating fragment, additionally enhances the overall initiator performance.

The TAs of FBz, FBz Iso, and F_2Bz attract particular attention due to their very low optical densities and – in contrast to all other investigated photoinitiators in this study – their purely triexponential decay.

Figure 3. Combined analytical results for the investigation of FBz, FBz Iso, and F₂Bz. Upper part: Initiation efficiency ratios of FBz vs. benzoin, FBz Iso vs. 4MB, F₂Bz vs. benzoin, and FBz vs. FBz Iso determined by PLP-ESI-MS. Middle part: Transient spectra of FBz (A.), FBz Iso (B.), and F₂Bz (C.) from femtosecond pump-probe experiments with probe pulses at 500 nm. UV-Vis extinction and results from TD-DFT calculations with electronic states and transitions (D.). Bottom part: Radical fragments of FBz, FBz Iso, F₂Bz, benzoin, and 4MB and their corresponding rate coefficients for the addition to MMA, k_{sol} .

All corresponding time constants retrieved at a probe wavelength of 500 nm are similar. For τ_1 a decay of 2-4 ps is obtained (see Table S2) and for τ_2 20-50 ps with a third time constant exceeding the experimental maximum delay range of 2 ns. The time constants are in very good agreement with previous work on benzoin and 4MB.¹⁷

TDDFT calculations showed that FBz, FBz Iso, and F₂Bz have an S_1 singlet state around 350 nm with a dominant share of $n\pi^*$ character. For FBz, FBz Iso, and F₂Bz two triplet states are located below the excited singlet state S_1 , as already observed for the efficient photoinitiators benzoin and 4MB. First,

a T_1 triplet state with a prevailing $n\pi^*$ character for FBz, FBz Iso, and F₂Bz and second, a T_2 triplet state with $\pi\pi^*$ character for FBz, with $\pi\pi^*/n\pi^*$ character for FBz Iso and a mixed $\pi\pi^*/n\pi^*$ character for F₂Bz. Thereby, FBz Iso exhibits a smaller energy gap $S_1 \rightarrow T_2$ compared to FBz and F₂Bz. However the energy gap $T_2 \rightarrow T_1$ is smaller for FBz and F₂Bz compared to FBz Iso. A combination of ISC and IC, enabled by the energetic positioning of T_1 and T_2 , presumably contributes to the fast decay in the dynamics of the transient spectra of FBz ($\tau_1 \sim 2.7$ ps), FBz Iso ($\tau_1 \sim 2.0$ ps), and F₂Bz ($\tau_1 \sim 2.7$ ps). Theoretical calculations also confirm an increased

Figure 4. Combined analytical results for the investigation of NMe₂Bz, NMe₂Bz Iso, and FNMe₂Bz. Transient spectra of NMe₂Bz (A.), NMe₂Bz Iso (B.), and FNMe₂Bz (C.) from femtosecond pump-probe experiments with probe pulses at 500 nm. UV-Vis extinction and results from TD-DFT calculations with electronic states and transitions (D.). Bottom part: Radical fragments of NMe₂Bz, NMe₂Bz Iso, and FNMe₂Bz and their corresponding rate coefficients for the addition to MMA.

reactivity of the FB radical fragment (rate coefficient of $6.3 \cdot 10^4$ L·mol⁻¹·s⁻¹ for the addition to MMA) compared to the B fragment. However, FBz presumably forms less radicals than benzoin. Thus, the positive effect of radical reactivity of FB is compensated.

NMe₂Bz, NMe₂Bz Iso, and FNMe₂Bz

Benzoin derivatives carrying an amine group have been previously reported in literature.²⁴⁻²⁶ Due to the strongly electron-releasing effect of the dimethyl amine group, this substituent was chosen for our study. The strongly elevated extinction coefficients as well as the red-shifted absorption bands compared to benzoin and 4MB raised our expectations for creating highly reactive photoinitiators. However, after the first PLP-ESI-MS experiments we found that our dimethyl amine substituted benzoin derivatives showed very poor polymer yields (≤ 0.5 %) compared to benzoin (~ 4.5 %), under identical PLP conditions. In order to improve the polymer yield, FNMe₂Bz was synthesized: While maintaining the amine substitution at the hydroxy-carrying side of the benzoin structure, the para-position of the benzoyl moiety was simul-

taneously substituted with a fluorine group. However, in contrast to the results for FBz and FBz Iso described above, the fluorine substitution in FNMe₂Bz did not increase the polymer yield. Due to this very low polymer output of the amine-carrying benzoin derivatives, a quantitative comparison of the initiation efficiencies via PLP-ESI-MS could not be performed.

On the other hand, due to the high extinction coefficients of the amine-carrying molecules, their investigation via transient absorption spectroscopy was well-accessible. Upon absorption of UV light at 350 nm NMe₂Bz is excited into the S₁ state with $n\pi^*$ character, whereas NMe₂Bz Iso and FNMe₂Bz are excited into the S₂ state. The S₁ states of the latter can be described by a $\pi\pi^*$ character and are therefore not suitable for photoinitiator purposes. Their S₁ states, however, offer an $n\pi^*$ (FNMe₂Bz) and a mixed character (NMe₂Bz Iso), respectively. All three amine-carrying benzoin derivatives possess a multitude of triplet states, offering a $\pi\pi^*$ or a mixed character. The ISC from $n\pi^*$ singlet states into $\pi\pi^*$ triplet states can be easily performed due to the change of the molecular orbital configuration, as predicted by the El-Sayed selection rule.²³ However,

the multitude of triplet states can lead to an overlay of several processes, explaining the long delay times for the transient spectra, exhibiting the formation of a plateau that is reached after a few picoseconds. Thus, the amine-carrying species show completely different TA traces compared to those of FBz, FBz Iso, and F₂Bz. The strongly differing extinction coefficients of NMe₂Bz compared to NMe₂Bz Iso and FNMe₂Bz are striking. At the same time the calculated transition of the three benzoin derivatives show a corresponding trend. Transitions of FNMe₂Bz and NMe₂Bz Iso are comparable, whereas those of NMe₂Bz differ. At the same time NMe₂Bz Iso and FNMe₂Bz exhibit similar transient absorption spectra. This similar trend for NMe₂Bz Iso and FNMe₂Bz can presumably be explained by the identical positioning of the dimethyl amine substituent. An additional factor that could explain the poor polymerization ability of the amine-carrying photoinitiators are the theoretically calculated rate coefficients of the addition of the radical fragments to MMA. The dimethyl amine para-substituted benzoyl fragment (BNMe₂, 4.2·10⁴ L·mol⁻¹·s⁻¹) shows a 33 % lower rate coefficient compared to

the benzoyl fragment (B, 6.3·10⁴ L·mol⁻¹·s⁻¹). However, the fluorine substituted benzoyl fragment (FB, 1.6·10⁵ L·mol⁻¹·s⁻¹) shows a considerably higher rate coefficient than the benzoyl fragment. Yet, the polymer yield of FNMe₂Bz and NMe₂Bz is similar. Thus, we assume that the numerous triplet states of the dimethyl amine-substituted benzoin derivatives – and their overlay – are the main cause for the very low polymer yield, preventing the excited molecules from performing radical scission. Thus, the radicals that can initiate a polymerization cannot be formed in a sufficient number.

DfB and Benzil

The positive influence of fluorine substitution, as observed for FBz Iso and F₂Bz, was further investigated for the photoinitiator system of benzil. Since benzil is known to be a poor photoinitiator for low irradiation energies, the influence of fluorine substitution is of particular interest. The direct comparison of para-substituted difluoro

Figure 5. Combined analytical results for the investigation of DFB and benzil. Upper part: Initiation efficiency ratios of DFB and benzil determined by PLP-ESI-MS. Middle part: Transient spectra of DFB (A.) and benzil (B.) from femtosecond pump-probe experiments with probe pulses at 500 nm. UV-Vis extinction and results from TD-DFT calculations with electronic states and transitions (C.). Bottom part: Radical fragments of DFB and benzil and their corresponding rate coefficients for the addition to MMA.

benzil (DFB) with benzil showed indeed a clearly higher initiation efficiency for DFB. An initiation efficiency ratio of 1.67 / 1 for the initiator fragments FB / B of DFB and benzil was determined via PLP-ESI-MS. In their transient absorption spectra, both benzil as well as DFB show low absorptivities for all probe wavelengths. Thereby, for different probe wave-

lengths, a shift in the development of the TA can be observed. In particular the absorption at 500 nm probe (see **Figure 5**) results in a positive increase of some hundreds of fs for DFB whereas for benzil the signal rises much slower (some ps). This increase is further illustrated by the positive sign of the amplitudes and by the decay on a picosecond timescale for

both systems. Femtosecond experiments showed that both DFB and benzil are excited into the S_2 singlet state upon irradiation with UV light at 350 nm.

The transition into the first singlet state could comprise a dark state possessing a particularly low oscillator strength. Singlet singlet transitions (S-S) via conical intersection – as is the case for mesitol¹⁷ – could be possible. The required singlet states S_1 and S_2 of benzil and DFB both have $n\pi^*$ character. Below the S_1 state six triplet states can be found. Thereby, only T_1 and T_4 exhibit an $n\pi^*$ character, whereas T_1 is presumably not accessible. The remaining triplet states, offering $\pi\pi^*$ or mixed characters, are unsuitable for radical formation. Thus, the small amount of formed radicals could cause the poor initiation ability of benzil derivatives in general. The higher rate coefficient for addition to MMA for the fragment FB compared to B explains the better initiation efficiency of DFB compared to benzil. Both, DFB as well as benzil form a small amount of radicals. However, the higher reactivity of fluorine-substituted benzoyl radicals promotes the initiation efficiency of DFB.

In summary, seen from the PLP-ESI-MS experiments, the substitution with electron withdrawing groups has a negative influence on the initiation efficiency of a benzoin-like photoinitiator. Regardless of its position in the aromatic system – alongside the carbonyl group (NMe₂Bz) or hydroxy group (NMe₂Bz Iso) – the dimethylamine substituted derivatives show lower initiation efficiencies compared to benzoin. Additionally, the dimethylamine substituent has a deteriorating effect on fluorine substituted benzoin derivatives, as seen for FNMe₂Bz. For FBz, the benzoin derivative with fluorine substitution on the aromatic system alongside the carbonyl group shows a slightly negative influence on the initiation efficiency. However, for its regioisomer FBz Iso, the initiation efficiency is increased compared to FBz and strongly increased compared to 4MB. For F₂Bz the initiation efficiency is increased compared to benzoin.

As noted above, for the prediction of the initiation efficiencies of a photoinitiator, Hammett parameters are sometimes taken into account. They enable the gradual increase of the extinction coefficient for the desired excitation wavelength (i.e., at 351 nm), shown above in the discussion of the UV-Vis absorption of the photoinitiator library. However, as discussed in the further course of this study, Hammett parameters do not allow for a qualitative, let alone a quantitative prediction of the initiation efficiency. Instead, a set of characteristic properties and structural requirements for an ideal photoinitiator can be derived from our results.

A significant factor for the efficiency of a photoinitiator is the character of its electronic states that are involved during the process of excitation and ISC. Good photoinitiators exhibit only few (≤ 2) triplet transitions located below the excited singlet states. Besides the character of the triplet state,²⁷ further characteristics are crucial for the initiation efficiency of a photoinitiator. A good initiator exhibits an excitation into a singlet state with $n\pi^*$ character and performs a subsequent transition into a triplet state offering an equal character ($n\pi^*$). However, a poor initiator offers a multitude of triplet states below the S_1 state (partly with $\pi\pi^*$ character). A great number of triplet states presumably results in an overlay of different electronic processes that can be traced due to their residual absorption for long delay times (triplet dynamics). Therefore, intense transient absorptions are an indication for a relatively poor initiation behavior of a photoinitiator, caused by its long-

term abundance in triplet states prior to the radical fragmentation process. On the basis of our results, we conclude that a good benzoin-like photoinitiator should fulfil the following criteria:

(i) The extinction coefficient should be close to 60 L·mol⁻¹·cm⁻¹. Smaller values may represent dark singlet states that can result in conical overlap, as observed for mesitol.¹⁷ However, higher values are no inevitable sign for a good photoinitiator, but can – on the contrary – imply transitions from $n\pi^*$ to $\pi\pi^*$ excited states, having an inappropriate character for radical formation (refer to Figure 4).

(ii) After the excitation into a singlet state a fast ISC process in the time range of 2-4 ps ensures the sufficient formation of photoinitiator species in triplet states.

(iii) As a further selective criterion for a good photoinitiator, we observed a time frame of maximum 100 ps for the formation of radicals which derive from the initiators' triplet state. At this stage – radicals are formed and could initiate a polymerization – yet the selective criteria for a good photoinitiator are not exhausted.

(iv) Radicals can vary immensely in their reactivity towards monomer double bonds, as illustrated by the rate coefficient k_{sol} for the addition of a radical fragment to MMA in Figure 3 – 5 and Table 2. Thus, a photoinitiator that fulfils all the above criteria, yet generates a high amount of unreactive radicals, will most likely not possess a high initiation efficiency. On the other hand, a photoinitiator that generates highly reactive radical fragments but in only very low numbers, will presumably not perform with a high initiation efficiency, as observed for the amine substituted benzoin NMe₂Bz, NMe₂Bz Iso, and FNMe₂Bz in Figure 4.

Conclusions

Our study of benzoin-type photoinitiators demonstrates that a set of parameters are required in order to quantify their efficiencies. Among these are low ground state absorption at the excitation wavelength – usually characterized by an $n\pi^*$ singlet state. In agreement with recent results,³ the subsequent ISC should occur on a time scale of 2 ps. Ideally the resulting triplet state is of $n\pi^*$ character as well, which is in line with previous findings.²⁷ The number of triplet states below the lowest singlet states should not exceed two with at least one of them being of $n\pi^*$ character. The time constant for the α -cleavage should be within 100 ps (typically 25 to 50 ps). Further, the number of singlet states below the lowest singlet state, so-called dark states (one-photon forbidden states), should be zero since otherwise the internal conversion is too fast with respect to ISC – presumably due to the occurrence of conical intersections. This has been shown previously for mesitol.¹⁷ Finally, using molecules with two highly reactive radical species such as DFB is not beneficial owing to the existence of too many triplet states below the lowest excited singlet state. Note that these rules do not necessarily make those molecules useless in case they do not fulfil all of these issues perfectly. However, they will certainly lack a considerable amount of conversion efficiency as observed for benzil and difluorobenzil, for instance.

As implied by the preceding conclusions an a priori identification of good photoinitiators is not possible by simply inspecting one of the aforementioned properties. It is the interplay between different characteristics that needs to be addressed. It remains for future investigations to examine this approach for other types of photoinitiators.

ASSOCIATED CONTENT

Supporting Information. Results of quantum chemical calculations, evaluation of transient data, amplitude calculations, normalized TA traces, and singlet absorption bands. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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