Quantifying the Efficiency of Photoinitiation Processes in Methyl Methacrylate Free Radical Polymerization via Electrospray Ionization Mass Spectrometry

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ABSTRACT: Photolytically generated radicals (at a wavelength of 351 nm) derived from the acetophenone-type photoinitiators benzoin (2-hydroxy-1,2-diphenylethanone) and mesitil (1,2-dimesitylethane-1,2-dione) (specifically the benzoyl and mesitoyl radicals) are quantified in their ability to serve as initiating species in methyl methacrylate (MMA) bulk free radical polymerizations at 5 °C. The polymerizations are initiated by the pulsing action of a high-frequency excimer laser (100 Hz) operated at the 351 nm XeF line. The pulsing action of the laser serves to limit the molecular weight of the generated polymer to allow its analysis via electrospray ionization mass spectrometry (ESI-MS) employing a quadrupole ion trap analyzer. MMA-derived propagating radicals terminate to a large proportion via disproportionation. These disproportionation products can be unambiguously detected via ESI-MS. The resulting disproportionation signals can—within each repeat unit and over the entire mass spectrum—be quantitatively evaluated. The ratio of benzoyl and mesitoyl end groups is demonstrated to be independent of the polymer chain length, and no mass bias is observed in the ESI-MS spectra. Benzoin and mesitil are employed in variable ratios in the reaction mixture as a cocktail. A plot of the ratio of benzoyl to mesitoyl end groups vs the ratio of both initiators in the reaction mixture indicates that the benzoyl radical is 8.6 times more likely to initiate the polymerization process than the mesitoyl fragment.

Introduction

Photopolymerizations constitute an important avenue for the preparation of synthetic polymers in both industry and academia and can be achieved through the use of photoinitiators, photo-cross-linkable polymers, and photo-cross-linking agents.[1] Photoinitiators are used for the polymerization of functional monomers, oligomers, and polymers[2] for use in applications including UV-curing of coatings and inks as well as for more specialized applications such as dental restorative materials[3,4] and biomaterials.[5,6] In here, we employ electrospray ionization mass spectrometry (ESI-MS) to quantitatively assess the ability of two specific photolytically generated radical fragments to initiate the bulk free radical polymerization of methyl methacrylate (MMA) at 5 °C. Despite a range of studies on photoinitiation processes of various photoinitiators, there is almost no quantitative information available on the initiation efficiency of photoinitiators obtained from polymerizing systems, which provides concrete numbers on the effectiveness of one radical species over another to serve as initiating species. Such quantitative information is of significant help when choosing optimum radical fragment combinations for applications ranging from photocuring in the realm of material science to mechanistic and kinetic investigations, where the selection of radical fragments that exclusively terminate polymerization activity can be of importance.[7] For the present initial quantitative study we select MMA as the monomer, as it is a key monomer in several UV-curing applications, photoimaging, and kinetic studies (see for example refs 8−11). In previous investigations employing mass spectrometry to qualitatively study photoinitiation process via ESI-MS mass spectrometry,[12−14] we have mapped in great detail the reaction products which are generated during the pulsed laser-induced photoinitiation employing variable acetophenone-type initiators with a wide range of monomer classes including acrylates, methacrylates, and itaconates. Such detailed polymer end-group analysis has become feasible by the rise of soft-ionization mass spectrometry techniques, namely, matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-ToF-MS)[15,16] and ESI-MS coupled with quadrupole ion trap and/or time-of-flight detectors.[17−19] The potential of mass spectrometric analysis for synthetic polymers has been discussed in numerous publications and review articles.[20−23] ESI-MS is one of the most powerful mass spectrometry techniques (as it provides very soft ionization conditions) and has been employed to study the mechanism and kinetics of a wide range of polymer systems, ranging from living/controlled radical polymerizations[24−26] to thermal initiation processes.[27−29]

The reason for employing a pulsed laser as UV radiation source in the present study to deposit photons into the polymerization system is twofold: First, and most importantly, the rapid pulsing action of the laser allows for fine control over the molecular weight of the generated polymers. The length of the generated polymer chains is essentially controlled via the time a polymer chain has to grow between two consecutive laser pulses; a higher pulsing frequency leads to a lower DP_n. Thus, the use of a pulsed laser system is a paramount precondition for studying photoinitiation processes with ESI-MS, as it represents a convenient avenue to providing low molecular weight polymers which fall within the ESI-MS m/z window of below 4000 m/z. Second, the laser light is highly monochromatic (in here a wavelength of 351 nm is employed) and thus provides a defined and stable energy input into the polymerization system.

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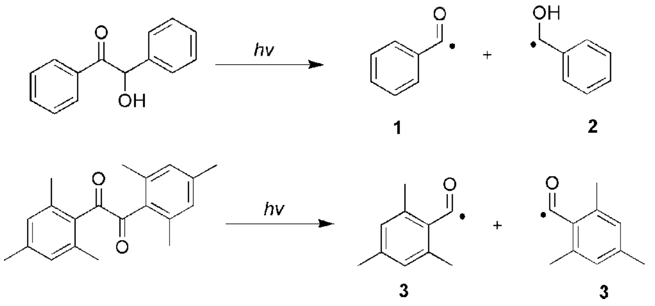
Scheme 1. Photolytic Decomposition Pattern of Benzoin and Mesitil into Their Radical Fragments[a]



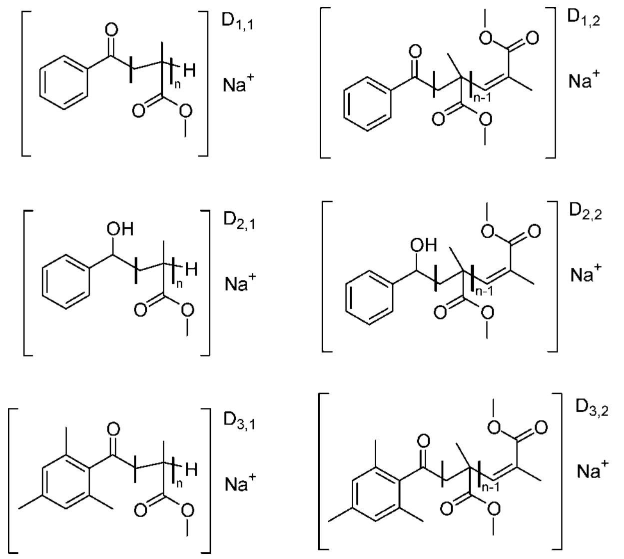
[a] In the present study, the efficiency of the benzoyl fragment (**1**) to initiate the free radical bulk polymerization of methyl methacrylate (MMA) is quantitatively compared to that of the mesitoyl (**3**) fragment. For this purpose mixtures of benzoin and mesitil are employed (for details see text).

The choice of studying the comparative reactivity of benzoyl vs mesitoyl radicals is driven by our previous qualitative finding that the mesitoyl fragment seems to display a very poor ability to react with MMA or other monomers after its generation from a phosphoryl-type photoinitiator (and thus initiate its polymerization).[12] This finding is in contrast to the generally high ability of benzoyl radical fragments to initiate macromolecular growth.[12] The primary aim of the current study is thus to quantify this efficiency difference (observed when using benzoin and mesitil initiators) via the following experimental strategy: Mixtures of benzoin and mesitil (ranging from equimolar composition to a large excess of mesitil) are prepared and subjected to pulsed laser initiation. The generated polymer is isolated and subjected to direct infusion ESI-MS.[23] Via the mass spectral evaluation procedure described in detail below, the ratio of benzoyl to mesitoyl radical fragments that have initiated macromolecular growths is plotted as a function of the ratio of both initiators in the reaction mixture. Evaluation of such a plot (see below for a procedure describing this process) provides a quantitative measure of the ratio of the initiation ability of both radical fragments. Within the present study we thus introduce a methodology that may be employed to quantitatively assess comparative radical reactivities for a range of photoinitiators.

Scheme 1 shows the chemical structure of both employed initiators as well as their UV-light-induced radical decomposition products. Scheme 2 depicts the expected disproportionation products which are (almost exclusively at this temperature)[30] formed in the presence of MMA as monomer. Note that the disproportionation product having radical fragment **2** as end group is not subject of the present study (for details why this is the case see below).

Before discussing the results of the investigation in detail, it is important to clarify a particular aspect of the present work. In here, we determine in a quantitative fashion the ratio in which the benzoyl and the mesitoyl radical fragments are initiating macromolecular growth. However, knowledge of this ratio does not necessarily allow a conclusion about the reactivity of both fragments toward MMA because it is possible that the observed ratio of the initiation ability is a reflection of the fact that the number of each radical species that is available to react with MMA is different. It is a well-known fact that the initiators' ability to absorb UV light, the primary quantum yields, and cage reactions directly after the birth of the individual radical fragments may indeed be different for both initiators so that the amount of radicals generated from each initiator may differ, and a different number of radicals is available to initiate macromolecular growth. It is, however, very important to note that beyond the difficulty in clarifying the actual individual radical reactivity toward a vinyl monomer, the data presented in here may be viewed from the perspective of the employed initiators rather than from the perspective of the generated radicals. Via such an approach, the data presented in the current study provide an unambiguous value for the effectiveness of the benzoin vs mesitil initiators to provide benzoyl and mesitoyl radicals to initiate the free radical polymerization of methyl methacrylate.

Scheme 2. Expected Polymeric Disproportionation Peaks in the Photochemically Initiated Bulk Free Radical Polymerization of Methyl Methacrylate (MMA) in the Presence of a Cocktail of the Benzoin and Mesitil Photoinitiators Depicted in Scheme 1[a]



[a] Note that the position of the double bond in the unsaturated disproportionation product may also be at the site of the (former) α-methyl group. See Table 1 for a collation of the mass of the individual radical fragments.

Table 1. Collation of the Polymeric Product Signals Observed during ESI-MS of Poly(methyl methacrylate) Samples Generated during the Pulsed Laser Initiated Bulk Free Radical Polymerization of MMA at Ambient Temperature[a]

species	ionization	$(m/z)^{\mathrm{theo}}$/Da	$(m/z)^{\mathrm{exp}}$/Da	$\Delta m/z$
$D_{1,2}$	Na^+	1327.6	1327.7	0.1
$D_{1,1}$ and $D_{2,2}$	Na^+	1329.7	1329.6	0.1
$D_{2,1}$	Na^+	1331.7	1331.7	0
$D_{3,2}$	Na^+	1369.7	1369.7	0
$D_{3,1}$	Na^+	1371.7	1371.7	0

[a] The table provides experimentally observed as well as the theoretically expected masses for the found disproportionation products (that consist of 11 monomer units, i.e., for $n = 11$ in Scheme 2). The structures corresponding to the individual peaks are depicted in Scheme 2. The tabulated values correspond to the peaks displayed in Figure 1.

Experimental Section

Materials. Methyl methacrylate (MMA, Fluka, 99%) monomer was deinhibited over a column of activated basic alumina. Benzoin (Aldrich) was recrystallized twice in ethanol prior to use. Tetrahydrofuran (THF, Aldrich, 99%), *tert*-butyllithium (*t*-BuLi, Aldrich) and carbon monoxide (CO, BOC gases, 5.0) were used as received without any further purification.

Synthesis of 1,2-Dimesitylethane-1,2-dione (Mesitil). The following preparation procedure was adapted from a combination of refs 31 and 32. 5 g (25 mmol) of mesitil bromide was dissolved into 25 mL of dry tetrahydrofuran (THF). 2 mol equiv of *t*-BuLi solution (1.7 M) in hexane was added dropwise under oxygen- and water-free conditions. Argon was used as inert gas in the reaction flask. The reaction flask was placed into an acetone/liquid nitrogen mixture while adding the *t*-BuLi. The reaction mixture was stirred for 2 h and was subsequently allowed to thaw to ambient temperature. Once at ambient temperature, $CO_{(g)}$ was percolated through the reaction flask for ~45 min. A color change from red/brown to dark green occurs as soon as the CO is introduced into the reaction mixture. After the CO percolation, saturated NH_4Cl solution was added dropwise to the reaction flask, which was subsequently separated into an aqueous and organic phase. The organic phase was dried over $MgSO_4$ followed by the evaporation of all solvent. Primary purification is achieved via column chromatography using a 1:4 mixture of ethyl acetate/hexane. The first column chromatography results in a crude product, and a second column chromatography is carried out on the collected crude product to further purify the compound. Recrystallization in ethanol gives the final mesitil product in the form of orange plate crystals. ESI-MS: 294.2 Da (found), 294.16 Da (calculated). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.20 (s, 12H), 2.30 (s, 6H), 6.88 (s, 4H).

Polymerizations. All MMA samples consisted of monomer (sample volume ~ 1.0 mL) with a mixture of both photoinitiators with an overall concentration of $c_{PI} = 5 \times 10^{-3}$ mol L^{-1}. The samples were carefully freed of oxygen prior to laser irradiation by purging the reaction mixture with high-purity nitrogen. Polymerization was achieved (at $T = 5$ °C) by laser pulses generated from a Lambda Physik COMPex Pro 110 XeF (351 nm, 20 ns pulse width) excimer laser system at constant frequency of 100 Hz for an overall polymerization time of ~15 min. Single pulse energy ranged between 5 and 25 mJ. More details regarding the laser setup and sample methodology have been described previously.[14]

UV Spectra. UV/vis spectra were recorded at ambient temperatures using a Varian Cary 300 Bio photospectrometer.

Electrospray Ionization Mass Spectrometry. ESI-MS experiments were carried out using a Thermo Finnigan LCQ Deca quadrupole ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA) as well as a Thermo Finnigan LXQ linear quadrupole ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA) in positive ion mode. The ESI-MS is equipped with an atmospheric pressure ionization source which operates in nebulizer-assisted electrospray mode. The instrument was calibrated with caffeine, MRFA, and Ultramark 1621 (all from Aldrich) in the mass range 195−1822 amu. All spectra were acquired over the mass-to-charge range (*m/z*) of 150−2000 Da with a spray voltage of 5 kV, a capillary voltage of 39 V, and a capillary temperature of 275 °C. Nitrogen was used as sheath gas (flow: 40% of maximum) while helium was used as auxiliary gas (flow: 5% of maximum in all experiments). The eluent was a 3:1 v/v mixture of dichloromethane:methanol with polymer concentration being around 0.4 mg mL^{-1}.

Results and Discussion

The upper part of Figure 1 provides a depiction of an entire ESI mass spectrum recorded from a polymer sample generated via the pulsed laser polymerization of MMA in the presence of a 1:2.5 mixture of benzoin and mesitil. The lower part of the figure shows a representative repeat unit from the above mass spectrum, with every peak being labeled according to the following nomenclature: Disproportionation peaks occur in pairs removed by 2 amu. Thus, each peak is labeled $D_{n,1 \text{ or } 2}$ where n denotes the radical fragment that has initiated the polymerization. The expected and found masses for the depicted representative repeat unit are collated in Table 1. The also (to a much lesser part) occurring combination products can be found at double the molecular weight of the disproportionation products.

Inspection of Table 1 shows that the found and theoretically expected masses agree well within the accuracy of the mass spectrometric analysis (±0.2 Da). Such excellent agreement is found in every repeat unit and is representative for any initiator cocktail composition employed within the current study. Before proceeding to a quantitative analysis of the individual disproportionation peaks, it is worthwhile to briefly provide a qualitative description of how the ESI-MS spectrum changes with increasing amounts of mesitil in the initiation cocktail.

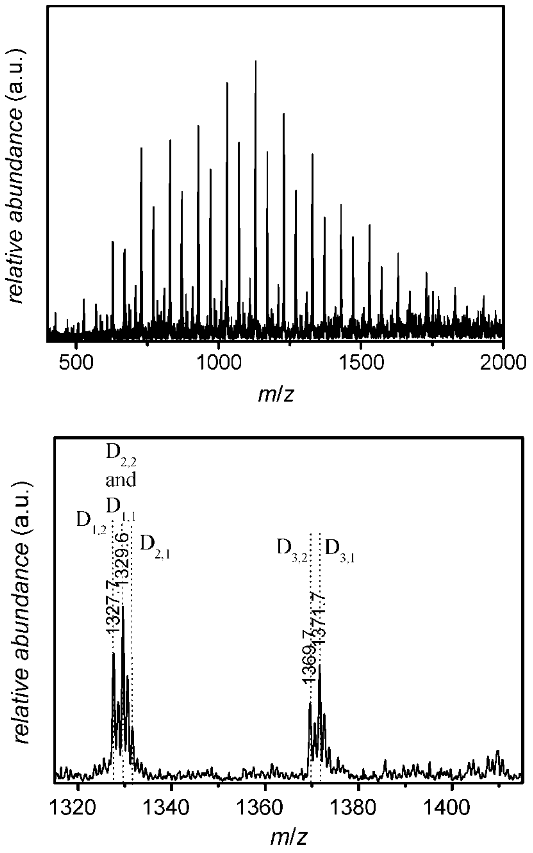


Figure 1. ESI-MS spectra of the polymeric material obtained from the benzoin/mesitil-initiated ($c_{\text{ini},0} = 5 \times 10^{-3}$ mol L^{-1}) PLP of MMA_{bulk} at 5 °C at a laser intensity of 5 mJ and a frequency of 100 Hz. Top: full scan between 400 and 2000 *m/z*. Bottom: zoom scan of one monomer repeat unit between 1315 and 1415 *m/z*. The nomenclature employed to identify the individual disproportionation products is provided in Scheme 2.

Figure 2 depicts the *m/z* region (from a representative repeat unit) of the disproportionation peaks $D_{3,1}$ and $D_{3,2}$ as a function of the initiator cocktail composition. For each cocktail composition, the spectrum was normalized (within the repeat unit under consideration) to the peak $D_{1,2}$ (at 1127.7 Da), i.e., the (free from isobaric interference, see below) disproportionation product peak corresponding to polymer chains initiated with a benzoyl fragment. Inspection of Figure 2 demonstrates that with increasing amounts of mesitil in the reaction mixture the number of chains carrying a mesitoyl end group increases. Qualitatively, one can also note that relatively large amounts of mesitil in the initiation cocktail need to be present to achieve a significant signal. To put this qualitative observation onto a quantitative basis, the disproportionation peaks corresponding to the chains initiated with mesitoyl radicals (**3**) depicted in Figure 2 are placed in relation to the peaks associated with chains initiated by benzoyl fragments (**1**). The specific evaluation procedure applied to arrive at quantitative ratios of **1** to **3** as species that have started macromolecular growth will be detailed below. Before progressing to the particulars of the analysis procedure, the following should be noted: The signals which are directly compared via eq 1 and/or eqs 2−4 have to show no isobaric overlap with any other peak. The depicted exemplary disproportionation peak ensemble (see Figure 3) for chains initiated with **1** or **2** demonstrates that only the peak labeled $D_{1,2}$ is free of isobaric interference. The isotopic pattern associated with $D_{1,1}$, $D_{2,2}$, and $D_{2,1}$ all overlap with each other, making their quantitative evaluation nonfeasible. These isobaric overlaps also do not allow obtaining quantitative information about the initiation ability of **2** to be obtained. In addition, it is important

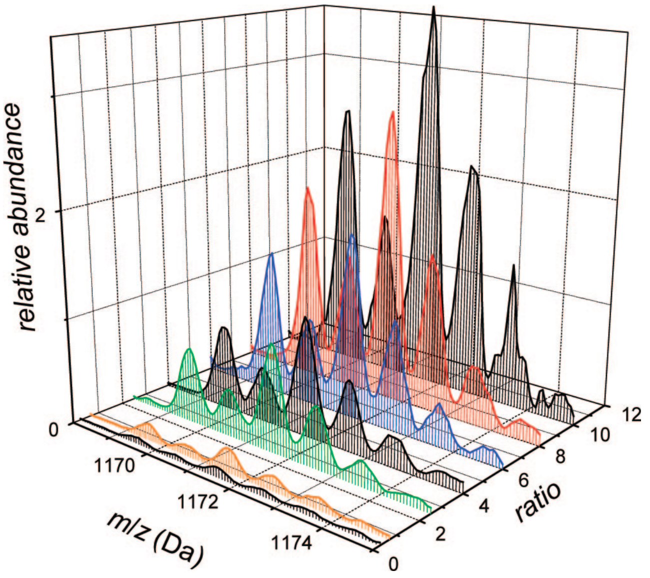


Figure 2. 3-Dimensional plot of the intensity of the variation of the mass spectroscopic signal of the disproportionation peak $D_{3,1}$ and $D_{3,2}$ (i.e., chains which have been initiated via a mesitoyl radical) as a function of the composition of the photoinitiator cocktail (ratio = n_{mesitil}:n_{benzoin}). Clearly visible is the constant increase of the amount of mesitil initiated polymer chains with increasing amounts of mesitil in the cocktail. The relative abundance was determined by normalizing each individual spectrum with respect to the (benzoin derived) peak at 1127.7 Da ($D_{1,2}$).

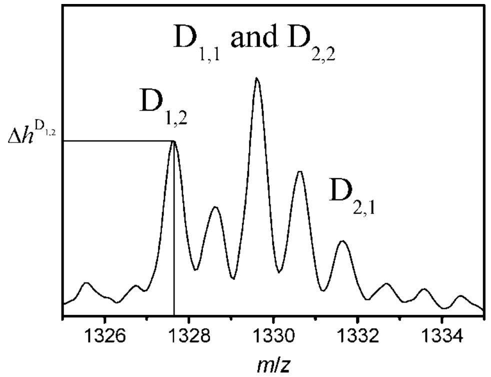


Figure 3. Enlarged section of the disproportionation peak ensemble associated with polymer chains initiated by radical fragment **1** or radical fragment **2**. The signal employed for evaluation purposes is $D_{1,2}$ as it is the only isotopically nonoverlapping signal.

to compare disproportionation products that carry the same end group, i.e., saturated vs nonsaturated. Given the isobaric overlap of $D_{2,1}$ with $D_{2,2}$, the only choice for quantitatively evaluating the mass spectra is a comparison between $D_{1,2}$ and $D_{3,2}$. Figure 3 also shows how the height $\Delta h^{D_{1,2}}$ is defined which is employed in the mass spectrometric data evaluation procedure, which is now described in detail.

Data Analysis and Evaluation of the ESI-MS Spectra. In the following the procedure of evaluating the obtained ESI-MS spectra will be detailed. In an ideal scenario, one would have mass spectra at hand that display no mass bias at all. In reality, there may always be a certain amount of mass bias present, and it is important to test for its occurrence. In the most simple and straightforward approach for evaluating the mass data in the present study, the height of the only two peaks that do not show isobaric overlap (i.e., $D_{1,2}$ and $D_{3,2}$, the species of interest), $\Delta h^{D_{n,2}}$, is evaluated in each repeat unit. Figure 3 provides a graphical representation on how $\Delta h^{D_{n,2}}$ is determined. As the height of the peak (alternatively the integral could be employed)[33] is proportional to the number of molecules corresponding to the associated mass, the individual peak heights can be employed to arrive at the mole fraction of the disproportionation product $D_{1,2}$, F, via eq 1. Note that F is given as $F(i)$, as it can be evaluated in every repeat unit, with i being the chain length to which the repeat unit corresponds. It is important to note that this mole fraction does not consider the entirety of all disproportionation products generated during the polymerization (i.e., $D_{1,2}$, $D_{1,1}$, $D_{2,2}$, $D_{2,1}$, $D_{3,1}$, and $D_{3,2}$; see Scheme 2 for the corresponding structural definitions), but only $D_{1,2}$ and $D_{3,2}$. The factor 2 in front of $\Delta h^{D_{1,2}}$ arises because each mesitil initiator yields two mesitoyl radicals, whereas each benzoin fragment only generates one benzoyl radical fragment. Further below, a detailed account is provided on the results of evaluating the mass spectrometry data via eq 1.

$$F(i) = \frac{\Delta h^{D_{3,2}}(i)}{\Delta h^{D_{3,2}}(i) + 2\Delta h^{D_{1,2}}(i)} \tag{1}$$

While eq 1 can be a valuable tool, it does not take into account any potential chain length dependent ionization mass biases other than evaluation of every repeat unit. However, there exist approaches which can be employed to try to eliminate the mass biases. In here, we adopt (and modify for our purposes) the elegant approach taken by Günzler et al. in previous quantitative mass spectrometric evaluations.[33] The modified approach we take in here is as follows: Let $G(i)$ be the ratio of the peak heights of $D_{3,2}$ and $D_{1,2}$ $\forall\ i$. Nota bene: This ratio may directly be plotted against chain length, i, and yields identical information to $F(i)$ as $F(i) = G(i)(G(i) + 1)^{-1}$. Now define $G'(i,i-1)$ and $G''(i,i+1)$ in a similar manner to $G(i)$, however taking the height of $D_{3,2}$ ($\Delta h^{D_{3,2}}$) from one repeat unit higher than $D_{1,2}$ (eq 3) or lower than $D_{1,2}$ (eq 4). Thus, the vectors $G(i)$, $G'(i,i-1)$, and $G''(i,i+1)$ are obtained.

$$G(i) = \frac{\Delta h^{D_{3,2}}(i)}{2\Delta h^{D_{1,2}}(i)} \tag{2}$$

$$G'(i, i-1) = \frac{\Delta h^{D_{3,2}}(i)}{2\Delta h^{D_{1,2}}(i-1)} \tag{3}$$

$$G''(i, i+1) = \frac{\Delta h^{D_{3,2}}(i)}{2\Delta h^{D_{1,2}}(i+1)} \tag{4}$$

In a subsequent step, $G(i)$, $G'(i,i-1)$, and $G''(i,i+1)$ are individually averaged $\forall\ i$, yielding the average values $\langle G\rangle$,$\langle G'\rangle$, and $\langle G''\rangle$. $\langle G\rangle$ corresponds to the average ratio of $\Delta h^{D_{n,2}}$ within the same repeat unit (mass difference between the compared peaks is $\Delta m/z = 42$ Da), $\langle G'\rangle$ corresponds to the average ratio of $\Delta h^{D_{n,2}}$ within two repeat units with the second repeat unit being at smaller molecular weights ($\Delta m/z = -58$ Da), and $\langle G''\rangle$ corresponds to the average ratio of the $\Delta h^{D_{n,2}}$ within two repeat units with the second repeat unit being at larger molecular weights ($\Delta m/z = +142$ Da). With $\langle G\rangle$, $\langle G'\rangle$, and $\langle G''\rangle$ now at hand, one can plot these values against $\Delta m/z$. The y-intercept ($\Delta m/z = 0$) of such a plot yields $\langle G\rangle_{\Delta m/z,0}$, which represents the mass bias free ratio of the two disproportionation products $D_{3,2}$ and $D_{1,2}$ in the polymer sample. In systems where the mass bias is negligible, all the evaluation procedures, i.e., averaging $F(i)$, $G(i)$ and calculating $\langle G\rangle_{\Delta m/z,0}$, should give (near) identical results. In the present system, nearly ideal conditions are observed, as will be demonstrated below.

As shown in the data analysis section above, it is relatively simple to arrive at eq 1 which gives the mole fraction, $F(i)$, of mesitoyl radicals that have initiated the polymerization process as a function of the analyzed chain length, i. Figure 4 depicts how $F(i)$ varies with increasing amounts of mesitoyl initiator

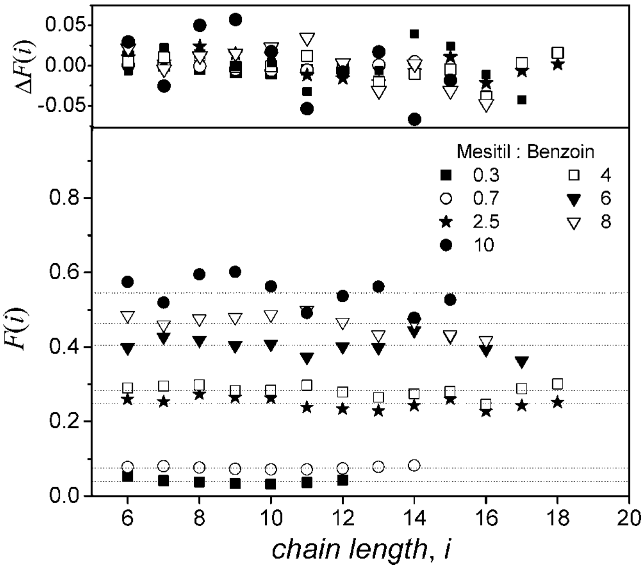


Figure 4. Intensity-derived mole fractions of polymer chains initiated with mesitoyl radicals, $F(i)$, vs the chain length, i. The dotted lines give the average of the mole fraction over the entire chain length range. The upper part of the figure depicts the residual ($\Delta F(i)$, the deviation of each measured data point from the average value derived from all data points as a function of chain length for a given ratio of mesitil to benzoin), demonstrating that $F(i) = F$.

in the initiator cocktail. Two important observations can be made from Figure 4: (i) $F(i) = F$, i.e., there is no dependence of F on the mass range that has been analyzed, implying that mass bias effects are not pronounced. The upper part of Figure 4 shows the residual $\Delta F(i)$, and one can clearly observe that all data points scatter around the zero line, indicating that no systematic dependence of F on i is observed. (ii) Between 8 and 10 times excess of mesitoyl over benzoin is required to have an identical number of chains initiated with mesitoyl and benzoyl radical fragments. Note that equal initiation ability would be observed at $F = 0.5$, which lies between the data series representing the ratios of 10:1 (closed circles) and 8:1 (open triangles).

As has been detailed above, it is possible to not plot F but rather G (or more correctly $\langle G\rangle_{\Delta m/z,0}$, the mass bias corrected variant of $G(i)$) vs the initiator cocktail composition, as such a plot (which gives the direct ratio of chain initiated with mesitoyl fragments over those initiated with benzoyl radicals) allows for a direct and quantitative comparison of the initiation efficiency of benzoin and mesitoyl with respect to the derived benzoyl and mesitoyl radicals. Such a plot is given in Figure 5. Inspection of Figure 5 immediately reveals that a linear correlation exists between the ratio of benzoin to mesitil in the reaction mixture and the mass bias corrected ratio, $\langle G\rangle_{\Delta m/z,0}$, of the benzoyl and mesitoyl radicals that have initiated the polymerization process. Parity in the initiation between mesitil and benzoin derived fragments ($\langle G\rangle_{\Delta m/z,0} = 1$) occurs at an initiator cocktail composition of 8.6 (as indicated in the figure).

Upon inspection of Figure 5, one could come to the conclusion that benzoyl radicals are a factor 8.6 more efficient in reacting with MMA monomer units and initiating macromolecular growth. However, it is also possible that the number of radicals which are available to initiate macromolecular growth differs for both photoinitiators. Two main factors can contribute to this: (i) the efficiency with which both initiators absorb the incident UV light differs and thus a different number of radicals is generated per laser pulse and (ii) the quantum yield for primary radical production, Φ. The primary quantum yield is composed of processes that occur after irradiation and absorption has taken place and consists of several deactivation mechanisms including the quantum yield for intersystem crossing Φ_{ISC} (going from an S_1 state to a T_1 state), the radical quantum yield, Φ_R (i.e., efficiency with which the triplet state of the photoinitiator molecule is depopulated by processes that do not lead to the formation of primary radicals), and the efficiency at which the generated radicals escape in-solvent-cage reactions, Φ_{RM}. The quantum yield for intersystem crossing is rather high for ketones,[34] so that in a good approximation Φ_{ISC} can be set to unity. Thus, the overall quantum yield of the initiation process only depends on Φ_R and Φ_{RM}. In free radical polymerization, these reactions include deactivation by molecular oxygen. In the present study, the reaction mixture was carefully freed of oxygen prior to laser irradiation, and thus a significant deviation of Φ_R from unity is unlikely. In addition, the shorter the lifetime of the triplet state T_1, the fewer the chances that deactivation processes can reduce Φ_R. An initiator similar to benzoin and mesitil is 2,2-dimethoxy-2-phenylacetophenone (DMPA), which features a rather short triplet lifetime of $\tau < 0.1$ ns.[35] Given these short triplet lifetimes coupled with the fact that the reaction solutions were freed of oxygen places Φ_R—as stated above—close to unity. The quantum yield Φ_{RM}, which governs the formation of the available initiating radicals, is often termed the initiator efficiency. The initiator efficiency (i.e., Φ_{RM}) is influenced by the ability of the nascent radicals to diffuse from their birth solvent cage to the reaction site, i.e., the monomer units. For both initiators, there is currently no information available on the value of Φ_{RM}. Recall, however, that the absolute value of Φ_{RM} is irrelevant for the present study as we are comparing the efficiency of two radicals to initiate macromolecular growth. Given that both the benzoin and mesitil photoinitiators are structurally similar, one could expect that the difference in Φ_{RM} may not be overly large and may be not as large as the factor 8.6 difference observed in the initiating end-group amounts. Clearly, a firm statement on Φ_{RM} and its difference for both initiators is not possible; however, two points should be kept in mind. First, the value of Φ_{RM} will depend strongly on the solvent environment and nature of the solvent cage, as this will determine the radicals' ability to escape and initiate the polymerization process. Second, the rate of recombination of the nascent radical fragments within the solvent cage may differ for the mesitoyl and the benzoyl radicals. Within the solvent cage, these reactions are governed by the individual radical reactivities (determined by the electronic and steric situation at the radical site) that may indeed be different for both fragments and thus lead to different Φ_{RM} values.

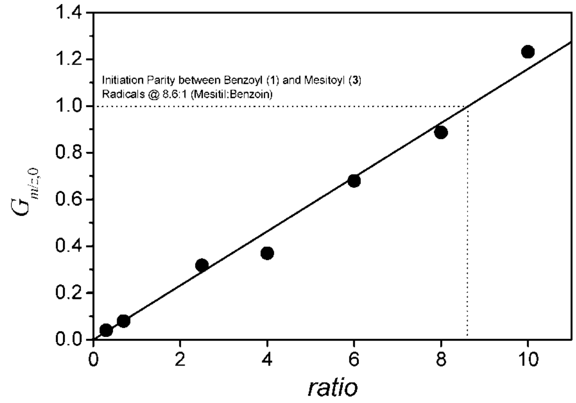


Figure 5. Plotted is the ratio of the intensities of the disproportionation signals corresponding to polymer chains initiated with a benzoyl and a mesitoyl radical vs the ratio of both initiators in the reaction mixture (ratio = $n_{\text{mesitil}}:n_{\text{benzoin}}$). An evaluation procedure has been adopted, which allows for the minimization of mass bias and yields the mass bias free intensity ratio $\langle G\rangle_{\Delta m/z,0}$ (refer to the Data Analysis section for a detailed description of the evaluation procedure).

We have not yet considered in detail the possibility that both initiators absorb UV light with a very different efficiency at 351 nm (see point i in the above section), and thus the observed end-group difference is a reflection of the initiators ability to absorb photons. To some extent, one can estimate whether an absorption phenomenon can contribute to the difference: If benzoin and mesitil have a different absorptivity at 351 nm (at equal concentrations), then it is a corollary that they also have a different efficiency in absorbing the photons. At a concentration of 10^{-3} mol L^{-1} (in methanol) and an optical path length of 10 mm, benzoin and mesitil have an absorption of 0.09 and 0.9, respectively, as measured in the current study. This is a highly interesting result: The initiator (mesitil) which absorbs *more* photons (by a factor of 10) yields radicals that are a factor of 8.6 *less* likely to be found as initiating groups in the polymer. Under the premise that Φ_{RM} is equal for both initiators, one is tempted to multiply both factors to arrive at the true reactivity of the mesitoyl vs the benzoyl radicals toward MMA (and obtain a factor 86 in reactivity difference). However, we wish to abstain from such an exercise and merely note that, on the balance of the above arguments, it is highly likely that a significant part of the observed difference in the ability of benzoin and mesitil to provide respectively benzoyl and mesitoyl initiated chains is caused by a difference in their reactivity toward the monomer MMA and not solely by a potential difference in the respective Φ_{RM} values. To even achieve a parity in radical reactivity, the primary radical yield of mesitil would have to be a factor of 86 less than that of benzoin: a highly unlikely scenario.

Conclusions

In the present contribution we have provided—for the first time from a polymerizing system—quantitative information on the initiation abilities of two radical moieties commonly contained in acetophenone photoinitiators. Benzoin and mesitil were employed as sources for benzoyl and mesitoyl radicals. To quantitatively assess the relative efficiency of each radical fragment to initiate macromolecular growth, pulsed laser polymerizations (at 351 nm) of MMA were initiated with cocktails of benzoin and mesitil of varying composition (1:0.3 to 1:10 benzoin vs mesitil). A plot of the relative amounts in which both fragments were found in the disproportionated chains in the polymer indicates that benzoyl radicals are close to a factor 8.6 more likely to initiate macromolecular growths than mesitoyl radicals. This quantitative finding is in good agreement with earlier qualitative observations that mesitoyl radicals may be poor initiating entities. It is also pleasing to note that—at least in the present system—mass-dependent ionization biases are minimal. At least for MMA, one can come to the conclusion that initiators containing mesitoyl (such as 2,4,6-trimethylbenzoyldiphenyl phosphinoxide) may be improved by exchanging the mesitoyl moiety by a benzoyl fragment.[12,36] On the balance of all available data, the strong discrepancy in initiating macromolecular growth is due to a significant part to the reactivity difference between mesitoyl and benzoyl radicals and probably only to a lesser degree to different effective radical concentrations generated from mesitil and benzoin. Ongoing studies in our laboratories are also currently exploring whether the origin of a radical species (i.e., from which photoinitiator) has an influence on its ability to serve as an initiating species for various monomers.

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References and Notes

(1) Gruber, H. F. *Prog. Polym. Sci.* **1992**, *17*, 953–1044.
(2) Kaur, M.; Srivastava, A. K. *J. Macromol. Sci., Part C: Polym. Rev.* **2002**, *42*, 481–512.
(3) Ge, J.; Trujillo, M.; Stansbury, J. W. *J. Dent. Mater.* **2005**, *21*, 1163–1169.
(4) Anseth, K. S.; Newman, S. M.; Bowman, C. N. *Adv. Polym. Sci.* **1995**, *122*, 177–217.
(5) Fisher, J. P.; Dean, D.; Engel, P. S.; Mikos, A. G. *Annu. Rev. Mater. Res.* **2001**, *31*, 171–181.
(6) Anseth, K. S.; Metters, A. T.; Bryant, S. J.; Martens, P. J.; Elisseeff, J. H.; Bowman, C. N. *J. Controlled Release* **2002**, *78*, 199–209.
(7) Junkers, T.; Wong, E. H. H.; Szablan, Z.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2008**, *29*, 503–510.
(8) Buback, M.; Feldermann, A.; Barner-Kowollik, C.; Lacik, I. *Macromolecules* **2001**, *34*, 5439–5448.
(9) Buback, M.; Junkers, T.; Vana, P. *Macromol. Rapid Commun.* **2005**, *26*, 796–802.
(10) Buback, M.; Egorov, M.; Felderman, A. *Macromolecules* **2004**, *37*, 1768–1776.
(11) Szablan, Z.; Stenzel, M. H.; Davis, T. P.; Barner, L.; Barner-Kowollik, C. *Macromolecules* **2005**, *38*, 5944–5954.
(12) Szablan, Z.; Junkers, T.; Koo, S. P. S.; Lovestead, T.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromolecules* **2007**, *40*, 6820–6833.
(13) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Aust. J. Chem.* **2002**, *55*, 315–318.
(14) Szablan, Z.; Lovestead, T. M.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromolecules* **2007**, *40*, 26–39.
(15) Nielen, M. W. F. *Mass Spectrom. Rev.* **1999**, *18*, 309–344.
(16) Raeder, H. J.; Schrepp, W. *Acta Polym.* **1998**, *49*, 272–293.
(17) Tanaka, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3861–3870.
(18) Saf, R.; Mirtl, C.; Hummel, K. *Acta Polym.* **1997**, *48*, 513–526.
(19) Lovestead, T. M.; Hart-Smith, G.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromolecules* **2007**, *40*, 4142–4153.
(20) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527–569.
(21) Montaudo, G. *Trends Polym. Sci.* **1996**, *4*, 81–86.
(22) Scrivens, J. H.; Jackson, A. T. *Int. J. Mass Spectrom.* **2000**, *200*, 261–276.
(23) Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Polymer* **2004**, *45*, 7791–7805.
(24) Chaffey-Millar, H.; Hart-Smith, G.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1873–1892.
(25) Gruendling, T.; Hart-Smith, G.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromolecules* **2008**, *41*, 1966–1971.
(26) Hart-Smith, G.; Lovestead, T.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Biomacromolecules* **2007**, *8*, 2404–2415.
(27) Buback, M.; Frauendorf, H.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4266–4275.
(28) Buback, M.; Frauendorf, H.; Günzler, F.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2453–2467.
(29) Buback, M.; Frauendorf, H.; Günzler, F.; Vana, P. *Polymer* **2007**, *48*, 5590–5598.
(30) It is worthwhile to note the Russell and colleagues observe up to 40% combination products in their ESI-MS assessment of MMA polymerizations.[33] Nota bene: the amount of combination does not affect the methodology of our present approach.
(31) Rathman, T. L.; Woltermann, C. J. *PharmaChem* **2003**, *2*, 6–8.
(32) Nudelman, N.; Schulz, H. *J. Chem. Res.* **1999**, 422–423.
(33) (a) Günzler, F. PhD Thesis, Göttingen, **2008**. (b) Buback, M.; Günzler, F.; Russell, G. T.; Vana, P. *Macromolecules* **2009**, *42*, 652−662.
(34) Turro, N. J. In *Macromolecular Photochemistry*; University Science Books: Sausalito, 1991, ISBN 0-935702-71-7.
(35) Fouassier, J. P.; Jacques, P.; Lougnout, D. J.; Pilot, T. *Polym. Photochem.* **1984**, *5*, 57–76.
(36) Wyzgoski, F. J.; Polce, M. J.; Wedemiotis, C.; Arnould, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2161–2171.

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