

Benzoin Type Photoinitiator for Free Radical Polymerization

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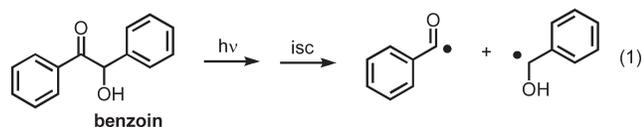
ABSTRACT: Benzoin, a popular photoinitiator for free radical polymerization of vinyl monomers, was improved by introduction of two methyl thioether substituents. This new benzoin derivative showed an about 50 times higher light absorption in the near-UV spectral region and performed better than the unsubstituted benzoin in polymerization experiments in bulk solutions or films of acrylate monomers when low initiator concentrations are used. Laser flash photolysis, low temperature luminescence experiments and photoproduct

studies by mass spectrometry suggest that a slow α -cleavage mechanism ($k_x = 2.2 \times 10^5 \text{ s}^{-1}$) from the electronic triplet state with a quantum yield of 0.1 is the primary photoreaction to generate the initiating free radicals. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 1865–1871

KEYWORDS: laser flash photolysis; photoinitiator; photopolymerization; photochemistry; photophysics; radical polymerization

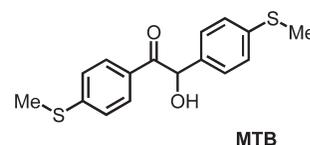
INTRODUCTION

Benzoin and its ether derivatives have long been known to be efficient photoinitiators for free radical polymerization of vinyl monomers and have found wide application in the polymer industry.^{1–3} Benzoin after photoexcitation and efficient intersystem crossing populates the triplet state, which undergoes efficient α -cleavage (Norrish Type I reaction) to generate benzoyl and α -hydroxy radicals (eq 1).^{4–10}



In the presence of vinyl monomers, these radicals can initiate free radical polymerization. The major disadvantage of benzoin and its ether derivatives is the poor light absorption in the near-UV, a spectral region which is most attractive for industrial photopolymerizations.

Here, we present a benzoin derivative, MTB, which shows the desired bathochromic shifted absorption and higher molar absorptivity compared to benzoin. We show that although the mechanism of radical generation is different from the α -cleavage mechanism of unsubstituted benzoin, this new photoinitiator efficiently initiates free radical polymerization.



RESULTS AND DISCUSSION

The light absorption properties of benzoin and MTB are shown in Figure 1. From the absorption spectrum it can be seen that MTB has a significantly stronger absorption in the near UV spectral region compared to benzoin with orders of magnitude higher molar absorptivity. Benzoin has a weakly absorbing $n\pi^*$ transition at 323 nm with a molar absorptivity of only $328 \text{ M}^{-1} \text{ cm}^{-1}$ and a strongly absorbing $\pi\pi^*$ transition at 247 nm with a molar absorptivity of $11,600 \text{ M}^{-1} \text{ cm}^{-1}$. For MTB, the strongly absorbing $\pi\pi^*$ transition shifted bathochromically to 313 nm accompanied by an increase in molar absorptivity ($18,800 \text{ M}^{-1} \text{ cm}^{-1}$). The two orders of magnitude improved light absorption of MTB compared to benzoin in the near UV spectral region should make MTB attractive to be studied as candidate of a photoinitiator.

Comparative polymerization experiments of methyl methacrylate (MMA) in DMF solutions were performed using MTB or benzoin as photoinitiators. Table 1 summarizes the

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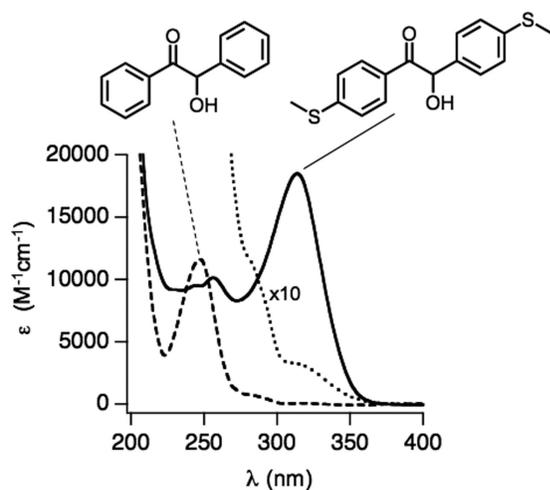


FIGURE 1 Absorption spectra of benzoin (dashed line) and MTB (solid line) in acetonitrile.

gravimetrically determined polymer yields under different experimental conditions, such as initiator concentration, presence or absence of a co-initiator (amine) or molecular oxygen (nitrogen or air saturated solutions). In general, at high initiator concentrations (10 mM; Table 1, entries 1–4) benzoin generates higher polymer yields compared to MTB. This is expected, because at these high concentrations of benzoin the photolysis light is efficiently and evenly absorbed throughout the sample solution. However, at high concentrations of MTB (10 mM), the photolysis light can not penetrate the entire sample solution because of the high molar absorptivity of MTB. Light absorption and initiator radical generation occurs only at the surface but not deeper in the bulk sample solution leading to reduced polymer yields. At lower initiator concentrations (1 mM and 0.1 mM; entries 5–9) where light can penetrate the entire sample sol-

TABLE 1 Free Radical Polymerization of MMA (4.7 M) in DMF Using MTB or Benzoin as Photoinitiators^a

Entry	[Initiator] (mM)	N ₂ ^b	H-donor ^c	Conversion (%) ^d	
				MTB	benzoin
1	10	–	–	17.2	33.4
2	10	+	–	21.9	31.3
3	10	+	+	14.5	34.1
4	10	–	+	17.8	31.3
5	1	–	–	14.6	7.8
6	0.1	–	–	4.3	0
7	0.1	+	–	5.5	3.7
8	0.1	+	+	11.3	5.1
9	0.1	–	+	9.5	1.3

^a 60 min photolysis in photoreactor with $\lambda_{\text{max}} = 350$ nm.

^b N₂ (+) or air saturated (–) solutions.

^c *N*-methyl-diethanolamine (10 mM).

^d Gravimetrically determined.

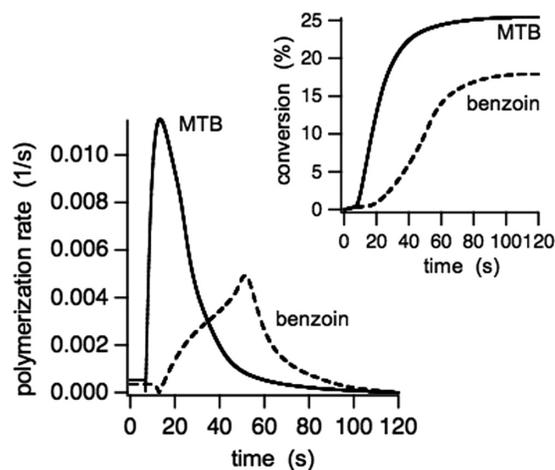


FIGURE 2 Photo-DSC profiles for polymerization of TPGDA/EA mixtures (20% TPGDA + 80% EA) using MTB (solid line) or benzoin (dashed line) (0.1% w/w). Inset: conversion of acrylate monomers vs. photolysis time. (Light intensity: 15 mW/cm²).

utions, MTB generates significantly higher polymer yields than benzoin. The superiority of MTB at low concentrations probably is mostly attributed to the two orders of magnitude higher molar absorptivity compared to benzoin.

Photo-differential scanning calorimetry (Photo-DSC) has been widely used to compare the efficiencies of photoinitiators for polymerization. The technique is based in the interpretation of heat generated by the polymerization reaction. We selected the diacrylate mixture Etercure 621A-80 as monomers because it forms films, which are suitable for DSC measurements. Etercure 621A-80 contains 20% tripropylene glycol diacrylate (TPGDA) and 80% of a bisphenol-A epoxy diacrylate (EA). Figure 2 shows a representative example of the photo-DSC profiles generated under our experimental conditions. It can be seen that photopolymerization using MTB as initiator proceeds with a significantly faster polymerization rate compared to initiation with benzoin. In addition, higher acrylate conversions are observed for MTB. A quantitative conversion of all monomer double bonds is not expected due to hindered diffusion in crosslinked polymer films.

These polymerization experiments show that MTB is an efficient photoinitiator and performs under some conditions better than benzoin. Photophysical studies were performed to investigate the mechanism of radical generation upon photolysis.

The triplet state of benzoin is known to have a $n\pi^*$ configuration, the configuration which favors α -cleavage (eq 1).¹¹ Phosphorescence experiments were performed to investigate the nature of the triplet state of MTB. Figure 3 shows the steady-state emission spectrum of MTB in ethanol glass at 77 K. This emission was assigned to the phosphorescence, because of its long lifetime (66 ms). The excitation spectrum matches well the absorption spectrum of MTB, which

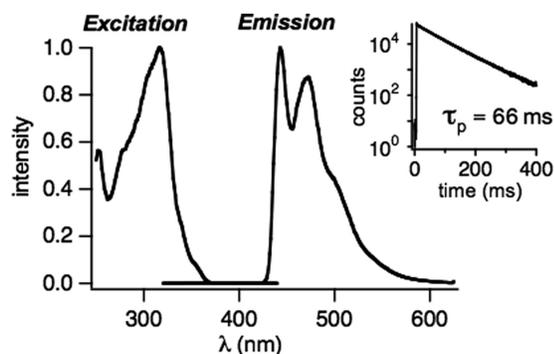


FIGURE 3 Luminescence spectra of MTB in methylcyclohexane and ethanol glass at 77 K. The observed emission is assigned to phosphorescence of MTB. Inset: phosphorescence decay trace. $\lambda_{\text{ex}} = 314$ nm, $\lambda_{\text{em}} = 445$ nm.

demonstrates that the observed emission originates from MTB and not from impurities. No fluorescence was detectable, which indicates efficient intersystem crossing into the triplet state. The triplet energy of 270 kJ/mol was obtained from the phosphorescence spectrum. The long phosphorescence lifetime of 66 ms suggests that MTB has a $\pi\pi^*$ configuration of its lowest triplet state, a configuration less favorable to α -cleavage reaction.

Laser flash photolysis experiments were performed to investigate if MTB triplet states undergo a similar α -cleavage as benzoin at room temperature (eq 1). Deoxygenated acetonitrile solutions of MTB were excited with laser pulses ($\lambda_{\text{ex}} = 355$ nm, 5 ns pulse width). Figure 4 shows transient absorption spectra at different delay times after the laser pulse. The observed transient absorption with a maximum at 460 nm and a shoulder at ~ 620 nm shows a lifetime of 4.5 ± 0.2 μs .

Quenching experiments were performed to investigate the nature of this transient absorption. Transient decay traces were recorded of solutions containing different amounts of dissolved molecular oxygen. Increased oxygen concentration

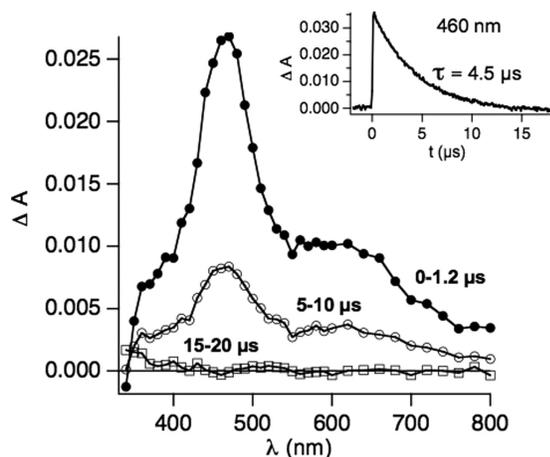


FIGURE 4 Transient absorption spectra of MTB in argon saturated acetonitrile solutions recorded at different delay times after the laser pulse (355 nm). Inset: decay trace at 460 nm.

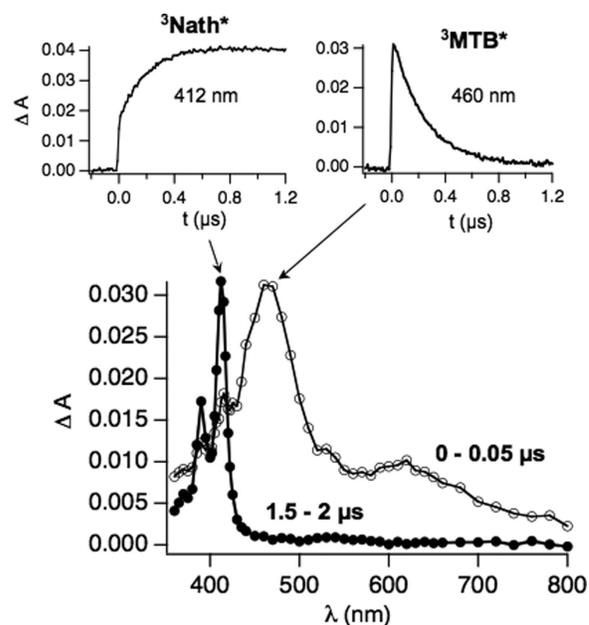


FIGURE 5 Transient absorption spectra of argon saturated acetonitrile solutions of MTB and naphthalene (0.5 mM) recorded at different delay times after the laser pulse (355 nm). Insets: decay traces at 412 and 460 nm.

caused a decreased lifetime of the transient at 460 nm, which indicates oxygen quenching. From the slope of the plot of the pseudo-first order decay constant (inverse lifetime) and the oxygen concentration¹² the bimolecular rate constant of oxygen quenching of 3.4×10^9 $\text{M}^{-1} \text{s}^{-1}$ was determined (eq 2) (Fig. S1 in Supporting Information). This rate constant is typical for reactions of oxygen with carbon centered radicals or triplet states.

$$k_{\text{obs}} = k_0 + k_q [\text{quencher}] \quad (2)$$

Quenching experiments with naphthalene were performed to differentiate the transient assignment to triplet states or radicals. Naphthalene does not absorb at 355 nm, the excitation wavelength for MTB in our laser flash photolysis experiments. Naphthalene has a lower triplet state energy (255 kJ mol^{-1}) than MTB (270 kJ mol^{-1}). Therefore, quenching of MTB triplet states by naphthalene should generate naphthalene triplet states, which are known to have a distinct absorption at 412 nm. Laser flash photolysis experiments in the presence of naphthalene showed efficient quenching of the transient absorption at 460 nm and the formation of a new transient at 412 nm, typical of naphthalene triplets (Fig. 5). The rise kinetic at 412 nm (naphthalene triplet) matches well the decay kinetic at 460 nm. The bimolecular quenching constant was determined (7.5×10^9 $\text{M}^{-1} \text{s}^{-1}$) using variable naphthalene concentrations (Fig. S2 in Supporting Information). This rate constant is typical for triplet energy transfer. From these naphthalene quenching experiments we conclude that the observed transient at 460 nm is caused by the triplet absorption of MTB. The long triplet lifetime of 4.5 μs suggests that α -cleavage analog eq 1 is

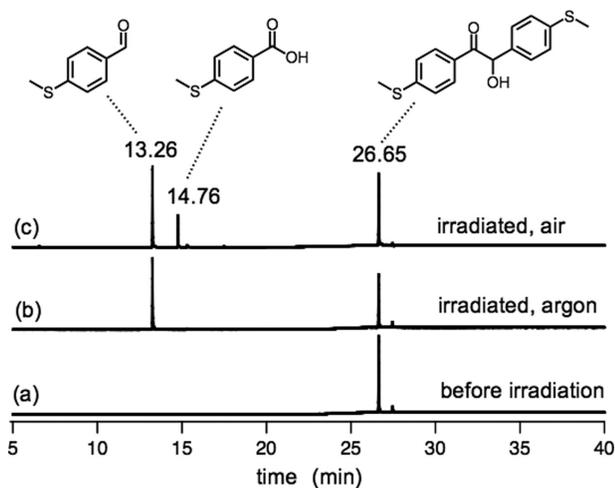


FIGURE 6 GC-MS traces of MTB in acetonitrile. (a) non-irradiated; (b) irradiated after argon degassing; (c) irradiated in air-equilibrated conditions.

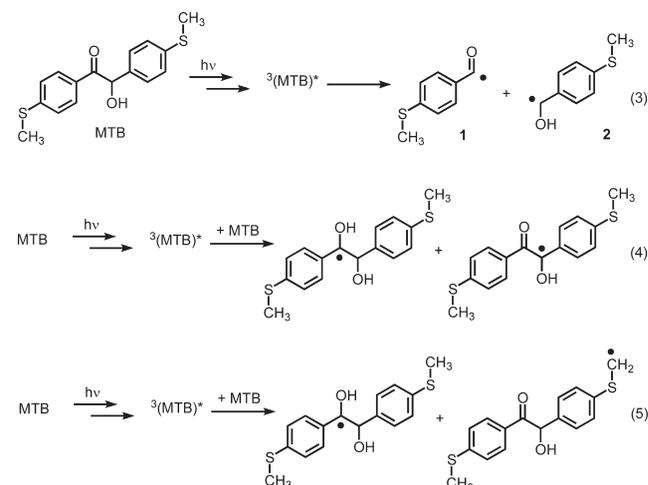
slow or not the dominating reaction pathway to generate free radicals to initiate polymerization.

To investigate the photochemistry of MTB and its radical generation mechanism, product studies were performed after photolysis of MTB solutions under various conditions. Figure 6 shows GC-MS traces of acetonitrile solutions of MTB before (a) and after irradiation at 313 nm (b,c). After irradiation in deoxygenated solutions, the peak at 26.65 min, assigned to MTB, decreased and a new peak at 13.26 min was observed (trace b). This new peak was assigned to 4-(methylthio)-benzaldehyde. In the presence of molecular oxygen (air saturated solutions), the reaction proceeded much slower and an additional photoproduct was observed at 14.76 min (trace c), which was assigned to 4-(methylthio)-benzoic acid. The assignments were based on the mass spectral fragmentation patterns (Supporting Information, Figs. S3–S5) and on the mass spectral data base NIST05.¹³

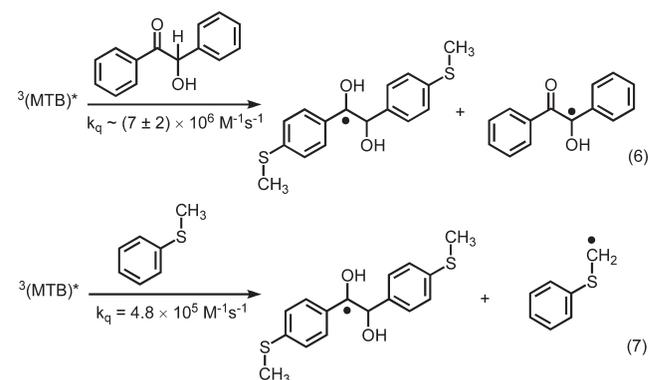
The photoproducts were further studied by LC-MS. MTB can be detected under both, positive and negative ionization conditions (Fig. S3, Supporting Information). The same main photoproducts, 4-(methylthio)-benzaldehyde and 4-(methylthio)-benzoic acid, were also detected by LC-MS (Figs. S4–S7, Supporting Information). Larger photoproducts, such as dimerization products of MTB were found in trace amounts.

The observed photoproduct 4-(methylthio)-benzaldehyde can be rationalized by α -cleavage of MTB to generate 4-(methylthio)-benzoyl radical (**1**) and the corresponding α -hydroxy radical (**2**) (eq 3). Radical recombination could lead to the starting material (MTB; coupling of **1** + **2**), a benzil derivative (coupling of **1** + **1**) or a diol (coupling of **2** + **2**). H-abstraction of the radical **1** from a H-donor would lead to the observed 4-(methylthio)-benzaldehyde.⁵ In the presence of molecular oxygen (air saturated solutions) radicals **1** and **2** can be oxidized through peroxide intermediates to 4-(methylthio)-benzoic acid as observed in Figure 6(c). Other

possible mechanisms include H-abstraction of triplet states of MTB from another MTB molecule in the ground state according to eqs 4 and 5. This would lead to large ketyl radicals, which might stabilize by fragmentation to generate 4-(methylthio)-benzaldehyde or stabilize by radical recombinations. However, no significant amounts of other intermediates or photoproducts were observable by GC-MS or LC-MS under our experimental conditions.



To determine if self-reaction according to eqs 4 and 5 are the dominant reactions to generate radicals, laser flash photolysis experiments were performed. The rate constants for both H-abstraction reactions were estimated using model compounds (benzoin and methylphenyl thioether) which are relatively transparent at the wavelength for laser excitation of MTB (355 nm). The use of these model compounds allowed the use of pseudo-first order quenching kinetics to determine the rate constants of MTB triplet quenching (Fig. S8, Supporting Information). The observed rate constant for MTB triplet quenching by H-abstraction at the α -hydroxy position of benzoin ($\sim 7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$; eq 6) is higher than for H-abstraction at the thioether position ($4.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; eq 7). However, both rate constants are relatively low and, therefore, self-reaction according to eqs 4 and 5 can only compete at higher MTB concentrations ($>10 \text{ mM}$).

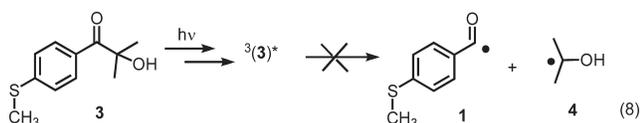


To determine the photodecomposition quantum yield of MTB, photolysis experiments at 313 nm in deoxygenated

acetonitrile solutions were performed (see Supporting Information). Low concentrations of MTB ($1 \mu\text{M}$) were used to rule out the self-reaction according to eqs 4 and 5. Using benzoin as actinometer with it is known α -cleavage quantum yield of 0.41,⁵ a quantum yield of MTB decomposition of 0.1 ± 0.02 was determined in deoxygenated acetonitrile solutions. In the presence of molecular oxygen (air saturated acetonitrile) the quantum yield decreased to 0.015 ± 0.003 . The decreased photodecomposition quantum yield in the presence of oxygen is consistent with the oxygen quenching of MTB triplet states observed by laser flash photolysis.

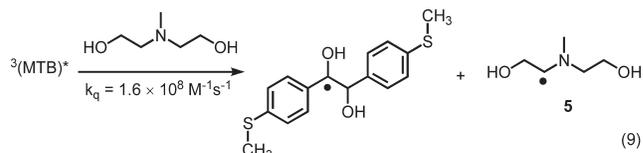
The above experimental results indicate that radical generation after photoexcitation of MTB occurs from the triplet state under α -cleavage (eq 3). Considering the relatively short triplet lifetime of $4.5 \mu\text{s}$ and the relatively low rate constants for self-reaction according to eqs 4 and 5, radical generation should occur through a monomolecular process. In addition, efficient radical generation of MTB to initiate free radical polymerization was observed (Table 1, entries 2 and 7).

However, the low-temperature phosphorescence spectra of MTB indicate that the nature of the lowest triplet state is $\pi\pi^*$. Ketones with $\pi\pi^*$ triplet states are known for low α -cleavage rate constants whereas α -cleavage is reported to be much more efficient from ketones with $n\pi^*$ triplet states, such as benzoin.¹⁴ The structurally similar ketone to MTB, 4'-methylthio-2-hydroxy-2-methyl-1-phenyl propanone (**3**), shows also a lowest triplet state of $\pi\pi^*$ nature and the photodecomposition quantum yield is only 0.01.¹⁵ In deoxygenated acetonitrile solution, this ketone shows a lifetime of $7 \mu\text{s}$,¹⁵ which is significantly longer than the triplet lifetime of MTB under the same conditions ($4.5 \mu\text{s}$). The shorter triplet lifetime of MTB suggests that in addition to thermic deactivation to the ground state (major pathway), MTB triplets display also a reactive pathway, α -cleavage according to eq 3. This is consistent with the low decomposition quantum yield of 0.1. To rationalize why the structurally similar ketone **3** shows no measurable α -cleavage and MTB undergoes some α -cleavage, we look at the stability of the resulting radicals. The benzoyl radicals **1** are identical for both reactions (eqs 3 and 8). However, the ketyl radicals **2** and **4** (π radicals) are structurally different. It is expected that the ketyl radical **2** is more stable compared to **4** because the extended aromatic conjugation in **2** stabilizes this π radical. This radical stabilization in **2** might provide the driving force for α -cleavage in MTB. Alternatively, orbital mixing of the lowest $\pi\pi^*$ triplet state with the energetically higher $n\pi^*$ triplet state might be more favorable in MTB compared to **3**. Orbital mixing would provide the lowest energy triplet state with a small amount of $n\pi^*$ character and allowing for slow α -cleavage.¹⁴



Tertiary amines, such as *N*-methyldiethanolamine (MDEA) are often used as co-initiators and additives in photopolymeriza-

tion formulations. Tertiary amines are known to efficiently react with triplet states of aromatic ketones to generate radicals by H-abstraction or by electron transfer followed by fast proton transfer. For unsubstituted benzoin, it is expected that the primary photochemistry (α -cleavage according to eq 1) does not change with addition of moderate amounts of amine, because α -cleavage from the triplet state is too fast to compete with amine reactions. However, the triplet state of MTB is longer lived and easier to be intercepted by amines. The rate constant for quenching of MTB triplet states by MDEA was determined by laser flash photolysis (355 nm excitation) by monitoring the MTB triplet absorption decay kinetics at different concentrations of MDEA. From the plot of the inverse MTB triplet lifetime vs. the MDEA concentration a rate constant of $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was obtained (Supporting Information, Fig. S9) which confirms efficient reaction. The transient absorption spectrum in the presence of MDEA showed a buildup of a transient absorption at 350 nm during the course of the reaction of MTB triplets with MDEA (Supporting Information, Fig. S10, red spectrum). This transient absorption is quenched by molecular oxygen and was tentatively assigned to the α -amino radical **4** (eq 9) based on similarities with the previously reported spectra of aliphatic α -amino radicals.¹⁶



This α -amino radical is able to initiate free radical polymerization in the presence of monomers, such as MMA. Because of the relatively slow α -cleavage reaction (eq 3) the photochemistry of MTB in the presence of MDEA at concentrations as low as 10 mM is dominated by amine reaction according to eq 9. This switches the initiation mechanism of MMA polymerization from initiation by radicals **1** and **2** in the absence of amine to initiation by radical **5** in the presence of amine. This switch in initiation mechanism contributes to the different observed polymer yields shown in Table 1.

Because the photoreaction of MTB with amines causes a loss of the ketone chromophore at 313 nm, the quantum yield of this photo reaction can be conveniently measured by photo bleaching studies. Deoxygenated acetonitrile solutions of MTB in the presence of 10 mM MDEA were photolyzed at 320 nm for different times and subsequent absorbance spectra were recorded (Fig. 7). From the loss of MTB absorbance and using Aberchrome 456 as actinometer,¹⁷ a quantum yield of MTB decomposition in the presence of amine of $\Phi = 0.20 \pm 0.04$ was determined. This high quantum yield suggests efficient radical generation which should lead to efficient initiation of free radical polymerization of monomers, such as MMA.

CONCLUSIONS

The benzoin derivative MTB initiated free radical polymerization of vinyl monomers efficiently in the absence of

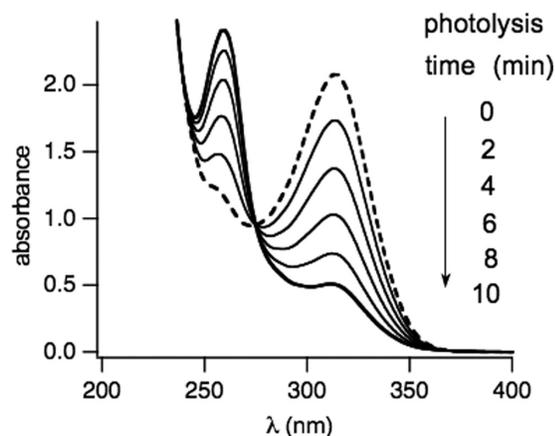


FIGURE 7 Absorption spectra of MTB (0.1 mM) and MDEA (10 mM) in deoxygenated acetonitrile before (dashed line) and after photolysis at 320 nm for different times.

co-initiators, such as amines. Although MTB shows a lowest triplet state of $\pi\pi^*$ nature, our experimental results suggest that slow α -cleavage with a quantum yield of 0.1 is the primary photoreaction to generate the initiating free radicals. Because MTB shows an about 50 times higher absorption in the near-UV spectral region compared to the unsubstituted benzoin, MTB performs better than benzoin in polymerizations. This should make MTB attractive for practical applications as photoinitiator where low initiator concentrations are required or for thin films.

EXPERIMENTAL

Materials

See Supporting Information for the synthesis procedure of 2-hydroxy-1,2-bis-(4-methylsulfonyl-phenyl)-ethanone (MTB)¹⁸ and details of other materials.

Photopolymerization

Solutions (0.5 mL) of monomer, photoinitiator and co-initiator were placed into a Pyrex tube (inner diameter 9 mm), sealed with a septum cup and, if specified, deoxygenated by N_2 bubbling. The tubes were irradiated for 60 min in a photoreactor equipped with 12 low-pressure Hg-lamps emitting nominally at 350 nm. The polymer was obtained after precipitation in methanol and drying under vacuum. Conversions were calculated gravimetrically.

Photoinitiated polymerization was also followed by differential scanning calorimetry (Photo-DSC) using a DSC Q100 (TA Instruments). Appropriate sample mixtures (2.0 ± 0.1 mg) were placed on the sample trays and UV light was applied from a medium-pressure Hg lamp (15 mW/cm^2 at the sample). The measurements were performed in isothermal mode at room temperature under N_2 flow (50 mL/min). A reaction heat of conversion of acrylate double bonds of $\Delta H_0^{\text{theory}} = 86 \text{ kJ/mol}$ was used for calculating polymerization rates and conversions.¹⁹

Measurements

UV-vis spectra were recorded on an Agilent 8453 spectrometer. Steady-state luminescence spectra were recorded on a Fluorolog-3 fluorometer (HORIBA Jobin Yvon) at 77 K using 3 mm (inner diameter) quartz tubes inside a quartz liquid nitrogen dewar. The phosphorescence lifetime at 77 K was measured by multichannel scaling on an OB920 spectrometer (Edinburgh Analytical Instruments) in conjunction with a pulsed Xe-lamp. Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150-30 Nd:YAG laser (355 nm, ca 5 mJ/pulse, 5 ns) and a computer controlled system that has been described elsewhere.²⁰ Solutions of MTB were prepared at concentrations such that the absorbance was ~ 0.3 at the excitation wavelength (355 nm).

Photoproducts

The photoproduct distributions were studied by GC-MS and LC-MS. The GC-MS was a Hewlett Packard 6890N equipped with a 5973 series mass selective detector (E.I. 70 eV). A Rtx-5MS capillary column with 30-m length, 0.25-mm I.D., and 0.25- μm film thickness (Restek) was used with the following oven temperature program: 70 °C for 2 min, 10 °C min^{-1} increase until a final temperature of 280 °C. The injector was set to 280 °C and the injection volume was 1 μL . The LC-MS system is an Agilent Technologies 1200 Series LC coupled to a Bruker Daltonics HCT *ultra* (ion trap), able to carry out MS^n , $n = 11$. A Hamilton PRP-1 reversed phase LC column (15.0-cm length, 2.1-mm internal diameter, 5 μm), stabilized at 25 °C was used. The used eluent system was acetonitrile (A) and water (B), both with 10 μM of NaCl. The gradient started with 20% of A, followed by a linear increase up to 100% in 20 min. A final cleaning step using 100% of A during 4 min was made after each run. The eluent was then allowed to recover the initial conditions in 5 min.

Quantum Yields

The photodegradation quantum yields of MTB were determined using benzoin with a quantum yield of 0.41 (in benzene)⁵ as reference (see Supporting Information for details).²¹ The initial concentrations of MTB and benzoin were 1 and 20 μM , respectively. MTB and benzoin were quantified by UV absorbance using a diode array detector at 315 and 280 nm, respectively, and/or by LC-MS under positive polarity by monitoring the ions at m/z 327 $[\text{M}+\text{Na}]^+$ and 235 $[\text{M}+\text{Na}]^+$, respectively for MTB and benzoin.

Photobleaching quantum yields of MTB in the presence of MDEA (10 mM) were determined under 320 nm photolysis using a xenon lamp (LX300UV, Varian) in conjunction with a monochromator (Kratos, Schoeffel Instruments). The changes in optical absorption were measured on an Agilent 8452A spectrophotometer. The absorbed light dose was determined by actinometry using Aberchrome 540 (Aberchromics Ltd., U.K.) and its quantum yield of 0.20 in toluene.¹⁷

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