Investigation of Barton Esters as Radical Photoinitiators

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ABSTRACT: Different photoinitiators based on Barton thiohydroxamic esters, O-acyl-N-hydroxy-pyridine-2(1H)-thione and O-acyl-N-hydroxy-thiazole-2(3H)-thione derivatives, were tested in photopolymerization reactions through time-resolved FTIR spectroscopy. Good rates of polymerization and final monomer conversion were obtained for some compounds. The excited state processes, investigated by time resolved absorption spectroscopy, lie on a fast singlet state cleavage leading to thiyl and alkyl radicals. Both the pyridine-2(1H)-thiyl and alkyl radicals are able to initiate a polymerization, in contrast with the thiazole-2(3H)-thiyl radical. A triplet state is observed for some derivatives. Computational studies help to describe the excited state properties and show a strong difference in the spin localization in the formed thiyl initiating radicals. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 825–833, 2008

Key words: photochemistry; photopolymerization; photoinitiator

INTRODUCTION

The search for new photoinitiators (PI) has continuously received a considerable attention in the last two decades.[1–6] Many aspects have been studied such as the effects of the chemical structures and the introduction of suitable substituents on a given chromophoric group to improve the desired properties. Available interesting cleavable structures developed so far are based on the benzoyl chromophore and involve an α-cleavable C—C bond (benzoin ethers, hydroxy alkyl phenyl acetophenones, dialkoxy acetophenones, morpholino ketones), an α-cleavable C—P bond (phosphine oxide derivatives), a β-cleavable C—C bond, etc.[1–6] Recent attempts have been made for example to change the acetophenone nucleus for a heterocyclic containing carbonyl chromophore,[7,8] to design difunctional photoinitiators,[9,10] or to introduce a new chromophoric group in sulfonyl ketones.[11]

Barton esters were developed in the 1980s, with the aim to promote radical chemistry with amplification by radical chain reactions.[12–14] Although these compounds were primarily designed to decompose by heat, most of the molecules exhibit a high photochemical activity. The most widely used family of compounds were derived from N-hydroxy-pyridine-2(1H)-thione, which exhibits a broad and intense absorption band centered around 350–360 nm. Many compounds were synthesized and many organic reactions were studied.[14–28] In the field of polymer science, it was recently proposed to use some Barton esters as grafting agents for vinyl polymers.[29] Other studies have shown that these compounds can act as efficient chain transfer agents for free radical polymerization.[30,31] More interestingly, it was shown that Barton esters have both thermal and photochemical initiating properties toward double bonds.[19,32] Therefore, it turns out that the photoinitiating ability of this class of compounds for radical polymerization has to be studied.

In the present article, we will investigate both the photochemical reactivity and the polymerization initiation ability of radical photoinitiators based on thiohydroxamic esters, such as O-acyl-N-hydroxy-pyridine-2(1H)-thiones (TP) and O-acyl-N-hydroxy-thiazole-2(3H)-thiones (TT) (Scheme 1). Such TP appear as good candidates for the production of radicals although their storage is somewhat tricky as already reported.[33] Interestingly, TTs exhibit a better resistance to hydrolysis and a better photochemical stability.[33] Moreover, the latter presents a novelty character as not much is known on their photochemistry. As a consequence, the present article will be mainly focused on TT derivatives while the TPs are used as reference compounds. Time resolved laser spectroscopy and molecular modeling will help to study and to characterize the excited state processes. Some aspects of the structure–properties relationships will be discussed.
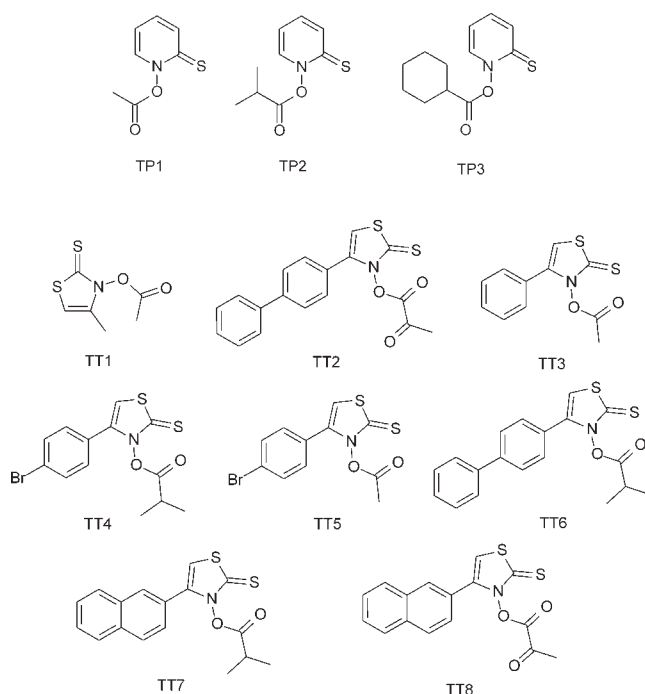
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EXPERIMENTAL

O-Acetyl-*N*-hydroxy-pyridine-2(1H)-thione (TP1), *O*-isobutyryl-*N*-hydroxy-pyridine-2(1H)-thione (TP2), *O*-cyclohexanecarbonyl-*N*-hydroxy-pyridine-2(1H)-thione (TP3), *O*-acetyl-*N*-hydroxy-4-methyl-thiazole-2(3H)-thione (TT1), *O*-(2-oxopropionyl)-*N*-hydroxy-4-(biphenyl-4-yl)-thiazole-2(3H)-thione (TT2), *O*-acetyl-*N*-hydroxy-4-phenyl-thiazole-2(3H)-thione (TT3), *O*-isobutyryl-*N*-hydroxy-4-(4-Bromo-phenyl)-thiazole-2(3H)-thione (TT4), *O*-acetyl-*N*-hydroxy-4-(4-Bromo-phenyl)-thiazole-2(3H)-thione (TT5), *O*-isobutyryl-*N*-hydroxy-4-(biphenyl-4-yl)-thiazole-2(3H)-thione (TT6), *O*-isobutyryl-*N*-hydroxy-4-naphthalen-2-yl-thiazole-2(3H)-thione (TT7), *O*-(2-oxopropionyl)-*N*-hydroxy-4-naphthalen-2-yl-thiazole-2(3H)-thione (TT8) were synthesized according to the standard procedures.[19,28] The chemical structures are shown in Scheme 1.

The nanosecond laser absorption set-up consists in a Nd:YAG laser and a classical transient absorption analysis system already described.[34] The excitation wavelength can either be 266 or 355 nm. The picosecond time resolved absorption set-up is based on a classical pump-probe arrangement using a picosecond tripled Nd:YAG laser as an excitation source (355 nm). All the characteristics have been already reported elsewhere.[35]

The photolysis experiments are conducted in solution by following the evolution of the absorption spectra as a function of the irradiation time. The photolysis quantum yields were determined accord-ing to a classical treatment, provided that no photolysis product absorbs.[36]

The polymerizable formulation contained Ebecryl 605 (bisphenol A epoxydiacrylate/tripropylene glycoldiacrylate 75/25, from UCB Chem.) and 1% of photoinitiator. All the samples were laminated between two polypropylene films (100 μm thick). Two well known photoinitiators were used as references: 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, Esacure KB-1 or Irgacure 651) and 2-methyl-1-[4-(methylthio)-phenyl]-2-(4-morpholinyl)-1-propanone (TPMK, Irgacure 907). The irradiation was performed with the polychromatic light of a Hg/Xe Lamp (LC6, Hamamatsu) at 10% of its maximal intensity for 5 min. The polymerization reactions were followed by monitoring the disappearance of the IR absorption of the acrylic double bond at 1635 cm^{-1} with a FTIR spectrometer (Nexus 870, Nicolet).[35] The rates of polymerization were deduced from the linear part of the conversion versus time curve and normalized by using a value of 100 for DMPA. A delay of 3 s was set up before opening the shutter of the irradiation lamp. However, do to the use of a FTIR system, and the intrinsic time for the positioning of the mobile mirror, the induction time is not reliable. The experimental error is about 5% for both R_p values and final monomer conversions.

The modeling calculation procedures were carried out using Gaussian 03,[37] following a procedure described elsewhere.[38] Density functional theory was used to calculate the structure of the molecules. Relaxed ground states and radicals produced after cleavage were fully optimized using the B3LYP functional with the 6-31G* basis set. The absorption properties were computed with a time dependant method at a B3LYP/6-311++G** level.

RESULTS AND DISCUSSION

Ground state absorption

Typical ground state absorption spectra for TP and TT derivatives are reported in Figure 1. High molar extinction coefficient was found at 366 nm in acetonitrile. For example, values of 5700 and 400 M^{-1} cm^{-1} were found for TP2 and TT6, respectively. The introduction of suitable substituents at the 4- position of the five-membered thiazole ring of TTs allows a red shift of the absorption band; however, TPs still exhibit better absorptions than TTs between 280 and 400 nm.

Scheme 1 Formula and abbreviations of the products studied.

The polymerization activity of the different derivatives

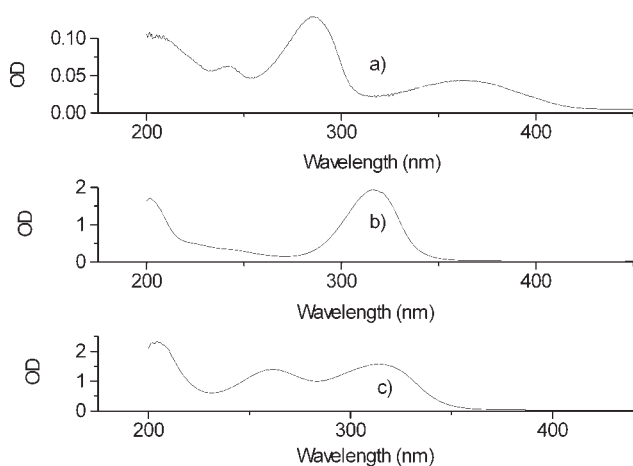Typical photopolymerization profiles obtained under a polychromatic irradiation in the presence of TPs

Figure 1 Typical ground state absorption spectra in acetonitrile. (a) TP2, (b) TT1, and (c) TT6.

TABLE I
Relative Rates of Polymerization (R_p) and Final Conversion Results Using Representative TP and TT Derivatives as Photoinitiators

Compound	R_p (a.u.)	Conversion (%)
TPMK	70	93
DMPA	100	91
TP2	35	57
TT1	15	65
TT2	15	60
TT3	20	62
TT4	<1	25
TT5	23	54
TT6	<2	27
TT7	<2	25
TT8	15	44

and TTs are displayed in Figure 2. Corresponding relative rates of polymerization are reported in Table I.

TPs and TTs are found less reactive than the commercial photoinitiators. As exemplified by TP2, the R_p is three times lower and the final conversion is 60% lower than those of DMPA. The polymerization rates when using some typical TTs strongly depend on the compound used: these differences cannot only be explained by the change of the absorption properties. The photodegradation of the starting product as well as the modification of the chromophoric group or the change of the R leaving group play a significant role. The substitution by a phenyl group on the five-membered ring enhances the efficiency (compare TT1 and TT3). This holds also true through the introduction of a substituent at the para-position of the phenyl (compare TT3 and TT5) as
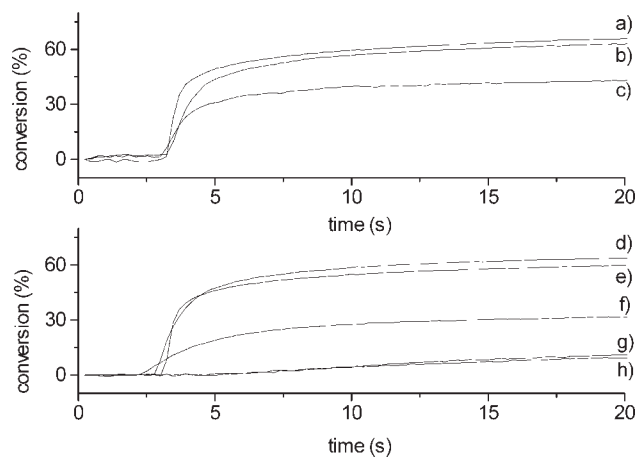
well as the change of the O-acyl moiety (compare either TT4 and TT5 or TT7 and TT8). Changing the phenyl for a biphenyl does not improve the efficiency (compare TT3 and TT2). Similarly, the incorporation of a naphthalene does not improve the efficiency (compare TT2 and TT8).

Steady state photolysis

The photolysis of TPs under irradiation at 366 nm was studied in acetonitrile by following the changes of the UV spectra between 340 and 450 nm (Fig. 3): there is a progressive disappearance of the absorption at 366 nm and an increase of the absorption at 250 nm.

The photolysis is due to the cleavage process already mentioned in the literature[18–21] that corresponds to a N—O bond breaking presumably followed by a fast decarboxylation and generation of a R radical (Scheme 2).
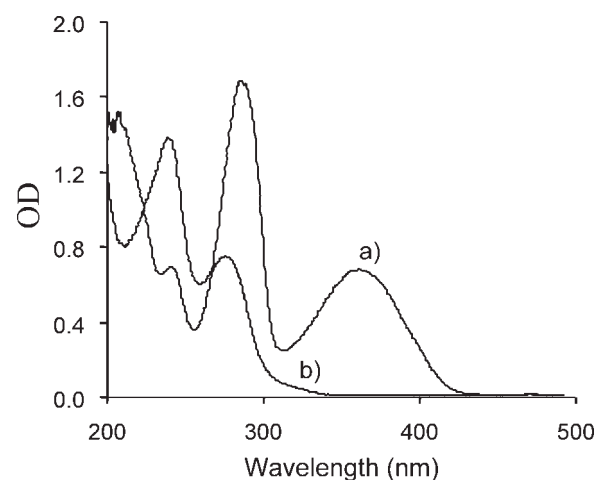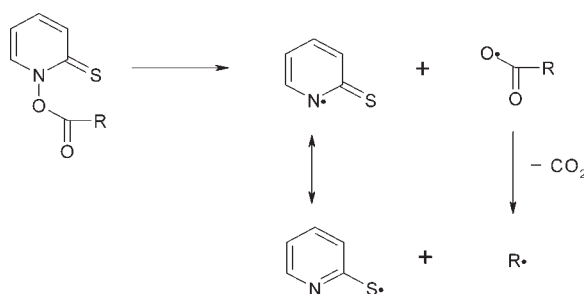

Figure 2 Typical photopolymerization profiles of Ebecryl 605 in the presence of various photoinitiators: (a) TPMK, (b) DMPA, (c) TP2, (d) TPMK, (e) DMPA, (f) TT8, (g) TT6, and (h) TT7.

Figure 3 Absorption spectra of TP2 in acetonitrile before (a) and after (b) irradiation.

Scheme 2 NO bond cleavage in TPs.

The photolysis is extremely efficient and leads to a photolysis quantum yield of 3.8 and 3.4 for TP2 and TP3, which confirms the involvement of a chain reaction[22]: the thiyl or the alkyl radical produced by photocleavage react with a ground state molecule (Scheme 3).

This chain reaction does not lead to a higher amount of radicals but rather leads to the bleaching of the photoinitiator. Subsequent detrimental reactions (that involve the alkyl radical, oxygen, or a hydrogen transfer from hydrogen donors (HD) such as the monomer unit or the polymer)[19] toward the initiation step efficiency are also expected (Scheme 4).

An attempt was made to scavenge the radicals formed by this reaction to determine the photolysis quantum yield in the absence of the chain reaction. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical), BHT (2,6-di-*tert*-butyl-4-methylphenol), and MEHQ (4-methoxyphenol) were used as radical scavengers. The photolysis quantum yields obtained for TP3 in acetonitrile upon irradiation at 366 nm under argon are 3.4, 5.9, and 7.7 in the presence of MEHQ (0.1 M), BHT (0.1 M), and TEMPO (0.2 M), respectively. Instead of reducing the detrimental reactions, the scavengers enhance the chain reaction. In the case of MEHQ and BHT, the new radical formed during the interaction may have some reactivity towards the TP ground state.

The degradation of TT1 was studied under irradiation at 366 nm by following the changes in the UV spectra between 355 and 450 nm. Under argon bubbling, a progressive increase of a band near 360 nm was observed. The quantum yield of photolysis can-
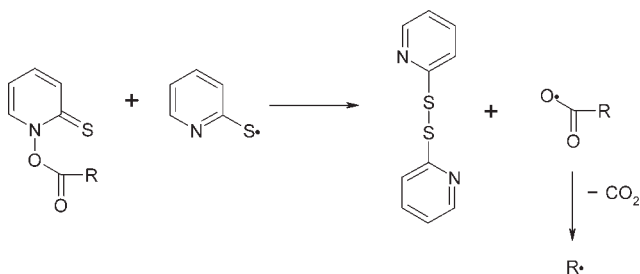
Scheme 3 Chain reactions in TPs.
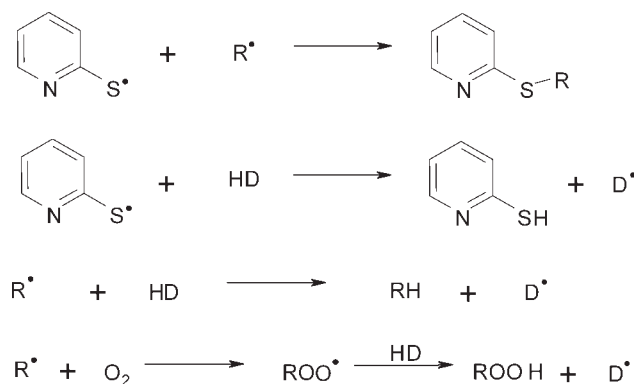
Scheme 4 Reactivity of TP derived radicals.

not be determined because of the absorption of the photoproducts in the TT1 absorption band, but the primary process involved should be presumably similar to that described in Scheme 2.

Computational study

Some molecular modeling calculations were carried out to give a more theoretical insight into the excited states. In TPs, the HOMO and LUMO orbitals exhibit a n and π^* nature, respectively. Accordingly, the long wavelength absorption of the studied TPs corresponds to a n-π^* transition. Ground state absorption is predicted for TP1 at 434 nm with a low oscillator strength ($f = 0.0001$) and 367 nm with a high oscillator strength ($f = 0.0532$). This is the latter transition that is experimentally observed. Similarly, the two lowest electronic transitions of TP2 are predicted at 434 nm ($f = 0.0001$) and 367 nm ($f = 0.0532$), respectively, in good agreement with Figure 1.

The triplet state of TP1 can not be computed. Indeed, the triplet state molecule was optimized as two separated moieties showing that the triplet state is dissociative. According to time-dependent computation, the singlet and triplet states are located at $E_S = 66.4$ kcal/mol and $E_T = 52.6$ kcal/mol with respect to the ground state, respectively. The N—O bond dissociation energy BDE was found to be rather small (28.2 kcal/mol). The low bond dissociation energy makes this molecule a rather good photocleavable agent but it could have a detrimental effect on the thermal stability of this compound. The spin density of the pyridine-thiyl radical formed after cleavage in the triplet state is clearly localized on the sulfur atom (Fig. 4). This could explain the observed high reactivity of this radical in organic chemistry.[17–22]

For TT1, the HOMO-LUMO transition is n-π^*. Time-dependant computations lead to predicted UV transitions at 345 nm ($f = 0.0002$), 304 nm ($f = 0.0016$), and 292 nm ($f = 0.17$). When a biphenyl group is introduced (e.g., in TT6), the lowest energy transitions are globally red shifted and predicted at
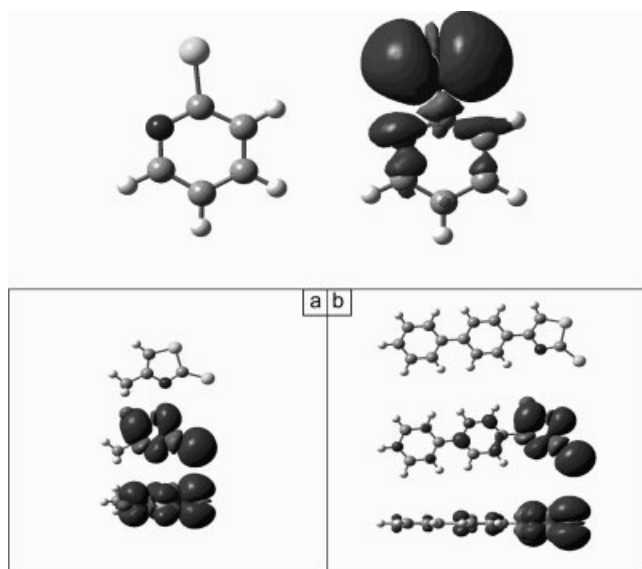
Figure 4 Spin localization on the radical obtained after the N—O bond cleavage at a B3LYP/6-31G* level. Top: in a TP derivative. Bottom: (a) TT1; (b) TT6.

350 nm ($f = 0.0037$) and 349 nm ($f = 0.1208$). These data satisfactorily agree with the spectra of Figure 1, a shift from about 10–20 nm between the experimental data and the calculations being noted. As for the TPs, the first transition exhibits a $n\pi*$ character and the second a $\pi\pi*$ character. Changing the biphenyl for a naphthalene (e.g., in TT7) slightly shifts the absorption (361 nm with $f = 0.0633$) which, however, becomes a $\pi\pi*$ transition. The calculated triplet state energies are lying in the range of 61 kcal/mol (e.g., for TT6 and TT7) to 64 kcal/mol (e.g., for TT1). The BDE of TT1 and TT6 are still quite low with values of 24.7 and 19.2 kcal/mol, respectively, at B3LYP/6-31G* level. The computed absorption spectrum of the TT6 thiyl radical shows numerous transitions—the most important being located at 320 nm ($f = 0.3592$) and 809 nm ($f = 0.1416$)—that could explain the broad transient absorption band observed (see below).

For TT1, calculations at UB3LYP/6-31G* level show that the thiyl radical is not localized on the S atom but delocalized over the π system (Fig. 4). When introducing a substituent on the five-membered cycle TTs (e.g., TT6), the spin localization occurs on the five-ring moiety in the same manner as in TT1. Therefore, the same reactivity is expected for the TT6 and TT1 radicals if the sterical hindrance does not play a significant role. The calculated absorption maxima of the TT1 thiyl radical are located at 315 nm ($f = 0.1472$) and 515 nm ($f = 0.0480$).

Excited state processes of the TP compounds

It is known that a nanosecond laser excitation of the TP ground states (^{0}TP) in deaerated solutions leads to the generation of a rather long-lived transient ascribed to the pyridine-thiyl radical (PS•).[13] The spectra obtained on the picosecond time scale upon laser excitation of TP1 correspond to this radical (Fig. 5). No other transient appears in this time scale. The generation of this radical occurs within 10 ps which clearly demonstrates that the direct cleavage of the N—O bond should occur in the first excited singlet state (^{1}TP), a fact that prevent any triplet state formation.

Nanosecond laser spectroscopy (excitation at $\lambda = 355$ nm) allows to monitor the bleaching of the ground state around 360 nm (Fig. 6). The three TPs exhibit similar kinetics. The first part of the kinetics at 380 nm is very fast and corresponds to the cleavage of the molecule (Scheme 5). The second part is slower and depends on the concentration of the starting molecule: it corresponds to the addition of the PS• radical to TP (Scheme 5). This reaction was already described in the literature to be nearly diffusion-controlled (~ 3–4×10^9 M^{-1} s^{-1}).[19] The lifetime of the thiyl radical, monitored at 490 nm, that depends on the ground state concentration (pseudo-first order decay), was determined in acetonitrile: $\tau \approx 1.7$ μs in our experimental conditions ([TP] = 2 × 10^{-4} M). The kinetics are not affected by the presence of oxygen in agreement with the low sulfur radical/oxygen interaction.[22,32,39]

The quantum yield for the primary process of dissociation of TPs can be calculated by monitoring the
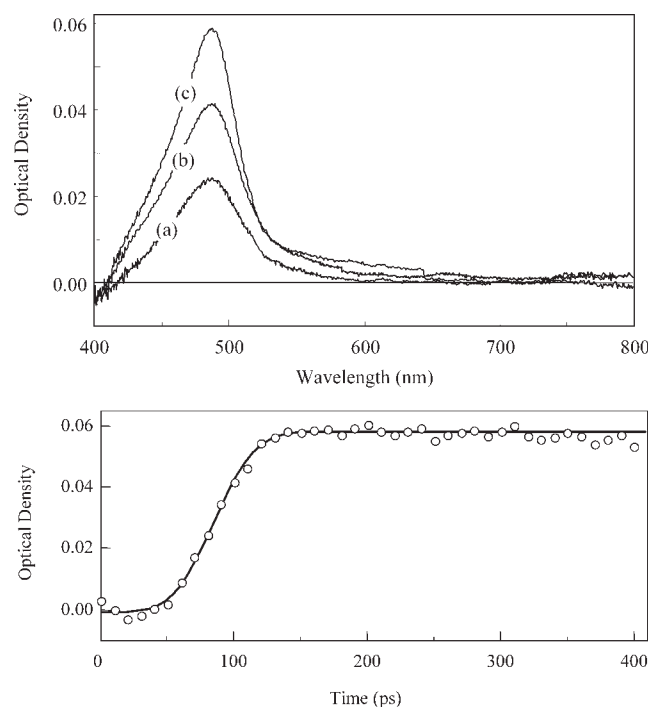

Figure 5 Top: absorption spectra of TP1 in acetonitrile (a) 80 ps, (b) 100 ps, and (c) 280 ps after excitation. Bottom: growth of the absorption as a function of time at 488 nm.
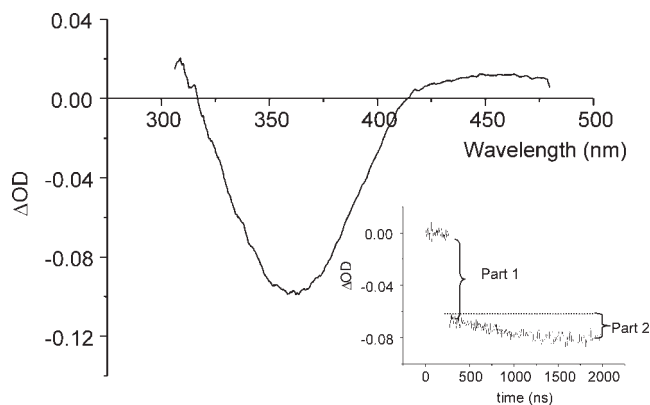
Figure 6 Transient spectrum of TP3 obtained 600 ns after the excitation. Insert: decay observed for TP3 in acetonitrile at 380 nm under argon.

initial optical density of the thiyl radical and determining the concentration of the excited states according to:

$$\phi_{diss} = (\Delta OD(TP) \cdot \varepsilon_{3BP})/(\Delta OD(BP) \cdot \varepsilon_{TP}) \quad (1)$$

where ε_{3BP} is the molar extinction coefficient of the benzophenone triplet state used as an actinometer (6500 M^1 cm^1 at 525 nm), ε_{TP} is the molar extinction coefficient of the TP ground state (4812 M^1 cm^1 at 380 nm). $\Delta OD(BP)$ and $\Delta OD(TP)$ are the changes observed in the transient absorption of BP and TP, respectively. Applying this equation leads to values of 0.8 and 0.9 for TP2 and TP3, respectively, showing the high efficiency of the cleavage process.

The triplet state energy level was determined for TP1 by energy transfer experiments using a set of well established triplet energy donors and using a procedure described elsewhere.[40,41] This yields to a value of 50–56 kcal/mol for TP1 in good agreement with previous expectations on *N*-hydroxypiridine-2-thione (between 59.5 and 63 kcal/mol)[12] and computational results (52.6 kcal/mol, see above).

Excited state processes of the TT compounds

The TT transient absorption spectra, obtained in acetonitrile under argon upon laser excitation at 355 or 266 nm, spread in the whole investigated wavelength range (from 340 to 780 nm) and exhibit a maximum between 350 and 450 nm. Figure 7 shows typical spectra recorded for TT1 and TT6.

For the unsubstituted compound TT1, the transient exhibits two maxima at 340 and 580 nm. The ratio between the two absorption maxima of the

experimental spectrum (2.96) is very close to that of the calculated oscillator strengths (3.06, see above), supporting the attribution of the transient species to the corresponding thiyl radical TS*. The formation of the transient species is very fast (within the nanosecond time scale) and the decay obeys to a second-order kinetics as observed at 570 and 350 nm. The decay and the initial maximum concentration are not affected by the presence of oxygen. The thiyl radicals are therefore presumably formed through a cleavage process in the singlet state ^{1}TT1 (Scheme 6), through a mechanism which should be similar to that of TPs. At 350 nm, a second and very long-lived species appears as a residual, which could not yet be safely attributed.

The laser excitation of TT6 (which contains a biphenyl moiety) leads to a broad transient absorption around 370–420 nm totally different to that of TT1. The kinetics are rather complex. At 510 nm, a short lived transient decays according to a first order law. The corresponding lifetime changes from 3 μs under argon to 130 ns under air. This species is likely ascribed to a triplet state ^{3}TT6 (absorption spectrum a in Fig. 7). At 380 nm, in addition to this short transient, a long-lived transient (in the ms time scale) appears that might be a photoproduct (spectrum c in Fig. 7). At 650 nm, the decay trace is totally different. A new transient decays according to a second order law and is not quenched by oxygen. This transient can be likely attributed to the thiyl radical. In addition, the corresponding absorption spectrum, ranging from 600 to 800 nm (spectrum b in Fig. 7), is in very good agreement with the calculated one. The initial optical density of this species is not significantly affected by oxygen: one can safely assume that the cleavage mainly occurs in the singlet state (Scheme 7). The behavior of the other substituted TT (such as TT3, TT7) is similar to that of TT6.

The assignment to a triplet state was confirmed by energy transfer observed at 450 nm. Camphorquinone (CQ; whose triplet state is located at 51.6 kcal/mol) was found to efficiently quench the short lived transient species with a quenching rate constant of 2 10^9 M^{-1} s^{-1}. By contrast, energy transfer with 1-methylnaphtalene (the triplet energy being 60.7 kcal/mol) was not successful. These experimental results lead to an estimate of the triplet state around 52–60 kcal/mol in good agreement with the evaluation of the spectroscopic triplet state for these kinds of compounds by molecular modeling, keeping in mind that the relaxed triplet state from which the energy transfer occurs is lower than the spectroscopic triplet state.

Polymerization initiation

The initiation of the polymerization in TPs occurs according to Scheme 8. It is known that sulfur radicals
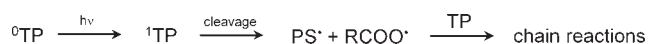
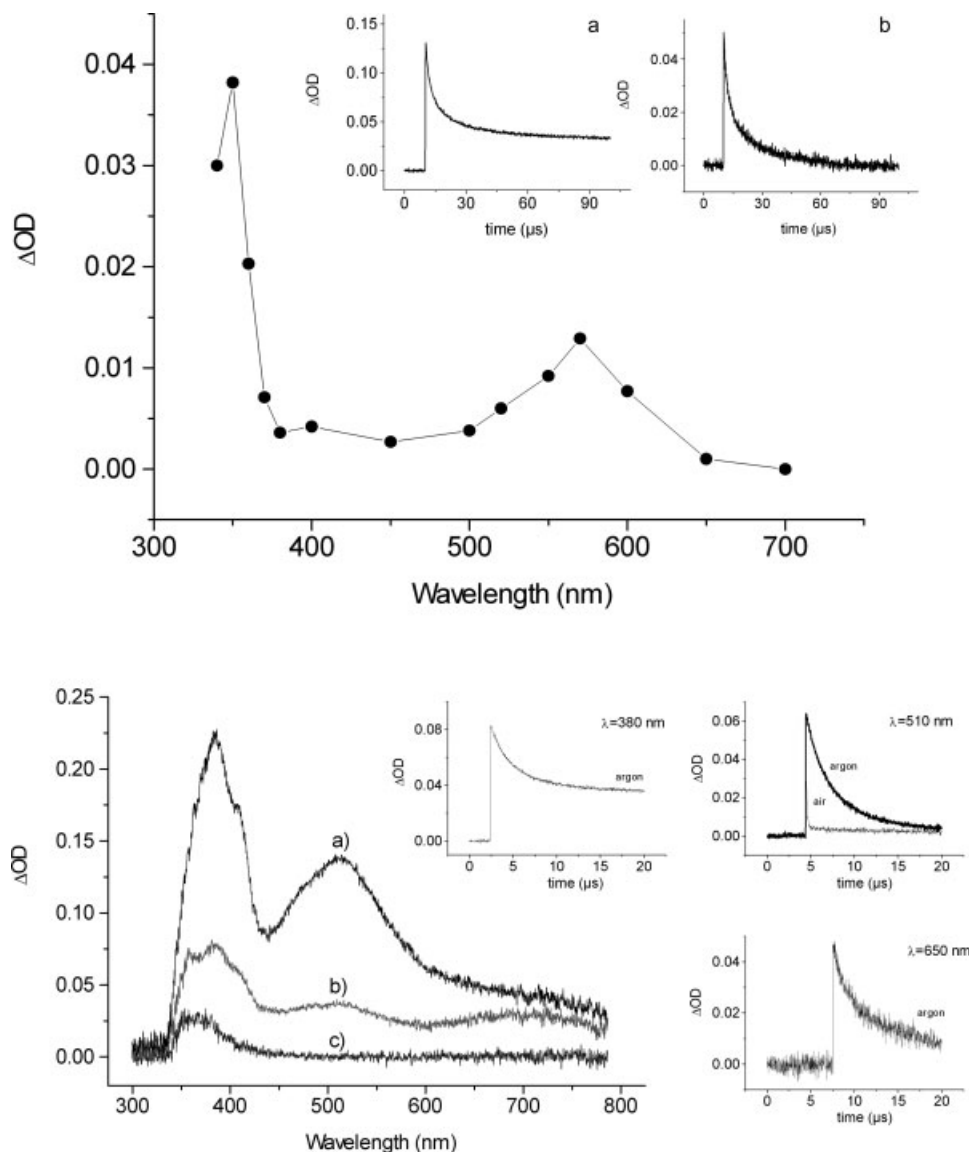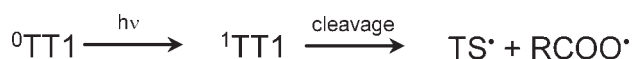**Scheme 5** Reactivity of TPs upon light excitation.

Figure 7 Transient absorption spectra for TT1 and TT6 in argon saturated acetonitrile. Top: TT1. Absorption observed immediately after the laser pulse. Insert: decay traces at two analyzing wavelengths: (a) $\lambda = 350$ nm; (b) $\lambda = 570$ nm. Excitation wavelength: 266 nm. Bottom: TT6. Absorption recorded at time $t = 0$ (a), $t = 7$ µs (b), and $t = 2$ ms (c). Insert: decay traces at 380, 510, and 650 nm. Excitation wavelength: 355 nm.

react very efficiently toward double bonds.[39,42] Because of the values of the rate constants of interaction of sulfur centered radicals with hydrogen donors (HD) and double bonds,[17–20,22,24] the thiyl radical should be the most efficient initiating radical. The rate constant of the PS radical addition onto methylmethacrylate has been measured to be 1×10^8 M^{-1} s^{-1}.[19,20] The detrimental chain reaction in TPs (Scheme 3) does not lead to a higher amount of radicals but it consumes both the highly localized initiating thiyl radical and the starting compound: the ability of the

system to initiate a polymerization is therefore not as high as it would be expected. However, this effect was demonstrated to have a beneficial effect leading to chain transfer processes and therefore opening new opportunities to control the molecular weight in free radical photopolymerization.[30,31]

By contrast with TPs derivatives, the thiyl radical in TTs is delocalized. In that case, the chain reaction

$$^0TT6 \xrightarrow{h\nu} {}^1TT6 \longrightarrow {}^3TT6$$
$$\xrightarrow{cleavage} TS^{\bullet} + RCOO^{\bullet}$$
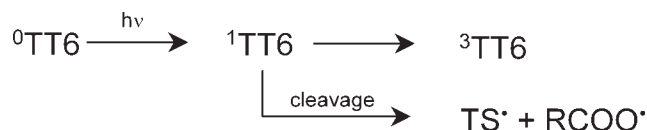
Scheme 7 Reactivity of TT6 upon light excitation.

$$^0TT1 \xrightarrow{h\nu} {}^1TT1 \xrightarrow{cleavage} TS^{\bullet} + RCOO^{\bullet}$$

Scheme 6 Reactivity of TT1 upon light excitation.
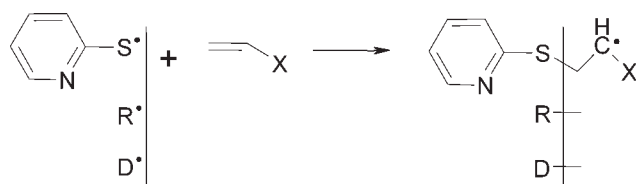
Scheme 8 Initiation reactions.

with the starting molecules should be reduced, but this would also reduce the reactivity of this radical towards the addition to the monomer unit. The relative overall efficiency in TPs and TTs will depend on the amount of light absorbed, the dissociation quantum yield, the decarboxylation process, the ability of the radicals to add to the monomer, and the side reactions which consume the initiating radicals.

CONCLUSIONS

Thiohydroxamic esters TPs (O-acyl derivatives of N-hydroxy-pyridine-2(1H)-thione) and TTs (O-acyl derivatives of N-hydroxy-thiazole-2(3H)-thiones) can effectively act as photoinitiators of radical polymerization. However, the intrinsic photoreactivity of these compounds is lower than that of commercially available photoinitiators. From a practical point of view, the shell life could remain a drawback in TPs, but the design of TTs appears as promising for getting a better photochemical stability. Indeed, working on the ring substitution or the nature of the radical derived from the acyloxy moiety might lead to more efficient compounds. The cleavage of the N—O bond of the newly investigated family of TTs occurs in the singlet state, a behavior which is similar to that of TPs. The introduction of a naphthalene, a phenyl, or a biphenyl moiety on the five-membered ring increases the intersystem crossing quantum yield and allows to form a triplet state, which might lead to a cleavage of the molecule to some extent. New insights in the photochemistry of TTs were given, especially on the thiyl radicals whose reactivity is completely different than that of TPs. In the TT series, compared to TPs, the destruction of the starting molecules by the thiyl radicals is reduced or suppressed: this should also help to reduce the photolysis of TTs. The modification of the chromophoric group (which plays a crucial role in the excited state processes), the structure of the thiyl radical, and the R leaving group (leading to a competition between initiation and degradation of the starting compound) presumably have a strong influence on the balance between the different processes. This work could serve as a starting point to design more efficient systems.

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