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Heteroaromatic Thiols as Co-initiators for Type II Photoinitiating Systems Based on Camphorquinone and Isopropylthioxanthone

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ABSTRACT: The heteroaromatic thiols (imidazole, oxazole, and thiazole derivatives) were investigated in regard to their abilities to function as co-initiators in free-radical photopolymerizations induced by camphorquinone and isopropylthioxanthone. As shown by the kinetic data, these heteroaromatic thiols are efficient co-initiators with activities comparable to aromatic amines. They quenched the triplet states of isopropylthioxanthone and camphorquinone with rate constants determined to be on the order of 10^9 and 10^8 M^{-1} s^{-1}, respectively. The results suggested that rates of polymerization of a low-viscosity monomer (triethylene glycol dimethacrylate) in an inert atmosphere are dependent on the quantum yields of formation of primary thiyl radicals Φ. However, this effect was also moderated by the reactivities of the thiyl radicals that were generated in the photosensitization stage. The observed activities of the initiator/thiol systems also depended on the possibility of initiator photoreduction by the monomer and, in air, on the ability of the co-initiators to reduce oxygen inhibition.

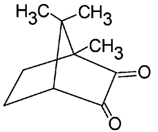
Introduction

Photoinitiators for free-radical polymerizations generally function in two distinct manners. The type I photoinitiators undergo intramolecular bond cleavage, notably α-cleavage of an aromatic ketone group in the photoinitiator itself. On the other hand, type II photoinitiators, typically benzophenone or quinone derivatives, act via intermolecular H abstraction from a hydrogen donor.[1,2] The long-lived triplet excited states of type II initiators, mainly diaryl ketones, can rapidly abstract hydrogen atoms from suitable donors (called co-initiators). The role of a co-initiator is to produce an initiating species, normally, by the reduction of the photoinitiator. Thus, such a co-initiator must contain labile hydrogens. In this reaction of the co-initiator with the electronically excited photoinitiator, the photoinitiator's carbonyl group is reduced to an alcohol. The reduction products can arise through two different pathways, namely: hydrogen abstraction from the hydrogen-donating compound by the excited ketone and electron transfer from an electron donor to the excited ketone and subsequent proton transfer.

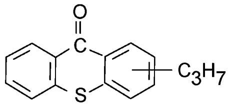
To adequately utilize these reactions with excited ketones, a variety of compounds can be used, such as alcohols, ethers, amines, phosphines, sulfides, etc. Tertiary amines are more reactive than alcohols and ethers, and as a consequence, these amines are the most frequently used co-initiators.

The popular type II photoinitiators are isopropylthioxanthone (ITX), widely used in photocurable compositions, and camphorquinone (CQ), the only photoinitiator employed in dentistry. CQ absorbs visible light in region of 400−500 nm (which is responsible for its yellow color) with a maximum at 470 nm due to an n,π* transition of the α-dicarbonyl chromophore.[3,4] The molar absorption coefficient of this transition is very low ($\epsilon = 40$ M^{-1} cm^{-1}). ITX absorbs at about 330−410 nm with a maximum at 384 nm due to a π,π^* transition. Its molar absorption coefficient at the λ_{max} is 6.9×10^3 M^{-1} cm^{-1}.[5]

To produce radicals efficiently, CQ and ITX are commonly used with amine co-initiators, often aromatic ones. Because there are many serious disadvantages of using amines (e.g., their mutagenicity and their tendency to induce substrate corrosion), investigations of new efficient co-initiators for ITX and CQ are important undertakings. Thiols are a class of compounds having readily abstractable hydrogens. Many thiols have the ability to quench the triplet states of type II photoinitiators with the subsequent formation of thiyl radicals:[6]



CQ



ITX

$$Ar_2CO \xrightarrow{h\nu} Ar_2CO^* \xrightarrow{RSH} RS^\bullet + Ar_2C^\bullet OH \qquad (1)$$

The resulting thiyl radicals are able to add to monomer double bonds. Reaction 1 is facilitated by the relatively low S−H bond dissociation energies (87 kcal/mol)[7] of thiols.

Thiols are relatively good quenchers of the triplet states of benzophenone and acetophenone.[8] Quantum yields for the photoreduction of benzophenone by amines are substantially increased by aliphatic thiols and decreased by aromatic thiols. In contrast, quantum yields for the photoreduction of benzophenone by alcohols were shown to be decreased by both aromatic and aliphatic thiols. These results are related to the propensity of thiols to undergo hydrogen abstraction readily, even by the triphenylmethyl radical. Moreover, thiols have unusual properties. In particular, while the hydrogen atom may be abstracted very rapidly from the thiol's sulfur, the resulting thiyl radicals are highly reactive (mainly, but not exclusively) in H-abstraction

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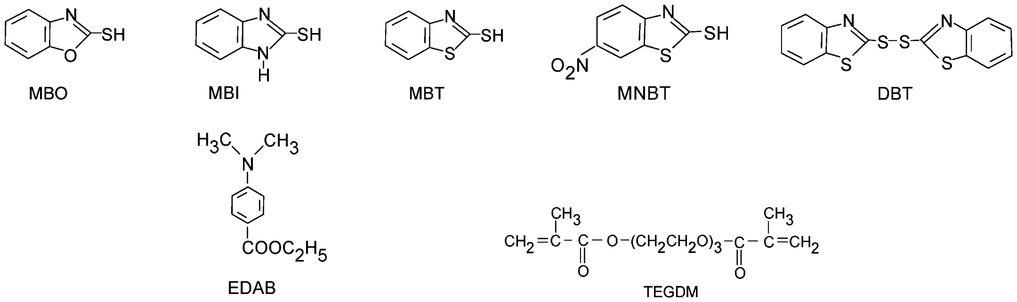
Chart 1



reactions. Such hydrogen transfers, to and from sulfur, compete effectively with other possible hydrogen abstractions and with radical recombinations. They may lead to inhibition, or to a change in the products, as in photoreductions by alcohols.[8] The strong hydrogen-donating character of thiols has been used in thiol−ene photopolymerizations.[9]

Aromatic thiols are especially strong hydrogen donors. Because of their ability to donate hydrogen atoms readily, some of them have been used as co-initiators for hexaarylbisimidazoles (HABI); in particular, the heteroaromatic thiols 2-mercaptobenzthiazole (MBT), 2-mercaptobenzimidazole (MBI), and 2-mercaptobenoxazole (MBO) were used.[10−13] Chemical reductions in these systems can occur either by direct hydrogen abstraction or by electron transfer to give the imidazole derivative and a sulfur-centered radical. The most frequently used thiol co-initiators in the HABI system have been found to react predominantly by an electron-transfer pathway.[1,10,13]

A combination of 9-phenylacridine with certain heteroaromatic thiols, such as MBI, provided high photosensitivity for the polymerization of pentaerythritol tetraacrylate.[14] MBO and MBT have also been used in two- and three-component photoinitiating systems based on coumarin derivatives.[15] They were able to initiate photopolymerizations without any photoinitiator although the efficiencies were low.[16]

This paper presents the high polymerization efficiencies for some heteroaromatic thiols, functioning as co-initiators for excited CQ and ITX, with efficiencies comparable to those of aromatic amines. The thiols in this study were MBO, MBI, MBT (which do not have the unpleasant smell of most thiols), and their derivatives. Their activities were compared to the activity of an aromatic amine, 4-ethyl-(*N*,*N*-dimethylamino)benzoate (EDAB), which due to its high efficiency, is widely used as a co-initiator in type II initiating systems. Triethylene glycol dimethacrylate (TEGDM) was used as a model monomer. The preliminary results of these investigations were published elsewhere.[17,18]

Experimental Section

Materials. The following compounds were investigated as co-initiators: 2-mercaptobenzoxazole (Aldrich, purity: 95%), 2-mercaptobenzimidazole (Aldrich, purity: 98%), 2-mercaptobenzothiazole (Aldrich, 98%), 2-mercapto-6-nitrobenzothiazole (MNBT Acros Organics, purity: 96%), 2,2′-dithiobis(benzothiazole) (DBT, Aldrich, 99%), and 4-ethyl-(*N*,*N*-dimethylamino)benzoate (Aldrich, ≥99%). They were used as received. Triethylene glycol dimethacrylate (Aldrich, purity: 95%) was purified by column chromatography before use. Camphorquinone (purity 97%) and isopropyl-9*H*-thioxanthen-9-one (isopropylthioxanthone), mixture of 2- and 4-isomers (purity 97%), were purchased from Aldrich.

Polymerization Kinetics. Reaction rate (R_p) profiles and conversions (p) were determined by differential scanning calorimetry (DSC) under isothermal conditions at 40 ± 0.01 °C in a high-purity argon atmosphere (<0.0005% of O_2) using a DSC 605M instrument (UNIPAN-TERMAL, Warsaw, Poland). It was equipped with a lid especially designed for photochemical measurements. The DSC instrument was calibrated with a standard Indium sample of known mass, melting point temperature, and known associated enthalpy change. The response time of the instrument is about 2.5 s. The 10 mg samples were polymerized in open aluminum pans having a diameter of 6.6 mm. The DSC chamber was purged with argon of high purity (<0.0005% of O_2) for 10 min prior to irradiation in order to remove oxygen from the chamber and that dissolved in the sample. The polymerizations were initiated by the light from a halogen lamp (Phillips 500 W GY 9,5, total light intensity 415 mW/cm^2). The initiating systems consisted of equimolar amounts (0.06 M) of the initiator (CQ or ITX) and the co-initiator, with the exception of DBT (0.006 M). All DSC photopolymerization experiments were conducted at least in triplicate. The reproducibility of the results was about ±3%. For computations, the heat of polymerization was taken to be 56 kJ/mol per double bond.[19]

Nanosecond Laser Flash Photolysis. The nanosecond laser flash photolysis setup has been described elsewhere.[20,21] For the MBO and MBI investigations, a nitrogen laser operating at 337 nm, 4−6 mJ/pulse (pulse width about 8 ns), was used, and for the MBT experiments, a Quanta Ray DCR-1 YAG laser operating at 355 nm, 2−12 mJ, 10 ns pulse width was used. Transient absorption spectra and quantum-yield measurements were performed using a flow-cell system with rectangular quartz cells (0.5 × 1 cm). The transients were monitored with a pulsed 1 kW xenon lamp, with the monitoring beam perpendicular to the laser beam. All solutions were routinely degassed with argon. The monitoring light path length was 0.5 cm. In quantum yield determinations an external relative actinometer was used.[22] The actinometry employed the triplet of 4-carboxybenzophenone in water taking $\epsilon_{535} = 6250\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$.[23]

The quantum yields of the transients were determined using the following equation:

$$\phi = \frac{\Delta A_t}{\epsilon_t}\frac{\epsilon_{CB}}{\Delta A_{CB}} \qquad (2)$$

in which ΔA_t is the transient absorption change (i.e., thiyl radicals) extrapolated to the end of pulse, ΔA_{CB} is the absorption change in the actinometer immediately after the laser flash due to the 4-carboxybenzophenone (CB) triplet (535 nm), and ϵ_t and ϵ_{CB} are the corresponding molar absorption coefficients of the transient and the CB triplet, respectively.

Molar absorption coefficients for MBO- and MBT-derived thiyl radicals were taken to be 27 000 and 29 000 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$, respectively.[24] The literature value for the molar absorption coefficient of the MBI-derived radical is not known; we therefore assumed that it is the same as for MBO-derived radicals.

The triplet quenching rate constants, ^3k_q, were measured by monitoring the decays of the triplet−triplet absorption of ITX at 640 nm in acetonitrile. The concentration of ITX was held fixed (7×10^{-5} M), while the concentrations of the thiols varied over a range (up to 8×10^{-4} M) that reduced the lifetime of the triplet. The ^3k_q values were determined by a linear least-squares fit to plots of the observed pseudo first-order rate constants k_{obs} for the ITX

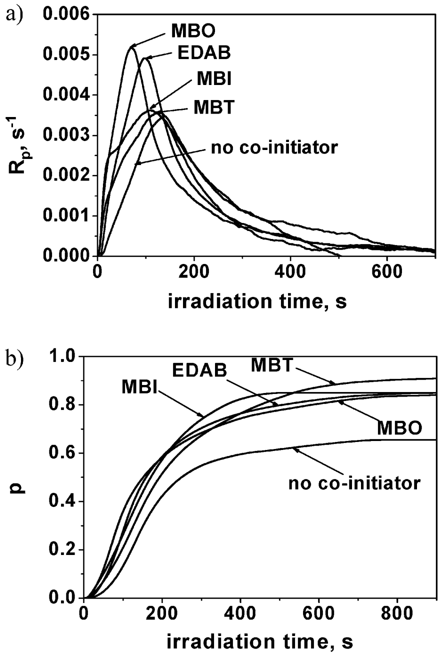


Figure 1. Polymerization rate R_p (a) and the degree of double-bond conversion *p* (b) as a function of irradiation time for triethylene glycol dimethacrylate (TEGDM) bulk photopolymerizations in Ar at 40 °C, initiated by camphorquinone (CQ, 0.06 M) in the absence and presence of co-initiators (0.06 M). MBO = 2-mercaptobenzoxazole, MBI = 2-mercaptobenzimidazole, MBT = 2-mercaptobenzothiazole, and EDAB = 4-ethyl-(*N*,*N*-dimethylamino)benzoate.

triplet decay vs the quencher concentrations [Q]. The fitting function was

$$k_{obs} = (^3\tau_0)^{-1} + {^3k_q}[Q] \tag{3}$$

in which $^3\tau_0$ is the ITX triplet-state lifetime in the absence of quencher.

Spectrofluorimetry. The spectrofluorimetric measurements were performed using a Perkin-Elmer MPF-3 spectrofluorimeter. The rate constant for the quenching of CQ fluorescence by MBO was determined in acetonitrile. The concentration of CQ was 3.6×10^{-3} M, and that of the thiol was in the range of 0.4×10^{-4}–1.1×10^{-4} M. The fluorescence quenching at 500 nm was measured in air, which enabled elimination of triplet emission. We were unable to determine the quenching rate constant of the CQ triplet by phosphorescence quenching because its phosphorescence intensity was too low for our observation at room temperature.

Cyclic Voltammetry. The oxidation potentials (E_{ox}) of thiols and the reduction potentials (E_{red}) of the initiators were measured in acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte using an AUTOLAB PGSTAT 30 instrument. The reference electrode was an AgCl electrode, and the scanning rate employed was 100 mV/s. The concentration of CQ and ITX was 10^{-2} M and that of the co-initiators 10^{-3} M.

Results and Discussion

Polymerization Kinetics. *CQ as the Photoinitiator*. The rate profiles of TEGDM photopolymerization (Figure 1a) show an immediate onset of autoacceleration typical for the polymerization of multifunctional monomers. The kinetic curves presented in Figure 1 reflect the activity of the investigated thiols, functioning as co-initiators for CQ, in TEGDM photopolymerizations.

The overall polymerization rate is determined by rates of the elementary reactions shown in Scheme 1, in which In is the initiator and M is a monomer molecule; $P^{\bullet}$ is a macroradical; k_q^{M} and k_q^{RSH} are the quenching rate constants by the monomer and the thiol, respectively; k_i^{M} and k_i^{RS} are the rate constants of addition to the monomer by the monomer- and thiol-derived radicals, respectively; k_p is the propagation rate coefficient; k_t^{b} and k_t^{m} are bi- and monomolecular (radical trapping) termination rate coefficients; k_t^{RS}, $k_t^{M(-H)}$, and k_t^{InH} are the termination rate coefficients by the primary radicals; k_{tr} is the chain transfer rate constant; k_{re} ($= k_i^{RS}$) is the reinitiation rate coefficient; k_{ox} includes both physical quenching by oxygen and the reactions of In* with oxygen; k_{O_2} is the rate constant of oxygen addition to carbon-centered radicals; and k_O^{RSH} and k_O^{M} are the rate constants of hydrogen abstraction by peroxy radicals from the thiol and the monomer, respectively.

Scheme 1

initiation

$$\text{In}^* + \text{M} \xrightarrow{k_q^{M}} \text{InH}^{\bullet} + \text{M(-H)}^{\bullet} \tag{4}$$

$$\text{In}^* + \text{RSH} \xrightarrow{k_q^{RSH}} \text{InH}^{\bullet} + \text{RS}^{\bullet} \tag{5}$$

$$\text{M(-H)}^{\bullet} + \text{M} \xrightarrow{k_i^{M}} \text{M(-H)M}^{\bullet} \tag{6}$$

$$\text{RS}^{\bullet} + \text{M} \underset{k_{-i}^{RS}}{\overset{k_i^{RS}}{\rightleftarrows}} \text{RSM}^{\bullet} \tag{7}$$

propagation

$$\left.\begin{matrix}\text{RSM}^{\bullet}\\ \text{M(-H)M}^{\bullet}\end{matrix}\right\} + n\text{M} \xrightarrow{k_p} \text{P}^{\bullet} \tag{8}$$

termination

$$\text{P}^{\bullet} + \text{P}^{\bullet} \xrightarrow{k_t^{b}} \text{dead polymer} \tag{9}$$

$$\text{P}^{\bullet} \xrightarrow{k_t^{m}} \text{radical trapping} \tag{10}$$

termination by primary radicals

$$\left.\begin{matrix}\text{P}^{\bullet} + \text{RS}^{\bullet} & \xrightarrow{k_t^{RS}}\\ \text{P}^{\bullet} + \text{M(-H)}^{\bullet} & \xrightarrow{k_t^{M(-H)}}\\ \text{P}^{\bullet} + \text{InH}^{\bullet} & \xrightarrow{k_t^{InH}}\end{matrix}\right\} \text{dead polymer} \tag{11}$$

chain-transfer

$$\text{P}^{\bullet} + \text{RSH} \xrightarrow{k_{tr}} \text{PH} + \text{RS}^{\bullet} \tag{12}$$

re-initiation

$$\text{RS}^{\bullet} + \text{M} \xrightarrow{k_{re}} \text{RSM}^{\bullet} \tag{13}$$

oxygen inhibition

$$\text{In}^* + \text{O}_2 \xrightarrow{k_{ox}} \text{oxidation products of In and physical quenching} \tag{14}$$

$$\text{P}^{\bullet} + \text{O}_2 \xrightarrow{k_{O2}} \text{POO}^{\bullet} \tag{15}$$

reduction of oxygen inhibition

$$\text{POO}^{\bullet} + \text{RSH} \xrightarrow{k_O^{RSH}} \text{POOH} + \text{RS}^{\bullet} \tag{16}$$

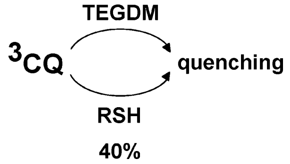
$$\text{POO}^{\bullet} + \text{M} \xrightarrow{k_O^{M}} \text{POOH} + \text{M(-H)}^{\bullet} \tag{17}$$

In the above set of elementary reactions, the initiation by the photoinitiator-derived ketyl radicals $\text{InH}^{\bullet}$ has not been included because ITX and CQ ketyl radicals are not able to initiate the polymerization; they rather participate in the termination[1,6,25] (reaction 1).

The rates of the reactions in the polymerization scheme can be diffusion-controlled, depending on the viscosity of the polymerizing medium (termination is diffusion-controlled from the beginning of the reaction). The TEGDM viscosity at 40 °C (measured in this work) is 6 mPa·s. Thus, the diffusion rate coefficient estimated from the Stokes–Einstein–Smoluchowski equation is on the order of 1.2×10^{9} M^{-1} s^{-1}. This means that in the early stages of TEGDM polymerization only processes with markedly higher rate constants (occurring with the participation of small molecules) will be diffusion-controlled.

In the absence of any co-initiator, the hydrogen-donor molecule is the monomer itself (reaction 4); thus, the polymerization may occur if the monomer contains labile hydrogen atoms. TEGDM contains three oxyethylene units which may serve as a source of abstractable hydrogens (reaction 8). Radical

Scheme 2



formation is then possible because the lowest excited triplet state of CQ has n,π^* character which enables it to react efficiently with ethers.[6] This is the mechanism of the initiation in the absence of co-initiators, and it is the reason the polymerization is quite efficient.

$$-O-CH_2-CH_2- + CQ^* \rightarrow -O-C^{\bullet}H-CH_2- + C^{\bullet}QH \quad (18)$$

Addition of the thiols or the amine resulted in a significant acceleration of primary radical formation leading to an increase in the polymerization rate. In the case of the thiols, the primary radicals are the $RS^{\bullet}$ radicals (reactions 5 and 19):

$$CQ^* + RSH \rightarrow C^{\bullet}QH + RS^{\bullet} \quad (19)$$

Up to about 4% of double-bond conversion, the polymerization rates in the presence of MBO and MBI are very similar and are higher than in the presence of MBT. At this stage of the polymerization process, the initiation rate will depend mainly on the rate constants for the quenching of excited CQ by the co-initiators and the monomer and, in addition, on the quantum yields of radical formation.

The probability $\alpha_{In,Q}$ for quenching an excited photoinitiator molecule by a co-initiator is given by eq 20

$$\alpha_{In,Q} = \frac{^3k_q[Q]}{^3k_q[Q] + {^3k_q}^M[M] + k_d} \quad (20)$$

in which ^3k_q is the rate constant of quenching by the co-initiator, ${^3k_q}^M$ is the rate constant of quenching by the monomer, k_d is the rate constant for intramolecular deactivation of the triplet state equal to reciprocal triplet lifetime in the absence of co-initiator and monomer, [Q] is the co-initiator concentration, and [M] is the monomer concentration.

Taking into account that the quenching rate constant of ^{3}CQ by TEGDM is 2.6×10^6 M^{-1} s^{-1} [26] ([M] = 3.5 M) and that the quenching rate constants of ^{3}CQ by the heteroaromatic thiols are on the order of 10^8 M^{-1} s^{-1} (see below), one obtains, from eq 20, that the CQ triplet is quenched by thiols (0.06 M) only to the extent of about 40% (Scheme 2). This points to the important role that the monomer's hydrogen-donating ability plays in the production of initiating radicals in this particular case. Since the triplet lifetime of CQ is in the range of 400 μs,[27] k_d in eq 20 was neglected in this calculation.

The rate constant for quenching ^{3}CQ by an aromatic amine is on the order of 4.6×10^9 M^{-1} s^{-1},[28] which means that 96% of ^{3}CQ would be quenched by the amine, when [amine] = 0.06 M. This indicates that α-aminoalkyl radicals would be the main initiating species when aromatic amines are used as the co-initiator in CQ-induced polymerizations.

Another factor determining the rate of the initiation is the rate for the addition of the thiyl radical to the monomer double bond (reaction 7). This reaction is reversible. The rate constant for addition of the MBT-derived radical to the methyl methacrylate double bond was determined by Ito to be 2.8×10^7 M^{-1} s^{-1},[29] and the elimination rate constant estimated from Ito's results is $<10^6$ s^{-1}. However, the high concentration of double bonds would shift the equilibrium away from the thiyl radical, and addition of $RSM^{\bullet}$ radicals to the monomer would deplete the macroradical's side of the equilibrium (7), further driving the equilibrium away from the thiyl radical. Thus, the elimination reaction (reverse reaction in equilibrium (7)) of the adduct radical can be neglected in our case.

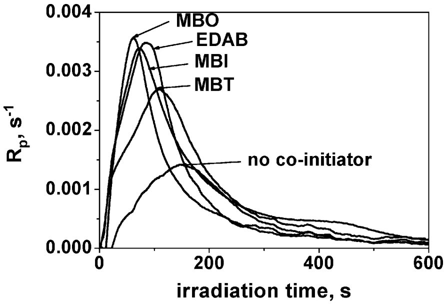


Figure 2. Polymerization rate R_p as a function of irradiation time for TEGDM bulk photopolymerizations in air at 40 °C, initiated by CQ (0.06 M) in the presence of the co-initiators (0.06 M). Abbreviations as in Figure 1.

The influence of other factors becomes more important in later stages of the polymerization process as the system's viscosity increases, and the concentration of macroradicals increases. These additional factors, e.g., the chain-transfer reaction (reaction 2) and/or the reactivity of $RS^{\bullet}$ radicals, may further differentiate polymerization rates. The influence of chain-transfer reactions is to accelerate bimolecular termination, slowing in this way the polymerization. This effect has been discussed elsewhere.[30]

The largest increase in the maximum polymerization rate R_p^{max} was observed in the presence of MBO, whose influence on the acceleration of the polymerization was comparable to that shown by the amine.

The high activity of MBO in accelerating the polymerizations suggests a high efficiency for radical formation in the CQ/MBO initiating system and/or a high reactivity for the MBO-derived thiyl radicals. The ability of MBI to accelerate the polymerization, which is high at the beginning of the reaction, decreased substantially after the polymerizing system reached conversions of about 10% and became similar to that shown by MBT. Despite differences between the co-initiators with regard to their effects on the polymerization rates, all the co-initiators increase the final conversions to a similar degree. (An increase in the efficiency of CQ/MBO-induced polymerization was reported also for 2-hydroxyethyl methacrylate[18] and for methyl methacrylate.[31])

In the presence of air, the polymerization rates were significantly lower (Figure 2), and the accelerating effect of the co-initiators was stronger. Assuming that the quenching rate constant of ^{3}CQ by oxygen is 0.22×10^9 M^{-1} s^{-1} [32] and that the oxygen concentration in the organic solvents is on the order of 2×10^{-3} M, we obtain from an equation analogous to eq 20 that oxygen quenching of ^{3}CQ at the beginning of the polymerization is only 5% in the absence of co-initiators and <3% in their presence, reaction 14.This indicates that the influence of oxygen on the initiation stage was minimal and that most of the oxygen inhibition resulted mainly from radical capture. Thus, the observed accelerating effect of the co-initiators, in the presence of air, results both from the acceleration of radical formation and from reduction of oxygen inhibition (removing of oxygen in the peroxidation process, reactions 15 and 16).[9,33]

A possible reason for the relatively low efficiency of MBT in an Ar atmosphere might be the low reactivity of the derived

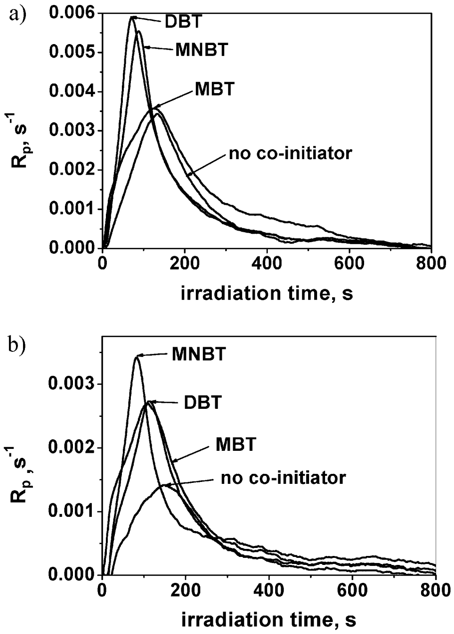


Figure 3. Polymerization rate R_p as a function of irradiation time for TEGDM bulk photopolymerizations at 40 °C initiated by CQ (0.06 M) in the presence of MBT and MNBT (0.06 M) and DBT (0.006 M): (a) Ar; (b) air. DBT = 2,2′-dithiobis(benzothiazole) and MNBT = 2-mercapto-6-nitrobenzothiazole; other abbreviations as in Figure 1.

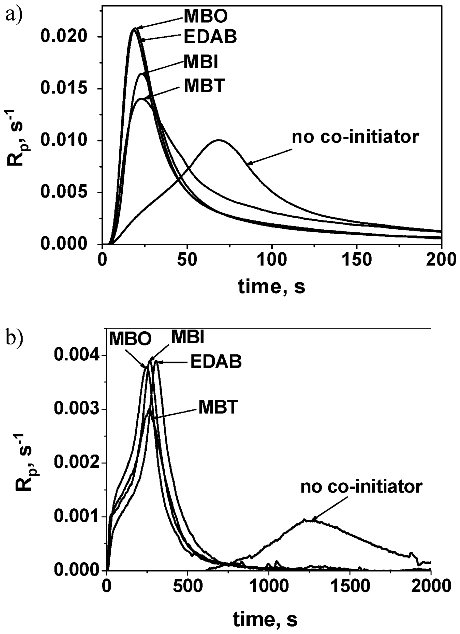


Figure 4. Polymerization rate R_p as a function of irradiation time for the bulk photopolymerizations in Ar at 40 °C initiated by CQ (0.06 M) in the absence and presence of co-initiators (0.06 M), with monomers (a) tetraethylene glycol diacrylate and (b) 2-hydroxyethyl methacrylate. Abbreviations as in Figure 1.

thiyl radicals. However, this same thiyl radical can be formed alternatively by homolytic cleavage of DBT. We tested DBT as a co-initiator for ^{3}CQ. Because of the limited solubility of DBT, it was employed at a concentration 10 times lower (0.006 M) than we used for the other co-initiators. Despite its low concentration, the polymerization initiated by the CQ/DBT system occurred with a rate comparable to that of MBO (Figures 1 and 3a) as the co-initiator. Thus, the high activity of DBT suggests that its dissociation in the presence of ^{3}CQ is very efficient and that the derived thiyl radicals do efficiently initiate the polymerization. (A polymerization was attempted with DBT in the absence of CQ, and it led to a very low yield of polymerization. This indicates that the S−S cleavage of DBT is mainly photoinduced via CQ under the photolysis conditions we employed.) Comparing the MBT and DBT reactivities, one should also take into account that the rate constants for chain transfer to disulfides are much lower than those to thiols.[7]

Introduction of an electron-withdrawing group, such as introducing the nitro moiety into the benzene ring of MBT, yielding the co-initiator MNBT, resulted in a significant acceleration of the polymerization at medium conversions (Figure 3a). It was suggested[34] that this type of substitution in tertiary aromatic amines enhances the reactivity of the derived aminoalkyl radicals.

A comparison of the relative behavior of MBT and DBT in air (Figure 3b) and under argon (Figure 3a) showed the influence of oxygen inhibition. The ability of DBT to accelerate the polymerization in air is weaker than that of MNBT and is almost the same as that of MBT (not compensating for the different concentrations used). This is because MBT and MNBT are effective in their reduction of oxygen inhibition via the extractable hydrogens on their thiol groups, whereas DBT has no such easily extractable hydrogens and cannot reduce oxygen inhibition via reaction 16.

Other heteroaromatic thiols tested in this work, such as 2-mercaptoimidazole (MI), 2-mercapto-5-methylimidazole (MMBI), and 2-mercapto-1-methylimidazole (MMI) plus some aromatic (4,4′-thiobis(benzenethiol), MAS) and aliphatic (dodecanethiol, DDM) thiols were very poor co-initiators. They often retarded the TEGDM photopolymerization in Ar under the conditions used, but they accelerated polymerizations in air (due to their reduction of oxygen inhibition).

It is also worth mentioning that increasing the co-initiator concentration from 0.03 up to 0.09 M resulted in an increase in the polymerization rate.

Qualitatively similar results using initiator/(heteroaromatic thiol) systems were also obtained employing other monomers, e.g., tetraethylene glycol diacrylate and 2-hydroxyethyl methacrylate (Figure 4, polymerization in Ar).

The relative efficiency of the CQ/heteroaromatic thiol system changes when the monomer (or mixtures of monomers) is highly viscous. An example is TEGDM/bis-GMA (2,2-bis[4-(2-hydroxymethacryloxypropoxy)phenyl]propane) (30/70 by weight) mixture, widely used in dental applications. Its viscosity is 0.63 Pa•s (at 40 °C), which makes the diffusion-limited rate coefficient on the order of only 10^7 M^{-1} s^{-1} in such a mixture. Thus, the reactions between CQ and the co-initiators will be diffusion controlled from the very beginning of the polymerization. As a consequence, the main factor controlling the polymerization rate will be the reactivity of the primary radicals. The polymerization rate profiles of the TEGDM/bis-GMA mixture initiated by the CQ/co-initiator systems in Ar are shown in Figure 5, which demonstrates that the most efficient co-initiator was the aromatic amine. The ability of MBT to accelerate the polymerization was much higher than that of MBI (which correlates well with the reactivities of their radicals in the literature[24,35]). Even the thiols which retarded TEGDM polymerization were quite efficient co-initiators for CQ in the polymerization of the TEGDM/bis-GMA mixture. The presence of oxygen has almost no influence on the polymerization, probably due to limited oxygen diffusion into the highly viscous medium.

ITX as the Photoinitiator. The initiation process occurring in the presence of ITX should differ from that in the presence of CQ because of the different photochemical properties of the two photoinitiators. ITX has a π,π^* state for its lowest triplet

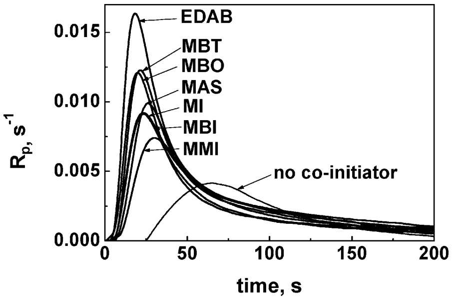


Figure 5. Polymerization rate R_p as a function of irradiation time for the bulk photopolymerizations in Ar at 40 °C initiated by CQ (0.06 M) in the absence and presence of co-initiators (0.06 M), with the TEGDM/bis-GMA (30/70 by weight) mixture. MMI = 2-mercapto-1-methylimidazole, MMBI = 2-mercapto-5-methylimidazole, and MAS = 4,4′-thiobis(benzenethiol); other abbreviations as in Figure 1.

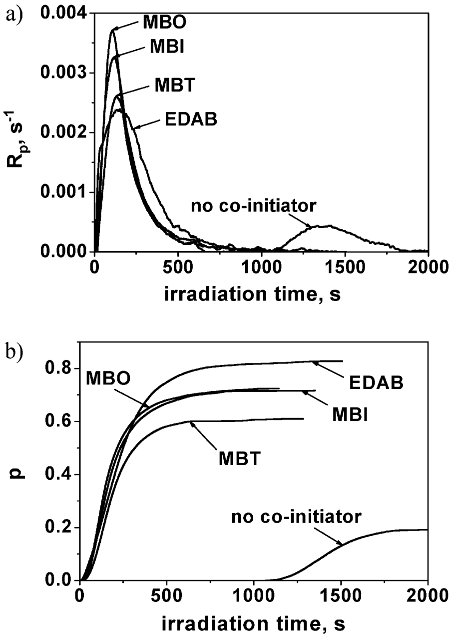


Figure 6. Polymerization rate R_p and degree of double-bond conversion *p* as a function of irradiation time for TEGDM bulk photopolymerization in Ar at 40 °C initiated by isopropylthioxanthone (ITX, 0.06 M) in the absence and presence of co-initiators (0.06 M). Abbreviations as in Figure 1.

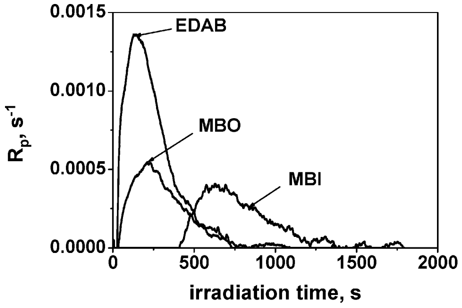
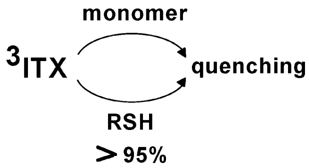


Figure 7. Polymerization rate R_p as a function of irradiation time for TEGDM bulk photopolymerizations in air at 40 °C initiated by ITX (0.06 M) in the presence of the co-initiators (0.06 M). In the presence of MBT and in the absence of co-initiators no polymerization occurred. Abbreviations as in Figures 1 and 6.

Scheme 3



(T_1) while the T_1 state of CQ is n,π*. Triplet n,π* states are generally much better hydrogen abstractors than are π,π* T_1 states because of the electrophilicity of the localized hole left by the excitation of the nonbonded orbital in an n,π* T_1 state.[6] Thus, ITX is should be less effective than CQ as a type II photoinitiator.

The kinetic curves of TEGDM photopolymerizations initiated by ITX in the presence of MBO, MBI, MBT, and EDAB are shown in Figures 6 and 7. On the basis of the difference in the T_1 states of ITX and CQ, mentioned above, it is not surprising that the rates of TEGDM polymerization initiated by the ITX/thiol systems were markedly lower than in the CQ/thiol systems. However, this difference may also result in part from differences in the intensities of the light absorbed by ITX and CQ, resulting from their respective differences in the overlap between the light source spectrum and the spectra of ITX and CQ.

As can be seen, the most striking difference between polymerizations initiated by CQ and ITX occurs when no co-initiator was present. Even in an inert atmosphere (Figure 6), this ITX-initiated polymerization occurred only after a long induction period and was characterized by a low polymerization rate and a low conversion. This behavior probably results from inefficient production of initiating radicals in the reaction between ^{3}ITX and TEGDM since ethers react efficiently only with n,π* triplet states. As reported earlier,[36] the initiation of the polymerization in the ITX/(methyl methacrylate) system does not occur probably because of the absence of readily abstractable hydrogens.

Addition of co-initiators significantly increased the polymerization rates (Figure 6) due to efficient photoreduction of ^{3}-ITX. Even thiols, which retarded TEGDM polymerization when photoinitiated by CQ (for instance MMBI, MI, MMI), showed an accelerating effect with ITX. The order of the polymerization efficiencies of the three heteroaromatic thiols was the same as in the presence of CQ, namely at low double-bond conversion (up to ~8% of double-bond conversion) MBO ≈ MBI > MBT and at higher conversions MBO > MBI > MBT. When EDAB was used as the co-initiator along with ITX, the strongest accelerating effect was observed at the beginning of the polymerization. However, the maximum polymerization rate (R_p^{max}) was lower than those in the presence of the thiols, which was in contrast to the corresponding polymerizations initiated by CQ. With all the co-initiators, the polymerizations went to high conversions with a somewhat better result for EDAB compared to the heteroaromatic thiols.

Another difference between polymerizations initiated by CQ and ITX was that, at the beginning of the polymerizations, the primary radicals in ITX-initiated polymerizations were almost exclusively formed in the reaction between ITX and the co-initiators. Assuming (1) that the monomer's rate constant for quenching the triplet of ITX is similar to that of methyl methacrylate (3×10^6 M^{-1} s^{-1})[5] and (2) that the rate constants for quenching ^{3}ITX by EDAB[5] or the heteroaromatic thiols (see below) are on the order of $(3-6) \times 10^9$ M^{-1} s^{-1}, it can be shown from eq 20 that >95% of ^{3}ITX should be quenched by the thiols or the amine (0.06 M, Scheme 3). Thus, hydrogen abstraction from the monomer practically does not affect the production of initiating radicals at low conversions in the presence of the hydrogen donors under investigation. (In eq 20, k_d was ignored because the triplet lifetime of ITX is 20 μs, as measured from T−T absorption decay, Figure 8.)

Kinetic curves of the polymerizations carried out in air are presented in Figure 7 and show a very strong inhibitory effect

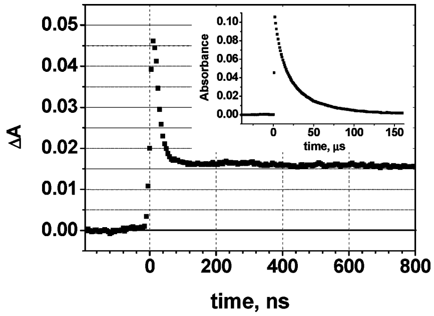


Figure 8. Kinetic trace at 640 nm following laser flash photolysis of ITX (7×10^{-5} M) and MBO (1.9×10^{-2} M) in acetonitrile. Inset: kinetic trace of decay of ITX triplet state measured at 640 nm (ITX concentration 7×10^{-5} M). Abbreviations as in Figure 6.

from oxygen. Because oxygen quenching of ^{3}ITX in the presence of co-initiators was below 5%, the oxygen inhibition resulted mainly from radical capture, and its strong effect was probably due to the low rates of radical production under the conditions used. In the absence of co-initiators, about 95% of the ^{3}ITX was quenched by oxygen. This, along with the low efficiency of radical formation from the monomer, was why polymerization did not occur in the absence of co-initiators.

The best results were obtained in the presence of the amine. This, along with the lack of a significant induction period, indicates that its efficiency was highest due to the reduction of oxygen inhibition. The complete suppression of the induction period was also observed in the presence of MBO, suggesting that this compound was the most efficient of the thiols investigated in reducing oxygen inhibition.

No polymerization was observed in the presence of MBT. This may indicate that (like in the absence of co-initiators) the efficiency of radical formation was too low to allow the reaction to occur in the presence of oxygen under the conditions used.

Investigation of the Initiation Mechanism. The initiating radicals (derived from the corresponding thiols) were the same whether the light-absorbing species was CQ or ITX. From the discussion above, it may be expected that the activities of the thiols in accelerating polymerizations depend on the reactivities of the thiyl radicals generated, the efficiency of their formation, and the extent of chain transfer to the co-initiators. The efficiency of radical formation (measured by quantum yields of radical formation Φ) was, in turn, critically dependent on the co-initiators' rate constants for quenching the excited photoinitiator. Thus, the relative polymerization efficiencies of the thiols may be determined in large part by photophysical and photochemical properties of the photosensitizers relative to the co-initiators.

These photophysical and photochemical parameters can be quantified using laser flash photolysis. In particular, rate constants ^3k_q of triplet quenching of the photoinitiators by the co-initiators and the quantum yields Φ of thiyl radical formation were determined for the ITX/thiol (MBO, MBI, and MBT) systems.

Following laser excitation of ITX at 355 nm in acetonitrile, a transient absorption spectrum was seen with a peak at 640 nm. The transient absorption has a lifetime of 21 μs and corresponds to the triplet−triplet absorption of ITX.[37] The inset to Figure 8 shows the kinetic curve of the ITX triplet's decay.

When the thiols were present, the ITX triplet was rapidly quenched. The kinetic curve of the ^{3}ITX quenching process occurring in the presence of MBO is depicted in Figure 8. After a rapid initial drop in the 640 nm decay trace, Figure 8 shows a much longer-lived absorption with a lifetime greater than even the unquenched triplet. This long-lived absorption indicates the formation of a new species generated in the quenching reaction. Transient absorption spectra, taken in time windows following the rapid decay of the ITX triplet, show the appearance of a new absorption band at 590 nm. Examples of these transient absorptions are presented in Figure 9. The absorption spectra are ascribed to thiyl radicals on the basis of literature data for MBO- and MBT-derived radicals.[24] These spectra were produced from the reactions of the corresponding thiols with ^{3}ITX and were taken in various times after the laser flash.

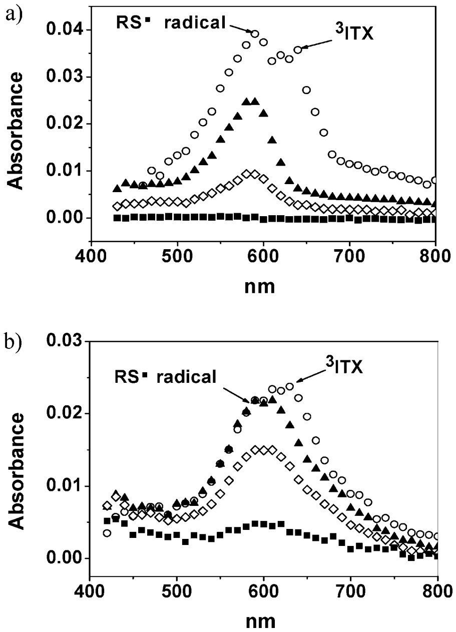


Figure 9. Transient absorption spectra following quenching of the ITX triplet in acetonitrile: (a) by MBI taken 40 ns (circles), 150 ns (triangles), 100 μs (diamonds), and 150 μs (squares) after the flash; (b) by MBO taken 40 ns (circles), 200 ns (triangles), 5 μs (diamonds), and 30 μs (squares) after the flash. [ITX] $= 7 \times 10^{-5}$ M, [MBI] $= 10^{-2}$ M, and [MBO] $= 1.9 \times 10^{-2}$ M. Excitation at 355 nm. Abbreviations as in Figures 1 and 6.

In addition, at long delay times after the ^{3}ITX absorption disappears, the weak absorption of the ITX ketyl radical with $\lambda_{max} = 425$ nm[37] was visible.

Rate constants ^3k_q for quenching of the ITX triplet were determined using pseudo-first-order plots of the observed reciprocal lifetimes (k_{obs}) of the triplet state vs [Q] (see Experimental Section). Because of the strong inhibitory oxygen effect, the rate constant for quenching by oxygen was also determined in an analogous manner. Quantum yields of thiyl radical formation Φ were determined by laser flash photolysis using relative actinometry and the extinction coefficients cited in the Experimental Section. These quenching rate constants and quantum yields are given in Table 1.

The rate constants for quenching of the ITX triplet by the investigated thiols were very high, similar to that of the aromatic amine. They were also much higher than the rate constants for quenching of the ITX triplet by aliphatic thiols, such as dodecanethiol.[5] The quantum yields of radical formation are rather low, on the order of those reported for triplet benzophenone quenching by 1-pentanethiol ($\Phi = 0.03$).[8] The Φ values are very similar for MBO and MBI, but these two values are about 3 times higher than that for MBT. This result correlates well with the activity of thiols in accelerating the TEGDM polymerizations at low double-bond conversions.

The quenching rate constant of the CQ triplet by heteroaromatic thiols has only been estimated. Determination of the

Table 1. Rate Constants for Quenching of the ITX Triplet (^3k_q) by Thiols, an Amine, and Oxygen plus Quantum Yields of Thiyl Radical Formation (Φ) during Photoreduction of ITX by Thiols in Acetonitrile

quencher	^3k_q (M^{-1} s^{-1})	Φ
O_2	$(4.8 \pm 0.2) \times 10^9$	
MBO[a]	$(3.44 \pm 0.01) \times 10^9$	0.050
MBI[b]	$(6.2 \pm 0.2) \times 10^9$	0.053
MBT[c]	$(4.7 \pm 0.1) \times 10^9$	0.015
EDAB[d]	4×10^9, ref 5	
DDT[e]	7×10^7, ref 5	

[a] 2-Mercaptobenzoxazole. [b] 2-Mercaptobenzimidazole. [c] 2-Mercaptobenzothiazole. [d] 4-Ethyl-(*N*,*N*-dimethylamino)benzoate. [e] Dodecanethiol.

quenching rate constant of the CQ singlet by MBO gave the value $^1k_q = (7.50 \pm 0.06) \times 10^8$ M^{-1} s^{-1}. Because the quenching rate constant of the triplet state is usually lower or close to the quenching rate constant of the singlet state, we assumed that the quenching rate constant of the CQ triplet by heteroaromatic thiols is $\leq 10^8$ M^{-1} s^{-1}. This value is similar to that for aliphatic amines and is lower than for aromatic amines ($^3k_q \sim 10^9$ M^{-1} s^{-1}).[28]

The large rate constants for quenching the triplets of the photoinitiators suggest that the formation of radicals in the photoinitiator/(heteroaromatic thiol) systems may occur via photoinduced electron transfer (PET) followed by proton transfer shown in eq 21:

$$\mathrm{In}^* + \mathrm{HS{-}R} \xrightarrow{\mathrm{ET}} [\mathrm{ITX}^{\bullet-}...\mathrm{HS}^{\bullet+}{-}\mathrm{R}]^* \rightarrow \mathrm{In}^{\bullet} + \mathrm{S}^{\bullet}{-}\mathrm{R} \qquad (21)$$

The thermodynamic condition for spontaneous electron transfer is that the Gibbs free energy $\Delta G°$, expressed by the Rehm–Weller equation,[38] has negative values:

$$\Delta G° = E_{ox}(D^{\bullet+}/D) - E_{red}(A/A^{\bullet-}) - Ze^2/\epsilon a - E_{oo} \qquad (22)$$

in which $E_{ox}(D^{\bullet+}/D)$ is the oxidation potential of the electron donor molecule (thiol), $E_{red}(A/A^{\bullet-})$ is the reduction potential of the electron acceptor (ITX, CQ), $Ze^2/\epsilon a$ is the Coulombic energy, normally considered negligible in high-dielectric solvents, and E_{oo} is the triplet energy of the photoinitiator.

The driving force for the electron transfer is $-\Delta G°$. If the PET process is not diffusion controlled, it could be the rate-determining step for the polymerization. In such a case, the polymerization rate would increase with an increase in the $-\Delta G°$ value, at least up to the diffusion-controlled limit. The rate of electron transfer cannot be the rate-determining step if it approaches the diffusion-controlled limit (then it becomes independent of $\Delta G°$). In such a situation, other factors (for example, the reactivity of the primary radicals) would control the polymerization rate.[39] Thus, the effectiveness of any PET mechanism decreases as the viscosity of the polymerizing medium increases, and the formation of reactive radicals by the PET mechanism may be effective only at the beginning of the polymerization. Figure 10 presents the natural logarithm of the TEGDM polymerization rate at 8% of double-bond conversion as a function of the $-\Delta G°$ value for the initiating systems. (Note the PET driving forces of ^{3}ITX quenching are greater than those of the ^{3}CQ associated ones, with ^{3}ITX triangles displaced to the right of the circles for the corresponding ^{3}CQ data points in Figure 10.) $\Delta G°$ values were calculated from the measured oxidation potentials of the co-initiators given in Table 2 and the measured reduction potentials of the initiators $E_{red} = -1.596$ V vs AgCl (for ITX) and $E_{red} = -1.296$ V vs AgCl (for CQ).

It is clearly seen that there is a correlation between the $-\Delta G°$ value of the PET step of initiation and the polymerization rate although the dynamic range of the changes in ln R_p is not large. This suggests that at the beginning of the TEGDM polymerizations electron transfer may be the rate-determining step in the radical formation. Figure 10 shows also, for comparison, the parameters for the EDAB-containing initiating systems. However, the EDAB positions cannot be compared directly to the positions of the thiols because of the difference in the structure of its functional group that serves as the hydrogen donor.

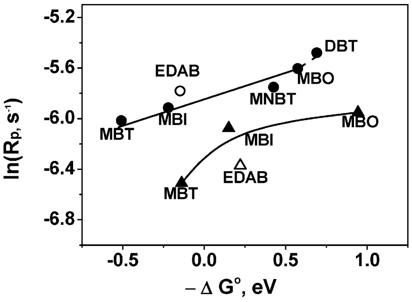


Figure 10. Rates of polymerization R_p (in Ar at 40 °C) of TEGDM at 8% of double-bond conversion as a function of Gibbs free energy of the electron-transfer reactions from the various co-initiators to the triplet sensitizer. Triangles: $[\mathrm{ITX}] = 6 \times 10^{-2}$ M, $[\text{co-initiator}] = 3 \times 10^{-2}$ M; circles: $[\mathrm{CQ}] = 6 \times 10^{-2}$ M, $[\text{co-initiator}] = 6 \times 10^{-2}$ M except for $[\mathrm{DBT}] = 6 \times 10^{-3}$ M. The curves are not fits to the data points but are meant as a guide to the eye of the reader. Abbreviations as in Figures 1 and 3.

Table 2. Oxidation Potentials (in V vs AgCl Electrode) of the Co-initiators

co-initiator	MBO[a]	MBI[b]	MBT[c]	MNBT[d]	DBT[e]	EDAB[f]
E_{ox} (V)	0.336	1.13	1.419	0.484	0.219	1.058

[a] 2-Mercaptobenzoxazole. [b] 2-Mercaptobenzimidazole. [c] 2-Mercaptobenzothiazole. [d] 2-Mercapto-6-nitrobenzothiazole. [e] 2,2′-Dithiobis(benzothiazole). [f] 4-Ethyl-(*N*,*N*-dimethylamino)benzoate.

Conclusion

The current studies show that heteroaromatic thiols can be efficient co-initiators for free-radical polymerizations induced by the popular photosensitizers ITX and CQ. The co-initiators employed have a much stronger influence on the rates of ITX-induced polymerizations than on CQ-induced polymerizations. This general trend may be due to the combination of two factors: (i) the lower efficiency of radical formation directly from the monomers when the lowest excited triplet state of the initiator has π-π* character (ITX) and/or (ii) the higher driving force $-\Delta G°$ for the excited-state quenching (larger PET driving force for ITX). As our results show, there is a correlation between the initial polymerization rate of TEGDM (the low-viscosity monomer) and the quantum yield of radical formation as well as a correlation between the initial polymerization rate of TEGDM and the $-\Delta G°$ for the PET of the initiating system.

According to the literature, the reactivities of thiyl radicals change in the order MBT ≥ MBO ≫ MBI.[24,35] However, the existence of the correlation between the polymerization rates at low conversions and the quantum yields of radical formation (MBO ≈ MBI > MBT) suggests that these quantum yields are more important than radical reactivities as far as they affect the initial polymerization rates under inert atmospheres. On the other hand, when there are small differences in Φ, the reactivities of the thiyl radicals may be the deciding factor in determining the relative importance of the polymerization rates at medium and higher conversions. The observed activities of the initiator/thiol systems are also associated with the possibility of initiator photoreduction by the monomer.

In the presence of air, an additional factor appears that can influence a co-initiator's effectiveness. This factor is the ability of a co-initiator to reduce oxygen inhibition. If the efficiency of primary radical formation is high, the reaction of oxygen consumption is less important. However, in the case of slow initiation, it can have a significant effect (e.g., EDAB in the ITX-induced polymerization).

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