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Sulfur-containing initiators and coinitiators of free radical polymerization

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Abstract

Initiation of polymerization of a number of monomer molecules by the absorption of one photon is a form of chemical amplification. The process is started by system called "photoinitiation system" or "photoinitiator system". The photoinitiator system generates the free radicals that initiate radical chain polymerization of vinyl monomers. It may be a single compound that absorbs the light and then undergoes homolytic bond cleavage to form a pair of free radicals, or it may consist of several different compounds that undergo series of complex reactions to produce initiating radicals. This brief review summarizes a part of results obtained by members of our research group on the photochemistry and application of sulfur-containing organic compounds used as photoinitiators and coinitiators of free radical polymerization.

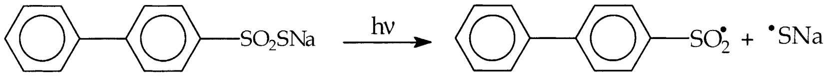
Keywords: Sulfur-containing initiator; Coinitiators; Polymerization

1. Photofragmentable (photodecomposed) sulfur-containing initiators

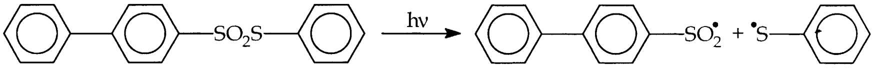
Photofragmentation occurs when a photoexcited molecule undergoes bond cleavage that gives a pair of free radicals. One or both of the resulting radicals can initiate free radical polymerization. There are several groups of sulfur-containing organic compounds studied in our laboratory and described in literature. These include the following.

1.1. Thiosulfonate [1–3]

This group includes sodium 4-phenyl-phenylthiosulfonate (**I**) and phenyl ester of diphenyl-4-thiosulfonic acid (**II**). These compounds are known to undergo the decomposition on the light irradiation to yield sulfur radicals



I



II

Since sodium 4-phenyl-phenylthiosulfonate is soluble in water, it can be used both as a photoinitiator of polymerization of aqueous monomer solution and as photoinitiator of an emulsion polymerization. Polymerization of styrene in water–Triton-X-100 emulsion indicates, as it is shown in Fig. 1 that **I** is a very efficient photoinitiator of free radical polymerization.

Polymerization of acrylamide performed in water shows that 4-phenyl-phenylthiosulfonate also very efficiently initiates polymerization of this monomer. The measurements have shown that the rate of polymerization and masses of polymer obtained depend on the photoinitiator concentration. Replacement of sodium atom by phenyl group changes the solubility of **I** that becomes soluble in nonpolar solvents. The modification gives as a result an ester of biphenyl-4-thiosulfonic acid (**II**). The initiator obtained is rather poor one in the polymerization of styrene in benzene solution. The rate of polymerization can be accelerated by

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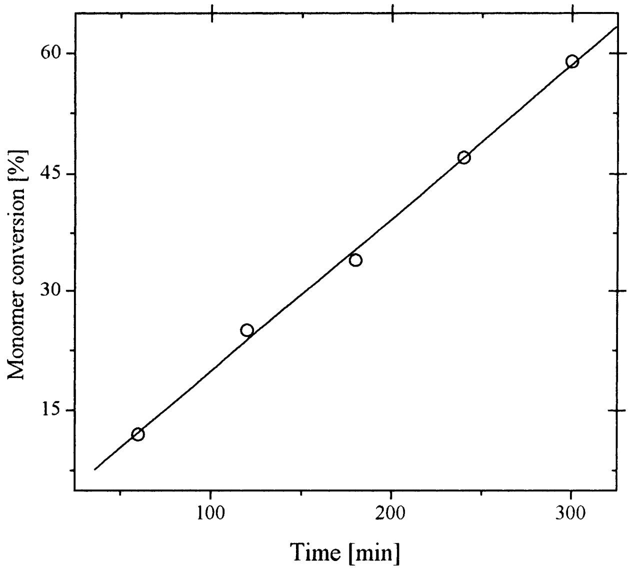


Fig. 1. Conversion of styrene in water–Triton-X-100 emulsion; concentration of emulsifier 5% by mass, concentration of 4-phenylphenylthiosulfonate 1.8×10^{-2} M.

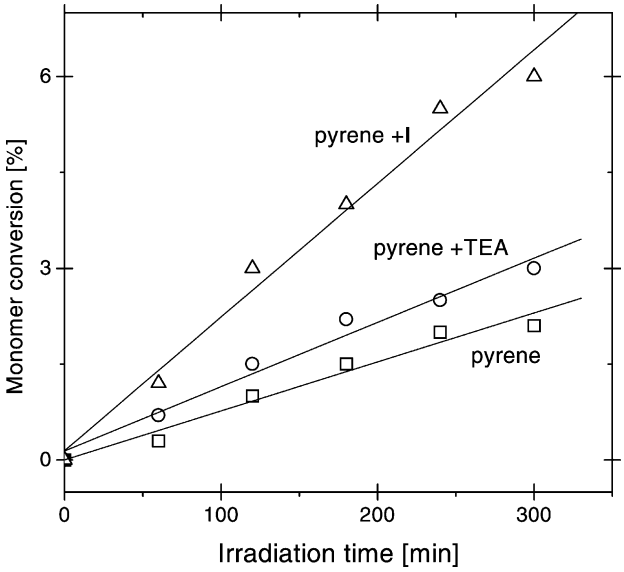


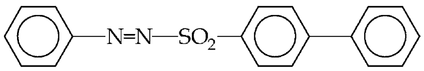
Fig. 2. Conversion of styrene in benzene, concentration of sulfoester 5×10^{-3} M, concentration of pyrene and triethylamine (TEA) 1×10^{-3} M.

using pyrene as a component of the photoinitiation system (Fig. 2).

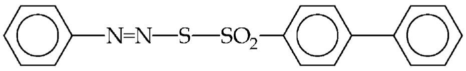
1.2. *Sulfur-containing azoinitiators [4,5]*

This class of the compounds include:

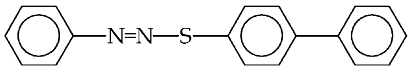
(a) phenylazo-4-biphenylsulfone (**III**)



(b) phenylazo-4-biphenyltiosulfone (**IV**)

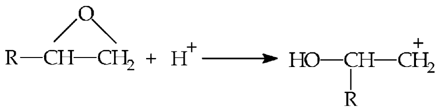


(c) phenylazo-4-biphenylsulfide (**V**)



The sulfur-containing azoinitiators photodecompose on the light irradiation giving radicals (in nonpolar solvents) and ions (in polar solvents). These initiators are rather poor photoinitiators of free radical polymerization (see Fig. 3). Instead they are very good thermal initiators. For instance, phenylazo-4-biphenylsulfide more effectively thermally initiate free radical polymerization than commonly applied azodiizobutyronitryle (see Fig. 4).

Sulfur-containing azoinitiators can also be used as photocross-linking agent [5]. Obtained in the photodecomposition process sulfonyl, thiosulfonate and sulfide radicals, abstract hydrogen atom from the medium of the reaction to give appropriate Brönsted acids that can crosslink poly(2,3-epoxypropyl methacrylate) by cationic mechanism according to equation:



$$R{-}\overset{\overset{O}{\wedge}}{CH{-}CH_2} + H^{+} \longrightarrow HO{-}\underset{\underset{R}{|}}{CH}{-}\overset{+}{CH_2}$$

Fig. 5 presents photocrosslinking process of poly(2,3-epoxypropyl methacrylate) by compounds (**III**–**V**). As can be seen the best photocrosslinking properties possesses

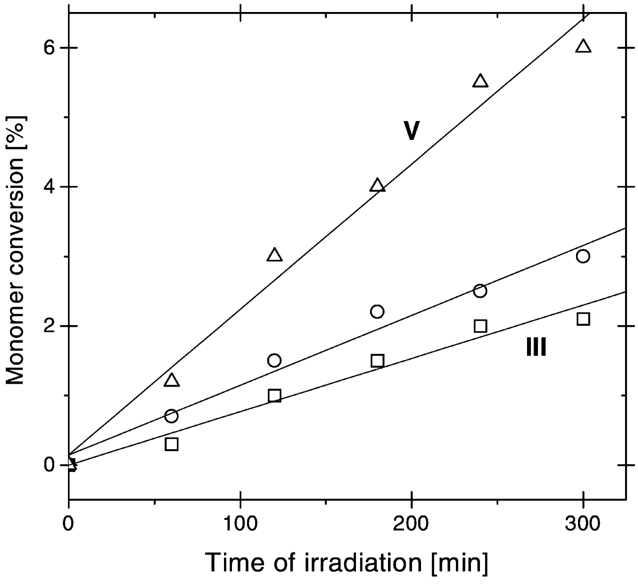


Fig. 3. Photoinitiated polymerization of styrene by: 1 (**III**), 2 (**IV**), 3 (**V**). Concentration of compounds (**III**–**V**) equal 5×10^{-3} M.

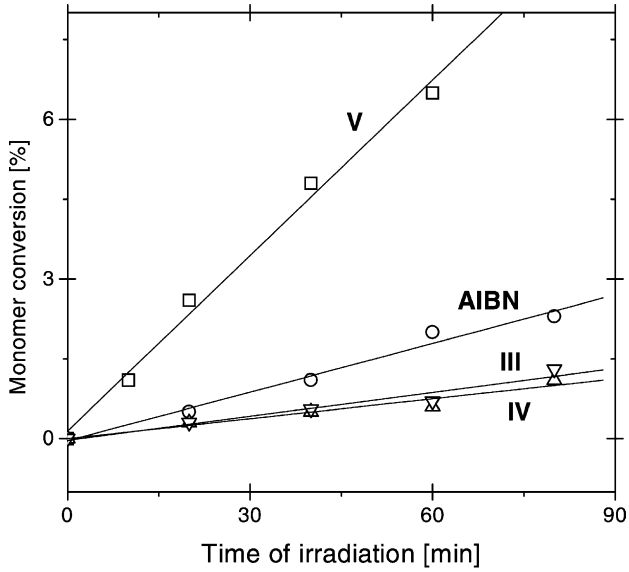


Fig. 4. Thermal polymerization of styrene by: 1 (**III**), 2 (**IV**), 3 (**V**) at 65 °C. Concentration of compounds (**III–V**) equal 1×10^{-3} M.

phenylazo-4-diphenylsulfone. The variation in the rate of photocrosslinking is probably due to the difference in the power of Brönsted acids rather than in difference in the rate of photodecomposition of sulfur-containing compounds.

1.3. Sulfur derivatives of benzophenone [6–9]

Benzophenone alone weakly polymerizes vinyl monomers. But certain substituted benzophenones act as efficient photoinitiators [10–13]. The first example of the benzophenone sulfur derivatives investigated by authors of this paper was *N*-[(*p*-benzoyl)benzenesulfonyl] benzene-sulfonamide (**VI**) [9]. The compound is soluble in both in organic solvents and in water. Solubility in organic solvents is due to the benzophenone residue and solubility in water is caused by strong hydrogen bonding between water and sulfonamide group. The initiator dissociates upon light irradiation according to Scheme 1.

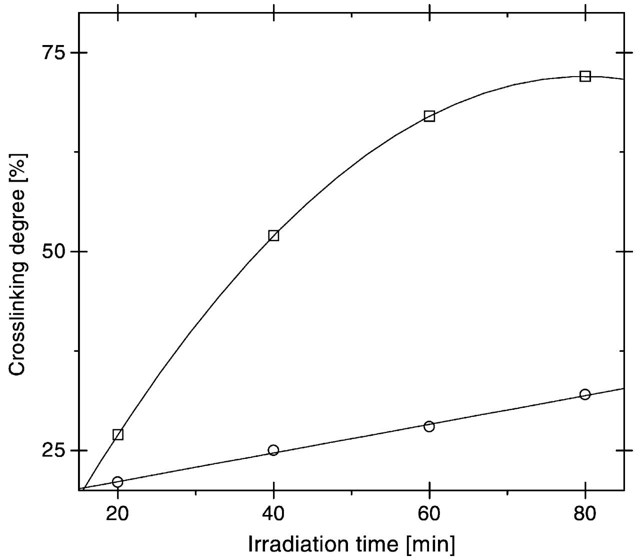
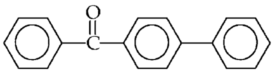
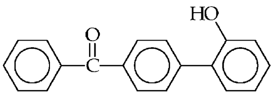


Fig. 5. Photocrosslinking of poly(2,3-epoxy propyl methacrylate) by compounds (**III–V**), concentration of compounds (**III–V**) 2% by mass.

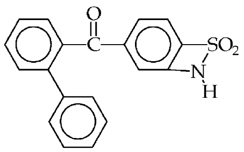
The above mechanism is postulated based on **VI** photolysis in an aqueous solution [14]. The photoproduct (95%) consists of four main components

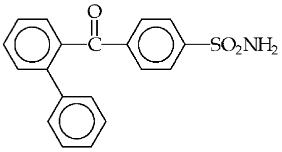


4-benzoylbiphenyl (**VII**)

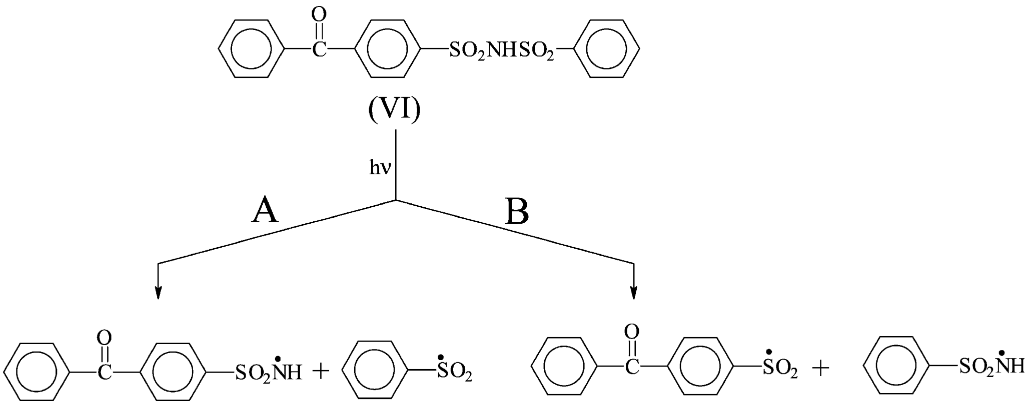


2-hydroxy-4’-benzoylbiphenyl (**VIII**)

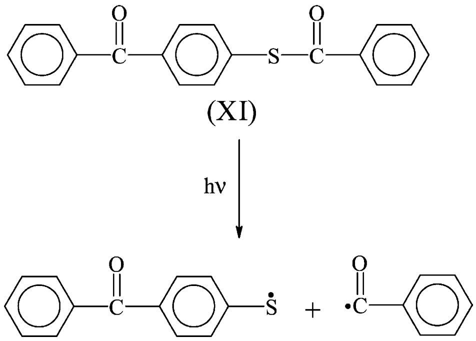




The presence of compounds **VII** and **VIII** confirms the leg **B** of photoprocesses. However, the formation efficiency of these products is quite low (3 and 5%, respectively). The dominating path of photoreaction (leg **B**),



Scheme 1.



Scheme 2.

according to the data obtained, is proofed by the efficiency of 4-(2-phenyl-benzoyl)-benzene-sulfonic acid amide (**X**) formation, which reaches the value of 80%.

N-[(4-benzoyl)benzenesulfonyl]benzene-sulfonamide (**VI**) as photoinitiator can be used for polymerization of monomer in aqueous solution as well as the initiator of polymerization of monomers in bulk [6,9]. In the nonionic emulsion, the rate of the polymerization depends on the concentration of the photoinitiator as well on the concentration of emulsifier Triton X-100 [6]. Polymerization of methyl methacrylate in bulk shows that the rate of the polymerization is proportional to the square root of the photoinitiator concentration. It should be noted that the dependence of the reciprocal of the chain length versus the rate of polymerization shows that the chain transfer to monomer can be neglected. The change of hydrogen atom on methyl group changes the solubility of photoinitiators, which after this transformation can be used for the initiation of polymerization of acrylamide in DMSO solution [7].

The last compound of this class is *S*-(4-benzoyl)phenylthiobenzoate (**XI**), which photodecomposes to yield benzoylphenylsulphonyl and benzoyl radicals (Scheme 2). It was initially postulated that the decomposition of the photoinitiator occurs exclusively by the triplet mechanism [7]. Measurements of photopolymerization performed showed that the rate of the polymerization of methyl methacrylate is proportional to the square root of the photoinitiator concentration. The change of the sulfur atom on the oxygen in photoinitiator molecule results in a sharp decrease of the photoinitiation ability (Fig. 6).

The detailed study on the mechanism of *S*-(4-benzoyl)phenylthiobenzoate photodissociation, performed with the use of laser flash photolysis evidently documented the formation of benzoylphenylsulphonyl and benzoyl radicals (Fig. 7).

Fig. 8 shows the transient absorption spectra recorded for *S*-(4-benzoyl)phenyl thiobenzoate in MeCN solution. A similar experiment performed for 4-benzoylphenyl benzoate gives quite a different picture of the process (see Fig. 9).

Comparison of the spectra in Figs. 8 and 9 reveals that *S*-(4-benzoyl)phenyl thiobenzoate (BpSBz) behaves quite differently than 4-benzoylphenyl benzoate (BpOBz). In addition, it is worth noting that there is a significant difference of the effect of oxygen on the two spectra. In the case of *S*-(4-benzoyl)phenyl thiobenzoate, at short times, its spectrum in an oxygen-saturated solution is almost identical in shape to that in Fig. 8; however, at longer times, a broad band develops in the spectral region between 350 and 400 nm. From the inset of Fig. 8, the decay of the transient in argon-saturated solution is seen to be second-order, and its decay in the presence of oxygen is the same for kinetic traces monitored at 500 nm. On the other hand, for oxygen-saturated solutions of BpOBz, the transient in Fig. 9 disappears within 50 ns. This is in contrast to oxygen-free solutions of BpOBz where the decay is monoexponential with a lifetime of 10.4 μs (see inset of Fig. 9).

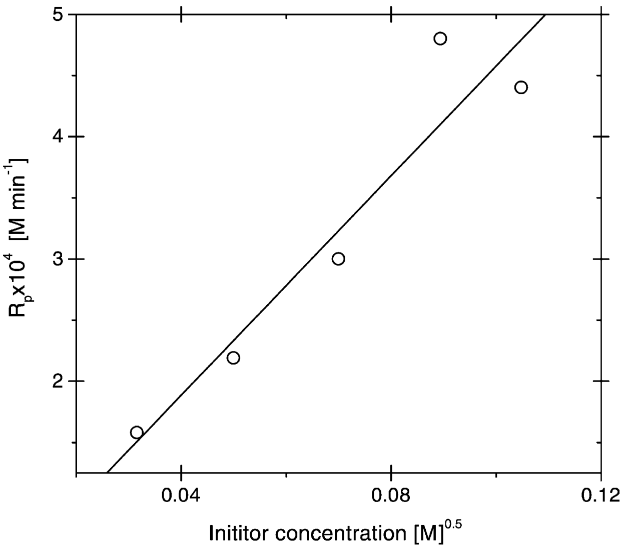


Fig. 6. Initial polymerization rate (R_{p}) of methyl methacrylate (MMA) as a function of the square root of the *N*-[(*p*-benzoyl)benzenesulfonyl] benzenesulfonamide concentration.

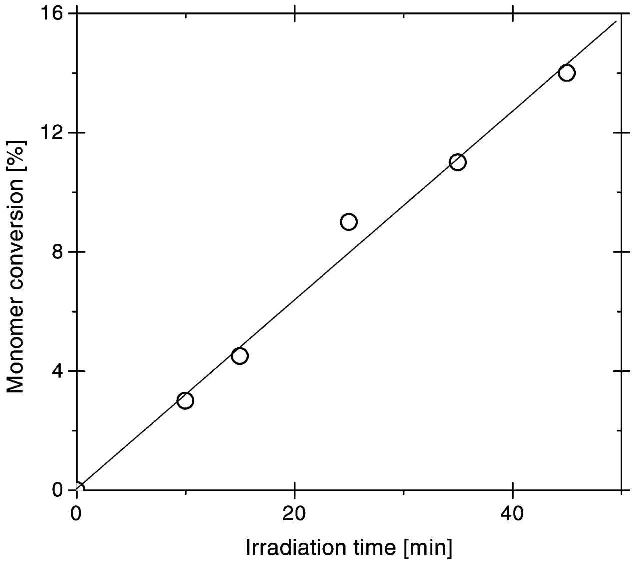


Fig. 7. Conversion of methyl mathacrylate by *S*-(benzoyl)phenyl thiobenzoate. Concentration of initiator equal 3×10^{-3} M.

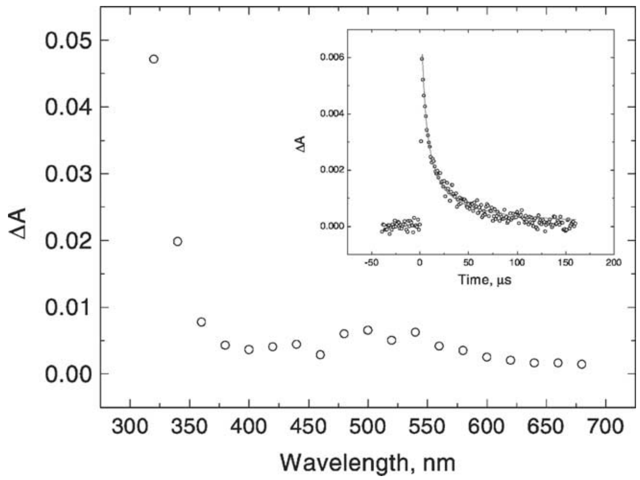
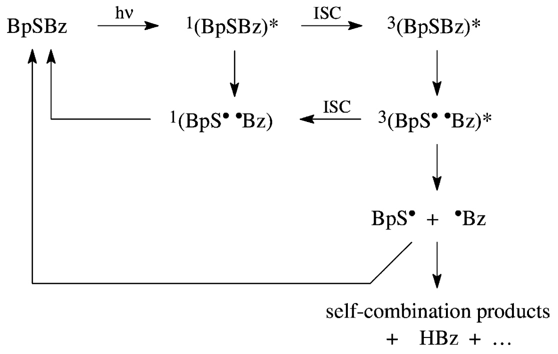


Fig. 8. Transient absorption spectrum obtained during 308 nm photolysis of *S*-(4-benzoyl)phenyl thiobenzoate in MeCN (argon-saturated) solution after 450 ns delay. Inset: kinetic trace recorded at 500 nm, second-order decay decay with $2k/\varepsilon l = 2.5 \times 10^7\,\mathrm{s}^{-1}$.



Scheme 3.

On the basis of the spectral characteristics and the behavior in the presence of oxygen, one can assign the transient in Fig. 8 as the 4-benzoylphenylthiyl radical (BpS$^\bullet$). The spectral characteristics of the species being assigned as the BpS$^\bullet$ radical (absorption spectrum slightly red-shifted, compared with the spectrum of phenylthiyl radical [15]) are almost identical to the features of the optical spectrum of the BpS$^\bullet$ radical found by Autrey et al. [16] in the photolysis of bis(4-benzoylphenyl)disulfide (BpSSBp). In addition to the similarity in the transient's spectrum to that of BpS$^\bullet$, its second-order decay is consistent with the unknown species being a radical. Furthermore, its lack of reactivity with oxygen is consistent with the normally low reactivity of aromatic thiyl radicals with oxygen ($k < 10^4\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) [17]. The transient in Fig. 9 is assigned as the triplet state of 4-benzoylphenyl benzoate. Its spectral position and shape are reminiscent of benzophenone triplet–triplet absorption. Its decay is monoexponential in argon-saturated solutions, and it is quenched by oxygen, both of which are consistent with the transient being a triplet state absorption.

The energetic considerations indicate the possibility of two separate pathways for photocleavage, via the singlet excited state and the triplet state (see Scheme 3, which is in analogy to the scheme for the photolysis of BpSSBp [16]). The singlet mechanism involves a singlet radical pair in which the radicals, BpS$^\bullet$ and $^\bullet$Bz, would likely recombine efficiently. The triplet mechanism, on the other hand, would result in a triplet radical pair that could permit substantial escape of free radicals because of spin restrictions on recombination in the solvent cage. The triplet mechanism may also be substantial since the intersystem crossing rate constant in analogous substrates, e.g., BpSMe generates triplets within 17 ps [16].

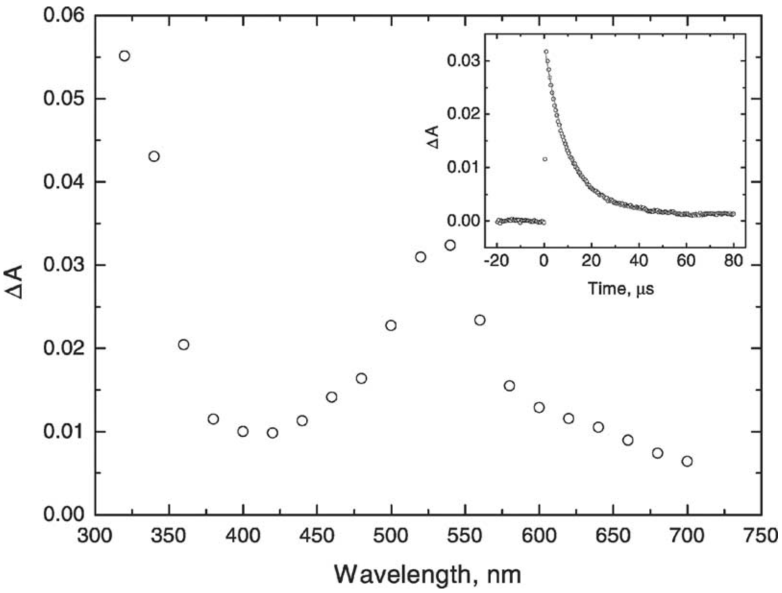


Fig. 9. Transient absorption spectrum obtained in the 308 nm photolysis of 4-benzoylphenyl benzoate in MeCN (argon-saturated) solution, recorded after 250 ns delay. Inset: kinetic trace recorded at 540 nm, monoexponential decay; $\tau = 10.4\,\mu\mathrm{s}$.

2. Two components photoinitiation systems

Photoinduced intermolecular electron transfer is an important process giving as an intermediate free radical able to initiate polymerization chain reaction [18–21]. The panchromatic sensitization of vinyl polymerization requires the presence of suitable dye as a primary absorber. For such a case, photophysical energy transfer between dye excited state and other chromophore which yields free radicals, is generally disfavored. As an alternative other processes avoiding typical energy restriction should be considered. The photoinduced intermolecular electron transfer, which is nonclassical, endothermic energy transfer process, represents such as alternative. This process involves the use of light to initiate electron transfer from a donor to an acceptor molecule. Scheme 4 is a good starting point to begin the analysis of the process.

k_d is the rate constant representing the rate of diffusive encounters between reactants, k_{-d} denotes the rate of separation of the reactants after collision, k_{el} is the first-order rate constant of electron transfer. The reverse step is designated by the rate constant k_{-el} and finally k_r denotes the rate of return electron transfer.

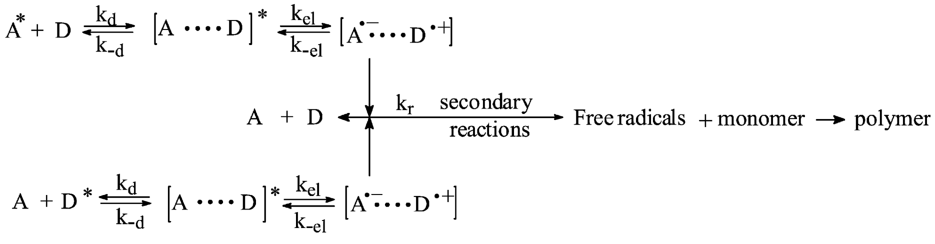
In translating these to sensitization of free radical polymerization one should anticipate that two types of sensitization should occur.

(1) Photoreducible dye sensitization reported first by Oster in 1954 [22]. Oster identified several groups of effective dyes, which are photoreduced during photochemical reaction in the presence of suitable reductants. The tested dyes included the classes of acridine, xanthene and thiazine dyes.

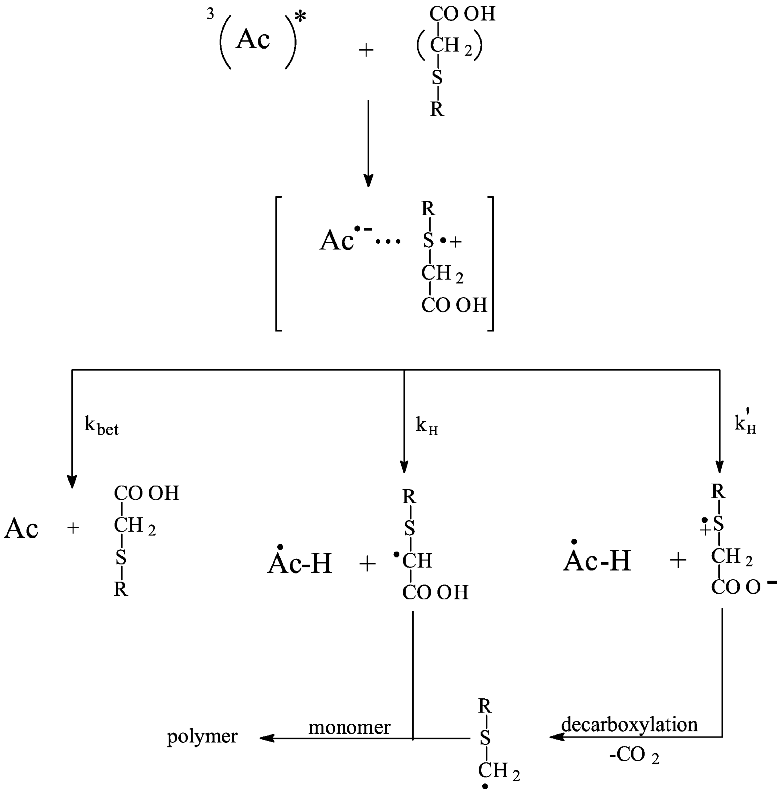
(2) Photooxidiazable dye sensitization. This sensitization requires molecules being in its ground state a strong electron acceptor. Onium salts of xanthene dyes prepared by Linden and Neckers [23–25] undergo photochemical reaction, which is pure electron transfer process.

The mechanistic aspects of secondary reactions following photoinduced electron transfer between an electron acceptor and sulfur-containing amino-acids, sulfur-containing carboxylic acids (SCCAs), both aromatic and alifatic, depend strongly on the polarity of polymerizing mixture. Marciniak et al. [26–32] examined quenching of triplet states of benzophenones by sulfur-containing amino-acids and SCCAs in water/acetonitrile solution and they found that the mechanism of photoinduced electron transfer between sulfur-containing amino-acids and carboxylic acids, tested using steady-state and laser photolysis techniques, involves an electron transfer from the sulfur atom to the triplet state of benzophenone followed by: (i) the diffusion apart of the charge-transfer complex, (ii) the intramolecular proton transfer within CT complex. The first, more efficient process led to the formation of sulfur-centered radical cations and ketyl radicals anions which undergo fast protonation. The slow formation of the ketyl radicals is assigned to the one electron reduction of benzophenone by the α′-aminoalkyl-type radicals produced from the free-radical cation of the amino-acids as a result of intramolecular electron transfer from the carboxyl group to the sulfur-centered radical cation followed by decarboxylation. Scheme 5 shows the photoprocesses that occur in the electron acceptor–sulfur-containing electron donor photoredox pair. Based on this, the study with the use of xanthene dyes as electron acceptors and sulfur-containing acids and amino-acids as electron donors, were tested as potential systems able to photoinitiate free radical polymerization. Taking into account the photochemistry of xanthene dyes [33–36] and properties of sulfur-containing acids and amino-acids, one can expect that this type of photoredox pairs are able efficiently to initiate free radical polymerization.

Based also on the study on the photochemistry of xanthene dyes [33–36] and properties of sulfur-containing amino-acids acting as electron donors [26–32], one can propose the scheme (see Scheme 6) illustrating major processes that may occur during photoinitiated free radical polymerization. The ratio between the rate of diffusion apart of radical ions and the rate of intramolecular proton transfer within CT complex depends on the properties of a solvent (monomer). Since sulfur-containing amino-acids are weakly soluble even in moderate polar solvents, the reaction of photoinitiated polymerization is possible in formulation containing water. Under this condition, the dominating path of the reaction, after an electron transfer, begins from the separation of radical ions. Since sulfur-containing amino-acids are biologically less-toxic, less-allergic and probably nonmutagenic compounds, they can probably replace harmful amines as coinitiators used for preparation of dental restorative formulations [37].



Scheme 4.



Scheme 5.

The kinetics of free radical polymerization were measured based on measurement of the rate of heat evolution during polymerization [38–41]. Photopolymerization was initiated using an Omnichrome argon-ion laser Model 543-500 MA. The average power of irradiation was 30 mW/0.785 cm^2. All irradiation procedures were made on the one type of formulation which consists of the mixture of poly(ethylene glycol)diacrylate—1% NH_4OH in water (7:3), dye concentration: 10^{-3} M. and electron donor concentration 10^{-1} M.

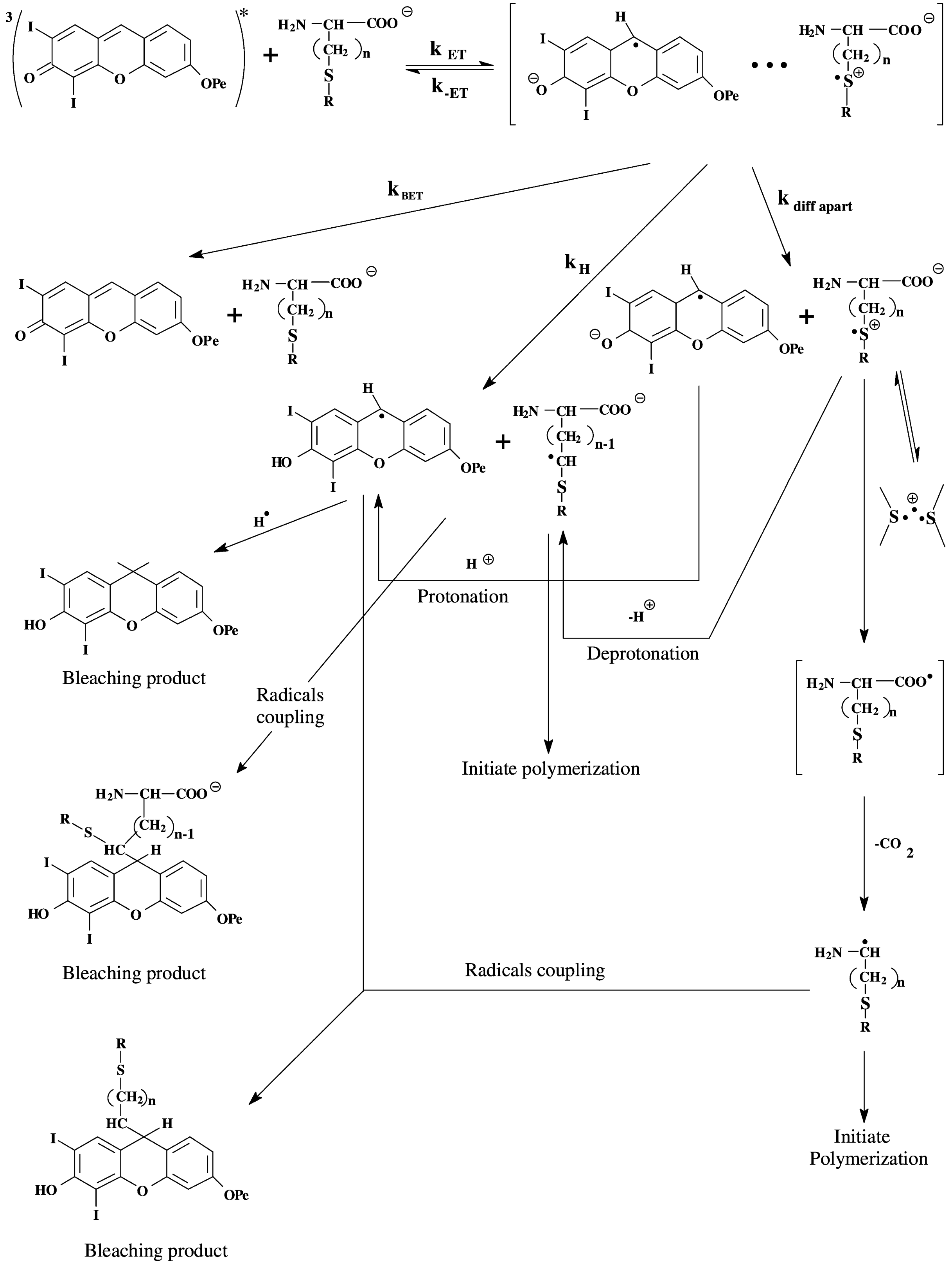
As electron acceptors xanthene dyes were used. These included the following:

1. *RBAX*. The Rose Bengal derivative was prepared from Rose Bengal according to procedure described by Neckers and co-workers [42]. Its reduction potential is assumed to be equal to the reduction potential of Rose Bengal C2′ benzyl ester, sodium salt [21], e.g., $E_{red}(A^{\bullet-}/A) = -0.80$ V and its triplet $E_{oo} = 1.7$ eV [43,44].
2. *TIHF*. Tetraiodohydrofluorescein (2,4,5,7-tetraiodo-6-hydroxyfluorone) was synthesized according to the method of Shi et al. [33,34]. Its reduction potential and triplet state energy according to Rodgers and Neckers are $E_{red}(A^{\bullet-}/A) = -0.99$ V (V(SCE)) (our measurement $E_{red}(A^{\bullet-}/A) = -0.940$ V (V (1 M. Ag–AgCl)) and $E_{oo}^{(T)} = 1.83$ eV. For photopolymerization experiments TIHF was acetylated using a similar procedure as for RBAX.
3. *DIPF*. Diiodohydrofluorescein (3-pentoxy-5,7-diiodo-6-fluorone) was synthesized according to the method of Shi et al. [34]. Its reduction potential measured using cyclic voltammetry is $E_{red}(A^{\bullet-}/A) = -0.94$ V and $E_{oo}^{(T)} = 2.25$ eV.

As electron donors amino-acids and SCCAs as well as sulfur-containing amino-acids were applied. In order to reduce the effect of diffusion-controlled termination, the effect of network formation and the Norrish-Troomsdorf effect [45–49], the initial rates of polymerization were taken into account for further consideration (initial rates of polymerization are slopes of the lines drawn on the flow of heat versus time curves at initial time of polymerization). Fig. 10 shows the family of kinetic curves recorded during the photoinitiated polymerization of mixture composed of: poly(ethylene glycol)diacrylate—1% NH_4OH in water (7:3), and TIHF as light absorber and selected sulfur-containing amino-acids.

Initial rates of polymerization [au] obtained for all tested amino-acids, sulfur-containing acids and amino-acids are summarized in Table 1.

Precisely, the chemistry of sensitized photooxidation of sulfur-containing amino-acids in neutral aqueous solution was explained with the use of 4-carboxybenzophenone (CB) as electron acceptor and series of sulfur-containing amino-acids [26,50]. Sensitized photoreaction of sulfur-containing amino-acids occurs via electron transfer from the sulfur to the triplet state of the sensitizer according to the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Protonation
-H⊕
Deprotonation
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Radicals coupling
Initiate polymerization
-CO 2
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Initiate Polymerization
Bleaching product
Bleaching product
Bleaching product

Scheme 6.

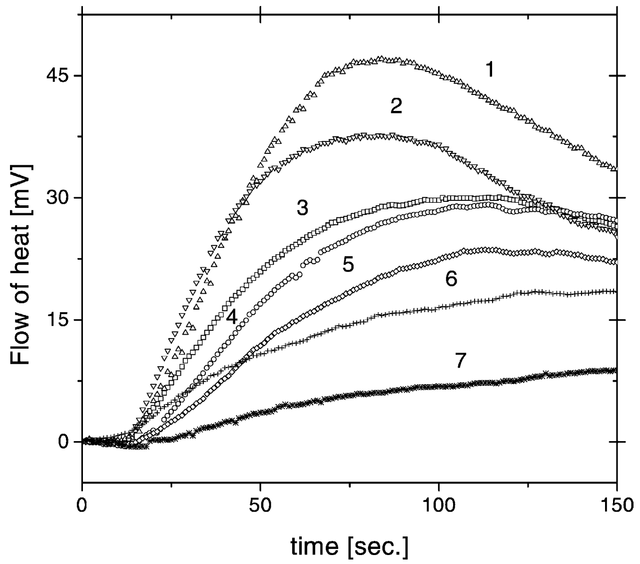


Fig. 10. Rate of heat evolution during photoinitiated polymerization of mixture composed of: poly(ethylene glycol)diacrylate—1% NH_4OH in water (7:3); TIHFE concentration: 10^{-3} M and (1) L-methionine, (2) ethionine, (3) thiaproline, (4) *S*-methyl-L-cysteine, (5) *S*-carboxyethyl-L-cysteine, (6) penicilamine, (7) L-cysteine. Electron donor concentration 0.1 M.

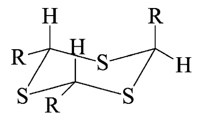
Table 1
Coinitiation efficiency of tested amino-acids and carboxylic acids

Number	Coinitiators	Rate of polymerization (au)		
		DIPF	TIHF	RBAX
1	L-Cysteine	1.652	0.219	0.049
2	Homocysteine	3.293	0.506	0.164
3	*S*-methyl-L-cysteine	3.410	0.554	0.168
4	*S*-ethyl-L-cysteine	3.288	0.679	0.161
5	*S*-carboxymethyl-L-cysteine	0.231	0.193	0.027
6	*S*-carboxyethyl-L-cysteine	0.262	0.352	0.029
7	L-Methionine	4.849	0.937	0.235
8	Ethionine	6.032	0.997	0.483
9	*N*-acethyl-L-methionine	1.516	0.244	No polymer
10	Thiaproline	1.338	0.571	0.161
11	3-Mercapto-propionic acid	0.461	0.165	No polymer
12	2-Mercapto-propionic acid	0.487	0.222	No polymer
13	(Phenylothio)acetic acid	0.277	0.318	No polymer
14	*S*-benzylothioglycolic acid	No polymer	0.119	No polymer
15	Thiosalicylic acid	0.001	0.129	No polymer
16	Glicyne	4.067	0.937	0.890
17	Alanine	1.922	0.185	0.0232
18	Proline	3.653	1.838	0.457

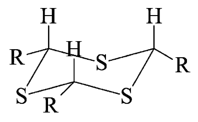
mechanism shown in Scheme 5. A series of SCCAs demonstrate similar photophysical and photochemical features as electron donors [51]. Laser flash photolysis experiments allow one to establish the mechanism (see Scheme 5) of the major processes occurring during irradiation of CB–SCCA photoredox pairs. Steady-state and laser flash photolysis allowed also to determine the basic photophysical and photochemical properties of CB–SCCA photoredox pairs. These are collected in Table 2. Photopolymerization experiments were carried out to compare the efficiency of the photoinitiated polymerization as a function of the SCCA structures. The rates of polymerization determined from the efficiencies of the photopolymerization after 6 min of irradiation are also presented in Table 2. A reference sample containing CB and other components, but without any coinitiator, did not show any polymerization. The results in Table 2 show that the rate of photoinitiated polymerization depends on the SCCA used.

Aliphatic sulfides can be efficient coinitiators for the photoinduced polymerization induced by benzophenone [52,53]. The model reaction for free radical formation during photoreduction of an initiator triplet state, is the photoreduction of benzophenone by dimethyl sulfide [28,54–56]. In this process it was established that electron transfer from the sulfur atom to the triplet state of the benzophenone is a primary photochemical step. In this step, one forms radical ions. The overall quantum yields of photoproducts (ketyl radicals and radical anions) are low: ($\sum \Phi \approx 0.26$) in aqueous solution, oscillate in the range 0.16–0.20 in mixed water-acetonitrile solution and less then 0.01 in pure acetonitrile. These results suggest that, in organic solvents, back electron transfer within the radical ion pair to regenerate the reactants is the dominant process.

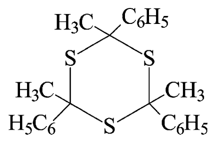
An exceptionally strong effect was observed for 2,4,6-trimethyl-1,3,5-trithiane (TMT). Polymerization of butane-1,4-diol dimethacrylate, sensitized by benzophenone in the presence three different sulfides, has been described by Andrzejewska and co-workers [57]. The measurements show that in the absence and in the presence of propyl sulfide and 2,2′-thiobisethanol no polymer was formed. This can be explained by the effective back electron transfer process that occurs in the radical ion pair in organic solvents. Effective polymerization was observed only in the presence of TMT. Laser flash photolysis studies performed for the benzophenone–TMT pair, allow one to construct the scheme (Scheme 7) explaining characteristic features of the mechanism of polymerization initiated by the system. The results prompted the authors to study other symmetrically substituted 1,3,5-trithianes as electron donors for benzophenone sensitized free radical polymerization [58].



α - form (cis-trans)

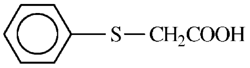
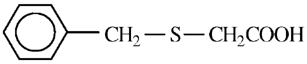
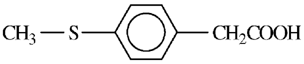
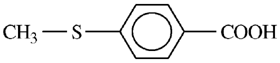
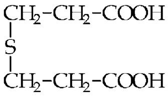


β - form (cis-cis)



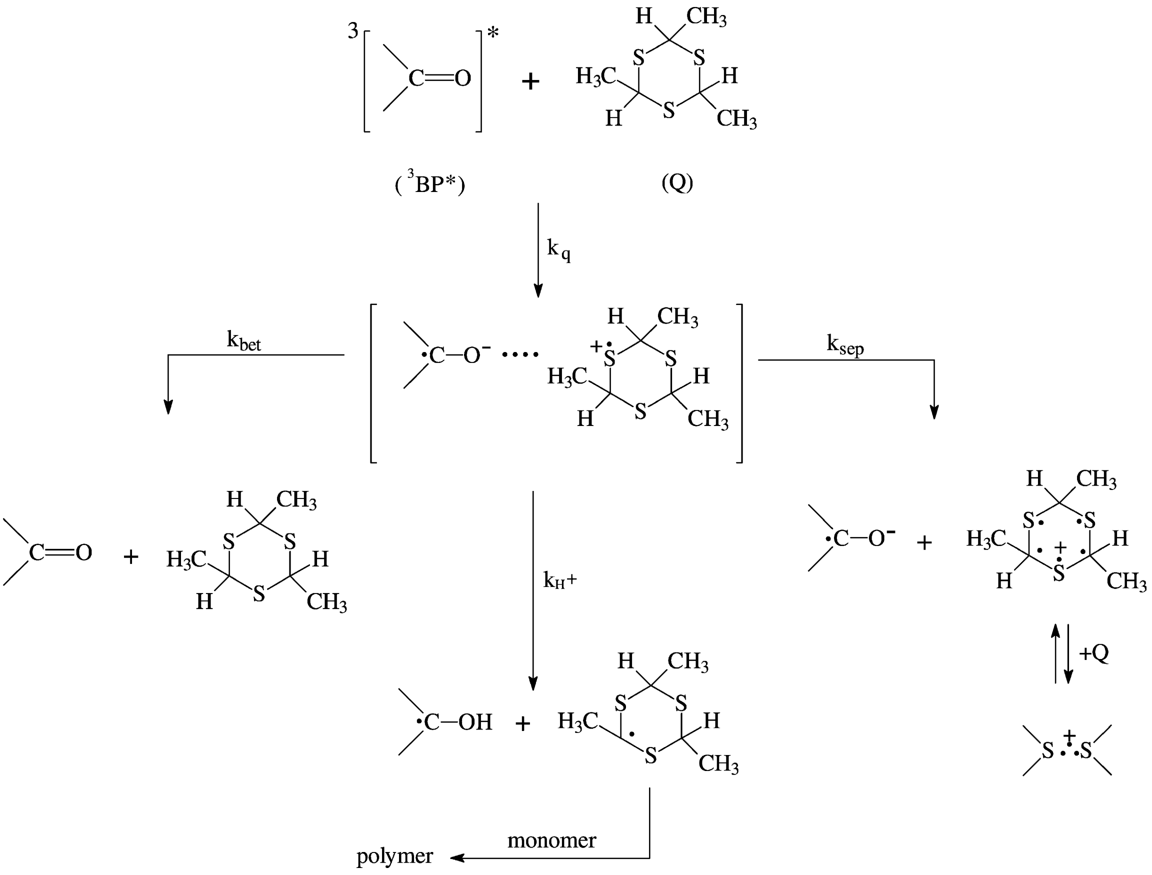
TMTPT (cis-trans)

Table 2
Photophysical and photochemical properties of SCCAs tested as electron donors in 4-carboxybenzophenone sensitized polymerization

Number	Coinitiator structure	k_q ($\times 10^{-9}$ M^{-1} s^{-1})	ϕ_{CO_2}[a]	ϕ_{CB^-}[b]	ϕ_{CBH}[b]	R_p (%) (6 min)
1		1.85	0.92 (±0.09)	0.97	0	70
2		1.54	0.57	0.84	0.16	48
3		1.9	0.29			43
4	$CH_3–S–CH_2COOH$	2.1	0.86	0.87	0.12	42
5		1.9	<0.05			6
6	$HOOC–CH_2–S–CH_2–COOH$	0.95	0.80	0.84	0.16	7
7	 $S(CH_2–CH_2–COOH)_2$	1.0	<0.03	0.90	0.09	no
8	$CH_3–S–CH_3$	4.9	–	0.16	0.10	8

[a] From steady-state measurements, extrapolated to zero percent of CB conversion.
[b] From the laser flash photolysis estrapolated to end of the flash.

Most 1,3,5-trithianes are active coinitiators in benzophenone-induced polymerization. The most efficient is β-TMT, whose reactivity significantly exceeds that of the α-isomer. Consideration of the order of the quantum yields (Table 3) suggests that the most active coinitiator should be β-TPT. In general, it was found that the polymerization efficiency of the coinitiators did not follow the efficiency of photoinduced free radical formation.



Scheme 7.

Table 3
Trithianes studied and their basic photochemical properties

Substituent	Trithiane	Abbreviation	k_q (M^{-1} s^{-1})	$\Phi_{BPH^\bullet}$
R = H	1,3,5-Trithiane	TT	2.5×10^8	0.28
R = CH_3	α-TMT	α-TMT	4.2×10^8	0.62
R = CH_3	β-TMT	β-TMT	3.4×10^8	0.53
R = C_6H_5	α-2,4,6-Triphenyl-1,3,5-trithiane	α-TPT	2.1×10^8	0.81
R = C_6H_5	β-2,4,6-Triphenyl-1,3,5-trithiane	β-TPT	1.6×10^8	0.32
	2,4,6-Trimethyl-2,4,6-triphenyl-1,3,5-trithiane	TMTPT	$\leq 5 \times 10^6$	

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