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New water-soluble benzophenone derivatives as initiators of free radical polymerization of acrylates

Summary — Triplet state quenching of benzophenone derivatives in the presence of amino-acids undergoes *via* photoinduced intermolecular electron transfer mechanism (PET), which is followed by the transformations yielding free radicals able to initiate polymerization. This paper describes a series of water soluble free radical photoinitiating systems consisting of sodium 4-benzoylbenzenesulfonate (BBS) and sodium 4,4′-dibenzoylbenzenesulfonate (DBBS) as the light absorbing chromophores and amino acids or sulfur-containing amino acids acting as the electron donors. Photoinitiated polymerization were carried out for the mixture composed of poly(ethylene glycol)diacrylate (PEGDA) — 1 % NH_4OH (3:1).

The mechanistic aspect of photoinitiating processes was investigated by the measurement of polymerization kinetics and by the nanosecond laser flash photolysis. The photoreduction of benzophenone derivatives in the presence of the electron donors was studied in acetonitryle and water solutions. Nanosecond laser flash photolysis indicated a weak efficiency of ketyl radical formation (λ_{max} = 550 nm), which is due to the hydrogen atom abstraction by the excited triplet state of the sulfobenzophenone chromophore. It is also documented that in the presence of amino acids or sulfur containing amino acids PET process leads to formation of α-aminoradicals that can initiate PEGDA polymerization. Based on photochemistry of tested benzophenone derivatives, photochemistry of sulfur-containing amino acids and obtained results the mechanism describing primary and secondary processes occurring during photoinitiated polymerization *via* PET process is proposed.

Key words: photoinitiated radical polymerization, poly(ethylene glycol) diacrylate, redox systems, water-soluble benzophenone derivatives, sulfur-containing aminoacids.

NOWE ROZPUSZCZALNE W WODZIE POCHODNE BENZOFENONU JAKO INICJATORY RODNIKOWEJ POLIMERYZACJI AKRYLANÓW

Streszczenie — Wygaszanie stanu trypletowego benzofenonu przez aminokwasy przebiega zgodnie z mechanizmem fotoindukowanego międzycząsteczkowego przeniesienia elektronu (PET), prowadząc do generowania wolnych rodników mogących inicjować polimeryzację. Opisano wyniki badań inicjowania z wykorzystaniem procesu PET polimeryzacji rodnikowej za pomocą rozpuszczalnej w wodzie kompozycji składającej się z soli sodowej kwasu 4-benzoilo-benzenosulfonowego (BBS) lub soli disodowej kwasu di(benzoilobenzofenono-4,4′-sulfonowego) (DBBS) pełniących role absorbera promieniowania i aminokwasu jako donora elektronów. Stosowano przy tym aminokwasy zawierające siarkę bądź jej niezawierające — odpowiednio SAAc i AAc (tabela 1). Polimeryzacji poddano mieszaninę diakrylanu glikolu polioksyetylenowego (PEGDA) z 1-proc. roztworem NH_4OH w stosunku objętościowym 3:1.

Mechanizm procesu fotoinicjowania polimeryzacji analizowano korzystając z pomiarów kinetyki polimeryzacji rodnikowej metodą oznaczania ilości wydzielającego się ciepła (rys. 10, tabela 1) oraz badania procesu fotoredukcji sulfonowych pochodnych benzofenonu w obecności donorów elektronu metodą nanosekundowej fotolizy błyskowej (tabele 2 i 3, rys. 1—9). W procesie pierwotnym następuje przeniesienie elektronu z aminokwasu do stanu trypletowego sulfonowej pochodnej benzofenonu (absorpcja przejściowa BBS^3 przy 530 nm) dające w rezultacie parę rodnikojonów (widmo przejściowe $BBS^{-\bullet}$ z maksimum przy 630 nm). Szybkie protonowanie rodnikoanionu prowadzi do utworzenia rodnika ketylowego badanego benzofenonu, obserwowanego w widmie przejściowym przy 545 nm. Zachodzący równolegle proces fotoindukowanego utleniania aminokwasu prowadzi w wyniku sekwencji reakcji następczych do utworzenia rodników α-aminoalkilowych mogących inicjować polimeryzację rodnikową akrylanów. Na podstawie uzyskanych wyników zaproponowano mechanizm podstawowych procesów fotochemicznych zachodzących w trakcie polimeryzacji (schematy A—D).

Słowa kluczowe: fotoinicjowana polimeryzacja rodnikowa, diakrylan glikolu polioksyetylenowego, układy redoksy, rozpuszczalne w wodzie pochodne benzofenonu, aminokwasy zawierające siarkę.

Photoreduction of aromatic ketones [1—3] or xanthene dyes [4—6] or cyanine dyes [7] in the presence of electron donors undergoes *via* photoinduced intermolecular electron transfer mechanism (PET) which is followed by the transformations yielding free radicals able to initiate polymerization [8, 9]. Several types of composition containing photoredox pair that can be used for photoinitiation of polymerization were examined.

The photoredox pair possesing the sulfur organic compounds, *e.g.* thiols, thioethers and amino acids as electron donors, have been a subject of several studies [10—12]. It is well known that the initiation ability of this group of photoinitiators is based on the radical production from the interaction between an excited triplet state of electron acceptor and an electron donor [13—16]. Marciniak, Bobrowski, Hug and Rozwadowski [17, 18] examined the quenching of carboxybenzophenone triplet state by amino acids and sulfur-containing carboxylic acids in water or water/acetonitryle solutions. According to these authors, benzophenone excited states are quenched by a mechanism that involves an electron transfer from the electron donor to the triplet state of benzophenone. This process yields a radical ion pair. In the next step, a rapid proton transfer from the electron donor radical cation to the ketone radical anion yields the benzophenone ketyl radical and a neutral radical formed from electron donor.

In our earlier papers [19, 20] we described the study on the quenching of the triplet state of xanthene dyes by amino acids or sulfur-containing amino acids. We have shown that these photoredox pairs can be used for the photoinitiation of free radical polymerization in aqueous media. The proposed mechanism describing the major processes occurring during the photoinitiated polymerization of poly(ethylene glycol)diacrylate (PEGDA) was established using the steady-state and laser flash photolysis techniques.

It is our intention to describe in this work a series of free radical polymerization photoinitiation systems based on water-soluble benzophenone derivatives as the absorbing chromophore and amino acids or sulfur-containing amino acids as the electron donors.

EXPERIMENTAL

Materials

Poly(ethylene glycol)diacrylate (PEGDA, $\overline{M}_n$ *ca.* 575, viscosity in 25 °C 57 cps) as monomer and substrates for initiator synthesis were purchased from Aldrich.

Amino acids (AAc), sulfur-containing amino acids (SAAc) and 4-(dimethylamino)benzonitrile (DMABN) were also from Aldrich as the best available purity grades and were used without further purification.

The light absorbing chromophores, namely sodium 4-benzoylbenzenesulfonate ($C_6H_4COC_6H_4SO_3Na$, BBS) and sodium 4,4′-dibenzoylbenzene sulfonate ($NaO_3SC_6H_4COC_6H_4SO_3Na$, DBBS) were synthesized using methods described below.

Chromophores synthesis

Sodium 4-benzoylbenzenesulfonate

4-Chlorobenzophenone (21.9 g, 0.1 M), $Na_2SO_3 \cdot 7H_2O$ (252.16 g, 1 M) and $CuSO_4 \cdot 5H_2O$ (1.564 g) was added to 2.4 L of water. Mixture was kept at 200—210 °C for 3 h under the pressure of 1.8—2.0 MPa. Then reaction mixture was cooled to room temperature and filtrated. The filtrate was evaporated under reduced pressure and obtained crystals after precipitation were isolated by the filtration; yield 13.1 g, (46 %).

UV (water, pH = 7) — $S_1(\pi\text{-}\pi^*)$: $\lambda_{max.}$ (ε) = 258 (20300); $S_2(n\text{-}\pi^*)$: 340 nm (130 $L \cdot mol^{-1} \cdot cm^{-1}$);

(water, pH = 11.4) — $S_1(\pi\text{-}\pi^*)$: $\lambda_{max.}$ (ε) = 257 (15400); $S_2(n\text{-}\pi^*)$: 344 nm (1580 $L \cdot mol^{-1} \cdot cm^{-1}$).

IR (KBr, cm^{-1}) — 1654 (C=O), 1188 (SO_3), 1239 (SO_3).

^1H NMR (DMSO), δ ppm: 7.500—7.820 (m, 9H, phenyl).

Elementary anal. — calcd. S 11.28, found S 10.19.

Sodium 4,4′-dibenzoylbenzene sulfonate

4,4′-Dichlorobenzophenone (24.58 g, 0.1 M), $Na_2SO_3 \cdot 7H_2O$ (378.24 g, 1,5 M) and $CuSO_4 \cdot 5H_2O$ (3.128 g) was added to 2.4 L of water. Mixture was kept at 200—210 °C for 3 h at pressure of 1.8—2.0 MPa. The resulting reaction mixture was cooled to room temperature and filtrated. From the obtained solution the solvent was evaporated under reduced pressure and after precipitation the resulting crystals were filtrated, yield 13.8 g (36 %).

UV (water, pH = 7) — $S_1(\pi\text{-}\pi^*)$: $\lambda_{max.}$ (ε) = 259 (20500); $S_2(n\text{-}\pi^*)$: 348 nm, (180 $L \cdot mol^{-1} \cdot cm^{-1}$);

(water, pH = 11.4): $S_1(\pi\text{-}\pi^*)$: $\lambda_{max.}$ (ε) = 259 (21150); $S_2(n\text{-}\pi^*)$: 348 nm, (3280 $L \cdot mol^{-1} \cdot cm^{-1}$).

IR (KBr, cm^{-1}) — 1651 (C=O), 1186 (SO_3), 1239 (SO_3).

^1H NMR (DMSO); δ ppm: 7.500—7.820 (m, 9H, phenyl).

Elementary anal. — calcd.: S 16.6, found S 14.84.

Electrochemical measurements

The oxidation potentials of amino acids and reduction potentials of benzophenone derivatives were measured using cyclic voltammetry. An Electroanalitycal MTM System model EA9C-4z was used for the measurements. A platinum (1 mm) disk electrode served as the working electrode, a Pt wire constituted the counter electrode and an Ag-AgCl electrode was used as a reference electrode. The measurements were carried out under argon in a 0.1 M solution of tetrabutylammonium perchlorate in dry acetonitryle.

Polymerization

The kinetics of free radical polymerization was analysed based on measurement of the rate of heat evolution during the polymerization. As a temperature sensor a semiconducting diode immersed in the 2 mm thick layer of a cured sample was used. The temperature signal was transformed with an analog-digital data acquisition board to a computer.

Photopolymerization was initiated using argon ion laser model INNOWA 90 (Coherent) emitting two lines of equal intensity at 351 and 361 nm. The average power of irradiation was 30 mW/0.785 cm^2 (38 mW/cm^2). All irradiation procedures were made on the one type of formulation which consists of the mixture of PEGDA — 1 % NH_4OH in water (7:3); initiator concentration: $4.4 \cdot 10^{-3}$ M for BBS and $2 \cdot 10^{-3}$ M for DBBS, co-initiator concentration 0.02 M, pH of polymerizing mixture was 11.4.

In order to evaluate the photoredox pairs composition on their photoinitiation abilities as a reference sample a corresponding novel benzophenone derivative in monomer formulation without co-initiator was used.

Laser flash photolysis

Nanosecond laser flash photolysis experiments were performed using a LKS.60 Laser Flash Photolysis apparatus (Applied Photophysics). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from a Lambda Physik/model LPY 150 operating at 65 mJ/pulse (pulse width about 4—5 ns) was used for the excitation. Transient absorbances at preselected wavelengths were monitored by a detection system consisting of a monochromator, a photomultiplier tube (Hamamatsu R 955) and a pulsed xenon lamp (150 W) as a monitoring source. The signal from the photomultiplier was processed by a Hewlett-Packard/Agilent an Agilent Infiniium 54810A digital storage oscilloscope and an Acorn compatible computer.

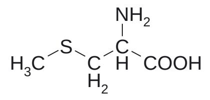
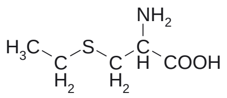
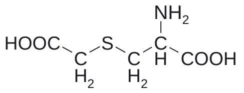
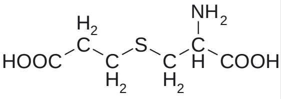
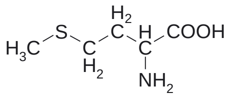
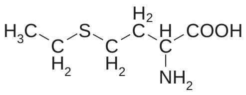
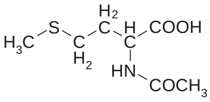
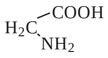
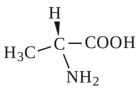
The concentration of amino acids and sulfur containing amino acids in the quenching experiments were in the range from $3 \cdot 10^{-5}$ M to $8 \cdot 10^{-4}$ M. In all experiments, the BBS and DBBS concentration was $2 \cdot 10^{-5}$ M. Quantum yields of BBS ketyl radical formation process (Φ'_{ketyl}) at pH = 7 were measured using amino acids at concentration of $1.7 \cdot 10^{-3}$ M. Concentration of SAAc in alkaline solution (pH = 12) was $3 \cdot 10^{-4}$ M, of AAc $3 \cdot 10^{-3}$ M. Concentration of benzhydrole was 0.3 M and 0.6 M at pH = 7 and pH = 12 respectively. The pH of the solutions was adjusted by adding sodium hydroxide. All solutions were deoxygenated by bubbling high purity argon.

RESULTS AND DISCUSSION

The structure and oxidation potentials (E_{ox}) of tested amino acids as well as reduction potentials ($E_{red.}$) and triplet excited-state transition energies (E_{00}) for synthesized novel benzophenone derivatives are compiled in Table 1 and Table 2 respectively.

Laser flash irradiation of benzophenone derivatives recorded in acetonitryle yielded a transients whose absorption spectra are peaked at $\lambda_{max.}$ = 530 nm for BBS and $\lambda_{max.}$ = 550 nm for DBBS respectively. The spectrum, shown in Fig. 1, is very similar to that of benzophenone (Bp) triplet spectra in benzene and 4-carboxybenzophe-

Table 1. The structure and oxidation potentials (E_{ox}) of amino acids or sulfur-containing amino acids, as well as relative rates of polymerization (R_p)

Coinitiators			Initiators	
Structure	AAc and SAAc	E_{ox} [eV]	BBS R_p[a.u.]	DBBS R_p[a.u.]
	S-methyl- -L-cysteine	1,100	1,519	2,133
	S-ethyl- -L-cysteine	1,164	1,000	2,002
	S-carboxy- methyl- -L-cysteine	0,966	2,029	2,405
	S-carboxy- ethyl- -L-cysteine	0,970	2,501	3,504
	L-methionine	1,340	1,529	1,695
	Ethionine	1,244	1,419	2,239
	N-acetyl-DL- -methionine	1,016	1,955	1,653
	Glicyne	0,620	2,150	3,250
	Alanine	0,740	2,120	1,570

none (CB) triplet in water [21, 22] and can be assigned to the triplets of corresponding benzophenone derivatives.

Table 2. The quenching rate constants (k_q) of benzophenone derivatives triplets by amino acids and sulfur-containing amino acids

AAc and SAAc	$k_q \cdot 10^{-9}$, $M^{-1}s^{-1}$		
	BBS E_{red} = -1.242 V E_{00} = 2.961		DBBS E_{red} = -1.236 V E_{00} = 2.940
	pH = 7*)	pH = 12**)	pH = 7*)
S-methyl-L-cysteine	1.38	1.19	2.25
S-ethyl-L-cysteine	1.73	1.32	2.17
S-carboxymethyl-L-cysteine	0.67	0.70	0.84
S-carboxyethyl-L-cysteine	0.68	0.48	1.20
L-methionine	1.48	5.52	2.70
Ethionine	1.68	3.36	2.33
N-acetyl-DL-methionine	1.66	1.20	2.33
Glicyne	0.023	0.022	0.032
Alanine	0.00075	0.012	0.038

*) In water solutions.
**) In 0.01 M NaOH solutions.

Triplet lifetimes and quenching rate constants of BBS and DBBS by amino acids and SAAc was studied by means of nanosecond laser flash photolysis in acetonitryle or water solutions. Seven SAAc and two AAc (alanine and glicyne) were used as quenchers of the triplet states of tested benzophenones (see Table 2).

The quenching rate constants, k_{obs}, were obtained by monitoring the transient decays at maximum of the triplet-triplet absorption for various quenchers concentrations. The resulting pseudo-first-order values of k_{obs} were linear for applied concentration of donor and the primary reaction rate constants, k_q were obtained from slope of relationship described by equation (1):

$$k_{obs} = k^0 + k_q[Q] \qquad (1)$$

where: k^0 — *the quenching rate constant of the benzophenones triplet in the absence of an electron donor, [Q] — the quentcher concentrations.*

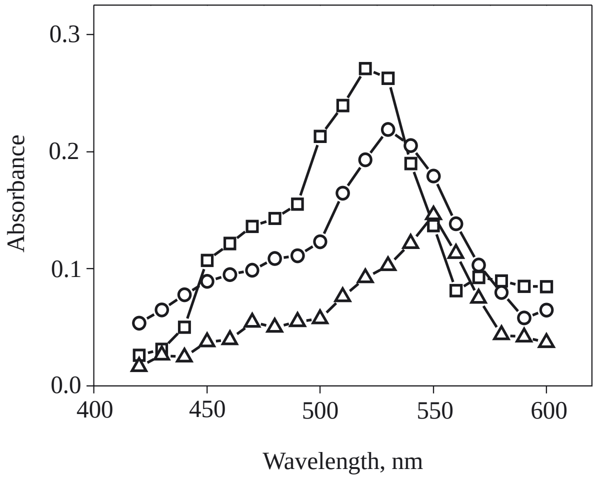


Fig. 1. Triplet absorption spectra of benzophenone (Bp) in MeCN (□), BBS in water (○) and DBBS in water (Δ); the transient absorption spectra recorded 0.12 μs after the pulse

A comparison of the kinetic data in Table 2 shows that for amino acids containing methionine group the value of k_q measured in alkaline solutions is visibly higher then those obtained in neutral solutions. It suggests, that the rate of quenching of BBS triplet is not affected by changing the degree of protonation of the amino group. For alanine and glicyne, which lack a sulfur atom, the values of k_q, measured in water solutions are some orders lower then the corresponding k_q's obtained for the SAAc. At the same time, the quenching rate constant of BBS triplet by alanine obtained in alkaline solution is almost 3 orders of magnitude higher then the analogues values in neutral solution. Bobrowski *et al.* [23] explained this behavior by the change of amino acids structure from the zwitterionic form at pH = 7 to the anionic at pH = 12. It should be noted that the nitrogen atom in the deprotonated amino group can participate in the quenching of BBS triplet as well.

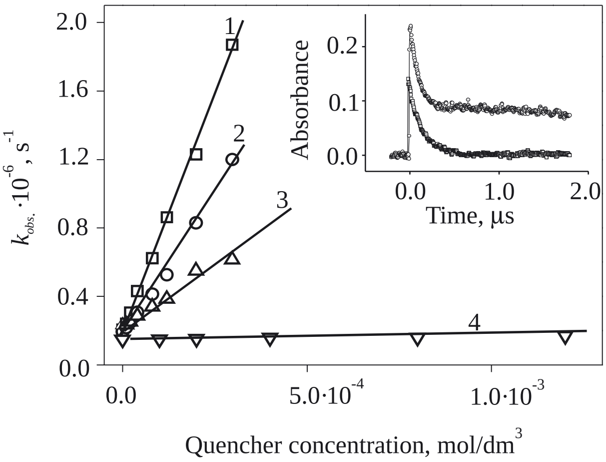


Fig. 2. Stern-Volmer plots for the quenching of BBS triplet by selected amino acids in water solution: 1 — methionine, 2 — ethionine, 3 — cysteine, 4 — alanine. Inset: experimental traces for the BBS triplet decay at 530 nm in acetonitryle (lower curve) and for BBS in the presence of $3 \cdot 10^{-4}$ M methionine in water solution (upper curve)

Stern-Volmer plots for the quenching of BBS triplet by selected amino acids are presented in Fig. 2 for illustration. A typical experimental traces for the triplet decay in acetonitryle or water solutions shows inset of this Figure; the long-lived absorption observed for the water solution containing methionine as electron donor (upper curves) is attributed to the presence of ketyl radical [24].

Calculated k_q values can be correlated with the standard free energy change for electron transfer process

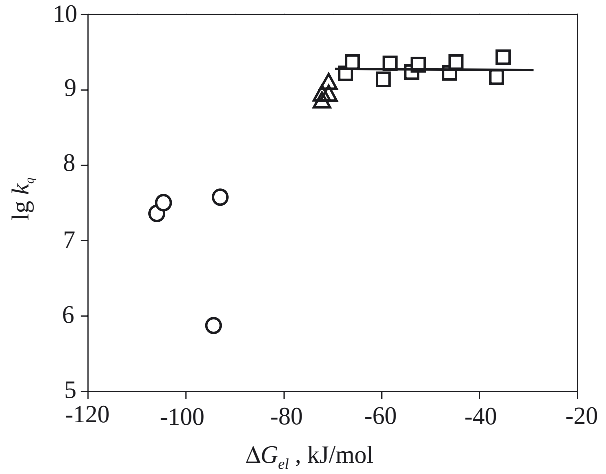


Fig. 3. Dependence of the quenching rate constant (k_q) on ΔG_{el} for quenching of tested benzophenone derivative triplets by SAAc (□), alanine and glicyne (○) and carboxyamino acids (Δ)

(ΔG_{el}), given by the Rehm-Weller equation [25, 26] [eq. (2)].

$$\Delta G_{el} = (E_{ox} - E_{red}) - E_{oo} + C \qquad (2)$$

where: C — *(Coulombic energy) — the free energy gained by bringing the radical ions formed to an encounter distance in a solvent with dielectric constant* ε.

For the SAAc, the ΔG_{el}, values calculated from eq. (2) are in the range from -67 to -35 kJ/mol for all combinations of AAc and the substituted benzophenones. The dependence of the quenching rate constant on the standard free energy change is presented in Fig. 3. As ΔG_{el} increases in algebraic value, the plateau region for the exoergonic processes is observed. Similar observation for $\Delta G_{el} < 20$ kJ/mol were described by Marciniak *et al.* [13] for 4-carboxybenzophenone/sulfur-containing amino acids photoredox pairs. This behavior is predicted by the classical theory of photoinduced electron transfer and can be taken as evidence for the operation of an electron-transfer mechanism in the quenching of the triplet state of benzophenone by the tested amino acids. The amino acids without sulfur atom (○) and amino acids containing two carboxylic groups (Δ) in neutral solution as well as in alkaline solution show evidently lower value of the quenching rate constant (see Table 2).

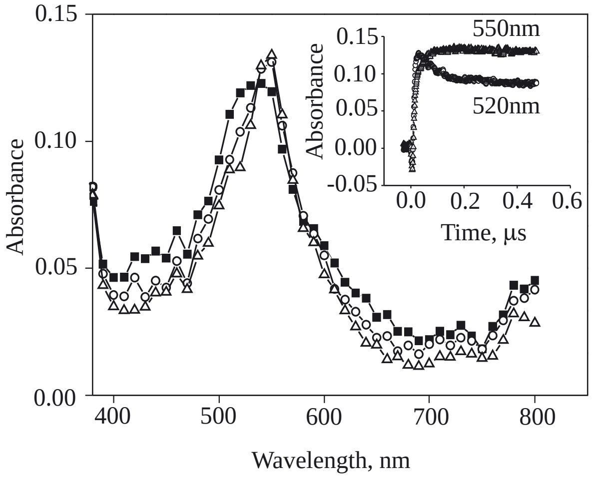


Fig. 4. The transient absorption spectra recorded at different delay obtained from Bp ($2 \cdot 10^{-5}$M) in MeCN in the presence of 0.08 M DMABN; delay time: ■ — 12 ns, ○ — 40 ns, Δ — 100 ns. Inset: kinetic traces for decay of Bp triplet (λ = 520 nm) and formation of ketyl radical (at 550 nm) in MeCN in the presence of 0.02 M DMABN

Figure 4 shows the transient absorption spectra from Bp in the presence of 0.08 M DMABN. It can be seen in Fig. 4 that the absorption of triplet benzophenone (λ = 520 nm) decays, simultaneously forming a new absorption band with the maximum at 550 nm [27]. The experimental traces (inset of Fig. 4) clearly indicate the process

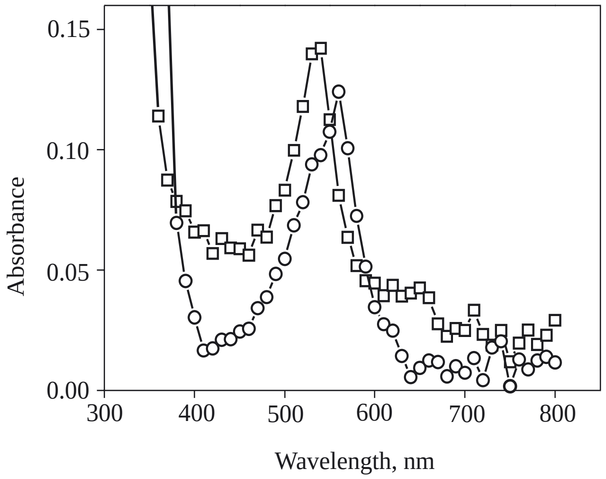
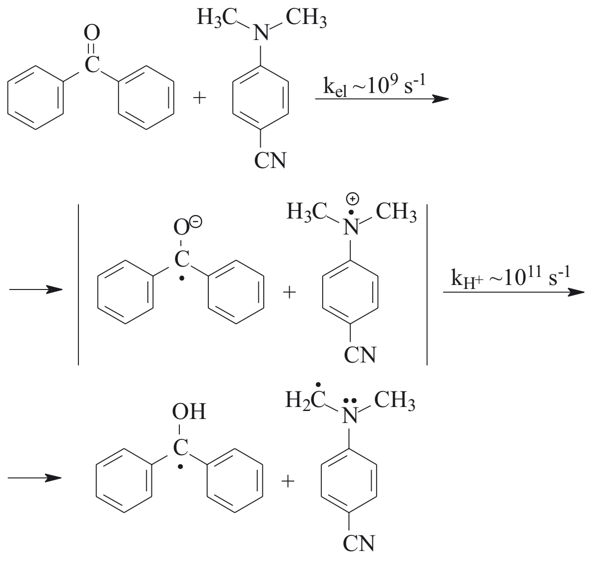


Fig. 5. The transient absorption spectra of BBS triplet (□) and transient absorption spectra following the quenching of BBS triplet by 0.02 M DMABN (○) in acetonitryle recorded 2 μs after the flash



Scheme A

of ketyl radical formation. Similar behavior is observed in Fig. 5 for BBS. At high amine concentration the triplet of BBS quenching is complete in the very short time after the laser pulse.

In the present case, one can assume two possible ways of the ketyl radical formation. The first is the hydrogen atom abstraction from DMABN by the BBS triplet. The second is the sequence of electron-proton transfer reactions. Thus, taking into account the high value of rate constant for triplet quenching by electron transfer mechanism one can eliminate the photoreduction of BBS by hydrogen atom abstraction [28].

The lack of transient absorption band indicating the presence of radical anion as intermediate can be explained by a very fast proton transfer process that follows electron transfer according to the Scheme A [29, 30].

Triplet and radical decay for all tested photoredox pairs were followed at 550 nm (Fig. 6). The yield of BBS ketyl radical formation from the triplet is proportional to the ratio *r* described by equation (3):

$$r = \frac{\Delta D_R^{\infty}}{\Delta D_T^{0}} \tag{3}$$

where: ΔD_T^0 — *the initial increment in absorbance immediately after the flash,* ΔD_R^∞ — *the change in absorbance corresponding to the formation of a radical after the complete decay of the triplet [31].*

To convert values of *r* [eq. (3)] into quantum yields, we assume $\Phi'_{\text{ketyl}} = 2$ for used as reference benzophenone-benzhydrol pair, in which benzophenone triplet is entirely trapped by benzhydrol. The photochemical reduction of benzophenone by benzhydrol produces only benzpinacol, *i.e.* has a one hydrogen transfer product, only a single kind of radical — namely ketyl radical of benzophenone. At high concentration of the alcohol the quantum yields of triplet state quenching approaches unity [32]. Having in mind fact that the reaction between benzophenone triplet and benzhydrol produces two benzophenone ketyl radicals, it is obvious that for complete triplet quenching the quantum yield of the ketyl radical formation, Φ'_{ketyl}, is equal 2. In Figure 6, A_0 is the value of absorption immediately after the flash and A_{rad} is a corresponding value of absorbance obtained by an extrapolation of the suitable radical decay curve to the zero time. The yields of ketyl radical formation measured using this methodology for the all tested SAAc's and AAc's from table 2 are compiled in Table 3.

Table 3. Quantum yields of BBS ketyl radical formation (Φ'_{ketyl}) during the intermolecular photoinduced electron transfer process

Amino acid	Φ'_{ketyl}	
	pH = 7[*)]	pH = 12[**)]
Benzhydrole[***)]	2	2
S-methyl-L-cysteine	0.60	0.66
S-ethyl-L-cysteine	0.44	0.60
S-carboxymethyl-L-cysteine	0.35	0.76
S-carboxyethyl-L-cysteine	0.48	0.68
L-methionine	0.88	0.98
Ethionine	0.87	0.94
N-acetyl-DL-methionine	0.40	0.57
Glicyne	0.68	0.82
Alanine	0.84	0.95

[*)] In water solutions, concentration of all tested amino acids $1.7 \cdot 10^{-3}$ M.
[**)] In 0.01 M NaOH solutions, concentration of sulfur containing amino acids $3 \cdot 10^{-4}$ M, glicyne and alanine $3.0 \cdot 10^{-3}$ M.
[***)] Concentration 0.3 M and 0.6 M for pH = 7 and pH = 12 respectively.

Transient absorption spectra following the quenching of BBS triplet by SAAc show Fig. 7 and Fig. 8. Spectra

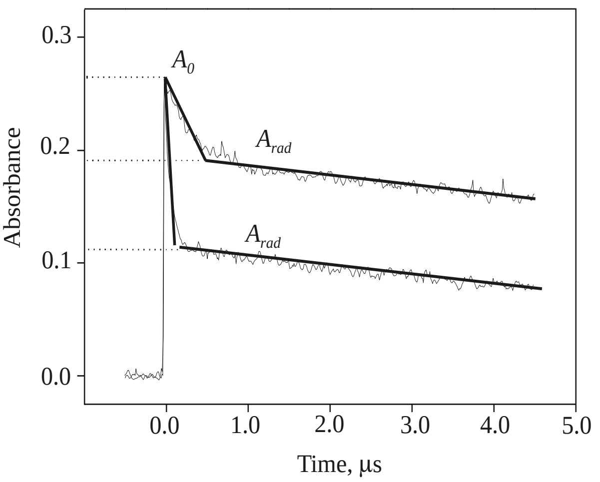


Fig. 6. The ketyl radical formation and decay profiles detected at 550 nm, obtained from Bp in the presence of benzhydrol (upper curve) and BBS in the presence of N-acetyl-DL-methionine (lower curve) (for symbols — see text)

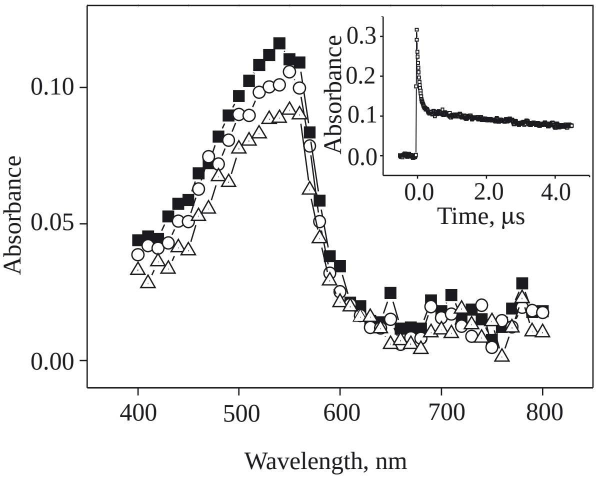


Fig. 7. The transient absorption spectra recorded at different delay times obtained from BBS ($2.0 \cdot 10^{-5}$M) in the presence of N-acetyl-DL-methionine ($3.0 \cdot 10^{-3}$M) in H_2O (pH = 7); delay time: ■ — 300 ns, ○ — 700 ns, Δ — 2.5 ns. Inset: kinetic trace at λ = 540 nm for BBS^3 decay

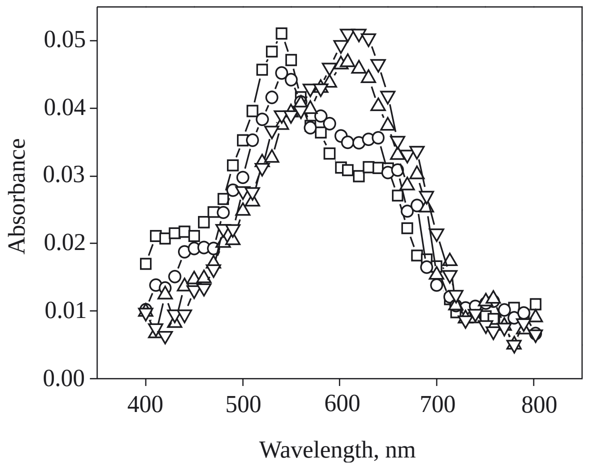


Fig. 8. The transient absorption spectra recorded at different delay times obtained from BBS (2.0 · 10^{-5}M) in the presence of methionine (1.5 · 10^{-3} M) in 0.1 M NaOH solution (pH = 12); delay time: ☐ *— 300 ns,* ○ *— 500 ns,* Δ *— 1.5 μs,* ∇ *— 2.5 μs*

obtained in aqueous solution at pH = 7 are strikingly different from those in alkaline solution. At pH = 7, in the presence of methionine derivative, the absorption at 540 nm is disappearing and simultaneously a new absorption with the maximum at 550 nm is appearing (Fig. 7). We assigned this new absorption to the BBS ketyl radical. At alkaline solution (Fig. 8) an absorption band at the maximum at 630 nm is appearing. This transient we assigned to the BBS radical anion ($BBS^{-\bullet}$).

The course of the kinetic traces shown in Fig. 9 indicate that both BBS radical anion and BBS ketyl radical are formed during two different processes. A very fast process occurring on a few nanoseconds time scale is likely due to the formation or decay of either ketyl radical ($\lambda_{max.}$ = 540 nm), and the $BBS^{-\bullet}$ radical anion ($\lambda_{max.}$ = 630 nm). A high initial absorbance recorded at 630 nm is due to the contribution of BBS triplet exhibiting a significant absorbance at 630 nm (see Fig. 5).

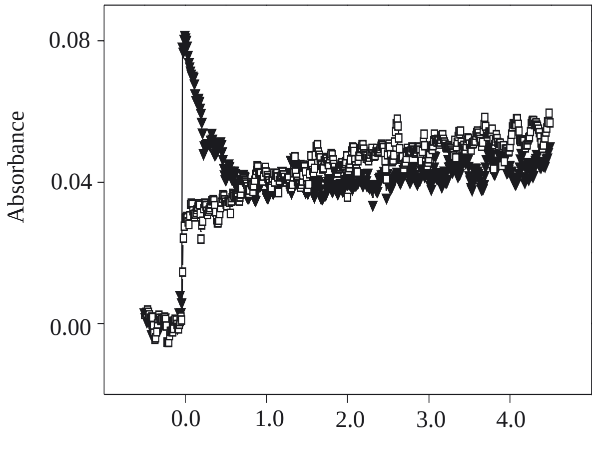
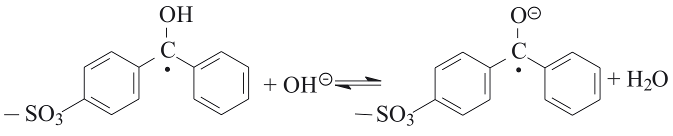


Fig. 9. Kinetic traces at λ = 530 nm for decay of BBS^3 (▲) and at 630 nm (☐) for $BBS^{\bullet-}$ formation

All these data, together with the weak acidity (pK_a = 9.2 for the benzophenone ketyl radical [30] and pK_a = 8.2 for the 4-carboxybenzophenone ketyl radical [24]) strongly suggest that after initial sequence of electron-proton transfer reaction within the charge-transfer complex (CTC), BBS radical anion is produced by the deprotonation of the BBS ketyl radical caused by high pH of solution. Alternatively, the radical anion ($BBS^{-\bullet}$) is formed in the diffusion apart of radical ion pair components that occurs after electron transfer. Because of high pH of solution, after all mentioned above processes, the equilibrium between BBS ketyl radical and BBS radical anion is immediately reached (see Scheme B).

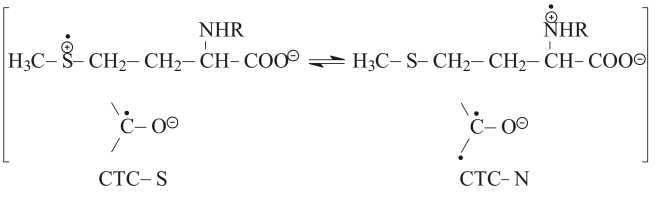


Scheme B

The existence of the isosbestic point at about 550 nm (Fig. 8) suggests that the BBS radical anion is the main product of the reaction. This, in turn, indicates that equilibrium described in Scheme 1 is strongly shifted to the radical anion formation as pH of solution increases.

The kinetic traces presented in Fig. 9 clearly show that after the formation of ketyl radical and BBS radical anion in fast process, a slow process of both intermediates formation is observed when methionine is the quencher. By analogy to Bobrowski *et al.* studies, the slow process of ketyl radical formation can be attributed to one electron reduction of BBS ground state by the α-aminoalkyl radicals produced from the decarboxylation of the methionine sulfur-centered radical cation [2]. Considering fact that this reaction consumes free radicals needed for photoinitiation process, one can treat the oxidation of α-aminoalkyl radicals as the reaction that competes with initiation reaction of free radical polymerization.

According to the mechanism proposed by Inbar *et al.* [33] for the quenching of benzophenone triplet by molecules possessing the thioether moiety, the initial step involves the formation of a CTC between benzophenone



Scheme C

triplet and electron donors. For methionine [34] (Scheme C) two charge-transfer complexes have been proposed — CTC-S and CTC-N — but only the first can decarboxylate and form α-aminoalkyl radicals able to start free radical polymerization of acrylates.

Bobrowski *et al.* [2] based on both, the laser flash photolysis and puls radiolysis experiments, proposed the mechanism of the 4-carboxybenzophenone-sensitized photooxydation of sulfur containing amino acids. The initial step is ascribed to electron transfer from the sulfur atom to the 4-carboxybenzophenone triplet to form a radical ion pair that can undergo: (i) the back electron transfer process that recovers the substrates, (ii) the formation of α-(alkylthio)alkyl radical caused by proton transfer within radical ions complex, and (iii) the diffusion apart of benzophenone radical anion and sulfur centered radical cation. The last pathway leads to the formation of the α-aminoalkyl radicals being the result of the decarboxylation reaction of the sulfur centered radical cation.

Concluding, one can state that adopting the mechanism proposed by Bobrowski *et al.* it is possible to predict that the photoreduction of BBS and DBBS by amino acids leads to the formation of two different types of free radicals that can start radical polymerization.

The photoinitiated polymerization of acrylates was monitored based on the measurement of the rate of heat evolution during the polymerization. Figure 10 shows the characteristic kinetic curves obtained for photoinitiated free radical polymerization of PEGDA with the use of BBS as the electron acceptor and selected amino acids acting as electron donors. The measured initial rates of photoinitiated polymerization (R_p) for tested photoinitiating systems are summarized in Table 1. A comparison of the kinetic data in Table 1 indicate that for the tested photoredox pairs, the rate of photoinitiation depends significantly on the structure of radicals obtained after PET, namely on the structure of electron donors.

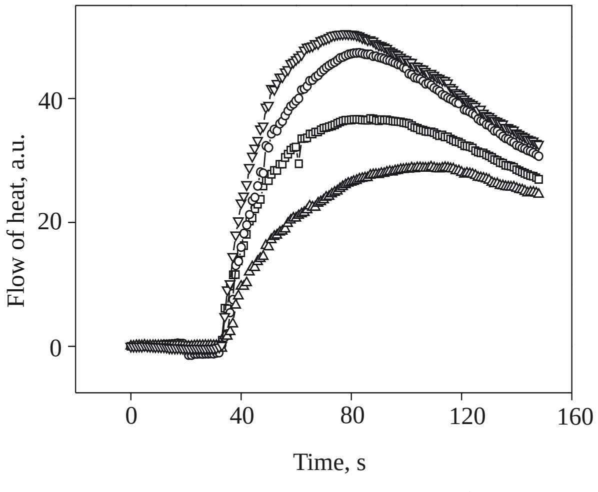


Fig. 10. Kinetic curves recorded during polymerization of PEGDA initiated by BBS as the light absorber and selected amino acids used as electron donors; □ — L-methionine, ○ — N-acetyl-D-methionine, Δ — S-ethyl-L-cysteine, ∇ — S-carboxymethyl-L-cysteine

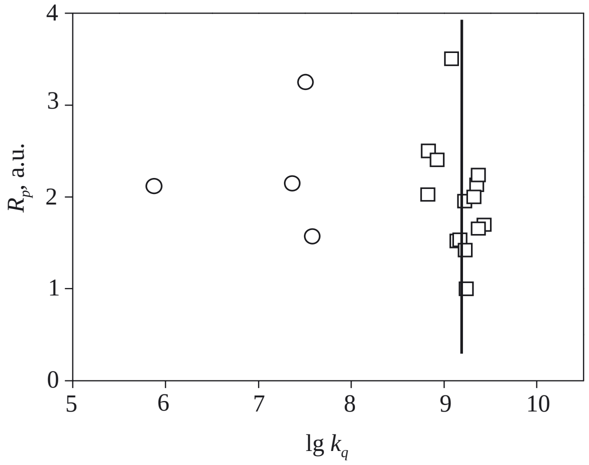


Fig. 11. Dependence of the rate of polymerization of PEGDA (R_p) on quenching rate constant (k_q) for tested benzophenones by glicyne and alanine (○) and SAAc (□)

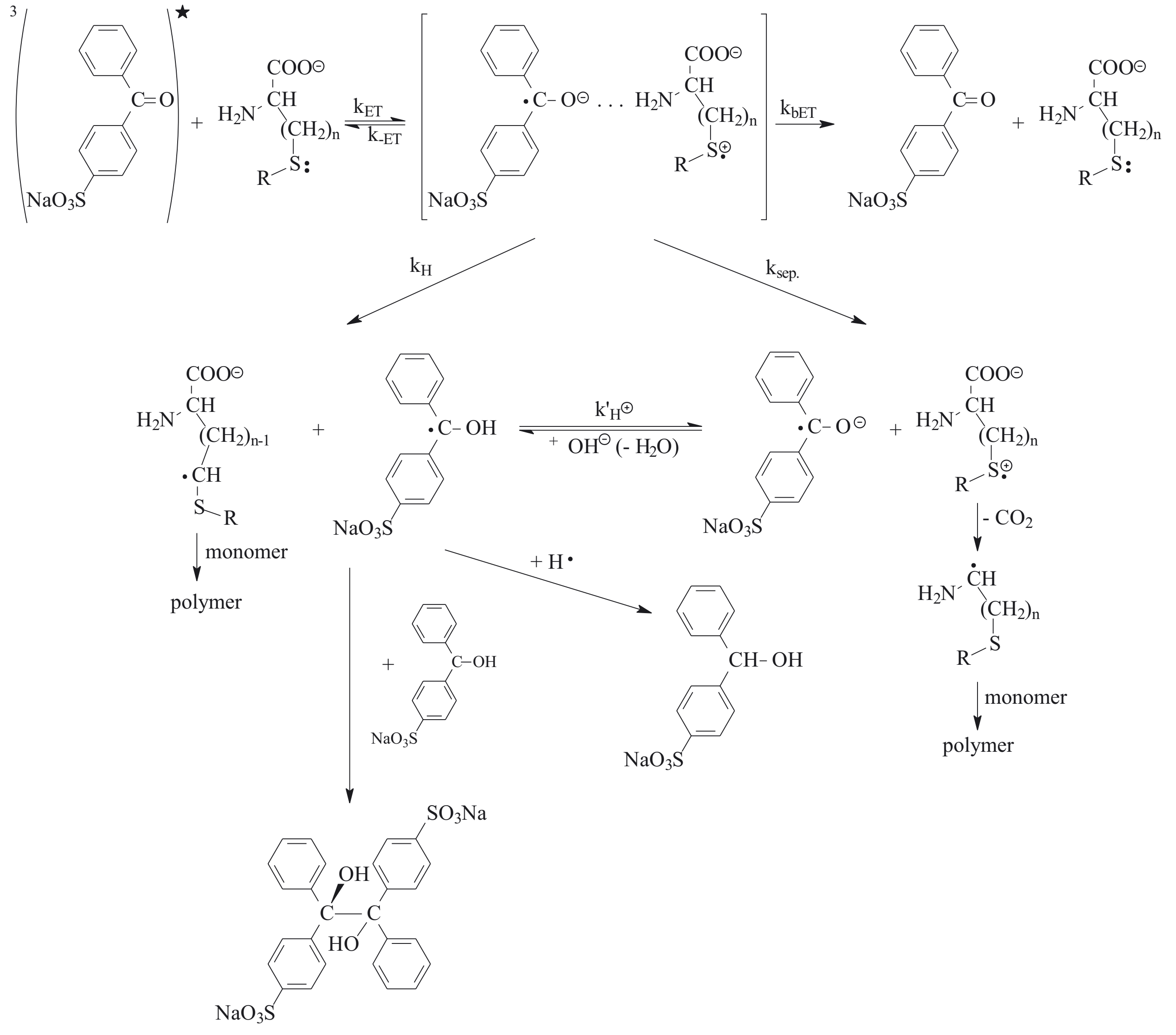
The question that is coming in mind is whether there is a direct link between the rate of polymerization and the rate of photoinduced electron transfer process, namely, whether the electron transfer step controls an overall efficiency of photoinitiated polymerization. For the photoredox pairs under the study this relationship is shown in Fig. 11. Inspection of this data reveals that there in no relation between the quenching rate constant (k_q) of tested benzophenones by amino acids and R_p value.

For the tested initiating systems the intermolecular electron transfer process is not the limiting step controlling the overall efficiency of polymerization. In fact, the efficiency of the polymerization initiation step closely depends on the structure and the yield of products formed during the reactions that follow electron transfer, namely the reactivity of radical arising from the decarboxylation of radical cation.

CONCLUSION

Basing on the general kinetic scheme for polymerization *via* PET process [35] the mechanistic aspects for the quenching of benzophenone [27, 28] or carboxybenzophenone [29] triplets by thioethers, amino acids, sulfur-containing amino acids and on the basis of our results obtained during the flash photolysis experiments and polymerization kinetics measurements we propose the scheme illustrating the major processes occurring during initiation of polymerization of acrylates by photoredox pair composed of benzophenone derivative/sulfur-containing amino acid.

According to this scheme (Scheme D), the initial step involves the quenching of benzophenone derivative triplet state. The rate of triplet quenching (measured using laser flash photolysis techniques), as it is shown in Table 2, is slightly below the diffusion limit for sulfur-containing amino acids, whereas is at least two orders of



Scheme D

magnitude lower for amino acids without sulfur atom. It should by point out that for methionine and ethionine the quenching rate constant is significantly higher at pH = 12 in comparison to the process carried out in neutral solution. The quenching rates are not reflected by the suitable rates of photoinitiation of the radical polymerization.

Described above photoredox pairs benzophenone derivative/sulfur-containing amino acid can be effectively used as photoinitiators in free radical polymerization of PEGDA.

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