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High speed three-component photoinitiating systems composed of cyanine dyes borate salt and heteroaromatic thiols

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ABSTRACT

Three heteroaromatic thiols (2-mercaptobenzothiazole, 2-mercaptobenzoxazole and 2-mercaptobenzimidazole) were investigated in regard to their abilities as a co-initiator in free radical polymerization induced by cyanine dye/borate salt photoinitiating system. The kinetic results shown that the new three-component photoinitiating systems are more effective than two-component ones. The mechanism of photochemical and chemical processes occurring during the irradiation of the three-component initiators was proposed on the basis of the laser flash photolysis. The addition to the cyanine dye borate salt of a second co-initiator (thiol) results in the generation besides butyl radical the second free radical which can start the polymerization chain reaction.

1. Introduction

Typical photoinitiating systems acting under visible light are classified as follow [1,2]:

- One-component system (such as bis-acylphosphine oxides, irone arene salts, peresters, organic borates, titanocenes, iminosulfonates, oxime esters, etc) [3,4].
- Two-component system (working through the electron transfer/proton transfer, energy transfer, processes that generate free radicals during the secondary reactions) [1,4].
- Three-component systems, where the basic idea is to try to enhance of photosensitivity by a combination of several components that form the photoinitiating systems.

In the basic concept developed several years ago in a three-component system I/II/III working through electron transfer (Scheme 1) the light is absorbed by **I** and radicals are formed trough **I**/**II** interaction [1,5,6].

Radicals $R_i^\bullet$ playing a detrimental role (through a reaction with the growing macromolecular chains) are quenched by **III**. The use of this suitable quencher **III** allows to scavenge the $R_i^\bullet$ radicals and, if possible, to generate new initiating radicals through an electron transfer reaction. It is apparent that the rate of polymerization (R_p) will increase since, the concentration of terminating radicals decreases and new initiating species are generated from the deactivation process of the side radicals $R_i^\bullet$.

- Multi-component systems (more than three partners).

Organoborate salts of carbocyanine dyes, described by G.B. Schuster in 1988 are the first commercial used two-component photoinitiating systems operating in the visible light region [7–9]. In this photoinitiating system the cyanine dye acts as a light absorber of a visible light and as an electron acceptor. The irradiation of cyanine borate salts leads to the formation of an excited singlet state of cyanine dye. One of the deactivation processes that follow this process is an electron transfer reaction from borate anion to the excited state of a dye. As a result an unstable boranyl radical is formed. The boranyl radical can undergo the C–B bond cleavage giving triphenylboron and butyl radical. The butyl radical is capable of initiating the radical polymerization of the acrylate monomers.

The photoinitiating ability of such photoinitiating systems depends on the:

- Structure of polymethine dye (symmetrical or unsymmetrical)
- Type of a heteroatom in dye heterocyclic ring
- Type of a substituent in the "*meso*" position of polymethine chain

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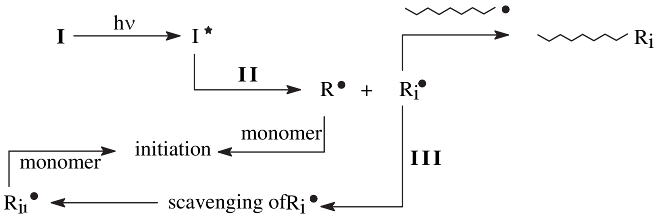


Scheme 1.

- Type of a substituent in the phenyl ring
- Structure of an alkylamino group in the styryl moiety (only for hemicyanine dyes)
- Structure of the borate anion.

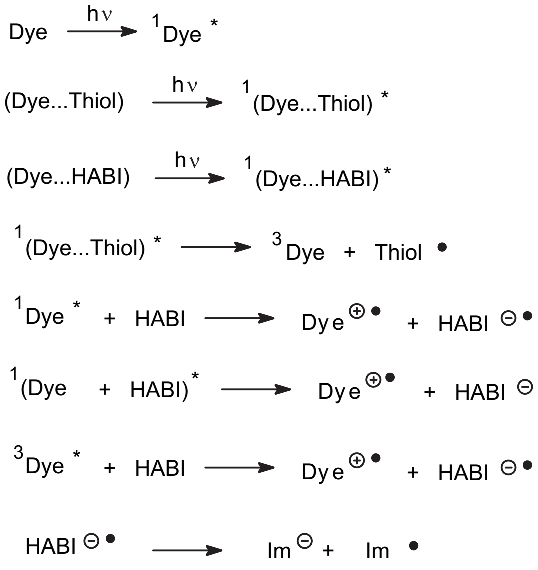
Generally, the photoinitiating ability of mono-cationic cyanine dye photoinitiating systems is lower than the photoinitiating ability of dye photoinitiating systems in which after irradiation with visible light the long-lived excited triplet state of dye is formed.

Since, the three-component systems have consistently been found to be faster, more efficient and more sensitive than their two-component counterparts we decided to focus our studies on application of the cyanine dyes borate salts in three-component photoinitiating systems [1,2,4–7,10–13].

In order to accelerate the rate of polymerization initiated by photoinitiating systems composed of mono-cationic cyanine dye borate salt different compounds were used as a second co-initiator (e.g. N-alkoxypiridinium salts, 1,3,5-triazine derivatives, N-methylpicolinium esters) [10–13].

The present paper is focused on the effect of the heteroaromatic mercaptans on the efficiency of the photoinitiating systems. The three-component photoinitiating system under study was composed of: cyanine dye (electron acceptor), borate salt (electron donor) and mercaptan working as a second co-initiator.

More recently, Suzuki studied the photochemical reactions in the three-component photoinitiating system, composed of aminostyryl sensitizing dye, bis-imidazole derivative (HABI) and 2-mercaptobenzothiazole as a co-initiator. The mechanism of the formation of free radicals, which can start the polymerization chain reaction is as follows (Scheme 2) [14]:



Scheme 2.

In the case of three-component photoinitiating system, the initial absorption of imidazolyl radicals (Im•) was increased by the addition of 2-mercaptobenzothiazole. It is suggested that, the quantum yield of triplet state of aminostyryl dye formation was increased by 2-mercaptobenzothiazole and additional sensitization, that is, triplet electron transfer from aminostyryl dye to imidazole derivative might occur. Suzuki concluded, that the electron transfer occurs *via* both singlet and triplet states of aminostyryl dye, resulting in the improvement of the photosensitivity [14].

Other, high speed photoinitiating systems were composed of cyanine (Scheme 3) or merocyanine dyes or 3,3′-carbonylbis-(coumarine) derivatives (as a sensitizer), 1,3,5-triazine derivative and a heteroaromatic mercaptan (like 2-mercaptobenzimidazole or 2-mercaptobenzothiazole) which acts as an efficient chain transfer agent which greatly enhances the sensitivity [15–17]. The activated initiator dissociates into radical fragments which abstract hydrogen from the mercaptan. Polymerization is subsequently mainly initiated by the sulphur-centred radical.

Alternatively, the mercaptan can act as a co-initiator for the excited dye on its own [17].

2-Mercaptobenzoxazole (MO) and 2-mercaptobenzothiazole (MS) have also been used in two- and three-component photoinitiating systems based on coumarin derivatives [18].

Other mechanism can be involved in multi-component combinations such as in the dye/bis-imidazole derivative/thiol system (Scheme 4) [1].

This paper presents the influence of the heteroaromatic thiols on the photoinitiating ability of the cyanine dye borate salts. The thiols in this study were 2-mercaptobenzothiazole (MS), 2-mercaptobenzoxazole (MO) and 2-mercaptobenzimidazole (MI). Their activities were compared with the activity of two-component photoinitiating systems composed of cyanine dye borate salt. Basing on the laser flash photolysis experiments the mechanism of primary and secondary reactions occurring in the three-component photoinitiating system was proposed.

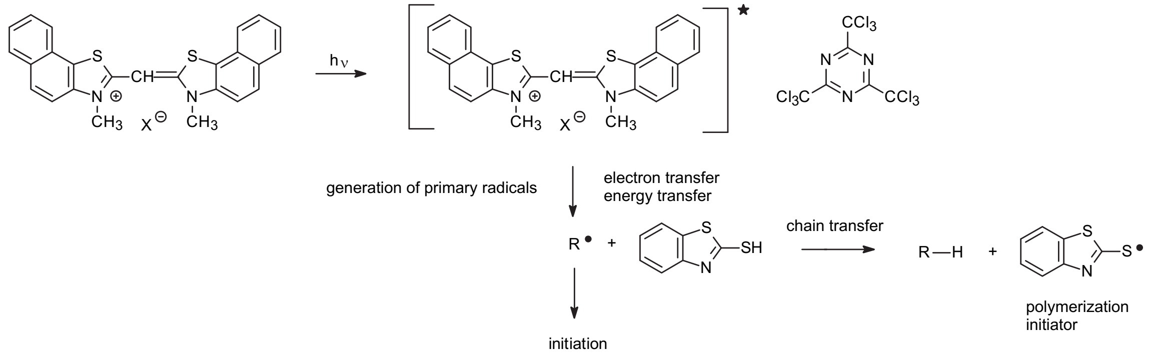
2. Experimental

2.1. Materials

The following compounds were investigated as co-initiators: 2-mercaptobenzothiazole (Aldrich, purity 98%), 2-mercaptobenzoxazole (Aldrich, purity 95%), and 2-mercaptobenzimidazole (Aldrich, purity 98%). They were used as received. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich and were used as monomer and solvent, respectively.

2.2. Cyclic voltammetry

The reduction and oxidation potentials of cyanine dye and co-initiators were measured by cyclic voltammetry. An Electroanalitical MTM System model EA9C-4z (Krakow, Poland), equipped with a small-volume cell was used for the measurements. A 1 mm platinum disc electrode was applied as the working electrode. A Pt wire constituted the counter electrode, and an Ag–AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. The solution was deoxygenated by bubbling argon gas through the solution. The potential was swept from −1.6 to 1.6 V and with the sweep rate of 500 mV/s to record the current–voltage curve.



Scheme 3.

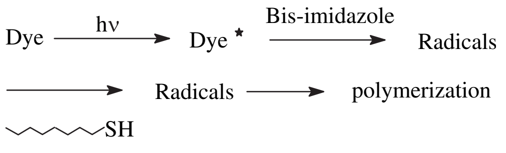
2.3. Polymerization kinetics

Photoinitiated polymerization rate (R_p) profiles were determined by a differential scanning calorimetry (DSC), under isothermal conditions at room temperature using a photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. The 0.035 ± 0.002 g of sample was polymerized in open aluminium pans having the diameter of 6.6 mm. The irradiation of the polymerization mixture was carried out using the visible emission (514 nm) of an argon-ion laser Air-cooled Ion Laser Systems model 177-G01 (Spectra-Physics, USA). The average power of irradiation was 20 mW/0.196 cm^2 at 514 nm. The light intensity was measured by a Coherent Model Fieldmaster power meter.

A polymerization solution was composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The cyanine dyes concentrations used in experiments were 7.5×10^{-4} M, 1×10^{-3} M and 5×10^{-3} M. The co-initiators concentrations were varied from 1×10^{-3} M to 1×10^{-1} M. The monomer was used without purification. As a reference sample, a polymerizing mixture containing cyanine iodide (dye without a co-initiator) was used. The polymerizing mixture was not deareated. In order to reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish–Troomsdorff effect and radicals trapping effect, the initial rates of polymerization were taken into account for further consideration. For computations, the heat of polymerization was taken to be 78 kJ/mol per acrylic double bonds [19].

The rate of polymerization (R_p) was calculated using the formula (1) where dH/dt is maximal heat flow during reaction, M is the molar mass of the monomer, *m* is the mass of the sample, *n* is the number of double bonds per monomer molecule and ΔH_p^{theor} is the theoretical enthalpy for complete conversion of acrylates' double bonds.

$$R_p = \left(\frac{dH}{dt}\right)\frac{M}{n\Delta H_p^{theor} m} \tag{1}$$



Scheme 4.

2.4. Fluorescence quenching

The fluorescence lifetime measurements were performed using an F900 Edinburgh Instruments Fluorescence Spectrometer. The apparatus uses a picosecond diode laser (465 nm) generating pulses of about 50 ps for the excitation. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals in the range of single picoseconds possible. The dyes were studied at a concentration able to provide equivalent absorbance at 465 nm (0.2–0.25 in the 10 mm cell). The rate constant for the quenching of thiacarbocyanine dye by all co-initiators under studies were determined in ethyl acetate:1-methyl-2-pyrrolidinone (4:1) mixture. The concentration of carbocyanine dye was 2×10^{-5} M and that of the co-initiators was in the range from 2×10^{-3} M to 1.6×10^{-2} M. The fluorescence quenching at 600 nm was measured in air.

2.5. Nanosecond laser flash photolysis

Transient absorption spectra and decay kinetics were carried out using the nanosecond laser flash photolysis method. The nanosecond laser flash photolysis experiments were performed using an LKS.60 Laser Flash Photolysis apparatus (Applied Photophisics). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from a Lambda Phisik/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 R955) and a pulsed xenon lamp (150 W) as a monitoring source. The signal from the photomultiplier was processed by a Helwett–Packard/Agilent an Agilent Infiniium 54810A digital storage oscilloscope and an Acorn compatible computer.

3. Results and discussion

3.1. The kinetics of polymerization. Efficiency of photoinitiation of two- and three-component photoinitiating systems

The photoinitiating systems composed of cyanine dye as a photosensitizer with various co-initiators (borate salt and heteroaromatic thiols) were used for the initiation of free radical polymerization. The structures of dyes and co-initiators tested are given in Chart 1. The polymerization solution was consisted of 7.5×10^{-4} M (TS1), 1×10^{-3} M (P3), 5×10^{-3} M (SH1) of sensitizer (as an iodide or *n*-butyltriphenylborate salt) and heteroaromatic thiol with concentrations varied from 1×10^{-3} M to

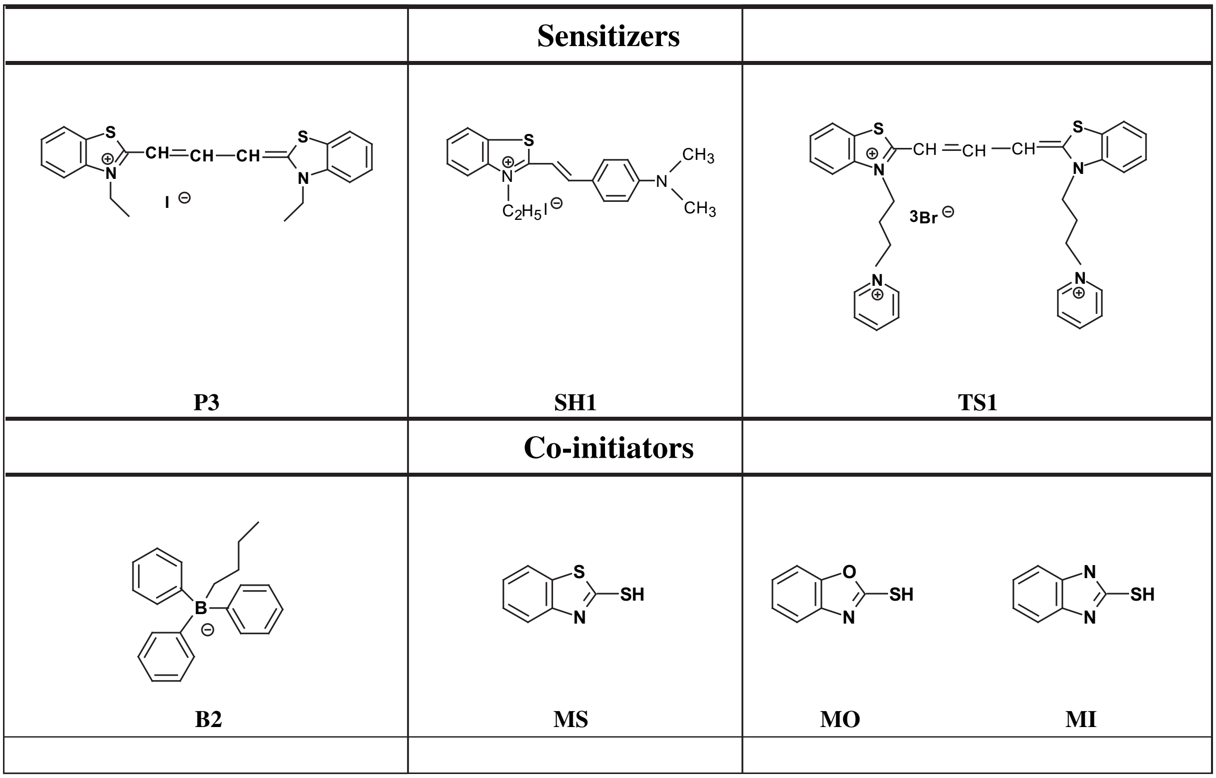


Chart 1.

1×10^{-1} M. The polymerization process was initiated by irradiation at 514 nm. At this wavelength only the sensitizer absorbs the light.

In order to optimize a photoinitiation mixture composition, at the beginning, the cyanine borate concentration effect on the observed rate of polymerization was determined. It is well known that the photoinitiator concentration plays a key role in the photopolymerization. In the conventional UV/Vis photopolymerization, R_p increases when more initiator is used, however it decreases rapidly if too much initiator is added. This effect is rendered to the "inter filter effect" and becomes more significant for photoinitiators with high molar extinction coefficient (for tested dyes ε is about 100 000 M^{-1} cm^{-1}). Fig. 1 presents the relationship between the initial rate of polymerization and concentration of photoinitiator.

It is evident that as the photoinitiator concentration is increasing, the initial rate of polymerization increases and reaches a maximum followed by continuous mild decrease. For the tested photoinitiators, under experimental conditions, the highest rate of polymerization was achieved at the initiator concentrations of about 7.5×10^{-4} M (TS1B2), 1×10^{-3} M (P3B2) and 5×10^{-3} M (SH1B2), respectively. The reduction of the photoinitiated polymerization rate at higher initiator concentration (for applied technique of polymerization rate measurement) can by easily understood taking into account the decrease of the penetration depth of the laser beam. Therefore, basing on this, all polymerization kinetic measurements were curried out at concentration equal 5×10^{-3} M (P3B2), 5×10^{-3} M (SH1B2) and 7.5×10^{-4} M (TS1B2), respectively.

The comparison of the polymerization rates observed for cyanine–borate ion pair and cyanine–borate–heteroaromatic thiol three-component system indicates that the lowest rates of polymerization were observed for the two-component photoinitiating system.

The addition of heteroaromatic thiol into photoinitiating systems results in a significant acceleration of the polymerization process.

The kinetic curves obtained during the photoinitiated polymerization of TMPTA/MP (9:1) mixture photoinitiated by cyanine borates in a presence of thiols, under irradiation with a visible light are shown in Fig. 2 for illustration.

The rate profiles of TMPTA photopolymerization (Fig. 2) show an immediate onset of autoacceleration typical for the polymerization of multifunctional monomers [19].

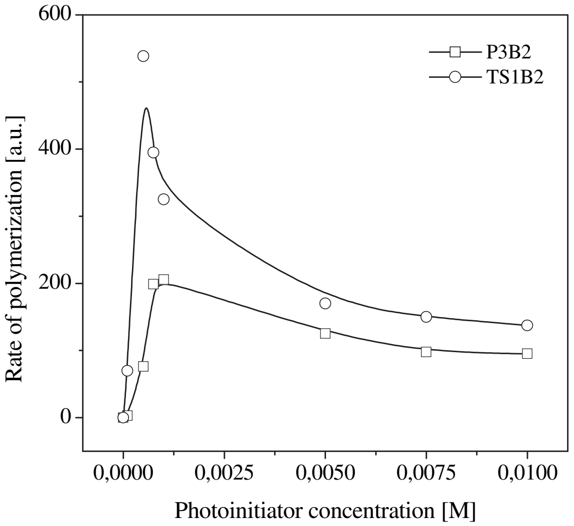


Fig. 1. Rate of polymerization versus photoinitiators concentration (marked in the Figure).

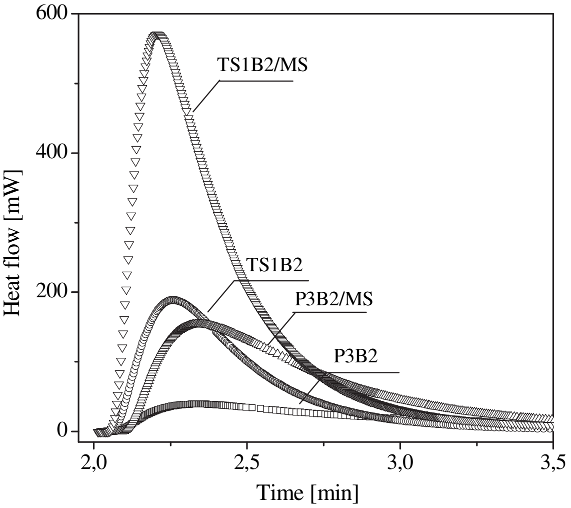


Fig. 2. Family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA/MP (9:1) mixture initiated by three-component photoinitiating systems composed of cyanine dye *n*-butyltriphenylborate in presence of thiols marked in the Figure. The thiols concentrations were 5×10^{-2} M, $I_a = 20$ mW/0.196 cm^2.

It is apparent from the inspection of the initial rates of polymerization that the efficiency of the tested photoinitiating system depends on the structure of heteroaromatic thiol.

The relative rates of photoinitiated polymerization measured for all the tested photoinitiating systems are collected in Table 1.

The kinetic curves presented in Fig. 2 and data complied in Table 1 reflect the activity of the investigated heteroaromatic thiols.

From the obtained kinetic results it is seen that the addition of thiol to monomeric formulation containing cyanine borate as photoinitiator increases the rate of polymerization about 2–8 times.

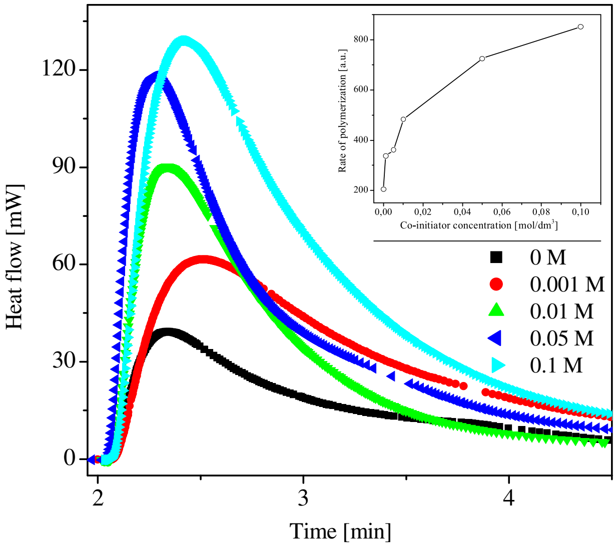


Fig. 3. Kinetic curves recorded during the measurements of the flow of heat during the photoinitiated polymerization of the TMPTA/MP (9:1) mixture initiated by N,N′-diethylthiacarbocyanine *n*-butyltriphenylborate in presence of different concentration (marked in the Figure) of 2-mercaptobenzothiazole (MS). Inset: The influence of the thiol concentration on the rate of polymerization for MS as a second co-initiator.

Fig. 3 presents the kinetic traces recorded during an argon-ion laser photoinitiated polymerization of TMPTA/MP (9:1) mixture in the presence of N,N-diethylthiacarbocyanine *n*-butyltriphenylborate and functioning as a second co-initiator 2-mercaptobenzothiazole (MS) at its various concentrations.

As can be seen in Fig. 3 the addition into the photoinitiating system of the second co-initiator changes the photoinitiation ability in complex fashion.

It should be also noted, that the irradiation of photosensitizer (cyanine dye) in the presence of heteroaromatic thiols without of *n*-butyltriphenylborate salt also leads to the TMPTA polymerization but with lower photoinitiating rates (Fig. 4). This property indicates that the presence of borate anion is crucial for a more effective polymerization.

Table 1

The rates of free radical polymerization of TMPTA photoinitiated by two- and three-component photoinitiating systems tested.

Concentration [mol/dm^3]	MS R_p [μmol s^{-1}]	MO R_p [μmol s^{-1}]	MI R_p [μmol s^{-1}]
P3B2			
0	**0.511**	**0.511**	**0.511**
0.001	0.665	0.793	0.256
0.005	0.818	0.857	0.064
0.01	0.971	1.151	0.384
0.05	1.969	1.510	0.537
0.1	2.01	1.637	0.780
SH1B2			
0	**0.127**	**0.127**	**0.127**
0.001	0.448	0.499	0.383
0.005	0.524	0.486	0.933
0.01	0.780	0.320	0.767
0.05	0.742	0.908	1.036
0.1	0.678	0.793	1.112
TS1B2			
0	**1.982**	**1.982**	**1.982**
0.001	1.342	2.967	2.532
0.005	3.670	2.621	3.644
0.01	3.990	2.954	1.918
0.05	7.263	1.637	2.455
0.1	4.706	2.609	1.662

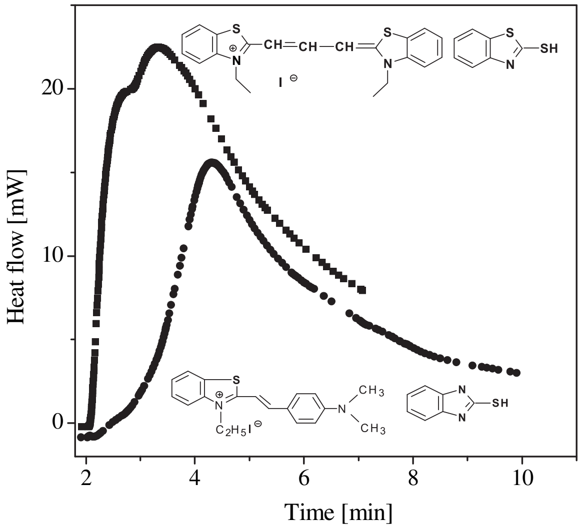


Fig. 4. The kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA/MP (9:1) mixture initiated by cyanine dye in the presence of different co-initiators (marked in the Figure). The cyanine dye and co-initiators concentrations were 1×10^{-3} M and 5×10^{-2} M, respectively. $I_a = 20$ mW/0.196 cm^2.

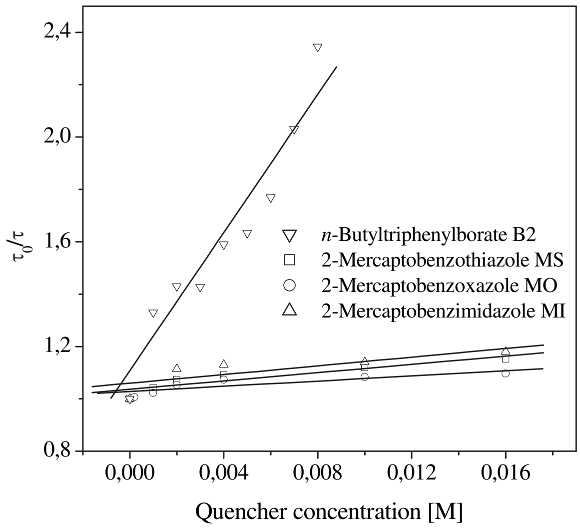


Fig. 5. The Stern–Volmer plots of fluorescence quenching of dye N,N′-diethylthiacarbocyanine iodide by borate salt (B2) and heteroaromatic thiols (MS, MO, MI), respectively.

3.2. Excited state processes in the cyanine dye/n-butyltriphenylborate anion and cyanine dye/thiol photoinitiating systems

In order to explain the thiol and *n*-butyltriphenylborate anion (B2) effect on the photochemical behavior of the light absorbing dye the steady-state fluorescence experiments were applied to observe the quenching of the dye fluorescence as a function of a co-initiator concentration.

The influence of both co-initiators on the rate of fluorescence decay of the dye suggests that the primary photoreaction occurs between the dye and both borate salt and thiol, respectively.

In all tested photoinitiating systems the co-initiator decreases the cyanine dye fluorescence lifetime, e.g. quenches the excited singlet state of cyanine dye.

The results obtained from fluorescence quenching experiments were analyzed with the use of the Stern–Volmer relationship:

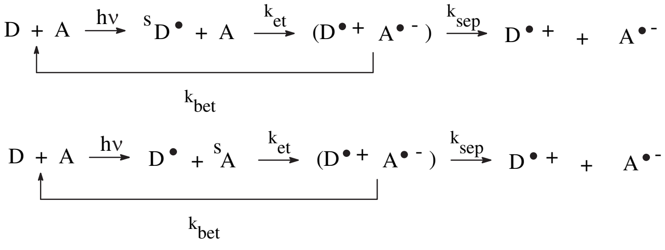
$$I/I_0 = 1 + k_{sv}[Q] = 1 + k_q\tau[Q] \qquad (2)$$

where: I_0 and I are the fluorescence intensities of the thiacarbocyanine dye in the absence and presence of quencher, respectively; k_{sv} is the Stern–Volmer constant, k_q is the quenching constant. From the fluorescence lifetime τ_f and the slope of the linear relationship of Stern–Volmer plot (Fig. 5), one can calculated the k_q value.

Analysis of the data collected in Table 2 shows that the quenching rate constants of excited singlet state of cyanine dyes by heteroaromatic thiols in ethyl acetate:1-methyl-2-pyrrolidinone solution (4:1) are about 10^{10} M^{-1} s^{-1} e.g. are controlled by the diffusion. The quenching of the excited singlet state of the dye by borate anion is much more efficient (Table 2). The rate constants obtained for dye-borate ion pairs are greater than those commonly observed for intermolecular electron transfer reactions since ion pairing eliminates the limitation caused by diffusion and are about one order of magnitude higher than those measured for thiols (Table 2).

Table 2
The fluorescence quenching rate constants for N,N′-diethylthiacarbocyanine iodide quenched by thiols and *n*-butyltriphenylborate anion in solution composed of ethyl acetate:1-methyl-2-pyrrolidinone (4:1).

Co-initiator	MS	MO	MI	B2
k_q [M^{-1} s^{-1}]	2.92×10^{10}	2.44×10^{10}	2.78×10^{10}	7.47×10^{11}



Scheme 5.

The addition of heteroaromatic thiol to the two-component photoinitiating system induced a strong synergic effect (Fig. 2). However, the efficiency of the cyanine dye/borate salt/thiol three-component system is not a simple sum of the efficiencies of the two-component dye/borate salt or dye/thiol photoinitiating systems acting separately. Therefore, it seems that the improvement in photoinitiation for the system cyanine dye/borate/thiol in comparison to cyanine/borate salt may be a result of reactions between thiol and the excited singlet state of the dye.

It is well known that the electron transfer reaction can be depicted accordingly to the following scheme (Scheme 5):where D is an electron donor, A is an electron acceptor, s is the spin multiplicity of the excited state (s = 1 or 3), k_{et}, k_{bet} and k_{sep} are the rate constants of electron transfer, back electron transfer, and ion separation, respectively. In general, the Rehm–Weller equation is used for evaluating the possibility of an electron transfer reaction. The free energy change (ΔG_{el}) of the reactions can be calculated by using the following equation [20]:

$$\Delta G_{ET} = E_{ox}(D^{\bullet+}/D) - E_{red}(A/A^{\bullet-}) - Ze^2/\varepsilon a - E_{00} \qquad (3)$$

here E_{ox} ($D^{\bullet+}/D$) is the oxidation potential of the electron donor molecule, E_{red} ($A/A^{\bullet-}$) is the reduction potential of electron acceptor, $Ze^2/\varepsilon a$ is the Coulombic energy, normally considered negligible in high-dielectric solvents, and E_{00} is an excited state energy of the photosensitizer.

PET reactions compete with rapid photophysical deactivation of the sensitizer excited state.

Since the last term is relatively small in polar or medium polarity media, it can be neglected in the estimation of ΔG_{el}. The E_{ox} and E_{red} of both photoredox pair components were determined from the cyclovoltameric measurements in acetonitrile and are gathered in Table 3.

For the three-component photoinitiating system theoretically following primary reactions are possible:

$$\text{Dye}* + \text{B2} \rightarrow \text{Dye}^\bullet + \text{B2}^\bullet$$

$$\text{Dye}* + \text{Thiol} \rightarrow \text{Dye}^\bullet + \text{Thiol}^{\bullet+}$$

The values of ΔG_{el} calculated for above reactions are in the range from −0.454 eV to 0.094 eV.

Table 3
The oxidation and reduction potentials and the excited singlet state energy of tested compounds.

Compound	E_{red} [eV]	E_{ox} [eV]	E_{00} [eV]
P3	−1.30	1.0	2.08
SH1	−1.09	–	2.156
TS1	−1.02	–	2.164
B2	−1.00	1.16	–
MS	−0.42	0.816	–
MO	−0.36	0.69	–
MI	–	0.90	–

Table 4
Calculated free energy changes (ΔG_{el}) of the electron transfer reaction between the excited singlet state of the dyes and borate or thiols, respectively.

Dye	Oxidation of B2 (ΔG_{el}) [eV]	Oxidation of MS (ΔG_{el}) [eV]	Oxidation of MO (ΔG_{el}) [eV]	Oxidation of MI (ΔG_{el}) [eV]
P3	−0.02	−0.004	−0.13	0.08
SH1	0.094	−0.25	−0.376	−0.166
TS1	−0.016	−0.328	−0.454	−0.244

Calculated by $\Delta G_{el} = E_{ox}$ (Thiol or B2) $- E_{red}$ (dye) $- E_{00}$.
The Coulombic stabilization term is not taken into account. It is usually negligible in polar solvents like acetonitrile.

The free energy changes of the electron transfer reactions between the excited states of the dye and heteroaromatic thiols show that an electron transfer from the thiol to the excited singlet state of the dye is more feasible, leading to reduction of the dye and oxidation of thiol (Table 4).

Therefore, for two-component photoinitiating system composed of cyanine dye and thiol, the efficiency of thiyl radical formation and, hence, initiation of polymerization depends on the observed efficiency of electron transfer from the thiol to the excited singlet state of cyanine dye. The kinetic results obtained for this photoinitiating pair seems confirming this prediction.

All results of these investigations on excited state processes reveal that an effective interaction can take place between *n*-butyltriphenylborate anion, thiol, and the photosensitizer in its excited singlet state.

The following electron transfer processes can occur:

(i) from the borate anion to the excited singlet state of cyanine dye
(ii) from the ground state of the thiol to the excited singlet state of the cyanine dye.

According to literature the second reaction is followed by a hydrogen abstraction which leads to the formation of radicals [1,15,19]. In the present case radicals capable of initiating polymerization of TMPTA are present (Fig. 4). Thus, this process plays also a significant role in photoinitiation of free radical polymerization.

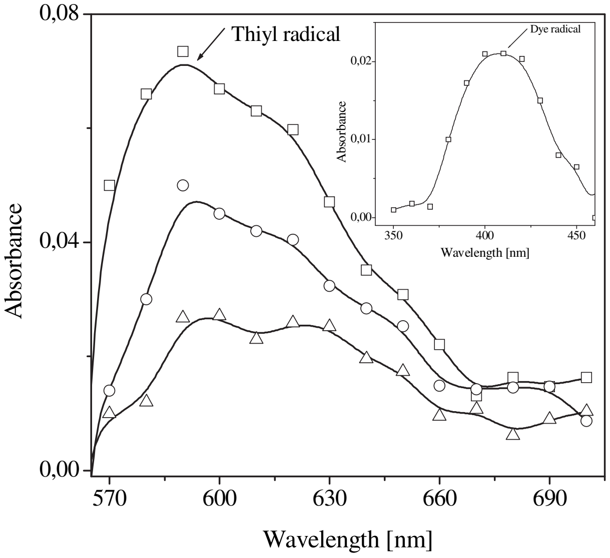


Fig. 6. Transient absorption spectra of cyanine dye in the presence of 2-mercaptobenzothiazole (MS) recorded: 1 μs (squares), 4 μs (circles) and 10 μs (triangles) after laser pulse. Inset: Transient absorption spectra of cyanine dye in the presence of 2-mercaptobenzothiazole (MS) recorded 100 ns after laser pulse (circles) (concentration of 2-mercaptobenzothazole 1×10^{-2} M) in acetonitrile solution. Dye concentration was 2×10^{-4} M.

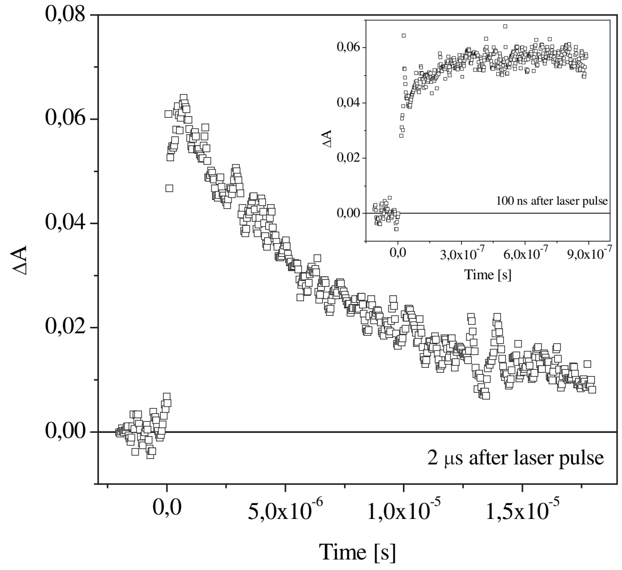


Fig. 7. Transient absorption kinetic observed at 600 nm after different delay time (100 ns and 2 μs) for two-component system: N,N′-diethylthiacarbocyanine iodide/2-mercaptobenzothiazole. Dye concentration equals 5×10^{-4} M, 2-mercaptobenzothiazole concentration was 1×10^{-2} M.

3.3. Laser flash photolysis

The transient absorption spectra of N,N′-diethylthiacarbocyanine iodide in the presence of 2-mercaptobenzothiazole are presented in Fig. 6.

Following laser excitation of thiacarbocyanine dye in the presence of thiol at 355 nm in acetonitrile, a transient absorption spectrum show the appearance of two absorption bands at 420 and 600 nm, respectively.

The irradiation of the carbocyanine dye with visible light leads to the excited singlet state formation. This can be quenched by electron transfer process by heteroaromatic thiol. The absorption band observed at 420 nm in the transient absorption spectra after

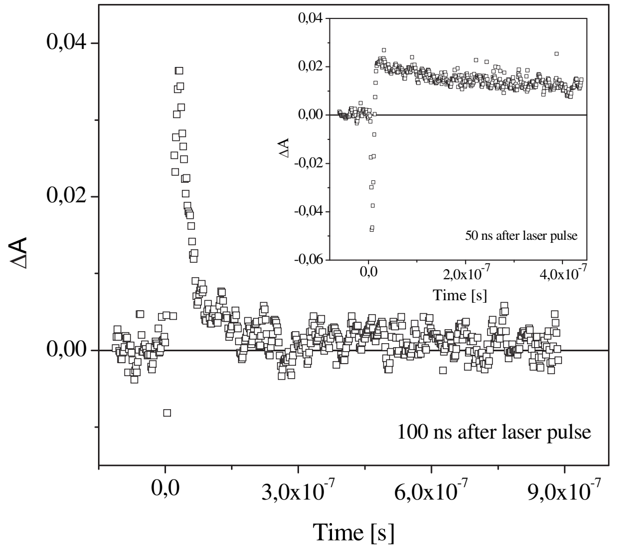


Fig. 8. Transient absorption kinetic observed at 420 nm after different delay time (50 ns and 100 ns) for two-component system: N,N′-diethylthiacarbocyanine iodide/2-mercaptobenzoxazole. Dye concentration equals 5×10^{-4} M, 2-mercaptobenzoxazole concentration was 2×10^{-2} M.

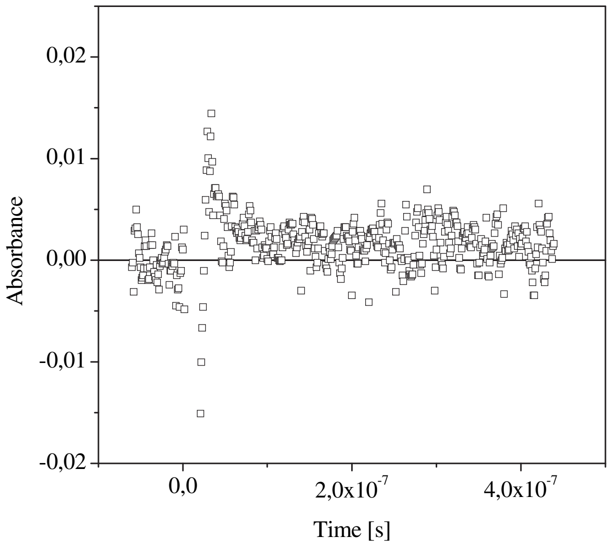


Fig. 9. Transient absorption kinetics observed at 420 nm after 100 ns delay time for three-component system: cyanine dye/borate salt/thiol. Dye concentration equal 2×10^{-5} M, borate salt and thiol concentrations were 1×10^{-2} M, respectively.

Schuster [8,9,21] can be assigned to the cyanine dye radical formed in electron transfer reaction.

The laser flash photolysis recorded for two-component system composed of cyanine dye/2-mercaptobenzothiazole ($c = 1 \times 10^{-2}$ M) gives the second absorption band at 600 nm. This behavior is similar to that described by Andrzejewska et al. [19] for system composed of camphorquinone and 2-mercaptobenzothiazole, and quite different from results obtained by Suzuki et al. [14] for three-component photoinitiating system, composed of: neutral cyanine dye/bis-imidazole derivative/thiol.

This characteristic band was attributed to the presence of the oxidation product of thiol. It is ascribed to thiyl radicals on the basis of literature data for 2-methylbenzothiazole- and 2-methylbenzoxazole-derived radicals [19]. The spectra were produced from the reactions of the thiol with an excited singlet state of cyanine dye and were taken in various times after the laser flash (Fig. 6).

The formation of thiyl radical after electron transfer process from 2-mercaptobenzothiazole to the excited singlet state of N,N′-diethylthiacarbocyanine iodide and its disappearance in the time about 10 μs is shown in Fig. 7.

The curves traces observed at 420 nm in the case of two-component system composed of cyanine dye and 2-mercaptobenzoxazole are presented below. From inspection of the Fig. 8 it is seen that cyanine radical is formed (band at 420 nm).

Basing on these results, one can conclude, that there is the possibility of donating an electron from heteroaromatic thiol to thiacarbocyanine dye, which is thermodynamically allowed [19].

Therefore, one may conclude, that excited carbocyanine dye may act as an electron acceptor in the two-component photoinitiating system, composed of cyanine dye/heteroaromatic thiol.

The kinetics of the disappearance of cyanine dye radical after electron transfer process observed for three-component photoinitiating system composed of cyanine dye/borate anion/thiol is shown in Fig. 9.

On the basis of the nanosecond laser flash photolysis experiments, it appears that excited singlet state of cyanine dye can be reduced by both *n*-butyltriphenylborate anion and heteroaromatic thiol.

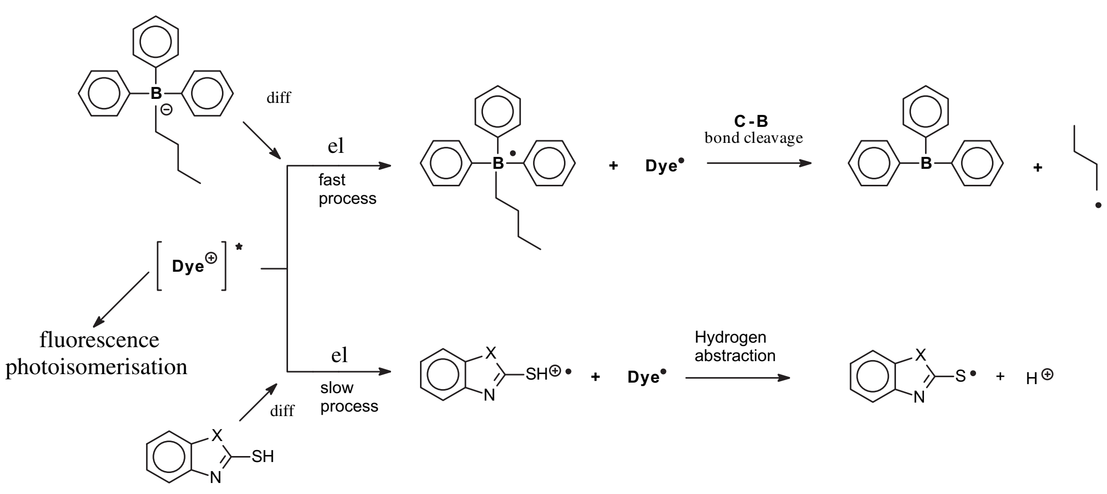
This reactions produce:

- cyanine dye radical and boranyl radical, which undergoes C—B bond cleavage, giving butyl radicals and triphenylboron and cyanine dye radical and thiyl radical.

3.4. Mechanism of free radicals formation

On the basis of the nanosecond laser flash photolysis and the thermodynamical analysis presented above, a mechanism for the primary and secondary reactions occurring in the three-component photoinitiating systems under study is proposed (Scheme 6). After irradiation of the three-component photoinitiating system with a visible light, the excited singlet state of chromophore is formed. The deactivation of excited state occurs by fluorescence, photoisomerization or electron transfer process. In the presence of alkyltriphenylborate anion the cyanine dye undergoes one-electron reduction. The cyanine dye radical and boranyl radical are formed. The boranyl radical undergoes the C—B bond cleavage, giving an alkyl radical that can start the polymerization reaction.

On the other hand, in the presence of heteroaromatic thiol the excited singlet state of cyanine dye may undergo deactivation *via* electron transfer process. The rate of this process is about two orders of magnitude lower than for cyanine borate photoredox ion pair. As a result of this process, the cyanine dye radical and thiyl radical cation are formed. The thiyl radical cation undergoes the



Scheme 6.

hydrogen abstraction, giving a thiyl radical that can start the polymerization reaction.

4. Conclusions

Presented paper is focused on the photochemistry of a very efficient three-component photoinitiating system that can be used for initiation of free radical polymerization.

The studies show that the heteroaromatic thiols can be efficient second co-initiators for free radical polymerization initiated by cyanine dye, a popular photosensitizer. The estimated, according to the Rehm—Weller equation, values of free energy activation for the electron transfer process from an electron donor (thiol, borate salt) to an electron acceptor (cyanine dye) shows that the electron transfer process between these substrates is thermodynamically allowed. An electron transfer process from thiol to the excited singlet state of cyanine dye enhances the efficiency of photoinitiation of polymerization by tested cyanine borate salt in the presence of different heteroaromatic thiols.

Generally, a combination of heteroaromatic thiols and alkyltriphenylborate anion with suitable cyanine dye, enhances the overall polymerization efficiency.

Acknowledgments

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