Journal of Photochemistry and Photobiology A: Chemistry 214 (2010) 276–283

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Tetramethylammonium phenyltrialkylborates as co-initiators with novel two-cationic styrylbenzimidazolium dyes in highly efficient, visible light polymerization of acrylate

Beata Jędrzejewska*, Marek Pietrzak, Jerzy Pączkowski

University of Technology and Life Sciences, Faculty of Chemical Technology and Engineering, Seminaryjna 3, 85-326 Bydgoszcz, Poland

ARTICLE INFO

Article history:
Received 15 April 2010
Received in revised form 6 July 2010
Accepted 9 July 2010
Available online 16 July 2010

Keywords:
Photopolymerization
Radical polymerization
Initiators
Hemicyanine dyes

ABSTRACT

New phenyltrialkylborate salts have been treated as co-initiators with mono- and dicationic styrylbenzimidazole chromophores for the photopolymerization of acrylic monomer. The relative initiator efficiency of the phenyltrialkylborate salts as compared to the *n*-butyltriphenylborate salt with the same type of chromophore was determined. The phenyltrialkylborate salts coupled with selected hemicyanine dye are more efficient photoinitiators of free radical polymerization in comparison to the corresponding photoinitiating system containing *n*-butyltriphenylborate salt as an electron donor. The study showed that, the photoinitiating ability of dicationic styrylbenzimidazolium dyes coupled with the same borate salts is higher in comparison to monocationic chromophore. The significant increase of the efficiency of photoinitiation of free radical polymerization is a result of the generation of more than one radical after one photon absorption (phenyltrialkylborate salts as co-initiators) and an increase of an electron donor concentration in close proximity to a hemicyanine dye moiety (mono- and dicationic styrylbenzimidazole dyes as light absorbers).

1. Introduction

Using visible or UV light to initiate polymerization is an area of intense interest in organic photochemistry. Photopolymerization can be specially directed and turned on or off. In free radical processes triggered by light, rates can be controlled by a combination of factors: source(s) of radicals, light intensity, and temperature [1].

The traditional way to initiate polymerization through photochemistry is carried out by direct photolysis of a precursor that provides free radicals by direct bond scission. Panchromatic sensitization of acrylic polymerization has also been extensively used as a more flexible alternative, but it has its own limitations because it requires the presence of suitable dyes to serve as a primary absorber. In particular, it is necessary to choose a sensitizer (absorber) and a co-initiator so that energy transfer can occur between these components. Photoinduced intermolecular electron transfer represents an alternative to such a restriction. This process involves the use of light to initiate an electron transfer from a donor to an acceptor molecule [2].

Photoinduced electron transfer reaction represents an important route to free radicals among whose uses are the initiation of acrylic polymerization. It is apparent that borate anions are especially beneficial electron transfer donors, and these have many important applications in free radical polymerizations initiated by different electron acceptor sensitizers [3].

Williams et al. were the first to report a systematic study on the photochemistry of tetraarylborates [4]. They found that irradiation of sodium tetraphenylborate in oxygen-free aqueous solution produces 1-phenyl-1,4-cyclohexadiene in nearly quantitative yield. These studies showed that the new carbon–carbon bond is formed intramolecularly between carbon atoms originally bound to boron.

In the eighties of the 20th century, Schuster and his co-workers [5–7] reported that carbocyanine alkyltriphenylborate salts dissolved in nonpolar solvents exist predominantly as ion pairs. Irradiation of the ion pair with visible light absorbed by the cyanine leads to formation of a locally excited singlet state of the dye. The singlet excited cyanine in the ion pair is capable of oxidizing the borate anion to the boranyl radical. The boranyl radical undergoes very fast carbon–boron bond cleavage to generate a free alkyl radical. The rate of bond cleavage depends directly on the stability of an alkyl radical formed. When the stabilized alkyl radicals are formed, carbon–boron bond cleavage is faster than the back electron transfer reaction that regenerates the cyanine borate ion pair. The free alkyl radicals formed by the irradiation–electron transfer–bond cleavage sequence may be used in meaningful chemical processes such as the initiation of polymerization.

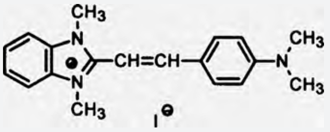
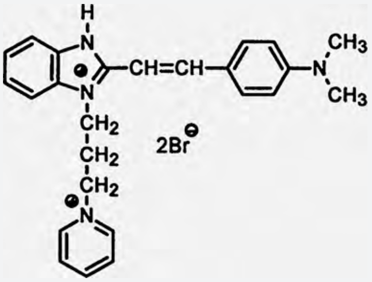
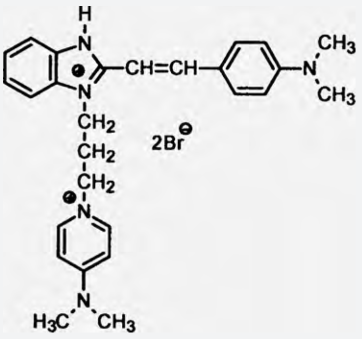
The electron transfer photooxidation of borates may also occur with uncharged acceptors [8,9]. Hassoon and Neckers have

---

* Corresponding author. Tel.: +48 52 374 9034; fax: +48 52 374 9009.
E-mail address: beata@utp.edu.pl (B. Jędrzejewska).

1010-6030/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2010.07.012

Table 1
The steady-state spectral properties of tested hemicyanine dyes in tetrahydrofurane and 1-methyl-2-pirrolidinone.

No	Dye	λ_{max}^{A} (nm)		λ_{max}^{Fl} (nm)		$\Delta\nu$ (cm^{-1})	
		THF	MP	THF	MP	THF	MP
BI1		430.5	429.0	537.4	546.2	4620.7	5001.7
HDBI2		429.0	428.0	558.0	558.0	5388.9	5443.3
HDBI3		428.5	428.0	559.6	559.2	5467.3	5481.8

reported that photoreduction of fluorine dyes by triphenylbutylborate salts is an intermolecular electron transfer reaction from borate anion to the triplet state of the dye that leads to the formation of butyl radicals which initiate polymerization [9].

From literature [10–14] it is known that cyanine borates act as efficient photoinitiators and are able to satisfy the requirement in the field of photopolymerization. The focus of the present report is on tetraorganyl borate salts. Upon electron transfer, tetraorganyl borate anions produce alkyl radicals making this class of compounds useful radical initiators. Herein we describe the novel systems in which phenyltrialkylborate salts dissolved in acrylic monomer are activated by excited styrylbenzimidazole dye to initiate radical polymerization.

2. Experimental

2.1. Materials

Monomer, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), co-initiators, thiophenoxyacetic acid (TPAA), N-phenylglycine (NPG), N-phenyliminodiacetic acid (DNPG), ethyl 4-N,N-dimethylaminobenzoate (ENB), 2-mercaptobenzoic acid (MBA), N-methoxy-4-phenylpyridinium tetrafluoroborate (NO) and solvents, 1-methyl-2-pyrrolidinone (MP), tetrahydrofurane (THF), acetonitrile and ethyl acetate (EtOAc) were purchased from Aldrich Chemical Co. and were used without further purification. Dyes were synthesized in our laboratory using procedures described earlier [10]. DIBF – 5,7-diiodo-3-butoxy-6-fluorone was obtained by applying methodology given by Neckers and co-workers [15].

Phenyltrialkylborate tetramethylammonium salts were synthesized based on the method described by Polykarpov and Neckers [16]. The final products were identified by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy when it was needed. The obtained spectra suggest that the reaction products were of desired structures. The purity of synthesized compounds was determined using thin layer chromatography and by measuring the melting points. The molecular structure and denotations of the dyes under the study are given in Table 1.

2.2. Spectral measurements

The UV–vis absorption spectra were recorded with a Shimadzu UV–vis Multispec-1501 spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. The fluorescence measurements were performed at an ambient temperature.

The fluorescence lifetimes were measured using a FLS920P Spectrometers produced by Edinburgh Instruments. The apparatus utilizes for the excitation a picosecond diode laser generating pulses of about 55 ps at 375 nm. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals with resolution in the range of few picoseconds possible. The dyes were studied at concentration able to provide equivalent absorbance at 375 nm (0.2–0.3 in the 10 mm cell) to be obtained. The measurements were performed in the ethyl acetate–1-methyl-2-pyrrolidinone (10:2) solution.

2.3. Electrochemical measurements

The reduction potentials of the dyes and the oxidation potential of the borates were measured by cyclic voltammetry using an Electroanalytical Cypress System Model CS-1090. The typical three-

Table 2
The rates ($R_p^{\max}$) and the quantum yields (Φ_p) of free radical polymerization of TMPTA/MP (9/1) mixture for tested photoredox couples.

Dye concentration (M)	Co-initiator concentration (M)	$R_p^{\max}$ (μmol/s)	Φ_p	$R_p^{\max}$ (μmol/s)	Φ_p	$R_p^{\max}$ (μmol/s)	Φ_p	$R_p^{\max}$ (μmol/s)	Φ_p
		TB2		TB5		TB7		TB8	
BI1									
0.001	0.001	0.05	0.57	0.14	1.65	0.32	3.73	0.73	8.54
0.005	0.005	0.18	2.14	1.64	19.11	4.20	48.93	6.38	74.30
0.0075	0.0075	0.18	2.12	0.51	5.97	4.22	49.11	6.92	80.61
HDBI2									
0.001	0.002	0.05	0.62	0.24	2.74	1.09	12.68	0.83	9.63
0.005	0.01	1.26	14.65	2.94	34.21	12.88	149.90	10.08	117.37
0.0075	0.015	2.91	33.88	7.70	89.58	24.00	279.35	15.04	175.06
HDBI3									
0.001	0.002	0.04	0.46	0.04	0.48	1.18	13.76	0.83	9.71
0.005	0.01	1.13	13.20	5.00	58.16	13.91	161.95	15.42	179.54
0.0075	0.015	2.80	32.60	5.01	58.28	14.83	172.65	18.87	219.60

electrode setup was employed for electrochemical measurements. The electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile, which was purged with argon prior to a measurement. Platinum 1 mm electrode was applied as working electrode and platinum and no-leak Ag/AgCl were used as auxiliary and reference electrodes, respectively.

2.4. Polymerization measurements

The kinetics of free radical polymerization was studied using a polymerization solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The styrylbenzimidazolium iodide or bromide was used as light absorber whereas the tetramethylammonium borate constituted the electron donor in the photoinitiator system. Their concentration is given in Table 2. A reference formulation contained dye without an electron donor (styrylbenzimidazolium iodide or bromide).

The kinetics of free radical polymerization were measured based on the measurements of the rate of the heat evolution during polymerization in thin film cured sample (0.035 ± 0.002 g; 1 mm thick layer). The measurements were performed by measuring photopolymerization exotherms using photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. Irradiation of the polymerization mixture was carried out using the emission (line at 488 nm) of an argon ion laser Model Melles Griot 43 series with intensity of light of 100 mW/cm^2. The light intensity was measured by a Coherent Model Fieldmaster power meter. An average value of the rate of polymerization was established based on measurements performed at least three times.

The rate of polymerization (R_p) was calculated using the formula (1) where dH/dt is maximal heat flow during reaction and $\Delta H_p^{\text{theor}}$ is the theoretical enthalpy for complete conversion of acrylates' double bonds. $\Delta H_p^{\text{theor}}$ for acrylic double bond is equal 78.2 kJ/mol [17]:

$$R_p = \left(\frac{dH}{dt}\right)\frac{1}{\Delta H_p^{\text{theor}}} \qquad (1)$$

The reaction heat liberated in the polymerization is directly proportional to the number of vinyl groups reacting in the system. By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to Eq. (2):

$$C = \frac{\Delta H_t \cdot M}{n\Delta H_p^{\text{theor}} m} \qquad (2)$$

where ΔH_t is the reaction heat evolved at time t, M is the molar mass of the monomer, m is the mass of the sample and n is the number of double bonds per monomer molecule.

The quantum yield of polymerization Φ_p was defined as the number of polymerized double bonds per absorbed photon [18].

2.5. Determination of the relative initiation efficiency

Since the borate concentration, monomer structure, irradiation and measurement conditions, and the initiator concentration were identical for all borate pair studied, the kinetic profiles allow one to compare the rate of initiation of TMPTA polymerization with each borate.

The classical equation for the polymerization rate is:

$$R_p = k_p\sqrt{\frac{R_i}{2k_t}}[\text{M}]_0 \qquad (3)$$

where R_p is the rate of polymerization, R_i is the rate of initiation, k_p and k_t are the propagation and termination rate constants, respectively, and $[\text{M}]_0$ is the concentration of functional groups (the starting concentration of monomer). In the case of photochemical initiation Eq. (3) takes the form:

$$R_p = k_p\sqrt{\frac{\Phi \cdot I_a}{k_t}}[\text{M}]_0 \qquad (4)$$

because

$$R_i = 2\Phi \cdot I_a \qquad (5)$$

where Φ is the quantum yield for initiation and I_a is the absorbed light intensity.

It results from the Eq. (4), that the rate of polymerization calculated for maximal heat evolution during reaction is related to the rate of initiation. For the same monomer k_p, k_t and $[\text{M}]_0$ are constant. What is more, if concentration and absorption characteristics of the initiators are the same for all cases of the pairs of borates studied, the light absorbed is identical. Hence, the ratio of the polymerization rates for two initiators a and b is equal to the square root from the rates of initiation under particular conditions and in consequence to the square root from the ratio of initiation quantum yields of the initiators [19]:

$$\frac{R_{p_\text{b}}}{R_{p_\text{a}}} = \sqrt{\frac{R_{i_\text{b}}}{R_{i_\text{a}}}} = \sqrt{\frac{\Phi_\text{b}}{\Phi_\text{a}}} \qquad (6)$$

Table 3
Reduction potentials (E_{red}) data and the influence of the type of chromophore on relative initiation efficiency (Φ_{rel}) of phenyltrialkylborates (TB5, TB7 and TB8) compared to *n*-butyltriphenylborate (TB2).

No	E_{red} (V)	Φ_{rel}		
		TB5	TB7	TB8
BI1	−0.524	7.95	538.18	1449.59
HDBI2	−0.514	6.99	68.00	26.71
HDBI3	−0.510	3.20	28.05	45.39

The relative initiation efficiency of the initiators can be defined by Eq. (7):

$$\Phi_{rel} = \frac{\Phi_b}{\Phi_a} = \frac{R_{i_b}}{R_{i_a}} = \frac{(R_p)_b^2}{(R_p)_a^2} \tag{7}$$

where Φ_{rel} is the relative initiation efficiency, Φ_a and Φ_b are the initiation quantum yields, R_{i_a} and R_{i_b} are the rates of initiation, and $(R_p)_a$ and $(R_p)_b$ are the rate of polymerization in the presence of initiators a and b, respectively [19].

Eq. (7) was used to determine the relative initiation efficiency of the initiator pairs studied. The R_p values were calculated based on the kinetic profiles obtained in the presence of *n*-butyltriphenylborates (b) and phenyltrialkylborates (a) with the same chromophore as the cation. The relative initiation efficiencies of the phenyltrialkylborates compared to the corresponding triphenylbutylborate (TB2) are listed in Table 3.

3. Results and discussion

Each of the photoinitiators absorbed UV–vis light with a significant absorption shoulder above 400 nm. This allowed us to apply the excitation beam of the argon ion laser for the initiation of the radical polymerization. The efficiency of radical polymerization photoinitiated by styrylbenzimidazolium dyes under the study coupled with different co-initiators was evaluated by monitoring the rate of heat evolution during the radical polymerization of multiacrylate. Fig. 1 shows example of polymerization profiles for polymerization of TMPTA initiated by phenyltri-*sec*-butylborate salts with mono- and dicationic styrylbenzimidazolium dyes. Similar in shape kinetic curves were obtained for the other initiator pairs.

Fig. 1 presents kinetic curves, representing monomer conversion as a function of time, obtained by photo-DSC. After an induction period during which polymerization inhibitors are consumed, the polymerization starts causing an increase of medium microviscosity. With progress of polymerization, reactive functional groups are consumed and polymerization stops as indicated by the plateau on the kinetic profile (Fig. 1).

The analysis of the kinetic cures obtained for the photoinitiated polymerization of TMPTA/MP (9:1) mixture recorded for styrylbenzimidazolium dyes–tetramethylammonium borate salts photoinitiator systems, under irradiation with an argon ion laser (line at 488 nm) revealed that the rate of polymerization depends on both dye and borate structure (Figs. 1 and 2).

Data presented in Fig. 3 show that the polymerization photoinitiation ability of dicationic photoinitiating system is comparable to the photoinitiating ability observed for DIBF, common triplet state photoinitiator with the same borate salt used as an electron donor [15].

Because photoinitiator performance remarkably affects the overall performance of polymerization systems, significant effort to optimize this important component of the polymerization system has been underway.

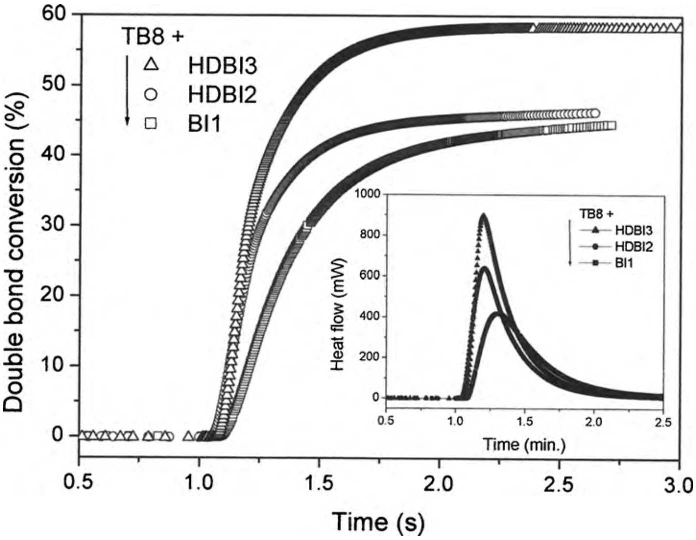


Fig. 1. Comparison of the TMPTA/MP (9/1) mixture polymerization kinetic curves recorded for photoinitiated polymerization initiated by mono- and dicationic styrylbenzimidazolium dyes and tetramethylammonium phenyl-tri-*sec*-butylborate salt (TB8) as measured by photo-DSC with the incident light intensity of 100 mW/cm^2. For all samples the electron donor concentration was 7.5×10^{-3} M calculated for a single absorbing chromophore. Inset: 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 the photoinitiating systems marked in the figure.

Fig. 4 presents the family of kinetic curves recorded during an argon-ion laser initiated polymerization of a solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP), 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and different photoinitiating systems with a sensitizer concentration of 1×10^{-3} M and a co-initiator concentration of 1×10^{-1} M. The experiments were carried out to illustrate the influence of co-initiator structure on the rate of photoinitiated polymerization. The results clearly show that the rate of polymerization is very low (or polymerization does not occur) when typical co-initiators, such as thiophenoxyacetic acid (TPAA), N-phenylglycine (NPG), N-phenyliminodiacetic acid (DNPG), ethyl 4-N,N-dimethylaminobenzoate (ENB), 2-mercaptobenzoic acid (MBA), were used. The highest rates of free radical polymerization of TMPTA–MP mixture were obtained

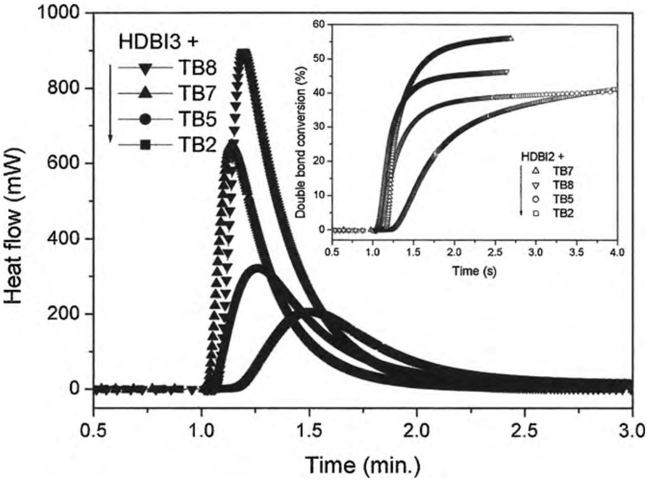


Fig. 2. Visible light polymerization of the acrylic formulation (TMPTA–MP 9/1) with dicationic styrylbenzimidazolium dye (HDBI3) and tetramethylammonium borates as photoinitiator systems. Inset: Double bond conversion vs. time for dicationic styrylbenzimidazolium dye (HDBI2) and tetramethylammonium borates mixtures as photoinitiators.

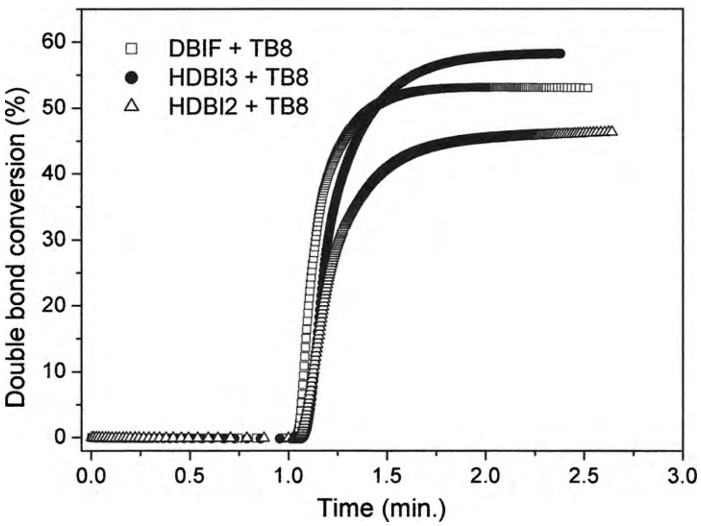


Fig. 3. Comparison of the TMPTA/MP (9/1) mixture polymerization initiated by HDBI2–TB8, HDBI3–TB8 and DIBF–TB8 systems as measured by photo-DSC with the incident light intensity of 100 mW/cm^2. For all samples the electron donor concentration was 7.5×10^{-3} M calculated for a single absorbing chromophore. DIBF – 5,7-diiodo-3-butoxy-6-fluorone (triplet state photoinitiator) [15].

for photoinitiator systems composed of the dye and tetramethylammonium phenyltri-*n*-butylborate (TB7) salt. In presence of N-methoxy-4-phenylpyridinium tetrafluoroborate (NO) the rate of polymerization is about 20 times lower in comparison to photoinitiating systems consisting of TB7 at the same concentration of the electron donor.

The steps determining the reaction of the free radical initiated polymerization *via* intermolecular electron transfer (PET) process are dependent on the nature of the dye and the electron donor (or acceptor). For the tertiary aromatic amines, the electron transfer between an excited acceptor and an electron donor is followed by a proton transfer from the electron donor radical cation to the dye radical anion, which yields a neutral radical initiating polymerization and the reduced radical of the dye [20]. The use of NPG as electron donor gives even more complex processes following the electron transfer that yield the free radicals being a result of N-phenylglycine radical cation decomposition [21]. Very complex is also the photochemistry of the dye–aromatic thiocarboxylic acid photoredox pair [22]. The initiation of the polymerization for dye–N-methoxy-4-phenylpyridinium tetrafluoroborate systems results from the cleavage of the nitrogen–oxygen bond of N-methoxy-4-phenylpyridinium radical cation obtained after electron transfer from the excited dye molecule to the ground state of N-methoxy-4-phenylpyridinium salt. This reaction forms a methoxy radical which initiates the radical polymerization. It should be noted that for this type of photoinitiating system the dye changes its role from an electron acceptor (for dye–MBA, dye–ENB, dye–TPAA, dye–NPG and dye–TB7 systems) to an electron donor.

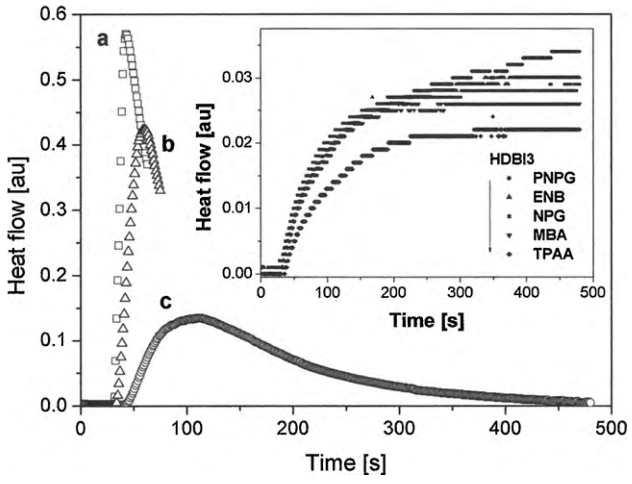


Fig. 4. The kinetic traces recorded for photoinitiated polymerization of the TMPTA–MP (9:1) mixture initiated by sensitizer HDBI3 (1×10^{-3} M) in the presence of (a) tetramethylammonium phenyltri-*n*-butylborate (TB7) salt (0.01 M) and N-methoxy-4-phenylpyridinium tetrafluoroborate (NO) in concentration equals 0.01 M (c) and 0.1 M (b), respectively. Inset: The kinetic traces recorded for photoinitiated polymerization of the TMPTA–MP (9:1) mixture initiated by sensitizer HBDI3 (1×10^{-3} M) in the presence of different co-initiators. The concentration of co-initiator was 1×10^{-1} M. Light intensity was 64 mW/cm^2 (line at 457 nm). The electron donors marked in the figure.

The experimental results suggest that the intermolecular electron transfer process may be the limiting step in the photoinitiated polymerization.

In general, the tetramethylammonium phenyltrialkylborates studied are better co-initiators than the *n*-butyltriphenylborates at the same initiator concentration and irradiation conditions as indicated by the rate of polymerization (Table 2). It should be added, however, that the difference in the initiation efficiencies between the phenyltrialkylborates and the *n*-butyltriphenylborate strongly depends on the structure of the chromophore as well (Tables 2 and 3).

From the data obtained during the measurements, it was deduced that the conversion of monomer double bonds is ranging from about 21% to 60%, while the quantum yields of photopolymerization oscillate between 33 and 280 for the light absorber concentration equals 0.0075 M (Table 2). It was also found that the degree of monomer conversion and the quantum yield of photopolymerization depend on the photoinitiator pair's structure and pair's components concentration. It is noteworthy that the photoinitiating systems composed of DIBF and TB8 is comparable to the dicationic styrylbenzimidazolium dye–TB8 borate salt, photoinitiation ability with a quantum yield of polymerization of about 290, a conversion of monomer double bonds of about 54% and the polymerization rate equals 24.9 μmol/s.

When one takes into account that the rate of polymerization is proportional to the square root of the initiator efficiency, the difference between rates of polymerization induced by HDBI3 coupled with TB2 and TB5 borates becomes even less; the rate of polymerization in the presence of HDBI3 and TB5 photoinitiating system increases only two times in comparison to HDBI3 and TB2 photoredox pair, whereas for BI1–TB8 couple with reference to BI1–TB2 photoinitiating system the rate of polymerization increases about 40 times (compare data in Tables 2 and 3).

From Neckers and co-workers' studies [19], it is known that the relative initiation efficiency can be strongly depended on the reduction potential of the dye cation in the borate initiators. According to the author, the easier it is to reduce the chromophore of the initiator (i.e., the less negative is its reduction potential), the smaller the difference in initiation efficiency observed between the tetraphenyl- and alkyltriphenylborate photoinitiating systems. This causes that the electron transfer processes (i.e., the forward and the competitive back electron transfer between the excited chromophore and the borate anion within the ion pairs) can be dominant factors effecting the kinetics of the free radical generation from the borate anion, if the E_{00} energy of the chromophores and oxidation potential of the borates under the study are similar [19].

In photoinitiating systems described in this paper, the chromophore structure in the tested dyes is the same. This causes that the reduction potential of the styrylbenzimidazolium derivatives is very similar and this factor cannot significantly affect the relative initiation efficiency. For studied systems the factors which might have an impact on the final rate of photoinitiated polymerization

Table 4
The rate constants of electron transfer process (k_{el}) for tested photoredox pairs.

No	$10^{-11}k_q \approx 10^{-11}k_{el}$ (M^{-1} s^{-1})		
	BI1	HDBI2	HDBI3
TB2	0.92	3.35	3.60
TB5	1.06	5.13	5.52
TB7	2.16	12.2	12.4
TB8	2.08	13.0	13.9

are the oxidation potential of the tetrametylammonium borate salts, their concentration in close proximity of the excited chromophore, the number of the free radicals formed after one photon absorption and their reactivity.

As it was mentioned in Section 1, the mechanism for photoinitiation with cyanine dye/tetraalkylammonium alkyltriarylborate has been previously described by Schuster [5]. Electron transfer from the borate anion to the singlet excited state of cyanine leads to the formation of cyanine radical and the boranyl radical which rapidly and irreversibly decomposes producing an alkyl radical. According to Polykarpov and Neckers studies [16] the initial step, in the case of phenyltrialkylborate salts, is anticipated to be also an electron transfer from borate to excited state of sensitizer followed by formation of the alkyl radical and phenyldialkylborane. An alkyl radical, when formed, reacts with acrylic monomers. The second product phenyldialkylborane is also capable of initiating a chain radical reaction. It can react either with the oxygen centered radical product of addition of the alkyl radical to the double bond of monomers or with the excited state of sensitizer [23,24] forming additional radicals. In the case of styrylbenzimidazolium phenyltrialkylborate salts, we confirmed this hypothesis by measuring a yield of a monofunctional monomer and butyl radicals adduct formation [25].

Irradiation of a deaerated solution containing styrylbenzimidazolium phenyltri-*n*-butylborate, and methyl methacrylate in benzene/acetonitrile gives an adduct with yield equals 155%. This result indicates that the photoinduced one electron oxidation of phenyltri-*n*-butylborate anion by the excited state of styrylbenzimidazolium cation produces substantially more than one equivalent of the butyl radicals. The obtained result is in good agreement with the Polykarpov and Neckers [16] studies.

The occurrence of the electron transfer between cyanine cation and borate ions leads to quenching and simultaneous shortening of the fluorescence lifetime of hemicyanine chromophore. The quenching rate constant of the fluorescing state of the hemicyanine under the study can be estimated based on a Stern–Volmer analysis. The lifetimes of the dye in the absence (τ_0) and presence (τ_q) of a quencher (Q) are measurable, thus we can determine k_q from Eqs. (8) and (9):

$$\text{Lifetime of a dye; no Q}: \frac{1}{\tau_0} = k_1 \tag{8}$$

$$\text{Lifetime of a dye; Q present}: \frac{1}{\tau_q} = k_1 + k_q[\mathrm{Q}] = \frac{1}{\tau_0} + k_q[\mathrm{Q}] \tag{9}$$

Experimentally, this was done by plotting $1/\tau_q$ as a function of quencher concentration [Q]. The slope of such a plot is equal to k_q.

The quenching rate constants (k_q) for the photoinduced electron transfer reaction between the singlet state of hemicyanine cations and the borate anion are collected in Table 4. If the electron transfer is the only quenching process of styrylbenzimidazolium singlet, the electron transfer rate constants are equal to those of singlet quenching (Fig. 5).

The measured electron transfer rate constants for photoredox pairs are well above the diffusion limit. This is the pure evidence that the reaction of electron transfer occurs mostly in an intra ion-pair assembly. Similar observation for other cyanine dyes was described by Schuster and co-workers [6].

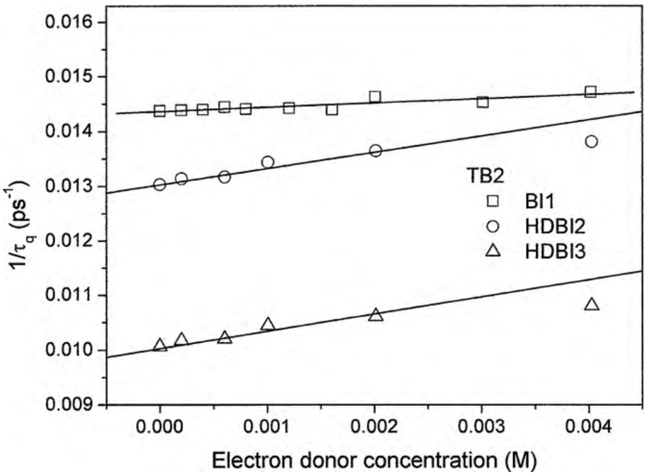


Fig. 5. Experimental plot of $1/\tau_q$ vs. TB2 electron donor concentration for styrylbenzimidazolium dyes tested (marked in figure). For the analysis the main component of the fluorescence decay curve (mostly above 90%) was taking.

The classical Schuster's photoinitiating systems apply as chromophore cyanine dyes that do not form long-lived triplet state. Since the lifetime of cyanine singlet is short (typical lifetime about or less than 1 ns), an efficient electron transfer between borate anion and an excited dye molecule is possible only in nonpolar solvent where the process can occur between components of the tight-ion-pair [6,7,26]. The ion pair electron transfer rates from borate to an excited state of cationic acceptor are anticipated to be above the diffusion limit [6]. Unfortunately, the efficiency of tight-ion-pair formation is high only in really nonpolar solvents such as benzene. Even small amount of polar solvent, as documented by Neckers, may sharply change a degree of such ion pair formation [3]. In polymerizing mixture (acrylates; medium polarity solvent), the photoinitiating photoredox pair composed of cyanine cation and borate anion exists as tight-pair and solvent separated ions. This fact was confirmed experimentally, firstly by an investigation of the influence of borate anion concentration on the efficiency of photoinitiation and secondly by fluorescence quenching experiments.

The studies on the influence of the borate concentration on the rate of photoinitiated polymerization indicate, that for styrylbenzimidazolium-*n*-butyltriphenylborate initiating system about 71.5% exists as ion pair at the concentration of the dye equal 7.5×10^{-3} M. In the case of electron donors, which are able to generate more than one radical after one photon absorption, there is no significant influence of borate concentration on the polymerization rate. What is more, styrylbenzimidazolium halide and tetramethylammonium borate salt applying as photoinitiating system initiated the polymerization reaction with the rate comparable to the styrylbenzimidazolium borate salt, as it is shown in Fig. 6. This is evidence that the electron transfer reaction between borate and an excited state of acceptor is not controlled by the diffusion limit.

The free energy of activation (ΔG_{el}) for the electron transfer reaction between chromophore cation and an electron donor is expressed by the Rehm–Weller equation [27]:

$$\Delta G_{el} = E_{ox}\left(\frac{D}{D^{\bullet+}}\right) - E_{red}\left(\frac{A^{\bullet-}}{A}\right) - \frac{Ze^2}{\varepsilon a} - E_{00} \tag{10}$$

where $E_{ox}(D/D^{\bullet+})$ is the oxidation potential of the electron donor, $E_{red}(A^{\bullet-}/A)$ is the reduction potential of the electron acceptor, E_{00} is the excited state energy of electron accepting molecule, and $Ze^2/\varepsilon a$ is the Coulombic energy, which is the free energy gained by bringing the radical ions formed to an encounter distance *a* in a solvent with dielectric constant *ε*.

The Rehm–Weller equation (10) for photoinduced electron transfer suggests a dependence of the free energy change (ΔG_{el}) on the oxidation potentials of borates (E_{ox}). The cyclic voltammetry gives irreversible oxidation waves for each of the borates examined with peak potentials that vary systematically with the structure of the borate.

One should underline that since the oxidation of borate is irreversible, the oxidation potentials of the borates could not be precisely measured by electrochemical techniques [28]. However, the peak potentials obtained by either cyclic or square wave voltammetry usually follow the same trend as those measured by kinetic methods [5,28]. Therefore, they can be used for the comparison of the borates properties. The measured oxidation potentials of the tetramethylammonium tetraorganylborates are compiled in Table 5.

From Schuster and co-workers studies [5–7], it is known that the rates of alkyl radical formation, as the result of the boranyl radical degradation, are directly related to the known stabilities of the alkyl radicals formed. Since the decay of the boranyl radical is found to be very fast and irreversible, the rate of back electron transfer is negligible [5]. Therefore, the efficiencies of alkyl radical formation and, hence, initiation of polymerization depend on the rate of electron transfer from the borate anion to the singlet state of styrylbenzimidazolium dye cation.

The ease of oxidation of the borates is seen from their oxidation potentials. The tendency is that the more stable radical can be formed, the easier it is to oxidize the borate. Secondary alkyl radicals are more stable than primary, and phenyltri-*sec*-butylborate (TB8) was found to be more reactive than phenyltri-*n*-butylborate (TB7). The same trend is followed for trialkylaryl-, and alkyltriarylborates. Thus, tri-*n*-butylphenylborate (TB7) has a less electropositive peak potential and faster electron transfer rate than *n*-butyltriphenylborate (TB2). Rates of the initiation of photopolymerization follow the same trend under conditions where the borate concentration, relative to the concentration of the dye, is low enough so that a trend can be distinguished (Table 2).

It has been noted that replacement of phenyl ligands on boron by alkyl ligands makes the borates less stable and easier to oxidize. We find that there is a marked difference between the rates of photoinitiation of polymerization under the conditions described above when the trialkylphenylborates, as opposed to

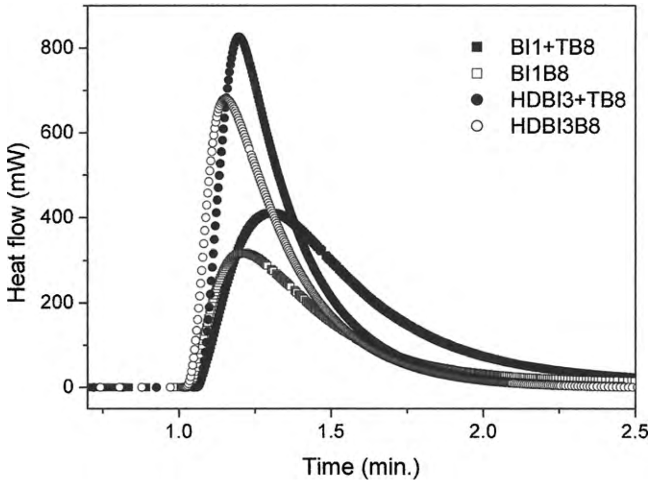
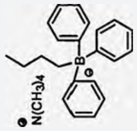
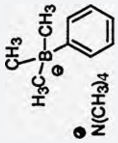
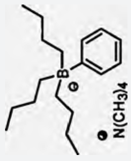
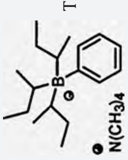


Fig. 6. Comparison of the TMPTA/MP (9/1) mixture polymerization initiated by either styrylbenzimidazolium phenyltrialkylborate (BI1B8, HDBI3B8) or styrylbenzimidazolium dye halide (BI1, HDBI3) and tetramethylammonium borate (TB8) as photoinitiator systems. The light intensity of 100 mW/cm^2.

Table 5
Oxidation (E_{ox}) potential data, energy of the excited state (E_{00}) involved in electron transfer reaction and calculated free energies (ΔG_{el}) of the electron transfer reaction between the singlet excited state of the dyes and electron donor tested.

Dye	E^S_{00} (eV)		ΔG_{el} (eV)							
	THF	MP	THF	MP	THF	MP	THF	MP	THF	MP
			 TB2: E_{ox} = 1.244 V		 TB5: E_{ox} = 0.888 V		 TB7: E_{ox} = 0.708 V		 TB8: E_{ox} = 0.664 V	
BI1	2.494	2.492	−0.726	−0.724	−1.082	−1.080	−1.262	−1.260	−1.306	−1.304
HDBI2	2.413	2.456	−0.655	−0.698	−1.011	−1.054	−1.191	−1.234	−1.235	−1.278
HDBI3	2.427	2.452	−0.673	−0.698	−1.029	−1.054	−1.209	−1.234	−1.253	−1.278

ΔG_{el} – calculated using the Rehm–Weller equation.

the alkyltriphenylborates, are used as co-initiators. Thus, tributyl- and trimethylphenylborates definitely show faster initiation of polymerization than *n*-butyltriphenylborates, respectively (Fig. 2). Tri-*sec*-butylphenyl- and tri-*n*-butylphenylborates are even more reactive. Similar observations are described by Neckers and co-workers [15], who tested the series of tetraorganoborates in the presence of 5,7-diiodo-3-butoxy-6-fluorone, the triplet state sensitizer.

4. Conclusions

The presented paper is focused on photoinitiation of radical polymerization initiated by photoreducible dye sensitization. Phenyltrialkylborate salts or *n*-butyltriphenylborate salts in the presence of mono- and dicationic styrylbenzimidazolium dyes have been evaluated as novel, singlet state, visible light initiators. The comparative analysis of the borate salts as co-initiators with styrylbenzimidazolium dyes shows that the number of alkyl groups per boron determines reactivity. Trialkylphenylborates initiate polymerization much more rapidly than *n*-butyltriphenylborate (TB2). The tri-*sec*-butylphenyl- and tri-*n*-butylphenylborates as co-initiators in the presence of dicationic styrylbenzimidazolium dyes are very efficient radical producers.

Acknowledgment

This work was supported by The Ministry of Science and Higher Education (MNiSW) (grant no. N N204 054135).

References

[1] A.A. Ermoshkin, E.S. Nikolaeva, D.C. Neckers, A.V. Fedorov, New tetraalkylborate initiators for remote polymerization, Macromolecules 41 (2008) 9063–9066.

[2] D.F. Eaton, in: D.H. Volman, K. Gollnick, G.S. Hammond (Eds.), Advances in Photochemistry, vol. 13, Wiley-Interscience, New York, 1986 (Chapter 4).

[3] S. Hassoon, A. Sarker, A.Y. Polykarpow, M.A.J. Rodgers, D.C. Neckers, Photoinduced inter- and intra-ion-pair electron transfer reactions in N-(*p*-benzoylbenzyl)-N,N,N-tri-*n*-butylammonium triphenyl-*n*-butylborate and -gallate salts, J. Phys. Chem. 100 (1996) 12386–12393.

[4] J.L.R. Williams, J.C. Doty, P.J. Grisdale, T.H. Regan, G.P. Happ, D.P. Maier, Boron photochemistry. II. Irradiation of sodium tetraarylborates in alcohol solutions, J. Am. Chem. Soc. 90 (1968) 53–55.

[5] G.B. Schuster, Photochemistry of organoborates: intra-ion pair electron transfer to cyanines, Pure Appl. Chem. 62 (1990) 1565–1572.

[6] S. Chatterjee, P.D. Davis, P. Gottschalk, M.E. Kurz, B. Sauerwein, X. Yang, G.B. Schuster, Electron transfer and the chemistry of boranyl radicals, J. Am. Chem. Soc. 112 (1990) 6329–6338.

[7] S. Chatterjee, P. Gottschalk, P.D. Davis, G.B. Schuster, Electron-transfer reactions in cyanine borate ion pairs: photopolymerization initiators sensitive to visible light, J. Am. Chem. Soc. 110 (1988) 2326–2328.

[8] J.Y. Lan, G.B. Schuster, Photoalkylation of dicyanoarenes with alkyltriphenylborate salts, J. Am. Chem. Soc. 107 (1985) 6710–6711.

[9] S. Hassoon, D.C. Neckers, Electron transfer photoreduction of 5,7-diiodo-3-butoxy-6-fluorone with tetrabutylammonium triphenylbutylborate and N,N-dimethyl-2,6-diisopropylaniline, J. Phys. Chem. 99 (1995) 9416–9424.

[10] B. Jędrzejewska, J. Kabatc, M. Pietrzak, J. Pączkowski, Styrylpyridinium borate salts as dye photoinitiators of free radical polymerization, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 1433–1440.

[11] B. Jędrzejewska, M. Tur, J. Pączkowski, Styrylbenzimidazolium dye–borate complex as an effective, singlet state photoinitiator in an argon laser induced TMPTA photopolymerization, J. Photochem. Photobiol. A: Chem. 209 (2010) 32–40.

[12] B. Jędrzejewska, J. Jeziórska, J. Pączkowski, Studies on an argon laser induced photopolymerization employing both mono- and bischromophoric hemicyanine dye–borate complex as a photoinitiator, J. Photochem. Photobiol. A: Chem. 195 (2008) 105–115.

[13] B. Jędrzejewska, M. Tur, J. Pączkowski, Styrylquinolinium borates as donor–acceptor initiators for sensitized photopolymerization of TMPTA, Mater. Chem. Phys. 117 (2009) 448–454.

[14] B. Jędrzejewska, A. Marciniak, J. Pączkowski, Studies on an argon laser induced photopolymerization employing both mono- and bischromophoric hemicyanine dye–borate complex as a photoinitiator. Part II, Mater. Chem. Phys. 111 (2008) 400–408.

[15] A.Y. Polykarpov, S. Hassoon, D.C. Neckers, Tetramethylammonium tetraorganylborates as coinitiators with 5,7-diiodo-3-butoxy-6-fluorone in visible light polymerization of acrylates, Macromolecules 29 (1996) 8274–8276.

[16] A.Y. Polykarpov, D.C. Neckers, Tetramethylammonium phenyltrialkylborates in the photoinduced electron transfer reaction with benzophenone. Generation of alkyl radicals and their addition to activated alkenes, Tetrahedron Lett. 36 (31) (1995) 5483–5486.

[17] J. Brandrup, E.H. Immergut, Polymer Handbook, third edition, John Wiley & Sons, Inc., New York/Chichester/Brisbane/Toronto/Singapore, 1989, p. II/298.

[18] S. Zhang, B. Li, L. Tang, X. Wang, D. Liu, Q. Zhou, Studies on the near infrared laser induced photopolymerization employing a cyanine dye–borate complex as the photoinitiator, Polymer 42 (2001) 7575–7582.

[19] R. Popielarz, A.M. Sarker, D.C. Neckers, Applicability of tetraphenylborate salts as free radical initiators, Macromolecules 31 (4) (1998) 951–954.

[20] J.J.M. Lamberts, D.R. Schumacher, D.C. Neckers, Novel rose bengal derivatives: synthesis and quantum yield studies, J. Am. Chem. Soc. 106 (1984) 5879–5883.

[21] B. Marciniak, K. Bobrowski, G.L. Hug, Quenching of triplet states of aromatic ketones by sulfur-containing amino acids in solution. Evidence for electron transfer, J. Phys. Chem. 97 (1993) 11937–11943.

[22] K. Bobrowski, M. Marciniak, G.L. Hug, A reinvestigation of the mechanism of photoreduction of benzophenones by alkyl sulfides, J. Photochem. Photobiol. A: Chem. 81 (1994) 159–168.

[23] G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structures of Organometallic Compounds, vol. 7, Pergamon Press, Oxford, 1982, pp. 291–293, 335.

[24] A.-G. Davies, J.C. Scaiano, Homolytic organometallic reactions. Part X. Kinetics of the homolytic photoreductions of aromatic ketones by trialkylboranes, J. Chem. Soc. Perkin Trans. 2 (1972) 2234–2238.

[25] M. Pietrzak, B. Jędrzejewska, J. Pączkowski, Unusually highly efficient, singlet state, visible light photoinitiators based on styrylbenzimidazolium phenyltributylborate photoredox pairs for vinyl monomers free radical polymerization, J. Polym. Sci. Part A: Polym. Chem. 47 (2009) 4119–4129.

[26] X. Yang, G.B. Schuster, C. Zou, Photo-initiated electron transfer reactions in dye–borate ion pairs: energy, distance and solvent dependence, J. Photochem. Photobiol. A: Chem. 65 (1992) 191–196.

[27] D. Rehm, A. Weller, Kinetics of fluorescence quenching by electron and H-atom transfer, Isr. J. Chem. 8 (1970) 259–271.

[28] D. Murphy, G.B. Schuster, A kinetic method for determination of redox potentials: oxidation of tetraarylborates, J. Phys. Chem. 99 (1995) 511–515.