

Development of New Heterobicationic Monomethine Dyes as Effective Photoinitiator of Free Radical Polymerization in Visible-Light Region

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ABSTRACT: The dye initiators consisting of *N*-[3-(*p*-alkylpyridine)propyl]-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodides as chromophores and *n*-butyltriphenylborate anion as electron donor were prepared to achieve an efficient photoinitiator of free radical polymerization in a visible-light region. The relative photoinitiating efficiencies of novel photoinitiators of vinyl monomers polymerization were evaluated. The results

obtained clearly documented that the bicationic photoinitiators exhibit a marked increase in the photoinitiation ability compared to the initiators consisting of a single charged hemicyanine dye. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1636–1645, 2008

Key words: bicationic monomethine dye; initiator; photopolymerization; kinetics

INTRODUCTION

The search for efficient polymerization photoinitiating systems operating under UV excitation has been extensively developed because of the wide applications of UV curing technologies.^{1,2} Designing systems that are photosensitive under visible light meant for use in photocurable pigmented coatings, in high speed laser imaging, and capable of superseding the harmful mercury-based UV lamps by new, environmental friendly, energy saving, visible lamps such as excimer or metal halide doped lamps, are the subject of intensive research work.² Very few cleavable radical photoinitiators (Type I) working under visible light are known as yet.^{1–4} Accordingly, it is necessary to use two-component or multicomponent photoinitiating systems. Improvement of these combinations has led, for example, to the design of photoinitiating systems such as dye/amine dye/onium or dye/borate salt ion pairs.^{1–6}

Application of cyanine dye borate salt photoinitiating systems give opportunity of changing the usefulness region of these photoinitiators by changing the structure of a cyanine dye.

The modification of the structure of the dye by shortening or extending of the polymethine chain,

by introducing a substituent in heterocyclic moiety or in the “*meso*” position of polymethine chain, leads to the change in absorption spectra and to the change in efficiency of free radical polymerization of vinyl monomers.^{5–8} From our earlier studies, it is known that modification of the hemicyanine dye structure by introduction of the second, not conjugated with the dye molecule, quaternary nitrogen significantly enhances the efficiency of the photoinitiation.⁹

This work presents the study on the synthesis and both photophysical and photochemical properties of novel, singlet-state free radical photoinitiators with enhanced photoinitiation ability caused by an artificial increase of a donor concentration in proximity to an absorbing chromophore. This unique and easily achieved improvement was carried out by covalent bonding of quaternary pyridinium cation to cationic monomethine dyes.

The photoinitiating abilities of the novel photoredox pairs were compared to the photoinitiation of their monocationic equivalents, e.g., *N*-methyl-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium *n*-butyltriphenylborate (D0B2), as well as Rose Bengal derivative (RBAX), e.g., typical triplet state photoinitiator.

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EXPERIMENTAL

Materials

1,3-Dibromopropane, pyridine, 4-picoline, 4-(*N,N*-dimethylamino)pyridine, 2-methylbenzothiazole, 4-

chloroquinoline, monomer, and solvents were obtained from Aldrich Chemical Co. (Poland) RBAX was prepared using procedure given by Neckers and Co-workers.¹⁰

Measurements

About $1.0 \times 10^{-5}M$ solutions of heterobicationic monomethine dyes: *N*-(3-pyridinepropyl)-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D1), *N*-[3-(4-methylpyridine)propyl]-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D2), and *N*-[3-(4-*N,N*-dimethylaminopyridine)propyl]-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D3) in various solvents were prepared for the measurements of the absorption and fluorescence spectra. Absorption spectra were recorded at room temperature using a Shimadzu UV-vis Multispec-1500 spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter (Tokyo, Japan). Absorption and fluorescence spectra were recorded using spectroscopic quality acetonitrile (MeCN) and *N,N*-dimethylformamide (DMF). The fluorescence measurements were performed at an ambient temperature.

The reduction potentials of the dyes and the oxidation potential of tetramethylammonium *n*-butyltriphenylborate were measured using cyclic voltammetry technique. An Electroanalytical MTM System Model EA 9C-4z (Crakov, Poland), equipped with a small volume cell, was used for the measurements. A 1-mm platinum disc electrode served as a working electrode, a Pt wire constituted the counter electrode, and an Ag-AgCl electrode was used as a reference electrode. The supporting electrolyte was 0.1M tetrabutylammonium perchlorate in dry acetonitrile.^{5,11}

The photoinitiated polymerization kinetics was followed *in situ* by measuring the rate of heat evolution during polymerization in 2- to 3-mm thick sample. The measurements were performed in a homemade micro-calorimeter. A semiconducting diode immersed in 2-mm thick layer (0.25 mL) of a cured sample was used as a temperature sensor. The irradiation of the polymerization mixture was carried out using the emission of an Omnicrome model 543-500 MA argon-ion laser (Chino, California, USA), which emits two visible light wavelengths at 488 and 514 nm. The irradiation intensity was measured with a Coherent Power Meter Type 543-500 mA and was 64 mW/cm^2 .

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 initiator (dye) concentration was equal to $7.5 \times 10^{-4}M$. A polymerizing mixture containing the dye without an electron donor was used as a reference sample. The monomer was used with-

out purification. The polymerizing mixture was not deaerated.

The ¹H-NMR spectra were recorded with the use of a Varian Gemini 200 spectrometer operating at 200 MHz. Dimethylsulfoxide (DMSO-*d*₆) was used as the solvent and tetramethylsilane as internal standard.

Melting points (uncorrected) were determined on the Boëthius apparatus-PGH Rundfunk-Fernsehen Niederdorf KR. Stollberg/E.

Synthesis

The synthesis of novel visible-light photoinitiators is based on the condensation reaction of 1-[3-(2-methylbenzothiazolium)]-3-(*p*-alkylpyridinium) propane dibromide derivatives (B1, B2, B3) with 4-chloro-*N*-(3-bromopropyl)quinoline (C1). The dyes were obtained according to the methodology given by Gadjev et al.¹²

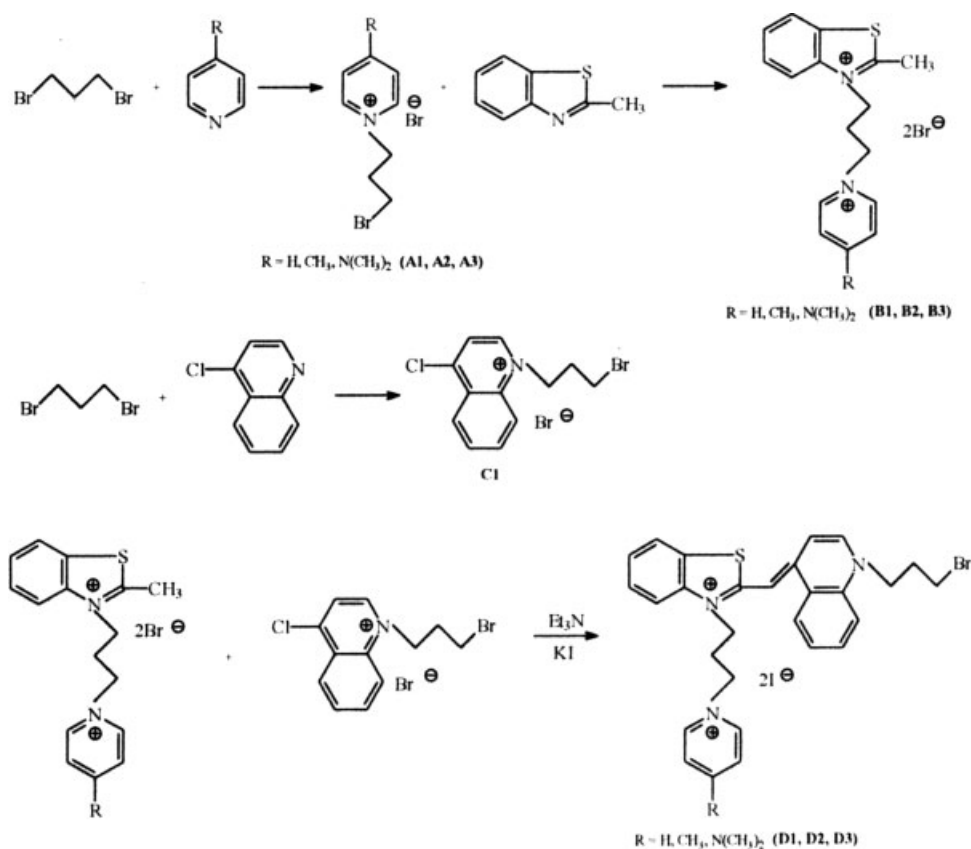
A general route for the synthesis of novel heterobicationic monomethine dyes is shown in Scheme 1.

The synthesis of the new heterobicationic monomethine dyes undergoes via four steps as shown in Scheme 1:

1. The quaternization reaction of a *p*-substituted pyridine with 1,3-dibromopropane giving *N*-(3-bromopropyl)pyridinium bromide (A1, A2, A3).
2. The quaternization reaction of 2-methylbenzothiazole with an appropriate *N*-(3-bromopropyl) pyridinium bromide (A1, A2, A3) leading to the formation of corresponding 1-[3-(2-methylbenzothiazolium)]-3-(*p*-alkylpyridinium) propanedi-bromide (B1, B2, B3).
3. The quaternization reaction of 4-chloroquinoline with 1,3-dibromopropane yielding 4-chloro-*N*-(3-bromopropyl)quinolinium bromide (C1).
4. The condensation reaction of 1-[3-(2-methylbenzothiazolium)]-3-(*p*-alkylpyridinium) propanedi-bromide derivatives (B1, B2, B3) with 4-chloro-*N*-(3-bromopropyl)quinolinium bromide (C1) resulting in the formation of the appropriate heterobicationic monomethine dyes (D1, D2, D3).

N-(3-bromopropyl)pyridinium bromide (A1), *N*-(3-bromopropyl)-4-methylpyridinium bromide (A2), *N*-(3-bromopropyl)-4-*N,N*-dimethylaminopyridinium bromide (A3) were prepared using Colichman's method.¹³ The synthesis details are described in our previous paper.⁹

1-[3-(2-Methylbenzothiazolium)]-3-(*N*-pyridinium) propane dibromide (B1), 1-[3-(2-methylbenzothiazolium)]-3-(4-methylpyridinium) propane dibromide (B2), 1-[3-(2-methylbenzothiazolium)]-3-(4-*N,N*-dimethylaminopyridinium) propane dibromide (B3) were prepared using a method described by Gadjev



Scheme 1 The synthesis of the new heterobicationic monomethine dyes.

et al.¹² The detailed synthesis procedure has been described elsewhere.⁹

Synthesis of *N*-(3-bromopropyl)-4-chloroquinolinium bromide (C1)

N-(3-bromopropyl)-4-chloroquinolinium bromide (C1) was prepared using a method described by Gadjev et al.¹² Five grams (0.03 mol) of 4-chloroquinoline was suspended in 7 mL of chlorobenzene. To the suspension, 6.1 mL (12.1 g, 0.06 mol) of 1,3-dibromopropane was added. The reaction mixture was refluxed and stirred for 2 h. Then additional 4.04 g (2 mL) of 1,3-dibromopropane was added and reflux was continued for two more hours. The reaction mixture was cooled yielding solid product. The compound was filtered and dried under vacuum. Yield of the crude product was 10.35 g (85%).¹² *N*-(3-bromopropyl)-4-chloroquinolinium bromide is highly hygroscopic and requires storing in a desiccator. The product obtained was used in the next reaction steps without additional purification.

C1: C₁₂H₁₂ClBr₂N

¹H-NMR (DMSO-d₆) δ (ppm): 2.484–2.563 (m, 2H, –CH₂–), 3.677–3.818 (m, 2H, –CH₂Br), 5.319 (m, 2H, –CH₂N), 8.059–8.200 (m, 2H, pyr), 8.299–8.409 (m, 2H, pyr), 8.486–8.735 (m, 2H, pyr).

The synthesis of the corresponding heterobicationic monomethine dyes (D1, D2, D3)

N-(3-pyridinepropyl)-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D1), *N*-[3-(4-methylpyridine)propyl]-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D2), and *N*-[3-(4-*N,N*-dimethylaminopyridine)propyl]-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D3) were obtained by refluxing of *N*-(3-bromopropyl)-4-chloroquinolinium chloride (C1) (0.0035 mol) with appropriate 1-[3-(2-methylbenzothiazolium)]-3-(*p*-alkylpyridinium)] dibromide (B1, B2, B3; 0.0035 mol) in methanol (15 mL) in the presence of triethylamine (0.97 mL, 0.007 mol) for 30 min. A triple excess of saturated aqueous potassium iodide solution was added to the hot dye solution. The precipitate formed after cooling the reaction mixture was filtered and recrystallized from either aqueous ethanol or methanol.¹²

N-(3-pyridinepropyl)-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D1)

D1: C₂₈H₂₈N₃SBr₂I₂; yield 74.1%; mp 204°C;

¹H-NMR (DMSO-d₆) δ (ppm): 1.139–1.212 (m, 2H, –CH₂–), 3.058–3.154 (2H, –CH₂–), 3.410–3.655

(2H, $-\text{CH}_2-$), 4.329 (m, 2H, $-\text{CH}_2\text{N}$), 4.784–5.143 (m, 4H, $-\text{CH}_2\text{N}^+$), 6.934 (1H), 7.395–7.468 (m, 2H, Ar), 7.630–7.675 (2H, pyr), 7.886–7.899 (4H, Ar), 8.099–8.134 (d, 1H, $J = 7$ Hz, pyr), 8.261–8.298 (d, 1H, $J = 7.6$ Hz, pyr), 8.439–8.826 (5H, Ar).

N-[3-(4-methylpyridine)propyl]-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D2)

D2: $\text{C}_{29}\text{H}_{30}\text{N}_3\text{SBrI}_2$; yield 64.6%; mp 223°C;

$^1\text{H-NMR}$ (DMSO- d_6) δ (ppm): 1.080–1.209 (s, 3H, CH_3), 1.820–1.857 (2H, $-\text{CH}_2-$), 3.143–3.168 (2H, $-\text{CH}_2-$), 3.611–3.648 (2H, $-\text{CH}_2-$), 4.333 (m, 2H, $-\text{CH}_2\text{N}$), 4.831–5.102 (m, 4H, $-\text{CH}_2\text{N}^+$), 6.915 (1H), 7.432–7.524 (m, 2H, Ar), 7.530–7.677 (2H, Ar), 7.690–7.769 (2H, pyr), 7.941–7.996 (m, 4H, Ar, $J = 11$ Hz), 8.212–8.490 (2H, pyr), 8.611–8.805 (2H).

N-[3-(4-*N,N*-dimethylaminopyridine)propyl]-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (D3)

D3: $\text{C}_{30}\text{H}_{33}\text{N}_4\text{SBrI}_2$; yield 63.9%; mp 208°C;

$^1\text{H-NMR}$ (DMSO- d_6) δ (ppm): 1.005–1.074 (2H, $-\text{CH}_2-$), 1.142–1.213 (2H, $-\text{CH}_2-$), 3.138–3.312 (6H, $-\text{N}(\text{CH}_3)_2-$), 3.393–3.488 (2H, $-\text{CH}_2-$), 4.330–4.376 (m, 2H, $-\text{CH}_2\text{N}$), 4.495–4.735 (m, 2H, $-\text{CH}_2\text{N}^+$), 4.907–5.153 (m, 2H, $-\text{CH}_2\text{N}^+$), 6.878 (1H), 6.980–7.019 (d, 2H, $J = 7.8$ Hz, pyr), 7.398–7.453 (m, 2H, Ar, $J = 11$ Hz), 7.608–7.814 (2H, pyr), 7.912–8.088 (2H), 8.183–8.273 (4H), 8.669–8.828 (2H).

To transform the obtained monomethine dyes into efficient free radical polymerization initiating systems, an anion exchange from iodide to borate was necessary. The ion exchange reaction was performed using the procedures given by Damico¹⁴ and Schuster and Co-workers.¹⁵ The final products were identified by $^1\text{H-NMR}$. The spectra and results obtained were the evidence that the tested salts were of the desired structures.

RESULTS AND DISCUSSION

Synthesis

The structures of the novel heterobicationic monomethine dyes are presented in Chart 1.

Details of the synthesis are given in the Experimental Section. An inspection of the experimental

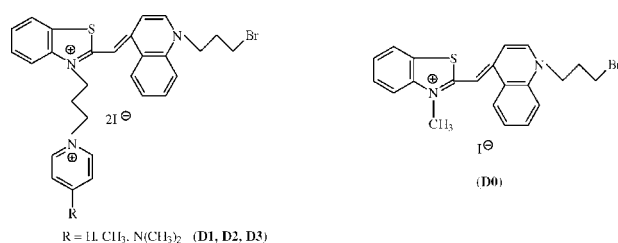


Chart 1 The structure of the monomethine dyes tested.

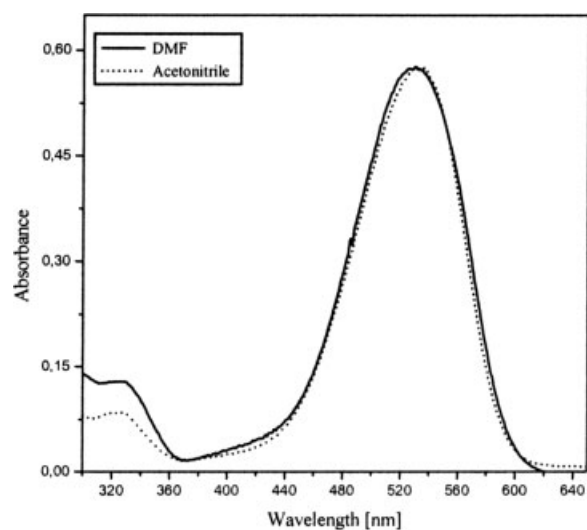


Figure 1 Electronic absorption spectra of D2 obtained in DMF and acetonitrile as a solvent at 293 K.

data shows that the melting points for all compounds are sharp, indicating high purity and crystalline phase of the resulting salts. It is noteworthy that the $^1\text{H-NMR}$ spectra of monomethine dyes D1, D2, and D3 display one characteristic bond localized at about 6.8–7 ppm, which can be attributed to the hydrogen atom in the methine group. The bands that appeared in the range from about 7.3 to 8.8 ppm are the signal for the aromatic protons.

A comparative analysis of the $^1\text{H-NMR}$ spectra of the *n*-butyltriphenylborate salt of the prepared monomethine dye (DOB2) confirms that the amount of borate anion in heterobicationic monomethine cyanine borate is twice as high as that in the salt of the monocationic dye (DOB2). This finding indicates that both cations in the bicationic dyes are coupled with *n*-butyltriphenylborate anions in a 1 : 1 ratio.

The *N*-(3-bromopropyl)pyridinium bromide derivatives are white powders, whereas the monomethine dyes are intensely red. According to thin-layer chromatography analysis (silica gel 60, F-254), with the use of methanol–acetone mixture (2 : 1) as the eluent, the monomethine dyes are of high purity.

Spectroscopic and electrochemical properties

The benzothiazole-based cyanine dyes studied display several specific properties that are similar to the properties of other monomethine dyes reported in literature.^{16–19} They have a common structural feature, namely, they possess an electron-donor and electron-acceptor moieties located on the opposite sides of the monomethine bond.

Figure 1 shows the illustrative electronic absorption spectra recorded for a selected monomethine dye in DMF and acetonitrile as a solvent, respectively.

TABLE I
Steady State Spectroscopic Properties of the Mono- and Heterobicationic Monomethine Dyes Under the Study

Dye	Solvent	λ_{ab} (nm)	ϵ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	λ_{fl} (nm)	Stokes shift (cm^{-1})
D0	DMF	510	12,500	556	2829
	Acetonitrile	507	5,200	550	2775
D1	DMF	511	21,700	557	1616
	Acetonitrile	507	45,000	551	1575
D2	DMF	535	28,800	607	2393
	Acetonitrile	530	40,100	603	2108
D3	DMF	510	20,900	581	2396
	Acetonitrile	507	40,800	579	2453

Table I collects the values of the absorption maximum positions, molar absorption coefficients, the fluorescence maximum positions, and Stokes shifts for all dyes measured in DMF and MeCN. The data for monocationic monomethine cyanine dye *N*-methyl-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium iodide are presented as well for comparison.

The electronic absorption spectra of all the dyes display a broad band with a maximum at about 510 nm for D1 and D3 and at 530 nm for D2, and a molar absorption coefficient is varying from 21,000 $\text{dm}^3 \text{ mol}^{-1}$ to 45,000 $\text{dm}^3 \text{ mol}^{-1}$ depending on the nature of the solvent.

It has also been observed (Fig. 2) that the precursor dye, e.g., monocationic dye methyl-2-[*N*-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium iodide (D0) and its dicationic equivalents (except D2) show the absorption band with the maximum located at about 510 nm in DMF. The mechanism causing the red shift observed for dicationic dye (D2) is not clear.

The difference in energy between the absorbed and emitted radiation is known as the Stokes shift.²⁰ The Stokes shift values obtained for novel heterobicationic monomethine dyes tested are shown in Table I. The highest value of Stokes shift in both solvents ($> 2000 \text{ cm}^{-1}$) is observed for dyes D0, D2, and D3, and the lowest about (1600 cm^{-1}) for D1.

It is well known that the main prerequisite for a photoinduced electron transfer (PET) reaction (vital for free radical formation) is that the thermodynamic driving force for the electron transfer reaction between an excited state of a dye and an electron donor should have a negative value. The free energy of activation for the PET (ΔG_{el}) process can be easily estimated on the basis of the Rehm-Weller²¹ eq. (1) as follows:

$$\Delta G_{el} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - E_{00} - Ze^2/\epsilon a, \quad (1)$$

where: $E_{ox}(D/D^{\bullet+})$ is the oxidation potential of the electron donor, $E_{red}(A^{\bullet-}/A)$ is the reduction poten-

tial of the electron acceptor, E_{00} is the energy of the excited state involved in electron transfer reaction, and $Ze^2/\epsilon a$ is the Coulombic energy associated with the process. Because 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 cyclic voltammetry measurements (Table II). The electrochemical reduction of the dyes is reversible. However, the oxidation of alkyl triphenyl borate is dissociative and this, in turn, causes the electrochemical process to be irreversible.

The thermodynamically meaningful oxidation potential can be established using an indirect, kinetic method described by Murphy and Schuster.²² Oxidation potentials measured electrochemically and kinetically differ by about 0.3 V.

Therefore, the obtained electrochemical values for both components of photoredox pairs may have only approximate thermodynamic meaning, yet allow us to estimate roughly the free energy of activation (ΔG_{el}) for the PET process.

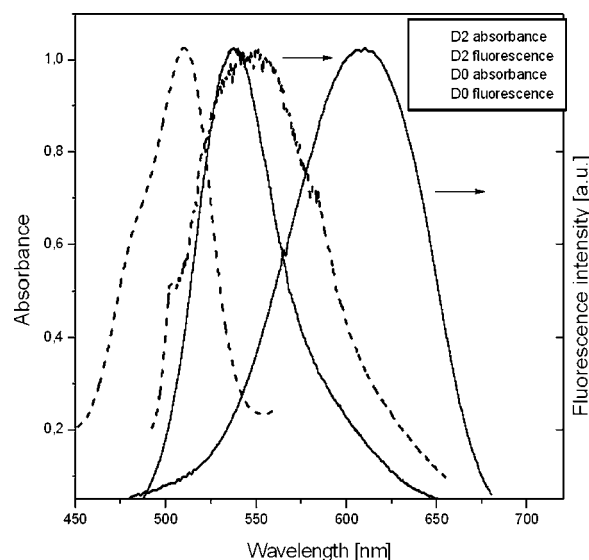


Figure 2 Absorption and emission spectra of both D2 (full line) and D0 (dotted line) in DMF.

TABLE II
Reduction and Oxidation Potential Data, Energy of the Excited State Involved in Electron Transfer Reaction (E_{00}) and Calculated Free Energies (ΔG_{el}) of the Electron Transfer Reaction Between the Singlet Excited State of the Tested Dyes and Electron Donor

Dye	E_{00}^a (eV)	E_{00}^b (eV)	E_{red} (V)	ΔG_{el}^a (kJ/mol)	ΔG_{el}^b (kJ/mol)
D1	2.352	2.064	-0.98	-20.45	7.33
D2	2.145	2.032	-0.90	-8.20	2.70
D3	2.335	2.042	-0.77	-39.08	-10.81

The oxidation potential of tetramethylammonium *n*-butyltriphenylborate is equal to 1.16 V.

^a Measured in DMF as a solvent.

^b Measured in acetonitrile as a solvent.

The measured values of the dyes reduction potentials, the electron donor (*n*-butyltriphenylborate anion) oxidation potential ($E_{ox} = 1.16$ V), and the singlet state energy of the dyes, allow us to calculate the free energy change for the photoinduced intermolecular electron transfer process with the Rehm-Weller equation.²¹ The estimated data are summarized in Table II.

The values of ΔG_{el} for the tested photoinitiating systems oscillate in the range from -39.08 to 7.33 kJ/mol. The calculations clearly show that in monomers of various polarities for the tested photoredox pairs, the electron transfer process is thermodynamically allowed. This, in turn, allows us to predict that the tested dyes in combination with borate anion should effectively generate free radicals that can start polymerization of vinyl monomers.

Photoinitiating abilities

Three photoredox pairs, consisting of the heterobicationic monomethine dyes (acting as electron acceptors) and *n*-butyltriphenylborate anion (acting as electron donor) were tested as photoinitiating systems for the polymerization of multifunctional vinyl monomers. Since the maximum of the absorption band of the tested dyes is located at about 510 and 530 nm for the photoinitiation of polymerization, the emission of an argon-ion laser emitting at 488 and 514 nm (Omnichrome) was used. The kinetic curves obtained for the polymerization of TMPTA-MP (9 : 1) mixture employing monomethine cyanine borate salts (DB2) as photoinitiators, under irradiation with a visible light, are shown in Figure 3.

The relative rates of photoinitiated polymerization measured for all tested photoredox pairs are collected in Table III.

It is apparent from the inspection of the initial rates of polymerization that the photoinitiation efficiency of the tested photoinitiators depends strongly on their structure.

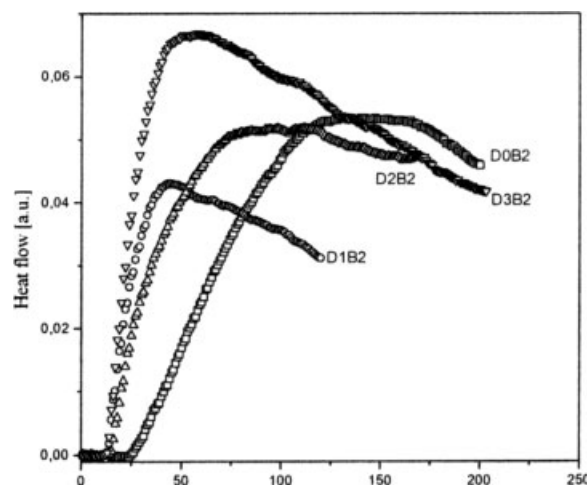


Figure 3 The family of kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of the TMPTA/MP (9/1) mixture initiated by the tested borate salts. The dye concentration was $7.5 \times 10^{-4} M$, $I_a = 64$ mW/cm². The applied dyes possessed various chromophores and identical borate anions.

Generally, the initiators that couple two electron donors in one molecule of a photoinitiating dye exhibit significantly higher rate of heat evolution (the slope of the linear part of the kinetic curve at its initial time) in comparison to the model mono-cationic monomethine dye (D0). However, these initiators exhibit lower photoinitiation in comparison to the photoinitiation ability observed for their hemicyanine analogs.⁹

From the data obtained during the measurements, it was deduced that the conversion of monomer ranges from 8.3% to 11.4%, whereas the quantum yields of photopolymerization vary between 8.3 and 33 (Table III). The photoinitiating systems containing two borate anions in one molecule show much better photoinitiation ability with quantum yield of polymerization being three times (D1B2), two times (D2B2), and four times (D3B2) higher in comparison to the classical photoinitiating system, in which the concentration of electron donor is equal to the concentration of monomethine cyanine cation (D0B2). It was also found that the degree of monomer conversion depends on the structure of the dye.

TABLE III
The Rate of Free Radical Polymerization (R_p) of TMPTA for Tested Photoinitiators

Dye	R_p ($\mu\text{mol/s}$)	Monomer conversion (%)	Φ_{polym}
D0B2	1.96	8.43	8.31
D1B2	6.94	8.96	29.45
D2B2	3.60	8.32	15.28
D3B2	7.32	11.32	33.06

The initiation of polymerization via photoinduced intermolecular electron transfer process involves many steps. Those include PET from an electron donor to an excited state of a dye or from an excited electron donor to the ground state of an electron acceptor followed by secondary reactions yielding a neutral radical initiating polymerization.

The steps determining the reaction rate of the free radical initiated polymerization via intermolecular electron transfer process (PET) are dependent on the nature of the dye and the electron donor (or acceptor). In the case of alkyltriphenylborate anion acting as an electron donor, the alkyl radical is formed as a result of rapid cleavage of the alkyl-boron bond within the boranyl radical produced after the electron transfer.^{23,24} According to Chatterjee et al., studies on symmetrical cyanine borate initiators in nonpolar or medium polarity solvents, one can treat cyanine cation and borate anion as an ion pair. However, our studies on the influence of the borate anion concentration on the rate of photoinitiated polymerization show a distinct increase in the rate of polymerization as the concentration of borate anion increases for an identical monomer-dye formulation.^{5,6,11} This finding suggests that at the concentration of borate anion equal to the concentration of cyanine cation, only a part of the photoredox pairs exists as ion pairs. Since the electron transfer in cyanine dyes occurs in their singlet state, the existence of a cyanine cation and borate anion as ion pair is the basic prerequisite for the effective electron transfer. It is obvious that the additional amount of borate anion in the polymerizing composition should shift the equilibrium between free ions-ion pairs to a higher ion pair concentration and cause an increase in the photoinitiation efficiency of the dye-borate salt. It seems to be obvious that an artificial increase of the number of electron donor moieties within one molecule achieved by the coupling of the second borate anion to the dye molecule should improve the photoinitiating ability. Our experiments confirm this notion. From the inspection of the data presented in Figure 4 it is clear that the rate of polymerization initiated by monomethine cyanine-borate pairs increases when the concentration of coinitiator increases. This finding suggests that one can treat heterobicationic monomethine cyanine cation and borate anion in non polar or medium polarity solvents as an ion pair. However, a more precise study on the influence of borate concentration on the rate of photoinitiated polymerization indicates that under conditions of the polymerizing formulation (medium viscosity and medium polarity), one observes a distinct increase in the rate of photopolymerization as the concentration of borate anion increases. Figure 4 illustrates this relationship.

On the basis of this experiment, it appears that under the experimental conditions, only a part of

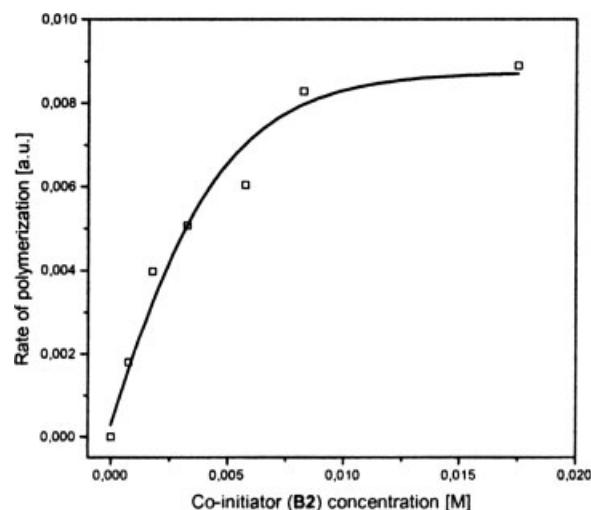


Figure 4 Dependence of the rate of photoinitiated polymerization on concentration of the electron donor (B2). The initiating dye-borate (D2B2) concentration was $7.5 \times 10^{-4}M$.

photoredox pairs exist as ion pair. Detailed analysis of the data presented in Figure 4 indicates that for D2B2 initiating system only about 18% of photoredox couples exist as ion pairs. At concentration of the dye equal to $7.5 \times 10^{-4}M$, these values give an equilibrium constant of $\sim 2.8 \times 10^{-3}M$ for D2B2.

The supporting experiments that can clarify the presence of both dissociated and undissociated forms of the tested photoinitiators may come from the fluorescence-quenching experiments. The absorption spectra measurements show that the exchange of iodide anion on borate has no effect on the electronic absorption spectra. Thus, if there is a certain contribution of a ground state equilibrium between the monomethine cyanine cation and the borate anion leading to the formation of a nonfluorescing ion pair, then the evidence for the ground state ion pair formation may come from fluorescence intensity quenching measurements. To estimate the contribution of the quenching from the ground state ion pair (static quenching, K_S) and diffusion controlled quenching (dynamic quenching, $K_D = k_q \times \tau^0$) the fluorescence quenching data were analyzed by combining both effects described by equation^{24,25}:

$$\frac{I_f^0}{I_f} = (1 + K_D[Q]) \times (1 + K_S[Q]), \quad (2)$$

where:

$$K_S = \frac{[D^+ \dots B2^-]}{[D^+] \times [B2^-]}. \quad (3)$$

The result of such treatment allows us to separate the two types of quenching and calculating the K_S value. The steady-state fluorescence quenching data

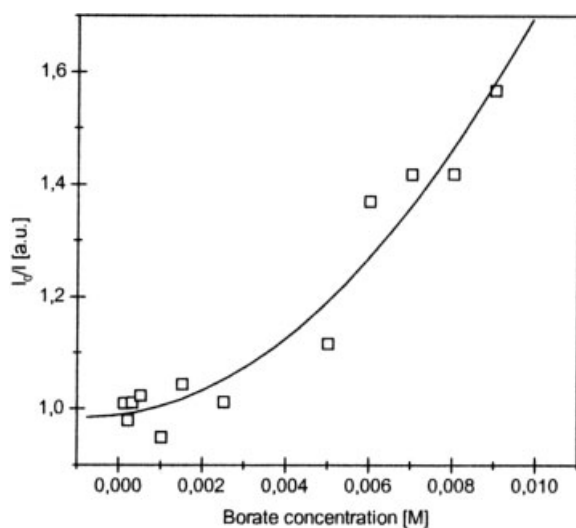


Figure 5 Stern–Volmer plot for quenching of fluorescence of D2B2 by Tetramethylammonium *n*-butyltriphenylborate (B2) in ethyl acetate.

for D2B2 in the presence of *n*-butyltriphenylborate (B2) (see Fig. 5) leads to the conclusion that an upward curvature for the high concentration of quenchers indicates the existence of both forms of hemicyanine borates, e.g., the form of the free ions and the form of the ion pairs.

Figure 5 shows that the data recorded for the quenching measurements obtained for D2B2 do not follow a linear Stern–Volmer relationship, reflected by a significant curvature upward for the high concentration of the electron donor. The lack of the linear relationship for the photoredox pairs indicates that the quenching of fluorescence occurs by both dynamic and static mechanisms. Thus, we infer that the dye cation and the electron donor anion form a ground state complex, namely, a ground state ion pair. In that case, K_S can be identified by the association constant of the complex. All the discussed properties show that the fraction of monomethine cyanine borate present as ion pairs in ethyl acetate significantly varied within the range of borate concentration studied in the described experiments. It is noteworthy that only the unassociated monomethine cyanine cations fluoresce, there is no (or very little) fluorescence from the cyanine borate ion pair.^{23,24} One can calculate the dissociation constant of these pairs from the Stern–Volmer relationship obtained for D2B2 pairs [(eqs. (2) and (3)]. Assuming that for a low concentration of borate anion only dynamic quenching occurs, from the linear relationship observed in a low concentration region, one can estimate the K_D value. For D2B2 photoredox pair, this parameter is equal to $48.96M^{-1}$. Plugging this value into eq. (3) gives K_S equal to $127.42M^{-1}$. This, in turn, allows calculation of the degree of dissociation equal to 84.7% for D2B2. Finally, the dissociation

constant is calculated to be $K = 3.62 \times 10^{-3}M$ for D2B2. The analysis presented clearly shows that the bicationic monomethine cyanine borate (D2B2) probably exists mostly as a separated ion pair. The artificial increase of the electron donor moieties in close proximity to the chromophore causes both a decrease in the dissociation constant and a sharp improvement of the photoinitiating abilities of the heterobicationic monomethine cyanine borates.

It is worth noting that the values of dissociation constants obtained for the relationships between the rate of photoinitiated polymerization versus borate anion concentration and from the fluorescence quenching experiments are in very good agreement. This supports the notion of the photoinitiating pair existing in both dissociated and undissociated forms.

Another interesting feature of the tested dyes is worthy of attention. Analyzing the data summarized in Table III, one can find that the type of substituent present in the pyridine moiety attached to the benzothiazole ring causes a significant variation in the photoinitiating abilities of the tested two-cationic cyanine borates. Asymmetric cyanine dyes usually consist of an electron donating moiety, and a heterocyclic or polyaromatic moiety, which can function as an electron-deficient acceptor. Furthermore, donor and acceptor can be in direct electronic conjugation via a mono- or polymethine π -system and the acceptor moiety itself can be charged or uncharged.⁶ We tested asymmetric cyanine dyes with electron donor–acceptor moieties on the opposite sides of the monomethine bond with additionally bonded pyridinium ring possessing different substituents in *para* position. On the basis of our experiments, it appears that the initiator possessing the dimethylamino group in *para* position of the pyridinium moiety (D3B2), initiates the free radical polymerization with the highest rate. For the cationic photoredox systems, the photoinitiating ability of tested dyes decreases in order: D3B2 > D1B2 > D2B2. This suggests that the presence of $-N(CH_3)_2$ group in pyridinium moiety causes an enhancement of the electron donor concentration (borate anion) in the proximity to the absorbing dye.

The best photoinitiation efficiency has been observed for D3B2 photoredox pair as shown in Figure 3. Its sensitivity is lower than the sensitivity of a RBAX-based initiation system (a triplet state photoinitiator) as shown in Figure 6.

The data presented in Figure 6 clearly show that the polymerization photoinitiation ability of D3B2 is lower than that observed for RBAX–B2 couple. It is also apparent that heterobicationic monomethine cyanine borate (D3B2) initiates free radical polymerization with the rate significant lower than RBAX–NPG initiating photoredox pair (where NPG is *N*-phenylglycine) in contrast to heterobicationic hemicyanine borate described in our earlier paper.⁹

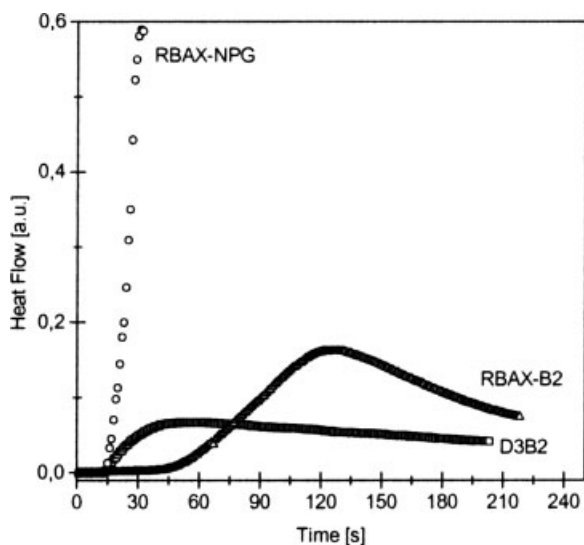


Figure 6 Comparison between the photoinitiation ability of D3B2 ($7.5 \times 10^{-4}M$) and RBAX ($7.5 \times 10^{-4}M$)-*N*-phenylglycine ($1 \times 10^{-2}M$), RBAX ($7.5 \times 10^{-4}M$)-B2 ($c_2 = 7.5 \times 10^{-4}M$) photoinitiation systems; $I_a = 64 \text{ mW/cm}^2$.

However, it should be emphasized that such high efficiency for RBAX–NPG pair is observed when the electron donor concentration is as high as $1 \times 10^{-2}M$, that is, when the electron donor concentration is about one order of magnitude higher than that present in D3B2 photoredox pair.

The concentration of the photoinitiator itself also plays a key role in the photopolymerization. In a conventional UV–vis photopolymerization R_p increases with the increase of concentration of the initiator up to a certain level, than it decreases. This behavior is attributed to the “internal filter effect.”

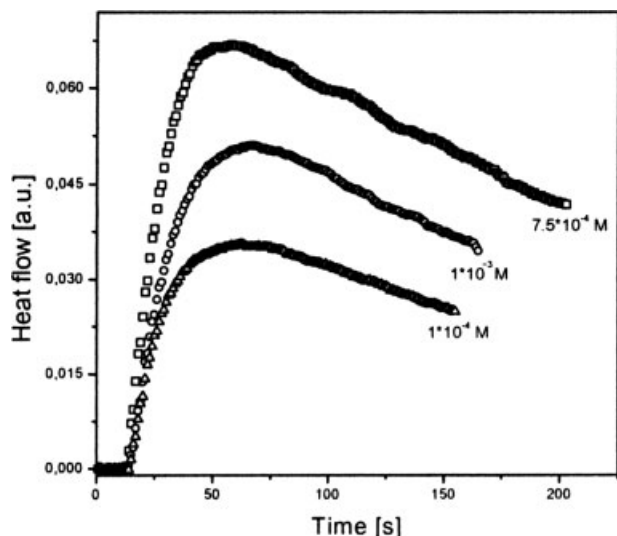


Figure 7 The family of kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of the TMPTA/MP (9/1) mixture, initiated by D3B2 at its different concentration, $I_a = 64 \text{ mW/cm}^2$.

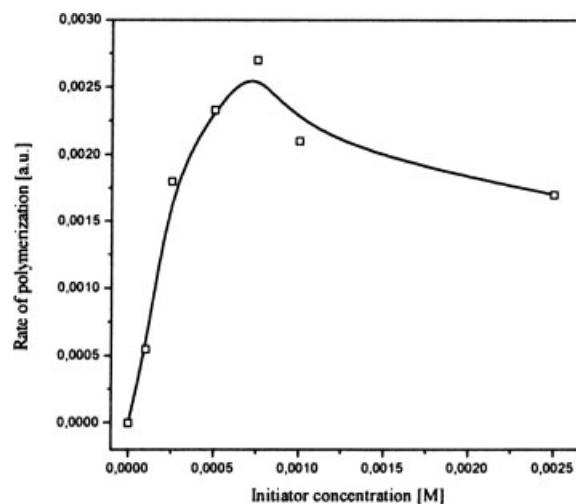


Figure 8 Rate of polymerization versus (D3B2) photoinitiator concentration.

This becomes more significant for photoinitiators with high molar absorption coefficient.^{5,6,25} The kinetic curves recorded for photoinitiated polymerization at different initiator concentrations are presented in Figure 7.

Data in Figure 7 show that the time needed to reach the curve maximum decreases when the initiator (D3B2) concentration increases. The observed property is related to the rate of heat evolution in the initial time of polymerization (slope of the linear part of kinetic curve).

Figure 8 presents the relationship between the initial rate of polymerization (the slope of the linear part of the kinetic curve at its initial time) and the concentration of D3B2 photoinitiator.

It is evident that as the photoinitiator concentration increases, the initial rate of polymerization increases and reaches a maximum followed by continuous mild decrease. The highest rates of polymerization (for 3-mm thick sample; Fig. 8) were achieved at an initiator concentration of about $7.5 \times 10^{-4}M$ for the tested photoinitiators with two electron donors in one molecule. The reduction of the photoinitiated polymerization rate at high initiator concentration can be easily understood when taking into account the decrease of the penetration depth of the laser beam being a result of the so-called internal filter effect.²⁵

CONCLUSIONS

The spectroscopic properties of bicationic monomethine dyes tested are similar to that of their monocationic analogs. Therefore, these compounds paired with organic borate salts can act as an absorber of the light in visible-light photoinitiators of vinyl monomer polymerization. The introduction to the

monocationic monomethine dye additional organic cation, for example, pyridinium moiety artificially increased concentration of the *n*-butyltriphenylborate anion (acting as an electron donor) in proximity to the electron accepting excited cyanine dye chromophore. The artificial increase of an electron donor concentration in cyanine chromophore proximity causes an enhancement of the photoinitiating abilities of the bicationic photoredox pair in comparison to their monocationic analog.

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