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The synthesis, spectroscopic and electrochemical properties, and application of new dyeing photoinitiator systems for acrylate monomers polymerization

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ABSTRACT

New symmetrical bicationic polymethine dyes were synthesized and their spectroscopic and electrochemical properties were described. The bichromophoric dyes (benzothiazole, benzoxazole, indolinium derivatives) were investigated as sensitizers in the free radical photopolymerization initiated by their borate salts. The obtained kinetic results shown that bicationic polymethine dyes as the organoborate salts are much efficient photoinitiating systems of acrylate monomers polymerization than monocationic parent dyes. The rate of polymerization depends on ΔG_{ET} of electron transfer from borate anion to the excited singlet state of bicationic polymethine dye. The relationship between the rate of polymerization and the free energy of electron transfer process shows the dependence predicted by the classical theory of electron transfer.

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1. Introduction

The development of the selective bond-breaking reactions that are triggered by the absorption of a photon is a fundamental goal of photochemistry. These reactions have also many practical applications. For example, photolithographic techniques create nanometer scale images on a surface by selectively breaking bonds in a photoinitiator molecule, creating free radicals or cations [1].

In recent years photoinitiators operating in the visible light region were developed which is mostly due to a fact that this light is cheap, safe and possesses higher penetration in comparison with UV light [2].

Photoinduced free radical polymerization of multifunctional monomers produces highly crosslinked polymers with high thermal stability, mechanical strength and resistance to organic solvents. These polymers have many industrial applications as coatings for flooring and furniture, dental restorative materials, optical fiber coating, hard and soft contact lenses and photolithography [3]. The photopolymerization can be initiated either by direct UV photolysis of a precursor which provides free radicals by bond decomposition or by panchromatic sensitization which requires the presence of suitable dye as a primary absorber of a light. In the last case, the formation of free radicals often occurs *via* photoinduced electron transfer process (PET) from electron donor molecule to the excited state of an electron acceptor.

Photoinduced electron transfer (PET) processes were attracted the interest of a generation of chemists. Previous works were elucidated many of the factors that control the rates of these reactions [4,5]. Therefore, many current efforts are aimed at identifying and demonstrating useful applications of these processes. Applications include solar energy conversion, photolithography, molecular electronics, the design of novel synthetic transformations and mentioned above the photoinitiation of free radical polymerization of acrylate monomers [6–9]. The initiation of the free radical polymerization in the visible light region needs the presence of the two-component photoinitiating systems acting *via* electron transfer process. As a result of electron transfer process a high-energy radical and radical ion pairs were formed. Such radical pairs are interesting because they are capable of undergoing bond-forming or bond-fragmentation reactions that are difficult to carry out using conventional techniques. The example, of such ion pair was indocarbocyanine dyes alkyltriphenylborate salts studied by Schuster and co-workers [10,11]. The irradiation of ion pair with visible light leads to the one-electron oxidation of the borate anion and carbon-boron bond cleavage what results in free alkyl radicals formation. These compounds were the first, color-tunable, operating in the visible region, commercial photoinitiators. Analysis of chemical, physical and spectral properties of these salts shows that, in nonpolar solvents, they form ion pairs.

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Under this condition irradiation of cyanine dye with visible light causes in efficient sensitization of the borate and the generation of free alkyl radicals. The formation of ion pairs guarantees an efficient electron transfer between borate anion and excited dye molecule in its short-lived singlet excited state. However, it was soon discovered that the even small amount of polar solvent might sharply change a degree of the tight-ion-pair formation [12]. In polymerizing mixture (acrylates, medium polarity solvent), the photoinitiating photoredox pair exists as a tight-pair and solvent separated ions. Since an efficient electron transfer between singlet excited state of cyanine cation and borate anion is efficient only between paried components of photoredox couple, it is obvious that a dissociation of ion pair causes sharp decrease in efficiency of electron transfer process. This finally decreases the rate of polymerization. Therefore, the improvement of a photoinitiating efficiency of such photoinitiating systems might be achieved by few methods. First, was an increase of an electron donor concentration in close proximity to an excited singlet state of polymethine dye moiety. Traditionally, such approach was possible to achieve by attaching to an absorbing chromophore an additional organic cation that could form an ion pair with borate anion [13]. Second method was the addition to the polymerizing formulation a third component that can participate in consecutive reaction yielding one more radical [14]. The third possibility was the application of bicationic dyes composed of two identical chromophores covalently linked to each other.

In this paper, reactivity of several photoinitiating systems composed of bicationic polymethine dye acting as light absorber, *n*-butyltriphenylborate anion acting as an electron donor were presented.

2. Experimental

2.1. Materials

2-Metylbenzothiazole, 2-methylbezoksxazole, 1,3,3-trimethylindolenine, 1,5-diiodopentane, 1,10-diiododecane, triethyl orthoformate and solvents were obtained from Aldrich Chemical Co. *n*-Butyltriphenylborate tetramethylammonium salt (**B2**) was used as a co-initiator and synthesized based on the method described by Damico [15]. 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. Measurements

(i) All final products were identified by ^{1}H NMR spectroscopy and elemental analysis.

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

The elemental analysis was made with a Vario MACRO 11.45-0000 Elementar Analysesysteme GmbH (Germany), operating with a software VARIOEL 5.14.4.22.

Melting points (uncorrected) were determined on the Boëthius apparatus.

(ii) Spectroscopic measurements: UV/vis absorption spectra: obtained using Shimadzu UV–vis Multispec – 1500 Spectrophotometer, and steady-state fluorescence: using a Hitachi F-4500 Spectrofluorimeter.

(iii) The reduction and oxidation potentials of dyes and *n*-butyltriphenylborate salt were measured by cyclic voltammetry. An Electroanalitical MTM System model EA9C-4z (Cracow, Poland), equipped with a small-volume cell was used for the measurements. A 1 mm platinum disc electrode was used 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 degassed by bubbling argon gas through the solution. The potential was swept from −1.6 to 1.6 V with the sweep rate of 500 mV/s to record the current–voltage curve.

(iv) 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. 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 photoinitiators concentration used in experiments was 1×10^{-3} M. The monomer was used without purification. As a reference sample, a polymerizing mixture containing polymethine perchlorates (dye without a co-initiator) was used. The polymerizing mixture was not deaerated. In order to reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish–Troomsdorf effect and radicals trapping effect, the initial rates of polymerization were taken into account for further consideration. The initial rates of polymerization were the slopes of the lines drawn on the flow of heat versus time curve at the initial time of polymerization.

2.3. Synthesis

The synthetic approaches that were applied are outlined below and are based on the condensation reaction of 1,5-bis-[*N*,*N*′-(2-methylbenzothiazolium)pentane diiodide, 1,5-bis-[*N*,*N*′-(2-methylbenzoxazolium)pentane diiodide, 1,5-bis-[*N*,*N*′-(2,3,3-trimethylindoleninum)pentane diiodide, 1,10-bis-[*N*,*N*′-(2-methylbenzothiazolium)-decane diiodide, 1,10-bis-[*N*,*N*′-(2-methylbenzoxazolium)decane diiodide, 1,10-bis-[*N*,*N*′-(2,3,3-trimethylindoleninum)decane diiodide (**S5**, **S10**, **O5**, **O10**, **I5**, **I10**) with a quadruple excess of triethyl orthoformate.

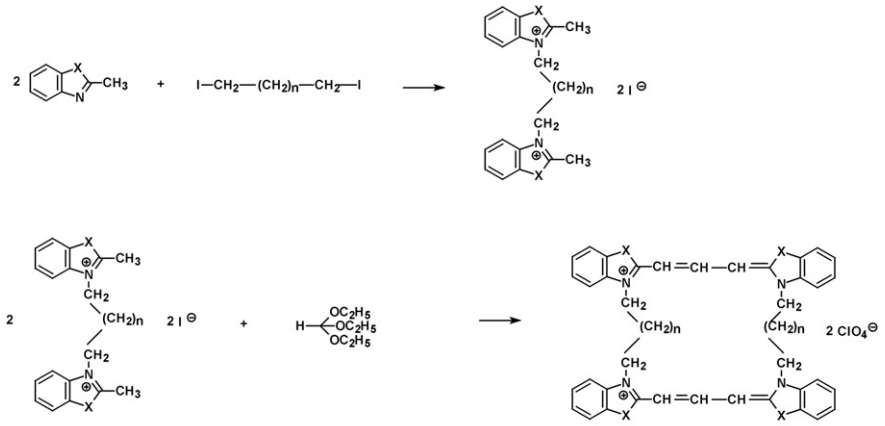
A general route for the synthesis of novel homobicationic polymethine dyes is shown in Scheme 1.

As it is shown in Scheme 1 the synthesis of the bichromphoric polymethine dyes undergos *via* two steps:

- The quaternization reaction of 2-methylbenzothiazole, 2-methylbenzoxazole and 1,3,3-trimethylindolenine with 1,5-diiodopentane and 1,10-diiododecane yielding corresponding diheterocyclic salts (**S5**, **S10**, **O5**, **O10**, **I5**, **I10**).
- The condensation reaction of diheterocyclic salts (**S5**, **S10**, **O5**, **O10**, **I5**, **I10**) with triethyl orthoformate resulting in the formation of the corresponding bichromophoric polymethine dyes (**TS5**, **TS10**, **TO5**, **TO10**, **TI5**, **TI10**).

2.3.1. General procedure for synthesis of quaternary salts of heterocycles (*S5*, *S10*, *O5*, *O10*, *I5*, *I10*)

A mixture of 0.011 mol of corresponding heterocycle and 0.005 mol α,ω- dihalogenalkane in 5 ml of dioxane was boiled for 6 h. Obtained salt was precipitated by diethyl ether and filtered off.



where X is S, O or $C(CH_3)_2$, respectively and n = 3 or 8

Scheme 1.

Precipitate was washed with 10 ml of isopropanol and 10 mlof ether. Quaternary salts were used without further purificaltion [16].

*2.3.2. General procedure for synthesis of bichromophoric polymethine dyes (**TS5**, **TS10**, **TO5**, **TO10**, **TI5**, **TI10**)*

A mixture of 0.001 mol of quaternary salt, 0.002 mol of triethyl orthoformate in 3 ml of acetic anhydride was boiled for 10 min. Obtained dye was precipitated by diethyl ether and filtered off. Dye obtained was washed with alcohol and crystallized from ethanol [16].

3. Results and discussion

3.1. Molecular design and synthetic procedures

Six possessing two identical chromophores polymethine dyes were synthesized by the condensation reaction of appropriate diheterocyclic diiodides with triethyl orthoformate (Scheme 1). In the first step a corresponding heterocycle (2-methylbenzothiazole, 2-methylbenzoxazole, 1,3,3-trimethylindolenine) was boiled in dioxane with α,ω-dihalogenalkane. Then triethyl orthoformate was added to the obtained in the first reaction quaternary salts and the mixture was boiled in acetic anhydride. Details of the synthetic procedures and structures of tested dyes (see Scheme 1) are described in Section 2. The dyes were purified by crystallization from ethanol and flash chromatograpy. The structure and purity of the prepared compounds were confirmed by ^{1}H NMR spectroscopy, elemental analysis and thin layer chromatography. The data of the structural analysis of all dyes are given in Table 1.

The spectra obtained were the evidence that the reaction products were of the desired structures. The purity of synthesized compounds was determined using thin layer chromatography and by measuring of the melting points. The purity of the dyes was as it is required for spectroscopic studies (99.5%–99.9%).

3.2. The spectroscopic properties of polymethine dyes

The spectroscopic properties of compounds under the study are listed in Table 2.

The symmetrical bichromophoric polymethine dyes such as thiacarbocyanines (**TS**), oxacarbocyanines (**TO**) and indocarbocyanine dyes (**TI**) are characterized by an intense absorption band in the orange spectral region, with the more intense peaks ($\varepsilon_{max} \approx 4 \times 10^4$ dm^{3}mol^{-1}cm^{-1}) located for thiacarbocyanines in the range between 560–570 nm and the second, less intense, shifted to the blue of about 6000 cm^{-1}. The absorption bands of oxacarbocyanines and indocarbocyanines are hypsochromic shifted about 70–80 nm and about 20 nm in comparison with the absorption bands of benzothiazole derivative, respectively. The two bands are assigned to the 0,0 and 0,1 vibronic transitions within the first excited state of the dye. The position of absorption band λ_{max} depends on the type of heterocyclic ring (Fig. 1), but essentially does not depend on the number of chromophores and on the number of the carbon atoms in alkyl chain linked both chromophores and weakly depends on the solvent polarity (Fig. 2, Table 2).

The fluorescence spectra of the dyes tested are roughly a mirror image of the absorption spectrum. The typical room temperature normalized absorption and emission spectra for indocarbocyanine diperchlorates in tetrahydrofuran as a solvent are shown in Fig. 3.

The fluorescence emission in *N*,*N*-dimethylformamide and tetrahydrofuran solution exhibits a maximum which is red-shifted in comparison to the absorption maximum by less than 1200 cm^{-1}. Since the Stockes shift is not large and the half width of the absorption and emission bands are almost the same, therefore one can conclude that the geometry of the dye molecule is almost the same in its ground and excited states.

3.3. Efficiency of polymethine dye/borate salt as photoinitiating systems in radical polymerization

The photoinitiating abilities of several combinations of cyanine dye/borate salt in the polymerization of TMPTA were measured. Six

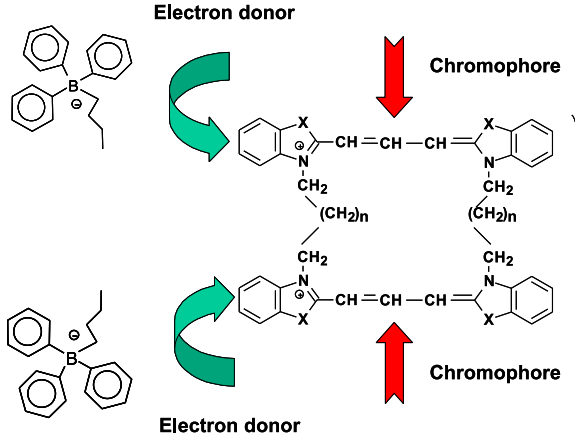


Chart 1.

Table 1
Characteristics of the homobichromophoric carbocyanine dyes tested.

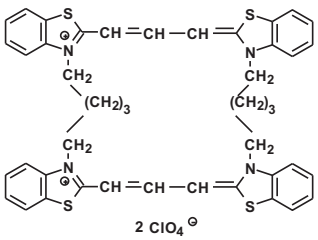
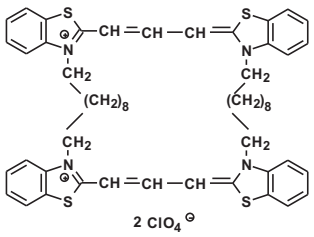
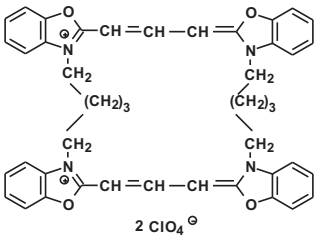
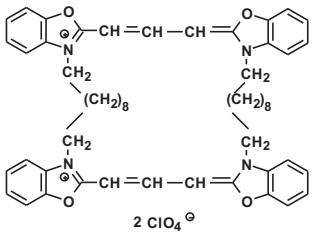
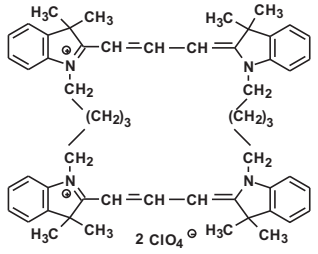
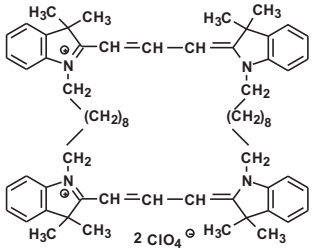
Dye	Empirical formula Molecular mass [g/mol] m.p. [°C]	^{1}H NMR (DMSO) δ (ppm)
 **TS5**	$C_{44}H_{42}S_4N_4O_8Cl_2$ 953 136	1.604–1.633 (m, 6H, $-CH_2-$); 1.787–1.897 (m, 6H, $-CH_2-$); 3.959–4.022 (t, 2H, N$-CH_2$), 4.329 (m, 4H, $N^+(CH_2)$); 4.703 (m, 2H, N$-CH_2$); 6.633 (d, 4H, $-CH=$); 7.274–7.454 (m, 4H, Ar); 7.516–7.589 (t, 2H, $-CH=$); 7.732–7.846 (m, 8H, Ar); 7.912–8.018 (t, 2H Ar); 8.274–8.406 (d, 2H, Ar)
 **TS10**	$C_{54}H_{62}S_4N_4O_8Cl_2$ 1093 73	1.598–1.855 (m, 32H, $-CH_2-$); 4.188–4.316 (t, 4H, N$-CH_2$), 4.522–4.719 (m, 4H, N^+CH_2)); 6.551–6.617 (d, 4H, $-CH=$); 7.379–7.452 (t, 4H, Ar); 7.533–7.606 (t, 2H Ar); 7.723–7.775 (d, 2H, $-CH=$); 7.833–7.921 (m, 2H, Ar), 8.112–8.178 t, 4H, Ar); 8.288–8.324 (d, 2H, Ar); 8.405–8.441 (d, 2H, Ar); 8.559–8.632 (t, 2H, Ar)
 **TO5**	$C_{44}H_{42}O_{12}N_4Cl_2$ 889 95	1.635–1.814 (m, 6H, $-CH_2-$); 1.944–2.070 (m, 6H, $-CH_2-$); 3.955–3984 (m, 4H, N$-CH_2$); 4.189 (m, 4H, $N^+(CH_2)$); 5.990–6123 (m, 2H, $-CH=$); 7.088–7.178 (m, 2H, $-CH=$); 7.392–7.434 (m, 8H, Ar); 7.68–7.770 (m, 8H, Ar); 8.266–8.314 (m, 2H, $-CH=$)
 **TO10**	$C_{54}H_{62}O_{12}N_4Cl_2$ 1029 76	1.497–1.644 (m, 32H, $-CH_2-$); 3.592–3.697 (m, 4H, N$-CH_2$); 3.926–4.182 (m, 4H, $N^+(CH_2)$); 6.039–6.107 (d, 4H, -CH=); 6.779–6.861 (t, 4H, Ar); 6.861–6.951 (d, 4H, Ar); 7.052–7.195 (m, 4H, Ar); 7.394–7.456 (m, 4H, Ar); 7.667–7.770 (t, 2H, $-CH=$)
 **TI5**	$C_{46}H_{66}N_4O_8Cl_2$ 873 104	1.183–1.212 (t, 6H, CH_2); 1.513 (s, 12H, CH_3); 1.666 (s, 12H, CH_3); 1.897 (m, 6H, $-CH_2$); 3.765–3.846 (T, 4H, N$-CH_2-$); 4.432–4.571 (t, 4H, N^+-CH_2-); 6.406–6.469 (d, 4H, $-CH=$); 6.531–6.710 (m, 2H, Ar); 6.992–7.131 (m, 4H, Ar); 7.293–7.509 (t, 4H, Ar); 7.816–7.937 (m, 2H, Ar); 8.124–8.181 (t, 2H, $-CH=$); 8.304 (d, 2H, Ar)

Table 1 (*continued*)

Dye	Empirical formula Molecular mass [g/mol] m.p. [°C]	^{1}H NMR (DMSO) δ (ppm)
 **TI10**	$C_{56}H_{86}N_4O_4Cl_2$ 1013 83	1.221 (t, 24H, $-CH_2$); 1.512 (s, 12H, CH_3); 1.675 (s, 12H, CH_3); 3.794 (d, 4H, N$-CH_2$); 4.09 (t, 4H, N^+CH_2); 6.436–6.502 (t, 4H, $-CH=$); 7.026–7.110 (m, 2H, Ar); 7.290–7.340 (4H, Ar); 7.425–7.502 (d, 4H Ar); 7.610–7.632 (d, 4H, Ar); 7.803–7.872 (t, 2H, $-CH=$); 8.145–8.176 (t, 2H, Ar); 8.252–8.289 (t, 2H, Ar)

bichromophoric polymethine dyes as *n*-butyltriphenylborate salts were used as two-component photoinitiating systems. The structure of the photoinitiators tested is presented in Chart 1.

Kinetic studies were performed with irradiation at 514 nm e.g. at the wavelength where the light is absorbed by dye cation.

It is necessarily to emphasize that, in order to transfer the bicationic polymethine dyes into efficient photoinitiating system, the exchange of an anion type from perchlorate on borate anion was needed.

The kinetic curves obtained for the polymerization of TMPTA/MP (9:1) mixture initiated by selected polymethine dyes borate salts, under irradiation with a visible light (514 nm) are shown in Fig. 4 for illustration.

Fig. 5 presents the kinetic curves observed for free radical polymerization of TMPTA/MP mixture initiated by both symmetrical mono- and bichromophoric polymethine borates for comparison.

The relative rates of photoinitiated polymerization measured for all the tested photoinitiators are collected in Table 3.

It is apparent from the inspection of the initial rates of polymerization that the efficiency of the tested photoinitiating systems strongly depends on their structure. The highest rates of photoinitiated polymerization were observed for bichromophoric polymethine dyes possessing a linkage group with 5 carbon atoms between the heterocyclic rings as a spacer. The differences in photoinitiating ability of the photoinitiating systems composed of sensitizers with five carbon atoms and ten carbon atoms covalent linkage of two identical chromophores may orginate from the differences in the degree of dissociation of polymethine dye borate salts.

In general, the initiators that couple two electron donors in one molecule of sensitizer exhibit a significantly higher rate of heat evolution (the slope of the linear part of the kinetic curve at its initial part) in comparison with monocationic polymethine ones (*N*,*N*′-diethylthiacarbocyanine iodide (**P3**), *N*,*N*-diethyloxacarbocyanine iodide (**P19**) and 1,1′,3,3′,3,3-hexamethylindocarbocyanine iodide (**P60**)).

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 attributed to the "inter filter effect" and becomes more significant for photoinitiators with high molar extinction coefficient (for tested bichromophoric polymethine dyes borate salt ε is reaching value 4×10^4 M^{-1} cm^{-1}). Fig. 6 presents the relationship between the initial rate of polymerization (taken as the slope of linear part of kinetic curve at its initial time) and concentration of photoinitiator.

It is evident that as the photoinitiator concentration is increasing, the initial rate of polymerization increases and reaches

Table 2
Spectroscopic properties of the bichromophoric carbocyanine dyes in both *N*,*N*-dimethylformamide (DMF) and tetrahydrofurane (THF) as the solvent.

Dye	$\lambda_{ab\ max}$ [nm]	ε [M^{-1} cm^{-1}]	$\lambda_{fl\ max}$ [nm]	E_{00} [eV]	Stokes shift [cm^{-1}]
N,N-dimethylformamide ($\varepsilon = 36.71$, $n_D = 1.4305$)					
TS5	565	34 000	595	2.15	892
TS10	564	33 000	596	2.13	952
TO5	491	39 000	522	2.46	1210
TO10	491	37 000	524	2.46	1282
TI5	554	30 200	582	2.18	868
TI10	555	32 000	582	2.19	836
Tetrahydrofurane ($\varepsilon = 7.58$, $n_D = 1.4072$)					
TS5	571	51 000	613	2.15	1200
TS10	569	43 800	607	2.13	1100
TO5	494	41 000	517	2.46	900
TO10	492	36 000	513	2.47	832
TI5	556	39 200	586	2.18	920
TI10	556	38 000	588	2.19	979

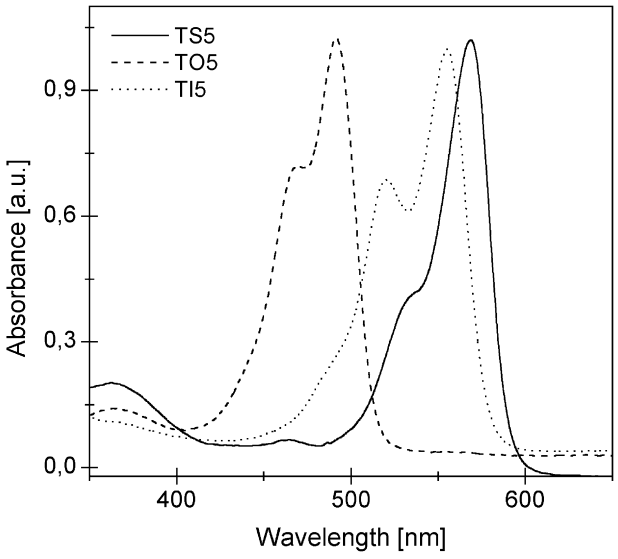


Fig. 1. Electronic absorption spectra of selected bichromophoric dyes (concentration was equal 1×10^{-5} M) in tetrahydrofuran as a solvent at 293 K (dye marked in the figure).

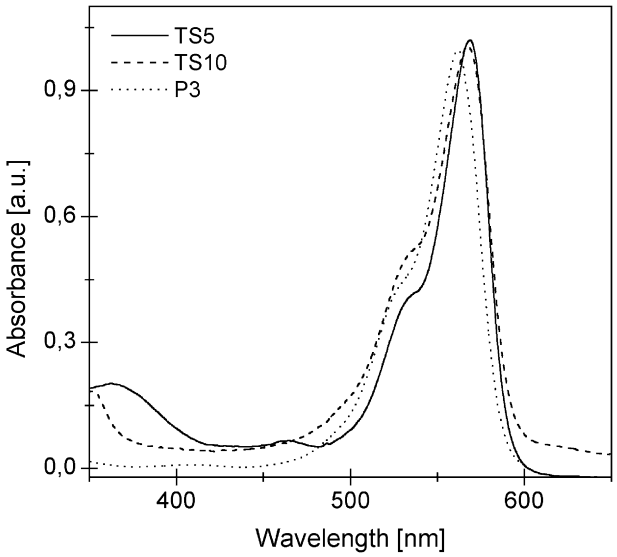


Fig. 2. Electronic absorption spectra of selected bichromophoric dyes and monochromophoric analoque (*N,N′*-diethylthiacarbocyanine iodide) (concentrations were equal 1×10^{-5} M) in tetrahydrofuran as a solvent at 293 K (dye marked in the figure).

a maximum by continuous gradual decrease. For the tested photoinitiator (**TI5B2)**, the highest rate of polymerization under experimental conditions was achieved at the initiator concentration of about 1×10^{-3} M. The reduction of the photoinitiated polymerization rate at higher initiator concentration (for applied technique of polymerization rate measurement) can by easily understood talking into account the decrease of the penetration depth of the laser beam [17].

3.4. The influence of the free energy of electron transfer process on the rate of the free radical polymerization

The formation of free radicals in photoinitiating systems studied occurs *via* photoinduced electron transfer process (PET). The thermodynamic condition for spontaneous electron transfer is that the

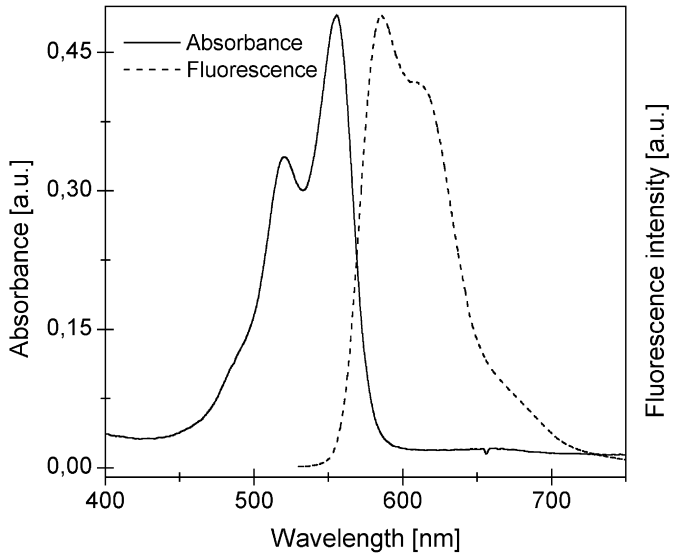


Fig. 3. The normalized electronic absorption and fluorescence spectra of bichromophoric indocarbocyanine diperchlorate in tetrahydrofuran as a solvent (concentration was equal 1×10^{-5} M).

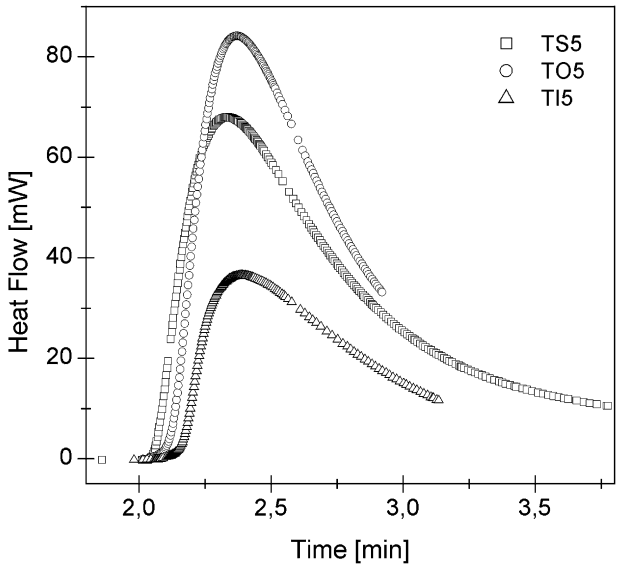


Fig. 4. Family of kinetic curves recorded during the measurements of the flow of heat emitted during the polymerization of the TMPTA/MP (9:1) mixture initiated by bichromophoric polymethine borates marked in the figure. The photoinitiating system concentration was 1×10^{-3} M, $I_a = 20$ mW/0.196 cm^2. The applied dyes possessed various chromophores and identical borate anion.

free energy change ΔG_{ET}, expressed by the Rehm–Weller equation (eq. (1)) has negative value [18,19]:

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

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

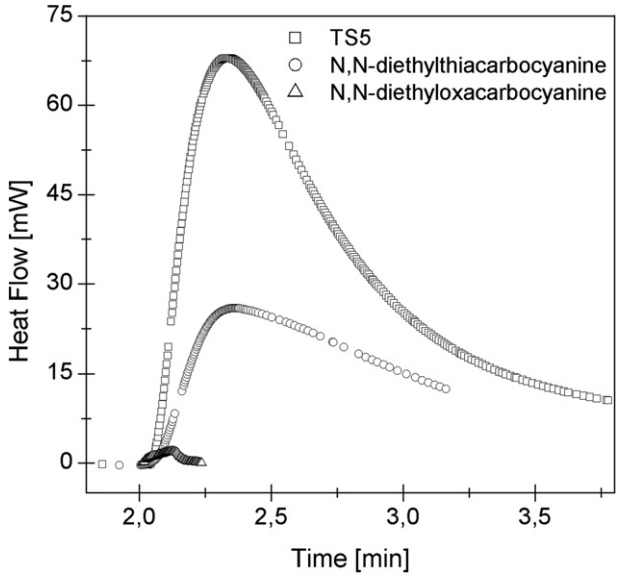


Fig. 5. Family of kinetic curves recorded during the measurements of the flow of heat emitted during the polymerization of the TMPTA/MP (9:1) mixture initiated by mono- and bichromophoric carbocyanine borates, respectively. The photoinitiating concentrations were 1×10^{-3} M and 5×10^{-3} M for bi- and monochromphoric dyes, respectively. $I_a = 20$ mW/0.196 cm^2.

Table 3
The rate of photoinitiated polymerization and the relative rates of photoinitiation abilities of the monocationic and bicationic carbocyanine borates tested.

Photoinitiator	R_p [mW/s]	$1 + \ln R_p$
TS5	410	5.36
TS10	165	4.23
TO5	479	5.43
TO10	122	4.16
TI5	286	5.01
TI10	169	4.48
P3	108	4.03
P19	20.8	2.39
P60	5.2	1

As a rule, PET reactions compete with rapid photophysical deactivation of the sensitizer excited state. The excited singlet state of polymethine dye can undergo three possible deactivation processes: fluorescence, photoizomerization or electron transfer process. As a consequence such reactions are expected to proceed efficiently only when the initial electron-transfer step is exergonic. In other words, the driving force for the electron transfer is $-\Delta G_{ET}$. Values for ΔG_{ET} were estimated for the electron transfer from *n*-buthyltriphenylborate anion on the excited singlet state of the dye, using the oxidation potential of borate salt (1.16 eV) and the reduction potential of sensitizers.

The obtained data and reduction potentials of bicationic polymethine dyes tested are given in Table 4.

For sensitizers empolyed in this study, ΔG_{ET} is predicted to range between −0.68 and 0.19 eV. The estimated, according the Rehm–Weller equation, values of free energy activation for the electron transfer process from borate anion to the excited polymethine dyes show that for the tested photoredox pairs the electron transfer process is thermodynamically allowed (negative values of ΔG_{el}) only in the case of the following photoinitiators: **TS5** and **TO5**. Basing on this, only these photoinitiators should initiate free radical polymerization. But the kinetic results obtained and presented in Table 3 do not confirmed the thermodynamical requirement. Therefore, one should conclude, that there are other factors which may effect on the overall rate of free radical polymerization.

If the electron transfer process is not diffusion controlled, it could be the rate-determining step for the polymerization. In such a case, the polymerization rate would increase with the an increase

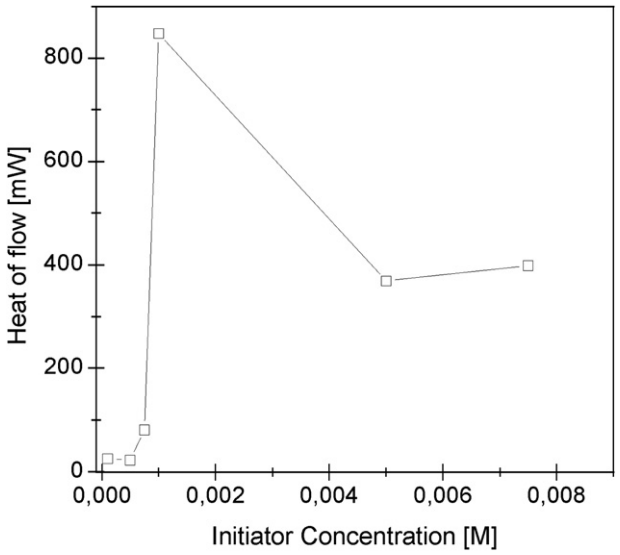


Fig. 6. The relation between the rate of polymerization and selected photoinitiator concentration (**TI5B2**), $I_a = 20$ mW/0.196 cm^2.

Table 4
Reduction potentials and calculated free energies (ΔG_{ET}) of the electron transfer reaction between the singlet excited state of the dyes and electron donor tested.

Co-initiator	E_{red} [eV]	ΔG_{ET} [eV]
TS5	−0.97	−0.025
TS10	−1.16	0.19
TO5	−0.60	−0.675
TO10	−0.93	0.05
TI5	−1.08	0.06
TI10	−1.14	0.11

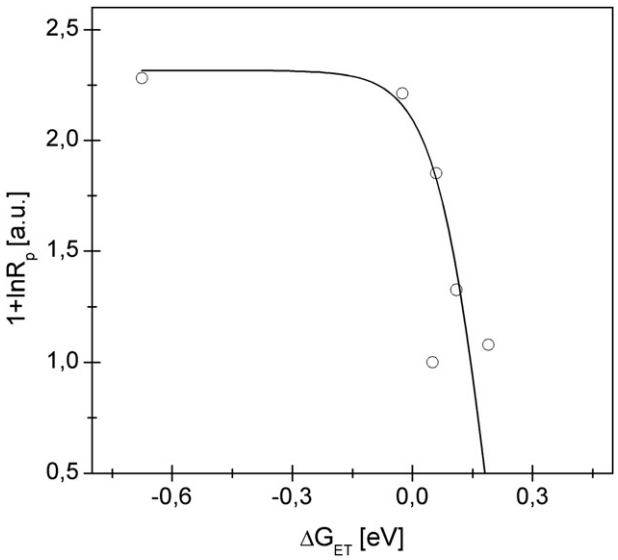


Fig. 7. Rates of polymerization R_p of TMPTA as a function of the free energy change for the electron transfer reaction from the borate anion to the excited single state of bicationic polymethine dyes.

in the $-\Delta G_{ET}$ values, at least up to the diffusion-controlled limit. The rate of electron transfer cannot be the rate-determining step if it approaches the diffusion-controlled limit (then it becomes independent of ΔG_{ET}). In such a situation, other factors (for example, the reactivity of the primary radicals) would control the polymerization rate [18]. Thus, the efficiency of any PET mechanism decreases as the viscosity of the polymerizing medium increases, and the formation of reactive radicals by the PET mechanism may be effective only at the beginning of the polymerization. Fig. 7 presents the normal logarithm of the TMPTA polymerization rate as a function of the ΔG_{ET} value for the initiating systems.

It is apparent from the inspection of the relationship presented in Fig. 7 that the plot exhibits predicted by classical Marcus theory of photoinduced electron transfer. This suggests that at the beginning of the TMPTA polymerization electron transfer process may be the rate-determining step in the radical formation.

4. Conclusion

Six symmetrical bicationic polymethine dyes were synthesized and their steady-state absorption and fluorescence spectra have been investigated. The presented paper is focused on photoinitiation of free radical polymerization initiated by photoreducible dye sensitization.

It was shown that the homodimeric polymethine dyes with linkage group length of 5 carbon atoms paried with *n*-butyltriphenylborate anion significantly increase the efficiency of photoinitiation of free radical polymerization in comparison to the identical series of monochromophore polymethine dyes.

Several important conclusions follow from the experimental data: (1) The estimated, according the Rehm–Weller equation, values of free energy activation for the electron transfer process from an electron donor to the excited electron acceptor show that for the tested photoredox pairs the electron transfer process is thermodynamically allowed (negative values of ΔG_{el}) only in the case of the following photoinitiators: **TS5** and **TO5**. (2) The rates of polymerization depend on the structure of the dye (The dyes possessing the 5 carbon atoms linkage group are the better photoinitiating systems). (3) Since the rate of polymerization is increased when the thermodynamic driving force of electron transfer process (ΔG_{el}) is increased one concludes that the intermolecular electron transfer process may be the limiting step in the photoinitiated polymerization.

Acknowledgments

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