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Novel 6-bromo-3-ethyl-2-styrylbenzothiazolium *n*-butyl-triphenylborates as photoinitiators of trimethylolopropane triacrylate (TMPTA) polymerization

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Summary

The series of 6-bromo-3-ethyl-2-styrylbenzothiazolium *n*-butyltriphenylborates was synthesized and evaluated as photoinitiators of free radical polymerization. The dyes were obtained by the condensation reaction of the 6-bromo-3-ethyl-2-methylbenzothiazolium salts with different alkylaminobenzaldehydes. The resulting styrylbenzothiazole dyes (hemicyanine dyes) paired with *n*-butyltriphenylborate anion (**SBrB2**), are shown to be efficient photoinitiators for free radical polymerization of trimethylolpropane triacrylate (TMPTA) induced with the visible emission of an argon-ion laser. The photochemistry of the novel hemicyanine borates was compared to the photochemistry of identical series of the dyes that do not possess the bromo substituent at benzothiazolium residue. The comparison has shown that the introduction of the bromine into benzothiazolium residue causes a small red shift of the electronic absorption maxima, changes the reduction potential of the dye and, finally, increases a photoinitiation ability of the dye.

Introduction

Photoinitiation of free radical polymerization requires a compound that forms initiating species to be incorporated into the formulation. This material should be capable of producing of active species from the excited states either by direct bond dissociation or by bimolecular reactions. The bimolecular processes include, most commonly, either hydrogen abstraction by sensitizer triplet state or electron transfer process followed by various secondary reactions yielding free radical capable to start chain reaction.

The secondary reactions may include proton transfers [1-3] or a bond cleavage in short-lived intermediates obtained after electron transfer process. These are: (i) boron-carbon bond decomposition applied in cyanine borate photoinitiating systems [4-6], carbon-carbon bond cleavage leading to a decarboxylation of sulfur-containing carboxylic acids [7,8] and aminoacids [9] or C-N bond fragmentation observed for methoxypyridine radicals [9-12].

The electron transfer photoinitiators allow shifting the sensitivity of the initiating system to visible part of the electromagnetic spectra and allow easily match the spectral absorbance of photoinitiator with the spectral output of the light source. This, in turn, maximizes the photoinitiation efficiency.

It is reasonable to focus research attempts on the developments of photoinitiators that have visible absorption around 500 nm, the region where the two main lines of argon-ion laser (488 and 513 nm) are observed. Research carried out in our laboratory has resulted in the synthesis of a series of dye photoinitiators that have good absorption around 500 nm that allows a good matching between the dyes absorption and argon-ion laser emission. This paper reports the results obtained from the studies on the series of such "tunable" photoinitiators composed of 6-bromo-3-ethyl-2-styryl benzothiazolium *n*-butyltriphenylborate salts. The properties of novel dyes are compared to these observed for 3-ethyl-2-styryl benzothiazolium *n*-butyltriphenylborate salts, described earlier by our research group [13,14].

Experimental

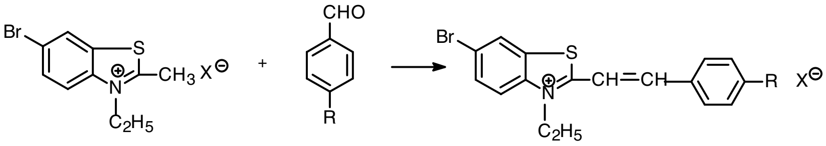
Materials

Substrates used for the preparation of the dyes and electron donor were purchased from Fluka, Merck, or Aldrich Chemical Co. All chemicals and solvents were of the best grade quality and were used without further purification.

Synthesis

The electron donor, tetramethylammonium *n*-butyltriphenylborate was prepared according to the procedure described in our earlier paper [15].

All tested sensitizers were prepared according to the general method presented in Scheme 1.



Scheme 1. A general route for the synthesis of hemicyanine dyes.

The dyes were obtained by the condensation of 6-bromo-3-ethyl-2-methylbenzothiazolium salt with appropriate *p*-(alkylamino)benzaldehyde that yields 6-bromo-3-ethyl-2-styrylbenzothiazolium dyes (**SBr**).

*6-Bromo-3-ethyl-2-(4-N,N-dimethylaminostyryl)benzothiazole p-toluene sulphate (**SBr1**)*

To a warm solution of 6-bromo-3-ethyl-2-methylbenzothiazole *p*-toluene-ethyl sulphate (0.01 mol) and *p*-N,N-dimethylaminobenzaldehyde (0.01 mol) in ethanol (6 mL) few drops of triethyl amine were added. After cooling to ambient temperature the precipitated product was filtered and crystallized from ethanol; m.p. 224-238°C.

^{1}H NMR (DMSO) δ (ppm): 1.043-1.125 3H, –CH_3; 1.354-1.426 3H, –CH_3; 3.116 6H, –$N(CH_3)_2$; 4.762-4.799 2H, N^+-CH_2; 6.817-6.863 2H, Ar; 7.535-7.612 J≈15Hz 1H, –CH=; 7.907-7.960 3H Ar; 8.035-8.072 1H, Ar; 8.147 1H, –CH= ; 8.572-8.581 1H, Ar.

*6-Bromo-3-ethyl-2-(4-N,N-diethylaminostyryl)benzothiazole ethyl sulphate (**SBr2**)*

A mixture of 6-bromo-3-ethyl-2-methylbenzothiazole ethyl sulphate (1 mol), *p*-N,N-diethylaminobenzaldehyde (1 mol) and acetic anhydride (20 mL) was refluxed for 20 min. The precipitate obtained after cooling the reaction mixture was filtered and crystallized from ethanol; m.p. 197-218°C.

^{1}H NMR (DMSO) δ (ppm): 1.054-1.188 6H, –CH_3; 1.349-1.418 3H, –CH_3; 3.335-3.561 4H, –$N(C_2H_5)_2$; 3.667-3.774 3H, –CH_3; 4.748-4.784 2H, N^+-CH_2; 6.804-6.850 2H; 7.493-7.568 J≈14Hz, 1H, –CH=; 7.883-7.949 3H Ar; 8.019-8.063 1H, Ar; 8.123 1H, –CH= ; 8.557-8.566 1H, Ar.

*6-Bromo-3-ethyl-2-(2-methyl-4-N,N-dimethylaminostyryl)benzothiazole ethyl sulphate (**SBr3**)*

It was synthesized according to the method applied for the preparation of the dye **SBr2**; m.p. 198-248°C.

^{1}H NMR (DMSO) δ (ppm): 1.054-1.125 3H, –CH_3; 1.348-1.418 3H, –CH_3; 1.898 3H, –CH_3; 3.107 6H, –$N(CH_3)_2$; 4.758-4.792 2H, N^+-CH_2; 6.648-6.659 1H, Ar; 6.703-6.748 1H, Ar; 7.480-7.554 J≈15Hz, 1H, –CH= ; 7.894-7.948 1H, Ar; 8.021-8.064 1H, Ar; 8.120-8.165 2H, Ar; 8.513-8.523 1H, –CH=.

*6-Bromo-3-ethyl-2-(2,6-dimethyl-4-N,N-dimethylaminostyryl) benzothiazole ethyl sulphate (**SBr5**)*

The dye was synthesized according to the procedure described for preparation of the dye **SBr2**; m.p. 163-199°C.

^{1}H NMR (DMSO) δ (ppm): 1.363-1.435 3H, –CH_3; 2.471-2.561 6H, –CH_3; 2.993-3.079 6H, –$N(CH_3)_2$; 4.724-4.759 2H, N^+-CH_2; 6.614 2H, Ar; 7.057-7.134 J≈15Hz, 1H, –CH=; 7.920-7.975 1H, Ar; 8.075-8.123 2H, Ar; 8.202 1H, –CH=.

*6-Bromo-3-ethyl-2-(p-pyrolidinylstyryl)benzothiazole iodide (**SBr7**)*

A mixture of 6-bromo-3-ethyl-2-methylbenzothiazole ethyl sulphate (1 mol), *p*-pyrolidinylaldehyde (1 mol) and acetic anhydride (20 mL) was refluxed for 20 min, then poured into a warm solution of potassium iodide (4 mol) in water (200 mL). The washed with water product was extracted with ether and recrystallized from methanol or ethanol; m.p. 188-236°C.

^{1}H NMR (DMSO) δ (ppm): 1.349-1.488 3H, –CH_3; 1.898-1.992 4H, –CH_2; 3.167-3.427 4H, –CH_2–; 4.715-4.784 2H, N^+-CH_2; 6.614-6.726 1H, –CH=; 7.376-7.429 1H, Ar; 7.504-7.621 1H, Ar; 7.911-7.949 1H, Ar; 8.017-8.096 1H, J≈15Hz, –CH=; 8.132 1H, Ar; 8.281-8.325 1H, Ar; 8.563-8.568 1H, Ar; 8.702-8.709 1H, Ar.

*6-Bromo-3-ethyl-2-(p-piperidinylstyryl)benzothiazole iodide (**SBr8**)*

The dye was prepared according to the method described for the dye **SBr7**; m.p. 159-206°C.

^{1}H NMR (DMSO) δ (ppm): 1.355-1.487 3H, –CH_3; 1.615 4H, –CH_2-; 1.897-3.315 6H, –CH_2–; 4.714-4.945 2H, –N^+-CH_2; 7.025-7.069 1H, Ar; 7.560-7.637 J≈15Hz, 1H, –CH=; 7.893-7.967 1H, Ar; 8.040-8.135 2H, Ar; 8.267-8.311 1H, Ar; 8.586-8.597 2H, Ar; 8.696 1H, –CH=.

*6-Bromo-3-ethyl-2-(N-methyinodolyl)benzothiazole ethyl sulphate (**SBr9**)*
The compound was synthesized according to the method applied for the preparation of the dye **SBr2**; m.p. 170-219°C.
^{1}H NMR (DMSO) δ (ppm): 1.384-1.458 9H, $-CH_3$; 2.718-2.871 4H, $-CH_2$; 4.677-4.787 2H, N^+-CH_2-; 7.377 1H, Ar; 7.578-7.633 1H, –CH=; 7.809-7.853 2H, Ar; 8.047-8.095 2H, Ar; 8.267-8.311 2H, Ar; 8.692-8.703 1H, –CH=.

The borate anion-exchange reaction was performed according to the procedure given by Damico [16].

Measurements

Absorption spectra were recorded with a Varian Cary 3E Spectrophotometer, and fluorescence spectra were obtained using a Hitachi F-4500 Spectrofluorimeter. The absorption and emission spectra were recorded using spectroscopic quality ethyl acetate as a solvent. The measurements were performed at ambient temperature.
The fluorescence quantum yields for the dyes in tetrahydrofurane (THF) were determined as follows. The fluorescence spectrum of a dilute (< 25 μM) dye solution was recorded by excitation at the absorption band maximum of the standard. A dilute Rhodamine B in ethanol (Φ = 0.55 [17]) was used as reference. The fluorescence spectrum of Rhodamine B was obtained by excitation at its absorption peak at 530 nm. The quantum yield of the tested dye (Φ_{dye}) was calculated using equation:

$$\Phi_{dye} = \Phi_{ref} \frac{I_{dye} A_{ref}}{I_{ref} A_{dye}} \tag{1}$$

where:
Φ_{ref} is the fluorescence quantum yield of reference (Rhodamine B) sample in ethanol, A_{dye} and A_{ref} are the absorbances of the dye and reference samples at the excitation wavelengths (530 nm), I_{dye} and I_{ref} are the areas arbitrary units of the corrected fluorescence spectra (plotted in frequency scale) for the dyes and reference samples, respectively.

The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical MTM System (Krakow) Model EA9C-4z was used for the measurements. A platinum 1 mm disk electrode was used as the working electrode, a Pt wire constituted the counter electrode, and Ag-AgCl electrode served as a reference electrode. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium perchlorate in dry acetonitryle.

Polymerization

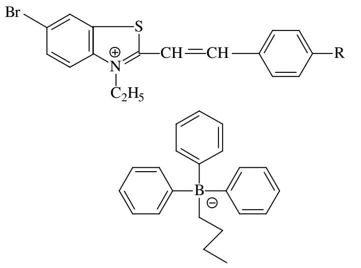
The kinetics of free radical polymerization was studied using a polymerization solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The sensitizer's concentration was $1x10^{-3}$ M. As a reference sample a polymerizing mixture containing sensitizer without an electron donor was used. The measurements were carried out at ambient temperature and the polymerizing mixture was not deaerated before curing.

Measurements of the kinetics of free radical polymerization were performed in a home-made microcalorimeter. As a temperature sensor a semiconducting diode immersed in the 2 mm thick layer (0.25 mL) of a cured sample was used. The amplified signal was transformed with an analog/digital data acquisition board to a computer. In order to avoid the possibility of non-isothermal reaction conditions, for further discussion only the data for initial time of polymerization were used for the calculation of the polymerization rates. An average value of the rate of polymerization was established based on measurements performed at least twice.

Irradiation of the polymerization mixture was carried out using the visible emission of an Omnichrome model 543-500 MA argon-ion laser (488 and 514 nm) with intensity of light of 64 mW/cm^2. The light intensity was measured by a Coherent Model Fieldmaster power meter [18].

Results and discussion

SBrB2 is a complex of hemicyanine dye cation acting as electron acceptor and *n*-butyltriphenyl borate anion being the electron donor.



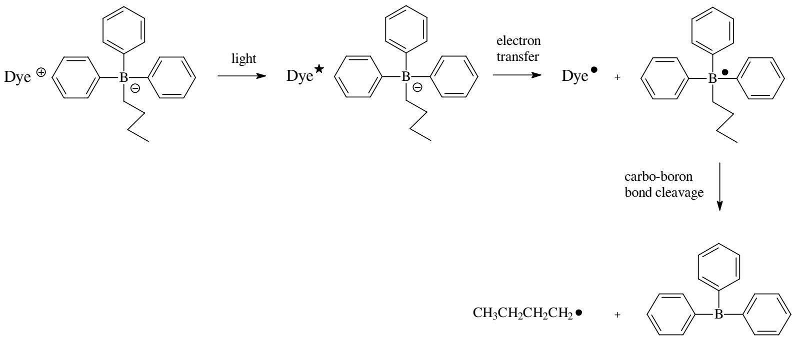
Sensitizer

Electron acceptor

Co-initiator

Electron donor

As it has been mentioned earlier, Chatterjee et al. [4,5] studied the photoreactions mechanism of several similar complexes in visible region. Under irradiation of visible light, the cationic cyanine dye absorbs a photon and is excited; an electron is then transferred from the borate to the cyanine excited state, which results in the formation of an unstable boranyl radical. The n-butyl radical released from the boranyl radical is capable of initiating radical polymerization of vinyl monomers. The mechanism is illustrated in Scheme 2.



Scheme 2. A general route for the generation of free radical starting a polymerization chain-reaction.

The analysis of the kinetic scheme for photoinduced polymerization via the inter- or intramolecular electron transfer process allows the prediction of several principal requirements that should be considered during a design of the photoinitiating photoredox pair [19,20]. First, the rate of photoinitiated free-radical polymerization depends on the quantum yield of a deactivation processes of singlet excited state or quantum yield of the singlet state formation and yields of processes that deactivates this state. Second, it depends on both, the thermodynamic (ΔG_{el}) and kinetic (λ) aspects of electron-transfer process. Finally, it may depend on the reactivity of free radicals resulting from the electron transfer process [19]. The influence of all these parameters on the rate of polymerization can be also deduced during the analysis of spectroscopic, electrochemical and structural properties of new styrylbenzothiazole dyes.

Figure 1 depicts the electronic absorption spectra of the selected tested dyes, and Table 1 lists the structures and spectroscopic properties as well as the electrochemical data of all the dyes studied.

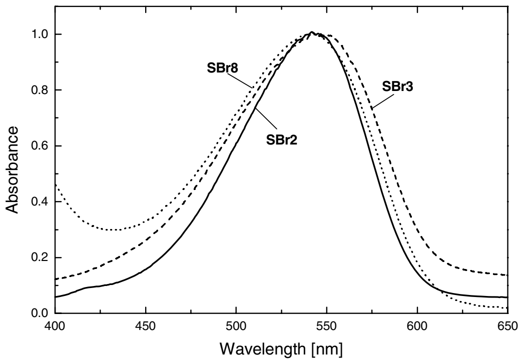


Fig. 1. Electronic absorption spectra for selected dyes tested in ethyl acetate (type of the dye shown in the legend).

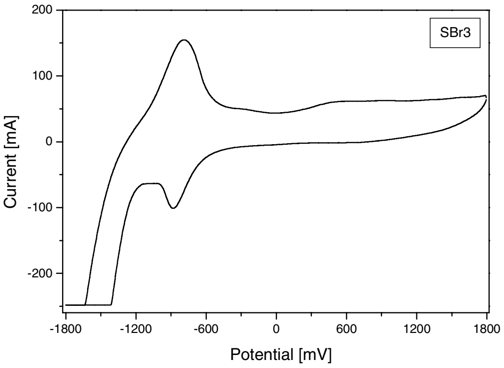
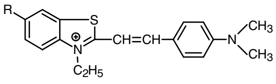
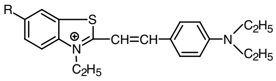
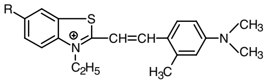
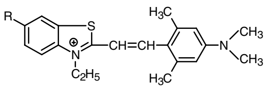
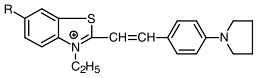
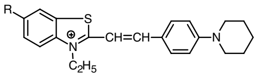
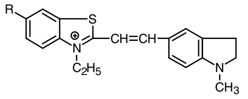


Fig. 2. Cyclovoltammetric curve recorded for 6-bromo-3-ethyl-2-(2-methyl-4-N,N-dimethylaminostyryl)benzothiazole ethylsulphate (**SBr3**).

Table 1. Structure, Spectroscopic and Electrochemical Properties of Tested Dyes.

Cation structure	Dye	R = Br			Dye	R = H		
		λ_{ab} [nm]	ε [M^{-1} cm^{-1}]	E_{red} [mV]		λ_{ab} [nm]	ε [M^{-1} cm^{-1}]	E_{red} [mV]
	SBr1	538	23000	-750	SH1	521	30600	-965
	SBr2	546	28000	-1130	SH2	536	21400	-1005
	SBr3	550	30000	-780	SH3	532	17000	-920
	SBr5	540	32000	-1100	SH5	531	26000	-945
	SBr7	560	34000	-1115	SH7	535	41800	-1070
	SBr8	544	26000	-1250	SH8	527	35700	-1084
	SBr9	553	17000	-1165	SH9	538	34800	-915

The electrode potential at which dye undergoes reduction was determined by cyclic voltammetry. The obtained voltamperograms for tested dyes show a reversible reduction (Fig. 2).

The value of the reduction potential depends on the structure of the dye and oscillates in the range from –1250 to –750 mV.

The influence of the dye structures on their polymerization ability is very significant. Figure 3 presents the illustrative photopolymerization kinetic curves recorded for all novel dyes in presence of n-butyltriphenylborate as an electron donor.

Essentially one method of dye modification was applied in our study. The modification was based on the introduction of bromine substituent into phenyl ring of benzothiazolium skeleton and the change of structure of the dialkilamino group in styrylamino residue. The analysis of the kinetic curves presented in Figure 3 allows one to conclude that there is significant substituent effect on the photoinitiation ability of the novel dyes. The highest rates of photoinitiated polymerization for the **SBr** dyes were observed for compounds **SBr1**, **SBr2**, **SBr3** and **SBr5**. These are dyes for which the rotation about the bond linking the dialkylamino group and benzene ring is not limited.

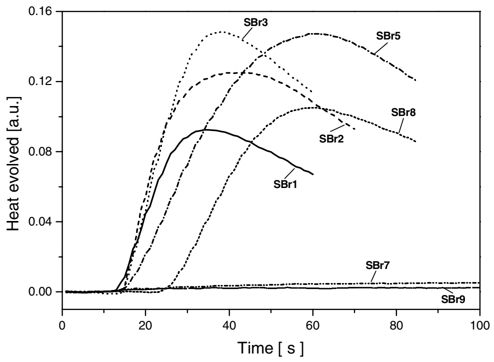


Fig. 3. Family of photopolymerization kinetic curves recorded for the novel tested dyes; electron donor: n-butyltriphenylborate (E_{ox} = 1160 mV, concentration 0.005 M), monomer formulation: 1 mL of MP and 9 mL of TMPTA. Light intensity of argon-ion laser irradiation was 64 mW/cm^2 (photoinitiating dyes marked in the figure).

Figure 4 presents the effect of the heavy atom substituted in benzothiazolium part of the dye, on the rate of photoinitiated polymerization. The relative rates of photoinitiated polymerization measured for all the tested photoredox pairs are collected in Table 2.

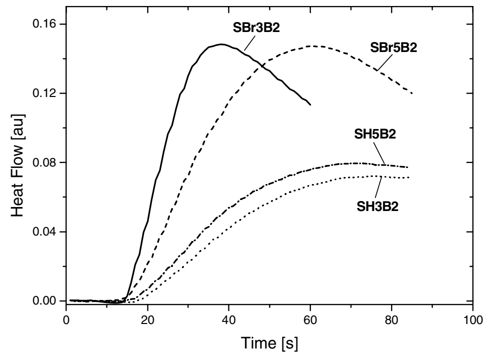


Fig. 4. Family of the kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of the TMPTA/MP (9/1) mixture initiated by hemicyanine borate salts illustrating the effect of the heavy atom on the polymerization rate.

Additionally the data obtained from the photoinitiated polymerization kinetics measured for dyes without bromide substituent at 6 position of benzothiazolium residue are presented for comparison as well.

Summarizing the results collected in Table 2, one can conclude that not only the electron-donating substituents but also the heavy atom substituted into the electron-withdrawing moiety of the molecules strongly affect the photoinitiation ability of tested photoredox systems. In principle, the 6-bromo-3-ethyl-2-styryl benzothiazolium *n*-butyltriphenylborate salts have slightly higher rate of heat evolution (slop of the linear part of kinetic curve) observed during photouinitiated polymerization in comparison to described earlier by our research group [13,14] similar series of styrylbenzothiazolium dyes without heavy atom.

Table 2. The Spectroscopic, Electrochemical, Thermodynamical Properties and the Rates of Free Radical Polymerization of TMPTA Characterizing the Dyes under the Study.

Dye	λ_{fl}[1] [nm]	Φ[2] [-]	E_{00} [eV]	ΔG_{el}[3] [eV]	R_p [a.u.]	R_p [μmol/s]
SBr1	601	0.016	2.062	-0.152	4.35	13.5
SBr2	604	0.019	2.053	0.237	4.81	21.3
SBr3	605	0.006	2.049	-0.109	4.54	16.3
SBr5	644	0.001	1.926	0.334	4.08	10.3
SBr7	599	0.003	2.070	0.205	1	0.47
SBr8	611	0.005	2.030	0.38	3.74	7.31
SBr9	614	0.004	2.019	0.306	2.3	1.74
SH1	596	0.015	2.213	-0.088	3.39	5.16
SH2	601	0.009	2.170	-0.005	3.3	4.73
SH3	608	0.003	2.178	-0.098	3.26	4.51
SH5	601	0.008	2.170	-0.065	3.3	4.73
SH7	602	0.006	2.209	0.021	3.04	3.65
SH8	601	0.008	2.155	0.089	2.92	3.22
SH9	616	0.003	2.144	-0.069	3.16	4.08

[1] measured in ethyl acetate

[2] measured in THF

[3] calculated according to Rehm-Weller equation; borate anion $E_{ox}(D/D^{\bullet-}) = 1.160$ V

Discussion on the hemicyanine borates photochemistry should also include the estimation of the thermodynamic driving force of the photoinduced electron transfer (PET) between components forming photoredox pair. It is well known that the main prerequisite for PET reaction is described by Rehm–Weller [21] equation (2), which states that the free energy of activation for the PET (ΔG_{el}) process should have negative value.

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

where:

$E_{ox}(D/D^{\bullet+})$ is the oxidation potential of electron donor, $E_{red}(A^{\bullet-}/A)$ is the reduction potential of electron acceptor, E_{00} is the excited state energy, $Ze^2/\varepsilon a$ is the Coulombic energy, which for products of analyzed reaction, is considered negligible with respect to the overall magnitude of ΔG in the present system.

The dye fluorescence emission peak measured in ethyl acetate (EtOAc), the oxidation potential of the electron donor and the reduction potential of the dye allow to calculate the value of free energy for electron transfer process (ΔG_{el}) between the tested dyes cation and applied as electron donor n-butyltriphenylborate anion. The measured values of the mentioned above variables and the calculated values of the free energy change (ΔG_{el}) for the photoinduced intermolecular electron transfer process are also summarized in Table 2. The data indicate, that for the series of 6-bromo-3-ethyl-2-(4-N,N-dialkylaminostyryl)benzothiazole borates, possessing n-butyltriphenylborate counterion, the free energy of activation (ΔG_{el}) for an electron transfer reaction between cyanine cation and borate anion is positive (with the exception of dyes **SBr1** and **SBr3**). The practical application of the theory of electron transfer [22] in the polymerization photoinitiation process can be limited to certain conditions (identical free radical formed), assuming that the rules regulating the primary processes might also be applied for secondary reactions. The results of such treatment are presented in Figure 5.

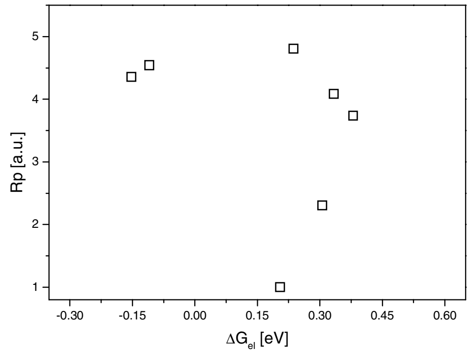


Fig. 5. Relationship between the rate of polymerization (TMPTA/MP) and the free energy change (ΔG_{el}) for asymmetric cyanine – borate photoredox pairs. Irradiation of the polymerization mixture was carried out using visible emission of an argon laser with intensity of irradiation, I = 64W/cm^2.

Figure 5 shows relationship between the rate of polymerization and the thermodynamic driving force (ΔG_{el}) for PET process obtained for the dyes tested. From the inspection of the data presented in this Figure, it is seen, that the rate of free radical polymerization initiated by tested dyes does not give the relationship predicted by Marcus theory e.g. is not showing an increase of polymerization rate as the driving force of electron transfer process is increasing. The lack of such correlation for tested photoredox systems can be explained by properties of borate ion.

The occurrence of electron transfer between cyanine and borate ions leads to quenching and simultaneous shortening of fluorescence lifetime of cyanine chromophore. Under this assumption and according to the theory of the electron transfer, the state, which is quenched should be the fluorescing state. If the cyanines are not quenched in their fluorescing state the relationship predicted by the Marcus equation can be not observed. In addition to this, if the oxidation of borate anion is dissociative or nearly so the Marcus theory may not predict rates of its electron transfer reaction. It should be noted that the Marcus theory [22] is based upon the assumption that the oxidized and reduced forms of substrates have long enough lifetimes of establish a new equilibrium. If the electron transfer is dissociative, this new equilibrium cannot be reached and the application of the Marcus theory may not be quite appropriate. Concerning the previously discussed specific feature of cyanine borates [23], one can predict that even a slight change in the radical-ion pair electrochemical properties or size, may cause distinct deviation of the rate constant for the electron transfer from the value predicted by the Marcus theory.

Conclusion

The asymmetric cyanine dyes combined with borate salts (6-bromo-3-ethyl-2-styryl benzothiazolium n-butyltriphenylborate salts) can be used as visible-light photoinitiators. They initiate radical polymerization of multiacrylate monomers under irradiation of a 514 nm argon laser. The initiation ability of studied photoinitiating systems depends on the hemicyanine cation and increases when the structure of the dye was modificated by the introduction of simple N,N-dialkylamino group in the phenyl ring of styryl moiety. One can also conclude that not only the electron-donating substituents but also the heavy atom substituted into the electron-withdrawing moiety of the molecules affects the photoinitiation abilities of tested photoredox systems. In principle, the 6-bromo-3-ethyl-2-styryl benzothiazolium *n*-butyltriphenylborate salts have slightly higher rate of photoinitiated polymerization in comparison to described earlier by our research group [13,14] similar series of styrylbenzothiazolium dyes without heavy atom.

The relationship between the rate of polymerization and the free energy change (ΔG_{el}) do not display normal Marcus kinetic behavior. The lack such correlation for tested photoredox systems can be explained by properties of borate ion.

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