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Journal of Photochemistry and Photobiology A: Chemistry 195 (2008) 105–115

Journal of Photochemistry and Photobiology A:Chemistry

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Studies on an argon laser-induced photopolymerization employing both mono- and bischromophoric hemicyanine dye–borate complex as a photoinitiator

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Received 4 June 2007; received in revised form 21 September 2007; accepted 24 September 2007
Available online 29 September 2007

Abstract

Dye photoinitiators consisting of either 1,3-bis-[4-(*p*-*N*,*N*-dialkylaminostyryl)pyridinyl]propane (C1B2–C8B2) or 1,3-bis-[4-(*p*-*N*,*N*-dialkylaminostyryl)-pyridinyl]xylene (A1B2–A8B2) dications, acting both as light absorbers and as electron acceptors and *n*-butyltriphenylborate anions being electron donors were tested in order to reveal the effect of a dye structure on the efficiency of multiacrylate photoinitiated polymerization. The kinetic studies clearly demonstrated that the bischromophoric stilbazolium borate photoredox pairs exhibit a significant increase in the efficiency of TMPTA free radical polymerization in comparison to the pairs containing structurally related, monochromophoric styrylpyridinium borates (SP1B2–SP8B2). The efficiency of tested systems depends on the ΔG_{el} of electron transfer between borate anion and styrypyridinium cation. The latter value was experimentally determined for 24 photoredox pairs. The relationship between the rate of polymerization and the free energy of activation of electron transfer reaction shows the dependence predicted by the classical theory of electron transfer phenomena. This relation is independently observed for mono- and bischromophoric hemicyanine borate salts.

Keywords: Dyeing photoinitiators; Radical polymerization; Marcus theory

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1. Introduction

The cyanine dyes were first reported more than 150 years ago [1]. They are characterized by two heterocyclic residues connected by a polymethine bridge having an odd number of carbons. Variation of the heterocycle structure and bridge length leads to absorption and emission maxima that span the visible and near-IR regions of the spectrum. Cyanines exhibit large excitation coefficients ($\varepsilon_{max} > 10^4\ M^{-1}\ cm^{-1}$) and moderate fluorescence quantum yields, leading to widespread applications as photosensitizers, stains, fluorescent labels and probes [2].

One report concerning cyanine dyes was especially interesting for us and motivated our entry into this field. In 1990s, Schuster et al. reported that irradiation of cyanine dyes with visible light in the presence of borate anion was sufficient to initiate the polymerization of vinyl monomers [3]. The mechanism for photoinitation with cyanine–alkyltriarylborate complex involves an alkyl radical formation as a result of photoinduced electron transfer from a borate anion to the singlet excited state of the cyanine dye cation, followed by addition of the alkyl radical formed to the carbon–carbon double bond of the acrylate (Scheme 1).

From the Schuster et al. initial studies on such photoinitiating system [4], it is well known that the cyanine–borate photoinitiating system forms a tight-ion pair in non-polar solvents. This guarantees an efficient electron transfer between borate anion and excited dye molecule in spite of its short-lived singlet excited state. However, it was soon discovered that an even small amount of polar solvent might sharply change a degree of the tight-ion-pair formation [5]. In polymerizing mixture (acrylates; medium polarity solvent), the photoinitiating photoredox pair exists as a tight-pair and solvent-separated ions. This fact was confirmed by both dynamic and static quenching experiments and the relationship between the concentration of borate anion and the efficiency of photoinitiation [6,7]. These experiments show the need of an increase of an electron donor concentration in close proximity

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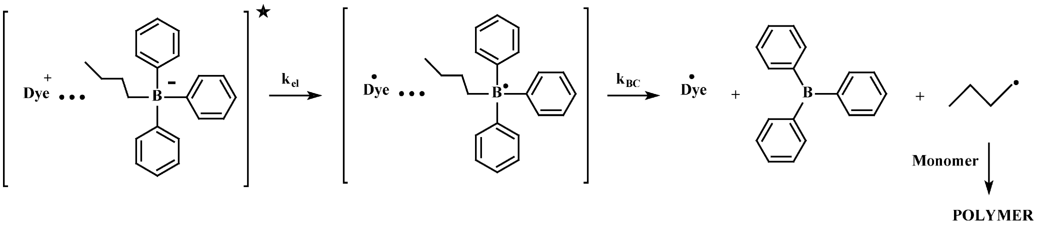
doi:10.1016/j.jphotochem.2007.09.011



Scheme 1. Radical initiation from cyanine–borate complex.

to a cyanine dye moiety. Traditionally, such approach is possible to achieve by attaching to an absorbing chromophore an additional organic cation that can form an ion pair with borate anion [6,8–10].

In literature there are many review articles on various aspects of photoinitiated polymerization [11–15]. The key steps of the mechanism are the quenching of the excited chromophore, either singlet or triplet states, by the electron transfer mechanism and various steps that follow the primary process. Marcus [16] has provided a simple approach allowing to predict the kinetic of the process, using thermodynamic parameters and spectroscopic measurements. The Marcus theory assumes that the bimolecular electron transfer occurs in three stages: (1) the formation of the precursor complex, (2) the electron transfer and (3) the change in organization of the solvent cage in which electron transfer primary products exist. This theory leads to the prediction that the rate of electron transfer first should increase with an increase in the thermodynamic driving force up to a maximum and then decrease with an increase of the thermodynamic driving force.

The practical application of the Marcus theory is commonly used for the study of the primary photochemical processes. The description of the kinetics of the photoinitiated polymerization *via* intermolecular electron transfer process is one more example applying this theory to practice.

In this paper, we describe the kinetic studies of the novel photoinitiating systems consisting of different bischromophoric hemicyanine dyes (the light absorbers) coupled with butyltriphenylborate anions (co-initiators). The photoinitiating ability of tested photoredox systems are compared to the photochemistry of structurally related, monochromophoric styrylpyridinium borates. It is also our intention to show that the Marcus equation can be applied for the description of the kinetics for dye–borate photoinitiated polymerization *via* an intermolecular electron transfer process.

2. Experimental

2.1. Materials

Monomer, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), 1-methyl-2-pyrrolidinone (MP), 2,4,6-tris(chlorodifluoromethyl)-*s*-triazine (DFCT) and the spectroscopic grade solvents for spectral measurements were purchased from Aldrich Chemical Co. and were used without further purification.

2.2. Techniques

(i) The synthesis of the dyes was described in our earlier papers [7,17,18]. *n*-Butyltriphenylborate tetramethylammonium salt (B2) was synthesized based on the method described by Damico [19]. The ion-exchange reaction was performed using the procedures given by Damico [19] and Murphy et al. [20]. The final products were identified by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy when it was needed. The obtained spectra suggest that the reaction products were of desired structures. The purity of synthesized compounds was determined using thin layer chromatography and by measuring of the melting points. All these results are described in our earlier papers as well [7,17,18]. It is necessary to mention that some of the dyes, i.e. monochromophoric ones and C1 and A1 were synthesized previously by other research group [21–25] but they have not been used as photoinitiators of free radical polymerization earlier.

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

(iii) *Electrochemical measurements*: 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.

(iv) *Polymerization measurements*: the kinetics of free radical polymerization were 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 styrylpyridinium borate (photoinitiator) concentration was 1×10^{-3} M. In order to eliminate the thermal effect of laser irradiation on polymerization kinetics curve the flow of heat evolution traces for reference samples were recorded. A reference formulation contained styrylpyridinium iodide or bromide (dye without an electron donor; e.g. A1) instead of styrylpyridinium borate salt (photoinitiator). The reference data were subtracted from the data of heat flow obtained during polymerization of formulation containing the photoinitiator.

The measurements were carried out at an ambient temperature and the polymerizing mixture was not deaerated before curing. The measurements of the kinetics of free radical polymerization were performed in a homemade 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. The initial rates of polymerization are the slopes of the lines drawn on the flow of heat versus time curve at the beginning of polymerization. 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 emission (two lines of equal intensity at 488 and 514 nm) of an Omnichrome argon ion laser Model 543-500 MA with intensity of light of 64 mW/cm^2. The light intensity was measured by a Coherent Model Fieldmaster power meter.

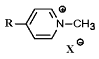
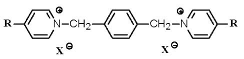
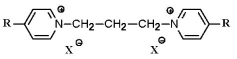
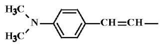
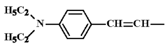
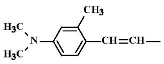
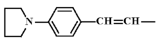
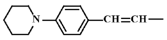
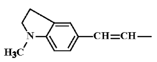
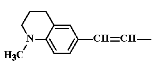
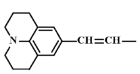
3. Results and discussion

3.1. Spectroscopic and photophysical properties of hemicyanine derivatives

The molecular structure and denotations of the dyes under the studies are given in Scheme 2.

In our studies polymerization of TMPTA photoinitiated by both mono- and bischromophoric hemicyanine borate salts were performed under irradiation at 488 and 514 nm, e.g. at the wavelengths where the light is absorbed by cyanine cation (Fig. 1).

All salts possess similar absorption spectra with two maxima at about 300 and 500 nm. The shortest wavelength bands are attributed to the $\pi \rightarrow \pi^*$ transitions whereas the long-wavelength bands, generally characterized by higher molar absorption coefficients, are attributed to CT transitions. On vary-

Substituent R	Denotation 					
	X=I	X=n-$C_4H_9B(C_6H_5)_3$	X=Br	X=n-$C_4H_9B(C_6H_5)_3$	X=Br	X=n-$C_4H_9B(C_6H_5)_3$
	**SP1**	**SP1B2**	**A1**	**A1B2**	**C 1**	**C 1B2**
	**SP2**	**SP2B2**	**A2**	**A2B2**	**C2**	**C2B2**
	**SP3**	**SP3B2**	**A3**	**A3B2**	**C3**	**C3B2**
	**SP4**	**SP4B3**	**A4**	**A4B2**	**C4**	**C4B2**
	**SP5**	**SP5B2**	**A5**	**A5B2**	**C5**	**C5B2**
	**SP6**	**SP6B2**	**A6**	**A6B2**	**C6**	**C6B2**
	**SP7**	**SP7B2**	**A7**	**A7B2**	**C7**	**C7B2**
	**SP8**	**SP8B2**	**A8**	**A8B2**	**C8**	**C8B2**

Scheme 2.

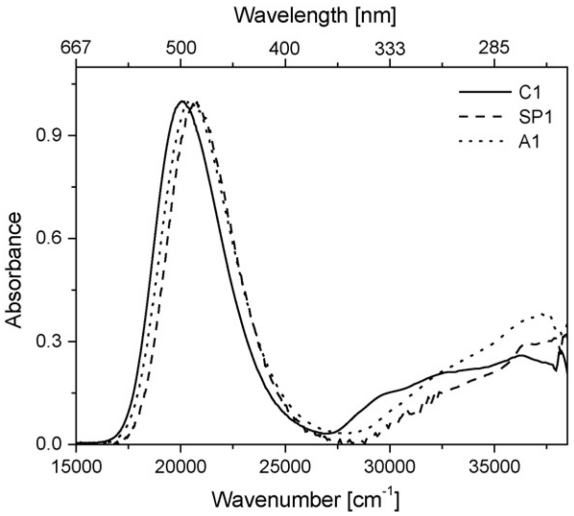


Fig. 1. Electronic absorption spectra of mono- (SP1) and bischromophoric (C1 and A1) dyes in DMF.

ing of the solvent polarity, relatively weak shifts of the absorption maxima are observed [17,18,26]. The type of anion has no significant effect on the position and intensity of the absorption band. The spectroscopic properties of the dyes under the study are presented in Table 1 for illustration. Full data associated with the spectroscopic properties of the tested compounds can be found in our earlier papers [17,18,26].

Tested photoinitiators represent mono- and bischromphoric molecules that show large Stokes shift (about 4000–5000 cm^{-1} in polar solvents and 2000–3000 cm^{-1} in non-polar ones) [17,18,26]. This indicates that an emitting state is not the Franck–Condon S_1 state reached in the absorption transition but different, the solvent relaxed state, from which the fluorescence originates. The nature of an emitting state in D-S-A molecules may change with the solvent [17,18,24] or can be changed with the dye structure (the nature of the electron donor part of molecule) that is forcing or precluding the excited state relaxation *via* selected channels [27] or may be controlled by the viscosity of the medium [28].

Theoretically [29] the energy level of the molecule excited CT state, relative to its ground state can be expressed by Eq. (1), where $E_{\mathrm{ox}}(D)$ and $E_{\mathrm{red}}(A)$ are the one-electron oxidation and reduction potentials of donor and acceptor and C is a constant that depends on the degree of charge separation.

$$E_{\mathrm{CT}} = E_{\mathrm{ox}}(D) - E_{\mathrm{red}}(A) + C \qquad (1)$$

Verhoeven and coworkers [30], analysing the properties of rod-shaped donor–acceptor systems, illustrated that fluorescence frequency of intermolecular exciplexes and excimers as well as intramolecular donor–acceptor systems is a linearly dependent on the value described by Eq. (1), namely on the value of $E_{\mathrm{ox}}(D) - E_{\mathrm{red}}(A)$. As it is shown in Fig. 2 such properties are also observed for compounds described in this paper. Fig. 2 clearly shows that the emitting states of the dyes are charge-transfer in character.

What is more, for tested compounds on varying of the solvent polarity, relatively strong shifts of the fluorescence maxima are observed [17,18,26]. Generally, we observed a positive solvatochromism in the emission (a redshift in the emission with increasing polarity of the solvents). The strong polarity dependence of the dye emission spectra [17,18,26] suggests that the

Table 1
The steady-state spectral properties of tested hemicyanine dyes in selected organic solvents

No.	λ^{A}_{max} (nm)[a]	λ^{A}_{max} (nm)[b]	λ^{Fl}_{max} (nm)[a]	λ^{Fl}_{max} (nm)[b]	$\Delta\nu$ (cm^{-1})[a]	$\Delta\nu$ (cm^{-1})[b]
A1B2	500	491.5	623	635	3950	4600
A2B2	501	504	611	633	3590	4040
A3B2	500	502	612	637	3660	4220
A4B2	501	503	611	638	3590	4210
A5B2	500	503.5	619	641	3845	4260
A6B2	504	503.5	627	653	3890	4550
A7B2	505	511.5	628	649	3880	4140
A8B2	530	535	639	661	3220	3560
C1B2	500	489	608	628	3550	4530
C2B2	501	501	606	624	3460	3930
C3B2	501	494	603	627	3380	4290
C4B2	501	497.5	614	629	3670	4200
C5B2	500	476	612	635	3660	5260
C6B2	502	497.5	623	652	3870	4760
C7B2	508	504.5	620	644	3560	4290
C8B2	527	526.5	628	656	3050	3750
SP1B2	469	479.5	596	621	4540	4750
SP2B2	484	484.5	588	619	3650	4485
SP3B2	479	480.5	600	625	4210	4810
SP4B2	482	479.5	599	625	4050	4855
SP5B2	462	461	606	626	5140	5720
SP6B2	474	484	615	643	4840	5110
SP7B2	488	489	611	637	4125	4750
SP8B2	495	511.5	631	651	4350	4190

[a] Measured in ethyl acetate.

[b] Measured in 1-methyl-2-pirrolidinon.

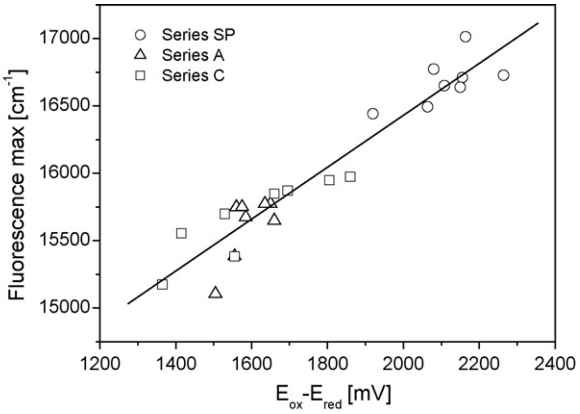


Fig. 2. Fluorescence frequency of compound tested vs. $E_{ox}(D) - E_{red}(A)$ in DMF.

energy of singlet state on which electron transfer from an electron donor occurs may be affected by polarity of an environment. This, in turn, may have an effect on the value of free energy change for electron transfer process predicted by Rehm–Weller equation [31]. Transferring this to the practical application of the electron transfer theory into photoinitiation, one may expect that photoinitiation ability of the photoredox pair can be strongly affected by the monomer polarity (besides of its reactivity).

It is well known that the main prerequisite for the electron transfer (PET) reaction, vital for free radicals formation, states that the thermodynamic driving force of the electron transfer reaction between the excited state of the dye cation and alkyltriphenylborate anion should have negative value. The free energy of activation for the PET (ΔG_{el}) process can be easily estimated on the basis of the Rehm–Weller [31] equation:

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

where $E_{ox}(D/D^{\bullet+})$ is the oxidation potential of the electron donor, $E_{red}(A^{\bullet-}/A)$ the reduction potential of the electron acceptor, E_{00} the excited state energy of electron accepting molecule, and $Ze^2/\varepsilon a$ is the Coulombic energy, which is the free energy gained by bringing the radical ions formed to an encounter distance "a" in a solvent with dielectric constant ε. This term, for products of analyzed reaction, is considered negligible with respect to the overall magnitude of the ΔG in the present system. Since the oxidation of the borate anion is irreversible, the oxidation potential of borate could not be precisely measured by electrochemical techniques [32]. However, the peak potential obtained by either cyclic or square wave voltammetry usually follow the same trend as those measured by kinetic methods [3,32]. Therefore, these can be used for the calculation of the ΔG. The measured oxidation potential of the tetramethylammonium *n*-butyltriphenylborate is estimated to be equal 1.17 V and reduction potentials measured for dyes are compiled in Table 2.

The measured values of the dyes reduction potentials, the electron donor (*n*-butyltriphenylborate anion) oxidation potential (E_{ox} = 1.17 V) and the singlet state energy of the dyes, allows one to calculate (using the Rehm–Weller equation (2)) the free energy change for the photoinduced intermolecular electron transfer process. The estimated data are summarized in Table 2.

Table 2
Electrochemical and thermodynamic properties of the asymmetric cyanine borates tested

No.	E_{red} (V)	E_{ox} (V)	E^{S}_{oo} (eV)[a]	E^{S}_{oo} (eV)[b]	ΔG_{el} (eV)[a]	ΔG_{el} (eV)[b]
A1B2	−0.76	0.890	2.19	2.14	−0.259	−0.213
A2B2	−0.735	0.900	2.17	2.22	−0.268	−0.315
A3B2	−0.81	0.750	2.17	2.22	−0.193	−0.240
A4B2	−0.8	0.785	2.18	2.20	−0.211	−0.234
A5B2	−0.96	0.830	2.19	2.23	−0.062	−0.098
A6B2	−0.725	0.850	2.14	2.18	−0.244	−0.286
A7B2	−0.825	0.730	2.13	2.14	−0.133	−0.144
A8B2	−0.765	0.740	2.11	2.12	−0.172	−0.183
C1B2	−0.94	0.920	2.23	2.26	−0.118	−0.146
C2B2	−0.735	1.070	2.19	2.23	−0.284	−0.327
C3B2	−0.67	0.990	2.19	2.24	−0.349	−0.400
C4B2	−0.91	0.785	2.19	2.21	−0.112	−0.128
C5B2	−0.78	0.750	2.19	2.24	−0.242	−0.294
C6B2	−0.86	0.695	2.22	2.21	−0.186	−0.178
C7B2	−0.915	0.500	2.16	2.19	−0.077	−0.104
C8B2	−0.89	0.475	2.12	2.14	−0.065	−0.079
SP1B2	−0.405	1.859	2.24	2.33	−0.667	−0.751
SP2B2	−0.54	1.616	2.24	2.29	−0.528	−0.584
SP3B2	−0.63	1.478	2.23	2.28	−0.434	−0.483
SP4B2	−0.615	1.549	2.23	2.30	−0.443	−0.513
SP5B2	−0.635	1.429	2.25	2.30	−0.449	−0.495
SP6B2	−0.595	1.485	2.19	2.24	−0.422	−0.479
SP7B2	−0.65	1.500	2.19	2.25	−0.370	−0.430
SP8B2	−0.605	1.315	2.13	2.19	−0.355	−0.414

ΔG: calculated using the Rehm–Weller equation; B2: $E_{ox}(D/D^{\bullet+})$ = 1.170 V.
[a] Measured in 1-methyl-2-pirrolidinon.
[b] Measured in ethyl acetate.

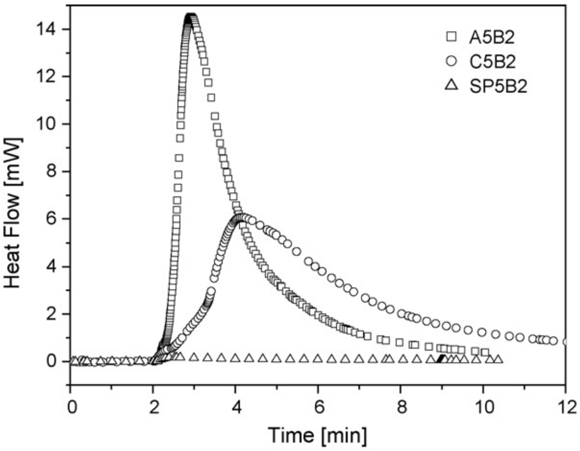


Fig. 3. Family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA/MP (9/1) mixture initiated by asymmetric cyanine borates marked in the figure. The dye concentration was 7.5×10^{-4} M, $I_a = 30$ mW/cm^2. The applied dyes possessed various chromophores and identical borate.

The values of ΔG_{el} for tested photoinitiating systems oscillate in the range from −0.062 to −0.751 eV. The calculations clearly show that for the tested photoredox pairs the electron transfer process is thermodynamically allowed. This, in turn, allows to predict that the tested dyes in combination with borate anion should effectively generate free radical that can start polymerization of acrylic monomers.

3.2. Kinetics study of multifunctional acrylates polymerization

The kinetic curves obtained for the photoinitiated polymerization of TMPTA-MP (9:1) mixture recorded for selected hemicyanine borate salts, under irradiation with a visible light laser, are shown in Fig. 3 for illustration. The rates of photoinitiated polymerization measured for all the tested photoredox pairs are collected in Table 3.

It is apparent from the inspection of the initial rates of polymerization that the efficiency of the tested photoinitiators depends strongly on their structure. The highest rates of photoinitiated polymerization were observed for the bis-chromophoric dyes possessing xylene moiety as the spacer separating hemicyanine chromophores.

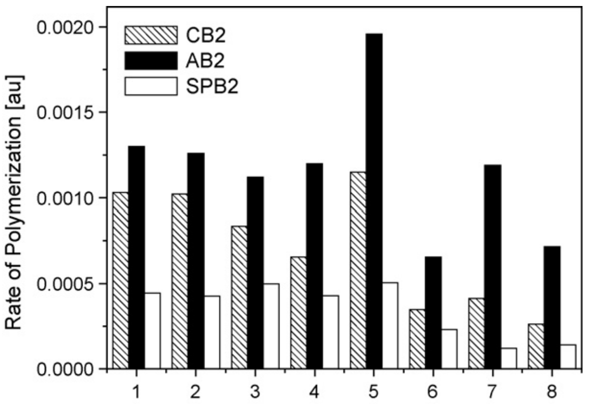


Fig. 4. Comparison of photoinitiating efficiency for visible photoinitiating systems under the study. The cyanine borate concentration was 1×10^{-3} M, $I_a = 64$ mW/cm^2. The type of photoinitiator is marked in figure.

Additionally, it was found that the photoinitiation efficiency of the tested hemicyanine borates depends on a character of dialkylamino substituent in electron donating part of molecule. The best photoinitiating abilities exhibit the photoredox pairs possessing dimethyl- (A1, C1, SP1), diethyl- (A2, C2, SP2) and “cyclic” (A5, C5, SP5) amino substituents in the dye molecule. Generally, the initiators with electron-donating groups for which the free rotation is possible indicate higher rate of heat evolution (slop of the linear part of kinetic curve at its initial time of reaction) in comparison to the dyes possessing a stiffened dialkylamino group (see data in Table 3 and Fig. 4).

3.3. Influence of initiator concentration

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 ‘inner filter effect’ and becomes more significant for photoinitiators with high molar extinction coefficient (for tested hemicyanine borate salts ε is reaching value of 4×10^4 M^{-1} cm^{-1}) [17,18,26].

Fig. 5 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 photoinitiators.

Table 3
Rate of free radical polymerization of TMPTA for tested photoinitiators

No.	Relative rate of polymerization	Rate of polymerization (μmol/s)	No.	Relative rate of polymerization	Rate of polymerization (μmol/s)	No.	Relative rate of polymerization	Rate of polymerization (μmol/s)
A1B2	3.38	2.79	C1B2	3.15	2.21	SP1B2	2.31	0.95
A2B2	3.35	2.71	C2B2	3.14	2.19	SP2B2	2.27	0.92
A3B2	3.23	2.41	C3B2	2.94	1.79	SP3B2	2.43	1.07
A4B2	3.30	2.58	C4B2	2.99	1.41	SP4B2	2.27	0.92
A5B2	3.53	4.21	C5B2	3.26	2.47	SP5B2	2.44	1.09
A6B2	2.79	1.41	C6B2	2.10	0.75	SP6B2	1.65	0.81
A7B2	3.29	2.56	C7B2	2.24	0.89	SP7B2	1.00	0.87
A8B2	2.78	1.54	C8B2	1.77	0.56	SP8B2	1.15	0.60

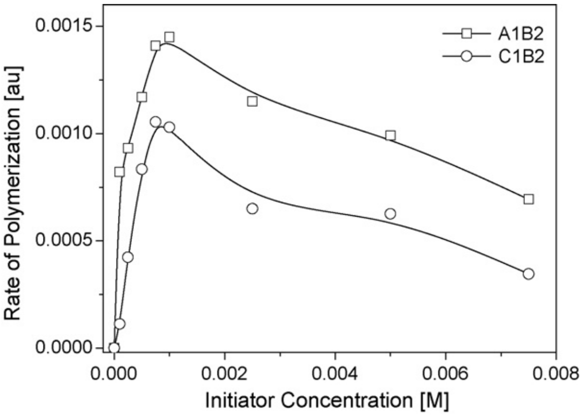


Fig. 5. Rate of polymerization vs. photoinitiator concentration (type of the dye marked in figure).

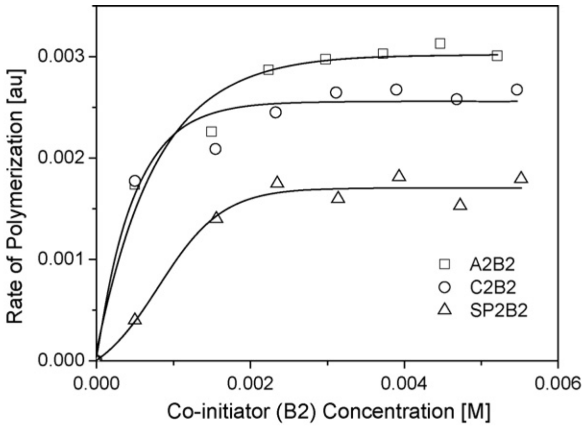


Fig. 6. Dependence of the rate of photoinitiated polymerization on the concentration of the electron donor (B2). The initial dye–borate complex concentration was 1×10^{-3} M.

It is evident that as the photoinitiator concentration is increasing, the initial rate of polymerization increases and reaches a maximum followed by continuous mild decrease. For the tested photoinitiators, the highest rates of polymerization for 2 mm thick sample (Fig. 5) were 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 be easily understood taking into account the decrease of the penetration depth of the laser beam [33].

3.4. *Influence of co-initiator concentration*

The mechanism of photoinitiation, consistent with Schuster et al. [34] observations for cyanine–alkyltriarylborate complex has been previously suggested [35]. Electron transfer from the borate anion to the excited state of chromophore (being either in singlet or triplet excited state) leads to the formation of cyanine radical and boranyl radical, which rapidly decomposes producing an alkyl radical. The latter is the most likely initiator of the polymerization of acrylates.

The classical Schuster's photoinitiating systems apply as chromophore cyanine dyes that do not form long-lived triplet state. Since the lifetime of cyanine singlet is short (piocoseconds time scale), an efficient electron transfer between borate anion and an excited dye molecule is possible only in non-polar solvent where the process can occur between components of the tight-ion pair [4,36]. The intra-ion-pair electron transfer rates from borate to an excited state of cationic acceptor are anticipated to be above the diffusion limit. Unfortunately, the efficiency of tight-ion-pair formation is high only in really non-polar solvents such as benzene. Even small amount of polar solvent, as documented by Neckers, may sharply change a degree of such ion-pair formation [5]. In polymerizing mixture (acryletes; medium polarity solvent), the photoinitiating photoredox pair composed of cyanine cation and borate anion exists as tight-pair and solvent-separated ions. This fact was confirmed experimentally, firstly by an investigation of the influence of borate anion concentration on the efficiency of photoinitiation and secondly by fluorescence quenching experiments.

The studies on the influence of the borate concentration on the rate of photoinitiated polymerization indicate, that for identical monomer-dye formulation, a distinct increase in the rate of polymerization is observed as the concentration of borate anion increases. Fig. 6 illustrates this relationship.

On the basis of this experiment, it appears that at the concentration of borate anion equal to the concentration of asymmetric cyanine cation, only a part of the photoredox pairs exist as the ion pair. Analysis of the data presented in Fig. 6 indicates that for monochromophoric initiating system only about 20% and for bischromophoric photoredox couples about 55% exist as ion pair at the concentration of the dye equal 1×10^{-3} M. These values give an equilibrium constant equal 3×10^{-3} M and 3×10^{-4} M for mono- and bischromophoric dyes, respectively. The differences in both dissociation constants and degree of dissociations seems to be obvious because in the case of the dimeric dyes there are two donor molecules in close neighborhood to an excited chromophore that causes an increase of the formation of free radical starting polymerization chain reaction.

The supporting experiments that can clarify the presence of both dissociated and undissociated forms of the tested initiators may come from the fluorescence quenching experiments (Fig. 7).

The absorption spectra measurements show that the exchange of iodide or bromide anion on borate has no effect on the electronic absorption spectra. Thus, if there is a certain contribution of a ground state equilibrium between hemicyanine cation and borate anion leading to the formation of a non-fluorescence ion pair, then the evidence for the ground state ion pair formation may come from the fluorescence intensity quenching measurements. To estimate the contribution of the quenching deriving from the ground state ion pair (static quenching, K_S) and diffusion controlled quenching (dynamic quenching, $K_D = k_q \times \tau^0$) terms, the fluorescence quenching data for the selected dye–borate pairs were analyzed by combining of both effects that can be described by the following equation [37,38]:

$$\frac{I_f^0}{I_f} = (1 + K_D[Q]) \times (1 + K_S[Q]) \tag{3}$$

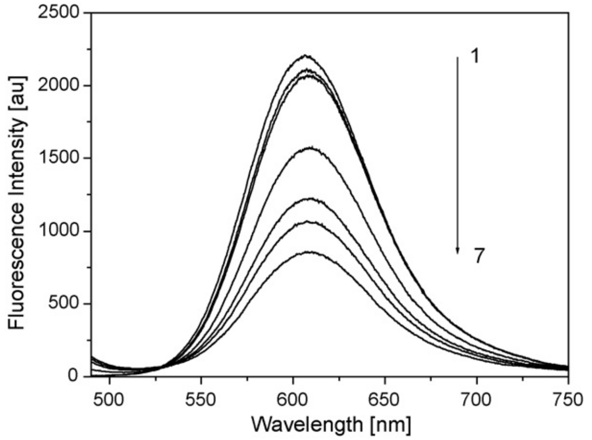


Fig. 7. Fluorescence spectra of dye C2 in presence of tetra-methylammonium *n*-butyltriphenylborate (B2) in ethyl acetate. Concentration of the dye was 1×10^{-5} M. Concentration of borate salt: (1) 0; (2) 0.8×10^{-3}; (3) 1.1×10^{-3}; (4) 3.0×10^{-3}; (5) 4.0×10^{-3}; (6) 4.8×10^{-3}; (7) 5.4×10^{-3} M.

where

$$K_S = \frac{[HC^+ \ldots Bo^-]}{[HC^+] \times [Bo^-]} \tag{4}$$

The result of such a treatment allows to separate both type of quenching and calculate the K_S value. The steady-state fluorescence quenching data for both C2B2 and SP2B2 in the presence of *n*-butyltriphenylborate (B2) (Fig. 8) lead 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.

The data recorded for the quenching measurements obtained for C2B2 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 a linear relationship for tested photoredox pairs indicate that the quenching of fluorescence occurs by both dynamic and static mechanism. Thus, we infer that the dye cation and the electron donor anion form the ground state complex, namely the ground state ion pair. In that case K_S can be identified with the association constant of the complex. All these discussed properties show that over the borate concentration range studied in the described above experiments, the fraction of hemicyanine borate present as ion pairs in ethyl acetate significantly varied. It is noteworthy that only the unassociated hemicyanine cations fluorescence, there is no (or very little) fluorescence from the cyanine borate ion pair [34,36]. From the Stern–Volmer relationship obtained for both A2B2 and SP2B2 pairs one can calculate, based on Eqs. (3) and (4), the dissociation constant of these pairs. 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 A2B2 photoredox pair this parameter is equal 17.3 M^{-1} whereas for SP2B2 photoredox pair this parameter is equal 38.8 M^{-1}. The introduction of this value into Eq. (4) gives K_S equal 10,062and 2185 M^{-1}, respectively and this, in turn, allows calculating a degree of dissociation equal 82.4% and 48.5% (SP2B2 and A2B2 dissociation constants equal $K = 3.9 \times 10^{-3}$ M and 4.5×10^{-4} M, respectively). The presented above analysis clearly shows that some part of hemicyanine borate salts probably exist in a monomeric formulation in dissociated form, namely as separated ions pair.

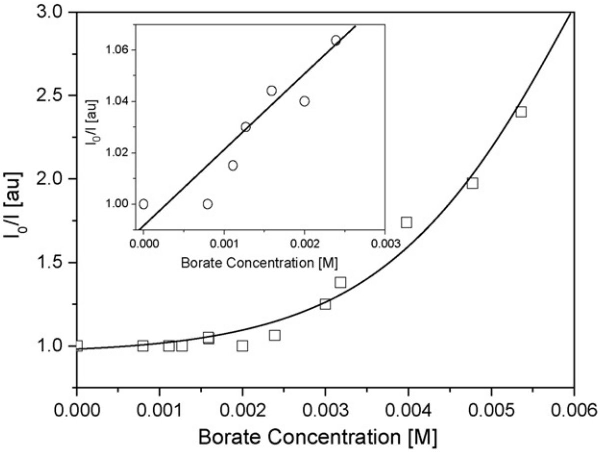


Fig. 8. Stern–Volmer plot for quenching of fluorescence of C2B2 by tetra-methylammonium *n*-butyltriphenylborate (B2) in ethyl acetate. *Inset*: the Stern–Volmer plot for low-borate concentration.

Obtained using the fluorescence methodology data are in excellent agreement with the results obtained from the analysis of the rate of polymerization versus donor concentration relationship (Fig. 6).

Since the electron transfer for cyanine dyes occurs on their singlet state, the existence of cyanine cation and borate anion as ion pair is the basic prerequisite for the effective electron transfer. The additional amount of borate cation shifts the equilibrium between free ions–ion pair to the higher concentration of ion pair. That is why the presence of the additional amount of the co-initiator causes an increase of the photoinitiation efficiency.

It seems to be obvious that in the case of bischromophoric dyes the concentration of electron donor in proximity to each single chromophore is increased because of the presence of neighboring second chromophore that couples electron donor. It is also obvious that under continues laser irradiation (relatively low light intensity) only one chromophore from bischromophoric system can be excited. Under these circumstances the excited molecule can be quenched by both, its own coupled electron donor or by a donor that is associated with its dimeric partner. Namely, such organization of electron donor artificially increases a concentration of electron donor in proximity to an excited molecule. This, in turn, should substantially increase the rate of singlet excited state quenching, causing, in effect, an increase in efficiency of free radical formation. Our experiments confirmed this suggestion (see data presented in Fig. 4 and collected in Table 3).

3.5. Influence of thermodynamics parameter

As was previously reported for the alkyltriphenylborates, [3,34,36] the rates of alkyl radical formation, as the result of the boranyl radical decomposition, are directly related to the stabilities of the alkyl radicals formed. Since the decay of the boranyl radical is found to be very fast and irreversible, the rate of back electron transfer is negligible [3]. Therefore, the efficiencies of alkyl radical formation and, hence, initiation of polymerization depend on the observed efficiency of electron transfer from the borate anion to the singlet state of cyanine molecule.

The Marcus theory [16] allows to predict the rate of the primary process, e.g. the rate of photoinduced electron transfer process. The use of cyanine borates creates a unique opportunity to study the possibility of the application of this theory for the description of the rate of polymerization *via* an intermolecular electron transfer process. For these dyes the change of the driving force of the electron transfer process has no influence on the type of the yielding free radical.

In our earlier papers [39,40] we have shown that in the very viscous media, the rate of polymerization initiated *via* a photoinduced intermolecular electron transfer can be described as follows:

$$\ln R_\mathrm{p} = A - \frac{(\lambda + \Delta G_\mathrm{el})^2}{8\lambda RT} \qquad (5)$$

where A for the initial time of polymerization is the sum: $\ln k_\mathrm{p} - 0.5 \ln k_\mathrm{t} + 1.5 \ln [\mathrm{M}] + 0.5 \ln I_\mathrm{a}$ (here k_p, k_t denote the rate constant of polymerization and termination, respectively, [M] the monomer concentration, and I_a is intensity of absorbed light), λ is the reorganization energy necessary to reach the transition states both of excited molecule and solvent molecules.

Eq. (5) clearly indicates that if the primary process, e.g. the rate of electron transfer process controls the observed rate of photopolymerization, one should observe a parabolic relationship between the logarithm of polymerization rate and the free energy change ΔG_el. For the photoinitiating photoredox pairs examined it is shown in Fig. 9.

It is apparent from the inspection of the relationships presented in Fig. 9 that the plot exhibits predicted by Marcus or more likely by the Rehm–Weller [31] and Agmon–Levine [41] equations. Seems to be obvious that for the tested initiating photoredox pairs two independent curves should be observed; one for the monochromophoric and second for the bischromophoric dyes. According to Fig. 9, the rate of free radical polymerization initiated by the series of hemicyanine borates increases as the driving force of the electron transfer reaction increases. This behavior is predicted by the classical theory of photoinduced electron transfer [16,42].

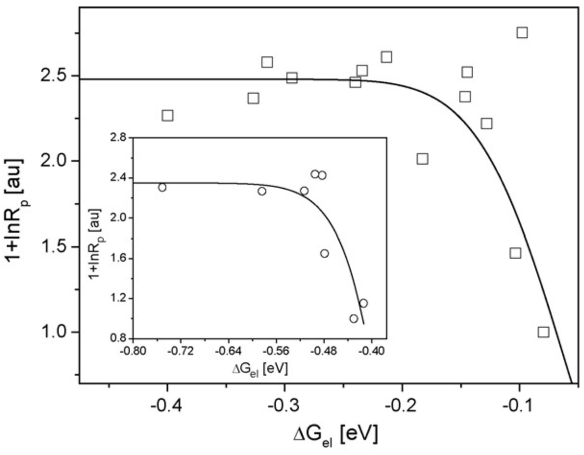


Fig. 9. Dependence of the rate of photoinitiated polymerization on the free energy (ΔG_el) for the photoinduced electron-transfer process from borate to the excited state of bischromophoric cyanine dye. *Inset*: dependence of $\ln R_\mathrm{p}$ vs. ΔG_el for monochromophoric cyanine–borate photoredox pairs.

3.6. Three components photoinitiating system

From the literature it is well known that the distance between the electron donor and the electron acceptor is quite important for the photoinduced electron transfer reaction, especially when the process occurs in the short-lived singlet excited state. In the case of cyanine borate salts the process is efficient in non-polar solvents in which the electron transfer occurs between components of a tight-ion pair [4]. Our study reveals that only about 50% of the tested photoinitiating pairs exists in polymerizing mixture as a tight-ion pair. What is more, a degree of dissociation is depending on concentration of solute in complex fashion. However, in the simple approximation a degree of dissociation is decreasing as concentration of solute is increasing (or a concentration of non-dissociated salt is enhancing when concentration of solute increases). That is why, the simplest way to increase the efficiency of polymerization process consists on adding an additional amount of co-initiator (B2) into polymerization mixture. The other way enhancing the rate of polymerization is to find consecutive reaction forming free radical. This can be achieve by adding to the polymerizating mixture second co-initiator, which is able to react with the dye free radical obtained from dye–borate electron transfer reaction.

In studied by our group [43] three component photoinitiating system composed of dye cation, borate anion and triazine it was documented that the presence of additional co-initiator do not enhance the concentration of the dye cation and borate anion ion pair.

Fig. 10 presents the kinetic traces recorded during an argon ion laser photoinitiated polymerization of TMPTA–MP (9:1) mixture in the presence of bischromophoric cyanine–borate

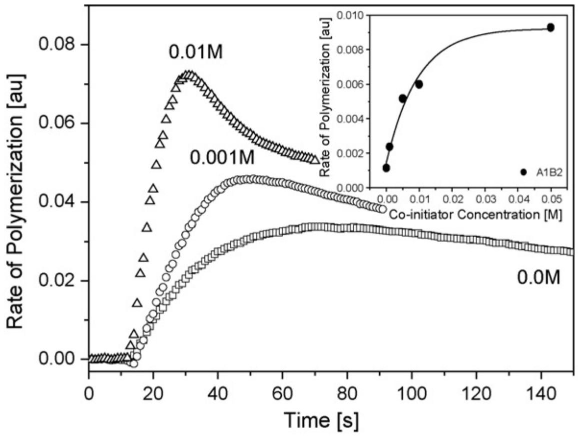


Fig. 10. Kinetic curves of the TMPTA/MP (9:1) mixture recorded during the measurements of the flow of heat during the photoinitiated polymerization initiated by asymmetric cyanine borate (A1B2) in the presence of different concentration (marked in the figure) of DFCT. *Inset*: The influence of the DFCT concentration on the rate of polymerization for A1B2 photoredox pair.

complex and functioning as additional co-initiator 2,4,6-tris(chlorodifluoromethyl)-*s*-triazine (DFCT).

As can be seen in Fig. 10, the photoinitiating system composed of hemicyanine borate and triazine much more efficiently initiates free radical polymerization of TMPTA in comparison to the photoinitiating systems composed of dye and borate anion exclusively. An addition into the initiating mixture of an unimolar amount of triazine increases the rate of polymerization at least twice.

In the literature, there are known photoinitiating systems possessing cyanine dye, which yield dye free radicals able to the initiate a reductive cleavage of 2,4,6-tris(trichloromethyl)-*s*-triazine (TCT) [44,45]. The formation of radical starts from an electron transfer from the cyanine dye radical to the ground state of TCT, yielding a TCT radical anion. Subsequently, a TCT radical anion decomposes, by cleavage of the C–Cl bond, to give a starting polymerization dichloromethylenetriazine radical and a chlorine anion [44,45].

The photoinitiating system being the mixture of dye cation–borate anion pair and triazine exhibits higher photoinitiation ability in comparison to the ability presented by dye cation–borate anion pair.

4. Conclusion

Presented paper is focused on photoinitiation of free radical polymerization initiated by photoreducible dye sensibilization. Three different groups of hemicyanine *n*-butyltriphenylborate salts were employed as visible-light photoinitiators of vinyl monomers polymerization. They were examined in order to verify the possibility of the Marcus equation application for the description of the kinetics of free radical polymerization photoinitiated *via* the photoinduced electron transfer process (PET). The kinetics of polymerization of trimethylolpropane triacrylate, using hemicyanine borates as photoinitiators, was studied by microcalorimetric method. The experimental data revealed that:

(i) Hemicyanine borate salts are shown to be effective photoinitiators for the polymerization of vinyl monomers when irradiated with the visible emission of an argon-ion laser.
(ii) The efficiency of the polymerization depends on the structure of the hemicyanine cation used as an electron acceptor. The resulting bischromophoric hemicyanine dyes paired with *n*-butyltriphenylborate anion (series: AB2 and CB2), are shown to be more efficient photoinitiators of free radical polymerization in comparison to the identical series of the single-chromophore dyes.
(iii) The inspection of the initial rates of polymerization showed that that both initiator and co-initiator concentration affects the rates of photopolymerization.
(iv) The free energy change (ΔG_{el}) of the electron transfer process between an excited acceptor and a donor were experimentally determined for 24 organic photoredox pairs.
(v) The relationship between the rate of polymerization and the free energy change (ΔG_{el}) displays typical Marcus kinetic behavior. This relation is independently observed for mono- and bischromophoric hemicyanine borate salts.
(vi) The bischromophoric cyanine dyes were found to be potentially very useful as a visible light sensitizers in the multi-components photoinitiation system.

Acknowledgement

This work was supported by the State Committee for Scientific Research (KBN) (grant no. 3 T09B 101 28).

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