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Styrylbenzimidazolium dye–borate complex as an effective, singlet state photoinitiator in an argon laser-induced TMPTA photopolymerization

Beata Jędrzejewska*, Marcin Tur[1], Jerzy Pączkowski

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

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ABSTRACT

Dye photoinitiators consisting of styrylbenzimidazolium cations, 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 efficiency of tested systems depends on the ΔG_{el} of electron transfer between borate anion and hemicyanine cation. The latter value was experimentally determined for 9 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. The kinetic studies clearly demonstrated that the styrylbenzimidazolium borate photoredox pairs are very promising photoinitiators for multiacrylates free radical polymerization. They initiate the polymerization reaction with the efficiency comparable to RBAX, Rose Bengal derivative, common triplet state initiator.

1. Introduction

Over the last 25 years, radiation curing science and technology has grown from a laboratory research subject into a major industrial development and is now a field of central importance in polymer science and technology. Applications include resists, paper, wood and metal coatings, dentistry, imaging science and printing. Inherent in these technologies is the use of a photoactivator system which is capable of absorbing the incident UV and/or visible radiation wavelengths employed for converting a monomer or prepolymer system into a crosslinked network [1–5].

In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiator molecules with more desirable properties, such as higher activity coupled with greater speed and a low migration rate to the surface of the cured coating in order to reduce loss of adhesion and to minimize toxicity where food contact is important. One area of importance in this regard is the development of photoinitiators having great spectral sensitivity to the visible region of the spectrum [6]. These initiators absorb visible light with a high speed and cause the same photopolymerization events described above to take place—namely a conversion of a highly functionalized liquid acrylate monomer to a solid polyacrylate. In practice, most monomers used in fast photoinitiated polymerization are acrylates or modified acrylates whose structure lends to rapid crosslinking. Some of the photoinitiators have been widely discussed in the literature for they are the backbone of the photopolymerization. In one such process, the initiators are cyanine borate ion salts, so-called ion pair initiators, which utilize single electron transfer to the excited state of the light absorbing dye from the partner ion acting as electron donors, starting the crucial first step in the initiation of the radical chain. Thus, the cyanine dye, in its excited state, accepts an electron from the partner borate and subsequent boranyl radical chemistry initiates polymerization [7]. The photochemistry of different cyanine borate salts in photoinitiated free radical polymerization was first described by Schuster [8] and later by Zhang [9] and by our research group [10–14].

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 [15] 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

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

[1] Master degree student of University of Technology and Life Sciences.

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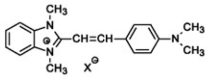
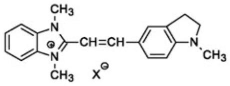
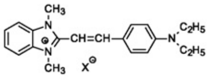
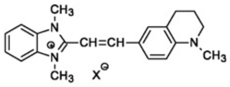
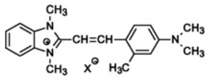
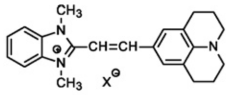
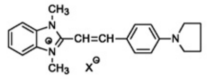
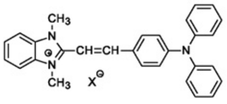
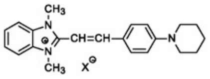
Structure	Denotation		Structure	Denotation	
	X=I	X=n-$C_4H_9B(C_6H_5)_3$		X=I	X=n-$C_4H_9B(C_6H_5)_3$
	**BI1**	**BI1B2**		**BI6**	**BI6B2**
	**BI2**	**BI2B2**		**BI7**	**BI7B2**
	**BI3**	**BI3B2**		**BI8**	**BI8B2**
	**BI4**	**BI4B3**		**BI9**	**BI9B2**
	**BI5**	**BI5B2**			

Chart 1. Monocationic hemicyanine salts tested as photoinitiators for free radical polymerization of vinyl monomers.

description of the kinetics of the photoinitiated polymerization *via* intermolecular electron-transfer process is one more example applying this theory to technological practice.

In this paper, we describe the kinetic studies of the novel photoinitiating systems consisting of different styrylbenzimidazolium dyes (the light absorbers) coupled with butyltriphenylborate anions (co-initiators). Additionally, it is 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) and ethyl acetate (EtOAc) were purchased from Aldrich Chemical Co. and were used without further purification. Dye photoinitiators were synthesized in our laboratory using procedures described in the literature [12].

The molecular structure and denotations of the dyes under the study are given in Chart 1. n-Butyltriphenylborate tetramethylammonium salt (TB2) was synthesized based on the method described by Damico [16]. The ion-exchange reaction was performed using the procedures given by Damico [16] and Murphy et al. [17]. 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.

2.2. Techniques

2.2.1. Spectral measurements

The UV–vis absorption spectra were recorded with a Shimadzu UV-vis Multispec-1501 spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. The fluorescence measurements were performed at an ambient temperature. The fluorescence lifetimes were measured using an Edinburgh Instruments (FLS920P Spectrometers). The apparatus utilizes for the excitation a picosecond diode laser generating pulses of about 55 ps at 375 nm. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals with resolution in the range of single picoseconds possible. The dyes were studied at concentration able to provide equivalent absorbance at 375 nm (0.2–0.3 in the 10 mm call) to be obtained.

2.2.2. Electrochemical measurements

The reduction potentials of the dyes (BI1-BI9) and the oxidation potential of tetramethylammonium n-butyltriphenylborate (TB2) were measured by cyclic voltammetry using an Electroanalytical Cypress System Model CS-1090. The typical three-electrode setup was employed for electrochemical measurements. The electrolyte was 0.1 M tertrabutylammonium perchlorate, which was purged with argon prior to a measurement. Platinum 1 mm electrode was applied as working electrode and platinum and Ag/AgCl were used as auxiliary and reference electrodes, respectively.

2.2.3. Polymerization measurements

The kinetics of free radical polymerization was studied using a polymerization solution composed of 1 mL of 1-methyl-

2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The styrylbenzimidazolium borate (photoinitiator) concentration was 7.5×10^{-3} M. A reference formulation contained styrylbenzimidazolium iodide or bromide (dye without an electron donor; e.g. BI1) instead of styrylbenzimidazolium borate salt (photoinitiator). The polymerizing mixture was not deaerated before curing.

The kinetics of free radical polymerization were measured based on the measurements of the rate of the heat evolution during polymerization in thin film cured sample (0.035 ± 0.002 g). The measurements were performed by measuring photopolymerization exotherms using photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. Irradiation of the polymerization mixture was carried out using the emission (line at 488 nm) of an argon-ion laser Model Melles Griot 43 series with intensity of light of 20 mW/0.196 cm^2. The light intensity was measured by a Coherent Model Fieldmaster power meter.

The rate of polymerization (R_p) was calculated using the formula (1) where dH/dt is maximal heat flow during reaction and $\Delta H_p^{\text{theor}}$ is the theoretical enthalpy for complete conversion of acrylates' double bonds. $\Delta H_p^{\text{theor}}$ for acrylic double bond is equal 78.2 kJ/mol [18]

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

3. Results and discussion

3.1. Spectroscopic and photophysical properties of hemicyanine derivatives

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

All salts possess similar absorption spectra with two maxima at about 300 and 430 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 varying of the solvent polarity, red shifts of the CT absorption maxima are observed. 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.

Tested photoinitiators represent monochromphoric molecules that show large Stokes shift (ranging from 4000 to 8000 cm^{-1} depending on the solvent polarity and the dye structure). 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-π-A molecules may change with the solvent [19] 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 [19] or may be controlled by the viscosity of the medium [20].

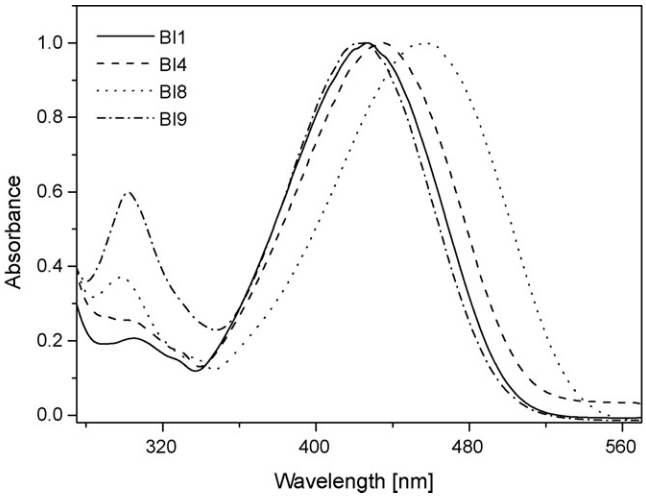


Fig. 1. Normalized electronic absorption spectra of selected hemicyanine dyes (marked in Figure) in MP.

Theoretically [21] the energy level of the molecule excited CT state, relative to its ground state can be expressed by Eq. (2), where $E_{\text{ox}}(\text{D})$ and $E_{\text{red}}(\text{A})$ 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

$$E_{\text{CT}} = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) + C \qquad (2)$$

Verhoeven [22], 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 linearly dependent on the value described by Eq. (2), namely on the value of $E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A})$. 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 weak shifts of the fluorescence maxima are observed. Generally, we observed a positive solvatochromism in the emission (a red shift in the emission with increasing polarity of the solvents). The polarity dependence of the dye electronic absorption and emission spectra suggests that the 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

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

No	$\lambda_{\text{max}}^{\text{A}}$ [nm]^a	$\lambda_{\text{max}}^{\text{A}}$ [nm]^b	$\lambda_{\text{max}}^{\text{Fl}}$ [nm]^a	$\lambda_{\text{max}}^{\text{Fl}}$ [nm]^b	$\Delta\nu$ [cm^{-1}]^a	$\Delta\nu$ [cm^{-1}]^b
BI1B2	399	409	543	546	6646	6135
BI2B2	412	424	542	545.6	5822	5256
BI3B2	402	428	549	552.2	6661	5255
BI4B2	414	427	541	548.4	5670	5184
BI5B2	404	416	549	551.6	6538	5909
BI6B2	421	429	562.6	564	5978	5580
BI7B2	415	430	553	555.4	6013	5251
BI8B2	452	457	564	569	4393	4307
BI9B2	416	422	600	623	7372	7645

$\Delta\nu$ – Stokes shift.

[a] Measured in ethyl acetate.

[b] Measured in 1-methyl-2-pyrrolidinone

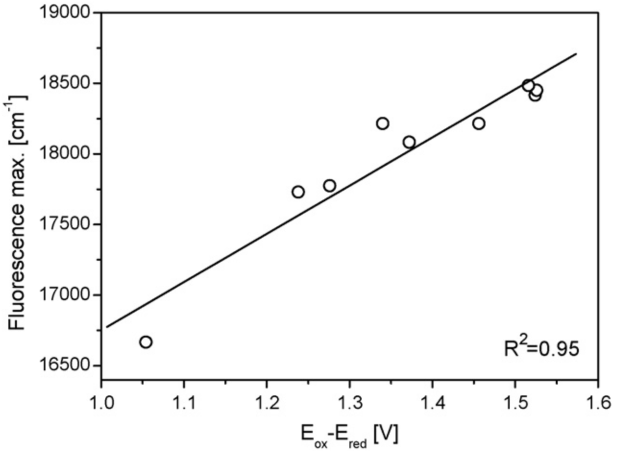


Fig. 2. Fluorescence frequency of styrylbenzimidazolium dyes under the study versus $E_{ox}(D) - E_{red}(A)$ in EtOAc.

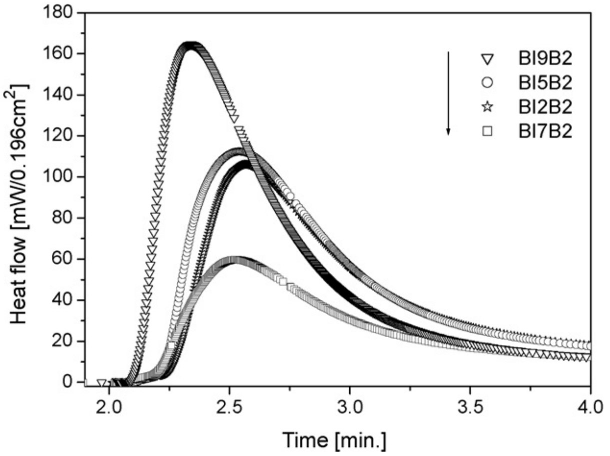


Fig. 3. Family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA-MP (9:1) mixture initiated by asymmetric cyanine borates marked in the Figure. The dye concentration was 7.5×10^{-3} M, $I_a = 100\,\text{mW/cm}^2$. The applied dyes possessed various chromophores and identical borate.

for electron-transfer process predicted by Rehm-Weller equation [23].

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 [23] equation:

$$\Delta G_{el} = E_{ox}\left(\frac{D}{D^{\bullet +}}\right) - E_{red}\left(\frac{A^{\bullet -}}{A}\right) - \frac{Ze^2}{\varepsilon a} - E_{00} \qquad (3)$$

where $E_{ox}(D/D^{\bullet +})$ is the oxidation potential of the electron donor, $E_{red}(A^{\bullet -}/A)$ is the reduction potential of the electron acceptor, E_{00} is the excited state energy of electron accepting molecule, and $Ze^2/\varepsilon a$ is the Coulombic energy, which is the free energy gained by bringing the radical ions formed to an encounter distance "*a*" in a solvent with dielectric constant ε. This term, for products of analyzed reaction, is considered negligible with respect to the overall magnitude of the ΔG_{el} 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 [24]. However, the peak potential obtained by either cyclic or square wave voltammetry usually follow the same trend as those measured by kinetic methods [24,25]. Therefore, these can be used for the calculation of the ΔG_{el}. The measured oxidation potential of the tetramethylammonium *n*-butyltriphenylborate is estimated to be equal 1.14 V and reduction potentials measured for the dyes, the singlet state energy of the dyes and the free energy change for the photoinduced intermolecular electron-transfer process are compiled in Table 2.

The values of ΔG_{el} for tested photoinitiating systems oscillate in the range from −0.845 eV to −1.106 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 vinyl 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 rates of polymerization that the efficiency of the tested photoinitiators depends strongly on their structure. 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 diphenyl- (BI9), dimethyl- (BI1) and "cyclic" (BI4, BI5) amino substituents in the dye molecule. Generally, the initiators with electron-donating groups for which the free rotation between benzene ring carbon and nitrogen of N-alkylamino group is possible

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

No	E_{red} [V]	E_{ox} [V]	E_{00}^S [eV][a]	E_{00}^S [eV][b]	ΔG_{el} [eV][a]	ΔG_{el} [eV][b]
BI1B2	−0.468	1.056	2.490	2.570	−0.886	−0.966
BI2B2	−0.456	1.07	2.469	2.534	−0.877	−0.942
BI3B2	−0.512	0.826	2.460	2.539	−0.812	−0.891
BI4B2	−0.426	1.09	2.469	2.549	−0.907	−0.987
BI5B2	−0.434	1.022	2.469	2.539	−0.899	−0.969
BI6B2	−0.414	0.862	2.413	2.408	−0.863	−0.858
BI7B2	−0.444	0.928	2.434	2.491	−0.854	−0.911
BI8B2	−0.412	0.826	2.390	2.393	−0.842	−0.845
BI9B2	−0.316	0.738	2.479	2.558	−1.027	−1.106

ΔG_{el} – calculated using the Rehm-Weller equation; E_{red} – measured for dyes as iodide salts (BI1–BI9); E_{ox} – measured for tetramethylammonium n-butyltriphenylborate TB2: $E_{ox}(D/D^{\bullet -}) = 1.14\,\text{V}$.

[a] Measured in 1-methyl-2-pyrrolidinone.

[b] Measured in ethyl acetate.

Table 3
Rate of free radical polymerization of TMPTA and the rate constant of electron-transfer process for tested photoinitiators.

No	$\mathrm{d}H/\mathrm{d}t$[a] [mW]	R_p [μmol/s]	$1 + \ln R_p$	$k_q \approx k_{el}$ [$M^{-1}\,s^{-1}$]
BI1B2	164.4	2.10	2.98	9.22E+10
BI2B2	106.8	1.37	2.55	8.67E+10
BI3B2	58.99	0.75	1.95	8.12E+10
BI4B2	126.0	1.61	2.71	8.89E+10
BI5B2	120.3	1.54	2.67	8.99E+10
BI6B2	37.55	0.48	1.50	8.20E+10
BI7B2	64.51	0.82	2.04	8.27E+10
BI8B2	22.71	0.29	1.00	7.57E+10
BI9B2	216.4	2.77	3.25	1.53E+10

[a] Maximal heat flow during reaction.

indicate higher rate of heat evolution in comparison to the dyes possessing a stiffened dialkylamino group (see data in Table 3).

As Fig. 4 shows, the photoinitiation capability observed for selected styrylbenzimidazolium borate photoredox pairs (singlet state photoinitiators) is comparable to the Rose Bengal based initiation system (triplet state photoinitiator [26]).

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 $4 \times 10^4\ M^{-1}\,cm^{-1}$) [12,19].

Fig. 5 presents the relationship between the rate of polymerization and photoinitiator concentration.

It is evident that as the photoinitiator concentration is increasing, the rate of polymerization increases and reaches a maximum followed by continuous mild decrease. For the tested photoinitiators, the highest rates of polymerization for 1 mm thick sample (Fig. 5) were achieved at the initiator concentration of about 7.5×10^{-3} M. This is the typical behavior observed for all photoinitiating systems attributed to the decrease of the penetration depth of the laser beam in cured sample as concentration of a photoinitiator increases [2,7,9].

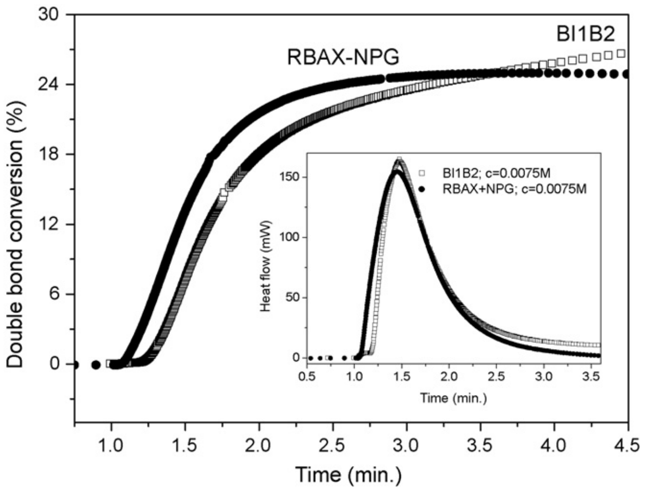


Fig. 4. Comparison of the photoinitiation ability of styrylbemzimidazolium borate (BI1B2) salt (7.5×10^{-3} M) and RBAX-NPG (7.5×10^{-3} M) photoinitiating systems. RBAX – Rose Bengal derivative (triplet state photoinitiator) [26]; $I_a = 100\ mW/cm^2$.

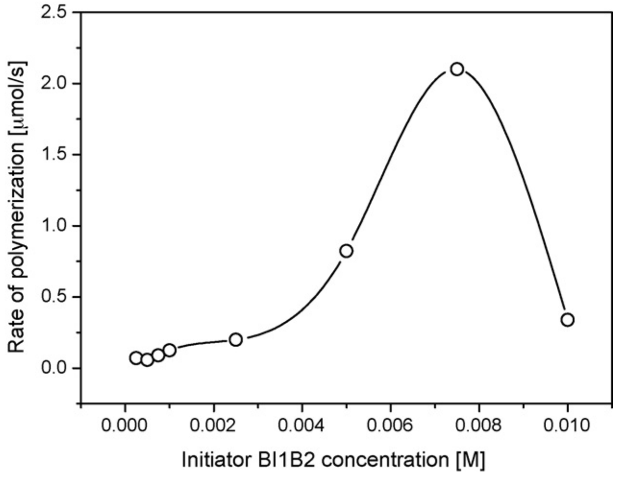


Fig. 5. Rate of polymerization versus photoinitiator BI1B2 concentration.

3.4. Influence of co-initiator concentration

The mechanism of photoinitiation, consistent with Schuster et al. [8,24] observations for cyanine–alkyltriarylborate complex has been previously suggested [8,10]. 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 the most likely starts 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 (typical lifetime about or less than 1 ns), an efficient electron transfer between borate anion and an excited dye molecule is possible only in nonpolar solvent where the process can occur between components of the tight-ion-pair [8,24,27]. The ion pair electron-transfer rates from borate to an excited state of cationic acceptor are anticipated to be above the diffusion limit [24]. Unfortunately, the efficiency of tight-ion-pair formation is high only in really nonpolar solvents such as benzene. Even small amount of polar solvent, as documented by Neckers, may sharply change a degree of such ion pair formation [28]. In polymerizing mixture (acrylates; medium polarity solvent), the photoinitiating photoredox pair composed of cyanine cation and borate anion exists as tight-pair and solvent separated ions. This fact was confirmed experimentally, firstly by an investigation of the influence of borate anion concentration on the efficiency of photoinitiation and secondly by fluorescence quenching experiments.

The studies on the influence of the borate concentration on the rate of photoinitiated polymerization indicate, that for 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 about 71.5% exist as ion pair at the concentration of the dye equal 7.5×10^{-3} M. These values give an equilibrium constant equal 8.56×10^{-4} M for styrylbenzimidazolium borate salts. The dissociation equilibrium constant (K) was calculated based on the following equation

$$K = \frac{[HC^+][Bo^-]}{[HC^+ \cdots Bo^-]} = \frac{\alpha^2 c}{1 - \alpha} \tag{4}$$

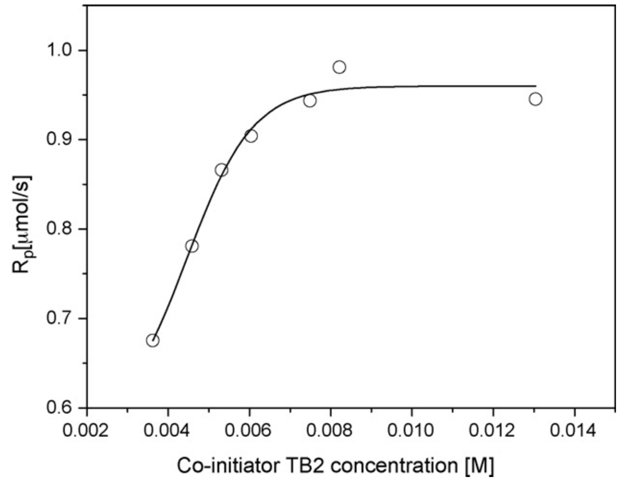


Fig. 6. Dependence of the rate of photoinitiated polymerization on the concentration of the electron donor (TB2). The initial dye–borate complex BI2B2 concentration was 7.5×10^{-3} M.

where α is the degree of dissociation of hemicyanine borate salt, and c is the molar concentration of the salt.

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.

Traditionally, if a quencher is added to the system, the quenching of an excited state is a simple diffusion-reaction. Another limiting condition exists in which the quencher exists in proximity to the excited state. In many systems intermediate situations are often observed. If the quenching molecule can form, for example, a contact ion pair with fluoresceing molecule, the plot of I_0/I_q may differ from predicted by Stern–Volmer linear relationship (I_0 is the fluorescence intensity of fluorophore in the absence of a quencher and I_q is the fluorescence intensity in the presence of quencher).

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 Eq. (5) [29–31]:

$$\frac{I_0}{I_q} = (1 + K_D[Q]) \times (1 + K_S[Q]) \tag{5}$$

where

$$K_S = \frac{[HC^{+}\cdots Bo^{-}]}{[HC^{+}] \times [Bo^{-}]} \tag{6}$$

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 BI2B2 in the presence of tetramethylammonium *n*-butyltriphenylborate (TB2) (Fig. 7) lead to the conclusion that an upward curvature for the high concentration of quenchers indicates the existence of both forms of hemicyanine borate, e.g. the form of the free ions and the form of the ion pairs. Interestingly, the plots of I_0/I_q and τ_0/τ_q may significantly differ (τ_0 and τ_q are the fluorophore fluorescence lifetime in the absence and in the presence of quencher, respectively) (Fig. 7).

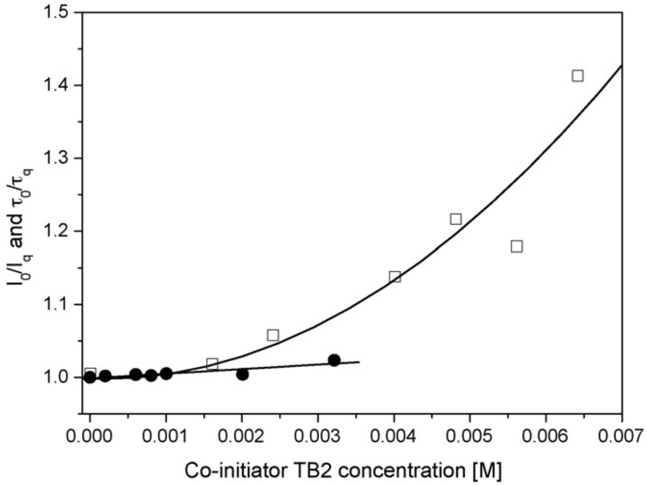


Fig. 7. Stern–Volmer plot for quenching of fluorescence of BI2B2 by tetramethylammonium *n*-butyltriphenylborate (TB2) in ethyl acetate–MP (10:2) solution based on fluorescence lifetimes (dark circle) and fluorescence intensity (squares) measurements.

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 conclude 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 [24,27]. From the Stern–Volmer relationship obtained for both BI2B2 pairs one can calculate, based on Eqs. (5) and (6), 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 BI2B2 photoredox pair this parameter is equal to 8.835 M^{-1}. The introduction of this value into Eq. (6) gives K_S equal 1495.6 M^{-1} and this, in turn, allows calculating a degree of dissociation equal 25.7% (dissociation constants equal $K = 6.69 \times 10^{-4}$ M). The presented above analysis clearly shows that large part of hemicyanine borate salts probably exist in a monomeric formulation as non-separated ions pair.

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).

3.5. Thermodynamics

As was previously reported for the alkyltriphenylborates [24,25,27], 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 [25]. 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 [15] allows predicting 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 an application of this theory for the description of the rate of polymerization *via* an intermolecular electron-transfer process. This is because for all photoredox couples under the study the identical radical is formed, e.g. the driving force of the electron-

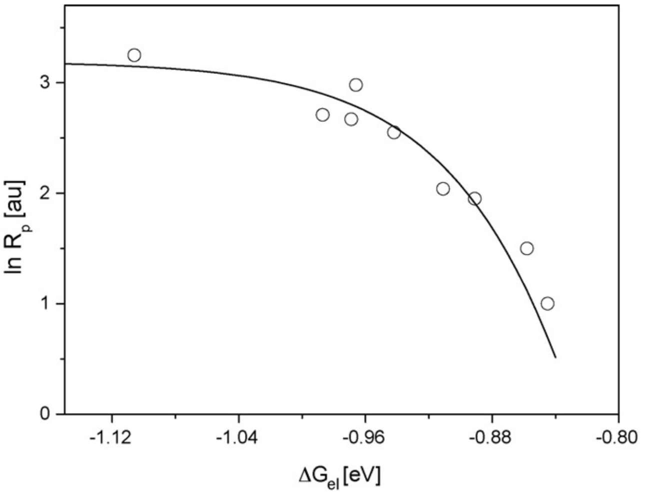


Fig. 8. Dependence of the rate of photoinitiated polymerization on the free energy ($\Delta G_{\rm el}$) for the photoinduced electron-transfer process from borate to the excited state of monochromophoric hemicyanine dye.

transfer process has no influence on the type of the yielding free radical.

As described in literature [32,33] the rate of the photoinitiated polymerization can by described by the following equation:

$$R_{\rm p} = -\frac{d[{\rm M}]}{dt} = k_p[{\rm M}]\left[\frac{I_{\rm a}k_{\rm el}}{k_t}\right]^{0.5} \quad (7)$$

where [M] is the monomer concentration, $k_{\rm t}$ is the rate constant of termination process, and $I_{\rm a}$ is the light intensity.

The rate of the electron-transfer process can be expressed by the following equation:

$$k_{\rm el} = \chi Z \exp\left(\frac{-\Delta G^{\#}}{RT}\right) \quad (8)$$

where Z is an universal frequency factor ($6 \times 10^{12}\,{\rm s}^{-1}$) at 25 °C, χ is the transmission coefficient and $\Delta G^{\#}$ is the total energy of activation described by the Marcus equation:

$$\Delta G^{\#} = \frac{\lambda}{4}\left(1 + \frac{\Delta G_{\rm el}}{\lambda}\right) \quad (9)$$

where λ is defined as the total reorganization energy necessary to reach the transition states both of excited molecule and solvent molecules and $\Delta G_{\rm el}$ is expressed by the Rehm-Weller equation (Eq. (3)).

After taking into account the Marcus relationship, as a final equation describing the rate of the photoinitiated polymerization for very viscous or solid monomer can be described as follows:

$$R_{\rm p} = -\frac{d[{\rm M}]}{dt} = k_p[{\rm M}]\sqrt{\frac{I_a\chi Z\exp[-(\lambda+\Delta G_{\rm el})^2/4\lambda RT]}{k_t}} \quad (10)$$

or in logarithmic form:

$$\ln R_{\rm p} = A - \frac{(\lambda + \Delta G_{\rm el})^2}{8\lambda RT} \quad (11)$$

where A is the sum for the initial time of polymerization: $\ln k_{\rm p} - 0.5\ln k_{\rm t} + 1.5\ln[{\rm M}] + 0.5\ln I_{\rm a}$.

Eq. (11) 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 $\Delta G_{\rm el}$. For the photoinitiating photoredox pairs examined it is shown in Fig. 8.

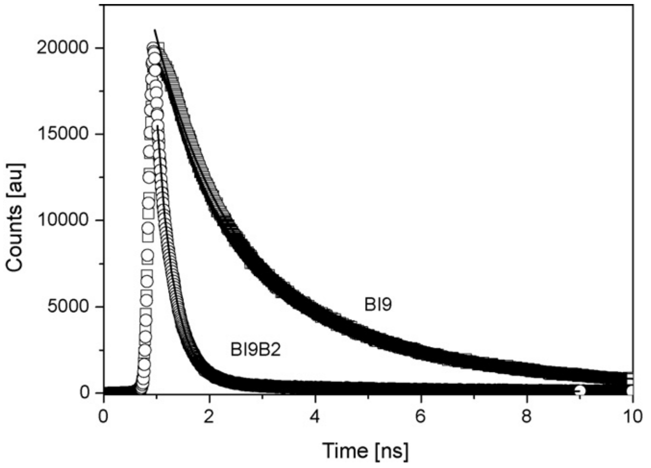


Fig. 9. The influence of the borate ion (B2) on the fluorescence decay recorded for hemicyanine BI9. Fluorescence measurements performed for dyes in ethyl acetate–1-methyl-2-pyrrolidinone (10:2) solution.

It is apparent from the inspection of the relationship presented in Fig. 8 that the plot exhibits behavior predicted by Marcus or more likely by the Rehm-Weller [23] and Agmon-Levine [34] equations. According to Fig. 8, 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 type of behavior is predicted by the classical theory of photoinduced electron transfer [35].

In order to clarify the relationship between the rate of the polymerization and the photophysical properties of the hemicyanine dyes tested, fluorescence lifetime measurements were performed, allowing the decay of the lifetime to be established with the resolution of few picoseconds. The fluorescence lifetime were measured for the dyes with iodine and parallel with borate ions as the counterions. A typical example of fluorescence decay behavior is given in Fig. 9, which presents a graphical report for the picosecond lifetime measurement recorded for BI9 and BI9B2. Similar properties were observed for all styrylbenzimidazolium dyes under the study. The results are in good agreement with data obtained for styrylpyridinium dyes described earlier in literature [36].

The occurrence of electron transfer between cyanine and borate ions leads to quenching and simultaneous shortening of the fluorescence lifetime of hemicyanine chromophore.

The quenching rate constant of the fluorescing state of the hemicyanine under the study can be estimated based on a Stern–Volmer analysis. Since the lifetimes of the dye in the absence (τ_0) and presence ($\tau_{\rm q}$) of a quencher (Q) are measurable, we can determine $k_{\rm q}$ from Eqs. (12) and (13). Experimentally, this is done by plotting $1/\tau_{\rm q}$ as a function of quencher concentration [Q]. The slope of such a plot is equal to $k_{\rm q}$ (Fig. 10)

$$\text{Lifetime of a dye; no Q}: \quad \frac{1}{\tau_0} = k_1 \quad (12)$$

$$\text{Lifetime of a dye; Q present}: \quad \frac{1}{\tau_q} = k_1 + k_{\rm q}[{\rm Q}] = \frac{1}{\tau_0} + k_q[{\rm Q}] \quad (13)$$

The quenching rate constants ($k_{\rm q}$) for the photoinduced electron-transfer reaction between the singlet state of hemicyanine cations and the butyltriphenylborate anion are collected in Table 3. For the sake of comparison we analyzed the quenching rate constant established for BI2 hemicyanine cation using the steady state and lifetime measurements methodologies. We found that the first method gave the rate constant equals about $1.2 \times 10^{11}\,{\rm M}^{-1}\,{\rm s}^{-1}$, while the second method gave the rate equals about $8.7 \times 10^{10}\,{\rm M}^{-1}\,{\rm s}^{-1}$.

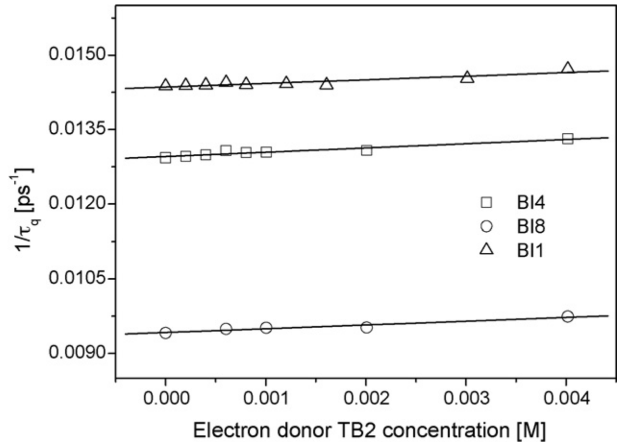


Fig. 10. Experimental plot of $1/\tau_q$ versus tetramethylammonium *n*-butyltriphenylborate (TB2) concentration for selected dyes.

The measured electron-transfer rates constants for photoredox pairs are well above the diffusion limit. This is the pure evidence that the reaction of electron transfer occurs mostly in an intra-ion-pair assembly. Similar observation for other cyanine dyes was described by Schuster and co-workers [24].

It is well known that the rate of the electron transfer is related to the free energy of the reaction through the classical Marcus equation [15].

The data presented in Fig. 11 behave as predicted by the theory of the electron transfer and allows concluding that the state which is quenched is the fluorescing state. It is necessary to emphasize that the relationship predicted by the Marcus equation is fulfilled for the whole series of hemicyanines tested with the exception of BI9.

It should be added, however, that this dye differs substantially from others. Its fluorescence is characterized by three-exponential decay with the main component (about 90%) lifetime of about 3433 ps, e.g. about 50 times longer than main-component lifetime recorded for other dyes under the study. Such difference suggests that BI9 does not fulfill all requirements needed for the series that can be described in a way similar to that applied for other dyes.

As shown in Fig. 8 the rate of polymerization might be a function of the thermodynamic driving force of the electron-transfer process (ΔG_{el}). Since the rate of the electron-transfer process is much faster than the rate of polymerization, this conclusion may be quite surprising. However, it is obvious that for a consecutive reaction mechanism, an increase in the reaction rate for the primary step should automatically increase the rate of the reaction that follows. The photoinitiated polymerization reaction represents such a type of process. Since the one-electron oxidation of an alkyl triphenyl borate generates identical type of an alkyl radical, this type of photoinitiating donor–acceptor system is the best for the testing of the relationship between the rate of the primary process (electron transfer) and the rate of the photoinitiated polymerization. Therefore, if there is a relationship between the rate of the electron-transfer process and the rate of the photoinitiated polymerization, one should observe the linear relationship between the rate of the electron-transfer process and the rate of the photoinitiated polymerization. These type of relationship is shown in Fig. 12.

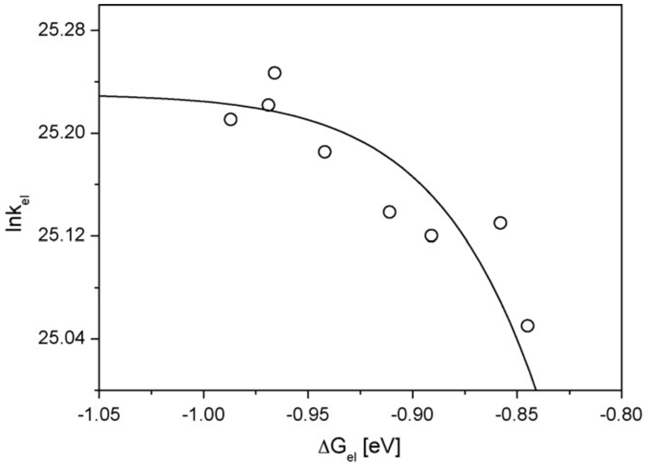


Fig. 11. The dependence of the rate for electron transfer on free energy for transfer of an electron from *n*-butyltriphenylborate ion to the dye cation for monochromophoric hemicyanine photoredox pairs under the study.

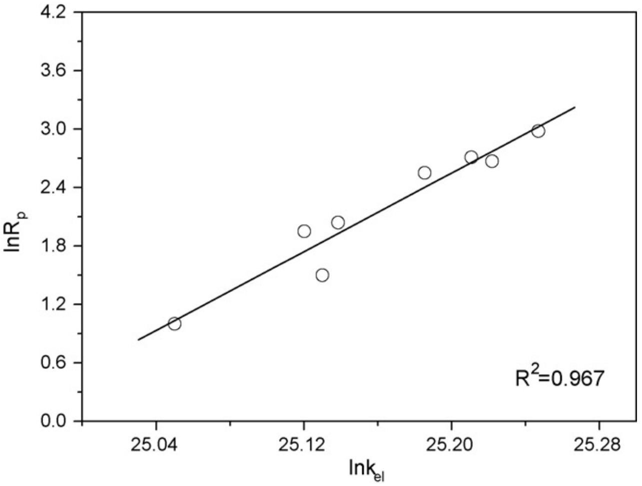


Fig. 12. The dependence of the rate of photopolymerization on the rate constant for electron transfer for styrylbenzimidazolium *n*-butyltriphenylborates.

On the basis of the data presented in Fig. 12 one can conclude that there is a linear relationship between the logarithm of the polymerization rate and logarithm of the rate of the primary process of the electron-transfer reaction with the exception of BI9B2. Transferring this to the practical application of Marcus theory into photoinitiated polymerization, one can conclude that for tested photoredox pairs it is possible to apply the Marcus relationship.

4. Conclusion

Presented paper is focused on photoinitiation of free radical polymerization initiated by photoreducible dye sensibilization. A series of hemicyanine *n*-butyltriphenylborate salts were employed as visible-light, singlet state 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 styrylbenzimidazole borates as photoinitiators, was studied by differential scanning calorimetric method. The experimental data revealed that:

(i) Hemicyanine borate salts are shown to be very 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. (iii) The inspection of the rates of polymerization showed that that both initiator and co-initiator concentration affects the rates of photopolymerization. (iv) The relationship between the rate of polymerization and the free energy change (ΔG_{el}) for electron-transfer reaction displays typical Marcus kinetic behavior.

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References

[1] N.S. Alien, Photopolymerisation and Photoimaging Science and Technology, Elsevier Applied Science, Barking, 1989.

[2] J.P. Fouassier, Photoinitiation, Photopolymerisation and Photocuring: Fundamentals and Applications, Hanser Publishers, Munich, 1995.

[3] D.R. Randell, Radiation Curing of Polymers II, Royal Society of Chemistry, Cambridge, 1991.

[4] R.S. Davidson, Polymeric and polymerisable free radical photoinitiators, J. Photochem. Photobiol. A: Chem. 69 (1993) 263–275.

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

[6] R. Podsiadly, The synthesis of novel, visible-wavelength oxidizable polymerization sensitizers based on the 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine skeleton, Dyes Pigments 80 (2009) 86–92.

[7] J.P Fouassier, J.F. Rabek, Radiation Curing in Polymer Science and Technology, vol. 2, Elsevier Applied Science, London, 1993.

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

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

[10] J. Kabatc, M. Pietrzak, J. Pączkowski, Cyanine borates revisited. Application of the Marcus equation for the description of the kinetics of photoinitiated free radical polymerization. IV, Macromolecules 31 (1998) 4651–4654.

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

[12] B. Jędrzejewska, A. Rudnicki, The synthesis and spectroscopic investigation of dichromophoric hemicyanine dyes, Dyes Pigments 80 (2009) 297–306.

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

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

[15] (a) R.A. Marcus, On the theory of oxidation–reduction reactions involving electron transfer. I, J. Chem. Phys. 24 (1956) 979;
(b) R.A. Marcus, On the theory of electron-transfer reactions. VI. Unified treatment for homogeneous and electrode reactions, J. Chem. Phys. 43 (1965) 679.

[16] R. Damico, Preparation, characterization, and reactions of lithium and sodium tetraalkylboron compounds, J. Org. Chem. 29 (1964) 1971–1976.

[17] S. Murphy, X. Yang, G.B. Schuster, Cyanine borate salts that form penetrated ion pairs in benzene solution: synthesis, properties, and structure, J. Org. Chem. 60 (1995) 2411–2422.

[18] E. Andrzejewska, M. Andrzejewski, Polymerization kinetics of photocurable acrylic resins, J. Polym. Sci. A: Polym. Chem. 36 (1998) 665–673.

[19] S. Wróblewski, K. Trzebiatowska, B. Jędrzejewska, M. Pietrzak, R. Gawinecki, J. Pączkowski, Development of fluorescence probes based on stilbazolium salts for monitoring free radical polymerization processes, J. Chem. Soc. Perkin Trans. 2 (1999) 1909–1917.

[20] B. Strehmel, M. Younes, V. Strehmel, S. Wartewig, Fluorescence probe studies during the curing of epoxy systems, Progr. Colloid Polym. Sci. 90 (1992) 83–87.

[21] R. Foster, Organic CT Complexes, Academic Press, London, 1969.

[22] R.M. Hermant, N.A.C. Bakker, T. Scherer, B. Krijnen, J.W. Verhoeven, Systematic study of a series of highly fluorescent rod-shaped donor–acceptor systems, J. Am. Chem. Soc. 112 (1990) 1214–1221.

[23] D. Rehm, A. Weller, Ber. Bunsen-Ges Phys. Chem. 73 (1969) 834–839.

[24] S. Chatterjee, P.D. Davis, P. Gottschalk, M.E. Kurz, B. Sauerwein, X. Yang, G.B. Schuster, Photochemistry of carbocyanine alkyltriphenylborate salts: intra-ion-pair electron transfer and the chemistry of boranyl radicals, J. Am. Chem. Soc. 112 (1990) 6329–6338.

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

[26] O. Valdes-Aquilera, C.P. Pathak, J. Shi, D. Watson, D.C. Neckers, Photopolymerization studies using visible light photoinitiators, Macromolecules 25 (1992) 541–547.

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

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

[29] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Plenum, New York, 1983, p. 266.

[30] W. Augustyniak, A. Maciejewski, B. Marciniak, Some remarks on the quenching terminology, EPA Newlett. 34 (1988) 13–17.

[31] S.E. Webber, The role of time-dependent measurements in elucidating static versus dynamic quenching processes, Photochem. Photobiol. 65 (1997) 33–38.

[32] J. Pączkowski, Z. Kucybała, Generalization of the kinetic scheme for a dye-photosensitized free-radical polymerization initiating system via an intermolecular electron-transfer process. Application of Marcus theory, Macromolecules 28 (1995) 269–273.

[33] J. Pączkowski, M. Pietrzak, Z. Kucybała, Generalization of the kinetic scheme for photoinduced polymerization via an intermolecular electron transfer process. 2. Application of the Marcus theory, Macromolecules 29 (1996) 5057–5064.

[34] N. Agmon, R.D. Levine, Energy, entropy and the reaction coordinate: thermodynamic-like relations in chemical kinetics, Chem. Phys. Lett. 52 (1977) 197–201.

[35] L. Eberson, Electron Transfer in Organic Chemistry, Springer-Verlag, New York, 1987.

[36] B. Strehmel, H. Seifert, W. Rettig, Photophysical properties of fluorescence probes. 2. A model of multiple fluorescence for stilbazolium dyes studied by global analysis and quantum chemical calculations, J. Phys. Chem. B 101 (1997) 2232–2243.