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One photon–two radical-electron transfer photoinitiators. 2-(*o*-, *m*-, or *p*-Methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfates as photoinitiators of free radical polymerization

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Abstract

In this paper, the novel hemicyanine dye–borate pair, e.g. 2-((*o*, *m*, or *p*)-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfates (MeOSp)–tetramethylammonium *n*-butyltriphenyl borate (TBAB) were evaluated and employed as the photoinitiating pairs of multiacrylate monomer polymerization. The kinetic studies clearly demonstrate that the modification of the dye structure by the exchange of the *N*-alkyl group on *N*-alkoxy one in pyridinium moiety causes a marked increase in the efficiency of photoinitiation of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) polymerization.

Keywords: Photoinitiating pair; Electron-transfer process; Photoinitiated free radical polymerization

1. Introduction

Bond dissociation reactions are the predominant reactions used to photoinitiate polymerization in the UV and blue-region of visible area of the spectrum. However, the bond decomposition of organic compounds requires energy upward from 280 kJ/mol and visible light energies are insufficient to cause bond dissociation even for appropriately designed molecules. This problem can be avoided taking into account fact that excited states are, very often, much easier to oxidize and reduce than their ground state equivalents. The possibility of such excited state oxidation or reduction can be predicted by the Rehm–Weller equation [1]. This equation predicts that if the difference between the oxidation potential of the donor (in its excited or ground state), the reduction potential of the acceptor (in its ground or excited state) and the energy of the excited state is negative, the electron transfer process between electron donor and electron acceptor will be spontaneous (thermodynamically allowed). The thermodynamics of redox processes, fortunately, can be applied also to other reactions, including the reaction between free radicals (or radical ions) and molecules in its ground state.

Such approach was presented by Farid et al. in the paper on energies of electron transfer reactions of dye-sensitized fragmentation of *N*-alkoxypyridinium salts [2]. The idea of such dye-sensitized fragmentation came from the pioneer Schuster's work on photoinduced nitrogen–oxygen bond cleavage in alkoxypyridinium salts [3]. The most interesting feature of this reaction is the possibility of the doubling the photoresponse by the coupling of the reductive cleavage of N–O bond of *N*-alkoxypyridinium moiety with an oxidative cleavage of C–B bond of an alkyltriphenylborate [2,4].

In this paper, we present the synthesis and the experimental results of the photoinitiation properties of the photoredox systems composed of 2((*o*-, *m*- and *p*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfate (*o*-, *m*-, *p*-MeOSP) and tetramethylammonium *n*-butyltriphenylborate (TBAB) as photoinitiators of free radical polymerization. The photoinitiating system under the study, in contrast to well-known electron transfer initiators, applied photoredox pair in which both components of such pair after electron transfer undergo effective bond cleavage. From literature it is known that, most commonly, only one component of the photoredox pair after electron transfer process undergoes bond fragmentation. The butyltriphenylboranyl radical B–C bond cleavage [5–9], C–C bond fragmentation in radical cation of sulfur-containing aromatic carboxylic acids [10,11] or *N*-phenylglycine

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derivatives radical cation C–C bond fragmentation [12] are good illustration of such photoinitiation systems. In described in this paper photoinitiating pairs, after electron transfer both products of this process, e.g. the radicals obtained from an electron acceptor and an electron donor undergo efficient fragmentation.

2. Experimental

The substrates used for the preparation of the dyes: 2-picoline *N*-oxide, 3-picoline *N*-oxide, 4-picoline *N*-oxide, dimethyl sulfate and 4-*N*,*N*-dimethylaminobenzaldehyde, monomer: 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and solvent: 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich. The hemicyanine dyes and tetramethylammonium *n*-butyltriphenylborate were prepared in our laboratory. Tetramethylammonium *n*-butyltriphenylborate salt (TBAB) was synthesized based on the method described by Damico [13].

All final products were identified by ^{1}H, ^{13}C NMR spectroscopy (Varian Spectrophotometer Gemini 2000, 200 MHz) and IR spectroscopy (Bruker Spectrophotometr Vector 22). The spectra obtained were the evidence that the synthesized products were of the desired structures. The purity of synthesized dyes was controlled by thin layer chromatography and by measuring of the melting points. The purity of the dyes was as it is required for spectroscopic studies. The measurements showed that the synthesized compounds are high purity.

Spectroscopic measurements: UV/vis absorption spectra: Varian Cary 3E Spectrophotometer, and steady-state fluorescence: Hitachi F-4500 Spectrofluorimeter.

The reduction and oxidation potentials of dyes and tetramethylammonium *n*-butyltriphenylborate were measured by cyclic voltammetry. An Electroanalitical MTM System model EA9C-4z (Cracow, Poland), equipped with a small-volume cell, was used for the measurements. A 1 mm platinum electrode was used as the working electrode. A Pt wire constituted the counter electrode, and an Ag–AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. The solution was degassed by bubbling argon gas through the solution for 20 min. The potential was swept from −1.8 to 1.8 V with the sweep rate of 250 mV/s to record the current–voltage curve.

The kinetics of free radical polymerization were measured based on the measurements of the rate of the heat evolution during polymerization in a sample 2–3 mm thick (10 mm

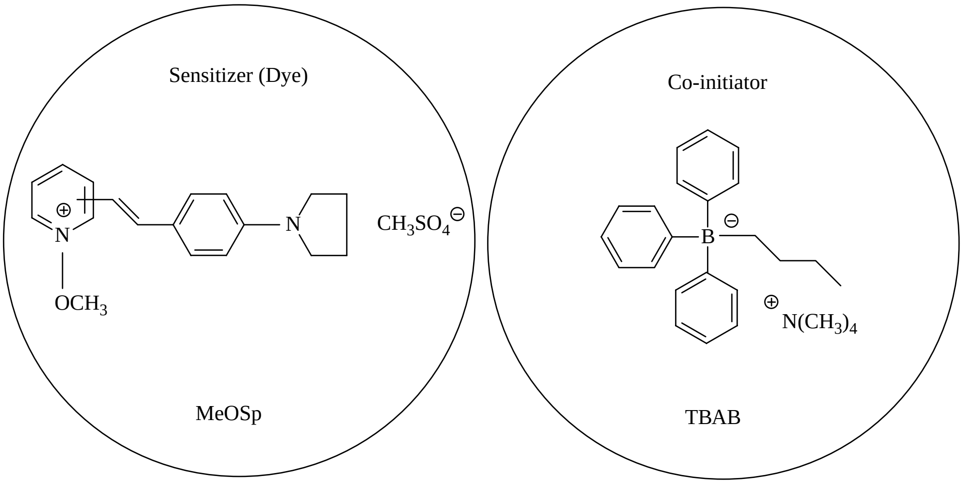
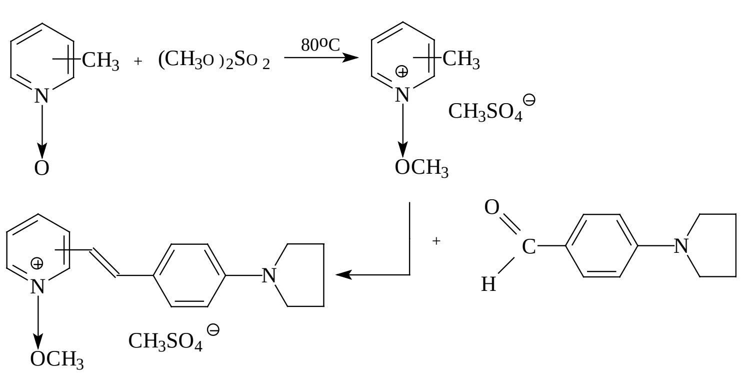


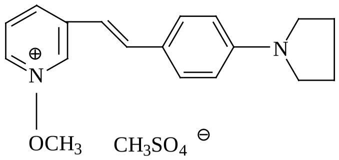
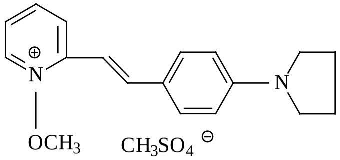
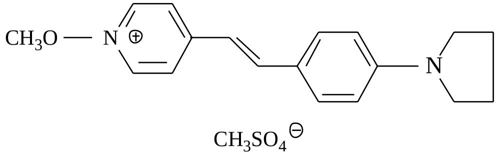
Chart 1.



o-MeOSp, m-MeOSp, p-MeOSp

Scheme 1.

Table 1
Characteristics of the hemicyanine dyes tested

Dye	Yield (%)	Mp (°C)	^{1}H NMR, ^{13}C NMR δ (DMSO), (ppm) IR ν (cm^{-1})
	22.3	71–80	^{1}H NMR; 1.992–2.090 (t, 8H,–*CH$_2$*–), 3.704 (s, 3H,–*OCH$_3$*), 4.565 (s, 3H, $^{+}$NO–*CH$_3$*), 6.552–6.596 (d, J=8.8 Hz, 4H, Ar), 7.249–7.316 (d, J=13.4 Hz, 1H, –*CH*=), 7.707–7.751 (3H, Pyr), 8.191–8.258 (d, J=13.4 Hz, 1H, –*CH*=). ^{13}C NMR; 24.960, 47.237 (–*CH$_2$*–), 60.2 (–*OCH$_3$*), 120.841, 121.241 (–*CH*=*CH*–), 126.990, 129.290 (C, Ar), 130.0, 141.0, 145.7 (C, Pyr). IR (KBr) ν; 1640 cm^{-1} (–*CH*=*CH*–)
	16.0	63–70	^{1}H NMR; 1.991–2.117 (t, 8H, –*CH$_2$*–), 3.730 (s, 3H, –*OCH$_3$*), 4.611 (s, 3H, $^{+}$NO–*CH$_3$*), 6.549–6.593 (d, J=8.8 Hz, 4H, Ar), 7.181–7.263 (d, J=16.4–Hz, 1H, –*CH*=)1, 7.707–7.751 (3H, Pyr), 8.142–8.224 (d, J=16.4 Hz, 1H, –*CH*=). ^{13}C NMR; 27.018, 47.374 (–*CH$_2$*), 61.256 (–*OCH$_3$*), 122.341, 124.781 (–*CH*=*CH*–), 128.790, 129.990 (C, Ar), 130.1, 141.9, 145.7 (C, Pyr). IR (KBr) ν; 1640 cm^{-1} (–*CH*=*CH*–)
	10.0	65–69	^{1}H NMR; 2.02–2.110 (t, 8H,–*CH$_2$*–), 3.744 (s, 3H, –*OCH$_3$*), 4.558 (s, 3H, –*OCH$_3$*), 6.548–6.592 (d, J=8.8 Hz, 4H, Ar), 7.181–7.248 (d, J=13.4 Hz, 1H, –*CH*=), 7.691–7.761 (3H, Pyr), 8.214–8.281(d, J=13.4 Hz, 1H, –*CH*=). ^{13}C NMR; 24.960, 47.237 (–*CH$_2$*–), 61.621 (–*OCH$_3$*), 120.841, 124.182 (–*CH*=*CH*–), 121.36, 126.990 (C, Ar), 130.209, 131.656, 144.374, 151.575 (C, Pyr). IR (KBr) ν; 1640 cm^{-1} (–*CH*=*CH*–)

diameter; 0.25 mL of cured sample). The measurements were performed in a homemade microcalorimeter [10,14–17]. A semiconducting diode immersed in a 2 mm thick layer of a cured sample was used as a temperature sensor. The irradiation of the polymerization mixture was carried out using the emission of an Omnichrome model 543-500 MA argon-ion laser, which emits two visible light wavelengths at 488 and 514 nm. The average power of irradiation was 64 mW/cm^2.

A polymerization solution was composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The dyes (MeOSp) and co-initiator (TBAB) concentrations used in experiments were 4.5×10^{-2} M. The monomer was used without purification. As a reference sample, a polymerizing mixture containing hemicyanine methyl sulfate (dye without a coinitiator) was used. The polymerizing mixture was not deaerated. In order to reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish–Troomsdorf effect and radicals trapping effect, the initial rates of polymerization were taken into account for further consideration. The initial rates of polymerization are the slopes of the lines drawn on the flow of heat versus time curve at the initial time of polymerization.

3. Results and discussion

The general formula of the photoredox systems under the study is shown in Chart 1.

The general method of synthesis of hemicyanine dyes is presented in Scheme 1.

The preparation of the quaternary salt of picoline *N*-oxides was the first step of synthesis of the dyes. Detailed study on the synthesis has shown that, a more convenient method of *N*-methoxy salts preparation involves the treatment of the appropriate *N*-oxides with dimethyl sulfate [18]. This method yields the *N*-methoxymethyl sulfate salts with high yield. The reaction was mildly exothermic and nearly quantitative.

3.1. Synthesis

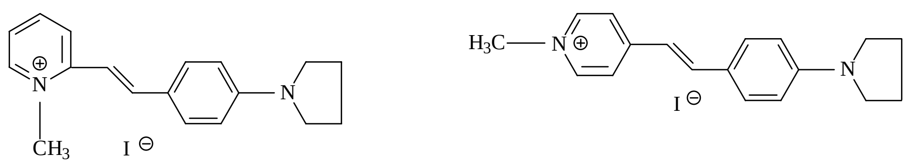
3.1.1. Synthesis of 2-, 3- or 4-methyl-N-methoxypyridinium methyl sulfate

To 109 g (1 mol) of a powdered 2-picoline *N*-oxide 126 g (1 mol) of dimethyl sulfate was added with the rate allowing temperature of the reaction mixture to maintain at about 80 °C throughout the dimethyl sulfate addition. When the addition was complete (about 1 h) the solution was heated on steam bath for an additional 2 h. After cooling the precipitated salt was filtered and recrystallized from anhydrous acetone giving white prisms [18].

The final dye was obtained by the condensation of obtained quaternary salts with *p*-pyrrolidinebenzaldehyde according to the method described in our earlier paper [19].

3.1.2. Synthesis of 2-(o-, m-, and p-methoxypyridine)-p-pyrrolidinestyrilium methyl sulfate

A mixture of 2-, 3- or 4-methyl-*N*-methoxypyridinium methyl sulfate (1 mol), *p*-pyrrolidinebenzaldehyde (1 mol) and



o-MeSp

E_{red} = -580 meV

p-MeSp

E_{red} = -615 meV

Chart 2.

acetic anhydride (20 mL) was refluxed for 20 min. After cooling the purple powder was obtained. It was recrystallized from methanol or ethanol.

The structure and purity of the prepared compounds were confirmed by ^{1}H and ^{13}CNMR spectroscopy and thin layer chromatography. The structural analysis data for the dyes are compiled in Table 1.

The inspection of the data from Table 1 shows that all dyes melt in quite large temperature region. This can be attributed to the liquid crystal properties of the hemicyanine dyes [19]. It is noteworthy that the ^{1}H NMR spectra display two characteristic doublets localized at chemical shifts about 7 and 8 ppm. They are attributed to both vinyl hydrogen atoms. The data in Table 1 characterizing the spectra of all prepared compounds also show all the relevant protons.

For comparative studies two more, described earlier dyes, whose structures are shown in Chart 2 were prepared [19].

3.2. The spectroscopic and photophysical properties of 2-(o-, m-, and p-methoxypyridine)-p-pyrrolidinestyrilium methyl sulfates

Fig. 1 shows the illustrative electronic absorption and fluorescence emission spectra for 2-(*p*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfate in *N*,*N*-dimethylformamide solution. For comparison the electronic absorption spectra recorded for *p*-MeSp is presented as well.

Table 2 collects the values of the absorption and fluorescence maximum positions as well the Stokes shifts for all the tested dyes.

Analysis of the electronic absorption spectra of *N*-methoxypyridine-*p*-pyrrolidinestyrilium cation indicates the presence of the absorption bands that correspond to the $S^0 \rightarrow CT$ transition appearing at the red-energy side of the absorption spectrum (Fig. 1).

A well-separated CT absorption band is observed for all methoxypyridine-*p*-pyrrolidinestyrilium dyes. The position and intensity of the CT absorption band only insignificantly depends on the molecular structure. An interesting is the comparison of the absorption spectra recorded for novel dyes and *p*-MeSp. The spectra of *p*-MeSp shows a much more prominent long-wave shoulder attributed to $S^0 \rightarrow CT$ transition in comparison to the similar absorption bands observed for tested methoxypyridine-*p*-pyrrolidinestyrilium dyes. The latter finding is probably generated by relatively low reduction potential of methoxypyridine-*p*-pyrrolidinestyrilium dyes (Table 3) in comparison to similar potentials measured for corresponding *o*-MeSp ($E_{red} = -580$ mV) and *p*-MeSp ($E_{red} = -615$ mV). This property increases the CT states formation energy barrier in methoxypyridine-*p*-pyrrolidinestyrilium dyes with respect to similar dyes possessing methyl group at pyridine nitrogen.

The fluorescence emission in *N*,*N*-dimethylformamide solution exhibit a maximum which is redshifted in comparison to the absorption maximum by less than 1800 cm^{-1}. Since the Stokes shift is relatively small and the half width of the absorption ($S^0 \rightarrow CT$ transition) and emission bands are almost the same, one can conclude that the geometries of the dyes in their ground and emitting excited states are similar.

The electrochemical reduction and oxidation of hemicyanine cation, shown in Fig. 2, in acetonitrile solution are reversible.

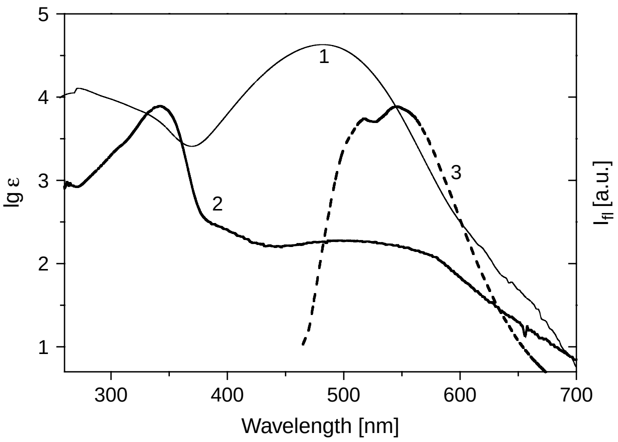


Fig. 1. The electronic absorption spectra (1) of *N*-methyl-2-(*p*-pyrrolidinestyrilium) pyridinium iodide, the electronic absorption spectra (2) and fluorescence spectra (3) of 2-(*p*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfate in DMF.

Table 2
Spectroscopic properties of the hemicyanine dyes tested in *N*,*N*-dimethylformamide solution

Dye	λ_{ab} (nm)	λ_{fl} (nm)	Stokes shift (cm^{-1})
o-MeOSp	515	540	880
m-MeOSp	555	560	200
p-MeOSp	545	563	1600

Table 3
Electrochemical, thermodynamical and photoinitiation properties of hemicyanine dyes–TBAB photoinitiating systems

Dye	E_{00} (eV)	E_{red} (V)	E_{ox} (V)	ΔG_{el}[a] (eV)	Initial R_p[b] (μmol/s)	R_p[c] (a.u.)
o-MeOSp	2.35	−0.955	1.315	−0.235	158.0	335
m-MeOSp	2.21	−0.910	1.265	−0.14	328.0	579
p-MeOSp	2.17	−0.840	1.255	−0.17	236.0	417

[a] The oxidation potential of tetramethylammonium *n*-butyltriphenylborate is equal 1.16 V.
[b] Measured for cylindrical sample ($r=5$ mm, $h=3$ mm).
[c] The rates of polymerization compared to the rate obtained for *o*-MeSp–borate system (0.47 (μmol/s)).

On the other side the oxidation of applied in this study, as electron donor borate anion, is irreversible [20]. This is caused by the very short lifetime of alkyltriphenylboranyl radical. The oxidation of alkyltriphenyl borate is dissociative and this, in turn, causes the electrochemical process to be irreversible. Therefore, the obtained electrochemical values for both components of photoredox pairs may have only approximate thermodynamic meaning yet, allow roughly estimate the free energy of activation (ΔG_{el}) for the photoinduced electron transfer process (PET). It is well know from the basic Rehm–Weller [1] requirement that the free energy of activation for the PET (ΔG_{el}) process should have a negative value Eq. (1)

$$\Delta G_{\mathrm{el}} = E_{\mathrm{ox}}(D/D^{\cdot +}) - E_{\mathrm{red}}(A^{\cdot -}/A) - Ze^2/\varepsilon a - E_{00} \qquad (1)$$

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

The measured electrochemical, as well as calculated (using the Rehm–Weller equation) thermodynamical properties of novel hemicyanine-borate photoinitiating systems are listed in Table 3. For the calculation of ΔG_{el} the energy of excited state on which the electron transfer occurs was established based on fluorescence spectra of MeOSp. The energy corresponding to the fluorescence λ_{max}, was taken into account for this purpose.

The values of ΔG_{el} of tested photoinitiating systems oscillate in the range from −0.235 to −0.14 eV. These results clearly indicate that the electron transfer between *N*-methoxypyridinine-*p*-pyrrolidinestyrilium cation and *n*-butyltriphenylborate anion is thermodynamically favorable.

3.3. The kinetics of free radical polymerization

As it is mentioned earlier, in this paper we present the synthesis and the possible application as free radical photoinitiators of vinyl polymerization the three novel, absorbing a visible light, photoinitiating systems possessing the styrylpyrydinium dyes as sensitizer.

Fig. 3 presents the kinetic curves recorded during an initial time of an argon-ion laser initiated polymerization of a solution composed of 1 mL of MP and 9 mL of TMPTA. Polymerization was photoinitiated by pair composed of *o*-MeOSp and TBAB as well as, for comparison, photoinitiating pair possessing as components *o*-MeSp and TBAB.

The analysis of the data presented in Fig. 3 and summarized in Table 3 clearly show that the modification of the dye structure by the replacement of methyl group by the *N*-methoxy group at the nitrogen atom of pyridine ring sharply increases the rate photoinitiation process of TMPTA free radical polymerization. The experimental results (Table 3) evidently show that this modification causes of an increase in photoinitiation of TMPTA polymerization about 300–500 times. The activity of photoinitiating systems described here to the initiation of the photopolymerization of TMPTA is

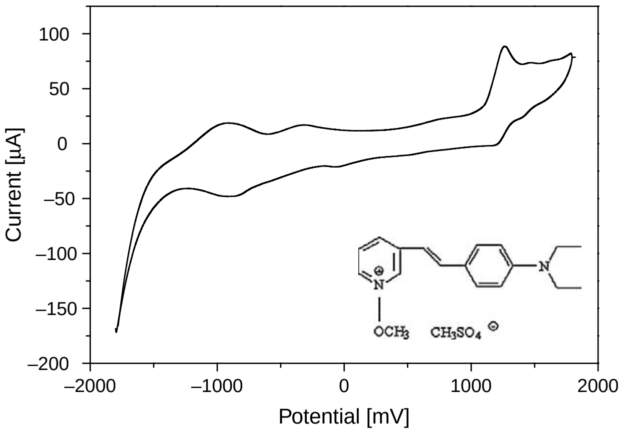


Fig. 2. Illustrative cyclic voltammetric curve of 2-(*m*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfate.

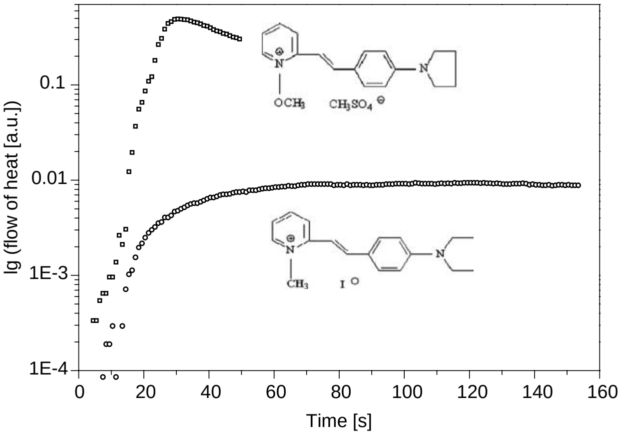


Fig. 3. The family of the photopolymerization kinetic traces recorded for the initial time of polymerization of the TMPTA–MP (9:1) mixture initiated by (*o*-MeSp and *o*-MeOSp)–borate (TBAB) system. Dye concentration: 4.5×10^{-2} M, light intensity $I_a=50$ mW/0.785 cm^2. For clarity of presentation the rate of polymerization is expressed in logarithmic fashion.

comparable to that for three-component photoinitiating systems: dye/*n*-butyltriphenylborate salt/*N*-alkoxypyridinium salt [4].

Described earlier hemicyanine dye–borate pairs are not particularly efficient photoinitiators [19–23]. This essentially disqualifies such photoinitiating pairs as photoinitiators applied in practice. The reason of the low sensitivity is caused by the fact that the electron transfer process in such system occurs via short-lived singlet excited state.

The most important reason of the synthesis and the analysis of the photoinitiation efficiency of novel, possessing *N*-alkoxy group hemicyanine dyes was an increase in the quantum yield of free radical formation, caused by the fragmentation of electron acceptor radical obtained after electron transfer. Such approach, as it is shown in Fig. 3, is very successful.

Fig. 4 presents the illustrative kinetic curves recorded during an initial time of an argon-ion laser initiated polymerization of a solution composed of 1 mL of MP, 9 mL of TMPTA, possessing the methoxypyridine-*p*-pyrrolidinestyrilium dyes being the electron acceptor and tetramethylammonium *n*-butyltriphenylborate acting as electron donor. All results obtained during the measurements of polymerization kinetics are also collected in Table 3.

The kinetic curves presented in Fig. 4 show that the type of methoxypyridine-*p*-pyrrolidinestyrilium dye isomer, not significantly but visibly affect the photoinitiation ability of the described in this communication photoinitiating systems. The analysis of the kinetic curves in Fig. 4 shows, additionally, relatively long polymerization induction time. This specific behavior can be attributed to the presence of oxygen in polymerizing formulation.

The efficiencies of polymerization initiation (expressed by the initial rates of polymerization) do not correspond to the value of ΔG_{el} of electron transfer between MeOSp and TBAB (Table 3). Analyzing the ΔG_{el} values, one can expect that the best photoinitiation efficiency should present *o*-MeOSp–TBAB photoredox pair and the lowest efficiency should exhibit *m*-MeOSp–TBAB pair. The observed in Fig. 4 order of sensitivity is quite opposite. This behavior can be attributed to the different rates of N–O bond cleavage for all tested dyes isomers. The thermodynamical prediction of such rate is practically impossible, because of unknown thermodynamics of the N–O bond cleavage reaction of methoxypyridine-*p*-pyrrolidinestyrilium radicals. However, basing on obtained kinetic data, one can judge that the stability of the methoxypyridine-*p*-pyrrolidinestyrilium radicals is in order

$$o-\text{MeOSp} > p-\text{MeOSp} > m-\text{MeOSp}.$$

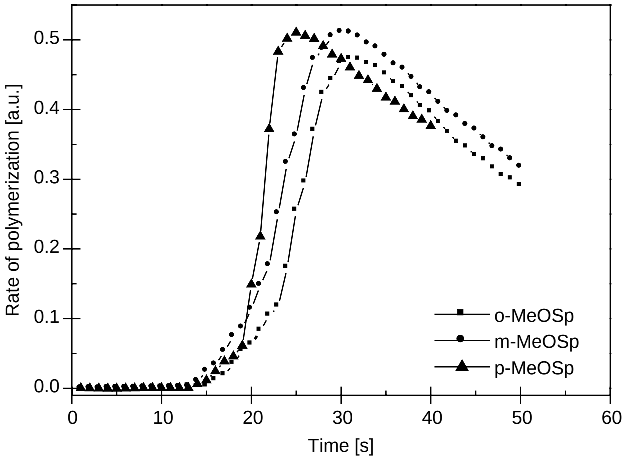
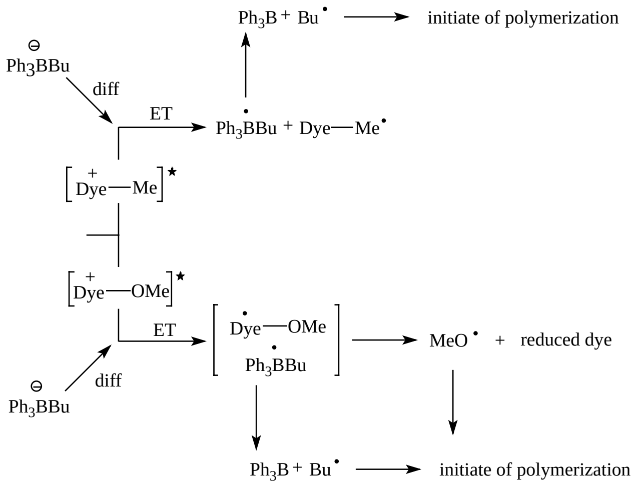


Fig. 4. Family of curves recorded during the measurements of the flow of heat during the polymerization of the TMPTA–MP (9:1) mixture photoinitiated by systems composed of novel hemicyanine dyes and tetramethylammonium *n*-butyltriphenylborate borate. The dye and co-initiator concentration was 4.5×10^{-2} M, $I_a=64$ mW/cm^2.

The data in Fig. 3 depict the striking difference between the photoinitiating system composed of: (i) *o*-MeOSp dye acting as electron acceptor and TBAB as electron donor and (ii) *o*-MeSp dye in the presence of TBAB. For the analysis of the data in Fig. 3 one should recall the scheme proposed for cyanine dyes–borate photoredox pair, and remember the basic photochemical principles for such systems described by Schuster [5,6]. In the case of dye MeSp in the presence of TBAB, after dye excitation, first, excited dye and TBAB must diffuse to each other for effective electron transfer. After electron transfer the radical formed from TBAB, according to Schuster, decomposes yielding an alkyl radical and triphenylboron. The radical formed from MeSp can not decompose, because of high stability of N–C bond. In this photoinitiating system only alkyl radical can initiate free radical polymerization.

In other hand, in photoinitiating systems composed of dye MeOSp and TBAB, after absorption of light the excited molecule of the dye and TBAB encounter (diffusion controlled process) for effective electron transfer reaction. After electron transfer process, resulting *n*-butyltriphenylboranyl radical decomposes yielding *n*-butyl radical (first radical) and triphenylboron. The second product of electron transfer process, 2-(*o*, *m* or *p*-pyrrolidinestyryl)-*N*-methoxypyridinium radical, being unstable, decomposes giving methoxy radical (second initiating radical) and 1-(*p*-pyrrolidenephenyl)-2-(2-pyridine) ethen.



Scheme 2.

On the basis of the Schuster's studies on the photochemistry of photoinitiating system composed of dye/borate salt [5,6], the Gould's studies on the photochemistry of photoinitiating systems: dye/*N*-alkoxypyridinium salt and our studies on the photochemistry of three-component photoinitiating systems composed of dye/borate salt/*N*-alkoxypyridinium salt we proposed the mechanism in Scheme 2 which is consistent with our earlier observations [4]. The mechanism of photochemical reactions that occurs after electron transfer for the photoinitaiting systems under the study was suggested on the basis of the laser flash photolysis experiments, described in our earlier paper [4].

In summary the photoinitiating systems composed of hemicyanine dye possessing *N*-methoxy group in the pyridine moiety and *n*-butyltriphenylborate after absorption of one photon generate two radicals that can initiate the free radical polymerization of vinyl monomers. Scheme 2 summarizes the photochemical processes which occur in photoinitiating systems composed of methoxypyridine-*p*-pyrrolidinestyrilium dye and *n*-butyltriphenylborate (bottom leg) and methypyridine-*p*-pyrrolidinestyrilium dye and *n*-butyltriphenylborate (upper leg), respectively.

4. Conclusions

Tetramethylammonium *n*-butyltriphenyl borate as co-initiator and three novel hemicyanine dyes, possessing *N*-methoxy group (2-(*o*-, *m*- and *p*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfates) as sensitizers can be used as visible-light photoinitiators of polymerization of vinyl monomers. The rate of polymerization depends on the structure of dye. The photoinitiator system, composed of borate salt and possessing *N*-alkoxy group hemicyanine dye, initiates multi-acrylate polymerization with much higher rate in comparison to the photoinitiation rate of hemicyanine-borates possessing the methyl group at nitrogen atom of pyridine moiety.

Finally, from a combination of alkyltriphenylborate salts with suitable sensitizer, two radicals can be generated per one absorbed photon, thus enhancing the overall polymerization efficiency.

Acknowledgements

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