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Journal of Photochemistry and Photobiology A: Chemistry 184 (2006) 184–192

Journal of Photochemistry and Photobiology A:Chemistry

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# Acceleration of the free radical polymerization by using *N*-alkoxypyridinium salt as co-initiator in hemicyanine dye/borate salt photoinitiating system

Janina Kabatc *, Jerzy Pączkowski

*Faculty of Chemical Technology and Engineering, University of Technology and Agriculture, Seminaryjna 3, 85-326 Bydgoszcz, Poland*

Received 9 February 2006; received in revised form 7 March 2006; accepted 10 April 2006

## Abstract

Results of kinetic studies of the two-component and three-component photoinitiator system used in visible-light photoinduced polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMPTA) are presented. Five different hemicyanine dyes ((6-bromo-3-ethyl-2-(*p*-alkylamino)styryl) benzothiazolium salts **SBr**) were used as sensitizers in photoinitiator systems, with four different co-initiators. The rates of polymerization were compared with the rate of polymerization photoinitiated by well known photoinitiator composed of hemicyanine dye and *n*-butyltriphenylborate anion as co-initiator. Reactive radicals that initiate the polymerization are formed by a mechanism of photoinduced electron transfer process and are different for all co-initiators tested.

In this paper we shown that photoinitiator system composed of sensitizer and co-initiator is less efficient to the photoinitiation of free radical polymerization of TMPTA than photoinitiator system possessing dye as sensitizer and two types of co-initiators.

*Keywords:* Photoinitiator; Photopolymerization; Dye

## 1. Introduction

In recent years, photoinitiators that operate in the visible region of the spectrum have been developed. This is mostly due to the fact that visible light is safe and possesses higher penetration ability (compared to ultraviolet light) in the presence of UV absorbing monomers, pigments and substrates [1]. Generally, the photoinitiators can be classified into three different groups:

- the dissociative photoinitiators, such as peroxides, benzoin or acetophenone derivatives [2,3],
- the compounds which generate free radicals in the hydrogen atom transfer reaction [4],
- the dyes [5]—in this case the radicals are formed in a non-classical energy transfer process.

The panchromatic sensibilization of polymerization of vinyl monomers requires such a dye which can act as a primary absorber of a radiation. The excitation of the dye by the visible light and then the transfer of the sensitizer energy is not an efficient way of free radicals formation, because the excitation energy are not high enough for the dissociation of the majority of the chemical bonds [6]. However, a different mechanism is also possible, namely the photoinduced energy transfer process connected with an electron transfer from a donor to an acceptor molecule.

The secondary reaction following after electron transfer process is the fragmentation reaction (cleavage). This type of reaction can occur as reductive cleavage or as oxidative cleavage, depending on whether the compound that undergoes the cleavage reaction has been initially reduced or oxidized [7].

Examples of oxidative cleavage of anions and reductive cleavage of cation are provided by the reactions of alkyltriarylborate and *N*-alkoxypyridinium salts, respectively. These reactions are useful in many photoinitiating systems.

There are a few one-component systems and two-component systems which were first used as photoinitiators of free radical polymerization under visible light. For example, dyes such as Rose Bengal, Eosin or cyanine dyes (symmetrical and unsymmetrical) are empolyed as photosensitizers in the presence of free radical sources [8,9–13]. To improve the efficiency of the polymerization and the sensitivity of such systems multi-component

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[*] Corresponding author. Tel.: +48 523749045; fax: +48 523749009.
*E-mail address:* nina@atr.bydgoszcz.pl (J. Kabatc).

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doi:10.1016/j.jphotochem.2006.04.013

combinations have been developed. For example, the use of three-component photoinitiating systems, the analysis of the mechanisms involved, the photochemical behaviour and the evaluation of the photopolymerization activity have been studied and discussed by Fouassier and co-workers [1,14] and Gould et al. [7] for a large variety of three-component combinations:

- ketone/amine/$CBr_4$;
- ketone/amine/onium salt;
- thioxanthene dyes/amine/onium salt;
- ketone/amine/ferrocenium salt;
- ketone/bis-imidazole derivatives/thiol derivatives;
- thioxanthene dyes/amine/1,3,5-triazine derivatives;
- thioxanthene dyes/*N*-alkoxypyridiniun salt/borate salt; and four-component dye photoinitiating systems;
- Rose Bengal/amine/ferrocenium salt/hydroxyperoxide [14,15].

It is well known that photoinitiated polymerization occurs by a chain reaction between the free radicals formed from photoinitiating system and the monomer. Considering the dye (**SBr**)/borate (**B2**) or dye (**SBr**)/*N*-alkoxypyridinium salt (**NO**, **Bp**) photoinitiator systems, the reactive free radicals, which initiate the polymerization, may arise simultaneously from different reactions such as:

$$\mathrm{Cy}^{\oplus}[\mathrm{RB(Ph)_3}]^{\ominus}\xrightarrow{h\nu}[\mathrm{Cy}^{\bullet}]+\mathrm{R}^{\bullet}+\mathrm{Ph_3B} \quad (1)$$

$$\mathrm{Cy}^{*}[\mathrm{R{-}O{-}Pyr}]^{\oplus}\xrightarrow{h\nu}[\mathrm{Cy}^{\oplus\bullet}]+\mathrm{RO}^{\bullet}+\mathrm{Pyr} \quad (2)$$

It is also well known that the irradiation of cyanine borate salts with visible light results in the efficient sensitization of borate anion and the generation of free alkyl radicals (Eq. (1)) [9]. In such photoinitiator system the dye in its excited singlet state acts as an electron acceptor. On the other hand, there are photoinitiator system composed of cyanine dye and *N*-alkoxypyridinium salt in which the sensitizer plays a role of an electron donor. In such system free *N*-alkoxy radicals are formed (Eq. (2)) [7,16]. These both different reactions are useful for the photoinitiation of polymerization of vinyl monomers.

Photoinitiating systems containing *N*-alkoxypyridinium salts or *N*,*N*′-dialkoxy-bipyridilium salts were presented in few papers [7,16]. In our previous paper it was demonstrated that the addition of *N*-alkoxypyridinium salt to the two-component photoinitiating system composed of 3-ethyl-2-(*p*-*N*,*N*-dialkylaminostyryl)benzothiazolium iodide/*n*-butyltriphenylborate salt clearly leads to an increase in the efficiency of the polymerization under visible light irradiation [17]. A reaction mechanism was elaborated which shows that *N*-alkoxypyridinium salt (**NO**) mainly acts as a second source of free radical formed in the second photochemical reaction between dye radical (dye$^{\bullet}$) and the *N*-alkoxypyridinium salt (**NO**).

The cyanine borate salts first described by Schuster in 1988 themselves can photoinitiate polymerization, however, only at a low rate [9]. In order to accelerate the polymerization, *N*-alkoxypyridinium salts are used as co-initiators. The alkoxy radicals that are formed in such type photoinitiator system beside *n*-butyl radical initiate the free radical polymerization. The efficiency of this process depends on the composition of the photoinitiator system.

The aim here is to report the polymerization activity of other two-component and three-component photoinitiating systems that are based on the hemicyanine dye/*n*-butyltriphenylborate salt/*N*-alkoxypyridinium derivatives, to discuss the results as a function of the thermodynamic parameters and the spectroscopic properties of the dyes. We discuss a particularly useful example of visible-light initiating system based on the chemistry of (6-bromo-3-ethyl-2-(*p*-alkylaminostyryl) benzothiazolium salts (**SBr**, hemicyanine dye). We also presented the interesting kinetic results obtained during the free radical polymerization of triacrylate monomer initiated by two-component and three-component initiators, employing the hemicyanine dye, which plays the role of a primary absorber of the visible light. We also consider the effect of the photoinitiator system composition on the rate of photoinitiated free radical polymerization.

## 2. Experimental

### 2.1. Materials

The substrates used for the preparation of the dyes, *N*-methoxy-4-phenylpyridinium tetrafluoroborate (**NO**), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich.

### 2.2. Techniques

(i) The synthesis of dyes (**SBr**) was described in our earlier paper [8]. *n*-Butyltriphenylborate tetramethylammonium salt (**B2**) was synthesized based on the method described by Damico [18]. The *N*-methoxy-4-phenylpirydinium-*n*-butyltriphenylborate (**NOB2**) was prepared in our laboratory following methodology developed by Schuster for synthesis of cyanine borate salts [9]. All final products were identified by $^1$H NMR spectroscopy. The obtained spectra suggest that the reaction products were of the desired structures. The purity of synthesized compounds was determined using thin layer chromatography and by measuring of the melting points. These results are described in our earlier paper [8,17] Synthesis of **NOB2**—yield 76.3%, melting point 120–122 °C, $^1$H NMR (DMSO) $\delta$ (ppm); 0.698–0.796 (t, 3H, $CH_3$–), 0.835 (4H, –$CH_2$–), 1.153 (2H, –$CH_2$–), 4.431 (s, 3H, O–$CH_3$), 6.714–6.772 (m, 3H, Ar), 6.839–6.947 (m, 6H, Ar), 7.162–7.195 (m, 6H, Ar), 7.635–7.671 (2d, 3H, Ar), 8.051–8.100 (m, 2H, Ar), 8.572–8.606 (d, 2H, Pyr), 9.474–9.508 (d, 2H, Pyr). The purity of the dyes was spectroscopic grade.

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

(iii) The reduction and oxidation potentials of dyes, the oxidation potential of *n*-butyltriphenyl borate and reduction potentials of *N*-methoxy-*p*-phenylpyridinium salt and

*N*,*N*'-diethoxy-2,2'-bipyridilium salt were measured by cyclic voltammetry. An Electroanalitical MTM System model EA9C-4z (Cracow, Poland), equipped with a small-volume cell, was used for the measurements. A 1 mm platinum 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. $O_2$ was removed by bubbling argon gas through the solution. The potential was swept from −1.6 to 1.6 V with the sweep rate of 250 mV/s to record the current–voltage curve.

(iv) 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 diameter; 0.25 mL of cured sample). The measurements were performed in a homemade microcalorimeter [19–23]. 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 (**SBr**) and co-initiators (**B2**, **NO**, **BP**, **NOB2**) concentrations used in experiments were $1 \times 10^{-3}$ and $1 \times 10^{-2}$ M, respectively. The monomer was used without purification. As a reference sample, a mixture containing hemicyanine iodides or *p*-toluene sulfates (dye without a co-initiator) was used. The polymerizing mixture was not deaerated. In order to reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish–Troomsdorf effect and radicals trapping effect, the initial rates of polymerization were taken into account for further consideration. The initial rates of polymerization are the slopes of the lines drawn on the flow of heat versus time curve at the initial of polymerization.

## 3. Results and discussion

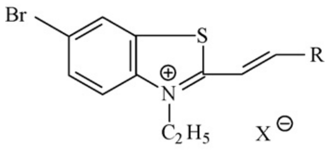
### 3.1. Efficiency of dye/n-butyltriphenylborate salt and dye/n-butyltriphenylborate salt/N-alkoxypyridinium salt photoinitiating systems in free radical polymerization

Five various sensitizers (**SBr** electron acceptor/electron donor) and four co-initiators were used in our study. The structure of dyes used in studies is given in Chart 1.

Chart 2 presents the structure and electrochemical properties of co-initiators studied.

Table 1 presents the structures and spectroscopic properties of all tested dyes.

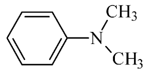
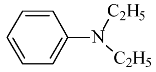
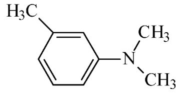
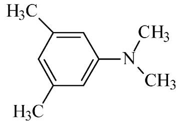
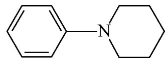
Belonging to the hemicyanine dyes (6-bromo-3-ethyl-2-*p*-alkylaminostyryl) benzothiazolium salts (**SBr**) absorb the visible light in the region of 450–600 nm (responsible for their purple color) due to the $\pi,\pi^*$ transition of vinyl conjugated chromophore. The tested dyes show an intensive absorption band with maximum localized in the range from 538 to 550 nm. The presence of various substituents in the dye structure, as shown in Table 1, only slightly affects the position of electronic absorption spectra maximum. The typical room temperature absorption and emission spectra for 6-bromo-3-ethyl-2-(*p*-*N*,*N*-dimethylaminostyryl) benzothiazolium *p*-toluene sulfate (**SBr1**) in ethyl acetate solution are shown in Fig. 1.



**(SBr)**

Chart 1.

Table 1
Characteristics of hemicyanine dyes

| Dye | R | $\lambda_{ab}$[a] [nm] | $\lambda_{fl}$[a] [nm] | $E_{00}$ [eV] |
|---|---|---|---|---|
| **SBr1** |  | 538 | 601 | 2.062 |
| **SBr2** |  | 546 | 604 | 2.053 |
| **SBr3** |  | 550 | 605 | 2.049 |
| **SBr5** |  | 540 | 644 | 1.926 |
| **SBr8** |  | 544 | 617 | 2.03 |

[a] $\lambda_{ab}$ and $\lambda_{fl}$ are the absorption and fluorescence maximum in ethyl acetate solution, respectively. $E_{00}$ is the excited singlet state energy.

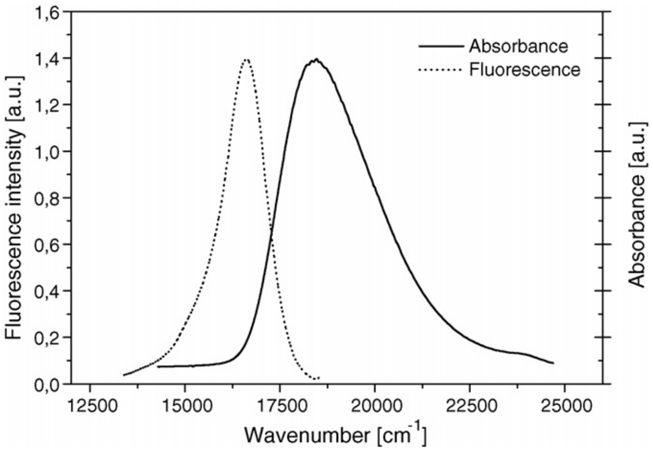
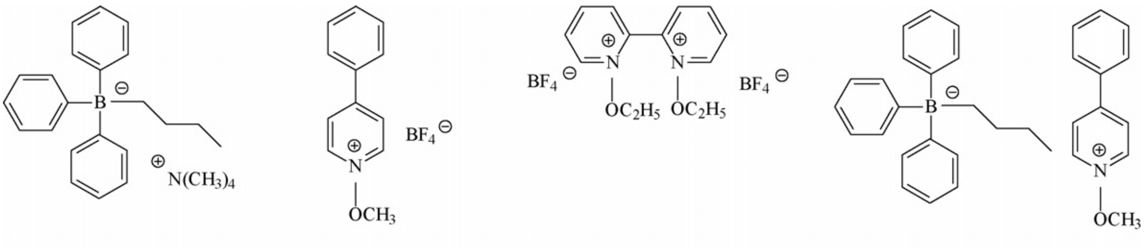


Fig. 1. Electronic absorption and fluorescence spectra of **SBr1** dye, recorded in ethyl acetate.



tetramethylammonium *n*-butyltriphenylborate
**B2**
$E_{ox}$ = 1.16 eV

N-methoxy-4-phenylpyridinium tetrafluoroborate
**NO**
$E_{red}$ = - 0.67 eV

N,N'-diethoxy-2,2'-bipyridilium ditetrafluoroborate
**Bp**
$E_{red}$ = - 0.645 eV

N-methoxy-4-phenylpirydinium-*n*-butyltriphenylborate
**NOB2**

Chart 2.

The fluorescence spectra of these dyes are roughly a mirror image of the absorption spectra. Fluorescence emission in ethyl acetate solution exhibits a maximum which is redshift in comparison to the absorption maximum by less than 2500 $cm^{-1}$.

For the analysis of the photoinitiating properties of the novel photoinitiator systems the selected combinations of hemicyanine dyes (**SBr**) and co-initiators (**B2**, **NO**, **Bp**) were used:

in two-component photoinitiator systems:
I. Hemicyanine dye and tetramethylammonium *n*-butyltriphenylborate (**SBr + B2**).
II. Hemicyanine dye and *N*-methoxy-4-phenylypyridinium tetrafluoroborate (**SBr + NO**).
III. Hemicyanine dye and *N*,*N*′-diethoxy-2,2′-bipyridilium ditetrafluoroborate (**SBr + Bp**).
in three-component photoinitiator systems:
IV. Hemicyanine dye, tetramethylammonium *n*-butyltriphenylborate and *N*-methoxy-4-phenylpyridinium tetrafluoroborate (**SBr + B2 + NO**).
V. Hemicyanine dye and *N*-methoxy-4-phenylpyridinium *n*-butyltriphenylborate (**SBr + NOB2**).
VI. Hemicyanine borate and *N*-methoxy-4-phenylpyridinium tetrafluoroborate (**SBrB2 + NO**).
VII. Hemicyanine borate and *N*,*N*′-diethoxy-2,2′-bipyridilium ditetrafluoroborate (**SBrB2 + Bp**).

It is clearly visible that there are two significant structural differences between the main system under study in the current work and that reported by Schuster and co-workers [9,10]. Firstly, the absorbing dyes are positively charged and this after an electron transfer allows to obtain a neutral radical. Secondly, we use both co-initiators paired either with different counterions or in form of an ion pair, which allows substrates of electron transfer reactions in a specific form to organize and minimize the diffusion effect on overall efficiency of photoinitiation.

The irradiation of photoinitiator systems tested with visible light may generate following radicals: *n*-butyl, methoxy, ethoxy that can initiate free radical polymerization of triacrylate monomers. Therefore, one can conclude that on the overall efficiency of the photoinitiation of free radical polymerization can influence: (i) the rate of electron transfer process, (ii) the rate of carbon–boron bond cleavage and the rate of nitrogen–oxygen bond cleavage or (iii) the reactivity of free radicals formed.

Table 2
Measured rates of free radical polymerization (μmol $s^{-1}$) of TMPTA photoinitiated by all photoinitiator systems tested

| Dye | B2 | NO | NO[a] | Bp | Bp[a] | NO + B2 | NOB2 |
|---|---|---|---|---|---|---|---|
| **SBr1** | 23.37 | 1.13 | 9.91 | 0.47 | 0.47 | 93.0 | 227.36 |
| **SBr2** | 17.70 | 0.94 | 8.50 | 0.71 | 5.90 | 94.68 | 240.8 |
| **SBr3** | 13.45 | 0.47 | 7.56 | 0.47 | 5.43 | 86.1 | 134.8 |
| **SBr5** | 11.33 | 0.47 | 4.01 | 0.19 | 3.30 | 59.0 | 108.6 |
| **SBr8** | 11.10 | 0.24 | 6.61 | 0.12 | 2.60 | 91.60 | 115.70 |

The other photoinitiator systems composed of hemicyanine dye as iodide (**SBr**).
[a] For photoinitiator system composed of hemicyanine dye as *n*-butyltriphenylborate salt (**SBrB2**).

The data illustrating the kinetics of free radical polymerization of TMPTA initiated by tested photoinitiator systems are summarized in Table 2.

The sensitivity of photoinitiator systems depends on the structure of the dye as well as on the type of co-initiator. This is

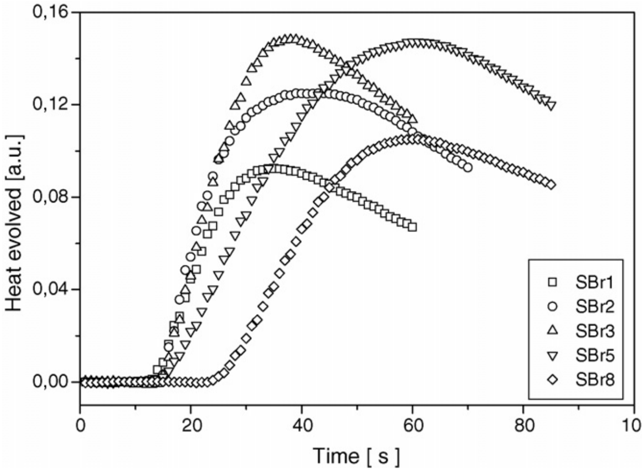


Fig. 2. Photopolymerization kinetic curves recorded for various sensitizers (**SBr**) and one type of co-initiator (**B2**). Monomer formulation: 1 mL of MP and 9 mL of TMPTA. Dye concentration was $1 \times 10^{-3}$ M and photoinitiating co-initiator concentration was $1 \times 10^{-2}$ M. Light intensity of argon-ion laser irradiation was 50 mW/0.785 $cm^2$.

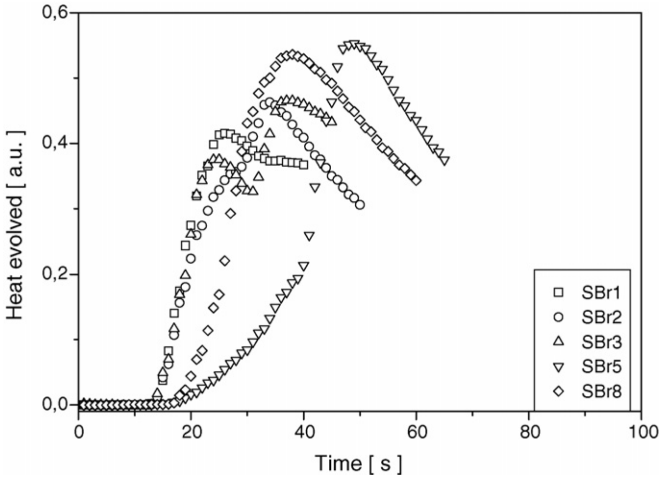


Fig. 3. Photopolymerization kinetic curves recorded for various sensitizers (**SBr**) and two types of co-initiators (**B2** and **NO**). Monomer formulation: 1 mL of MP and 9 mL of TMPTA. Dye concentration was $1 \times 10^{-3}$ M and photoinitiating co-initiator concentration was $1 \times 10^{-2}$ M. Light intensity of argon-ion laser irradiation was 50 mW/0.785 cm$^2$.

illustrated in Fig. 2 (for two-component photoinitiator system: dye **SBr**/co-initiator **B2**) and 3 (for three-component photoinitiator system: dye **SBr**/co-initiators: **B2** and **NO**), respectively, as well as is summarized in Table 2. The analysis of the kinetic curves in Figs. 2 and 3 shows, additionally, relatively long polymerization induction time. This specific behavior can be attributed to the presence of oxygen in polymerizing mixture.

The data in Fig. 2 and Table 2 clearly show that hemicyanine borates are effective initiators of free radical polymerization.

The apparent efficiency of the well known two-component dye/*n*-butyltriphenylborate photoinitiating system is dependent on the dye as expected (Fig. 2; Table 2). Some combinations such as **SBr5/B2** and **SBr8/B2** behave very inefficient, leading to a long inhibition time.

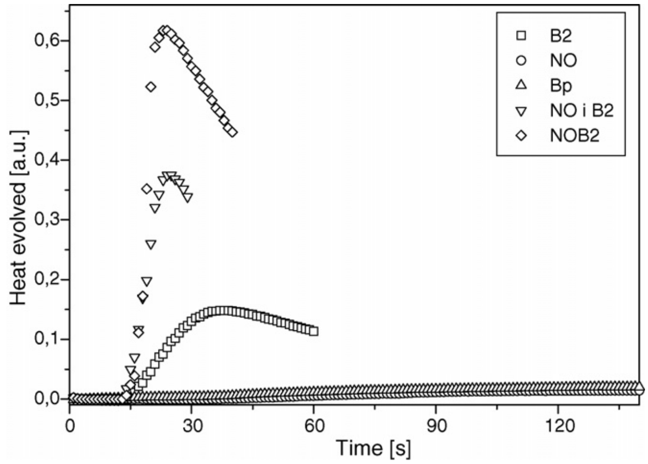


Fig. 4. The kinetic curves of TMPTA-MP mixture polymerization initiated by 6-bromo-3-ethyl-2-(2-methyl-4-*N*,*N*-dimethylaminostyryl) benzothiazole ethyl sulfate (**SBr3**) ($c = 1 \times 10^{-3}$ M) in the presence of: **B2**, **NO**, **Bp**, **NO + B2** and **NOB2**, respectively. Concentration of each co-initiator equal $1 \times 10^{-2}$ M. Light intensity equal 50 mW/0.785 cm$^2$.

Table 3
The relative rates ($R_p$) to the rates of the initiation of free radical polymerization by hemicyanine *n*-butyltriphenyl borate ion pair (**SBrB2**)

| Dye | B2 | NO | NO[a] | Bp | Bp[a] | NO + B2 | NOB2 |
|---|---|---|---|---|---|---|---|
| **SBr1** | 1 | 0.084 | 0.737 | 0.035 | 0.351 | 6.91 | 10.02 |
| **SBr2** | 1 | 0.040 | 0.364 | 0.03 | 0.252 | 4.05 | 9.73 |
| **SBr3** | 1 | 0.027 | 0.427 | 0.027 | 0.307 | 4.87 | 13.6 |
| **SBr5** | 1 | 0.042 | 0.354 | 0.017 | 0.292 | 5.2 | 9.6 |
| **SBr8** | 1 | 0.021 | 0.59 | 0.01 | 0.23 | 8.25 | 10.49 |

[a] For photoinitiator system composed of hemicyanine dye as *n*-butyltriphenylborate salt (**SBrB2**).

Fig. 4 presents the kinetic traces recorded during an argon-ion laser photoinitiated polymerization of TMPTA-MP (9:1) mixture in the presence of 6-bromo-3-ethyl-2-(2-methyl-4-*N*,*N*-dimethylaminostyryl) benzothiazole ethyl sulfate (**SBr3**) as the light absorber and functioning co-initiators defined in the figure.

The relative rates of polymerization photoinitiated by all dye/co-initiators combinations tested are summarized in Table 3.

Fig. 5 presents the comparison of photoinitiating efficiency for selected two- and three-component photoinitiating systems

The photoinitiating systems possessing cyanine dye and *N*-alkoxypyridinium salt yield free radicals able to the initiate polymerization as a result of reductive cleavage of *N*-alkoxypyridinium salts [7]. Single electron transfer from the excited singlet state of the dye to *N*-alkoxypyridinium salt results in N–O bond cleavage and the formation of an alkoxy radical, which can initiate a radical polymerization. The driving force for the fragmentation reaction in this case results from the formation of a stable pyridine molecule [7].

From the inspection of the kinetic data it appears that the two-component dye/*N*-alkoxypyridinium or dye/*N*,*N*′-dialkoxybipyridilium photoinitiating systems are not able to the initiate a radical polymerization as did other dye based systems (xanthene or cyanine dye/**NO**) under the same irradiation conditions [7]. This means that under sensitization conditions and using these dyes as sensitizers, the interaction between the dye and **NO** or **Bp** does not efficiently lead to the initiating species.

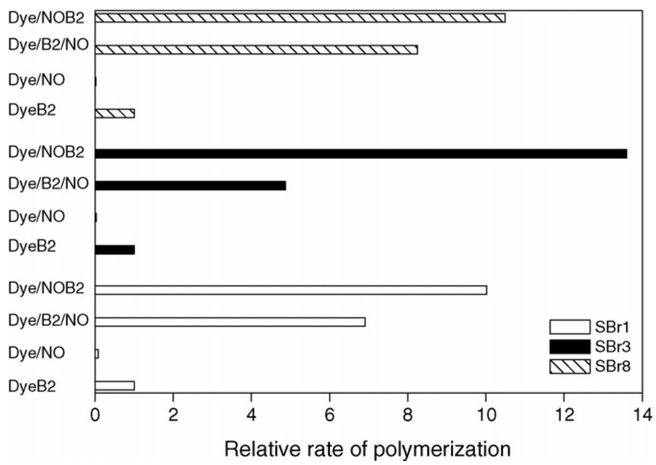


Fig. 5. Comparison of photoinitiating efficiency for different visible photoinitiating systems. The type of photoinitiator is marked in figure.

Generally the type of applied co-initiator also has effect on the overall sensitivity of a dye. Therefore, one can conclude that the rate of photoinitiated polymerization may depend on the structure of a radical that is obtained during a secondary reaction occurring after electron transfer. It is clearly seen, if we compare the rate of free radical polymerization of TMPTA initiated by photoinitiator systems: **SBr/B2**, **SBr/NO** and **SBr/Bp**. Only *n*-butyl radicals initiated the free radical polymerization of TMPTA. However, such photoinitiating systems initiate a free radical polymerization with the lower rate ($R_p$) than the three-component photoinitiating system under this study.

Here it also was demonstrated that the addition of *N*-alkoxypyridinium salt to the two-component **SBr/B2** photoinitiator system leads to an enhancement of the polymerization efficiency for all the systems studied. *N*-Alkoxypyridinium salt (**NO**) has the most striking effect on the photoinitiating system that contains **SBr1** and **SBr8** dyes. For all photoinitiating systems tested the rate of free radical polymerization exhibits a seven-/eight-fold increase in the presence of **NO** (Table 3; Fig. 5).

The use of two co-initiators as the ion pair causes an additional acceleration in polymerization rate. Unexpectedly, the highest rate of polymerization, as it is shown in Fig. 4 and in Tables 2 and 3, is observed for such *n*-butyltriphenyl borate and *N*-methoxy-4-phenylpyridinium ion pair acts as co-initiating pair.

In such photoinitiator system the light intensity have only insignificant influence on the rate of free radical polymerization of TMPTA. In Fig. 6 it is shown that if the light intensity was decreased from 50 to 15 mW/0.785 cm$^2$ the efficiency to the initiation of polymerization by three-component photoinitiator system is still very high.

The experiments show that the rate of polymerization photoinitiated by all hemicyanine dyes tested (**SBr**) in the presence of tested co-initiators ($c = 1 \times 10^{-2}$ M) increases in a sequence:

**Bp < NO < B2 < B2 + NO < NOB2**

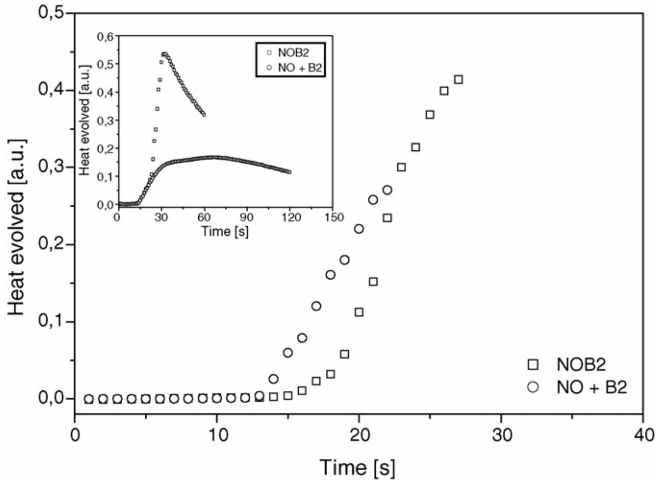
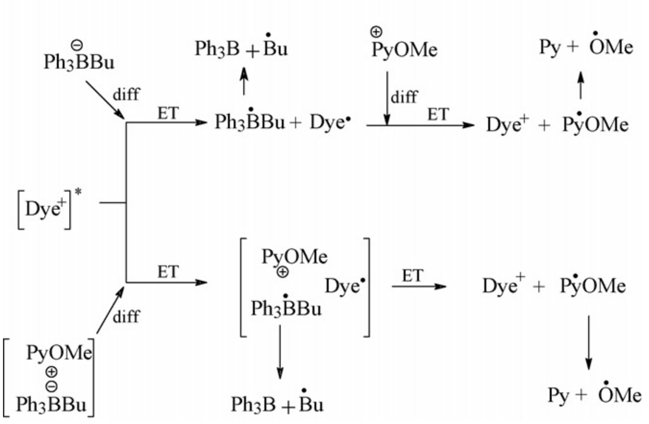


Fig. 6. The kinetic curves of TMPTA-MP mixture polymerization initiated by 6-bromo-3-ethyl-2-(4-*N*,*N*-dimethylaminostyryl) benzothiazole ethyl sulfate (**SBr1**) ($c = 1 \times 10^{-3}$ M) in the presence of **B2 + NO** and **NOB2**, respectively. Concentration of each co-initiator equal $1 \times 10^{-2}$ M. Light intensity equal 50 mW/0.785 cm$^2$ (inset $I_a = 15$ mW/0.785 cm$^2$).



Scheme 1.

As it was mentioned above the photoinitiating system of the mixture of dye and *N*-alkoxypyridinium borate ion pair exhibits higher photoinitiation ability in comparison to that of dye–borate salt–*N*-alkoxypyridinium salt photoinitiator system.

All this specific behaviors can be explained by assuming that there is an additional factor affecting the rate of photoinitited polymerization [17]. We believe that the observed difference comes from the specific spatial arrangement of all components of photoinititing system. Based on the photochemistry of borate anion [9,10] and photochemistry of *N*-alkoxypyridinium cation [7] we propose the mechanism in Scheme 1 that is consistent with the observations described above.

In this scheme, two possible mechanisms of free radical generation are considered. The upper path describes the processes that can occur when all initiating components are not organized, e.g. they are present in formulation as salts of photochemically inert counterions.

After excitation, in order to make an electron transfer effective the electron donor and electron acceptor must diffuse to each other to form encounter complex, in which electron transfer reaction takes place. Resulted boranyl radical decomposes yielding neutral triphenylboron and butyl radical [9,10]. The other product of electron transfer reaction, dye radical, could participate in a second electron transfer reaction with alkoxypyridinium cation to form alkoxypyridinium radical and in this way to generate a second radical. The mechanism of the processes occurring after irradiation of the photoinitiator systems tested was established by us using the laser flash photolysis [17]. It was found that, if co-initiators are present in solution as ion pair, after excitation, the dye and co-initiators ion pair diffuse and form encounter complex. An electron transfer from borate ion follows this process forming boranyl and dye radicals. However, in this case the borate ion that is reaching excited dye is accompanied by alkoxypyridinium cation. This artificially enhances the concentration of alkoxypyridinium cation in proximity to the dye radical. This, in turn, increases the effective rate of dye radical quenching. As a result one observes an increase in speed of photoinitiated polymerization.

### 3.2. *Criteria of selection of the dye in the photoinitiating system dye/**B2**/**NO***

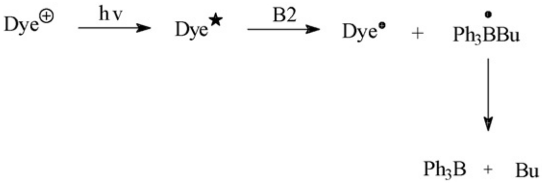
As it was mentioned above the addition of *N*-methoxy-*p*-phenylpyridinium salt (**NO**) to a classical hemicyanine dye/*n*-butyltriphenylborate salt photoinitiating system (in which the dye is the only absorbing species) clearly leads to an increase in the rate of polymerization of acrylic monomers. This confirms the results that were obtained when 3-ethyl-2-(*p*-dialkylaminostyryl) benzothiazolium iodide were present [17].

As it is shown in Scheme 1 after light absorption by the dye, the excited state of the dye is quenched by **B2**. This interaction leads to the generation of the initiating radicals (*n*-butyl radicals). The reaction between dye radical and **NO** leads to dye and second initiating radical. As a consequence, it appears that the efficiency of the photoinitiating system dye/borate salt **B2**/*N*-alkoxypyridinium salt **NO** lies on the involvement of electron transfer reaction between the dye, **B2** and **NO**.

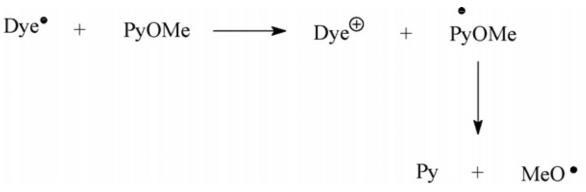
All the dyes studied exhibit the same kind of photophysics and photochemistry [8,11,17]. They possess a short lived singlet excited state. Borate salt interaction occurs in the excited singlet state and generates boranyl radical and dye$^{\bullet}$ radical. The *N*-alkoxypyridinium salt acts as an electron acceptor in its ground state and reacts with a dye$^{\bullet}$ radical.

Basing on this, the a priori selection of efficient systems should obey at least to two major criteria:

(i) the interaction between the excited singlet state of the dye and *n*-butyltriphenylborate **B2** must be strong in order to generate a large number of initiating radicals



(ii) the interaction between the dye radical and *N*-alkoxypyridinium salt **NO** must also be important in order to generate a large number of initiating radicals



$\Delta G_{\mathrm{el}\,1}$ and $\Delta G_{\mathrm{el}\,2}$ denote the free energy changes.

It appears that the first condition (i) involves reduction of excited state of the dye by **B2**, whereas (ii) is the oxidation of the reduced state of dye (radical) by **NO**. Therefore, the studies of the kinetics of the free radical polymerization via electron transfer process should include the estimation of the thermodynamic driving force for the electron-transfer reaction. The main prerequisite for photoinduced intermolecular electron-transfer process (PET) reactions has been described by the Rehm–Weller equation [24], which states that the free energy of activation for the PET ($\Delta G_{\mathrm{el}}$) process should have a negative value. For the calculation of $\Delta G_{\mathrm{el}}$, several important data are needed: (1) the reduction or oxidation potential of the dye, (2) the oxidation potential of electron donor (*n*-butyltriphenylborate anion **B2**), (3) the reduction potential of electron acceptor (**NO**, **Bp**), and (4) the singlet or tryplet state energy of the dye. An analysis based on the calculated free energy changes of electron transfer reactions mentioned above $\Delta G_{\mathrm{el}\,1}$, $\Delta G_{\mathrm{el}\,2}$ was carried out for all dyes (Table 4).

Table 4
Electrochemical and thermodynamic properties of the hemicyanine dyes and co-initiators tested

| Compound | $E_{\mathrm{red}}$ [eV] | Dye reduction by **B2** | Dye$^{\bullet}$ oxidation by **NO** and **Bp** | |
|---|---|---|---|---|
| | | $\Delta G_{\mathrm{el}\,1}$ [eV][a] | $\Delta G_{\mathrm{el}\,2}$ [eV][b] | $\Delta G_{\mathrm{el}\,2}$ [eV][c] |
| **SBr1** | −0.750 | −0.152 | −0.08 | −0.105 |
| **SBr2** | −0.780 | −0.109 | −0.11 | −0.135 |
| **SBr3** | −1.130 | 0.237 | −0.46 | −0.485 |
| **SBr5** | −1.100 | 0.334 | −0.43 | −0.455 |
| **SBr8** | −1.250 | 0.38 | −0.58 | −0.605 |

[a] Free energy changes ($\Delta G_{\mathrm{el}\,1}$) in acetonitrile calculated by $\Delta G_{\mathrm{el}} = E_{\mathrm{ox}}$ (**B2**) − $E_{\mathrm{red}}$ (dye) − $E_{00}$.

[b] Free energy changes ($\Delta G_{\mathrm{el}\,2}$) in acetonitrile calculated by $\Delta G_{\mathrm{el}} = E_{\mathrm{red}}$ (dye) − $E_{\mathrm{red}}$ (**NO**).

[c] Free energy changes ($\Delta G_{\mathrm{el}\,2'}$) in acetonitrile calculated by $\Delta G_{\mathrm{el}} = E_{\mathrm{red}}$ (dye) − $E_{\mathrm{red}}$ (**Bp**).

$(\Delta G_{\mathrm{el}\,1})$

The results of $\Delta G_{\mathrm{el}}$ calculation presented in Table 4 clearly indicate that the electron transfer process is thermodynamically allowed only in a few photoinitiator system tested.

$(\Delta G_{\mathrm{el}\,2})$

On the basis of the above experiments, it appears that alkoxypyridinium cation is reduced by dye radical. This reaction yields the dye cation and alkoxypyridinium radical that undergoes fragmentation giving stable pyridine and alkoxy radical.

It is necessary noting that the dye-sensitized oxidation of alkoxypyridinium cation requires the transfer of an electron from the excited state of the dye to the pyridinium cation. Gould et al. have documented that exothermic photochemical electron transfer reaction requires the reduction potential of the donor molecule to be more negative in comparison to the reduction potential of alkoxypyridinium cation [7]. Reduction of *N*-methoxy-4-phenylpyridinium salt and the dyes under the study by cyclic voltametry is irreversible in almost all cases. Therefore, the potentials measured by cyclic voltametry reduction potentials may have only approximate thermodynamical significance. Thus, calculated using the Rehm–Weller equation [24] the driving force of electron transfer process ($\Delta G_{\rm el}$) with cyclic voltametry potentials can be treated as only rough estimation. According to the Rehm–Weller model [24], significant quenching rate constants through electron transfer ($>10^9\,{\rm M}^{-1}\,{\rm s}^{-1}$) should be observed when $\Delta G_{\rm el}$ values are negative.

The dyes under the study reduce in the range from −1.250 eV dye **SBr8** to −0.75 eV dye **SBr1**, respectively (versus Ag–AgCl). The measured value of reduction potential for alkoxypyridinium cation and *N*,*N*′-dialkoxy-2,2′-bipyridilium dication is about −0.67 and −0.645 eV, respectively. Under this condition, in the presence of alkoxypyridinium cation or *N*,*N*′-dialkoxy-2,2′-bipyridilium dication, only dyes **SBr3**, **SBr5** and **SBr8** can initiate polymerization, because only the energetic of this photoredox pair is close to the region when the electron transfer becomes exothermic (the negative value of $\Delta G_{\rm el}$ calculated from Rehm–Weller equation). As it is seen from the data presented in Tables 3 and 4 the efficiencies of polymerization initiation (expressed by the initial rates of polymerization) do not correspond to the value of $\Delta G_{\rm el}$ of electron transfer between hemicyanine dye (**SBr**) and *N*-alkoxypyridinium salt (**NO**) and between hemicyanine dye (**SBr**) and *N*,*N*′-dialkoxy-2,2′-bipyridilium salt (**Bp**) (see Tables 3 and 4). Analyzing of $\Delta G_{\rm el}$ values, one can expect that the best photoinitiation efficiency should present the photoredox pair composed of dye **SBr8** and *N*-alkoxypyridinium salt (**NO**) or *N*,*N*′-dialkoxy-2,2′-bipyridilium salt (**Bp**) as co-initiator. The lowest efficiency should be observed in the photoinitiator system composed of dye **SBr1** and **SBr2**. The observed order of sensitivity in Table 3 is quite opposite. This behavior can be attributed to the different rates of N–O bond cleavage for both alkoxy salts: *N*-methoxy-4-phenylypyridinium (**NO**) and *N*,*N*′-diethoxy-2,2′-bipyridilium (**Bp**) for all tested two-component photoinitiator systems or, more precisely, to the ratio between the rate of the bond cleavage and the rate of the back electron transfer process. In the photoinitiator systems composed of hemicyamine dye and *n*-butyltriphenyl borate salt as co-initiator the rate of free radical polymerization increases if the driving force of electron transfer process becomes more negative. This behavior is consistent with the Marcus electron transfer theory [6,19,20].

Because the main property that differentiates the system under study and that from that described by Schuster comes from the properties of products obtained after an electron transfer process, which in our case are neutral radicals, therefore one can conclude that the overall rate of free radical formation reaction is not controlled either by the back electron transfer reaction or by the solvation process. Under this condition the rate of electron transfer, the diffusion, or spatial arrangement of both, substrates and short-lived intermediates limit the rate of photoinitiated polymerization. The reactivity of free radicals formed after electron transfer process can also influence on the rate of free radical polymerization. There are three different radicals initiating free radical polymerization: *n*-butyl, methoxy and ethoxy radicals. Analyzing the data presented in Table 3 one can conclude, that the rate of *n*-butyltriphenylboranyl radical decomposition is greater than that of *N*-methoxy-4-phenylypyridiunium and *N*,*N*′-diethoxy-2,2′-bipyridilium radicals. This suggests that the stability of radicals formed after electron transfer process is in order:

*N*,*N*′-diethoxy-2,2′-bipyridyl > *N*-methoxy-4-phenylypyridyl > *n*-butyltriphenylboranyl.

In summary, in fact, the thermodynamic conditions that have to be fulfilled on $\Delta G_{\rm el}$ are necessary but not enough to the selection of the dye. It was demonstrated that the kinetics also plays an important role.

## 4. Conclusions

Two-component photoinitiating system and three-component photoinitiating system, possessing (6-bromo-3-ethyl-2-(*p*-alkylaminostyryl)) benzothiazolium salts (**SBr**) as a primary absorber of visible light can be used to the initiate of free radical polymerization. Only two-component photoinitiator systems possessing hemicyanine dye and *n*-butyltriphenyl borate initiate polymerization with good efficiency. The three-component photoinitiator systems, possessing hemicyanine dye, borate anion and *N*-alkoxypyridinium cation or hemicyanine dye and *N*-alkoxypyridinium borate ion pair initiate free radical polymerization five and ten times faster than two-component photoinitiator system. By combination of *N*-alkoxypyridinium and alkyltriphenylborate salts with suitable dye cation two radicals can be generated by one absorbed photon.

## Acknowledgement

This work was supported by the State Committee for Scientific Research (KBN) (grant No. 3 T09 B 101 28).

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