

N-methylpicolinium esters as the second co-initiators in three-component visible light photoinitiating systems for vinyl monomers polymerization.

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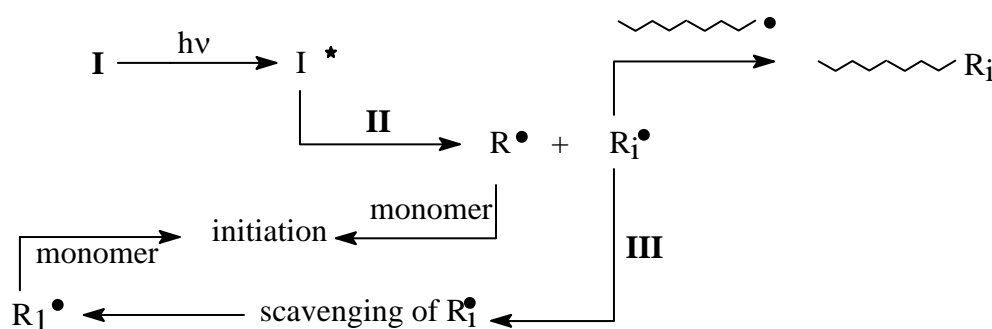
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Introduction

Typical photoinitiating systems acting under visible lights are classified as follow [1,2]:

- One-component system (such as bis-acylphosphine oxides, irone arene salts, peresters, organic borates, titanocenes, iminosulfonates, oxime esters, etc) [3,4].
- Two-component system (working through the electron transfer/proton transfer, energy transfer, processes that generate free radicals during the secondary reactions) [1,4].
- Three-component systems, where the basic idea is to try to enhance of photosensitivity by a combination of several components, that form the photoinitiating systems.

In the basic concept developed several years ago [1,5-7) in a three-component system I/II/III working through electron transfer (Scheme 1) the light is absorbed by I and radicals are formed trough I/II interaction. Radicals R_i^\bullet playing a detrimental role (through a reaction with the growing macromolecular chains) are quenched by III. The use of this suitable quencher III allows to scavenge the R_i^\bullet radicals and, if possible, to generate new initiating radicals through an electron transfer reaction. It is apparent that R_p will increase since, the concentration of terminating radicals decreases and new initiating species are generated from the deactivation process of the side radicals R_i^\bullet .

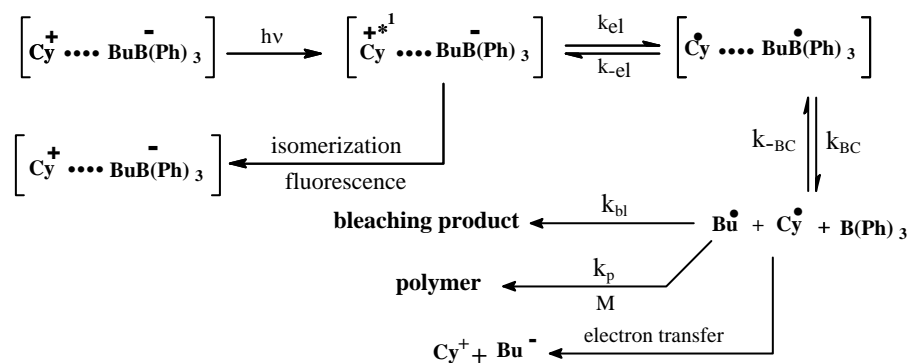


Scheme 1

- Multi-component systems (more than three partners).

Cyanine dyes as sensitizers in photoinitiating systems

Organoborate salts of carbocyanine dyes, described by G.B. Schuster in 1988, are the first commercial used two-component photoinitiating systems operating in the visible light region [8-10]. In this photoinitiating system the cyanine dye acts as a light absorber of a visible light and as electron acceptor. Basing on the Schuster's and our studies the mechanism of the processes occurring during the free radical polymerization initiated by cyanine borates photoredox pair was proposed (Scheme 1) [8-10].



Scheme 1

From this mechanism it can be deduced that the irradiation of cyanine borate salts leads to the formation of an excited singlet state of cyanine dye. One of the deactivation process that follows this process is an electron transfer reaction from borate anion to the excited state of a dye. As a result an unstable boranyl radical is formed. The boranyl radical can undergo the C-B bond cleavage giving triphenylboron and butyl radical. The butyl radical is capable of initiating the radical polymerization of an acrylate monomers.

In such photoinitiating systems the cyanine dye is an electron acceptor and only one type of free radical obtained initiates a chain reaction. The described above system represents a oxidative cleavage type of fragmentation.

The photoinitiation ability of such photoinitiating systems depends on the:

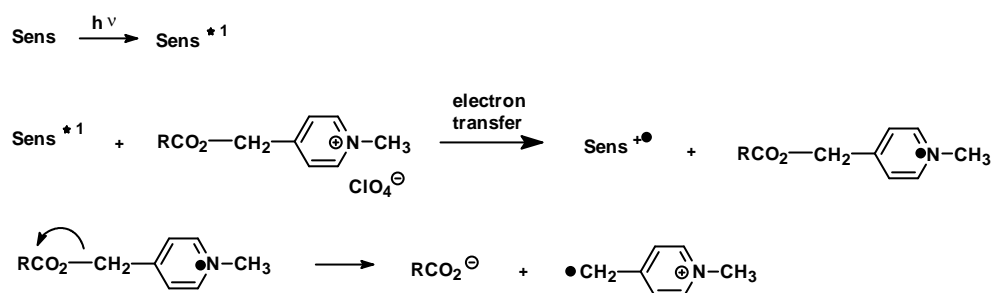
- Structure of polymethine dye (symmetrical or unsymmetrical)
- Type of a heteroatom in dye heterocyclic ring
- Type of a substituent in the "meso" position of polymethine chain
- Type of a substituent in the phenyl ring
- Structure of an alkylamino group in the styryl moiety (only for hemicyanine dyes)
- Structure of the borate anion.

Generally, the photoinitiating ability of mono-cationic cyanine dye photoinitiating systems is lower than the photoinitiating ability of dyeing photoinitiating systems in which after irradiation with visible light the long-lived excited triplet state of dye is formed.

Since, the three-component systems have consistently been found to be faster, more efficient, and more sensitive than their two-component counterparts we decided to focus our studies on application of the symmetrical carbocyanine dyes borate salts in three-component photoinitiating systems.

In order to accelerate the rate of polymerization initiated by photoinitiating systems composed of mono-cationic carbocyanine dye, borate salt and N-methyl picolinium esters were used as second co-initiator.

More recently, Sunderarajan's studies on the photochemical reduction of several N-methyl-4-picolinium derivatives by using laser flash photolysis demonstrated the formation of the radical anions. It was shown that the radical anion formed in this reaction readily undergoes C-O fragmentation to yield a carboxylic acid and a 4-pyridylmethyl radical. The mechanistic pathway of this photofragmentation reaction is as follows (Scheme 2) [11,12]:

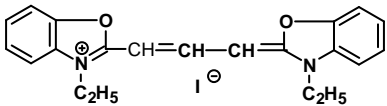
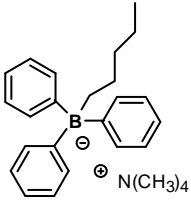
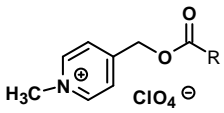


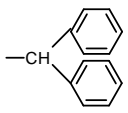
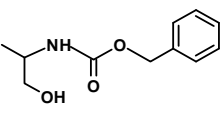
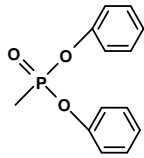



Scheme 2

Upon irradiation, the photosensitizer molecule absorbs light and is promoted to its excited singlet state. The latter transfers an electron to the picolinium derivative. The pyridyl radical subsequently releases the carboxylate anion, along with pyridylmethyl radical fragment. The pyridylmethyl radical can start the polymerization chain reaction.

The perchlorates of N-methylpicolinium derivative used as co-initiators and cyanine dye employed as a photosensitizer in this study, along with some relevant photophysical parameters including their redox potentials are listed in Table 1.

Table 1
The electrochemical properties of both sensitizer and co-initiators tested.

						
<p style="text-align: center;">Absorbing dye (Cy 19) $E_{red} = -1.26 \text{ eV}$, $E_{ox}(\text{dye}^*) = -1.04 \text{ eV}$, $E_{00} = 2.41 \text{ eV}$</p>						
Co-initiators						
I						II
						
where R is:						
						
B2 $E_{ox} = 1.16 \text{ eV}$	E1A $E_{red} = -0.92 \text{ eV}$ $E_{ox} = 0.25 \text{ eV}$	E1B $E_{red} = -0.77 \text{ eV}$ $E_{ox} = 0.27 \text{ eV}$	E1D $E_{red} = -0.60 \text{ eV}$ $E_{ox} = 0.27 \text{ eV}$	E1E $E_{red} = -0.65 \text{ eV}$ $E_{ox} = 0.60 \text{ eV}$	E1G $E_{red} = -0.94 \text{ eV}$ $E_{ox} = 0.23 \text{ eV}$	

Analyzing the possible reduction-oxidation reactions between components of photoinitiating system, one should consider all processes that can occur between them. This should include interactions between all reactants and possible reactions between photoinitiating system components in their ground state and short-lived intermediates obtained after electron transfer process.

Analysis of cyclovoltametric curve recorded for sensitizing dye (Fig. 1) suggests that the dye easily reduces and does not oxidizes. This observation allows concluding that the dye can not be an electron donor in N,N'-diethylcarbocyanine - N-methylpicolinium derivative photoredox couple. Thus, adopting this observation to application of this type of photoredox pair as photoinitiating system, one can predict that the couple composed of N,N'-diethylcarbocyanine cation and N-methylpicolinium derivative can not act as effective photoinitiator.

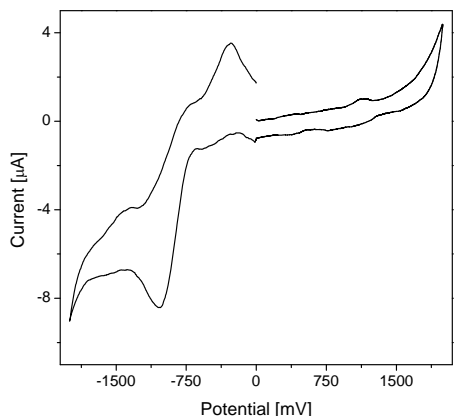


Figure 1. Cyclic voltammogram of N,N'-diethylcarbocyanine iodide in 0.1 M tetrabutylammonium perchlorate solution in dry acetonitrile as the supporting electrolyte.

The second possibility concerns the redox reaction between and N-methylpicolinium derivatives and borate anion. Knowing the oxidation potential of borate anion (1.160 eV), the reduction potentials of and N-methylpicolinium derivatives (oscillating from -0.94 eV to -0.60 eV, see Figure 2 and data in Table 1), and taking into account fact that and N-methylpicolinium derivative can not be transferred into its excited state at 514 nm, one can easily calculate that the free energy change (ΔG_{el}) for reactions between N-methylpicolinium derivatives and borate anion oscillates from 1.760 eV to 2.10 eV. This observation clearly states that analyzed type of reaction is not thermodynamically allowed.

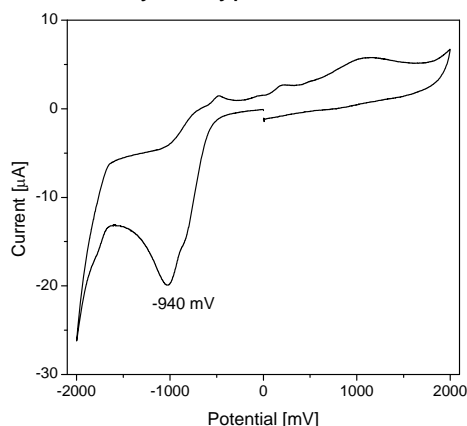


Figure 2. Cyclic voltammogram of N-methylpicolinium derivative (**E1B**) in 0.1 M tetrabutylammonium perchlorate solution in dry acetonitrile as the supporting electrolyte.

The third possibility concerns a reaction that can take place between the N,N'-diethylcarbocyanine radical, obtained after photoinduced electron transfer between dye cation and borate anion (E_{ox}^*). Such intermediate can be treated as electron donating individual in the reaction with N-methylpyridinium derivative ground state. The free energy change for these reactions depends on the N-methylpicolinium derivative structure and varies between -0.44 and -0.1 eV. The negative values of ΔG_{el} , in contrast to positive ones obtained for other possible reactions, suggests that there is a possible secondary reaction between the dye radical and ground state of N-methylpicolinium derivative. This reaction yields N-methylpicolinium derivative radical that decomposes giving picolyl radical and carboxylic acid anion.

Summarizing, the thermodynamics considered predicts that the system composed of cyanine dye/borate anion/N-methylpicolinium derivative theoretically can give two photoinitiating radicals after absorption of one photon.

The cyclovoltammetric curves shown in Figures 1 and 2 demonstrate two different specific properties. Both analyzed compounds undergo reduction. However, in the case of the cyanine dye this process is fully reversible, while N-methylpicolinium derivative reduces irreversibly. The dye cation reduction yields dye radical that, as it is shown in Figure 1, can undergo back electron, namely can be easily oxidized (can be an effective reductor). On the other hand methylpicolinium radical obtained does not undergoes back electron transfer

reaction. This specific behavior is commonly observed for the products of redox reaction that very fast decomposes. Nice illustration of such behavior is well known property of borate anion [7,8]. The above analysis strongly supports a possibility of an interaction between the dye radical and N-methylpicolinium cation. This redox reaction yields as a product methylpicolinium radical that based on data presented in Figure 2 decomposes giving methylpicolinium radical and organic acid anion [11,12].

The kinetics of polymerization. Efficiency of photoinitiation of two- and three-component photoinitiating systems.

The photoinitiating systems composed of N,N'-diethylcarbocyanine dye as a photosensitizer with various co-initiators (borate salt and N-methylpicolinium derivatives) were used for the initiation of free radical polymerization.

The kinetic curves obtained for the photoinitiated polymerization of 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) (9:1) mixture photoinitiated by N,N'-diethylcarbocyanine borate in a presence of selected N-methylpicolinium derivatives, under irradiation with a visible light are shown in Figure 3 for illustration.

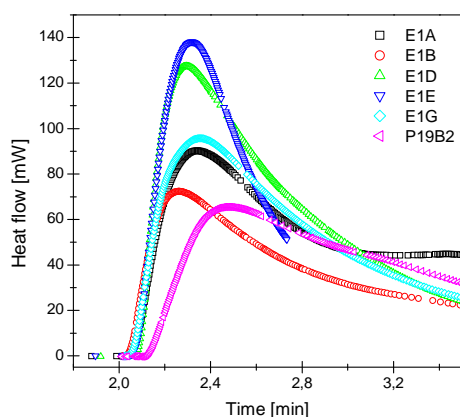


Figure 3. Family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA/MP (9/1) mixture initiated by N,N'-diethylcarbocyanine *n*-butyltriphenylborate in presence of N-methylpicolinium derivative perchlorates marked in the Figure. The cyanine borate and N-methylpicolinium derivative concentrations were 5×10^{-3} M, $I_a = 20$ mW/0.196cm⁻¹.

The rate profiles of TMPTA photopolymerization (Figure 3) show an immediate onset of autoacceleration typical for the polymerization of multifunctional monomers [13].

It is apparent from the inspection of the initial rates of polymerization that the efficiency of the tested photoinitiating system depends on the structure of N-methylpicolinium salt. The lowest rate of photoinitiated polymerization was observed for acyl derivative (**E1G**).

The relative rates of photoinitiated polymerization measured for all the tested photoinitiating systems are collected in Table 2.

Table 2

The relative rates of photoinitiated polymerization and the values of the free energy of activation change for the PET (ΔG_{el}) process between the dye radical and N-methylpicolinium salt.

Co-initiator	Rate of polymerization [a.u.]	ΔG_{ET} [eV]
<i>n</i> -butyltriphenyl borate salt	266	-0.05*
E1A	608	-0.124**
E1B	826	-0.274**
E1D	1013	-0.444**
E1E	893	-0.394**
E1G	522	-0.104**

ΔG_{ET}^* was calculated form $\Delta G_{ET} = E_{ox}(B2) - E_{red}(Dye) - E_{00}$

ΔG_{ET}^{**} was calculated form $\Delta G_{ET} = E_{ox}(Dye^{\bullet}) - E_{red}(E)$

The kinetic curves presented in Figure 3 and data compiled in Table 2 reflect the activity of the investigated N-methylpicolinium derivatives.

From the obtained kinetic results it is seen that the addition of N-methylpicolinium derivative to monomeric formulation containing cyanine borate as photoinitiator increases the rate of polymerization about 3 – 4 times. The best photoinitiating ability exhibits the photoinitiating system possessing L-serine and phosphoryl (**E1D**, **E1E**) residues in N-methylpicolinium molecule.

Figure 4 presents the kinetic traces recorded during an argon ion laser photoinitiated polymerization of TMPTA-MP (9:1) mixture in the presence of N,N-diethylcarbocyanine *n*-butyltriphenyl borate and functioning as second co-initiator N-methylpicolinium derivative perchlorate at its various concentration.

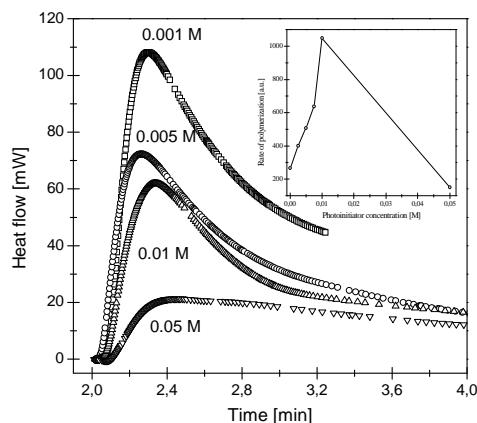


Figure 4. Kinetic curves recorded during the measurements of the flow of heat during the photoinitiated polymerization of the TMPTA/MP (9/1) mixture initiated by N,N'-diethylcarbocyanine *n*-butyltriphenylborate in presence of different concentration (marked in the Figure) of N-methylpicolinium derivative perchlorate (**E1B**). Inset: The influence of the picolinium ester concentration on the rate of polymerization for **E1A** as a second co-initiator.

From the inspection of the data presented in Table 2 one can see that the addition a N-methylpicolinium ester as a second co-initiator to cyanine dye/borate salt photoinitiating system causes a synergistic effect in the polymerization reactions (Figures 3 and 4). For all third components tested the polymerization rate increases compared to the parent cyanine dye/borate salt system. The three-component dye/borate salt/N-methylpicolinium ester initiators exhibit a high reactivity: the rate of polymerization (R_p) is 3-4 times higher than measured for dye/borate salt two-component photoinitiating system.

In order to explain the *n*-butyltriphenylborate salt, N-methylpicolinium ester (**E1B**) effect on the photochemical behavior of the light absorbing dye (sensitizing component) the steady-state fluorescence experiments were applied to measure the quenching of the dye fluorescence as a function of co-initiator concentration. The fluorescence quenching experiment was performed for and N,N'-diethyloxcarbocyanine iodide in the presence of borate salt (B2), and N-methylpicolinium ester, respectively. Experiments show that the efficiency of the fluorescence quenching of carbocyanine dye by borate salt is significantly higher than those observed for N-methylpicolinium ester.

The Stern-Volmer plot for quenching of N,N'-diethyloxcarbocyanine iodide fluorescence by borate salt is shown in Figure 5

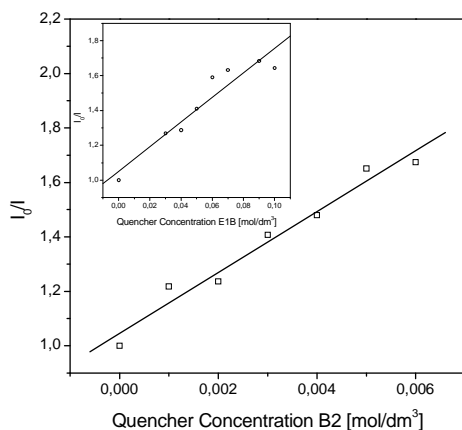
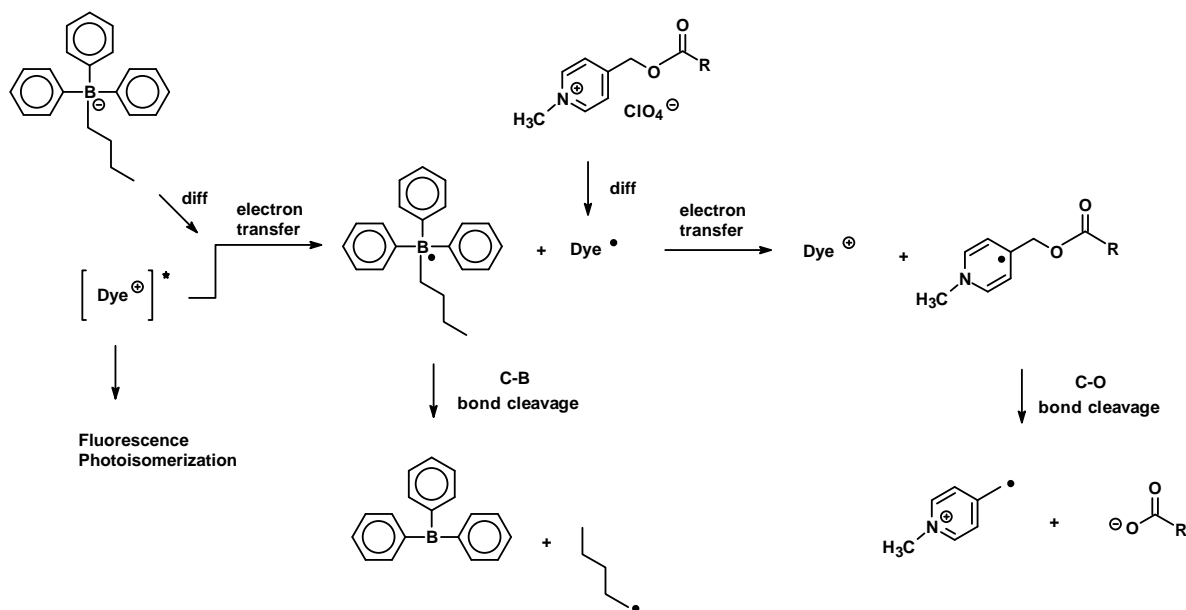


Figure 5. The Stern-Volmer plots of fluorescence quenching of mono-cationic dye: N,N'-diethyloxacarbocyanine iodide by borate salt (**B2**) and N-methylpicolinium ester (**E1B**), respectively.

Analysis of the data obtained from the fluorescence quenching experiments shows, that the quenching rate constants (under experimental conditions equal to the electron transfer rate constant) of the excited singlet state of carbocyanine dye by second co-initiator in ethyl acetate : 1-methyl-2-pyrrolidinone solution (1:1) are about $10^{10} \text{ M}^{-1}\text{s}^{-1}$ e.g. are controlled by the diffusion. The quenching of the excited singlet state of the carbocyanine dye by borate anion is much more efficient, reaching the value of k_q close to $10^{12} \text{ M}^{-1}\text{s}^{-1}$. The rate constant obtained for dye-borate pair are greater, than those commonly observed for intermolecular electron-transfer reactions, since ion pairing eliminates the limitation caused by diffusion. The quenching rate constant of the cyanine excited singlet state by N-methylpicolinium ester is about one order of magnitude lower than those measured for borate anion.

The mechanism of photochemical processes in three-component photoinitiating system

Basing on the photochemical and photophysical properties of alkyltriphenylborate salts and N-alkylpicolinium esters the following mechanism of processes occurring in the three-component photoinitiating system composed of carbocyanine dye/borate salt/N-methylpicolinium ester was proposed (Scheme 3).



Scheme 3

After irradiation with a visible light of the three-component photoinitiating system, the excited singlet state of chromophore is formed. The deactivation of excited state occurs by fluorescence, photoisomerization or electron transfer process. In presence of

alkyltriphenylborate salt the cyanine dye undergoes one-electron reduction. The cyanine dye radical and boranyl radical are formed. The boranyl radical undergoes the C-B bond cleavage giving an alkyl radical which can start the polymerization reaction. The cyanine radical in presence of N-alkylpicolinium ester can participate in the second electron transfer process giving cyanine cation and N-alkylpicolyl radical. The last undergoes fast decomposition forming pyridylmethyl radical which can also initiate free radical polymerization.

Mechanism of this reaction was concluded on the basis of the nanosecond laser flash photolysis results for cyanine dye in presence of (i) tetramethylammonium *n*-butyltriphenyl borate, (ii) perchlorate N-methylpicolinium ester and (iii) cyanine *n*-butyltriphenylborate in presence of perchlorate N-methylpicolinium ester.

The transient absorption spectra of cyanine dye recorded in the presence of tested co-initiators are presented in Figure 6

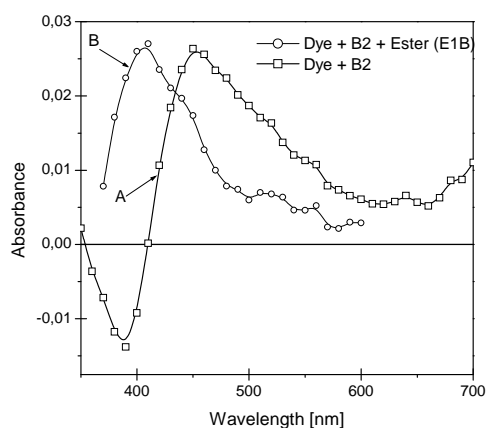


Figure 6. Transient absorption spectra of: (A) cyanine dye in presence of borate salt (**B2**) recorded 50 ns after laser puls (squares) and (B) for cyanine dye in presence of equimolar ratio of tetramethylammonium *n*-butyltriphenyl borate and N-methylpicolinium perchlorate (**E1B**) 100 ns after laser puls (circles) (concentration of both equal 2×10^{-3} M) in acetonitrile solution. Dye concentration was 2×10^{-5} M.

As it was mentioned above the irradiation of the carbocyanine dye with visible light leads to the excited singlet state formation. This can be quenched in electron transfer process by *n*-butyltriphenylborate salt. The absorption band observed at 430 nm in the transient absorption spectra is assigned to the cyanine dye radical formed in electron transfer process [7-9]. There are no characteristic bands after irradiation of cyanine dye and N-methylpicolinium ester solution. However, laser flash photolysis of the three-component system composed of cyanine dye/borate salt/N-methylpicolinium ester in acetonitrile as a solvent (concentration 2×10^{-3} M) gives the new absorption band at 410 nm, that appears at expense of that observed at 430 nm. This behavior is similar to that described by Sundararajan [11,12] for system composed of dye and N-alkylpicolinium ester. The characteristic band at 410 nm can be attributed to the product of N-methylpicolinium ester reduction.

Taking into consideration, the results described by Sunderarajan and et. al. for dye/ester system one can conclude, that the addition N-methylpicolinium ester into two-component system: cyanine dye/borate salt causes the quenching of the cyanine radical formed after electron transfer process.

The formation of N-methylpicolyl ester radical after electron transfer process from cyanine radical to ground state of N-methylpicolinium ester and its disappearance occurs during a period of time about 170 ns (see Figure 7).

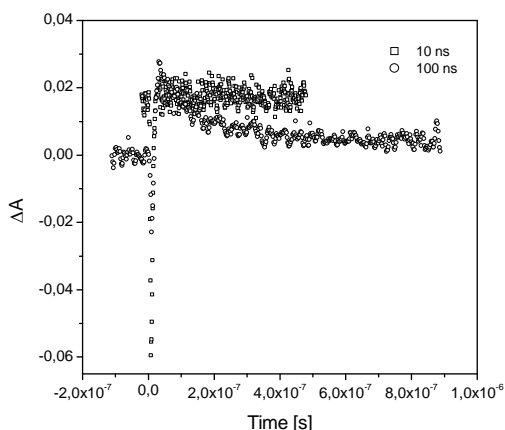


Figure 7. Transient absorption kinetic traces observed at 410 nm after different delay time (10 ns and 100 ns) for three-component system: cyanine dye/borate salt/N-methylpicolinium ester. Dye concentration equal 2×10^{-5} M, borate salt and ester concentration was 2×10^{-3} M.

The traces curves recorded at 410 nm and 430 nm in the case of two-component system composed of cyanine dye and borate salt are presented below. From the inspection of the Figure 8 it is seen that cyanine radical is formed (band at 430 nm) and no individual at 410 nm (pyridylmethyl radical) is observed.

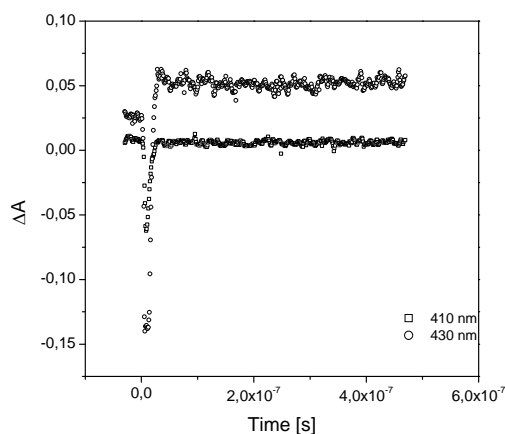


Figure 8. Transient absorption kinetic traces observed at wavelength 410 nm and 430 nm recorded for cyanine dye in presence of *n*-butyltriphenylborate salt in acetonitrile as a solvent. Borate salt concentration was 2×10^{-3} M.

On the basis of the nanosecond laser flash photolysis experiments, it appears that N-methylpicolinium ester is reduced by dye radical. This reaction yields the dye cation and N-methylpicolyl radical that undergoes C-O fragmentation giving carboxylic acid and 4-(N-methyl)pyridylmethyl radical.

In summary, cyanine dye was found to be very useful as a visible light sensitizer in the three-component photoinitiating system. An electron transfer process from the dye radical to the ground state of N-methylpicolinium derivative enhances the high efficiency of photopolymerization of tested cyanine borate salt in presence of different N-methylpicolinium derivatives. The efficiency of initiation depends on the chemical structure of N-methylpicolinium derivative and changes in the order alkyl > phosphoryl > L-serine derivatives.

Generally, a combination of N-methylpicolinium derivative and alkyltriphenylborate anion with suitable carbocyanine dye, two radicals can be generated per one absorbed photon, thus enhancing the overall polymerization efficiency.

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