

# Novel *N*-ethyl-2-styrylquinolinium Iodides as Sensitizers in Photoinitiated Free Radical Polymerization of Trimethylolpropane Triacrylate (TMPTA), Part 3

Janina Kabatc, Jerzy Pączkowski

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

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**ABSTRACT:** Three-component systems, which contain a light-absorbing species (dye), an electron donor (*n*-butyltriphenylborate salt), and a third component (*N*-alkoxy-pyridinium salt or 1,3,5-triazine derivative), have emerged as efficient, visible-light sensitive photoinitiators of free radical polymerization. It was found that three-component systems are more efficient than their two-component counterparts. Kinetic studies based on microcalorimetry revealed a significant increase in polymerization rate with increasing concentration of *N*-alkoxy-pyridinium salt. Such results were not obtained for photoinitiating systems possessing 1,3,5-triazine derivative as a second coinitiator.

Based on the experimental results we concluded that the primary photochemical reaction involves electron transfer from the borate anion to the excited dye followed by the reaction of resulting dye-based radical with second coinitiator that regenerates the original dye and simultaneously produces the alkoxy radical or triazynyl radical which could start the polymerization chain reaction. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2669–2675, 2010

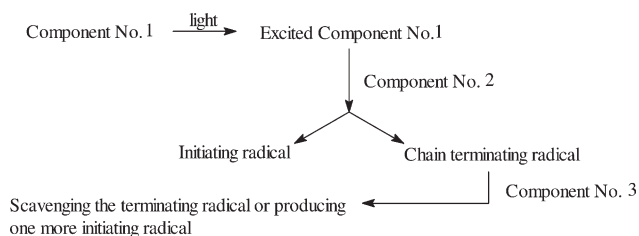
**Key words:** photopolymerization; three-component photoinitiating system; styrylquinolinium dyes; visible-light initiator

## INTRODUCTION

The visible-light photoinitiators consist of one or two components (in this case, one is a dye that absorbs visible-light, while the other are the reacting with the dye a radical generator). Until recently, the need for visible-light radical photoinitiators has been addressed primarily by using bimolecular initiator systems.

In these systems, active radicals are generally produced via electron transfer (ET) from an electron donor to a photoexcited molecule. Using this approach, the system can be tailored to a specific wavelength range by a choice of the light-absorbing species.

To enhance the sensitivity, three-component photoinitiators have been recently studied. In these systems, the third component is usually supposed to scavenge the chain-terminating radicals that are generated by primary ET reaction or produce an additional initiating radical.<sup>1,2</sup>



Like the two-component systems, the three-component initiators include a light-absorbing moiety, which are typically a dye and an electron donor. The third component is usually an onium salt. Three-component photoinitiators are extremely flexible since a wide variety of dyes that can be used. Similarly to the two-component systems, the selection of the dye determines the active wavelength. Classes of dyes that have been reported for three-component systems include ketones, xanthenes, thioxanthenes, coumarins, thiazines, cyanines, hemicyanines, merocyanines and polycyclic heterocycles and many others.<sup>2–13</sup> These photoinitiating systems have consistently been found to be faster, more efficient, and more sensitive than their two-component parent photoredox pairs.<sup>2,14,15</sup>

In this paper, the search for more effective photoinitiating systems of free radical polymerization of vinyl monomers, the styrylquinoline dyes in the three-component photoinitiating systems is

Correspondence to: J. Kabatc (nina@utp.edu.pl).

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described. The photoinitiators consisting of these dyes parried with borate anion in the presence of *N*-alkoxypyridinium salt or 1,3,5-triazine derivative as a second coinitiator were investigated through polymerization experiments.

## EXPERIMENTAL

### Materials

All chemicals and solvents were purchased from Fluka, Merck, or Aldrich Chemical Co. (Poland) and used without further purification.

### Measurements

The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical MTM System (Krakow) Model EA9C-4z was used for the measurements. A platinum 1 mm disk electrode was used as the working electrode, a Pt wire constituted the counter electrode, and Ag-AgCl electrode served as a reference electrode. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium perchlorate in dry acetonitrile.

The kinetics of free radical polymerization was monitored by determining the rate of heat evolution during the polymerization of a cured sample. The measurements were carried out under pseudo-adiabatic condition and was based on recording polymerization formulation temperature using a single-cell calorimeter based on a thick film temperature sensor (calibrated semiconducting diode) immersed in polymerizing formulation (0.25 mL,  $0.3 \pm 0.015$  g).<sup>16</sup> The irradiations of the polymerizations were carried out with Air-cooled Ion Laser Systems model 177-G01 (488 and 514 nm) (Spectra-Physics). The average incident power of the irradiations (64 mW/

cm<sup>2</sup>) was measured by a Coherent Model Fieldmaster power meter (Germany).

A polymerization formulations were composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), and an appropriate amount of the photoinitiating systems. The styrylquinolinium dye (SQ) and styrylquinolinium borate salt and second coinitiators concentrations used in experiments were  $1 \times 10^{-3}$ M and  $3 \times 10^{-3}$ M, respectively. Blank photochemical experiments were also performed on the polymerizing mixture containing styrylquinolinium iodide (dye without coinitiator). The kinetic measurements were performed under air atmosphere and at an ambient temperature. In order to avoid the possibility of temperature effect on a polymerization rate, only the data for initial times of the polymerizations (about 3–5% of monomer conversion) were used for the evaluation of the polymerization rates. The initial rates of polymerization are the slopes of the lines drawn on the heat released versus time curve at the beginning of polymerization. The average values for the rates of polymerization were calculated based on at least two measurements.

## RESULTS

Synthesis and spectroscopic properties of the dyes under the study were described earlier.<sup>17</sup> The exchange of an anion type from iodide on borate (*n*-butyltriphenylborate anion), transferring this group of the dyes into efficient free radical polymerization initiating systems (SQB2) was performed following the guidelines given by Schuster.<sup>18</sup>

The structures of the series of *N*-ethyl-2-(4-*p*-alkylaminostyryl)quinolinium dyes tested along with their properties are summarized in Table I.

TABLE I  
Electrochemical, Spectroscopic, and Thermodynamic Properties of the Styrylquinolinium Borates Tested

Dye	Structure	$E_{\text{red}}$ [V] SQ	$E_{\text{ox}}^{\text{a}}$ [V] SQ	$\lambda$ [nm] SQ	$\lambda$ [nm] SQ	$E_{00}$ [eV] SQ	$R_p^{\text{b}}$ [au] SQB2	$R_p$ [au] SQB2
SQ1		-0.75	-0.715	526	652	2.156	0.00096	1.68
SQ2		-0.93	-0.71	537	658	2.13	0.00067	1.17
SQ7		-1.085	-0.860	538	658	2.116	0.00097	1.70
SQ8		-0.96	-0.850	522	664	2.112	0.00057	1.0

<sup>a</sup> Is the oxidation potential of styrylquinolinium dye radical (SQ).

<sup>b</sup> The slope of the linear part of the kinetic curve observed during free radical polymerization measurements.

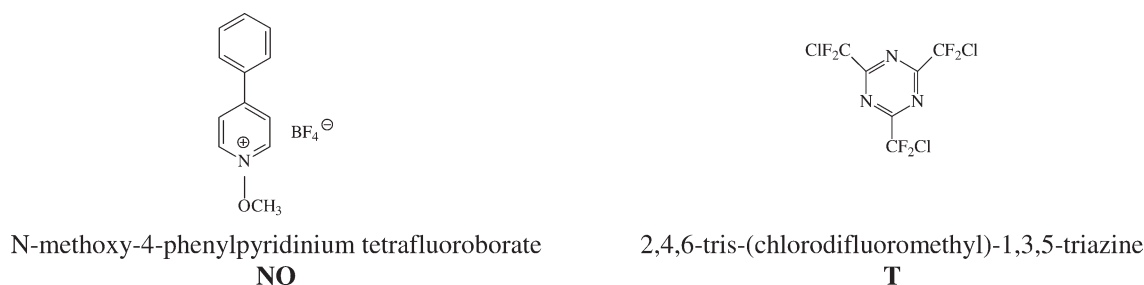


Chart 1

The value of the reduction potential of the dye depends on its structure and oscillates in the range from  $-1.085$  V to  $-0.75$  V.

The measured values of the dyes reduction potentials, the electron donor (*n*-butyl-triphenylborate anion) oxidation potential (equal 1.16 eV) and the singlet state energy of the dyes, allow one to calculate the free energy change for the photoinduced intermolecular ET process. For further discussion it is assumed that the oxidation potential of the dye radical is approximately equal to the reduction potential of this dye.

#### Kinetic study of multifunctional acrylate polymerization initiated by three-component photoinitiating systems

For the comparison of the photoinitiating abilities of three-component photoinitiating systems with two-component photoinitiating pairs, four photoredox pairs consisting of styrylquinolinium dye (acting as electron acceptor) and *n*-butyltriphenylborate anion (acting as an electron donor) were tested as photoinitiators of the multiacrylate monomer polymerization. The rates of photoinitiated polymerization measured for all the tested two-component photoredox pairs are collected in Table I.

It is apparent from the inspection of the initial rates of polymerization that the efficiency of the tested photoinitiators depends on their structure and is higher than those previously described for styrylpyridinium borates.<sup>19,20</sup>

From the kinetic results obtained for the two-component photoinitiating systems, it is clearly evident that styrylquinolinium borate salts can be used as visible-light photoinitiators of vinyl monomers polymerization. However, their ability to the photoinitiation is significantly lower than those observed for symmetric cyanine dyes.<sup>19-23</sup> In order to the accelerate the photopolymerization process initiated by styrylquinolinium borate salts to formation a second coinitiator was added. The structures of compounds used as second coinitiator are presented in Chart 1.

By the comparison of the results obtained by Grotzinger for three-component photoinitiating system composed of dye/amine/1,3,5-triazine and our

results obtained for system possessing cyanine dye/borate salt/*N*-alkoxy pyridinium salt one can conclude that in such photoinitiating formulations more than one free radicals, able to the initiate the free radical polymerization, are formed after absorption of one photon.<sup>6,24</sup>

Irradiation of three-component photoinitiating systems under the study with visible-light leads, according to our previous communications,<sup>20,25</sup> to the formation of following radicals: alkoxy or 1,3,5-triazynyl radicals beside *n*-butyl radical that is formed after first ET reaction. The efficiency of these processes depends on the composition of the photoinitiator system. Thus, one can conclude that the overall efficiency of the photoinitiation of free radical polymerization can be affected by: (i) the rate of primary ET process, (ii) the rate of carbon-boron bond cleavage, (iii) the rate of secondary ET process, (iv) the rate of nitrogen-oxygen bond or the rate of carbon-halogen bond cleavage, namely on yields of free radical formation, and finally (v) on the reactivity of free radicals obtained.

The data illustrating the kinetics of free radical polymerization of TMPTA initiated by both two- and three-component photoinitiator systems are summarized in Table II.

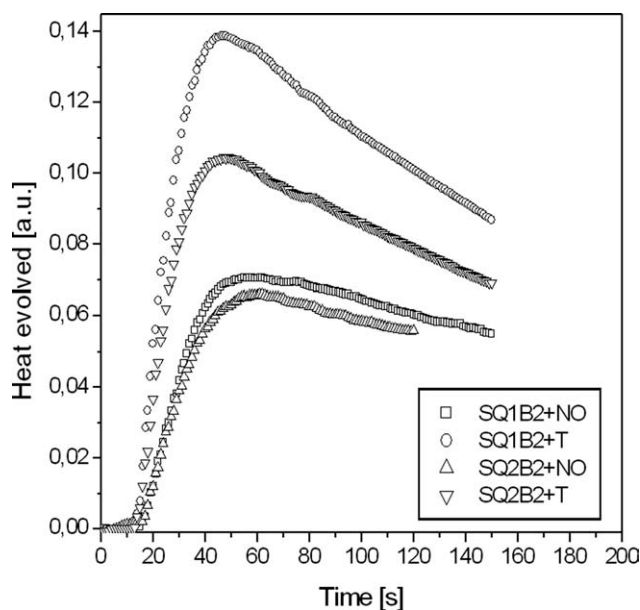
**TABLE II**  
Measured Rates ( $R_p$ ) of Free Radical Polymerization of TMPTA and the Quantum Yields ( $\Phi_p$ ) of Free Radical Polymerization Photoinitiated by Two- and Three-Component Photoinitiating Systems Tested

Dye	The rates ( $R_p$ ) of free radical polymerization [ $\mu\text{mol s}$ ]					The quantum yields ( $\Phi$ )		
	B2	NO	NO <sup>a</sup>	T	T <sup>a</sup>	B2	NO <sup>a</sup>	T <sup>a</sup>
<b>SQ1</b>	2.29	0	5.07	0	14.56	9.62	25.95	61.81
<b>SQ2</b>	1.58	0	4.33	0.34	12.84	6.71	21.24	54.50
<b>SQ7</b>	0.69	0	6.3	0	10.03	9.72	26.75	42.58
<b>SQ8</b>	1.13	0	5.41	0	10.0	5.71	21.54	42.08

<sup>a</sup> Photoinitiator composed of styrylquinolinium dye as *n*-butyltriphenylborate salt (**SQB2**) and **NO** or **T**, respectively.

Other photoinitiating systems are composed of styrylquinolinium dye as iodide (**SQ**) and **NO** or **T**, respectively.

The coinitiator (**NO** or **T**) concentration was  $3 \times 10$  M.



**Figure 1** Photopolymerization kinetic curves recorded for various sensitizers (SQ) and two types of coinitiators (B2/NO and B2/T). Monomer formulation: 1 mL of MP and 9 mL of TMPTA. Dye borate salt concentration was  $1 \times 10^{-3}$  M and second coinitiators concentration was  $3 \times 10^{-3}$  M. Light intensity of argon-ion laser irradiation was  $64 \text{ mW/cm}^2$ .

The examples of the polymerization kinetic curves are shown in Figure 1. From the analysis of the kinetic curves in Figure 1 and the data compiled in Table II it is seen that, the sensitivity of three-component photoinitiating systems depends on the structure of second coinitiator.

Figure 2 presents the comparison of photoinitiating efficiency for selected two- and three-component photoinitiating systems.

From the inspection of the kinetic data shown in Table II, it appears that the two-component dye/*N*-alkoxy pyridinium or dye/1,3,5-triazine photoinitiating systems are not able to initiate the radical polymerization under applied irradiation conditions ( $64 \text{ mW/cm}^2$ ). It means no free radicals able to start polymerization chain are generated.

Generally, the type of applied second coinitiator in three-component photoinitiating system has effect on the overall efficiency of the photoinitiation. It is demonstrated that the addition of *N*-alkoxy pyridinium salt or 1,3,5-triazine derivative to the two-component **SQB2** photoinitiating system leads to an enhancement of the polymerization efficiency for all dyes studied. The rate of free radical polymerization is several times more higher in the presence of **NO** or even greater in the presence of **T** in comparison to the two-component photoinitiating system (styrylquinolinium borate salt) (Table II and Fig. 2).

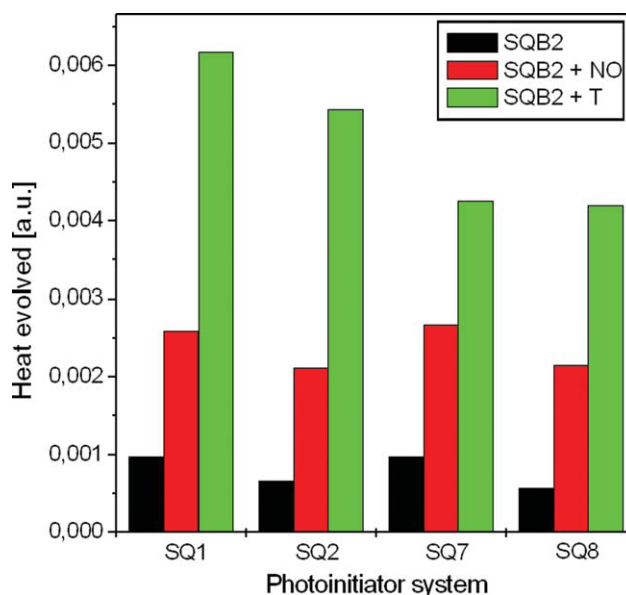
From the data, obtained during measurements, it was also deduced that the conversion of monomer double bonds is ranging from 2 to 20.5%, while the

quantum yields of photopolymerization oscillates between 5.71 to 61.81 (Table II). It was also found that the degree of monomer conversion and the quantum yields of photopolymerization depend on the photoinitiating system composition. It is noteworthy that the two-component photoinitiating systems composed of hemicyanine dye as borate salt show a lower photoinitiating ability with quantum yield of polymerization of about 9 and the polymerization rates equal  $1\text{--}2 \text{ }\mu\text{mol/s}$ .

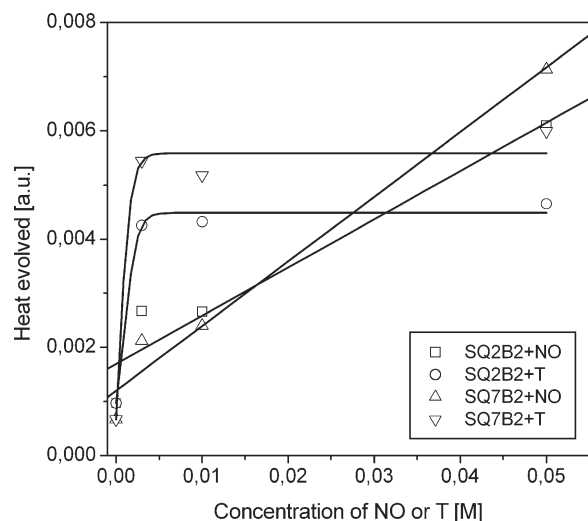
We have documented earlier that cyanine dye/borate salt ion pair is partially dissociated even in medium polarity solvents.<sup>22</sup> A degree of dissociation depends on a concentration of solute in complex fashion. However, in the simple approximation a degree of dissociation is decreasing as concentration of solute is increasing (or a concentration of nondissociated salt is enhancing when concentration of solute increases).

The study on the influence of the borate concentration on the rate of photoinitiated polymerization indicates, for identical monomer-dye formulation, a distinct increase in the rate of polymerization as the concentration of borate anion increases. Figure 3 illustrates this relationship.

Based on this experiment, it appears that at the concentration of borate anion equal to the concentration of asymmetric cyanine cation, only a part of the photoredox pairs exist as the ion pair. Analysis of the data presented in Figure 4 indicates that for **SQ7B2** initiating system only about 30% of photoredox couples exist as ion pairs. At the concentration



**Figure 2** The comparison of photoinitiating efficiency for different visible-light photoinitiating systems. The type of photoinitiator is marked in Figure. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

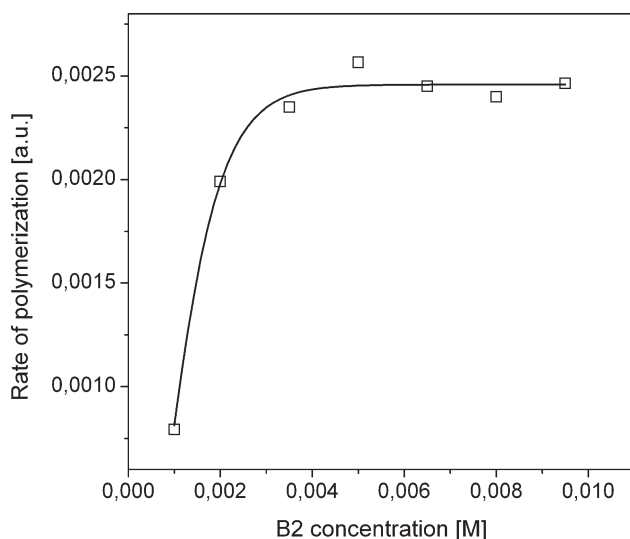


**Figure 3** Dependence of the rate of photoinitiated polymerization on concentration of the electron donor (B2). The initial dye (SQ7B2) – borate concentration was  $1 \times 10^{-3} M$ .

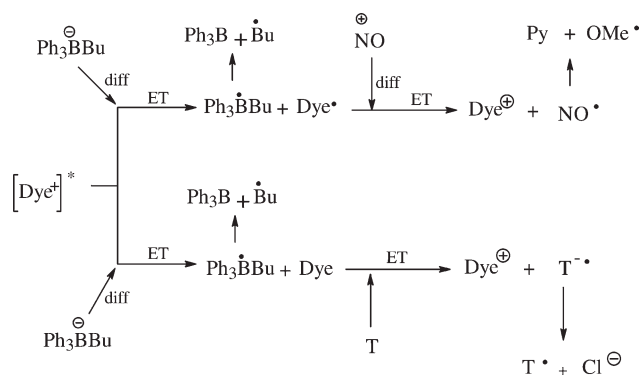
of the dye equal  $1 \times 10^{-3} M$  this value gives an equilibrium constant of approximately  $1.58 \times 10^{-3} M$ .

As it was mentioned above the photoinitiating system composed of styrylquinolinium borate salt and 1,3,5-triazine exhibits higher photoinitiation ability in comparison to that of styrylquinolinium borate salt - *N*-alkoxypyridinium salt photoinitiator system.

The influence of *N*-alkoxypyridinium salt and 1,3,5-triazine concentration on the rate of free radical polymerization initiated by three-component photoinitiating system confirmed these observations. From Figure 4, it is clearly evident that the addition of an *N*-alkoxypyridinium salt causes a significant enhancement of the polymerization rate in a wide range of **NO** concentration. This behavior is not observed for 1,3,5-triazine derivative.



**Figure 4** The dependence of the polymerization rates on type and coinitiator concentration.



**Scheme 1**

Based on the photochemistry of borate anion,<sup>21</sup> *N*-alkoxypyridinium cation<sup>26</sup> and 1,3,5-triazine derivatives<sup>6,2,27</sup> we propose the following mechanism (Scheme 1) that is consistent with the observations described earlier.

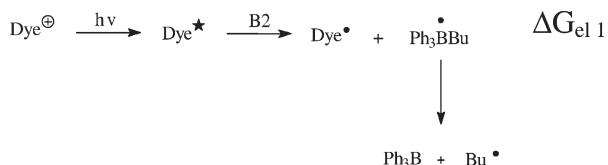
After excitation, in order to make an ET effective the electron donor and electron acceptor must diffuse to each other to form encounter complex, in which ET reaction takes place. Resulted boranyl radical ( $Ph_3B^{\bullet}Bu$ ) decomposes yielding neutral triphenylboron ( $Ph_3B$ ) and butyl radical ( $Bu^{\bullet}$ ).<sup>16,24</sup> The other product of ET reaction, dye radical ( $Dye^{\bullet}$ ), could participate in a second ET reaction with alkoxyypyridinium cation ( $NO^+$ ) (upper leg) to form alkoxyypyridinium radical ( $NO^{\bullet}$ ) 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.<sup>24</sup> The bottom path describes the process that can occur when three-component photoinitiating system is composed of cyanine dye/borate salt and 1,3,5-triazine used as a second coinitiator. In this case the triazynyl radical ( $T^{\bullet}$ ) is formed as a result of a second ET process from cyanine dye radical ( $dye^{\bullet}$ ) to the 1,3,5-triazine derivative (T). This radical, beside butyl radical, can initiate free radical polymerization. That is why, as a result one observes an increase in speed of photoinitiated polymerization.

All the dyes studied exhibit similar photophysical and photochemical behaviors.<sup>28,29</sup> They possess a short lived singlet excited-state. Cyanine borate salt interaction occurs in the dye excited singlet state and generates boranyl radical and dye radical ( $dye^{\bullet}$ ). The *N*-alkoxypyridinium salt and 1,3,5-triazine derivative act as an electron acceptor in their ground state and reacts with a dye radical ( $dye^{\bullet}$ ), yielding secondary products.

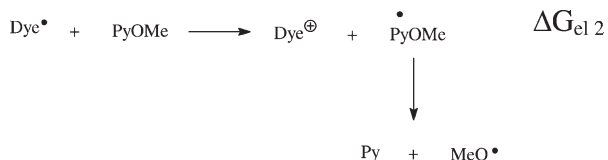
Basing on these observations the primary selection of efficient systems under the study should obey several major criteria:

1. The interaction between the excited singlet state of the dye and *n*-butyltriphenylborate **B2** must

be efficient in order to generate a large number of initiating radicals.

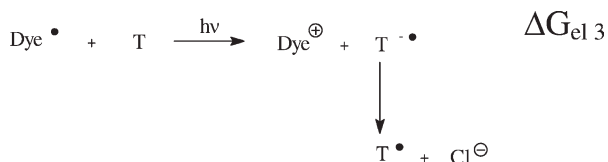


- ii. The interaction between the dye radical (dye<sup>•</sup>) and *N*-alkoxy-pyridinium salt **NO** should also be efficient in order to generate a large number of the second type of initiating radicals.



or similar

- iii. The interaction between the dye radical (dye<sup>•</sup>) and 1,3,5-triazine **T** should yields a large number of initiating radicals of a second type.



The thermodynamic driving forces for all presented above reactions can be marked as:  $\Delta G_{\text{el}1}$  for first reaction,  $\Delta G_{\text{el}2}$  for the second and  $\Delta G_{\text{el}3}$  for third reaction, respectively.

It appears that the first step (i) involves reduction of the excited-state of the dye by **B2**, whereas (ii) and (iii) are the oxidation of dye radical (dye<sup>•</sup>) by **NO** or **T**. Therefore, the studies of the kinetics of the free radical polymerization via ET process should include the estimation of the thermodynamic driving force for the electron – transfer reaction for both steps. The free energy change ( $\Delta G_{\text{el}}$ ) for ET from a donor D to an acceptor A in the excited-state is expressed by the Rehm-Weller eq. (1).<sup>30</sup>

$$\Delta G_{\text{el}} = E_{\text{ox}}(\text{D}/\text{D}^{\bullet+}) - E_{\text{red}}(\text{A}^{\bullet-}/\text{A}) - E(S_1) - e^2/\epsilon R_{\text{DA}} \quad (1)$$

where  $E(S_1)$  is the excited-state energy of the acceptor (styrylquinolinium dye in this case) in ET reaction,  $E_{\text{ox}}(\text{D}/\text{D}^{\bullet+})$  is the oxidation potential of the electron donor (in this case *n*-butyltriphenylborate salt),  $E_{\text{red}}(\text{A}^{\bullet-}/\text{A})$  is the reduction potential of the electron acceptor. The last term accounts for the Coulombic energy associated with the separation of charges in the ET products. This factor can be ignored in systems under study. It is well known that the main prerequisite for PET reactions is

**TABLE III**  
The Thermodynamic Properties of the Hemicyanine Dyes and Coinitiators Tested

Compound	Dye oxidation by <b>NO</b> and <b>T</b>		
	Dye reduction by <b>B2</b>		
	$\Delta G_{\text{el}1}$ [eV] <sup>a</sup>	$\Delta G_{\text{el}2}$ [eV] <sup>b</sup>	$\Delta G_{\text{el}3}$ [eV] <sup>c</sup>
<b>SQ1</b>	−0.246	−0.045	−0.225
<b>SQ2</b>	−0.04	−0.04	−0.22
<b>SQ7</b>	0.129	−0.19	−0.37
<b>SQ8</b>	0.008	−0.18	−0.36

<sup>a</sup> Free energy changes ( $\Delta G_{\text{el}1}$ ) in acetonitrile;  $\Delta G_{\text{el}} = E_{\text{ox}}(\text{B2}) - E_{\text{red}}(\text{dye}) - E_{00}$ .

<sup>b</sup> Free energy changes ( $\Delta G_{\text{el}1}$ ) in acetonitrile;  $\Delta G_{\text{el}} = E_{\text{ox}}(\text{dye}) - E_{\text{red}}(\text{NO})$ .

<sup>c</sup> Free energy changes ( $\Delta G_{\text{el}1}$ ) in acetonitrile;  $\Delta G_{\text{el}} = E_{\text{ox}}(\text{dye}) - E_{\text{red}}(\text{T})$ .

described by the Rehm-Weller<sup>30</sup> eq. (1), which states that the free energy change for the PET ( $\Delta G_{\text{el}}$ ) process should have negative value.

As it was mentioned earlier for two-component photoinitiating systems the calculation of  $\Delta G_{\text{el}}$  needs several important data: (1) the reduction potential of a dye and oxidation potential of a dye radical, (2) the oxidation potential of electron donor (*n*-butyltriphenylborate anion **B2**), (3) the reduction potential of electron acceptor (**NO**, **T**), and (4) the singlet state energy of the dye. The calculated free energy changes  $\Delta G_{\text{el}1}$ ,  $\Delta G_{\text{el}2}$  and  $\Delta G_{\text{el}3}$  of ET reactions for systems under the study are collected in Tables I and III.

The results of  $\Delta G_{\text{el}}$  calculation presented in Table III supports the ET mechanism involved in free radicals generation in consecutive reactions that are characteristic for three-component photoinitiating systems.

On the basis of the above experiments, it appears that alkoxy-pyridinium cation and 1,3,5-triazine are reduced by dye radical. This reaction yields the dye cation and alkoxy-pyridinium radical that undergoes fragmentation giving stable pyridine and alkoxy radical or triazynyl radical and chlorine anion, respectively.

According to the mechanism presented above it is clear that there are two couples of different radicals initiating free radical polymerization: *n*-butyl, methoxy for **SQB2** and **NO** triplet and *n*-butyl and triazynyl radicals for **SQB2** and **T** triplet.

In summary, the thermodynamic conditions that have to be fulfilled for  $\Delta G_{\text{el}}$  are necessary but not enough for the selection of the dye as effective light-absorbing chromophore.

## CONCLUSION

In this article, the efficiency of the visible-light induce polymerization of multifunctional acrylate in

the presence of two-component and three-component photoinitiating systems based of styrylquinolinium dyes/borate salt was ascertained. The initiation ability of studied photoinitiating systems increases when both the initiator and the coinitiators concentration increases.

The two-component photoinitiator systems possessing styrylquinolinium dye and *n*-butyltriphenyl borate initiate polymerization with a very low efficiency. Acceleration of this process was achieved by the addition of a second coinitiator. The three-component photoinitiating systems, possessing styrylquinolinium borate salt and *N*-alkoxyppyridinium salt or styrylquinolinium borate salt and 1,3,5-triazine derivative initiate free radical polymerization two and ten times faster in comparison to parent two-component system. By combination of alkoxyppyridinium or 1,3,5-triazine derivative with borate salts of suitable dye cation two radicals can be generated by one absorbed photon.

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