

# Novel *N*-ethyl-2-styrylquinolinium Iodides as Sensitizers in the Photoinitiated Free-Radical Polymerization of Trimethylolpropane Triacrylate. II

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Received 22 November 2008; accepted 29 January 2009

DOI 10.1002/app.30125

Published online 19 May 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Results of kinetic studies of two-component photoinitiator systems used in the visible-light photoinduced polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate are presented. Nine different styrylquinolinium dyes coupled with *n*-butyltriphenylborate as a coinitiator have been used as photoinitiating systems. Reactive radicals that initiate the polymerization are formed

by the well-known mechanism of photoinduced electron transfer between dye cations acting as electron acceptors and borate anions acting as electron donors. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 165–172, 2010

**Key words:** dyes/pigments; initiators; kinetics (polym.); photopolymerization

## INTRODUCTION

The use of dyes as light-absorbing components in photoinitiating systems for radical polymerization under visible-light irradiation is of great interest because such systems have widespread applications in practical fields, such as high-speed photopolymers in computer-to-plate laser imaging, holographic recording films, and three-dimensional polymerization systems.<sup>1,2</sup> Currently, the application of photopolymer materials to holographic data storage is attracting a great deal of attention because holographic data storage can potentially meet the demand for high-capacity data storage as it holds the promise of a digital storage system with terabyte storage capacity, faster transfer rates in the gigabytes per second range, and short access times of less than 100  $\mu$ s.

Because of practical issues such as cost, compatibility, and mass production, photopolymers offer a better choice for holographic data storage materials. In these systems, photopolymers highly responsive and highly photosensitive to visible-light lasers are required.<sup>1</sup>

As already mentioned, photopolymers are widely used in various fields.<sup>3</sup> Nowadays, photopolymers sensitive to visible-light lasers are widely studied from the viewpoint of designing efficient systems for direct imaging technology. Very effective visible-light photoinitiators consisting of one or two components (in this case, one is a dye that absorbs visible light, whereas the other is a radical generator reacting with the dye) are still being sought.

We have recently developed new photosensitized photoinitiating systems in which a photosensitizing chromophore, hemicyanine dye, is tethered to a radical-generating part, *n*-butyltriphenylborate anion.<sup>4–7</sup>

## EXPERIMENTAL

### Materials

The substrates used for the preparation of the dyes and electron donor, monomer, and solvents were purchased from Fluka, Merck, or Aldrich Chemical Co. (Poland). All chemicals and solvents were the best grade and were used without further purification.

### Synthesis

The general route and methodology for the synthesis of the styrylquinolinium dyes prepared for these studies were the same as those for styrylpyridinium dyes and have been described elsewhere.<sup>8</sup>

The ion-exchange reaction was performed with the procedure reported by Damico<sup>9</sup> and Murphy et al.<sup>10</sup>

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Contract grant sponsor: The Ministry of Science and Higher Education; contract grant numbers: N N204 219734, BS-13/2006.

## Measurements

Absorption spectra were recorded with a Shimadzu Multispec 1500 ultraviolet–visible spectrophotometer (Kyoto, Japan), and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorometer (Tokyo, Japan). The absorption and emission spectra were recorded with spectroscopic-quality *N,N*-dimethylformamide (DMF) as the solvent. The measurements were performed at the ambient temperature.

The reduction potentials of the dyes were measured with cyclic voltammetry. An Electroanalytical MTM System (Krakow, Poland) model EA9C-4z was used for the measurements. A 1-mm platinum disk electrode was used as the working electrode, a platinum wire was the counter electrode, and a silver/silver chloride electrode served as the reference electrode. The supporting electrolyte was 0.1M tetrabutylammonium perchlorate in dry acetonitrile.

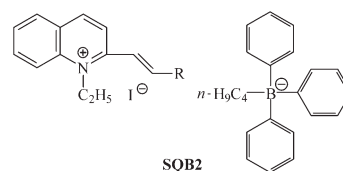
The kinetics of free-radical polymerization were monitored by the determination of the rate of heat evolution during the polymerization of an actual cured sample. The measurements were carried out under pseudo-adiabatic conditions and were based on recording the polymerization formulation temperature with a single-cell calorimeter based on a thick-film temperature sensor (a calibrated semiconducting diode) immersed in the polymerizing formulation (0.25 mL,  $0.3 \pm 0.015$  g). The irradiation of the polymerization was carried out with an Omnicrome model 543-500 MA argon-ion laser (488 and 514 nm) (Chino, CA). The average incident power of the irradiation ( $64 \text{ mW/cm}^2$ ) was measured with a Coherent Fieldmaster power meter (Germany).<sup>11</sup>

Polymerization formulations consisted of 1 mL of 1-methyl-2-pyrrolidinone (MP), 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate [or trimethylolpropane triacrylate (TMPTA)], and an appropriate amount of the photoinitiating systems. Blank photochemical experiments were also performed with the polymerizing mixture containing styrylquinolinium iodide (a dye without a coinitiator). The kinetic measurements were performed under an air atmosphere and at the ambient temperature. To avoid the possibility of a temperature effect on the polymerization rate, only the data for the initial times of the polymerization (ca. 3–5% monomer conversion) were used for the evaluation of the polymerization rates. The initial rates of polymerization were the slopes of lines drawn on the curve of the released heat versus time at the beginning of polymerization. The average values for the rates of polymerization were calculated on the basis of at least two measurements.<sup>11</sup>

## RESULTS

In polymer photochemistry, hemicyanine dyes such as styrylpyridinium salts have been investigated as fluo-

rescence probes for monitoring the progress of free-radical polymerization and measuring the curing of epoxy resins.<sup>12,13</sup> The photophysics and spectroscopic behavior of this class of compounds have been described by Fromherz's<sup>14–16</sup> and Rettig's<sup>17</sup> research groups. The exchange of an anion type from iodide on borate was performed according to the guidelines of Schuster et al.,<sup>18</sup> and this group of the dyes was transferred into an efficient free-radical polymerization initiating system (SQB2, the styrylquinolinium dye as *n*-butyltriphenylborate salt). The general structure of the tested styrylquinolinium borates can be depicted as follows:



**Chart 1** General structure of styrylquinolinium borates tested.

Tested in this study, a large number of asymmetric cyanine salts, possessing different characteristic substituents in the benzene ring, were examined to achieve a better understanding of their initiating properties.

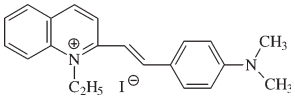
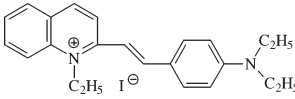
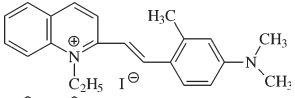
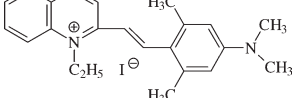
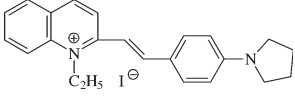
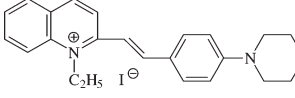
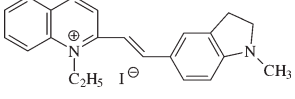
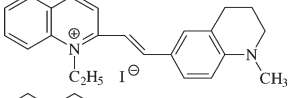
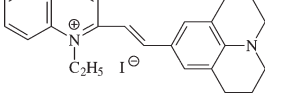
The structures of a series of tested *N*-ethyl-2-(4-*p*-alkylaminostyryl)quinolinium dyes are compiled in Table I.

Figure 1 shows illustrative electronic absorption spectra and fluorescence spectra recorded for selected dyes in DMF solutions. The basic spectroscopic properties of the tested dyes are also summarized in Table I.

The analysis of the electronic absorption spectra clearly indicates the presence of two absorption bands. The more intensive absorption band corresponds to the  $S^0$ -CT (where  $S^0$  is the singlet state and CT is the charge transfer state) transition, which appears at the red-energy side of the absorption spectrum (see Fig. 1). This absorption is caused by intramolecular charge transfer from the nitrogen atom on the quaternary nitrogen atom in the quinolinium moiety. A well-separated CT absorption band can be observed for almost all dyes tested in polar and medium-polarity solvents. An inspection of the illustrative absorption spectra presented in Figure 1 shows that the position and intensity of the CT absorption band strongly depend on the molecular structure. The type of anion has no significant effect on the position or intensity of the absorption band. The second, less intensive short-wavelength absorption band can be attributed to the  $\pi$ - $\pi^*$  transition.

Just like the absorption spectra, the fluorescence spectra of the tested dyes show the presence of two emission bands. The position of the fluorescence

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

Dye	Structure	SQX			SQB2		
		$E_{\text{red}}$ (eV)	$\lambda_{\text{ab,max}}$ (nm)	$\lambda_{\text{fl,max}}$ (nm)	$E_{00}^{\text{S}1}$ (eV)	$\Delta G_{\text{el}}$ (eV)	$\ln R_p$ (au)
SQ1		-0.71	526	652	2.156	-0.286	2.27
SQ2		-0.93	537	658	2.13	-0.04	1.89
SQ3		-0.965	538	650	2.119	0.006	1.95
SQ5		-0.985	516	674	2.238	-0.093	2.27
SQ7		-1.085	538	658	2.116	0.129	2.268
SQ8		-0.96	522	664	2.112	0.008	1.74
SQ9		-1.045	547	667	2.066	0.139	1.064
SQ10		-0.96	547	662	2.073	0.047	1.566
SQ11		-1.04	573	683	2.006	0.194	1

$\Delta G_{\text{el}}$  = free energy change;  $E_{00}^{\text{S}1}$  = excited-state energy of the acceptor;  $E_{\text{red}}$  = reduction potential;  $R_p$  = polymerization rate; SQX = styrylquinolinium dye as an iodide salt;  $\lambda_{\text{ab,max}}$  = the maximum of absorption;  $\lambda_{\text{fl,max}}$  = the maximum of fluorescence.

band from the CT state, depending on the structure of the dye, can be observed in the range of 650–682 nm in DMF as the solvent.

Because the absorption of the dyes is extended up to about 500 nm, we can consider the tested dyes potentially useful for dental applications.

The electrode potential at which the dyes undergo reduction has been determined by cyclic voltammetry. The obtained voltamperograms for the tested dyes show reversible reduction (Fig. 2).

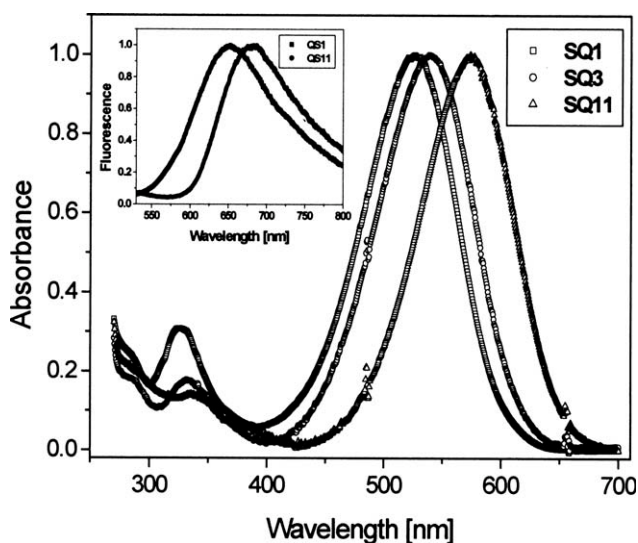
The value of the reduction potential depends on the structure of the dye and oscillates from -1085 to -710 mV (Table I).

The measured values of the dye reduction potentials, the electron donor (*n*-butyl-triphenylborate anion) oxidation potential, and the singlet-state energy of the dyes allow us to calculate the free energy change for the photoinduced intermolecular electron transfer process.

#### KINETIC STUDY OF MULTIFUNCTIONAL ACRYLATE POLYMERIZATION INITIATED BY A TWO-COMPONENT PHOTOINITIATING SYSTEM

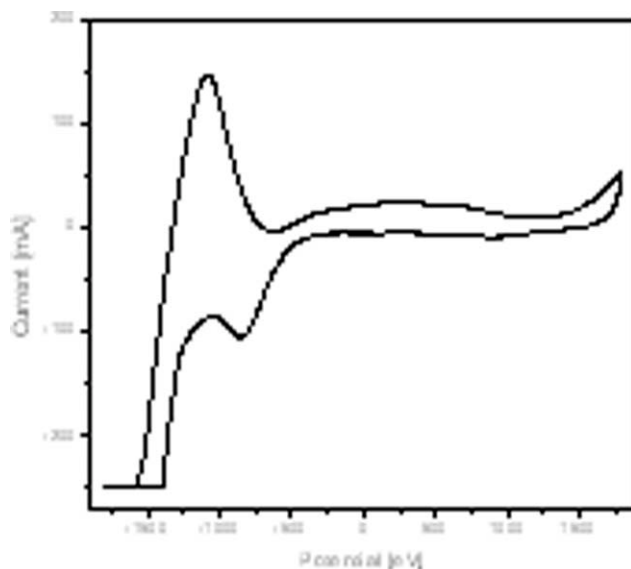
Nine photoredox pairs consisting of a styrylquinolinium dye (acting as an electron acceptor) and an *n*-butyl-triphenylborate anion (acting as an electron donor) were tested as photoinitiating systems for the polymerization of the multiacrylate monomer. The kinetic curves for the photoinitiated polymerization of a TMPTA/MP (9/1) mixture, recorded for selected styrylquinolinium borate salts (SQB2) under irradiation with visible light, are shown in Figure 3 for illustration. The relative rates of photoinitiated polymerization measured for all the tested photoredox pairs are also collected in Table I.

It is apparent from the inspection of the initial rates of polymerization that the efficiency of the



**Figure 1** Illustrative electronic absorption spectra of selected dyes recorded in DMF solutions. The inset shows the fluorescence spectra of selected dyes recorded in DMF solutions at room temperature.

tested photoinitiators depends strongly on their structure and is higher than that of the styrylpyridinium borates described earlier.<sup>5-7</sup> The highest rates of photoinitiated polymerization were observed for SQ1, SQ2, SQ5, and SQ7. For the most part, these are dyes (SQ1, SQ2, and SQ5) for which the rotation around the bond linking the dialkylamino group and benzene ring is possible. In the case of dyes SQ9–SQ11, this motion is largely restricted because of a semibridged anilino bond.



**Figure 2** Cyclic voltammogram recorded for *N*-ethyl-2-(4-pyrrolidinylstyryl)quinolinium iodide (SQ7).

### Influence of the light intensity

Generally, the polymerization rate ( $R_p$ ) can be expressed as follows:

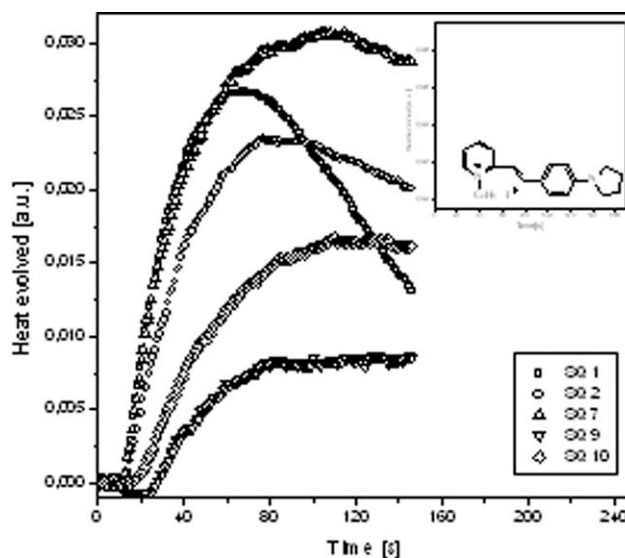
$$R_p = \frac{d[M]}{dt} = k_p \left( \frac{\phi_d I_a}{2k_t} \right)^{0.5} [M] \quad (1)$$

where  $k_p$  is the rate constant of the propagation step,  $k_t$  is the rate constant of the termination step,  $\phi_d$  is the quantum yield of free-radical formation,  $I_a$  is the absorbed light intensity,  $t$  is the time, and  $[M]$  is the monomer concentration.

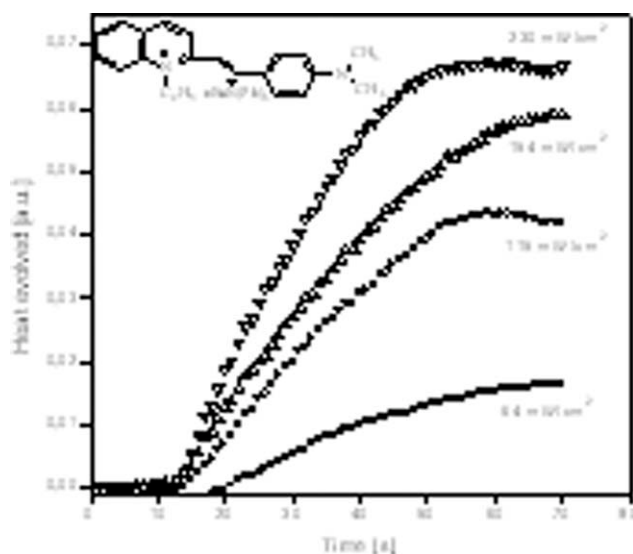
In this expression, the polymerization rate depends on the square root of the absorbed light intensity and is directly proportional to the monomer concentration. Figure 4 shows the effect of the light intensity on the rate of polymerization photoinitiated by asymmetric cyanine borate photoredox pairs.

An increase in the light intensity leads to an increase in the polymerization rate. The observed trend is in good accordance with eq. (1). The slopes of the linear part of the curve observed for the initial time of polymerization (assumed to be the polymerization rates) are, as shown in Figure 5, proportional to the square root of  $I_0$ , the absorbed light intensity.

This observation indicates that the light intensity has no effect on the quantum yield of free-radical formation.<sup>19</sup> Moreover, this suggests that the



**Figure 3** Family of kinetic curves recorded during the measurement of the flow of heat during the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by styrylquinolinium borates. The dye concentration was  $1 \times 10^{-3}$  M, and the absorbed light intensity was 64 mW/cm<sup>2</sup>. The applied dyes possessed various chromophores and the same borate. The inset shows the kinetic curve recorded during the measurement of the flow of heat during the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by styrylpyridinium borate (SP7).



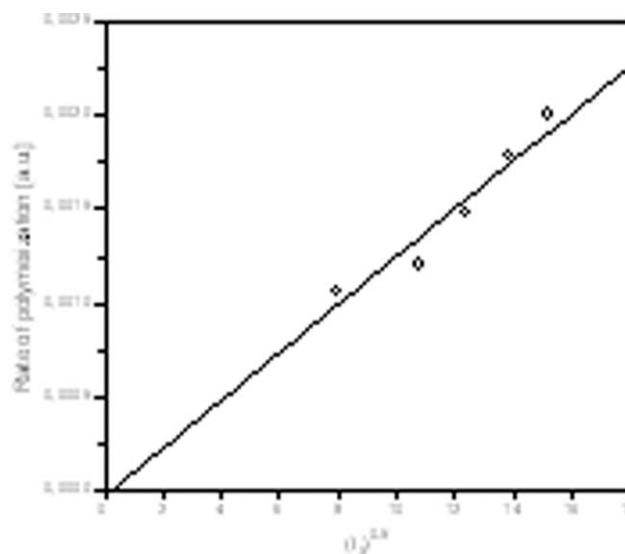
**Figure 4** Family of kinetic curves recorded during the measurement of the flow of heat for the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by SQ1B2. The effect of the light intensity on the polymerization rate is illustrated.

photoinitiated polymerization of the system proceeds by a conventional mechanism in which bimolecular termination occurs through a reaction between two macroradicals. This allows us to conclude that the free radicals formed from styrylquinolinium cations after the photoinduced electron transfer (PET) process do not act as terminators of polymer chains.

#### Influence of the initiator concentration

The kinetic curves recorded for photoinitiated polymerizations at different initiator concentrations are presented in Figure 6.

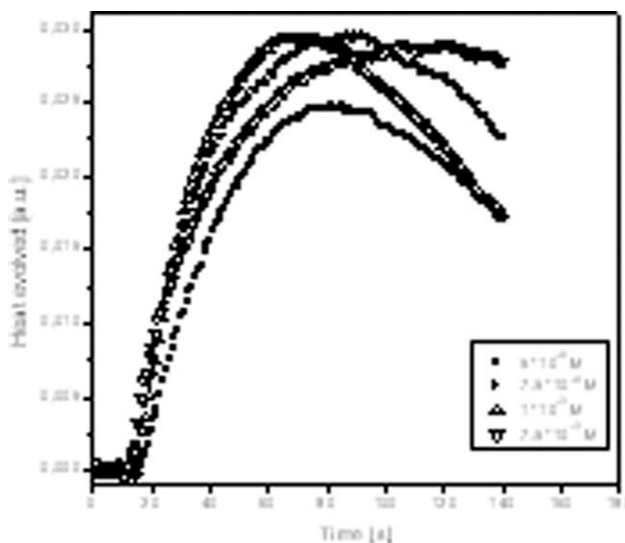
The data in Figure 6 show that the time needed to reach the curve maximum decreases when the initiator [SQ1B2, the styrylquinolinium dye (SQ1) as *n*-butyltriphenylborate salt] concentration increases. The observed property is caused by two differences in character-specific behaviors. The first is related to the rate of heat evolution for the initial time of polymerization (the slope of the linear part of the kinetic curve), and the second is related to the time needed for polymerization to start (the induction time). Under similar experimental conditions, with a low concentration of the initiator, the induction time is about 20 s, whereas for a concentration about 1 magnitude higher, the induction time decreases to 16 s. Simultaneously, the slope of the linear parts of the kinetic curves increases when the concentration of the initiator increases.



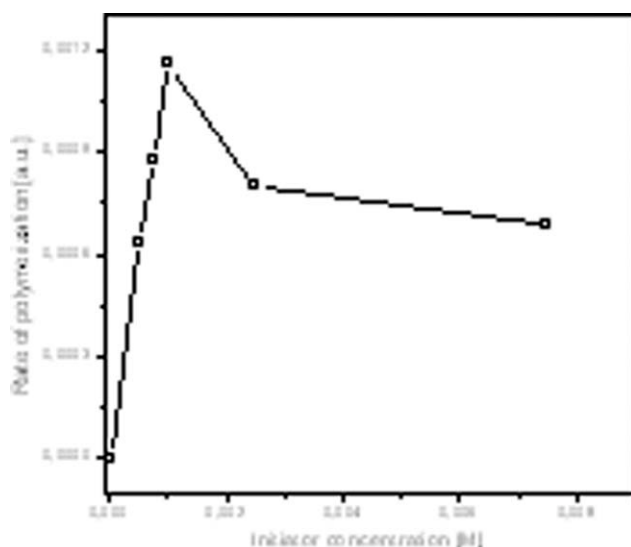
**Figure 5** Rate of polymerization versus the light intensity for the styrylquinolinium borate system (SQ1B2). The photoinitiator concentration was  $1 \times 10^{-3}$  M.

Figure 7 presents the relationship between the initial rate of polymerization (the slope of the linear part of the kinetic curve) and the concentration of the photoinitiator (SQ1B2).

It is evident that as the photoinitiator concentration increases, the initial rate of polymerization increases, and it reaches a maximum followed by a continuous mild reduction. For the tested photoinitiators, the highest rates of polymerization for 3-mm-thick samples (Fig. 7) were achieved at the initiator concentration of about  $1 \times 10^{-3}$  M. The reduction of the photoinitiated polymerization rate at a higher



**Figure 6** Family of kinetic curves recorded during the measurement of the flow of heat for the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated with different concentrations of SQ1B2. The absorbed light intensity was  $64 \text{ mW/cm}^2$ .

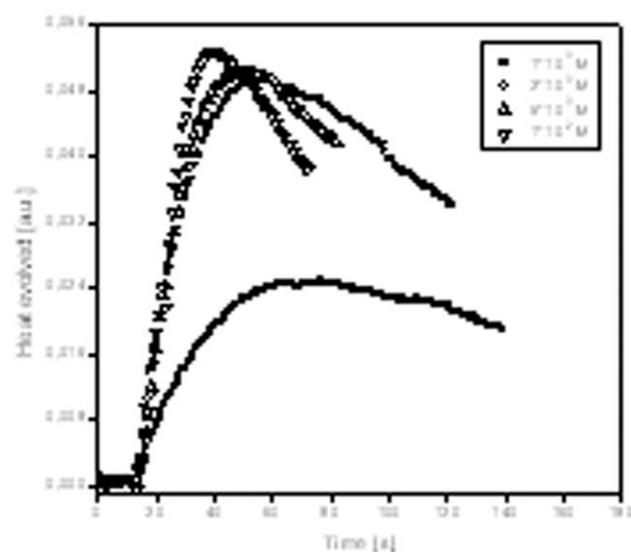


**Figure 7** Rate of polymerization versus the photoinitiator (SQ1B2) concentration.

initiator concentration for an applied technique of polymerization rate measurement can be easily understood if we take into account the reduction of the penetration depth of the laser beam, which is a result of a so-called internal filter effect.<sup>20</sup>

#### Influence of the coinitiator concentration

The kinetic curves shown in Figure 8 were recorded for the polymerizations initiated by photoredox pairs with different initiator/coinitiator concentration ratios under irradiation with visible light. The data in Figure 8 apparently show that the rate of photoi-

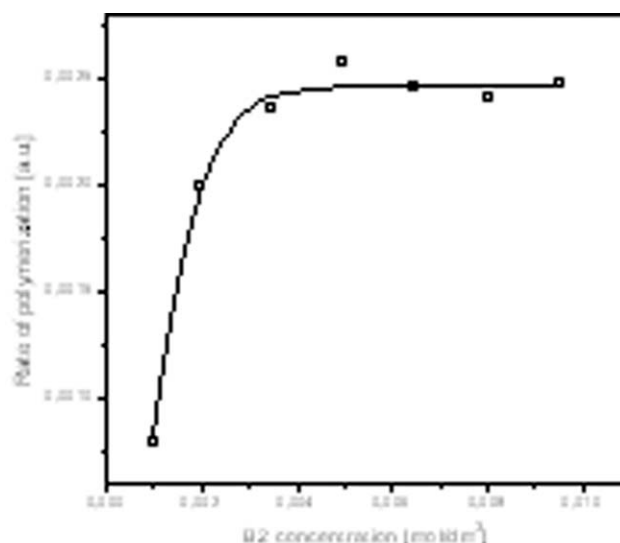


**Figure 8** Family of kinetic curves recorded during the measurement of the flow of heat for the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by SQ7B2 with various concentrations of the electron donor (B2).

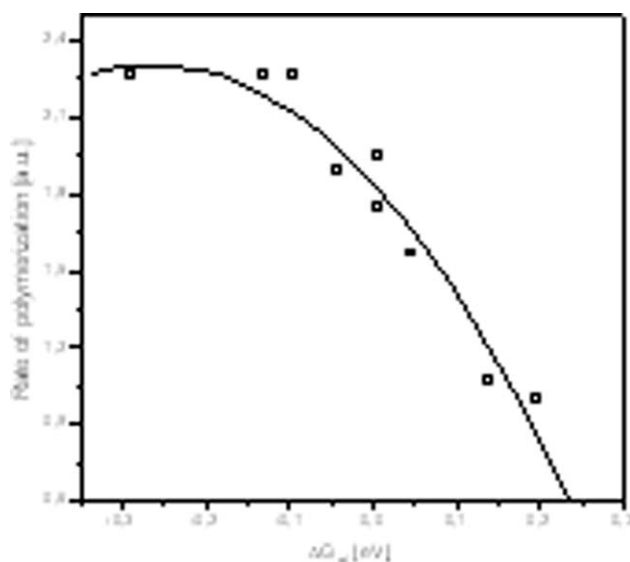
nitiated polymerization by a dye-coinitiator pair strongly depends on the concentration of the coinitiator. The insertion of an additional amount of the coinitiator (B2) into the dye leads to an enhancement of the polymerization rates for all the systems studied.

According to Chatterjee et al.'s<sup>21</sup> studies on symmetrical cyanine borate initiators, in nonpolar or medium-polarity solvents, one can treat the asymmetric cyanine cation and borate anion as an ion pair. However, the study on the influence of the borate concentration on the rate of photoinitiated polymerization indicates, for an identical monomer-dye formulation, a distinct increase in the rate of polymerization as the concentration of the borate anion increases. Figure 9 illustrates this relationship.

On the basis of this experiment, it appears that when the borate anion concentration is equal to the styrylquinolinium cation concentration, only some of the photoredox pairs exist as ion pairs. An analysis of the data presented in Figure 9 indicates that for the SQ7B2 initiating system, only about 30% of the photoredox couples exist as ion pairs. At a concentration of the dye equal to  $1 \times 10^{-3}$  M, these values give an equilibrium constant of approximately  $1.58 \times 10^{-3}$  M. Because the electron transfer for cyanine dyes occurs in their singlet state, the existence of the cyanine cation and borate anion as an ion pair is the basic prerequisite for effective electron transfer. From the relationship shown in Figure 9, it is clear that an additional amount of the borate cation shifts the equilibrium between free ions: from the ion pair to the higher concentration of the ion pair. This is why the addition of the coinitiator causes an



**Figure 9** Dependence of the rate of photoinitiated polymerization on the concentration of the electron donor (B2). The initial dye (SQ7B2)-borate concentration was  $1 \times 10^{-3}$  M.



**Figure 10** Relationship between the rate of polymerization (TMPTA/MP) and the free energy change ( $\Delta G_{el}$ ) for styrylquinolinium borate photoredox pairs (initiator concentration =  $1 \times 10^{-3}$  M). The irradiation of the polymerization mixture was carried out with the visible emission of an argon laser with an irradiation intensity of  $64 \text{ mW/cm}^2$ .

increase in the photoinitiation efficiency, which is enhanced by the more efficient electron transfer reaction.

### Influence of the thermodynamic parameter

A discussion of the photochemistry of styrylquinolinium borates should also include an estimation of the thermodynamic driving force for the PET process.

The free energy change ( $\Delta G_{el}$ ) for electron transfer from donor D to acceptor A in the excited state is expressed by the Rehm–Weller equation<sup>22</sup>:

$$\Delta G_{el} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - E_{00}^{S_1} - e^2/\epsilon R_{DA} \quad (2)$$

where  $R_{DA}$  is the distance between donor and acceptor molecule in an ion pair  $\epsilon$ , a dielectric constant and  $E_{00}^{S_1}$  is the excited-state energy of the acceptor (styrylquinolinium dye) in the electron transfer reaction (calculated from the intersection of the normalized absorption and fluorescence spectra recorded in the same solvent),  $E_{ox}(D/D^{\bullet+})$  is the oxidation potential of the electron donor (*n*-butyltriphenylborate anion), and  $E_{red}(A^{\bullet-}/A)$  is the reduction potential of the electron acceptor. The last term accounts for the Coulombic energy associated with the separation of charges in the electron transfer products. This factor can be ignored for these cases. It is well known that the main prerequisite for PET reactions is described by the Rehm–Weller equa-

tion<sup>22</sup> [eq. (2)], which states that the free energy of activation for the PET process should have a negative value.

The measured values of the above mentioned variables and the calculated values of the free energy change for the photoinduced intermolecular electron transfer process are also summarized in Table I. The free energy change of this system can be estimated to be in the range of  $-0.286$  to  $0.194$  eV with the reduction potentials of hemicyanine dyes ( $-1.085$  to  $-0.71$  eV), the excitation energy of hemicyanine dyes ( $2.00$ – $2.24$  eV), and the oxidation potential of *n*-butyltriphenylborate salt ( $1.16$  eV).<sup>4</sup> Calculations clearly show that for the tested photoredox pairs, the electron transfer process is thermodynamically allowed only for three tested dyes (SQ1, SQ2, and SQ5; negative values of the free energy change).

The practical application of the theory of electron transfer<sup>23,24</sup> in the polymerization photoinitiation process can be limited to certain conditions (an identical free radical formed), under the assumption that the rules regulating the primary processes can also be applied to the secondary reactions. The results of such treatment are presented in Figure 10.

From an inspection of the data presented in Figure 10, we can see that the rate of free-radical polymerization initiated by the styrylquinolinium borate salts increases as the driving force of the electron transfer reaction increases. It is noteworthy that this behavior is predicted by the classical theory of the electron transfer process.<sup>23,24</sup>

## CONCLUSIONS

In this article, the efficiency of visible-light-induced polymerization of a multifunctional acrylate in the presence of two-component photoinitiating systems based on styrylquinolinium dyes and borate salt has been ascertained. The initiation ability of the studied photoinitiating systems increases when both the initiator and coinitiator concentrations and the light intensity increase. The relationship between the rate of polymerization and the free energy change for the electron transfer process displays normal Marcus kinetic behavior.

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