

## Cyclic acetals as the second co-initiators in three-component photoinitiating systems

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**Abstract** Cyclic acetals were used as a second co-initiator in three-component photoinitiating systems. The mixtures of cyanine dye borate ion salt and cyclic acetals were used to initiate the visible light polymerization of triacrylate monomer (TMPTA). The kinetics of polymerization was recorded by differential scanning calorimetry (DSC). The results showed that the addition of cyclic acetals increases the rate of polymerization ( $R_p$ ).

**Keywords** Photoinitiators · Acetals · Free radical polymerization · Electron transfer process

### Introduction

Photoinitiated free radical polymerization is a technologically important process owing to extensive applications in the curing and coating on various materials, adhesives, printing inks, and photoresists [1, 2]. In these systems, a key to control the photopolymerization process is photoinitiator, which absorbs light and generates active radicals to initiate the polymerization [3]. Photoinitiated free radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators [1]. The type I photoinitiators undergoes a direct photofragmentation process ( $\alpha$ - or less common  $\beta$ -cleavage) upon absorption of light and formation of initiating radicals capable of start the polymerization chain reaction. The type II photoinitiators are a second class of photoinitiators based on compounds whose triplet excited states readily react with hydrogen donors or electron donors, thereby producing an initiating radical [1].

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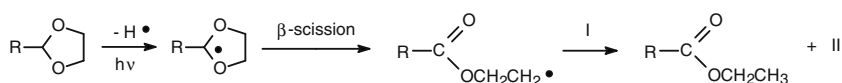
Although the rate of the type II photoinitiators are slower than the type I photoinitiators due to a bimolecular initiation reaction, so far efficient polymerization, the bimolecular reaction (e.g., H-abstraction or electron transfer process) must compete with other side reactions, such as the quenching of excited triplet state by oxygen, by monomer or self quenching with low triplet energy [1, 4]. Therefore, these systems are more sensitive to oxygen, and polymerization in air may lead to relatively low curing rates.

Among the most commonly used photoinitiators for free radical polymerization, bimolecular initiating systems, which undergo intermolecular hydrogen abstraction process from a co-initiator that contains labile hydrogen [5–7]. Tertiary amines are the most frequently employed co-initiators due to its higher reactivity. However, amines are known to mutagenicity and tend to induce substrate corrosion and cause yellow of the cured film [5]. Other examples of hydrogen donating photoinitiators are heteroaromatic thiols [8, 9] and cyclic acetals [1, 5]. The acetal function is a well-known protecting group with unique reactivity [5, 10]. It has been reported that the monoester radical generated by the photoirradiation of cyclic acetal could initiate the polymerization of vinyl compounds and methyl methacrylate [1, 11]. Recently, photosensitized hydrogen abstraction from 2-alkyl-1,3-dioxolanes by triplet state of benzophenone gives the corresponding 1,3-dioxolan-2-yl radicals and provides a viable alternative for synthesis of 1,4-diketones [1, 12]. More recently, Shi reported that cyclic acetals were used as hydrogen donors for bimolecular photoinitiating systems and a natural component 1,3-benzodioxole was used as a co-initiator for replacing the conventional amine for dental composite [1, 13].

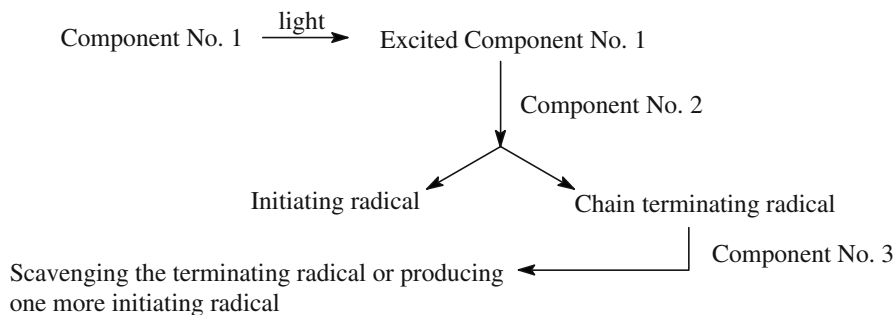
Since the active hydrogen between two alcohxy groups in the cyclic acetals is abstractable and could form a radical, Elad and Youssefeyeh proposed the photochemical rearrangement mechanism of 1,3-dioxolane compounds to give esters is shown in Scheme 1 [1, 14].

To enhance the sensitivity, very often the three-component photoinitiating systems have been used. In these systems, the third component is usually supposed to scavenge the chain-terminating radicals that are generated by primary electron transfer reaction or produce an additional initiating radical (Scheme 2) [15, 16].

Like the two-component systems, the three-component initiators include a light absorbing moiety, which is 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, polycyclic heterocycles and many others [16–27]. These



**Scheme 1** The photochemical rearrangement mechanism of 1,3-dioxolane



**Scheme 2** The general mechanism the free radicals formation in three-component photoinitiating system

photoinitiating systems have consistently been found to be faster, more efficient, and more sensitive than their two-component parent photoredox pairs [16, 28, 29].

In this paper, the search for more effective photoinitiating systems of free radical polymerization of acrylate monomers, composed of cyanine dyes in the three-component photoinitiating systems is described. The photoinitiators consisting of these dyes parried with borate anion in the presence of cyclic acetal as a second co-initiator were investigated through polymerization experiments. In this study, cyclic acetals were used as hydrogen donors for three molecular photoinitiating systems. The synergistic effect of cyclic acetals was investigated by differential scanning calorimetry (DSC) technique.

## Experimental

### Materials

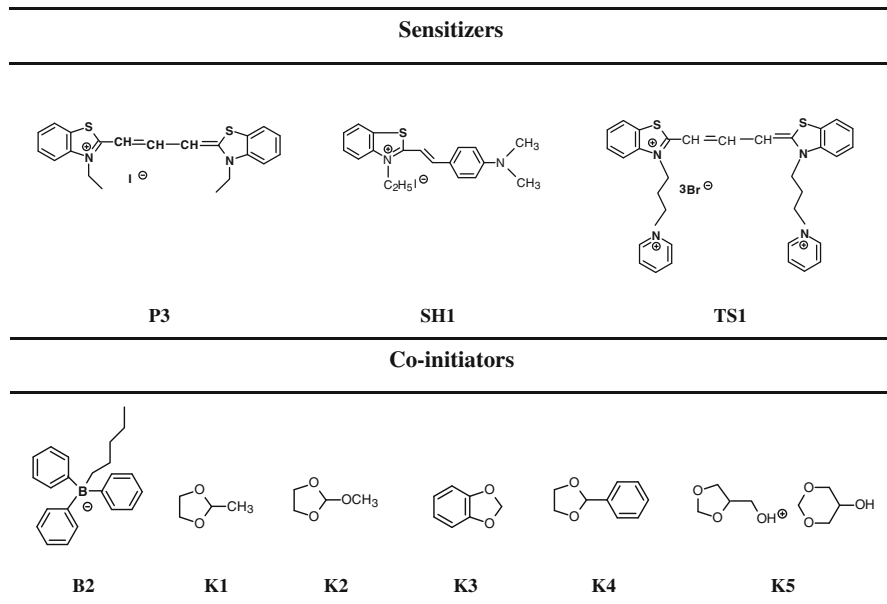
2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich and were used as monomer and solvent, respectively.

Cyclic acetals: 2-methyl-1,3-dioxolane (**K1**), 2-methoxy-1,3-dioxolane (**K2**), 1,3-benzodioxolane (**K3**), 2-phenyl-1,3-dioxolane (**K4**), glycerol formal (mixtures of 40% 4-hydroxymethyl-1,3-dioxolane and 60% 5-hydroxy-1,3-dioxolane) (**K5**) were purchased from Aldrich Co. and used without further purification.

The chemical structure of sensitizers and co-initiators are shown in Chart 1.

### Cyclic voltammetry

The reduction and oxidation potentials of cyanine dyes and co-initiators were measured by cyclic voltammetry. An Electroanalytical MTM System model EA9C-4z (Krakow, Poland), equipped with a small-volume cell was used for the measurements. A 1 mm platinum disc electrode was applied 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



**Chart 1** The chemical structure of sensitizers and co-initiators tested

tetrabutylammonium perchlorate in dry acetonitrile. The solution was deoxygenated by bubbling argon gas through the solution. The potential was swept from  $-1.6$  to  $1.6$  V and with the sweep rate of  $500$  mV/s to record the current–voltage curve.

### Polymerization kinetics

Photoinitiated polymerization rate ( $R_p$ ) profiles were determined by a differential scanning calorimetry (DSC), under isothermal conditions at room temperature using a photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. The  $0.035 \pm 0.002$  g of sample was polymerized in open aluminum pans having the diameter of  $6.6$  mm. The irradiations of the polymerizations were carried out with Air-cooled Ion Laser Systems model 177-G01 (488 and 514 nm) (Spectra-Physics, USA). The average power of irradiation was  $20$  mW/ $0.196$  cm<sup>2</sup> at 514 nm. The light intensity was measured by a Coherent Model Fieldmaster power meter.

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 cyanine dyes concentrations used in experiments were  $7.5 \times 10^{-4}$  M,  $1 \times 10^{-3}$  M, and  $5 \times 10^{-3}$  M, respectively. The co-initiators concentrations were varied from  $1 \times 10^{-3}$  M to  $1 \times 10^{-1}$  M. The monomer was used without purification. As a reference sample, a polymerizing mixture containing cyanine iodide (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 reproducibility of the results was about  $\pm 3\%$ . For computations, the heat of polymerization was taken to be 78 kJ/mol per for acrylic double bonds.

## Results and discussion

### The kinetics of polymerization: efficiency of two- and three-component photoinitiating systems

The photoinitiating systems composed of cyanine dye as a photosensitizer with various co-initiators (borate salt and cyclic acetals) were used for the initiation of free radical polymerization. The polymerization solution consisted of  $7.5 \times 10^{-4}$  M (**TS1**),  $1 \times 10^{-3}$  M (**P3**),  $5 \times 10^{-3}$  M (**SH1**) of sensitizer (as an iodide or *n*-butyltriphenylborate salt), and cyclic acetals with concentrations varied from  $1 \times 10^{-3}$  M to  $1 \times 10^{-1}$  M. The polymerization process was initiated by irradiation at 514 nm. At this wavelength only a sensitizer absorbs the light.

Cyanine dye borate salts are the most prominent representatives of visible light bimolecular photoinitiating systems [30–32]. Various factors had great influence on the rate of polymerization such as a chemical structure of the dye, chemical structure of co-initiator, the light intensity, etc. [26].

The comparison of the polymerization rates observed for cyanine–borate pair and cyanine–borate–cyclic acetal triplets indicates that the lowest rates of polymerization for cyanine–borate photoredox pair were observed.

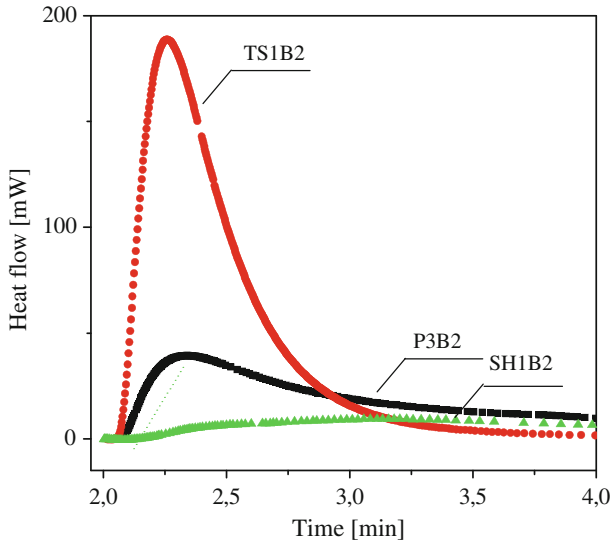
For comparison of the photoinitiating abilities of tested photoinitiating systems, the kinetic curves obtained during the photoinitiated polymerization of TMPTA-MP (9:1) mixture photoinitiated by two-component photoinitiating systems composed of cyanine borates, under irradiation with a visible light are shown in Fig. 1 for illustration.

As it was shown below, the addition of cyclic acetals resulted in an acceleration of the polymerization process.

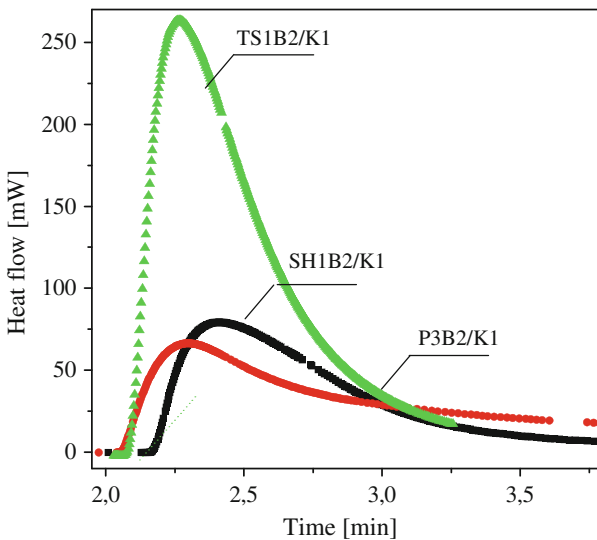
The kinetic curves obtained for the photoinitiated polymerization of TMPTA-MP (9:1) mixture photoinitiated by cyanine borates in a presence of cyclic acetals, under irradiation with a visible light are shown in Fig. 2 for illustration.

From the data presented in Figs. 1 and 2 it is clear that the three-component systems dye/borate salt/cyclic acetal exhibit the highest reactivity. The rates of polymerization ( $R_p$ ) are 1.5–2 times higher than those observed for two-component dye/borate salts photoinitiating systems.

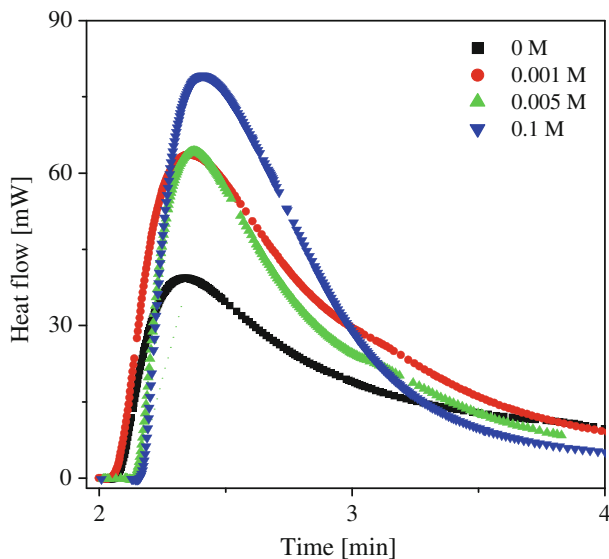
The couple **SH1B2** was the worst photoinitiating system used. However, addition of cyclic acetal into **SH1B2** considerably enhanced the efficiency of the polymerization that became as good as those obtained in the presence of other dyes under the identical conditions (sevenfold increase in the polymerization rate, Fig. 2).



**Fig. 1** 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 two-component photoinitiating systems composed of cyanine dye *n*-butyltriphenylborate marked in the figure. The photoinitiators concentrations were  $7.5 \times 10^{-4}$  M (TS1B2),  $1 \times 10^{-3}$  M (P3B2), and  $5 \times 10^{-3}$  M (SH1B2), respectively.  $I_a = 20$  mW/0.196 cm<sup>2</sup>



**Fig. 2** 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 three-component photoinitiating systems composed of cyanine dye *n*-butyltriphenylborate in presence of 2-methyl-1,3-dioxolane, marked in the figure. The acetal concentration was  $1 \times 10^{-2}$  M,  $I_a = 20$  mW/0.196 cm<sup>2</sup>



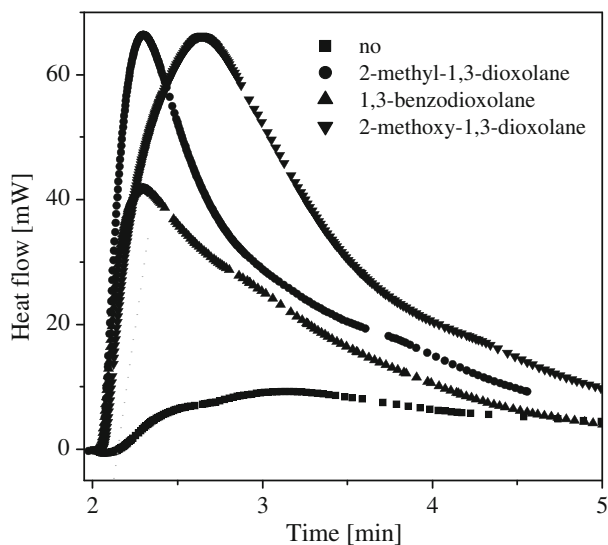
**Fig. 3** Effect of 2-methyl-1,3-dioxolane (**K1**) concentration on the rate of free radical polymerization of TMPTA/MP polymerizing mixture initiated by three-component photoinitiating system (**P3B2**). Concentration of dye =  $1 \times 10^{-3}$  M. Light intensity equal 20 mW/0.196 cm<sup>2</sup>

The photoinitiating efficiency of tested three-component systems depends on the concentration of both co-initiators (borate salt and cyclic acetal). Figure 3 illustrates 2-methyl-1,3-dioxolane (**K1**) concentration effect on the rate of photoinitiated polymerization.

The increase of the concentration of cyclic acetal from 0 to 0.1 M caused the increase of the rate of polymerization ( $R_p$ ) about two times.

The next factor, which has significant influence on the photoinitiating ability of three-component photoinitiating systems is the structure of a second co-initiator. The effect of the structure of cyclic acetal on the rate of free radical polymerization photoinitiated by cyanine borate salt is shown in Fig. 4.

The relative rate of hydrogen atom abstraction by photogenerated radicals from a variety of cyclic ethers, acetals and orthoformates had been investigated using EPR spectroscopic technique [5, 33]. There was pronounced stereoelectronic effect, which produced high rates of abstraction from cyclic acetal carbon. Thus, methyl group attached to the acetal carbon atom exerted a significant effect on the hydrogen abstraction. However, the activating effect of phenyl group was proved to be smaller than that of methyl group, probably because of the delocalization of the unpaired electron on to the unsaturated group came at the expense of planarization at acetal carbon [5, 34]. In addition to the stereoelectronic factor, molecular conformation also affected the abstraction rate. For example, Malatesta and Ingold [33] found that the more mobile envelope conformation of five-numbered cyclic acetals had higher hydrogen abstraction rate than that of six-numbered ones. Ouchi and Hamada [11] also reported the results that the strain of ring could affect the ability to promote the polymerization.



**Fig. 4** Effect of cyclic acetals structure on the rate of free radical polymerization of TMPTA:MP polymerizing mixture initiated by three-component photoinitiating system (SH1B2). Concentration of dye =  $5 \times 10^{-3}$  M. Light intensity equal 20 mW/0.196 cm<sup>2</sup>

In this study, 2-methyl-1,3-dioxolane (**K1**) had relatively higher rate of polymerization  $R_p$ , than that of 2-phenyl-1,3-dioxolane (**K4**), which was consistent with the reported rate of hydrogen abstraction from cyclic acetals. Formal glycerol (**K5**) with 60% six-numbered cyclic acetal had lower reactivity. 1,3-Dioxolane (**K3**) indicated an effective second co-initiator for cyanine dye/borate salt photoinitiating systems.

Summarizing, the addition of cyclic acetal to the two-component photoinitiating system induced a strong synergic effect (Figs. 2, 3, and 4). However, the efficiency of the cyanine dye/borate salt/cyclic acetal three-component system is not a simple sum of the efficiencies of the two-component photoinitiating system: dye/borate salt or dye/acetal systems acting separately. Therefore, it seems that the improvement in photoinitiation for the system cyanine dye/borate/cyclic acetal in comparison to cyanine/borate salt is a result of secondary reactions between cyclic acetal and the species deriving from the first step of interaction, e.g., the reaction between the excited singlet state of the dye and borate salt.

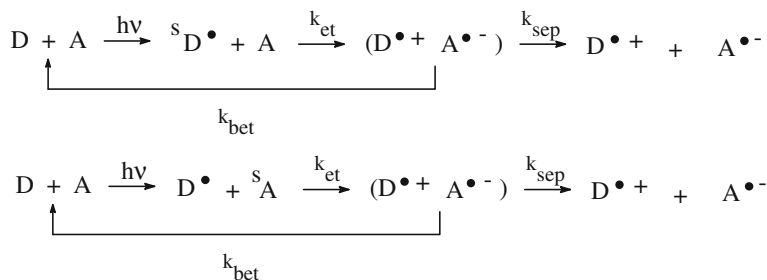
It is well-known that the electron transfer reaction can be depicted according to Scheme 3.

In general, the Rehm–Weller equation is used for evaluating the possibility of an electron transfer reaction. The free energy change ( $\Delta G_{el}$ ) of the reactions can be calculated by using the following equation (Eq. 1) [36]:

$$\Delta G_{el} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - E_{00} - Ze^2/\epsilon a \quad (1)$$

where:



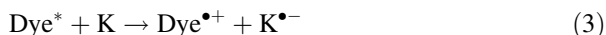
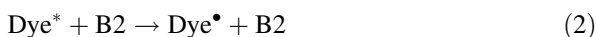


**Scheme 3** The mechanism of an electron transfer processes. D is an electron donor, A is an electron acceptor,  $s$  is the spin multiplicity of the excited state ( $s = 1$  or  $3$ ),  $k_{\text{et}}$ ,  $k_{\text{bet}}$ , and  $k_{\text{sep}}$  are the rate constants of electron transfer, back electron transfer, and ion separation, respectively [35]

$E_{\text{ox}}(\text{D}/\text{D}^{\bullet+})$  is the oxidation potential of the electron donor,  $E_{\text{red}}(\text{A}^{\bullet-}/\text{A})$  is the reduction potential of the electron acceptor,  $E_{00}$  is the energy of the excited state involved in electron transfer reaction and  $Ze^2/\epsilon a$  is the Coulombic energy associated with the process.

Since the last term is relatively small in polar or medium polarity media, it can be neglected in the estimation of  $\Delta G_{\text{et}}$ . The  $E_{\text{ox}}$  and  $E_{\text{red}}$  of both photoredox pair components were determined from the cyclic voltametric measurements in acetonitrile and are summarized in Table 1.

For three-component system theoretically following primary reactions are possible (Eqs. 2–4):



As it is seen, from the electrochemical measurements only electron transfer from borate anion to the excited singlet state of cyanine dye is possible reaction (Eq. 2). The calculated  $\Delta G_{\text{et}}$  for this reaction are in the range from  $-0.02$  to  $0.094$  eV.

**Table 1** The oxidation and reduction potentials and the excited singlet state energy of tested compounds

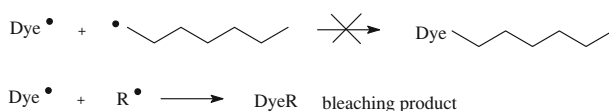
| Compound   | $E_{\text{red}}$ (eV) | $E_{\text{ox}}$ (eV) | $E_{00}$ (eV) |
|------------|-----------------------|----------------------|---------------|
| <b>P3</b>  | -1.30                 | 1.0                  | 2.08          |
| <b>SH1</b> | -1.09                 | -                    | 2.156         |
| <b>TS1</b> | -1.02                 | -                    | 2.164         |
| <b>B2</b>  | -1.00                 | 1.16                 |               |
| <b>K1</b>  | -1.18                 | -                    |               |
| <b>K2</b>  | -1.07                 | -                    |               |
| <b>K3</b>  | -1.02                 | -                    |               |
| <b>K4</b>  | -1.055                | -                    |               |
| <b>K5</b>  | -1.03                 | -                    |               |

Because tested dyes do not undergo electrochemical oxidation, the electron transfer from the excited singlet state of the dye to the cyclic acetal is not possible, leading to oxidation of the dye and reduction of cyclic acetal (Eq. 3). From the same reason, the electron transfer process from the ground state of cyclic acetal on the excited singlet state of cyanine dye could not occur (Eq. 4).

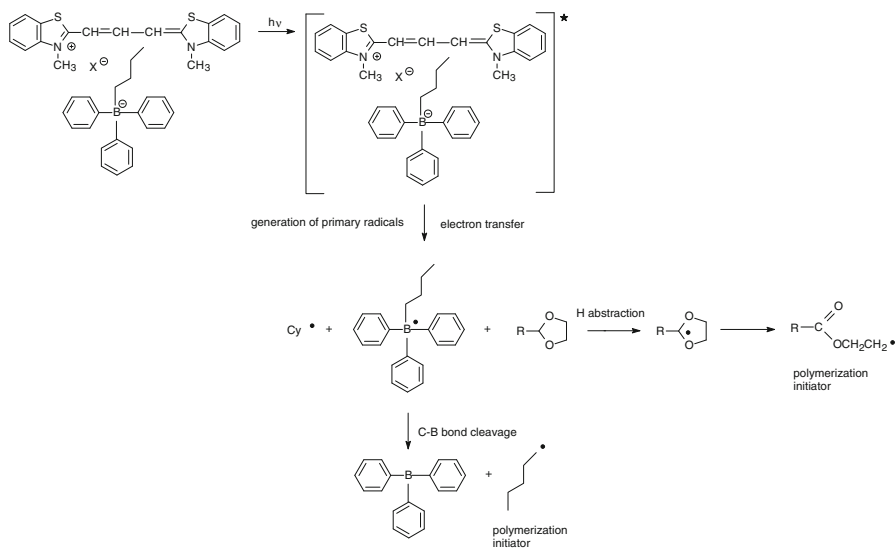
Basing on this, one can conclude that the primary process is an electron transfer from borate anion to the excited state of cyanine dye, leading to the formation of cyanine dye radical and boranyl radical.

All results, reveal that an effective interaction can take place between cyclic acetal and the products formed as a result of primary process (cyanine dye radical, boranyl radical). If the electron transfer reaction from the cyclic acetal to excited state of the dye occurs, leading to the formation of radicals capable of initiating polymerization of TMPTA we should observe the initiation of free radical polymerization of TMPTA by two-component photoinitiating systems composed of cyanine dye/cyclic acetal. In the present case no radicals capable of initiating polymerization of TMPTA are present. Thus, this process does not play a significant role in photoinitiation.

There are at least two possible explanations of the observed phenomena. The first reasonable hypothesis suggests, that the synergic effect of the cyanine dye/borate salt/cyclic acetal system behavior could be explained by an electron transfer interaction of the reduced dye (dye radical), boranyl radical or butyl radical (product decomposition of boranyl radical) with the cyclic acetal. Cyanine dye radical is known as weak terminator of the growing macromolecular chains. However, it reacts efficiently with an alkyl radical [37–39]. The linear relationship between the rate of polymerization and the square root of the light intensity absorbed confirms this postulate, suggesting that photoinitiated polymerization of the system proceeds by a conventional mechanism in which bimolecular termination occurs by the reaction between two macroradicals. This allows concluding that the free radicals formed from cyanine radical do not act as terminator of polymer chains [40].



Such interaction can sharply decrease an efficiency of initiation process, and this in turn, causes a decrease in observed rate of polymerization. The possible explanation of the observed synergic effect for three-component system may consider possible redox reaction between cyanine dye radical, boranyl radical or butyl radical and cyclic acetal. Similar reaction was well documented for dye radical and *N*-methoxy-pyridine cations or *N*-methypicolinium ester [38, 41]. The second explanation considers the interactions between the cyanine dye radical and cyclic acetal can strongly reduce a terminating effect caused by dye radical, or interaction between cyanine dye radical, boranyl radical or butyl radical and cyclic acetal and additionally to form a new initiating radicals as a results of hydrogen abstraction. Similar observations were observed for three-component photoinitiating systems composed of cyanine dye/triazine/thiol [42].



**Scheme 4** The primary and secondary processes occurring in the three-component photoinitiating system: cyanine dye/borate salt/cyclic acetal after absorption of the visible light

Based on the discussion presented above, we suggest that the radical formation reactions proceed as illustrated in Scheme 4.

The photoexcited dye molecule encounters *n*-butyltriphenylborate anion and accepts an electron from borate anion, forming boranyl radical, and cyanine radical. In the next step the hydrogen abstraction from cyclic acetal to free radicals, formed in primary photochemical process occurs.

## Conclusions

Cyclic acetals showed the potential as second co-initiators for three-component photoinitiating systems for triacrylate monomer (TMPTA). The photoinitiation ability of three-component photoinitiating systems composed of cyanine dye/borate salt/cyclic acetal depends on the chemical structure and concentration of cyclic acetals. The initial rates of polymerization are increasing as the concentration of acetal increases. The addition of cyclic acetal to the well-known two-component photoinitiation system caused in increasing of the rate of free radical polymerization of about two times.

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