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The Comparison of the Photoinitiating Ability of the Dyeing Photoinitiating Systems Acting via Photoreducible or Parallel Series Mechanism

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1. Introduction

Light-induced polymerization reaction is largely encountered in many industrial applications. For example, laser direct imaging, graphics arts, holography, and dental materials require irradiation in the visible light region to benefit from laser technologies or simply to avoid UV damaging effects on skin [1]. The basic idea is to readily transform a liquid resin or a soft film into a solid film upon light exposure to form either a coating as developed in the UV curing area or an image as used in the (laser) imaging area. The starting resin is in fact a formulation that consist in an oligomer, a monomer, a photoinitiating system, and various additives depending on the applications (formulation agents, stabilizers, pigments, fillers, etc.).

The imaging technology industries where lasers are very often used currently, appear in high-tech sectors combining photochemistry, organic and polymer chemistry, physics, optics, electronics such as (i) microelectronics – photoresists for the printed circuits, integrated circuits, very large and ultralarge scale integration circuits and laser direct imaging (LDI) technology that allows to write complex relief structures for the manufacture of microcircuits or to pattern selective areas in microelectronic packaging, and so on, (ii) graphic arts – manufacture of conventional printing plates, computer-to-plate technology that directly helps to reproduce a document on a printing plate, and so on (iii) 3D machining (or three-dimensional photopolymerization or stereolithography) which is giving the possibility to make objects for prototyping applications, (iv) optics – holographic recording and information storage, computer generated and embossed holograms, manufacture of optical elements (diffraction grating, mirrors, lenses, waveguide, array illuminators, and display applications), design of structured materials on the nanoscale size.

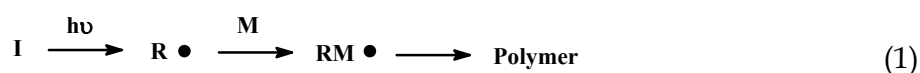
Great effort is taken at present in the design the new photosensitive systems being able to work in well-defined conditions. As far as the polymerization reactions are concerned in UV curing and imaging areas, they are mostly based on a radical process.

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In this chapter, we will focus on photosensitive systems that are used in free radical photopolymerization reactions. We will give the most exhaustive presentation of potentially interesting systems developed on a laboratory scale together with the characteristic of their excited-state properties. We will also show how modern time resolved laser spectroscopy techniques allows to probe the photophysical/photochemical properties as well as the chemical reactivity of a given photoinitiating system [2].

2. Properties of photoinitiating system

A photoinitiating system (PIS) consist at least in a photoinitiator (I). Very often, a co-initiator (coI), a radical scavenger (RS) or a photosensitizer S can be added. Basically, a photoinitiating system leads to radicals that can initiate the polymerization (1).



The photoinitiator (I) is usually an organic molecule. Upon excitation by light, (I) is promoted from its ground singlet state S_0 to its first excited singlet state S_1 and then converted into its triplet state T_1 via a fast intersystem crossing. In many cases, this transient T_1 state yields the reactive radicals R^\bullet that can attack a monomer molecule and initiate the polymerization [1, 2].

Radicals of photoinitiators are produced through several following typical processes:

- A photolysis of a C-C, C-S, C-B and C-P bonds (most cleavable compounds are based on the benzoyl chromophore),
- An hydrogen abstraction reaction between (I) and (coI), which plays the role of a hydrogen donor (such as an alcohol, a thiol, etc.); two radicals are formed: one on a donor and another on (I),
- An electron transfer process between (I) and (coI).

The spectral absorption range of photoinitiator is a decisive factor: the wavelength range of the (I) absorption has to match the spectral emission range of the light source. Therefore, when pigmented or colored media are used, a spectral window has to be found to excite. It may happen that the direct excitation of photoinitiator is impossible. In that case, a photosensitizer (S) must be added. The role of sensitizer is to absorb the light and to transfer the excess of energy to the photoinitiator through the well-known energy transfer process. The process is efficient only if the energy level of a donor is higher than that of an acceptor.

The panchromatic sensitization of free radical polymerization under visible light can occur in a presence of the dye alone (one-component) or in a presence of two-, three- or multi-component photoinitiating systems composed of dye molecule (sensitizer) and second compound acting as a co-initiator (either as electron or hydrogen atom donor).

Commonly, visible-light activated initiators are typically two-component initiator systems: a light-absorbing photosensitizer and co-initiator. In this type of photoinitiating system, the photo-excited dye may act as either an electron acceptor (for example, if an amine is used as the second component), or an electron donor (for example, when an iodonium salt is used as the second component) [3]. Although both reaction pathways are known, electron transfer

from an electron donor to the photo-excited dye and the generation of radicals followed by either proton transfer from radical cation of electron donor or bond cleavage in electron donor is more common [3]. The intrinsic characteristics of two-component initiator systems leads to numerous kinetic limitations. For example, since the back electron transfer step is invariably thermodynamically feasible, back electron transfer and radical recombination decrease the potential concentration of free radical active centers. Furthermore, an inefficient radical is often produced simultaneously in this electron transfer/proton transfer reaction step because the dye-based radical is not active for initiation but is able to terminate a growing polymer chain [3]. These cumulative effects significantly limit polymerization kinetics of two-component initiator systems and tend to make visible light polymerization less attractive, than UV photocuring in applications where reaction rate is a primarily consideration [3].

Some dyes absorbing in the visible region have been reported to be photoreduced in the presence of amines [1]. These compounds belong to the families of xanthenes, fluorones, acridines, phenazines, thiazenes, and so on. For example, methylene blue is well known to react from its triplet state with amine to initiate the photopolymerization of acrylates. The photoreduction is accompanied with an important photobleaching of the dye, rendering the photopolymerization of thick samples under visible light. The photobleaching is not so important in the case of xanthenes or fluorones, although the polymerization can be very efficient. Very good efficiencies were reported using thionine, rose bengal, eosin Y, erythrosin, riboflavin, polymethine dyes as photosensitizers, and co-initiators, such as amines, sulfinates, carboxylates, organoborate salts [1]. In the case of amine as co-initiator, the reaction involves a hydrogen abstraction from a amine to semireduced form of a dye. But in the case of organoborate salts acting as a co-initiator, the reaction involves an electron transfer from borate anion to polymethine dye in its excited singlet state. These systems are able to shift the spectral sensitivity of photopolymers up to the red region of the visible spectrum. However, dye/co-initiator systems were not developed significantly in the industry. Very often, dark reactions take place that lead to poor shelf life of the formulation, an effect that was detrimental to their industrial use for a long time. In addition, the conversion of the monomer to polymer was generally limited. Indeed, for most of the industrial applications, conversion of more than 60% have to be reached, a goal that is difficult to achieve with conventional dye/co-initiator photoinitiating systems (PIS) [1].

In the last decade, three-component photoinitiating systems have emerged as an attractive alternative for visible light polymerization based on numerous demonstrations that the kinetic effectiveness of a two-component electron/proton transfer initiator system can be improved by the addition of a third component.

Like the two-component system, the three-component (PIS) include a light absorbing moiety, an electron donor (ED) and an electron acceptor (EA). In such systems, the third component is supposed to scavenge the chain-terminating radicals that are generated by the photoreaction between other two components or produce the additional initiating radicals. This process leads to an increase of the free radical polymerization rate. Therefore, certain additives improve the polymerization efficiency, leading to the development of the so-called three-component photoinitiating systems [3-12]. Three-component initiator systems have consistently been found to be faster, more efficient, and more sensitive than their two-component counterparts [3]. The mechanism involved is rather complex and is based on

chemical secondary reactions. It was reported, that different radical intermediates generated during the irradiation and in the subsequent polymerization reaction react with the additive to give new reactive radicals.

The development of new photoinitiating systems remains an interesting challenge. In specific areas, for example in graphic arts or in conventional clear coat and overprint varnish applications, the photoinitiators must exhibit particular properties, among them a high photochemical reactivity leading to high curing speeds.

Kim et al. [4], used the thermodynamic feasibility and kinetic considerations to study photopolymerization initiated with rose bengal or fluorescein as photosensitizer to investigate the key factors involved with visible-light activated free radical polymerization involving three-component photoinitiating systems. Many of the same photosensitizers used for two-component electron-transfer initiating systems may also be used in three-component ones [3]. Examples include coumarin dyes, xanthene dyes, acridine dyes, thiazole dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrins, aromatic polycyclic hydrocarbons, *p*-substituted aminostyryl ketone compounds, aminotriaryl methanes, merocyanines, squarylium dyes, and pyridinium dyes [3, 13-17].

A number of kinetic mechanisms have been suggested to explain the enhanced kinetics and sensitivity for three-component initiator systems.

There are few mechanisms of free radicals generation in dyeing three-component photoinitiating systems:

- Photooxidizable series mechanism,
- Photoreducible series mechanism (dye/amine/iodonium salt),
- Parallel series mechanism.

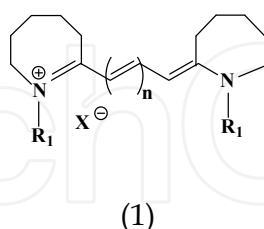
The photoreducible series mechanism is the well-known representative kinetic mechanism for three-component photoinitiating systems. Until now, photoreducible series mechanism for (PIS) containing camphoquinone or methylene blue dye have been reported as a representative kinetic mechanism. However, alternative kinetic mechanisms must be considered since a variety of dyes used in three-component initiator systems impose different thermodynamic and kinetic constraints. For this study, we used three-component photoinitiator systems containing thiocarbocyanine dye (Cy). This dye has excellent attributes that make it attractive for these mechanistic studies. Because this photosensitizer has both reduction potential as well as oxidation potential, the photo-excited dye allows thermodynamically feasible direct interactions with an electron donor as well as with an electron acceptor simultaneously.

In this chapter, the efficiency of the three-component photoinitiating system based on thiocarbocyanine dye to induce visible light polymerization of triacrylate monomer will be described. The ability of both photoinitiating systems formed by Cy/*n*-butyltriphenylborate/second co-initiator and Cy/1,3,5-triazine derivative/heteroaromatic thiol to initiate polymerization under visible light will be reported.

To understand their efficiency in terms of monomer conversion, the photochemistry of these systems was investigated by means of steady state and time resolved spectroscopy.

2.1 Polymethine dyes as sensitizer in photoinitiating system

Polymethine dyes were first synthesized in 1856 by Greville Williams. Classical polymethine dyes are cationic molecules in which two terminal nitrogen heterocyclic subunits are linked by a polymethine bridge as shown by the general structure 1.



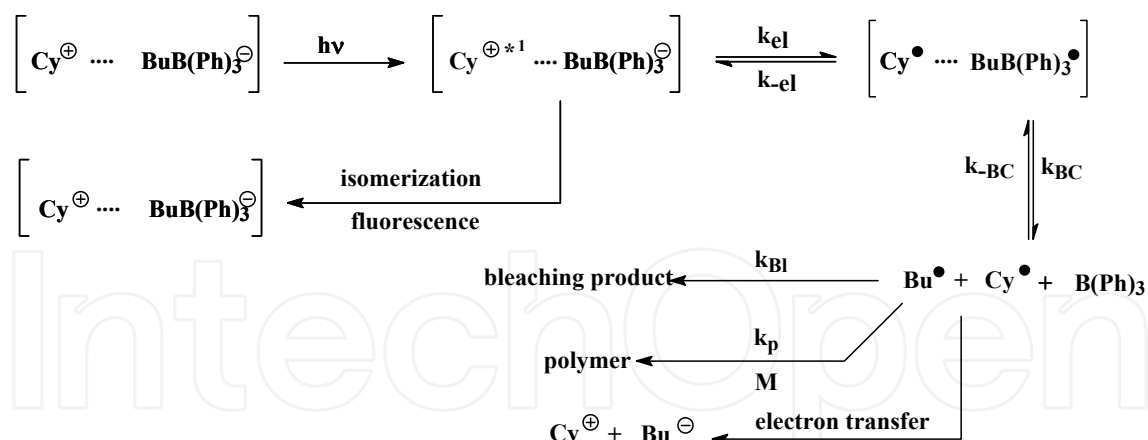
In the ensuing 150+ years, thousands more cyanines have been synthesized due to demand based on diverse applications of these versatile dyes [18]. As it is known, these dyes present intense absorption and fluorescence bands in the green-red visible region of the electromagnetic spectrum and exhibit high fluorescence quantum yields. The best known application of these dyes is in the laser field, where they showed higher laser efficiency than rhodamine dyes. Besides their use as laser dyes, polymethines have also shown very good performance as sensitizing dyes in free radical photopolymerization, with the idea of using the photopolymers in industrial applications, such as photoimaging, holography, computer-to-plate, and so on. They have been used as sensitizer dye with organoborate or 1,3,5-triazine derivatives as a radical generating reagent. The ion pair composed of cyanine dye cation and an alkyltriarylborate anion was first described by G. B. Schuster et al. [19, 20].

The work of Schuster and co-workers [19, 20] on the photochemistry of cyanine borates led to the preparation of the color-tunable, operating in the visible region commercial photoinitiators [21]. This research group discovered that, photolysis of 1,4-dicyanonaphthalene containing an alkyltriphenylborate leads to one electron oxidation of alkyltriphenylborate salts yielding an alkyltriphenylboranyl radical that undergoes carbon-boron bond cleavage and the formation of free radicals [22].

The laser flash photolysis data allows one to describe the mechanism of the polymerization initiation process. The initiation step of the reaction involves alkyl radical formation as a result of photoinduced electron transfer from borate anion to the excited singlet state of cyanine dye, followed by the rapid cleavage of the carbon-boron bond of the boranyl radical (see Scheme 1).

Scheme 1 summarizes possible primary and secondary processes, which may occur during the free radical photoinitiated polymerization with the use of cyanine borate initiators; where k_{BC} denotes the rate of the carbon-boron bond cleavage, the reverse step is designated as k_{-BC} , and k_{bl} is the rate constant of the free radicals cross-coupling step yielding bleached dye.

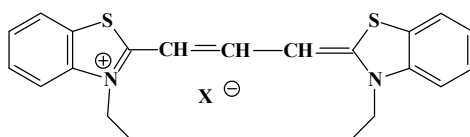
As it was mentioned above this chapter reports the use of polymethine dye as a part of a three-component photoinitiating system for radical polymerization in the visible region of the spectrum, together with an alkyltriphenylborate salt and different additives as co-initiators. In the study, we examined the ability of the systems formed by Cy/borate salt,



Scheme 1. Primary and secondary processes occurring during the free radical photoinitiated polymerization with the use of cyanine borate photoinitiators.

Cy/borate salt/different derivatives, and Cy/1,3,5-triazine/heteroaromatic tiol to initiate polymerization under visible light (Scheme 2).

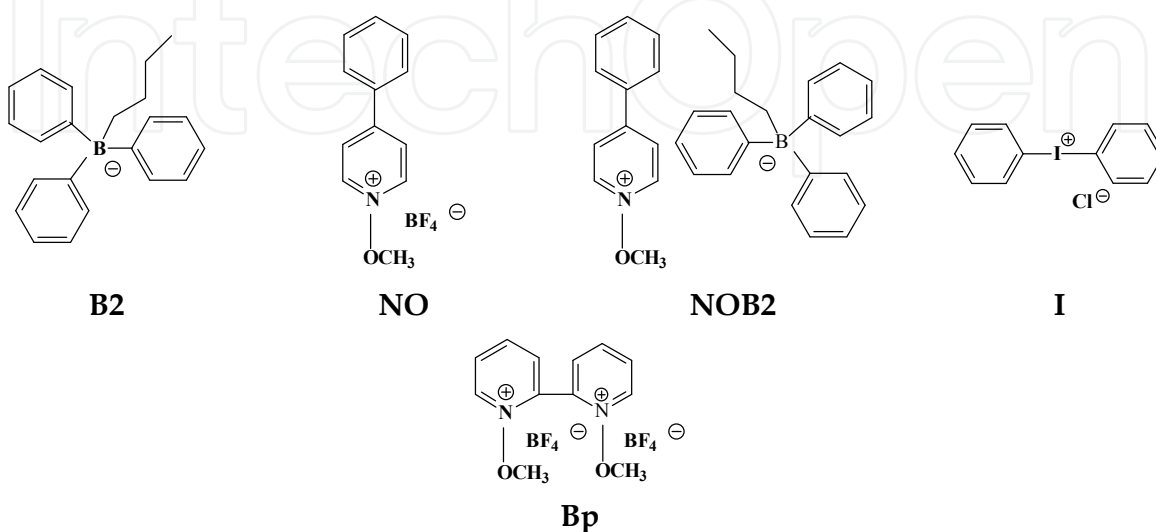
Photosensitizer



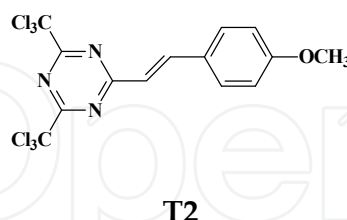
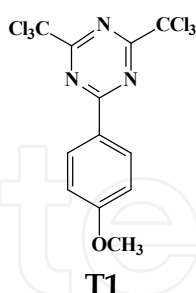
Cy

Co-initiators:

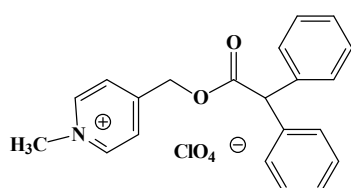
Onium salts



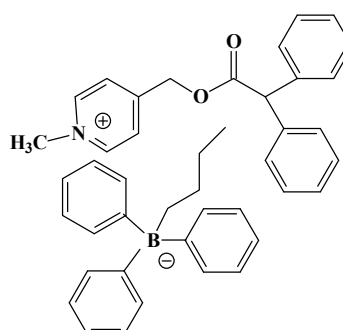
1,3,5- Triazine derivatives



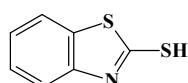
Other co-initiators



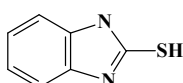
E1B



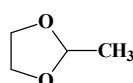
E1BB2



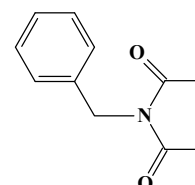
MS



MI



K1



EPM

Scheme 2. Compounds used in this study

2.1.1 Kinetic key factors for visible-light activated free radical polymerizations

The efficiency of different combinations of polymethine dye and additives as (PIS) for the polymerization of triacrylate, was evaluated using the differential scanning calorimetry (DSC), under isothermal conditions at room temperature, using a photo-DSC apparatus constructed on the basis of the TA Instruments DSC 2010 Differential Scanning Calorimeter.

The different formulations, in molecular ratio of each component, for dye studied are detailed in Table 1. No significant photopolymerization was detected in the absence of the dye. Figures 1-4 show the corresponding kinetic observed for N,N'-diethylthiacarbocyanine dye, and Table 1 shows the final conversions, polymerization rates and inhibition times for all runs after 5 min of irradiation.

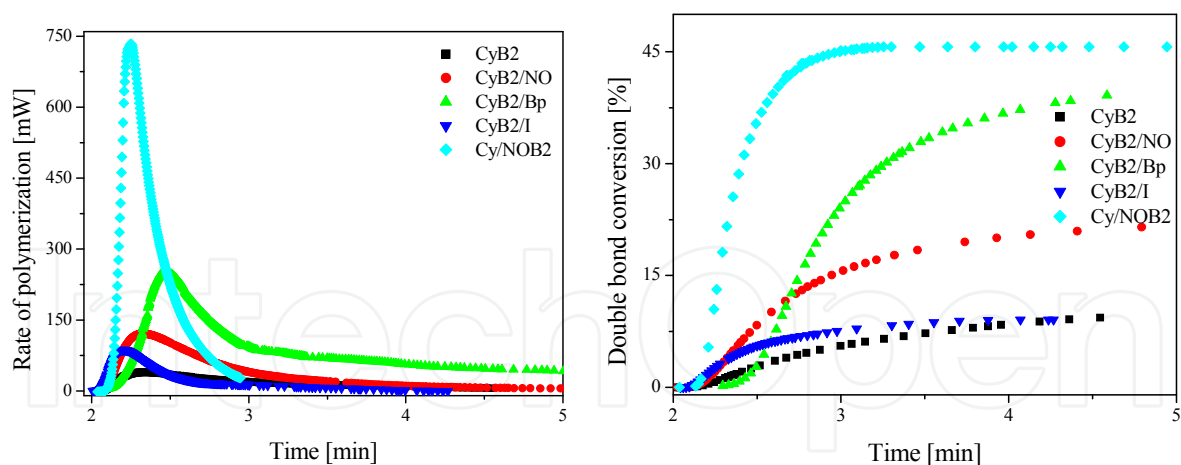


Fig. 1. Comparative study of the photopolymerization of TMPTA/MP mixture (9:1) (2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate/1-methyl-2-pyrrolidinone) using different photoinitiating systems based on the polymethine dye and onium salts.

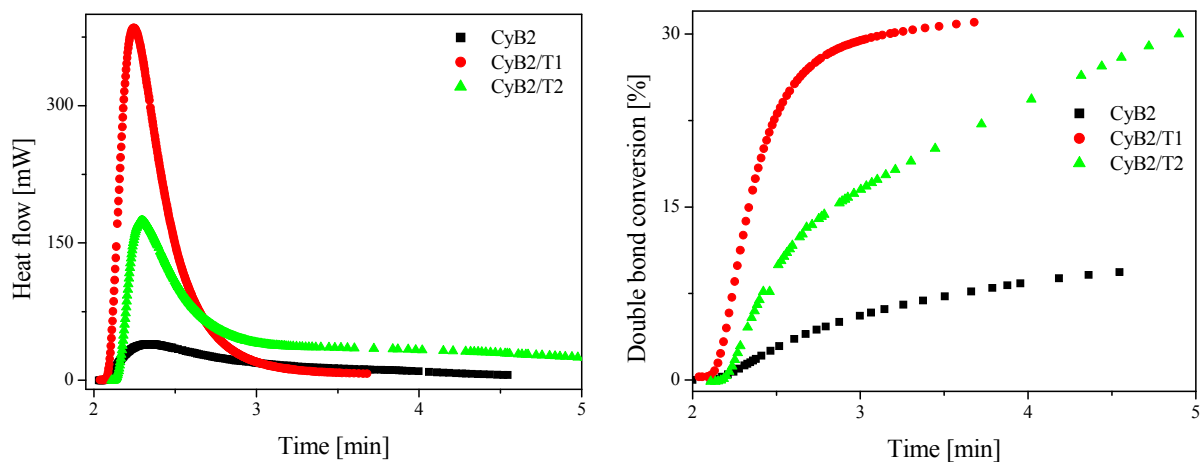


Fig. 2. Comparative study of the photopolymerization of TMPTA/MP mixture (9:1) using different photoinitiating systems based on the polymethine dye and 1,3,5-triazine derivatives.

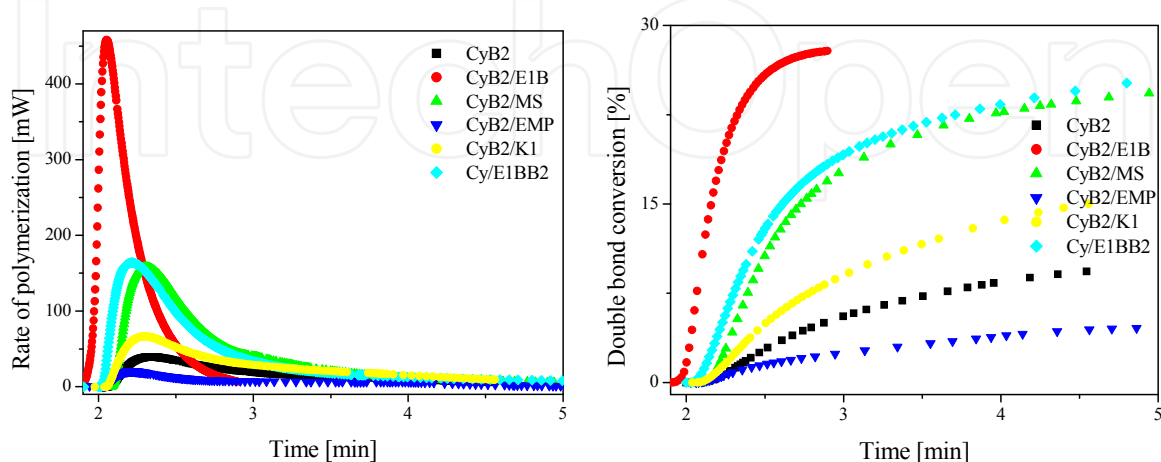


Fig. 3. Comparative study of the photopolymerization of TMPTA/MP mixture (9:1) using different photoinitiating systems based on the polymethine dye and other additives.

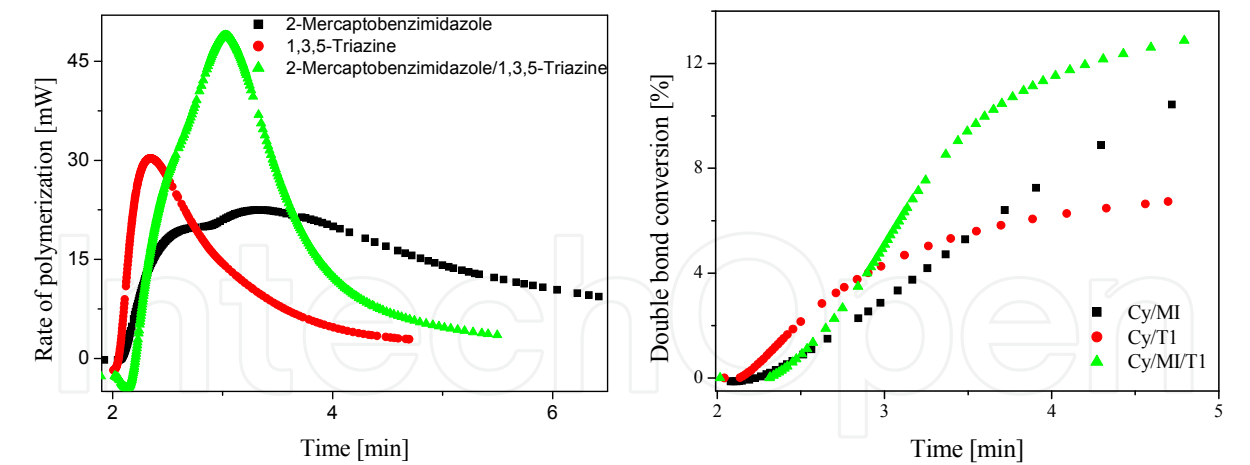


Fig. 4. Comparative study of the photopolymerization of TMPTA/MP mixture (9:1) using photoinitiating systems based on the polymethine dye, heteroaromatic thiol and 1,3,5-triazine derivative.

Co-initiator	Dye [M]	B2 [M]	Other Additives [M]	Molar ratio B2/other additives	Inhibition time [s]	R _p [μmol/s]	Final conversion (%)
B2	5 × 10 ⁻³	5 × 10 ⁻³	0	0	6.5	0.502	10
NO	5 × 10 ⁻³	5 × 10 ⁻³	5 × 10 ⁻⁴	10	1	1.54	22
NOB2	5 × 10 ⁻³	1 × 10 ⁻²	1 × 10 ⁻²	1	0	9.38	46
Bp	5 × 10 ⁻³	5 × 10 ⁻³	5 × 10 ⁻⁴	10	0	3.20	39
I	5 × 10 ⁻³	5 × 10 ⁻³	3 × 10 ⁻³	1.67	0.8	1.11	10
T1	5 × 10 ⁻³	5 × 10 ⁻³	5 × 10 ⁻²	0.1	0	4.92	31
T2	5 × 10 ⁻³	5 × 10 ⁻³	1 × 10 ⁻²	0.5	1.4	2.24	30
E1B	5 × 10 ⁻³	5 × 10 ⁻³	1 × 10 ⁻²	0.5	1	5.86	28
E1BB2	5 × 10 ⁻³	1 × 10 ⁻²	1 × 10 ⁻²	1	1.5	2.11	25
MS	5 × 10 ⁻³	5 × 10 ⁻³	5 × 10 ⁻²	0.1	9	2.02	24
K1	5 × 10 ⁻³	5 × 10 ⁻³	1 × 10 ⁻¹	5	9	0.84	15
EPM	5 × 10 ⁻³	5 × 10 ⁻³	5 × 10 ⁻³	1	0	0.261	4
T1	5 × 10 ⁻³	0	5 × 10 ⁻²	0	3	0.388	7
MS	5 × 10 ⁻³	0	5 × 10 ⁻²	0	8	0.29	10.7
T1 + MS	5 × 10 ⁻³	0	5 × 10 ⁻²	0	9	0.63	13

Table 1. Molar composition of the samples, corresponding B2/other additive molar ratio, final conversion obtained after 5 min of irradiation, maximum polymerization rate R_p and inhibition time.

It has been reported that to enhance the kinetics of a visible-light activated initiation process, it is important to: (1) retard the back electron transfer and recombination reactions and (2) use the secondary reaction step to consume the nonproductive dye-based radical and thereby regenerate the original photosensitizer (dye) [3]. Figures 1-4 provide a comparison of the visible-light activated free radical polymerizations initiated by two-component

initiator systems (CyB2, Cy/MS and Cy/T) with the corresponding three-component PIS. These examples clearly show that the three-component initiator systems produce the highest rates and final conversion as predicted.

Figures 1-3 demonstrate that the photoreducible series mechanism (Cy/B2/second co-initiator) produces the highest conversion and the fastest rates of polymerization. In such photoinitiating system, since Cy^* reacts directly with borate salt (ED), this kinetic pathway can prevent photon energy wasting steps such as back electron transfer [23]. But it is well known, that in a case when stable alkyl radical (initiating radical) is formed as a result of carbon-boron bond cleavage in boranyl radical (product of primary photochemical reaction) the back electron transfer process does not occur. Therefore, in the EA-based secondary reaction step, the dye-based radical can be consumed and photosensitizer (Cy) can be regenerated.

The parallel-series mechanism (Figure 4 (Cy/thiol/triazine)) showed intermediate reaction kinetics because this kinetic pathway simultaneously involves both the photoreducible and photooxidizable mechanisms in the primary photochemical reaction. These results are also supported by Table 1 which illustrates that the photoreducible series mechanisms (Cy/B2/second co-initiator) produced the highest reaction kinetics and photo-sensitivity then the alternative kinetic pathway.

The comparison of Cy/MS and Cy/T systems also illustrates the importance of preventing of back electron transfer reaction. Grotzinger and coworkers reported that when 1,3,5-triazine derivative accepts an electron, it produce 1,3,5-triazine radical anion which fragments to produce an active, initiating 1,3,5-triazynyl radical and a chloride anion [12]. Thus, triazine (T) accepts an electron from Cy^* , and the product obtained undergoes a rapid unimolecular fragmentation reaction that limits back electron transfer. Because of the reduced back electron transfer between the Cy^* and T, Cy/T system leads to the generation of higher concentrations of active centers than Cy/MS system (however, complete bleaching of the dye in the photochemical reactions results in the low conversion in the two-component systems and the conversion reaches < 10 %).

On the other hand, the excited dye wastes photon energy in an electron transfer process between dye and co-initiator because of the back electron transfer competes with separation of gemine radical pair. It has generally been reported than only 10% of the absorbed light energy may be used for photo-induced electron transfer in the bimolecular organic electron transfer reaction [23]. Hence the Cy/MS initiator system only reached ~ 10 % of final conversion. The Cy/MS/T three-component initiator system produced enhanced conversion about 13 %.

As expected, this behavior is strongly dependent on the composition of the photoinitiating system. The photoinitiating ability of the (PIS) under study depends mostly on the nature of the co-initiator. The use of diphenyliodide or N-phenylethylmaleimide in the CyB2 photoinitiating system leads to poor and slow conversion of the monomer.

On the other hand, the Cy/B2/second co-initiator photoinitiating systems produced dramatically enhanced conversion ranging from 15 to 46 % because of effective retardation of the recombination reaction step and consumption of the dye-based radical to regenerate

of the original photosensitizer (dye) in the secondary reaction step. The enhanced conversion relative to the two-component initiator system also arises from production of two radicals: an active initiating butyl radical and an active alkoxy, triazinyl, picolinium ester, thyl or phenyl radical. These results are supported by Table 1, which illustrates the reaction rate as well as the final conversion of monomer with photoinitiating systems under study. The data clearly indicate that the three-component initiator system (Cy/B2/second co-initiator) is the most effective in overall radical active centre production as well as the rate of initiation from the onset of polymerization.

On the contrary, the system Cy/T1 exhibits a good reactivity with both higher rate of polymerization and final conversion. However, the best results were obtained for the three-component system CyB2/T1 and CyB2/T2. The addition of 1,3,5-triazine derivative to the CyB2 system increased the polymerization rate as well as the final conversion of the triacrylate compared with the two-component systems.

Finally, all these kinetic results provide very useful information in terms of the selection criteria for each component of photoinitiating system. Because once photosensitizer with both reduction and oxidation potentials is selected, the kinetic pathway is controlled by selection of an electron donor or an electron acceptor based on the thermodynamic feasibility, thereby influencing the conversion and rate of polymerization kinetic data.

As before, these kinetic differences of two kinetic pathways are ascribed to differences in the efficiency of retarding back electron transfer as well as regenerating photosensitizer through the secondary reaction step.

2.1.2 Excited state reactivity

Because polymethine dye tested exhibits medium fluorescence quantum yield (Table 2), the fluorescence quenching by co-initiators was first studied.

	Cy
λ_{\max} [nm]	556
ϵ_{\max} [mol ⁻¹ dm ³ cm ⁻¹]	113 000
E_s [kJ/mol]	203
ϕ_f	0.05
τ_0 [ps]	139, 392
E_{ox} [V/SCE]	1.0
E_{red} [V/SCE]	-1.34

Maxiumum absorption wavelength λ_{\max} , molar extinction coefficient ϵ_{\max} , singlet state energy E_s , fluorescence quantum yield ϕ_f , singlet state lifetime τ_0 , half-wave oxidation and reduction potentials E_{ox} and E_{red} , respectively.

Table 2. Photophysical and Electrochemical Properties of Polymethine Dye

The quenching rate constants k_q of the singlet excited state by co-initiators tested were determined in ethyl acetate:1-methyl-2-pyrrolidinone mixture (4:1) (Table 3), and showing values close to the diffusion rate constant ($k_q = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$).

	k_q [M ⁻¹ s ⁻¹]	ΔG_{el} [kJ/mol]
B2	9.5×10 ¹¹	-1.93
NO	6.15×10 ¹⁰	-64.64
Bp	1.96×10 ¹⁰	-67.06
T1	3.6×10 ¹⁰	-27.02
E1B	7.42×10 ⁹	-26.44
Thiol	2.78×10 ¹⁰	-12.54

Table 3. Fluorescence Quenching Data k_q and Gibbs Free Energy ΔG_{el} Changes for Thiocarbocyanine Dye with Co-initiators Tested.

2.1.3 Thermodynamics of photo-induced electron transfer reaction

Before investigating the kinetic mechanisms for efficient design of photoinitiator systems, thermodynamic feasibility for electron transfer reactions must be verified. The Rehm-Weller equation was used to predict the thermodynamic feasibility for electron transfer reaction as shown below [24]. In this study, N,N'-diethylthiocarbocyanine dye was selected as photosensitizer because allows thermodynamic feasibility for direct simultaneous interaction with an electron donor as well as with an electron acceptor previously described. B2 or MS are used as electron donor (ED) and NO, Bp, I, T1, T2, E1B, K or EMP is used as (EA).

Because of the redox properties of the dye (Table 2) and the co-initiators, the mechanism for the quenching of sensitizer's excited state likely involves an electron transfer process. The values of the Gibbs free energy change for the photoinduced electron transfer ΔG_{et} on excited state is given by the Rehm Weller equation (2) [24].

$$\Delta G_{el} = E_{ox} - E_{red} - E^* + C \tag{2}$$

where:

E_{ox} and E_{red} are the half-wave oxidation and reduction potentials for the acceptor (Cy; $E_{red} = -1.34$ V/SCE) and the donor (B2; $E_{ox} = 1.16$ V/SCE), respectively, and E^* is the energy of the excited state. The coulombic term C is usually neglected in polar solvents.

The ΔG_{et} values are very useful for determining the potential kinetic pathway. As can be seen in Table 3, the calculated values for the intermolecular singlet electron transfer reactions are favorable, indicating that the dye can be reduced in the presence of the electron donors, such as: B2 or heteroaromatic thiol or oxidized with 1,3,5-triazine derivative.

From these results, one can conclude that the carbocyanine dye reacts with the co-initiators mainly through the quenching of the first excited singlet state. The reaction proceeds through the formation of a geminate radical pair, which can recombine through a back electron transfer process or separate into free radicals. The latter process explains the formation of the dye-based radical when alkyltriphenylborate salt is used as a quencher, or the radical cation of the dye when 1,3,5-triazine is used instead.

These results can lead to two initiator systems with two corresponding thermodynamically feasible kinetic pathways, which are (i) photoreducible series mechanism: Cy/B2/onium

salt, Cy/B2/N-methylpicolinium ester, Cy/B2/acetal, Cy/B2/thiol, Cy/B2/triazine, (ii) parallel-series mechanism: Cy/thiol/triazine.

2.2 Mechanism of free radicals formation

From the transient absorption spectra obtained during laser flash photolysis, the ground state photobleaching of sensitizer under addition of borate salt, heteroaromatic thiol or 1,3,5-triazine derivative can be observed at 420 nm. Laser flash photolysis experiments were carried out in acetonitrile solution, exciting at 355 nm. Accordingly, it can be seen in Scheme 3 that the depletion increases with increasing concentration of borate salt, as a consequence of the formation of the dye-based radical and boranyl radical.

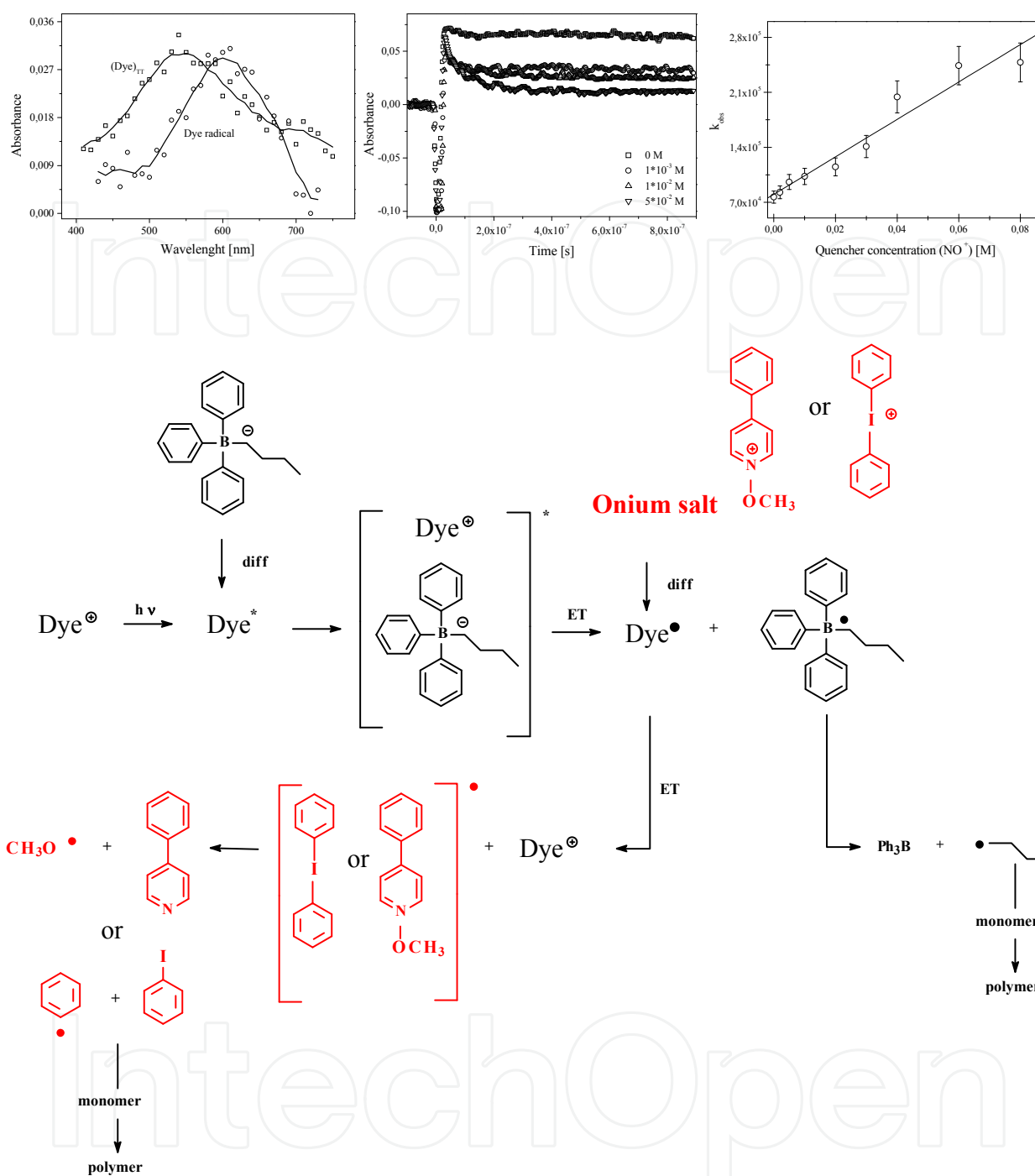
2.2.1 Photoreducible series mechanisms

As illustrated in Scheme 3, the kinetic pathway involves electron transfer and carbon-boron bond cleavage from borate salt to the photo-excited dye (Dye*) and produces an active initiating radical (such as butyl radical) as the primary photochemical reaction. The second onium salt (N-alkoxypyridinium or diphenyliodonium salt), as an electron acceptor, consumes an inactive radical and produces another active radical (alkoxy or phenyl), thereby regenerating the original dye in the secondary reaction step. The regenerated (PS) may re-enter the primary photochemical reaction. This kinetic pathway is designed as a photoreducible series mechanism. It is the well-known representative kinetic mechanism for three-component initiators. In this mechanism, the second co-initiator increases the photopolymerization kinetics in two ways: (1) it consumes an inactive dye-based radical (Dye*) and produces an active initiating radical, thereby regenerating the original (PS) (dye), and (2) it reduces the recombination reaction of dye-based radical and boranyl radical.

Unfortunately, the latter species can not be observed under our experimental conditions. The initiating radicals in this case could come mainly from the boranyl radical, which undergoes rapid and irreversible fragmentation as a result of carbon-boron bond cleavage. It should be noted that this reaction will compete with the back electron transfer from dye-based radical (Dye*) to boranyl radical within the gemine radical pair; as well with the recombination of the both radicals.

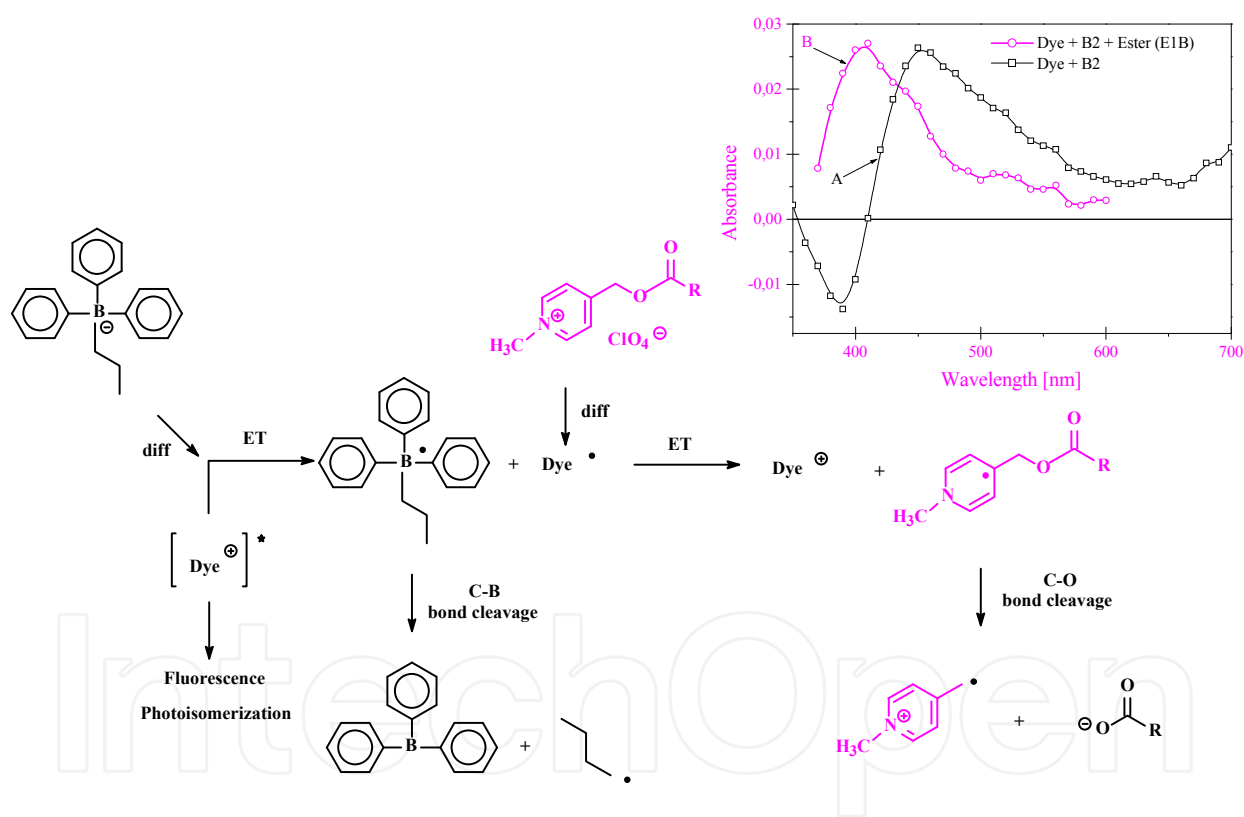
As stated above, when carbocyanine dye is used with borate salt as co-initiator the excited singlet state is quenched with the rate close to the diffusion rate constant, observing an increase in the signal of dye-based radical: as borate salt acts as an electron donor, the electron transfer reaction of sensitizer excited state and B2 leads to (Dye*) and (B2*) radicals (Schemes 1 and 3). Monitoring the dye radical formation at 420 nm leads to the observation of a increasing absorbance of the dye-based radical, in line with the results obtained for heteroaromatic thiol. This demonstrates that the reaction between carbocyanine dye-excited state and borate salt behaves similar to that of thiol. From all these results, the low conversion observed in the photopolymerization for Cy/MS photoinitiating system could be explained by a low quantum yield of radical formation from MS*+.

Turning now to the study of the three-component system, transient absorption spectroscopy at 420 nm shows that the signal of (Dye*) formed from the interaction Dye/B2 (with excess of borate salt with respect to other additives) decreases under addition of N-alkoxypyridinium

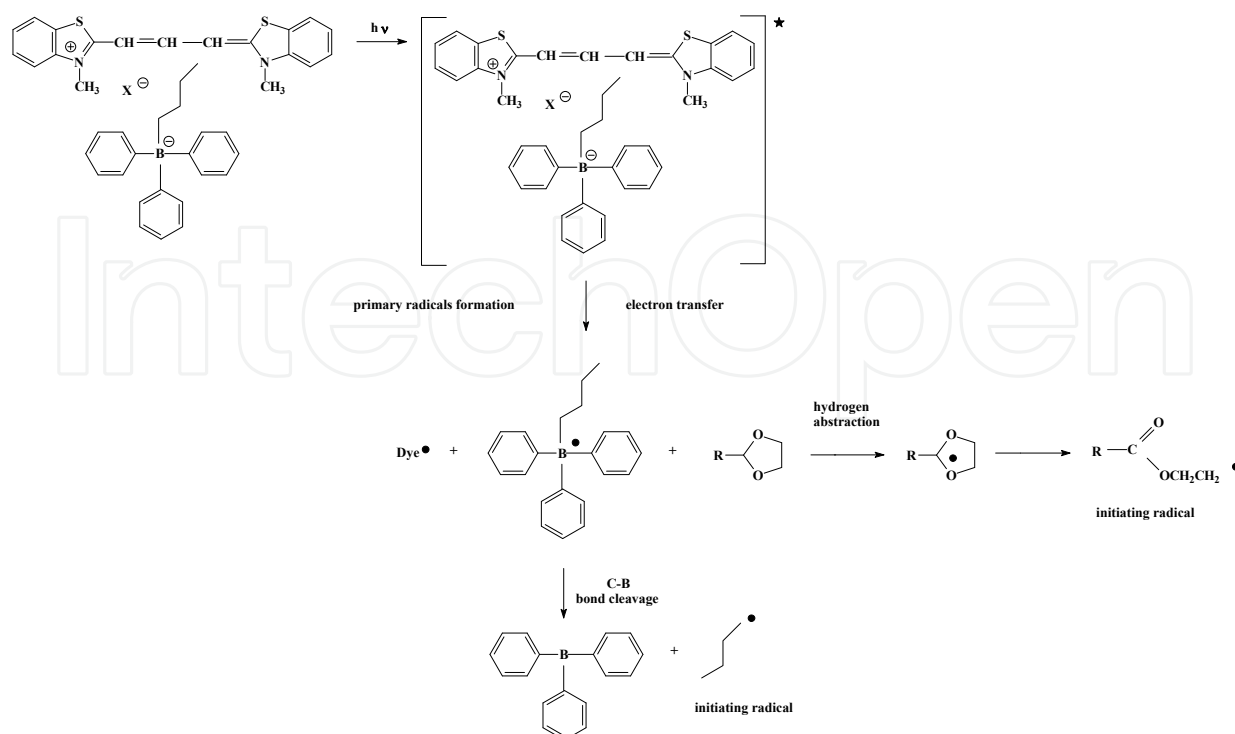


Scheme 3. Mechanism of the reactions occurring in three-component photoinitiating systems based on carbocyanine dye, borate salt and other onium salt. Inset: Left: Transient absorption spectra recorded 100 ns after laser flash (355 nm) for dye in MeCN (squares) and 500 ns after flash for dye in presence *n*-butyltriphenylborate salt presented dye-based radical formation. In the midst of: Kinetic traces for dye-based radical decay at 610 nm in the presence of various amount of N-methoxy-*p*-phenylpyridinium salt. The concentration of quencher is marked in Figure. Right: The Stern-Volmer plot of the fluorescence quenching of cyanine dye-based radical by onium salt.

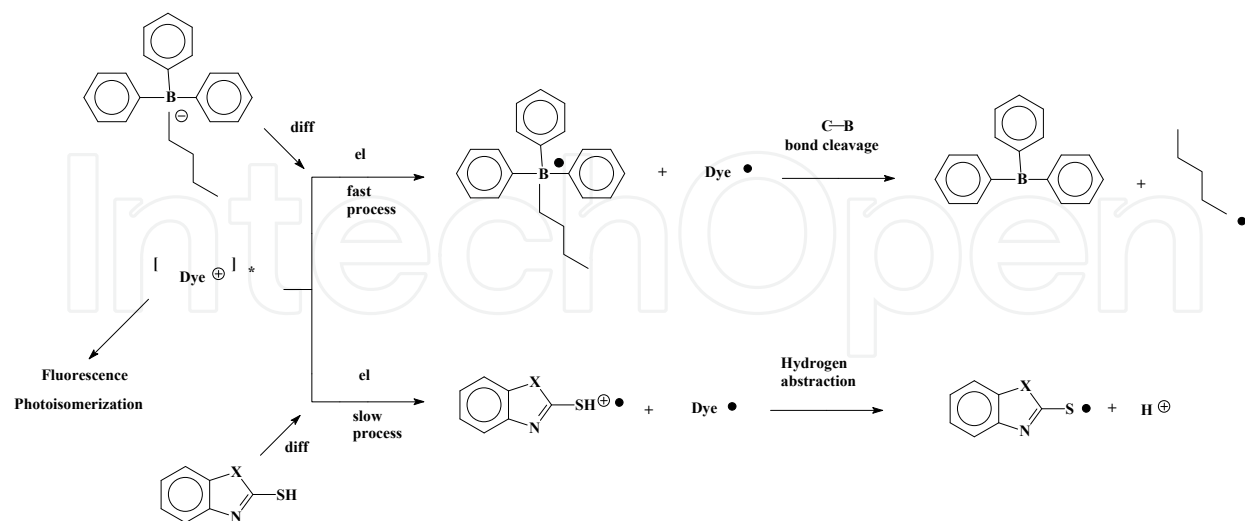
salt, iodonium salt, 1,3,5-triazine derivative, N-methylpicolinium ester or other co-initiators (Schemes 3-6). This indicates that onium salt, triazine or other co-initiators (with the exception of heteroaromatic thiol) react with the Dye-based radical (Dye^\bullet) formed from the interaction of dye excited state with borate salt (Schemes 1-6). At the same time, the photobleaching of sensitizer ground state is lowered when second co-initiator is added to the Dye/B2 system. This means that the reaction of second co-initiator with (Dye^\bullet) leads to recovery of the dye ground state. The reaction is expected to proceed through an electron transfer process from dye-based radical to second co-initiator. From the value of the oxidation potential of (Dye^\bullet) ($E_{\text{ox}} = 1.0 \text{ V/SCE}$), the free energy of the electron transfer reaction between (Dye^\bullet) and second co-initiator is estimated to be in a range from -0.13 eV to 0.08 eV (e.g. $-12.54 \text{ kJ}\cdot\text{mol}^{-1}$ to $7.72 \text{ kJ}\cdot\text{mol}^{-1}$), this value would lead to a fast rate constant of interactions (Schemes 3-6).



Scheme 4. Mechanism of the reactions occurring in three-component photoinitiating systems based on carbocyanine dye, borate salt and N-methylpicolinium ester. Inset: Transient absorption spectra of: (A) cyanine dye in a presence of borate salt recorded 50 ns after laser puls (squares) presented dye-based radical formation and (B) for cyanine dye in presence of equimolar ratio of tetramethylammonium *n*-butyltriphenylborate and N-methylpicolinium perchlorate recorded 100 ns after laser puls (circles) presented N-methylpicolinium ester radical formation.



Scheme 5. Mechanism of the reactions occurring in three-component photoinitiating systems based on carbocyanine dye, borate salt and cyclic acetal.



Scheme 6. Mechanism of the reactions occurring in three-component photoinitiating systems based on carbocyanine dye, borate salt and heteroaromatic thiol.

Similarly, if the deactivation of the excited state of the dye proceed through a photoinduced electron transfer with heteroaromatic thiol or triazine (Schemes 6 and 7), the dye-based radical and (Dye^{•+}) are formed, respectively. In this case, one can assume that the oxidation and reduction potentials of dye are 1.0 V/SCE and -1.34 V/SCE, respectively. But the oxidation potential of thiol and reduction potential of triazine are in the range from 0.69 V/SCE to 0.90 V/SCE and -0.84 V/SCE, respectively. This leads to the calculation of ΔG_{el} values of -12.54 and -27.02 kJ/mol for thiol and triazine, respectively, showing that this reaction is exergonic and to be feasible.

In summary, when N,N'-diethylthiacarbocyanine dye is used as photosensitizer, the kinetic pathway is seen for the three-component initiator system composed of onium salt, picolinium ester, cyclic acetal, 1,3,5-triazine derivative or maleimide as second co-initiator enhances photopolymerization kinetics as previously described. As an example, the Cy/B2/NO photoinitiator system may be used to explain photoreducible series mechanism (Scheme 3). Because Cy/NO is not a thermodynamically feasible system, the primary photoinduced electron transfer reaction only proceeds between photo-excited dye and borate salt. Then, subsequent electron transfer involves the electron acceptor (NO) in a secondary reaction step.

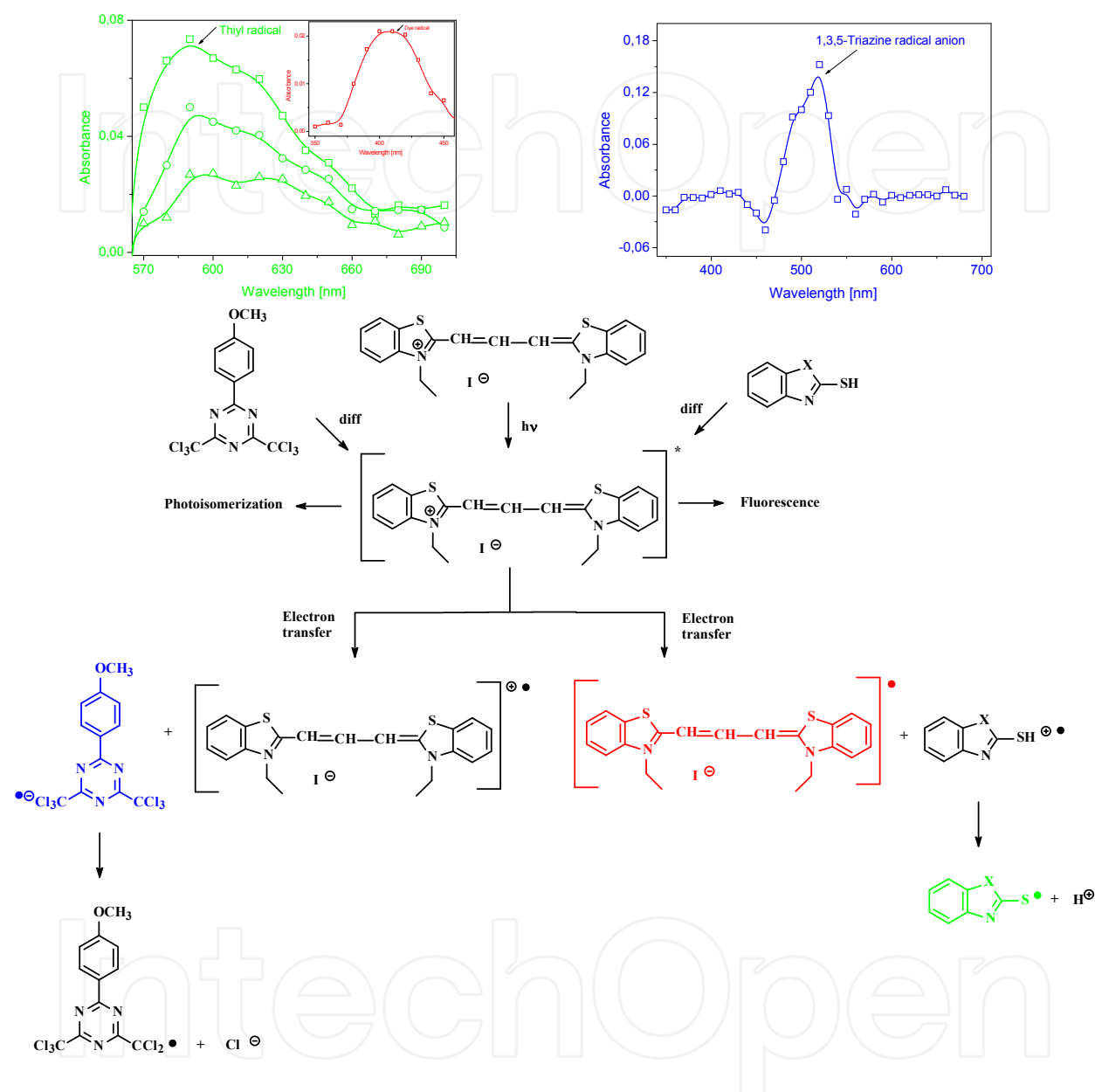
2.2.2 Parallel-series mechanism

On the other hand, under conditions where photosensitizer (dye) has both reduction and oxidation potentials, the photoexcited dye may act as both an electron donor and an electron acceptor, resulting in a parallel-series mechanism [3]. In this kinetic pathway, the electron transfer between the excited dye molecule and an electron donor competes with an electron transfer between the excited dye and an electron acceptor, as the primary photochemical reaction. The Cy/thiol/1,3,5-triazine photoinitiating system provides example of the combined parallel-series mechanism. Because Cy/MS initiator system is thermodynamically feasible (which did produce free radical active centers as a two-component initiator system; Figure 4) and Cy/T system is also thermodynamically feasible (free radical active centers were also produced), the Cy/MS/T initiator system may engage in the parallel-series mechanism.

For such system composed of polymethine dye/1,3,5-triazine derivative, the photobleaching of the ground state increases with increasing concentration of triazine. This indicates that the photochemical reaction between Dye-excited state and T yields to the formation of transient species. According to the electron transfer reaction, the radical anion (T^{•-}) is easily detected at 510 nm (Scheme 7).

It can be seen from Scheme 7 that (T^{•-}) is formed within the laser pulse, as a consequence of its formation mainly in the electron transfer process from the excited singlet state of dye to triazine. This leads to the formation of radical cation of dye and the radical anion of triazine. The latter species afterwards loses chloride anion to give the initiating radical (T^{•-}), as was demonstrated for other triazine derivatives in presence of rose bengal [12]. Interestingly, the recorded cyclic voltammogram for T1 in acetonitrile (Figure 5 right) exhibits an irreversible reduction wave at -0.84 V/SCE and a noticeable oxidation wave at 1.270 V/SCE indicating a cleavage process within the radical anion (T^{•-}). It is expected that the chloride anion is

expelled in a fast time scale, preventing the $(\text{Dye}^{\bullet+})/(\text{I}^{\bullet-})$ system to undergo a back electron transfer process.



Scheme 7. Mechanism of the reactions occurring in three-component photoinitiating systems based on carbocyanine dye, heteroaromatic thiol and 1,3,5-triazine derivative. Inset: Left: Transient absorption spectra of cyanine dye in a presence of 2-mercaptobenzothiazole (MS) recorded: 1 μs (squares), 4 μs (circles) and 10 μs (triangles) after laser pulse presented the thiyl and dye-based radicals formation. In: Transient absorption spectra of cyanine dye in a presence of 2-mercaptobenzothiazole (MS) recorded 100 ns after laser pulse (circles) in acetonitrile solution. Right: Transient absorption spectra of cyanine dye in a presence of 2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine (I) recorded 50 ns after laser pulse presented the 1,3,5-triazinyl radical formation.

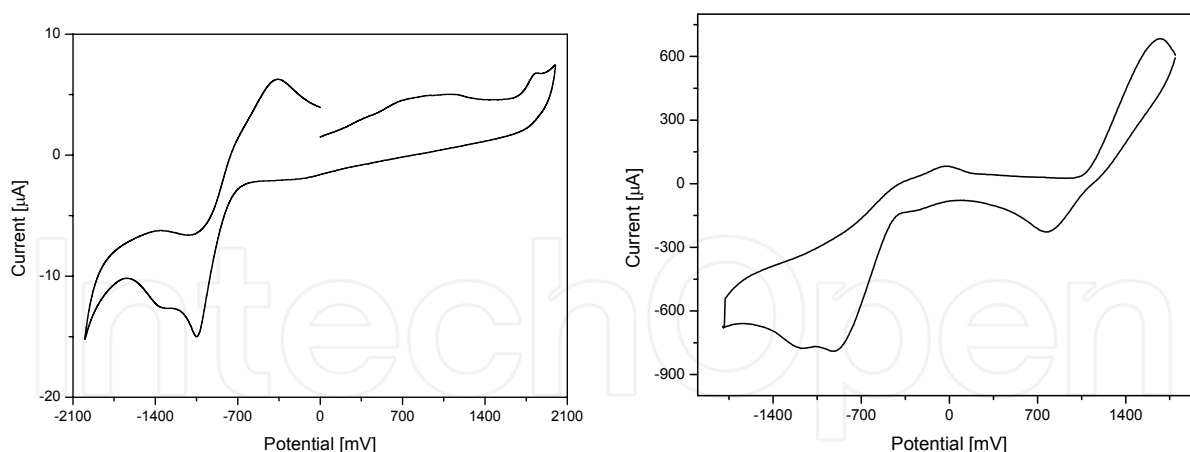


Fig. 5. Cyclic voltammograms of Dye (Cy) and 1,3,5-triazine derivative (T) in 0.1 M tetrabutylammonium perchlorate solution in dry acetonitrile as the supporting electrolyte.

At 510 nm (Scheme 7) it is possible to observe an increase of ($T^{\bullet-}$) signal, which clearly evidences the electron transfer process from sensitizer to triazine.

2.3 Photoinitiation efficiency

From all these experiments, it turns out that the photoreactions from the excited state of the carbocyanine dye are very efficient with both borate salt and second co-initiator. These photoreactions lead to the formation of initiating species, and therefore, to the conversion of monomer. A rough estimate of the diffusion rate constant can be given by equation 3:

$$k_d = \frac{8RT}{3\eta} \quad (3)$$

This leads to the value of $k_d = 1.84 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for the monomer used. Consequently, the quantum efficiency of dye excited state deactivation by a given quencher Q will depend on $k_d \times [Q]$ for most of the photoreactions reported in Table 3. Therefore, the relative efficiency of the corresponding photochemical processes will be mainly dependent on the concentration of the co-initiators.

In the case of the three-component photoinitiating systems, the highest concentration of additive makes the excited state quenched by second co-initiator, leading to initiating radical (after electron transfer process) and the dye-based radical (Dye^{\bullet}). This latter is able to react with second co-initiator leading to the recovery of the dye ground state and additional initiating species (Schemes 3-7). The fact that three-component photoinitiating systems have higher efficiencies than two-component ones is in good agreement with the expected reaction of second co-initiator with the dye-based radical. The combination of co-initiators B2 and others have clearly a beneficial effect on the photopolymerization process.

By contrast, in a case of three-component photoinitiating system composed of dye/thiol/triazine, the deactivation of the (Cy) excited state will be mainly governed by the photoreaction with both thiol and 1,3,5-triazine derivative (Scheme 7). This leads to the formation of initiating radicals and radical cation ($\text{Dye}^{\bullet+}$).

It was shown that three-component photoinitiating systems acting via photo-reducible series mechanism produce the highest rates of polymerization and final conversion of monomer (Figure 6).

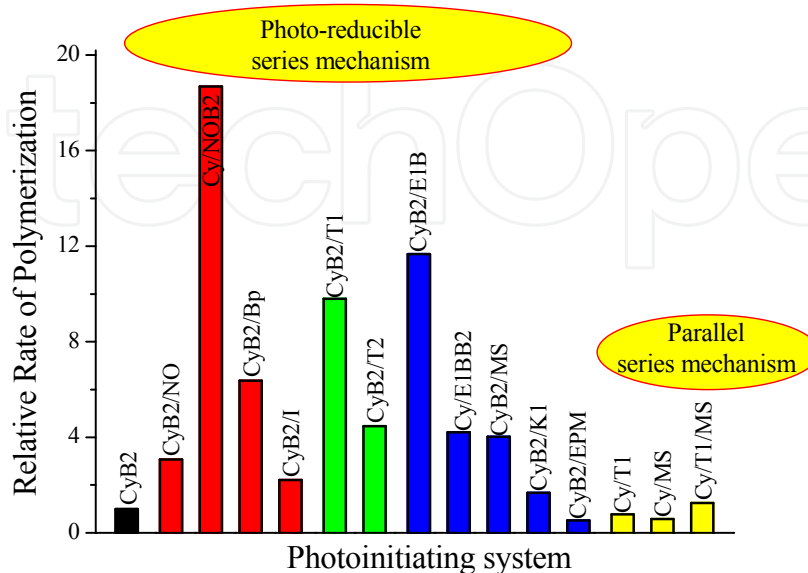


Fig. 6. The comparison of the photoinitiating ability of the dyeing photoinitiating systems acting via photoreducible series mechanism and parallel series mechanism.

3. Conclusions

In this chapter, we have characterized two different kinetic mechanisms using thermodynamic feasibility and key kinetic factors with three-component visible light photoinitiating systems containing thiacyanocyanine dye as a photosensitizer. We used the Rehm-Weller equation to verify the thermodynamic feasibility for the photoinduced electron transfer reaction. Based on this, we have suggested two different kinetic mechanisms, which are (i) photoreducible series mechanism (Cy/B2/second co-initiator) and (ii) parallel series mechanism (Cy/thiol/triazine). In addition, based on experimental kinetic data, we have evaluated two kinetic pathways. The photo-DSC kinetic experiments revealed that the photoreducible series mechanism produced the highest rates of polymerization and final conversion of monomer values. It was found, that three-component PIS showed the best performance. Laser spectroscopy studies allowed the understanding the processes that may explain the behavior observed in terms of photopolymerization. The sensitizer reacts mainly through a singlet electron transfer mechanism from the borate salt or heteroaromatic thiol to the dye and from the dye to the triazine derivative. Beneficial side-reactions were shown to limit the photobleaching of the dye, resulting in higher final monomer conversion.

Although, these two kinetic pathways presented here can not govern the detailed interactions in all initiator mechanisms, this approach will provide useful information for selection criteria for each component, as well as provide a straightforward manner for classifying the photopolymerization process.

4. Acknowledgment

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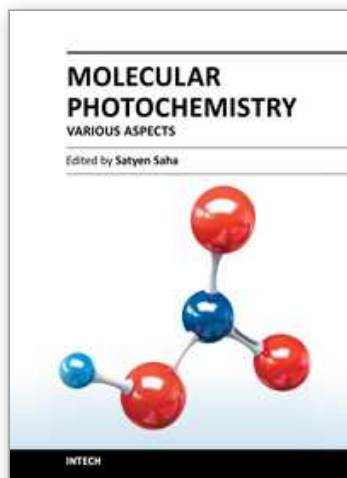
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There have been various comprehensive and stand-alone text books on the introduction to Molecular Photochemistry which provide crystal clear concepts on fundamental issues. This book entitled "Molecular Photochemistry - Various Aspects" presents various advanced topics that inherently utilizes those core concepts/techniques to various advanced fields of photochemistry and are generally not available. The purpose of publication of this book is actually an effort to bring many such important topics clubbed together. The goal of this book is to familiarize both research scholars and post graduate students with recent advancement in various fields related to Photochemistry. The book is broadly divided in five parts: the photochemistry I) in solution, II) of metal oxides, III) in biology, IV) the computational aspects and V) applications. Each part provides unique aspect of photochemistry. These exciting chapters clearly indicate that the future of photochemistry like in any other burgeoning field is more exciting than the past.

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