

# **Hemicyanine dyes based on the benzimidazole ring systems as effective photoinitiators in an argon laser induced TMPTA photopolymerization.**

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## **INTRODUCTION**

Radical polymerization is one of the most widely used processes for the commercial production of high-molecular weight polymers. The main factors responsible for the preeminent position of radical polymerization are (i) the ability to polymerize a wide variety of monomers, including (meth)acrylates, (meth)acrylamides, acrylonitrile, styrenes, dienes, and other vinyl monomers; (ii) tolerance of unprotected functionality in monomer and solvent (e.g., OH, NR<sub>2</sub>, COOH, CONR<sub>2</sub>, and SO<sub>3</sub>H; polymerizations can be carried out in aqueous or protic media); (iii) compatibility with reaction conditions (e.g., bulk, solution, emulsion, mini-emulsion, and suspension); and (iv) it is simple to implement and inexpensive in relation to competitive technologies [1,2].

The traditional way to initiate polymerization through photochemistry has been by direct photolysis of a precursor that provides free radicals by direct bond scission. Panchromatic sensitization of acrylic polymerization has also been extensively used as a more flexible alternative, but it has its own limitations because it requires the presence of suitable dyes to serve as the primary absorber. In particular, it is necessary to choose the sensitizer (absorber) and co-initiator so that energy transfer occurs to the co-initiator. Photoinduced intermolecular electron transfer represents an alternative to such a restriction. This process involves the use of light to initiate electron transfer from a donor to an acceptor molecule [3].

In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiator molecules with more desirable properties, such as higher activity coupled with greater speed and a low migration rate to the surface of the cured coating in order to reduce loss of adhesion and to minimize toxicity where food contact is important. One area of importance in this regard is the development of photoinitiators having great spectral sensitivity to the visible region of the spectrum [4]. These initiators absorb visible light with a high speed and cause the same photopolymerization events described above to take place - namely a conversion of a highly functionalized liquid acrylate monomer to a solid polyacrylate. In practice, most monomers used in fast photoinitiated polymerization are acrylates or modified acrylates whose structure lends to rapid cross-linking. Some of the photoinitiators have been widely discussed in the literature for they are the backbone of the photopolymerization. In one such process, the initiators are photoredox pair initiators, which utilize single electron transfer to the excited state of the light absorbing dye from the partner acting as electron donors, starting the crucial first step in the initiation of the radical chain.

It is apparent that borate anions are especially beneficial electron transfer donors, and they have many important applications in free-radical polymerizations initiated by different electron accepting sensitizers.

The electron transfer photooxidation of borates may occur with either charge or uncharged acceptors [5,6]. Neckers et al. have reported that photoreduction of fluorine dyes by triphenylbutylborate salts is an intermolecular electron transfer reaction from borate anion to the triplet state of the dye that leads to the formation of butyl radicals which initiate polymerization [5].

Schuster and his co-workers [6-8] have studied the photochemistry and photophysics of carbocyanine alkyltriphenylborate salts and shown that electron transfer occurs from the

borate to the singlet state of the cyanine cation. Since the lifetime of the cyanine singlet is short (picoseconds), the said electron transfer is observed only in nonpolar solvents where the process can occur in the tight ion pair [8]. The photochemistry of different cyanine borate salts in photoinitiated free radical polymerization was later described by Zhang [9] and by our research group [10-13].

The key steps of the mechanism are the quenching of the excited chromophore, either singlet or triplet states, by the electron transfer mechanism and various steps that follow the primary process. Marcus [14] has provided a simple approach allowing to predict the kinetic of the process, using thermodynamic parameters and spectroscopic measurements. The Marcus theory assumes that the bimolecular electron transfer occurs in three stages: (1) the formation of the precursor complex, (2) the electron transfer and (3) the change in organization of the solvent cage in which electron transfer primary products exist. This theory leads to the prediction that the rate of electron transfer first should increase with an increase in the thermodynamic driving force up to a maximum and then decrease with an increase of the thermodynamic driving force.

The practical application of the Marcus theory is commonly used for the study of the primary photochemical processes. The description of the kinetics of the photoinitiated polymerization *via* intermolecular electron transfer process is one more example applying this theory to technological practice.

In this paper, we describe the kinetic studies of the novel photoinitiating systems consisting of different styrylbenzimidazolium dyes (the light absorbers) coupled with butyltriphenylborate or phenyl-trialkylborate anions (co-initiators). Additionally, it is our intention to show that the Marcus equation can be applied for the description of the kinetics for dye – borate photoinitiated polymerization *via* an intermolecular electron transfer process.

## EXPERIMENTAL

### Materials

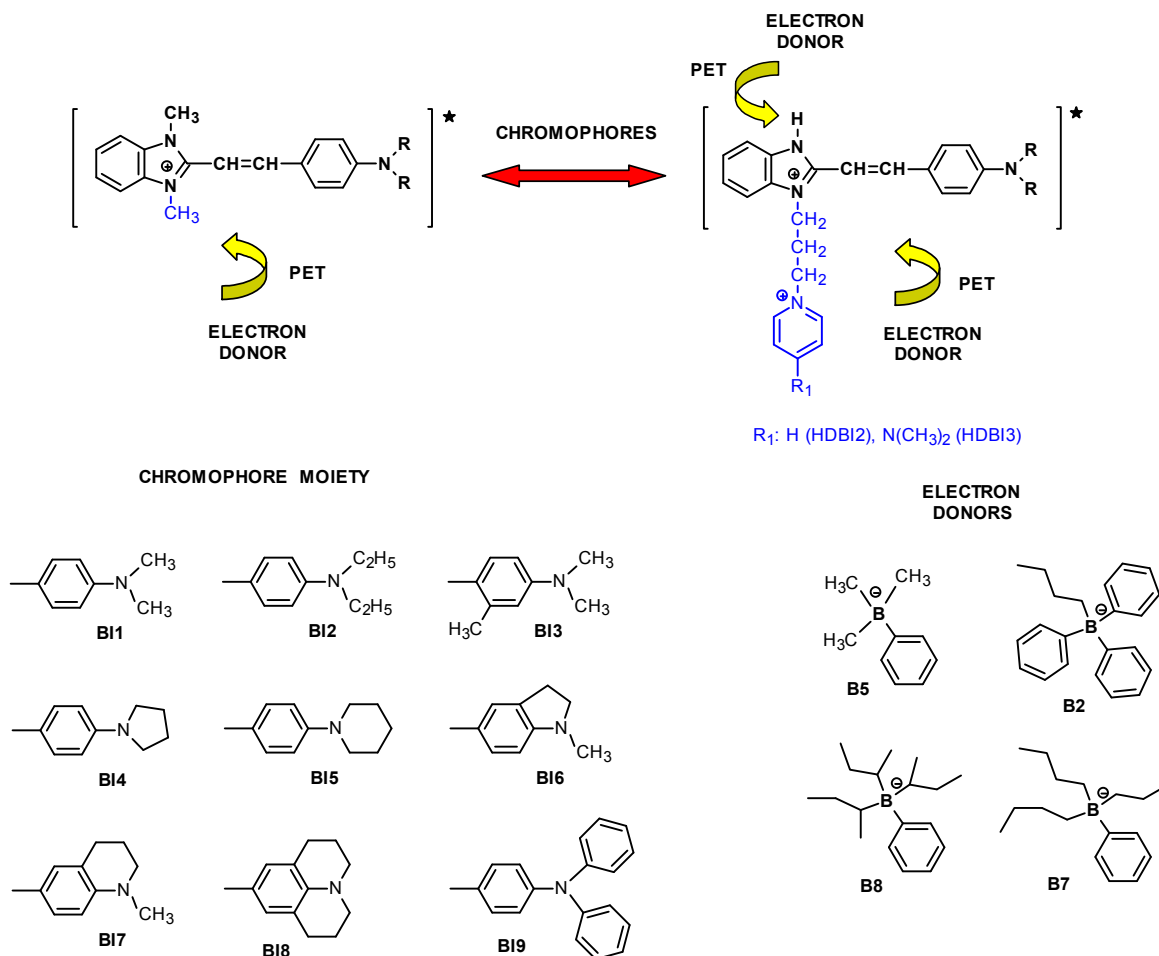
For the analysis of the photoinitiating properties of novel photoredox pairs, being the selected combinations of *n*-butyltriphenylborate (**B2**) or phenyl-trialkylborate (**B5**, **B7** and **B8**) anion and mono- and dicationic styrylbenzimidazolium dyes, were used. Their structures are shown in Scheme 1.

### Polymerization

The kinetics of free radical polymerization were measured based on the measurements of the rate of the heat evolution during polymerization in thin film cured sample ( $0.035 \pm 0.002$  g). The measurements were performed by measuring photopolymerization exotherms using photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. Irradiation of the polymerization mixture was carried out using the emission (line at 488 nm) of an argon ion laser Model Melles Griot 43 series with intensity of light of  $20 \text{ mW}/0.196 \text{ cm}^2$ .

Photo-DSC is a unique method of obtaining a fast and accurate indication of the photoinitiator performance. With a single measurement, various important parameters are accessible. The time to reach the maximum polymerization exotherm reveals information about the photoinitiator activity. Double bond conversion was calculated from the overall enthalpy evolved, which corresponds to the area under the peak. The polymerization rate was determined from the height of the peak.

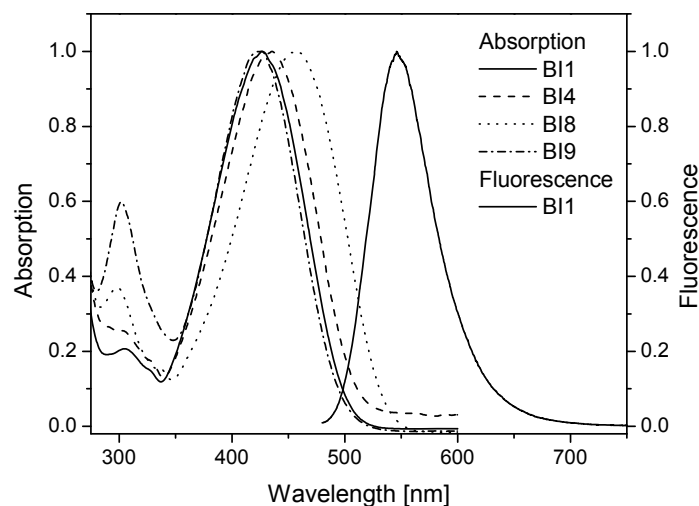
## Scheme 1



## RESULTS AND DISCUSSION

Each of the photoinitiators tested absorb UV-vis light with a significant absorption shoulder above 400 nm. This allowed us to apply the excitation beam of an argon ion laser for the initiation of the free radical polymerization. Figure 1 presents the illustrative electronic absorption and fluorescence spectra for selected styrylquinolinium dyes as iodide salts in 1-methyl-2-pyrrolidinone (MP).

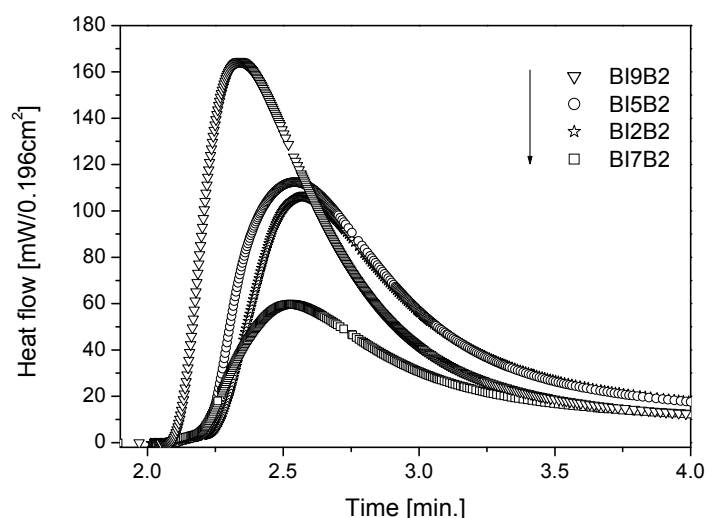
All salts possess similar absorption spectra with two maxima at about 300 and 430 nm. The shortest wavelength bands are attributed to the  $\pi \rightarrow \pi^*$  transitions whereas the long-wavelength bands, generally characterized by higher molar absorption coefficients ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), are attributed to CT transitions.



**Figure 1.** Electronic absorption and fluorescence spectra of an example of hemicyanine dyes in MP.

### Kinetics study of multifunctional acrylates polymerization

The kinetic curves obtained for the photoinitiated polymerization of triactylate trimethylolpropane – 1-methyl-2-pyrrolidinone (TMPTA-MP) (9:1) mixture recorded for selected hemicyanine borate salts, under irradiation with a visible light laser, are shown in Figure 2 for illustration.



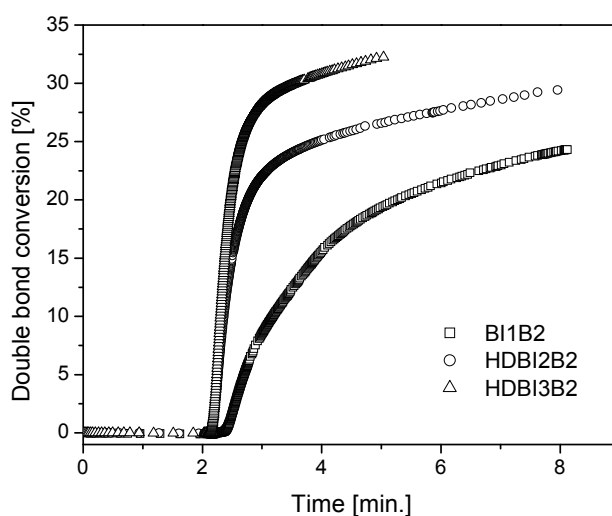
**Figure 2.** Family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA-MP (9:1) mixture initiated by asymmetric cyanine *n*-butyltriphenylborates marked in the Figure. The dye concentration was  $7.5 \times 10^{-3}$  M,  $I_a = 100$  mW/cm<sup>2</sup>. The applied dyes possessed various chromophores and identical borate.

It is apparent from the inspection of the rates of polymerization that the efficiency of the tested photoinitiators depends strongly on their structure. It was found that the photoinitiation efficiency of the tested hemicyanine borates depends on a character of dialkylamino substituent in electron donating part of molecule. The best photoinitiating abilities exhibit the photoredox pairs possessing diphenyl- (BI9), dimethyl- (BI1) and “cyclic” (BI4, BI5) amino substituents in the dye molecule. Generally, the initiators with electron-donating groups for which the free rotation between benzene ring carbon and nitrogen of N-alkylamino group is

possible indicate higher rate of heat evolution in comparison to the dyes possessing a stiffened dialkylamino group.

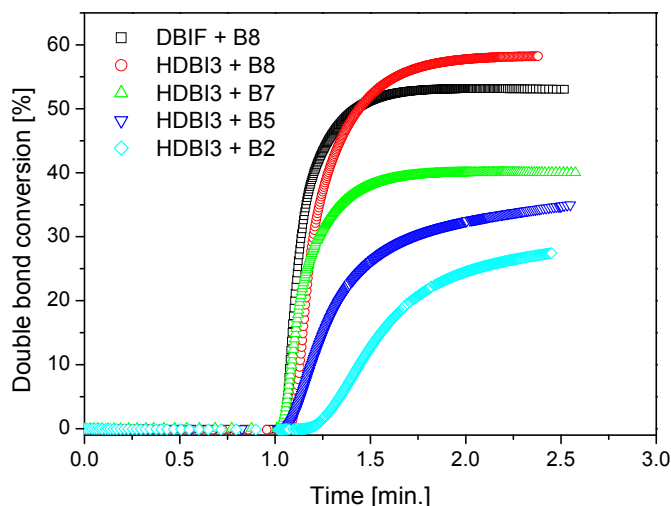
The classical Schuster's photoinitiating systems apply as chromophore cyanine dyes that do not form long-lived triplet state. Since the lifetime of cyanine singlet is short (typical lifetime about or less than 1 ns), an efficient electron transfer between borate anion and an excited dye molecule is possible only in nonpolar solvent where the process can occur between components of the tight ion pair [6-8]. The ion-pair electron transfer rates from borate to an excited state of cationic acceptor are anticipated to be above the diffusion limit [7]. Unfortunately, the efficiency of tight-ion-pair formation is high only in really nonpolar solvents such as benzene. Even small amount of polar solvent, as documented by Neckers, may sharply change a degree of such ion-pair formation [3]. In polymerizing mixture (acrylates; medium polarity solvent), the photoinitiating photoredox pair composed of cyanine cation and borate anion exists as tight-pair and solvent separated ions. This fact was confirmed experimentally, firstly by an investigation of the influence of borate anion concentration on the efficiency of photoinitiation and secondly by fluorescence quenching experiments [10,12,13]. Dissociation causes a sharp decrease of an electron donor concentration in proximity of an electron acceptor and inefficient formation of free radical initiating polymerization reaction. The electron donor concentration in such systems can be artificially increased by the covalent bonding to the electron acceptor molecule an additional positively charged species. The nature of the bonded additional positively charged molecule fragment in such approach, decides on an enhanced concentration of the electron donor molecule in proximity to an electron acceptor.

As it has been expected, dicationic hemicyanine borate salts gave significantly higher reactivity compared to monocationic equivalent (Figure 3). The increase of borate anion concentration in close proximity to the dye chromophore revealed the increase in the rate of TMPTA polymerization.



**Figure 3.** Comparison of the TMPTA/MP (9/1) mixture polymerization initiated by mono- (BI1B2) and dicationic (HDBI2B2 and HDBI3B3) styrylbenzimidazolium borate systems as measured by photo-DSC with the incident light intensity of 100mW/cm<sup>2</sup>.

On the other hand, the photoinitiating ability of the tested photoredox pairs depends on an electron donor structure. The phenyl-trialkylborate salts treated as co-initiators with styrylbenzimidazole chromophores for the photopolymerization of acrylic monomer composition revealed better initiation efficiency as compared to the butyltriphenylborate salts with the same type of chromophore. The dicationic styrylbenzimidazolium phenyl-tri-sec-butylborate salts initiated the free radical polymerization in the rate comparable to the observed for 5,7-diiodo-3-butoxy-6-fluorone (DIBF) common triplet state photoinitiator with the same borate used as an electron donor (Figure 4) [15].



**Figure 4.** Comparison of the TMPTA/MP (9/1) mixture polymerization initiated by dicationic styrylbenzimidazolium dye (HDBI3) and different tetramethylammonium tetraorganylborates and DIBF-B8 systems as measured by photo-DSC with the incident light intensity of  $100\text{mW}/\text{cm}^2$ . For all samples the electron donor concentration was  $7.5 \times 10^{-3}$  M. DIBF – 5,7-diiodo-3-butoxy-6-fluorone (triplet state photoinitiator) [15].

In general, the phenyl-trialkylborates studied reacted faster than the triphenylbutylborates at the same initiator concentration and irradiation conditions as indicated by the rate of polymerization (Table 1). However, the difference in the initiation efficiencies between the phenyl-tri-alkylborates and the triphenylbutylborate strongly depends on the structure of the chromophore.

From the data, obtained during the measurements, it was also deduced that the conversion of monomer double bonds is ranging from about 21 % to 60 %, while the quantum yields of photopolymerization oscillates between 33 and 280 for the light absorber concentration equals 0.0075 M (Table 1). It was also found that the degree of monomer conversion and the quantum yields of photopolymerization depends on the photoinitiator pairs structure. It is noteworthy that the photoinitiating systems composed of DIBF and B8 shows a comparable to the bicationic styrylbenzimidazolium dye - B8 borate system, photoinitiation ability with a quantum yield of polymerization of about 290, a conversion of monomer double bonds of about 54 % and the polymerization rate equals  $24.9 \mu\text{mol}/\text{s}$ .

**Table 1.** The Rates ( $R_p$ ) and the Quantum Yields ( $\Phi_p$ ) of Free Radical Polymerization of TMPTA for Tested Photoredox Couples.

Dye concentration (M)	Co-initiator concentration (M)	$R_p^{\text{max}}$ ( $\mu\text{mol s}^{-1}$ )	$\Phi_p$	$R_p^{\text{max}}$ ( $\mu\text{mol s}^{-1}$ )	$\Phi_p$	$R_p^{\text{max}}$ ( $\mu\text{mol s}^{-1}$ )	$\Phi_p$	$R_p^{\text{max}}$ ( $\mu\text{mol s}^{-1}$ )	$\Phi_p$
		<b>B2</b>		<b>B5</b>		<b>B7</b>		<b>B8</b>	
<b>BI1</b>									
0.0075	0.0075	0.18	2.12	0.51	5.97	4.22	49.11	6.92	80.61
<b>HDBI2</b>									
0.0075	0.015	2.91	33.88	7.70	89.58	24.00	279.35	15.04	175.06
<b>HDBI3</b>									
0.0075	0.015	2.80	32.60	5.01	58.28	14.83	172.65	18.87	219.60

The significant increase of the efficiency of photoinitiation of free radical polymerization in the case of styrylbenzimidazolium phenyltrialkylborate salts is the result of the generation of more than one radical after one photon absorption, which was confirmed by measuring a yield of a monofunctional monomer and butyl radicals adduct formation [16].

Irradiation of a deaerated solution containing styrylbenzimidazolium phenyl-tri-*n*-butylborate, and methyl methacrylate in benzene/acetonitrile gives an adduct with yield equals 155%. This result indicates that the photoinduced one electron oxidation of phenyl-tri-*n*-butylborate anion by the excited state of styrylbenzimidazolium cation produces substantially more than one equivalent of the butyl radicals. The obtained result is in good agreement with the Neckers' et al. [17] studies.

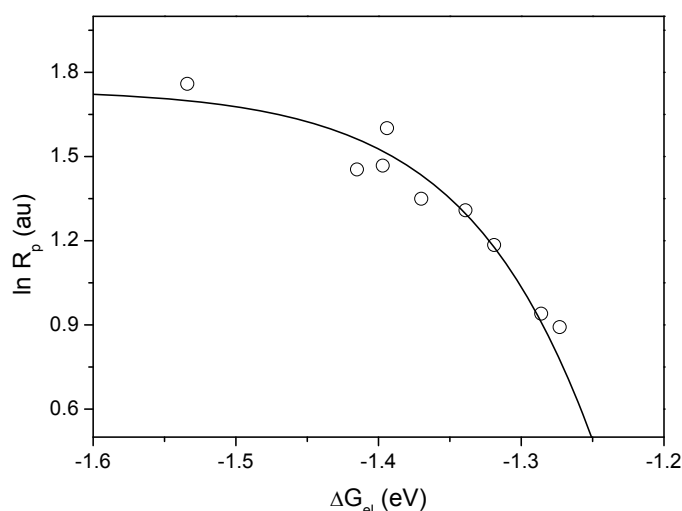
As was previously reported for the alkyltriphenylborates [6-8], the rates of alkyl radical formation, as the result of the boranyl radical decomposition, are directly related to the stabilities of the alkyl radicals formed. Since the decay of the boranyl radical is found to be very fast and irreversible, the rate of back electron transfer is negligible [8]. Therefore, the efficiencies of alkyl radical formation and, hence, initiation of polymerization depend on the observed efficiency of electron transfer from the borate anion to the singlet state of cyanine molecule.

The Marcus theory [14] allows predicting the rate of the primary process e.g. the rate of photoinduced electron transfer process. The use of cyanine borates creates a unique opportunity to study the possibility of an application of this theory for the description of the rate of polymerization *via* an intermolecular electron transfer process. Under the assumption that for all photoredox couples under the study the identical radical is formed, e.g. the driving force of the electron transfer process has no influence on the type of the yielding free radical, one should observe a parabolic relationship between the logarithm of polymerization rate and the free energy change  $\Delta G_{el}$  as follows:

$$\ln R_p = A - (\lambda + \Delta G_{el})^2 / 8\lambda RT \quad (1)$$

where: A for the initial time of polymerization is the sum:  $\ln k_p - 0.5 \ln k_t + 1.5 \ln [M] + 0.5 \ln I_a$ .

For the photoinitiating photoredox pairs examined this relationship is shown in Figure 5.



**Figure 5.** Dependence of the rate of photoinitiated polymerization on the free energy change ( $\Delta G_{el}$ ) (calculated for ethyl acetate solution) for the photoinduced electron-transfer process from phenyl-tri-*n*-butylborate to the excited state of monochromophoric hemicyanine dye.

It is apparent from the inspection of the relationship shown in Figure 5 that the presented plot exhibits trend predicted by the classical Marcus theory for photoinduced electron-transfer reaction [14]. This suggests that at the beginning of the TMPTA

polymerization electron transfer process may be the rate determining step in the radical formation process.

## CONCLUSION

Presented paper is focused on photoinitiation of free radical polymerization initiated by photoreducible dye sensitization. A series of hemicyanine *n*-butyltriphenylborate or phenyl-trialkylborate salts were employed as visible-light, singlet state photoinitiators of acrylic monomers polymerization. They were examined in order to verify the possibility of the Marcus equation application for the description of the kinetics of free radical polymerization photoinitiated *via* the photoinduced electron transfer process (PET). The kinetics of polymerization of trimethylolpropane triacrylate, using styrylbenzimidazole borates as photoinitiators, was studied by differential scanning calorimetric method. The experimental data revealed that:

(i) Hemicyanine borate salts are shown to be very effective photoinitiators for the polymerization of acrylic monomers when irradiated with the visible emission of an argon-ion laser. (ii) The efficiency of the polymerization depends on the structure of the hemicyanine cation used as an electron acceptor. (iii) The inspection of the rates of polymerization showed that the dicationic styrylbenzimidazolium salts initiated polymerization more effectively than monocationic equivalents. (iv) The comparative analysis of the borate salts as co-initiators with styrylbenzimidazolium dyes shows that the number of alkyl groups per boron determines reactivity. Trialkylphenylborates initiate polymerization much more rapidly than do *n*-butyltriphenylborate (B2). (v) The relationship between the rate of polymerization and the free energy change ( $\Delta G_{ei}$ ) for electron transfer reaction displays typical Marcus kinetic behavior.

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