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## Tetramethylammonium phenyltrialkylborates as co-initiators with novel two-cationic styrylbenzimidazolium dyes in highly efficient, visible light polymerization of acrylate

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## ABSTRACT

New phenyltrialkylborate salts have been treated as co-initiators with mono- and dicationic styrylbenzimidazole chromophores for the photopolymerization of acrylic monomer. The relative initiator efficiency of the phenyltrialkylborate salts as compared to the *n*-butyltriphenylborate salt with the same type of chromophore was determined. The phenyltrialkylborate salts coupled with selected hemicyanine dye are more efficient photoinitiators of free radical polymerization in comparison to the corresponding photoinitiating system containing *n*-butyltriphenylborate salt as an electron donor. The study showed that, the photoinitiating ability of dicationic styrylbenzimidazolium dyes coupled with the same borate salts is higher in comparison to monocationic chromophore. The significant increase of the efficiency of photoinitiation of free radical polymerization is a result of the generation of more than one radical after one photon absorption (phenyltrialkylborate salts as co-initiators) and an increase of an electron donor concentration in close proximity to a hemicyanine dye moiety (mono- and dicationic styrylbenzimidazole dyes as light absorbers).

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## 1. Introduction

Using visible or UV light to initiate polymerization is an area of intense interest in organic photochemistry. Photopolymerization can be specially directed and turned on or off. In free radical processes triggered by light, rates can be controlled by a combination of factors: source(s) of radicals, light intensity, and temperature [1].

The traditional way to initiate polymerization through photochemistry is carried out 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 a primary absorber. In particular, it is necessary to choose a sensitizer (absorber) and a co-initiator so that energy transfer can occur between these components. Photoinduced intermolecular electron transfer represents an alternative to such a restriction. This process involves the use of light to initiate an electron transfer from a donor to an acceptor molecule [2].

Photoinduced electron transfer reaction represents an important route to free radicals among whose uses are the initiation of acrylic polymerization. It is apparent that borate anions are espe-

cially beneficial electron transfer donors, and these have many important applications in free radical polymerizations initiated by different electron acceptor sensitizers [3].

Williams et al. were the first to report a systematic study on the photochemistry of tetraarylborates [4]. They found that irradiation of sodium tetraphenylborate in oxygen-free aqueous solution produces 1-phenyl-1,4-cyclohexadiene in nearly quantitative yield. These studies showed that the new carbon–carbon bond is formed intramolecularly between carbon atoms originally bound to boron.

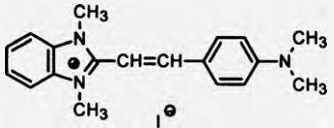
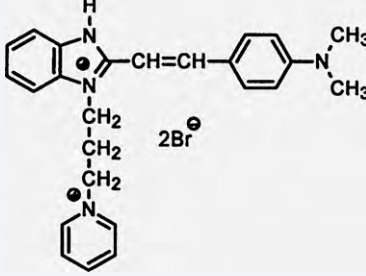
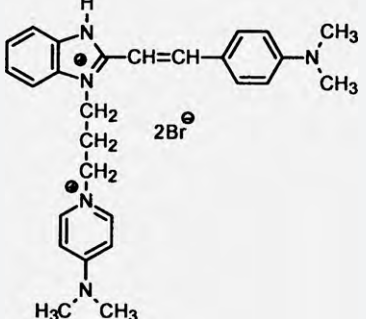
In the eighties of the 20th century, Schuster and his co-workers [5–7] reported that carbocyanine alkyltriphenylborate salts dissolved in nonpolar solvents exist predominantly as ion pairs. Irradiation of the ion pair with visible light absorbed by the cyanine leads to formation of a locally excited singlet state of the dye. The singlet excited cyanine in the ion pair is capable of oxidizing the borate anion to the boranyl radical. The boranyl radical undergoes very fast carbon–boron bond cleavage to generate a free alkyl radical. The rate of bond cleavage depends directly on the stability of an alkyl radical formed. When the stabilized alkyl radicals are formed, carbon–boron bond cleavage is faster than the back electron transfer reaction that regenerates the cyanine borate ion pair. The free alkyl radicals formed by the irradiation–electron transfer–bond cleavage sequence may be used in meaningful chemical processes such as the initiation of polymerization.

The electron transfer photooxidation of borates may also occur with uncharged acceptors [8,9]. Hassoon and Neckers have

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**Table 1**

The steady-state spectral properties of tested hemicyanine dyes in tetrahydrofuran and 1-methyl-2-pyrrolidinone.

No	Dye	$\lambda_{\text{max}}^{\text{A}}$ (nm)		$\lambda_{\text{max}}^{\text{Fl}}$ (nm)		$\Delta\nu$ (cm <sup>-1</sup> )	
		THF	MP	THF	MP	THF	MP
BI1		430.5	429.0	537.4	546.2	4620.7	5001.7
HDBI2		429.0	428.0	558.0	558.0	5388.9	5443.3
HDBI3		428.5	428.0	559.6	559.2	5467.3	5481.8

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 [9].

From literature [10–14] it is known that cyanine borates act as efficient photoinitiators and are able to satisfy the requirement in the field of photopolymerization. The focus of the present report is on tetraorganyl borate salts. Upon electron transfer, tetraorganyl borate anions produce alkyl radicals making this class of compounds useful radical initiators. Herein we describe the novel systems in which phenyltrialkylborate salts dissolved in acrylic monomer are activated by excited styrylbenzimidazole dye to initiate radical polymerization.

## 2. Experimental

### 2.1. Materials

Monomer, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), co-initiators, thiophenoxyacetic acid (TPAA), N-phenylglycine (NPG), N-phenyliminodiacetic acid (DNPG), ethyl 4-N,N-dimethylaminobenzoate (ENB), 2-mercaptobenzoic acid (MBA), N-methoxy-4-phenylpyridinium tetrafluoroborate (NO) and solvents, 1-methyl-2-pyrrolidinone (MP), tetrahydrofuran (THF), acetonitrile and ethyl acetate (EtOAc) were purchased from Aldrich Chemical Co. and were used without further purification. Dyes were synthesized in our laboratory using procedures described earlier [10]. DIBF – 5,7-diiodo-3-butoxy-6-fluorone was obtained by applying methodology given by Neckers and co-workers [15].

Phenyltrialkylborate tetramethylammonium salts were synthesized based on the method described by Polykarpov and Neckers

[16]. The final products were identified by <sup>1</sup>H NMR spectroscopy and <sup>13</sup>C NMR spectroscopy when it was needed. The obtained spectra suggest that the reaction products were of desired structures. The purity of synthesized compounds was determined using thin layer chromatography and by measuring the melting points. The molecular structure and denotations of the dyes under the study are given in Table 1.

### 2.2. Spectral measurements

The UV–vis absorption spectra were recorded with a Shimadzu UV–vis Multispec-1501 spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. The fluorescence measurements were performed at an ambient temperature.

The fluorescence lifetimes were measured using a FLS920P Spectrometers produced by Edinburgh Instruments. The apparatus utilizes for the excitation a picosecond diode laser generating pulses of about 55 ps at 375 nm. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals with resolution in the range of few picoseconds possible. The dyes were studied at concentration able to provide equivalent absorbance at 375 nm (0.2–0.3 in the 10 mm cell) to be obtained. The measurements were performed in the ethyl acetate–1-methyl-2-pyrrolidinone (10:2) solution.

### 2.3. Electrochemical measurements

The reduction potentials of the dyes and the oxidation potential of the borates were measured by cyclic voltammetry using an Electroanalytical Cypress System Model CS-1090. The typical three-

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