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Phenyltrialkylborates as co-initiators with cyanine dyes in visible light polymerization of acrylates

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ABSTRACT

Photoredox pairs consisting of selenocarbocyanine dye cations and phenyltrialkylborate anions were employed as the novel, effective visible-wavelength initiators of the radical polymerization of acrylic monomer. The influence of the sensitizers and electron donor structure on the photopolymerization kinetics of multiacrylate monomer was investigated by photo-DSC. It was found that the polymerization rate and the final conversion degree were dependent on both dye and borate structure. The kinetic studies of the free radical polymerization revealed an increase in the polymerization rate with a decrease of the borate oxidation potentials which was additionally reflected by the linear relationship between the Hammett constant and rate of polymerization. The efficiency of these initiators was discussed on the basis of the free energy change for electron transfer from an excited cyanine dye cation to a borate anion. The ΔG_{el} values were estimated for photoredox pairs containing a series of phenyltrialkylborate anions and one selenocarbocyanine dve cation. The relationship between the rate of polymerization and the free energy of activation for electron transfer reaction gives the dependence predicted by the classical theory of electron transfer. The photoreduction of cyanine phenyltrialkylborate complex was studied using nanosecond laser flash photolysis. The dye triplet was found to be quenched by the electron donors via an electron transfer process. Rate constants (k_q) for the quenching of the excited states were high and approached diffusion-controlled limits and were found to depend on the borate structure.

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1. Introduction

Although photopolymerization is a rather old technique for the curing of acrylate-based formulations, numerous new applications are added regularly. Especially, visible light curing is still a challenge due to the high demands in modern applications such as dental filling materials [1], reprography (photoresists, printing plates, integrated circuits), laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. Therefore, important components such as monomers and photoinitiators (PIs) [1–4] have to be adapted.

A photoinitiator or photoinitiator system can be considered to be a molecule or combination of molecules which, when exposed to irradiation, initiate polymerization at a much faster rate than would occur in their absence. Most photoinitiation processes involve a uni- or bimolecular process [5].

Photoinitiators for radical polymerization are classified as cleavage (type I) and H-abstraction type (type II) initiators [4–7]. The majority of type I photoinitiators are aromatic carbonyl compounds

with appropriate substitution. For example, upon absorption of light, benzoin and derivatives, benzil ketals, acetophenones, aminoalkyl phenones, O-acyl- α -oximino ketones, α -hydroxyalkyl ketones, and acyphosphine oxides all spontaneously undergo " α -cleavage", generating free radicals. Due to relatively lower absorbance, the other cleavage initiator-based azo, peroxy, and halogenated compounds are not widely used as photoinitiators. Each photoinitiator has advantages and disadvantages, and the selection of a photoinitiator very much depends on the requirements of a particular application.

The generation of free radicals from type II photoinitiators and curing rates is generally slower than the generation of free radicals from type I photoinitiators, which are based on unimolecular formation of radicals. These systems are, therefore, more sensitive to quenching of excited triplet states of the photoinitiators, which are the reactive precursors of light-induced chemical changes for carbonyl compounds. Indeed, quenching by monomers with low triplet energy (e.g., styrene or N-vinylcarbazole) or by oxygen is often observed and may lead to relatively low curing rates when type I photoinitiators are employed [7].

Visible photoinitiation systems often involve dyes as lightabsorbing chromophores. Numerous photoinitiated free radical polymerizations using dyes have been described and reviewed by





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several authors [2,7–16]. Initiating radicals are typically generated by photoinduced electron transfer and involve a co-initiator that participates in the electron transfer process. Energy transfer to monomers is not thermodynamically favorable in these systems due to the low excitation energies of dyes. Depending on the nature of the dye involved, namely photoreducible or photooxidizable dyes, two distinct mechanisms need to be considered. These are electron transfer from the co-initiator to the excited, photoreducible dye and electron transfer from the excited, photooxidizable dye to the co-initiator (Scheme 1). These systems include aromatic ketone–amine combinations, dye–co-initiators pairs, as well as certain organometallic photoinitiators [6].

The excited-state electron transfer process often plays a key role in visible light-induced free radical polymerizations [1-6]. This process leads to the formation of free radicals that are effective initiators of polymerizations. The efficiency of the initiating radical formation depends on two main factors. The first factor is the precise nature of the reacting partners taking part in the electron transfer process. The second is the efficiency of any subsequent fragmentations yielding secondary radicals and radical ions [8–16] that are often much more effective in initiating polymerizations than the primary radicals. Therefore, a detailed knowledge of such primary and secondary photochemical mechanisms is critical for the design of practical systems used in initiating polymerizations.

In the past decade, there have been several extensive studies on the photooxidation of borate-containing organic compounds and the subsequent fragmentation reactions of the photon-generated borate-centered radical anions. These studies are of general interest because of their potential application in photopolymerization [9,10,17–22], and their importance as intermediates in organic synthesis [23–26]. In the area of polymerization, for example, it was recently shown for a series of phenyltrialkylborate salts, which type of radicals would be the most effective co-initiators of polymerizations [17–20].

Upon oxidation, phenyltrialkylborate anions have been shown to be very useful as free radical sources. Paired with an appropriate cationic chromophore, the tetraorganylborates are used as co-initiators in visible light photoinitiator systems. The mechanism of photoinitiation with a cyanine—borate complex involves alkyl radical formation as a result of photoinduced electron transfer from a borate anion to the singlet excited state of the cyanine dye cation, followed by the addition of an alkyl radical formed to the carbon—carbon double bond of the acrylate [9,10]. The relationship between the rate of polymerization and the free energy of the activation of the electron transfer reaction shows the dependence predicted by the classical theory of electron transfer phenomena [6].

Phenyltrialkylborates have been found to have better reactivity in comparison to traditionally used alkyltriphenylborate salts. The significant increase in the efficiency of the photoinitiation of free radical polymerization is a result of the generation of more than one radical after the absorption of one photon [9].

$$A^{*} + D \frac{k_{d}}{k_{-d}} [A \cdots D]^{*} \frac{k_{cl}}{k_{-cl}} [A^{-} \cdots D^{+}]$$

$$A + D \xleftarrow{k_{r}} \underbrace{secondary}_{reactions} \text{Polymerization initiation species}$$

$$A + D^{*} \frac{k_{d}}{k_{-d}} [A \cdots D]^{*} \frac{k_{cl}}{k_{-cl}} [A^{-} \cdots D^{+}]$$

Scheme 1. Schematic presentation of both the photoreducible and the photooxidizable sensitization of free radical polymerization. Note: k_d is the rate constant that represents the rate of diffusive encounters between reactants, k_{-d} denotes the rate of separation of the reactants after collision, k_{el} is the first order rate constant of electron transfer. The reverse step is designated by the rate constant k_{-el} , and finally k_r denotes the rate of return electron transfer. In this paper, the polymerization kinetics of trimethylolpropane triacrylate (TMPTA) in the presence of several pairs of borate initiators is compared. Each pair of the borate salts contained the same light-absorbing chromophore as the cation and either different phenyltrialkylborate or butyltriphenylborate as the counterion. The borates studies are shown in Scheme 4.

2. Experimental

2.1. Materials

Monomer, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), all chemicals and solvents were purchased from Aldrich Chemical Co. and were used without further purification. As sensitizers selenocarbocyanine dyes were used. The 3,3'-dimethylthiacar bocyanine iodide (S4), 5,7-diiodo-3-butoxy-6-fluorone (DIBF), campherchinone (CQ) and titanocene (Ti(C₆F₅)₂(C₅H₄)₂; T) were applied as light absorber for comparison. As co-initiators the following compounds were tested: tetramethylammonium phenyltriethylborate (B6), tetramethylammonium *p*-methoxyphenyltriethyl-borate (B62), tetramethylammonium *p*-phenoxyphenyltriethyl-borate (B63), tetramethylammonium *p*-cyanophenyltriethylborate (B65), tetramethylammonium *n*-butyltriph enylborate (B2), N-phenylglycine (NPG) and ethyl 4-N,N-dimethylaminobenzoate (ENB).

2.2. Techniques

2.2.1. Spectral measurements

Absorption (the concentration of the dye 1.0×10^{-5} mol/L) and emission spectra (the concentration of the dye 3.0×10^{-6} mol/L) in N,N-dimethylformamide (DMF), acetonitrile (AcCN), and tetrahydrofurane (THF) were recorded at room temperature using a Shimadzu UV–vis Multispec-1501 spectrophotometer and a Hitachi F-4500 spectrofluorimeter, respectively.

The nanosecond laser flash photolysis experiments were performed using a LKS.60 Laser Flash Photolysis apparatus (Applied Photophisics). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from a Lambda Phisik/model LPY 150 operating at 65 mJ/pulse (pulse width about 4–5 ns) was used for the excitation. Transient absorbances at preselected wavelengths were monitored by a detection system consisting of a monochromator, a photomultiplier tube (Hamamatsu R955) and a pulsed xenon lamp (150 W) as a monitoring source. The signal from the photomultiplier was processed by a Helwett-Packard/ Agilent an Agilent Infiniium 54810A digital storage oscilloscope and an Acorn compatible computer.

2.2.2. Electrochemical measurements

The reduction potentials of the dyes were measured by cyclic voltammetry using an Electroanalytical Cypress System Model CS-1090. The typical three-electrode setup was employed for electrochemical measurements. The electrolyte was 0.1 M ter-trabutylammonium perchlorate, which was purged with argon prior to a measurement. Platinum 1-mm electrode was applied as working electrode and platinum and Ag/AgCl were used as auxiliary and reference electrodes, respectively.

2.2.3. Polymerization measurements

The kinetics of free radical polymerization were studied using a polymerization solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The seleno- and thiocarbocyanine borate salts (photoinitiator) concentration was 0.0015 M. A reference formulation contained seleno- and thiocarbocyanine iodide or bromide (dye without an electron donor) instead of seleno- and thiocarbocyanine borate salt (photoinitiator). The measurements were carried out at an ambient temperature and the polymerizing mixture was not deaerated before curing.

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 ± 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 514 nm) of an argon-ion laser Model Melles Griot 43 series with intensity of light of 100 mW/cm². The light intensity was measured by a Coherent Model Fieldmaster power meter.

The rate of polymerization (R_p) was calculated using the Equation (1) where dH/dt is maximal heat flow during reaction and ΔH_p^{theor} is the theoretical enthalpy for complete conversion of acrylates' double bonds. ΔH_p^{theor} for acrylic double bond is equal 78.2 kJ/mol [27].

$$R_p = \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) \frac{1}{\Delta H_p^{theor}} \tag{1}$$

The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups reacting in the system. By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to Equation. (2).

$$C = \frac{\Delta H_t \cdot M}{n \Delta H_n^{\text{theor}} m} \tag{2}$$

where ΔH_t is the reaction heat evolved at time *t*, *M* is the molar mass of the monomer, *m* is the mass of the sample and *n* is the number of double bonds per monomer molecule.

The quantum yield of polymerization Φ_p was defined as the number of polymerized double bonds per absorbed photon [28].

2.3. Synthesis

2.3.1. Synthesis of phenyltrialkylborate salts

Simple synthetic procedures were developed to prepare suitably substituted stable phenyltrialkylborate tetramethylammonium salts [18,19]. The synthetic approaches that were applied are outlined below and are based on the addition of alkyl or phenyllithium reagents to a triorganylborane. A general route for the synthesis of tetramethylammonium phenyltrialkylborate is shown in Scheme 2.

Typical procedure: To a solution of triethylborane in hexane (15 mmol, 15 mL, 1 M), anhydrous diethyl ether (25 mL) was added. To the vigorously stirred solution, under nitrogen, *p*-substituted phenyllithium (16.6 mmol) was added dropwise at -85 °C over 10 min. The mixture was allowed to warm slowly to room temperature and stirred for a further 2 h. The solvent was removed under reduced pressure, the residue was dissolved in 10 mL of



Scheme 2. A general route for the synthesis of B6 borate series.

water and poured into 100 mL of saturated aqueous N(CH₃)₄Cl. The white precipitate which formed was filtered, washed with water, dried and recrystallized from ethanol.

The detailed synthetic procedures as well as the basis of analytical results and spectral evidences of the tetramethylammonium phenyltrialkylborates the readers can find in our previous paper [29].

2.3.2. Synthesis of selenocarbocyanine dyes

The methodology for the synthesis of the trimethine cyanine dyes is illustrated in Scheme 3. The classical orthoester approach to carbocyanines was applied. It involves the condensation, under basic conditions, of orthoesters with quaternary heterocyclic salts substituted with an activated methyl group [30].

General procedure: A solution of 1.72 mmol of quaternary heterocyclic salts, 0.76 g (0.86 mL, 5.16 mmol) of triethyl orthoformate and 7 mL of dry pyridine was refluxed for 2 h. After cooling to room temperature, diethyl ether was added and the resulting



Scheme 3. Synthesis of trimethine cyanine dyes.

mixture allowed to complete precipitation. The crystalline product obtained was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry methanol or dimethylformamide/diethyl ether system [30].

2.3.2.1. 3-(3-(Pyridinium-1-yl)propyl)-2-((1E,3Z)-3-(3-(3-(pyridinium-1-yl)propyl)benzo[d] [1,3]selenazol-2(3H)ylidene)prop-1-enyl)benzo[d] [1,3]selenazol-3-ium bromide (Se1).



The title compound was obtained by crystallization from MeOH. Yield 62%.

¹H NMR (200 MHz, DMSO-*d*₆): δ = 2.42 (m, 4H; 2× CH₂), 4.47 (m, 4H; 2× CH₂), 5.11 (m, 4H; 2× CH₂), 7.35 (t, *J* = 7.6 Hz, 2H; 2× CH), 7.53–7.63 (m, 4H), 7.82 (d, *J* = 8.2 Hz, 2H; 2× CH_ar), 7.95 (t, *J* = 11.8 Hz, 1H; CH), 8.10 (d, *J* = 8.2 Hz, 2H; 2× CH_ar), 8.19 (t, *J* = 6.8 Hz, 4H; 4×CH_ar), 8.62 (t, *J* = 7.6 Hz, 2H; 2× CH_ar), 9.41 (d, *J* = 6.2 Hz, 4H, 4×CH_ar) ppm.

(d, J = 6.2 Hz, 4H, 4×CH_{ar}) ppm. ¹³C NMR (50.3 MHz, DMSO- d_6): $\delta = 29.3$ (2× CH₂), 44.2 (2× CH₂), 57.2 (2× CH₂), 105.0 (CH), 114.9 (2× CH), 125.1 (2× CH), 125.4 (2×C), 126.6 (2× CH), 127.9 (2× CH), 128.1 (4×CH), 142.3 (2×C), 144.9 (4×CH), 145.7 (2× CH), 151.0 (2×C), 168.6 (2×C) ppm.

2.3.2.2. 3-Ethyl-2-((1E,3Z)-3-(3-ethylbenzo[d] [1,3]selenazol-2(3H)ylidene)prop-1-enyl)benzo[d] [1,3]selenazol-3-ium ethyl sulfate (Se2).



The title compound was obtained by crystallization from dry DMF/Et₂O. Yield 78%.

¹H NMR (200 MHz, DMSO-*d*₆): $\delta = 1.09$ (t, J = 7.2 Hz, 3H; CH₃), 1.33 (t, J = 7.0 Hz, 6H; 2× CH₃), 3.74 (q, J = 7.2 Hz, 2H; CH₂), 4.35 (q, J = 7.4 Hz, 4H; 2× CH₂), 6.75 (d, J = 12.6 Hz, 2H; 2× CH), 7.34 (t, J = 7.4 Hz, 2H; 2× CH_ar), 7.54 (t, J = 7.4 Hz, 2H; 2× CH_ar), 7.70 (d, J = 8.0 Hz, 2H; 2× CH_ar), 7.78 (t, J = 12.6 Hz, 1H; CH), 8.06 (d, J = 8.0 Hz, 2H; 2× CH_ar) ppm.

¹³C NMR (50.3 MHz, DMSO- d_6): $\delta = 12.6$ (2× CH₃), 15.2 (CH₃), 42.3 (2× CH₂), 61.2 (CH₂), 103.2 (CH), 114.7 (2× CH), 125.0 (2× CH), 125.4 (2×C), 126.4 (2× CH), 128.0 (2× CH), 142.2 (2×C), 150.6 (2× CH), 168.8 (2×C) ppm.

2.3.2.3. 6-Methoxy-2-((1E,3Z)-3-(6-methoxy-3-methylbenzo[d] [1,3] selenazol-2(3H)-ylidene)prop-1-enyl)-3-methylbenzo[d] [1,3]selena-zol-3-ium iodide (Se3).



The title compound was obtained by crystallization from dry DMF/Et₂O. Yield 40%.

¹H NMR (200 MHz, DMSO- d_6): $\delta = 3.75$ (s, 6H; 2× CH₃), 3.83 (s, 6H; 2× CH₃), 6.64 (d, J = 12.2 Hz, 2H; 2× CH), 6.94 (d, J = 8.8 Hz, 2H;

 $2 \times$ CH_{ar}), 7.20 (s, 2H; $2 \times$ CH_{ar}), 7.69 (t, J = 12.2 Hz, 1H; CH), 7.89 (d, J = 8.8 Hz, 2H; $2 \times$ CH_{ar}) ppm.

¹³C NMR (50.3 MHz, DMSO-*d*₆): δ = 34.6 (2× CH₃), 55.9 (2×OCH₃), 100.6 (2× CH), 103.7 (CH), 112.4 (2× CH), 115.6 (2×C), 126.7 (2× CH), 144.5 (2×C), 149.3 (2×C), 159.9 (2× CH), 170.4 (2×C) ppm.

2.3.2.4. 3-Methyl-2-((1E,3Z)-3-(3-methylbenzo[d] [1,3]selenazol-2 (3H)-ylidene)prop-1-enyl)benzo[d] [1,3]selenazol-3-ium iodide (Se4).



The title compound was obtained by crystallization from dry DMF/Et₂O. Yield 37%.

¹H NMR (200 MHz, DMSO-*d*₆): δ = 3.87 (s, 6H; 2× CH₃), 6.48 (d, *J* = 12.8 Hz, 2H; 2× CH), 7.00 (m, 2H; 2× CH_{ar}), 7.28 (m, 2H; 2× CH_{ar}), 7.44 (m, 2H; 2× CH_{ar}), 7.69 (t, *J* = 12.8 Hz, 1H; CH), 7.82 (d, *J* = 8.8 Hz, 2H; 2× CH_{ar}) ppm.

¹³C NMR (50.3 MHz, DMSO-*d*₆): δ = 33.5 (2× CH₃), 98.8 (CH), 112.7 (2× CH), 123.4 (2×C), 124.7 (2× CH), 127.5 (2× CH), 129.0 (2× CH), 139.8 (2×C), 146.0 (2× CH), 159.8 (2×C) ppm.

2.3.2.5. 2-((1E,3Z)-3-(3-Ethylbenzo[d]thiazol-2(3H)-ylidene)prop-1enyl)-3-methylbenzo[d] [1,3]selenazol-3-ium iodide (Se6).



The title compound was obtained by crystallization from dry DMF/Et₂O. Yield 18%.

¹H NMR (200 MHz, DMSO-*d*₆): δ = 1.33 (t, *J* = 6.6 Hz, 3H; CH₃), 3.78 (s, 3H; CH₃), 4.37 (q, *J* = 6.6 Hz, 2H; CH₂), 6.60–6.70 (m, 2H), 7.28–7.79 (m, 7H), 7.98–8.06 (m, 2H) ppm.

¹³C NMR (50.3 MHz, DMSO-*d*₆): δ = 12.7 (CH₃), 34.5 (CH₃), 41.6 (CH₂), 98.7 (CH), 99.6 (CH), 102.7 (CH), 113.5 (CH), 114.9 (CH), 123.2 (CH), 124.8 (CH), 125.4 (CH), 126.3 (CH), 127.9 (CH), 128.2 (CH), 140. 8 (C), 143.4 (C), 146.4 (C), 148.5 (C), 164.5 (C), 169.7 (C) ppm.

2.3.2.6. 3-Methyl-2-((1E,3Z)-3-(3-methylbenzo[d]thiazol-2(3H)-ylidene)prop-1-enyl)benzo[d]thiazol-3-ium iodide (S4).



The title compound was obtained by crystallization from dry MeOH. Yield 46%.

¹H NMR (200 MHz, DMSO- d_6): $\delta = 3.81$ (s, 6H; 2× CH₃), 6.52 (d, J = 12.8 Hz, 2H; 2× CH), 6.94 (d, J = 7.2 Hz, 2H; 2× CH_{ar}), 7.56 (t, J = 7.0 Hz, 2H; 2× CH_{ar}), 7.72 (m, 3H; 3×CH_{ar}), 7.97 (d, J = 7.0 Hz, 2H; 2× CH_{ar}), ppm.

¹³C NMR (50.3 MHz, DMSO-*d*₆): δ = 33.5 (CH₃), 98.9 (CH), 113.6 (2× CH), 123.0 (2× CH), 124.9 (2×C), 125.2 (2× CH), 128.0 (2× CH), 141.8 (2×C), 146.2 (2× CH), 165.0 (2× C) ppm.

For the analysis of the photoinitiating properties of novel photoredox pairs, the selected combinations of *n*-butyltriphenylborate (B2) or phenyltrialkylborate (B6, B61, B62, B63, B64 and B65) anion and mono- and tricationic cyanine dyes, were used.



Fig. 1. Normalized absorption spectra of selected cyanine dyes (marked in Figure) in acetonitrile.

3. Results and discussion

3.1. Spectroscopic and photophysical properties of cyanine derivatives

In our studies, polymerization of TMPTA photoinitiated by mono- and tricationic trimethine cyanine borate salts was performed under irradiation at 514 nm, e.g. at the wavelengths where the light is absorbed by cyanine cation (Fig. 1).

Dithiacarbocyanine and diselenocarbocyanine dyes are characterized by an intense absorption band in the orange spectral region, with the more intense peaks ($\epsilon_{max} = 8 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) located for dithiacarbocyanine (S4) at about 550–560 nm and the second, less intense, blue-shifted by about 6000 cm⁻¹ (Fig. 1). For diselenocarbocyanines the absorption bands are shifted to the red area of visible light of about 20 nm. The spectral data are listed in Table 1.

It is evident that for tested cyanine dyes only relatively small solvent dependence of their absorption and emission spectra is observed. Generally, we observed a blue shift in the absorption with an increase of solvents polarity and a positive solvatochromism in the emission.

Table 1

Spectral properties o	of cyanine	dyes under	the study in	THF,	DMF and	AcCN.
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Solvent	Dye	$\lambda_{\max}^{Ab}(nm)$	$\lambda_{\max}^{Fl}(nm)$	Stokes shifts (cm ⁻¹)
Tetrahydrofurane (THF)	Se1	586	600	398.2
	Se2	578	597	550.6
	Se3	593	615	603.2
	Se4	582	600	515.5
	Se6	568	583	453.0
	S4	563	579	490.8
N,N-dimethylformamide	Se1	583	601	513.7
(DMF)	Se2	577	596	552.5
	Se3	585	617	886.6
	Se4	580	602	630.1
	Se6	567	586	571.8
	S4	562	580	552.2
Acetonitrile (AcCN)	Se1	577	595	524.3
	Se2	568	588	598.8
	Se3	586	613	751.6
	Se4	572	593	619.1
	Se6	559	579	617.9
	S4	554	572	568.0

The difference in energy between the absorbed and emitted radiation is known as the Stokes' shift. The Stokes' shift values for novel cyanine dyes are collected in Table 1. The absorption and emission spectra of dye under the study show small Stokes' shift. The fluorescence spectra are roughly a mirror image of the absorption spectra (Fig. 2). This indicates that the structure of the dyes upon excitation is unchanged.

3.2. Kinetics study of multifunctional acrylates polymerization

The photoinitiating systems composed of mono- and tricationic cyanine dyes (electron acceptor) coupled with phenyl-trialkylborates (electron donor) were used for the initiation of free radical polymerization of multifunctional acrylate monomer. The structures of the photoinitiators are given in Scheme 4.

The polymerization solution consisted of 1.5×10^{-3} M of sensitizer as a phenyltrialkylborate salt. The polymerization process was initiated by irradiation at 514 nm. At this wavelength only the sensitizer absorbs the light.

In order to optimize the photoinitiation mixture composition, at the beginning, the cyanine borate concentration effect on the rate of polymerization was determined. It is well known that the photoinitiator concentration plays a key role in photopolymerization. In conventional UV/Vis photopolymerization, R_p increases when more initiator is used, however it decreases rapidly if too much initiator is added. This effect is rendered to the "inter filter effect" and becomes more significant for photoinitiators with a high molar extinction coefficient (for tested dyes ε is about 8 × 10⁵ M⁻¹ cm⁻¹). Fig. 3 presents the relationship between the rate of polymerization and concentration of photoinitiator.

It is evident that as the photoinitiator concentration increases, the rate of polymerization increases and reaches a maximum followed by continuous mild decrease. For the tested photoinitiators, under experimental conditions, the highest rate of polymerization was achieved at initiator concentrations of about 1.5×10^{-3} M. The reduction of the photoinitiated polymerization rate at higher initiator concentration (for applied technique of polymerization rate measurement) can be easily understood taking into account the decrease of the penetration depth of the laser beam across the polymerizing formulation layer. Thus, all kinetic measurements for cyanine borate salts were carried out at a concentration equal to 1.5×10^{-3} M.

The kinetic curves obtained for the photoinitiated polymerization of TMPTA–MP (9:1) mixture recorded for selected cyanine borate salts, under irradiation with a visible light laser, are shown in



Fig. 2. Normalized absorption and fluorescence spectra of Se3 dye in THF and DMF.



Scheme 4. Conceptual presentation of an artificial increase of an electron donor concentration in close neighborhood to the excited chromophore for trimmeric cyanine dyes in comparison to monomeric ones.

Fig. 4 for illustration. The rates of photoinitiated polymerization measured for all the tested photoredox pairs are collected in Table 2.

It is apparent from the inspection of the rates of polymerization that the efficiency of the tested photoinitiators depends on both the dye and the borate structure. Among monocationic cyanine borates the highest rates of photoinitiated polymerization were observed for 6,6'-dimethoxy-N,N'-dimethylselenocarbocyanine phenyl-triethylborate (Se3B6) used as initiator.

For the comparison of the photoinitiating efficiency, Fig. 5 presents the kinetic curves observed for free radical polymerization of TMPTA/MP mixture initiated by different photoinitiating systems.

Data presented in Fig. 5 show that the structure of both an electron donor and an electron acceptor in the photoinitiating systems plays an important role in polymerization reaction and has influence on the overall rate of polymerization process. It was found

that the photoinitiator system composed of CQ – NPG couple initiates the free radical polymerization with the highest rate. Additionally, it is evident that the photoinitiating ability of tricationic carbocyanine borate salt (Se1B2) is lower than that observed for the well known visible light photoinitiators.

The differences in photoinitiating abilities of tested systems result from the efficiency of free radical formation. For the tertiary aromatic amines, the electron transfer between an excited acceptor and an electron donor is followed by a proton transfer from the electron donor radical cation to the dye radical anion, which yields a neutral radical initiating polymerization and the reduced radical of the dye [6]. The use of NPG as electron donor gives even more complex processes following the electron transfer that yield the



Fig. 3. Rate of polymerization vs. photoinitiator concentration.



Fig. 4. Family of kinetic curves recorded during the measurements of the heat flow emitted during the photoinitiated polymerization of the TMPTA–MP (9:1) mixture initiated by cyanine dyes–borates complexes marked in the Figure. The dye concentration was 1.5×10^{-3} M, $l_a = 100$ mW/cm². The applied photoinitiators possess identical borates. Inset: Comparison of the photoinitiation ability of cyanine borate salts. The photoinitiators possess the same chromophore and either *n*-butyl-triphenylborate or phenyltriethylborate as an electron donor.

Table 2

No	$E_{red}\left(V\right)$	$E_{00} (eV)^{a}$	$R_p (\mu mol/s)^b$	$\Phi_p^{\ b}$	No	$E_{ox}\left(V\right)$	$\Delta G_{el} (eV)^c$		$R_p \ (\mu mol/s)^c$		Φ_p^{c}	
							Se1B	Se4B	Se1B	Se4B	Se1B	Se4B
Se1	-1.072	2.09	3.90	45.36	B6	0.888	-0.253	-0.187	1.57	0.65	18.29	7.60
Se2	-1.282	2.11	1.64	19.13	B61	0.708	-0.311	-0.245	1.78	0.56	20.71	6.53
Se3	-1.158	2.05	2.06	23.96	B62	0.618	-0.385	-0.319	2.08	0.47	24.32	5.43
Se4	-1.142	2.09	1.30	15.13	B63	0.684	-0.269	-0.203	1.49	0.59	17.36	6.92
Se6	-1.154	2.15	1.29	15.06	B64	0.890	-0.127	-0.061	1.38	0.42	14.82	4.85
S4	-1.184	2.17	1.36	15.78	B65	0.954	-0.063	0.003	1.00	0.18	11.63	2.07

The reduction potentials of the cyanine dyes, the oxidation potential of the tetramethylammonium borate salts, the singlet state energy (E_{00}) of the dyes, the rates (R_p) and the quantum yields (Φ_p) of free radical polymerization of TMPTA/MP (9/1) mixture for tested photoredox couples.

^a Calculated for THF.

^b Calculated for cyanine dyes paired with phenyltriethylborate (series Se1-6B6 and S4B6).

^c Calculated for a series of borates (B6-B65) paired with either Se1 or Se4 cyanine dyes (series Se1B6-65 and Se4B6-65).

free radicals being a result of N-phenylglycine radical cation decomposition [6]. Very complex is also the potochemistry of the titanocene photoinitiators [6,31].

The experimental results suggest that the intermolecular electron transfer process may be the limiting step in the photoinitiated polymerization.

From literature it is well known that the distance between the electron donor and the electron acceptor is guite important for the photoinduced electron transfer reaction, especially when the process occurs in the short-lived singlet excited state. In the case of cvanine borate salts the process is efficient in non-polar solvents in which the electron transfer occurs between components of a tightion pair [9,10]. Our study reveals that a degree of dissociation of such pairs depends on both the structure and concentration of the solute in a complex fashion [20-22,32-34]. However, in simple approximation, a degree of dissociation decreases as the concentration of solute increases (or the concentration of non-dissociated salt is enhanced when the concentration of the solute increases). That is why, the simplest way to increase the efficiency of the polymerization process is the adding of an extra amount of coinitiator (an electron donor) into the polymerization mixture. Traditionally, such a situation is achieved by the attachment of an organic cation that can form an ion pair with a borate anion to an absorbing chromophore [35-37]. In cationic dyes, this is possible



Fig. 5. Family of kinetic curves recorded during the measurements of the heat flow emitted during the photoinitiated polymerization of the TMPTA–MP (9:1) mixture initiated by: A) T (0.001 M); B) DIBF (0.001 M) – NPG (0.001 M); C) CQ (0.01 M) – NPG (0.001 M); D) CQ (0.01 M) – ENB (0.001 M) and E) Se1B2 (0.001 M). Irradiation of the polymerization mixture was carried out using the emission (line at 457 nm or 556 nm) of DDPS lasers (Shanghai Dream Lasers Technology) with intensity of light of 25 mW/ cm².

by the covalent bonding of an extra organic cation that is not a part of the chromophore, which can form an ion pair with the electron donor anion.

Fig. 6 presents kinetic curves, representing monomer conversion as a function of time, obtained by photo-DSC for mono- and tricationic photoinitiators. After an induction period during which polymerization inhibitors are consumed, the polymerization starts causing an increase of medium microviscosity. With the progress of polymerization, reactive functional groups are consumed and polymerization stops as indicated by the plateau on the kinetic profile (Fig. 6).

It was found that the degree of monomer conversion and the quantum yield of photopolymerization depend on the photoinitiator pair's structure. From the data obtained during the measurements, it was also deduced that the conversion of monomer double bonds rises from about 10% to 22%, while the quantum yields of photopolymerization changes from 10 to 48 for the light absorber concentration equals 0.0015 M for mono- (Se4) and tricationic (Se1) photoinitiators, respectively. Generally, the photoinitiator that couple three electron donors in one molecule (Se1) exhibits better photoinitiating ability in comparison to the model monocationic cyanine dye (Se4).

The higher photoinitiating abilities of three-cationic cyanine borate salts can be attributed to an increase of an electron donor concentration in a close proximity to an excited dye molecule



Fig. 6. Family of kinetic curves recorded during the measurements of the heat flow emitted during the photoinitiated polymerization of the TMPTA–MP (9:1) mixture initiated by cyanine dyes – *n*-butyltriphenylborate complexes. The dye concentration was 1.5×10^{-3} M, $I_a = 100$ mW/cm². The applied dyes possess various chromophores and identical borate (B2).

180

150

caused by the presence of the extra borate anions coupled by the covalently linked to dye molecule additional organic cations.

The efficiency of radical polymerization initiated *via* intermolecular electron transfer process (PET) is dependent on the nature of the dye and the electron donor. As can be seen in Fig. 4 (inset), the phenyltriethylborate salt reacted faster than the corresponding *n*-butyltriphenylborate at the same initiator concentration and irradiation conditions.

From Schuster and his co-workers [9,10] reports, it is well known that the irradiation of carbocyanine alkyltriphenylborate salts with visible light absorbed by cyanine leads to the 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 the 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. What is more, Neckers' et al. studies [19] revealed that, in the case of phenyltrialkylborates, the second product formed after an electron transfer process, phenyldialkylborane, is also capable of initiating a chain radical reaction. It can react either with the oxygen centered radical product of addition of the alkyl radical to the vinyl bond of monomers or with the excited state of the sensitizer [38,39] forming additional radicals.

Thus, the overall efficiency of the photoinitiation of radical polymerization can be affected by: (i) the rate of the primary electron transfer process, (ii) the rate of carbon–boron bond cleavage, (iii) the rate of secondary processes and finally (iv) the reactivity of free radicals formed.

Because photoinitiator performance remarkably affects the overall performance of polymerization systems, a significant effort to optimize this important component of the polymerization system is underway.

The efficiency of radical polymerization photoinitiated by the cyanine dyes under study coupled with different co-initiators was evaluated by monitoring the rate of heat evolution during the radical polymerization of multiacrylate.

Fig. 7 presents the family of kinetic curves recorded during an argon-ion laser initiated polymerization of a solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP), 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and different photoinitiating systems with a sensitizer and a co-initiator concentration equal 1.5×10^{-3} M.

From the inspection of the kinetic curves presented in Fig. 7 and data collected in Table 2, it is seen that the initiation ability depends on of the borate anion in the photoinitiators. In the photoinitiating systems shown in Fig. 7, the chromophore structure is the same. This causes that the reduction potential of cyanine dye cannot affect the initiation efficiency. Since the borate salts are efficient electron donor in the photoredox pairs, the difference in their reactivity in the system investigated is related to substantial differences in the oxidation potentials of the borates. The tetramethylammonium *n*-butyltriphenylborate has an oxidation potential of about 1.2 V. This is higher than that of tetramethylammonium phenyltriethylborates, which are in the range of 0.95–0.62 V, meaning that phenyltriethylborate salts are much more reductive than *n*-butyltriphenylborate salt. What is more, substitution on the benzene ring strongly influences the reduction properties of tetramethylammonium phenyltriethylborates. 4-Methoxyphenyltriethylborate (B62), which bears a strong electron releasing substituent, has an oxidation potential of about 0.62 V, while the



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Fig. 7. Family of kinetic curves recorded during the measurements of the heat flow emitted during the photoinitiated polymerization of the TMPTA–MP (9:1) mixture initiated by cyanine dyes–borates complexes marked in the Figure. The dye concentration was 1.5×10^{-3} M, $I_a = 100$ mW/cm². The applied dyes possess identical chromophore and different borates.

4-cyanophenyltriethylborate (B65), which bears a strong electron withdrawing group, has an oxidation potential of about 0.95 V.

The effect of the borate oxidation potential on photoinitiating abilities can be explained on the basis of the Rehm–Weller [40] Equation (3).

$$\Delta G_{el} = E_{ox} \left(D_{/D^{\bullet+}} \right) - E_{red} \left(A^{\bullet-} / A \right) - \frac{Ze^2}{\varepsilon a} - E_{00}$$
(3)

where: ΔG_{el} is the free energy of activation for the photoinduced electron transfer (PET) process, $E_{ox}(D/D^{+})$ is the oxidation potential of the electron donor, $E_{red}(A^{-}/A)$ is the reduction potential of the electron acceptor, E_{00} is the excited state energy of the electron accepting molecule, and $Ze^2/\epsilon a$ is the Coulombic energy, which is the free energy gained by bringing the radical ions formed to an encounter distance "*a*" in a solvent with dielectric constant ϵ . This term, for products of an analyzed reaction, is considered negligible with respect to the overall magnitude of the ΔG_{el} in the present system. The E_{ox} and E_{red} of both photoredox pair components were determined from cyclovoltametric measurements (Table 2). The electrochemical reduction of the dyes is reversible. However, the oxidation of phenyltrialkylborate is dissociative and this in turn causes the electrochemical process to be irreversible as is shown in Fig. 8.

The thermodynamically meaningful oxidation potential can be established using an indirect, kinetic method described by Murphy and Schuster [41]. However, the peak potentials obtained by either cyclic or square wave voltammetry usually follow the same trend as those measured by kinetic methods. Oxidation potentials measured electrochemically and kinetically differ by about 0.3 eV. Therefore, these can be used for the comparison of the borates.

The measured oxidation potential of the borate, the reduction potentials of the dyes, the singlet state energy of the dyes and the free energy change for the photoinduced intermolecular electron transfer process are compiled in Table 2 together with the polymerization results.

The values of ΔG_{el} for tested photoinitiating systems oscillate in the range from 0.003 eV to -0.385 eV. The calculations show that for the tested photoredox pairs the electron transfer process is thermodynamically allowed.



Fig. 8. Cyclic voltammperograms for selected tetramethylammonium phenyltrialkylborates under the study in acetonitrile. Solution contained tetra-*n*-butylammonium perchlorate as the supporting electrolyte and was deoxygenated prior to analysis by purging with argon for 15 min.

Fig. 9 presents the relationship between the free energy of the activation of electron transfer process and either the Hammett constant or the rate of polymerization initiated by the series of phenyltriethylborates and Se1 dye.

Presented in Fig. 9 data show a linear relationship between the free energy of the activation of electron transfer process and Hammett constants of the substituents presented in the benzene ring of the borate salts. This indicates that ΔG_{el} increases as the Hammett constant increases. Since the alkyl radicals formed from borate anion after an electron transfer are the same for all borate salt series, the difference in their reactivity in the system investigated is related to substantial differences in the oxidation potentials of the borates.

A linear relationship is also observed between the free energy of the activation of electron transfer process. According to Fig. 9, the rate of free radical polymerization initiated by the series of cyanine borates increases as the driving force of the electron transfer reaction increases. This type of behavior is predicted by the classical theory of photoinduced electron transfer [42]. This suggests that at the beginning of the TMPTA polymerization, the electron transfer process may be the rate determining step in the radical formation process.

As was previously reported for the alkyltriphenylborates [9,10], the rates of alkyl radical formation, as the result of the boranyl radical degradation, are directly related to the known 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 (k_{-el}) is negligible [9,10]. Therefore, the efficiencies of alkyl radical formation and, hence, the initiation of polymerization depend on the rate of electron transfer from the borate anion to the excited state of the sensitizer.

In an attempt to measure the intramolecular electron transfer, a nanosecond flash photolysis experiment was conducted. The occurrence of the electron transfer between the cyanine cation and borate ions leads to the quenching and simultaneous shortening of the excited state lifetime of the cyanine chromophore. If the electron transfer is the only quenching process of cyanine triplet, the electron transfer rate constants are equal to those of triplet quenching. The quenching rate constant of the triplet state of the cyanine dye can be estimated based on a Stern–Volmer analysis.

A nanosecond time-resolved transient absorption spectroscopy with excitation at 355 nm using the third harmonics of a Q-switched Nd:YAG laser was used to determine the rate



Fig. 9. Relationship between free energy of activation of electron transfer process and either Hammett constant or rate of polymerization initiated by the series of phenyl-triethylborates and Se1 dye.

constants (k_q) for the quenching of the excited state of the dye. The triplet decay rates and transient absorption spectra of Se3 were measured in acetonitrile (MeCN). In the case of Se3 when no electron transfer is expected from the iodide counteranion to the excited triplet state of cyanine cation, the triplet transient absorption spectrum was obtained. The transient absorption spectrum of Se3, showing the triplet decay, obtained in acetonitrile at a different time after the pulse, is shown in Fig. 10, inset.

At the wavelengths above 600 nm we observed positive absorption which decays with a lifetime of about $40-50 \ \mu$ s, depending on the exact quality of the removal of oxygen from the solution. By analogy to the other works described in literature [43,44], we assign it to the triplet absorption of the cyanine moiety.

The triplet state of Se3 was found to be quenched by tetramethylammonium phenyltrialkylborate salts with a concomitant observation of absorptions at 630 nm. Rate constants for quenching were determined by measuring the effects of the additive on the lifetimes of the dye triplet state. Linear Stern–Volmer plots were observed (Fig. 11).

The quenching rate constants obtained by linear fitting of the data in Fig. 11 are $2.32 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $2.48 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $1.29 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for B6, B62 and B65, respectively. The quenching rate is affected by the substituents on the benzene ring in the



Fig. 10. Transient absorption kinetic curve observed at 630 nm at 2 µs after the pulse for 6,6'-dimethoxy-N,N'-dimethylselenocarbocyanine (Se3). Inset: Transient absorption spectra of Se3 in acetonitrile recorded at a different time after the pulse assigned to the triplet state.



Fig. 11. Concentration dependence of the triplet decay rate of the Se3 in MeCN.

borate molecule. For the tested borate series, the B62 borate possessing a strong electron releasing substituent has a less electropositive peak potential and faster electron transfer rate than the B65 salt bearing a strong electron withdrawing group. Rate constants (k_q) for the quenching of the excited states were high and approached diffusion-controlled limits.

4. Conclusion

Cyanine borate salts are shown to be effective photoinitiators for the polymerization of acrylic monomers when irradiated with the visible emission of an argon-ion laser. The efficiency of the polymerization depends on the structure of both the cyanine cation used as an electron acceptor and the borate anion used as an electron donor. The inspection of the rates of polymerization showed that the tricationic cyanine salts initiated polymerization more effectively than monocationic equivalents. The comparative analysis of the borate salts as co-initiators with cyanine dyes shows that the number of alkyl groups per boron determines reactivity. The reactivity of borate anion is determined by the Hammett constants. Generally the rate of polymerization increases when the value of Hammett constants decreases.

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