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Electron transfer processes in photoinitiating systems composed of hemicyanine *sec*-butyltriphenylborate ion pairs

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Summary

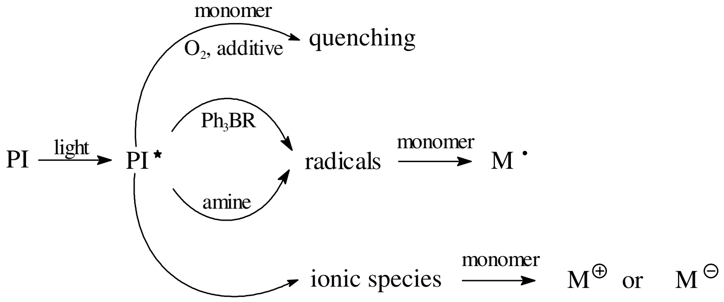
Borate hemicyanine salts, namely *sec*-butyltriphenyl styrylbenzoxazole borates are shown to be effective photoinitiators for the polymerization of vinyl monomers. Mechanism of the photoinitiation involves *sec*-butyl radicals formed from the heterolytic cleavage of carbon-boron bond that follows the electron transfer process. The capability of the salts to act as initiators for the polymerization of multifunctional monomer is documented.

Introduction

Photoinitiated polymerization forms the basis of numerous applications in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics. Almost all of the commercially significant photoinitiators are organic compounds that produce free radicals and/or cationic species upon irradiation. The most widely used free radical photoinitiators include benzoin and its derivatives, benzyl ketals, acetophenone derivatives, aromatic ketone/amine combinations, while onium salts belonging to iodonium, sulphonium and alkoxy pyridinium families represent a class of cationic photoinitiators [1].

Direct photoinduced polymerization reactions concern the creation of a polymer through a chain reaction initiated by light. Since a formation of reactive species from a monomer by direct light absorption is not an efficient route, the initiation step of the polymerization reaction requires the presence of a photoinitiator (PI) which, under light excitation, is capable of generating reactive species that can start polymerization chain reaction (see Scheme 1).

The intrinsic reactivity of PI which plays an important role on curing speed is directly connected with its molecular structure, which governs the intensity of the light absorbed, the absorption wavelength range, the electron transfer reactions ability and the efficiency of the photophysical and photochemical processes involved in the excited states deactivation (which determines the yield of cleavage reactions, the rate of electron transfer reactions, the yield of the quenching by monomer, oxygen or other additives such as, hydrogen donors, light stabilizers, etc.) [2].



Scheme 1. Schematic presentation of reactions following after light absorption by a photoinitiator.

Generally, there are two types of photoinitiators of free radical polymerization:

- Photofragmentable (photodecomposed). Photogeneration of free radicals occurs when a photoexcited molecule undergoes bond cleavage that gives a pair of such species. One or both of the resulting radicals can initiate free radical polymerization
- Two components photoinitiation systems

Photoinduced intermolecular electron transfer is an important process giving as an intermediate free radical able to initiate polymerization chain reaction. The panchromatic sensitization of vinyl polymerization requires the presence of suitable dye as a light absorber. For such a case, photophysical energy transfer between dye excited state and other chromophore which yields free radicals, is generally disfavored. As an alternative other processes avoiding typical energy restriction is usually considered. The photoinduced intermolecular electron transfer, which is nonclassical, endothermic energy transfer process, represents such an alternative. This process involves the use of light to initiate electron transfer from a donor to an acceptor molecule [3,4].

In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiating systems [4,5]. Initiators possessing alkyltriphenylborate anion paired with symmetrical and unsymmetrical cation of cyanine dyes represent such novel group. This group of photoinitiators has been synthesized and has been examined in terms of their efficiency as photoinitiators of free radical polymerization in our laboratory [6-8]. The ability of polymerization photoinitiation of multifunctional acrylate by *sec*-butyltriphenylborate salts of the styrylbenzoxazole chromophoric groups is documented in this paper.

Experimental

Materials

Substrates used for the preparation of the dyes, monomers and solvents were purchased from Fluka, Merck and Aldrich. Dyes listed in Table 1 were obtained in our laboratory by the method described elsewhere [9-14].

Instruments

Absorption spectra were recorded using a Varian Cary 3E spectrophotometer and fluorescence spectra were obtained using a Hitachi F-4500 spectrofluorimeter.

Absorption and emission spectra were recorded using a spectroscopic quality ethyl acetate (EtOAc) as a solvent. Fluorescence measurements were performed at an ambient temperature.

The reduction potentials of hemicyanine dyes and the oxidation potential of the tetramethylammonium *sec*-butyltriphenylborate were measured by cyclic voltammetry. An Electroanalytical MTM System model EA9C-4z (Cracow, Poland), equipped with a small volume cell was used for measurements. A 1-mm platinum disc electrode was used as the working electrode, a Pt wire constituted the counter electrode and an Ag-AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile [6].

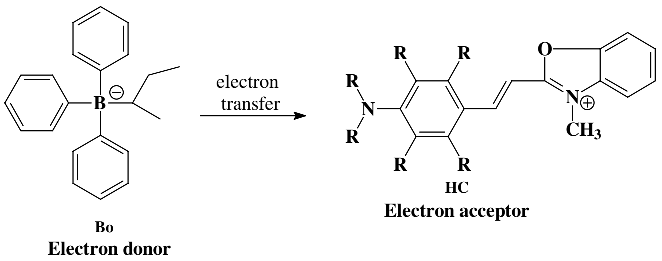
Polymerization

The kinetics of free radical polymerization measurements was carried out by measuring of the rate of heat evolution during polymerization [6-8,15,16]. Measurements were performed in a homemade microcalorimeter. A semiconducting diode immersed in a 2 mm thick layer (0.25 mL) of a cured sample was used as a temperature sensor. Irradiation of the polymerization mixture was carried out using the emission of an Omnichrome model 543-500 MA argon-ion laser, which emits two wavelengths, at 488 and 514 nm. The average power of irradiation was 64 mW/cm^2.

A polymerization solution was composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The hemicyanine borate (**HCBo**) concentration in the formulation was 1×10^{-3} M. As a reference sample, a polymerizing mixture containing hemicyanine iodides (dye without an electron donor) were used.

Results and discussion

The structure of the salts used in the study are shown below:



Scheme 2. Electron transfer reaction from borate anion to hemicyanine cation.

As electron acceptors styrylbenzoxazole dyes (hemicyanine dyes) were used. As electron donor *sec*-butyltriphenyl borate was applied.

Analysis of the kinetic scheme for photoinduced polymerization *via* intermolecular electron transfer process has shown [5,15,16] that for a negligible efficiency of the absorbing chromophore bleaching process (for very low quantum yield of the dye color loss process), and taking into account the Marcus relation [17-19], the following equation can be used for the description of the rate of polymerization in viscous media:

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

where A for the initial time of polymerization is the sum: $\ln k_p - 0.5 \ln k_t + 1.5 \ln[M] + 0.5 \ln I_A$ (where k_p, k_t, [M] and I_a have conventional meanings), λ is the reorganization energy necessary to reach the transition states both of the excited molecule and the solvent molecules and finally ΔG_{el} is the free energy change expressed by the Rehm-Weller equation [20,21].

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

where $E_{ox}(D/D^{\bullet +})$ is the oxidation potential of the electron donor, $E_{red}(A^{\bullet -}/A)$ is the reduction potential of the electron acceptor, E_{00} is the excited state energy, and $Ze^2/\varepsilon a$ is the Coulombic energy, which for products of analyzed reaction is considered negligible with respect to the overall magnitude of the ΔG_{el}. For the evaluation of ΔG_{el} the reduction potential of an electron acceptor is needed. The electrochemical reduction of the selected hemicyanine cation (**B6**), serving as an example in acetonitrile solution is shown in Figure 1 for illustration.

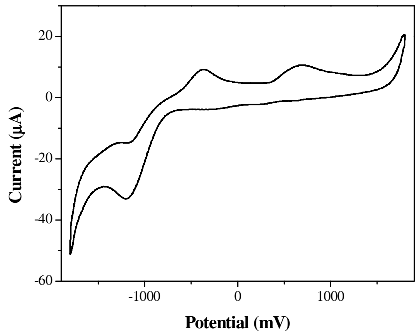


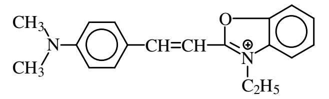
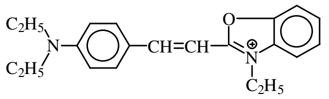
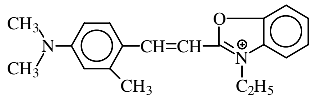
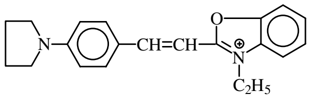
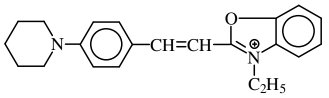
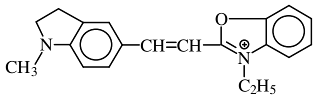
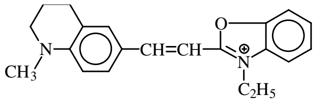
Figure 1. Serving as example cyclic voltaic curve of selected dye. Type of molecule tested shown in the inset.

From the cyclovoltaic curve shown in Figure 1 it is apparent that the electrochemical reduction of hemicyanine cation is reversible, therefore the reduction potentials values for novel dyes may have the thermodynamic meaning. Knowing the reduction potentials of hemicyanine dyes, knowing their singlet state energy (calculated based on the fluorescence spectra, see Table 1) and knowing the oxidation potential of tetramethylammonium *sec*-butyltriphenylborate ($E_{ox} = 0.78$ V) and using the Rehm-Weller equation [20,21] one can calculate the free energy change (ΔG_{el}) for the electron transfer process between hemicyanine cation and borate anion. The structures of the hemicyanine dyes prepared, their electrochemical properties along with all calculated data are collected in Table 1.

Negative values of ΔG_{et} indicate that for all combinations of hemicyanine borate pairs the electron transfer reaction yielding free radicals is thermodynamically allowed, and that the tested salts should initiate the free radical polymerization of the vinyl monomers.

Figure 2 presents typical kinetics curves observed during an argon-ion laser initiated polymerization of the solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP), 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and initiating hemicyanine borate salts with concentration of $1\text{x}10^{-3}$ M. The relative rates of the initial rates of photoinitiated polymerization measured for all the tested photoredox pairs are collected in Table 2.

Table 1. Structures, basic electrochemical and thermodynamical properties of hemicyanine dyes tested.

Dye	Structure of acceptor cations tested	E_{red} [V][a]	E_{00} [eV][b]	ΔG_{el} [eV][c]
B1		-0.575	2.314	-0.857
B2		-0.550	2.309	-0.877
B3		-0.445	2.276	-0.949
B4		-0.470	2.249	-0.989
B5		-0.360	2.288	-1.046
B6		-0.440	2.271	-0.949
B7		-0.460	2.247	-0.951

[a] Measured in MeCN.

[b] Measured in Ethyl Acetate (EtOAc).

[c] Calculated using the Rehm-Weller equation: E_{ox} (D/D$^{\bullet-}$) = 0.790 V.

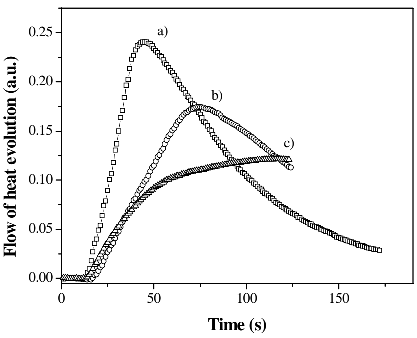


Figure 2. Family of curves recorded during the measurements of the flow of heat during the photoinitiated polymerization of the TMPTA-MP (9:1) mixture initiated by hemicyanine borates. The dye concentration was 1×10^{-3} M and I_a=64 mW/cm^2. The applied pairs possess various chromophores and identical borates (*sec*-butyltriphenylborate): (a) B3Bo, (b) B4Bo, (c) B7Bo.

Table 2. Measured relative rates of polymerization, degree of monomer conversion and quantum yields of the photobleaching process for tested novel hemicyanine borates.

No	Time [s]*	tgα**	1+lnR$_p$ [a.u.]	Monomer conversion [%]	Φ_{polym}	Φ_{bl}
B1	12	0.000069	1.00	0.11	0.69	0.28
B2	19	0.000103	1.40	0.26	1.08	0.71
B3	34	0.003901	5.03	27.78	64.43	0.14
B4	34	0.003971	5.05	15.60	36.18	0.00
B5	20	0.000072	1.04	0.21	0.84	0.70
B6	15	0.000079	1.14	0.08	0.40	0.85
B7	19	0.002825	4.71	6.66	27.67	0.00

„*„ irradiation time for the initial rates of photoinitiated polymerization
„**„ slope of the linear part of photoinitiated polymerization kinetic curve for the initial time of polymerization

The analysis of the initial rates of polymerization shows that the photoinitiation efficiency of tested initiators depends on the structure of hemicyanine borate photoredox pair. It is obvious that only three initiators (dyes: **B3**, **B4** and **B7**) initiate the polymerization with the high observed rate.

From the data, obtained during the measurements, it was also deduced that the conversion of monomer is ranging from 0.1% to 28%, while the quantum yields of photopolymerization oscillates between 0.4 and 64 (Table 2) for the all photoinitiating pairs tested. It is noteworthy that the ion pair marked as **B3Bo** and **B4Bo** shows the best photoinitiation ability with quantum yield of polymerization of about 36 and 64, respectively. It was also found that the degree of monomer conversion depends on the structure of the photoinitiating pair.

The relationship between the rate of photoinitiated polymerization and the free energy of electron transfer process is shown in Figure 3.

It is apparent from the inspection of the data presented in Figure 3 that there is not good correlation between the rate of polymerization and the driving force of electron

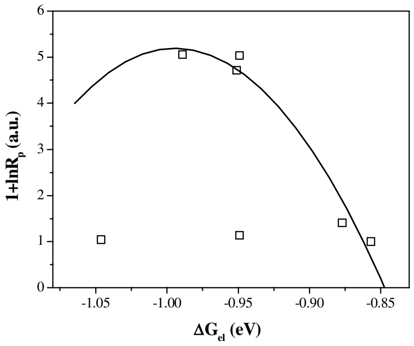


Figure 3. Marcus plot obtained for the rates of polymerization of TMPTA-MP mixture initiated by hemicyanine – borate photoredox pairs (for dyes listed in Table 1).

transfer reaction. We observe only a trend, which is predicted by the classical theory of photoinduced electron transfer [17-19].
Irradiation of hemicyanine borates causes, as it is shown in Figure 4, a bleaching of the dye.

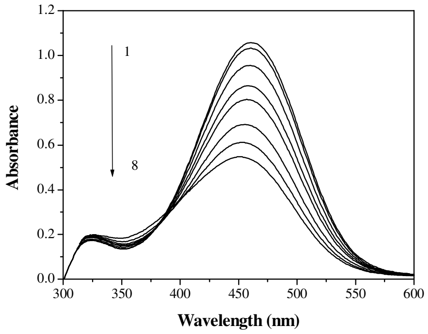


Figure 4. Changes of the electronic absorption spectra of **B3Bo** during an argon-ion laser irradiation ($I_a = 50$ mW/cm^2) in EtOAc solution. Time of irradiation: (1) – 0 s, (2) – 2 s, (3) – 20 s, (4) – 50 s, (5) – 90 s, (6) – 210 s, (7) – 510 s, (8) – 1110 s.

According to the general kinetic scheme for polymerization photoinduced by cyanine dyes in the presence of alkyltriphenylborate salts, the colorless product obtained during the polymerization originates from cross-coupling reaction between an *sec*-butyl radical and a cyanine radical formed from both an electron donor and an electron acceptor [6,8,22-25]. The analysis of the bleaching process shows that the quantum yields of these reactions for radicals pairs under study oscillate between 0.00 and 0.85. For initiators **B2, B5, B6** the values of the quantum yields of the bleaching process is close to the value of the quantum yield of *sec*-butyl radical formation ($\phi = 0.78$), determined for the symmetrical cyanine dyes [23] (see Table 2). This observation permits to conclude that the bleaching process might decrease the efficiency of the free radical polymerization. From the inspection of the data presented in Table 2 one can also conclude that the styrylbenzoxazole borate salts are characterized by the highest value of the quantum yield of the bleaching process and are rather poor photoinitiators of the free radical polymerization of TMPTA.

Conclusion

Photoinitiated by **HCBo** pairs polymerization occurs through the electron transfer process. The efficiency of the polymerization significantly depends on the structure of the hemicyanine cation used as an electron acceptor. It is obvious that the bleaching process is competing with polymerization process.

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