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Difluoroboranyl derivatives as efficient panchromatic photoinitiators in radical polymerization reactions

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Abstract Photoinitiating systems based on BF_2 derivatives and tetramethylammonium phenyltriethylborate salt were tested in photopolymerization reactions through the photo-DSC method. The good rates of TMPTA polymerization and final monomer conversion were obtained for tested system. The effect of the type of heterocycle on their properties was revealed. The excited state processes, investigated by nanosecond flash photolysis, lie on a fast excited state photoinitiated cleavage leading to reactive species. A triplet state is observed for investigated derivatives.

Keywords Polymers · Radical polymerization · Photochemistry · Difluoroboranyls

Introduction

Compounds containing BF_2 moiety are a class of fluorescent dyes. They are usually characterized by: (a) high extinction coefficient, (b) high fluorescence quantum yield, (c) narrow emission band, (d) relatively long excited-state lifetime, (e) great photostability and (f) large two-photon absorption cross-section [1–3]. The photophysical and photochemical properties of the fluorescent difluoroboranyl dyes can be easily modified, e.g. by an introduction of the suitable substituent [2], by

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altering atoms through, which the BF_2 group is attached to the molecule [4, 5] or by changing the conjugation path [6, 7] or their structure from symmetrical to unsymmetrical one [8–10]. Among various compounds carrying the BF_2 moiety the most common are boron–dipyrromethenes (BODIPYs) [8, 11]. The core of the dyes is a complex of dipyrromethane with a disubstituted boron atom, typically a BF_2 unit [12]. This means that BF_2 group is attached to two nitrogen atoms. Another examples are β-diketonate (OBF_2O) and β-ketoiminate (NBF_2O) difluoroboranyls [13]. Their easy functionalization makes the dyes very attractive as immobilized [13] probes or indicators [2, 14], as dyes for biolabelling [15], chemodosimeters [16]. They also are used in solar cells applications [17]. Furthermore, they can find an application in the other fields of technology making use of interaction of light with matter.

Polymerization is any process of converting monomer molecules into linear chains or three-dimensional network of polymer chains [14, 15]. A lot of studies have been published in this area because polymerization process is very important from practical viewpoint. There are many kinds of polymerization and different systems exist to categorize them. Photopolymerization is one of the most important processes in that field. It makes use of radiation in the ultraviolet (UV) or visible (Vis) range of light to generate reactive species such as radicals or ions [16, 17] that reacts in a chain reaction. Thus, the photoinitiation of polymerization requires the presence of molecule capable of absorbing light of the appropriate wavelength (photoinitiator, PI) and generating reactive species alone. Moreover, radicals or ions can be formed by primary or subsequent reactions involving, beside PI, one or more additional compounds (photoinitiating system, PIS). Photoinitiated radical polymerization, which is one of the most common and useful polymerization reactions, may be initiated by one-component system leading to homolytic cleavage process (type I PI) or by two-component systems producing radicals through a hydrogen transfer, an electron/proton transfer or an energy transfer (type II PI). The type II PIs are generally composed of PI and either a hydrogen donor (HD) or a photosensitizer (PS) [18–22]. One- and two-component systems are also used to start photoinduced cationic polymerization. Classical cationic PIs are onium salts [23].

The light-induced polymerization reactions are very important in different industrial sectors, such as radiation curing, imaging, microelectronics, medicine or optics [15]. The development of high-performance PISs operating upon visible light exposure is still a challenge. Recently Lalevée et al. [15, 24] have reported the photoinitiators based on the BODIPY and boranil chromophores. These dyes are characterized by high tunability of the absorption allowing triggering the cationic polymerization at any wavelengths in the 400–600 nm range. Upon visible light exposure these dyes are able to photosensitize the iodonium salt decomposition. This results in the formation of radical cation of the dye (dye$^{·+}$) and aryl radical of the iodonium salt (Ar·) and then by subsequent reactions leads to cationic polymerization of epoxy, epoxy-silicone and vinyl ether monomers [24, 25]. What is more, the addition of silanes to the BODIPY/iodonium salt couples increases the efficiency of the polymerization. The boron–dipyrromethenes were also introduced in PISs in combination with a photoacid generator for the design of photoresists. On the other hand, the three-component system boranil/methyldiethanolamine/

phenacylbromide or pyrromethane dye/amine/triazine derivatives were proposed as PISs for radical photopolymerization. However, they initiated trimethylolpropane triacrylate (TMPTA) polymerization with low final conversions [18].

The present study was undertaken to reveal the polymerization initiation ability of new photoinitiating system based on difluoroboranyl dyes of the type NBF_2O and phenyltriethylborate salt. Our intention was to show that panchromatic sensibilization of radical polymerization can be achieved by benzannulation of the parent dye.

Experimental

Materials and methods

The general method of the synthesis of tetramethylammonium phenyltriethylborate salt (**B6**) and dyes **1**, **2**, **3** and **4** together with their spectral characteristic are described elsewhere [26–30]. Solvents and monomers [trimethylolpropane triacrylate (TMPTA), 1,6-hexanediol diacrylate (HDODA), lauryl acrylate (LA)] were obtained commercially from Aldrich Chemical Co. and used as received.

Absorption and fluorescence spectra were measured with 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^{-1} (pulse width about 4–5 ns) was used for the excitation. Transient absorbances at pre-selected 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.

The electrochemical characteristics of the compounds were investigated using a cyclic voltammetry (Electroanalytical Cypress System Model CS-1090) employing a 1 mm platinum electrode as working electrode, a platinum wire as counter electrode and an Ag/AgCl (3.0 M KCl) electrode as reference electrode. The cyclic voltammograms were obtained from a one-compartment glass cell in 0.1 M tertrabutylammonium perchlorate as a supporting electrolyte, where the scan rate was 100 or 400 mV s^{-1}.

The investigation of the polymerization kinetics was based on the measurements of the rate of the heat evolution during the chain reaction in thin film cured sample (0.035 ± 0.002 g) using photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. Irradiation of the polymerization mixture was performed using a diode pumped solid state (DPSS) laser (line at 473 nm) with the intensity of light of 100 mW cm^{-2} (or a DPSS laser line at 457 nm with the intensity of light of 150 mW cm^{-2}; or an argon ion laser Model Melles Griot 43 series line at 488 nm with the intensity of light of 100 mW cm^{-2}). Polymerization solution was composed of γ-butyrolactone (1 mL),

2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA; 9 mL), difluoroboranyl derivative ($A_{473nm} = 2$) and **B6** (0.003 M). A reference formulation did not contain an electron donor (**B6**).

The rate of polymerization (R_p), the conversion of the vinyl groups (C) and the quantum yield of polymerization Φ_p were determined based on the well known equations [31–33].

Results and discussion

We focused our attention on the possibility of an application of difluoroboranyl dyes as a component in the photoinitiating systems for the polymerization of acrylic monomers. The tested difluoroboranyl derivatives (dyes **1**, **2**, **3** or **4**) were applied as visible light absorbing molecules in the presence of phenyltriethylborate tetramethylammonium salt (**B6**) used as an efficient electron donor in the excited state (see Fig. 1).
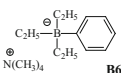
The crucial parameters in photopolymerization are a compatibility of the PIS absorption spectrum with an emission spectrum of the light source and the number of available incident photons. Thus, the spectral properties of the PI have a big impact on the polymerization rate, R_p, which is directly connected with the amount of light absorbed [34]. As shown in Figs. S1 and S2 (in Supporting Information), the difluoroboranyls exhibit absorption in the visible wavelength range (for λ_{max} see Table 1), which allows a good matching with the visible-light emission of various sources, for example, diode lasers at $\lambda = 408, 457$ or 473 nm. At these irradiation wavelengths the electron donor is transparent.

For tested photoinitiator systems we assumed that the initiation of polymerization proceeds by an electron transfer mechanism. The electron transfer from the borate salt to the excited difluoroboranyls is feasible if the change of the free enthalpy for the photoinduced electron transfer (PET) process (ΔG_{el}) is negative [35, 36]. The ΔG_{el} values for the tested photoredox pairs were estimated on the basis of the oxidation potential (E_{ox}) of the borate salt, singlet (E_{00}) and triplet (E^T) state energy of the dyes and their reduction potential (E_{red}) using Rehm–Weller equation
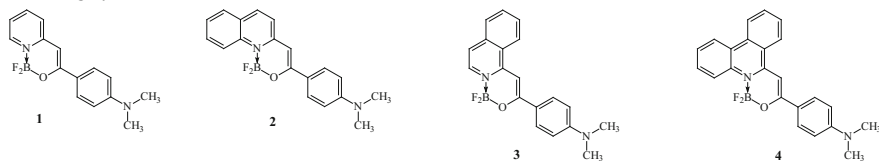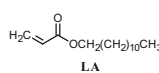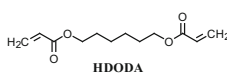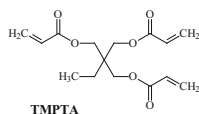

Fig. 1 Structures of the sensitizing dyes, co-initiator and monomers under the study

Table 1 Spectral characteristic of difluoroboranyl derivatives in ethyl acetate (EtOAc) ($\lambda_{ex} = 404$ nm for **1**, **2** and **3**, and $\lambda_{ex} = 450$ nm for **4**)

	1	**2**	**3**	**4**
λ_{max}^{ab} (nm)	416	468	458	475
ε (10^4 M^{-1} cm^{-1})	3.67	4.52	3.03	6.41
λ_{max}^{fl} (nm)	499	534	520	536
Δv (cm^{-1})	3998	2641	2603	2396
ϕ_{fl}	0.699	0.614	0.663	0.655
τ_1^{fl} (ns)	0.442	0.358	0.255	0.314
α_1 (%)	3.76	3.41	3.40	2.69
τ_2^{fl} (ns)	2.647	2.777	2.695	2.746
α_2 (%)	96.24	96.59	97.6	97.31
τ_{av}^{fl} (ns)	2.56	2.69	2.61	2.68
k_r (10^8 s^{-1})	2.73	2.28	2.54	2.45
k_{nr} (10^8 s^{-1})	1.17	1.43	1.29	1.29
λ_{00} (nm)	456.6	496.9	489.2	501.2
E_{00} (eV)	2.716	2.495	2.535	2.474
λ_T (nm)	511	560	535	570
E^T (eV)	2.43	2.21	2.32	2.18

Absorption (λ_{max}^{ab}; nm), fluorescence maxima (λ_{max}^{fl}; nm), Stokes shift (Δv; cm^{-1}), maximum extinction coefficient (ε; 10^4 M^{-1} cm^{-1}), fluorescence quantum yield (ϕ_{fl}), fluorescence lifetimes (τ; ps), their amplitudes (α), average lifetime, τ_{av} calculated as $\tau_{av} = (\Sigma_i \alpha_i \tau_i)/(\Sigma_i \alpha_i)$, radiative ($k_r$; 10^8 s^{-1}) and non-radiative (k_{nr}; 10^8 s^{-1}) rate constants and singlet (E_{00}) and triplet (E^T) state energy

[37]. The obtained data are collected in Table 2. The reduction potential of the dyes and the oxidation potential of the borate salt were measured by cyclic voltammetry. The oxidation potential of the **B6** is 0.764 V, the excitation energies of the sensitizers and their reduction potentials are summarized in Tables 1 and 2. The values of ΔG_{el} for tested photoinitiating systems oscillate in the range from -0.778 to -0.990 eV for the S$_1$ excite state and from -0.480 to -0.701 eV for the T$_1$ excited state. The calculations clearly show that the electron transfer in both the singlet (S) and triplet (T) excited states of the difluoroboranyls-**B6** systems is thermodynamically favorable and suggest that the photoredox pairs should effectively generate free radical initiating polymerization of acrylic monomers.

The good polymerization profiles were obtained using two-component systems containing difluoroboranyl dyes and **B6** upon blue light irradiation (Fig. 2). The formation of the polyacrylate network was easily characterized by measuring photopolymerization exotherms using photo-DSC apparatus. The polymerization under UV–Vis light irradiation in the presence of tested difluoroboranyls without a co-initiator was not observed.

The heterocyclic ring in the difluoroboranyl dyes affects the initiating ability of these two-component systems with a reactivity following the order: **3**, **2**, **4**, and **1**. These results highlight the interest of an appropriate selection of the difluoroboranyl derivatives to improve the polymerization process. For the best initiating system (0.001 M **3** + 0.0075 M **B6**; $I_0 = 100$ mW cm^{-2} at 488 nm), the polymerization rate is ca. 15 µmol s^{-1}, the conversion of carbon–carbon double bonds reaches about 70% after 60 s of irradiation. Figures 3 and S3 illustrate the photo-DSC profiles of TMPTA and HDODA initiated by **1**+**B6**, **2**+**B6**, **3**+**B6** and **4**+**B6** systems. The obtained data are collected in Table S2 in SI.

Table 2 Reduction potential of the difluoroboranyl derivatives (E_{red}), free energy of activation for the PET process (ΔG_{el}), rates (R_p), quantum yields (Φ_p) and monomer conversion (C) for TMPTA polymerization for tested photoinitiators

No.	E_{red} (A/A^{-}) (V)	$\Delta G_{el}^{(S)}$ (eV)[a]	$\Delta G_{el}^{(T)}$ (eV)[a]	[b]473 nm, 100 mW cm^{-2}			[c]457 nm, 150 mW cm^{-2}			[d]488 nm, 100 mW cm^{-2}		
				R_p (µmol s^{-1})	Φ_p	C (%)	R_p (µmol s^{-1})	Φ_p	C (%)	R_p (µmol s^{-1})	Φ_p	C (%)
1	− 0.962	− 0.990	− 0.701	2.64	33.5	44	6.95	60.7	57	–	–	–
2	− 0.936	− 0.795	− 0.514	3.25	41.1	38	7.87	68.7	64	11.9	145.3	59
3	− 0.964	− 0.807	− 0.590	3.37	44.1	49	8.47	73.9	66	15.2	186.5	71
4	− 0.932	− 0.778	− 0.480	2.97	37.7	39	7.22	63.0	52	9.14	112.0	62

[a]For the ΔG_{el} calculation the oxidation potential of the tetramethylammonium phenyltriethylborate salt (**B6**) was 0.764 V

[b]Co-initiator (**B6**) concentration was 0.003 M, optical density (OD) of the dyes was 2 at the excitation wavelength (473 nm)

[c]c(**B6**) = 0.003 M, OD$_{457nm}$ = 2

[d]c(**B6**) = 0.0075 M, c(dye) = 0.001 M

Fig. 2 Family of kinetic curves recorded by the measurements of the heat flow emitted during the photoinitiated polymerization of the TMPTA initiated by difluoroboranyl derivative—phenyltriethylborate salt marked in figure. The optical density of the photoinitiator was 2, $I_0 = 100$ mW cm^{-2} at 473 nm. The applied systems possess different BF$_2$-dyes and the identical borate salt

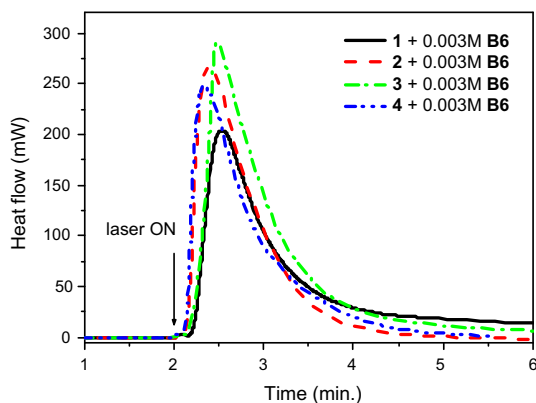**Fig. 3** Rate vs. conversion for photopolymerization initiated by **1**+**B6**, **2**+**B6**, **3**+**B6** and **4**+**B6**, cured at r.t. by visible light (457 nm) with an intensity of 150 mW cm^{-2}. The optical density of the photoinitiator was 2, the **B6** concentration was 0.005 M (solid line denotes data of TMPTA polymerization; dash line—HDODA polymerization)
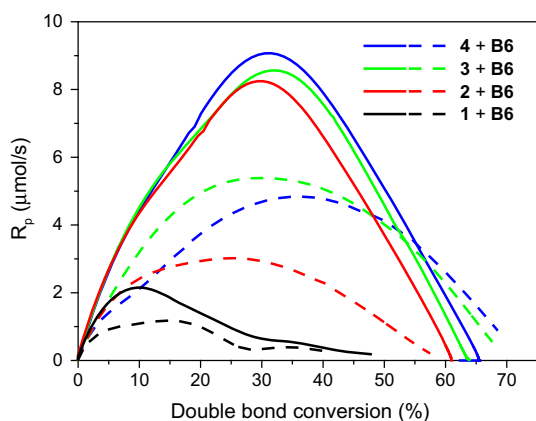
Fig. 4 Comparison of photoinitiating abilities of photoinitaing systems based on difluoroboranyls— phenyltriethylborate salt (**B6**) to analogous systems containing suitable styryl dyes as a sensitizer (structures presented in SI). The optical density of the photoinitiator was 2, $I_0 = 150$ mW cm^{-2} at 457 nm, the **B6** concentration was 0.003 M
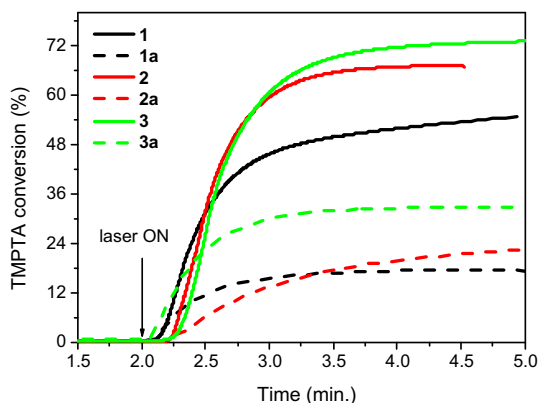
Based on the kinetic data presented in Figs. 4 (for structures **1a**–**3a** see Table S1) and S4, it is also seen that the rigidity of the sensitizer molecules by introduction of BF$_2$ unit increases significantly the photoinitiating ability of the tested systems. The

observed rates of polymerization and monomer conversion (for the same experimental conditions) are about 2.5 times higher than that observed for styryl dyes—borate salts for which these parameters are in range from 1.21 to 3.98 μmol s^{-1}, and from 12 to 30%, respectively. Therefore, tested difluoroboranyls appear to be highly efficient to photosensitize the tetramethylammonium phenyltriethylborate salt decomposition.

It must be pointed out, that not only photoinitiator type influences the photoinitiating ability but also a relative amount of the dye in the solution (Fig. S5 in SI). Our studies have shown that the highest rates of polymerization, for a given condition, were achieved at the initiator concentration related to the optical density that equals 2. For this condition, almost whole incident light is absorbed across the entire polymerizing formulation layer. Furthermore, the TMPTA final conversion is dependent on the co-initiator concentration in the polymerizing formulation and increases from ca. 25–35 to 55–70% with an increase in the **B6** content of about 7.5 times (Figs. S6, S7 in SI).

The photoinitiating abilities of the systems composed of difluorobaranyls and phenyltriethylborate salt are comparable to the commercial photoinitiators for acrylates photopolymerization such as Irgacure 819 [BAPO; bis(2,4,6-trimethyl-benzoyl)-phenylphosphineoxide] and Darocur TPO [TMDPO; diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide]. For example, as it is known from Arsu et al. studies [38], for one-component photoinitiating system based on either TMDPO or BAPO, the degree of double bond conversion in TMPTA is equal 30%, and 40% for addition of mercaptothioxanthone (TX–SH) to the initiator formulation [38]. According to Fouassier et al. [39], photopolymerization profile of TMPTA in laminate in the presence of the commercial photoinitiator BAPO on the exposure to
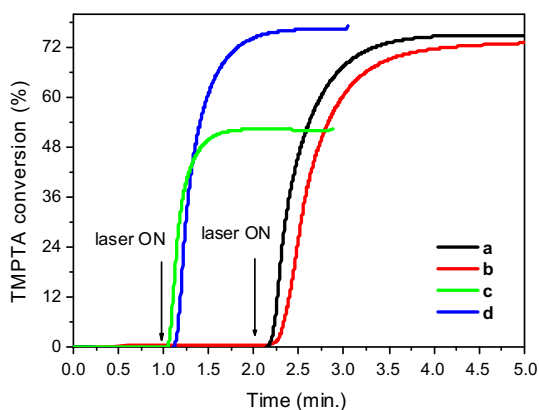

Fig. 5 Comparison of the TMPTA polymerization initiated by following systems: **a 3** (0.001 M) + **B6** (0.0075 M), laser beam $\lambda = 488$ nm 100 mW cm^{-2}, solvent: γ-butyrolactone; **b 3** ($A_{457nm} = 2$) + **B6** (0.0075 M), laser beam $\lambda = 457$ nm 150 mW cm^{-2}, solvent: γ-butyrolactone; **c DIBF** (5,7-diiodo-3-butoxy-6-fluorone, 0.001 M) + **NPG** (N-phenylglycine, 0.01 M), laser beam $\lambda = 488$ nm 100 mW cm^{-2}, solvent: 1-methyl-2-pyrrolidinone; **d** titanocene [Ti(C$_6$F$_5$)$_2$(C$_5$H$_4$)$_2$, 0.001 M], laser beam $\lambda = 488$ nm 100 mW cm^{-2}, solvent: 1-methyl-2-pyrrolidinone. Arrows indicate start of irradiation

LED at 405 nm indicates 56% of monomer conversion. As illustrated in Figs. 5 and S8, when using the laser at 488 nm the photoinitiating system composed of difluoroboranyl **3** and **B6** is capable of initiating the TMPTA polymerization with similar degree of double bonds conversion (ca. 70%) to the popular one-component visible light initiator—titanocene but led to relatively lower polymerization rates (15 vs. 29 μmol s^{-1}). It is also noteworthy that the **3–B6** photoredox pair exhibits only slightly worse photoinitiating ability with lower polymerization rates but higher conversion than two-component system based on common triplet state photoinitiator (**DIBF–NPG**).

From the comparison, it seen that, the new photoinitiating systems are efficient and yielded good final conversion of TMPTA, which endows the system with potential applications in the manufacture of coatings. Furthermore, during the photopolymerization, a noticeable bleaching of the dyes in the presence of **B6** was observed. The said loss of color indicates that, beside the initiation of radical polymerization, PET process in the donor–acceptor systems leads to the bleaching of the primary absorber.

According to the general equation (Eq. 1) [40], the polymerization rate (R_p) depends on the square root of the absorbed light intensity (I_a) and is directly proportional to the monomer concentration ([M]).

$$R_p = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = k_p \left(\frac{\phi_d I_a}{2k_t} \right)^{0.5} [M]. \tag{1}$$

Analysis of the kinetics of radical polymerization indicates that the linear relationship is observed when one radical obtained after PET is an initiating radical while the second type of radical terminates the chain [35]. Figure 6 presents relationship between the rate of TMPTA polymerization as a function of power of laser beam. The observed trend is in good accordance with Eq. (1). The polymerization rates are proportional to the I_0 square root. This observation shows that the light intensity has no effect on the quantum yield of free radical formation ϕ

Fig. 6 The rate of polymerization vs. light intensity for the **4-B6** system (photoinitiator concentration = 0.001 M)

y=1.0098x - 1.9767
R^2=0.988
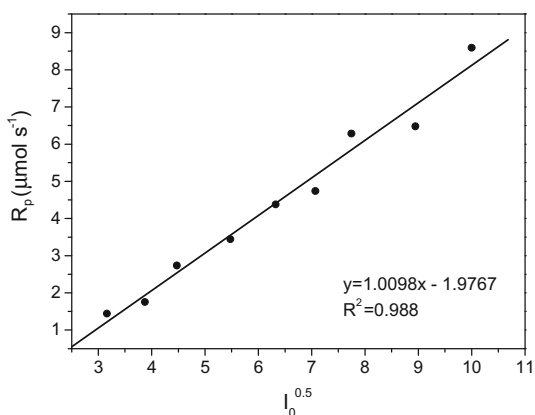
[41] and suggests that the polymerization follows a typical radical chain mechanism with second-order termination [35].

It is well-known that the alkyl radical formed from borate salts as a results of the electron transfer from borate anion to the excited state of sensitizer leading to boranyl radical followed by its decomposition initiates radical polymerization of acrylates [42, 43]. To study the photochemical process that occurs in the excited state of the difluoroboranyl complexes, the nanosecond laser flash photolysis was used. Transient absorption spectra of the tested dyes have been performed in acetonitrile at room temperature, on exciting at 355 nm (see Fig. 7 for compound **4** and Fig. S9 in SI). For **4**, the bleaching in the range 400–500 nm is formed immediately after excitation, coupled with a transient absorption growing at wavelengths longer than 500 nm. The bleaching band is probably due to the depletion of ground state of the difluoroboranyl. The same trend was observed for compounds **1**, **2** and **3** (see Fig. S9 in SI). The positive absorption band observed in helium-saturated acetonitrile solution exhibits a maximum at ca. 520–570 nm (Figs. 7, S9). Based on the literature data connected with triplet state absorption spectra of BODIPY derivatives [44–50] this band may be attributed to the triplet state of currently investigated complexes.

Absorption of the T_1 state decays completely in 5 μs after the excitation in a first-order kinetics. The triplet-state lifetimes were determined as 2.3, 2.7, 2.3, and 2.1 μs, for **1**, **2**, **3** and **4**, respectively, which is much shorter than a classical BODIPYs, e.g. *trans*-bis(trialkylphosphine) bisacetylide complex with BODIPY ligand (not styrylBODIPY ligand, $\tau_T = 128$ μs) [51] or a C_{60}-styrylBODIPY dyad (71–123 μs) [52]. However, this lifetime is close to that observed with heavy atom effect ($\tau_T = 1.8$ μs) [53] or *trans*-bis-(trialkylphosphine) Pt(II) bisacetylide binuclear complex with BODIPY ligand ($\tau_T = 5.8$ μs) [54]. It is fair to mention that the spectra are noisy and difficult to more precise interpretation.

The triplet state of the difluoroboranyls is quenched by tetramethylammonium phenyltriethylborate salt (**B6**) with a concomitant observation of absorptions at 550–570 nm (see Figs. S10, S11 in SI). Figure S11 presents a transient absorption kinetic curve at 1 μs after pulse for compound **4** in deoxygenated solution without and with the presence of borate salt **B6**. Taking into account the T_1 state lifetime in

Fig. 7 Transient absorption spectra of **4** in helium-saturated acetonitrile recorded at a different time after the pulse assigned to the triplet state
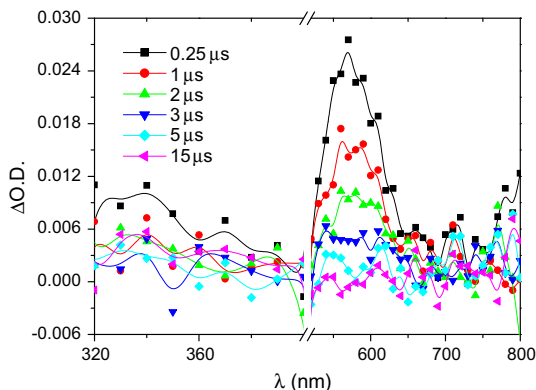
the presence of borate salt **B6** and its concentration in the solution, the rate constant of T_1 state quenching (k_q) was estimated based on the classical Stern–Volmer plot (Fig. 8).

Assuming that the electron transfer is the only quenching process of the difluoroboranyls, the electron transfer rate constants (k_{el}'s) are equal to those of triplet quenching [35]. According to the data shown in Fig. 8, the quenching rates (k_q) are affected by the heterocycle ring in the dye molecule and are lower than the rate constant of the diffusion controlled reaction. For the tested photoinitiating systems, the triplet state of compound **3** was the most effectively quenched by **B6**. The slowest electron transfer rate was determined for dye **1**–**B6** photoredox pair. These results demonstrate that the quenching rates are in quite good agreement with polymerization data (see polymerization rates collected in Table 2). Thus, for more effective photo initiating system higher quenching rate was observed.

The obtained results confirmed that tested difluoroboranyl dye–phenyltriethylborate salt photoredox pairs are efficient initiators of free radical polymerization initiated by the light in visible region. Having in mind a wide range of developed applications, there are a lot of advantages of such a panchromatic sensibilization, e.g.: (1) more efficient utilization of mercury lamp due to the absorption of visible photons by a UV–Vis PI, (2) the possibility to use lasers as a light source which gives a better matching of the emission spectrum of the emitter to the absorption spectrum of the sample, (3) the opportunity to use the sunlight for polymer curing [54]. It is also common that the spectral properties of organic compounds and difluoroboranyls may be turned by a variety of methods [26]. However, our previous studies revealed that the influence of the substituent on the main absorption band is limited [26–28]. In this work, we demonstrated that an extension of the spectral sensitivity to visible lights might be achieved by benzannulation. As shown in Table 1, the absorption maximum shifts to the red of about 42–59 nm depending on the position of the benzannulation and the number of aromatic rings adapting the difluoroboranyls to irradiation with light emitting diodes (LEDs), diode-pumped solid-state lasers (DPSSLs) and other conventional light sources. Furthermore, extension of the spectral sensitivity does not reduce the photochemical reactivity of

Fig. 8 Concentration dependence of the triplet decay rate of the difluoroboranyls tested in acetonitrile in the presence of borate salt (**B6**)
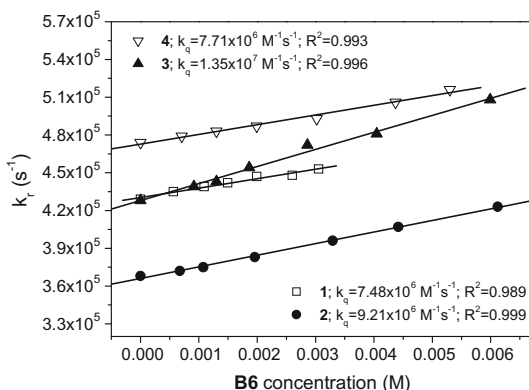
these systems, but it increases the polymerization rate and the double bonds conversion of the monomer.

Our studies also revealed that crucial effects on polymerization rate have the concentration of both components of the photoinitiating systems and the light intensity. It was found that the addition of an electron donor to the composition accelerates the chain reaction. Furthermore, laser flash photolysis experiments showed the excited singlet state of the difluoroboranyls may undergo intersystem crossing to give the excited triplet state (^{3}PI). ^{3}PI interacts with borate salt to produce reactive species. Rate constants (k_q) for the quenching of the excited states of the dyes were low, below diffusion controlled limits and they were dependent on the heterocyclic ring in the sensitizer molecule.

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