Applicability of Hemicyanine Phenyltrialkylborate Salts as Free-Radical Photoinitiators in the Visible-Light Polymerization of Acrylate

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ABSTRACT: The photoinitiation ability of photoredox pairs composed of a hemicyanine dye cation and different borate anions for the radical polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate was investigated. In such a system, the excited dye chromophore is reduced by different tetraorganylborate anions. Upon irradiation at 488 nm, reductive carbon–boron bond cleavage occurs, producing reactive radicals, which start the chain reaction. The efficiency of bond-breaking processes was found to be dependent on the nature of both the acceptors and the donors. The experimental results show that the photoinitiating ability of the tested photoredox pairs were controlled by both the driving force of the electron-transfer process between the electron donor and the electron acceptor and the reactivity of the free radical that resulted from the secondary reactions occurring after the photoin-duced electron-transfer process. Using the nanosecond flash photolysis method, we studied the spectral and kinetic characteristics of the triplet state of cyanine dye and determined the rate constants of the triplet quenching by phenyltrialkylborate salts. The results obtained show that the tetramethylammonium phenyl-tri-*n*-butylborate (TB7) has a faster electron-transfer rate than the tetramethylammonium *n*-butyltriphenylborate (TB2) salt, which bore only one butyl group attached to the boron. The relative initiator efficiency of the triphenylbutylborate salts, as compared to the corresponding phenyltrialkylborate salts with a common chromophore, was determined. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3535–3544, 2012

Key words: dyes/pigments; initiators; kinetics (polym.); photopolymerization, radical polymerization

INTRODUCTION

Photoinduced electron-transfer reactions represent an important route to free radicals, among whose uses is the initiation of vinyl polymerization.[1,2] It is apparent that borate anions are especially beneficial electron-transfer donors, and these have many important applications in the free-radical polymerizations initiated by different electron-acceptor sensitizers. The one-electron photooxidation of tetraorganylborate anions forms a boranyl radical, which lives for a very short time and cleaves rapidly to yield a free radical, which initiates polymerization:[3]

$$R_4B^- - le^- \rightarrow R_3B + R^\bullet \qquad (1)$$
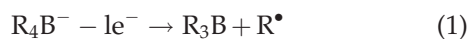
It is a common belief that useful organoborate salts must contain at least one alkyl group directly linked to the boron to be effective co-initiators for the photoinitiation of free-radical polymerization. Tetraarylborate salts have been thought to be inefficient on the basis of the general notion that aryl radicals are poorer initiating species, less stable, and more difficult to generate from oxidized borates than alkyl radicals. In fact, in model studies with triphenylbutylborate co-initiators, there has been no evidence whatsoever for a free phenyl radical.[4] However, tetraarylborates and, in particular, tetraphenylborates are more stable and easier to make than the corresponding arylalkylborates; this suggests an important advantage.[4,5]

Schuster et al.[6] showed that carbocyanine alkyltriphenylborates underwent electron transfer to yield an alkyl radical and triarylborane when the anion/cation was assembled as a tight ion pair. As a result of these studies, the alkyltriphenylborates are probably best known as free-radical initiators for vinyl photopolymerization,[7,8] but they are also a potential source of Lewis acids. Zhu and Kochi[9] first reported intramolecular alkyl transfer from alkyltriphenylborates to pyridinium, quinolinium, and isoquinolinium cations.

Several related photoinitiating systems, which include various visible-light and IR absorbing dyes in combination with a variety of borates,[10–14] have been investigated. However, there have been almost
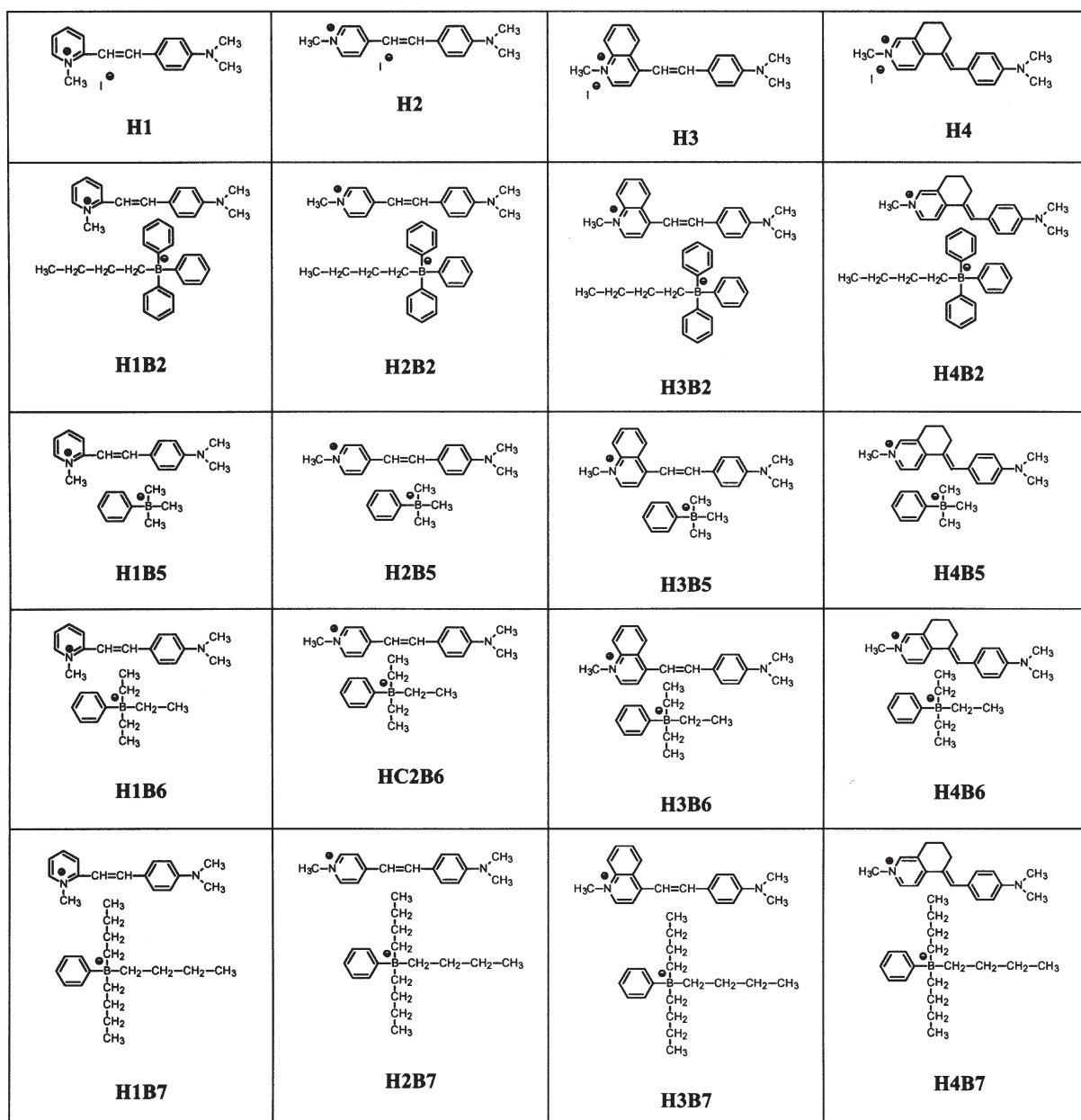
Figure 1 Structure of the hemicyanine borate salts applied as photoinitiators in the visible-light polymerization of TMPTA.

no studies of the structural relationships in borates with more than one alkyl ligand on boron. Most of the reports have been confined to triarylalkylborate or tetraarylborate systems.[10–12]

In this study, the polymerization kinetics of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) in the presence of three pairs of borate initiators were compared. Each pair of borate salts contained the same light-absorbing chromophore as the cation and either phenyltrialkylborate or *n*-butyltriphenylborate (B2) as the counter anion. The hemicyanine borate photoredox pairs under study are shown in Figure 1.

EXPERIMENTAL

Materials

TMPTA, 1-methyl-2-pyrrolidinone (MP), tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) were purchased from Aldrich Chemical Co. (Poznań, Poland) and were used without further purification. Dyes were synthesized in our laboratory with procedures described earlier.[12–15]

Phenyltrialkylborate tetramethylammonium salts [tetramethylammonium phenyltrimethylborate (TB5), tetramethylammonium phenyltriethylborate (TB6) and tetramethylammonium phenyl-tri-*n*-butylborate

TABLE I
R_p and Φ_p Values of the Free-Radical Polymerization of the TMPTA/MP (9/1) Mixture for the Tested Photoredox Couples

Dye concentration (M)	R_p^{max} (μmol/s)	Φ_p	R_p^{max} (μmol/s)	Φ_p	R_p^{max} (μmol/s)	Φ_p	R_p^{max} (μmol/s)	Φ_p
H1	B2		B5		B6		B7	
0.001	0.58	3.40	0.60	7.01	0.89	10.36	1.05	12.24
0.005	0.39	2.61	0.55	6.41	0.71	8.21	1.11	12.96
H2								
0.001	0.28	3.22	0.18	2.07	0.31	3.65	0.64	7.49
0.005	0.20	2.32	0.06	0.69	0.34	3.96	0.48	5.55
H3								
0.001	0.15	1.72	0.16	1.91	0.12	1.43	0.52	6.01
0.005	0.24	2.80	0.32	3.67	0.40	4.65	0.87	10.09
H4								
0.001	0.11	0.90	0.25	2.95	0.62	7.25	0.85	9.85
0.005	0.10	1.15	0.20	2.28	0.46	5.34	0.35	4.09

B2, n-butyltriphenylborate anion; B5, phenyltrimethylborate anion; B6, phenyltriethylborate anion and B7, phenyl-tri-n-butylborate anion in the fotoredox pairs.

(TB7)] were synthesized on the basis of the method described by Polykarpov and Neckers.[5] The final products were identified by ^{1}H-NMR spectroscopy and ^{13}C-NMR spectroscopy when needed. The obtained spectra suggest that the reaction products had the desired structures.[16] The purity of the synthesized compounds was determined with thin-layer chromatography and by measurement of the melting points.

Techniques

Spectral measurements

The ultraviolet–visible (UV–vis) absorption spectra were recorded with a Shimadzu Multispec-1501 UV–vis spectrophotometer (Kyoto, Japan), and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter (Tokyo, Japan). The fluorescence measurements were performed at ambient temperature.

The nanosecond laser flash photolysis experiments were performed with an LKS.60 laser flash photolysis apparatus (Applied Photophisics, Leatherhead, United Kingdom). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from a Lambda Phisik model LPY 150 instrument operating at 65 mJ/pulse (pulse width ≈ 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 (Applied Photophisics, Leatherhead, United Kingdom). The signal from the photomultiplier was processed by a Helwett-Packard/Agilent Agilent Infiniium 54810A digital storage oscilloscope and an Acorn compatible computer.

Electrochemical measurements

The reduction potentials (E_{red}'s) of the dyes and the oxidation potential of the borates $[E_{ox}(D/D^{\bullet+})]$ were measured by a cyclic voltammeter (Electroanalytical Cypress Systems model CS-1090, Lawrence, KS, USA). A typical three-electrode setup was employed for electrochemical measurements. The electrolyte was $0.1M$ tertabutylammonium perchlorate, which was purged with argon before measurement. A 1-mm platinum electrode was applied as a working electrode, and platinum and Ag/AgCl were used for the auxiliary and reference electrodes, respectively.

Polymerization measurements

The kinetics of free-radical polymerization were studied with a polymerization solution composed of 1 mL of MP and 9 mL of TMPTA. The hemicyanine phenyltrialkylborate salts or hemicyanine B2 salts were used as photoinitiators. Their concentrations are given in Table I. The reference formulation contained dye without an electron donor [hemicyanine iodides: 1-methyl-2-(4-(N,N-dimethylamino)styryl)pyridinium iodide (H1), 1-methyl-4-(4-(N,N-dimethylamino)styryl)pyridinium iodide (H2), 1-methy- 4-(4-(N,N-dimethylamino)styrylo)quinolinium iodide (H3) and 4-[(N-(5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-N,N-dimethylaniline iodide (H4)].

The kinetics of free-radical polymerization were measured on the basis of 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 measurement of the photopolymerization exotherms with a photo-differential scanning calorimetry apparatus constructed on the basis of a TA Instruments DSC 2010 differential scanning calorimeter. Irradiation of the

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TABLE II
E_{red} Data, E_{00}, ΔG_{el} for Photoinduced Electron Transfer Process (PET), and Influence of the Type of Chromophore on Φ_{rel} of the Phenyltrialkylborates (B5, B6, and B7) Compared to B2

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No.	$E_{red}(A^{\bullet-}/A;$ V)	$E_{red}(A/A^{\bullet-};$ V)	E_{00} (eV)	ΔG_{el} (eV)				Φ_{rel}		
				B2	B5	B6	B7	B5	B6	B7
H1	−0.484	−1.234	2.11	−0.38	−0.73	−0.86	−0.91	1.09	2.39	3.34
H2	−0.474	−1.246	2.05	−0.33	−0.68	−0.81	−0.86	0.41	1.28	5.39
H3	−0.536	−1.264	1.80	−0.02	−0.38	−0.50	−0.56	1.23	1.35	12.27
H4	−0.524	−1.296	2.04	−0.27	−0.62	−0.75	−0.80	5.42	32.82	60.55

polymerization mixture was carried out with the emission (line at 488 nm) of an argon-ion laser model Melles Griot 43 series (Cambridge, United Kingdom) with an 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 with eq. (2), where dH/dt is the maximal heat flow during the reaction and ΔH_p^{theor} is the theoretical enthalpy for complete conversion of acrylate double bonds (ΔH_p^{theor} for acrylic double bonds = 78.2 kJ/mol):[17]

$$R_p = \left(\frac{dH}{dt}\right)\frac{1}{\Delta H_p^{theor}} \qquad (2)$$

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, we could determine the conversion of the vinyl groups (C) or the extent of reaction according to eq. (3):

$$C = \frac{\Delta H_t M}{n\Delta H_p^{theor} m} \qquad (3)$$

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.[18]

Determination of the relative initiation efficiency (Φ_{rel})

Because the borate concentration, monomer structure, irradiation and measurement conditions, and initiator concentration were identical for all borate pairs studied, the kinetic profiles allowed us to compare the rate of initiation of TMPTA polymerization with each borate.

Φ_{rel} of the initiators could be defined by eq. (4):

$$\Phi_{rel} = \frac{\Phi_b}{\Phi_a} = \frac{R_{i_b}}{R_{i_a}} = \frac{(R_p)_b^2}{(R_p)_a^2} \qquad (4)$$

where Φ_a and Φ_b are the initiation quantum yields, R_{ia} and R_{ib} are the rates of initiation, and $(R_p)_a$ and

$(R_p)_b$ are the rates of polymerization in the presence of initiators a and b, respectively.[4,19]

Equation (4) was used to determine the Φ_{rel} values of the initiator pairs studied. The R_p values were calculated on the basis of the kinetic profiles obtained in the presence of B2s (b) and phenyltrialkylborates (a) with the same chromophore as the cation. The Φ_{rel} values of the phenyltrialkylborates compared to the corresponding B2s are listed in Table II.

RESULTS AND DISCUSSION

Spectral properties of the photoredox pairs

Figure 1 shows the structure of the hemicyanine borate salts applied as photoinitiators in the visible-light polymerization of TMPTA.

The H1, H2, and H3 hemicyanine dyes were characterized by an intense absorption band in the blue spectral region, with the more intense peaks (4×10^4 dm³ mol⁻¹ cm⁻¹) located in the range 459–471 nm and the second, less intense, blueshifted by about 11700 cm⁻¹ (Fig. 2). For H3, the absorption bands were shifted to the red area of visible light of about 80–90 nm, depending on the solvent polarity. The position of absorption (λ_{max}) essentially did not depend on the type of borate ion. The main band was assigned to the $S^0 \rightarrow CT$ transition, whereas the shortest wavelength band was attributed to the $\pi \rightarrow$
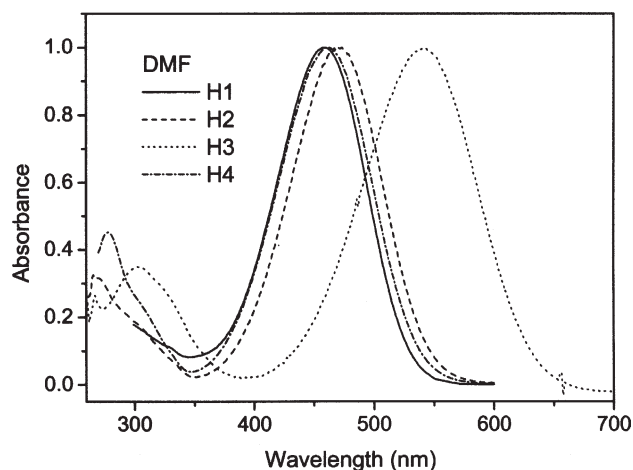

Figure 2 Illustrative normalized absorption spectra of the hemicyanine dyes recorded in DMF.

TABLE III
Steady-State Spectral Properties of the Tested Hemicyanine Dyes in THF and DMF

Dye	λ^A_{max} (nm)[a]	$\lambda^A_{max}\ \varepsilon$ $(M^{-1} cm^{-1})$[b]	λ^{Fl}_{max} (nm)[a]	λ^{Fl}_{max} (nm)[b]	$\Delta\nu$ (cm^{-1})[a]	$\Delta\nu$ (cm^{-1})[b]
H1		459	589	598	4527	5064
	465	38×10^3				
H2		470	606	624	4730	5251
	471	39×10^3				
H3		543	689	699	3472	4110
	556	37×10^3				
H4		462	609	620	5178	5516
	463	35×10^3				

[a] Measured in THF.
[b] Measured in DMF.
λ^A_{max}, wavelength of maximum absorption; λ^{Fl}_{max}, wavelength of maximum fluorescence; $\Delta\nu$, Stokes' shift.

π^* transitions. Inspection of the illustrative absorption spectra, presented in Figure 2 and with data collected in Table III, showed that the position and intensity of the CT absorption band, to some extent, depended on the dye molecule structure and solvent polarity.

The basic spectroscopic properties of the H1–H4 dyes are summarized in Table III.

It was established experimentally that the molecules with π-electrons, for which the charge distribution in the electronic ground state was considerably different from that in the excited state, exhibited pronounced solvatochromism. Thus, for the tested organic compounds, only a comparatively small solvent dependence of their UV–vis absorption spectra was observed. A solvent change from THF to DMF caused a hypsochromic shift of only about a few nanometers for its longest wavelength absorption band.

The fluorescence emission in THF exhibited a maximum, redshifted by more than 3500 cm^{-1}, in comparison to the CT absorption band. The value of the Stokes shift slightly depended on the type of dye and was higher for the polar solvent. The fluorescence emission spectra were roughly a mirror image of the absorption spectra.

Effect of the hemicyanine borate structure on the efficiency of the radical polymerization of TMPTA

Figure 3 presents kinetic curves, representing monomer the conversion as a function of time, obtained by photo-differential scanning calorimetry. After an induction period, during which polymerization inhibitors were consumed, the polymerization started causing an increase in the medium microviscosity. With the progress of polymerization, the reactive functional groups were consumed, and poly-

merization stopped, as indicated by the plateau on the kinetic profile (Fig. 3).

The R_p and Φ_p values of the photoinitiated polymerization measured for all of the tested photoredox pairs are collected in Table I.

It was apparent from the inspection of the R_p values that the efficiency of hemicyanine borates tested, when they were used as photoinitiators, depended strongly on their structure. It is notable that initiators possessing phenyl tri-n-butylborate anions were better co-initiators than the B2s at the same initiator concentration and irradiation conditions as indicated by R_p (Table I). It should be added, however, that the difference in the initiation efficiencies between the phenyltrialkylborates and B2 also strongly depended on the structure of the chromophore (Table I).

The analysis of the R_p values showed that the photoinitiation efficiency of the tested initiators
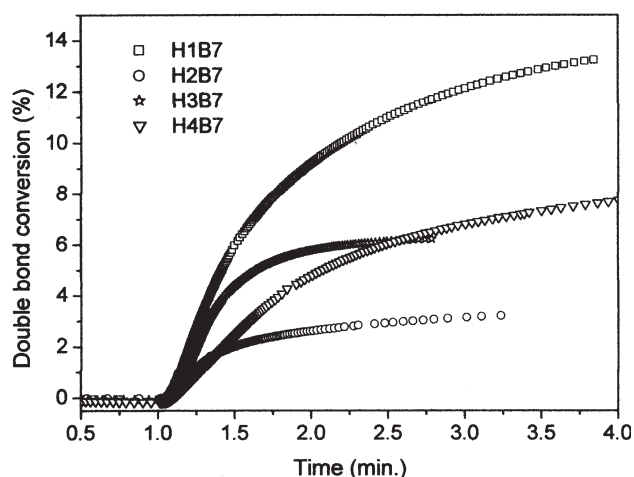

Figure 3 Double-bond conversion versus time for H1–H4 phenyltri-n-butylborate salts used as photoinitiators in TMPTA polymerization.
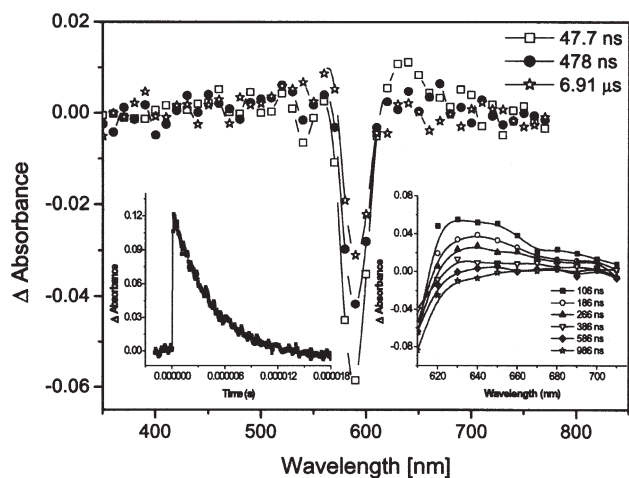
Figure 4 Transient absorption spectra of Se3 in acetonitrile recorded at a different times after the pulse. Inset: (left) Transient absorption kinetic curve observed at 630 nm at 2 μs after the pulse for Se3 and (right) transient absorption spectra of Se3 in acetonitrile recorded at a different times after the pulse assigned to the triplet state.

depended on the type of electron-accepting part of the molecule. The best photoinitiating abilities exhibited photoredox pairs possessing a pyridinium heterocycle ring.

From the data obtained during the measurements, it was determined that the quantum yields of photopolymerization oscillated between 0.69 and 12.96 (Table I) for all of the photoinitiating pairs tested. It is noteworthy that the ion pair marked as H1B7 showed the best photoinitiation ability, with a quantum yield of polymerization of about 12.96 and an R_p value of 1.11 μmol/s. It was also found that the degree of monomer conversion depended on the structure of the photoinitiating pairs.

When one takes into account that R_p was proportional to the square root of the initiator efficiency, the difference between the R_p values induced by H1 cation coupled with *n*-butyltriphenylborate anion (B2) and phenyltrimethylborate anion (B5) became even less; R_p in the presence of the H1B5 photoinitiating system was only 5% faster than in the case of the H1B2 photoredox pair, whereas for the H4B7 couple, with reference to the H4B2 photoinitiating system, R_p increased about eight times (cf. data in Tables I and II). The only exception was the H2B5 photoredox pair, which initiated the TMPTA polymerization with a lower rate than the H2B2 couple. This caused Φ_{rel} of B5 compared to B2 to be below 1 (0.41).

From the study of Neckers et al.,[4] it is known that Φ_{rel} can be strongly dependent on E_{red} of the dye cation in the borate initiators. According to the authors, the easier it is to reduce the chromophore of the initiator (i.e., the less negative is its E_{red}), the smaller difference in the initiation efficiency will be

observed between the tetraphenylborate and alkyltriphenylborate photoinitiating systems.[4]

In the photoinitiating systems described in this article, the chromophore structure in the tested dyes was similar. This causes E_{red} of the hemicyanine derivatives to not vary very much, and this factor could not significantly affect Φ_{rel}. For the studied systems, the factors that might have had an impact on the final rate of photoinitiated polymerization were the oxidation potential (E_{ox}) of the borate salts, the number of free radicals formed after one photon absorption, and their reactivity.

Factors determining the hemicyanine borate reactivity

The steps determining the reaction of the free-radical-initiated polymerization via the intermolecular electron-transfer process were dependent on the nature of the dye and the electron donor (or acceptor). For the cyanine borate salts applied as photoinitiators, the polymerization initiation involved two main steps. First, electron transfer from the borate anion to the excited state of the chromophore (being either in a singlet or triplet excited state) resulted in the formation of a cyanine radical and a boranyl radical, which rapidly decomposed to produce an alkyl radical and phenyldialkylborane. Second, the addition of the alkyl radical(s) formed an acrylic monomer and initiated a chain process that led to polymer formation. Additional pathways of radical initiation may be available because of the initiating capabilities of phenyldialkylborane,[5,20–22] a second active component produced during the first step of the initiation process.

In an attempt to measure the intramolecular electron transfer, a nanosecond flash photolysis experiment was conducted, in which the carbocyanine dye
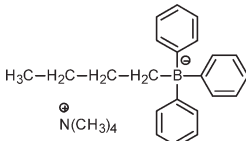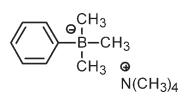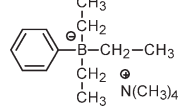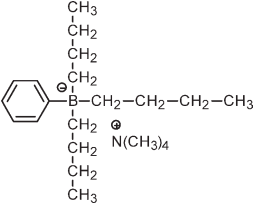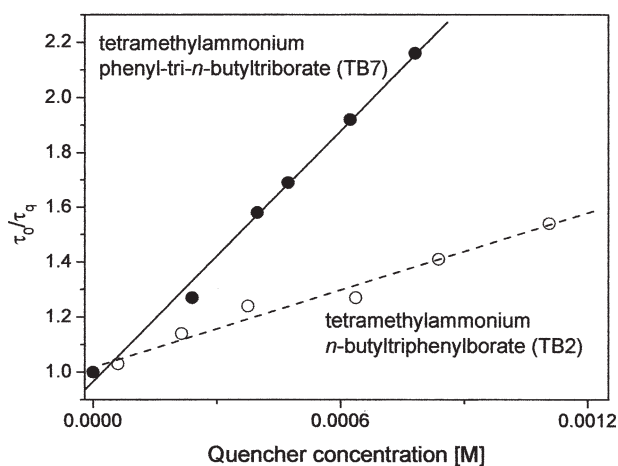

Figure 5 Concentration dependence of the triplet decay rate of the Se3 in MeCN in the presence of borate salts. t_0 and t_q lifetimes of the dye (Se3) in the absence and presence of a quencher (borate salt), respectively.

TABLE IV
E_{ox} and k_{el} Values for the Tested Photoredox Pairs

Abbreviation	Borate	$E_{ox}(D/D^{\bullet+})$ (V)	$10^{-9} k_q \approx 10^{-9} k_{el}$ $(M^{-1} s^{-1})^a$
TB2	$H_3C{-}H_2C{-}H_2C{-}H_2C{-}B^{\ominus}$ (triphenyl) $N(CH_3)_4^{\oplus}$	1.244	1.854
TB5	phenyl$-B^{\ominus}$(CH_3)_3 $N(CH_3)_4^{\oplus}$	0.888	1.846
TB6	phenyl$-B^{\ominus}$(CH_2CH_3)_3 $N(CH_3)_4^{\oplus}$	0.764	2.320
TB7	phenyl$-B^{\ominus}$(CH_2CH_2CH_2CH_3)_3 $N(CH_3)_4^{\oplus}$	0.708	5.329

^{a} The k_q values were determined for the Se3 dye–borate photoredox pairs.

[6,6′dimethoxy-N,N′-dimethylselenocarbocyanine (Se3)] triplet state was formed rapidly and used as an electron acceptor from borate anions instead of hemicyanine dye. The dye triplet decay rates were measured for each of the tetraorganylborates studied. When the electron transfer was the only quenching process of the cyanine triplet, the electron-transfer rate constants (k_{el}'s) were equal to those of triplet quenching. The transient absorption spectrum of Se3, showing the triplet decay, obtained in acetonitrile at a different time after the pulse, is illustrated in Figure 4.

At wavelengths above 600 nm, we observed positive absorption, which decayed with a lifetime of about 40–50 μs, depending on the exact quality of the removal of oxygen from the solution. By analogy to other works described in the literature,[7,23] we assigned 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 (k_q) were determined by measurement of the effects of the additive on the lifetimes of the dye triplet state. Linear Stern–Volmer plots were observed (Fig. 5). The k_{el}'s obtained for the borates of interest are listed in Table IV.

The k_q's obtained by linear fitting of the data presented in Figure 5 were affected by the substituents attached to the boron atom in the electron-donating

molecule. For the tested borate series, the TB7 boron possessing three butyl substituents had a less electropositive peak potential and faster electron-transfer rate than the TB2 salt bearing only one butyl group. k_q's of the excited states were high and approached diffusion-controlled limits.

The transient absorption spectra recorded at different times after laser excitation of a cyanine solution containing tetramethylammonium
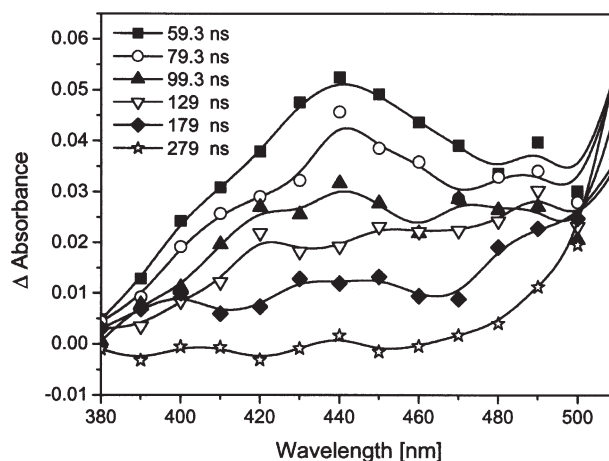

Figure 6 Transient absorption spectra recorded at a different times after laser excitation of a cyanine solution containing 0.024M tetramethylammonium phenyltrimethylbotate salt.
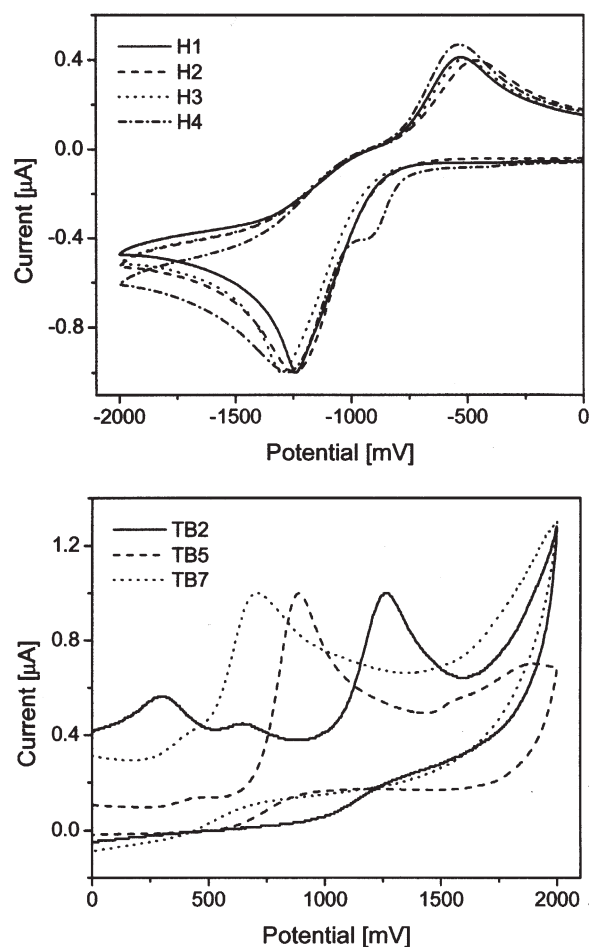
Figure 7 Cyclic voltammograms of selected compounds. The types of molecules are marked in the figure.

phenyltrialkylborate salts showed formation of a new peak at 430 nm; this suggested that by quenching the triplet, a new transient formed at this wavelength (Fig. 6). According to the literature,[7,8,24] this was the cyanine radical formed. The new feature, with absorption at 430 nm, decayed with a lifetime of about 170 ns.

The results show that the limiting step in the photoinitiated polymerization by the intermolecular electron-transfer mechanism was the process related to the intermolecular electron transfer.

Therefore, the quantum yields for product formation in many photoinduced electron-transfer reactions (among others, polymerization) are equivalent to the efficiency with which separated radical ions are formed. Considering these, one can conclude that for initiation via an intermolecular electron-transfer process, R_p can be described by the generalized eq. (5):

$$\ln R_p = A - \frac{(\lambda + \Delta G_{el})^2}{8\lambda RT} \quad (5)$$

where T - temperature; R - gas constant 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 and k_t denote the rate constant of polymerization and termination, respectively, [M] is the monomer concentration, and I_a is the intensity of absorbed light), λ is the reorganization energy necessary to reach the transition states both the excited molecule and solvent molecules, and finally, ΔG_{el} is the free-energy change expressed by the Rehm–Weller equation:[25]

$$\Delta G_{el} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - \frac{Ze^2}{\varepsilon a} - E_{00} \quad (6)$$

where $E_{red}(A^{\bullet-}/A)$ is the reduction potential of the chromophores, E_{00} is the excited state energy, and $Ze^2/\varepsilon a$ 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 ΔG_{el} in this system. E_{ox} and E_{red} of both photoredox pair components were determined from cyclovoltammetric measurements. The electrochemical reduction of the hemicyanine cation and oxidation of the borate anions in acetonitrile are shown in Figure 7 for illustration.

The electrochemical reduction of hemicyanine cation (Fig. 7 top) in acetonitrile solution was reversible. However, the cyclic voltammetry gave irreversible oxidation waves for each of the borates examined with peak potentials that varied systematically with the structure of the borate (Fig. 7 bottom). This was caused by the very short lifetime of the boranyl radical. The structures of the borate salts, along with their electrochemical properties, are collected in Table IV.

Knowing E_{red}'s of hemicyanine dyes, knowing their singlet state energy (calculated on the basis of the fluorescence spectra), knowing E_{ox} of tetramethylammonium borates, and using the Rehm-Weller equation [eq. (6)],[25] one can calculate ΔG_{el} for the electron-transfer process between the hemicyanine cation and the borate anion. The measured electrochemical and calculated thermodynamic properties of the hemicyanine borate salts are listed in Tables II and IV.

Negative values of ΔG_{el} indicated that for all combinations of hemicyanine borate pairs, the electron-transfer reaction yielding free radicals was thermodynamically allowed.

Equation (5) shows that if an intermolecular transfer process between the excited dye and an electron donor is a limiting step for photoinitiated polymerization, one should observe a parabolic relationship between log R_p and the thermodynamic parameter ΔG_{el}.

For the hemicyanine dye–borate salts initiating pairs, the rate of TMPTA polymerization increased as the

driving force of the electron-transfer reaction increased. This behavior was predicted by the classical theory of photoinduced electron-transfer process.[26–28]

In general, for the photoredox pairs tested, the overall efficiency of the photoinitiation of radical polymerization could be affected by (1) the rate of the primary electron-transfer process, (2) the rate of carbon—boron bond cleavage, (3) the rate of secondary processes, and (4) finally, the reactivity of free radicals formed.

Single electron transfer from the alkyltriphenylborates to the excited cyanine occurs with a rapid rate. The Rehm–Weller equation[25] for photoinduced electron transfer suggests a dependence of ΔG_{el} on $E_{ox}(D/D^{\bullet+})$ when E_{00} and $E_{red}(A^{\bullet-}/A)$ are similar.

The difference in E_{ox} was indicative of the relative ease of electron removal from each borate anion. The E_{ox} values increased in the following order: TB7 < TB6 < TB5 < TB2. The observed differences in E_{ox} between the borates provided additional support for the critical role of electron transfer in the initiation of the acrylate polymerization. The order of the electron-donating ability of the borates exactly corresponded to the order of reactivity of the borates in the polymerization initiation process (Table IV), but it is noteworthy to emphasize that the activity of the phenyltrialkyl borates did not solely depend on the ease of electron removal by an oxidizing agent.

In the symmetrically substituted borates, only one radical could be produced. If the boron atom had two different substituents, however, two different radicals may have been produced. In the latter case, the predominant formation of the most stable radical took place, resulting from the cleavage of the weakest bond. Of the borates examined, three different radical species may have been formed, having the following stability order n-Butyl > Ethyl > Methyl.

Borates producing the more stable n-butyl radical are more reactive than others. This applies to $N(CH_3)_4^+$-n-$C_4H_9B(C_6H_5)_3^-$ and $N(CH_3)_4^+$ (n-$C_4H_9)_3BC_6H_5^-$, which predominantly yield n-butyl radical. $N(CH_3)_4^+(C_2H_5)_3BC_6H_5^-$ yields ethyl radical, which is second in stability. $N(CH_3)_4^+(CH_3)_3BC_6H_5^-$ gives the least stable methyl radical. The reactivity order based on the stability of the radicals produced correlated reasonably with $E_{ox}(D/D^{\bullet+})$ studied and R_p, except for a reduced reactivity of $N(CH_3)_4^+$-n-$C_4H_9B(C_6H_5)_3^-$. However, in the case of phenyltrialkylborates, more than one radical is produced after one photon absorption. This influences both the overall efficiency of polymerization and the final degree of a double-bond conversion. Therefore, these electron donors initiate the polymerization reaction more efficiently than alkyltriphenylborate.

In the case of hemicyanine phenyltrialkylborate salts, we confirmed this hypothesis by measuring a yield of a monofunctional monomer and butyl radical adduct formation.[14]

Irradiation of a deaerated solution containing hemicyanine phenyltri-n-butylborate and methyl methacrylate in benzene/acetonitrile gave an adduct with a yield equaling 155%. This result indicated that the photoinduced one-electron oxidation of phenyltri-n-butylborate anion by the excited state of hemicyanine cation produced substantially more than 1 equiv of the butyl radicals. The obtained result was in good agreement with Polykarpov and Neckers's[5] studies.

The single electron transfer from the borate to the excited cyanine (the first step) occurred at diffusion-controlled rates (ca. 10^9 M^{-1} s^{-1}). The rate of the second step was determined by the ability of the radical formed during the first step to attack the acrylic double bond. Beckwith and Poole[29] reported the following rates of addition to methyl acrylate: 3.8×10^5 M^{-1} s^{-1} for methyl and 6.2×10^5 M^{-1} s^{-1} for pentyl radicals. However, the overall reactivity of the borate salt in the polymerization process should have been limited by the first step, with the assumption that the reaction conditions allowed for the second step to proceed. The reactivity order observed from the calorimetric measurements was affected by the electron-transfer processes (i.e., the forward and the competitive back electron transfer between the excited chromophore and the borate anion within the ion pairs), the rate of radical separation formed after the electron-transfer process, and the rate of decomposition of the boranyl radical. Thus, the overall rate of formation of alkyl radicals, which started a chain reaction, and their reactivity could have been dominant factors affecting the kinetics of the free-radical generation from the borate anions.

However, it is necessary to emphasize that several other factors, for example, the molecular geometry and structure effects, may have critically affected the overall efficiency of the polymerization.[30]

CONCLUSIONS

TB2 and phenyltrialkylborates as co-initiators with hemicyanine dyes could be used in the visible-light-induced polymerization of acrylates. The comparative analysis of the rate of the polymerization photo-initiated by hemicyanine borate salts showed that the photoinitiation ability of the photoredox pairs significantly depended on the electron-donor and electron-acceptor structures. The electron-transfer process was a dominant factor affecting the kinetics of the free-radical generation from the borate anion. It was apparent that the rate of the electron-transfer process was dependent on the nature and number of the alkyl groups bound to the boron atom in the borate molecule. Borates producing n-butyl radicals

displayed the best reactivity in TMPTA polymerization initiation. Then, the ethyl radicals were less efficient toward the conversion of a double bond. Finally, the methyl radicals displayed the smallest degree of a double-bond conversion.

References

1. Polykarpov, A. Y.; Hassoon, S.; Neckers, D. C. Macromolecules 1996, 29, 8274.
2. Eaton, D. F. Pure Appl Chem 1984, 56, 1191.
3. Hassoon, S.; Sarker, A.; Polykarpov, A. Y.; Rodgers, M. A. J.; Neckers, D. C. J Phys Chem 1996, 100, 12386.
4. Popielarz, R.; Sarker, A. M.; Neckers, D. C. Macromolecules 1998, 31, 951.
5. Polykarpov, A. Y.; Neckers, D. C. Tetrahedron Lett 1995, 36, 5483.
6. Murphy, S.; Xiquiang, Y.; Schuster, G. B. J Org Chem 1995, 60, 2411.
7. Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. J Am Chem Soc 1990, 112, 6329.
8. Chatterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. J Am Chem Soc 1988, 110, 2326.
9. Zhu, D.; Kochi, J. H. Organometallics 1999, 18, 161.
10. Schuster, G. B. Pure Appl Chem 1990, 62, 1565.
11. Murphy, S. T.; Zou, C.; Miers, J. B.; Ballew, R.; Dlott, D.; Schuster, G. B. J Phys Chem 1993, 97, 13152.
12. Jędrzejewska, B.; Pietrzak, M.; Pączkowski, J. J Photochem Photobiol A 2010, 209, 32.
13. Jędrzejewska, B.; Jeziórska, J.; Pączkowski, J. J Photochem Photobiol A 2008, 195, 105.
14. Pietrzak, M.; Jędrzejewska, B.; Pączkowski, J. J Polym Sci Part A: Polym Chem 2009, 47, 4119.
15. Jędrzejewska, B.; Marciniak, A.; Pączkowski, J. Mater Chem Phys 2008, 111, 400.
16. Pietrzak, M.; Jędrzejewska, B. J Organometal Chem 2011, 696, 2135.
17. Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley: New York, 1989; p II/298.
18. Zhang, S.; Li, B.; Tang, L.; Wang, X.; Liu, D.; Zhou, Q. Polymer 2001, 42, 7575.
19. Jędrzejewska, B.; Pietrzak, M.; Pączkowski, J. J Photochem Photobiol A 2010, 214, 276.
20. Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structures of Organometallic Compounds; Pergamon: Oxford, 1982; Vol. 7, pp 291, 335.
21. Davies, A.-G.; Scaiano, J. C. J Chem Soc Perkin Trans 1972, 2, 2234.
22. Ermoshkin, A. A.; Nikolaeva, E. S.; Neckers, D. C.; Fedorov, A. V. Macromolecules 2008, 41, 9063.
23. Krieg, M.; Bilitz, J. M.; Srichai, M. B.; Redmond, R. W. Biochim Biophys Acta 1994, 1199, 149.
24. Lan, L. Y.; Schuster, G. B. Tetrahedron Lett 1986, 27, 4261.
25. Rehm, D.; Weller, A. Ber Bunsen-Ges Phys Chem 1969, 73, 834.
26. Pączkowski, J.; Kucybała, Z. Macromolecules 1995, 28, 269.
27. Pączkowski, J.; Neckers, D. C. In Electron Transfer in Chemistry; Gould, I. R., Ed.; Wiley-VCH: New York, 2001; Vol. 5, p 516.
28. Eberson, L. Electron Transfer in Organic Chemistry; Springer-Verlag: New York, 1987.
29. Beckwith, A. L. J.; Poole, J. S. J Am Chem Soc 2002, 124, 9489.
30. Moad, G.; Solomon, D. H. The Chemistry of Radical Polymerisation; Elsevier: Oxford, 2006; Chapter 1, p 8.