Synthesis and studies of novel homodimeric styrylbenzimidazolium dyes applied as photoinitiators for the radical polymerization of acrylic monomers

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Abstract: A series of homodimeric styrylbenzimidazolium dyes were synthesized and applied as visible light initiators for the polymerization of acrylic monomer. In the photoinitiating system, hemicyanine dye cation acts as an electron acceptor whereas borate anion is an electron donor. The photochemistry of the series of bichromophoric hemicyanine borates: 1,3-bis{2-[4-(*N*-alkylamino)styryl]-1-methylbenzimidazolium}propane, 1,5-bis{2-[4-(*N*-alkylamino)styryl]-1-methylbenzimidazolium}pentane, 1,10-bis{2-[4-(*N*-alkylamino)styryl]-1-methylbenzimidazolium}decane, was compared to the photochemistry of structurally related monochromophoric hemicyanine borates. The photoinitiating efficiency of the donor-acceptor pairs is discussed based on the free energy change for the photoinduced electron transfer from borate anion to dye cation.

Keywords: radical polymerization, photoinitiators, kinetics of polymerization, styrylbenzimidazolium dyes.

Synteza i badania nowych, homodimerycznych barwników styrylobenzimidazoliowych jako fotoinicjatorów polimeryzacji rodnikowej monomerów akrylowych

Streszczenie: Otrzymano serię homodimerycznych barwników styrylobenzimidazoliowych i zastosowano je jako inicjatory polimeryzacji akrylanów działające w zakresie światła widzialnego. W badanych układach fotoinicjujących kation barwnika pełnił rolę akceptora elektronów, a anion boranowy — donora elektronu. Właściwości fotochemiczne soli boranowych dwuchromoforowych barwników hemicyjaninowych: 1,3-bis{2-[4-(*N*-alkiloamino)styrylo]-1-metylobenzimidazolo}propanu, 1,5-bis{2-[4-(*N*-alkiloamino)styrylo]-1-metylobenzimidazolo}pentanu, 1,10-bis{2-[4-(*N*-alkiloamino)styrylo]-1-metylobenzimidazolo}dekanu porównano z właściwościami ich monochromoforowych odpowiedników. Efektywność fotoinicjowania reakcji polimeryzacji przez badane pary donorowo-akceptorowe oceniono na podstawie zmiany energii swobodnej aktywacji procesu fotoindukowanego przeniesienia elektronu z anionu boranowego na kation barwnika.

Słowa kluczowe: polimeryzacja rodnikowa, fotoinicjatory, kinetyka polimeryzacji, barwniki styrylobenzimidazoliowe.

Free radical polymerization has been an important technological area for eighty years. It proceeds *via* a chain mechanism, which basically consists of four different types of reactions involving free radicals: (i) radical generation from a nonradical species (initiation), (ii) radical addition to a substituted alkene (propagation), (iii) atom transfer and atom abstraction reactions (chain transfer and termination by disproportionation), and (iv) radical-radical recombination reactions (termination by combination) [1].

Various methods can be used to initiate radical reactions and they can be divided into the broad areas of thermolysis, photolysis, and electron transfer reactions. Photochemical initiation of radical reactions is possible with a wide range of compounds. The photochemical event either creates a reactive state or cleaves a weak bond homolytically to produce radicals. Many of the commercial initiators are aryl ketones and phosphine oxides that are tuned for specific wavelength initiation [1].

Many dyes can be combined with different electron donors such as tertiary amines or thiols to provide an initiating system that is sensitive to visible light. Dyes can

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also be used as sensitizers with other photoinitiators [2—5].

Taking into account the nature of the mechanisms of radical formation, the photoinitiators can be classified as follows:

Type I — generates radical pairs through a highly efficient α-cleavage process. This class includes aromatic carbonyl compounds that are known to undergo a homolytic C-C scission upon UV exposure.

Type II — consists of two components, typically, an aromatic ketone in addition to a radical precursor containing a weak covalent bond. The initiation of polymerization occurs through the H-donor radical [6—9].

There are also systems that cannot be classified as type I or II. The class of photoinitiating systems works by inter- or intramolecular photoinduced electron transfer [3—6]. This process involves the use of the light to initiate electron transfer from a donor to an acceptor molecule [7—9].

There are two types of sensitization of radical polymerization *via* electron transfer processes: (i) photoreducible dye sensitization reported first by Oster in 1954 [10]; in such a photoinitiating system, the dye (acridine, xanthene and thiazine dyes) is photoreduced during a photochemical reaction in the presence of suitable reactants; (ii) photooxidizable dye sensitization. This sensitization requires molecules being in their ground state as a strong electron acceptor. Onium salts of xanthene dyes, merocyanine dyes and 1,3,5-triazine derivatives or cyanine dyes and *N*-alkoxypyridinium salts are such types of such photoinitiating systems [2, 6].

Considering the interaction between a chromophore and an electron donor in the ground state and after an electron transfer process, dye photoinitiators can be classified into three different groups [7—9]: (i) donor-acceptor pairs with electrostatic interactions in the ground state (ground state ion-pair) but neutral after the photoinduced electron transfer reaction; (ii) donor-acceptor pairs without electrostatic interactions in the ground state and, after electron transfer, at least one component that is neutral in the ground state and after electron transfer; (iii) donor-acceptor pairs that are neutral in the ground state and charged after electron transfer. In this case, the resulting product is a radical ion pair [6—9].

An example of the ground state ion-pair photoinitiators are borate salts.

Cyanine dyes based on the benzimidazole skeleton absorb around 400—480 nm but the nitrogen cation in the dye makes them almost insoluble in UV binders due to their ionic nature. Alkyltriaryl borates provide very efficient anions that can be combined with these dyes to give a good initiating system. Photoinduced electron transfer from the borate anion to the singlet excited state of cyanine dye leads to fragmentation of the anion and an alkyl radical is produced [7—9].

In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiating systems operating in the visible light region. Initiators possessing phenyltrialkylborate anion paired with the asymmetrical cation of hemicyanine dyes represent such a group. This group of photoinitiators has been synthesized and examined in terms of their efficiency as photoinitiators of radical polymerization. The ability of polymerization photoinitiation of acrylate monomers by homodimeric hemicyanine phenyltri-*n*-butylborate salts is documented in this paper.

EXPERIMENTAL PART

Materials

Monomers, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and acryloyloxyethyl trimethyl ammonium chloride (AETAC); solvents, 1-methyl-2-pyrrolidinone (MP), acetonitrile (MeCN), *N*,*N*-dimethylformamide (DMF) and ethyl acetate (EtOAc) were purchased from Aldrich Chemical Co. and were used without further purification. 4-Aminobenzaldehydes were prepared following the procedures given by Gawinecki *et al.* [11]. Dyes and borate salts were synthesized in our laboratory using procedures described in the literature [12—16]. The final products were identified by ^{1}H NMR spectroscopy. For comparison of the photoinitiating ability of the studied borate salts, the following compounds were applied: 2-[4-(*N*,*N*-dimethylamino)-styryl]-1,3-dimethyl-benzimidazolium phenyl-tri-*n*-butylborate (BI1B7), 5,7-diiodo-3-butoxy-6-fluorone (DIBF, triplet-state photoinitiator) and *N*-phenylglycine (NPG). The abbreviation B7 refers to phenyltri-*n*-butylborate anion.

Synthesis

The synthesis of the bichromophoric hemicyanine borates is *via* a few steps: (a) the quaternization reaction of 1,2-dimethylbenzimidazole with 1,3-dibromopropane, 1,5-diiodopentane or 1,10-diiodododecane yielding the corresponding diheterocyclic salts (P3, P5 and P10); (b) the condensation reaction of diheterocyclic salts (P3, P5 and P10) with 4-(*N*,*N*-dimethylamino)benzaldehyde (L1) [or 4-(*N*-pyrrolidino)benzaldehyde (L4)] yielding the corresponding bichromophoric hemicyanine dyes (as halides) (P3L1, P3L4, P5L1, P5L4, P10L1 and P10L4); (c) the reaction of phenyl lithium with tri-*n*-butylborane leading to phenyltri-*n*-butylborate tetramethylammonium salt (NMe_4B7); (d) the ion exchange reaction giving the homodimeric hemicyanine borate salts (P3L1B7, P3L4B7, P5L1B7, P5L4B7, P10L1B7 and P10L4B7).

Synthesis of alkane α,γ-bis[1,2-dimethylbenzimidazolium] dihalide

To a solution of α,γ-dihalidoalkane (0.1 mol) in anhydrous ethanol (50 cm^3), 1,2-dimethylbenzimidazole (0.2 mol) was added. The reaction mixture was refluxed for 6 h and then the solution was concentrated under vacuum to give a white solid [12, 13].

P3 — propane 1,3-bis[1,2-dimethylbenzimidazolium] dibromide

$C_{21}H_{26}N_4Br_2$; 494.27 g/mol; 64 %; ^{1}H NMR (DMSO-d_6) δ (ppm): 2.282 (m, 2H, $-CH_2-$), 2.944 (s, 6H, $-CH_3$), 3.982 (s, 6H, $N-CH_3$), 4.752 (t, 4H, N^+CH_2-), 7.627 (m, 4H, Ar), 7.979 (m, 4H, Ar).

P5 — pentane 1,5-bis[1,2-dimethylbenzimidazolium] diiodide

$C_{23}H_{30}N_4I_2$; 616.77 g/mol; 78 %; ^{1}H NMR (DMSO-d_6) δ (ppm): 1.451 (m, 2H, $-CH_2-$), 1.812 (m, 4H, $-CH_2-$), 2.867 (s, 6H, $-CH_3$), 3.977 (s, 6H, $N-CH_3$), 4.468 (t, 4H, N^+CH_2-), 7.623 (m, 4H, Ar), 7.975 (m, 4H, Ar).

P10 — decane 1,10-bis[1,2-dimethylbenzimidazolium] diiodide

$C_{28}H_{40}N_4I_2$; 686.45 g/mol; 72 %; ^{1}H NMR (DMSO-d_6) δ (ppm): 1.232 (m, 12H, $-CH_2-$), 1.272 (m, 4H, $-CH_2-$), 2.865 (s, 6H, $-CH_3$), 3.966 (s, 6H, $N-CH_3$), 4.464 (t, 4H, N^+CH_2-), 7.623 (m, 4H, Ar), 7.975 (m, 4H, Ar).

Synthesis of α,γ-bis{2-[4-(dialkylaminophenyl)ethenyl]benzimidazolyl}-alkane dihalides

Dicationic styrylbenzimidazolium dyes were synthesized by refluxing (5—6 h) the appropriate 4-aminobenzaldehyde (0.002 mol) with alkane α,γ-bis[1,2-dimethylbenzimidazolium] dihalide (0.001 mol) in ethanol (20 cm^3) in the presence of piperidine as a catalyst (few drops). The precipitate formed after cooling the reaction mixture was filtered and recrystallized from anhydrous ethanol or butanol [12, 13] (Table 1).

Synthesis of phenyltri-*n*-butylborate salts

The preparation of phenyltri-*n*-butylborate tetramethylammonium salt (NMe_4B7) is based on the addition of phenyl lithium reagent to a tri-*n*-butylborane in diethyl ether. The detailed synthetic procedure, as well as the basis of the analytical results and spectral evidence of the tetramethylammonium phenyltri-*n*-butylborates can be found in our previous paper [14].

Synthesis of dicationic styrylbenzimidazolium borate salts

The ion exchange reaction was performed using the procedure described in the literature [15].

A mixture of 0.15 mmol of dicationic styrylbenzimidazolium dyes and 0.3 mmol of phenyltri-*n*-butylborate tetramethylammonium salt in 10 cm^3 of an acetone-acetonitrile-ethanol-methanol mixture at a volume ratio of 1:1:1:1 was boiled for 10 min. Then, cold distilled water was added to the resulting hot solution until turbidity was achieved. The mixture was stored in a dark place where the salt crystallized. The precipitate was filtered and dried.

Methods of testing

Spectral measurements

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

— The ^{1}H NMR (200 MHz) spectra were recorded with the use of a Varian Gemini 200 NMR spectrometer (Palo Alto, CA, USA). Dimethylsulfoxide (DMSO-d_6) was used as the solvent. Melting points (uncorrected) were determined on Boëthius apparatus.

Electrochemical measurements

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

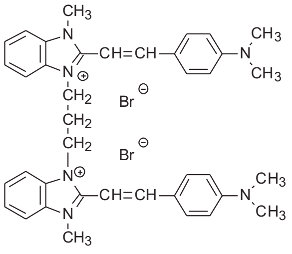
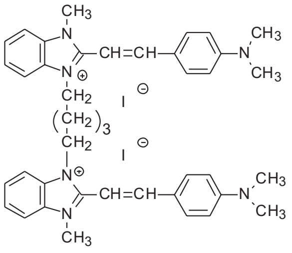
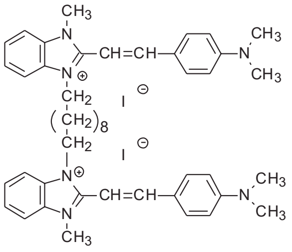
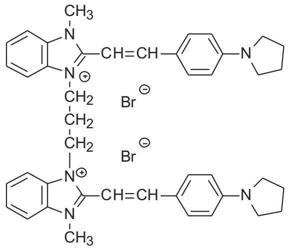
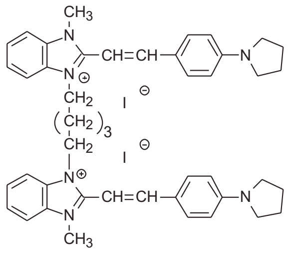
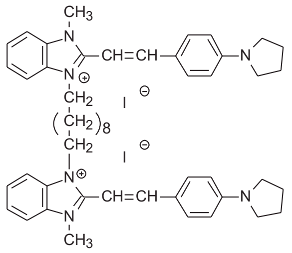
Polymerization measurements

The kinetics of free radical polymerization were studied using a polymerization solution composed of 1 cm^3 of 1-methyl-2-pyrrolidinone (MP) and 9 cm^3 of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) or acryloyloxyethyl trimethyl ammonium chloride (AETAC). The hemicyanine phenyltri-*n*-butylborate salts were used as a photoinitiator; their concentration was 0.0025 M. A reference formulation contained dye without an electron donor (hemicyanine iodide or bromide). The polymerizing composition was not deaerated before use.

— The kinetics of free radical polymerization were studied based on the measurements of the rate of the heat evolution during polymerization in thin film cured samples (0.035 ± 0.002 g). The investigations were performed by measuring photopolymerization exotherms using a 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 488 nm) of an argon ion laser Model Melles Griot 43 series with intensity of light of 100 mW/cm^2. The light intensity at the level of the measuring vessels in the cell (aluminum pots with an area of 0.196 cm^2) was 20 mW. The light intensity was measured by a Coherent Model Fieldmaster power meter.

— The maximum polymerization rate (R_p^{max}) was calculated using eq. (1) where: dH/dt — maximal heat flow

Table 1. Structures and ^{1}H NMR spectral data of the dicationic styrylbenzimidazolium salts

Structure	^{1}H NMR
 **P3L1**: $C_{39}H_{44}N_6Br_2$; 756.62 g/mol; 60 %; mp 244—247 °C	^{1}H NMR (DMSO-d_6) δ (ppm): 2.367 (m, 2H, –CH$_2$–), 3.039 (s, 12H, –CH$_3$), 4.079 (s, 6H, N–CH$_3$), 4.867 (m, 4H, N$^+$CH$_2$–), 6.717-6.755 (d, J=7.6 Hz, 4H, Ar), 7.107-7.189 (d, J=16.4 Hz, 2H, –CH=CH–), 7.535-7.577 (d, J=8.2 Hz, 4H, Ar), 7.601-7.682 (d, J=16.2 Hz, 2H, –CH=CH–), 7.722 (4H, Ar), 7.971-8.010 (d, J=7.8 Hz, 2H, Ar), 8.097-8.140 (d, J=8.6 Hz, 2H, Ar)
 **P5L1**: $C_{41}H_{48}N_6I_2$; 878.67 g/mol; 68 %; mp 274—277 °C	^{1}H NMR (DMSO-d_6) δ (ppm): 1.435 (m, 2H, –CH$_2$–), 1.856 (m, 4H, –CH$_2$–), 3.034 (s, 12H, –CH$_3$), 4.078 (s, 6H, N–CH$_3$), 4.550 (t, 4H, N$^+$CH$_2$–), 6.731-6.777 (d, J=9.2 Hz, 4H, Ar), 7.059-7.141 (d, J=16.4 Hz, 2H, –CH=CH–), 7.528-7.564 (m, 4H, Ar), 7.590-7.671 (d, J=16.2 Hz, 2H, –CH=CH–), 7.689-7.733 (d, J=8.8 Hz, 4H, Ar), 7.964 (m, 4H, Ar)
 **P10L1**: $C_{46}H_{58}N_6I_2$; 948.80 g/mol; 58 %; mp 196—200 °C	^{1}H NMR (DMSO-d_6) δ (ppm): 1.212 (m, 12H, –CH$_2$–), 1.731 (m, 4H, –CH$_2$–), 2.977 (s, 12H, –CH$_3$), 4.098 (s, 6H, N–CH$_3$), 4.550 (t, 4H, N$^+$CH$_2$–), 6.726-6.771 (d, J=9.0 Hz, 4H, Ar), 7.101-7.183 (d, J=16.4 Hz, 2H, –CH=CH–), 7.615 (m, 4H, Ar), 7.633-7.697 (d, J=12.8 Hz, 2H, –CH=CH–), 7.714-7.759 (d, J=9.0 Hz, 4H, Ar), 7.973 (m, 4H, Ar)
 **P3L4**: $C_{43}H_{48}N_6Br_2$; 808.70 g/mol; 43 %; mp 242—245 °C	^{1}H NMR (DMSO-d_6) δ (ppm): 1.993 (m, 8H, –CH$_2$–), 2.375 (m, 2H, –CH$_2$–), 3.323 (m, 8H, –CH$_2$–), 4.081 (s, 6H, N–CH$_3$), 4.855 (m, 4H, N$^+$CH$_2$–), 6.544-6.589 (d, J=9.0 Hz, 4H, Ar), 7.063-7.145 (d, J=16.4 Hz, 2H, –CH=CH–), 7.547-7.580 (d, J=6.6 Hz, 4H, Ar), 7.601 (2H, –CH=CH–), 7.669-7.712 (d, J=8.6 Hz, 4H, Ar), 7.984 (m, 2H, Ar), 8.098 (m, 2H, Ar)
 **P5L4**: $C_{45}H_{52}N_6I_2$; 930.75 g/mol; 47 %; mp 254—258 °C	^{1}H NMR (DMSO-d_6) δ (ppm): 1.444 (m, 2H, –CH$_2$–), 1.867 (m, 4H, –CH$_2$–), 1.993 (m, 8H, –CH$_2$–), 3.330 (m, 8H, –CH$_2$–), 4.078 (s, 6H, N–CH$_3$), 4.548 (t, 4H, N$^+$CH$_2$–), 6.574-6.616 (d, J=8.4 Hz, 4H, Ar), 7.022-7.105 (d, J=16.6 Hz, 2H, –CH=CH–), 7.586 (m, 4H, Ar), 7.590-7.671 (d, J=16.2 Hz, 2H, –CH=CH–), 7.685-7.727 (d, J=8.4 Hz, 4H, Ar), 7.958 (m, 4H, Ar)
 **P10L4**: $C_{50}H_{62}N_6I_2$; 1000.89 g/mol; 34 %; mp 203—207 °C	^{1}H NMR (DMSO-d_6) δ (ppm): 1.228 (m, 12H, –CH$_2$–), 1.728 (m, 4H, –CH$_2$–), 1.929 (m, 8H, –CH$_2$–), 3.248 (m, 8H, –CH$_2$–), 4.093 (s, 6H, N–CH$_3$), 4.522 (t, 4H, N$^+$CH$_2$–), 6.546-6.590 (d, J=8.8 Hz, 4H, Ar), 7.048-7.129 (d, J=16.2 Hz, 2H, –CH=CH–), 7.612 (m, 4H, Ar), 7.638 (2H, –CH=CH–), 7.699-7.743 (d, J=8.8 Hz, 4H, Ar), 7.971 (m, 4H, Ar)

during reaction and $\Delta H_p^{\text{theor}}$ — the theoretical enthalpy for complete conversion of the acrylate double bonds. $\Delta H_p^{\text{theor}}$ for the acrylic double bond is 78.2 kJ/mol [16].

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

The reaction heat liberated in the polymerization is 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 eq. 2.:

$$C = \frac{\Delta H_t M}{n\Delta H_p^{\text{theor}} m} \qquad (2)$$

where: ΔH_t — the reaction heat evolved at time t, M — the molar mass of the monomer, m — the mass of the sample, n — 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 [17].

RESULTS AND DISCUSSION

Synthetic procedures and spectral properties of the photoredox pairs

The dyes under study were obtained in reasonably good yields starting from the proper 4-aminobenzaldehydes and alkane α,γ-bis[1,2-dimethylbenzimidazolium] dihalide. They were purified by recrystallization and their structures were verified by ^{1}H NMR spectroscopy. The exchange of an anion type from iodide or bromide on borate anion, transfers this group of the dyes into efficient free radical polymerization initiating systems. The details are given in the experimental section.

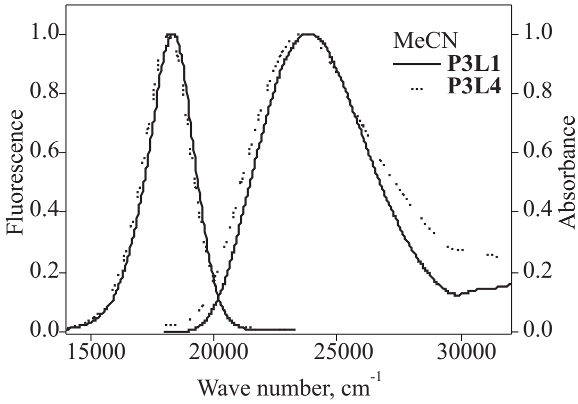


Fig. 1. Representative, normalized electronic absorption and fluorescence spectra of the P3L1 and P3L4 dyes recorded in MeCN at 293 K

Figure 1 show illustrative electronic absorption and fluorescence spectra recorded for selected dyes in MeCN. The basic spectroscopic properties of the tested dyes are summarized in Table 2.

Table 2. Spectroscopic properties of the dicationic hemicyanine dyes in EtOAc, DMF and MeCN

Dye	$\gamma^{Ab}_{\max}$ (nm) / ε (M^{-1} cm^{-1})	$\gamma^{Fl}_{\max}$ nm	Stokes Shift cm^{-1}	λ_{00} nm	E_{00} eV	ΔG_{el} eV
Ethyl acetate (EtOAc, ε = 6.053, n_D^{20} = 1.37239)						
P3L1	422	539	5144	492	2.52	-1.22
P3L4	412	545	5923	493	2.52	-1.39
P5L1	421	538	5166	488	2.54	-1.30
P5L4	429	543	4894	495	2.51	-1.40
P10L1	422	537	5075	488	2.54	-1.36
P10L4	423	545	5292	491	2.53	-1.45
N,N-dimethylformamide (DMF, ε = 36.71, n_D^{20} = 1.43047)						
P3L1	423/66700	546	5326	498	2.49	-1.19
P3L4	430/60800	551	5107	502	2.47	-1.34
P5L1	423/62300	546	5326	497	2.50	-1.25
P5L4	432/71700	551	4999	503	2.47	-1.36
P10L1	422/59100	546	5382	496	2.50	-1.32
P10L4	432/61200	551	4999	502	2.47	-1.39
Acetonitrile (MeCN, ε = 35.94, n_D^{20} = 1.34411)						
P3L1	419/61700	544	5484	496	2.50	-1.20
P3L4	423/48600	548	5392	503	2.47	-1.34
P5L1	419/61800	543	5450	494	2.51	-1.27
P5L4	424/58300	547	5303	500	2.48	-1.38
P10L1	419/57800	542	5416	491	2.53	-1.34
P10L4	424/57700	548	5337	493	2.52	-1.44

The analysis of the electronic absorption spectra clearly indicates the presence of absorption bands that correspond to the transition $S^0 \rightarrow CT$, which appears at the red-energy side of the absorption spectrum (see Fig. 1). A well-separated CT absorption band is observed for all tested dyes. The inspection of the illustrative absorption spectra, presented in Fig. 1, and data collected in Table 2 shows that the position and intensity of the CT absorption band slightly depends on the molecular structure and solvent used. It should be also noted that the type of anion has no significant effect on the position and intensity of the absorption band.

A study of the fluorescence of all tested dyes has been performed in EtOAc, DMF and MeCN at room temperature. All dyes show similar fluorescence characteristics with one broad emission band and a small red shift of about 6 nm on going from DMF to EtOAc. The fluorescence emission spectra bands are narrower than the absorption spectra. If the broadening of the spectra is understood as deriving from the population of the thermally available conformers, the observed reduction of fluorescence band width can be taken as evidence that some of these conformers are non emissive [18, 19].

The tested dyes represent bichromophoric non-conjugated molecules that show large Stokes' shift (see Table 2). This indicates that an emitting state is not the

Franck-Condon S_1 state reached in the absorption transition but different, the solvent relaxed state, from which the fluorescence originates. Also, it cannot be assumed that the excited state dipole moment remains unchanged during the transition from the Franck-Condon state to the emitting state.

Electrochemical properties of the photoredox pairs

It is well known that cyanine borate salts are a classical example of dye photoinitiators — donor-acceptor pairs with an electrostatic interaction in the ground state. The mechanism of the polymerization initiation process is based on photoinduced electron transfer process (PET) from an electron donor (borate anion) to the singlet excited state of an electron acceptor (dye cation). This process leads to the formation of alkyl radicals that initiate polymerization.

The rate of photoinduced electron transfer process is related to the free energy change of the electron transfer (ΔG_{el}) reaction according to classical Marcus theory [20]. Considerable attention has been made to testing the Marcus theory approach. Rehm and Weller were the first to point out a discrepancy between theory and experiment [21]. According to them, the ΔG_{el} can be calculated based on eq. (3):

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

where: E_{ox} $(D/D^{\bullet+})$ — the oxidation potential of the electron donor, E_{red} $(A^{\bullet-}/A)$ — the reduction potential of the electron acceptor, E_{00} — the excited state energy of electron accepting molecule, $Ze^2/\varepsilon a$ — the Coulombic energy associated with the process. Because, the last term is relatively small in polar or medium polarity media, it can be neglected in the estimation of ΔG_{el}.

The singlet state energy of the tested dyes was calculated based on the normalized electronic absorption and fluorescence spectra (Table 2). The electrochemical reduction of the hemicyanine dyes and the electron donor oxidation potentials were estimated using cyclic voltametry (see Table 3). The data of the free energy change for the photoinduced intermolecular electron transfer process are summarized in Table 2. The calculations clearly show that for the tested photoredox pairs, the electron transfer process is thermodynamically allowed (negative values of ΔG_{el}).

Kinetic study of radical polymerization

Several photoredox pairs consisting of a homodimeric hemicyanine dye (acting as electron acceptor) and phenyltri-*n*-butylborate salt (acting as electron donor) were tested as a photoinitiating system for the polymerization of acrylate monomers. Their structures are presented in Table 1.

In order to optimize the composition of the polymerization mixture, the cyanine borate concentration effect on the maximum polymerization rate was first determined. Figure 2 presents the relationship between the maximum polymerization rate and concentration of photoinitiator.

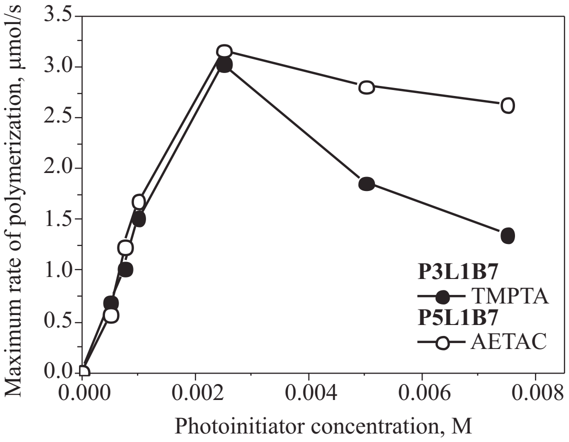


Fig. 2. The relation between the maximum polymerization rate and concentration of selected photoinitiators, I_0 equals 100 mW/cm^2

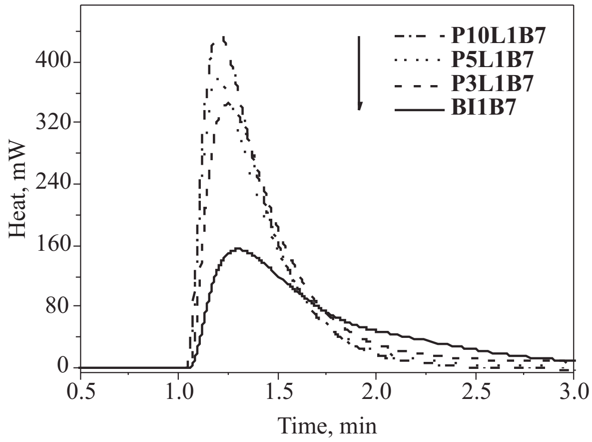


Fig. 3. Family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoininated polymerization of the TMPTA/MP (9/1) mixture initiated by homodimeric styrylbenzimidazolium borates marked in the figure; the initiator concentration was 0.0025 M; I_0 = 100 mW/cm^2; the applied dyes possessed various chromophores and identical borate; BI1B7 is 2-[4-(*N*,*N*-dimethylamino)-styryl]-1,3-dimethyl-benzimidazolium phenyl-tri-*n*-butylborate

It is evident that as the photoinitiator concentration increases, the rate of polymerization also increases and reaches a maximum before a continuous, gradual decrease. For the tested photoinitiators (P3L1B7 and P5L1B7), the highest rate of polymerization under experimental conditions was achieved at an initiator concentration of about 0.0025 M. The reduction of the photoinitiated polymerization rate at higher initiator concentration (for applied technique of polymerization rate measurement) can by understood, taking into account the decrease of the penetration depth of the laser beam [15, 17].

Figure 3 presents the kinetic curves observed for radical polymerization of TMPTA/MP mixture initiated by both mono- and bichromophoric hemicyanine borates.

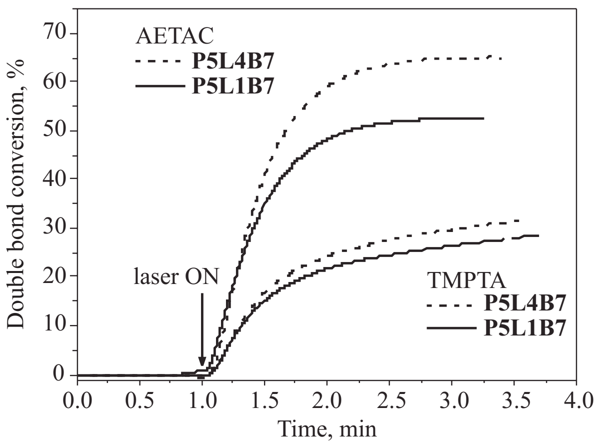


Fig. 4. Comparison of photoinitiating ability of hemicyanine borate salts to initiate polymerization of mono- and three-functional monomers; photoinitiator concentration was 0.0025 M, I_0 = 100 mW/cm^2

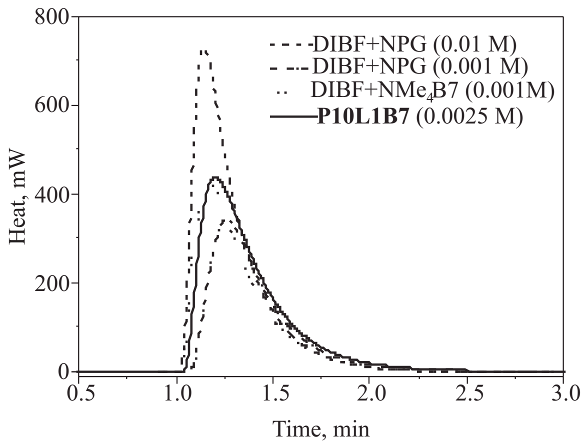


Fig. 5. Comparison of the TMPTA/MP (9/1) mixture polymerization initiated by P10L1B7, DIBF-NMe$_4$B7, and DIBF-NPG systems as measured by photo-DSC with incident light intensity 100 mW/cm^2; DIBF is a triplet state photoinitiator [22], its concentration was 0.001 M

It is apparent from inspection of Fig. 3 that the rates of polymerization of the tested photoinitiating systems depend on their structures. The highest rates of photoinitiated polymerization were observed for bichromophoric hemicyanine dyes possessing a linkage group of 10 carbon atoms between the heterocyclic rings as a spacer. The differences in the photoinitiating ability of the photoinitiating systems composed of sensitizers with five and three carbon atom covalent linkages of two identical chromophores may originate from the differences in the degree of dissociation of the hemicyanine borate salts.

Additionally, it was found that the photoinitiation efficiency of the tested hemicyanine borates depends on the character of dialkylamino substituents in the electron donating part of the molecule (see Fig. 4 and data in Table 3). The best photoinitiating abilities are exhibited by photoredox pairs possessing cyclic amino substituents in the dye molecule.

In general, the initiators that couple two electron donors in one molecule of the sensitizer exhibit a significantly higher rate of polymerization in comparison with monocationic hemicyanine (BI1B7).

For the comparison of the photoinitiating efficiency, Fig. 5 presents the kinetic curves observed for radical polymerization of the TMPTA/MP mixture photoinitiated by P10L1–phenyltri-*n*-butylborate, DIBF–phenyltri-*n*-butylborate and DIBF–NPG couples.

Data presented in Fig. 5 show that the photoinitiation ability of the homodimeric styrylbenzimidazolium phenyl-tri-*n*-butylborate is lower than that observed for the DIBF-NPG couple. It should be emphasized that such a high efficiency for tested photoinitiators is observed when the NPG (the electron donor) concentration is higher than the electron donor concentration in the P10L1B7 photoredox pair.

The polymerization quantum yields and maximal rates of photoinitiated polymerization measured for all photoinitiators in the study are collected in Table 3.

From the data, obtained during the measurements, it was deduced that the conversion of monomer double bonds ranges from 26 to 43 % for TMPTA and 47 to 81 % for AETAC, while the quantum yields of photopolymerization oscillate between 68.86 and 98.72 for TMPTA and 62.43 and 91.25 for AETAC (Table 3). It was also found that the degree of monomer conversion and the quantum yields of photopolymerization depend to some extent on the photoinitiator structures. It is noteworthy that the

Table 3. The maximal rates (R_p^{max}) and quantum yields (Φ_p) of radical polymerization and electrochemical properties for tested photoredox pairs

Dye	E_{red}(A$^{\bullet-}$/A), V	E_{red}(A/A$^{\bullet-}$), V	E_{ox}(D/D$^{\bullet-}$), V	R_p^{max}, μmol/s	Φ_p	R_p^{max}, μmol/s	Φ_p
				TMPTA		AETAC	
P3L1	-1.264	-0.592	0.890	5.92	68.86	5.09	62.43
P3L4	-1.374	-0.422	0.908	7.37	87.02	6.41	74.59
P5L1	-1.248	-0.534	0.916	7.73	90.00	5.75	70.48
P5L4	-1.362	-0.396	0.872	7.95	92.57	6.01	73.73
P10L1	-1.296	-0.476	0.918	8.48	98.72	6.98	85.61
P10L4	-1.376	-0.374	0.824	8.26	96.14	7.44	91.25

E_{ox}(D/D$^{\bullet-}$) of tetramethylamonium phenyltri-*n*-butylborate is 0.708 V.

photoinitiating systems composed of monochromophoric dye (BI1B7), at a concentration equal to 0.0025 M, shows a lower photoinitiation ability with a quantum yield of polymerization of about 32.67 and the maximum polymerization rate equal to 2.67 μmol/s. The observed differences can be easily explained taking into account the amount of the electron donor in close proximity to the excited chromophore.

The steps determining the reaction rate of the free-radical initiated polymerization *via* an intermolecular electron-transfer process (PET) are dependent on the nature of the dye and the electron donor (or acceptor). In the case of a borate anion acting as an electron donor, the alkyl radical is formed as a result of rapid cleavage of the alkyl-boron bond within the boranyl radical produced after the electron transfer [23, 24]. Therefore, the efficiencies of alkyl radical formation and, hence, initiation of polymerization depend on the rate of electron transfer from the borate anion to the singlet state of styrylbenzimidazolium dye cation. Since the lifetime of the hemicyanine singlet is short (usually less than 1 ns), an efficient electron transfer between borate anion and an excited dye molecule is possible only in nonpolar solvent where the process occurs between components of the tight-ion-pair [23, 24]. Even a small amount of polar solvent, as documented by Neckers, may sharply change the degree of such ion pair formation [25]. Our studies of the influence of the borate anion concentration on the rate of photoinitiated polymerization also confirm that when the borate anion and hemicyanine cation are present in a 1:1 mixture, only some of the photoredox pairs exist as ion pairs [15, 26]. However, the existence of a hemicyanine cation and a borate anion as a tight-ion-pair is the basic prerequisite for effective electron transfer. Therefore, an artificial increase in the number of electron donor moieties within one molecule achieved by the coupling of the second borate anion to the dye molecule improves the photoinitiating ability of the tested photoredox pairs. The electron transfer process for dimeric hemicyanine borate salts is more efficient and this results in an increase of the formation of the radical starting polymerization chain reaction.

The use of hemicyanine borates creates a unique opportunity to study the possibility of the application of the Marcus theory of the photoinduced electron transfer for the description of the polymerization rate. For these photoinitiators, the change of the driving force of the electron transfer process has no influence on the type of the yielding free radical. In our earlier papers [15, 26] we showed that in very viscous media, the rate of polymerization initiated *via* a photoinduced intermolecular electron transfer can be described as in eq. (4):

$$\ln R_p = A - \frac{(\lambda + \Delta G_{el})^2}{8\lambda RT} \tag{4}$$

where: A for the initial time of polymerization is the sum: $\ln k_p - 0.5 \ln k_t + 1.5 \ln [M] + 0.5 \ln I_a$ (here k_p, k_t denote the rate constant of polymerization and termination, respectively, [M] the monomer concentration, and I_a is intensity of absorbed light), λ is the reorganization energy necessary to reach the transition states both of the excited molecule and solvent molecules.

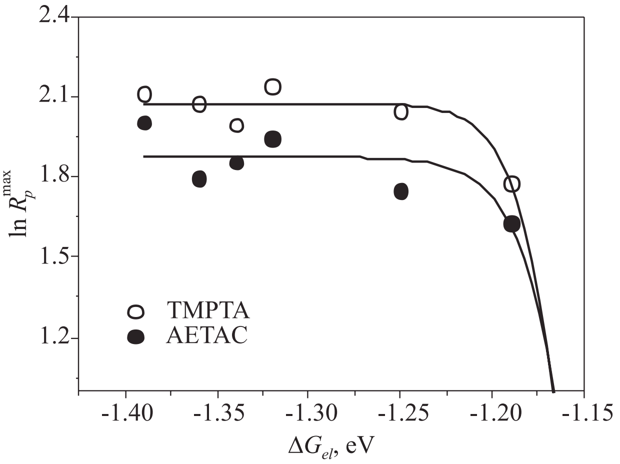


Fig. 6. Dependence of the maximal rate of photoinitiated polymerization on the free energy (ΔG_{el}) for the photoinduced electron-transfer process from borate to the excited state of bischromophoric hemicyanine dye

Equation (4) clearly indicates that if the primary process, *e.g.* the rate of electron transfer, controls the observed rate of photopolymerization, one should observe a parabolic relationship between the logarithm of maximum polymerization rate and the free energy change ΔG_{el}. This is shown in Fig. 6 for the examined photoinitiating photoredox pairs.

According to Fig. 6, the rate of free radical polymerization initiated by the series of homodimeric hemicyanine borates increases as the driving force of the electron transfer reaction increases. This behavior is predicted by the classic theory of photoinduced electron transfer [7—9].

CONCLUSIONS

The dicationic styrylbenzimidazolium dyes paired with an effective electron donor, such as phenyltrialkylborates, are good photoinitiators of radical polymerization. The homodimeric hemicyanine dyes have high electron affinity and participate in the photoreducible sensitization. The specially designed dyes bearing two electron donor moieties in one molecule initiate radical polymerization more effectively compared to their monocationic analogues. Their photoinitiation ability only slightly depends on the chemical structure of the dye. The limiting step in the photoinitiated polymerization is an electron transfer within the photoredox pair.

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