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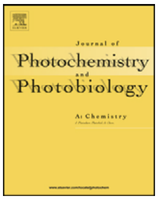

Multicationic monomethine dyes as sensitizers in two- and three-component photoinitiating systems for multiacrylate monomers

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ABSTRACT

This paper is focused on the description of the synthesis, spectroscopic and electrochemical properties, and the free radical photoinitiation abilities of new multi-cationic monomethine dyes.

The new monomethine dyes were employed both as the visible light photoinitiators of acrylate monomer polymerization and as fluorescence probes for monitoring the progress of polymerization. A degree of polymer cure from the measurement of the changes in the probe emission intensity and position shift during the thermally initiated polymerization of monoacrylate was obtained. A distinct increase in the intensity of the dyes fluorescence was observed during polymerization when the degree of monomer conversion was gradually increasing.

The second part of this work is the possibility of an application of the dyes synthesized in combination with borate anions, as photoinitiating systems.

Novel multi-cationic monomethine dyes paired with *n*-butyltriphenylborate anions are very efficient visible light photoinitiators of free radical polymerization of acrylate monomers. Their photoinitiating abilities were compared with the photoinitiation ability of Rose Bengal derivative, e.g. typical triplet state photoinitiator.

The addition of a second co-initiator to the two-component photoinitiating system (monomethine borate salts) enhances their photoinitiating abilities.

1. Introduction

Direct photoinduced polymerization reactions concern the creation of a polymer P through a chain reaction initiated by light (Scheme 1).

Since direct formation of reactive species on the monomer by light absorption is not an efficient route, the initiation step of the polymerization reaction requires the presence of a photoinitiator PI which, under light excitation, is capable of generating these reactive spaces (Scheme 2).

Extension of the spectral sensitivity (that corresponds to the best matching between the emission spectrum of the light source and the absorption spectrum of the formulation) can be achieved using photoinitiating systems (PSs): their role is absorb the irradiation energy at a wavelength where PI is unable to operate and to transfer the excitation to PI. In that case, the reaction is defined as a sensitized photoinduced polymerization (Scheme 3).

The intrinsic reactivity of photoinitiating system which plays an important role on the rate of photoinitiated free radical polymerization determines its interest an is directly connected with: (i) its molecular structure (which governs the intensity of the light absorbed, the absorption wavelength range, the energy or electron transfer reaction ability) and (ii) the efficiency of the photophysical and photochemical processes involved in the excited states (which determines the yield of cleavage reaction, electron transfer reactions, quenching by monomer or oxygen or other additives such as, e.g. hydrogen donors, light stabilizers, interaction with PS) [1].

Many photosensitive systems PI and PS for radical photopolymerization have been developed in recent years to take up the challenge of designing organic molecules working in well-defined conditions of laser excitations [1].

In radical photopolymerization reactions, examples include: ketocoumarins and coumarins derivatives (e.g. xanthene dyes such as Eosin or Rose Bengal, thioxanthene dyes); thioxanthones; bis-acylphosphine oxides, peresters; pyrylium and thiopyrylium salts in presence of additives such as a perester; cationic dyes containing a borate anion; dyes/bis-imidazole derivatives/thiols; PS/chlorotriazine/additives; metallocene derivatives (such as titanocenes); dyes or ketones/metallocene derivatives/amines; cyanine dyes in the presence of additives; dyes/bis-imidazoles; miscellaneous systems such as phenoxazones, quinolinones, phtalocyanines, squaraines, squarylium containing azulenes, novel fluorine visible light Pis, benzopyranones, rhodamines, riboflavines and two color sensitive systems [1–8].

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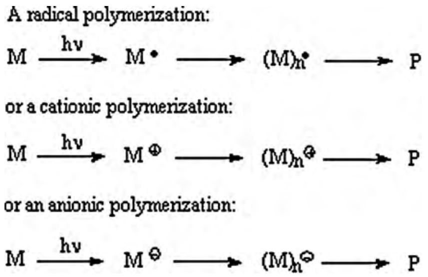
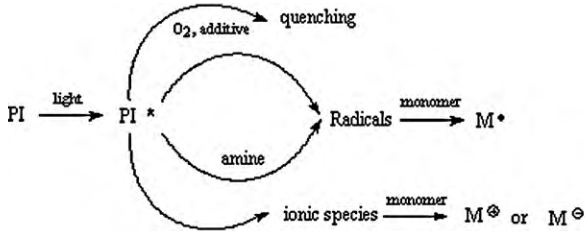


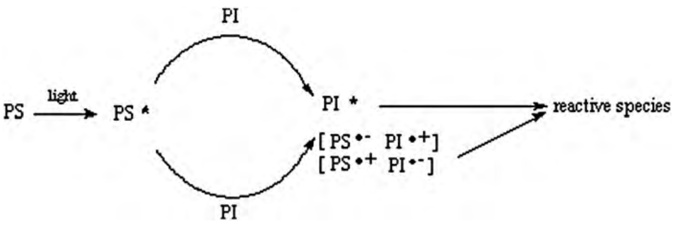
Scheme 1.



Scheme 2.

In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiator molecules with more desirable properties, such as higher activity coupled with greater speed and a low migration rate to the surface of the cured coating in order to reduce loss of adhesion and to minimize toxicity. One area of importance in this regard is the development of photoinitiators having great spectral sensitivity to the visible region of the spectrum [9]. These initiators absorb visible light with a high speed and cause the same photopolymerization events described above to take place – namely a conversion of a highly functionalized liquid acrylate monomer to a solid polyacrylate. In practice, monomers used in fast photoinitiated polymerization are acrylates or modified acrylates whose structure lends to rapid cross-linking. Some of the photoinitiators have been widely discussed in the literature for they are the backbone of the photopolymerization. In one such process, the initiators are cyanine borate ion salts, so called ion pair initiators, which utilize single electron transfer to the excited state of the light absorbing dye from the partner ion acting as electron donors, starting the crucial first step in the initiation of the radical chain. Thus, the cyanine dye, in its excited state, accepts an electron from the borate anion and subsequent boranyl radical decomposition leads to the formation of free radicals which initiate polymerization [10]. The application of different cyanine borate salts in photoinitiated free radical polymerization was first described by Schuster [10,11] and by our research group [12–16].

In this paper, the kinetic studies of the novel two- and three-component photoinitiating systems consisting of multichromphore monomethine dyes (the light absorbers) coupled with butyltriphenylborate anions (co-initiators) are described.



Scheme 3.

Here, it is demonstrated also that multi-cationic monomethine dyes can be used as fluorophores for monitoring the progress of the methyl methacrylate (MMA) polymerization. The relationship between the change in emission spectra of dye molecules and the degree of monomer conversion during thermally initiated polymerization is presented.

2. Experimental

2.1. Materials

All substrates for synthesis of multi-cationic monomethine dyes (2-methylbenzothiazole, methyl iodide, 4-chloroquinoline, 1,3-dibromopropane, pyridine, 2-methoxyethanol, N,N,N′N′-tetramethyl-1,3-propanediamine, N,N,N′,N′-tetramethyl-1,6-hexanediamine, 1,4-diazabicyclo[2,2,2]octane and 4,4′-bipirydyle) and tetramethylammonium *n*-butyltriphenylborate (triphenylboron, *n*-butyllithium, benzene) were purchased from Aldrich and used without further purification. *n*-Butyltriphenylborate tetramethylammonium (**B2**) was used as a co-initiator. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich and used as monomer and solvent, respectively.

2.2. Techniques

The synthesis of multi-cationic monomethine dyes was carried out using the method described by Deligeorgiev [17,18]. Tetramethylammonium *n*-butyltriphenylborate (**B2**) was synthesized according the method described by Damico [19]. All final products were identified by ^{1}H NMR spectroscopy. The spectra obtained were the evidence that the reaction products were of the desired structures. The purity of synthesized compounds was determined using thin layer chromatography and by measuring of the melting points. The purity of the dyes was as it is required for spectroscopic studies.

Spectroscopic measurements: UV/vis absorption spectra: obtained using Shimadzu UV–vis Multispec – 1500 Spectrophotometer, and steady-state fluorescence: using a Hitachi F-4500 Spectrofluorimeter.

The reduction and oxidation potentials were measured by cyclic voltammetry. An Electroanalitical MTM System model EA9C-4z (Cracow, Poland), equipped with a small-volume cell was used for the measurements. A 1-mm platinum electrode was applied as the working electrode. A Pt wire constituted the counter electrode, and an Ag–AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. The solution was deoxygenated by bubbling argon gas through the solution. The potential was swept from −1.6 to 1.6 V with the sweep rate of 500 mV/s to record the current–voltage curve.

2.2.1. Monitoring the free radical polymerization of monoacrylate

A deoxygenated MMA solution, containing of α,α′-azo-bisisobutyronitrile (AIBN) as a thermal free radical polymerization initiator (1%) and a tested probe at a concentration giving an intensity of the absorption at maximum about 0.2 were placed in Pyrex test tubes. The polymerization was initiated at 50 °C. The samples were periodically (20 or 30 min) removed from the water bath and cooled with ice to about 0 °C to stop the polymerization and then were warmed to the room temperature. The fluorescence of solutions was measured after the subsequent time of polymerization. The degrees of polymerization were estimated by a gravimetrical method after the precipitation of the polymer in ethanol [20].

2.2.2. Monitoring of the kinetics of the free radical polymerization of polyacrylate

It was based on the measurements of the rate of heat evolution during polymerization in a polymerizing sample. Photoinitiated polymerization rate (R_p) profiles were determined by a differential scanning calorimetry (DSC), under isothermal conditions at room temperature using a photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. The 0.035 ± 0.002 g of sample was polymerized in open aluminium pans having the diameter of 6.6 mm. Irradiation of the polymerization mixture was carried out using the emission (line at 514 nm) of an argon ion argon-ion laser Air-cooled Ion Laser Systems model 177-G01 (Spectra-Physics, USA) with intensity of light of 20 mW/0.196 cm^2. The light intensity was measured by a Coherent Model Fieldmaster power meter.

The rate of polymerization (R_p) was calculated using the formula (1) where dH/dt is maximal heat flow during reaction, M is the molar mass of the monomer, m is the mass of the sample, n is the number of double bonds per monomer molecule and $\Delta H_p^{\text{theor}}$ is the theoretical enthalpy for complete conversion of acrylates' double bonds. $\Delta H_p^{\text{theor}} = 78.2$ kJ/mol for acrylic double bonds.

$$R_p = \left(\frac{dH}{dt}\right)\frac{M}{n\Delta H_p^{\text{theor}} m} \qquad (1)$$

A polymerization solution was composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The photoinitiators concentration used in experiments was 5×10^{-3} M and 1×10^{-3} M for mono- and multi-cationic dyes, respectively. The second co-initiators concentration was 5×10^{-2} M. As a reference sample, a polymerizing mixture containing cyanine iodide (dye without a co-initiator) was used. The polymerizing mixture was not deaerated. In order to reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish–Troomsdorf effect and radicals trapping effect, the initial rates of polymerization were taken into account for further consideration.

2.3. Synthesis

The synthetic approaches that were applied are outlined below and are based on the reaction of 2,3-dimethylbenzothiazolium iodide with 1-(3-bromopropyl)-4-chloroquinolinium bromide in presence of triethylamine. The obtained dye A1 were quaternized with pyridine and bisquaternized with N,N,N′,N′-tetramethyl-1,3-propanediamine, N,N,N′,N′-tetramethyl-1,6-hexanediamine, 1,4-diazabicyclo[2,2,2]octane and 4,4′-bipirydyle.

A general route of the synthesis of multi-cationic monomethine dyes is shown in Scheme 4.

As it is shown in Scheme 4 the synthesis of the multi-cationic monomethine dyes undergoes *via* few steps:

1. The quaternization reaction of pyridine with 1,3-dibromopropane yielding 1-(3-bromopropyl)pyridinium bromide (**A1**).
2. The quaternization reaction of 2-methylbenzothiazole with 1-(3-bromopropyl)pyridinium bromide or methyl iodide, that leads to the formation following salts: 2-methyl-3-[3-(pyridino)propyl]benzothiazolium dibromide (**B1**) and 2,3-dimethylbenzothiazolium iodide (**B2**).
3. The quaternization reaction of 4-chloroquinoline with 1,3-dibromopropane, giving 1-(3-bromopropyl)-4-chloroquinolinium bromide (**C1**).
4. The condensation of 2-methyl-3-[3-(pyridino)propyl]benzothiazolium dibromide (**B1)** and 2,3-dimethylbenzothiazolium iodide (**B2**) with 1-(3-bromopropyl)-4-chloroquinolinium bromide (**C1**) in presence of triethylamine, yielding dyes **D1** and **D2**.
5. The additional quaternization of dyes **D1** and **D2** with pyridine, that leads to the formation of dyes **D3** and **D4**.
6. The bisquaternization of [1-(3-bromopropyl)-4-[(3-methyl-2-benzothiazolilyden)methylquinolinium iodide] with N,N,N′,N′-tetramethyl-1,3-propanediamine, N,N,N′,N′-tetramethyl-1,6-hexanediamine, 1,4-diazabicyclo[2,2,2]octane and 4,4′-bipirydyle, giving dyes **D5**–**D8**.

2.3.1. N-(3-bromopropyl)pyridinium bromide (*A1*)

N-(3-bromopropyl)pyridinium bromide (**A1**) was prepared using method described by Botero [21].

1,3-Dibromopropane (30 mmol) and pyridine (10 mmol) were heated at 45–50 °C in acetonitrile (60 mL) for 8 h. The solvent was removed in vacuum. The remaining oil was crystallized in ethanol-dichloromethane mixture (5:1).

2.3.2. 2-Methyl-3-[3-(pyridino)propyl]benzothiazolium dibromide (*B1*)

The quaternization reaction of 2-methylbenzothiazole with N-(3-bromopropyl)pyridinium bromide (**A1**) was carried out using method described by Deligeorgiev [17,18].

2-Methylbenzothiazole (0.1 mol) and N-(3-bromopropyl)pyridinium bromide (**A1**) were melted and the viscous alloy was stirred at 160 °C for 30 min. The melt was cooled to 60 °C and 30 mL of acetone was added to the reaction mixture. The acetone layer above the solidified melt was decanted. The semisolid salt was used without further purification in the reaction step giving the required dye [17,18].

2.3.3. 1-(3-Bromopropyl)-4-chloroquinolinium bromide (*C1*)

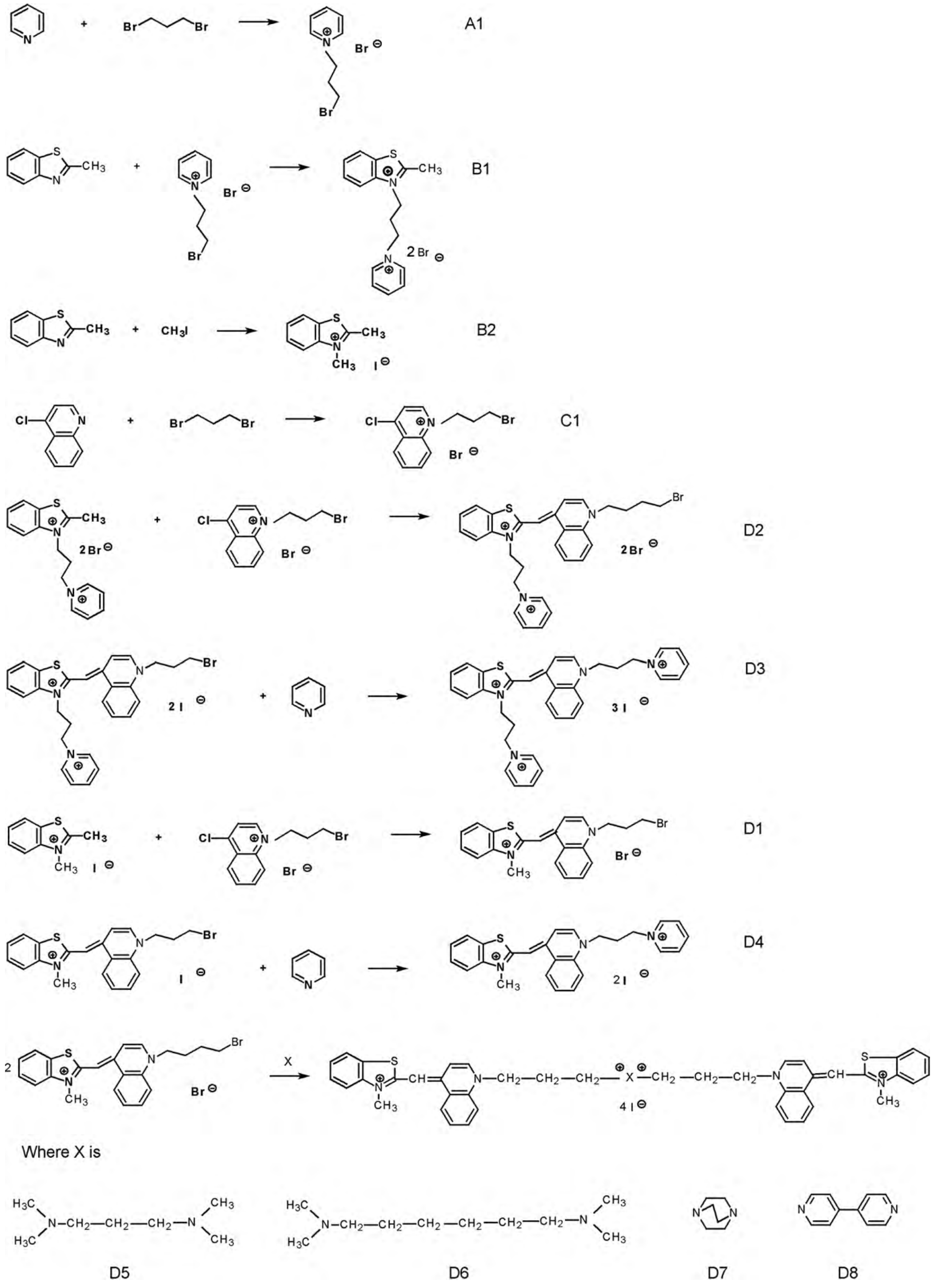
1-(3-Bromopropyl)-4-chloroquinolinum bromide (**C1**) was prepared using a method described by Gadjev [18]. Five grams (0.03 mol) of 4-chloroquinoline were suspended in 7 mL of chlorobenzene. To the suspension 6.1 mL (12.1 g, 0.06 mol) of 1,3-dibromopropane were added. The reaction mixture was refluxed and stirred for 2 h. Then additional 4.04 g (2 mL) of 1,3-dibromopropane were added and reflux was continued for 2 h. The reaction mixture was cooled yielding solid product. The compound was filtered and dried under vacuum. Yield of the crude product 10.35 g (85%) [19]. N-(3-bromopropyl)-4-chloroquinolinum bromide is highly hygroscopic and requires storing in a desiccator. The obtained product was used in the next reactions steps without additional purification.

2.3.4. The synthesis of the corresponding monomethine dyes (*D1, D2*)

N-methyl-2-[N-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (**D1**), N-[(3-(pyridinopropyl)]-2-[N-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (**D2**) were obtained by refluxing of 1-(3-bromopropyl)-4-chloroquinolinum chloride (**C1**) (0.0035 mol) with 2-methyl-3-[3-(pyridino)propyl]benzothiazolium dibromide (**B1)** and 2,3-dimethylbenzothiazolium iodide (**B2**) (0.0035 mol) in methoxyethanol (15 mL) in the presence of triethylamine (0.97 mL, 0.007 mol) for 30 min. A triple excess of saturated aqueous potassium iodide solution was added to the hot dye solution. The precipitate formed after cooling the reaction mixture was filtered and recrystallized from either aqueous ethanol or methanol [18].

2.3.5. N-methyl-2-[N-(3-bromopropyl)quinoline]-2-methyl enebenzothiazolium diiodide (*D1*)

D1: $C_{21}H_{20}N_2SIBr$; yield 54.1%; mp 110 °C.



Scheme 4.

^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.129–1.199 (t, 2H, –CH$_2$–), 3.045–3.208 (m, 2H, –CH$_2$–Br), 4.026 (d, 2H, N–CH$_2$), 4.181 (s, 3H, –CH$_3$–N$^+$–), 6.927 (s, 1H, –CH=), 7.744–7.918 (m, 5H, Ar), 8.253–8.295 (d, 3H, Ar), 8.400–8.442 (d, 2H, Ar).

*2.3.6. N-(3-pyridinopropyl)-2-[N-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (**D2**)*

D2: C$_{28}$H$_{28}$N$_3$SBrI$_2$; yield 74.1%; mp 204 °C.

^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.139–1.212 (m, 2H, –CH$_2$-), 3.058–3.154 (2H, –CH$_2$–), 3.410–3.655 (2H, –CH$_2$–), 4.329 (m, 2H, –CH$_2$N), 4.784–5.143 (m, 4H, –CH$_2$N$^+$), 6.934 (1H), 7.395–7.468 (m, 2H, Ar), 7.630–7.675 (2H, pyr), 7.886–7.899 (4H, Ar), 8.099–8.134 (d, 1H, J = 7 Hz, pyr), 8.261–8.298 (d, 1H, J = 7.6 Hz, pyr), 8.439–8.826 (5H, Ar).

*2.3.7. The synthesis of the corresponding multi-cationic monomethine dyes (**D3**, **D4**)*

The corresponding dyes **D1** and **D2** (0.00034 mol) and 0.08 mL of pyridine (0.001 mol) in 3 mL of 2-methoxyethanol were refluxed with stirring for 6 h. To the hot solution, a triple excess of saturated aqueous potassium iodide solution was added. After cooling the precipitated dye was filtered and dried [19].

*2.3.8. N-(3-bromopropyl)-4-{[N-(3-pyridinopropyl)-2-benzothiazolilydene)methyl]}quinolinium triiodide (**D3**)*

D3: C$_{33}$H$_{33}$SN$_4$I$_3$; yield 97%; mp.192 °C.

^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.117–1.187 (t, 2H, N–CH$_2$–), 3.110–3.465 (m, 4H, –CH$_2$–), 4.758–4.967 (s, 4H, N$^+$–CH$_{2,}$ Pyr), 5.157–5.260 (t, 2H, –CH$_2$–N$^+$–), 6.849 (s, 1H, –CH=), 7.355–7.545 (m, 4H, Ar), 7.725–8.326 (m, 6H, Ar), 8.545–8.805 (dd, 6H, Ar), 9.172–9.197 (d, 4H, Ar).

*2.3.9. N-(methyl)-4-{[N-(3-pyridinopropyl)-2-benzothiazolilydene)methyl]}quinolinium diiodide (**D4**)*

D4: C$_{26}$H$_{25}$SN$_3$I$_2$; yield 34.41%; mp. 292 °C.

^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.117–1.187 (t, 2H, –CH$_2$-), 3.125–3.136 (t, 2H, N–CH$_2$–), 4.157 (s, 3H, CH$_3$–N$^+$–), 4.758–4.967 (s, 2H, N$^+$–CH$_{2,}$ Pyr), 6.749 (s, 1H, –CH=), 7.355–7.545 (m, 2H, Ar), 7.725–8.326 (m, 6H, Ar), 8.545–8.805 (dd, 6H, Ar), 9.172–9.197 (d, 3H, Ar).

*2.3.10. The synthesis of the corresponding four-cationic monomethine dyes (**D5**–**D8**)*

The four-cationic monomethine dyes (**D5**–**D8**) were synthesized according method described by Deligeorgiev [17]. 0.002 mol of N-methyl-2-[N-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium diiodide (**D1**) and 0.001 mol of N,N,N′,N′-tetramethyl-1,3-propanediamine, N,N,N′,N′-tetramethyl-1,6-hexanediamine, 1,4-diazabicyclo[2,2,2]octane or 4,4′-bipirydyle were refluxed in 5–9 ml of 2-methoxyethanol for 15 min to 3 h. After cooling the precipitated dye was filtered and dried. The dye was dissolved in hot methanol and an excess of aqueous potassium iodide solution was added to the solution. The solution was cooled and the precipitated dye was filtered and dried. The dye was recrystallized from methanol [17].

*2.3.11. N,N′-bis{3-[4-{(3-methyl-2-benzothiazolilydeno)methylquinolinium-1-ylo]propyl}-1,4-diazobicyclo[2,2,2]oktane tetraiodide (**D5**)*

D5: C$_{48}$H$_{52}$I$_4$N$_6$S$_{2;}$ yield 45.6%; mp. 281 °C. ^{1}H NMR (DMSO-d$_6$) δ (ppm): 2.323–2.327 (m, 8H, –CH$_2$–), 2.794–3.010 (2s, 6H, N$^+$–CH$_3$), 3.938–4.034 (m, 16H, N$^+$–CH$_{2,}$ Pyr), 4.325 (dd, 4H, –CH$_2$–N–), 4.805 (dd, 4H, N$^+$–CH$_2$–), 6.837–6.927 (d, 2H, –CH=), 7.200 (d, 1H, Ar), 7.370–7.411 (d, 2H, Ar), 7.456–7.770 (t, 7H, Ar), 7.775–8.061 (tt, 7H, Ar), 8.194 (m, 2H, Ar), 8.610–8.647 (m, 2H, Ar).

*2.3.12. N,N,N′,N′-tetramethyl-N,N′-bis{3-[4-{(3-methyl-2-benzothiazolilydeno)methyl]-quinolinium-1-ylo]propyl}-1,6-hexanodiamine tetraiodide (**D6**)*

D6: C$_{52}$H$_{64}$I$_4$N$_6$S$_{2;}$ yield 74.6%; mp. 266–268 °C. ^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.315–1.327 (m, 8H, –CH$_2$–), 3.032 (s, 12H, N$^+$–(CH$_3$)$_3$), 3.915–3.946 (d, 8H, N$^+$–(CH$_2$)$_2$), 4.028 (s, 3H, N$^+$–CH$_3$), 4.667 (s, 2H, N–CH$_2$–), 4.816 (s, 2H, N–CH$_2$–), 6.848 (s, 2H, –CH=), 7.588 (d, 3H, Ar), 7.685–7.711 (d, 4H, Ar), 7.931–7.969 (d, 4H, Ar), 8.158–8.200 (d, 3H, Ar), 8.539–8.574 (d, 3H, Ar), 8.694–8.697 (m, 3H, Ar).

*2.3.13. N,N,N′,N′-tetramethyl-N,N′-bis{3-[4-{(3-methyl-2-benzothiazolilydeno)methyl]-quinolinium-1-ylo]propyl}-1,3-propanodiamine tetraiodide (**D7**)*

D7: C$_{49}$H$_{58}$I$_4$N$_6$S$_{2;}$ yield 80.6%; mp. 174–182 °C. ^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.315–1.327 (m, 6H, –CH$_2$–), 3.907–3.944 (d, 8H, N$^+$–(CH$_2$)$_2$), 4.667 (s, 6H, N$^+$–CH$_3$), 4.819 (s, 4H, N$^+$–CH$_2$), 6.847 (s, 2H, –CH=), 7.233–7.456 (m, 3H, Ar), 7.491–7.748 (m, 6H, Ar), 7.858–7.969 (d, 6H, Ar), 8.548–8.583 (d, 3H, Ar), 8.700–8.737 (d, 3H, Ar).

*2.3.14. N,N,N′N′-tetramethyl-N,N′-bis-{3-[4-[(3-methyl-2-benzothiazolideno)methyl]-quinolinium-1-ylo]propyl}-4,4’-bipirydyle tetraiodide (**D8**)*

D8: C$_{52}$H$_{48}$I$_4$N$_6$S$_{2;}$ yield 36.5%; mp. 148–150 °C. ^{1}H NMR (DMSO-d$_6$) δ (ppm): 1.960–1.970 (m, 4H, –CH$_2$–), 3.836–4.034 (d, 6H, N$^+$–CH$_3$), 4.440–4.500 (d, 4H, N–CH$_2$–), 4.839 (s, 4H, N$^+$–CH$_2$), 6.800 (s, 2H, –CH=), 7.200–7.256 (m, 4H, Ar), 7.370–7.384 (m, 8H, Ar), 7.863–8.037 (m, 8H, Ar), 8.196–8.233 (d, 4H, Ar), 8.597–8.781 (m, 4H, Ar).

3. Results and discussion

3.1. Synthesis

For the study eight different mono- and multi-cationic monomethine dyes were obtained. The dyes synthesis requires some intermediates to be prepared. 2-Methylbenzothiazole was quaternized with methyl iodide or 1-(3-bromopropyl)pyridinium bromide (**A1**) by melting together the components at around 160 °C for 30 min (Scheme 4), thus giving products **B1** and **B2**.

4-Chloroquinoline was quaternized with 1,3-dibromopropane for the preparation of compound **C1**. Dyes **D1** and **D2** were prepared by condensation reaction of the quaternized 2-methylbenzothiazolium salts **B1** and **B2** in the presence of triethylamine (Scheme 4). Dyes **D3** and **D4** with three and two positive charges were synthesized by additional quaternization of dyes **B1** and **B2** with pyridine.

In the next reaction [1-(3-bromopropyl)-4-[(3-methyl-2-benzothiazolilydeno)methylquinolinium iodide], were bisquaternized with N,N,N′,N′-tetramethyl-1,3-propanediamine, N,N,N′,N′-tetramethyl-1,6-hexanediamine, 1,4-diazabicyclo[2,2,2]octane and 4,4′-bipirydyle, given dyes **D5**–**D8** (Scheme 4).

In order to transform the monomethine dyes into the efficient free radical polymerization initiating systems an anion exchange from halogene to borate was necessary. The ion exchange reaction was performed using the procedures given by Damico [19] and Schuster [10]. The final products were identified by ^{1}H NMR. The spectra and results obtained were the evidence that the tested salts were of the desired structures.

3.2. Spectroscopic and electrochemical properties

The benzothiazole based monomethine dyes studied display several specific properties that are similar to the properties of other

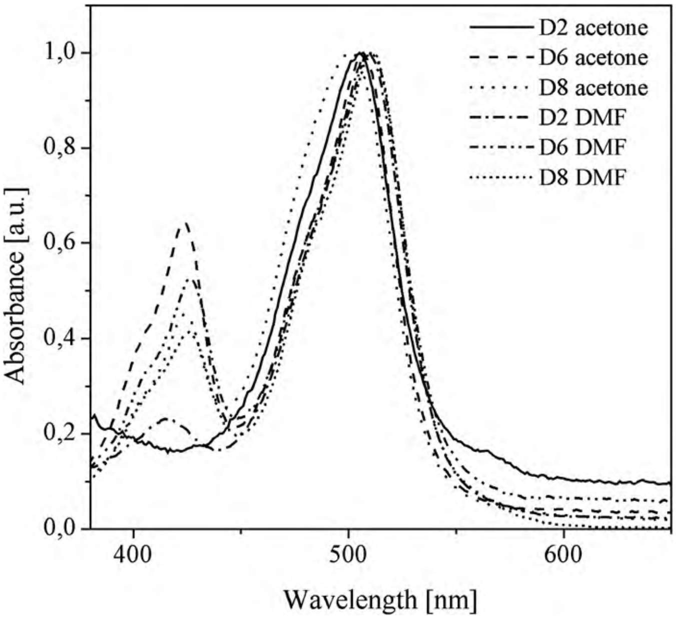


Fig. 1. The illustrative electronic absorption spectra of selected dyes (marked in figure) recorded in acetone and N,N-dimethylformamide (DMF) as a solvent, respectively.

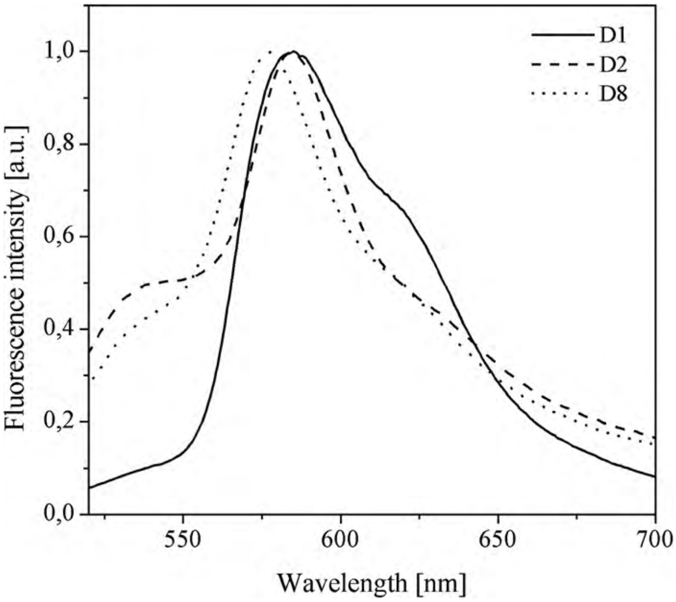


Fig. 2. The illustrative fluorescence spectra of selected dyes (marked in figure) recorded in N,N-dimethylformamide (DMF) as a solvent, λ_{ex} = 500 nm.

monomethine dyes reported in the literature [22–26]. They have a common structural feature namely, they possess an electron-donor and electron-acceptor moieties located on the opposite sides of the monomethine bond.

Figs. 1 and 2 show the illustrative electronic absorption and the fluorescence emission spectra recorded for the selected monomethine dyes in N,N-dimethylformamide and acetone as a solvent, respectively.

Table 1 collects the values of the absorption maximum positions, the fluorescence maximum positions and Stokes shifts for all dyes measured in DMF and acetone.

The electronic absorption spectra of all the dyes display two absorption bands, a main broad band with a maximum about 510 nm.

The difference in energy between the absorbed and emitted radiation is known as the Stokes shift [26]. The Stokes shift values obtained for novel multi-cationic monomethine dyes tested are shown in Table 1. The high value of Stokes shift in both solvents (>2000 cm^{-1}) is observed for all dyes under study.

It is well known that the main prerequisite for a photoinduced electron transfer (PET) reaction (vital for free radical formation) is that the thermodynamic driving force for the electron transfer reaction between an excited state of a dye and an electron donor should have a negative value. The free energy of activation for the PET (ΔG_{el}) process can be easily estimated on the basis of the Rehm–Weller equation (2) [27]:

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

where $E_{ox}\left(D/D^{\bullet+}\right)$ is the oxidation potential of the electron donor, $E_{red}\left(A^{\bullet-}/A\right)$ is the reduction potential of the electron acceptor, E_{00} is the energy of the excited state involved in electron transfer reaction and $Ze^2/\varepsilon a$ is 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 E_{ox} and E_{red} of both photoredox pair components were determined from cyclovoltameric measurements (Table 2). The electrochemical reduction of the dyes is reversible as it is shown in Fig. 3. However, the oxidation of alkyltriphenyl borate is dissociative and this in turn causes the electrochemical process to be irreversible.

The thermodynamically meaningful oxidation potential can be established using an indirect, kinetic method described by Murphy and Schuster [28]. Oxidation potentials measured electrochemically and kinetically differ by about 0.3 eV.

Therefore, the obtained electrochemical values for both components of photoredox pairs may have only approximate thermodynamic meaning, yet allow us to estimate roughly the free energy of activation (ΔG_{el}) for the photoinduced electron transfer process (PET).

The measured values of the dyes reduction potentials, the electron donor (*n*-butyltriphenylborate anion) oxidation potential (E_{ox} = 1.16 eV) and the singlet state energy of the dyes, allow us to calculate the free energy change for the photoinduced intermolecular electron transfer process with the Rehm–Weller equation [27]. The estimated data are summarized in Table 2.

The values of ΔG_{el} for the tested photoinitiating systems oscillate in the range from −16.41 to 7.72 kJ × mol^{-1}. The calculations clearly show that for the tested photoredox pairs the electron transfer process is thermodynamically allowed. This, in turn, allows us

Table 1
Steady state spectroscopic properties of the multi-cationic monomethine dyes under the study.

Solvent	Dye	λ_{ab} [nm]	λ_{fl} [nm]	Stokes shift [cm^{-1}]
DMF	D1	513	585	2399
	D2	509	585	2552
	D3	511	571	2056
	D4	513	578	2192
	D5	513	578	2192
	D6	511	577	2238
	D7	513	575	2101
	D8	510	578	2307
Acetone	D1	507	583	2571
	D2	505	581	2590
	D3	507	568	2118
	D4	507	574	2302
	D5	507	571	2211
	D6	506	572	2280
	D7	507	577	2393
	D8	502	571	2407

Table 2
Reduction potential data, energy of the excited state involved in electron transfer reaction (E_{00}) and calculated free energies (ΔG_{el}) of the electron transfer reaction between the singlet excited state of the tested dyes and electron donor and the rate of polymerization.

Dye	E_{ox} [eV]	E_{red} [eV]	ΔG_{el} [kJ × mol^{-1}]	R_p [μmol/s]
D1	2.18	−1.10	7.72	0.14
D2	2.34	−1.195	1.45	0.20
D3	2.36	−1.10	−9.65	0.40
D4	2.33	−1.05	−11.S8	0.015
D5	2.36	−1.03	−16.41	0.060
D6	2.37	−1.10	−10.62	0
D7	2.35	−1.10	−8.69	0.50
D8	2.33	−1.12	−4.83	0.79

to predicting that the tested dyes paired with borate anion should effectively generate free radicals that can start polymerization of acrylate monomers.

3.3. The kinetic of free radical polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA)

3.3.1. Two-component photoinitiating systems

The photoinitiating systems composed of multi-cationic monomethine dye (electron acceptor) as the photosensitizer coupled with *n*-butyltriphenylborate anion (electron donor) and for comparison corresponding parent mono-cationic monomethine dye paried with the same electron donor were used for the initiation of free radical polymerization. The structures of photoinitiators tested are given in Chart 1.

The polymerization solution consisted of 5×10^{-3} M of mono-cationic sensitizer and 1×10^{-3} M of multi-cationic sensitizer as an *n*-butyltriphenylborate salt. The polymerization process was carried out with irradiation at wavelength equal 514 nm.

In order to optimize the composition of a polymerization mixture, at the beginning, the influence of cyanine borate concentration on observed rate of polymerization was determined. Fig. 4 presents the relationship between the initial rate of polymerization (taken as the maximum value of heat evolved during polymerization time) and concentration of photoinitiator.

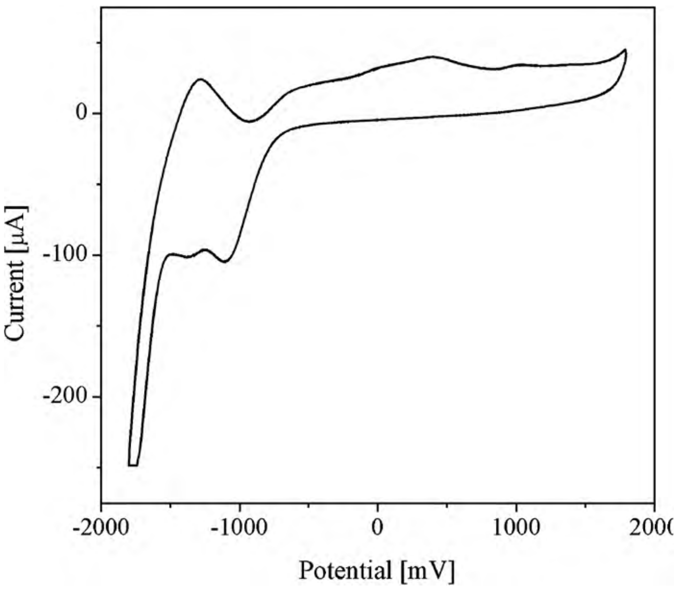


Fig. 3. Cyclic voltammograms of N-(3-bromopropyl)-4-{[N-(3-pyridinepropyl)-2-benzothiazolilydene)methyl]}quinolinium triiodide (**D3**) in acetonitrile.

It is evident, that as the photoinitiator concentration is increasing, the initial rate of polymerization increases and reaches a maximum followed by a continuous mild decrease. For the tested photoinitiator (both mono-cationic monomethine *n*-butyltriphenylborate and multi-cationic), under experimental conditions the highest rates of polymerization were observed at the initiator concentration of about 5×10^{-3} and 1×10^{-3} M, respectively.

The highest rates of polymerization photoinitiated by multi-cationic cyanine dyes were obtained at a concentration of photoinitiator of about five times lower than for its mono-cationic parent dye. This is probably caused by a higher concentration of co-initiator (*n*-butyltriphenylborate anion) in a close proximity to the excited multi-cationic chromophore in comparison to mono-cationic dye.

The reduction of the photoinitiated polymerization rate at higher initiator concentration can by easily understood taking into account the decrease of the penetration depth of the laser beam across the polymerizing formulation layer. Thus, all kinetic measurements for multi-cationic monomethine *n*-butyltriphenylborate salts were curried out at concentration equal 1×10^{-3} M.

The kinetic curves obtained for the photoinitiated polymerization of TMPTA/MP (9:1) mixture recorded for selected monomethine borate salts studied, under irradiation with a visible light, are shown in Fig. 5 for illustration.

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

It is apparent from the inspection of the initial rates of polymerization that the initiation efficiency of the tested photoinitiators depends on their structure. The highest rates of photoinitiated polymerization were observed for multi-cationic photoinitiators. It is also obvious that the four-cationic photoinitiators are much more effective in comparison to their three-, two- and mono-cationic equivalents (see Fig. 5 and Table 2). Higher photoinitiating abilities of multi-cationic monomethine borate salts can be attributed to an increase of an electron donor concentration in a close proximity to an excited dye molecule caused by the presence of the extra borate anions coupled by the covalently linked to a dye molecule additional organic cations.

3.3.2. Three-component photoinitiating systems

Three-component photoinitiating systems, which contain a light-absorbing species (dye), an electron donor (*n*-butyltriphenylborate salt), and a third component (N-alkoxypyridinum salt or 1,3,5-triazine derivative), have emerged as efficient, visible light sensitive photoinitiators of free radical polymerization. It was found that three-component photoinitiating systems are more efficient than their two-component counterparts.

To enhance the sensitivity, three-component photoinitiators have been recently studied. In these systems, the third component is usually supposed to scavenge the chain-terminating radicals that are generated by primary photochemical process or produce an additional initiating radical [29,30].

In the reach for obtain more effective photoinitiators for free radical polymerization of acrylate monomers, multi-cationic monomethine dyes in the three-component photoinitiatiating systems consisting of these dyes paried with borate anion in the presence of N-alkoxypyridinium salt or 1,3,5-triazine derivative as a second co-initiator were also investigated through polymerization experiments.

From the kinetic results obtained for the two-component photoinitiating systems, it is clearly evident that multi-cationic monomethine borate salts can be used as visible light photoinitiators of acrylate monomers. However, their ability to the

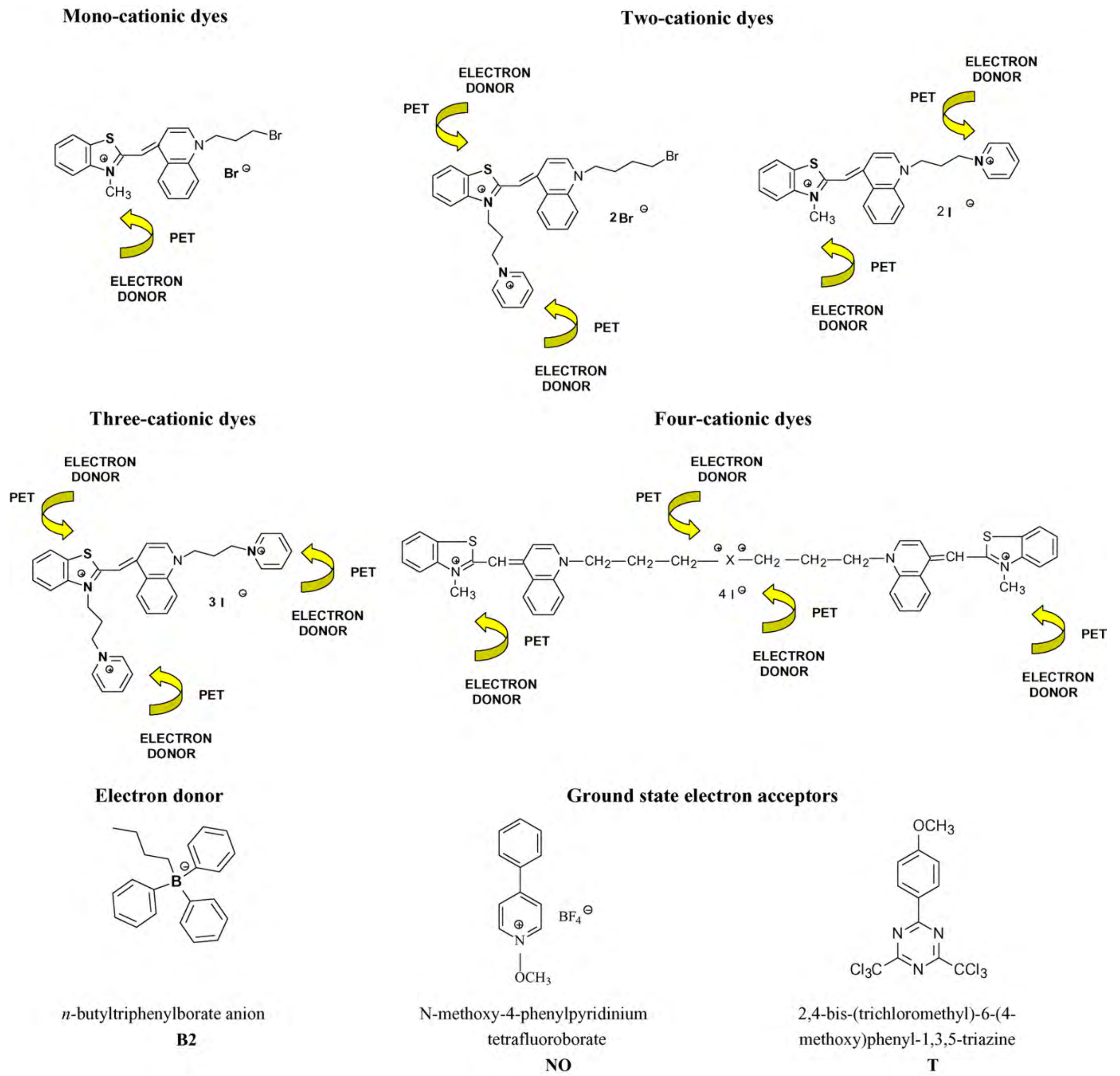


Chart 1.

photoinitiation of free radical polymerization is significantly lower than those observed for symmetrical cyanine dyes [12–14,31,32]. In order to accelerate the photopolymerization process initiated by monomethine dyes borate salts the second co-initiator was added to the two-component photoinitiating formulation. The structures of compounds used as a second co-initiator are presented in Chart 1.

Irradiation of three-component photoinitiating systems under the study with visible light leads, according to our previous communications [33,34], to the formation of following radicals: alkoxy or 1,3,5-triazynyl radicals beside *n*-butyl radical that is formed after first electron transfer reaction. The efficiency of these processes depends on the composition of the photoinitiator system. Thus, one can conclude that the overall efficiency of the photoinitiation of free radical polymerization can be affected by: (i) the rate of primary electron transfer process, (ii) the rate of carbon – boron bond cleavage, (iii) the rate of secondary electron transfer process, (iv) the rate of nitrogen – oxygen bond or the rate of carbon – halogen bond cleavage and finally (v) on the reactivity of free radicals formed.

The data illustrating the kinetics of free radical polymerization of TMPTA initiated by both two- and three-component photoinitiating systems are summarized in Table 3.

Fig. 6 presents the kinetic traces recorded during an argon ion laser photoinitiated polymerization of TMPTA/MP (9:1) mixture in the presence of monomethine dye-borate complex and functioning as additional co-initiator selected compounds.

As can be seen in Fig. 6, the photoinitiating system composed of mono- and multi-cationic dyes borate salts and second co-initiator much more efficiently initiates the free radical polymerization of

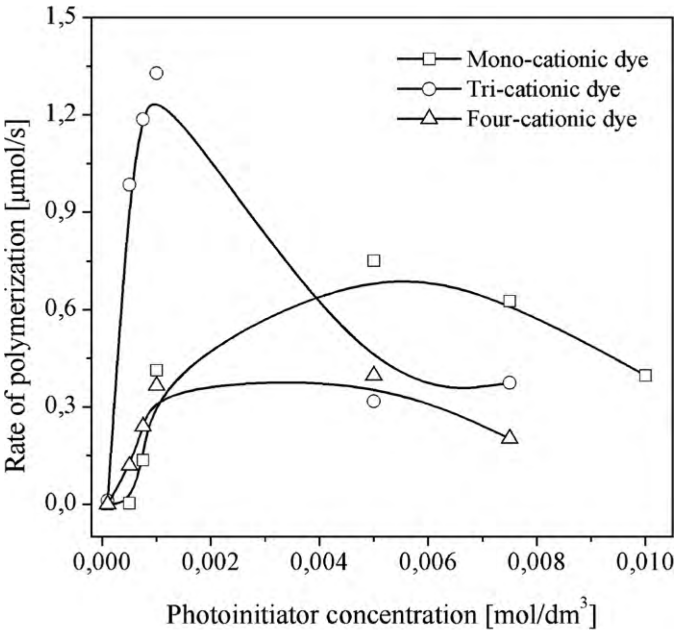


Fig. 4. Rate of polymerization versus N-methyl-2-[N-(3-bromopropyl)quinoline]-2-methylenebenzothiazolium borate **D1B2**, N-(3-bromopropyl)-4-{[N-(3-pyridinopropyl)-2-benzothiazolilydene)methyl]}quinolinium borate **D3B2** and N,N,N′N′-Tetramethyl-N,N′-bis-{3-[4-[(3-methyl-2-benzothiazolideno)methyl]-quinolinium-1-ylo]propyl}-4,4′-bipirydyle borate **D8B2** concentrations, respectively.

TMPTA in comparison to the two-component photoinitiating system composed of the dye and borate anion exclusively.

From the analysis of the kinetic curves in Fig. 6 and the data compiled in Table 3, it is seen that, the sensitivity of three-component photoinitiating systems depends on the structure of a second co-initiator.

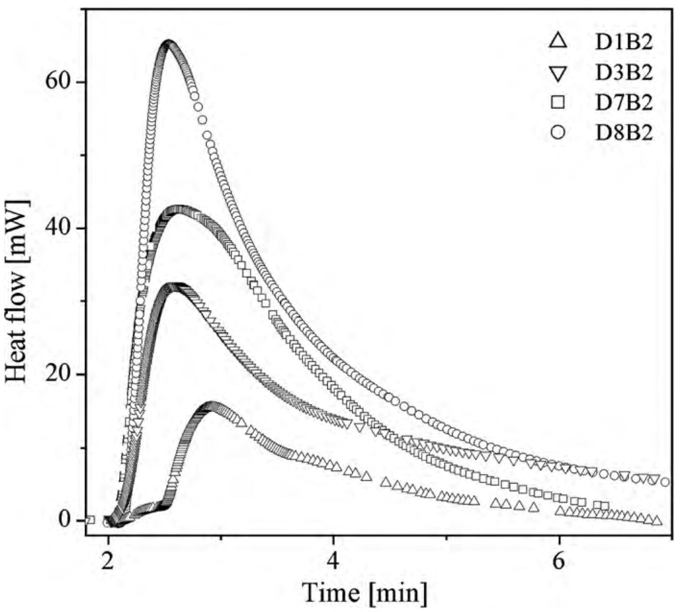


Fig. 5. The kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA/MP (9:1) mixture initiated by multi-cationic monomethine dye *n*-butyltriphenylborate and mono-cationic parent photoinitiator (marked in the figure). The cyanine borate concentration was 1×10^{-3} M, I_a = 20 mW/0.196 cm^{-1}.

Table 3

Measured rates (R_p) of free radical polymerization of TMPTA photoinitiated by three-component photoinitiating systems tested.

Initiator	R_P [μmol s^{-1}]		R_P[a]	
	NO	*T*	NO	*T*
D1B2	1.33	1.75	9.47	12.53
D2B2	0.54	2.38	2.67	11.88
D3B2	0.92	1.84	2.30	4.60
IMB2	0.17	10.94	11.52	729.36
DfB2	0.43	10.40	7.12	173.34
D6B2	0.57	6.72		
D7B2	0.92	8.07	1.84	16.15
D8B2	1.93	3.32	2.44	4.21

[a] The relative rates of polymerization in comparison to the rate of polymerization initiated by two-component photoinitiating system composed of monomethine dye as *n*-butyltriphenylborate salt (DB2).

Generally, the type of applied second co-initiator in three-component photoinitiating system has effect on the overall efficiency of the photoinitiation. It is demonstrated that the addition of N-alkoxypyridinium salt or 1,3,5-triazine derivative to the two-component DB2 photoinitiating system leads to an enhancement of the polymerization efficiency for all dyes studied. The rate of free radical polymerization is several times more higher in the presence of NO or even greater in the presence of T in comparison to the two-component photoinitiating system (Table 3 and Fig. 6).

The rate of free radical polymerization of TMPTA/MP mixture photoinitiated by systems under study changes in the order:

$$\mathrm{DB2/T > DB2/NO > DB2}$$

Presented in Fig. 6 data also clearly show that the polymerization photoinitiation ability of **DB2** in presence of a 1,3,5-triazine derivative as a second co-initiator is more efficient than this observed for **RBAX-NPF** couple (typical triplet photoinitiating system) [35,36].

On the basis of the our earlier experimental results we concluded that the primary photochemical reaction involves electron

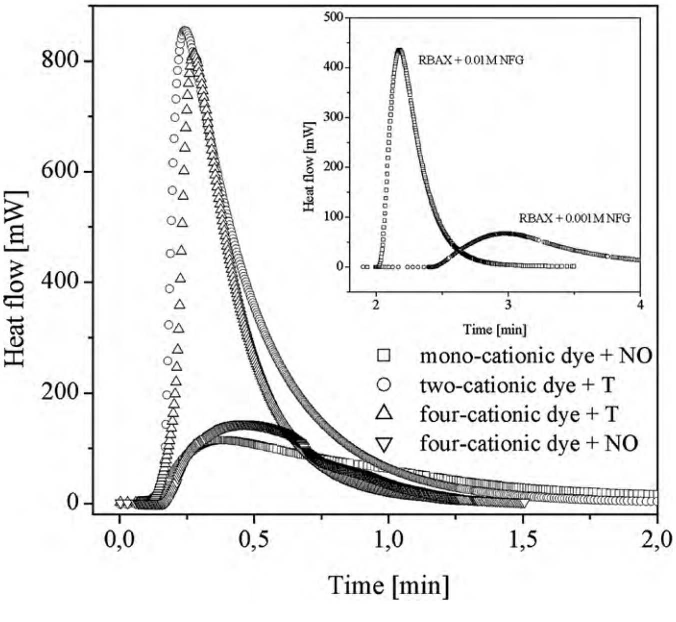


Fig. 6. Kinetic curves of the TMPTA/MP (9:1) polymerizing mixture recorded during the measurements of the flow of heat during the photoinitiated polymerization initiated by mono- (**D1B2**), two- (**D4B2**) nad four-cationic monomethine borates (**D5B2** and **D8B2**) in presence of different additional co-initiators (5.0×10^{-2} M) (marked in figure). Borate salt concentration was 1.0×10^{-3} M Inset: Comparison of photoinitiation ability of RBAX-NPG (N-phenylglycine concentration was 0.01 and 0.001 M) photoinitiating system, RBAX – Rose Bengal derivative (triplet state photoinitiator) [35,36].

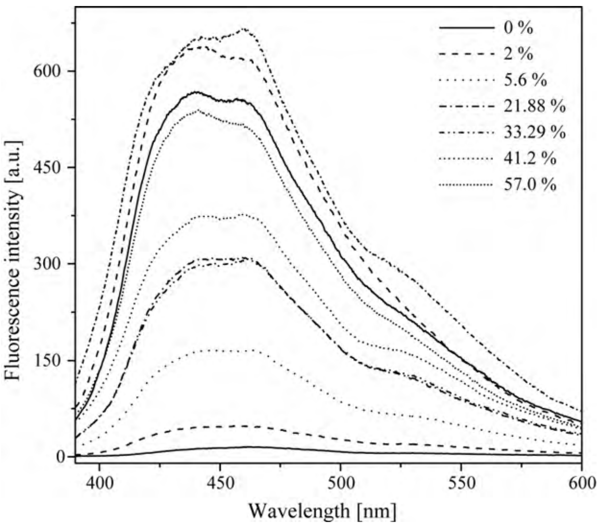


Fig. 7. Changes in the fluorescence spectra of **D3** during the thermally initiated polymerization of MMA recorded for conversions below the transition point of the liquid sample into a rigid polymer matrix.

transfer from the borate anion to the excited dye followed by the reaction of resulting dye-based radical with second co-initiator that regenerates the original dye and simultaneously produces the alkoxy radical or triazynyl radical which can start the polymerization chain reaction [33,34].

3.4. Fluorescence monitoring the free radical polymerization of monoacrylate

The second objective of this study was to investigate the fluorophore response to viscosity and polarity changes that occurred during the thermally initiated polymerization of methylmethacrylate (MMA). All the probes under study were quite soluble both in the monomers and in the solid polymers. There was no indication that during the course of polymerization molecular aggregates were formed or precipitation of the probes occurred. Figs. 7 and 8 show the fluorescence spectra of the **D3** probe during the thermally initiated polymerization of MMA for different degrees of polymerization.

The changes in the fluorescence intensity observed at the fluorescence maximum show gradual increase below the gel point. A distinct increase in the intensity of the probe fluorescence was observed during MMA polymerization when a liquid polymer solution was transferred into the solid polymer matrix (above the gel point). The fluorescence intensity increase because of changes in viscosity of the probe microenvironment that occur during the polymerization. This behavior can be attributed to the intramolecular charge-transfer excited-state relaxation to lower energy charge-transfer states obtained by rotation about the single or double bonds of the molecule [37]. In general, in such a case, the radiative deactivation constant is not affected, but a decrease in the nonradiative deactivation constant is related to an increase in the environment viscosity [37,38].

Fig. 9 summarizes the changes in the fluorescence intensity observed for **D** probe during thermally initiated polymerization of MMA.

Fig. 9 shows an “S” shape of the curve versus the polymerization time. This is a common behavior and is observed in the polymerization that shows a distinct transition from a fluid to a rigid glass. To quantify the results presented in Fig. 9, we have assumed that the probe emission intensity increases as the polymerization propagates. In other words, as the monomer consumption increases because of the polymerization, probe molecules are starting to be trapped in the rigid poly(methyl methacrylate) environment, and as a result, the emission intensity increases. Below the time needed for the onset of the gel effect, because the probe molecules are relatively free, they can easily relate to the ground state. This causes a low fluorescence intensity of the probe. However, above the time needed for the onset of the gel effect, because the reaction mixture is highly viscous, the relaxation processes become less effective, and the emission intensity can rise to high values. In general, the specific behavior of the probes in the transition area of a fluid monomer to a rigid polymer can be explained by the dramatic increase in the viscosity, and this, in turn, rapidly reduced the efficiency of nonradiative deactivation of the emitting state.

Changes in the probe emission intensities, measured at wavelengths specific for each of them, were also assumed as values

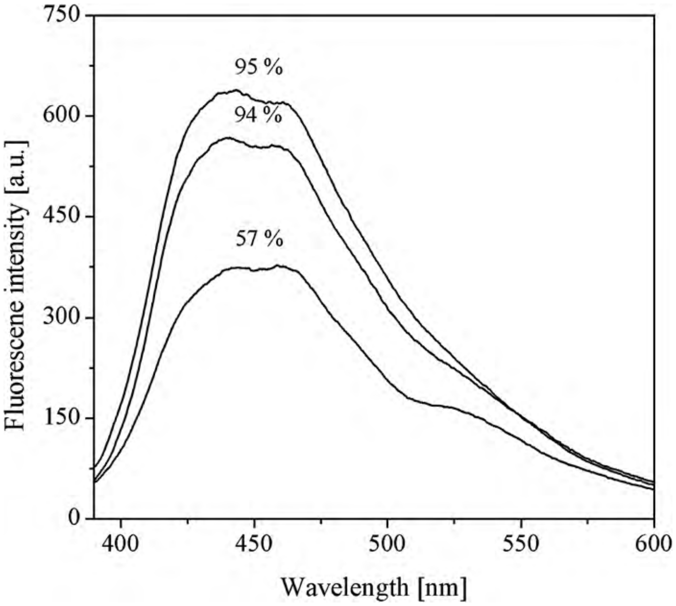


Fig. 8. Changes of the fluorescence spectra of **D3** during the thermally initiated polymerization of MMA above the point of transition of the liquid sample into a rigid polymer matrix.

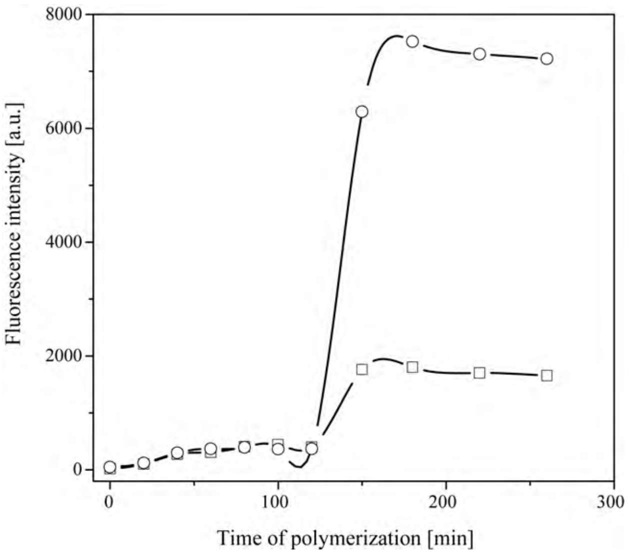


Fig. 9. Changes in the fluorescence intensity (measured at λ = 370 nm (circles) and λ = 530 nm (squares), respectively for **D8** probe during the thermally initiated polymerization of MMA in the presence of AIBN (1%).

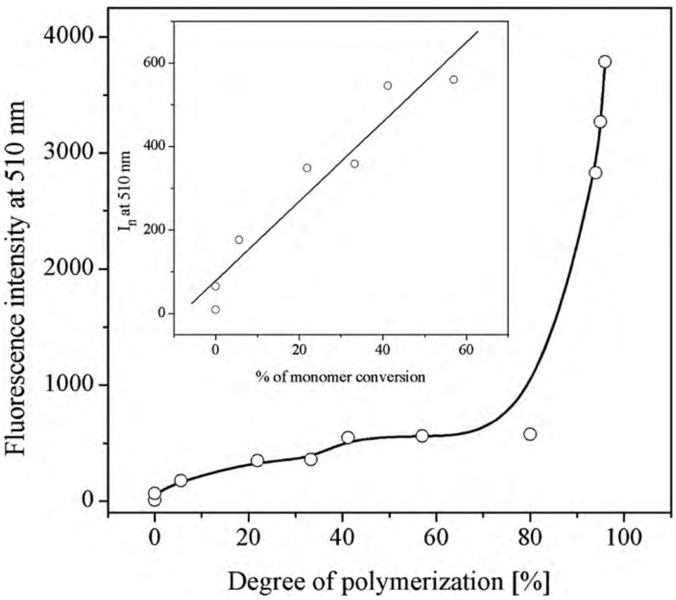


Fig. 10. Relationship between the probe emission intensity (probe **D1**, recorded at λ = 510 nm) versus the degree of monomer conversion into the polymer during the polymerization of MMA at 50 °C. The inset shows linear relationship between the fluorescence intensity and degree of polymerization recorded at λ = 510 nm for **D8** probe, illustrating their sensitivity (I_{FL} = fluorescence intensity).

characterizing the probe response to increases in the degree of polymerization. The illustrative experimental results are shown in Fig. 10.

The relationship between the changes in the probe emission and changes in the degree of monomer conversion into the polymer was linear for low degrees of polymerization (see the inset in Fig. 10). At higher degrees of monomer conversion, a sudden increase in the fluorescence intensity occurred, which was attributed to the effect connected with conversion of the polymer solution into the rigid polymer matrix (Fig. 10.). In principle, the probe intensity emission can be used to characterize the kinetics of polymerization, but only when a linear relationship between the increase in the fluorescence intensity and the amount of the obtained polymer is observed. For the tested probes, this property was observed for the degree of monomer conversion below the gel point. The probes sensitivity is about 10.

4. Conclusion

Eight monomethine dyes, possessing benzothiazole ring were synthesized and their spectroscopic and electrochemical properties were determined. The synthesized dyes were paried with borate anion and as photoredox pairs were used for photoinitiation of free radical polymerization. The efficiency of polymerization depends on the structure of monomethine dye used as an electron acceptor. The resulting multi-cationic monomethine dyes paried with *n*-butyltriphenylborate anion are shown to be more efficient photoinitiators of free radical polymerization in comparison to the identical series of mono-cationic dyes.

The two-component photoinitiating systems possessing monomethine dye and *n*-butyltriphenyl borate initiate polymerization with low efficiency. Acceleration of this process was achieved by the addition of a second co-initiator. The three-component photoinitiating systems, possessing monomethine dye borate salt and N-alkoxypyridinium salt or monomethine dye borate salt and 1,3,5-triazine derivative initiate free radical polymerization two and even hundred times faster in comparison to the parent two-component system. By combination of alkoxypyridinium or 1,3,5-triazine derivative with borate salts of suitable dye cation two initiating radicals can be generated by one absorbed photon.

Therefore, the mono- and multi-cationic monomethine dyes were found to be potentially very useful as a visible light sensitizers in the multi-component photoinitiating systems.

The studied monomethine dyes can be applied both as spectroscopic probes monitoring the degree of curve in their environment and as visible light photoinitiators of free radical polymerization. The fluorescence intensity of the tested probes, though low in the liquid monomer, increases considerably when the monomer goes into a rigid polymer matrix. This property makes monomethine dyes promising fluorophores for the monitoring of the free radical polymerization process.

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