One Photon−Two Free Radical Photoinitiating Systems. Novel Approach to the Preparation of Dissociative, Multicomponent, Electron-Transfer Photoinitiators for Free Radical Polymerization

Janina Kabatc* and Jerzy Pączkowski

Faculty of Chemical Technology and Engineering, University of Technology and Agriculture, Seminaryjna 3, 85-326 Bydgoszcz, Poland

Received July 18, 2005; Revised Manuscript Received September 22, 2005

ABSTRACT: The photoinitiation abilities of several photoinitiation systems composed of positively charged 3-ethyl-2-(*p*-(*N*,*N*-dimethylamino)styryl)benzothiazolium iodide (dye **I**) and 3-ethyl-2-(*p*-pyrrolidinestyryl)-benzothiazolium iodide (dye **II**) acting as light absorbers, *n*-butyltriphenylborate (Bo^-) anion being the electron donor, and alkoxypyridinium (AP^+) cation acting as ground-state electron acceptor, are compared. Both (Bo^-) and (AP^+) in polymerizing formulations were present either as Bo^- tetramethylammonium salt (TBAB) and AP^+ tetrafluoroborate salt (APTB), respectively, or as an ion pair composed of Bo^- anion and AP^+ cation (AP^+Bo^-). The best photoinitiating ability is observed for the system in which borate anion and pyridinium cation form an ion pair. On the basis of experimental results, it is postulated that an enhancement of photoinitiation ability observed for an ion pair is caused by a specific spatial organization of the reactants allowing the secondary reactions, yielding free radicals, in three-component encounter complex to occur. The mechanism of free radical generation is clarified with the use of laser flash photolysis experiments. Further modification of photoinitiating system concerns a possibility of diffusion elimination at least in one step of the reaction sequence. This was achieved by synthesis of a properly design dye-possessing alkoxypyridinium group. This dye after electron transfer forms radical localized on pyridine nitrogen that fragments forming alkoxy radical and reduced dye. Finally, from a combination of either alkoxypyridiunium or alkyltriphenylborate salts with suitable sensitizer or properly designed dye and alkyltriphenylborate salt, two radicals can be generated per one absorbed photon, thus enhancing the overall polymerization efficiency.

Introduction

There have been a number of studies on the dyeing photoinitiators forming a free radical via the photoinduced electron-transfer process. These include acridines, xanthenes, and thiazines, first reported by Oster,[1] a wide group of the fluorone dyes,[2] the cyanine dyes,[3,4] pyrene,[5] safranine T,[6] the dyes based on quinaxolin-2-one residue,[7] and many others.[8]

However, the research related to the photochemistry of dyeing photoinitiators is mostly focused on the development of new light absorbers, while there are only few papers describing the effect of an electron-donating molecule structure on the efficiency of the photoinitiation process.[8] Recently, Gould and Farid described reactions of photoinitiated polymerization that apply the electron transfer occurring between the excited state of dye and *N*-alkoxypyridinium salts, acting as the efficient ground-state electron acceptors.[10] The photochemistry of such electron-transfer reactions was, in part, clarified by Schuster et al.,[11] who concluded that for the singlet state reaction the nitrogen−oxygen bond cleavage competes successfully with the back electron transfer. When reaction occurs in an overall triplet state, back electron transfer cannot occur, and solvation and nitrogen−oxygen bond cleavage to form an alkoxy radical are competitive.

In this presentation, we have compared the reactivity of several photoinitiation three- or two-component systems composed of positively charged 3-ethyl-2-(*p*-(*N*,*N*-dimethylamino)styryl)benzothiazolium iodide (dye **I**) and 3-ethyl-2-(*p*-pyrrolidinestyryl)benzothiazolium iodide (dye **II**) acting as light absorbers, *n*-butyltriphenylborate (Bo^-) anion acting as electron donor, and alkoxypyridinium (AP^+) cation acting as ground-state electron acceptor. Both Bo^- and AP^+ in polymerizing formulations can be present either as tetramethylammonium salt (TBAB) and tetrafluoroborate salt (APTB), respectively, or can form an ion pair composed of Bo^- anion and AP^+ cation (AP^+Bo^-). Additionally, the mechanism of free radical generation is clarified with the use of laser flash photolysis experiments. Based on experiments performed for three-component photoinitiators, a two-component photoinitiating system composed of 2-(*o*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfate (dye **III**) and TBAB was designed. Dye **III** after electron transfer forms radical localized on pyridine nitrogen that fragments forming methoxy radical and reduced dye.

There are two significant structural differences between the main system under study in the current work and that reported by Schuster.[11] First, the absorbing dyes are positively charged and this after an electron transfer allows to obtain a neutral radical. Second, we use both co-initiators paired either with different counterions or in form of an ion pair, which allows substrates of electron transfer reactions in a specific form to organize and minimized a diffusion effect on overall efficiency of photoinitiation. The influence of diffusion additionally is limited in the two-component system, in which the light-absorbing dye possesses an alkoxypyridinium group.

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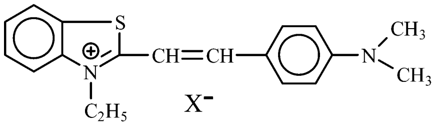
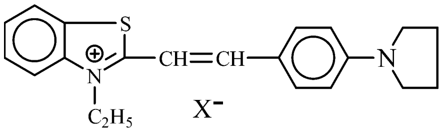
* Corresponding author: Tel ++48 52 3749045; Fax ++48 52 3749009, e-mail nina@atr.bydgoszcz.pl.

10.1021/ma051561j CCC: $30.25

Chart 1

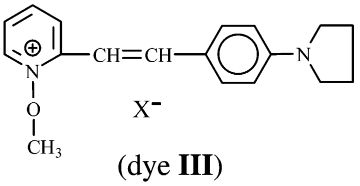


(dye **I**)

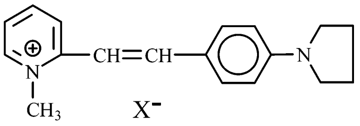


(dye **II**)

Chart 2



(dye **III**)



(dye **IV**)

Experimental Section

The substrates used for the preparation of the dye *N*-methoxy-4-phenylypyridinium tetrafluoroborate (APTB), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich and were the highest available purity and were used without further purification.

The synthesis of dyes possesing 3-ethyl-2-(*p*-(*N*,*N*-dimethylamino)styryl)benzothiazolium cation (dye **I**) and 3-ethyl-2-(*p*-pyrrrolidinestyryl)benzothiazolium cation (dye **II**) was described in our earlier paper.[12] *n*-Butyltriphenylborate tetramethylammonium salt (TBAT) was synthesized on the basis of the method described by Damico.[13] The *N*-methoxy-4-phenylpyridinium borate pair ($AP^{+}Bo^{-}$) was prepared in our laboratory with use of methodology described by Schuster for synthesis of cyanine borate salts.[4] All final products were identified by ^{1}H NMR spectroscopy. The spectra obtained were evidence that the reaction products were of the desired structures. The purity of the dyes were as it is required for spectroscopic studies.[12] The purity of co-initiators was determined using thin-layer chromatography and by measuring of the melting points. The measurements showed that the synthesized compounds are of high purity. For comparative studies several more dyes were prepared and evaluated as electron-transfer photoinitiating systems. These are the dyes possessing 2-(*o*-methoxypyridine)-*p*-pyrrolidinestyrilium cation (dye **III**) and 2-(*o*-methylpyridine)-*p*-pyrrolidinestyrilium cation (dye **IV**). These dyes were obtained starting either from *N*-methoxy-2-methylpyridinium methyl sulfate (dye **III**) or *N*-methyl-2-methylpyridinium iodide (dye **IV**) using methodology described in our earlier paper.[14] The reduction and oxidation potentials of dyes *N*-methoxy-*p*-phenylpyridinium and *n*-butyltriphenylborate salts were measured by cyclic voltammetry. An electroanalytical MTM system model EA9C-4z (Cracow, Poland), equipped with a small-volume cell, was used for the measurements. A 1 mm platinum electrode was used as the working electrode. A Pt wire constituted the counter electrode, and an Ag−AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. The solution was deoxidized by bubbling argon gas through the solution for20 min. The potential was swept from −1.6 to 1.6 V and back with the sweep rate of 250 mV/s to record the current−voltage curve.

The kinetics of free radical polymerization were measured based on the measurements of the rate of the heat evolution during polymerization in a sample 2−3 mm thick (10 mm diameter; 0.25 mL of cured sample). The measurements were performed in a homemade microcalorimeter.[9] A semiconducting diode immersed in a 2 mm thick layer of a cured sample was used as a temperature sensor. The irradiation of the polymerization mixture was carried out using the emission of an Omnichrome model 543-500 MA argon ion laser, which emits two visible light wavelengths at 488 and 514 nm. The average power of irradiation was 64 mW/cm^{2}.

A polymerization solution was composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The concentration of dyes was 1×10^{-3} M. The concentrations of co-initiators in the tested formulations were in the range form 1×10^{-3} to 1×10^{-1} M. The monomer was used without purification. As a reference sample, a polymerizing mixture containing hemicyanine iodides (dye without a co-initiator) was used. The polymerizing mixture was not deaerated.

The kinetics of free radical polymerization initiated by hemicyanine and styrylpyridinium dyes was measured for several different combinations of dyes and co-initiators. Three different co-initiators were applied. These are shown in Chart 3. To reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish−Troomsdorf effect, and the radicals trapping effect, the initial rates of polymerization were taken into account for further consideration. The initial rates of polymerization are the slopes of the lines drawn on the flow of heat vs time curve at the initial time of polymerization.

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

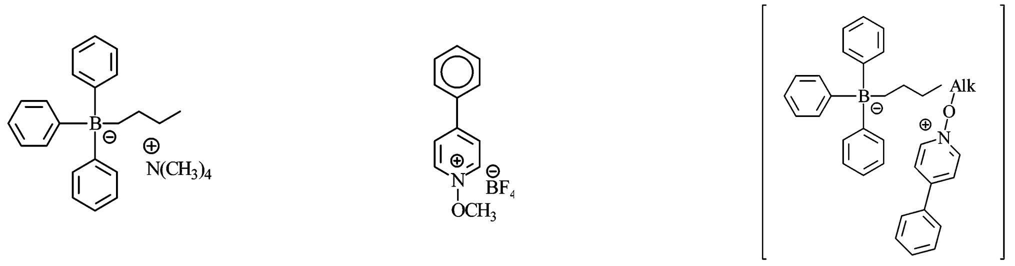
Results and Discussion

The main property that differentiates the system under study and from that described by Schuster[11] comes from the properties of products obtained after an electron-transfer process, which in our case are neutral radicals. Therefore, the overall rate of free radical formation reaction is not controlled either by the back-electron-transfer reaction or by the solvation process. Under this condition the rate of electron transfer, the diffusion, or spatial arrangement of both, substrates and short-lived intermediates limit the rate of photoinitiated polymerization.

Figure 1 shows two kinetic traces recorded during the photoinitiated polymerization of the mixture composed of TMPTA-MP (9:1) and tested hemicyanine (dyes **I** and **II**) borate salts ($DyeBo^{-}$).

The data in Figure 1 clearly show that hemicyanine borates are effective initiators of free radical polymerization. The analysis of the kinetic curves in Figure 1 shows, additionally, different polymerization induction times. This specific behavior can be attributed to the presence of oxygen in polymerizing formulation. The influence of oxygen on photoinitiation rate in tested system is not clear now and needs further study.

Chart 3



n-butyltriphenylborate tetramethylammonium (TBAB)

N-methoxy-4-phenylypyridinium tetrafluoroborate (APTB)

N-methoxy-4-phenylpyridinium-borate pair ($AP^+ Bo^-$)

However, there are known photoinitiating systems possessing cyanine dye, which yield free radicals able to the initiate polymerization as a result of reductive cleavage of *N*-alkoxypyridinium salts.[10] Single electron transfer to *N*-alkoxypyridinium salt results in N−O bond cleavage and the formation of an alkoxy radical. The driving force for the fragmentation reaction in this case results from formation of a stable pyridine molecule.

Figure 2 presents the kinetic traces recorded during an argon ion laser photoinitiated polymerization of TMPTA-MP (9:1) mixture in the presence of 3-ethyl-2-(*p*-(*N*,*N*-dimethylamino)styryl)benzothiazolium iodide as the light absorber and functioning as co-initiators: (i) n-butyltriphenylborate tetramethylammonium salt, (ii) mixture of n-butyltriphenylborate tetramethylammonium salt and *N*-methoxy-4-phenylpyridinium tetrafluoroborate, and finally (iii) the ion pair composed of n-butyltriphenylborate anion and *N*-methoxypyridinium cation.

The rates of polymerization photoinitiated by all dye−co-initiator combinations tested are summarized in Table 1. From the inspection of the data presented in Table 1, it is evident that the photoinitiating system composed of hemicyanine dye iodide and *N*-methoxy-*p*-phenylpyridinium salt (dye + APTB) do not initiate free radical polymerization of TMPTA even at a very high concentration of APTB.

In summary, unexpectedly, the highest rate of polymerization, as shown in Figure 2 and in Table 1, is observed for the formulation in which the n-butyltriphenylborate and *N*-methoxy-4-phenylpyridinium ion pair is acting as co-initiating pair. The rate of photoinitiated polymerization is the lowest for the system containing only TBAB as electron donor. An addition into the mixture of an unimolar amount of APTB causes, as is expected,[10] a sharp increase in the rate of polymerization. The use of a co-initiating system as the ion pair causes an additional acceleration in polymerization rate. The experiments show that the rate of polymerization photoinitiated by dye **I** in the presence of tested co-initiators ($c = 2 \times 10^{-2}$ M) increases in the sequence

$$\text{APTB } (R_r = 0.0004) < \text{TBAB } (R_r = 0.002) < \text{TBAB + APTB } (R_r = 0.042) < \text{AP}^+\text{ Bo}^- \ (R_r = 0.086)$$

There is one more specific feature that differentiates the AP^+Bo^- pair from a mixture of TBAB and APTB. Figure 3 demonstrates this interesting behavior.

On the basis of the results shown in Figure 3, it appears that the difference in co-initiation efficiency of $AP^+ Bo^-$ ion pair in comparison with TBAB and APTB mixture is widely increasing as concentration of co-initiators increases. There are also some observations and facts that are pertinent to the properties of co-initiating systems under the study. (i) There is almost no (dye **I**) or no (dye **II**) photoinitiated polymerization when only APTB was applied as co-initiator. (ii) The photoinitiating system being the mixture of dye cation−borate anion pair and APTB exhibits higher photoinitiation ability in comparison to the ability presented by dye cation−borate anion pair.

All this specific behaviors can be explained assuming that there is an additional factor affecting the rate of photoinitited polymerization. We believe that the ob-

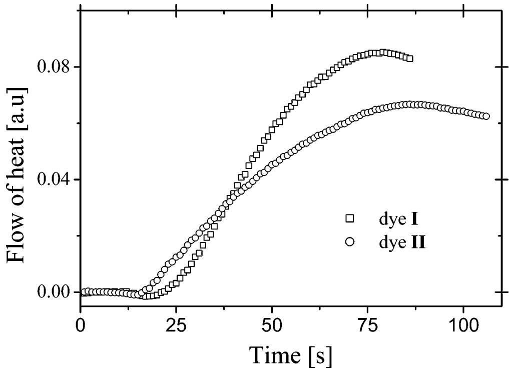


Figure 1. Family of curves recorded during the measurements of the flow of heat during the photoinitiated polymerization of the TMPTA-MP (9:1) mixture initiated by hemicyanine borates marked in the figure (see Chart 1). The dye concentration was 1×10^{-3} M, $I_a = 64$ mW/cm^2.

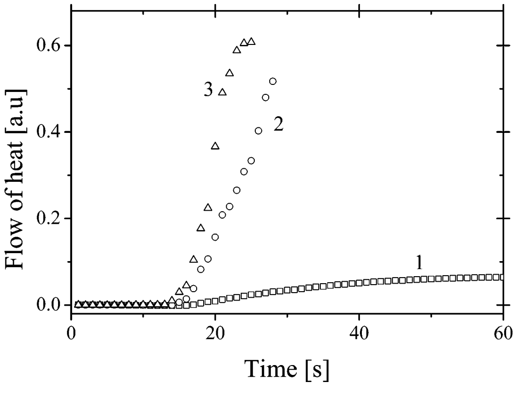
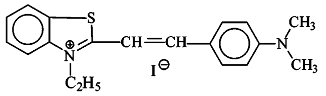
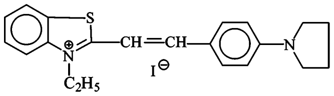


Figure 2. Kinetic curves of TMPTA−MP mixture polymerization initiated by 3-ethyl-2-(*p*-(*N*,*N*-dimethylamino)styryl)-benzothiazolium iodide (dye **I**; $c = 1 \times 10^{-3}$ M) in the presence of (1) TBAB, (2) TBAB and APTB mixture (1:1), and (3) (AP^+Bo^-). Concentration of each co-initiator was equal 2×10^{-2} M. Light intensity equal was 64 mW/cm^2.

Table 1. Rates of Polymerization (Measured for Light Intensity Equal to 64 mW/cm^2) Initiated by All Systems Tested and Relative Rates of Free Radical Polymerization

Photoinitiating System				
	Rate of polymerization [μmol/s]	Relative rate of polymerization	Rate of polymerization [μmol/s]	Relative rate of polymerization
DyeBo				
1×10^{-3} M	4.96	1	3.54	1
Dye + TBAB				
1×10^{-3} M	4.72	0.95	0.71	0.29
5×10^{-3} M	6.85	1.38	7.55	2.13
1×10^{-2} M	4.96	1	8.50	2.4
2×10^{-2} M	4.72	0.95	7.32	2.07
Dye + APTB				
1×10^{-3} M	0.0047	0.0095	---	---
1×10^{-2} M	0.11	0.02	---	---
1×10^{-1} M	0.73	0.15	---	---
2 × 10^{-1} M	0.94	0.20	---	---
Dye + APTB + TBAB				
1×10^{-3} M	14.2	2.86	15.8	4.5
5×10^{-3} M	56.7	11.43	12.5	3.53
1×10^{-2} M	68.0	13.71	21.0	5.93
2×10^{-2} M	98.4	19.86	36.5	10.33
5×10^{-2} M	89.7	18.1	46.3	13.07
DyeBo + APTB				
1×10^{-3} M	14.9	3.0	12.3	3.47
1×10^{-2} M	16.3	3.28	9.92	2.8
1×10^{-1} M	29.0	5.85	19.1	5.4
Dye + AP$^+$Bo$^-$				
1×10^{-3} M	4.72	0.95	0.71	0.2
2×10^{-3} M	15.11	3.05	2.12	0.6
5×10^{-3} M	74.8	15.1	43.2	12.2
1×10^{-2} M	126.5	25.6	66.3	18.73
2×10^{-2} M	203.0	40.1	141.9	40.07

served difference comes from the specific spatial arrangement of all components of photoinititing system. On the basis of the photochemistry of borate anion[3] and photochemistry of *N*-alkoxypyridinium cation,[10,11] we propose the mechanism in Scheme 1 which is consistent with the observations described above.

In this scheme, two possible mechanisms of free radical generation are considered. The upper path describes the processes that can occur when all initiating components are not organized; e.g., they are present in formulation as salts of photochemically inert counterions.

After excitation, to make an electron transfer effective, the electron donor and electron acceptor must diffuse to each other to form encounter complex, in which electron-transfer reaction takes place. The resulting boranyl radical decomposes, yielding neutral triphenylboron and butyl radical.[3,4] The other product of electron-transfer reaction, dye radical, could participate in a second electron-transfer reaction with alkoxypyridinium cation to form alkoxypyridinium radical and in this way to generate a second radical. The effective rate of dye radical quenching by alkoxypyridinium cation can be expressed by the equation

$$k_{\mathrm{obs}} = \tau_{\mathrm{T}}^{-1} + k_{\mathrm{q}}[\mathrm{AP}^+] \qquad (1)$$

in which τ_{T} is the lifetime of the dye radical in the

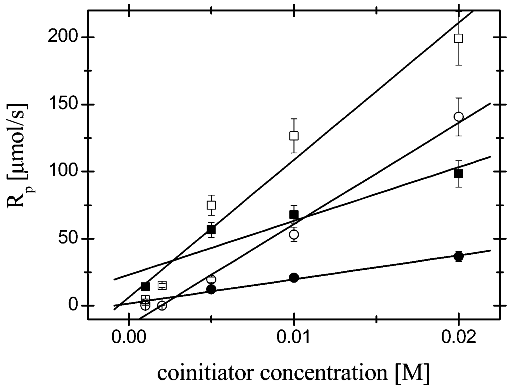
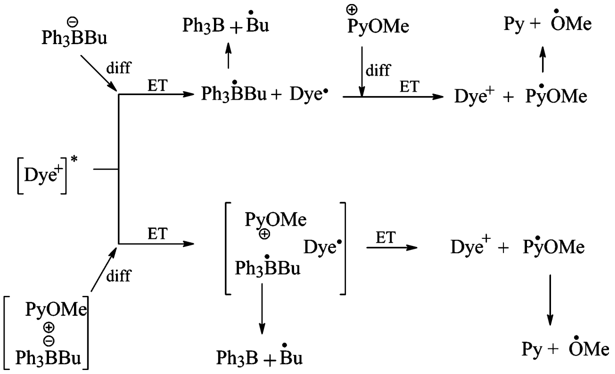


Figure 3. Dependence of the polymerization rates on co-initiator concentration. The solid points represent the system composed of TBAB and APTB mixture, and open points represent the AP^+Bo^- pair as co-initiator. Circles represent the data for dye **II** and squares for dye **I**. Error bars 10%.

Scheme 1



absence of an alkoxypyridinium cation (AP^+). It is obvious that the AP^+ concentration is uniform in an entire volume of the solution when alkoxypyridinium cation is used as its tetrafluoroborate salt. Situation is different when co-initiators are present in solution as ion pair. After excitation, the dye and co-initiators ion pair diffuse and form encounter complex. An electron transfer from borate ion follows this process forming boranyl and dye radicals. However, in this case the borate ion that is reaching excited dye is accompanied by an alkoxypyridinium cation. This artificially enhances the concentration of alkoxypyridinium cation in proximity to the dye radical. This, in turn, increases the effective rate of dye radical quenching. As a result, one observes an increase in speed of photoinitiated polymerization. Summarizing, from a combination of alkoxypyridinium and alkyltriphenylborate salts with suitable dye cation *two* radicals can be generated by *one* absorbed photon.

We have documented earlier that organic ion pair is partially dissociated even in medium polarity solvents.[14] A degree of dissociation is depending on concentration of solute in complex fashion. However, in the simple approximation a degree of dissociation is decreasing as concentration of solute is increasing (or a concentration of nondissociated salt is enhancing when concentration of solute increases). This behavior explains the relationships presented in Figure 3. For co-initiator introduced into solution as ion pair, its concentration increase causes higher concentration of nondissociated salt and, this in turn, starts to prefer the mechanism of polymerization described in Scheme 1 by the lower path. It is, thus, reasonable to conclude that the secondary reactions yielding free radicals occur in three-component encounter complex.

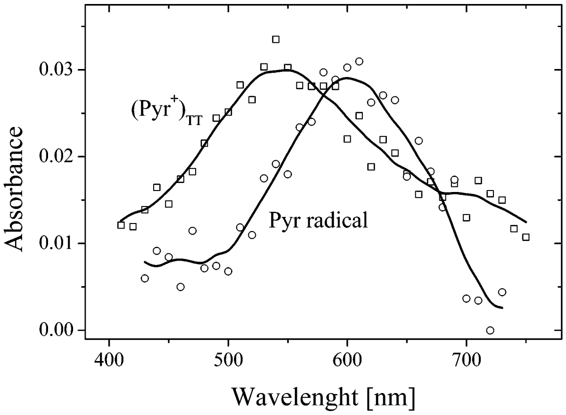


Figure 4. Transient absorption spectra recorded 100 ns after laser flash (355 nm) for *N*-(methylpurin-6-yl)pyridinium chloride (Pyr^+) in MeCN (squares) and 500 ns after flash for *N*-(methylpurin-6-yl)pyridinium chloride in the presence salt (TBAB) ($c = 5 \times 10^{-3}$ M) (circles). Concentration of Pyr^+ equal 2×10^{-4} M.

The mechanism of photochemical reactions that occurs after electron transfer for the photoinitiating three-component photoinitiating systems under the study may be suggested on the basis of the laser flash photolysis experiments performed for *N*-(methylpurin-6-yl)pyridinium cation (Pyr^+) in the presence of (i) tetramethylammonium *n*-butyltriphenylborate (TBAB), (ii) tetafluoroborate *N*-methoxy-4-phenylpyridinium (APTB), and (iii) ion pair AP^+Bo^- in MeCN solution. The transient spectra of *N*-(methylpurin-6-yl)pyridinium chloride (Pyr) and *N*-(methylpurin-6-yl)pyridinium chloride in the presence of salt (TBAB) are shown in Figure 4.

We selected Pyr^+ for examination because (i) the chromophore is positively charged, (ii) molecule undergoes intersystem crossing and its intermediates obtained after laser pulse and electron transfer are well described and may be monitored spectroscopically on the nanosecond time scale,[16] and (iii) the reduction potential of Pyr^+ is equal −0.57 V, e.g., is close to the corresponding value measured for *N*-methoxy-4-phenylpyridinium tetrafluoroborate (−0.67 V).[10] Irradiation of Pyr^+ with 5 ns laser pulse results in instantaneous appearance of its triplet state, which is characterized by absorption at 550 nm. The Pyr^+ triplet is quenched by TBAB, and a new transient with absorption at 610 nm is simultaneously formed. The new transient can be assigned to *N*-(methylpurin-6-yl)pyridinium radical ($Pyr^•$).[16] The rate constant, k_q, for the quenching of the triplet state of Pyr^+ by TBAB was determined in MeCN solution. The k_q value was obtained by monitoring the triplet−triplet absorption decays of Pyr^+ at fixed wavelength for various quencher concentrations by employing the Stern−Volmer equation. The established value of this rate constant is equal 3.94×10^{10} mol^{-1} s^{-1}, e.g., reaches the diffusion-controlled limit. The striking feature of the Pyr^+ behavior is the absence of an electron transfer reaction in the presence of *N*-methoxy-*p*-phenylpyridinium cation (similarly behave the dyes studied in this paper as photoinitiators). For high concentration of TBAB all triplets of Pyr^+ are quenched, and *N*-(methylpurin-6-yl)pyridinium radical ($Pyr^•$) is simultaneously formed (apparent $\lambda_{max} = 610$ nm). Bearing in mind the mechanism presented in Scheme 1, one should predict

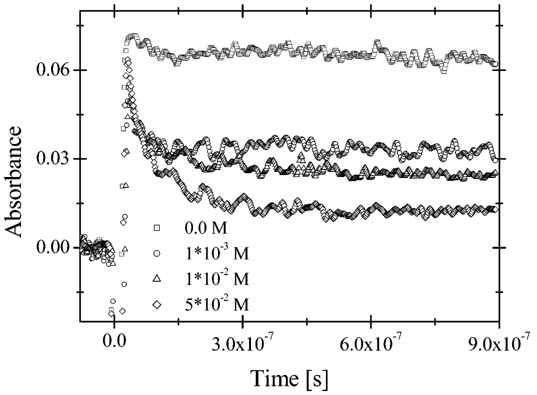


Figure 5. Kinetic traces for $\text{Pyr}^\bullet$ decay at 610 nm in the presence of various amount of *N*-methoxy-*p*-phenylpyridinium cation. The concentration of AP^+ marked in Figure.

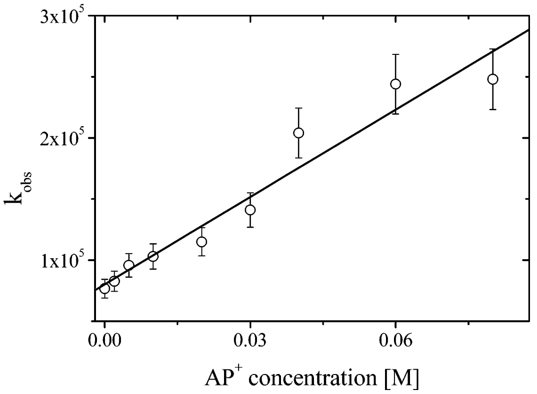


Figure 6. Stern−Volmer plot for quenching of $\text{Pyr}^\bullet$ by AP^+ in MeCN solution.

that the addition of *N*-methoxypyridinium cation should quench obtained radicals. This can be monitored by flash photolysis. Figure 5 shows the kinetic traces recorded at 610 nm for various concentrations of *N*-methoxy-*p*-phenylpyridinium cation in which triplets of Pyr^+ are quenched by TBAB.

The data presented in Figure 5 demonstrate that $\text{Pyr}^\bullet$ radical is quenched by AP^+ cation. The lifetime of $\text{Pyr}^\bullet$ in MeCN solution is about 10 μs and is decreasing as concentration of AP^+ increases. The Stern−Volmer plots obtained from the $\text{Pyr}^\bullet$ lifetime measurements, as is shown in Figure 6, is linear over the whole range of quencher concentration used.

On the basis of the above experiments, it appears that alkoxypyridinium cation is reduced by the dye radical. This reaction yields the dye cation and alkoxypyridinium radical which undergoes fragmentation, giving stable pyridine and alkoxy radical.

The dyes under study reduce at about −1.06 V for dye **I** and at about −0.73 V for dye **II** (vs Ag−AgCl). The measured value of reduction potential for the alkoxypyridinium cation is about −0.67 V. Under this condition, in the presence of alkoxypyridinium cation, only dye **I** can weakly initiate polymerization because energetic, calculated using the Rehm−Weller equation,[17] only for this photoredox pair is close to the region when the electron transfer becomes exothermic. A word of caution is required for the energy stored in the dye radical−alkoxypyridinium pair. For photoinduced electron transfer reaction between a donor and an acceptor, the energy stored in pair is define as the difference between the oxidation potential of a donor and reduction potential of an acceptor (referred also as the redox energy). The oxidation potential of the dye radical is approximately equal to the reduction potential of the dye cation. The reduction potentials for the dyes radical under the study are −1.06 V for dye **I** and −0.73 V for dye **II**. The reduction potential of the *N*-methoxy-4-phenylpyridinium cation is about −0.67 V. Thus, the driving force of electron transfer between the dye radical and *N*-methoxy-4-phenylpyridinium cation is −0.42 eV (−40.5 kJ mol^{-1}) for dye **I** and −0.06 eV (−5.8 kJ mol^{-1}) for dye **II**. The negative values indicate that the electron transfer between dye radicals and *N*-methoxy-4-phenylpyridinium cation is thermodynamically allowed.

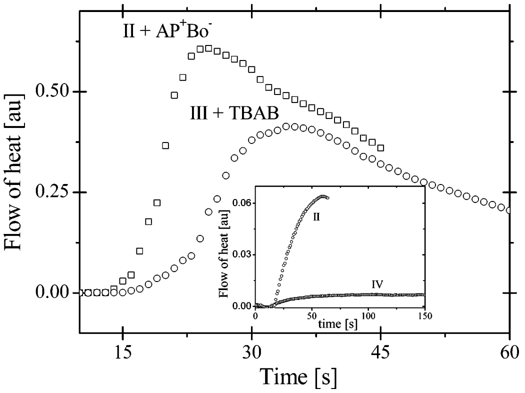


Figure 7. Kinetic curves of TMPTA−MP mixture polymerization photoinitiated by 3-ethyl-2-(*p*-pyrrolidinestyryl)benzothiazolium iodide (dye **II**) ($c = 1 \times 10^{-3}$ M) in the presence of (1) AP^+Bo^- (5×10^{-2} M) and 2-(*o*-methoxypyridine)-*p*-pyrrolidinestyrilium iodide (dye **III**) ($c = 1 \times 10^{-3}$ M) in the presence of TBAB (5×10^{-2} M). Inset: kinetic curves of TMPTA−MP mixture photopolymerization initiated by dyes **II** and **IV** ($c = 1 \times 10^{-3}$ M) in the presence of TBAB (5×10^{-2} M).

The next step of the novel photoinitiating system developing should be focused on the elimination of the process that causes decrease of its photoinitiation ability. Based on Scheme 1, for the photoinitiation occurring via singlet excited state the diffusion of photoinitiator components and the back electron transfer limits an overall efficiency of photoinitiation. The simplest way of the diffusion effect elimination is the covalent bonding of a dye with either electron donor or electron acceptor. Such an approach is clearly visible in dye **III**, which combines in one molecule the absorbing chromophore and ground-state electron acceptor. The reduction potential of **III** is equal −0.955 V. Thus, according to Gould's hypothesis,[10] this dye itself should be rather a poor photoinitiator. Indeed, the measurements of its photoinitiation efficiency explicitly confirmed this prediction. However, in the presence of TBAB 2-(*o*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfate (dye **III**) becomes extremely efficient as visible-light photoinitiator of free radical polymerization. Its photoinitiation ability is similar to that observed for initiating via triplet-state xanthene dyes described by Neckers.[18] Although the mixture of **III** and TBAB is less sensitive in comparison to the mixture of **II** and AP^+Bo^- (see Figure 7), the photoinitiating system composed of **III** and TBAB should be considered as very effective. The difference in sensitivity between **II** + AP^+Bo^- and **III** + TBAB mixtures may come from the different photoinitiation efficiency of 3-ethyl-2-(*p*-(*N*,*N*-dimethylamino)styryl)benzothiazolium dye and 3-ethyl-2-(*p*-pyrrolidinestyryl)benzothiazolium dye. The control measurements of the polymerization photoinitiation efficiency performed for 3-ethyl-2-(*p*-pyrrolidinestyryl)benzothia-

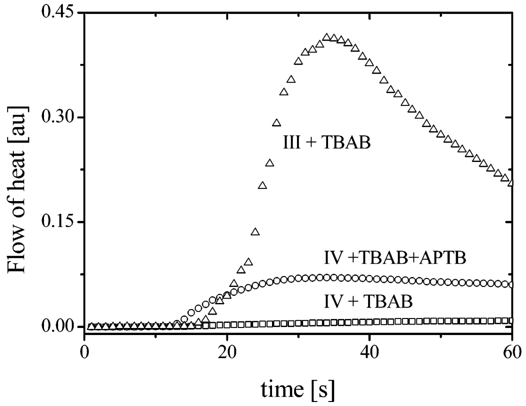


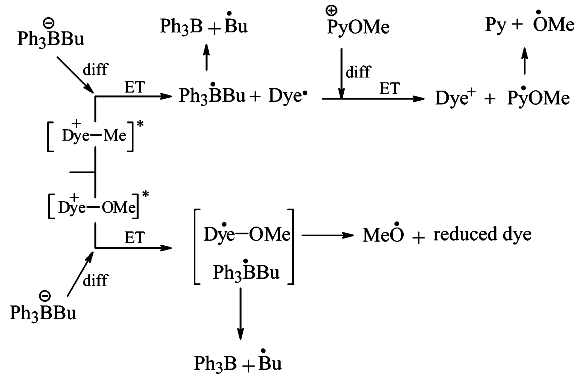
Figure 8. Kinetic traces recorded during polymerization photoinitiated by dyes **III** and **IV**. Photoinitiating systems marked in the figure.

zolium iodide (dye **II**) and *N*-methyl-2-(methylpyridinium) iodide (dye **IV**) in the presence of TBAB ($c = 5 \times 10^{-2}$ M) clearly demonstrated that the photoinitiation performance of the **II** + TBAB mixture is about 1 order of magnitude greater in comparison to the **IV** + TBAB photoredox pair (see inset in Figure 7). Thus, probably the type of chromophore plays an important role in relative lowering of the photoinitiation ability of the **IV** + TBAB photoredox pair in comparison to the **II** + AP^+Bo^- photoredox system.

One may suppose that 2-(*o*-methoxypyridine)-*p*-pyrrolidinestyrilium methyl sulfate (dye **III**) in combination with TBAB itself is very sensitive, and there is no one photon−two radical reaction. A simple way to verify this doubt is the comparison of the photoinitiation ability of **III** and **IV**. Figure 8 shows the kinetic traces recorded during photoinitiated polymerization of the TMPTA−MP (9:1) mixture photoinitited by **III** and **IV** in the presence of selected co-initiators.

The data in Figure 8 depict the striking difference between the photoinitiating system composed of (i) dye **IV** acting as electron acceptor and TBAB as electron donor, (ii) dye **IV** and two co-initiators TBAB (electron donor) and APTB (ground-state electron acceptor), and (iii) dye **III** in the presence of TBAB. For the analysis of the data in Figure 8 one should recall Scheme 1 underlining the influence of diffusion of photoinitiator components on its photoinitiation ability. In the case of dye **IV** in the presence of TBAB and APTB, after dye excitation, first, excited dye and TBAB must diffuse to each other for effective electron transfer. After electron transfer the radical formed from the dye and APTB in order to form an encounter complex should diffuse to each other as well. Since for dye **IV** no short-living intermediates are observed in nanosecond time scale, it is obvious that all processes occur in regime controlled by diffusion. Thus, elimination only one step that is diffusion-controlled should significantly increase the overall rate of entire reaction. The feasibility of this is demonstrated by system composed of dye **III** and TBAB, in which after absorption of light the excited molecule and TBAB encounter (diffusion-controlled process) for effective electron-transfer reaction. After the electron-transfer process, the resulting *n*-butyltriphenylboranyl radical decomposes, yielding *n*-butyl radical (first radical) and triphenyl borate. The second product of electron transfer, 2-(*p*-pyrrolidinestyryl)-*N*-methoxypyridinium radical, being unstable, decomposes to give methoxy radical (second initiating radical) and 1-(*p*-pyrrolidenephenyl)-2-(2-pyridine)ethene. It is clear that the decomposition process is not diffusion-controlled. Thus, using the photoinitiating pair composed of **III** and TBAT, one eliminates one of the rate-determining steps. This approach allows increase in speed of photoinitiation $\sim$1 one order in magnitude compared to those when either not modified initiator was used with TBAB and APTB. Scheme 2 summarizes the discussion presented above.

Scheme 2



There is one more feature that can strongly increase the yield of free radicals formation. The reaction between dye **III** and TBAB occurs via the singlet state. In such case a back electron transfer may be very efficient. The simplest way to avoid this energy loss is to find a competitive channel forming free radicals by bond cleavage reaction. In the case of dye **III** the nitrogen−oxygen bond cleavage competes successfully with the back electron transfer.

Conclusions

Practical and very efficient multicomponent sensitizing dye systems that are useful for photoinitiation of free radical polymerization reaction are described. The first approach considers a system contaning *n*-butyltriphenylborate anion as electron donor and *N*-methoxy-4-phenylpyridinium cation as the ground state electron acceptor. Both electron donor and electron acceptor can act separately or can be paired. The donor−acceptor pairing additionally enhances the rate of free radical formation, which is probably cased by partial elimination the diffusion that controls the overall efficiency of radical production. Further modification concerns a possibility of diffusion and back electron transfer at least in one step of the reaction sequence. This was achieved by synthesis of properly design dye possessing alkoxypyridinium group. This dye after electron transfer forms radical localized on pyridine nitrogen that fragments forming methoxy radical and reduced dye. Finally, from a combination of either alkoxypyridinium and alkyltriphenylborate salts with suitable sensitizer or properly design dye and alkyltriphenylborate salt, two radicals can be generated per one absorbed photon, thus enhancing the overall polymerization efficiency.

Acknowledgment. This work was supported by the State Committee for Scientific Research (KBN) (Grant 3 T09B 101 28).

References and Notes

(1) Oster, G. *Nature (London)* **1954**, *173*, 300−301.
(2) (a) Shi, J.; Zhang, X.; Neckers, D. C. *J. Org. Chem.* **1992**, *57*, 4418−4421. (b) Shi, J.; Zhang, X.; Neckers, D. C. *J. Org.*

Chem. **1993**, *58*, 2614−2618. (c) Polykarpov, A. Y.; Hassoon, S.; Neckers, D. C. *Macromolecules* **1996**, *29*, 8274−8276. (d) Hassoon, S.; Neckers, D. C. *J. Phys. Chem.* **1995**, *99*, 9416−9424.
(3) (a) Chatterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326−2328. (b) Kabatc, J.; Pietrzak, M.; Pączkowski, J. *Macromolecules* **1998**, *31,* 4651−4654. (c) Schuster G. B. *Adv. Electron Transfer Chem.* **1991**, *1*, 163−196.
(4) Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329−6338.
(5) (a) Encinas, M. V.; Majmund, C.; Lissi, E. A.; Scaiano, J. C. *Macromolecules* **1991**, *24*, 2111−2112. (b) Encinas, M. V.; Lissi, E. A.; Majmund, C.; Cosa, J. J. *Macromolecules* **1993**, *26*, 6284−6288.
(6) Previtali, C. M.; Bertolotti, S. G.; Neumann, M. G.; Pastre, I. A.; Rufs, A. M.; Encinas, M. V. *Macromolecules* **1994**, *27*, 7454−7458.
(7) (a) Kucybała, Z.; Pietrzak, M.; Pączkowski, J. *Chem. Mater.* **1998**, *10*, 2555−3563. (b) Kucybała, Z.; Pączkowski, J. *J. Photochem. Photobiol., A: Chem.* **1999**, *128*, 135−138.
(8) For exclusive reviews see: Pączkowski, J.; Neckers, D. C. Photoinduced Electron-Transfer I Iitiating Systems for Free-Radical Polymerization. In *Electron Transfer in Chemistry*; Gould, I. R., Ed.; Wiley-VCH: New York, 2001; Vol. 5, p 516. Pączkowski, J.; Kucybała, Z.; Ścigalski, F.; Wrzyszczyński, A. Dyeing Photoinitiators. Electron-Transfer Processes in Photoinitiating Systems. *Res. Trends* **1999**, *5,* 79−93.
(9) (a) Pączkowski, J.; Pietrzak, M.; Kucybała, Z. *Macromolecules* **1996**, *29*, 5057−5064. (b) Kabatc, J.; Kucybała, Z.; Pietrzak, M.; Ścigalski, F.; Pączkowski, J. *Polymer* **1999**, *40*, 735−745. (c) Wrzyszczyński, A.; Filipiak, P.; Hug, G. L.; Marciniak, B.; Pączkowski, J. *Macromolecules* **2000**, *33*, 1577−1582. (d) Andrzejewska, E.; Hug, G. L.; Andrzejewski, M.; Marciniak, B. *Macromolecules* **1999**, *32*, 2173−2179. (e) Wrzyszczyński, A.; Pietrzak, M.; Pączkowski, J. *Macromolecules* **2004**, *37*, 41−44.
(10) Gould, I. R.; Shukla, D.; Giesen, D.; Farid, S. *Helv. Chim. Acta* **2001**, *84*, 2796−2812.
(11) Wölfle, I.; Lodaya, J.; Sauerwein, B.; Schuster, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 9304−9309.
(12) Kabatc, J.; Jêdrzejewska, B.; Orliński, P.; Pączkowski, J. *Spectrochim. Acta*, *Part A*, in press.
(13) Damico, R. J. *Org. Chem.* **1964**, *29*, 1971−1972.
(14) Jędrzejewska, B.; Kabatc, J.; Pietrzak, M.; Pączkowski, J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1433−1440.
(15) Kabatc, J.; Jędrzejewska, B.; Pączkowski, J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3017−3026.
(16) Marciniak, B.; Hug, G. L.; Rozwadowski, J.; Bobrowski, K. *J. Am. Chem. Soc.* **1995**, *117*, 127−134.
(17) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271.
(18) (a) Shi, J.; Zhang, X.; Neckers, D. C. *J. Org. Chem.* **1992**, *57*, 4418−4421. (b) Tanabe, T.; Tores-Filho, A.; Neckers, D. C. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1691−1703.

MA051561J