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Novel dissociative electron transfer photoinitiators for free radical polymerization

Summary — Radical polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), photoinduced with redox system: electron donor-absorber, has been presented. Xanthene dyes: Rose bengal ditetrabutylammonium salt [RBTBAS — Formula (I)] and 5,7-diiodo-3-pentoxy-6-fluorone [DIPF — Formula (II)] were used as absorbers. Electron donors in the system investigated were: (phenylthio)acetic acid (PTAA), (phenylthio)acetic acid tetrabutylammonium salt (PTAA AS), ethyl (phenylthio)acetate (PTAA EE) or *n*-butyltriphenyl borate ($BuPh_3B^+$). Photopolymerization mechanism has been investigated using laser flash photolysis method. It has been found that photoreduction with PTAA or PTAA AS goes with electron transfer from sulfur atom to dye in triplet state (Schemes A and B). In case when RBTBAS is used as electron acceptor the anionic radicals of the dye [$RB^{\bullet 3-}$ — Formula (III) and $RB^{\bullet 2-}$ Formula (IV)] are obtained. The presence of these anionic radicals shows that after electron transfer the carboxylic group exists in an ionic form what let intramolecular electron transfer from carboxylate group to sulfur cationic radical, followed with rapid decarboxylation. As a result of decarboxylation the neutral thiomethylene radicals ($Ph\text{-}S\text{-}CH_2^{\bullet}$) are formed which, after escape from solvent cage, take part in photoinitiation of the polymerization. It has been stated that transformation of sulfur(II) containing carboxylic acids into their tetrabutylammonium salts significantly increases the sensitivity of the photoinitiating system (Fig. 6 and 7). It also increases photopolymerization rate (R_p) (Table 1, Fig. 10), which is a function of square root of the quantum yield of decarboxylation process (Φ_{CO_2}) (Fig. 9).

Key words: redox photoinitiators, xanthene dyes, trimethylolpropane triacrylate, electron transfer photoinitiated radical polymerization, initiation mechanism.

The process of the photoinitiated polymerization may be started by a direct photolysis of a precursor providing free radicals by a bond dissociation. The radicals may also be formed in bimolecular processes. The panchromatic sensitization of photoinitiated polymerization often requires the presence of a suitable dye as a primary light absorber. This can either transfer energy or undergo an electron transfer. The photoinduced intermolecular electron transfer uses light to initiate the electron transfer from a donor to an acceptor molecule. The process is possible because electronically excited states are both better oxidants and better reducers than their ground states equivalents.

There has been a number of studies on the dye photoinitiators forming free radicals *via* the photoinduced electron transfer process. These include the acridines, xanthenes and thiazines, first reported by Oster [1], a wide group of fluorone dyes [2—5], cyanine dyes [6—8], pyrene [9, 10], safranine T [11], dyes based on quinaxolin-2-one residue [12, 13] and many others [14]. However, it is necessary to emphasize that the research related to the photochemistry of dye photoinitiators is mostly focused on the development of new primary light absorbers, while there are only few papers describing the effect of an electron donating molecule structure on the efficiency of photoinitiation process [15—18].

In these papers it was shown that the reactivity and the type of free radicals that are formed after the electron

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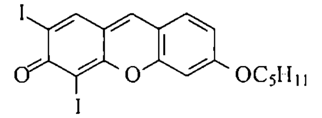
transfer depend on the structure of an electron donor and the properties of the polymerized mixture.

In this work, we have compared the reactivity of several photoredoxinitiation systems composed of xanthene dyes acting as light absorbers and a series of sulfur containing aromatic carboxylic acids and their tetrabutylammonium salts functioning as the electron donors in polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). For comparison, ethyl (phenylthio)acetate (PTAA EE), phenoxyacetic acid (PAA) and its tetrabutylammonium salt (PAA AS) were tested as well. (Phenylthio)acetic acid (PTAA) and other sulfur containing carboxylic aromatic acids were found to be very efficient electron donors (coinitiators) that, depending on the property of a formulation, may form two types of free radicals of a different initiation ability [17]. The proper modification of an electron donor structure allows one to control the path of secondary reactions that follow the electron transfer and allow to accelerate the rate of photoinitiated polymerization.

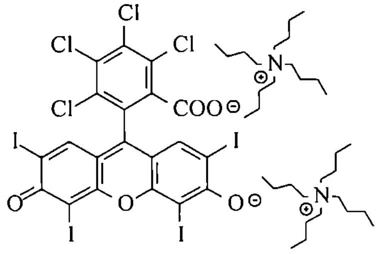
EXPERIMENTAL

Components of photoinitiation pairs

5,7-Diiodo-3-pentoxy-6-fluorone [DIPF — Formula (I)] was synthesized according to the method of Shi and Neckers [2, 3]. The preparation of Rose bengal ditetrabutylammonium salt [RBTBAS — Formula (II)] is also based on the method given by Neckers [19—21]. Both these dyes were used by us as light absorbers.



(I)



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Electron donors were prepared as follows: tetrabutylammonium salt (PTAA AS) of sulfur containing aromatic carboxylic acid [(phenylthio)acetic acid — PTAA] — were obtained by the treating of the corresponding acid dissolved in boiled water with a molar equivalent of tetrabutylammonium hydroxide. After the evaporation of water, the clammy residue was dried in a vacuum desiccator yielding transparent crystals.

Synthesis of *n*-butyltriphenyl borate ($BuPh_3B^+$) was described in [22, 23]. Ethyl (phenylthio)acetate (PTAA EE) was prepared using standard organic chemistry method.

2-Propanol (spectral grade) from Aldrich was used as hydrogen donor.

The dyes and substrates used for the preparation of the dyes and TMPTA were purchased from Aldrich.

Photopolymerization

The kinetics of free radical polymerization was studied using a polymerization solution composed of TMPTA and a photoinitiating photoredox pair. The concentration of DIPF was $1 \cdot 10^{-3}$ M and the concentration of RBTBAS was fixed on the level that assures at 500 nm, for a 3 mm thick layer, the absorbance of about 2.0 ($c = 6.7 \cdot 10^{-4}$ M). The concentrations of acids and their salts studied in the tested formulations were 0.1 M.

Nanosecond laser flash photolysis experiments in part were performed using the apparatus previously described [5] and in part using 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 Lambda Physik/model LPY 150 operating at 65 mJ/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 Hewlett-Packard/Agilent an Agilent Infiniium 54810A digital storage oscilloscope and Acorn compatible computer. The rates of Rose bengal and DIPF triplet decay and the transient spectra of short-lived photoreaction products were measured for $3 \cdot 10^{-5}$ M and $3 \cdot 10^{-4}$ M solution respectively in acetonitrile (MeCN).

Methods

The electronic absorption spectra were obtained using Varian Cary 3E spectrophotometer.

The kinetics of the polymerization measurements were carried out by measuring the polymerization heat evolution of a sample, irradiated with a laser beam through an optical system, in a home-made micro-calorimeter [15, 16]. The temperature sensor, a semiconducting diode, immersed in the 3 mm thick layer (about 290 mg) of a cured sample, was used for the detection of the heat flow. The amplified signals were transformed with an analog/digital data acquisition board to a computer. In order to avoid a possibility of non-isothermal reaction conditions, for further discussion only the data concerning the initial time of the polymerization were used for the calculation of the polymerization rates. The irradiation of the polymerization mixture was carried out using the emission of an Omnichrome Model 543-500 MA argon-ion laser. The light intensity was measured by a Coherent Model Fieldmaster power meter.

The final products were identified by ^{1}H NMR spectroscopy. The spectra obtained were the evidence that the reaction products were of the desired structures.

RESULTS AND DISCUSSION

The mechanism of the photoinitiation of polymerization by dye/sulfur(oxygen)-containing aromatic carboxylic acid in its ionic form may be suggested based on the transient absorption spectra recorded for RBTBAS and DIPF in the presence of: (*i*) sulfur containing aromatic carboxylic acid, (*ii*) sulfur containing aromatic carboxylic acid tetrabutylammonium salt, (*iii*) *n*-butyltriphenylborate in MeCN solution, and compared to the transient spectra recorded for the tested dyes in 2-propanol.

Transient absorption spectra of photoinitiation pairs

The consumption of both RBTBAS and DIPF (Fig. 1) is evident in the spectrum of the bleaching of their ground states absorption band (negative absorption). In the RBTBAS spectrum, shortly after the laser pulse, one can also see the bands characteristic for Rose bengal (apparent λ_{max} at 470 and 600 nm corresponding to the triplet-triplet absorption of the dye and an absorption band at 370 nm). According to Fouassier [24] at 470 nm both the triplet and the cation radical $RB^{\bullet +}$ issued from self-quenching, are responsible for the absorption. However, at this wavelength the absorption of $RB^{\bullet +}$ is much lower than the absorption of RB triplet, therefore the building up kinetics of $RB^{\bullet +}$ cannot be observed. The absorption intensity of the semi reduced RB ($RB^{\bullet 3-}$, appearing at 420 nm) is also low and is not observed in Fig. 1. The transient absorption spectra of DIPF reveals a typical absorption curve described earlier by Neckers [5].

In Figure 2 in the presence of borate, one sees a new absorption band with the absorption maximum at 420 nm. Since the $BuPhB^+$ acts as a one electron photoreducing agent, the observed transient can be assigned to the presence of RBTBAS (triple-negatively charged) radical anion [$RB^{\bullet 3-}$ — Formula (III)]. The peak position is in good agreement with the position recorded for this type of a radical anion assigned for RB [24]. On the other hand, when PTAA serves as the electron donor (curve 3), no Rose bengal radical anion ($RB^{\bullet 3-}$) is observed, but a new product absorbing at 375 nm grows as the triplet decays. This absorption transient can be assigned to different Rose bengal radical anion, *e.g.* protonated, a double negatively charged radical anion [$RB^{\bullet 2-}$ — Formula (IV)] obtained after the protonation of $RB^{\bullet 3-}$ by the deprotonation of a radical cation with sulfur centered positive charge ($Ph\text{-}S^{\bullet +}\text{-}CH_2\text{-}COOH$). Similar peak position is recorded when RBTBAS is irradiated in 2-propanol solution (curve 4). This additionally supports the conclusion that the observed transient can be assigned to Rose bengal double negatively charged radical anion, $RB^{\bullet 2-}$.

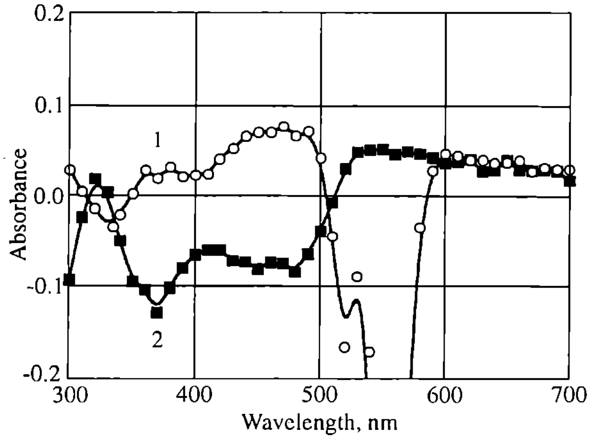


Fig. 1. Transient absorption spectra of RBTBAS (3 · 10^{-5} M, curve 1) and DIPF (3 · 10^{-4} M, curve 2) recorded in deaerated MeCN solution; delay time: RBTBAS — 6 μs, DIPF — 1 μs

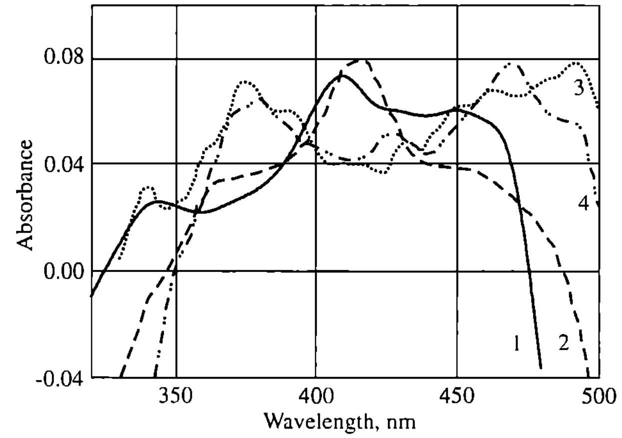
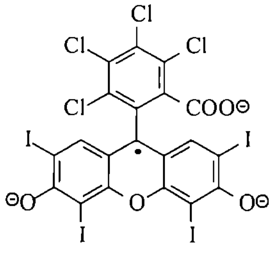


Fig. 2. Transient absorption spectra of RBTBAS (3 · 10^{-5} M) in MeCN in the presence of various electron donors (5 · 10^{-2} M) and hydrogen atom donors (2-propanol, 1.0 M) after 10 μs after the flash: 1 — PTAA AS, 2 — BuPh$_3$B$^+$, 3 — PTAA, 4 — 2-propanol



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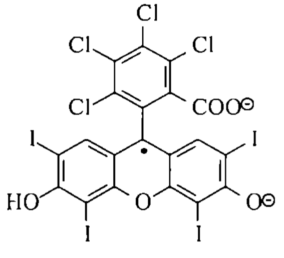


(IV)

The inspection of the transient spectrum obtained for Rose bengal in the presence of PTAA AS (curve 1) (5 · 10^{-2} M) shows quite different picture of the process. While the irradiation in the presence of PTAA yields as a product $RB^{\bullet 2-}$, under similar conditions, in the presence

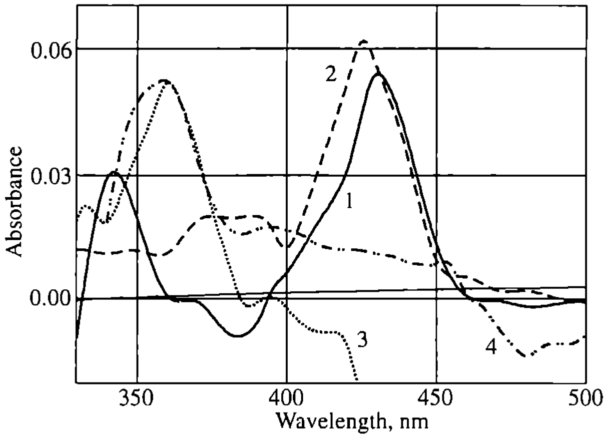
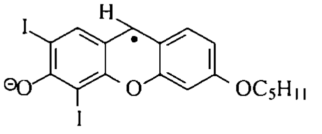


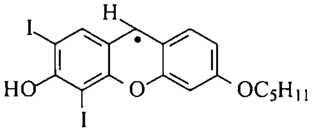
Fig. 3. Transient absorption spectra of DIPF ($3 \cdot 10^{-4}$ M) in MeCN in the presence of various electron donors ($5 \cdot 10^{-2}$ M) and hydrogen atom donors (2-propanol, 1.0 M) after 10 µs after the flash; for symbols see Fig. 2

of PTAA AS, one obtains a transient absorption with the maximum at 420 nm. The peak position suggests the presence of $RB^{\bullet 3-}$, no $RB^{\bullet 2-}$ can be detected in the recorded spectra.

Similar behavior as for RB^{2-} as the absorbing dye, as it is shown in Fig. 3, is observed for non-ionic dye — DIPF. The photoreduction of the dye by PTAA AS (curve 1) yields a stable DIPF radical anion [$DIPF^{\bullet -}$ — Formula (V)] and no presence of a neutral radical of $DIPF^{\bullet}$ [Formula (VI)] can be detected. On the other hand, the photoreduction of the dye by PTAA (curve 3) gives $DIPF^{\bullet}$ as



(V)



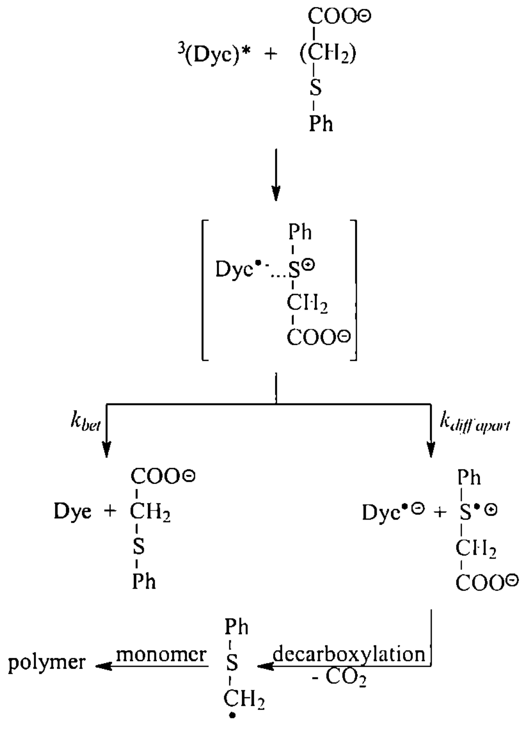
(VI)

a product. The photolysis of DIPF in a 2-propanol solution (curve 4) also gives a transient typical for the neutral radical of the dye ($DIPF^{\bullet}$).

In RB + PTAA and DIPF + PTAA cases, we were not able to detect $RB^{\bullet 3-}$ and $DIPF^{\bullet -}$. After the electron transfer from the sulfur to the dye triplet, $RB^{\bullet 3-}$ and $DIPF^{\bullet -}$ radical anions should be obtained. The dye radical anions have a negative charge centered on the oxygen at the 6 position. These intermediates act as a base and promote a rapid proton transfer from either carboxylate group or from the carbon α to the sulfur of the sulfur centered radical cation. Since the proton transfer within a radical ion pair occurs on the picosecond time scale, the described above processes can not be detected using the nonosecond time scale [25].

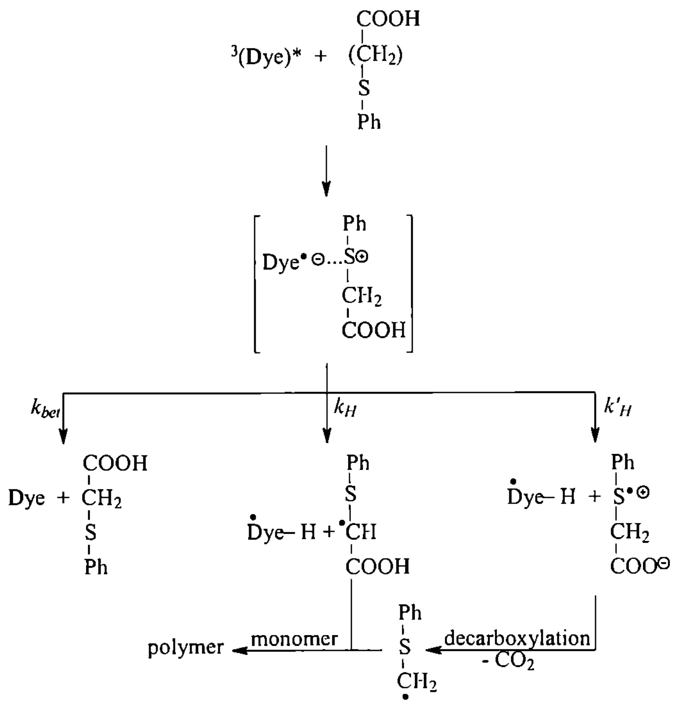
Mechanism of photooxidation of electron donors

All of the presented spectroscopic investigations of the photoreduction of the tested xanthene dyes allow to create the mechanism of the photooxidation of both PTAA and PTAA AS. Proposed mechanism is consistent with one proposed for the photooxidation of sulfur containing amino acids and one electron oxidation of similar types of molecules [29—32].



Scheme A. Proposed mechanism of photoinduced electron transfer process in the pair dye/PTAA AS

The flash photolysis results confirm that the photoreduction of the dyes in the presence of PTAA AS and PTAA as the electron donors, is one electron transfer process. The electron transfer from PTAA AS salt (Scheme A) results in the radical cation formation ($PTAA^{\bullet +}$) initially and $DIPF^{\bullet -}$ pair in the first case, and $PTAA^{\bullet +}$ and the Rose bengal triple-negatively charged radical anion ($RB^{\bullet 3-}$) pair in the other. This type of reaction is confirmed by the comparison with the photoreduction process of the dyes in the presence of tetrabutylammonium triphenylborate, the well-known one electron photoreducing agent [5]. The transient spectra in PTAA AS case show that $DIPF^{\bullet -}$ and $RB^{\bullet 3-}$ are the only products obtained after the triplet quenching of the tested dyes. This explicitly determines the structure of the reaction product obtained during the photooxidation of the electron donor. The only product obtained under these circumstances is the radical cation with a sulfur centered positive charge ($Ph\text{-}S^{\bullet +}\text{-}CH_2COO^-$). Based on the well established mechanism of the photooxidation of sulfur containing amino acids or one electron oxidation of similar types of molecules, one can easily predict the next steps of the process that may involve: the back electron transfer to reproduce the reactants in the ground state or the formation of the α-alkylthio-type radicals ($Ph\text{-}S\text{-}CH_2^{\bullet}$) produced from the free-radical cation of the



Scheme B. Proposed mechanism of photoinduced electron transfer process in the pair dye/PTAA

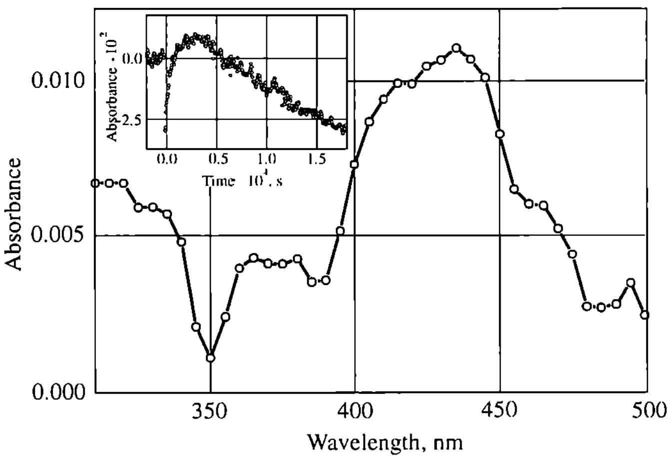


Fig. 4. Transient absorption spectrum of DIPF in 2-butoxyethyl acetate in the presence of PTAA AS as electron donor. Inset: radical anion (DIPF$^{\bullet -}$) formation and decay profile detected at 430 nm from DIPF (2.5 · 10^{-5} M) — PTAA AS (8.4 · 10^{-3} M)

sulfur containing carboxylic acid as a result of the intramolecular electron transfer from the carboxylate group to the sulfur-centered radical cation followed by decarboxylation with the rate constant to be in the range 10^6—10^7 [33, 34].

Different picture of the process is observed when PTAA is applied as an electron donor (Scheme B). The products obtained after one electron photoreduction of the dyes suggest that two different free radicals obtained after one electron photooxidation of PTAA are possible. Based on the pioneer works of Davidson [35—37] and the more current of Bobrowski, Hug and Marciniak [25—31] one can predict that these are: α-(alkylthio)carboxylic radical (Ph-S-CH$^{\bullet}$-COOH) and the α-alkylthio radical (Ph-S-CH$_2^{\bullet}$).

Summarizing the mechanistic studies of the analyzed photoreactions it is noteworthy that: (*i*) The insertion of an additional amount of tetraalkylammonium cation (as ClO$_4^-$ salt) into the reaction medium (both PTAA and PTAA AS) has no effect on the mechanism of the process. However, it slightly decreases the rate of the triplet state quenching [38]. The observed results suggest that the presence of tetraalkylammonium salt as electron donor is a basic prerequisite for the reaction with no deprotonation of radical cation. (*ii*) As it results from the comparison of Fig. 1, 2 and 4, substitution of MeCN with 2-butoxyethylacetate as a solvent *i.e.* the change of the solvent polarity does not affect shown mechanisms of the processes (Fig. 4). (*iii*) An extension of laser flash photolysis investigation of ethyl (phenylthio)acetate photooxigenation showed the presence of either DIPF$^{\bullet}$ or RB$^{\bullet 2-}$ that are the evidences of α-deprotonation reaction.

In our previous work on carboxybenzophenone-sulfur containing carboxylic acids photoredox pairs we also showed that α-alkylthio-type radicals (Ph-S-CH$_2^{\bullet}$) were more reactive in comparison with Ph-S-C$^{\bullet}$H-COOH radicals. The formation of α-alkylthio-type radicals requires the intramolecular electron transfer, and this in turn, needs the presence of the electron-donating group localized in the molecule. In the tested group of the electron donating molecules the carboxylate anion may show this function. Typically this process is possible in a highly polar solvent (for example MeCN-H$_2$O mixture). In non-polar or medium polarity monomers the sulfur containing carboxylic aromatic acids will not dissociate. It means that in this case, as it is documented experimentally, the electron transfer is followed by the proton transfer within the radical-ion pair and may involve a proton transfer either from the carboxylic group or from the alkyl group. The first path will produce Ph-S$^{\bullet +}$-CH$_2$COO$^-$, which after decarboxylation yields a more reactive α-alkylthio radical (Ph-S-CH$_2^{\bullet}$). The other path will give a less reactive α-(alkylthio)carboxylic radical (Ph-S-CH$^{\bullet}$-COOH). The ratio between the concentrations of both radicals will regulate the photoinitiaton efficiency of a photoredox pair. The sharp decrease in the photoinitiation efficiency in the presence of PTAA suggests that the leg forming Ph-S-CH$^{\bullet}$-COOH radical is a dominant one.

Kinetics of photopolymerization

We showed earlier that the rate of photoinitiated polymerization (R_p) can be expressed by the equation [14—16]:

$$R_p = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = k_p[M]\sqrt{\frac{I_a k_{el}}{k_t}} \qquad (1)$$

where: *[M] — monomer concentration, k_p — rate constant of propagation, I_a — intensity of absorbed light, k_t — rate constant of the termination of the macroradicals, k_{el} — rate constant of the electron transfer.*

Equation (1) predicts that the rate of the polymerization might be in part controlled by the rate of photoinduced electron transfer. The experimental verifications of the equation (1) for the tested photoinitiating systems is possible by measuring the rate of the primary process of the polymerization initiation process, *e.g.* the rate of the electron transfer between the tested dyes and the electron donors and the comparison of these rates with the rates of photoinitiated polymerization.

The quenching rate constants (k_q) (since the quenching of the dyes triplet by the electron donor is the only way of triplet deactivation, therefore under this condition one can assume that $k_q = k_{el}$) were obtained from the experimentally measured pseudo-first-order rate constant (k_{obs}) for the decay of the dyes triplet by the equation (2):

$$k_{obs} = \tau_{T^{-1}} + k_q[\mathrm{ED}] \qquad (2)$$

where: τ_T — *lifetime of the dye triplet in the absence of an electron donor (ED).*

Some typical plots based on eq. (2) are presented in Fig. 5 and the quenching rates constants ($k_{el} = k_q$) obtained for the selected electron donors are summarized in Table 1.

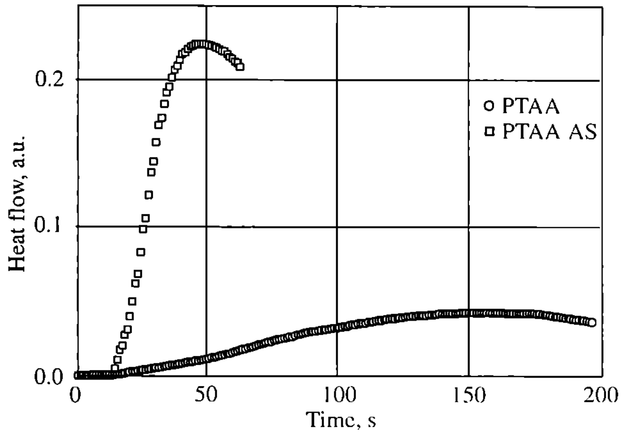


Fig. 6. Kinetic curves of TMPTA polymerization initiated by DIPF ($1.0 \cdot 10^{-3}$ M) in the presence of PTAA and PTAA AS; [ED] = 0.1 M, light intensity = 90 mW/cm^2, argon-ion laser

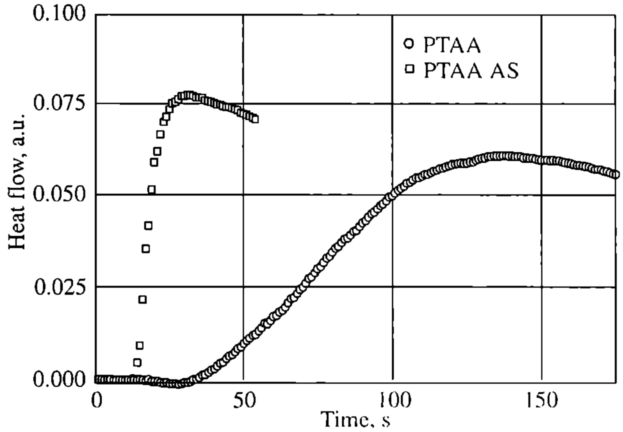


Fig. 7. Kinetic curves of TMPTA polymerization initiated by RBTBAS ($1.0 \cdot 10^{-4}$ M) in the presence of PTAA and PTAA AS; [ED] = 0.1 M, light intensity = 90 mW/cm^2, argon-ion laser

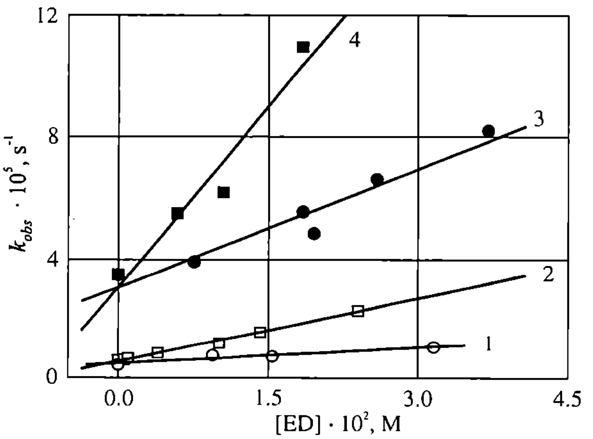


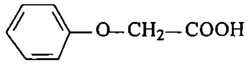
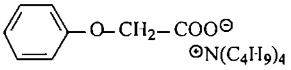
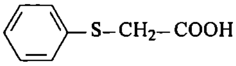
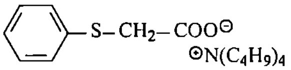
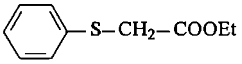
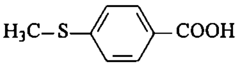
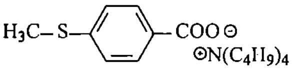
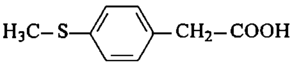
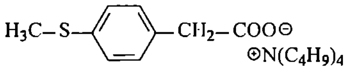
Fig. 5. Effect of electron donor concentration ([ED]) on observed rate constant (k_{obs}) of tested photoinitiator pair according to eq. (2); 1 — RB + PTAA ($k_q = 1.8 \cdot 10^6$ M^{-1} s^{-1}), 2 — RB + PTAA AS ($k_q = 6.57 \cdot 10^6$ M^{-1} s^{-1}), 3 — DIPF + PTAA ($k_q = 1.29 \cdot 10^7$ M^{-1} s^{-1}), 4 — DIPF + PTAA AS ($k_q = 3.93 \cdot 10^7$ M^{-1} s^{-1})

It is apparent from the inspection of the data shown in Fig. 6 that the transformation of PTAA into its tetrabutylammonium salt in the presence of DIPF dramatically increases the sensitivity of the photoinitiating system (more than one order of magnitude). Figure 7 presents the similar data obtained for RBTBAS. The observed phenomenon is similar to that observed for the system applying DIPF as the initiator.

Even more distinct differences are observed in the rates of polymerization when one compares the rate of polymerization photoinitiated by dye/PTAA AS and dye-ethyl (phenylthio)acetate (PTAA EE).

From the data collected in Table 1 it results that there is no simple correlation between the square roots of the rates of the electron transfer process and the rates of photoinitiated polymerization. Namely, it is easy to see that the change of PTAA into its tetrabutylammonium salt causes an increase in the rate constant of the electron transfer of about 2—3 times, while the rate of photoinitited polymerization increases at least one order of magnitude. This observation allow to conclude that there is an additional factor affecting the rate of photoinitiated polymerization. As it was mentioned earlier, in our previous work on carboxybenzophenone-sulfur containing

Table 1. Dyes and electron donors used as photoinitiating pairs, quantum yield of decarboxylation of electron donors (Φ_{CO_2}) and relative rates of polymerization of TMPTA initiated by the tested photoinitiating pairs

Structure		Electron donor	DIPF		RBTBAS	
		(Φ_{CO_2})	R_p, a.u.	k_{el}, M^{-1} s^{-1}	R_p, a.u.	k_{el}, M^{-1} s^{-1}
PAA		0.34	1.07	$0.88 \cdot 10^6$	—	—
PAA AS		—	1.75	—	2.21	—
PTAA		0.92	7.50	$1.29 \cdot 10^7$	8.01	$1.8 \cdot 10^6$
PTAA AS		—	183	$3.93 \cdot 10^7$	89.04	$6.57 \cdot 10^6$
PTAA EE		—	2.59	$3.86 \cdot 10^6$	1.50	$2.27 \cdot 10^6$
MTBA		<0.05	0.95	—	2.32	—
MTBA AS		—	2.90	—	2.42	—
MTPAA		0.29	1.74	—	4.37	—
MTPAA AS		—	36.70	—	7.15	—

carboxylic acids photoredox pairs, we have documented that α-alkylthio-type radicals (Ph-S-$CH_2^\bullet$) are more reactive in comparison with Ph-S-$C^\bullet$H-COOH radicals. We believe that the observed lack of correlation between the rates of the electron transfer and the rate of photoinitiated polymerization is caused by different reactivities of free radicals formed after the electron transfer between the dyes and the tested electron donors. As it was mentioned before, the inspection of the Schemes A and B reveals that in PTAA case two different radicals can be formed (Ph-S-$CH_2^\bullet$ and Ph-$S^\bullet$-CH_2COOH), while in the case of its ammonium salt only more reactive Ph-S-$CH_2^\bullet$ radical is the reaction product. In the first case the presence of less reactive Ph-$S^\bullet$-CH_2COOH radicals causes a sharp decrease in the sensitivity of the photoinitiating photoredox pair. On the basis of these observations it appears that the predicted from the kinetic Schemes A and B properties of the electron donating molecules can be regulated by their simple modification allowing to change of the type of free radicals that are formed after the primary, photoinduced electron transfer process.

It is worth noting that the free radical photoinitiating pair composed of Rose bengal ditetrabutylammonium salt and PTAA or PTAA AS was not selected accidentally. Figure 8 presents the electronic absorption spectra of Rose bengal disodium salt (typical commercial form of Rose bengal) in methanol and Rose bengal ditetrabutylammonium salt in ethyl acetate tested in this work. Both compounds, as it was documented earlier in Neck-

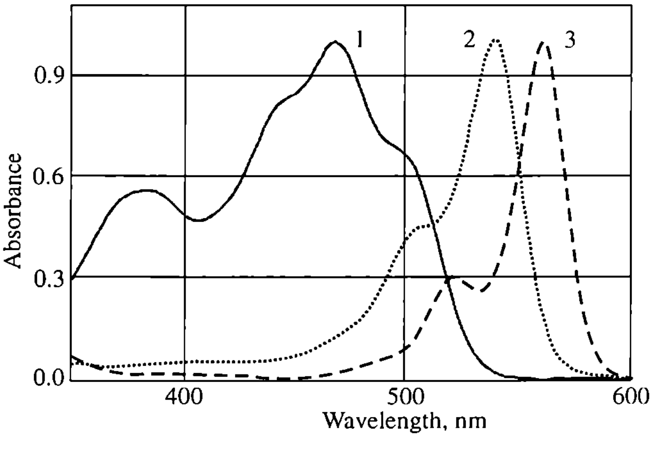


Fig. 8. Electronic absorption spectra of dyes in different solvents used as primary light absorbes; 1 — DIPF in EtAc, 2 — Rose bengal disodium salt in MeOH, 3 — Rose bengal ditetrabutylammonium salt in EtAc

ers' work, exist in the tested solutions in the ionic form [19—21]. On the basis of this observation, it is obvious that PTAA AS also exists in a non-polar solution exclusively in an ionic form. All these comparisons reveal to conclude that using PTAA AS instead of PTAA, one can change the route of the secondary reactions that follow the photoinduced electron transfer process. As a result, one can obtain a more efficient photoinitiation system.

In this study several other electron donors, being aromatic carboxylic acids, were tested. The results of the photoinitiation efficiency measured for all the dye-electron donor combinations are also summarized in 4 last lines of Table 1.

The first important feature shown in Table 1 is associated with the properties of phenoxyacetic acid (PAA) and its tetrabutylammonium salt (PAA AS). It is easy to see that these compounds are rather poor coinitiators. The reason of the very low photoinitiation efficiency observed for PPA as the electron donor might come from its low rate of the dyes triplet state quenching. Another explanation of the observed differences of R_p value between PAA and PAA AS in the photoinitiation efficiency might originate from the analysis of the efficiency of the secondary reactions observed for the tested acids after the electron transfer process. In our previous paper we documented that the degree of the monomer conversion is the linear function of the square root of the quantum yield of decarboxylation (Φ_{CO_2}) [17]. Only three among tested acids may be considered for this type of analysis in this paper, *e.g.* PAA ($\Phi_{CO_2} = 0.34$) [39], (phenylthio)acetic acid ($\Phi_{CO_2} = 0.92$) [17] and 4-(methylthio)phenylacetic acid (MTPAA) ($\Phi_{CO_2} = 0.29$) [17]. From the midst of 4 acids investigated only methylthiobensoic acid (MTBA) shows very small (<0.05) value of Φ_{CO_2}. The plot of the above mentioned relationship for the tested dyes is presented in Fig. 9.

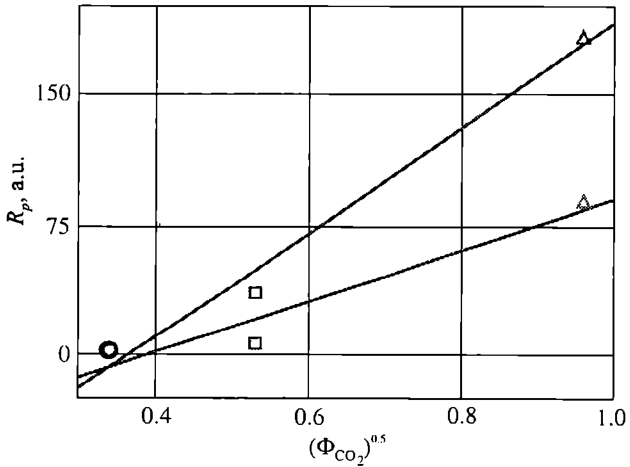


Fig. 9. Rate of photoinitiated polymerization (R_p) vs. square root of the quantum yield of decarboxylation (Φ_{CO_2})$^{0.5}$ for systems DIPF/electron donor (red) and RBTBAS/electron donor (blue); electron donors: o — MTBA, □ — MTPAA, Δ — PTAA

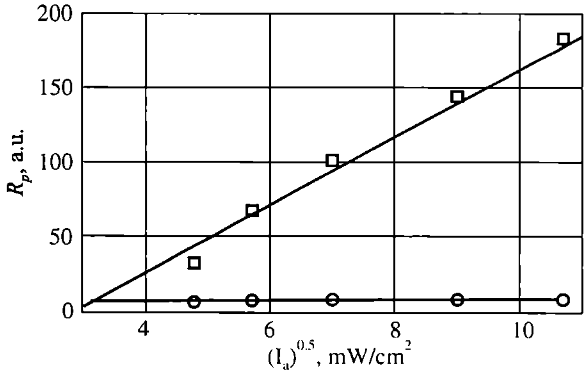


Fig. 10. Effect of absorbed light intensity (I_a) on the rate of photoinitiated polymerization (R_p) of TMPTA in the presence of PTAA AS (□) or PTAA (o) as electron donors and DIPF ($1 \cdot 10^{-3}$ M) as the dye

It is evident that the rate of photoinitiated polymerization is controlled by Φ_{CO_2}. This observation has very important consequences, as far as one considers the mechanistic aspects of the process. Finally, in order to clarify all the mechanistic problems of photoinitiation, we tested an influence of the light intensity (I_a) on the observed rate of polymerization (Fig. 10).

The presented in Fig. 10 results are quite surprising. However, a careful analysis of the process allows to conclude that for the case of Ph-S-CH_2-COOH (o) after the electron transfer, the ionic radical pair remains in the viscous and non-polar monomer cage. Therefore, the back electron transfer process starts to dominate the overall efficiency of the free radical formation. The same phenomenon is observed in the case of dimethyl sulfide, which behaves similarly in non-polar monomeric formulation [18]. For PTAA AS the situation is quite different. After the electron transfer the fast decarboxylation process produces the neutral radical, which easily escapes from the solvent cage, thus minimizing the back electron transfer effect on the overall efficiency of the free radical formation.

CONCLUSIONS

A new approach to the design of the electron transfer free radical photoredoxinitiating system, applying the light absorber (dye) and an electron donor of the structure allowing the formation of the leaving group and forming the neutral free radical, is presented.

The photoredoxinitiating system, analyzed in this paper, according to our best knowledge, is the third system described in literature that applies the dissociative electron transfer process for the effective production of free radicals able to initiate the radical polymerization.

The first, and the best known, based on cyanine borate ion pair, was presented by Schuster *et al.* [6, 7]. In this photoredox pair, photoinduced electron transfer from borate anion to the singlet excited state of cyanine dye is followed by rapid cleavage of the alkyl boron bond of the boranyl radical forming, as a leaving group, the alkyl radical which serves as the radical chain initiator.

Gould *et al.* described the other type of such system [40, 41]. The photoinitiating system applies one electron reduction of *N*-alkoxyheterocycles resulting in formation as leaving group a neutral heterocycle and an alkoxy radical that initiates free radical polymerization. Based on the known photochemistry of sulfur containing aromatic carboxylic acids, the chemical modification, giving the electron donating molecules the possibility of decarboxylation reaction after the electron transfer process, even in non polar monomeric formulation, is proposed. The experimental results show that after the transformation of the acid into its ammonium salt a substantial increase in the photoinitiation ability of the system is observed. The mechanism of the photoinitiated polymerization for the tested photoredox pairs is clarified based on the laser flash photolysis experiments obtained for an ionic form of dye (Rose bengal) or nonionic 5,7-diiodo-3-pentoxy-6-fluorone acting as electron acceptors and (phenylthio)acetic acid (Ph-S-CH$_2$-COOH) or its tetrabutylammonium salt in MeCN solution being electron donors. It is showed that the photoreduction of the dyes in the presence of (phenylthio)acetic acid occurs *via* the photoinduced electron transfer process. The evidence of this reaction, in the case of 5,7-diiodo-3-pentoxy-6-fluorone, comes from the presence of its radical anions and neutral radicals. When Rose bengal was applied as an electron acceptor the electron transfer mechanism was confirmed by the presence of Rose bengal triple-negatively charged radical anion ($RB^{\bullet 3-}$) and Rose bengal double negatively charged radical anion ($RB^{\bullet 2-}$). The photooxidation of Ph-S-CH$_2$-COOH in its ionic form allows a fast intramolecular electron transfer from the carboxylate group to the sulfur centered radical cation followed by rapid decarboxylation yielding neutral α-alkylthio-type radical (Ph-S-CH$_2^{\bullet}$) that can easily escape from the monomer cage. This causes an unexpectedly high increase in the photoinitiation efficiency. Concluding, the system described in this paper applies the dissociative electron transfer process for the effective production of free radicals able to initiate the radical polymerization.

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