

JERZY PAĆZKOWSKI^{1*)}, MAREK PIETRZAK¹⁾, BOŻENA PAĆZKOWSKA²⁾

Does the back electron transfer affect the rate of photoinduced free radical polymerization?

Summary — The specific behaviors of monomeric electron acceptor-electron donor bridged molecules and of polymeric initiator-coinitiator systems tested as free radical polymerization photoinitiating systems were observed. The obtained experimental and theoretical results suggest that the back electron transfer process probably does not control the rate of photoinitiated polymerization going with initiators tested. The phenomena observed more likely results from a different proton transfer between Rose bengal radical anion and a tertiary aromatic amine radical cation. This can be deduced on the basis of Marcus theory, describing the kinetics of photoinduced intermolecular and intramolecular electron transfer processes, and laser flash photolysis measurements.

Key words: polymer bond photoinitiators, Marcus theory, back electron transfer, kinetics of photopolymerization.

Recently the photoinitiators active in the visible range of the spectrum have been intensively studied [1—6]. The photoreduction of the absorbing dye in the presence of the appropriate coinitiator can be used to initiate polymerization. Electron donors, such as tertiary aromatic amines, reduce the dye excited states in the intermolecular electron transfer process, followed by a rapid proton transfer yielding a neutral reduced dye and aminoalkyl radical, which initiates free radical polymerization. Neckers and co-workers have studied the photochemistry and photophysics of these processes studying the properties of xanthene dyes, Rose bengal [7—9] and novel fluorone dyes [10, 11]. Though a mechanistic hypothesis concerning the photoreduction of xanthene dyes by tertiary amines is basically accepted, relatively little is known about the kinetics of photoinitiated polymerization *via* the photoinduced intermolecular electron transfer process. Paćzkowski and co-workers have shown, analyzing the photoinitiation process, that photoinduced polymerization involves many steps which can affect the final rate of polymerization [12—14].

The development of the photoinduced electron transfer (PET) applications, such as visible light curing or photochemical energy storage, is conditioned by the

generation of a high yield of free radicals or ions formation. The Gibbs energy dependence of the rate of the radical ion yield is the subject of the intense research. The classical theories of the reactions in condensed media lead to a suggestion that the rate of an electron transfer should be small for weakly exothermic reactions, should increase to a maximum in the thermodynamic driving force ($-\Delta G_{el}$) and should decrease for highly exothermic reactions in so-called "Marcus inverted region" [15—18]. The "Marcus inverted region" has been observed experimentally for the charge recombination or shift [19, 20] but not in the forward electron transfer (ET) in solution, where the rate constant as a function of Gibbs energy shows "Rehm—Weller" behavior [21]. However, in the polymerization photoinduced *via* ET process, for certain photoredox pairs the "Marcus inverted region" like kinetic behavior is observed [12, 14] and this property can not be explained by the reactivity of free radicals resulting from PET [22].

In this paper we would like to extend the kinetic consideration to one more process which can affect the final rate of polymerization. It is our intention to illustrate the effect of the back electron transfer or proton transfer process, following the electron transfer, on the final yield of photoinitiated polymerization.

EXPERIMENTAL

Materials

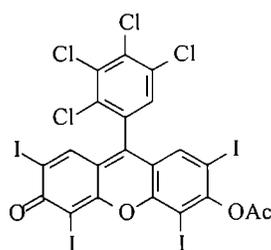
Substrates used for preparation of the dyes and electron donors, solvents, monomers (multifunctionalized

¹⁾ University of Technology and Agriculture in Bydgoszcz, Faculty of Chemical Technology and Engineering, ul. Seminaryjna 3, 85-326 Bydgoszcz.

²⁾ University of Technology and Agriculture in Bydgoszcz, Faculty of Civil and Environmental Engineering, ul. Prof. S. Kaliskiego 7, 85-791 Bydgoszcz.

^{*)} To whom all correspondence should be addressed; e-mail: paczek@atr.bydgoszcz.pl

acrylate or methacrylate) and the fluorescence probe were purchased from Fluka, Merck or Aldrich and Poly-science. Acetylated decarboxylated Rose bengal



RBAX

(RBAX) — Formula (I) was prepared using the procedure described earlier [1].

Synthesis

Synthesis of polymeric initiators and coiniciators were described in our earlier paper [23] and were based on known chemistry of Rose bengal polymeric derivatives [24].

Soluble polymer bond initiator-coinitiator: 6-O-acetylated Rose bengal and N-phenylglycine [PG-Poly-OC(O)RB-OAc] [see formula (IV) further]

3 g of Poly-OC(O)-RB-OAc obtained from bromomethylated polystyrene [24] [obtained using 4.03 g of bromomethylated polystyrene and 1.02 g (1 mmol) of Rose bengal] and 1.8 g of N-phenylglycine (NPG) were dissolved in 25 mL of DMF. The solution was stirred in the dark for 24 h at 60 °C, and the resulting product was precipitated by an excess of methanol and purified by repeated precipitation. Analytical data: the IR spectra indicated the presence of the groups typical for Poly-OC(O)-RB-OAc and poly-PG.

Covalently linked photoinitiator-coinitiator system

Synthesis of the covalently linked photoinitiator-coinitiator system is based on the well-known chemistry of Rose bengal [25—29].

— Hexane 1-[*p*-(dimethylamino)benzoate]-6-Rose bengal C2' ester (HDRB)

2.03 g (2 mmol) of Rose bengal disodium salt and 4.88 g (20 mmol) 1,6-dibromohexane were dissolved in 25 mL of dry DMF. The reaction mixture was stirred at 60 °C for 10 h. DMF and the excess of 1,6-dibromohexane were evaporated in a vacuum from the resulting red solution and to the dry solid residue 30 mL of DMF and 0.9 g (4.4 mmol) of potassium *p*-dimethylaminobenzoate were added. The reaction mixture was stirred at 60 °C for 24 h. The resulting red solution was evaporated in a vacuum and the residue was precipitated in water. The red colored product was obtained thoroughly washed with water and methanol to remove the excess of potassium 4-*N,N*-dimethylaminobenzoate then filtered off

and dried in a vacuum 0.63 g (25%) of the product was obtained. ¹H NMR (200 MHz, DMSO), 7.7842, 7.7402 ($J_{AB} = 8.8$ Hz, 2H), 7.5—7.0 (*m*, 2H, xanthene), 6.7375, 6.6936 ($J_{AB} = 8.78$ Hz, 2H, phenyl, benzoate), 4.0—4.20 (*m*, 4H, ester), 3.0018 [*s, s*, 6H, -N(CH₃)₂], 0.92—1.80 (*m*, 8H, methylene). UV-Vis (DMF): $\lambda_{max} = 560$ nm.

— Dodecane-1-[*p*-dimethylamino)benzoate]-12-Rose bengal C2' ester (DDRb)

Method of the synthesis was the same as used for HDRB. Reaction yield: 34%, ¹H NMR confirmed the structure of the compound. UV-Vis (DMF): $\lambda_{max} = 561$ nm.

— Butane-1-[*p*-(dimethylamino)benzoate]-4-Rose bengal C2' ester (BDRB)

Method of the synthesis was the same as used for HDRB. Reaction yield: 28%, ¹H NMR confirmed the structure of the compound. UV-Vis (DMF): $\lambda_{max} = 560$ nm.

— Propane-1-[*p*-(dimethylamino)benzoate]-3-Rose bengal C2' ester (PDRB)

Method of the synthesis was the same as used for HDRB. Reaction yield: 26%, ¹H NMR confirmed the structure of the compound. UV-Vis (DMF): $\lambda_{max} = 560$ nm.

— *p*-Xylyl- α -[*p*-(dimethylamino)benzoate]- α' -Rose bengal C2' ester (XDRB)

Method of the synthesis was the same as used for HDRB. Reaction yield: 20%, ¹H NMR confirmed the structure of the compound. UV-Vis (DMF): $\lambda_{max} = 560$ nm.

Methods

Measurements of the kinetics monitored by the fluorescence probe [30—34] were carried out using the solutions composed of 1 mL of 1-vinyl-2-pyrrolidinone (VP) or 1-methyl-2-pyrrolidinone (MP), 9 mL of the appropriate multifunctionalized acrylate or methacrylate, a Rose bengal derivative either monomeric or polymeric as the photoinitiator with an effective concentration of the dye oscillating in the range 10⁻³—10⁻⁴ M, and the monomeric or polymeric coiniciators with the concentration giving the donor concentration approximately equal $c = 0.05$ M.

The other method of the polymerization rate monitoring, applied for the measurements of the covalently linked acceptor-spacer-donor (A-S-D) system, is based on the measurements of the heat evolution during polymerization in a sample 2—3 mm thick [6]. A semiconducting diode (1 mm diameter) was used as a detector.

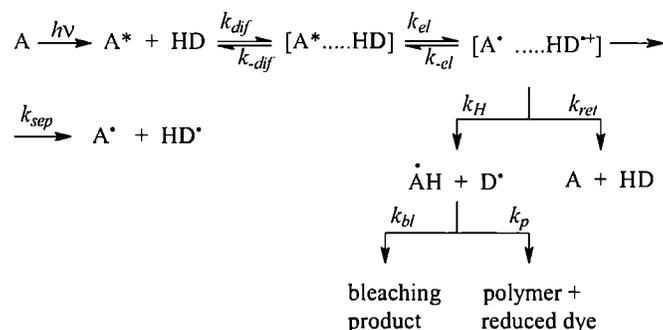
The nanosecond laser flash photolysis experiments were performed using LKS.60 Laser Flash Photolysis apparatus (Applied Photophysics). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from a Lambda Physik/model LPY 150 operating at 65 mJ/pulse (pulse width about 4—5 ns) was used for the excitation. The transient absorbances at the preselected wavelengths were monitored by a detection sys-

tem 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 Hewlett-Packard/Agilent an Agilent Infiniium 54810A digital storage oscilloscope and an Acorn compatible computer. The rates of Rose bengal and diiodopentoxyfluoron (DIPF) triplet decay and the transient spectra of the short-lived photoreaction products were measured for $3 \cdot 10^{-5}$ M and $3 \cdot 10^{-4}$ M solutions in acetonitrile.

RESULTS AND DISCUSSION

Rapid initiator systems for multiacrylate polymerization photoinitiated by visible light require a suitable dye acting in most cases as a reducing photoinitiator with an electron donor which may be either sulphur containing carboxylic acids [35], *N*-phenylglycine derivatives [13, 14, 36], triphenylalkyl borate [1, 2, 37, 38] or tertiary amines (most commonly aromatic tertiary amines) with α -hydrogen.

The process of free radical polymerization initiated *via* intermolecular electron transfer involves many steps, which depend on the type of an electron donor used [11]. Scheme A shows the possible processes which may occur during free radical photoinitiated polymerization in the presence of aromatic amines.



Scheme A

Symbol k_{dif} denotes the rate constant representing the rate of diffusive encounters between the reactants, which can dissociate apart with the rate constant k_{-dif} , k_{el} denotes the first-order rate constant of electron transfer with reverse step denoted by the rate constant k_{-el} , k_H denotes the rate constant of proton transfer between ion radicals, the cross-coupling (bleaching) step is denoted by the rate constant k_{bl} , the polymerization step — by k_p (rate constant of propagation) and k_{ret} denotes the process of the electron return.

As it can be seen from Scheme A, the rate of diffusion of reactants, the back electron transfer or the proton transfer process might be one of the limiting steps of the free radical formations, *i.e.* the limiting step of photoini-

tiated polymerization. In the simplest approach, one can organize a donor-acceptor in a close proximity that is required for the effective electron transfer process, by the attachment of these species to one polymeric chain.

The verification of the predicted phenomena of the polymer-bond photoinitiator is based on the real time and real condition measurements of the specific fluorescence probe emission intensity and structure, which are strongly affected by the changes in the environment [23—30]. As a fluorescence probe 5-dimethylamino-5-naphthalenesulfonamide (dansylamide — DA) compound showing ICT (Intramolecular Charge Transfer) properties is used.

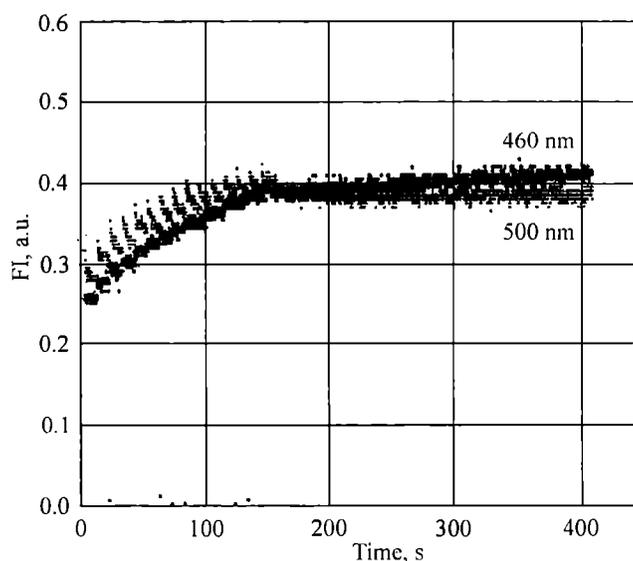


Fig. 1. The change of dansylamide fluorescence intensity (FI) recorded during the polymerization of TMPTMA/VP (9:1) mixture using photoinitiation system: RBAX ($10 \cdot 10^{-4}$ M), NPG (0.05 M); mode of irradiation: LRS (0.2 s—10 s—0.2 s—10 s...), 15 flashes, total time irradiation 3 s, 600 mW/1.54 mm², $\lambda = 514$ nm

During a polymerization process, the fluorescence spectrum of DA undergoes a large hypsochromic fluorescence shift accompanied by an increase in intensity when the degree of polymerization increases. Figure 1 shows the changes of fluorescence intensity of dansylamide observed at 460 nm and 500 nm during photoinitiated polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate (TMPTMA in VP). Polymerization was initiated by a series of argon-ion laser (514 nm) flashes [large relay sequence (LRS), time of single flash 200 ms, 15 flashes] using the initiator system (RBAX, $c = 5 \cdot 10^{-4}$ mol/L) and *N*-phenylglycine (NPG, $c = 0.05$ mol/L). Polymerization causes a decrease in the available free volume and this, in turn, affects the microenvironment of the probe. The ratio of the fluorescence intensities recorded at 460 nm and 500 nm indi-

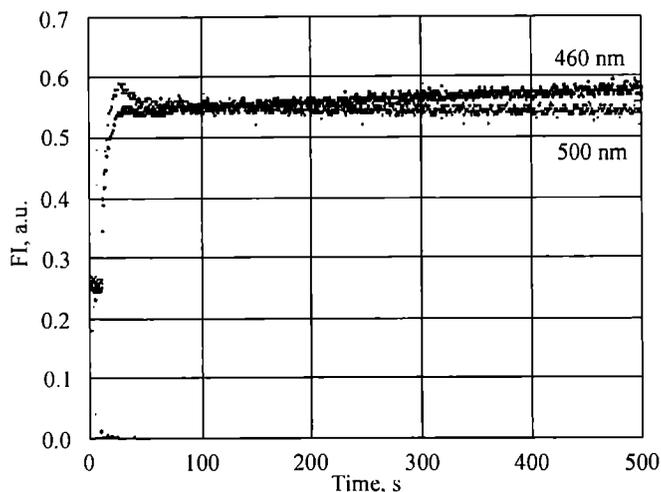
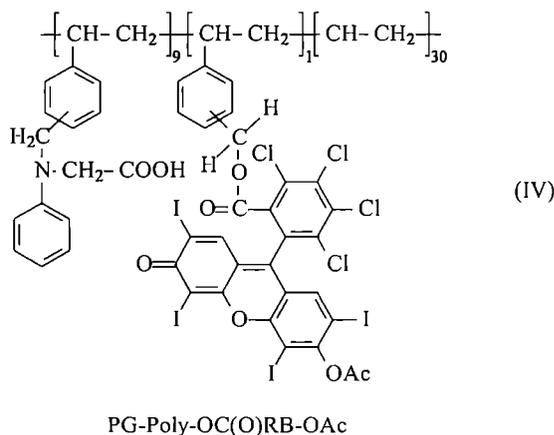


Fig. 4. The change of densylamide fluorescence intensity (FI) recorded during the irradiation of TMPTMA/VP (9:1) mixture; photoinitiation system: Poly-RB-OAc ($5 \cdot 10^{-4}$ M of RB-OAc molecules), NPG (0.05 M); mode of irradiation — see Fig. 1

Much more significant changes of the fluorescence probe were observed for the polymeric photoinitiator [Poly-RB-OAc, Formula (III)]. As Fig. 4 shows, after each flash the fluorescence intensity as well as the ratio of fluorescence intensities (I_{460}^F / I_{500}^F) increase. This clearly indicates that the polymerization goes rapidly.

Remarkable behavior is observed during the irradiation of polymerizing mixture with a polymeric acceptor-electron donor system in which the dye and an electron donor are covalently bonded into the same polymeric chain [PG-Poly-OC(O)RB-OAc — Formula (IV), Fig. 5].



The kind of the fluorescence probe response is not seen yet in the presented paper. After each flash the fluorescence intensity is sharply decreasing and coming back to its initial intensity. The irradiation does not initiate polymerization. A solid polymer is not observed even after a long time of irradiation. This specific behavior (in comparison with those in Fig. 1—4) can be explained assuming that the fluorescence intensity de-

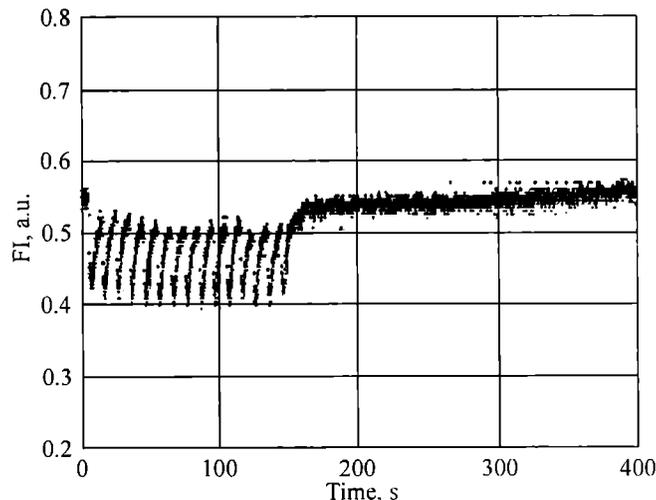


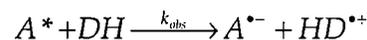
Fig. 5. The change of densylamide fluorescence intensity (FI) recorded during and after laser irradiation of TMPTMA/VP (9:1) mixture; initiation system: PG-Poly-OC(O)-RB-OAc ($5 \cdot 10^{-4}$ M of RB); mode of irradiation — see Fig. 1

crease is caused by the temperature increase without any chemical reaction (bleaching process). The rise of temperature is coming from the laser irradiation whose energy is changed directly into the heat instead of polymerization initiating (free radical formation). Since both polymeric initiator and cointiators initiate polymerization when they act with the monomeric photochemical partners, a possible explanation of the observed phenomenon is the idea of a back electron transfer or missing proton transfer process between radical ions pair. Since the polymeric chain makes the changes of the mutual orientation of geminate radical ions pairs more difficult, the back electron transfer process or the lack of amine radical cation deprotonation starts to dominate the overall efficiency of photoinitiation. As a result there is no free radicals formation and the laser energy is converted into a heat.

Kinetic analysis of the photoinitiation process can explain a possible cause of the observed feature of polymeric photoinitiation system. The steady state approximations applied to the donor neutral free radical (species initiating free radical polymerization) and for $[HD^{\bullet+}]$ ionradical gives:

$$k_{obs} - k_{ret}[HD^{\bullet+} \dots A^{\bullet-}] - k_t[D^{\bullet}M]^2 - k_{bl}[D^{\bullet} \dots A^{\bullet}H] = 0 \quad (1)$$

where: k_{obs} denotes the rate constant of simplified photochemical process



Dealing with a slow electron transfer (ET) step, one should take into account the fact that back ET in the successor complex might compete with its reactions, described by one composite unimolecular rate constant k_3 ($k_3 = k_{ret} + k_H + k_{sep}$). The steady state treatment applied

to the concentrations of the predecessor and successor complexes leads to the conclusion that k_{obs} should be related to the rate constant as in eq. (2):

$$k_{obs} = \frac{k_{dif}}{1 + \left(\frac{k_{-dif}}{k_{el}} \right) \left[1 + \frac{k_{-el}}{k_3} \right]} \quad (2)$$

Clearer is the inverted form of this equation:

$$\frac{1}{k_{obs}} = \frac{1}{k_{dif}} + \frac{1}{K_d k_{el}} + \frac{1}{K_d k_{el}} \left(1 + \frac{k_{-el}}{k_3} \right) \quad (3)$$

When k_{-el} becomes larger than k_3 , in such a case the first term of eq. (3) becomes negligible. Thus we obtain:

$$\frac{1}{k_{obs}} = \frac{1}{K_d K_{el} k_3}, \quad k_{obs} = K_d K_{el} k_3 \quad (4)$$

For Rose bengal derivatives $k_{bl}[D^+][A^-H]$ can be neglected [40], so under this condition the rate of free radical photoinitiated polymerization considering the steady state approximation $[D^+] = [D^+M]$ can be expressed as follows [14]:

$$R_p = -\frac{d[M]}{dt} = k_p[M] \sqrt{\frac{k_{obs}}{k_t}} \quad (5)$$

According to the authors of [40], Rose bengal undergoes photobleaching process, however the product of this process is dihydro dye, *i.e.* the electron transfer is followed by a proton transfer. Radical anion formed subtracts hydrogen either from electron donor or from a solvent.

An introducing of equation (4) into equation (5) gives the final equation describing the rate of polymerization (R_p):

$$R_p = -\frac{d[M]}{dt} = k_p[M] \sqrt{\frac{K_d K_{el} k_3}{k_t}} \quad (6)$$

For a high concentration of donor, k_{obs} becomes practically a first-order rate constant and it can be expressed in a form $k_{obs}I_a$, and the rate of photoinitiated polymerization can be described as follows:

$$R_p = -\frac{d[M]}{dt} = k_p[M] \sqrt{\frac{I_a K_d K_{el} k_3}{k_t}} \quad (7)$$

The final description of the rate of polymerization becomes more complex after the introduction into equation (7) the term describing the rate of the photoinduced intermolecular electron transfer. In the simplest form k_{el} can be expressed as:

$$k_{el} = \chi Z \exp(-\Delta G^\ddagger / RT) \quad (8)$$

where: Z — universal frequency factor (*ca.* $6 \cdot 10^{12} \text{ s}^{-1}$ at 25°C); χ — transmission coefficient; ΔG^\ddagger — total free energy of activation being the sum of the individual free energies: $\Delta G^\ddagger = \Delta G_v^\ddagger + \Delta G_s^\ddagger$.

ΔG^\ddagger is described by Marcus equation:

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G_{el}}{\lambda} \right)^2 \quad (9)$$

The subscripts "v" and "s" refer to the energy involving bond distortions of interacting molecules and solvent changes in the ionic sphere surrounding the reactants (s — solvent). λ is defined as the total reorganization energy. Thus, $\lambda = \lambda_v + \lambda_s$, where λ_v is the inner-sphere reorganization energy referring to the energy changes of the molecule geometry during the electron transfer step, λ_s is outer-sphere reorganization energy which is case of the energy change when the solvent shell surrounding the reactants rearranges.

Finally ΔG_{el}^0 is expressed by the Rehm—Weller [21] equation:

$$\Delta G_{el}^0 = E_{ox}(D/D^{*+}) - E_{red}(A^-/A) - Ze^2/\epsilon a - E_{ex} \quad (10)$$

where: $E_{ox}(D/D^{*+})$ — oxidation potential of the electron donor; $E_{red}(A^-/A)$ — reduction potential of the electron acceptor; E_{ex} — energy of the excited state of the electron acceptor; $Ze^2/\epsilon a$ — Coulombic energy which is considered negligible to the overall magnitude of the ΔG in the present systems.

The back electron transfer will have a different driving force than forward photoinduced ET, since the back process does not involve the excited state and because the charge types for the forward and reverse ET may differ [41]. Thus the ΔG_{-el} is expressed by equation:

$$\Delta G_{-el} = E_{ox}(D/D^{*+}) - E_{red}(A^-/A) - Ze^2/\epsilon a \quad (11)$$

Assuming that $K_{ET} = k_{el}/k_{-el}$, and introducing the Marcus equation for both processes, one obtains the equation describing the K_{ET} value in the form:

$$K_{ET} = \exp \left\{ \frac{\lambda}{4RT} \left[(\lambda + \Delta G_{-el})^2 - (\lambda + \Delta G_{el})^2 \right] \right\} \quad (12)$$

From the equation (12) one can conclude that for the given values of ΔG_{el} and ΔG_{-el} only the reorganization energy λ limits the value of K_{ET} .

The solvent reorganization energy (λ_s) for the spherical molecules is described in [15, 42] as:

$$\lambda_s = \frac{e^2}{2} \left(\frac{1}{r_a} + \frac{1}{r_d} - \frac{2}{r_{12}} \right) \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad (13)$$

where: r_a , r_d — radii of the electron acceptor and donor, respectively; r_{12} — distance between electron donor and acceptor; n — refractive index; ϵ — dielectric constant of a solvent.

Applying in eq. (13) the proper values for the polymerized mixtures, the solvent ($n = 1.4740$, $\epsilon = 13.102$) and approximated values of r_a and r_d (calculated using AM1 semiempirical method) which are 6.0 Å and 3.0 Å respectively, and assuming the closest distance between electron acceptor and electron donor as the sum of the mole-

cules radii (about 9.0 Å) and the greatest distance of about 17 Å for which an effective ET can occur [43], one can calculate that in the polymerization mixture for bridged Rose bengal/ethyl *p*-dimethylaminobenzoate the λ_s value oscillates between 1.4–1.8 eV. The combination of equations (12) and (13) allows to predict the changes of K_{ET} as a function of r_{12} , *i.e.* as a function of a distance separating the acceptor and donor molecules. A careful analysis of equation (13) shows that for $r_{12} \rightarrow \infty$, λ_s becomes constant and it means when r_{12} increases, K_{ET} value approaches a constant value. This is shown in Fig. 6.

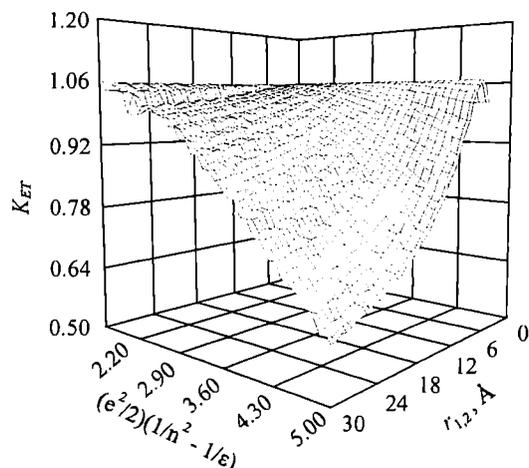


Fig. 6. Electron transfer process equilibrium constant K_{ET} versus the properties of solvent $[(e^2/2)(1/n^2 - 1/\epsilon)]$ and distance separating the donor and acceptor molecules (r_{12})

From the surface simulated in Fig. 6 it is also easy to conclude that K_{ET} value decreases when the distance

separating donor and acceptor molecules increases and approaches the constant value for very high r_{12} .

The experimental confirmation of the above mentioned theoretical consideration comes from the study of a series acceptor-spacer-donor systems (Rose bengal-flexible spacer-*p*-dimethylaminobenzoate/Rose bengal). The structures and the examples of stress-free molecules of the studied photoinitiators are shown in Scheme B.

The real-time kinetic curves recorded during an argon-ion laser initiated polymerization of TMPTA in the presence of the tested Rose bengal based initiators are depicted in Fig. 7.

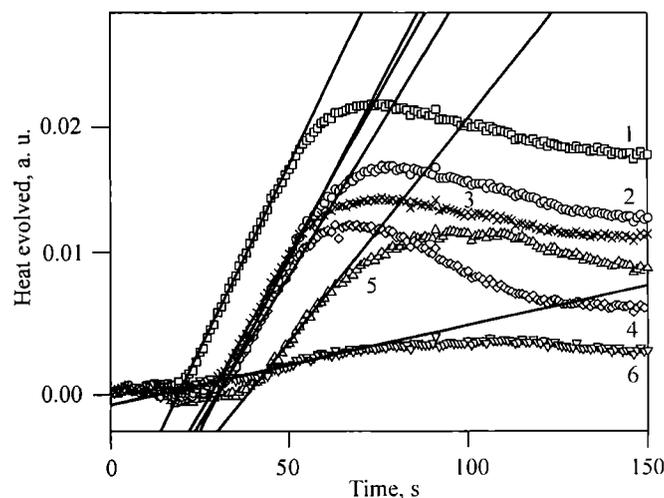
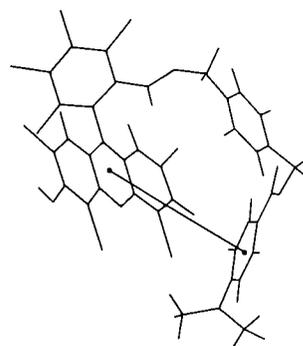
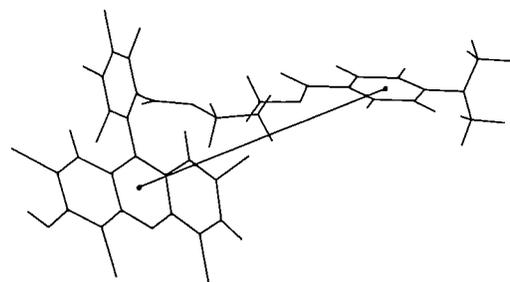
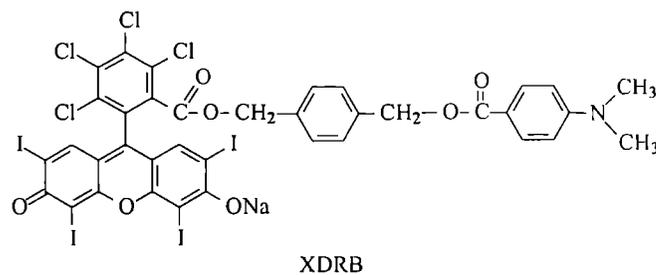
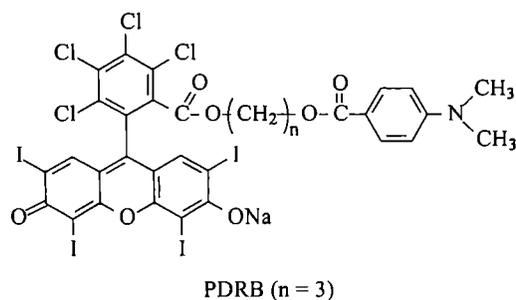


Fig. 7. The family of kinetic curves recorded during an argon-ion laser initiated polymerization of TMPTA in the presence of: 1 — Rose bengal C2' propyl ester ($c = 2 \cdot 10^{-4}$ M) and ethyl 4-*N,N*-(dimethylamino)benzoate ($c = 10^{-3}$ M), 2 — DDRB ($c = 10^{-3}$ M), 3 — HDRB ($c = 10^{-3}$ M), 4 — BDRB ($c = 10^{-3}$ M), 5 — PDRB ($c = 10^{-3}$ M), 6 — XDRB ($c = 10^{-3}$ M)



Scheme B

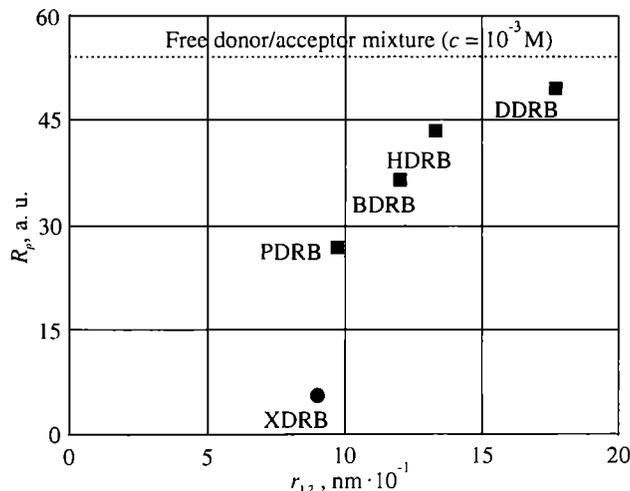


Fig. 8. Relationship between the rate of polymerization (R_p) and the distance separating the donor and acceptor moieties (r_{12}) (calculated for stress-free molecules using AM1 method) for tested A-S-D photoinitiators

Figure 8 summarizes the data presented in Figs. 6 and 7. Several important conclusions can result from the measurements. Firstly, the rate of polymerization increases when the length of the spacer separating donor and acceptor molecules increases. Secondly, the rate of polymerization initiated by the mixture of donor and acceptor, at the same concentration as for donor-acceptor bridged system, is much higher.

A possible explanation of the observed phenomenon is the idea of the back electron transfer process. Since the spacer in the A-S-D system does not allow to separate the geminate radical ions (or change enough the geometry in order to allow to occur the proton transfer process), the back electron transfer process starts to dominate in the reactions. Equation (7) can be written in simpler form as:

$$R_p = -\frac{d[M]}{dt} = k_p[M] \sqrt{\frac{I_a K_d k_3}{k_t}} \sqrt{K_{ET}} \quad (14)$$

For the given substrates of the photochemical reaction and for $I_a = \text{const.}$, one can assume that $k_3 = \text{const.}$, i.e. $(I_a K_d k_3 / k_t)^{0.5} = \text{const.}$ After these assumptions, it is obvious that equation (14) shows that for an initiating pair, for which the back electron transfer process may dominate the overall rate of polymerization, the final rate of polymerization is proportional to the square of the equilibrium constant K_{ET} . The comparison of theoretical consideration (Fig. 6) and experimental results (Fig. 8) shows that there is no correlation between theoretically predicted behavior and the observed experimental results. This finding allows to conclude that the back electron transfer process probably does not control the properties of the tested in our experiment A-S-D photoinitiating systems, or that the structures of the stress free A-S-D molecules are quite different from those predicted

by AM1 calculations (presumably for $n = 4, 6$ and 12 the structures are more folded).

Certain information about the processes that occur after an excitation of A-S-D type of photoinitiators comes from the analysis of the results obtained with the use of nanosecond laser photolysis. Figure 9 shows the transient absorption spectra of HDRB and PDRB in MeCN solution.

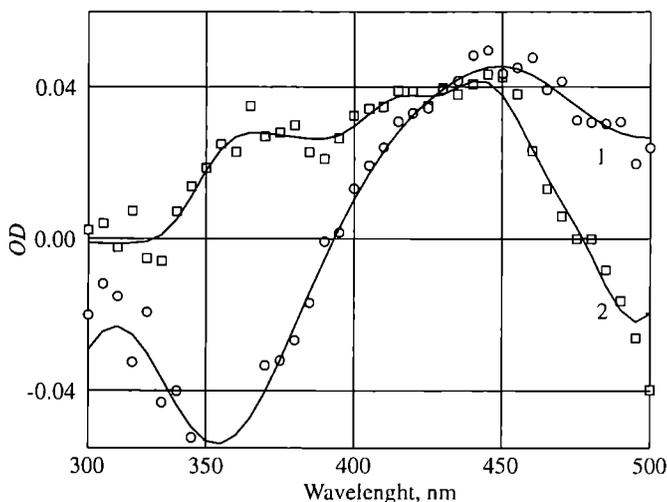


Fig. 9. Transient absorption spectra recorded $6 \mu\text{s}$ after the laser flash for selected A-S-D photoinitiating systems in MeCN; 1 — PDRB, 2 — HDRB

On the basis of the transient spectroscopy of Rose bengal derivatives [44, 45] one can conclude that for PDRB at 440 nm, both the triplet and the semi reduced RB ($\text{RB}^{\cdot 2-}$, appearing at 420 nm) issued from one electron reduction of Rose bengal molecule, are responsible for the absorption. On the other hand, when HDRB acts as an electron donor, Rose bengal radical anion ($\text{RB}^{\cdot 2-}$) is also observed, but a new product absorbing at 375 nm appears. This absorption transient can be assigned to a different Rose bengal radical anion, i.e. protonated, negatively charged radical anion ($\text{RB}^{\cdot -}$) obtained after the protonation of $\text{RB}^{\cdot 2-}$ by the deprotonation of tertiary aromatic amine yielding α -amino radical [46]. This radical initiates the polymerization. This observation let conclude that in the case of PDRB there is essentially no α -amino radical formation at the concentration detectable by the transient spectroscopy. The low concentration of this radical causes a sharp decrease in photoinitiation ability of PDRB in comparison with HDRB. These findings suggest that for a long alkyl chain separating acceptor and donor moieties of initiator certain folding of this chain may occur, making both electron and proton transfer processes possible. For a short chain only electron is transferred, however, the structure of the resulting radical ion pair does not allow proton transfer to occur.