PERKIN 2

Development of new dyeing photoinitiators for free radical polymerization based on the 1*H*-pyrazolo[3,4-*b*]quinoxaline skeleton. Part 2†

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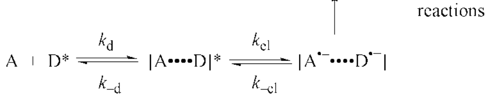
Several dyes containing a pyrazoloquinoxaline moiety have been synthesized and evaluated as novel photoinitiators for free radical polymerization induced with the argon-ion laser. The kinetic study of photoinitiated polymerization, performed for viscous monomeric formulations with the use of the most effective dye–*N*-phenylglycine derivative photoinitiating systems has shown unusual kinetic properties. The experimental data show the presence of "Marcus inverted region"-like kinetic behavior. Analysis of possible reasons for this specific feature suggests that one of the processes that may be responsible for such a specific property is the back electron transfer process. Study of photoinitiated polymerization has shown that there is a linear relationship between the rate of polymerization and the square root of the efficiency of singlet oxygen formation. This finding clearly indicates that the electron transfer process between the tested dyes and electron donors occurs *via* a triplet state. The observed relationship is also in good agreement with the general equation describing the rate of polymerization, which is (among other parameters) a function of the square root of the quantum yield of triplet state formation. In the paper, it is also shown that the structure of the dye has a strong effect on its polymerization photoinitiation ability. The dyes tested were prepared in such a way as to, (i) restrict the rotational freedom of selected parts of the molecule and (ii) increase the quantum yield of the triplet state formation. The latter was achieved by introducing to the molecule a heavy atom (ZCl2, CI) or different heavy atoms (CICl2).

Introduction

An area of intense interest in organic photochemistry involves the use of visible or ultraviolet light to initiate photopolymerization. This process is traditionally initiated by the direct photolysis of a precursor to provide free radicals by a bond photodecomposition. Panchromatic sensitization of vinyl polymerization requires the presence of a suitable dye as a primary absorber. For such a case, the photophysical energy transfer between the dye excited state and another chromophore, which yields free radicals, is generally disfavored. As an alternative other processes avoiding a typical energy restriction should be considered. The photoinduced intermolecular electron transfer which is a nonclassical, endothermic energy transfer process, represents such an alternative. This process involves the use of light to initiate electron transfer from a donor to an acceptor molecule.

Scheme 1 is a good starting point to begin the analysis of the process. Here k_d is the rate constant representing the rate of diffusive encounters between reactants, k_{-d} denotes the rate of separation of the reactants after collision, k_{el} is the first order rate constant of electron transfer. The reverse step is designated by the rate constant k_{-el} and finally k_r denotes the rate of return electron transfer.



Scheme 1

Translating these to the sensitization of free radical polymerization one should anticipate that two types of sensitization should occur.

1) *Photoreducible dye sensitization.* Oster first reported this type of photoinitiating process in 1954.[1] He identified several groups of effective dyes, which are photoreduced during photochemical reaction in the presence of suitable reductants. The tested dyes included the classes of acridine, xanthene and thiazine dyes.

2) *Photooxidizable dye sensitization.* This sensitization requires molecules that are strong electron acceptors in the ground state. Onium salts of xanthene dyes prepared by Linden and Neckers[2–4] undergo photochemical reaction, which is a pure electron transfer process. Systems comprised of onium salts, reducing agents and sensitizer, for example dye–amine–onium salts, are excellent photoinitiators for the polymerization of acrylates.[5–8]

Considering the interaction between the dye and an electron donor in the ground state and after an electron transfer process, dyeing photoinitiators can be classified in three different groups:

1) *Photoinitiating donor–acceptor pair with electrostatic interaction in the ground state (ground state-ion pair).* This type of photoinitiating system was first described by Schuster[9,10] and co-workers. This work was related to the photochemistry of cyanine borates and led to the preparation of color-tunable, operating in the visible region, and commercial photoinitiators.[11]

2) *Photoinitiating donor–acceptor pair without electrostatic interaction in the ground state and after an electron transfer.* The first system of this type described in the literature employed as electron acceptor a neutral derivative of Rose Bengal, which

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† For Part 1 see ref. 24.

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was first decarboxylated and then acetylated (RBAX), and triphenyl-*n*-butyl borate as electron donor.[12] Irradiation of this system also led to the formation of a free alkyl radical, which was capable of initiating polymerization. The photochemistry of the xanthene dye–triphenyl-*n*-butyl borate pair was clarified using novel xanthene dyes based on a 3-hydroxy-6-fluorone skeleton.[13–17]

3) *Photoinitiating donor–acceptor pair, neutral in the ground state and charged after an electron transfer (radical-ion pair)*. The photoreduction of 5,7-diiodo-3-butoxy-6-fluorone (DIBF) in the presence of *N*,*N*-dimethyl-2,6-diisopropylaniline is an example illustrating the properties of this specific dyeing photoinitiating system.[16] According to Neckers[15] the triplet state of the xanthene dyes, based on the 3-hydroxy-6-fluorone skeleton, is quenched by several electron donors, mainly aromatic amines or tertiary aliphatic amines. The process gives the dye anion radical,[18–21] which promotes a rapid proton transfer from the carbon α to the nitrogen of the amino cation radical, giving the neutral dye radical and the amine radical.[22]

In our earlier papers[23,24] we presented a new class of free radical photoinitiators based on pyrazolone azomethine dyes (PAM). Several dyes containing the azomethine moiety have been synthesized and evaluated as photoinitiators for free radical polymerization induced with the argon-ion or He–Ne lasers. Two ways of dye modification were applied in the study. The first was a change in the type of the substituent in the pyrazolone skeleton and the second elimination or limitation of the rotation of the phenyl group. It was also shown that one observes a dramatic increase in the photoinitiation efficiency and an increase in the quantum yield of the bleaching process when the twisting motion of the C=N bond is severely hindered by coplanarization of the azomethine residue with other parts of the dye. This stabilizes the molecule in its excited state and causes a red shift of the absorption spectra maximum allowing the initiation of polymerization using both argon-ion and He–Ne lasers.

In this paper, it is our intention to present studies on the third type of photoinitiation photoredox pairs, composed of newly prepared pyrazoloquinoxaline dyes (PQ) as primary absorbers and a series of *N*-phenylglycine derivatives as electron donors. It is also our intention to illustrate the relationship between the structures of PQ dyes and their photoinitiation ability, especially the kinetic study illustrating specific properties observed during the photoinitiated free radical polymerization with the use of the tested dyes.

Experimental

Substrates used for the preparation of dyes were purchased from Fluka, Merck or Aldrich. 2-Ethyl-2-(hydroxymethyl)propane-1,3-diol triacrylate (TMPTA), 1-methyl-2-pyrrolidinone (MP) and *N*-phenylglycine (NPG) were purchased from Aldrich. The properties of the series of *N*-phenylglycine derivatives used as electron donors were described in our earlier paper.[25]

Dyes: synthesis

4-(4-Diethylaminophenylimino)-5-methyl-2-phenyl-3,4-dihydro-2*H*-pyrazol-3-one was prepared using a previously described method.[26] 5-Methyl-2-phenyl-3,4-dihydro-2*H*-pyrazole-3,4-dione and 5-methyl-2-(4-iodophenyl)-3,4-dihydro-2*H*-pyrazole-3,4-dione were prepared using the method described by Tacconi *et al.*,[27] and 4-(2-aminophenylimino)-5-methyl-2-phenyl-3,4-dihydro-2*H*-pyrazol-3-one was prepared based on the procedure given by Ohle and Melkonian.[28] The final 1*H*-pyrazolo[3,4-*b*]quinoxalines (PQ) were synthesized according to the method given by Metwally *et al.*[29] The crude dyes were purified by column chromatography and finally by preparative thin layer chromatography. The final products were identified by ^{1}H NMR, ^{13}C NMR and 2D *z*-gradient selected ^{1}H, ^{15}N HMBC spectroscopy. The spectra obtained were evidence that the dyes were of the desired structures.

Absorption spectra were obtained using a Varian Cary 3E spectrophotometer. Fluorescence spectra were recorded using a Hitachi F-4500 spectrofluorimeter. Absorption spectra were recorded in ethyl acetate solution. Both fluorescence and phosphorescence spectra were recorded in 2-methyltetrahydrofuran solutions.

The kinetics of free radical polymerization were studied using a polymerization solution composed of 1 mL of MP and 9 mL of TMPTA. Dye concentration was varied from 1×10^{-3} to 5×10^{-3} M; concentrations of NPGs were also varied from 0.05 to 0.1 M; the polymerizing mixture was not deareated.

The kinetics of 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.[30] A temperature sensor, a semiconducting diode immersed in a 3 mm thick layer (about 290 mg) of cured sample, was used for detection of the heat flow. Amplified signals were transferred with an analog/digital data acquisition board to a computer. In order to avoid the possibility of non-isothermal reaction conditions, for further discussion only the data for the initial time of polymerization were used for the calculation of the polymerization rates.

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 reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical Cypress System Model CS-1090 was used for measurements, and an Ag–AgCl electrode served as a reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate.

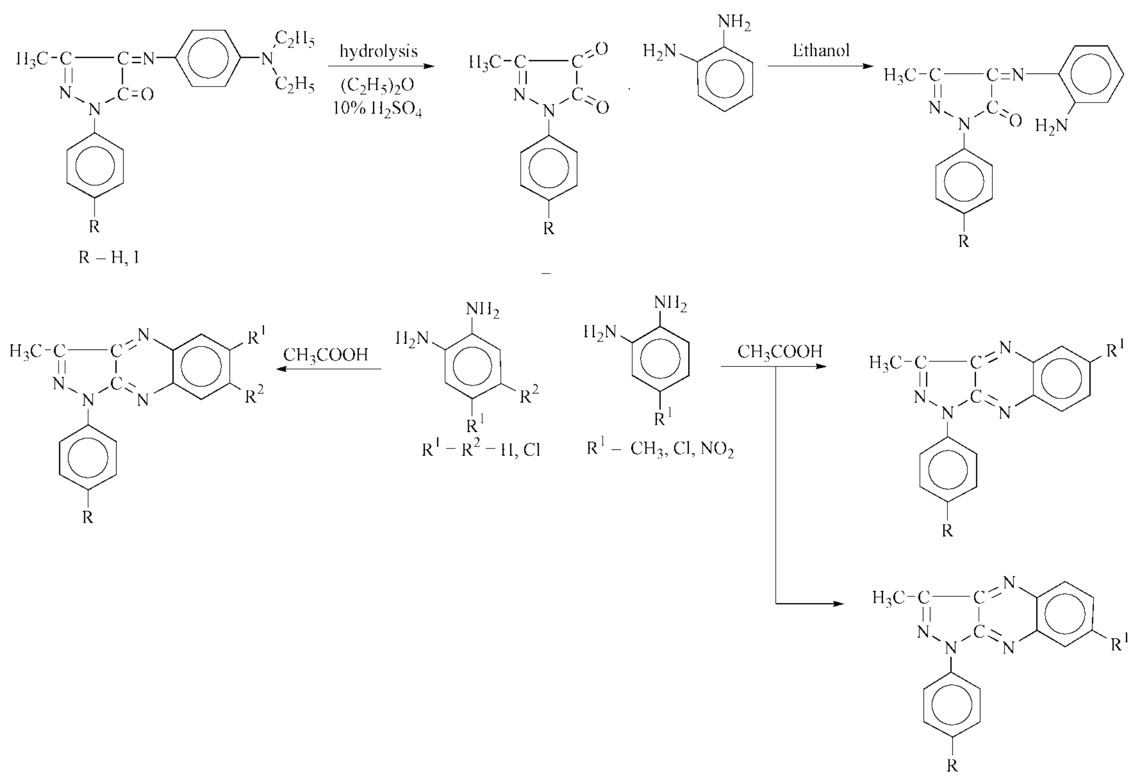
The quantum yields of singlet oxygen formation from pyrazoloquinoxaline dyes were obtained using the actinometric method described by Schaap *et al.*[31] For the quantum yield measurements the procedure was as follows: 3.45 mg of 2,3-diphenyl-1,4-dioxine was added to a 2 mL aliquot of a $CHCl_3$ solution of the dye that was present at a concentration that ensured that all incident light was absorbed. The solution (2 mL) was irradiated with an Omnichrome argon ion laser Model 543-500 MA with the intensity measured by a Coherent power meter Fieldmaster. The solution was agitated by a continuous flow of oxygen. The formation of the photooxygenated product (ethylene glycol dibenzoate) was followed by GLC analysis of the solution at 225 °C. The quantum yield of singlet oxygen formation, $\Phi(^1O_2)$, was calculated from the ratio of the rate of formation of ethylene glycol dibenzoate for the dye under study compared to the rate for polymer-based Rose Bengal,[32] using the known quantum yield for poly-(RB) ($\Phi(^1O_2) = 0.76$).[33] 2,3-Diphenyl-1,4-dioxine was prepared according to the method of Summerbell and Berger.[34]

Results and discussion

Analysis of the kinetic scheme for photoinduced polymerization *via* an intermolecular electron transfer process has shown[25,30] that for a negligible efficiency of the absorbing chromophore bleaching process (for very low quantum yield of the bleaching process, $2I_A\Phi_Tk_{el} \geqslant k_{bl}[D^\bullet \cdots A^\bullet]$), the following eqn. (1) can describe the rate of polymerization of monomer M in viscous media:

$$R_p = k_p[M]\left[\frac{2I_A\Phi_Tk_{el} - k_{bl}[D^\bullet \cdots A^\bullet H]}{k_t}\right]^{1/2} \cong k_p[M]\sqrt{\frac{2I_A\Phi_Tk_{el}}{k_t}} \quad (1)$$

Here I_A is intensity of absorbed light, Φ_T is the quantum yield of triplet state formation. The rate of free radical cross-



Scheme 2

coupling, yielding the dye bleaching products is denoted by k_{bl}, k_p and k_t denote the rate constants of polymerization and chain termination steps respectively and k_{el} is the first-order rate constant of electron transfer described by the Eyring eqn. (2).

$$k_{el} = \chi Z\exp(-\Delta G^{\ddagger}/RT) \qquad (2)$$

Here Z is a frequency factor, χ is the transmission coefficient, and $\Delta G^{\ddagger}$ is the free energy of activation given by the Marcus[35] equation (3) for neutral reactants, where λ is the reorganization

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ}_{el}}{\lambda}\right)^2 \qquad (3)$$

energy necessary to reach the transition states both of excited molecules and of solvent molecules, and ΔG° is expressed by the Rehm–Weller equation (4).[36]

$$\Delta G^{\circ}_{el} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - Ze^2/\varepsilon a - E_{oo} \qquad (4)$$

where $E_{ox}(D/D^{\bullet+})$ is the oxidation potential of the electron donor, $E_{red}(A^{\bullet-}/A)$ is the reduction potential of the electron acceptor, E_{oo} is the excited state energy, and $Ze^2/\varepsilon a$ is the Coulombic energy, which is considered negligible with respect to the overall magnitude of the ΔG in the present system.

Summarizing the above analysis, one can conclude that in order to compare the rates of the free radical initiated polymerization for different photoinitiators, several principal requirements should be considered. First, the rate of photoinitiated free radical polymerization depends on the yield of triplet state formation. Second, it depends on both the thermodynamic (ΔG°) and kinetic (λ) aspects of the electron transfer process, and third, it may depend on the reactivity of free radicals resulting from the electron transfer process.[37]

The azomethine dyes are so-called branched dyes. Their fluorescence quantum yields are very small. The short lifetime of the singlet excited state and low quantum yield of intersystem crossing[38] of dyes are probably due to the high freedom of rotation around bonds linking each part of the molecule with the pyrazolone skeleton. 1*H*-Pyrazolo[3,4-*b*]quinoxalines (PQ) have a more rigid structure and were prepared by the sequence of reactions described in Scheme 2.

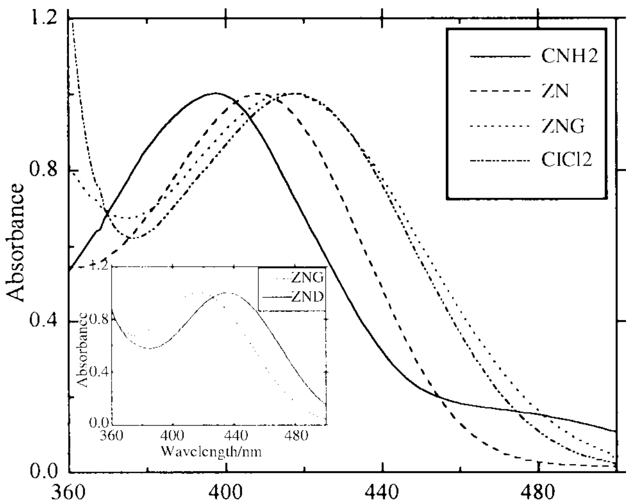


Fig. 1 The electronic absorption spectra for selected dyes tested in ethyl acetate solution. Type of dye shown in the legend. Inset: Electronic absorption spectra for two, marked in the legend, selected dye isomers.

As was published earlier, two different products can be formed, during the condensation of 4-substituted *o*-phenylenediamines and 5-methyl-2-phenyl-3,4-dihydro-2*H*-pyrazole-3,4-dione.[39] The spectroscopic properties of the isomers obtained, as is shown in Fig. 1, differ appreciably.

Fig. 1 shows the electronic absorption spectra of dyes tested, Fig. 2 presents the emission properties of selected dyes and Table 1 summarizes the structures, spectroscopic and electrochemical data. All dyes studied exhibit weak fluorescence characterized by a distinct Stokes shift (about 5000–6000 cm^{-1}). This behavior indicates that the emitting states of the dyes are charge-transfer in character. On the other hand, the calculated dyes' ground state dipole moments show low values (with the exception of ZNG and ZND) and this demonstrates that the

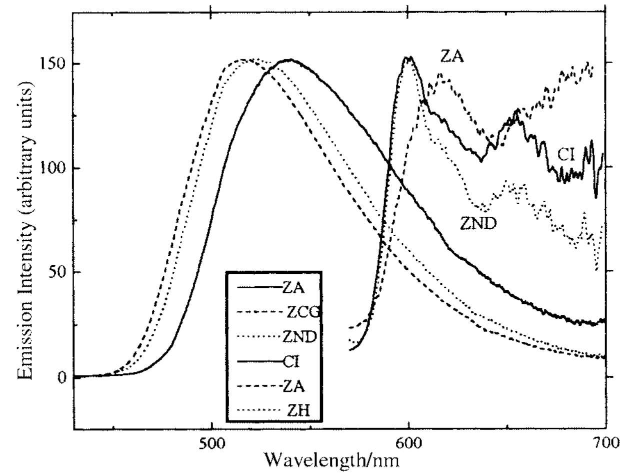


Fig. 2 Steady-state emission spectra of selected dyes tested. Spectra recorded in 2-methyltetrahydrofuran solution. Type of dye marked in legend.

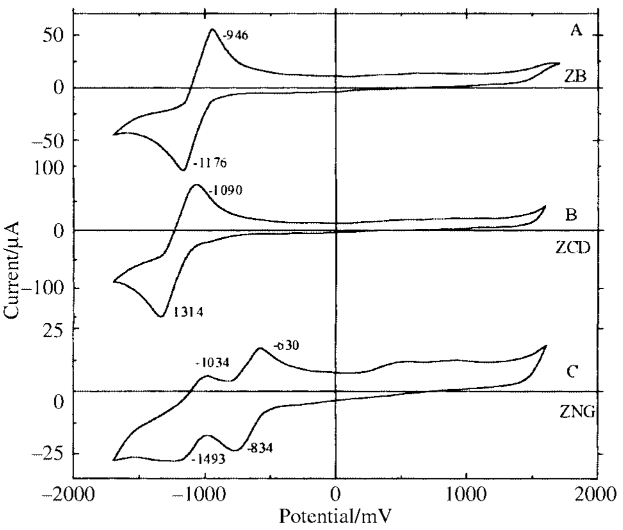
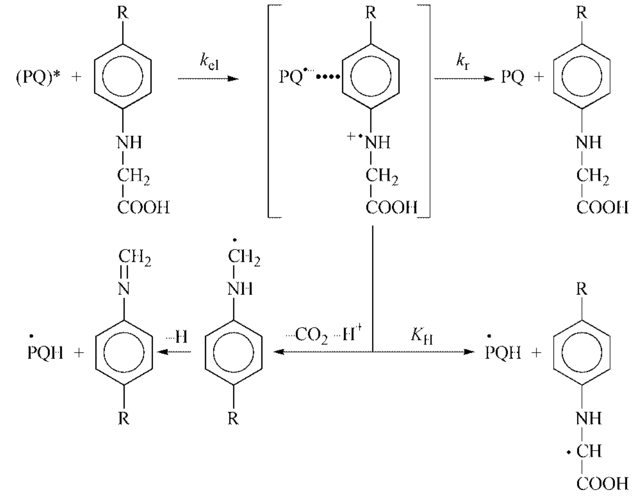


Fig. 3 Cyclovoltammetric curves recorded for selected chromophores. A, ZB; B, ZCD; C, ZNG.

dyes are essentially non-polar in their ground state. Fig. 2 also shows the steady-state phosphorescence spectra of studied dyes. From the phosphorescence spectra one can calculate the energy of the triplet state (E^{T}_{00}). The triplet state energy, as is summarized in Table 1, ranges from 190 to 200 kJ mol^{-1} (1.97 and 2.07 eV). The electrode potentials at which a compound undergoes reduction were located by cyclic voltammetry. The cyclic voltammograms for studied dyes show only one electron reversible reduction (see Fig. 3). The values of reduction potentials for the isomers tested are, within experimental error, identical. The two peaks observed for ZNG and ZND suggest that these dyes present a two-step reversible reduction.

As electron donors for the photoinitiated free radical polymerization *N*-phenylglycine derivatives (NPGs) were used. The free energy change for the electron transfer ($\Delta G°$) between a dye and *N*-phenylglycine was calculated from the Rehm–Weller equation [eqn. (4)]. For the calculation of $\Delta G°$ the reduction potentials of tested dyes (see Table 1), oxidation potentials of applied NPGs[25,40] and the measured triplet state energies of studied dyes (see Table 1) were used. The calculations showed that on the whole the free energy change for the electron transfer ($\Delta G°$) is negative. This means that the photoinduced intermolecular electron transfer for the studied bimolecular system is thermodynamically allowed. The positive values of $\Delta G°$ (photoinduced electron transfer thermodynamically forbidden) are observed only for the combination of ZH, ZCG, ZCD, ZND with *p*-nitro-*N*-phenylglycine, as well as for the combination of ZCG, ZCD with *p*-cyano-*N*-phenylglycine. It is also worth emphasizing that for the isomers the calculated values of $\Delta G°$, within experimental error, have very close values.

The mechanism of radical chain initiation by the PQ–NPGs system can be roughly predicted based on the photochemistry of the benzophenone–sulfur-containing amino acids system described by Marciniak, Bobrowski and Hug.[41] According to this mechanism, electron transfer is followed by (1) the diffusion apart of the charge transfer (CT) complex, (2) intramolecular proton transfer within the CT complex. In polar solvents the first process is more efficient and leads to decarboxylation, and this yields a radical centered on the α-carbon with respect to the carboxylic group. In less polar and viscous solvents there is no separation of the radical-ions and an addition-type secondary reaction is more likely, *e.g.* proton transfer, to produce a free radical centered on the α-carbon with respect to the carboxylate group, takes place. In this case, no decarboxylation of the amino acid is observed. Based on this and earlier-studied properties of *N*-phenylglycine,[42] one can derive Scheme 3 describing the photochemical properties of the PQ–NPGs system.



Scheme 3

Discussion is required concerning the path of free radical formation, which is decisive in the entire process, *e.g.* what type of free radical is formed after PET. The quantum yield of *N*-phenylglycine photooxidized decarboxylation, according to Nishimoto[42a] varies with the relative permittivity, ε, of the solvent. In our study monomers in the solvent (formulation of TMPTA–MP, 9 : 1) possess a relative permittivity of about 13. At this value of ε the quantum yield of *N*-phenylglycine decarboxylation varies in the range of 7–8%. However, two aspects of the tested system are worthy of attention. The first is that Nishimoto's measurements were made in non-viscous solvents (viscosity below or about 1 cP).‡ In our experiments the viscosity of polymerizing mixture was about 70 cP. Taking this into account, one can easily estimate that the rate of radical ion pair separation for the tested monomer formulation is at least two orders of magnitude lower than one estimated for non-viscous solvents. The second is the observation that the decarboxylation process requires radical ion pair separation.[41] The quantum yield of radical ion separation (Φ_{sep}) is determined by the competition between return electron transfer and separation (k_{sep}) within the geminate radical-ion [eqn. (5)].

$$\Phi_{sep} = k_{sep}/(k_{sep} + k_{-et}) \qquad (5)$$

Since for the geminate radical ion pair, the rate of back electron transfer (k_{-et}) is not viscosity dependent, it is obvious that

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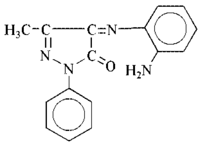
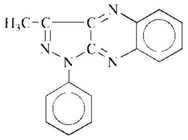
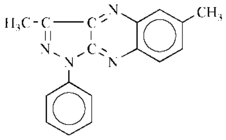
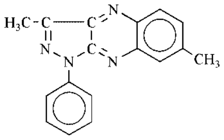
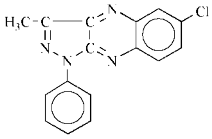
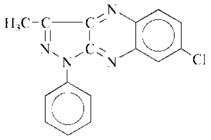
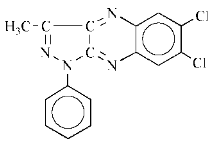
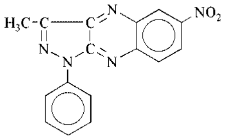
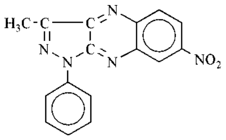
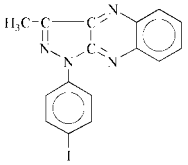
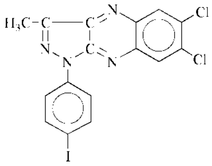
‡ cP = mPa s.

Table 1 Spectroscopic and electrochemical properties of tested dyes

No.	Structure	$\lambda^{\mathrm{abs}}_{\mathrm{max}}$/nm	$\lambda^{\mathrm{Fl}}_{\mathrm{max}}$/nm	Φ_{Fl}	$E^{\mathrm{T}}_{\mathrm{oo}}$/kJ mol^{-1}	E_{red}/mV	$\mu_{\mathrm{calc.}}$/D
CNH2		389	465	<0.0001	—	−1198	—
ZH		409	517	0.061	199	−1344	1.33
ZCG		413	514	0.088	198	−1324	1.73
ZCD		404	511	0.089	198	−1314	1.76
ZA		416	534	0.024	197	−1154	1.24
ZB		408	534	0.024	193	−1176	0.32
ZCl2		417	529	0.011	187	−1040	1.32
ZNG		417	560	0.0085	196	−834 −1493	5.65
ZND		435	525	0.0059	191	−752 −1504	4.32
CI		408	522	0.021	199	−1172	—
CICl2		418	539	0.036	196	−926	—

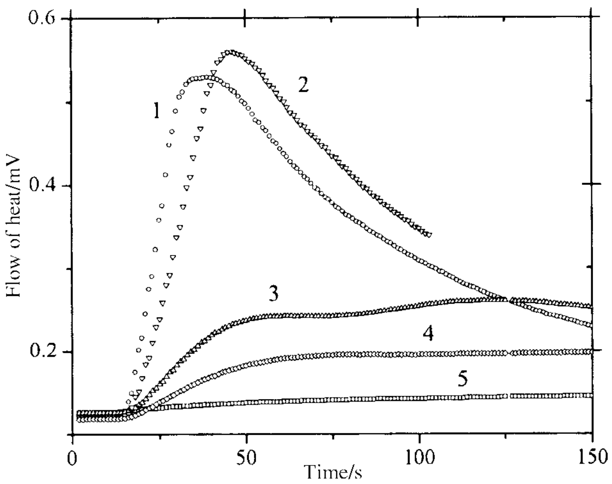


Fig. 4 Photopolymerization kinetic curves recorded for examples of novel tested dyes; electron donor: *N*-phenylglycine (0.1 M), monomer formulation: of 1 mL of MP and 9 mL of TMPTA. Photoinitiating dyes: (1) CICl2, (2) CI, (3) ZB, (4) ZH, (5) CNH2.

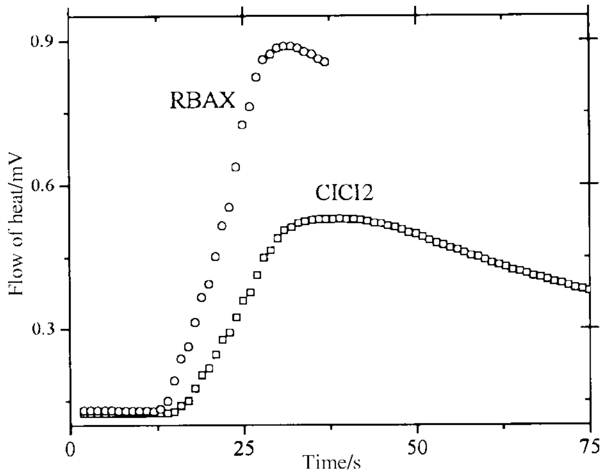


Fig. 5 Comparison between the photoinitiation ability of CICl2–*N*-phenylglycine and RBAX–*N*-phenylglycine photoinitiation systems.

a decrease of the rate of radical ion pair separation decreases the quantum yield of radical ion pair separation. The simulation indicates that the decrease of the rate constant of radical ion pair separation by two orders of magnitude causes a decrease of Φ_{sep} of about one order of magnitude. In other words, for the system described in this paper, the quantum yield of decarboxylation is about 10 times lower in comparison to that observed for non-viscous solvents. Therefore the path of free radical formation that involves a radical cation decarboxylation process (less than 1%) can be negligible.

The influence of the dye structure on their polymerization photoinitiation ability is very significant. As Fig. 4 shows, the best photoinitiation capability is presented by CI and CICl2. Their sensitivity is comparable, as is shown in Fig. 5, to the sensitivity of the Rose Bengal based initiation system described by Neckers.[12]

The dyes tested were prepared in such a way as to (i) restrict the rotational freedom of selected parts of molecule and, (ii) increase the quantum yield of triplet state formation. The latter was achieved by introducing to the molecule a heavy atom (ZCl2, CI) or different heavy atoms (CICl2). It is apparent from the inspection of the data presented in Fig. 4 that there is an observable significant heavy atom effect on the photoinitiation ability of the tested dyes. The relative efficiency of the photoinitiation ability of all dyes studied along with their quantum yields of singlet oxygen formation are summarized in Table 2.

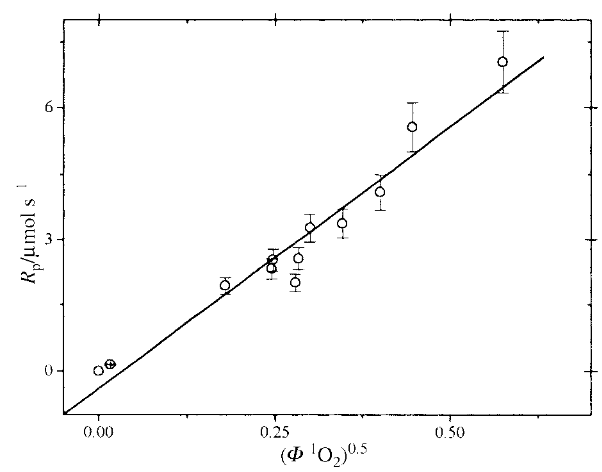


Fig. 6 Relationship between the photoinitiated polymerization rate and the square root of the quantum yields of singlet oxygen formation for dyes tested.

On the basis of the data listed in Table 2, it appears that there is a relationship between the rate of photoinitiated polymerization and the quantum yield of singlet oxygen formation. This is shown in Fig. 6.

It is clear from inspection of the data presented in Fig. 6 that there is a linear relationship between the rate of polymerization and the square root of the efficiency of singlet oxygen formation. This finding clearly indicates that the electron transfer process between the PQs and electron donor occurs *via* the triplet state of the tested dyes. The observed relationship shown in Fig. 6 is also in good agreement with a general equation describing the rate of polymerization, which is (among other parameters), a function of the square root of the quantum yield of triplet state formation [see eqn. (1)]. It is also important to emphasize that the precursor dye (CNH2, open, non-cyclized structure) displays the lowest efficiency of both: the photoinitiation ability as well as the efficiency of singlet oxygen formation. This finding apparently shows that the elimination of the rotation of the C=N bond, by the coplanarization of the azomethine residue with other parts of the dye, eliminates an effective channel of the dye excited state deactivation, *e.g.* eliminates *trans–cis* isomerization of the azomethine bond. This type of molecule modification increases the photoinitiation ability by about two orders of magnitude. A similar effect was observed for other, different types of azomethine dyes described earlier.[24] The introduction of iodine as a heavy atom additionally increases the photoinitiation efficiency by about 8 times, and of both iodine and chlorine atoms by about 12 times. It is also worth emphasising that the introduction of chlorine atoms into the molecule increases only slightly the quantum yield of singlet oxygen formation and photoinitiation ability. The above described behaviors are classical and similar to the properties observed for well-known xanthenes.[43]

One more interesting feature of the tested dyes is worthy of attention. Analyzing the data summarized in Tables 1 and 2, one can find that the quantum yield of singlet oxygen formation (it might be treated as an indirect method of measurement of the quantum yield of triplet state formation), differs for different dye isomers. This observed phenomenon is relatively common[44] and its explanation can be found in photochemistry textbooks.[45]

The efficiency of polymerization photoinitiation strongly depends on the type of electron donor. Fig. 7 presents kinetic curves recorded for CICl2 in the presence of various *N*-phenylglycine derivatives (which are present in the tested systems in their zwitterionic form). On the basis of these experiments, one can conclude that the rate of photoinitiation might be a function of the rate of the primary process, *e.g.* the

Table 2 Quantum yields of singlet oxygen formation and rates of photoinitiated polymerization for tested dyes

Dye	CNH2	ZH	ZCG	ZCD	ZA	ZB	ZCl2	ZNG	ZND	CI	CICl2
${}^1\Phi_{O_2}$	0.00025	0.078	0.060	0.160	0.090	0.120	0.061	0.080	0.032	0.199	0.311
R_p/µmol s^{-1}	0.024	4.014	5.40	16.73	10.73	11.39	6.37	6.58	3.72	30.93	49.58

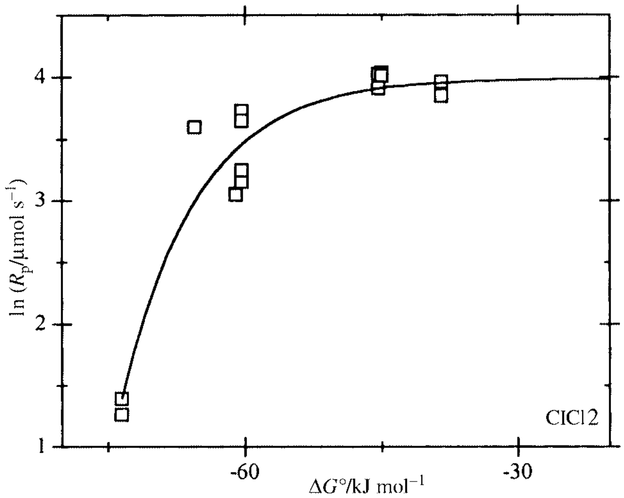


Fig. 7 Relationship between the rate of polymerization and the free energy change of the electron transfer process for ClCl2–NPGs photoredox pairs.

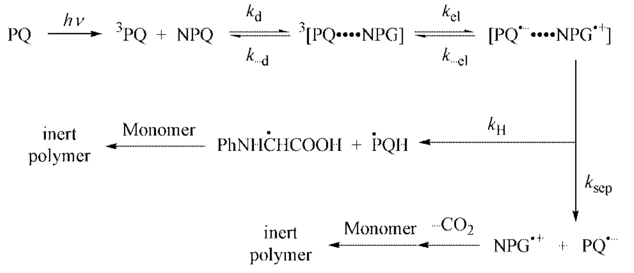
rate of electron transfer. Another possibility is that the photoinitiation ability of a photoredox pair is a function of the reactivity of the free radicals obtained as a result of the secondary processes that follow an electron transfer.

The verification of the first case is possible after plotting the rate of polymerization *versus* the free energy change for the electron transfer process [ΔG°, see eqn. (4)]. This type of relationship is shown in Fig. 7. It is apparent from inspection of the relationship presented in Fig. 7 that the plot exhibits "Marcus inverted region"-like properties. This behavior is very improbable for the tested system; therefore, one should consider another explanation, *e.g.* the effect of the free radicals' reactivity.

The kinetics of photoinitiated polymerization can be described by the following simplified eqn. (6), where In denotes

$$\mathrm{In} \xrightarrow{h\nu} \mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{RM}^{\bullet} + n\mathrm{M} \xrightarrow{k_p} \mathrm{RM}_{n+1} \xrightarrow{k_t} \mathrm{RM}_{2(n+1)} \quad (6)$$

a light sensitive initiator, k_i, k_p, and k_t have their conventional meanings. A kinetic scheme describing the photoinitiated polymerization *via* a photoinduced electron transfer process is more complex, because it should include a free radical generation step. For tested systems, Scheme 4 summarizes the processes which may occur during the free radical photoinitiated polymerization *via* the photoinduced electron transfer process.



Scheme 4

From a kinetic point of view a mechanism describing photoinitiated polymerization, which contains all the major processes (not considering the kinetics of an electron transfer process) can be presented as follows in eqns. (7)–(12).

$$\mathrm{PQ} \xrightarrow{h\nu,\ \mathrm{NPG}} \mathrm{PQ^{\bullet}H} + \mathrm{NPG}^{\bullet} \quad I_A\Phi_{\mathrm{NPG}^{\cdot}} \quad (7)$$

$$\mathrm{NPG}^{\bullet} \xrightarrow{k_q} \mathrm{NPG} \quad k_q[\mathrm{NPG}^{\bullet}] \quad (8)$$

$$\mathrm{NPG}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{NPGM}^{\bullet} \quad k_i[\mathrm{M}][\mathrm{NPG}^{\bullet}] \quad (9)$$

$$\mathrm{NPG}^{\bullet} + \mathrm{NPG}^{\bullet} \xrightarrow{k_c} \mathrm{NPG{-}NPG} \quad k_c[\mathrm{NPG}^{\bullet}]^2 \quad (10)$$

$$\mathrm{NPGM}^{\bullet} + n\mathrm{M} \xrightarrow{k_p} \mathrm{NPGM}^{\bullet}_{n+1} \quad k_p[\mathrm{M}][\mathrm{NPGM}^{\bullet}] \quad (11)$$

$$\mathrm{NPGM}^{\bullet}_{n+1} + \mathrm{NPGM}^{\bullet}_{m+1} \xrightarrow{k_t} \mathrm{NPGM}_{n+m+2} \quad k_t[\mathrm{NPGM}^{\bullet}_{n+1}][\mathrm{NPGM}^{\bullet}_{m+1}] \quad (12)$$

The reactivity of free radicals depends on structure; therefore, in the initiation process of the chain only some of the free radicals efficiently participate. For aromatic radicals, one can apply the Hammett equation for the description of the initiation rate constant, k_i, as eqn. (13), and then under a

$$k_i = e^{\rho\sigma} \quad (13)$$

steady-state condition eqn. (14) applies. Thus free radical

$$e^{\rho\sigma}[\mathrm{M}]\,[I_A\Phi_{\mathrm{NPG}^{\cdot}}] = k_t[\mathrm{NPGM}^{\bullet}_{n+1}][\mathrm{NPGM}^{\bullet}_{m+1}] = k_t[\mathrm{NPG}^{\bullet}]^2 \quad (14)$$

concentration is described as in eqn. (15). Under this condition

$$[\mathrm{NPG}^{\bullet}] = (\Phi_{\mathrm{NPG}^{\cdot}})^{0.5}(I_A)^{0.5}[\mathrm{M}]^{0.5}(e^{\rho\sigma})^{0.5}(k_t)^{-0.5} \quad (15)$$

the rate of polymerization is given by eqn. (16), or in

$$R_p = k_p[\mathrm{M}]^{1.5}(\Phi_{\mathrm{NPG}^{\cdot}})^{0.5}(I_A)^{0.5}\,(e^{\rho\sigma})^{0.5}(k_t)^{-0.5} \quad (16)$$

logarithmic form, eqn. (17), where A, the initial time of

$$\ln R_p = \ln A + 0.5\rho\sigma \quad (17)$$

polymerization, is the sum of ln k_p − 0.5 ln k_t + 1.5 ln [M] + 0.5 ln $\Phi_{\mathrm{NPG}^{\cdot}}$ + 0.5 ln I_A. Eqn. (17) clearly shows that the rate of polymerization depends on the reactivity of free radicals yielded after the photoinduced electron transfer process. Fig. 8 illustrates this type of relationship observed for ClCl2–NPGs photoredox pairs.

Surprisingly, there is no linear relationship between the rate of photoinitiated polymerization and the Hammett constants. This specific behavior, as is shown in Fig. 9, is also observed for other tested photoredox pairs (ZND–NPGs).

Typically, a Hammett's non-linear relationship occurs when the mechanism of a process is changing as the type of substituent varies. In our earlier papers it was demonstrated that for *N*-phenylglycine derivatives, used with Rose Bengal derivative RBAX[12] as well as with camphorquinone, a linear relationship between rate of polymerization and Hammett constants is

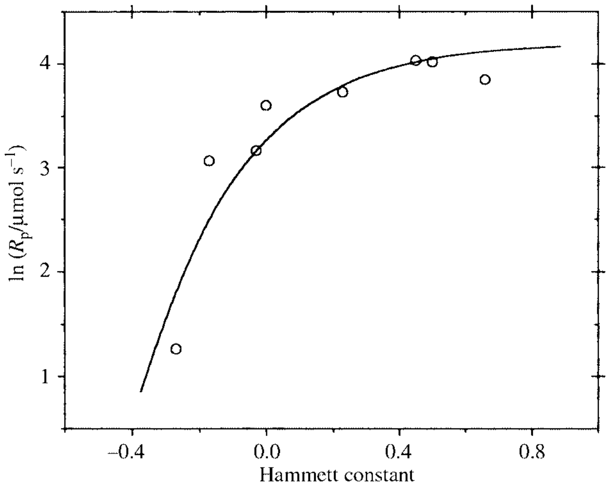


Fig. 8 Relationship between the rate of polymerization and the Hammett's constant of the *N*-phenylglycine derivative for ClCl2–NPGs photoredox pairs.

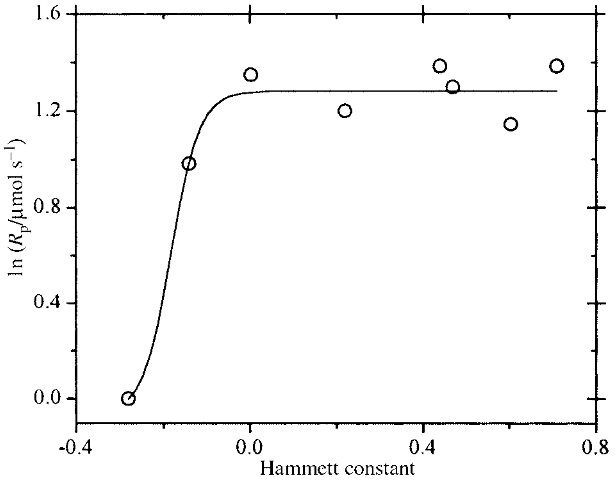


Fig. 9 Relationship between the rate of polymerization and the Hammett's constant of the *N*-phenylglycine derivative for ZND–NPGs photoredox pairs.

observed.[25,40,46] The non-linear Hammett's relationship obtained in this study for the rate of photoinitiated polymerization suggests that the reactivities of the free radicals, obtained as a result of PET, do not affect the final rate of photoinitiated polymerization.

Dealing with the PET process, one should take into consideration the fact that the PET process is the reversible one. The free-radical ion formation yields are determined by the competition between the rates of separation and the back electron transfer. Since for the tested system the yield of radical ion pair separation is negligible, the highly exothermic return electron transfer process might affect the final rate of the forward electron transfer process. Gould and his colleagues have documented that in a very exothermic region, the highly exothermic return electron transfer can cause a marked decrease (*ca.* 2 orders of magnitude) in the electron transfer rates.[47] Also, as a more plausible explanation suitable from the practical point of view, results presented by Marciniak *et al.*[41b,48] have suggested that even a slight change in the solvent (or mixture of solvents) polarity can strongly affect the mode of the radical ion pair decay and that the back electron transfer can only be a mode of decay of the radical ion pair (for example the change from water to a 1 : 1 mixture of MeCN–water). Taking these into consideration, one might suppose that the results presented in this paper could be interpreted in terms of possible influence of the back electron transfer on the rate of photoinitiated polymerization. An illustration of such an interpretation is given in Fig. 10.

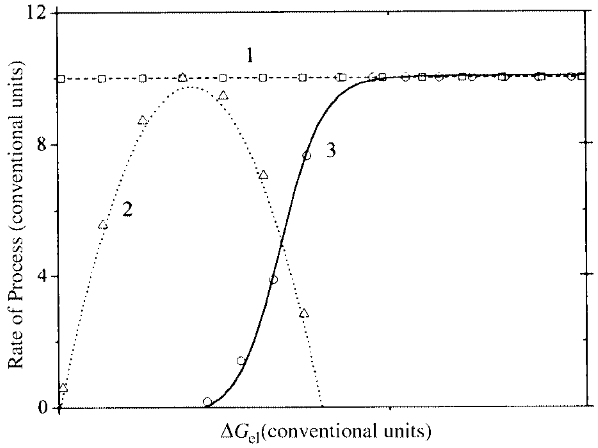


Fig. 10 Conceptual presentation of the effect of the back electron transfer process on forward electron transfer process yielding free radicals able to initiate free radical polymerization. (1) Rate of polymerization controlled by the diffusion, (2) hypothetical, exothermic Marcus parabolic relationship for the back electron transfer process, (3) theoretical curve for rate of polymerization as a function of free energy change affected by the back electron transfer process (obtained after abstraction of curve (2) from linear relationship (1)).

Data in Figs. 8 and 9 show that in the low value free energy change region the rate of photoinitiated polymerization is not dependent on the free energy change. A similar behavior is also observed for positive values of Hammett's constant. This specific feature can be explained by assuming the overall control of the process is by diffusion. In the highly exothermic region the back electron transfer process starts to affect the overall rate of electron transfer to a much greater degree than the diffusion controlled processes. The back electron transfer process decreases the efficiency of the forward electron transfer process and as a result the efficiency of free radical formation is decreased. This causes a significant lowering in the rate of the photoinitiated polymerization. Shown in Fig. 10 is a schematic presentation of the effect of the back electron transfer process on the rate of final photochemical reaction product formation (the rate of polymerization), simulated for the normal Marcus region for this process. It is obvious that a similar relationship can be obtained for processes that occur in a more exothermic region, *e.g.* for the back electron transfer process occurring at the inverted Marcus region.

Presented here is one interpretation of a specific kinetic behavior of a photoinitiating system, composed of a viscous monomeric mixture and a PQ–NPGs initiating system, to explain the presence of the observed "Marcus inverted region" -like kinetic behavior. However, one should mention that a detailed explanation of the mechanism of the process that occurs in this paper, without systematic study using laser flash photolysis techniques, is not possible.

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