Development of new dyeing photoinitiators for free radical polymerization based on 3-methyl-1-phenyl-1H-pentaazacyclopenta[b]naphthalene skeleton III

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Abstract

Two dyes containing pyrazoloquinoxaline moiety have been synthesized and evaluated as the novel photoinitiators for free radical polymerization induced with the argon-ion laser. The kinetic study of photoinitiated polymerization, performed for viscous monomeric formulation with the use of the most effective dye, N-phenylglycine derivatives photoinitiating photoredox pairs, has shown an unusual kinetic property. The experimental data show the presence of the 'Marcus inverted region' like kinetic behavior. The analysis of the possible reasons of this specific feature suggested two possible processes that might be responsible for such a specific property. The first is the back electron transfer process and the second is the rate of the proton transfer that follows the photoinduced electron transfer (PET) process. 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 a way that allows the coplanarization of the molecule skeleton and this causes an increase of the quantum yield of the triplet state formation. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dyeing photoinitiator; Effect of structure; Kinetics of photoinduced polymerization; Effect of the coinitiator

1. Introduction

The research on photopolymerization involves, most commonly, the use of organic photochemistry to initiate polymerization. This process is traditionally initiated by the direct photolysis of a precursor to provide free radicals by bond photodecomposition. However, the panchromatic sensitization of 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 other chromophore that yields free radicals, is generally disfavored. As an alternative, other processes avoiding typical energy restriction should be considered. The photoinduced intermolecular electron (PET) 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. In translating these to sensitization of polymerization one should anticipate that two types of sensitization should occur.
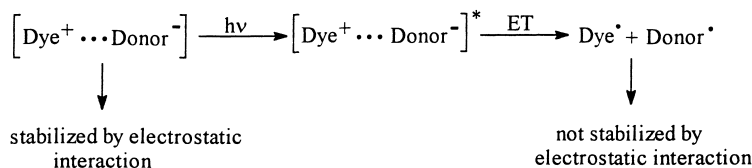
1. Photoreducible dye sensitization reported first by Oster in 1954 [1]. Oster identified several groups of effective dyes, which are photoreduced during a photochemical reaction in the presence of suitable reductants. The dyes included the classes of acridine, xanthene and thiazine dyes.
2. Photooxidiazable dye sensitization. This sensitization requires molecules being in its ground state a strong electron acceptor. Systems comprised of onium salts, reducing agents and sensitizer, for example dye/amine/onium salt, are excellent photoinitiators for the polymerization of acrylates [2–4].

In literature there are many review articles on various aspects of photoinitiated polymerization [5–11]. The key steps of the mechanism are the quenching of the chromophore excited, either singlet or triplet states, by the electron transfer mechanism and various steps that follow the primary process. Marcus [12–14] has provided a simple approach allowing to predict the kinetic of the process, using thermodynamic parameters and spectroscopic measurements. The Marcus theory assumes that the bimolecular electron transfer occurs in three stages: (1) the formation of the precursor complex, (2) the electron transfer and (3) the change in organization of the solvent cage in which electron transfer
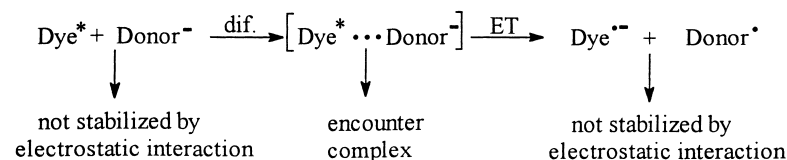
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primary products exist. Considering these principles and the interaction between the dye (chromophore) and an electron donor in the ground state and after an electron transfer process, dyeing photoinitiators can be classified into four different groups:
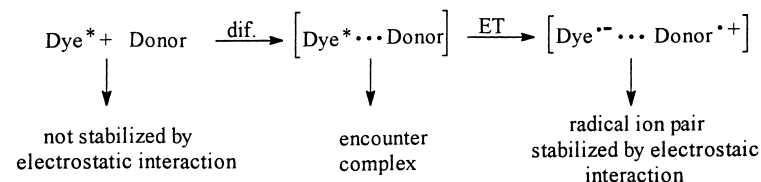
1. Photoinitiating donor–acceptor pairs with electrostatic interaction in the ground state (ground state–ion pair) and neutral after the photoinduced electron transfer process.

$$\left[\text{Dye}^+ \cdots \text{Donor}^-\right] \xrightarrow{h\nu} \left[\text{Dye}^+ \cdots \text{Donor}^-\right]^* \xrightarrow{ET} \text{Dye}^\bullet + \text{Donor}^\bullet$$

stabilized by electrostatic interaction

not stabilized by electrostatic interaction

2. Photoinitiating donor–acceptor pair without electrostatic interaction in the ground state and after an electron transfer (at least one component neutral in the ground state and neutral after an electron transfer process).

$$\text{Dye}^* + \text{Donor}^- \xrightarrow{dif.} \left[\text{Dye}^* \cdots \text{Donor}^-\right] \xrightarrow{ET} \text{Dye}^{\bullet-} + \text{Donor}^\bullet$$

not stabilized by electrostatic interaction

encounter complex

not stabilized by electrostatic interaction

3. Photoinitiating donor–acceptor pair neutral in the ground state and charged after an electron transfer (radical–ion pair).

$$\text{Dye}^* + \text{Donor} \xrightarrow{dif.} \left[\text{Dye}^* \cdots \text{Donor}\right] \xrightarrow{ET} \left[\text{Dye}^{\bullet-} \cdots \text{Donor}^{\bullet+}\right]$$

not stabilized by electrostatic interaction

encounter complex

radical ion pair stabilized by electrostaic interaction

4. Photoinitiating donor–acceptor pair, which consists of two negatively (or two positively) charged components. For this type of photoredox pair, in the ground state, between the components there is a strong electrostatic push away effect, which might decrease an efficiency of PET.

In our earlier papers [15,16] we presented a new class of free radical photoinitiators based on pyrazolone azomethine dyes (PAM). Several dyes containing 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 the dye modification were applied in the study. The first was a change in the type of the substituent in the pyrazolone skeleton or 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 C=N bond is severely hindered by the coplanarization of the azomethine residue with other parts of the dye. This stabilizes the molecule in its excited state and causes the 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 the studies on the third type of photoinitiation photoredox pair which consists of 3-methyl-1-phenyl-1H-pentaazacyclopenta[b]naphthalene isomers as primary absorbers and N-phenylglycine derivatives as electron donors. The newly prepared 1-H-pentaazacyclopenta[b]naphthalene dyes (PACN) presented in this paper allows to illustrate the relationship between their structures and their photoinitiation ability.

2. Experimental section

Substrates used for the preparation of dyes were purchased from Fluka, Merck or Aldrich. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), 1-methyl-2-pyrrolidinone (MP), 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 [17].

2.1. Dye synthesis

4-(Diethylamino-phenylimino)-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one was prepared using the method described elsewhere [18]. 5-Methyl-2-phenyl-2H-pyrazole-3,4-dione was prepared using the method described by Tacconi et al. [19]. 4-Spirobenzimidazole derivatives (CNH2, PNH2G), quinoxaline derivative (ZH) and the final 3-methyl-1-phenyl-1H-pentaazacyclopenta[b]naphthalenes

were synthesized according to the method given by Metwally et al. [20]. The crude dyes were purified using a column chromatography and finally by a 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 for ethyl acetate solutions. Both fluorescence and phosphorescence spectra were recorded for 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 deaerated.

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 [21]. A 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. 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 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 MTM (Krakow) Model EA9C-4z was used for measurements, and 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 dyes were obtained using the actinometric method described by Schaap et al. [22]. For the quantum yield measurements the procedure was as follows: 3.45 mg of 2,3-diphenyl-*p*-dioxene 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 [23], using the known quantum yield for poly-Ⓡ$_\text{RB}$ ($\Phi(^1O_2) = 0.76$) [24]. 2,3-Diphenyl-*p*-dioxene was prepared according to the method of Summerbell and Berger [25].

3. Results and discussion

Tested 1H-pentaazacyclopenta[b]naphthalene dyes (PACN) were prepared by the sequence of reactions described in Scheme 1.

As it was shown earlier, two different products can be formed, during the condensation of 2,3-diaminopyridine
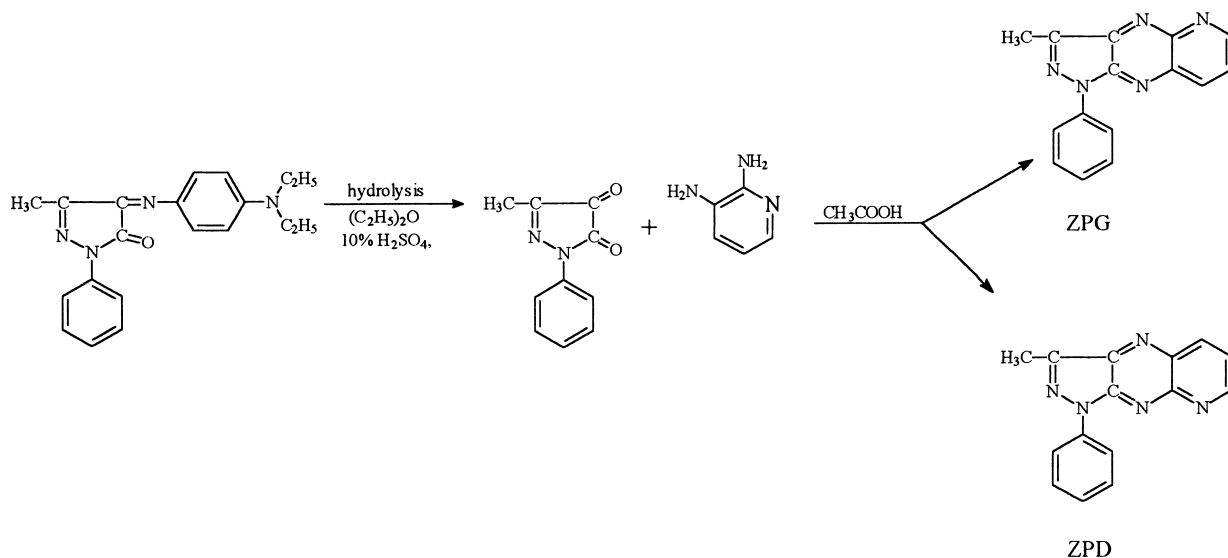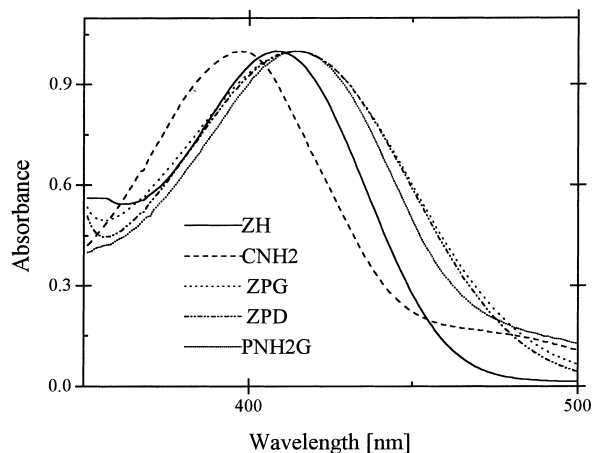

Scheme 1.

Fig. 1. The electronic absorption spectra for selected dyes tested in ethyl acetate solution. Type of dye shown in the legend.
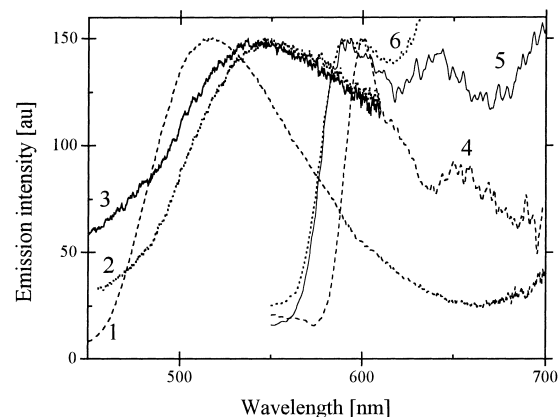

Fig. 2. Steady-state emission spectra of selected dyes tested. Spectra recorded in 2-methyltetrahydrofuran solution. Fluorescence: (1) ZH, (2) ZPG, (3) ZPD; Phosphorescence: (4) ZH, (5) ZPD, (6) ZPG.

and 5-methyl-2-phenyl-2H-pyrazole-3,4-dione [26]. The electronic absorption spectra of isomers obtained, as shown in Fig. 1 are almost identical.

Fig. 2 presents the emission properties of selected dyes and Table 1 summarizes the structures and spectroscopic properties as well as electrochemical data of all dyes tested. All dyes studied exhibit weak fluorescence characterized by distinct Stekes shift (about 5000–6000 cm^{-1}). This behavior indicates that the emitting states of the dyes

are charge-transfer in character. Fig. 2 also shows the steady-state phosphorescence spectra of the studied dyes. One can calculate the energy of triplet state (E_{oo}^{T}) from the phosphorescence spectra. The data summarized in Table 1 for the triplet state energies indicate that their values oscillate in the range of 200 kJ/mol. The electrode potential at which a compound undergoes reduction was located by cyclic voltammetry. The cyclic voltammograms for the studied dyes show only one electron reversible reduction

Table 1
Structures, spectroscopic and electrochemical properties of tested dyes

Dye	Structure	λ_{max}^{abs} (nm) EtAc	λ_{max}^{Fl} (nm) MTHF	ϕ_{Fl} MTHF	E_{oo}^{T} (kJ/mol)	E_{red} (mV)
CNH2		389	465	<0,0001	–	−1198
PNH2G		411	–	–	–	−1218
ZH		409	517	0.061	199	−1344
ZPG		413	545	0.009	202	−1108
ZPD		415	549	0.011	204	−1088

Fig. 3. Cyclovoltammetric curve recorded for ZPD.

Fig. 4. Photopolymerization kinetic curves recorded for novel tested dyes; electron donor: N-phenylglycine (0.1 M), monomer formulation of 1 ml of MP and 9 ml of TMPTA. Photoinitiating dyes marked in the figure.
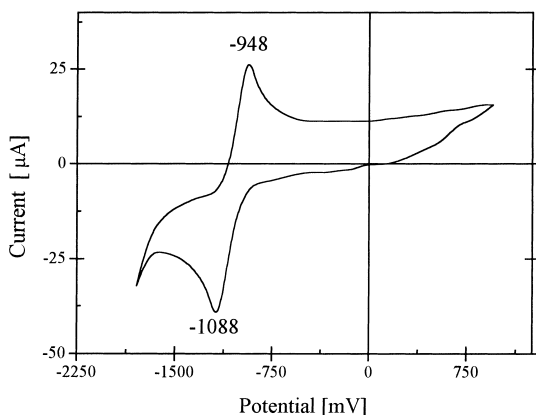
(see Fig. 3). The value of the reduction potentials for PACN isomers tested are, within an experimental error, identical.

N-phenylglycine derivatives (NPGs) as electron donors were used for the photoinitiated free radical polymerization. The free energy change for the electron transfer (ΔG^0) was calculated from Rehm–Weller equation [27,28]

$$\Delta G^0 = E_{ox}\left(\frac{D}{D^{\bullet+}}\right) - E_{red}\left(\frac{A^{\bullet-}}{A}\right) - \frac{Ze^2}{\varepsilon a} - E_{oo} \qquad (1)$$

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.

For the calculation of ΔG^0 the reduction potentials of the tested dyes (see Table 1), oxidation potentials of applied NPGs [17,21,29] and the measured triplet state energies of the studied dyes (see Table 1) were used. The calculations showed that the free energy change for the electron transfer (ΔG^0) is negative. It means that the photoinduced intermolecular electron transfer for the studied bimolecular system is thermodynamically allowed. It is also worth emphasizing that for isomers the calculated values of ΔG^0, within experimental error, have very close values.

The influence of the dye structure on their polymerization photoinitiation ability is very significant. As Fig. 4 shows, photoinitiation capabilities presented by ZPG and ZPD isomers are comparable and are significantly higher than one recorded for ZH.

The dyes tested were prepared in a way that allows the coplanarization of the molecule skeleton. This modification, as one can expect, should increase the singlet excited state lifetime, and possibly increase the quantum yield of the triplet state formation. The relative efficiency of the photoinitiation ability of all dyes studied along with their quantum yield of singlet oxygen formation (assumed as an indirect method of the efficiency of the triplet state formation measurement) are summarized in Table 2.
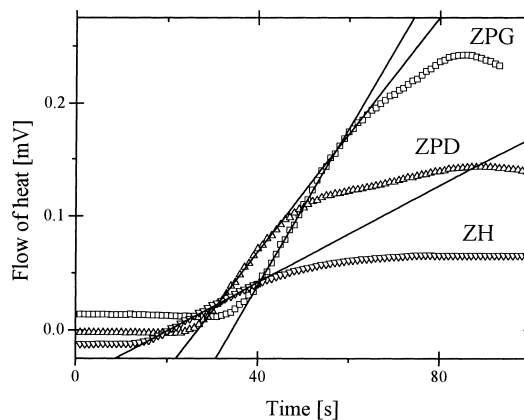
On the basis of the data lists in Table 2, it appears that there is a relationship between the rate of photoinitiated polymerization and the quantum yield of singlet oxygen formation. This is shown in Fig. 5.

It is clear from the inspection of the presentation in Fig. 5 that there is no linear relationship between the rate of polymerization and the square root of efficiency of the singlet oxygen formation.

The analysis of the kinetic scheme for photoinduced polymerization via an intermolecular electron transfer process has shown [17,30] that for a negligible efficiency of the absorbing chromophore bleaching process, the following equation can describe the rate of polymerization in viscous media:

$$R_p \cong k_p[M]\sqrt{\frac{2I_a\Phi_T k_{el}}{k_t}} \qquad (2)$$

where I_a is the intensity of absorbed light, Φ_T is the quantum yield of triplet state formation, k_p and k_t denote the rates constants of polymerization and chain termination steps, respectively, and k_{el} is the first-order rate constant of the electron transfer described by the Eyring equation

$$k_{el} = \chi Z \exp\left(-\frac{\Delta G^{\#}}{RT}\right) \qquad (3)$$

where Z is a frequency factor, χ is the transmission coefficient, and $\Delta G^{\#}$ is the free energy of activation given by the Marcus [12–14] equation for neutral reactants

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

Dye	CNH2	PNH2G	ZH	ZPG	ZPD
$\phi^1 O_2$	0.00025	0.0002	0.078	0.066	0.064
R_p (µmol/s)	0.024	0.030	4.02	12.42	11.13

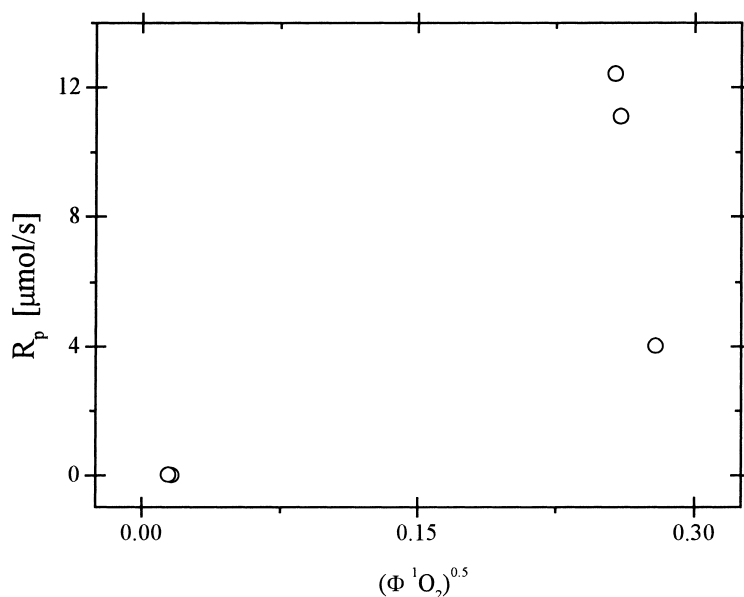[a] Electron donor: N-phenylglycine.

Fig. 5. Relationship between the photoinitiated polymerization rate and the square root of the quantum yields of singlet oxygen formation for dyes tested.

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

here λ is the reorganization energy necessary to reach the transition states both of excited molecules and of solvent molecules and ΔG_{el} is expressed by the Rehm–Weller [27,28] Eq. (1).

Summarizing the above analysis, one can conclude that in order to compare the rates of the free radical 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 thermodynamical (ΔG^0) and kinetic (λ) aspects of the electron transfer process, and third, it may also depend on the reactivity of free radicals resulting from the electron transfer process [31]. Since for data presented in Fig. 5 after PET one type of initiating radical is obtained, therefore, one can state that the observed nonlinear relationship between the rate photoinitiated polymerization and the square root of the quantum yield of singlet oxygen formation (usually equal to the quantum yield of intersystem crossing) is caused by different k_{el}. On the other hand, k_{el}, as Eqs. (3) and (4) show, depends on two parameters: thermodynamical (ΔG_{el}) and kinetic (λ). Taking into account the fact that the shape of the analyzed molecules are almost identical and the fact that polymerization reaction occurs for all cases in the same monomeric mixture, one can presume that the reorganization energy factor (λ) is approximately nearing. Therefore, the reorganization energy factor practically does not affect the rate of the electron transfer process. Explanation of the observed specific behavior might come from the analysis of the value of free energy change (ΔG_{el}) for the electron transfer process. Application of the Rehm–Weller Eq. (1) shows that for

ZH the free energy change (calculated for N-phenylglycine (NPG) as electron donor) is about 23–25 kJ mol^{-1} more positive in comparison to the free energy changes obtained for ZPD and ZPG. On the basis of these calculations, it appears that according to the Marcus equation, the rate constant of electron transfer for ZH–NPG pair should be smaller than that for ZPG–NPG and ZPD–NPG photoredox pairs. This is confirmed by the data presented in Table 2 and Fig. 5.

It is also important to emphasize that the precursor dye (CNH2), displays the lowest efficiency of both: the photoinitiation ability as well as the efficiency of the singlet oxygen formation. This finding apparently shows that the coplanarization of the 4-spirobenzimidazole residue with other parts of the dye, eliminates an effective channel of the dye excited state deactivation. This type of molecule modification increases the photoinitiation ability about two orders of magnitude. A similar effect was observed for other, different type of azomethine dyes described earlier [16,32].

The efficiency of polymerization photoinitiation strongly depends on the type of an electron donor. Fig. 6 presents kinetic curves recorded for ZPG 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 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 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^0, see Eq. (4)). This type of relationship is shown in Fig. 7.
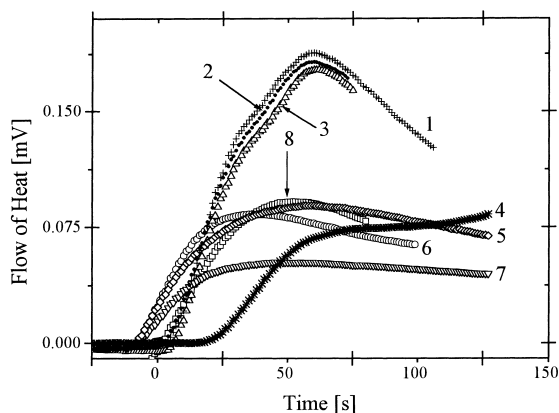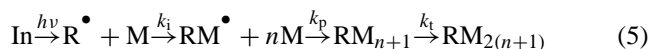
Fig. 6. Photopolymerization kinetic curves recorded for ZPG and various N-phenylglycine derivatives: ($c = 0.1$ M), monomer formulation: of 1 ml of MP and 9 ml of TMPTA. N-phenylglycine derivatives: (1) 4-C(O)CH$_3$, (2) 4-C(O)OEt, (3) 4-CN, (4) 4-NO$_2$, (5) -OPh, (6) 4-CH$_3$, (7) 4-OCH$_3$, (8) -H.

It is apparent from the inspection of the relationship presented in Fig. 7 that the plot exhibits 'the 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.

It has been shown earlier [32] that the kinetics of photoinitiated polymerization can be described by the following simplified equation

$$\text{In} \xrightarrow{h\nu} \text{R}^\bullet + \text{M} \xrightarrow{k_i} \text{RM}^\bullet + n\text{M} \xrightarrow{k_p} \text{RM}_{n+1} \xrightarrow{k_t} \text{RM}_{2(n+1)} \qquad (5)$$

where In denotes a lightsensitive initiator, k_i, k_p, and k_t have conventional meaning. A kinetic scheme describing the photoinitiated polymerization via photoinduced electron transfer process is more complex, because it should include a free radical generation step. For analysis of the rate of polymerization one can apply a simplified mechanism describing photoinitiated polymerization (not considering kinetics of an electron transfer process). Subsequently, one
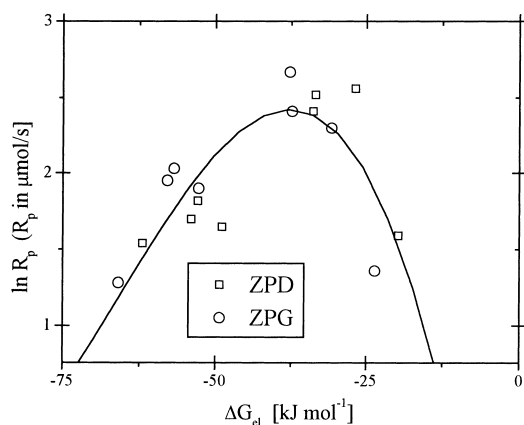

Fig. 7. Relationship between the rate of polymerization and the free energy change of the electron transfer process for ZPD–NPGs and ZPG–NPGs photoredox pairs.
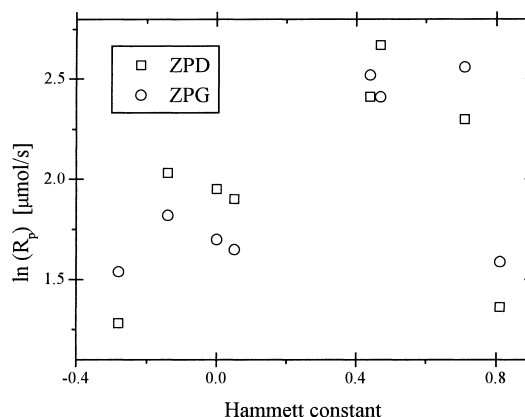

Fig. 8. Relationship between the rate of polymerization and the Hammett's constant of N-phenylglycine derivative for ZPD–NPGs and ZPG–NPGs photoredox pairs.

can assume the steady-state condition and assume that the reactivity of free radicals depends on their structure (for aromatic radicals, one can apply the Hammett equation for the description of initiation rate constant). Under these conditions for the description of the polymerization rate one obtains the following simple equation [32].

$$R_p = k_p[\text{M}]^{1.5}(\Phi_{\text{NPG}\bullet})^{0.5}(I_A)^{0.5}(e^{\rho\sigma})^{0.5}(k_t)^{-0.5} \qquad (6)$$

or in logarithmic form

$$\ln R_p = \ln A + 0.5\rho\sigma \qquad (7)$$

where A for the initial time of polymerization is the sum: $\ln k_p - 0.5 \ln k_t + 1.5 \ln[\text{M}] + 0.5 \ln \Phi_{\text{NPG}\bullet} + 0.5 \ln I_A$. Eq. (7) clearly shows that the rate of polymerization depends on the reactivity of free radicals yielded after photoinduced electron transfer process. Fig. 8 illustrates this type of relationship observed for ZPD–NPGs and ZPG–NPGs photoredox pairs.

Surprisingly, there is no linear relationship between the rate of photoinitiated polymerization and the Hammett constants. Typically, an existence of Hammett's non-linear relationship occurs when the mechanism of process is changing as the type of the substituent varies. Therefore, observed non-linear relationship between the rate of photoinitiated polymerization and the Hammett constants suggests that the reactivities of 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 two important features of the PET. The first is the fact that the PET process is a reversible one, and second that the rate of proton transfer (PT) (following after PET), is also free energy change of this process dependent [33].

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 the 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 [34–36]. Also, more suitable from the practical point of view, the results presented by Marciniak and coworkers [37] 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 the mode of decay of the radical ion pair (for example the change from water to 1:1 mixture of MeCN–water mixture). Taking these into consideration, one might suppose that the results presented in this paper might be interpreted in terms of possible influence of the back electron transfer on the rate of photoinitiated polymerization.

More recently, Peters et al. [34–36] have demonstrated that in low polarity solvents the rate for the proton transfer manifests a clear 'inverted region'. For the triplet radical ion pair, the back-electron transfer is a long time event (>10 ns) [38] in comparison to the proton transfer which occurs on the 100 ps time scale. Knowing this, one might suppose that the rate of proton transfer introducing to the process of free radical formation the 'inverted region' like behavior, might cause the observation of the 'inverted region' properties for the photopolymerization rate.

Acknowledgements

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