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Quinolineimidazopyridinium derivatives as visible-light photoinitiators of free radical polymerization

Ilona Pyszka, Zdzisław Kucybała*

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

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Abstract

Several dyes containing Quinolineimidazopyridinium moiety (QIPD) have been synthesized and evaluated as photoinitiators for free radical polymerization induced with the visible emission of a commercial dental lamp. The tested dyes were tested as photoinitiators in the presence of selected electron donors. Different substituents introduced into both the pyridine ring and quinoline moieties of the dyes influence photophysical properties of the investigated systems. Several different groups were tested including heavy atoms (−Cl, −Br, −I) and electron accepting (−NO_2) group. Analysis of the properties of the tested dyes allows one to conclude that there is a significant heavy atom effect on their photoinitiation efficiency. The type of the applied counter-ion has no effect on the overall performance of the photoinitiating system. QIPDs possess broad structured spectra with long-wavelength part located at the boundary of visible and UV parts of light spectrum. This makes QIPDs good candidates for the use as photoinitiating systems for dental restorative materials.

Keywords: Dyeing photoinitiator; Effect of structure; Kinetics of photoinitiated polymerization

1. Introduction

Since Oster's report [1], the fields of dye photoinitiated polymerization and photoimaging technology have made a great impact on both the scientific and industrial communities. In the recent years there have been many developments in the synthesis and photochemical studies of novel photoinitiating systems. They have been designed for many specific applications such as color printing [2], dentistry [3], or 3D modeling [4].

There is one striking point when considering thermodynamics of polymerization photosensitization by dyes. The energy transfer between an excited state of the dye and another chromophore, which is able to generate free radicals, is generally disfavored because the energy needed to dissociate a bond is larger than the energy transferred to the chromophore. However, with hydrogen or electron transfer involved it is possible to generate free radicals from molecules with low excitation energy.

There are numerous studies on the dye photoinitiators that form a free radical *via* the photoinduced electron transfer process. These include the acridines, the xanthenes and the thiazines, first reported by Oster [1], a wide group of fluorone dyes [5], cyanine dyes [2,6], pyrene [7], safranine T [8], dyes based on quinaxolin-2-one residue [9], styrylpyridinium residue [10], and many others [11]. It is noteworthy that only cyanine borates [6] are "tunable photoinitiators". Their color change can be achieved by altering the number of conjugated alkene units separating the aromatic parts of cyanine dye.

Nevertheless, there is still a need for the search of the new effective, visible-light photoinitiating systems that will fulfill specific properties, for example, properties required for dental materials. This paper is a part of these studies. We describe here an attempt to develop new photoinitiating systems, composed of the dye and suitable electron donor that can be initiated in the blue region of the visible light by the commercial dental lamps. They show a high molar absorption coefficient

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* Corresponding author. Tel.: +52 3749017; fax: +52 3749005.
E-mail address: kucybala@atr.bydgoszcz.pl (Z. Kucybała).

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in this spectral regime, which allows one to decrease their concentration in dental formulation.

2. Experimental

Substrates used for the preparation of the dyes and electron donors were purchased from Merck or Aldrich. (Phenylthio)-acetic acid (PTAA), phenoxyacetic acid (PAA), *N*-phenylglycine (NPG), ethyl 4-dimethylaminobenzoate (EDAB), *N*,*N*-dimethylaniline (DMA), tetrabutylammonium tetrabutylborate (TBATBB), 2-mercaptobenzoxazole (MBX), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), methyl methacrylate (MM), and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich and *N*-phenyliminodiacetic acid (PIDAA) was purchased from Lancaster.

The electron donors: tetramethylammonium *n*-butyltriphenyl borate (TMABTB) were prepared using the procedures described Damico [12], *N*-(4-acetyl-phenyl)glycine (APG), *N*-(4-cyano-phenyl)glycine (CPG) and *N*-(4-ethoxycarbonyl-phenyl)glycine (EPG), were prepared according to the method given by Dyer et al. [13] and Weisblat et al. [14], respectively. Quinoline[2,3-*b*]-1*H*-imidazo[1,2-*a*]pyridinium bromide (iodide, chloride) dyes (QIPDs) were obtained by a sequence of reactions. In the first step, 2-oxo-2,3-dihydro-1*H*-imidazo[1,2-*a*]pyridinium halogenates (ODIPHs) were synthesized in a condensation reaction of the corresponding 2-aminopyridine and ethyl halogenoacetate [15]. In the next step, ODIPHs were treated with 2-nitrobenzaldehyde and then reduced by iron in CH_3COOH to yield QIPDs. The borate anion exchange reaction was performed using the procedure given by Damico [12] and Murphy et al. [16]. The final products were purified with the use of preparative thin-layer chromatography and identified by ^1H NMR, ^{13}C NMR, and UV–vis spectroscopy.

3. Instruments and measurements

Absorption spectra were obtained using Varian Cary 3E spectrophotometer. Fluorescence spectra were measured using Hitachi F-4500 spectrofluorimeter. Absorption spectra were recorded for ethyl acetate solutions. Both fluorescence and phosphorescence spectra were obtained for 2-methyltetrahydrofuran solutions. The reduction potentials of the dyes were measured by cyclic voltammetry using Electroanalytical Cypress System Model CS-1090 with Ag–AgCl electrode serving as a reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate. The quantum yields of singlet oxygen formation were measured on Hewlett–Packard 5890 or 6890 gas chromatographs fitted with a glass capillary column using methodology given by Schaap et al. [17].

The kinetics of free radical polymerization was studied using a polymerization solution composed 1 mL of MP and 9 mL of TMPTA. Dye concentrations were varied from 1.3×10^{-3} to 2.8×10^{-3} M. The concentrations of electron donors were also varied in the range from 0.025 M to 0.15 M. The polymerization mixture was not deaerated. The kinetics measurements were carried out using the methodology described earlier [18]. For further discussion, only data for the initial times of polymerization were used for the calculation of the polymerization rates in order to avoid the possibility of non-isothermal reaction conditions.

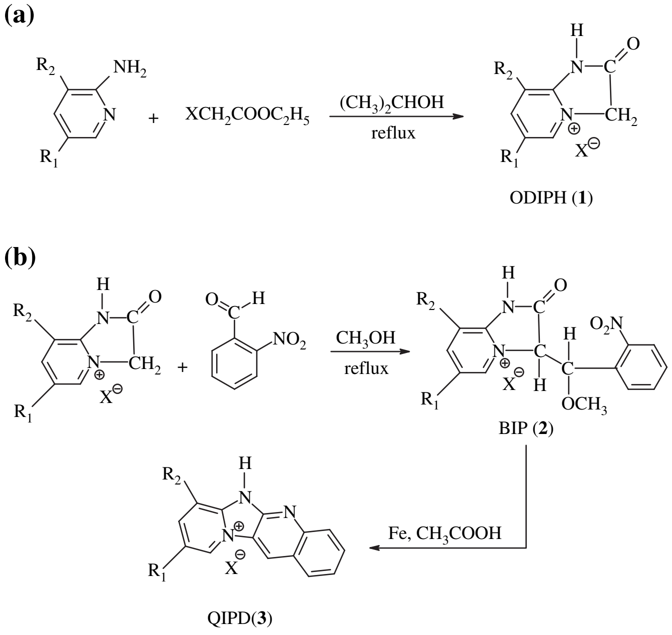
Irradiation of the polymerization mixture was carried out either with Luxor Model 4000 dental lamp (England) or the UV emission of Innova 90-4 argon-ion laser (351 and 361 nm lines). The incident light intensity at the sample position was measured with Coherent Model Fieldmaster power meter.

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 Lambda Physic/model LPY 150 operating at 65 mJ/pulse (pulse width about 4–5 ns) was used for the excitation.

4. Results and discussion

The parent compound **1** (see Scheme 1a), for all dyes synthesized is the corresponding 2-oxo-2,3-dihydro-1*H*-imidazo[1,2-*a*]pyridinium halogenate (ODIPHs). Its reaction with substituted benzaldehydes yields corresponding benzylideneimidazopyridinium halogenates, which were described in our earlier paper [19]. These dyes are rather poor photoinitiators and need further development. This was achieved by the condensation of ODIPHs with 2-nitrobenzaldehyde, followed by reduction, yielding halogenate of corresponding quinolineimidazopyridinium (QIPD) (**3**). The sequence of abovementioned reactions is shown in Scheme 1a and b.

The dyes tested were prepared in a way that allow to the study the various factors that can affect their final photoinitiation ability. These include: (i) the internal heavy atom effect,



Scheme 1. R_1, R_2, X^- marked in Table 1.

(ii) the external heavy atom effect, (iii) the correlation between the rate of photoinitiated polymerization and the free energy change for electron transfer reaction, and (iv) the effect of counter-anion on the rate of photoinitiated polymerization. It is worth noting that the compounds studied in this paper have not yet been described in the literature.

4.1. Physicochemical properties

QIPDs show the electronic absorption spectra typical for polycyclic aromatic heterocycles with characteristic vibrational structure. Fig. 1 shows the electronic absorption and emission spectra of quinoline[2,3-*b*]-1*H*-imidazo[1,2-*a*]pyridinium bromide (**S20**).

In contrast to benzylideneimidazopyridinium dyes, quinolineimidazopyridinium dyes exhibit strong fluorescence (see Fig. 1), characterized by moderate Stoke's shift of about 1000 cm^{-1}. The absorption and the fluorescence spectra are almost mirror images of each other with overlapping bands characterizing $0 \rightarrow 0$ transition. In 2-methyltetrahydrofuran, at liquid nitrogen temperature, the investigated dyes show phosphorescence, indicating the triplet state formation. Its energy depends on the type of dye and oscillates from 2.21 to 2.39 eV (213−221 kJ mol^{-1}).

The electrochemical reduction potentials for the dyes were determined by cyclic voltammetry. The one electron reduction of the dyes occurs in the range from -1.082 to -1.013 V. A type of counter-ion that forms the salt with a dye cation does not affect the reduction potential (within experimental error). The electrochemical reduction peaks are quasi-reversible indicating that the reduced dye molecules are kinetically unstable. The obtained electrochemical values may have thermodynamic meaning and allow the calculation of the free energy of activation (ΔG_{el}) for the photoinduced electron transfer process (PET).

It is well known that the basic Rehm−Weller [20] requirement states that the free energy of activation for the PET (ΔG_{el}) process should have a negative value.

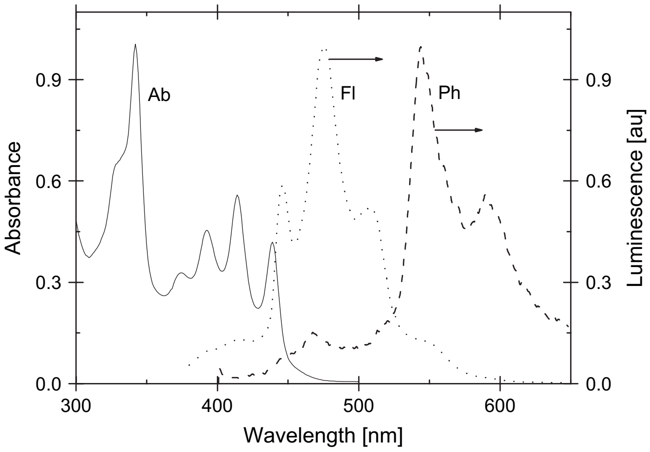


Fig. 1. Absorption and emission spectra of quinoline[2,3-*b*]-1*H*-imidazo[1,2-*a*]pyridinium bromide (**S20**). The absorption spectrum was recorded in ethyl acetate and the emission spectra were recorded in 2-methyltetrahydrofuran.

$$\Delta G_{\text{el}} = E_{\text{ox}}(D/D^{\bullet +}) - E_{\text{red}}(A^{\bullet -}/A) - \text{Ze}^2/\varepsilon a - E_{00} \qquad (1)$$

where $E_{\text{ox}}(D/D^{\bullet +})$ is the oxidation potential of the electron donor, $E_{\text{red}}(A^{\bullet -}/A)$ is the reduction potential of the electron acceptor, E_{00} is the energy of the excited state and $\text{Ze}^2/\varepsilon a$ is the Coulombic energy (considered to be negligible compared with the overall magnitude of ΔG in the present systems) gained by bringing the formed radical ions to an encounter distance in a solvent with dielectric constant ε. Table 1 shows the measured spectroscopic and electrochemical properties as well as the calculated thermodynamical values of the tested quinolineimidazopyridinium salts. For the calculation of ΔG_{el} from Eq. (1) the energy of the excited triplet state was used (E_{00}). The calculations showed that the free energy change values for the electron transfer (ΔG_{el}) in quinolineimidazopyridinium dye − *N*-(4-acetyl-phenyl)glycine systems are negative, indicating that the process is thermodynamically allowed.

4.2. Photoinitiated polymerization

Fig. 2 shows the family of kinetic curves recorded during polymerization photoinitiated by selected novel dyes.

The inspection of the experimental data shown in Fig. 2 reveals that the efficiency of photoinitiated polymerization strongly depends on the dye structure. From the data presented in Fig. 3 it is also evident that the rate of photoinitiated polymerization is strongly affected by the type of an electron donor.

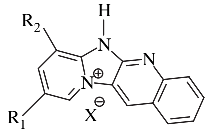
The data characterizing the photoinitiation capability of the tested dyes in the presence of *N*-(4-acetyl-phenyl)glycine, acting as electron donor, are compiled in Table 2. These data exhibit a wide range of values correlated to the structure of the dye. Based on the results listed in Table 2 one can conclude that there is quite significant internal heavy atom effect on the photoinitiation efficiency of the tested dyes. There is no evidence for such effect caused by the type of counter-anion forming salt with dye cation.

Since the tested dyes phosphoresce, one can assume that the reaction of free radical generation involves the excited triplet state. Eq. (2) describes the rate of the photoinitiated polymerization for this process.

$$R_{\text{p}} = -\frac{\text{d}[M]}{\text{d}t} = k_{\text{p}}[M]\sqrt{\frac{I_{\text{a}}\Phi_{\text{T}}}{k_{\text{t}}}} \qquad (2)$$

The symbols in Eq. (2) have conventional meaning. The equation predicts that the rate of the photoinitiated polymerization depends on the efficiency of the excited triplet state formation of an initiator. The experimental verification of Eq. (2) requires measuring quantum yield of the triplet state formation. Two types of measurements were applied for this purpose. The first method is based on the measurement of singlet oxygen formation [17] and the second approach allows one to determine the excited triplet state formation from the analysis of transient state bleaching curve obtained after short laser pulse excitation [21]. Table 2 shows the results obtained with the use of both the methods. It is evident that both methods produce practically identical results. In case **S25** laser flash methodology fails,

Table 1
Structures, spectroscopic and electrochemical properties and thermodynamical characteristics of tested dyes



Dye	R_1	R_2	X^-	Abs.[a] λ_{max} (nm)	ε_{max} ($M^{-1}\,cm^{-1}$)	Fl.[b] λ_{max} (nm)	Φ_{Fl}	E_T^{00} (eV)	E_{red} (mV)	ΔG^0 (eV)[c]
S20	−H	−H	−Br	387	2610	447	0.23	2.28	−1054	−0.591
				408	3040	477				
				432	2360	511				
S21	−Cl	−H	−Br	392	2530	453	0.26	2.29	−1044	−0.611
				417	1970	486				
				442	1590	519				
S22	−Br	−H	−Br	393	2000	442	0.29	2.30	−1013	−0.652
				417	1840	470				
				441	1330	515				
S23	−Br	−Br	−Br	389	2510	447	0.32	2.33	−1030	−0.665
				421	3020	476				
				447	2270	512				
S24	−H	$-NO_2$	−Br	389	1950	448	0.02	2.21	−1040	−0.535
				411	1720	480				
				435	1510	511				
S25	−H	−I	−Br	395	2540	458	0.37	2.39	−1034	−0.721
				418	3070	490				
				444	2340	525				
S26	−H	−H	−Cl	387	2450	447	0.22	2.27	−1053	−0.582
				408	3080	477				
				432	2310	512				
S27	−H	−H	−I	387	2520	447	0.23	2.28	−1052	−0.593
				408	2990	477				
				432	1920	512				
S28	−H	−H	n-Bu-B(C_6H_5)$_3$	387	2970	447	0.22	2.30	−1082	−0.583
				408	3710	477				
				432	2220	511				

[a] Ethyl acetate.
[b] 2-Methyltetrahydrofuran.
[c] $E_{ox} = 635$ mV (*N*-(4-acetyl-phenyl)glycine).

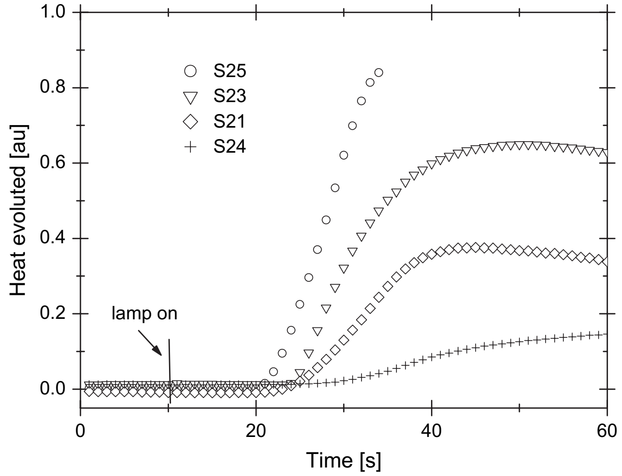


Fig. 2. Family of kinetic curves recorded during polymerization photoinitiated by novel dyes; electron donor: *N*-(4-acetyl-phenyl)glycine (0.1 M), monomer formulation: 1 mL of MP and 9 mL of TMPTA. Light intensity of dental lamp irradiation 20 mW/0.785 cm^2 (photoinitiating dyes marked in the figure).

because no appropriate wavelength can be found for which the ground state signal dominates over the absorption from the excited triplet state, which is the basic prerequisite for above-mentioned method. Thus, for compound **S25** we used the yield of the excited triplet state formation based on the quantum yield of singlet oxygen formation. Fig. 4 presents the relationship between the rates of the photoinitiated polymerization and the square root of quantum yield of the excited triplet state formation for the entire group of the tested dyes.

Overall, the majority of dyes (with the exception of **S24**) behave as predicted by Eq. (2). It is worth noticing that the value of intercept obtained for $\Phi_T = 0$ is low. This specific behavior is probably caused by a high induction period. This can be nicely confirmed by polymerization reaction profiles shown in Figs. 2 and 3.

For the sake of simplicity, we will analyze photoinitiation capability of the dyes using only one type of electron donor, (*N*-(4-acetyl-phenyl)glycine). The formation of the initiating radicals occurs *via* sequence of reactions, in which the

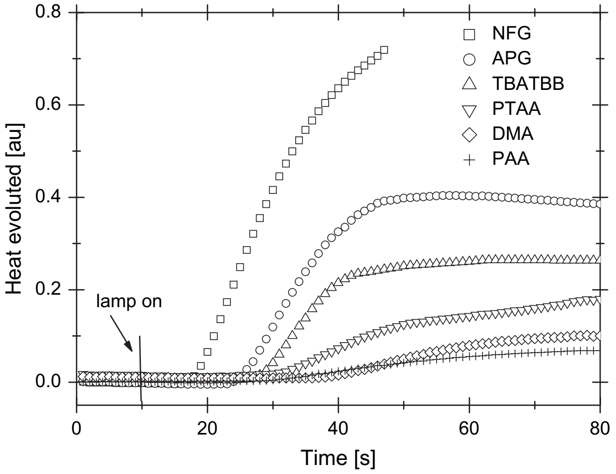


Fig. 3. Photopolymerization kinetic curves recorded for **S20** and various electron donors. Monomer formulation: 1 mL of MP and 9 mL of TMPTA. Photoinitiating electron donors (0.1 M) marked in figure. Light intensity of dental lamp irradiation: 20 mW/0.785 cm^2.

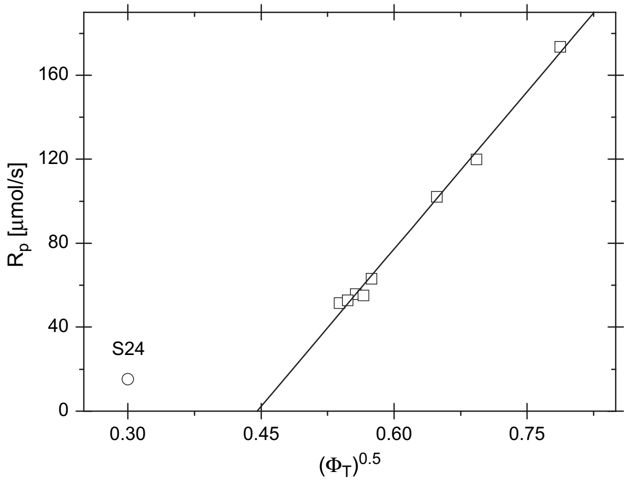


Fig. 4. Relationship between the rate of photoinitiated polymerization and square root of quantum yield of triplet state formation.

photoinitiated electron transfer process is the crucial step. Thus, it is interesting to check whether this step influences on the rate of polymerization or not. This is possible by measuring the rate of the primary process, e.g. the rate of the electron transfer between the tested dyes and electron donor, and next by comparing the measured values with the rates of photoinitiated polymerization. It should be noted, however, that this comparison is possible only when the identical type of free radical is released from the photoinitiating photoredox pair.

The quenching rate constants k_q (since the quenching of the dye's excited triplet state by the electron donor is the only way of the excited triplet state deactivation by which one can assume that $k_q = k_{el}$) were obtained from experimentally measured pseudo-first-order rate constant, k_{obs}, for the decay of the excited triplet state of the dyes using formula (3).

$$k_{obs} = \tau_T^{-1} + k_q[\mathrm{ED}] \tag{3}$$

where τ_T is the lifetime of the dye's excited triplet state in the absence of an electron donor (ED). Typical plots based on Eq. (3) are presented in Fig. 5 and the quenching rate constants obtained for *N*-(4-acetyl-phenyl)glycine as an electron donor are also summarized in Table 2.

The k_q values can be correlated to the standard free energy change for electron transfer. The free energy change (ΔG_{el}) associated with a single electron transfer from *N*-(4-acetyl-phenyl)glycine to the excited triplet state of the chromophore was calculated using the Rehm–Weller Eq. (1) [20].

The obtained ΔG_{el} values for the entire series of the dyes as electron acceptors and *N*-(4-acetyl-phenyl)glycine as electron donor are compiled in Table 1. The negative ΔG_{el} values reveal that the electron transfer processes from *N*-(4-acetyl-phenyl)glycine to the dyes triplet are thermodynamically favorable. The dependence of the quenching rate constant on ΔG_{el} is presented in Fig. 6.

For the tested photoredox pairs, typical "normal region" of Marcus plot is observed, strongly supporting the electron transfer mechanism in the quenching of the dyes triplet by *N*-(4-acetyl-phenyl)glycine. One data point shown in Fig. 6 deviates significantly from linearity (**S28**). The observed upward

Table 2

Rates of photoinitiated polymerization (R_p), quantum yield of singlet oxygen formation (Φ^1O_2), quantum yield of the triplet state (Φ_T), lifetime of triplet state (τ_T) formation, quenching rate constant (k_q) for the dyes under the study

Dye	[a]R_p (µmol/s)	[b]Φ^1O_2	[c]Φ_T	τ_T (µs)	[d]k_q ($M^{-1}\,s^{-1}$)
S20	55.69	0.31	0.29	1.01	3.44×10^8
S21	63.06	0.33	0.31	1.96	4.00×10^8
S22	102.14	0.42	0.41	8.72	1.11×10^9
S23	119.86	0.48	0.45	37.20	1.13×10^9
S24	15.26	0.09	0.08	0.74	2.75×10^8
S25	175.50	0.62	–	79.80	2.43×10^9
S26	51.43	0.29	0.29	0.89	3.62×10^8
S27	55.20	0.32	0.30	1.11	3.88×10^8
S28	52.74	0.30	0.28	1.52	8.61×10^8

[a] Measured for *N*-(4-acetyl-phenyl)glycine (APG) as an electron donor; visible-light intensity: 20 mW/0.785 cm^2.

[b] Measured using Schaap's methodology [17].

[c] Measured with the use of method given by Lament et al. [21].

[d] *N*-(4-acetyl-phenyl)glycine (APG) used as the triplet state quencher.

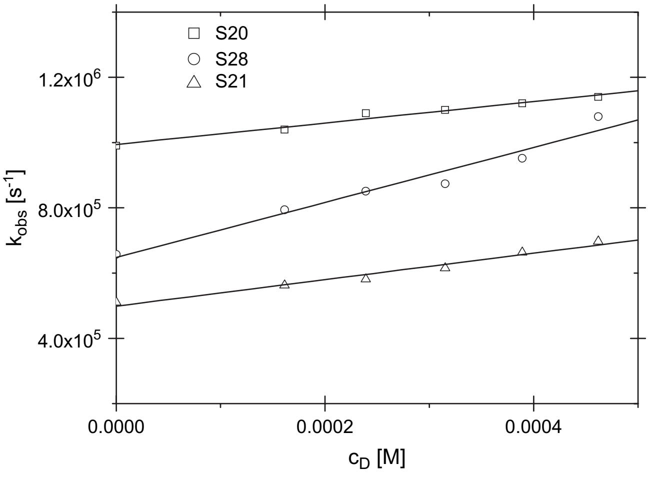


Fig. 5. Plot according to Eq. (3) for selected dyes triplet quenching. *N*-(4-acetyl-phenyl)glycine was applied as electron donor.

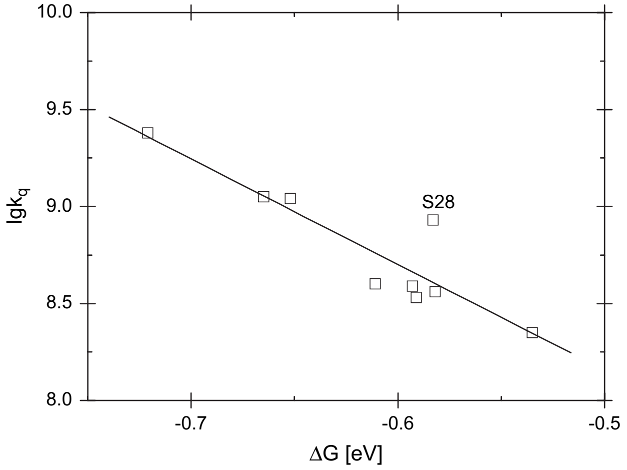


Fig. 6. Dependence of the quenching rate constant on ΔG_{el} for quenching of dyes triplet by *N*-(4-acetyl-phenyl)glycine.

is probably caused by the presence of an additional electron donor besides *N*-(4-acetyl-phenyl)glycine, e.g. *n*-butyltriphenyl borate anion. This increases the overall quencher concentration causing an increase of the quenching rate constant.

One can confirm the influence of the rate of electron transfer on the rate of polymerization by plotting the dependence of R_p on ΔG_{el}.

Inspection of the data shown in Fig. 7 reveals that the observed relationship fulfills the requirement predicted by classical electron transfer theory, e.g. the rate of polymerization increases as the driving force for the electron transfer process increases.

Fig. 8 presents the relationship between the rate of photoinitiated polymerization and the rate constant of the electron transfer process.

The linear relationship is obvious for the majority of the studied photoredox pairs indicating a direct link between the rate of polymerization and the rate constant of photoinduced electron transfer, namely, for the photoredox pairs under the study, the electron transfer step controls an overall efficiency of photoinitiated polymerization. The observed low photoinitiation capability of **S24** requires a comment. It is known from the literature that nitro compounds undergo photoreduction in the presence of electron donors, yielding corresponding nitroso derivatives [22], which are known to be efficient free radical scavengers [23]. It is also noteworthy, that nitro compounds themselves are known to be efficient inhibitors of free radical polymerization [24].

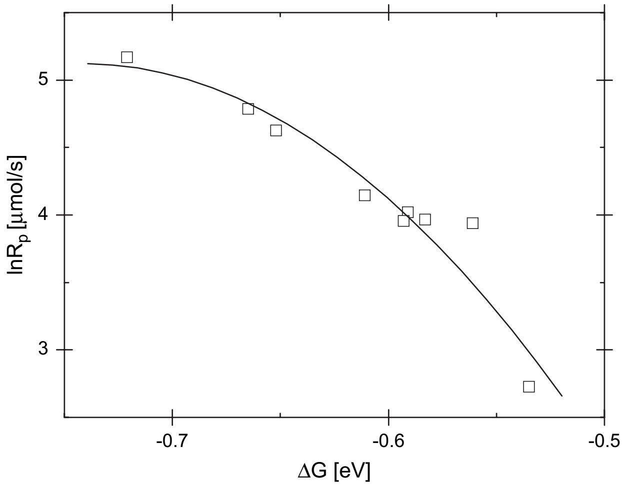


Fig. 7. Relationship between the rate of polymerization and the free energy change associated with electron transfer from *N*-(4-acetyl-phenyl)glycine to the triplet state of tested dyes.

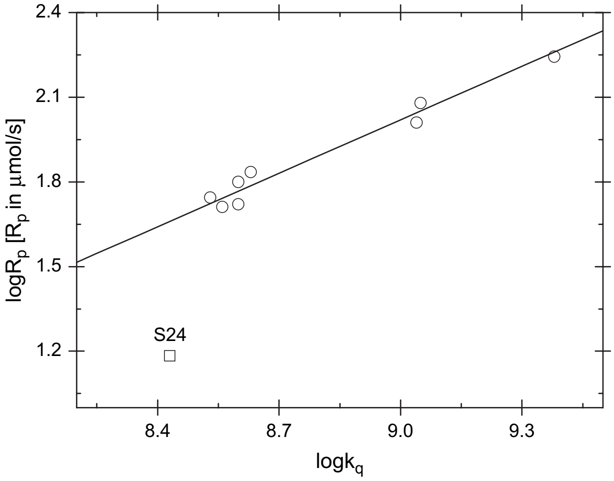


Fig. 8. Correlation between the rate of photoinitiated polymerization and the rate constant of electron transfer process for the tested dyes – *N*-(4-acetyl-phenyl)glycine photoredox pairs.

During the photoinitiation process there is a possibility of hydrogen atom abstraction either from the monomer or the polymer by the excited triplet state of the dye. It is also noteworthy that by analyzing the mechanistic aspects of photoinitiation process, one should avoid the complexity of the processes that are related with the polymerization of multiacrylates. In order to eliminate the above-mentioned effects on the mechanism of photoinitiation, a series of polymerization reactions of methyl methacrylate (MMA) in the bulk, initiated by the tested **S25**-coinitiator systems, were carried out. The obtained data are compiled in Table 3.

Table 3
The efficiencies of methyl methacrylate (MMA) (deoxygenated) polymerization and TMPTA–MP mixture polymerization rates photoinitiated by **S25**-coinitiator photoinitiating pair

Coinitiator	Initial R_p for multiacrylate TMPTA (μmol/s)	MMA conversion (%)
None	0.0	0.0
CPG	325.8	–
EPG	298.4	9.07
NPG	252.10	6.82
APG	175.50	5.57
EDAB	21.83	3.79
DMA	52.11	1.51
PTAA	34.20	1.73
PAA	8.72	0.47
TBATBB	121.21	3.08
PIDAA	–	10.68
MBX	–	9.09

Light source: xenon lamp fitted with glass filter; light intensity 600 mW/cm^2. Absorbance of dye at 418 nm = 1.5; time of irradiation 30 min.

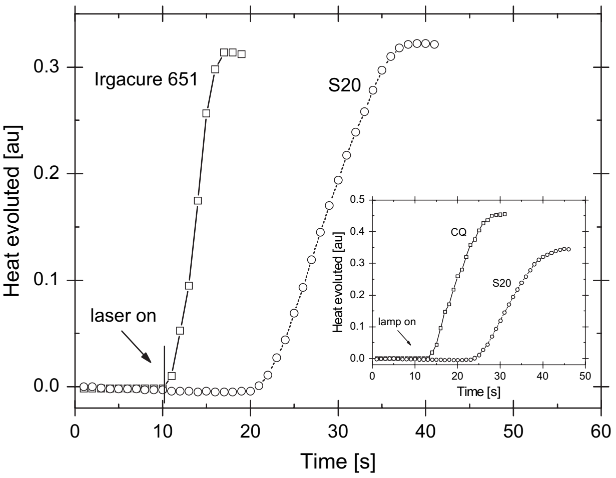


Fig. 9. Comparison of the kinetics of photoinitiated polymerization of the TMPTA–MP mixture initiated by **S20**-EDAB and Irgacure 651 systems. Light intensity of an argon-ion laser irradiation 20 mW/0.785 cm^2. Inset: polymerization initiated by **S20**-EDAB and CQ-EDAB photoredox pair. Light source dental lamp – irradiation intensity = 20 mW/0.785 cm^2.

It is clear that the rates of polymerization of TMPTA–MP mixture and the efficiencies of MM polymerization initiated by the studied photoinitiator pair correspond respectively.

The absorption spectra of the dyes under the study make them good candidates for the initiating system applied in dental materials. The above conclusion can be supported by comparison of the kinetics of polyolacrylate polymerization initiated by QIPD–EDAB and commercial initiator Irgacure 651 and camphorquinone–EDAB (CQ–EDAB) photoredox pair, commonly used in dentistry.

Analysis of the kinetic curves presented in Fig. 9 indicates that the tested dye requires a quite long time for the start of polymerization. This behavior does not make QIPDs the particularly good components of photoinitiating systems applied in dentistry.

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