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The dyes possessing diazine residue as effective photoinitiators of free radicals polymerization

Zdzisław Kucybała (✉), Anna Kosobucka

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

E-mail: kucybala@atr.bydgoszcz.pl

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Summary

The series of the dyes possessing diazine residue have been investigated as visible-light absorbing photoinitiators of free radical polymerization. The rates of photoinitiation depend on the structure of the dye. Mechanism of the photoinitiation involves the electron transfer process between the dye and the electron donor (co-initiator). The dyes possessing diazine residue in the presence of a suitable electron donor are very effective photoinitiators. This can be attributed to the high quantum yield of their triplet state formation and high rate constant of electron transfer reaction between the dye and electron donor.

Introduction

There are numerous of 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 [2], cyanine dyes [3], pyrene [4], safranine T [5], dyes based on quinaxolin-2-one residue [6], styrylpyridinium residue [7], and many others [8].

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 either blue light emitting lasers or by the commercial dental lamps. The dyes described in this paper possesses diazine residue that causes a high molar absorption coefficient at the boundary of UV and visible light, which makes the dyes under the study good candidates as initiators in restorative dental materials.

Experimental

Substrates used for the preparation of the dyes were purchased from Merck or Aldrich. Monomer, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich and were used without further purification. Electron donors: N-phenylglycine (NPG), N-phenyliminodiacetic acid (PIDAA), thiophenoxyacetic acid (TPAA), phenoxyacetic acid (PAA), N,N-dimethylaniline (DMA), ethyl 4-dimethylaminobenzoate (EDAB), tetrabutylammonium tetrabutylborate (TBATB), were purchased from Merck, Aldrich or Lancaster.

Instruments and Measurements

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. Fluorescence quantum yield was measured using 9-methylantracene as actinometer. The nanosecond laser flash photolysis experiments were performed using a LKS.60 Laser Flash Photolysis apparatus (Applied Photophysics). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd-YAG laser from Lambda Physik/model LPY 150 operating at 65 mJ/pulse (pulse width about 4-5 ns) was used for the excitation.

The reduction and oxidation potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical MTM (Krakow) Model EA9C-4z was used for measurements. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate.

The quantum yields of triplet state formation was established by measurement of the quantum yield of singlet oxygen formation using the actinometric method described by Schaap et. al. [9].

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 2.02×10^{-4} to 4.34×10^{-4} M; concentrations of electron donor were 0.1 M. The polymerizing mixture was not deareated.

TMPTA-MP kinetics of polymerization measurements were carried out by measuring the polymerization heat evolution of a sample irradiated with an Innova 90-4 argon-ion laser (351 and 361 nm lines), an Omnichrome model 543-500 MA argon-ion laser (visible emision, 488 and 514 nm) or a dental lamp (Luxor Model 4000) through an optical system, in a home-made micro-calorimeter as described earlier [10]. To avoid a possibility of nonisothermal reaction conditions, for further discussion only the data for the initial time of polymerization were used for the calculation of the polymerization rates. The irradiation intensity was measured by a Coherent model Fildmaster power meter and was varied from 5 or 70 mW/0.785cm^2.

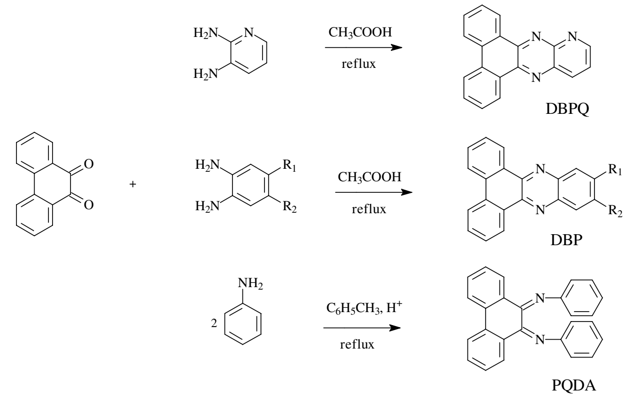
Synthesis

For the study dibenzo[f,h]pyrido[2,3-b]quinoxaline and several dibenzo[a,c]-phenazines were obtained by the condensation (Scheme 1) with either pyridine-2,3-diamine or corresponding 1,2-phenylenediamine derivative with 9,10-phenanthrenequinone according to procedure given by Hinsberg [11].

Preparation of 9,10-phenanthrenequinone dianil was performed according to method described by Sannicolo [12] and characterized using methodology given by MacPherson and Smith [13].

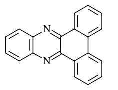
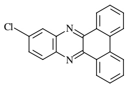
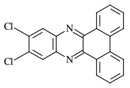
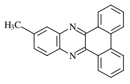
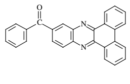
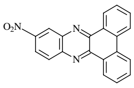
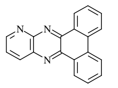
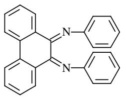
The products of condensation were purified with the use of preparative thin-layer chromatography and were characterized by proton and carbon NMR spectroscopy using a Varian Gemini 200 spectrometer.

Scheme 1.



where: R_1= H, Cl, NO_2, C(O)Ph, CH_3 and R_2= H, Cl

Table 1. Structures, abbreviations and basic spectroscopic, electrochemical and thermodynamical properties of the dyes under study.

Dye	Abb.	$^a\lambda_{max}$ [nm]	ε [$dm^3mol^{-1}cm^{-1}$]	$^b\lambda_{max}^{fl}$ [nm]	ϕ_{fl}	E_{red} [V]	E^T_{00} [eV]	$^c\Delta G_{el}$ [eV]
	DBP	373 393	19090 22600	415	0.004	-1.182	2.29	-0.68
	DBP-Cl	380 400	15000 20000	427	0.007	-1.202	2.23	-0.59
	DBP-Cl2	383 406	16600 23750	414	0.012	-1.198	2.21	-0.59
	DBP-CH3	378 397	11070 19790	423	0.005	-1.202	2.24	-0.61
	DBP-B	383 405	17470 20720	429	0.005	-1.134	2.28	-0.72
	DBP-NO2	392 410	17530 19080	-	-	-1.200	2.68	-1.05
	DBPQ	383 397	19240 18820	456	0.030	-1.150	2.53	-0.95
	PQDA	515	25600	N.O.*	-	-1.094	-	-

^{a} Ethyl acetate, ^{b} 2-Methyltetrahydrofuran, ^{c} Measured for N-phenylglycine (NPG) as electron donor E_{ox} = 0.426 [V]; Note: 1 eV= 96.488 kJmol^{-1}, N.O.* - not observed

Results and discussion

The tested dyes DBPQ and DBP show the electronic absorption spectra typical for polycyclic aromatic heterocycles with characteristic vibrational structure. Figure 1 shows absorption (in ethyl acetate) and emission (in 2-methyltetrahydrofurane) spectra of dibenzo[a,c]phenazine for illustration of the tested dyes spectroscopic properties.

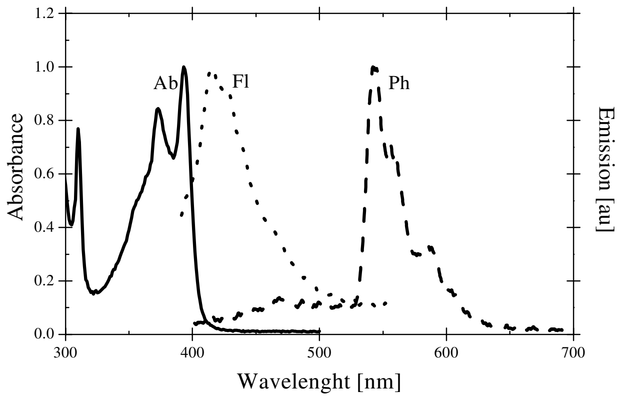


Figure 1. The electronic absorption and emission spectra of dibenzo[a,c]phenazine. The absorption spectra were recorded in ethyl acetate and the emission spectra in 2-methyltetrahydrofurane respectively.

The absorption and the fluorescence spectra are almost mirror images of each other with overlapping bands characterizing 0→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 213 to 244 kJ mol^{-1}. It should be noted, however, that PQDA do not fluorescence at ambient and at liquid nitrogen temperature. PQDA does not phosphorescence as well. The electrochemical reduction potentials for the dyes were determined by cyclic voltammetry. The one electron reduction of the dyes occurs in the range from –1.10 to -1.20 volts. The electrochemical reduction peaks are reversible indicating that the reduced dye molecules are kinetically stable.

The free radicals able to initiate polymerization are formed in bimolecular electron transfer process between the dye triplet state and suitable electron donor. The basic Rehm-Weller [14] requirement for such reaction states that the free energy of activation for the PET (ΔG_{el}) process should have a negative value. The free energies of activation for entire group of tested dyes were calculated using the Rehm-Weller equation.

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

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_{00} is the energy of the excited state and $Ze^2/\varepsilon a$ is the Coulombic energy gained by bringing the formed radical ions to an encounter distance in a solvent with dielectric constant ε. Table 1 compiles the measured spectroscopic and electrochemical properties as well the calculated thermodynamical values for the tested diazine dyes-N-phenylglycine photoredox pairs. For the estimation of ΔG_{el} the energy of the excited triplet state was used (E_{00}). The calculations showed that the values of free energy change for the electron transfer (ΔG_{el}) in diazine dyes - N-phenylglycine systems are negative, indicating that the process of the electron transfer is thermodynamically allowed.

Figures 2 and 3 show the family of kinetic curves recorded during an initial time of polymerization photoinitiated by novel tested dyes.

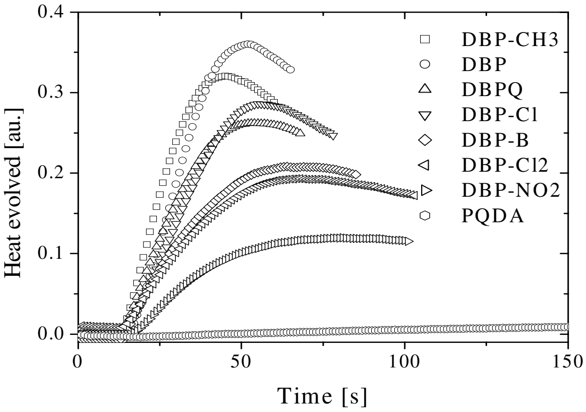


Figure 2. The photopolymerization kinetic traces recorded for novel tested dyes (marked in Figure). Polymerizing formulation: TMPTA-MP (9:1), coinitiator: N-phenylglycine (NPG). Light intensity of an argon-ion laser Innova 90-4 (DBP, DBPQ) irradiation 5 mW/0.785 cm^2, laser Omnichrome (PQDA) irradiation 70 mW/0.785cm^2.

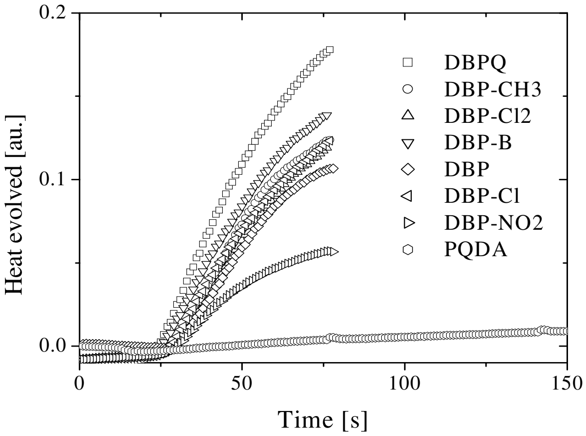


Figure 3. The kinetic traces recorded at the initial time of polymerization photoinitiated by novel tested dyes (marked in Figure). Polymerizing formulation: TMPTA-MP (9:1), coinitiator: N-phenylglycine (NPG). Light source a dental lamp - irradiation intensity 5 mW/0.785 cm^2 (DBP, DBPQ) and 70 mW/0.785cm^2 (PQDA).

The efficiency of photoinitiation of free radical polymerization of tested dyes depends strongly on their structure. It is apparent from the inspection of the experimental data shown in Figures 2 and 3 that the precursor, branched dye, initiates polymerization much less efficiently in comparison to its planar analogues. In our earlier papers we have demonstrated that the elimination or limitation of the rotation of the phenyl group in the azomethine part of molecule causes a significant increase of the photoinitiation ability observed for other, different type of azomethine dyes [6]. Elimination of the motion of C=N bond by co-planarization of the azomethine residue with other parts of the dye decreases the degree of branching of the dye, and this stabilizes the molecule in its excited state. From the data presented in Figure 4 it is also evident that the rate of photoinitiated polymerization is strongly affected by the type of an electron donor.

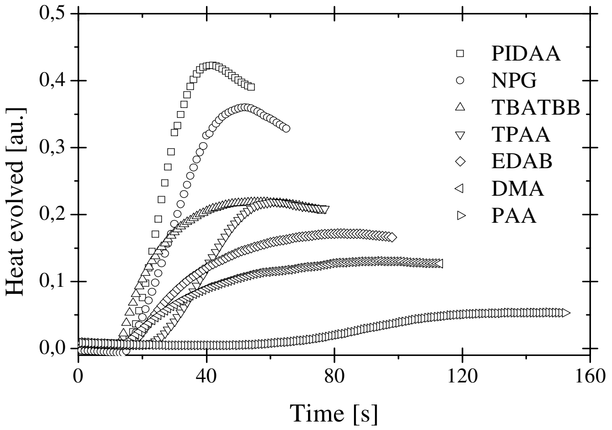


Figure 4. Photopolymerization kinetic traces recorded for an initial time of polymerization. Monomer formulation: TMPTA-MP (9:1). Initiating system: dibenzo[a,c]phenazine (DBP) and various electron donors (0.1 M): N-phenyliminodiacetic acid (PIDAA), N-phenylglycine (NPG), tetrabutylammonium tetrabutylborate (TBATB), thiophenoxyacetic acid (TPAA), ethyl 4-diethylaminobenzoate (EDAB), N,N-dimethylaniline (DMA), phenoxyacetic acid (PAA). Light intensity of an argon-ion laser Innova 90-4 irradiation 5 mW/0.785 cm^2.

Since the tested DBP and DBPQ dyes phosphorescence, one can assume that the reaction of free radical generation involves the excited triplet state. Equation 2 describes the rate of the photoinitiated polymerization for this process.

$$R_p = -\frac{d[M]}{dt} = k_p[M]\sqrt{\frac{I_a\Phi_T}{k_t}} \qquad (2)$$

The symbols in equation 2 have conventional meaning. The equation predicts that the rate of the photoinitiated polymerization depends on the efficiency of an initiator the excited triplet state formation.

The experimental verification of equation 2 requires measuring the 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 [9] 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 [15]. The measured values of quantum yield for triplet state formation oscillate from 0.22 for DBP-NO2 to 0.83 for DBP-Cl2.

Figure 5 presents the relationship between the rates of the photoinitiated polymerization and the square root of quantum yield of the triplet state formation for entire group of the tested dyes.

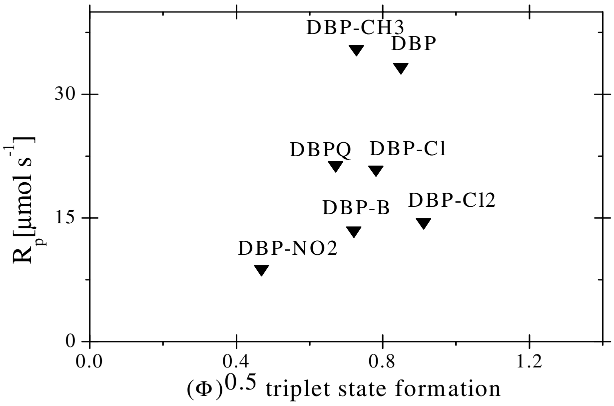


Figure 5. Relationship between the rate of photoinitiated polymerization and square root of quantum yield of triplet state formation. As co-initiator N-phenylglycine was applied.

The results in Figure 5 shows that there is no correlation predicted by equation 2. The luck of correlation between the rate of polymerization and quantum yield of triplet state formation suggests that there is another factor controlling the reaction rate of polymerization. In Pączkowski's earlier studies it was shown that for the photoinitiation process occurring *via* intermolecular electron transfer reaction, one can describe the rate of polymerization by following equation 3 [16].

$$R_p = -\frac{d[M]}{dt} = k_p[M]\sqrt{\frac{I_a k_{el}}{k_t}} \tag{3}$$

The equation 3 predicts that the rate of the polymerization might be, in part, controlled by the rate of photoinduced electron transfer.

The experimental verifications of the equation 3 for the tested photoinitiating systems is possible by measuring the rate of the primary process of the polymerization initiation process, e.g. the rate of the electron transfer between the tested dyes and the electron donors and the comparison of these rates to the rates of photoinitiated polymerization.

The quenching rate constants, k_q (since the quenching of the dyes triplet by the electron donor is the only way of triplet deactivation, therefore under this condition one can assume that $k_q=k_{el}$), were obtained from the experimentally measured pseudo-first-order rate constant, k_{obs}, for the decay of the dyes triplet. Figure 6 presents the relationship between the rates of photoinitiated polymerization and the rate constants of the electron transfer process.

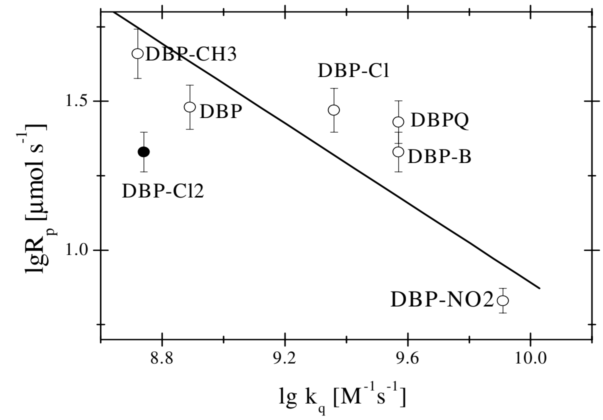


Figure 6. Correlation between the rate constants of electron transfer process and the rates of photoinitiated polymerization. As co-initiator N-phenylglycine was used.

As observed in Figure 6, the relationship is roughly linear. This observation allows concluding that the dyes under the study behave as predicts equation 3. Additionally the relationship presented in Figure 6 suggests that the electron transfer reaction is polymerization rate controlling limiting step.

Conclusion

Photoinitiated by the dyes (DBP and DBPQ) under the study free radical polymerization occurs trough the electron transfer process. The efficiency of the polymerization depends on the structure of the dye. The dyes in the presence of suitable electron donor (co-initiator) are very effective photoinitiators. This can be attributed to the high quantum yield of their triplet state formation and high rate constant of electron transfer reaction. One more important conclusion arises from the analysis presented; that is, the rotation and isomerization around dye C=N bound is the main channel of the dye PQDA excited state deactivation.

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