

Development of new dyeing photoinitiators for free radical polymerization based on 1H-pyrazolo[3,4-b]quinoline skeleton. IV.

Zdzisław Kucybała¹, Barbara Przyjazna¹, Lars-Åke Linden², Jerzy Paczkowski^{1,*}

¹ University of Technology and Agriculture, Faculty of Chemical Technology and Engineering
Seminaryjna 3, 85-326 Bydgoszcz, Poland
e-mail: paczek@atr.bydgoszcz.pl

² Polymer Research Group, Department of Dental Materials, Karolinska Institute,
Box 4064, S-14104 Huddinge (Stockholm), Sweden

Received: 30 June 2000/Revised version: 30 September 2000/Accepted: 10 October 2000

Summary

Several dyes containing 1H-pyrazolo[3,4-b]quinoline skeleton have been synthesized and evaluated as the novel photoinitiators for free radical polymerization induced in the UV region with the argon-ion laser. The kinetic study of photoinitiated polymerization, performed for viscous monomeric formulation with the use of thiophenoxyacetic acid has shown that the tested dyes are good dyeing photoinitiators. The results have shown that there is a linear relationship between the rate of polymerization and the square root of efficiency of the singlet oxygen formation. This finding clearly indicates that the electron transfer process between the tested dyes and electron donors occurs *via* triplet state. 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, firstly, the elimination of the rotational freedom of selected parts of molecule and secondly, to increase the quantum yield of the triplet state formation. The latest was achieved by introducing to the molecule a heavy atom. The tested dyes absorb at the boundary of UV and visible region, therefore they might be considered as the potential photoinitiators for dental application.

Introduction

Research on photopolymerization involves, most commonly, the use of organic photochemistry to initiate polymerization. This process is traditionally initiated by 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, photophysical energy transfer between 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 transfer (PET), which is nonclassical,

* Corresponding author

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. The key steps of the mechanism are the quenching of the chromophore excited either singlet or triplet states by electron transfer mechanism and various steps that follow the primary process. Recently, we described a series of new dyeing photoinitiating photoredox pairs composed of modified photographic dyes acting as the electron acceptor in their either singlet or triplet states and tertiary aromatic amines or N-phenylglycine derivatives serving as the electron donors [1-4]. The modification of the dyes allows obtaining effective initiators for free radical polymerization induced with the argon-ion laser. The dyes tested were prepared in a way that allows, firstly, the elimination of the rotational freedom of selected parts of molecule and secondly, to increase the quantum yield of the triplet state formation. The latest was achieved by introducing to the molecule heavy atoms. The present paper is an extension of this study and describes a new series of the modified photographic dyes absorbing at the boundary of UV and visible area, therefore they are considered as a potential initiating system for dental application.

Experimental

Materials

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

Tested 1H-pyrazolo[3,4-b]quinoline dyes (PQD) were prepared by the sequence of reactions described in Scheme 1. R₁, R₂, and R₃ substituents are specified in Table 1. The crude products of condensations were extracted with n-hexane and purified using preparative thin layer chromatography. Non-planar form of the dye, marked in Scheme 1 as **PCn**, was synthesized according to method described by Danel and Tomasik [5]. The final products were identified by ¹H NMR and ¹³C NMR spectroscopy (see Table 1). The spectra obtained were evidence that the dyes were of the desired structures.

Instruments

Absorption spectra were obtained using a Varian Cary 3E spectrophotometer. Fluorescence spectra were measured using a Hitachi F-4500 spectrofluorimeter. Absorption spectra were recorded for ethyl acetate solution. Both fluorescence and phosphorescence spectra were obtained for 2-methyltetrahydrofuran solutions. The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical MTM (Krakow) Model EA9C-4z 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 were measured on a Hewlett-Packard 5890 or 6890 gas chromatograph fitted with a glass capillary column.

Photoinitiated polymerization

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 2.6×10^{-3} to 3.42×10^{-3} M; concentrations of thiophenoxyacetic acid were also varied from 0.04 M to 0.14 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 using the method described earlier [6]. 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 UV (351 and 363 nm) emission of an Innova 90-4 argon-ion laser, Coherent, USA. The incident light intensity at the sample position was measured with a Coherent Power Meter Type 543-500 mA and was varied from 10 to 30 mW/0.75 cm².

Singlet oxygen formation

The quantum yields of singlet oxygen formation from pyrazoloquinoline dyes were obtained using the actinometric method described by Schaap et al. [7]

Scheme 1

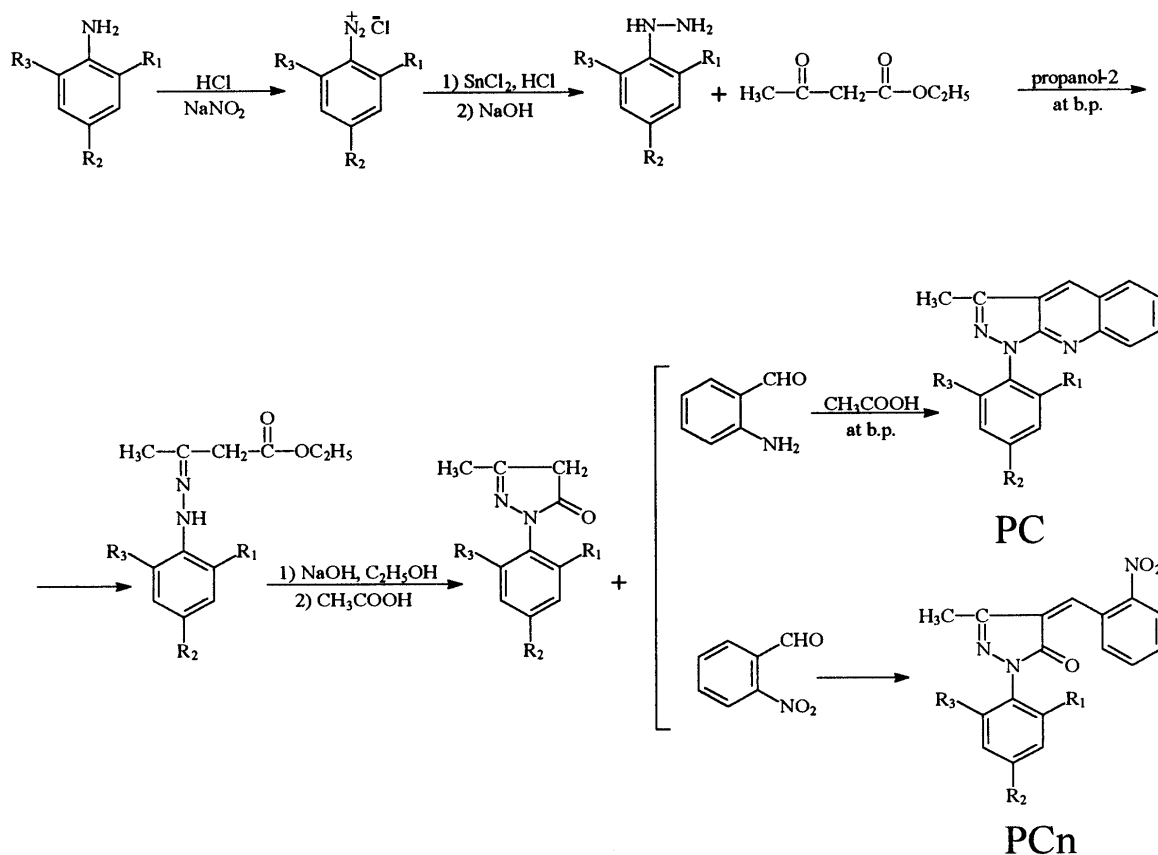


Table 1. Spectroscopic, electrochemical and thermodynamic characteristic of tested dyeing photoinitiators (oxidation potential of thiophenoxy-acetic acid is equal 1.092 V).

No.	PQD Dye (Abbreviation)	R ₁	R ₂	R ₃	λ_{\max} [nm]	m.p. [°C]	¹ H; CH ₃ δ [ppm] in CDCl ₃	¹³ C; CH ₃ δ [ppm] in CDCl ₃	ϵ [dm ³ mol ⁻¹ cm ⁻¹]	ϕ_{FI}	E _{red} [V]	E _T [kJ·mol ⁻¹]	ΔG_{el} [eV]
1	PC-H	H	H	H	379	85-86	2.710	12.641	3400	0.12	-1.175	239	-0.215
2	PC-Cl	H	Cl	H	382	151-153	2.679	12.616	4000	0.26	-1.191	238	-0.187
3	PC-Br	H	Br	H	382	150-151	2.742	12.598	4200	0.27	-1.142	234	-0.190
4	PC-3Br	Br	Br	Br	357 374	214-216	2.780	12.799	5800 5100	0.12	-1.411	245	-0.033
5	PC-3Cl	Cl	Cl	Cl	357 373	202-204	2.776	12.990	5700 5300	0.33	-1.213	232	-0.101
6	PC-OCH ₃	H	OCH ₃	H	397	103-104	2.717 3.862**	12.680 28.839**	4800	0.02	-1.241	238	-0.132
7	PC-NO ₂	H	NO ₂	H	319 353	164-166	2.781*	12.738*	4900 3800	-	-1.081	213	-0.034
8	PCn	H	H	H	430	158-160	2.381	12.891	3000	-	-1.084	-	-

* in DMSO, ** δ values for R₂ = OCH₃

Results and discussion

Spectroscopic, electrochemical and thermodynamic data of new tested dyeing photoinitiators are collected in Table 1. It is apparent from the inspection of these data that the dyes absorb the light at the boundary of UV and visible region. Since the absorption of the dyes is extended up to about 500 nm, one can consider the tested dyes as potentially useful for dental application. The photoinitiation abilities of the dyes were tested using thiophenoxyacetic acid as the electron donor photochemistry of which was clarified in our earlier paper [8]. The measured values of the dyes reduction potentials, the electron donor oxidation potential and the triplet state energy of the dyes, allow one to calculate (using the Rehm-Weller equation [9]) the free energy change for the photoinduced intermolecular electron transfer process. Calculations clearly show that for tested photoredox pairs the electron transfer process is thermodynamically allowed (negative values of ΔG_{et}).

Figure 1 shows the examples of photopolymerization kinetic curves. It is clear from the data presented in Fig. 1 that the photoinitiation capabilities presented by PC-NO₂ and PC-3Br substituted PQDs are comparable and are significantly higher than one recorded for PC-H. A control test showed that the photoinitiation abilities of PC-3Cl, PC-3Br and PC-Cl are comparable to the sensitivity of Rose bengal derivative, RBAX, described by Neckers [10].

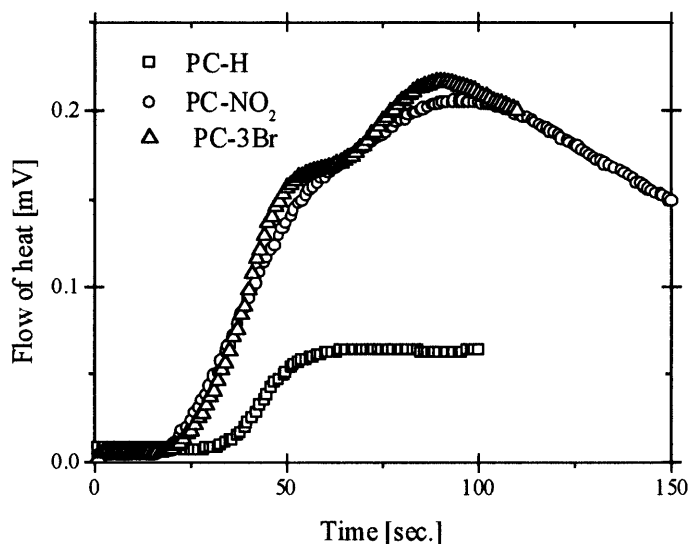


Figure 1. Photopolymerization kinetic curves recorded for novel tested dyes; electron donor: thiophenoxyacetic acid (0.1 M), monomer formulation: 1 mL of MP and 9 mL of TMPTA. Photoinitiating dyes marked in the Figure.

The data presented in Figure 1 and summarized in Table 2 evidently show the influence of the dye structure on their polymerization photoinitiation ability. It is apparent that the influence of the dye structure on their polymerization photoinitiation ability is quite significant.

The dyes tested were prepared in a way that allows firstly, the elimination of the rotational freedom of selected parts of molecule and, secondly, to increase the quantum yield of triplet state formation. The latest was achieved by introducing to the molecule a heavy atom (PC-Cl, PC-Br, PC-3Cl, PC-3Br).

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

Photoinitiating PQD	R_p [$\mu\text{mol}\cdot\text{s}^{-1}$]	$\Phi^1\text{O}_2$
PC-3Cl	19.21	0.56
PC-3Br	16.43	0.58
PC-Cl	15.25	0.43
PC-Br	11.79	0.43
PC-NO ₂	11.54	0.34
PC-H	6.94	0.32
PC-OCH ₃	1.98	0.16
PCn	0.50	0.046

On the basis of the data presented in Table 2 one can conclude that there is a quite significant heavy atom effect on the photoinitiation ability of the tested dyes.

The analysis of the kinetic scheme for photoinduced polymerization *via* an intermolecular electron transfer process has shown [6,11] that for a negligible efficiency of the absorbing chromophore bleaching process (for very low quantum yield of bleaching process, $2I_A\Phi_T k_{el} \gg k_{bl}[D^{\bullet}\dots A^{\bullet}H]$), the following equation can describe the rate of polymerization in viscous media:

$$R_p = k_p [M] \left[\frac{2I_A \Phi_T k_{el} - k_{bl} [D^{\bullet} \dots A^{\bullet} H]}{k_t} \right]^{0.5} \cong k_p [M] \sqrt{\frac{2I_a \Phi_T k_{el}}{k_t}} \quad (1)$$

Here I_A is intensity of absorbed light, Φ_T is the quantum yield of triplet state formation. The rate of free radicals cross-coupling, yielding the dye bleaching products is denoted by k_{bl} , 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 electron transfer. On the basis of equation 1 and the data listed in Table 2, one can suppose that a linear relationship between the rate of photoinitiated polymerization and the square root of quantum yield of singlet oxygen formation should be observed. This is shown in Figure 2. It is clear from the inspection of the data presented in Figure 2 that there is a linear relationship between the rate of polymerization and the square root of efficiency of singlet oxygen formation. This finding clearly indicates that the electron transfer process between the PQDs and electron donor occurs *via* the triplet state of the tested dyes. It is also important to emphasize that the precursor dye (PCn open, non-cyclized structure) displays the lowest

efficiency of both: the photoinitiation ability as well as the efficiency of singlet oxygen formation.

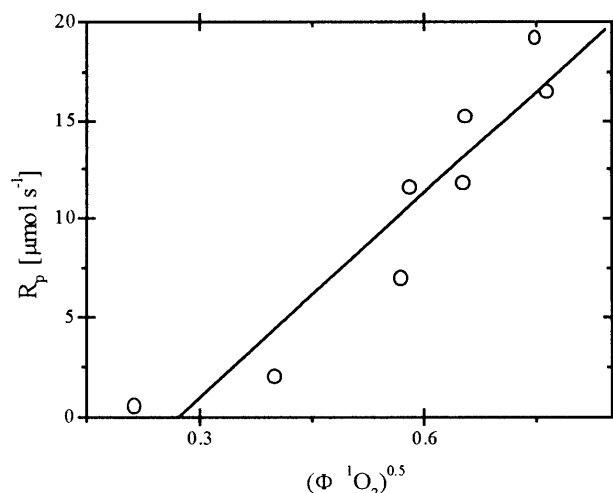


Figure 2. Relationship between the photoinitiated polymerization rate and the square root of the quantum yields of singlet oxygen formation for dyes tested.

This finding apparently shows that the elimination of the rotation of the C=C bond by the coplanarization of the benzylidene 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 alkene bond. This type of molecule modification increases the photoinitiation ability of about one order of magnitude. A similar effect was observed for different types of azomethine dyes described earlier [2,4]. The introduction of chlorine or bromine as heavy atom additionally increases the photoinitiation efficiency by 10 times. The above described behaviors are classical and similar to the properties observed for well-known xanthenes [12].

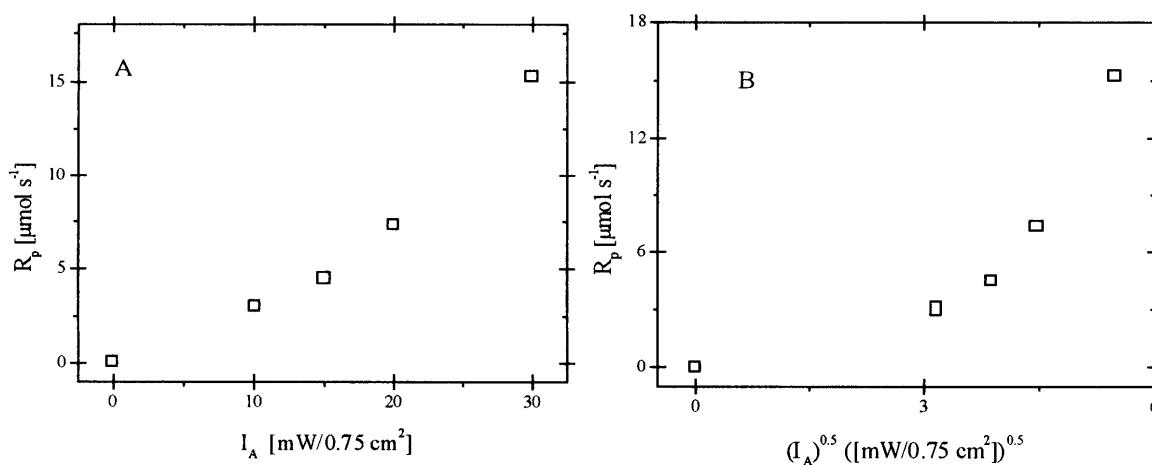


Figure 3. Rate of polymerization versus light intensity for PC-Cl

Photopolymerization initiated by PC-Cl photoredox pair, as is shown in Fig. 3 is not proceeded by conventional mechanism in which bimolecular termination occurs by reaction between two macroradicals. This type of behavior is predicted by equation 1 and

any observed deviation from linearity for relationship $R_p = f([I_a]^{0.5})$ suggests that free radicals formed from PQDs after the photoinduced electron transfer process might in part act as terminators of polymer chains.

Conclusions

Tested 1H-pyrazolo[3,4-b]quinoline dyes (PQD) are, in the presence of the effective electron donor (thiophenoxyacetic acid), good dyeing initiators of free radical polymerization. Photoinitiation ability strongly depends on the structure of the dye. The study on photoinitiated polymerization has shown that there is a linear relationship between the rate of polymerization and the square root of efficiency of the singlet oxygen formation. This finding clearly indicates that the electron transfer process between the tested dyes and electron donors occurs *via* 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. A control showed that the photoinitiation abilities of PC-3Cl, PC-3Br and PC-Cl are comparable to the sensitivity of Rose bengal derivative, RBAX. The dyes tested were prepared in a way that allows, first, the elimination of the rotational freedom of selected parts of molecule and second, to increase the quantum yield of the triplet state formation. The latest was achieved by the introducing to the molecule a heavy atom PC-Cl, PC-3Cl, PC-Br, PC-3Br.

Acknowledgment: This research was sponsored by the State Committee for Scientific Research (KBN), grant No. 3 TO9B 087 15.

References

1. Kucyba ła Z, Paczkowski J (1993) Polymer 34:1558
2. Kucyba ła Z, Pietrzak M, Paczkowski J (1998) Chem. Mater. 10:3555
3. Kucyba ła Z, Paczkowski J (1999) J. Photochem. Photobiol., A: Chem. 128:135
4. Kucyba ła Z, Pyszka I, Paczkowski J (2000) J. Chem. Soc., Perkin 2 1559.
5. Danel A, Tomasik P (1995) Polish J. Chem., 69:1013
6. Paczkowski J, Kucyba ła Z (1995) Macromolecules 28:269
7. Schaap AP, Thayer AL, Blossey EC, Neckers DC (1975) J. Am. Chem. Soc. 97:3741
8. Wrzyszczyński A, Filipiak P, Hug GL, Marciniak B, Paczkowski J (2000) Macromolecules 33:1577
9. Rehm D, Weller A (1969) Ber. Bunsen-Ges. Phys. Chem. 73:834
10. Valdes-Aquilera O, Pathak CP, Shi J, Watson D, Neckers DC (1992) Macromolecules 25:541.
11. Paczkowski J, Pietrzak M, Kucyba ła Z (1996) Macromolecules 29:5057
12. Neckers DC (1989) J. Photochem. Photobiol., A: Chem. 47:1