The dyes containing quinoline or quinoxaline skeleton as effective photoinitiators of free radicals polymerization

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Introduction

Panchromatic sensitization of radical polymerization requires a suitable dye as an absorber of light. Excitation of the dye in the visible area and the transfer of energy from the sensitizer is an inefficient way of creating free radicals because the excitation energy is not sufficient to cause dissociation of most chemical bonds. A different mechanism for generating free radicals, which occurs through the mechanism of photoinduced energy transfer with the transfer of an electron is possible.

It has been reported that the research on photoinitiating radical polymerization occurring *via* the mechanism of intermolecular electron transfer was used in many photoinitiated compositions. These compositions contain the following as an electron acceptor: azomethine dyes, benzylideneimidazopyridine dyes, quinolineimidazopyridine dyes, acridine dyes, thiazine dyes, xanthene dyes, cyanine dyes, camphorquinone, and many others. The composition, as electron donors, derivatives of N-phenylglycine, tertiary amines, alkyl triphenyl borates, compounds containing thioether groups and others were most commonly used [1÷8].

Nevertheless, there is still a need for the search of the new groups of dyes that are an effective photoinitiators of free radical polymerization. In this paper, the new dyes were synthesized and their photoinitiation properties were compared with free radical polymerization dyes obtained by us earlier [5, 8].

Experimental

Substrates used for the preparation of the dyes and electron donors were purchased from Aldrich and Lancaster. Phenoxyacetic acid (PAA), N,N-dimethylaniline (DMA), 2-mercaptobenzoxazole (MBX), 1-methyl-2-pyrrolidinone (MP) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) were purchased from Aldrich. (Phenylthio)acetic acid (PTAA) and tetra-n-butylammonium tetraphenylborate (TBATB) were purchased from Lancaster.

The electron donor: tetramethylammonium n-butyltriphenylborate (TMABTB) was prepared using the procedures described by Damico [9].

Dyes: Quinoline[2,3-b]-1H-imidazo[1,2-a]pyridinium bromide (QIPB) was prepared using the procedure described by us in the work [8]. 6H-indolo[2,3-b]quinoxaline (IQ) and 6-methyl-6H-indolo[2,3-b]quinoxaline (MIQ) were prepared according to the method given by Takekuma and other [10÷13] and 6H-indolo[2,3-b]quinoline (Iq) was synthesized using procedures described in the literature [14-15]. The final products were purified with the use of preparative thin–layer chromatography and identified by ^{1}H NMR, and by measuring the melting temperature.

Absorption spectra were obtained using Shimadzu UV-Vis Multispec-1501 spectrophotometer in ethyl acetate solution. Fluorescence spectra were measured using Hitachi F-4500 spectrofluorimeter. Registration of the fluorescence spectra were carried out in solution of 2-methyltetrahydrofuran at room temperature. The quantum yields of fluorescence was determined by comparison with a standard solution of 9-methylantracene [16] in 2-methyltetahydrofuran. Registration of the phosphorescence spectra was carried out in a solution of 2-methyltetrahydrofuran at liquid nitrogen temperature.

The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical MTM Model EA9C-4z was used for measurements, and Ag-AgCl electrode served as a reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate.
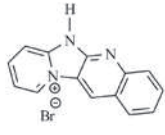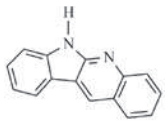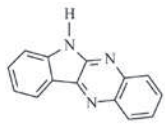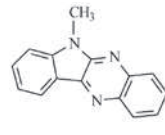
The study of the kinetics of polymerization was carried out using the methodology described earlier [1, 17, 18]. The kinetics of free radical polymerization was studied using a polymerization solution composed of 1 ml of MP and 9 ml of TMPTA. Dye concentrations varied from 2.7×10^{-4} to 1.8×10^{-3} M (depending on the molar absorption coefficient). The concentration of electron donors was 0.1 M. The polymerization mixture was not been deaerated. Irradiation of the polymerization mixture was carried out with the UV emission of Innova 90-4 argon-ion laser (351 and 361 nm lines of a total intensity 38 mW/cm^2). 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 355nm from the third harmonic of the Q-switched Nd:YAG laser from Lambda Physic/model LPY 150 operating at 65mJ/pulse (pulse width about 4-5ns) was used for the excitation.

Results and Discussion

Table 1 shows the structure, spectroscopic and electrochemical properties of the dyes used in the study.

Table 1

Structures and basic spectroscopic, electrochemical properties of tested dyes

Dye	Mark	[a]λ Abs. max	ε	[b]λ FL max	Φ_{Fl}	E_T^{00}	E_{red}
		nm	dm^3 mol^{-1} cm^{-1}	nm		kJ mol^{-1}	V
	QIPB	387 408 432	2610 3040 2360	447 477 511	0.23	228	-1.054
	Iq	316 330 367	14400 20150 3980	406	0.176	235	-0.98
	IQ	334 350 386	14100 16300 4200	465	0.039	227	-1.17
	MIQ	334 351 405	14100 16500 3400	476	0.040	226	-1.18

[a] measured in ethyl acetate
[b] measured in 2-methyltetrahydrofuran

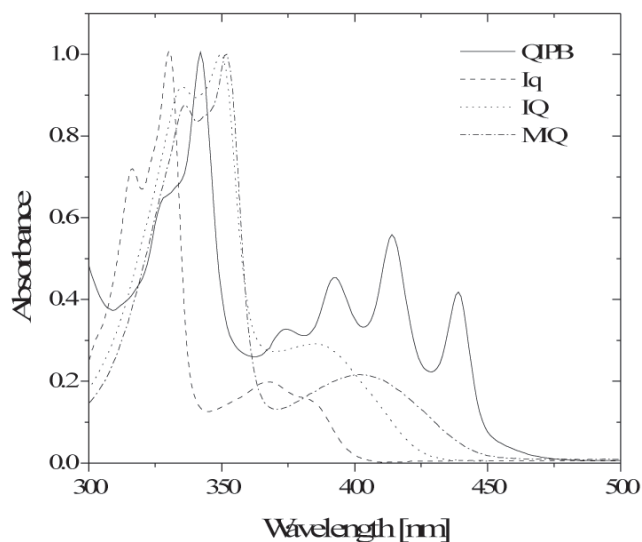Figure 1 shows the electronic absorption spectra of synthesized dyes.

Fig. 1. Electronic absorption spectra of the dyes tested obtained in ethyl acetate solution

The analysis of the electronic absorption spectra clearly indicates that the QIPB dye has spectrum typical for polycyclic aromatic heterocycles with characteristic vibrational structure. Other dyes used in this study have electronic absorption spectra of the intense absorption band located in the 320-350 nm and the other, usually less intense, absorption band shifted by about 35-50 nm. Electron emission spectra of synthesized dyes are shown in Figures 2 and 3.
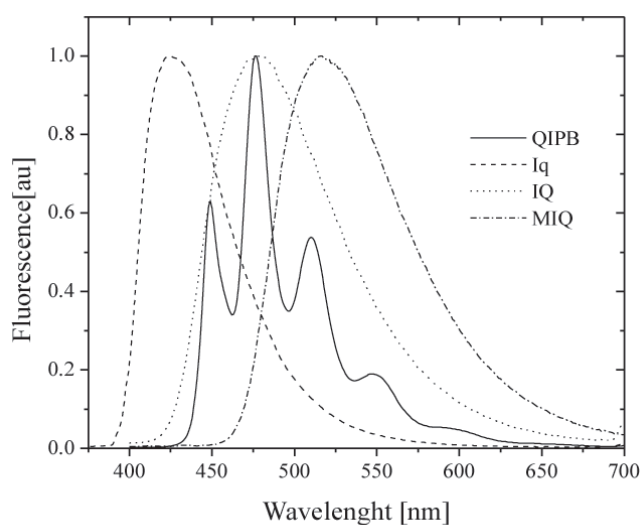

Fig. 2. Emission spectra of tested dyes. Spectra recorded in 2-methyltetrahydrofuran solution

QIPB and Iq dyes exhibit strong fluorescence and the IQ and MIQ emit very weak fluorescence. In 2-methyltetrahydrofuran, at liquid nitrogen temperature, the investigated dyes show phosphorescence, indicating the triplet state formation. The formation of the triplet state can be additionally confirmed by the laser flash photolysis experiments. From the phosphorescence spectra one can calculate the energy of the triplet state transition $T_1 \rightarrow S_0$ (E_T^{00}). The triplet state energy of the synthesized dyes ranges from 2.35 – 2.43 eV (226-235 kJ/mol[1]).

Figures 4 and 5 show examples of kinetic curves recorded during polymerization photoinitiated by tested dyes in the presence of PTAA (Fig. 4) and PAA (Fig. 5) as an electron donor.

The data characterizing the photoinitiation capability of the tested fotoredox pairs is compiled in Table 2. The kinetic curves shown in Figures 4 and 5 and the data in Table 2 show that the photoinitiation capability of free radical polymerization of TMPTA depends on the

structure of the electron acceptor, the quenching rate constant kq and the structure of the electron donor. Synthesized dyes photoinitiated free radical polymerization of TMPTA also *via* the mechanism of intermolecular transfer of hydrogen atom (MBX).
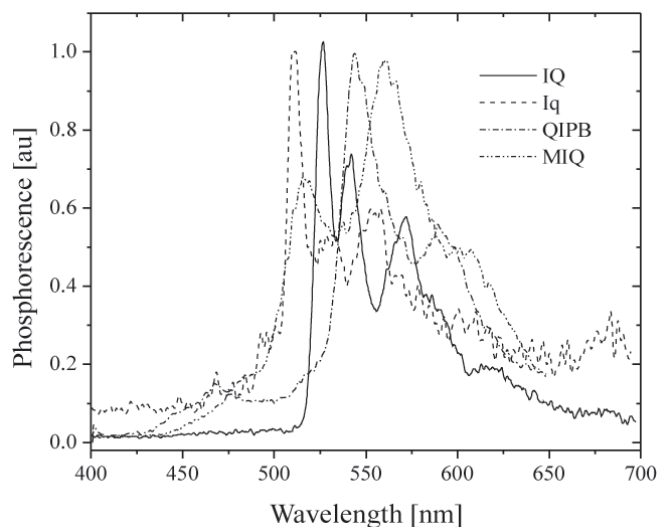

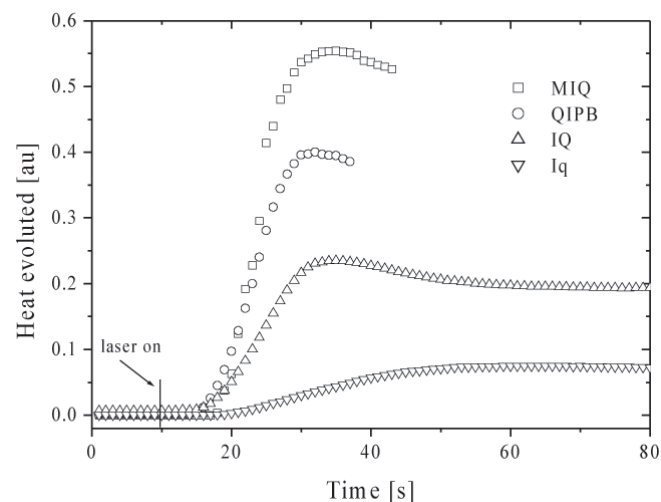**Fig. 3. Emission spectra of tested dyes. Spectra recorded in 2-methyltetrahydrofuran solution**

Fig. 4. Family of kinetic curves recorded during polymerization photoinitiated by tested dyes; electron donor: (Phenylthio)acetic acid (0.1M). Light intensity of argon-ion laser irradiation 38 mW cm⁻²
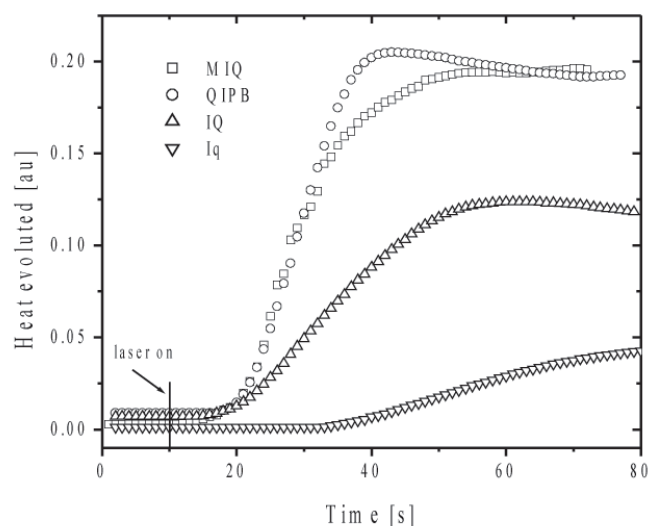

Fig. 5. Family of kinetic curves recorded during polymerization photoinitiated by tested dyes; electron donor: Phenylacetic acid (0.1M). Light intensity of argon-ion laser irradiation 38 mW/cm²

Table 2

Rates of photoinitiated polymerization (R$_p$) and quenching rate constant (k$_q$) for the dyes under the study

Electron donor	MIQ		QIPB		IQ		Iq	
	^{a}R$_p$, μmol/s^1	k$_q$x10^{-8}, M^{-1} s^{-1}	^{a}R$_p$, μmol/s^1	k$_q$x10^{-8}, M^{-1} s^{-1}	^{a}R$_p$, μmol/s^1	k$_q$x10^{-8}, M^{-1} s^{-1}	^{a}R$_p$, μmol/s^1	k$_q$x10^{-8}, M^{-1} s^{-1}
PTAA	78.74	24.71	75.34	25.10	38.40	18.00	6.59	9.66
TMABTB	62.34	17.80	61.26	16.20	21.53	12.30	7.07	6.62
DMA	48.95	7.09	56.04	6.94	24.62	5.92	5.01	3.16
PAA	28.56	2.65	27.01	2.79	9.37	4.61	2.65	2.33
TBATB	12.35	3.21	15.72	2.54	3.95	1.73	2.37	1.65
MBX*	134.06	2.98	113.16	3.36	75.02	3.11	5.78	1.97

^{a} light intensity: 38 mW/cm^2
* hydrogen atom donor

Since the investigated dyes exhibit phosphorescence, it can be assumed that the reaction of free radicals generation involves the excited triplet state. Equation 1 describes the rate of the photoinitiated polymerization for this process.

$$R_p = -\frac{d|M|}{dt} = k_p|M|\sqrt{\frac{I_a \Phi_T}{k_t}} \qquad (1)$$

Equation 1 shows that the rate of photoinitiated polymerization depends on the quantum yield of triplet state formation photoinitiator. The experimental verification of equation 1 requires the designation of the quantum yield of triplet state formation by for example Lament et al. [19]. For this purpose, photoinitiators triplet absorption spectra (Fig. 6) were registered, and from decay curves (Fig. 7) the quantum yield of triplet formation and its lifetime were determined by compiling the results in Table 3.
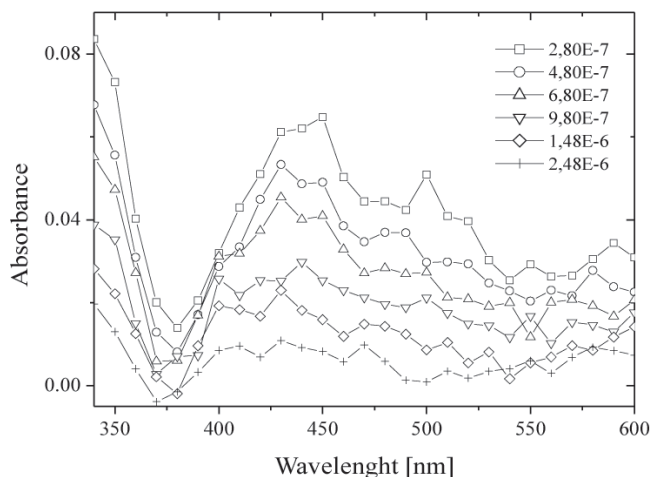

Fig. 6. Time resolved transient absorption spectra of IQ in argon deoxygenated acetonitryle

Table 3

Quantum yield of the triplet state (Φ_T) for the photoinitiators under the study and lifetime of triplet state (τ_T) formation

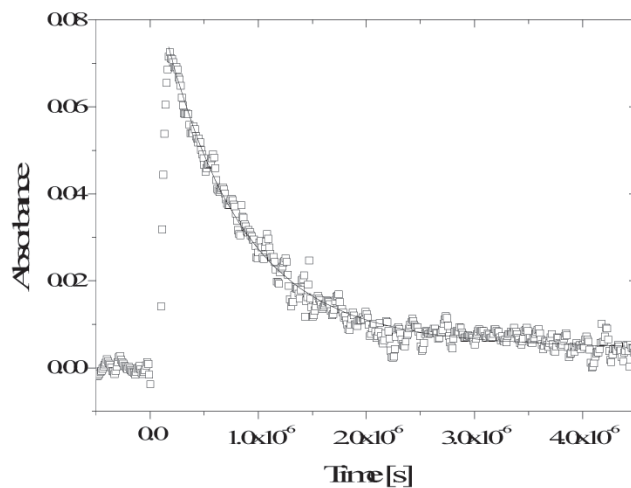| Photoinitiator	Φ_T	τ_T, μs
QIPB	0.293	1.52
IQ	0.210	1.31
Iq	0.124	0.74
MIQ	0.312	1.58

Fig.7. The experimental trace for the decay of the triplet state for IQ

Figure 8 presents the relationship between the rates of the photoinitiated polymerization of TMPTA and the square root of the quantum yield of the excited tryplet state formation for the tested dyes.
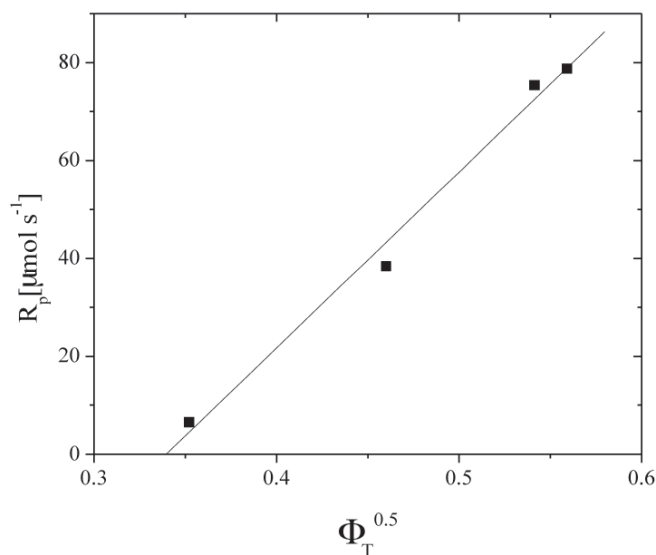

Fig. 8. Relationship between the rate of photoinitiated polymerization and square root of quantum yield of triplet state formation

The linear relationship shown in Figure 8 suggests that the electron transfer process between the dye and electron donor proceeds *via* the excited triplet state of the tested photoinitiators.

The triplet state of tested photoinitiators is effectively quenching the electron donors are used in this work.

The quenching rate constants k$_q$ (Tab. 2), were obtained by monitoring the triplet-triplet absorption decays at fixed wavelengths for various quencher concentrations and by employing the classical Stern-Volmer relation [20] (Fig. 9):

$$k_{obs} = \tau_T^{-1} + k_q[ED] \qquad (2)$$

where k$_q$ – the quenching rate constants, τ_T - the lifetime of the dyes excited triplet state in the absence of an electron donor, [ED] - concentration of electron donor.

If the only way to quench triplet state is by the electron donor, it can be assumed that the quenching rate constant is equal to the rate constant of the electron transfer process.

$$k_q = k_{el} \qquad (3)$$

Figure 10 presents the relationship between the rates of photoinitiated polymerization and the rate constants of the electron transfer process.
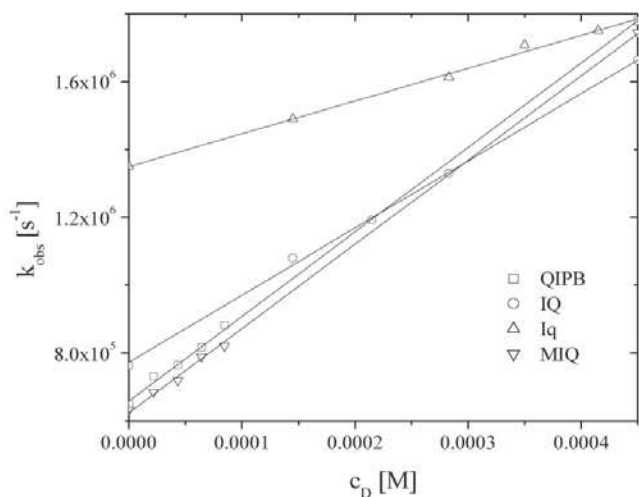
Fig. 9. Plot according to equation 2 for selected dyes triplet quenching. As electron donor (phenylthio)acetic acid was applied
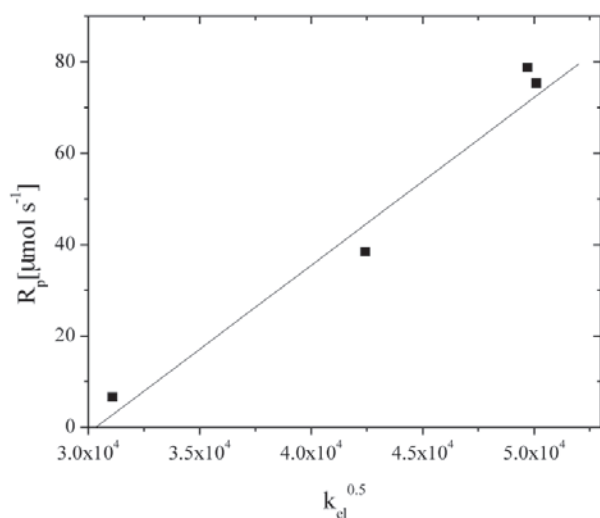

Fig. 10. Relationship between the rate of photoinitiated polymerization and square root of rate constant of electron transfer process

The relationship observed in Figure 10 is linear, which indicates that the limiting process of initial rate of free radical polymerization is an intermolecular electron transfer process.

Summary and conclusions

Photoinitiated by the dyes (MIQ, QIPB, IQ and Iq) under the study free radical polymerization occurs through the electron transfer process (hydrogen atom – MBX). The efficiency of the polymerization depends on the structure of the dye. The dyes in the presence of suitable electron donor (PTAA, TMABTB, DMA) or hydrogen atom donor (MBX) are very effective photoinitiators.

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