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Styryl dyes as new photoinitiators for free radical polymerization

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Abstract

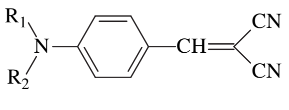
Several disperse and cationic styryl dyes have been synthesized and evaluated for the initiation of free radical polymerization of ethyl acrylate under UV–vis light. The kinetic study of photoinitiated polymerization performed with the use of suitable electron donors such as ethyl 4-*N*,*N*-dimethylaminobenzoate (DMB), phenylthioacetic acid (PhSAc) and phenoxyacetic acid (PhOAc) has proved that tested dyes are good electron acceptors. It has been shown that the intermolecular electron transfer is the limiting step in the photoinitiated polymerization process.

Keywords: Photoinitiator; Photopolymerization; Styryl dyes

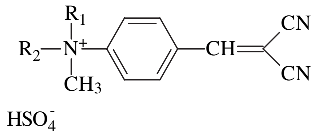
1. Introduction

In recent years photoinitiators operating in the range of the visible light have been developed which is mostly due to a fact that this light is cheap, safe and possesses higher penetration in comparison with UV light [1]. Photoinduced free radical polymerization of multifunctional monomers produces highly crosslinked polymers with high thermal stability, mechanical strength and resistance to organic solvents. These polymers have many industrial applications as coatings for flooring and furniture, dental restorative materials, optical fiber coating, hard and soft contact lenses and photolithography [2]. The photopolymerization can be initiated either by direct UV photolysis of a precursor which provides free radicals by bond decomposition or by panchromatic sensitization which requires the presence of suitable dye as a primary absorber. For this case the process following photoinduced intermolecular electron transfer (PET) yields free radicals initiating the polymerization. Two different types of dye sensitization may be considered. The first one is the photoreducible sensitization in which the dye (xantene, and acridine) is photoreduced in the presence of suitable reductant (*N*-phenylglycine [3], phenylthioacetic acid [4], *n*-alkyltriphenylborane [5]) and the second one is the photo-oxidation of the dye by strong electron acceptor (alkoxypyridinium salt) [6].

It is the intention of our paper to present the study on the styryl disperse **I** and cationic dyes **II** as primary absorbers initiating the polymerization of ethyl acrylate in the presence of electron donors such as ethyl 4-*N*,*N*-dimethylaminobenzoate (DMB), phenylthioacetic acid (PhSAc) and phenoxyacetic acid (PhOAc).



I



II

	R_1	R_2
a	CH_3	CH_3
b	C_2H_5	C_2H_5
c	C_2H_4OH	C_2H_4OH
d	C_2H_5	C_2H_4OH
e	C_2H_5	CH_2Ph

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2. Experimental

2.1. General

Substrates used for the preparation of dyes and chemicals used as electron donors were purchased from Aldrich (Poznan, Poland) and POCh (Gliwice, Poland). The final products were identified by ^{1}H NMR spectroscopy [Bruker Avance DPX 250, $CDCl_3$, TMS, δ (ppm), J (Hz)]. The absorption spectra (ethyl acetate – dyes **I**, DMF – dyes **II**) were recorded using a Perkin–Elmer Lambda 40 spectrophotometer. Fluorescence spectra (ethyl acetate – dyes **I**, DMF – dyes **II**) were recorded using a FluoroLog 3 spectrofluorimeter (Jobin Yvon–Spex). The electrochemical experiments were carried out in DMF and CH_3CN solutions containing 0.1 mol tetra-*n*-butylammonium perchlorate as supporting electrolyte. All solutions were degassed prior to experiments by bubbling with argon. During each experiment a blanket of argon was maintained over the solution. The concentration of the dyes was 1×10^{-3} mol dm^{-3}. In the measurements staircase voltammetry technique (SCV) was used. The experiments were carried out with the use of the potentiostat AUTOLAB (Ecochemie). Working hanging mercury drop electrode (HMDE), platinum auxiliary electrode and ferrocene reference electrode [7] were used. The polymerization was carried out in the solutions composed of 2 cm^3 of 1-methyl-2-pyrrolidone and 4 ml of ethyl acrylate. Dye concentration was 1.43×10^{-4} mol dm^{-3}. The concentration of electron donor was 1.43×10^{-2} mol dm^{-3}. The polymerization was carried out in Rayonet Reactor RPR 200 (The Southern New England Ultraviolet Co.) equipped with eight lamps emitting the light of 350 nm or 419 nm. The rate of polymerization (R_p) was calculated using the formula (1) [8] where Q/s is heat flow per second during reaction, M is the molar mass of the monomer, n is the number of double bonds per monomer molecule and ΔH_p is the theoretical enthalpy for complete conversion of acrylates' double bonds [9].

$$R_p = \frac{Q/sM}{n\Delta H_p m} \qquad (1)$$

For the detection of the heat flow a temperature sensor PT 401 (Elmerton) immersed in the sample was used. The light intensity was measured using the actinometric method described in Ref. [10]. In quantum chemical calculations the geometries of all species were optimized by the AM1 method [11] implemented in the Gaussian 98 suite programs [12].

2.2. Synthesis

The dye **Ic** was synthesized by condensation of *p*-*N*,*N*-diethanolaminebenzaldehyde (4.2 g, 0.02 mol) with malononitrile (1.6 g, 0.002 mol) in toluene (30 cm^3) in the presence of acetic acid (0.3 cm^3) and ammonium acetate (0.1 g) at boiling temperature for 3.5 h [13]. The crude product (3.86 g) precipitated after the evaporation of 15 cm^3 of toluene was recrystallized from ethanol. Yield: 75%, M.p. 128–130 °C [13]. ^{1}H NMR: 1.55 (s, 2H), 3.69 (t, 4H, $J = 7.5$), 3.96 (t, 4H, $J = 7.5$), 6.74 (d, 2H, $J = 10$), 7.53 (s, 1H), 7.90 (d, 2H, $J = 10$).

All other dyes **I** were synthesized according to the same procedure.

The dye **Ic** (0.52 g, 0.002 mol) was converted in **IIc** by heating at 120 °C in dimethyl sulfate (25 cm^3) within 18 h. The excess of dimethyl sulfate was hydrolyzed by heating in water (50 cm^3) at 50–60 °C. After neutralization with 30% NaOH the precipitated product was filtered off and dried. The crude product (0.47 g) was washed with acetone. Yield: 64%. M.p. > 360 °C. The chemical structure of the dye was confirmed indirectly by ^{1}H NMR analysis of its tetraphenylborate salt [14]: 3.29 (s, 8H), 3.37 (s, 5H), 6.80 (t, 4H, $J = 7.0$), 6.91 (t, 8H, $J = 7.3$), 7.14–7.19 (m, 9H), 7.25–7.50 (m, 2H), 7.70–7.85 (m, 1H), 7.98 (s, 1H).

All other dyes **II** were synthesized and identified according to the same procedure.

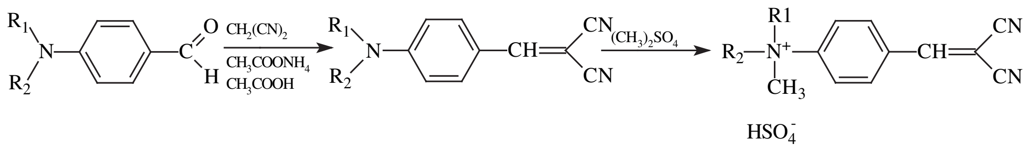
3. Results and discussion

The tested dyes were prepared by condensation of *p*-*N*,*N*-dimethylaminebenzaldehyde derivatives with malononitrile in boiling toluene (dyes **I**), followed by methylation with dimethyl sulfate (dyes **II**) according to Scheme 1.

The disperse dyes **I** were synthesized in 66–88% yield and their structure was confirmed by ^{1}H NMR spectroscopy and by the comparison of their physical properties with literature data [13]. The cationic dyes **II** were obtained in 59–79% yield. Since the solubility of these compounds is very poor in common solvents used in ^{1}H NMR spectroscopy, their structure was confirmed indirectly by ^{1}H NMR analysis of their tetraphenylborate salts. Table 1 summarizes the spectroscopic properties (absorption and fluorescence) of all tested dyes **I** and **II**.

In addition, the electronic absorption (UV–vis) and emission spectrum of selected dyes are presented in Fig. 1A and B.

All disperse dyes **I** have one absorption band in the visible region located approximately at 420 nm and strong emission



I **II**

Scheme 1.

Table 1
Yield, spectroscopic and electrochemical properties of dyes **I** and **II**

Dye	Yield (%)	$\lambda_{max\ abs}$ (nm)	$\lambda_{max\ fl}$ (nm)	E_{red} (V)	EA_s (eV)	EA_t (eV)
Ia	63	424[a]	457[a]	−1.690	2.13	2.95
Ib	88	429[a]	463[a]	−1.533	2.39	2.86
Ic	75	410[a]	448[a]	−1.490	2.33	2.99
Id	79	420[a]	457[a]	−1.675	2.17	3.01
Ie	68	425[a]	469[a]	−1.556	2.16	3.01
IIa	59	347[b]	356[b]	−2.731	5.38	6.15
IIb	79	358[b]	401[b]	−2.722	5.39	6.19
IIc	64	334[b]	444[b]	−2.740	5.22	6.06
IId	61	342[b]	364[b]	−2.769	5.35	6.15
IIe	61	351[b]	434[b]	−2.745	5.27	6.07

[a] Ethyl acetate.
[b] DMF.

band characterized by Stokes shift about 33–44 nm. Although the electronic and emission spectra of disperse dyes **I** and cationic dyes **II** were recorded in solvents with different polarity it is obvious that the absorption of cationic dyes **II** (~350 nm) is always blue shifted when compared with the absorption of their neutral precursors. In addition, they exhibit weak fluorescence in the range 356–444 nm characterized by Stokes shift depending on the structure of the dye. Similarly, the emission of all studied cationic dyes **II** is blue shifted in the comparison with their neutral analogues. Since in the photoreducible sensitization the dye is an electron acceptor [1,15,16], it is expected to have high electron affinity. Quantum chemical calculations of electron affinity (Table 1) proved that neutral and cationic dyes are good electron acceptors, both in the ground (EA_s) and excited state (EA_t) which makes them good candidates for free radical polymerization. In addition, the electrochemical studies (Fig. 2) showed that tested dyes **I** and **II** are reduced in two steps and the cationic dyes have higher reduction potentials than neutral analogues (Table 1).

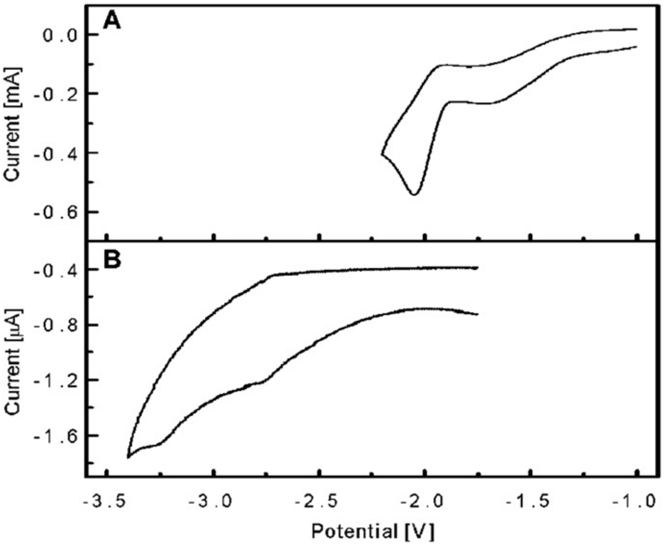


Fig. 2. Cyclic voltammograms of dye **Ia** and **IIa**. Scan rate: 0.1 V s^{-1}.

As electron donors for the photoinitiated free radical polymerization phenylthioacetic acid (PhSAc), phenoxyacetic acid (PhOAc) and ethyl 4-*N*,*N*-dimethylaminobenzoate (DMB) were used. The free energy change for the electron transfer (ΔG^0) between the dye and the electron donor was calculated from Rehm–Weller equation (2) [17]:

$$\Delta G^0_{el} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - Ze^2/\varepsilon_a - E_{00} \tag{2}$$

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 excited state energy and Ze^2/ε_a is the Coulombic energy (negligible with respect to the overall magnitude of the ΔG^0_{el}).

Oxidation potentials of electron donors used were estimated in the separate experiments (see Table 2). Singlet state energy was calculated from Eq. (3):

$$E_{00} = hcN/\lambda \tag{3}$$

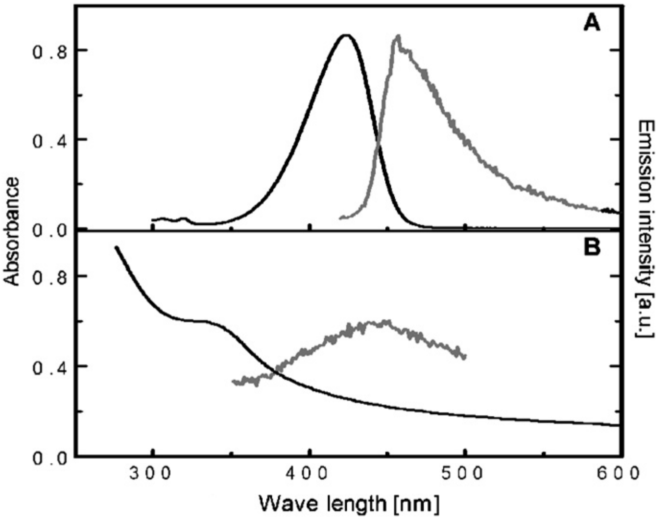


Fig. 1. Absorption and emission spectra of dye **Ia** (A) and **IIc** (B).

Table 2
Thermodynamic properties and rates of polymerization of tested photoredox pairs

Dye	ΔG^0_{el} [a] (eV)	ΔG^0_{el} [b] (eV)	ΔG^0_{el} [c] (eV)	E_{00} (kJ mol^{-1})	R_p [a] (µmol s^{-1})	R_p [b] (µmol s^{-1})	R_p [c] (µmol s^{-1})
Ia	−0.437	−0.546	−0.683	270.9	1.41[d]	1.58[d]	1.54[d]
Ib	−0.563	−0.672	−0.809	267.9	1.50[d]	1.89[d]	1.87[d]
Ic	−0.729	−0.838	−0.975	279.9	1.37[d]	1.67[d]	1.66[d]
Id	−0.484	−0.593	−0.730	274.0	1.48[d]	1.74[d]	1.56[d]
Ie	−0.571	−0.680	−0.817	270.0	1.48[d]	1.68[d]	1.79[d]
IIa	−0.053	−0.162	−0.299	334.3	6.51[e]	5.27[e]	5.91[e]
IIb	0.094	−0.015	−0.152	319.1	15.29[e]	6.30[e]	9.62[e]
IIc	0.130	0.021	−0.116	317.5	13.12[e]	7.74[e]	9.54[e]
IId	−0.015	−0.124	−0.261	334.3	8.16[e]	6.37[e]	6.70[e]
IIe	0.354	0.245	0.108	296.3	11.47[e]	3.62[e]	7.65[e]

[a] With PhSAc (oxidation potential: 0.780 V).
[b] With PhOAc (oxidation potential: 0.671 V).
[c] With DMB (oxidation potential: 0.680 V).
[d] Light (419 nm) intensity = 1.60×10^{17}quant s^{-1}.
[e] Light (350 nm) intensity = 1.58×10^{17}quant s^{-1}.

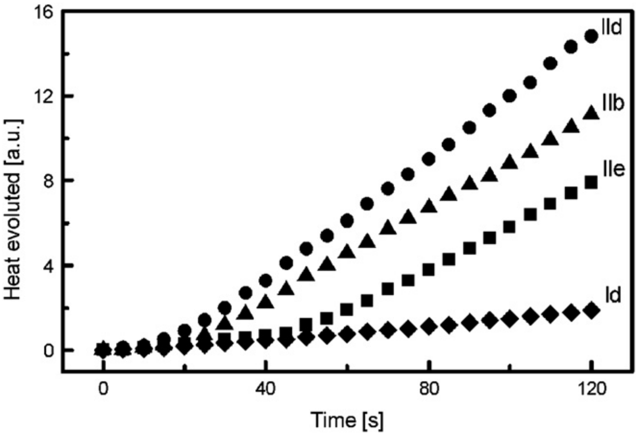


Fig. 3. Photopolymerization kinetic curves of ethyl acrylate recorded for PhSAc and **IId**, **IIb**, **IIe** and **Id**.

where h is Planck constant, c is the speed of light in vacuum (3×10^{17} nm s^{-1}), N is Avogadro constant and λ is the wavelength (nm). The results of ΔG_{el}^0 calculations for all photoredox pairs are reported in Table 2. It is apparent that the free energy change for the electron transfer (G_{el}^0) is in most cases negative which means that the photoinduced intermolecular electron transfer for studied photoredox pairs is thermodynamically allowed. Additionally, it is evident from Figs. 3 and 4 and calculated polymerization rate (Table 2) that the efficiency of polymerization strongly depends on the type of electron donor and on the structure of the dye.

It is apparent that the cationic dyes **II** combined with PhSAc are the most effective photoredox pairs initiating the polymerization of ethyl acrylate. The detailed revision of the data presented in Table 2 indicates that the rate of polymerization might be a function of the rate of the primary process, *e.g.* the rate of electron transfer within the photoredox pair. The relationship between the logarithm of the rate of polymerization ($\ln R_{\mathrm{p}}$) and the free energy change shown in Fig. 5 supports this mechanism.

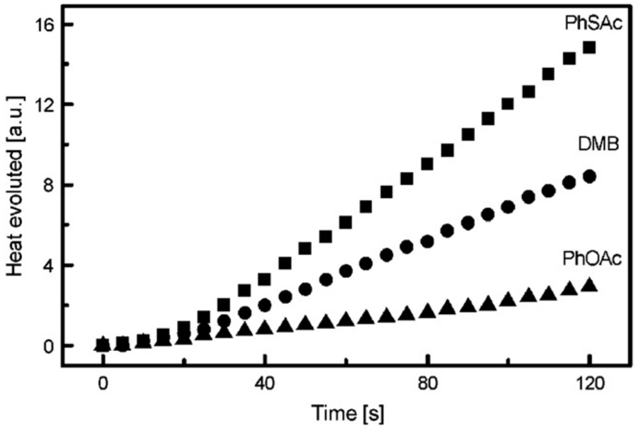


Fig. 4. Photopolymerization kinetic curves of ethyl acrylate recorded for dye **IIb** and PhSAc, PhOAc and DMB.

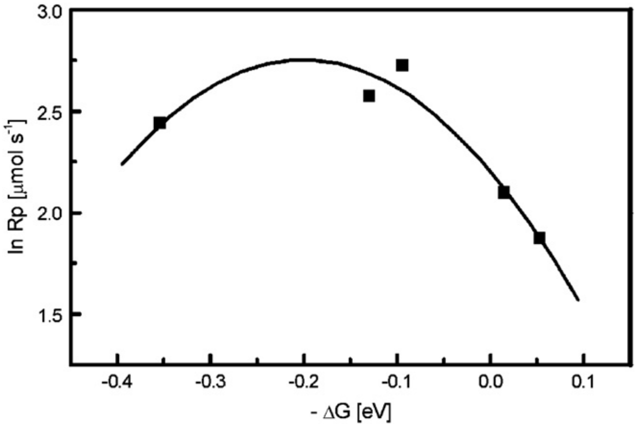


Fig. 5. Relationship between the rate of photoinduced polymerization and the free energy change of the electron transfer process for dyes **II** – PhSAc photoredox pairs.

4. Conclusions

The cationic styryl dyes are good photoinitiators of free radical polymerization in the presence of the effective electron donor such as phenylthioacetic acid. The photoinitiation ability strongly depends on the chemical structure of the dye and on the electron donor, as well. Styryl dyes have high electron affinity. They participate in the photoreducible sensitization and the limiting step in the photoinitiated polymerization is an electron transfer within photoredox pair.

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