

Multicationic styrylpyridinium dyes as sensitizers in photoinitiating systems of TMPTA radical polymerization

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1. Introduction

Photoinitiated polymerization is the basis for many applications in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics. Almost all of the commercially significant photoinitiators are organic compounds that produce free radicals and/or cationic species upon irradiation. The most widely used free radical photoinitiators include benzoin and its derivatives, benzyl ketals, acetophenone derivatives, aromatic ketone/amine combinations, while onium salts belonging to iodonium, sulphonium and alkoxy pyridinium families represent a class of cationic photoinitiators [1 ÷ 7].

The process of polymerization may be initiated by direct photolysis of a precursor providing free radicals by bond dissociation, or the radicals may be formed in bimolecular processes. Panchromatic sensitization of polymerization often requires the presence of a suitable dye as a primary absorber. This can either transfer energy, or undergo electron transfer [1, 4, 6].

Photoinduced intermolecular electron (PET) transfer uses light to initiate electron transfer from a donor to an acceptor molecule. The process is possible because electronically excited states are both better oxidants and better reductants than their ground states equivalents [6].

Considering the interaction between the chromophore and an electron donor in the ground state and after electron transfer process, dye photoinitiators can be classified in three different groups [6]:

1. Donor-acceptor pairs with electrostatic interaction in the ground state (ground state ion-pair) but neutral after the photoinduced electron transfer process
2. Donor-acceptor pairs without electrostatic interaction in the ground state and, after electron transfer; at least one component that is neutral in the ground state and after electron transfer
3. Donor-acceptor pairs that are neutral in the ground state and charged after electron transfer. In this case, the resulting product is a radical ion pair.

There have been a number 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 [2], a wide group of fluorone dyes [8], cyanine dyes [9, 10], pyrene [11], safranin T [12], dyes based on quinaxolin-2-one residue [13] and many others [5]. It is necessary to emphasize that the research related to the photochemistry of dye sensitizing photoinitiators is mostly focused on the development of new primary light absorbers that can either extend the range of light absorption or increase the efficiency of the photoinitiation process.

In present work we described the photoinitiating ability of different hemicyanine dyes (the light absorbers) coupled with *n*-butyltriphenylborate anion (co-initiator). The structures of the light absorbers used in our studies are presented in Scheme 1.

2. Experimental

2.1. Materials

Monomer, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), all chemicals and solvents were purchased from

Aldrich Chemical Co. and were used without further purification. As sensitizers four cationic styrylpyridinium derivatives were used. The tetramethylammonium *n*-butyltriphenylborate (B2) was applied as a co-initiator (an electron donor).

2.2. Techniques

2.2.1. Spectral Measurements

Absorption and emission spectra in *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were recorded at room temperature using a Shimadzu UV-vis Multispec-1501 spectrophotometer and a Hitachi F-4500 spectrofluorimeter, respectively.

2.2.2. Electrochemical Measurements

The reduction potentials of the dyes were measured by cyclic voltammetry using an Electroanalytical Cypress System Model CS-1090. The typical three-electrode setup was employed for electrochemical measurements. The electrolyte was 0.1 M tetrabutylammonium perchlorate, which was purged with argon prior to a measurement. Platinum 1-mm electrode was applied as working electrode and platinum and Ag/AgCl were used as auxiliary and reference electrodes, respectively.

2.2.3. Polymerization Measurements

The kinetics of free radical polymerization were studied using a polymerization solution composed of 0.1 ml of 1-methyl-2-pyrrolidinone (MP) and 0.9 ml of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The hemicyanine borate salts (photoinitiator) concentration was 0.0005 M. A reference formulation contained hemicyanine iodide or bromide (dye without an electron donor) instead of borate salt (photoinitiator). The measurements were carried out at an ambient temperature and the polymerizing mixture was not deaerated before curing.

The kinetics of free radical polymerization were measured based on the measurements of the rate of the heat evolution during polymerization in thin film cured sample (0.035 ± 0.002 g). The measurements were performed by measuring photo polymerization exotherms using photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. Irradiation of the polymerization mixture was carried out using the emission (line at 514 nm) of an argon ion laser Model Melles Griot 43 series with intensity of light of 100 mW/cm². The light intensity was measured by a Coherent Model Fieldmaster power meter.

The rate of polymerization (R_p) was calculated using the formula (1) where dH/dt is maximal heat flow during reaction and ΔH_p^{theor} is the theoretical enthalpy for complete conversion of of acrylates' double bonds. ΔH_p^{theor} for acrylic double bond is equal 78.2 kJ/mol [27].

$$R_p = \left(\frac{dH}{dt} \right) \frac{1}{\Delta H_p^{theor}} \quad (1)$$

The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups reacting in the system.

By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to eq. 2.

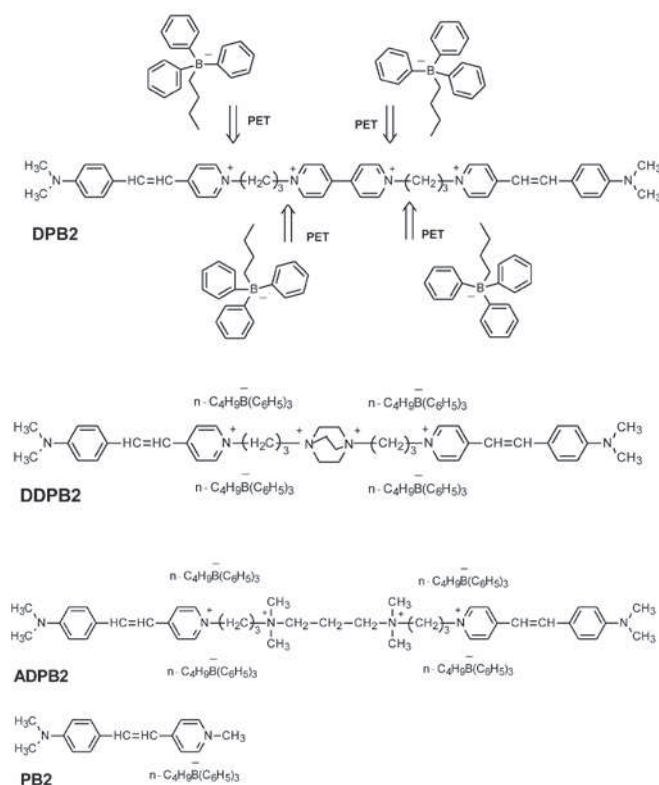
$$C = \frac{\Delta H_t \cdot M}{n \Delta H_p^{theor} \cdot m} \quad (2)$$

where ΔH_t is the reaction heat evolved at time t , M is the molar mass of the monomer, m is the mass of the sample and n is the number of double bonds per monomer molecule.

The quantum yield of polymerization Φ_p was defined as the number of polymerized double bonds per absorbed photon [28].

3. Results and discussion

For the analysis of the photoinitiating properties of novel photoredox pairs, the selected combinations of *n*-butyltriphenylborate and mono- and four-cationic hemicyanine dyes, were used. The structures of the salts under the study are shown in Scheme 1.



Scheme 1. Structures of the photoredox pairs tested as photoinitiators

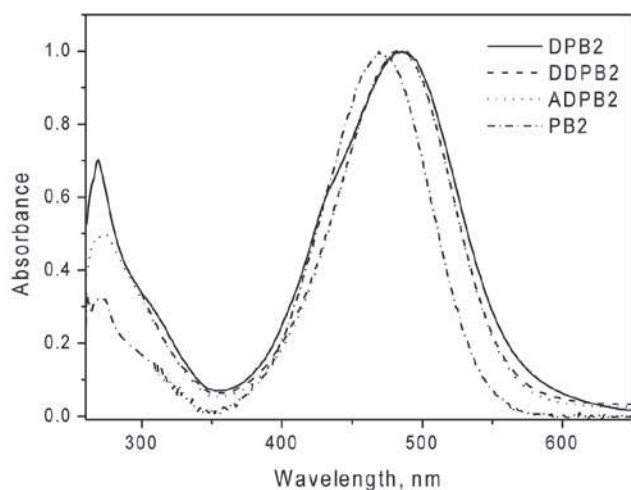


Fig. 1. Normalized absorption spectra of selected hemicyanine dyes (marked in Figure) in DMF

In our studies polymerization of TMPTA photoinitiated by mono- and four-cationic hemicyanine borate salts were performed under irradiation at 514 nm, e.g. at the wavelengths where the light is absorbed by cyanine cation (Fig. 1).

In order to optimize a photoinitiation mixture composition, at the beginning, the cyanine borate concentration effect on the rate of polymerization was determined. It is well known that the photoinitiator concentration plays a key role in the photopolymerization. In the conventional UV/Vis photopolymerization, R_p increases when more initiator is used, however it decreases rapidly if too much initiator is added. This effect is rendered to the "inter filter effect" and becomes more significant for photoinitiators with high molar extinction coefficient (for tested dyes ϵ is about $50\,000\text{ M}^{-1}\text{cm}^{-1}$) [14, 15]. Figure 2 presents the relationship between the rate of polymerization and concentration of photoinitiator.

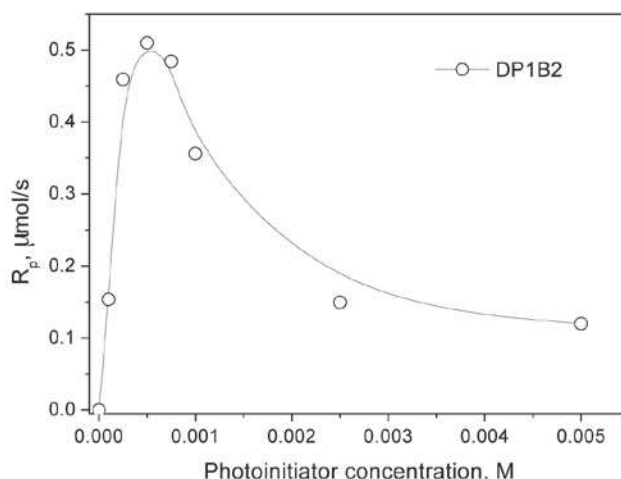


Fig. 2. Rate of polymerization vs. photoinitiator concentration

It is evident that as the photoinitiator concentration is increasing, the rate of polymerization increases and reaches a maximum followed by continuous mild decrease. For the tested photoinitiators, under experimental conditions, the highest rate of polymerization was achieved at the initiator concentrations of about $5 \times 10^{-4}\text{ M}$. The reduction of the photoinitiated polymerization rate at higher initiator concentration (for applied technique of polymerization rate measurement) can be easily understood taking into account the decrease of the penetration depth of the laser beam across the polymerizing formulation layer. Thus, all kinetic measurements for the hemicyanine borate salts were carried out at concentration equal $5 \times 10^{-4}\text{ M}$.

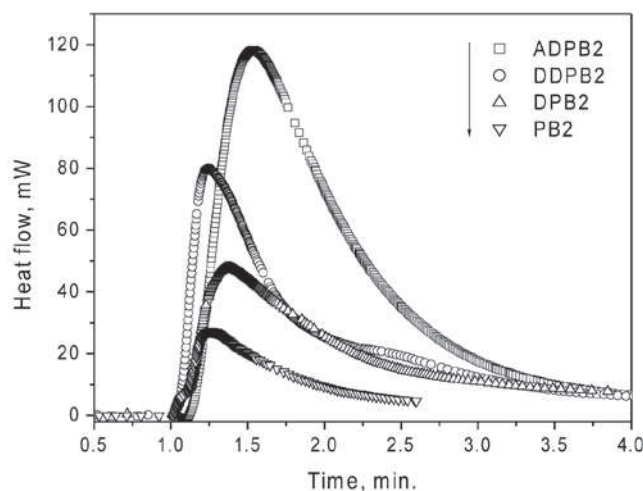


Fig. 3. Family of curves recorded during the measurements of heat flow during the photoinitiated polymerization of the TMPTA-MP (9:1) mixture initiated by hemicyanine borates. The dye concentration was $5 \times 10^{-4}\text{ M}$ and $I_a = 100\text{ mW/cm}^2$. The applied pairs possess various chromophores and identical borates (*n*-butyltriphenylborate)

Figure 3 presents typical kinetics curves observed during an argon-laser initiated polymerization of the solution composed of 0.1 ml of 1-methyl-2-pyrrolidinone (MP), 0.9 ml of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and initiating hemicyanine borate salts with concentration of 5×10^{-4} M. The rates of TMPTA polymerization photoinitiated by the photoredox pairs are collected in Table 1.

The analysis of the rates of polymerization shows that the photoinitiation efficiency of tested initiators depends on the structure of hemicyanine borate photoredox pair. It is obvious that four-cationic photoinitiators initiate the polymerization with higher rate. It is connected with the artificial increase of an electron donor concentration in close proximity to the excited chromophore [16, 17].

From the data, obtained during the measurements, it was deduced that the conversion of monomer is ranging from 4.2% to 26.4%, while the quantum yields of photopolymerization oscillates between 4.06 and 20.08 (Tab. 1) for the all photoinitiating pairs tested. It is noteworthy that the ion pair ADPB2 shows the best photoinitiation ability.

Table 1

Basic electrochemical and thermodynamical data, rates of polymerization, degree of monomer conversion and quantum yields of polymerization for tested novel hemicyanine borates

Dye	$E_{\text{red}}(\text{A}^-/\text{A})$ (V)	E_{00} (eV) ^a	ΔG_{el} (eV) ^b	R_p ($\mu\text{mol/s}$)	Φ_p	Monomer conversion (%)
DPB2	-0.27	2.16	-0.749	0.61	7.05	12.70
DDPB2	-0.42	2.27	-0.711	1.02	11.91	17.80
ADPB2	-0.40	2.27	-0.730	1.73	20.08	26.40
PB2	-0.41	2.30	-0.757	0.35	4.06	4.20

^a Measured in tetrahydrofuran (THF).

^b Calculated using the Rehm-Weller equation: $E_{\text{ox}}(\text{D}/\text{D}^{+\cdot}) = 1.14 \text{ V}$.

The free energy change (ΔG_{el}) for the electron transfer process between hemicyanine cation and borate anion was calculate based on the Rehm-Weller equation (Eq. 3) [18].

$$\Delta G_{\text{el}} = E_{\text{ox}}(\text{D}/\text{D}^{+\cdot}) - E_{\text{red}}(\text{A}^-/\text{A}) - Ze^2/\epsilon a - E_{00} \quad (3)$$

where $E_{\text{ox}}(\text{D}/\text{D}^{+\cdot})$ is the oxidation potential of the electron donor, $E_{\text{red}}(\text{A}^-/\text{A})$ is the reduction potential of the electron acceptor, E_{00} is the excited state energy, and $Ze^2/\epsilon a$ is the Coulombic energy, which for products of analyzed reaction is considered negligible with respect to the overall magnitude of the ΔG_{el} .

Negative values of ΔG_{el} indicate that for all combinations of hemicyanine borate pairs the electron transfer reaction yielding free radicals is thermodynamically allowed.

4. Conclusions

Photoinitiated by hemicyanine borate pairs polymerization occurs through the electron transfer process. The efficiency of the polymerization significantly depends on the structure of the hemicyanine cation used as an electron acceptor.

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