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Diazobenzo[a]fluorene derivatives as visible photosensitizers for cationic polymerization

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ABSTRACT

Photoredox pairs consisting of dyes based on diazobenzo[a]fluorene derivatives and commercially available onium salts (diaryliodonium and triphenylsulfonium salts) are tested as effective initiator systems for the cationic polymerization of cyclohexene oxide using visible light. The efficiency of these initiator systems is discussed based on the free energy change for the electron transfer from examined dyes to the onium compounds. The most efficient sensitizers are the dyes with the lowest oxidation potential and the highest $-\Delta G_{el}$. A linear relationship between the quantum yields of acid release $\Phi(H^+)$ and the conversion of CHO is observed.

1. Introduction

Light-induced photopolymerization has received considerable attention due to its numerous advantages including rapid curing at ambient temperatures and independence from solvents. These advantages have led to many important applications such as composite production, prototyping, coatings, adhesives, inks and electronics [1–4]. Cationic polymerization has several advantages over free radical processes. It may be used to polymerize important classes of monomers such as epoxides and vinyl ethers, which exhibit relatively low viscosity and toxicity, lower shrinkage upon curing, high mechanical performance and good adhesion [5]. Additionally, cationic curing of epoxides exhibits so-called dark-curing behavior in which the monomer continues to react slowly after the irradiation has ceased, progressively penetrating into areas inaccessible to the radiation source. Many early radiation-based systems for initiating cationic polymerization reactions act in response to UV light. During such reactions, the photoinitiators are directly fragmented into free radicals, cationic fragments and radical cation fragments (Scheme 1). The aryl cations and aryliodine radical cations generated from photolysis further react with the solvent molecules or monomers to generate a strong protic acid, H^+Y^-. This acid then initiates the polymerization of the monomers [6].

Onium salts used in cationic polymerization usually absorb within the range of 225–350 nm. To improve their spectral sensitivity to visible light, photosensitizers (Dye) applied with the onium salts have been proposed. Among the mechanisms by which the photosensitization of diaryliodonium [7] and triphenylsulfonium [8] salts is known to take place, electron transfer photosensitization is the most efficient and generally applicable process. This process involves absorption of light by the photosensitizer (Dye) to give the photo-excited sensitizer (Dye*) which is oxidized by the salt ($Ar-I^+-Ar$) to form a corresponding radical cation ($Dye^{\bullet+}$) and iodonium salt radical ($Ar-I-Ar^\bullet$) (Scheme 2). The radical cations ($Dye^{\bullet+}$) may initiate the cationic polymerization of the epoxide monomer. Alternatively, they may react with solvents or monomers resulting in the release of a strong protic acid which can also initiate cationic polymerization.

New initiating systems for cationic polymerizations effective over the long-wavelength UV and visible regions (430–490 nm) are subjects of intense study due to the increasing drive for the application of environmentally friendly technologies in areas such as imaging (stereolithography, printing, electronic transmission) and medicine (photocurable dental fillings and restoratives) in which lasers and light-emitting diodes are used as a light sources. There

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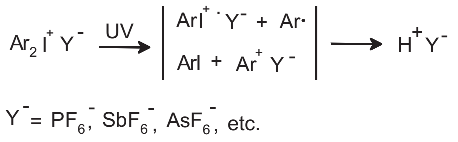
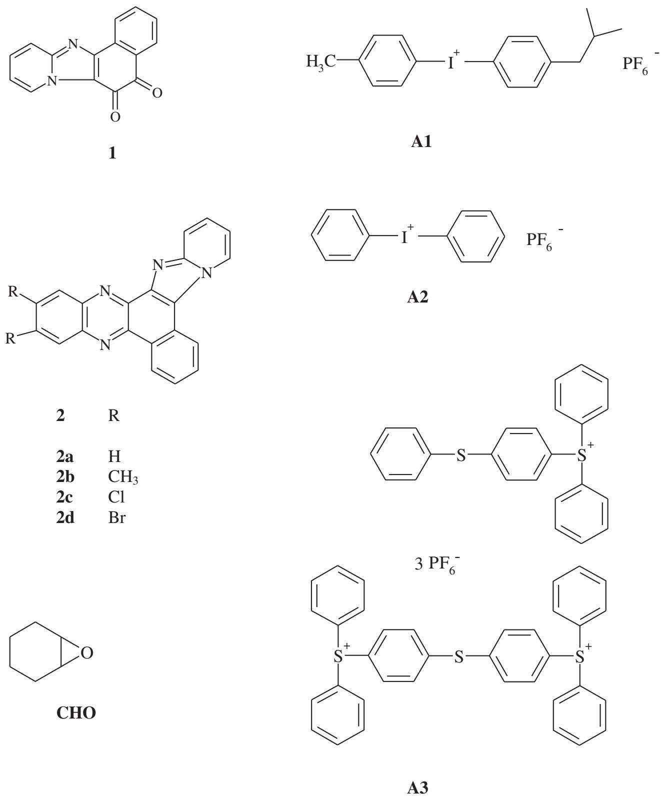


Scheme 1. Direct photolysis of iodonium salts.

are very few visible wavelength initiator systems available for cationic polymerization. This type of polymerization can be initiated by perylene [9], coumarin [10], curcumin [11], quinoxaline derivatives [12–14], benzophenothiazine and benzophenoxazine [15] or dithienothiophene derivatives [16] in the presence of appropriate onium salts that act as initiators.

In a previous paper [17], we presented the synthesis, spectroscopic and electrochemical properties of dyes **1** and **2**, which were used for the free radical polymerization of acrylates. It is the intention of this study to present the application of dyes **1** and **2** as photosensitizers for cationic polymerization. These dyes are combined with onium salts such as diphenyliodonium hexafluorophosphate (**A1**), Irgacure 250 (**A2**) and triarylsulfonium hexafluorophosphate (**A3**) to create visible photoinitiation systems. This paper also reports on the proton formation during photolysis of iodonium/sulfonium and diazobenzo[a]fluorene systems. Cyclohexene oxide (CHO) is chosen as the epoxide because it is widely applied as a monomer for cationic polymerization. The structure of the studied dyes, initiators and monomer are presented in Scheme 3.



Scheme 3. Structures of the studied dyes, initiators and monomer.

2. Experimental

2.1. General

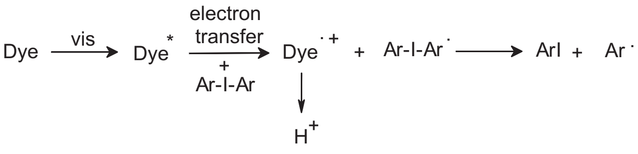
The dye-preparation procedure has been previously described [17]. The **A2** (Irgacure 250) salt was obtained from CIBA (Lodz, Poland). The **A1**, **A3** and CHO were purchased from Sigma–Aldrich (Poznan, Poland).

2.2. Photochemical experiments

In the photochemical experiments, a xenon lamp (Optel ZX 500 W, Poland) and a Rayonet photochemical reactor RPR-200 (Southern New England Ultraviolet Co., USA) equipped with eight lamps emitting light at 419 nm were used as the light source for dyes **2a**–**2d** and **1**, respectively. The specific wavelength of the xenon lamp was isolated with the application of a bandpass light filter (450 ± 10 nm). The xenon lamp and Rayonet reactor light intensities were measured using the potassium ferrioxalate $[K_3Fe(C_2O_4)_3 \times 3H_2O]$ actinometric method [18] and uranyl oxalate actinometry [19], respectively. A cationic polymerization of CHO (5 ml) was carried out under an ambient atmosphere and under a N_2 atmosphere using a specific time of exposure to the irradiation. The dye concentration was maintained at 0.1 mM and the concentration of the electron acceptors **A1**–**A3** was 10 mM. The resulting solution was poured into 50 ml methanol containing approximately 1 ml NH_3 (30%). The precipitated polymers were isolated by filtration, washed intensively with methanol from monomer, and dried for 2 h in a vacuum oven at 68 °C. The conversion of the monomers into polymers was then determined gravimetrically according to Eq. (1) as follows:

$$\% = \left(\frac{m_p}{m_m}\right) \times 100 \tag{1}$$

in which m_p is the mass of polymer obtained, and m_m is the mass of the monomer used in the polymerization. The quantum yield of the sensitized proton formation, $\Phi(H^+)$, under ambient atmosphere was determined using the sodium salt of bromophenol blue (**BPhBl**), which demonstrated a vanishing peak absorbance at approximately 600 nm during irradiation. The proton concentration was estimated from the calibration curve of the **BPhBl** optical density vs. that of water-free hexafluoroantimonic acid. The $\Phi(H^+)$ value was calculated using reactions that were 15 ± 5% complete.



Scheme 2. Photosensitization of iodonium salts.

Table 1
Thermodynamic properties of the tested photoredox pairs.

Dye[a]		A1	A2	A3
	E_{ox} [V] [15]	ΔG_{el} [kJ mol^{-1}]	ΔG_{el} [kJ mol^{-1}]	ΔG_{el} [kJ mol^{-1}]
2a	1.22	−63.90	−72.15	−37.23
2b	1.23	−67.77	−76.01	−41.09
2c	1.29	−51.70	−59.95	−25.03
2d	1.34	−54.04	−62.29	−27.37

A1 (E_{red}: −0.725 V) [20]; **A2** (E_{red}: −0.64 V) [21]; **A3** (E_{red}: −1.0 V) [21].

[a] In the case of **1**, the ΔG^0_{el} was not calculated because of a lack of measurable oxidation potential.