Dyes and Pigments 95 (2012) 74–78

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

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

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ARTICLE INFO

Article history:
Received 3 January 2012
Received in revised form
12 March 2012
Accepted 14 March 2012
Available online 5 April 2012

Keywords:
Cationic polymerization
Quantum yields of acid release
Diazobenzo[a]fluorene dyes
Onium salts
Electron transfer process
Cyclohexene oxide

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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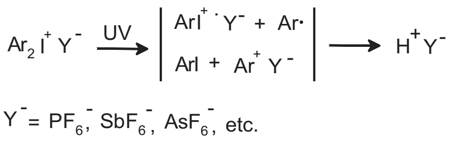
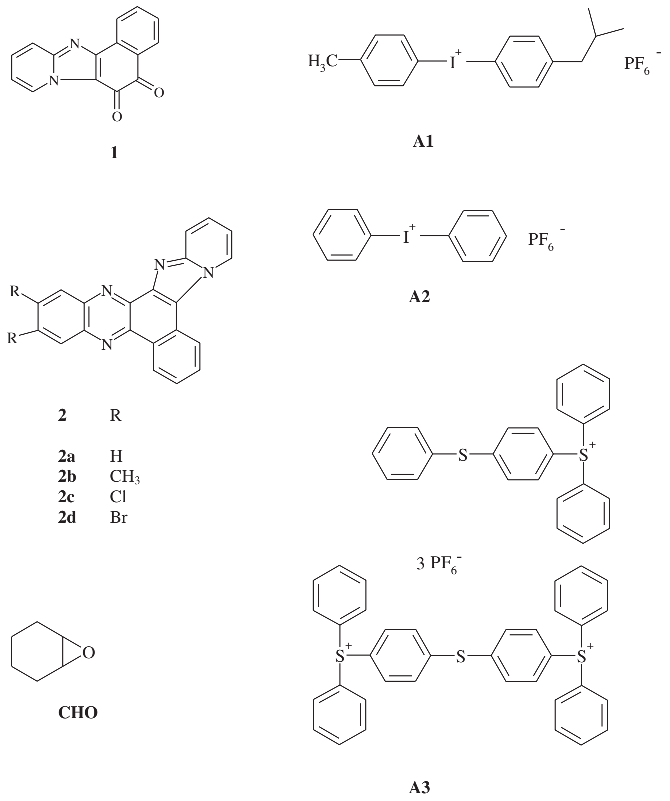
doi:10.1016/j.dyepig.2012.03.016



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.

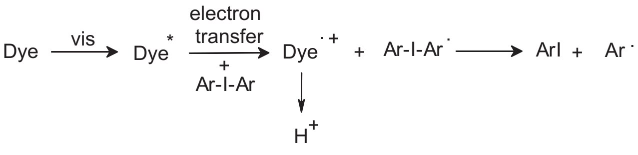
2. Experimental

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:



Scheme 2. Photosensitization of iodonium salts.

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

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.

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.

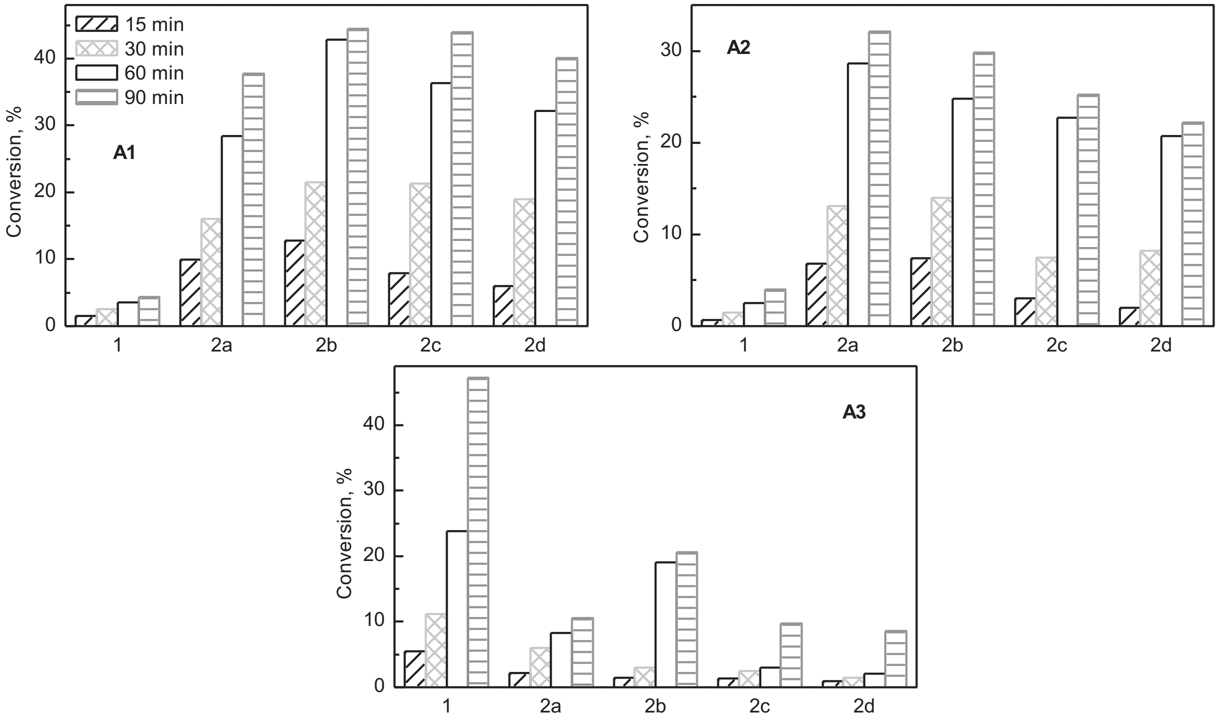


Fig. 1. Conversion of CHO under ambient atmosphere.

3. Results and discussion

3.1. Sensitized cationic polymerization

Onium salts are known to be efficient photoinitiators of cationic polymerization, but unfortunately, they absorb in the UV region. To extend their spectral sensitivity to visible light, the systems based on diazobenzo[a]fluorene derivatives **1** and **2** are used. As we reported in our previous paper [17] these dyes, with the exception of **1**, absorb in the region of 426–467 nm in CHO having a reasonable molar extinction coefficients that make them prime candidates for applications as sensitizers for the collection of light above

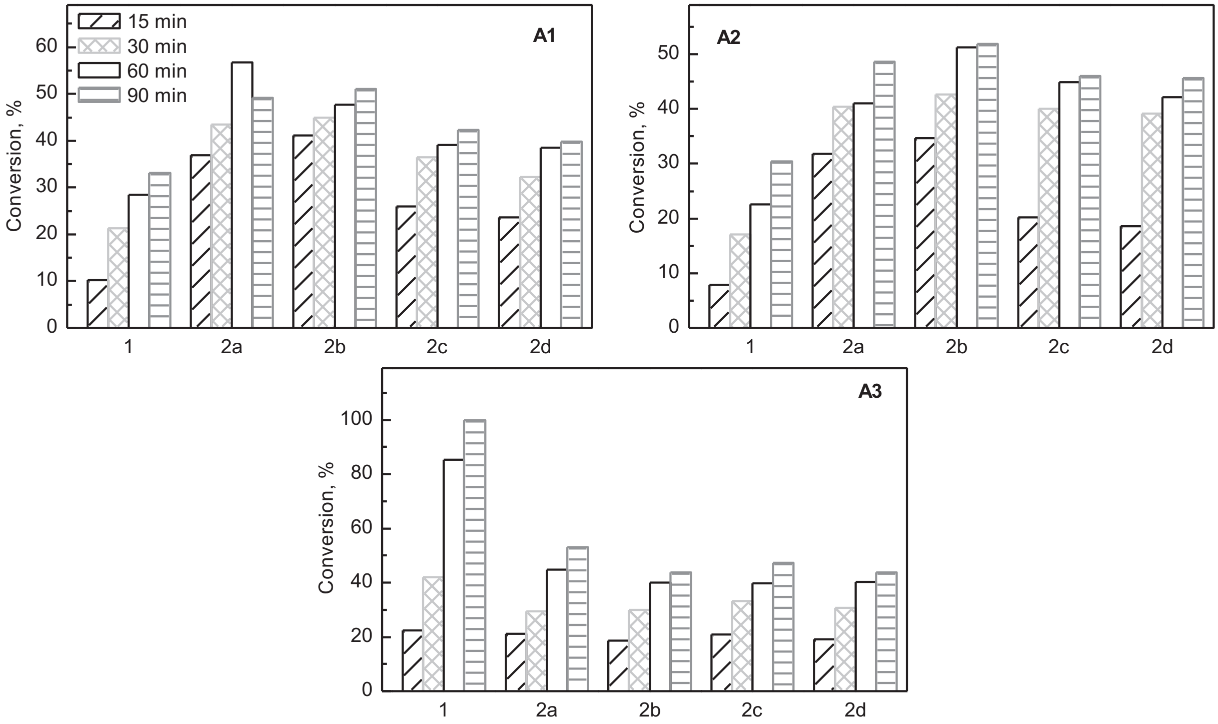


Fig. 2. Conversion of CHO under N_2 atmosphere.

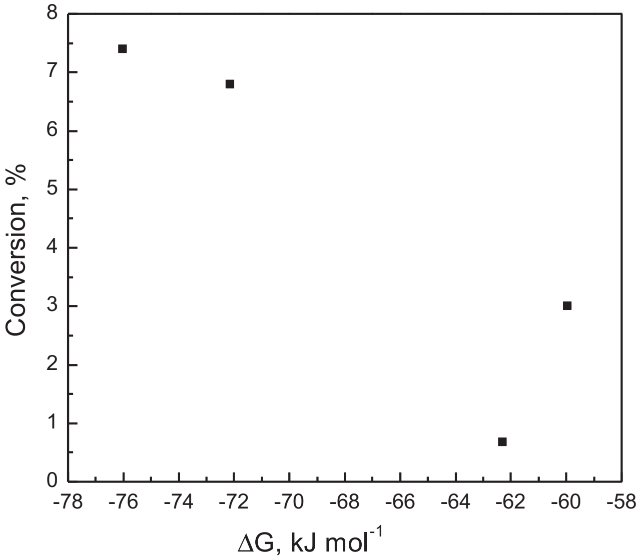


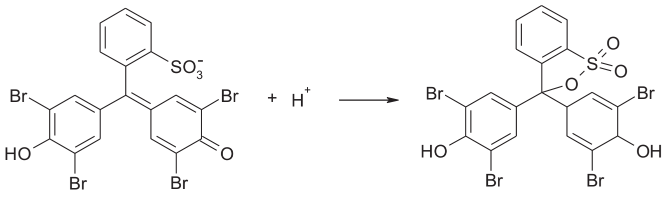
Fig. 3. Relationship between the free energy change and the conversion of **2**/**A2** compositions after 15 min of irradiation.

400 nm. In the dye-sensitized photodecomposition of onium salts, the irradiation of the photoredox pairs leads to an electron transfer from the excited photosensitizer (Dye*) to the onium salt (Ar–I$^+$–Ar) (Scheme 2) [8,9,20]. The resulting onium salt radical (Ar–I–Ar$^\bullet$) is then cleaved yielding a phenyl radical (Ar$^\bullet$), a neutral molecule (iodobenzene) and a photosensitizer radical cation (Dye$^{\bullet+}$). The rapid decomposition of the onium salt radical retards the back electron transfer and renders the overall process irreversible.

To facilitate the intermolecular photo-induced electron transfer from the excited dye to the onium salt, the corresponding free energy change ($\Delta G^0{}_{\mathrm{el}}$) must be negative. In our study $\Delta G^0{}_{\mathrm{el}}$ was calculated from the Rehm-Weller equation (2) [21] in which E_{ox} (D/D$^{\bullet+}$) and E_{red} (A$^{\bullet-}$/A) are the oxidation potential of the dye and reduction potential of the electron acceptor, respectively, and E_{00} is the excited singlet-state energy of the dye. The values of these parameters were taken from the literature [17,22–24]. In this calculation, the Coulombic energy, $Ze^2/\varepsilon\alpha$, was negligible with respect to the overall magnitude of the $\Delta G^0{}_{\mathrm{el}}$.

$$\Delta G^0_{\mathrm{el}}\left(\mathrm{kJmol}^{-1}\right) = 97\left[E_{\mathrm{ox}}\left(\frac{\mathrm{D}}{\mathrm{D}^{\bullet+}}\right) - E_{\mathrm{red}}\left(\frac{\mathrm{A}^{\bullet-}}{\mathrm{A}}\right)\right] - \frac{Ze^2}{\varepsilon\alpha} - E_{00} \qquad (2)$$

The calculated thermodynamic parameters are listed in Table 1. As observed, the $\Delta G^0{}_{\mathrm{el}}$ for the electron transfer process for all combinations of the dye/onium systems is negative, indicating that the photoelectron transfer process in the bimolecular systems studied occurs readily and proceeds via the excited state of the dye.



BPhBl

Scheme 4. Structure of sodium bromophenol blue.

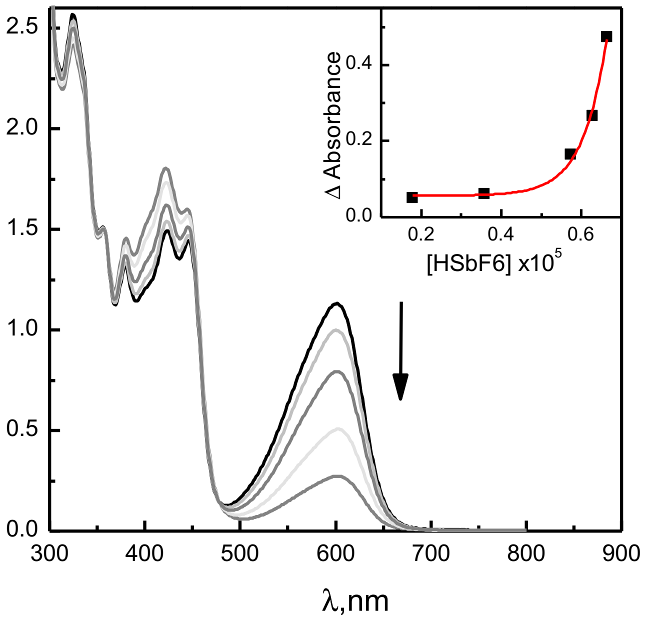


Fig. 4. Electronic absorption spectra obtained upon photolysis (time interval 3 s) of a solution of BPhBl (50 μM) and the dye **2b** (0.1 mM)/**A1** (10 mM) system in CHO. Inset: calibration curve of the change in BPhBl (20 μM) absorbance vs. $HSbF_6$ concentration (range 0–70 μM).

The dye **1**–**2**/onium photoredox pairs were examined for their usefulness as photoinitiators for the cationic polymerization of CHO. CHO was deliberately chosen as the monomer since it polymerizes only by cationic mechanisms and does not react with radicals to form oxidizable radicals. These experiments were conducted under ambient atmosphere (Fig. 1) and under N_2 atmosphere (Fig. 2). The reaction mixture was irradiated during 15, 30, 60 and 90 min intervals. The details regarding the conversion of CHO into a polymer are presented in Tables 2 and 3 (Supplementary Data).

It is evident that modifications within the cations of the onium salts have a marked influence on the cationic polymerization initiated by those salts. Among the tested onium salts, diphenyliodonium salts, **A1** and **A2**, exhibit higher polymerization efficiency in comparison with triarylsulfonium salt, **A3**, due to their lower reduction potentials [25]. In contrast, among the studied dyes numbered **2**, the most efficient sensitizers are dyes **2a** and **2b**, with the lowest oxidation potential and the highest $-\Delta G_{\mathrm{el}}$. This may suggest that the photosensitization occurs chiefly through an electron transfer process. Fig. 3, in which the relationship between the conversion of CHO in the presence of **2**/**A2** compositions after 15 min of irradiation and the free energy change, ΔG_{el}, is shown, supports this mechanism.

Additionally, our results clearly indicate that the polymerization of CHO under an N_2 atmosphere is much more efficient than that

Table 4
Quantum yield of acid release, $\Phi(\mathrm{H}^+)$ (in mmol quant^{-1}), under ambient atmosphere.

Dye	$\Phi(\mathrm{H}^+)$		
	A1	A2	A3
1	40.0	14.1	1.3
2a	41.9	34.5	5.1
2b	67.0	40.8	3.6
2c	26.6	13.6	5.3
2d	10.5	15.6	3.6

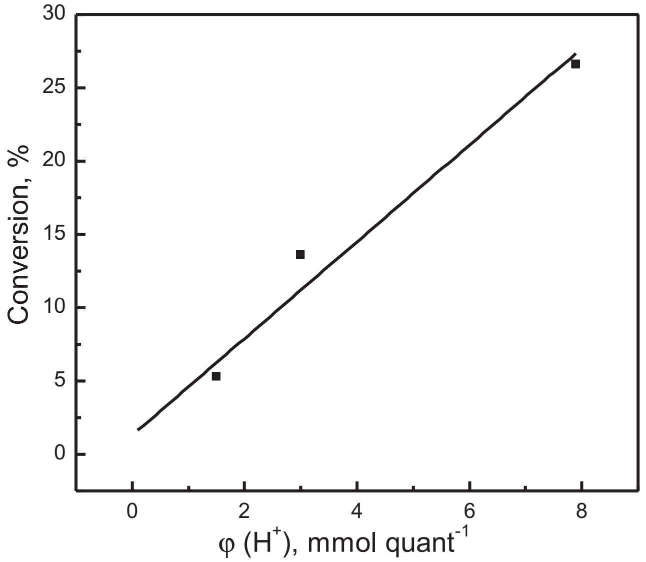


Fig. 5. Relationship between the conversion of **2c** after 15 min of irradiation and the quantum yield of acid release $\Phi(H^+)$ ($R = 0.97$).

under an ambient atmosphere. According to the mechanism shown in Fig. 2, an aryl radical ($Ar^•$) is formed, which possibly reacts with oxygen in the presence of air, resulting in a reduction in the conversion of CHO into polymer compared with that of the deoxygenated monomer [13].

Protic acid is a well-known initiator [7–9] for cationic polymerization processes. To confirm the formation of the acid during photolysis of the diazobenzo[a]fluorene dyes and the onium salt systems, the quantum yield of acid release [$\Phi(H^+)$] upon photolysis was measured using sodium bromophenol blue [(**BPhBl**), Scheme 4]. The quantity of acid released was estimated using a calibration curve relating the **BPhBl** absorbance as a function of $HSbF_6$ concentration (inset of Fig. 4). In the combinations studied, the solution acidity increased over time as the solution was irradiated, whereas the solution's **BPhBl** absorbance, $\lambda_{max} \approx 600$ nm, decreased correspondingly (Fig. 4). In contrast, the solution pH did not change when the dyes were photolyzed in the absence of the salt. The calculated values of the quantum yield of acid release are presented in Table 4. Dye **2b** clearly exhibits the highest quantum yield of acid release. Moreover, a linear relationship between $\Phi(H^+)$ and the conversion of CHO (Fig. 5) can be observed. This observation suggests that the proton formed upon photolysis of the **2**/electron acceptor compositions is the crucial factor initiating the cationic polymerization of CHO.

4. Conclusion

Polyheterocyclic dyes based on a diazabenzo[a]fluorene system, when combined with onium salts such as diphenyliodonium hexafluorophosphate (**A1**), Irgacure 250 (**A2**) and hexafluorophosphate triarylsulfonium (**A3**), may have practical applications as visible light photoinitiators for cationic polymerization. The ability of each dye to act as a photoinitiator depends on its chemical structure. The most efficient sensitizers are the dyes with the lowest oxidation potential and the highest $-\Delta G_{el}$ with the appropriate onium salt.

Acknowledgments

This work was supported by the National Science Center in Cracow, Poland (project no. N N209 032840).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2012.03.016.

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