# Dual Roles for Promoting Monomers to Polymers: A Conjugated Sulfonium Salt Photoacid Generator as Photoinitiator and Photosensitizer in Cationic Photopolymerization

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Received 5 April 2016; accepted 25 April 2016; published online 00 Month 2016 DOI: 10.1002/pola.28154

**ABSTRACT:** An efficient strategy for comprehensive utilization of the conjugated sulfonium salt photoacid generator (PAG), namely, 3-{4-[4-(4-*N*,*N*-diphenylamino)-styryl]phenyl}phenyl dimethyl sulfonium hexafluoroantimonate, was developed through photoinitiated cationic photopolymerization (CP) of epoxides and vinyl ether upon exposure to near-UV and visible light-emitting diodes (LEDs; e.g., 365, 385, 405, and 425 nm). Photochemical mechanisms were investigated by UV-vis spectra, molecular orbital calculations, fluorescence, cyclic voltammetry, and electron spin resonance spintrapping analyses. Compared with commercial PAGs, the prepared conjugated sulfonium salt generated H<sup>+</sup>, which can be used as photoinitiator. Moreover, the fluorescent byproducts from photo-

**INTRODUCTION** Photoacid generators (PAGs) constitute an important class of cationic photoinitiators and strategically used in photoresists.<sup>1</sup> PAGs are widely applied in various research domains, such as microelectronics,<sup>2</sup> photosensitized resins,<sup>3</sup> 3D microfabrication, and high-density optical data storage.<sup>4,5</sup> Diaryliodonium and triarylsulfonium salts are the most important PAGs because of their thermal stability, solubility in most cationic polymerized monomers, and efficiencies in generating strong protic acids during UV irradiation.<sup>6,7</sup> In recent years, light-emitting diodes (LEDs), which are cheaper and safer irradiation devices than UV lamps, have gained increased research attention.<sup>8,9</sup> New photoinitiating systems, for example, curcumin as a multicolor photoinitiator,<sup>10</sup> Nvinylcarbazole as versatile photoinaddimer,<sup>11</sup> hexaarylbiimidazole as visible light photoinitiator<sup>12</sup> using LEDs as light source gained good polymerization conversions. However, the size of aryl groups in commercial PAGs is small, and their absorption peaks are below 300 nm; hence, these materials are unsuitable when long-wavelength UV and visible LED sources are applied.<sup>13-15</sup> Two approaches can be used to achieve specific excitation of PAGs near UV- and visible-light ranges.7-9,16-23 The first approach is derived from sensitizing methods and

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decomposition can be used as photosensitizer of commercial iodonium salt in the photoinitiating systems of CP. These novel D- $\pi$ -A type sulfonium-based photoinitiating systems are efficient (epoxide conversion = 85–90% and vinyl conversion >90%; LEDs upon exposure to 365–425 nm) even in low-concentration initiators (1%, w/w) and low curing light intensities (10–40 mW cm<sup>-2</sup>). © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

**KEYWORDS**: cationic photopolymerization; conjugated sulfonium salt; near UV-visible LEDs; photochemistry; photoinitiator; photopolymerization; photosensitizer; radical polymerization

involves the association of a long-wavelength active sensitizer with commercial PAGs, such as onium salts. Acid generation proceeds through photoinduced electron transfer (PET) from the excited sensitizer to PAGs. However, the global kinetics of this bimolecular method is intrinsically limited by diffusion. Therefore, an integrated approach is proposed; this approach is based on the molecular association of the acid generator functionality into the structure of the low energy photon active chromophore.<sup>8,9,20–23</sup> Perry et al.<sup>20</sup> used this strategy to design a sulfonium-based bis[(diarylamino)styryl]benzene derivative, which exhibits maximum absorption at 390 nm and high quantum yield for acid generation ( $\sim 0.5$ ). We fabricated 4-ethoxystilbene and N,N-diphenylamino-substituted PAGs by using the D- $\pi$ -A system, in which a methyl(p-cyanobenzyl)sulfonium was monosubstituted in either para- or meta-position, and prolonged the absorption peak to approximately 400 nm.<sup>8,9,22,23</sup> Our prepared PAGs exhibited effective acid generation efficiency ( $\Phi_{\rm H}^{+}$  = 0.3–0.6). However, the molecular weights of PAGs with big conjugated systems decrease the molar contents of generated H<sup>+</sup> in the photoinitiating systems, and the ultimate conversion of cationic monomers is approximately 50-70%.8,9



**SCHEME 1** Chemical structures of the target sulfonium salt (PI-PAG), its precursor (Precursor), iodonium salt (Iod), and cationic monomers (EPOX, CHO, and DVE-3).

In this paper, we developed a  $\pi$ -conjugated sulfonium salt (PI-PAG, Scheme 1) characterized by a comprehensive utilization of two mechanisms, for example, integrated and sensitizing methods. The fabricated PI-PAG has high quantum yield of acid generation ( $\Phi_{\rm H}^+$  = 0.44) upon exposure to near UV-vis LEDs (365-425 nm). Photolysis byproducts, which have strong fluorescence, can synthesize iodonium salts to regenerate H<sup>+</sup> through PET. H<sup>+</sup> in the two steps can initiate the simultaneous photopolymerization of epoxides and vinyl ethers, which can greatly improve efficiency and energy consumption. The stepwise photoacid generation mechanism was studied using UV-vis spectra, fluorescent, cyclic voltammetry, and ESR spin-trapping analyses. The ability of the photoinitiating systems to start polymerization reactions was verified by real-time FTIR experiment.

#### **EXPERIMENTAL**

#### Materials

The PAG and monomers investigated here are presented in Scheme 1 and used with the best purity available. (3,4-Epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX), cyclohexene oxide (CHO), and triethyleneglycol divinyl ether (DVE-3) were purchased from Sigma-Aldrich or J&K Chemical and used as received without further purification. All chemicals for synthesis were purchased from Sinopharm Chemical Reagent; TCI; or J&K Chemical, and they were used without further purification unless otherwise specified. All solvents employed for photophysical measurements were J&K Chemical spectroscopic grade.

# **General Instruments**

<sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were recorded with a Bruker 400M NMR spectrometer and chemical shifts were reported in parts per million (ppm) downfield from the Me<sub>4</sub>Si resonance, which was used as the internal standard when recording NMR spectra. Elemental analysis was performed by Elementar Vario El III (Germany). Mass spectra were recorded on a Micromass GCTTM.

#### **Photochemical and Photophysical Experiments**

UV-vis spectra were recorded on a Mapada UV-6300 spectrophotometer. The photodecomposition processes in a solution of acetonitrile were studied by UV-vis spectra under an LED irradiation of 385 nm. Steady-state fluorescence spectra are collected from a Hitachi-2700 spectrofluorometer. Emission spectra are spectrally corrected, and fluorescence quantum yields include the correction due to solvent refractive index are determined relative to quinine bisulfate in 0.05 M sulfuric acid ( $\Phi_{\rm fl} = 0.52$ ).<sup>24</sup> The fluorescence lifetimes are measured using a Nano LED emitting at 372 nm as an excitation source with a Nano LED controller module, Fluorohub from IBH, operating at 1 MHz. The detection is based on an R928P type photomultiplier from Hamamatsu with high sensitivity photon-counting mode. The decays are fitted with the iterative reconvolution method on the basis of the Marquardt–Levenberg algorithm. Such a reconvolution technique allows an overall-time resolution down to 0.15 ns. The quality of the exponential fits is checked using the reduced  $\chi^2$  ( $\leq$ 1.2).

Quantum yields for acid generation were measured under irradiation at 385 nm using LED point curing (Uvata, Shanghai). The irradiated PAG dissolved in acetonitrile was previously N<sub>2</sub>-degassed. The progress of the photoreaction was monitored via UV-vis absorption spectra. The absorbance at the excitation wavelength was greater than 2.5 to assume a total absorption of the incident photons. The dose rates were maintained sufficiently small so that the changes of  $A_{\lambda}$ were lower than 10%. Rhodamine B (RhB) was used as a sensor of photoacid generation.<sup>25</sup> The acid generation in acetonitrile was also evaluated from a calibration curve of RhB, which was gradually protonated by the addition of p-toluenesulfonic acid. The incident light intensity was measured by ferrioxalate actinometry.

#### **Theoretical Calculations**

The theoretical calculations have been computed based on density functional theory (DFT). The overall computation strategy was defined as follows: After initial AM1 optimization calculations (in ACN), subsequent optimization of geometrical structures of the compounds were carried out using the B3LYP/6-31G(d) level of calculation. All calculations have been performed using GAUSSIAN 09 package.<sup>26</sup> The molecular orbitals involved in these transitions could be extracted, and the geometries were frequency checked.

#### **Redox Potentials**

The cyclic voltammetry experiments<sup>27</sup> (using a computercontrolled Radiometer Voltalab 6 potentiostat with a threeelectrode single-compartment cell, in which the working electrode is a platinum disk, and a saturated calomel electrode (SCE) that is used as a reference that placed in a separate compartment with a salt bridge containing the supporting electrolyte and saturated KCl performed at 300 K, in acetonitrile with a constant concentration (0.1 M) of n-Bu<sub>4</sub>NBF<sub>4</sub>. Ferrocene (Fc) is used as an internal reference.

#### **ESR Spin Trapping Experiment**

Electon spinning resonance spin trapping (ESR-ST) experiments carried out using a Bruker EMX-plus spectrometer (X-band). The radicals were generated at room temperature upon 365-nm LED exposure under Ar and trapped by phenyl-*N-tert*-butylnitrone (PBN) in *tert*-butylbenene.<sup>28</sup>



**SCHEME 2** Synthetic routes of the PAG. (a) NBS, CCl<sub>4</sub>, BPO; (b) P(OEt)<sub>3</sub>, 150 °C, 3 h; (c) potassium *tert*-butoxide, THF, 0 °C; (d) Pd(PPh<sub>3</sub>)<sub>4</sub>,  $K_2CO_3$ , toluene/ethanol/H<sub>2</sub>O; (e) CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, RT; and (f) NaSbF<sub>6</sub>, water, and acetone.

# **Photopolymerization Experiments**

The photopolymerization is monitored *in situ* by Fourier transform real-time infrared spectroscopy (FT-RTIR) with a Thermo-Nicolet iS5 instrument IR spectrometer. The photosensitive formulations are deposited on a KBr pellet in laminate (40  $\mu$ m thick) for irradiation at different wavelength LEDs (Uvata, Shanghai). The evolution of the epoxy group content of EPOX, the epoxy group content of CHO, the double bond (C = C) content of DVE-3 are continuously followed at about 790, 780, and 1620 cm<sup>-1</sup>, respectively.<sup>29,30</sup>

# Synthesis

The synthetic route of the precursor and PAG are shown in Scheme 2, and the details of synthesis and characterization are provided below. Compound **1**, **2**, and **3** were prepared following the procedure of literature.<sup>31,32</sup>

# Preparation of 4-(3-Methylthiophenyl)-4-N,N'diphenylamino-Stilebene (Precursor)

A 250-mL three-necked, round-bottomed flask fitted with an electromagnetic stirrer and a reflux condenser was charged with 3 (1.1 g, 2.5 mmol), 3-(methylthio)phenylboronic acid (420.1 mg, 2.5 mmol), potassium carbonate (1.0 g, 7.5 mmol), methyl trioctyl ammonium chloride 0.3 mL, Pd(PPh<sub>3</sub>)<sub>4</sub> (86.7 mg, 0.08 mmol), and toluene/ethanol/H<sub>2</sub>O (v/v/v, 5:3:1, 40 mL: 24 mL: 8 mL).<sup>33</sup> The resulting mixture was heated to reflux with stirring under nitrogen at approximately 90 °C for 48 h. The mixture was extracted by dichloromethane (50 mL  $\times$  3). Then column chromatography was used for separation and purification (dichloromethane: petroleum ether 1: 5, v/v, 500 mL) to obtain yellow product Precursor (1.1 g, 92.7% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): δ 7.57 (s, 4H, PhH), 7.49 (s, 1H, PhH), 7.44–7.33 (m, 4H, PhH), 7.31–7.21 (m, 5H, PhH), 7.17–6.99 (m, 10H, PhH, CH = CH), 2.54 (s, 3H, CH<sub>3</sub>).



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ, ppm): δ 147.57, 147.49, 141.46, 139.50, 139.06, 137.03, 131.45, 129.36, 129.26, 128.45, 127.46, 127.41, 126.79, 126.44, 125.40, 125.12, 124.58, 123.84, 123.58, 123.13, 16.34. MS (m/z): calcd. for C<sub>33</sub>H<sub>27</sub>NS, 469.19; found, 470.19 [M + H<sup>+</sup>]. Anal. calcd for C<sub>33</sub>H<sub>27</sub>NS: C, 84.40; H, 5.79; N, 2.98. Found: C, 84.31; H, 5.74; N, 2.90.

# Preparation of 3-(4-(4-(4-N,N'-Diphenylamino)-Styryl)Phenyl)Phenyl Dimethyl Sulfonium Hexafluoroantimonate (PI-PAG)

Precursor (197.7 mg, 0.4 mmol), Cs<sub>2</sub>CO<sub>3</sub> (274.3 mg, 0.8 mmol) was added to a 100-mL flask along with 20.0 mL of dry dichloromethane and the mixture was stirred under -78°C for 30 min. Then methyl trifluoromethanesulfonate (76.0 mg, 0.5 mmol) was syringed into the solution.<sup>34</sup> After stirring at this temperature for 2 h, the mixture was warmed to room temperature and stirred for another 48 h. Then, column chromatography was used for separation and purification (dichloromethane: methanol 1: 5, v/v, 500 mL) to obtain yellow product (sulfomium trifluoromethanesulfonate). Then, anion exchange of  $CF_3SO_3^-$  by  $SbF_6^-$  was performed using the Zhou et al. method.<sup>35</sup> A fresh 20-mL portion of NaSbF<sub>6</sub> (1.14 g, 4.40 mmol) in water was added to a solution of sulfomium trifluoromethanesulfonate (100 mg, 0.16 mmol) in 10 mL of acetone. The mixture was stirred for 2 h at room temperature in the dark. The solid was collected by filtration and redissolved in 10 mL of acetone. The above anion exchange was repeated three times. The resulting solid was washed three times with water and ether. The product was purified by two precipitations from a 10-mL acetone solution through the addition of 50 mL of diethyl ether. Yellow product was gained and the yield: 89.0%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): δ 7.92 (s, 1H, PhH), 7.72 (t, *J* = 7.3 Hz, 2H, PhH), 7.53 (m, 3H, PhH), 7.42 (d, *J* = 8.0 Hz, 2H, PhH), 7.31–7.14 (m, 6H, PhH), 7.04 (d, *J* = 7.9 Hz, 4H, PhH), 6.98 (m, 5H, PhH, CH = CH), 6.83 (d, *J* = 16.3 Hz, 1H), 3.11 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta_{ppm}$ ): δ 147.53, 147.39, 143.40, 138.05, 136.31, 132.58, 131.80, 130.90, 129.31, 129.11, 127.54, 127.45, 127.39, 127.05, 125.66, 125.36, 124.58, 123.23, 123.15, 28.39. MS (*m*/*z*): calcd for C<sub>34</sub>H<sub>30</sub>NS<sup>+</sup>, 484.21; found, 484.21 [sulfonium ion]. Anal. calcd for C<sub>34</sub>H<sub>30</sub>F<sub>6</sub>NSSb: C, 56.68; H, 4.20; N, 1.94. Found: C, 56.63; H, 4.14; N, 2.03.

#### **RESULTS AND DISCUSSION**

# Synthesis

The target PAG, named as PI-PAG, was prepared from 4-aldehyde-triphenylamine through four steps (Scheme 2) because the triphenylamine group is a good substituent in sulfonium salts.<sup>35</sup> The Suzuki reaction was performed with meta-(methylthio)-phenylboronic acid to produce precursor (Precursor) in high yields (over 90%). Finally, alkylation of the Precursor with  $CH_3CF_3SO_3$  generated a conjugated sulfonium triflate salt; subsequently, non-nucleophilic anions,



**FIGURE 1** The UV-vis spectra of PI-PAG and Precursor in acetonitrile. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

such as SbF<sub>6</sub>, were exchanged to improve the polymerization reactions.<sup>35</sup> The successful ions exchange can be proved by the elemental analysis due to the different molecular weight of anions (SbF<sub>6</sub><sup>-</sup>: 235.7 and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>: 149.1 as shown in Experimental section).

# Absorption Properties of the Sulfonium Salt and Precursor

The absorption spectra of sulfonium salt and its precursor (PI-PAG and Precursor) in acetonitrile are shown in Figure 1. The maxima for PI-PAG and Precursor are located at  $\lambda_{max} = 381 \text{ nm}$  ( $\varepsilon_{381 \text{ nm}} = 22,500 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $\lambda_{max} = 374 \text{ nm}$  ( $\varepsilon_{374 \text{ nm}} = 35,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), respectively (Table 1). The spectrum of PI-PAG presents a slight redshift but a lower  $\varepsilon$  value compared with its precursor (Precursor). The excellent absorption properties of the compounds are associated with the large delocalization of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are involved in the lowest energy transition.<sup>24,36</sup>

This result was further confirmed by DFT calculations, as shown in Figure 2. The HOMOs of both PI-PAG and precursor are mainly localized on the triphenylamine (donor) and stilbene (conjugated system) moieties; however, the LUMO of Precursor is distributed throughout the conjugated system. The  $\pi$ - $\pi$ \* transition of HOMO-LUMO orbitals explains the high  $\varepsilon$  values (Fig. 1). The LUMO of PI-PAG is located on the



**FIGURE 2** Representation of frontier molecular orbitals involved in the lowest energy electronic transitions of Precursor and PI-PAG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conjugated and sulfonium moieties, and an apparent  $\pi$ - $\sigma^*$ (sulfur-carbon bond, face to face) transition is involved in the LUMO orbital (Fig. 2), thereby decreasing the molar extinction coefficients of PI-PAG but increasing the electron delocalization in the molecular structure; these changes caused the spectra redshift relative to its precursor. Saeva confirmed that the photoacid generation reaction of arylsulfonium salts may occur either by direct excitation of  $\pi$ - $\sigma^*$ (sulfur-carbon bond) transition or excitation of the  $\pi$ - $\pi^*$ transition, followed by intramolecular electron transfer to  $\sigma^*$ on the sulfur-carbon bond.<sup>34,37</sup> In both cases, subsequent homolytic cleavage of the S-C bond leads to the formation of radical cation on the sulfur-containing fragment and a neutral radical on the carbon fragment.

A possible photolysis mechanism is proposed as shown in Scheme 3. The photogenerated proton can initiate the cationic polymerization of epoxides and vinyl ether.

### Cationic Photopolymerizations Photopolymerization of EPOX

The photopolymerization of EPOX in the presence of PI-PAG (1 wt %) in air were conducted through exposure to 365–425 nm LEDs because the PI-PAG showed considerable extinction coefficients within this range (Fig. 1 and Table 1). PI-PAG can initiate the polymerizations of EPOX; the conversion profile for the reaction and the conversion at t = 5 min, which is 52.3% at 365 nm LED, is depicted in Figure 3(a). Improved polymerization profiles were obtained upon addition of commercial iodonium salt (Iod), which is used in photosensitizing systems in visible-light photopolymerization, <sup>30</sup> to the PI-PAG system [Fig. 3(a)]. The conversions of

**TABLE 1** Light Absorption Properties of PI-PAG and Precursor and Their Molar Extinction Coefficients ( $\varepsilon$  in M<sup>-1</sup> cm<sup>-1</sup>) at the Maximum Emission Wavelengths of Different LEDs

Compound	$\lambda_{\max}$ (nm) <sup>a</sup>	e <sub>max</sub> a	b 365 nm <sup>8</sup>	b 385 nm <sup>8</sup>	b <sub>8405 nm</sub>	b 425nm	$\Phi_{H}{}^{+c}$
Precursor	374	35,000	32,000	32,000	14,500	1,900	-
PI-PAG	381	23,200	19,200	23,000	14,900	3,800	0.44

<sup>a</sup> In acetonitrile, and the error is approximately 10%.

<sup>b</sup> For different near UV/visible LEDs.

<sup>c</sup> Measured at 385 nm, and the error is approximately 15%.



**SCHEME 3** Proposed photolysis mechanism of sulfonium salt and photogenerated  $H^+$  and fluorescent byproducts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 3** (a) Photopolymerization profiles of EPOX in air and in the presence of lod (3 wt %), Precursor (1 wt %), PI-PAG (1 wt %), PI-PAG/lod (1%/3%, w/w), and Precursor/lod (1%/3%, w/w); and (b) Photopolymerization conversions of EPOX in air and in the presence of different initiating systems at different LED irradiation (40 mW cm<sup>-2</sup>). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can be considered as excellent photoinitiating systems for this viscous monomer.<sup>38</sup> The satisfactory performance of these two-component systems could be due to the contribution of a PET from the excited sensitizer to the Iod, as discussed in a previous report.<sup>19</sup> According to the photolysis mechanism shown in Scheme 3, the precursor (Precursor) exists in the photoinitiating systems; thus, the possible photosensitization process was studied in the present work.

the two component PI-PAG/Iod systems reach 82.0%, which

The related polymerization profiles are provided in Figure 3(a). Iod and Precursor could not initiate the conversion of EPOX. Precursor/Iod (1%/3%, w/w) system can initiate the polymerizations of EPOX, with a relative conversion of approximately 30-45%. Thus, we could preliminary conclude that the satisfactory performance of the PI-PAG/Iod system could be due to further photosensitization of byproducts of PI-PAG photolysis. The exposure wavelengths were redshifted to the visible range (425 nm), the dicomponent systems still exhibit good conversions compared with the PI-PAG itself [Fig. 3(b)]; this result is highly dependent on the photosensitizing process. Final tack free coatings are obtained within 5 min of LED irradiation in different wavelengths. Here,  $SbF_6^-$  was selected as counterion and it proves that it has better conversion of EPOX than  $PF_6^-$  as anion even the commercial Iod with  $PF_6^-$  as anion (the data are not shown).

#### **Photopolymerization of CHO And DVE-3**

These systems also initiated the cationic polymerizations of other types of monomers, for example, CHO and DVE-3. In this study, the conversion profiles of CHO and DVE-3 at 405 nm were selected as samples to compare their dynamics; the results are shown in Figure 4. These photoinitiating systems are very efficient, and 0.5 wt % of PI-PAG is sufficient to convert the monomer to polymers at approximately 100 s. At other wavelengths, the conversions of CHO reach 85–95% (Table 2).

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**FIGURE 4** Photopolymerization profiles of CHO and DVE-3 under air in the presence of PI-PAG (0.5 wt %) and PI-PAG/lod (0.5%/2%, w/w) at 405 nm LED irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The detailed photolysis and photosensitization processes were also studied to clarify the possible polymerization mechanism.

# Photochemical and Photophysical Properties of PI-PAG And Precursor

# Photodecomposition and Photoacid Generation of PI-PAG And PI-PAG(Precursor)/Iod Systems

The typical evolution of the absorption spectra of PI-PAG in acetonitrile upon irradiation by 385 nm LED at 1 mW cm<sup>-2</sup> is shown in Figure 5. With the appearance of a less intensive band located at 356 nm, the band located at approximately 280 nm increases slightly, whereas the maximum wavelength absorption band dramatically collapses. During photolysis,  $H^+$  is produced and the quantum yield of acid generation of PI-PAG is 0.44 at 385 nm LED irradiation (Table 1 and Fig. 6). Additionally, the photoacid generation of the PI-PAG/Iod system [Fig. 6(a)] and Precursor/Iod systems [Fig. 6(b)] was also studied and compared with that of the PI-PAG itself. The absorption peaks of RhB at 555 nm rapidly increases during

**TABLE 2** CHO and DVE-3 Conversions Obtained with 365–425 nm LED Illumination in the Presence of PI-PAG/lod (0.5%/2%, w/w) with Light Intensity 10 mW cm<sup>-2</sup>

Monomer	LEDs (nm)	Conversion (%)
СНО	365	87.5
СНО	385	85.2
СНО	405	83.5
СНО	425	84.9
DVE-3	365	90.6
DVE-3	385	89.0
DVE-3	405	90.3
DVE-3	425	88.4



**FIGURE 5** UV-vis spectra of PI-PAG in acetonitrile under irradiation of 385 nm LED (1 mW cm<sup>-2</sup>) at different periods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 6** (a) Photoacid generation curves of the PI-PAG/lod (1:2 mol/mol) mixture upon the LED exposure at 365 nm; UV-vis spectra recorded at different irradiation times; and (b) absorbance at 555 nm of RdB in different photoacid generating systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 7** ESR spectra of radicals generated in (a) PI-PAG, (b) PI-PAG/lod, and (c) Precursor/lod and trapped by PBN in *tert*-butylbenzene: spectra. PBN/free radical adducts: (a)  $a_N =$ 14.7 G;  $a_H = 3.13$  G; (b)  $a_N = 14.4$  G;  $a_H = 2.4$  G; and (c)  $a_N =$ 14.4 G;  $a_H = 2.4$  G. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the first 5 s and then increases slowly in the PI-PAG + 2 eq. Iod systems [Fig. 6(a)]. These results suggest that the photoacid generation could be divided into two stages [Fig. 6(b)]. The photolysis of PI-PAG is completed within 5 s under irradiation, and the byproducts are further sensitized the Iod to gradually produce  $H^+$ . Given that Precursor was used as sensitizer, a similar data could be obtained in the same experimental conditions. The photosensitization starts in the first seconds; the enlarged data are observed starting at 5 s. This finding suggests that  $H^+$  is produced during the photolysis of the PI-PAG + Iod system.

# EST-ST

The photochemical reactions were investigated through ESR-ST experiments, and the corresponding signals are shown in Figure 7. When PI-PAG was photodecomposed and the free radicals were trapped by PBN [Fig. 7(a)], the hyperfine coupling (*hfc*) constants of the radical adduct ESR of PI-PAG are  $a_{\rm N} = 14.7$  G and  $a_{\rm H} = 3.13$  G, which is due to CH<sub>3</sub><sup>•</sup> generation during the photolysis;<sup>28</sup> these findings are strong evidence for the photolysis mechanism of PI-PAG, as shown in Scheme 3. When Iod was added to the ESR-ST experiments [Fig. 7(b)], the *hfc* changed to  $a_{\rm N} = 14.4$  G and  $a_{\rm H} = 2.4$  G, which is similar to the mixture of Precursor + Iod:  $a_{\rm N} = 14.4$  G and  $a_{\rm H} = 2.4$  G [Fig. 7(c)]. These *hfc* values suggested that the trapped radicals are phenyl radicals generated from Iod, as discussed by Lalevee et al.<sup>39</sup> The PET process occurred between the sensitizers and Iod.

# **Photochemical Properties of Precursor**

Marder and Saeva et al. proved that the byproducts of PAG photodecomposition are the main precursor and free radical adducts.<sup>34,35</sup> Our study on the excited state dynamics of a D- $\pi$ -A type sulfonium-based alkoxystilbene PAG also led to the same conclusions.<sup>40</sup> Thus, the relative spectral properties of

Precursor were further investigated. Photopolymerization with the Precursor proved that it can be used as a cationic photoinitiator with iodonium or sulfonium salts, wherein the efficient production of reactive species (radicals and cations) play a very important role. The well-known mechanism of dye-sensitized photodecomposition of iodonium salts<sup>6</sup> is presented in reactions 1–6 ( $r_1$ – $r_6$ ). The key step is PET between dye/iodonium photoredox pair. The PET from the excited dye (Dye<sup>\*</sup>) to iodonium ( $Ph_2I^+$ ) leads to the dye radical cation (Dye<sup>•+</sup>) and neutral radical (Ph<sup>•</sup>). The rapid decomposition of the Iod retards reverse electron transfer and renders the overall process as irreversible. The radical cation ( $Dye^{+}$ ) may allow the CP of monomers of epoxides and vinyl ethers. Simultaneously, the hydrogen abstraction reaction between the radical cation and solvents or monomers generates strong protic acid, which can also initiate CP.

$$Dye \to Dye * (hv) \tag{r_1}$$

$$Dye * + Ph_2I^+ \rightarrow Dye^{\bullet +} + Ph^{\bullet} + Ph - I \qquad (r_2)$$

$$M-H + Dye^{\bullet +} \rightarrow Dye^{+}-H + M^{\bullet}$$
 (r<sub>3</sub>)

$$Dye^+ - H \rightarrow Dye + H^+$$
 (r<sub>4</sub>)

$$M-H + Ph^{\bullet} \rightarrow Ph-H + M^{\bullet} \qquad (r_5)$$

$$M^{\bullet} + Ph_2I^+ \rightarrow M^+ + Ph - I + Ph^{\bullet}$$
 (r<sub>6</sub>)

In this PET process, the Gibbs free energy that changes the electron transfer ( $\Delta G_{\rm et}$ ) from PIs to Iod (a kind of iodonium salt) should be obtained to determine the potential applicability of these dyes as electron donor in the excited state.<sup>19,41</sup> Free energy can be estimated according to Rehm-Weller equation (eq 1)<sup>41</sup> if we assume that this PET process proceeds from the singlet excited state. The electron transfer from the dyes to Iod is thermodynamically favorable if the free energy ( $\Delta G_{\rm et}$ ) is negative.

$$\Delta G_{\rm et}(\rm kJ\,mol^{-1}) = 97 \left[ E_{\rm ox}(S/S^{+}) - E_{\rm red}(\rm A^{-}/\rm A) \right] - E^{00}(S) - Z_1 Z_2 / \varepsilon r_{12}$$
(1)

In this equation,  $E_{\rm ox}$  and  $E_{\rm red}$  correspond to the oxidation potential of the Precursor  $[E_{ox} = 0.72 \text{ V (vs. SCE)}]$  and the reduction potential of Iod [ $E_{\rm red} = -0.2$  V (vs. SCE) in ref. 43], respectively.  $E^{00}$  is the energy of the singlet excited state determined by the normalized absorption and emission spectra ( $E^{00} = 2.94$  eV), and  $Z_1 Z_2 / \varepsilon r_{12}$  is the Coulombic energy characterizing the interaction of the generated radical ion pairs with charges  $Z_1$  and  $Z_2$  in a medium of dielectric constant  $\varepsilon$  for distance  $r_{12}$ . Given that the neutral radical of the Iod is formed during PET process (Z = 0),  $Z_1Z_2/\varepsilon r_{12}$ could be omitted in the calculation.<sup>24,44</sup> The calculated  $\Delta G_{\rm et}$ is --194.20 kJ mol<sup>-1</sup>, indicating that the combination of Precursor/Iod system possess a high driving force  $(-\Delta G_{\rm et} > 180 \text{ kJ mol}^{-1})$  upon light exposure. This finding confirms that the PET process easily occurs through the singlet excited state.



**FIGURE 8** Fluorescence quenching of Precursor by lod in ACN. Inset: Stern-Volmer plot of fluorescence quenching. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The intermolecular electron transfer from Precursor to Iod was also verified by fluorescence quenching measurements. Precursor show good fluorescent emission, wherein the fluorescence quantum yields are  $\Phi_{\rm fl} = 0.83$  in ACN. The presence of Iod leads to fluorescence quenching, as illustrated in Figure 8. The absence of any new peaks in the emission spectra excludes any exciplex formation.

The singlet quenching constant  $(k_q)$  is calculated from eq 219 by using the fluorescence lifetime of the dye  $(\tau_0 = 2.5 \text{ ns})$  in the absence of a quencher (Table 1).

$$I_0/I = k_q \tau_0 [\text{Iod}] + 1$$
 (2)

For this system, the singlet quenching constant ( $k_q$ ) shows that the value (5.35  $\times$  10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>) is close to the diffusion control limit.<sup>44</sup> These results confirm that fluorescence quenching proceeds via the PET process.<sup>45</sup> In addition, the



**FIGURE 9** Steady-state photolysis of Precursor and Precursor/ lod mixture upon the LED exposure at 385 nm;  $A/A_0$  recorded at different irradiation times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

accelerating photobleaching of the Precursor in the presence of Iod under irradiation of 385 nm LED further proves the photochemical process (Fig. 9). The photobleaching could also be used for other applications, for example, antiyellowing.

Photochemical and photophysical properties of PI-PAG and precursor explain the occurrence of polymerization.

## CONCLUSIONS

In conclusion, a new D- $\pi$ -A type sulfonium salts photoacid generator (PI-PAG) bearing the non-nucleophilic counterion  $\mathrm{SbF}_6^-$  were used as cationic photoinitiators. The key features of this sulfonium salt are as follows: (i) it produces H<sup>+</sup> efficiently upon exposure to 365-425 nm at very low light intensity and (ii) the resulting fluorescent byproducts (precursor and H-abstraction products) can sensitize the Iod in the cationic polymerization systems. Furthermore, they can also be used as two-component photoinitiators in different types of cationic monomers. Photochemically generated H<sup>+</sup> was useful for acid-activated material processing and fabrication in the solid phase. This approach suggested a new design strategy for the synthesis of  $\pi$ -conjugated sulfonium salts, which exhibits dual roles when applied to photocuring. Such PI-PAG can also be used as the sensitizer of sulfonium salts, such as commercial triphenylsulfonium salt. Further studies on the topic are in progress.

#### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51173134, 51573139); Fundamental Research Funds for the Central Universities and the Open Measuring Fund for Large Instrument and Equipment (0002015033) of Tongji University.

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