

# Synthesis and characterization of triarylsulfonium salts as novel cationic photoinitiators for UV-photopolymerization

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**Abstract** Using diaryliodonium salts as the arylating reagent and copper as a catalyst, a series of triarylsulfonium salts bearing benzoyl or benzoheterocyclic moieties were synthesized and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and high-resolution mass spectrometry. The photoinitiating behavior of the triarylsulfonium salts on photopolymerization of epoxy acrylate resin (UV6104) with hexane-1,6-diyldiacrylate (HDDA) as an activated monomer was investigated. The results showed that these triarylsulfonium salts could be utilized as cationic photoinitiators in the UV-curing process. A polymerization photoinitiation mechanism has been proposed.

Keywords UV-curing  $\cdot$  Cationic photoinitiators  $\cdot$  Synthesis  $\cdot$  Triarylsulfonium salt

# Introduction

The ultraviolet (UV)-curing technology, owing to its remarkable and unique properties such as slow energy consuming, high productivity, and low solvent emissions, has been widely used in coatings, varnishes, adhesives, printing inks and electronics [1, 2]. In normal conditions, a photopolymerization system is comprised of an oligomer or a reactive monomer, a photoinitiator and optional additives. The photoinitiator plays an important role in photo-curing and photopolymerization

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since it determines the photopolymerization speed and affects the polymer properties such as odor, yellowing and migration. Photoinitiators are divided into a free radical polymerization photoinitiator and a ationic polymerization photoinitiator based on the reaction mechanism [3, 4]. Benzophenone (BP) and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) are the most commonly used free radical photoinitiators owing to their low cost, high photoinitiation efficiency, and good solubility in the polymerization formulation. Compared with free radical polymerization initiation systems, a cationic photoinitiating system has many advantages such as rapid polymerization without oxygen inhibition, low shrinkage upon curing, strong adhesive force, high hardness, and good performance of abrasion resistance, etc. [5–7]. However, some limitations exist such as limited solubility of cationic photoinitiator in monomers and resins, long curing time and high cost. Thus, there is a great demand for the advantages of radical and cationic photoinitiators. Crivello et al. [8–11] introduced a phenacyl substituent into the triarylsulfonium salt, a kind of efficient cationic photoinitiator [12], in order to improve its compatibility with resins. Xie et al. [13] reported the preparation of diaryliodonium salts which bear a benzophenone group as free radical-cationic hybrid photoinitiators. Peter Pappas et al. [14] also reported the synthesis and photoactivity of anthracene-bound sulfonium salts, which efficiently absorb radiation between 330 and 410 nm due to the strong absorptivity of anthracene in this region. In addition, several ferrocenium salts have been synthesized and evaluated as novel cationic photoinitiators [15-18]. These compounds, however, usually involve complicated synthetic protocols characterized by low yield. Accordingly, the development of easily prepared photoinitiators with better properties such as low odor, low migration rate, low benzene release and good solubility in the formulation continues to be a growing area of interest. In the present work, a novel class of triarylsulfonium salts which bear benzophenone or aromatic heterocyclic moieties have been prepared and compared as cationic photoinitiators used in the UV-curing system.

# Experimental

# Materials

All starting materials for the preparation of triarylsulfonium salts were reagent grade and used without further purification. The monomer 1,6-hexanediol diacrylate (HDDA) was obtained from Specialty Chemicals (Jiangsu, China). The epoxy acrylate resin (UV6104) was obtained from Jiangsusanmu Specialty Chemicals (Jiangsu, China). 1-hydroxycyclohexyl phenyl ketone (Irgacure **184**) was purchased from Beijing Specialty Technology (Beijing, China). Scheme 1 depicts the chemical structures and abbreviations of the materials used in the polymerization.

# Instrumentation

 $^{1}$ H NMR and  $^{13}$ C NMR spectra were recorded in CDCl<sub>3</sub> and DMSO-d6 with a Bruker DRX 500 MHz and 600 MHz spectrometer. High-resolution mass spectra



Scheme 1 Chemical structures and abbreviations of the materials used in the polymerization

were obtained on a Bruker micrOTOF-Q III mass spectrometer. UV-vis absorption spectra were recorded in dichloromethane on a Hitachi UH-5300 UV spectrophotometer (Hitachi High-Technologies, Tokyo, Japan). A portable pencil scratch hardness tester (QHQ-A) was used, as were a manual coating machine (QTG) and a portable UV-Curing machine (LT4003).

### Synthesis

### S-aryldibenzo[b,d]thiophenium salts 1

To a single-neck flask were added dibenzo[b,d]thiophene (1 mol), diphenyliodonium triflate (1.2 mol) and Cu(OAc)<sub>2</sub> (10 mol%) as catalyst. The reaction mixture was stirred for 30 min at 130 °C. After cooling to room temperature, the precipitate was filtered off. The crude product was purified by silica gel chromatography using dichloromethane as the eluent to afford *S*-aryldibenzo[b,d]thiophenium salts **1**.

*S-phenyldibenzo*[*b,d*]*thiophenium triflate* **1***a* White crystal, mp: 197–198 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.51–7.67 (m, ArH, 4H), 7.61–7.78 (m, ArH, 3H), 7.79–7.84 (s, ArH, 2H), 8.30–8.60 (m, ArH, 4H). HRMS (ESI) clacd for C18H13S (M+ OTf)<sup>+</sup>: 261.0738, found: 261.0732.

*S*-(4-tolyl)dibenzo[b,d]thiophenium triflate **1b** Milky white crystal, mp: 179–181 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 2.32 (s, CH<sub>3</sub>, 3H), 7.37–7.40 (m, ArH, 2H), 7.45–7.48 (m, ArH, 2H), 7.71–7.96 (m, ArH, 4H), 8.30–8.33 (m, ArH, 2H), 8.48–8.51 (m, ArH, 2H). HRMS (ESI) clacd for C19H15S (M+ OTf)<sup>+</sup>: 275.0894, found: 275.0889.

*S*-(4-iodophenyl)dibenzo[b,d]thiophenium triflate **1***c* White crystal, mp: 253–254 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.37–7.40 (s, ArH, 2H), 7.76–7.81 (m, ArH, 2H), 7.96–8.01 (m, ArH, 4H), 8.39–8.42 (m, ArH, 2H), 8.54–8.56 (m, ArH, 2H). HRMS (ESI) clacd for C18H12IS (M+ OTf)<sup>+</sup>: 386.9704, found: 386.9699.

### S-arylsulfonium salts 2

Phenyl(4-(p-tolylthio)phenyl)methanone (1 mol), diphenyliodonium triflate (1.2 mol) and 1,1,2,2-tetrachloroethane (2 mL) were placed in a 50-mL roundbottom flask equipped with a mechanical stirrer, thermometer and reflux condenser. After thoroughly mixing, the combination of CuI (5 mmol%) and Cu (5 mmol%) was added as catalyst. The reaction mixture was stirred for 2 h at 110 °C. The resulting mixture was cooled, filtered and then excess solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography (dichloromethane: ethyl acetate = 7:3) to afford S-arylsulfonium salts **2**.

(4-Benzoylphenyl)(phenyl)(p-tolyl)sulfonium triflate **2a** Light yellow viscous liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.53–2.58 (s, CH<sub>3</sub>, 3H), 7.53–7.62 (m, ArH, 4H), 7.67–7.73 (m, ArH, 3H), 7.79–7.87 (m, ArH, 9H), 8.04–8.07 (m, ArH, 2H). <sup>13</sup>C NMR (DMSO)  $\delta$ : 20.92, 119.98, 124.17, 128.21, 128.46, 129.44, 130.53, 130.72, 131.04, 131.27, 131.76, 133.05, 134.18, 135.28, 141.63, 145.77, 193.57. HRMS (ESI) clacd for C26H21OS (M+ OTf)<sup>+</sup>: 381.1347, found: 381.1303.

(4-Benzoylphenyl)diptolylsulfonium triflate **2b** Light yellow viscous liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.44–2.50 (s, CH<sub>3</sub>, 6H), 7.56–7.63 (m, ArH, 6H), 7.70–7.72 (m, ArH, 1H), 7.78–7.80 (m, ArH, 6H), 7.88–7.91 (m, ArH, 2H), 8.00–8.03 (m, ArH, 2H). <sup>13</sup>C NMR (DMSO)  $\delta$ : 20.05, 120.46, 127.84, 128.69, 128.95, 129.88, 130.49, 131.00, 132.68, 134.77, 140.57, 144.65, 193.51. HRMS (ESI) clacd for C27H23OS (M+ OTf)<sup>+</sup>: 395.1463, found: 395.1469.

## S-arylsulfonium salts 3

Compounds 3 were synthesized following the same procedure as compounds 2, except that the reaction mixture was refluxed for 3 h.

*S-diphenyl-(1-methyl-2-phenylindole) sulfonium triflate* **3a** White crystal, mp: 204–205 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.83 (s, N-CH<sub>3</sub>, 3H), 6.96–7.19 (m, ArH, 4H), 7.22–7.44 (m, ArH, 5H), 7.45–7.64 (m, ArH, 5H), 7.67–7.73 (m, ArH, 5H). HRMS (ESI) clacd for C27H22 NS (M+ OTf)<sup>+</sup>: 392.1467, found: 392.1463.

*S-phenyl-(4-tolyl)-(1-methyl-2-phenylindole) sulfonium triflate* **3b** White crystal, mp: 174–176 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): 2.47 (s, CH<sub>3</sub>, 3H), 3.84 (s, CH<sub>3</sub>, 3H), 7.00–7.22 (m, ArH, 4H), 7.23–7.45 (m, ArH, 4H), 7.46–7.51 (m, ArH, 5H), 7.55–7.65 (m, ArH, 5H). HRMS (ESI) calcd for C28H24NS (M+ OTf)<sup>+</sup>: 406.1624, found: 406.1627.

*S-phenyl-(4-iodophenyl)-(1-methyl-2-phenylindole) sulfonium triflate* **3***c* White crystal, mp: 199–202 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): 3.84 (s, CH<sub>3</sub>, 3H), 7.19–7.22 (m, ArH, 1H), 7.45–7.47(m, ArH, 3H), 7.60–7.61 (m, ArH, 4H), 7.63–7.68 (m, ArH, 10H); HRMS (ESI) calcd for C27H21NSI (M+ OTf)<sup>+</sup>: 518.0434, found: 518.0437.

# Coating preparation and film property test

Polymeric composition for use as coating material comprises 15 wt% monomer (HDDA), 80 wt% epoxy acrylate resin (UV6104), 2 wt% triethanolamine and 3 wt% photoinitiator. The monomer and epoxy acrylate resin (UV6104) were mixed at room temperature under stirring and then triethanolamine and photoinitiator

were added dropwise. The resulting mixture was further heated for 30 min to obtain a transparent coating material. The liquid formulation was coated onto a clean glass using a coating machine and the coating thickness was 100  $\mu$ m. Then, the sample was exposed to UV radiation with a 400-W mercury lamp for a certain time. The pencil hardness and adhesion of the UV-cured films were measured by ASTM D 3363 and ASTM D 3359 test methods currently accepted by industry, respectively.

#### **Results and discussion**

#### Synthesis and characterization of triarylsulfonium salt

Our previous work demonstrated that diaryliodonium salts are excellent arylating reagents for the synthesis of *S*-phenylbenzothiophenium triflates [19–21]. In the present work, three kinds of *S*-arylated products were prepared as shown in Scheme 2. The reaction of dibenzo[b,d]thiophene with diaryliodonium salts were performed under solvent-free conditions using Cu(OAc)<sub>2</sub> as catalyst. Under mild conditions, the target products were obtained in good yields. Synthesis of triarylsulfonium salts **2** and **3** were attempted under analogous conditions but failed. Under the optimized reaction conditions, compounds **2** and **3** were prepared in tetrachloroethane in good yields using CuI and Cu as a cocatalyst. The synthesized triarylsulfonium salts exhibited good solubility in common organic solvents, such as ethanol, acetonitrile, acetone, ethyl acetate and dichloromethane, suggesting that as new cationic photoinitiators they possess good compatibility with other components of the polymerization system.



Scheme 2 Synthesis of the triarylsulfonium salts



Fig. 1 Absorption spectra of 1a, 2a, 3a, BP and Irgacure 184

#### UV-Vis absorption studies

Figure 1 depicts the UV absorption spectra of **1a**, **2a** and **3a** in dichloromethane. For comparison, the absorption spectra of **BP** and Irgacure **184** are also presented. These spectra were measured at an identical molar concentration  $(1 \times 10^{-4} \text{ M})$ , so that a direct comparison of absorbance can be made. As can be seen from Fig. 1, the absorption spectrum of the triarylsulfonium salts exhibits strong absorption in the 200–300 nm region, corresponding to  $\pi$ - $\pi$ \* transitions of the conjugated benzene ring. The absorption bands observed at 316 and 294 nm for **1a** and **3a**, respectively, could be attributed to n- $\pi$ \* transition of the thiophene and indole moieties. The maximum absorbances of **1a** and **3a** are red-shifted with respect to the absorption ( $\lambda_{max}$ 260 nm) of the triarylsulfonium salts previously reported [22]. In particular, the extended conjugation of **3a** due to the presence of the indole group induced a large shift of its main absorption band toward the near-UV wavelength range, which makes it more suitable for UV-curing with a UV high-pressure mercury lamp as a radiation source.

#### Photopolymerization studies

The synthesized triarylsulfonium salts were evaluated as photoinitiators for cationic polymerization of epoxy acrylate resin (UV6104) and activated monomer hexane-1,6-diyldiacrylate (HDDA). The triarylsulfonium salt was mixed with certain amounts of epoxy acrylate resin (UV6104), monomer and additive to produce a transparent coating. An experiment on UV-curing of the surface coating was carried out and the properties of the cured film were tested.

As summarized in Table 1, compared with **BP** and Irgacure **184**, the UV-cured coatings obtained by the photoinitiation with **1a** and **1b** have good hardness possibly due to the dibenzothiophene structure of these salts. Bearing the benzoyl moiety with high photoinitiation efficiency, **2a** and **2b** provide excellent performance in

Entry	Photoinitiator	Gloss	Curing time <sup>a</sup> (s)	Adhesion <sup>b</sup>	Pencil hardness <sup>c</sup>
1	1a	Smooth and transparent	10	1	4H
2	1b	Smooth and transparent	11	1	4H
3	1c	Smooth and transparent	12	3	2H
4	2a	Smooth and transparent	5	1	4H
5	2b	Smooth and transparent	5	1	4H
6	3a	Smooth and transparent	10	2	5H
7	3b	Smooth and transparent	10	2	5H
8	3c	Edge of coking	10	3	2H
9	BP	Smooth and transparent	10	3	3H
10	184	Smooth and transparent	11	2	2H

 Table 1
 Properties of UV-curable coating

<sup>a</sup> The curing time of the UV-curing coating was measured by the finger contact method

 $^{\rm b}$  The determination of curing film adhesion by the grid method, levels are classified into 0–5, with 0 the best, and level 5 the worst

<sup>c</sup> The determination of curing film hardness by using the pencil hardness

UV-curable coatings. The curing time was much shorter (5 s) and the pencil hardness was greater than 4H (Table 1, entries 4 and 5). **3a** and **3b** also have good pencil hardness due to the presence of indole ring (Table 1, entries 6 and 7). By contrast, **1c** and **3c** exhibit poor pencil hardness possibly due to the iodo substituent on the benzene ring, which may cause poor solubility of triarylsulfonium salts in the resin. All the UV-cured films are glossy and transparent except when using **3c** as a photoinitiator. Overall, the synthesized triarylsulfonium salts could be utilized as cationic photoinitiators for UV photopolymerization.

#### Photoinitiation mechanism

The photopolymerization mechanism was preliminarily discussed for the case of photoinitiator **2a** (Scheme 3). First, **2a** absorbs the photons and thereby goes to the



Scheme 3 Possible mechanism of photo-initiated polymerization

excited state (I). Possessing benzophenone and triarylsulfonium salt groups in its structure, the excited state (I) of **2a** could undergo photolysis in two ways: the homolytic cleavage of the C–S bond to form cationic radical (II) [23–26] since the bond energy of the C–S bond is low, and the electron transfer in the molecule to produce the benzoyl radical [27–30]. The cationic radical (II) extracts a hydrogen ion to produce a protonic acid and a free radical. The protonic acid is further deprotonated and the acidic proton generated ultimately initiates the oligomer polymerization. Thus, **2a** combines the advantages of radical and cationic photoinitiators. i.e., rapid polymerization without oxygen inhibition and good curing and post-curing ability.

### Conclusions

Three kinds of triarylsulfonium salts have been synthesized and their activity as cationic photoinitiators was studied. These triarylsulfonium salts could be utilized as cationic photoinitiators in the UV-curing process. The triarylsulfonium salts **3a** and **3b** showed strong absorptions at wavelengths above 294 nm and excellent photoinitiating activity. **2a** and **2b** can photoinitiate free radical and cationic polymerizations.

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