

SYNTHESES AND ACTIVE BEHAVIOR OF NOVEL UV PHOTOINITIATORS*

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Abstract A series of novel hybrid photoinitiators ($\text{YPhCOPhXPhI}^+\text{PhPF}_6^-$, $\text{Y} = 4\text{-NO}_2$, 4-MeO or 3-Cl , $\text{X} = \text{O}$, OCH_2 , or nothing), which contain multiple aromatic rings (PhCOPhXPh), were prepared by reaction of easily available aryl ketones (YPhCOPhXPh) with iodosobenzene diacetate [$\text{PhI}^+\text{OCOCH}_3(\text{CH}_3\text{CO}_2)^-$]. The inset of an aromatic ring into *p*-benzoyldiphenyliodonium hexafluorophosphate ($\text{PhCOPhI}^+\text{PhPF}_6^-$) (BDPIH, He-type photoinitiator) between diphenyliodonium and benzoyl is propitious both to the preparation and the photoinitiating activity of ketonic diphenyliodonium photoinitiators. The yield and performance of the novel hybrid photoinitiators are much better than those of the He-type initiator.

Keywords: Photoinitiator; Iodosobenzene diacetate; Synthesis.

INTRODUCTION

Photopolymerization has been developed tremendously for recent years due to its wide applications. Generally, there are two types of photopolymerization. One is radical photopolymerization, which uses radical photoinitiator, and another is cationic photopolymerization, which uses cationic photoinitiator^[1–3].

Radical photopolymerization has some advantages, such as faster polymerization rate, wide scope of monomers and being insensitive to moisture. But it would be severely affected by oxygen. What is more, the volume shrink of the coating material obtained from radical photopolymerization often takes place, which decreases the adherence intensity of the coating. On the contrary, the volume shrink of the coating material obtained from cationic photopolymerization never takes place, and the cationic photopolymerization is insensitive to oxygen. However, the cationic photopolymerization suffers from slow polymerization rate and is affected by moisture. Furthermore, compounds which contain functional groups bearing active hydrogen, such as hydroxyl, amino, carboxyl, *etc.*, would also affect the photopolymerization and consequently cannot be used as monomers for cationic photopolymerization.

In order to combine the advantages of radical photopolymerization and cationic photopolymerization and overcome their disadvantages, a development of new type of photoinitiators and/or photopolymerization methods is highly desirable. A desirable method is that the mixture of radical type monomer and cationic type monomer are polymerized in the presence of a mixture of benzophenone, which is a photosensitive agent, a radical type photoinitiator and diphenyliodonium hexafluorophosphate, which is a cationic type photoinitiator^[4]. In this case, the initiating process is bimolecular photosensitization, and the efficiency of this bimolecular system is usually limited by diffusion especially in highly viscous polymeric systems. Recently, He and co-workers reported a novel hybrid photoinitiator, *p*-benzoyldiphenyliodonium hexafluorophosphate (**1**) ($\text{PhCOC}_6\text{H}_4\text{I}^+\text{PhPF}_6^-$)^[5]. He's experiment showed that compound **1** could initiate not only the

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photopolymerization of cyclohexene oxide, which is a typical cationic polymerization monomer, but also the photopolymerization of methyl methacrylate, which is a typical radical polymerization monomer, with its cationic photoinitiating performance taking predominance.

However, the synthesis of He-type photoinitiator **1** encountered great difficulties, such as low yield (total yield: 0.9%), long reaction time, expensive starting material, caustic reaction conditions, *etc.*

We report here a kind of novel hybrid photoinitiators (**2**) by inseting an aromatic ring into He-type photoinitiator between benzoyl and diphenyliodonium groups. **2** can be synthesized more easily and its performance is much better than that of **1**^[6].

EXPERIMENTAL

UV spectrum was measured on a Shimadzu UV 265; NMR was measured on a Bruker AV 400 with tetramethylsilane as an internal standard.

A GZ 150 W high-pressure mercury lamp, made by Shanghai Yaming Lamp Limited Company, was used as a UV light source for the photocuring test.

Iodosobenzene diacetate was prepared according to the method reported by Sharefkin and co-workers^[7].

A Typical Synthesis Procedure of Benzoyl Compounds

Into a three-neck round flask equipped with a stirrer, a thermometer and a condenser bearing an anhydrous calcium chloride tube, were added 7.71 g (50 mmol) of biphenyl, 6.86 g (49 mmol) of benzoyl chloride and 9.25 g (69 mmol) of anhydrous aluminum chloride. The air in the flask was replaced by nitrogen. The mixture was stirred at 150°C for 8 h and then cooled down slowly to 100°C. 15 mL of 10% hydrochloric acid was added while stirring and then 20 mL of benzene. The mixture was refluxed for 5 min and then cooled to room temperature. The oil layer was separated and washed twice with water. The benzene was evaporated and the residue was purified by recrystallization to give 9.9 g of 4-phenylbenzophenone (**3**)^[8], yield 78%, m.p. 98–100°C.

4-Benzoyldiphenyl ether (**4**) was synthesized from diphenyl ether according to the method for the synthesis of **3**. Yield 79%, m.p. 62–64°C.

A Typical Synthesis Procedure of 4-Aryl Diphenyliodonium Hexafluorophosphates

Into a solution of **3** (5.17 g, 20 mmol) and iodosobenzene diacetate (**5**) (7.09 g, 22 mmol) in acetic anhydride (32 mL), were added dropwise a solution of acetic anhydride (6.5 mL) and concentrated sulfuric acid (13 mL). The reaction mixture was stirred at room temperature for 1 h and then stirred at 45–55°C for 12 h. After cooling to room temperature, the reaction mixture was added into 40 mL of water and filtered. The filtrate was extracted twice with ether and once with *n*-hexane. Into the extracted filtrate, an aqueous solution containing 7.73 g (42 mmol) of potassium hexafluorophosphate was added and white precipitate formed. The white precipitate was filtered, washed with water twice and then dried in vacuum at 50°C to afford 8.24 g (68% yield) of 4-(4-benzoylphenyl)diphenyliodonium hexafluorophosphate (**6**). m.p. 152–156°C. NMR (acetone-*d*₆): δ_{H} 7.56–7.60 (m, 2H), 7.64–7.71 (m, 3H), 7.79–7.82 (m, 3H), 7.90 (s, 4H), 7.98–8.02 (m, 2H), 8.41–8.44 (2H), 8.48–8.52 (m, 2H); δ_{C} 113.89, 114.87, 128.25, 129.37, 130.56, 131.41, 131.80, 133.38, 133.50, 133.93, 136.61, 137.22, 138.36, 138.60, 142.97, 145.16, 196.04.

Other diphenyliodonium hexafluorophosphates from substituted (or unsubstituted) 4-benzoyldiphenyl ether or 4-benzyloxybenzophenone were prepared according to the method for the synthesis of **6**.

p-(4-Benzoylphenoxy)diphenyliodonium hexafluorophosphate (**7**): yield 82.9%, m.p. 150–152°C, NMR (acetone-*d*₆): δ_{H} 7.25–7.31 (m, 4H), 7.55–7.58 (m, 2H), 7.62–7.69 (m, 3H), 7.77–7.80 (m, 3H), 7.87–7.91 (m, 2H), 8.38–8.45 (m, 4H); δ_{C} 106.79, 115.30, 120.23, 122.89, 129.32, 130.47, 133.20, 133.29 (2 kinds of C), 133.71, 134.98, 136.40, 139.54, 139.18, 159.65, 161.37, 195.29.

p-[4-(*p*-Methoxybenzoyl)phenoxy]diphenyliodonium hexafluorophosphate (**8**): yield 33%, m.p. 111–114°C, NMR (CDCl₃): δ_{H} 3.90 (s, 3H), 7.06–7.08 (m, 2H), 7.23–7.25 (m, 2H), 7.28–7.30 (m, 2H), 7.63–7.65 (m, 2H), 7.79–7.84 (m, 5H), 8.35–8.41 (m, 4H); δ_{C} (acetone-*d*₆), 56.00, 114.58, 120.24, 120.29,

122.77, 123.01, 132.93, 133.00, 133.08, 133.23, 133.28, 133.73, 136.29, 136.32, 136.87, 139.05, 139.09, 194.00.

p-[4-(*p*-Nitrobenzoyl)phenoxy]diphenyliodonium hexafluorophosphate (**9**): yield 67%, m.p. 100–105°C, NMR: δ_{H} (CDCl₃) 7.21–7.27 (m, 4H), 7.59–7.61 (m, 2H), 7.72–7.75 (m, 1H), 7.89–7.91 (m, 2H), 7.99–8.01 (m, 2H), 8.29–8.40 (m, 6H); δ_{C} (acetone-*d*₆) 107.55, 120.22, 123.14, 124.42, 129.70, 130.53, 131.47, 133.19, 133.58, 133.66, 133.71, 136.34, 139.11, 143.94, 160.47, 160.96, 193.93.

p-[4-(*o*-Chlorobenzoyl)phenoxy]diphenyliodonium hexafluorophosphate (**10**): yield 58.8%, m.p. 80–82°C, NMR (acetone-*d*₆): δ_{H} , 7.19–7.21 (m, 2H), 7.27–7.29 (m, 2H), 7.45–7.51 (m, 2H), 7.56–7.63 (m, 3H), 7.74–7.78 (m, 1H), 7.82–7.84 (m, 2H), 8.33–8.34 (m, 2H), 8.37–8.40 (m, 2H); δ_{C} , 107.68, 115.67, 120.19, 123.29, 128.12, 129.85, 130.81, 131.24, 132.38, 133.20, 133.27, 133.68, 133.80, 136.33, 139.09, 139.53, 160.80, 160.89, 193.83.

p-[4-Benzoylphenoxy]methylene]diphenyliodonium hexafluorophosphate (**11**): yield 48%, m.p. 149–151°C, NMR (acetone-*d*₆): δ_{H} , 5.51 (s, 2H), 7.42–7.51 (m, 5H), 7.53–7.62 (m, 5H), 7.67–7.71 (m, 1H), 7.73–7.78 (m, 3H), 8.12 (dd, $J_1 = 1.92$, $J_2 = 7.8$, 1H), 8.16 (d, $J = 7.8$, 2H), 8.73 (d, $J = 1.92$, 1H), δ_{C} , 73.24, 104.84, 113.91, 114.76, 129.22, 129.50, 129.68, 130.47, 133.11, 133.70, 133.72, 135.86, 136.67, 137.71, 138.05, 139.97, 159.93, 193.36.

The Photoinitiating Activity Test of Hybrid Iodonium Hexafluorophosphates

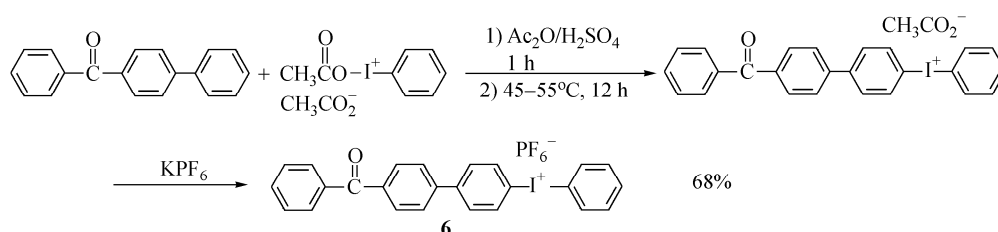
A sample trestle table was placed below the UV light, and the distance from the UV light tube to the sample table face was adjusted to 10 cm. The UV lamp was turned on and preheated for 15 min before the curing test. A test sample of photocoating-material was made by mixing 60 parts of biglycidyl 5,6-epoxynorbornane-2,3-diformate, 35 parts of glycidyl methacrylate and 5 parts of iodonium hexafluorophosphate. On a piece of 40 mm × 40 mm wood board, was coated 1.5 g of the photocoating-material sample. The thickness of the obtained photocoating-material film is 0.1 mm. Then the wood board was placed on the sample table and irradiated for 15 s or longer according to acquirement. The photopolymerization was tested by using finger method (*i.e.*, touching the coating surface with a finger to find out whether the coating surface was sticking or soft. If the surface was neither sticky, nor soft, the photopolymerization took place very well).

RESULTS AND DISCUSSION

The Synthesis of the Hybrid Iodonium Hexafluorophosphates

He-type photoinitiator **1** (PhCOC₆H₄I⁺PhPF₆[−]) has caused some attention for its hybrid photoinitiating performance. However, synthesis of compound **1** encountered great difficulty. He and co-workers synthesized compound **1** by coupling diphenylmethane with iodosobenzene diacetate and then oxidizing methene group to carbonyl. We cannot expect the reaction of benzophenone, which is cheap and conveniently available, with iodosobenzene diacetate to take place to give **1** because the benzoyl is an electron-withdrawing group. And also, Friedel-Crafts acylating reaction of diphenyliodonium salt with benzoyl chloride cannot take place. So, the He's synthetic path is reasonable. But there are many problem in He-type structure: (1) the synthetic steps are too many (6 steps) and the synthetic time is too long (total a week); (2) the start material Ag₂O and (NH₄)₂Ce(NO₃)₆ are too expensive; (3) the total yield is too low (10% reported by He, 4% found in our experiment). Therefore, it is not acceptable for compound **1** to be used as a photoinitiator.

We inserted phenyl group into compound **1** between the benzoyl group and the diphenyliodonium group, and the synthesis question became very simple. Unlike benzophenone, benzoyldiphenyl, in which the electronic-withdrawing group carbonyl is isolated efficaciously by the additional benzene ring, is an active nucleophile and can react with iodosobenzene diacetate directly without any difficulty. This makes it possible to make use of aromatic ketone as a start material in synthesizing carbonyl-bringing diphenyliodonium compounds. Our synthetic path is shown as Scheme 1.



Scheme 1 The synthetic route of 4-(4-benzoylphenyl)diphenyliodonium hexafluorophosphate

Compared with synthesis process of compound **1**, our novel compound **6** has many advantages: (1) the synthetic steps is very simple (2 steps) and the synthetic time is very short (only one day, total); (2) the start material benzoyldiphenyl is conveniently available and the expensive material AgO and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ are omitted; (3) the total yield is extremely high (68%). These advantages make it possible for our novel compound **6** to come to industry application.

The reactions of other ketones bearing multi-benzene ring with **5** were also examined. The results are shown in Table 1.

Table 1. The reaction of multiple benzene ring ketones reaction with **5**

Ar	Product		Yield
		(7)	82%
		(8)	33%
		(9)	67%
		(10)	58%
		(11)	48%

The inserting of oxygen into biphenyl group promotes the reaction because the unshared electron pair in oxygen participates in the conjugation of benzene rings with carbonyl and increases the electronic cloud density of the benzene ring. Therefore the yield of compound **7** comes to 82% and is much higher than that of compound **6**.

It was expected that addition of a CH_3O group at the other *p*-position of carbonyl could promote the reaction further because the CH_3O group was also an electronic donating group. But the experiment showed a negative result. The yield of **8** is the lowest among all of the iodonium compounds synthesized in this paper. The reason for the lowest yield of **8** was that the reaction took place on the ring bearing CH_3O group besides the desired ring and this side reaction also made difficulty in the product separation. The low yield of **11** is in anticipation because OCH_2 interrupts the conjugation of two aromatic rings. Even so, all of our novel compounds are much easier and more economical to be prepared than compound **1**.

The Photoinitiating Performance of the Hybrid Iodonium Hexafluorophosphates

In order to examine the photoinitiating activity of the synthesized hybrid iodonium hexafluorophosphates, a mixture comprising biglycidyl 5,6-epoxynorbornane-2,3-diformiate and glycidyl methacrylate was chosen as a photo curable material. After being added iodonium hexafluorophosphate, the mixture was coating on a piece of

wood to form a film whose thickness was 0.1 mm. Then, the film was irradiated by a 150 W UV light, which was 10 cm away from the film, to measure the solidification time. By comparing the solidification time at the same condition described in experimental, we could appraise the photoinitiating activity of iodonium hexafluorophosphates. To our delight, all these hybrid iodonium hexafluorophosphates synthesized in this paper had better photoinitiating activity than **1**. The photocurable material was solidified completely within 15 s when **6**, **7**, **8**, **9** or **11** was used as a photoinitiator, while the solidification time was 25 s when **1** was used as a photoinitiator. The excellent photoinitiating activity of **6**, **7**, **8** and **9** is probably attributed to their longer conjugation system. Unexpectedly, the photoinitiating activity of **10** was almost the same as **1**.

In order to further understand the conjugation effect on the photoinitiating activity, we determined the UV absorption of these photoinitiators. The results are summarized in Table 2. He *et al.* reported iodium salt **1** had three UV absorption peaks in 206, 250 and 342 nm. However, it was found that there were only two UV absorption peaks in the UV spectra of iodium salt **6**, **7**, **8**, **9**, **10** and **11**. Because the long wavelength absorption was considered to be important for photocuring under most commercially available UV lamp, we were interested in the absorption at 342 nm. In spite of no peak around 342 nm, we measured the extinction coefficient of **6**, **7**, **8**, **9**, **10** and **11** at 342 nm.

Table 2. The UV absorptions of iodium salts^a

Iodium salts	$\lambda_{\max 1}$ (nm), ($\epsilon_{\max}$)	$\lambda_{\max 2}$ (nm), ($\epsilon_{\max}$)	$\epsilon_{342 \text{ nm}}$
1	206 (6.9×10^4) ^b	250 (4.0×10^4) ^b	2.3×10^2 ^b
6	203.8 (6.4×10^4)	288.6 (3.6×10^4)	8.3×10^3
7	203.1 (7.5×10^4)	271.2 (3.3×10^4)	3.9×10^2
8	204.6 (4.9×10^4)	284.2 (2.3×10^4)	7.3×10^2
9	203.6 (6.9×10^4)	256.6 (2.9×10^4)	1.1×10^4
10	204.0 (6.4×10^4)	277.6 (2.5×10^4)	2.5×10^2
11	202.8 (5.2×10^4)	264.2 (1.9×10^4)	4.1×10^2

^aMeasured in MeOH; ^bReported by He *et al.*^[5]

Compared with the second absorption maximum (250 nm) of **1**, the second absorption maximum of **6**, **7**, **8**, **9**, **10** and **11** shifts bathochromically to 288.6, 271.2, 284.2, 256.6, 277.6 and 264.2 nm respectively. The extinction coefficients of the second peaks of **6**, **7**, **8**, **9**, **10** and **11** are higher than that of **1**. Especially, the extinction coefficient of **6** and **9** are much higher. It is this bathochromic shift and the high extinction coefficient that are responsible for their excellent photoinitiating activity.

It should be noted that the second absorption maximum wavelength of **6** is the longest among all above iodium salts, and **6** has very high extinction coefficient (8.3×10^3) at 342 nm and is very easy to be synthesized. Therefore, photoinitiator **6** will have the potential applications not only for laboratory research but also for industry.

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