

# Synthesis and Applications of Onium Salts for Photopolymerization Reactions

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**Abstract:** The synthesis and characterization of phosphonium and arsonium salts having anthraquinone and anthracene moiety was carried out by reacting equimolar amounts of halomethyl anthracene or anthraquinone with triphenylphosphine or triphenyl arsine in toluene solvent. The halide counter (Cl or Br) ion was exchanged with hexafluoro antimonate ( $\text{SbF}_6^-$ ) which proved to be a useful photoinitiator for polymerizing cyclohexene oxide, styrene, p-methyl styrene, and N-vinylcarbazole. The experimental results demonstrate the effects of salt, monomer structures, and the photolysis time on the rate of polymerization and the number average molecular weight of the obtained polymer. These salts are easy to handle, nonhygroscopic under laboratory conditions, and they have good solubility in halogenated solvents such as dichloromethane and chloroform.

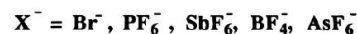
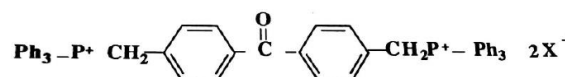
**Keywords:** Photopolymerization, 2-methyleneanthraquinonium, 9-methylantracencium salts, Cyclohexene oxide, styrene, p-methyl styrene, N-vinylcarbazole.

## 1. INTRODUCTION

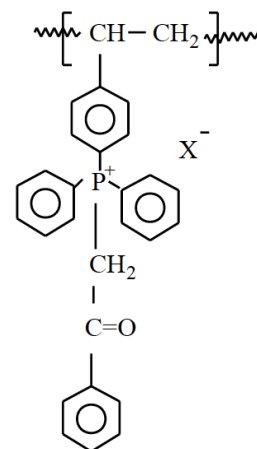
The use of photoinitiated polymerization is continuously growing in industry as reflected by the large number of applications in coatings, inks, adhesives, optoelectronics, laser imaging, stereolithography, 3D and 4D printings, and nanotechnology. The wavelength flexibility, and environmental and safety issues in photoinitiating systems design is very important in emerging applications of photoinitiated polymerizations in the field of biomaterials, surface modification, preparation of block and graft copolymers, and nanocomposites [1].

The photoinitiators are light-absorbing compounds that are active under low light intensity and in the visible range for polymerization reactions. Photoinitiations using diaryliodonium, triphenyl sulfonium, phosphonium, and arsonium salts, as monomeric soluble or polymeric insoluble (Structure 1) have found great applications in the graphics arts, packaging, dental, medical, and microelectronics, and environmentally friendly industries, as it has the advantage of operating at room temperature, and solvent free industry [2,3].

The polymeric salts are easy to handle, store, and sensitive to UV light. Therefore, they can be used as photocatalysts in polymerization or curing reactions at room temperature [4].



(A)



(B)

**Structure 1:** Monomeric (A), and polymeric (B) phosphonium salts.

Anthracene and anthraquinone moieties are versatile organic photocatalysts, they have low oxidation potential, they are extensively used in organic dyes for solar cells, photochromic materials, electrographic materials, and liquid crystal materials, [5], they have been identified as promising scaffolds for the design of photoinitiators in polymerizations reactions [6]. Photosensitization is used to increase the absorptivity of these photoinitiators to a longer wavelength [7].

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As part of our continuing effort to design new photoinitiators for polymerization reactions, we would like to report here on condensed aromatic whose photochemical reactivity drives from light absorption by anthracene and anthraquinone units attached to it triaryl phosphonium and arsonium salts having hexafluoroantimonate ( $\text{SbF}_6^-$ ) anion [8], initiation by these salts proceeds without complication, side reactions, or the need for co-catalysts and promoters. the synthesis and characterization of these salts are reported, and another part of the work is to examine them as photoinitiators for the production of polymers of cyclohexene oxide, p-methyl styrene, styrene, and N-vinylcarbazole, which have excellent potential for a broad range of applications in industrial products, surface coating and engineering plastics.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Materials

Starting materials and other reagents were obtained from Fluka Chemical Company and purified, where necessary, by standard procedures. The monomers cyclohexene oxide, p-methyl styrene, styrene, and N-vinyl carbazole (Fluka) were freed of inhibitors when necessary, then dried and distilled under reduced pressure just before use [9]. Solvents such as dichloromethane, chloroform, and diethyl ether (Fluka) were dried over calcium hydride and distilled before use. Acetone (Fluka) "AnalaR Grade" was used as received. Triphenylphosphine, triphenylarsine, 9-chloromethylantracene, 2-bromomethylantraquinone, and potassium hexafluoroantimonate were obtained from Fluka AG in good grade and used as received. The Elemental analysis for these salts was within the expected ranges.

### 2.2. Instruments

Ultraviolet spectra were obtained on a Cary-2390 UV-VIS-NIR Spectrometer. Infrared spectra were recorded on a Nicolet 5 DXB FTIR spectrophotometer using the KBr disk of the sample. Nuclear Magnetic Resonance Spectroscopy (NMR) Spectra were taken in  $\text{CDCl}_3$ , on an XL-200 pulsed Fourier transform NMR spectrometer with tetramethyl silane as internal standard.

The molecular weights of the obtained polymers were determined using a Waters Associates model 150-ALC/GPC at  $30^\circ$ , and were calculated based on polystyrene standards calibration, the systems were

analyzed in Tetrahydrofuran (THF) with a solvent flow rate of 1.5 mL/min and a polymer concentration of 1 mg/ml [10].

### 2.3. Polymerization Procedure

The selected amounts of the monomer and initiator in  $\text{CH}_2\text{Cl}_2$  were placed in a 12 mm diameter Pyrex tube, the solution degassed under vacuum by conventional freeze-thaw techniques and sealed off under a vacuum. Irradiation was carried out using a Xenon ARC Lamp, Varian Model PS-150-8 with power supply adjusted at 12 Ampere constant current, the light intensity was  $11.24 \times 10^{18}$  Photon  $\text{sec}^{-1} \cdot \text{cm}^2$ , the temperature of the tubes was maintained at  $25^\circ\text{C}$ . Reaction tubes were irradiated at 65 cm from the light source. The isolated polymer was precipitated in four-fold excess methanol containing a few drops of dilute hydrochloric acid, washed with methanol, filtered, and dried under a vacuum. The polymer recovered was a white solid, the rate of polymerization was calculated gravimetrically from the mass of the polymer isolated [11].

### 2.4. General Synthesis of the Onium Salts 2-9

The onium salts reported in Table 1 were prepared by refluxing an equimolar amount of the methyl bromide or chloride of anthraquinone or anthracene with triphenylphosphine or triphenylarsine in toluene for 4 hours. After that time, cooling to room temperature gives a white crystalline solid which was collected by filtration and dried. The salt was further purified by dissolution in a small volume of chloroform and precipitation in excess diethyl ether [12].

The obtained salt with halide counterion was converted to the required active counterion salt having anion  $\text{SbF}_6^-$  by adding a light excess from  $\text{KSbF}_6$  in water. After siring the solution was filtered, washed several times with water then diethyl ether and dried. Purification was achieved by dissolving the isolated salt in small-volume chloroform and adding excess diethyl ether which gives the pure salt in high yield [13].

The elemental analyses obtained for these salts were within the expected ranges. Melting points are uncorrected. The prepared onium salts are good crystals of white color. They are stable under laboratory conditions and are soluble in dichloromethane, chloroform, and THF. The physical and spectral parameters are shown in Table 1. The UV spectra of the salts are shown in Figures 1 and 2 in dichloromethane. The solution of the selected salt was

Table 1: Properties of the Onium Salts (1-8)

Salt no.	Anion (X)	Melting point °C	Carbonyl stretch	% Yield	NMR $\delta$ CH2	$\lambda_{\max}$ in CH <sub>2</sub> Cl <sub>2</sub>	$\epsilon_{\max}$ CH <sub>2</sub> Cl <sub>2</sub> M <sup>-1</sup> cm <sup>-1</sup> X10 <sup>4</sup>
2	Cl	285-86	-	75	6.5	400	7.34
						380	7.42
						375	7.34
						360	6.10
3	SbF <sub>6</sub>	246-47	-	94	5.8	400	7.90
						380	7.42
						360	6.82
						260	7.54
4	Br	312-15	1674	91	5.9	328	5.34
						259	8.75
						233	7.65
5	SbF <sub>6</sub>	243-45	1670	93	4.6	327	6.17
						272	20.00
						266	31.55
6	Cl	134-36	-	72	6.1	392	2.07
						372	2.33
						358	1.68
7	SbF <sub>6</sub>	132-39	-	90	5.6	391	1.88
						371	2.20
						353	1.61
8	Br	194-96	1675	74	5.8	328	1.28
						277	3.28
						258	9.39
9	SbF <sub>6</sub>	197-99	1671	92	4.7	328	1.78
						277	4.84

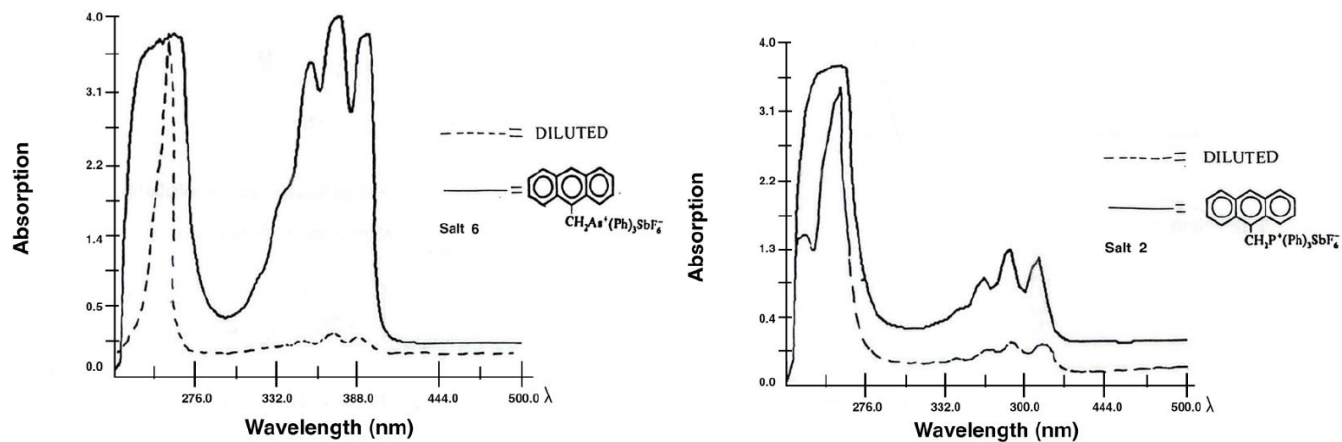
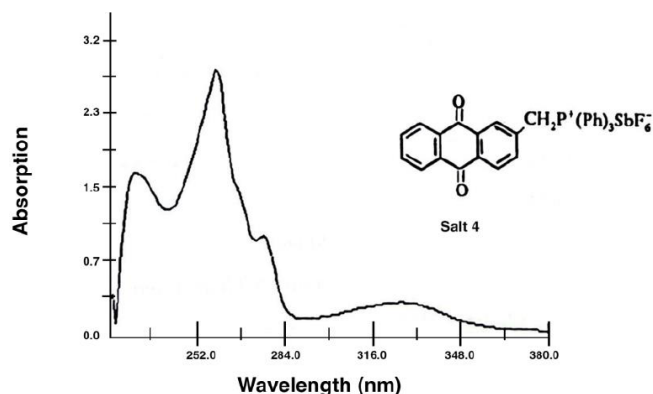


Figure 1: U.V. absorption spectra of salts 2 and 6 in dichloromethane.

diluted to reveal all the peaks in the spectral regions as shown in Figure 1.



**Figure 2:** U.V. absorption spectrum of salts 4 in dichloromethane.

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis and Characterization of the Onium Salts (Structure 2-9)

##### A. The Phosponium Salts (2-5)

##### 9-Methylene Anthracenyl Triphenylphosphonium Chloride (Structure 2)

1.13 g of 9-chloromethyl anthracene ( $5.00 \times 10^{-3}$  mole), 1.50 g of triphenylphosphine ( $5.73 \times 10^{-3}$  mole) were dissolved in 30 ml of toluene in a 100 ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 hours. After that time the mixture was cooled to room temperature. The precipitated salt was recovered and characterized as in Table 1.

##### 9-Methylene Anthracenyl Triphenylphosphonium Hexafluoroantimonate (Structure 3)

1.22 g of 9-methylene anthracenyl triphenylphosphonium chloride ( $2.50 \times 10^{-3}$  Mole), 0.85 g of  $\text{KSbF}_6$  ( $3.09 \times 10^{-3}$  mole) were stirred in 100 ml of solvent for 2 hours. The solvent used was a 50 / 50 mixture of water/methanol by volume. The precipitated salt was recovered and characterized as in Table 1.

##### 2-Methylene Anthraquinonyl Triphenylphosphonium Bromide (Structure 4)

1.50 g of 2-Bromomethyl anthraquinone ( $5.00 \times 10^{-3}$  mole), and 1.50 g of triphenylphosphine ( $5.72 \times 10^{-3}$  mole) were dissolved in 30 ml of toluene in 100 ml round-bottomed flask equipped with a Teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 hours. After that

time the mixture was cooled to room temperature. The precipitated salt was recovered and characterized as in Table 1.

##### 2-Methyleneanthraquinonyl Triphenylphosphonium Hexafluoroantimonate (Structure 5)

1.09 g of 2-Methylene anthraquinonyl triphenylphosphonium bromide ( $2.50 \times 10^{-3}$  Mole), 0.85 g of potassium hexafluoroantimonate ( $\text{KSbF}_6$ ) ( $3.09 \times 10^{-3}$  mole) were stirred in 100 ml of solvent for 2 hours. The solvent used was a 50/50 mixture of water/methanol by volume. The precipitated salt was recovered and characterized as in Table 1.

##### B. The Arsonium Salts 6-9)

##### 9-Methyleneanthracenyl Triphenylarsonium Chloride (Structure 6)

1.13 g of 9-chloromethyl anthracene ( $5.00 \times 10^{-3}$  mole), and 1.60 g of triphenylarsine ( $5.27 \times 10^{-3}$  mole) were dissolved in 30 ml of toluene in a 100 ml round-bottomed flask equipped with a Teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 hours, after which the mixture was cooled to room temperature. The precipitated salt was recovered and characterized as in Table 1.

##### 9-Methyleneanthracenyl Triphenylarsonium Hexafluoroantimonate (Structure 7)

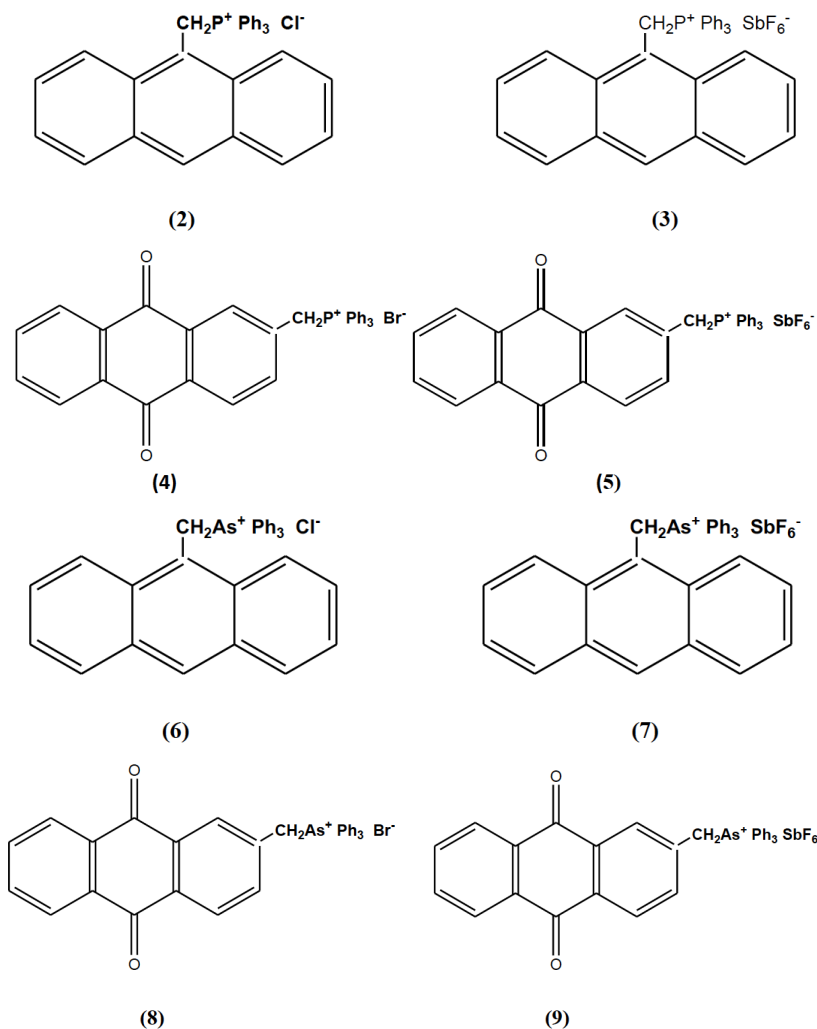
1.33 g of 9-methylene anthracenyl triphenylarsonium chloride ( $2.50 \times 10^{-3}$  Mole), and 0.85 g of  $\text{KSbF}_6$  ( $3.09 \times 10^{-3}$  mole) were stirred in 100 ml of solvent for 2 h. The Solvent used was a 50 / 50 mixture of water/methanol by volume. The precipitated salt was recovered and characterized as in Table 1.

##### 2-Methyleneanthraquinonyl Triphenylarsonium Bromide (Structure 8)

1.15 g of 2-Bromomethyl anthraquinone ( $5.00 \times 10^{-3}$  mole), and 10.0 g of triphenylarsine ( $5.23 \times 10^{-3}$  mole) were dissolved in 30 ml of toluene in a 100 ml round-bottomed flask equipped with a Teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 hours. After that time the mixture was cooled to room temperature. The precipitated salt was recovered and characterized as in Table 1.

##### 2-Methyleneanthraquinonyl Triphenylarsonium Hexafluoroantimonate (Structure 9)

1.20 g of 2-Methylenanthraquinonyl triphenylarsonium bromide ( $2.50 \times 10^{-3}$  Mole), 0.85 g of  $\text{KSbF}_6$



**Structure 2:** Chemical structure of the used onium salts (2-9).

( $3.09 \times 10^{-3}$  mole) were stirred in 100 ml of solvent for two hours. The solvent used was a 50/50 mixture of water/methanol by volume. The precipitated salt was recovered and characterized as in Table 1.

### 3.2. Photopolymerization

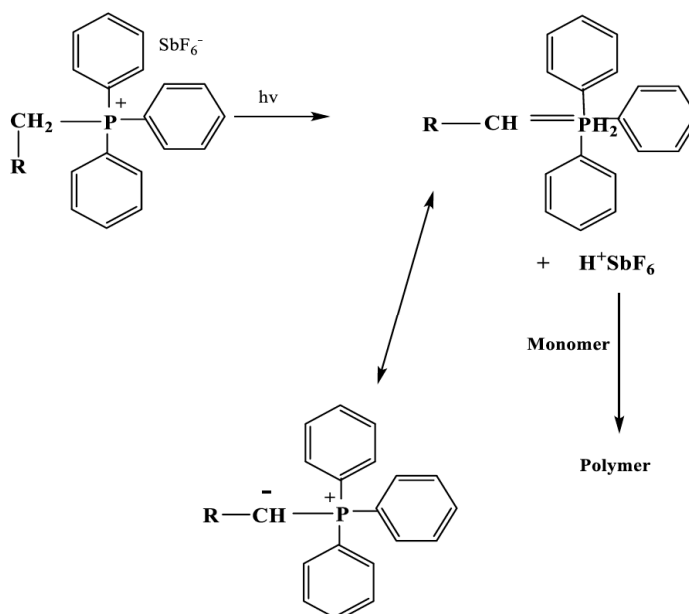
Under this work's experimental conditions, no polymerization occurs without photolysis. If any of the salts 3, 5, or 7 having anion  $\text{SbF}_6^-$  is photolyzed polymerization proceeds.

Based on the photopolymerization % conversion of each monomer presented in Table 2 shows that the rate of polymerization varies with monomer structure and reactivity of the monomers with the onium salts used falls in the following sequence: N-vinyl carbazole > cyclohexene oxide > p-methyl styrene > styrene, this reactivity order is related to factors such as the stability of the propagated chain against any termination process.

The anthracene phosphonium salt 3 and the arsonium anthracene salt 7 ( $X = \text{SbF}_6^-$ ) are the more reactive photoinitiators, than the anthraquinone phosphonium (5) and anthraquinone arsonium salt (9) having the counter ion ( $\text{SbF}_6^-$ ). This variation in reactivity is related to the intermediate phosphonium yield stability towards the propagated chain to compared to the arsonium yield, as shown in Scheme 1, where R group could be Anthracene or Anthraquinone unit.

Concerning counter-ion (X) effects the generated protonic acid  $\text{HSbF}_6$  is more stable and stronger than the  $\text{HAsF}_6$ , due to the low nucleophilicity of the  $\text{SbF}_6^-$  anion which minimizes the reaction of the growing chain with the anion. The number average molecular weight is also dependent on the rate of polymerization and the variation in the onium salt counter ion [14,15].

A typical absorption spectrum of diluted onium salts (2 and 4) in dichloromethane is shown in Figures 1 and



**Scheme 1:** Photoinitiation by onium salts.

**Table 2: Bulk Photopolymerization of Vinyl and Epoxide Monomers by Salts Number 2,4, and 6**

Salt #	Monomer	% conversion to polymer	$M_n$ average $\times 10^{-4}$ g/mol
2	CHO	48	2.81
4		24	1.63
6		32	2.22
2	PMS	48	2.81
4		24	1.63
6		32	2.22
2	Styrene	28	2.32
4		6	1.14
6		16	1.46
2	NVC*	82	3.23
4		40	2.44
6		52	2.90

**Monomers:** CHO = cyclohexene oxide, PMS = p- methyl styrene, NVC= N-vinylcarbazole.

Conditions: 25 °C, [salt] =  $5.0 \times 10^{-4}$ . Time = 20 minutes.

For NVC polymerization the time of polymerization reaction was 10 minutes.

2, it is worth mentioning here that all salts have shown the same characteristic absorption spectrum in dichloromethane regardless of the nature of the counter ion (X).

#### 4. CONCLUSION

Phosphonium and arsonium salts having anthracene or anthraquinone moiety have been

synthesized in good yield, and physical and spectroscopic properties were reported.

These onium salts were prepared with antimony hexafluoride ( $\text{SbF}_6^-$ ) anion and were used as polymerization photoinitiators for cyclohexene oxide, styrene, p-methylstyrene, and N-vinyl carbazole monomers. Based on the amount of polymer obtained in each case polymerization rate falls in the following

sequence: N-vinyl carbazole > cyclohexene oxide > p-methyl styrene > styrene. No polymer recovered without Photolysis of the reaction mixture.

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