

A Copolymeric Cationic Macrophotoinitiator Polystyrene-iodonium hexafluoroantimonate

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Abstract

A series of novel copolymeric Cationic Macrophotoinitiators Polystyrene-iodonium hexafluoroantimonate (PS-I·SbF₆) with different molecular weight were synthesized by the reaction of Polystyrene with [hydroxy(tosyloxy)iodo]benzene. The later product PS-I·SbF₆ was identified by ¹H-NMR, FTIR, GPC, DSC, and UV spectrum. Compared with [4-(2-hydroxy-3-butoxy-1-propoxy) phenyl] -phenyliodonium hexafluoroantimonate (BPI·SbF₆), the maximum absorption (λ_{\max}) of PS-I·SbF₆ red-shifted, its λ_{\max} moved from 227 to 260 nm, so it can well match the UV-A with mercury lamp. Photopolymerization of 3,4-Epoxy cyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (K126) initiated by Polystyrene-iodonium hexafluoroantimonate (PS-I·SbF₆) shows that different molecular weight of macrophotoinitiators exhibit different behaviors towards same monomer. The solubility and compatibility of PS-I·SbF₆ is better than low-molecular initiator Iodonium salts [4-(2-hydroxy-3-butoxy-1-propoxy) phenyl] -phenyliodonium hexafluoroantimonate (BPI·SbF₆), and its migration ratio in the cured film is much lower than the low-molecular initiator Iodonium salts BPI·SbF₆. The photoinitiation activities of the epoxy system in which PS-I·SbF₆ as a cationic photoinitiator were studied, results showed that it had good photosensitivity and the post-curing ability.

Key words: iodonium salt; cationic macrophotoinitiator; UV curing; photoinitiation activity

Introduction

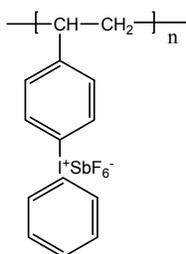
Photoinitiated cationic polymerization developed rapidly due to its many advantages: rapid cure speeds, pollution-free operation, and low energy consumption. One very important attractive feature is the lack of sensitivity of these polymerizations to the presence of oxygen. As a result of these attractive benefits, such photocured cationic polymerization systems are currently used in a wide variety of industrial applications, including coatings, adhesives, inks and microelectronics industries^[1, 2].

While the above stated advantages of diaryliodonium salts make them attractive photoinitiators, and there is considerable space for further improvement in these materials.

Diaryliodonium salts have received considerable attention as a cationic photoinitiators for the curing of vinyl or epoxy system. The range of the monomers polymerizable by a cationic mechanism encompasses both vinyl and ring-opening polymerizations. J. V. Crivello prepared a representative number of these compounds with various structures, functional groups, chromophores, and anions^[3]. Macrophotoinitiators have characteristics of low migration, low toxicity and so on^[4]. The impetus for much of the work has been due not only to the considerable academic interest in this field of polymer science but also to the rapid implementation of this technology into many commercial applications.

This article described a simple synthesis method of a macrophotoinitiator diaryliodonium salt, Polystyrene-iodonium hexafluoroantimonate (PS-I·SbF₆) and its application in UV curing system. After iodonium unit be induced to polymeric chain, the maximum absorption (λ_{\max}) of PS-I·SbF₆ red-shifted, its λ_{\max} moved from 227 to 260 nm, so it can well match the UV-A with mercury lamp. Its initiation reactivity was good, and its migration was lower than some low molecular products from the market.

The chemical structure of the cationic macrophotoinitiator was as below (Scheme 1):



Sche.1. The structure of polystyrene-iodonium hexafluoroantimonate (PS-I·SbF₆)

1 Experimental

1.1 Material and Characterization Techniques

All the organic reagents and solvents employed in this investigation were reagent-quality and were used as purchased from Reagent Company (Shanghai). n-butylglycidyl ether were obtained from Wells-Chem (Wuxi). NaSbF₆ was obtained from Ozark Fluorine Specialties Company. Mixed triarylsulfonium hexafluorophosphate salts in propylene carbonate (Omnicat 432), 3,4-Epoxy cyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (K-126) was obtained from Sartomer Company. 4,4'-dimethyl-diphenyl iodonium hexafluorophosphate (IHT-PI 820), IHT Group. [4-(2-hydroxy-3-butoxy-1-propoxy) phenyl]-phenyliodonium hexafluoroantimonate (BPI·SbF₆) was synthesized by ourselves.

¹H-NMR spectra was obtained with Bruker AM500 in DMSO; IR spectra were measured by FTLA2000—104; UV spectra was recorded on UV-1100; The melting-point was determined on MP - 51745. The Mn, Mw and PDI of PS and PS-I·SbF₆ were determined on Agilent-1100; Tg were measured by Mettler DSC822e.

1.2 Synthesis

Synthesis of [hydroxy(tosyloxy)iodo] benzene

Placed in a 250 ml. three-necked flask fitted with condenser, thermometer and paddle stirrer were 20.4g. (0.1 mol, 98%) iodobenzene. To the iodobenzene were added, with stirring, 51.0g. (0.45 mol) hydrogen peroxide, and 76.5g. (0.75 mol) acetic anhydride. The temperature was maintained below 50 °C. After addition was complete, the solution was maintained at 45 °C for 9 hours. Then there were added 20.9g. (0.11 mol) p-toluenesulfonic acid in portions, the reaction temperature was maintained at 40 °C for 2 hours after addition had been completed. Cooling, [hydroxy(tosyloxy)iodo] benzene was precipitated. The product was isolated by suction filtration, washed with ether and air dried. There were obtained 19.2g. [hydroxy(tosyloxy)iodo] benzene.

Synthesis of macrophotoinitiator (polystyrene-iodonium hexafluoroantimonate)

Combined together were 5.2g polystyrene and 3.92g (0.01 mol) [hydroxyl (tosyloxy) iodo] benzene, 50mL methylene chloride and 2mL glacial acetic acid. The reaction mixture was heated at reflux (40°C) for 12 hours to give a yellow, nearly transparent solution. The methylene chloride was removed on a rotary evaporator and then 100mL acetone was added. Next, There were added to the solution 2.59g (0.01mol) NaSbF₆ and the reaction mixture was stirred. Immediate formation of a white precipitate of sodium p-toluenesulfonate was formed, which was removed by centrifugal filter and suction filtration about three times. Then the residual solution was precipitated, and there was obtained the final product - a novel cationic macrophotoinitiator polystyrene-iodonium hexafluoroantimonate (PS-I·SbF₆). Yields ranged up to 66.8%.

1.3 Photopolymerizations

Photopolymerizations were carried out using the arc lamp. Photoinitiators were dissolved in the appropriate epoxy oligomers(K-126) to get the photosensitive resin. The photosensitive resin was coated on the clean glass, a coating layer which was 100µm thick was obtained. Then this coating layer was irradiated under 200W medium pressure arc lamp in different times, where the source light intensity was 33mW/cm², which got a transparent UV cured film.

1.4 Gel-yield measurements^[7]

The cured films were took into soxhlets extractor, distilled 8 hours in ethanol, air dried and weighted. The gel-yields were calculated using the following equation:

$$Gel - Yield = \frac{G_2}{G_1} \times 100\%$$

where G₂= the weight of before distilled; G₁= the weight of after distilled.

1.5 The migration measurements

Put the cured films in 95% ethanol (simulated fat liquid) in different hours at 40°C. Using UV-vis Spectrum to find their absorbencies and then calculate the migration of PS-I-SbF₆ with the following formulation.

$$C_i = \frac{A \cdot M}{\epsilon \cdot b} ; R = \frac{100 \cdot C_1}{C_2}$$

C_i: the relative concentration of photoinitiators (mol/L);

C₁: the relative concentration of PS-I-SbF₆;

C₂: the relative concentration of IHT-PI 820;

M: molecular weight of the photoinitiator(g/mol);

b: the sample cell thickness(cm);

A: Absorbency;

ε: molar absorptivity(L/mol·cm);

R: the migration of PS-I-SbF₆.

2 Results and discussion

2.1 Characterization of PS-I-SbF₆

Presented in Figure 1 was ¹H-NMR spectrum of PS-I-SbF₆ and. 1.5(b,2H,CH₂), 1.8 (a,H,CH), 3.3(a,H,CH₂), 6.63(c,H,CH), 6.68(d,H,CH), 7.15(e,H,CH), 7.23(f,H,CH), 7.5(g,H,CH), and δ=2.50ppm was DMSO. It was typical for this compound, and the final product was proved to be successfully synthesized. Figure 2 showed that comparison of the FTIR spectra of PS & PS-I-SbF₆. We found carbon-iodine bond in 568 cm⁻¹, this was indicative of graft reaction of [hydroxy(tosyloxy)iodo] benzene. The phenyl stretching vibration mode at 3025 and 2923cm⁻¹ were observed. Also, the absorption peaks of phenyl framework at 1493cm⁻¹and 1453cm⁻¹ were found. [hydroxy(tosyloxy)iodo] benzene was grafted to PS.

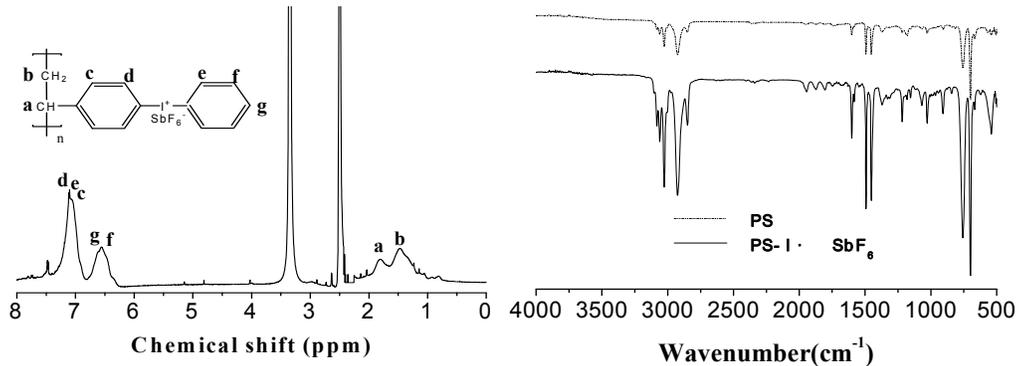


Fig 1. ¹H-NMR spectrum of PS-I-SbF₆ in DMSO

Fig 2. IR spectra of PS & PS-I-SbF₆

Table 1 The GPC, DSC and UV analysis of PS & PS-I-SbF₆

Compound	Mn/10 ⁴	Mw/10 ⁴	PDI	Tg/°C	λ _{max} (acetonitrile) /nm
PS	1.4	1.8	1.29	98	250
PS-I-SbF ₆	2.3	3.1	1.33	122.02	240-270

Table 1 gave the GPC, DSC and UV analysis of PS & PS-I-SbF₆. Because of additional phenyl group, the data showed that molecular weight, PDI and Tg became larger than PS.

Owing to the addition of rigid group, PS-I-SbF₆ boarden the the spectral sensitivity of diaryliodonium salts. The redshift phenomenon was observed in the ultraviolet spectrum of it, its λ_{\max} moved from 227 to 260 nm, so it could well match with mercury lamp. This redshift of 20nm nevertheless produced an appreciable enhancement of the efficiency of these photoinitiators when they were irradiated with conventional medium-pressure mercury arc lamps.

Table 2 The migration ratio of PS-I-SbF₆, Omniscat 432 and IHT-PT 820 in 95% ethanol

	24h	48h	72h	96h	120h
R(PS-I-SbF ₆)	0.12	2.01	2.08	2.06	1.40
R(Omniscat 432)	101.59	112.36	121.44	119.36	169.14
R(IHT-PT820)	100	100	100	100	100

According to Table 2, in comparison with some small photoinitiators(Omniscat 432, IHT-PI 820), the migration of PS-I-SbF₆ was much lower and might lead to very low toxicity and odor in the whole polymerization process. Because the residue of macrophotoinitiator in cured film or the migration of photolysis fragments were limited, PS-I-SbF₆ was more environment friendly.

Table 3 The solubility of PS-I-SbF₆, BPI-SbF₆^[8] and IHT-PT 820 in common solvents

	Acetone	Ethyl acetate	n-Butyl acetate	DMF	THF	n-Hexane	Dioxane	Chloroform
PS-I-SbF ₆	S	S	S	S	S	I	I	S
BPI-SbF ₆	S	S	S	S	S	I	I	S
IHT-PT820	S	S	S	S	S	I	I	I

(S : soluble I : insoluble)

Table 3 showed that the comparison of PS-I-SbF₆, BPI-SbF₆ and IHT-PT 820 in common solvents. The solubility and compatibility of PS-I-SbF₆ was little better than low-molecular initiator Iodonium salts BPI-SbF₆ and IHT-PT 820.^[8]

2.2 Photoinitiated Cationic Polymerization using PS-I-SbF₆

In this investigation, Gel-Yield measurement was employed to evaluate the efficiencies of PS-I-SbF₆ in the cationic polymerizations. K-126 is a highly reactive difunctional epoxy oligomer. A study of the photoinitiated cationic polymerizations of K-126 with PS-I-SbF₆ in various concentrations was shown in Figure 3. The best concentration of PS-I-SbF₆ in the system of K-126 is 3%. At first, crosslinking took place at very quick conversions, resulting in the solidification of the conversion, which retarded mobility and lowered the conversion. In terms of efficiency and economy, 5%wt was not necessary.

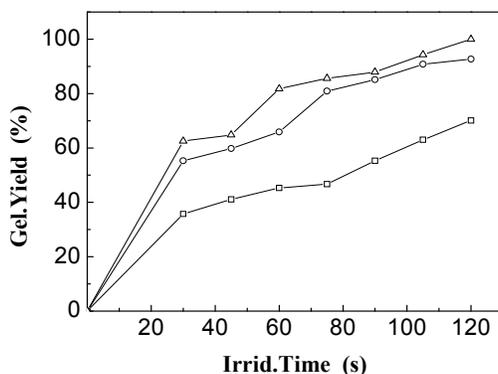


Fig 3. Characteristic curves of K-126 initiated by PS-I-SbF₆ in different concentrations

Film thickness=100μm ; Light intensity =33mW/cm²

□-1%wt ○-3%wt △-5%wt

2.3 Photosensitization of PS-I-SbF₆

One mean of effectively increasing the apparent efficiency of an onium salt photoinitiator was the use of photosensitization. The best photosensitizers were that compounds like polynuclear aromatic hydrocarbons that act as good electron donors in the excited state. By using radical photoinitiators as photosensitizers, it was possible to fit the spectral sensitivity of diaryliodonium salts with the medium-pressure mercury arc lamps and accelerate the photopolymerization. Complex initiator system could enlarge their photoinitiation activities^[5].

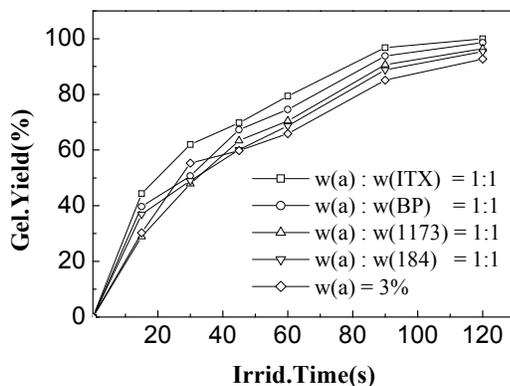


Fig 4. Characteristic curves of K-126, SR480/ PS-I-SbF₆ system initiated with different sensitizers

Concentration of photoinitiator=3%(wt) ;Film thickness=100μm ;Light intensity =33mW/cm²

The photoinitiated polymerization of K-126/ SR480 was carried out in the presence and absence of the radical photoinitiators ITX, BP, 1173, 184 with PS-I-SbF₆ as the photosensitizer, and the results are shown in Figure 4. There is a marked increase in the presence of above radical photoinitiators. As we saw in Figure 5, it was characteristic curves of K-126 / PS-I-SbF₆ system initiated with different molecular weights. The photoinitiation

activities of PS-I·SbF₆ increased with the decreasing of its molecular weight. The reason of this phenomenon might be the “cage” effect, which the active segment was surrounded and retarded in the macromolecule.

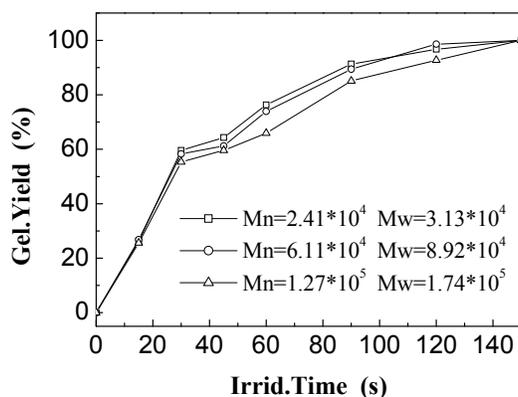


Fig. 5 Characteristic curves of K-126/PS-I·SbF₆ system initiated with different molecular weights

Concentration of photoinitiators=3%(wt) ; Film thickness=100μm ; Light intensity =33mW/cm²

2.4 Post-curing ability of PS-I·SbF₆

After the UV light was switched off, the dark polymerization still progressed and reached a considerable Gel-Yield^[7]. The experimental results obtained were analyzed and discussed to show that it had the post-curing ability, which was obvious in Figure 6.

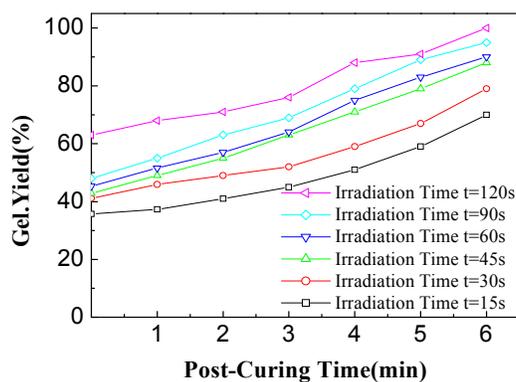


Fig 6. Characteristic post-curing curves of K-126/PS-I·SbF₆ system under different UV curing time

Concentration of PS-I·SbF₆=1%(wt) ; Film thickness=100μm ; Light intensity =33mW/cm²

Conclusions

This article described a simple synthesis method of a macrophotoinitiator diaryliodonium salt, Polystyrene-iodonium hexafluoroantimonate (PS-I·SbF₆) and its application in UV curing

system. PS-I·SbF₆ was prepared by the reaction of Polystyrene with [hydroxy(tosyloxy)iodo]benzene. The later product PS-I·SbF₆ was identified by ¹H-NMR, FTIR, GPC, DSC, and UV spectra. PS-I·SbF₆ possessed a greatly redshifted UV maximal absorption from 227 to 260 nm. The optimum ratio of PS-I·SbF₆ was about 3%wt, and it had the post-curing ability. As a result, it was an efficient cationic macrophotoinitiator, and its migration ratio in the cured film was much lower than the low-molecular photoinitiators. The resultant salt polystyrene-iodonium hexafluoroantimonate (PS-I·SbF₆) could be expected to be primarily used for food and drug packaging materials.

References and Notes

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