

Synthesis and Characterization of Alkoxy and Phenoxy-substituted Ferrocenium Salt Cationic Photoinitiators*

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Abstract Alkyl-substituted ferrocenium salts have limited solubility in epoxy oligomers and produce poisonous arene by photolysis. Herein, the synthesis and photoactivity of several alkoxy-substituted ferrocenium salts as long-wavelength UV light photoinitiators have been reported. [Cyclopentadien-Fe-anisole]PF₆, [Cyclopentadien-Fe-anisole]BF₄, [Cyclopentadien-Fe-diphenylether]PF₆, [Cyclopentadien-Fe-diphenylether]BF₄, and [Cyclopentadien-Fe-diethoxybenzene] PF₆ for polymerization of epoxy resin were prepared through the ligand exchange reaction between one ring of ferrocene and aromatic ether. They all display good solubility and photoinitiating activities in epoxy resins.

Keywords photoinitiator, cationic polymerization, ferrocenium salt, photoinitiating activity

1 INTRODUCTION

In recent years, the increasing commercial and technical demands of cationic photopolymerizations have led to an interest in the design and synthesis of optimized photopolymerization systems^[1]. Among the photopolymerization systems, the onium-type photoinitiators, such as sulfonium and iodonium salts play an important role due to their thermal stability and efficiency in generating reactive species upon photolysis^[2]. However, for the principal absorption bands in the short-wavelength (220—310nm) region of the UV spectrum, they could not match a number of important light sources (including high-pressure Hg lamp)^[3—5].

Ferrocenium salts are a different class of cationic photoinitiators^[6,7]. The absorptions caused by d-d up-field above 300nm make them attractive when the high-pressure Hg lamp was used as the light source. Alkyl-substituted ferrocenium salts have limited solubility in non-polar monomers and polymers. Hence, it was necessary to use polar solvents in order to ensure that homogeneous polymerization would take place. It was advantageous to have well-characterized ferrocenium salts with good solubility in epoxy oligomers. An additional problem with simple ferrocenium salts was the toxicity of arene produced by photolysis during the photoinitiating process. In this study, in order to improve the solubility and decrease the toxicity of arene, several ferrocenium salts with alkoxy-substituted arene ligands were synthesized and evaluated as cationic photoinitiators.

2 EXPERIMENTAL

2.1 Materials

All the starting materials were reagent grade and were used without purification unless otherwise noted. Cyclopentadiene-Fe-cymene hexafluorophosphate

(I-261) was obtained from Ciba-Geigy Corporation. Epoxy monomer is 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL-4221). Fig.1 summarizes the abbreviations and compound structures that were employed in this study.

2.2 Instruments

The UV absorption spectra were recorded at room temperature with a Hitachi U-3010 spectrometer. ¹H Nuclear magnetic resonance (NMR) spectra were recorded on DMX300 (300 MHz), CD₃COCD₃ as solvent. IR spectra were recorded on a Bruker VECIDR22 spectrometer. Elemental analysis was recorded on a Flash EA1112. The melting point was determined using a microscope melting point apparatus (XT4A).

2.3 Preparation of [cyclopentadien-Fe-1,4-diethoxybenzene] PF₆ (CFE-PF₆)

5.58g (0.03mol) of ferrocene, 11.7g (0.09mol) of anhydrous AlCl₃, 1.35g (0.05mol) of Al powder, 50.0ml of cyclohexane, and 4.98g (0.03mol) of 1,4-diethoxybenzene were added to the flask (250ml). The reaction mixture was then heated under reflux for 4h. The mixture was then slowly hydrolyzed. The aqueous solution was filtered into a concentrated aqueous solution of NaPF₆ and the light yellow colored solid was isolated. The solids were re-crystallized from a warm acetone-water solution. They were then dried for at least 24h in vacuum over P₂O₅. ¹H-NMR (acetone-d₆) δ6.24 (s,4H), δ5.14 (s,5H), δ4.25 (q,4H), δ1.39 (t,6H). Elemental analysis: Calc. for C₁₅H₁₉O₂FePF₆: C, 41.67%; H, 4.40%. Found: C, 41.87%; H, 4.58%.

2.4 Preparation of [cyclopentadien-Fe-anisole] PF₆/BF₄ (CFA-PF₆ and CFA-BF₄)

[Cp-Fe-anisole]⁺ PF₆/BF₄ was synthesized by the

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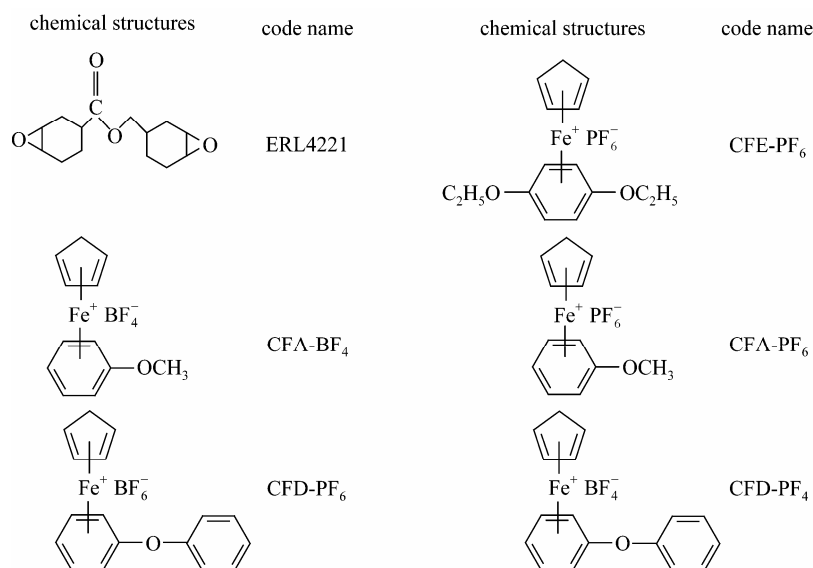


Figure 1 Chemical structures and code names of the discussed compounds

Table 1 Melting point and IR parameters of ferrocenium salts

(Cp-Fe-arene)+X ⁻	v _{max} [IR (KBr)]			mp, °C
	Cp/benzene	C-O-C	PF ₆ /BF ₄	
CFE-PF ₆	1496,1468	1245	843	169—170
CFA-PF ₆	1536,1470,1444,1421	1260	830	139—141
CFA-BF ₄	1534,1467,1439,1419	1261	1084	108—110
CFD-PF ₆	1591,1524,1490,1457	1251	831	132—133
CFD-BF ₄	1591,1522,1488,1457	1242	1072	104—106

reaction of ferrocene with anisole in a manner similar to CFE-PF₆. Ferrocenium tetrafluoroborate salt was prepared using NaBF₄ instead of NaPF₆. ¹H-NMR data (acetone-d₆) of CFA-PF₆ and CFA-BF₄ were the same: δ6.58-8.01 (m,5H), δ5.13 (s,5H), δ4.22 (s,3H).

2.5 Preparation of [cyclopentadien-Fe-1,4-diphenylether] PF₆ (CFD-PF₆)

[Cp-Fe-diphenylether]⁺ PF₆/BF₄ was synthesized by the reaction of ferrocene with diphenylether in a manner similar to CFA-PF₆ and CFA-BF₄. ¹H-NMR data (acetone-d₆) of CFD-PF₆ and CFD-BF₄ were the same: δ6.25-7.53 (m,10H), δ5.23 (s,5H).

Melting points (mp) and IR parameters of five ferrocenium salts are listed in Table 1.

2.6 Photopolymerization

0.04g of photoinitiator was added to 2g of epoxide and then stirred. The formulated mixture was then cast on a glass plate to a thickness of about 100μm. The mixture was irradiated by a 500W high-pressure Hg lamp with a measured intensity of the irradiation of 2.20mW·cm⁻² (365nm). The lamp was placed over the plate at a height of 10cm. After irradiation, the glass plate along with the mixture was weighed (*W*₁) and then was immersed into anhydrous alcohol/acetone for about 30min for the removal of un-

cured compositions. After removing from the anhydrous alcohol/acetone, the glass plate with the cured resin was dried in an oven at 80°C and was then weighed (*W*₂). The gel yield (%) was calculated according to the following formula:

$$\text{gel yield} = (W_2 - W_0) / (W_1 - W_0)$$

*W*₀: the mass of the glass plate, g.

3 RESULTS AND DISCUSSION

3.1 Synthesis

To enhance the solubility of ferrocenium salts and to decrease the toxicity of arenes, aromatic ring with alkoxy and phenoxy groups as ligand was incorporated into ferrocenium salts. The ferrocenium salts were prepared according to the Nesmeyarov and co-workers method as shown in Fig.2^[8]. Five ferrocenium salts: [cyclopentadien-Fe-anisole] PF₆ (CFA-PF₆), [cyclopentadien-Fe-anisole] BF₄ (CFA-BF₄), [cyclopentadien-Fe-diphenylether] PF₆ (CFD-PF₆), [cyclopentadien-Fe-diphenylether] BF₄ (CFD-BF₄), and [cyclopentadien-Fe-diethoxybenzene] PF₆ (CFE-PF₆) were prepared.

The ferrocenium salts were synthesized with long alkoxy group on the aryl ring by the ligand exchange reaction, but unfortunately the designed compounds were not obtained. It was found that when the number of carbon in alkoxy groups was more than four, the

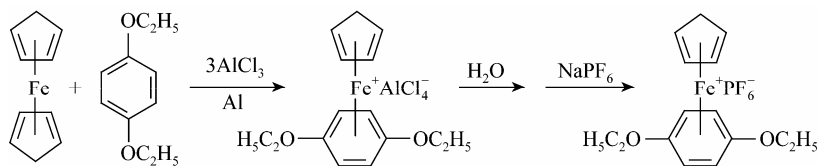


Figure 2 Synthetic method employed for the preparation of ferrocenium salts

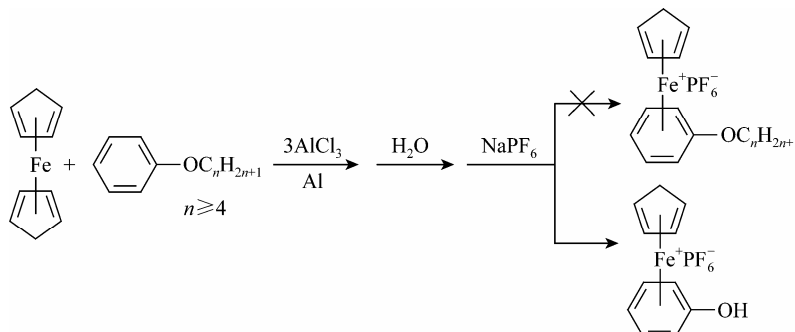


Figure 3 Reaction of ferrocene with arene ligands attaching long alkoxy groups

product of ligand exchange reaction was [cyclopentadien-Fe-phenol] PF₆ instead of [cyclopentadien-Fe-alkoxybenzene] PF₆ as shown in Fig.3.

Table 2 lists the solubility of the five ferrocenium salts in epoxy ERL-4221. Since the amount of photoinitiator that was used was within 5%, CFE-PF₆, CFA-PF₆, and CFA-BF₄ could be considered to be soluble in epoxy ERL-4221.

Table 2 The solubility of alkoxy and phenoxy-substituted ferrocenium salts in epoxy ERL-4221 at (30±1)°C

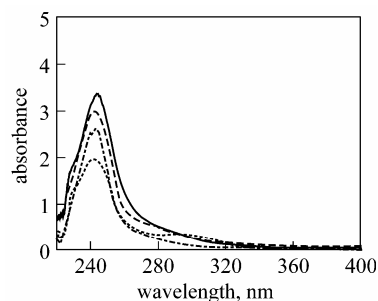
Photoinitiator	Solubility in ERL-4221, g·g ⁻¹
CFE-PF ₆	>0.05
CFA-PF ₆	>0.05
CFA-BF ₄	>0.05
CFD-PF ₆	0.022
CFD-BF ₄	0.029

3.2 UV absorption

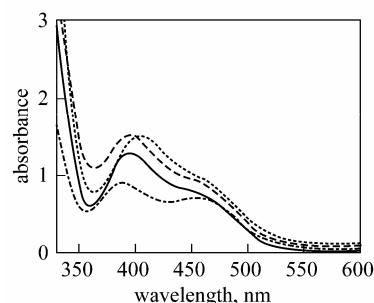
UV absorption is important, especially in the region above 300nm in the initiation of an epoxy system under high-pressure Hg lamp by a photoinitiator. In Fig.4 and Table 3, the UV spectra of CFE-PF₆, CFA-PF₆, CFDE-PF₆, and I-261 in dichloromethane are shown. The four spectra were recorded at the same molar concentration so that a direct comparison of their molar extinction coefficients could be made.

Table 3 Data of absorption spectra of [Cp-Fe-arene] PF₆ in dichloromethane

[Cp-Fe-arene]PF ₆	λ_{\max} (ϵ_{\max}), nm(L·mol ⁻¹ ·cm ⁻¹)
I-261	249(1.24×10 ⁴); 389(75); 465(59)
CFA-PF ₆	242(1.47×10 ⁴); 399(136); 466(72)
CFA-BF ₄	242(1.66×10 ⁴); 399(127); 466(75)
CFD-PF ₆	243(1.94×10 ⁴); 397(140); 462(75)
CFD-BF ₄	243(1.49×10 ⁴); 397(136); 462(78)
CFE-PF ₆	224(1.68×10 ⁴); 409(146); 465(59)



(a) $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ dichloromethane



(b) $2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ dichloromethane

Figure 4 UV-Vis spectra of CFE-PF₆, CFA-PF₆, CFD-PF₆, and I-261 in dichloromethane

— CFD-PF₆; ---- CFA-PF₆; CFE-PF₆; - - - - I-261

UV-Vis absorption spectra of these ferrocenium salts were similar, where the strongest absorptions lay in 200—300nm, which belonged to π - π upfield. The photoinitiating ability of ferrocenium salts under high pressure Hg lamp was caused by the absorptions above 300nm belonging to d-d upfield. Compared with I-261, the absorption of alkoxy group substituted ferrocenium salts were red-shifted by about 10—20nm and the molar extinction coefficient (ϵ) was almost 2 times that of I-261 above 300nm.

3.3 Photoinitiating activity comparison

The reactivities of alkoxy group substituted

ferrocenium hexafluorophosphate were determined in the cationic polymerizations of ERL4221 under a high-pressure mercury lamp. Fig.5 shows the photopolymerization curves of ERL4221 that were initiated by the ferrocenium salts. The reactivity of CFA-PF₆ and CFD-PF₆ was higher than that of I-261, however, CFE-PF₆ was less efficient than I-261. Though the absorption of alkoxy group substituted ferrocenium salts were higher than that of I-261, the denoting electricity of alkoxy group decreases the photolysis rate. The photoinitiating mechanism was the ferrocenium salts undergo photolysis in order to generate an iron-based Lewis with the loss of the arene ligand that coordinates with an epoxy monomer^[9,10]. Hence, the photolysis rate was important to the photoinitiating activity. In Fig.6, the photopolymerizations of ERL4221 photoinitiated by ferrocenium hexafluorophosphates and tetrafluoroborates were compared. It can be seen that the photoinitiating activity of ferrocenium hexafluorophosphate was higher than that of ferrocenium tetrafluoroborate.

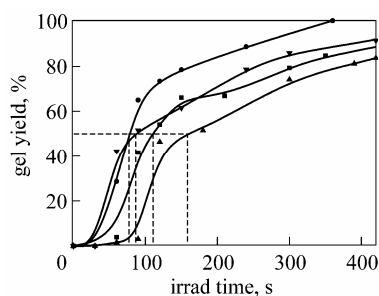


Figure 5 Photopolymerization of ERL-4221 photoinitiated by different 3% [Cp-Fe-arene] PF₆
 ■ I-261; ● CFA-PF₆; ▲ CFE-PF₆; ▼ CFD-PF₆

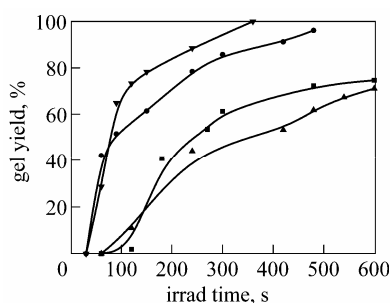


Figure 6 Photopolymerization of ERL-4221 photoinitiated by 3% [Cp-Fe-arene] PF₆ or [Cp-Fe-arene] BF₄
 ▼ CFA-PF₆; ● CFD-PF₆; ■ CFD-BF₄; ▲ CFA-BF₄

4 CONCLUSIONS

In this study, five alkoxy substituted ferrocenium salts were prepared and turned out to have good solubility in epoxy ERL4221. Compared with I-261, the absorption red shifted by about 10–20nm and the molar extinction coefficient (ϵ) was twice that of I-261 above 300nm. The photoinitiating activity of CFA-PF₆ and CFD-PF₆ for polymerization of epoxy monomer under irradiation of high pressure Hg lamp was higher than that of I-261, however, CFE-PF₆ was less efficient than I-261.

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