Several ferrocenium salts as efficient photoinitiators and thermal initiators for cationic epoxy polymerization

Tao Wang [*], Jian W. Chen, Zhi Q. Li, Ping Y. Wan

Department of Chemistry, Beijing University of Chemical Technology, P.O. Box 144, Beijing 100029, China

Abstract

A study of the photoinitiated and thermally initiated cationic polymerizations of epoxy oligomers with three ferrocenium salt photoinitiators bearing different arene ligands had been conducted. These photoinitiators were cyclopentadienyl-Fe-carbazole hexafluorophosphate ($[Cp-Fe-carbazole]^+PF_6^-$), cyclopentadienyl-Fe-*N*-ethylcarbazole hexafluorophosphate ($[Cp-Fe-n-ethylcarbazole]^+PF_6^-$) and cyclopentadienyl-Fe-aminonaphthalene hexafluorophosphate ($[Cp-Fe-aminonaphthalene]^+PF_6^-$). They were synthesized by the reaction of ferrocene and the corresponding arenes. These ferrocenium salts were capable of photoinitiating the cationic polymerization of epoxide directly on irradiation with long-wavelength UV light. Comparative studies demonstrated that they were more effective photoinitiators than I-261 due to the strong absorption above 300 nm. Preliminary studies had shown that these photoinitiators could also be employed as thermal initiators for the cationic ring-opening polymerization of epoxides at moderate temperatures.
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1. Introduction

Ferrocenium salts are attractive photoinitiators for cationic polymerization [1–4]. These compounds could be prepared by a synthetic method, from readily available and inexpensive starting materials. As photoinitiators, they are advantageous because they possess absorption maxima in the middle region of UV spectrum and their absorptions can be modified between long-wavelength UV and visible-wavelength regions through structure change in the ligands.

The increasing commercial and technical requirements for cationic photopolymerization had led to an interest in the design and synthesis of optimized photopolymerization systems [5–8]. To obtain more photosensitive cationic photoinitiators and improve their spectral absorption characteristics, carbazole, *n*-ethylcarbazole and aminonaphthalene-bound ferrocenium salts were synthesized and evaluated as photoinitiators in this work. Direct comparisons of these new photoinitiators with I-261 were presented. Their activities as thermal initiators for the cationic

ring-opening polymerization of epoxides were also evaluated by differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

All starting materials used in the preparation of ferrocenium salts were reagent grade and used without purification unless otherwise noted. Cyclopentadienyl-Fe-cymene hexafluorophosphate (I-261) was obtained from Ciba-Geiqy Corporation. Epoxy compounds used in this work were 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ERL-4221) and diglycidyl ether of bisphenol A (DGEBA E44). Scheme 1 summarized the abbreviations and structures of employed compounds in this study.

2.2. Preparation of [cyclopentadienyl-Fe-carbazole]PF₆ (CFC)

[Cyclopentadienyl-Fe-arene]PF₆ salts were prepared through the ligand exchange reaction between one ring of ferrocene and

* Corresponding author. Tel.: +86 10 64445350.
 E-mail address: wangtwj2000@163.com (T. Wang).
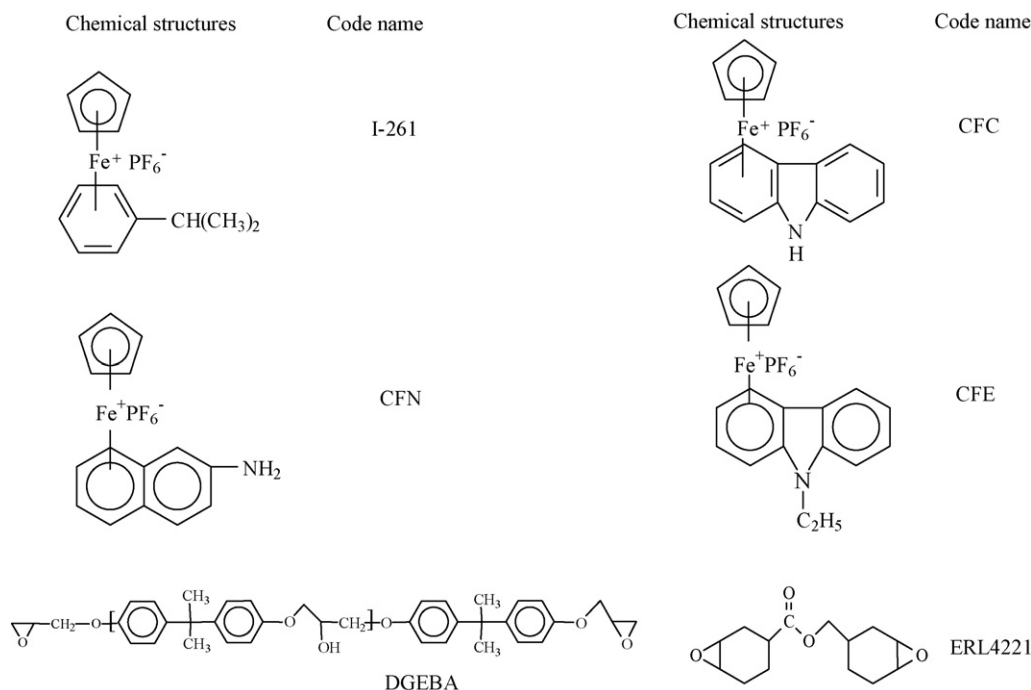
Scheme 1. Chemical structure and code name of initiator and epoxide.

arene according to the method described by Nesmeyanov and co-workers (Scheme 2) [9,10].

Ferrocene (5.23 g, 0.028 mol), carbazole (9.56 g, 0.057 mol), aluminum chloride powder (7.70 g, 0.058 mol), and aluminum powder (2.19 g, 0.081 mol) were stirred in decalin (50 ml) at 140–150 °C for 8 h. The mixture was than cooled with an ice bath and solvolyzed with 15% aqueous methanol. After filtration and separation of layers, the orange–brown water layer was washed with ether. It was then treated with sufficient $NaPF_6$ in water to give complete precipitation. After recrystallization from CH_2Cl_2/ether, the product was yellow-colored and weighed 4.9 g (41%). ^1H NMR (acetone-d_6): carbazole arene, δ 6.21–8.42 (m, 8H); cyclopentadienylyl, δ 4.67 (s, 5H). Elemental analy-

sis: calc. for $C_{17}H_{14}NFePF_6$: C, 47.14%; H, 3.26%. Found: C, 47.12%; H, 3.48%. IR (KBr): $\upsilon(PF_6)$ 829s.

### 2.3. Preparation of [cyclopentadienyl-Fe-n-ethyl carbazole]PF₆ (CFE)

CFE was synthesized by the reaction of ferrocene with *n*-ethyl carbazole in the similar procedure to CFC. ^1H NMR (acetone-d_6): carbazole arene, δ 6.21–8.42 (m, 8H); cyclopentadienyl δ 4.65 (s, 5H); –CH_2–, δ 1.63 (s, 2H); –CH_3, δ 2.42 (t, 3H). IR (KBr): $\upsilon(PF_6)$ 840s.

2.4. Preparation of [cyclopentadienyl-Fe-aminonaphthalene]PF₆ (CFN)

CFN was synthesized by the reaction of ferrocene with aminonaphthalene in the similar procedure to CFC. ^1H NMR (acetone-d_6): naphthalene,δ 6.28–7.68 (m, 7H); cyclopentadienyl δ 4.73 (s, 5H). IR (KBr): $\upsilon(PF_6)$ 838s.

2.5. Photopolymerization procedure

0.04 g of photoinitiator was added to 2 g of epoxide and then stirred. The formulated mixture was then cast on a glass plate to a thickness of about 100 μm and irradiated by a lamp. The lamp was placed over the plate with distance of 10 cm. After irradiation, the glass plate along with the mixture was weighed (W_1) and then was immersed into anhydrous alcohol/acetone for about 30 min to remove uncured compositions. After removing from the anhydrous alcohol/acetone, the glass plate with the cured resin was dried in oven at 80 °C and was weighed (W_2). The gel yield (%) was calculated according to the following
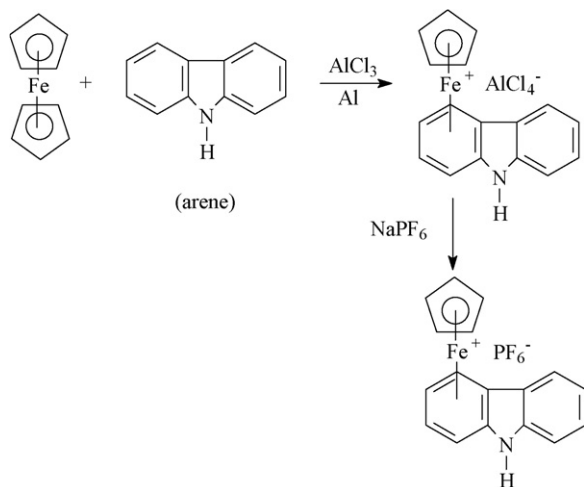
Scheme 2. The synthetic steps for the preparation of CFC through the ligand exchange reaction.

equation:

$$\text{gel yield} = \frac{W_2 - W_0}{W_1 - W_0}$$

where W_0 is the weight of the glass plate (g).

2.6. Thermally initiated cationic polymerizations

Studies of thermally initiated cationic polymerizations were carried out with differential scanning calorimeter (DSC). Samples (8–10 mg) containing 1.0 wt.% of the ferrocenium salt were dissolved in the epoxy monomer and heated in the calorimeter, from 50 to 200 °C under a nitrogen flow at a heating rate of 10 °C/min.

2.7. Instruments

UV absorption spectra were recorded at room temperature with Hitachi U-3010 spectrometer. [1]H nuclear magnetic resonance (NMR) spectra were recorded on DMX300 (300 MHz), CD_3COCD_3 as solvent. IR spectra were recorded on a Brucker VECIDR22 spectrometer. Elemental analysis was recorded on Flash EA1112. DSC thermograms were measured using dynamic DSC analysis (Perkin-Elmer Pyris 1).

3. Results and discussion

### 3.1. UV–vis absorption spectra of ferrocenium salts

In Fig. 1 and Table 1, the UV–vis spectra of CFC, CFN, CFE and I-261 in epihydrin were given. These four spectra were recorded at the same molar concentration (a: 1×10^{-4} M; b: 1×10^{-3} M), so that a direct comparison of absorbance can be made.

The UV–vis absorption spectra were similar to each other and the absorptions of CFC, CFN and CFE were much stronger than that of I-261. The strongest absorption lies in the region of 200–300 nm. They also possess stronger absorptions at wavelength, ranging from 300 nm to 400 nm which belong to d–d upfield of iron arene complexes.

Compared with I-261, the absorptions of CFC, CFN and CFE above 300 nm were obviously red-shifted and their molar absorptions were much higher than that of I-261. The molar extinction coefficient (ε) of CFC was 2.17×10^3 M^{-1} cm^{-1} at 347 nm, which was almost 30 times higher than that of I-261. CFN possesses the strongest absorption among these photoinitiators, especially at wavelength above 400 nm.
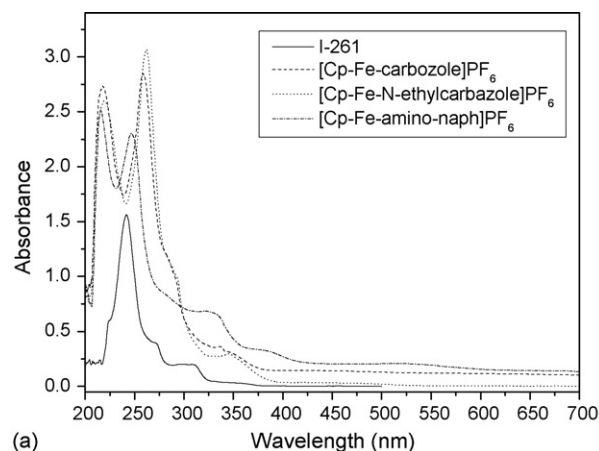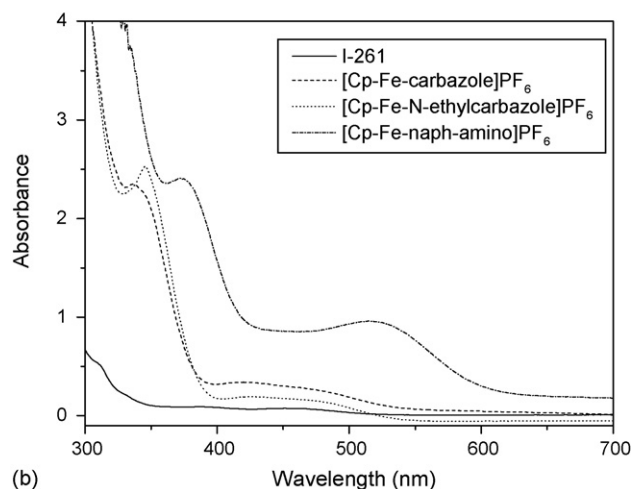
Fig. 1. UV spectra of CFC, CFE, CFN and I-261 in epihydrin in different concentration: (a) 1×10^{-4} M; (b) 1×10^{-3} M.

3.2. Photoinitiating activity comparison

The reactivities of ferrocenium salt CFC, CFN and CFE were determined and compared with I-261 in the cationic polymerization of ERL-4221. I-261 is the only commercial photoinitiator of iron arene complexes. ERL-4221 is a cycloaliphatic epoxy monomer with high reactivity.

Fig. 2 shows the photopolymerization curves of ERL-4221 initiated by these ferrocenium salts. The photopolymerization systems were irradiated by 700 W high-pressure Hg lamp which was cooled by a glass condenser which could cut off the light below 320 nm. From Fig. 2, the curing of epoxy ERL-4221 happened, as the result of the absorption of ferrocenium salts above 320 nm and the reactivity of CFC and CFE was

Table 1
Data of absorption spectra of [Cp-Fe-arene]PF_6 in epihydrin

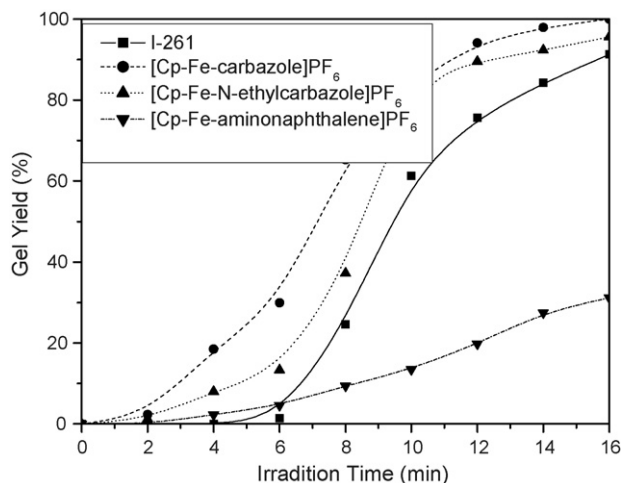| [Cp-Fe-arene]PF_6	λ_{max} (nm) (ε_{max} (1 mol^{-1} cm^{-1}))
I-261	249 (1.24×10^4); 297 (3.01×10^3); 375 (0.75×10^2)
CFC	219 (2.41×10^4); 259 (2.62×10^4); 347 (2.17×10^3); 421 (2.67×10^2)
CFE	219 (2.37×10^4); 259 (2.87×10^4); 352 (2.32×10^3); 429 (1.87×10^2)
CFN	213 (2.16×10^4); 242 (2.01×10^4); 376 (2.38×10^3); 546 (9.67×10^2)

Fig. 2. Photopolymerization of ERL-4221 with 2.0 wt.% of various photoinitiators irradiated by 700 W high-pressure Hg lamp with glass condenser. $I = 0.42$ mW/cm^2 (365 nm).
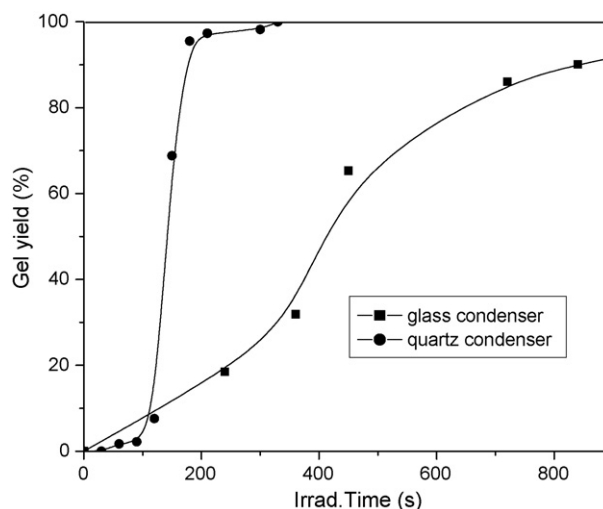

Fig. 3. Photopolymerization curves of ERL-4221 initiated by CFE at glass and quartz condenser $I = 0.42$ mW/cm^2 (365 nm).

higher than that of I-261, but, CFN was less efficient than I-261.

Fig. 3 shows the result of photopolymerization of ERL-4221 by 700 W high-pressure Hg lamp with different condenser. Unlike glass condenser, quartz condenser was unable to shed the UV light below 320 nm. For the strongest absorption in 200–300 nm, the photopolymerization of ERL-4221 with quartz condenser was much quicker than that of glass condenser.

Fig. 4 shows the results of the cationic ring-opening photopolymerizations of ERL-4221 with different photoinitiators irradiated by 1000 W D-lamp which major radiation wavelength at 420 nm. The same order of reactivity was obtained as the system radiated by high-pressure Hg lamp (Fig. 2).

Ferrocenium salts underwent photolysis to generate an iron-based Lewis acid with the loss of the arene ligand. Coordination of this latter species with an epoxy monomer was followed by ring-opening polymerization. The photoinitiated mechanism was shown in Scheme 3. Upon photolysis, CFN give out aminon-
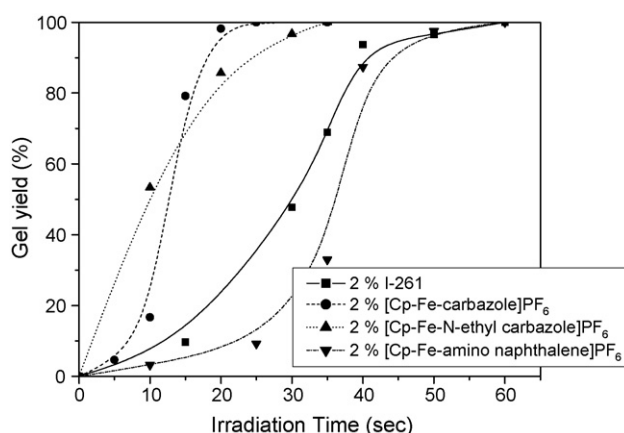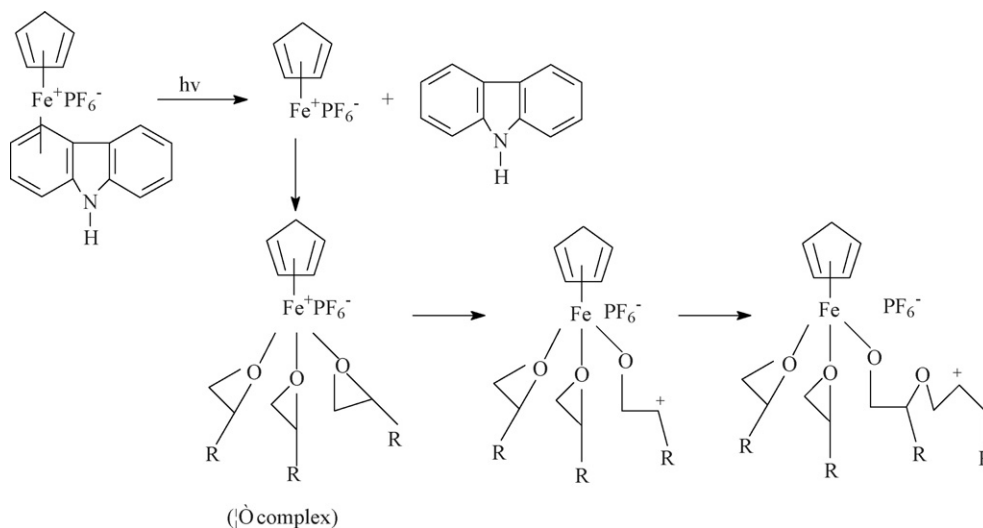

Fig. 4. Photopolymerization of ERL-4221 with 2.0 wt.% ferrocenium salts irradiated by D-lamp $I_{420\,nm} = 1.22$–1.25 mW/cm^2.

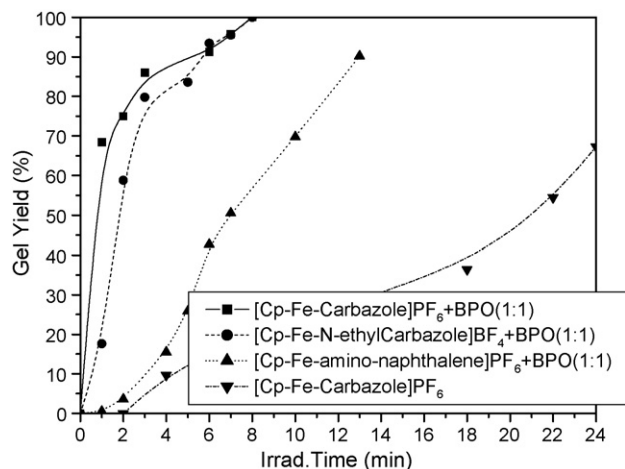Scheme 3. Typical ring opening reaction of epoxide initiated by an iron–arene complex.

Fig. 5. The effect of BPO on the curing rate of the system [Cp-Fe-*N*-ethylcarbazole]PF_6^+ ERL-4221. $I = 0.42$–0.45 mW/cm^2.

aphthalene belonging to strong electron donating material and might neutralize the Lewis acid (the initiating species). Therefore, CFN could photoinitiate the polymerization of ERL-4221, but much less efficiently than CFC, CFE and I-261.

The reactivity of carbazole-bound ferrocenium salt was highest. Compared to the electron density in the aminonaphthalene skeletons, the electron density in the carbazole molecule was distributed major into the aromatic rings and less onto the central nitrogen. Therefore, the carbazoles behave more "hydrocarbonlike" than "amine-like".

3.3. Photosensitization of ferrocenium salt photoinitiators

One way to increase efficiency of ferrocenium salt photoinitiators was the use of photosensitization. It was known that the reactivity of ferrocenium salts could be photosensitized with benzoyl peroxide (BPO):
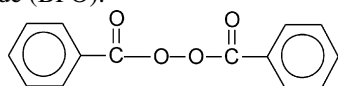
Fig. 5 was the results of photopolymerization of ERL-4221 photosensitized by BPO. It indicated that CFN, CFC, CFE allowed be photosensitized by BPO obviously. According to our previous study, the sensitizing effect was through oxidizing the iron cation to a higher valence [11].

3.4. Dark polymerization

A big difference between cationic and radical polymerization was the active center lifetime [12]. For cationic polymerization, the rate of consumption of active centers was very slow, the dark-cure could occur. In the previous studies, polymerization employing ferrocenium salts exhibited considerable dark polymerization. Accordingly, a study of the dark polymerization of ERL-4221 using CFN, CFC, and CFE as photoinitiators was performed after the samples were irradiated for 4-min, followed by the closing of the shutter, and the results were shown in Fig. 6. As can be noted, the polymerization of these three systems all can immediately resume.
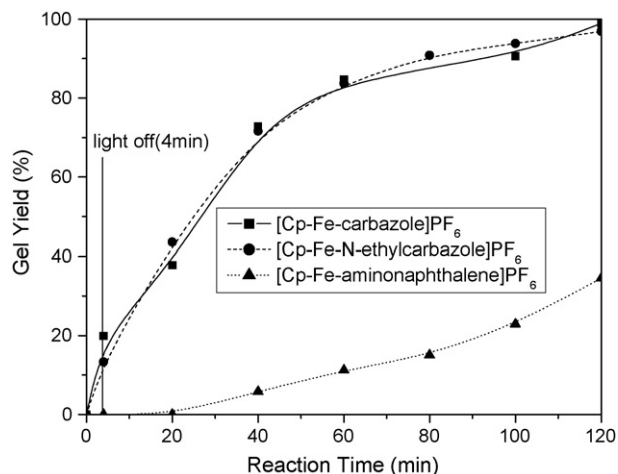

Fig. 6. Dark polymerization of ERL-4221with ferrocenium salt by the light off at 4 min.

3.5. Thermally induced cationic polymerizations

Recently, the use of a number of sulfonium salts for thermally induced cationic polymerization had been reported [13,14]. Ferrocenium salt photoinitiators were shelf-stable in the presence of even highly reactive monomers and oligomers, and long pot lives were observed in the dark. An important property of photoresists was the inherent thermal stability of the photoinitiator since pre- and post-exposure bakes could influence the physical state of the material. It was particularly true for cationic photoinitiator/epoxy blends because crosslinking of unexposed areas must be avoided in order to maximize the photoresist contrast. To assess this likelihood and the ability of thermally induced cationic polymerization, DSC was employed [15].

DEGBA and ERL-4221 are important epoxy oligomer and monomer and were employed in many applications for cationic polymerization. The thermally induced polymerizations of these two monomers were examined with 1 wt.% of CFC, CFE, CFN and the results was shown in Fig. 7. Table 2 was the summary of
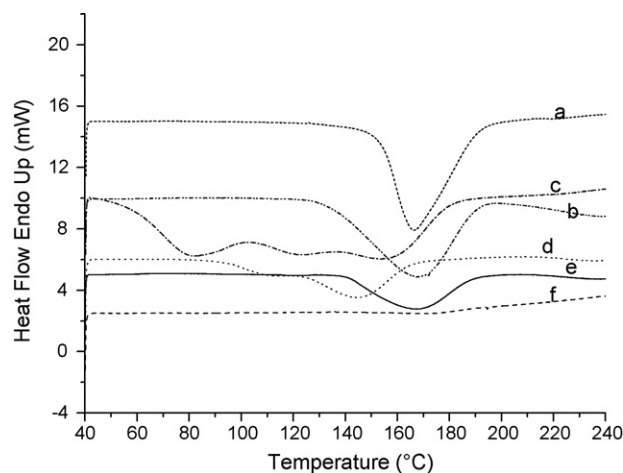

Fig. 7. Thermally induced polymerization of DEGBA and ERL-4221with 1.0 wt.% ferrocenium salts: (a) CFC + ERL-4221, (b) CFC + E44, (c) CFN + E44, (d) CFN + ERL-4221, (e) CFE + ERL-4221, and (f) CFE + E44.

Table 2

Data of thermally induced polymerization of ERL-4221 and E44 from DSC scans

1 wt.% of photoinitiator + epoxide	Onset temperature (°C)	ΔH (J/g)
(a) CFC + ERL-4221	153.6	166.9
(b) CFC + E44	136.8	205.5
(c) CFN + E44	59.7	342.7
(d) CFN + ERL-4221	120.2	90.5
(e) CFE + ERL-4221	143.3	167.3
(f) CFE + E44	–	–

the data for the thermally induced polymerization of ERL-4221 and DEGBA (E44). For CFC, the thermally induced polymerization of ERL-4221 began at approximately 153 °C and that of E44 began at approximately 136 °C. For CFE, the thermally induced polymerization of ERL-4221 began at approximately 143 °C. No exothermic peak could be observed in CFE + E44. The thermal stability of CFN was worst among these ferrocenium salts. The onset temperature of CFN + E44 is 60 °C and that of CFN + ERL-4221 is 120 °C and broad exothermic peaks could be observed.

4. Conclusion

Three ferrocenium salts were synthesized and their photointiating activities were studied. Compared with I-261, the absorption was much stronger above 300 nm; the photoinitiating reactivities were higher. They could be photosensitized by BPO obviously. The dark polymerization of ERL-4221 using CFN, CFC, and CFE as photoinitiators was observed. In epoxide DEGBA and ERL-4221, these photoinitiators could also be employed as thermal initiators at moderate temperatures.

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