Polymer Bulletin 53, 323–331 (2005)
DOI 10.1007/s00289-005-0346-9

Polymer Bulletin

Cationic photopolymerization of epoxy systems initiated by cyclopentadien-iron-biphenyl hexafluorophosphate ([Cp-Fe-biphenyl]$^+$PF$_6^-$)

Tao Wang (✉), Zhi H. Wang

College of Chemistry, Beijing University of Chemical Technology, Beijing, People's Republic of China

E-mail: wangtwj2000@163.com, Fax: 0086-010-64716545

Received: 29 December 2004 / Revised version: 23 January 2005 / Accepted: 27 January 2005

Summary

A study of the photoinitiated and thermally initiated cationic polymerizations of several epoxy systems with cyclopentadien-iron-biphenyl hexafluorophosphate ([Cp-Fe-biphenyl]$^+$PF$_6^-$) photoinitiator has been conducted. [Cp-Fe-biphenyl]$^+$PF$_6^-$ photointitiator is capable of photoinitiating the cationic polymerization of glycidyl ether and cycloaliphatic epoxides directly on radiation with long-wavelength UV light. Compared with the mono-arene iron complexes, the photoinitiating activity of [Cp-Fe-biphenyl] PF$_6$ is higher than that of mono-arene iron complex I-261. When the photosensitizer benzoyl peroxide (BPO) is employed, [Cp-Fe-biphenyl]$^+$PF$_6^-$ is rendered much more efficient than diaryliodonium salt SR1012. The thermally initiated polymerization of epoxide / [Cp-Fe-biphenyl]$^+$PF$_6^-$ system was evaluated by DSC. It was found that the heat polymerization can occur in the systems of TDE85/[Cp-Fe-biphenyl]$^+$PF$_6^-$ without UV radiation at 71.6. However, the GCC/[Cp-Fe-biphenyl]$^+$PF$_6^-$ and ERL4221/[Cp-Fe-biphenyl]$^+$PF$_6^-$ systems are stable under 200 ℃. The dark-cure of the system of epoxides/[Cp-Fe-biphenyl]$^+$PF$_6^-$ after UV radiation is obvious by DSC measure.

Introduction

UV-radiation curing is the most efficient technology presently available to transform quasi-instantly a liquid resin into a solid material. So it has been widely used in many applications, such as in the coating industry and in the graphic arts [1,2]. Most of the UV-curable resins currently used are based on free radical polymerization, which proceeds extensively within a fraction of a second. However, because of the advantage of oxygen insensitivity and the ability to polymerize monomers by both vinyl and ring opening mechanisms, there is growing commercial interest in the cationic photopolymerization [3,4].

The technically useful cationic photoinitiators are diaryl iodonium salts and triphenyl sulfonium salts [5]. Iron arene complexe was another different class of cationic photoinitiators, which was firstly reported by workers at the Ciba-Geigy Corporation in the 80th[6]. With the absorption above 300nm, iron arene complexes are more efficient than some cationic photoinitiators when used with high-pressure Hg lamp as light source. Cyclopentadien-Fe-cymene hexafluorophosphate (I-261) produced by Ciba-Geigy Corporation is the only commercial photoinitiator of iron arene complexes. For its lower molar extinction coefficients in dichloromethane at 389nm(ε=75M^{-1}. cm^{-1}), I-261 has not been used widely. However, the absorption of iron arene complexes can be varied over a wide range by structure changes in the ligands. An important way is to substitute mono-aromatics by polyaromatics [7].

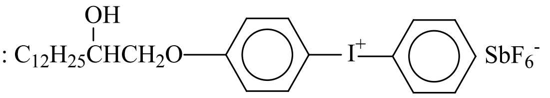
In this paper, as a cationic photoinitiator, [Cp-Fe-biphenyl] PF_6 was synthesized. The photoinitiating activity was compared with I-261 and SR-1012 in the epoxy systems. The thermal stability of four epoxy systems with $[\text{Cp-Fe-biphenyl}]^+ PF_6^-$ as photoinitiator without UV radiation was evaluated by DSC. The dark cure after UV radiation was also studied by DSC.

Experimental

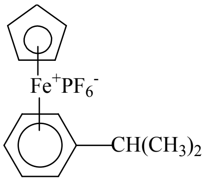
Materials

All reagents used in the preparation of [Cp-Fe-biphenyl] PF_6 were reagent grade. Ferrocene (Fc) was purified by recrystallization from ethanol, followed by sublimation. (4-n-(2-hydroxy-tetradecylphenyl))phenyl iodonium hexafluoro-antimonate(SR-1012) was obtained from Sartomer Corporation. Cyclopentadien-Fe-cymene hexafluorophosphate (I-261) was obtained from Ciba-Geiqy Corporation.

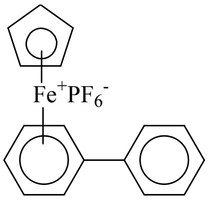
SR-1012:



I-261:

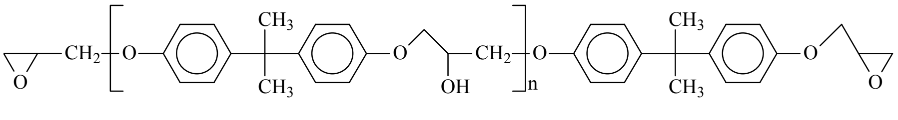


[Cp-Fe-biphenyl]PF_6:

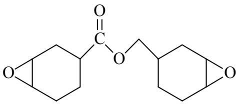


Epoxy oligomer is diglycidyl ether of bisphenol A (E44). Epoxy monomers: 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL-4221), di(2,3-epoxypropyl)3,4-epoxy-1,2-cyclohexanedioate(TDE-85), 1,2,3-(2,3-epoxypropyl)-glycidylether(GCC).

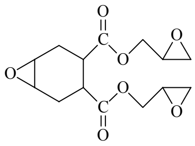
E44



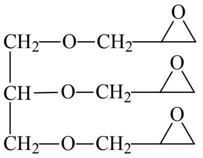
ERL4221:



TDE85:



GCC:



Instruments

Melting point determination was made using microscope melting point apparatus (XT4A); UV spectra were recorded on a Perkin Elmer Lambda 2 spectrometer; ^{1}H Nuclear magnetic resonance (NMR) spectrum was recorded on DMX300, CD_3COCD_3 as solvent.

Synthesis of [Cp-Fe-biphenyl] PF_6

[Cp-Fe-biphenyl] PF_6 salt was prepared through the ligand exchange reaction between one ring of ferrocene and biphenl according to the method of Nesmeyarov and Co-workers [8]. Under nitrogen, 5.58g (0.03mol) ferrocene, 11.7g (0.09mol) anhydrous aluminum chloride, 1.35g(0.05mol) aluminum powder, 50.0ml cyclohexane, and 3.8g (0.03mol) biphenyl were added to the 250ml flask. The reaction mixture is then heated under reflux, with rapid stirring, for 12 hr. Then the reaction flask was cooled to room temperature and placed in an ice bath, and the reaction mixture was slowly hydrolyzed with 50 ml of ice water. The aqueous layer was separated after washing with 30ml cyclohexane. The aqueous solution was filtered into a concentrated aqueous solution of $NaPF_6$.The solid was isolated and recrystallized from a warm acetone-water solution. They were then dried for at least 24hr in vacuum over P_2O_5. m.p. = 146-147 ℃. ^{1}H-NMR (acetone-d_6) δ 6.54-8.09 (m,10H,Ar), δ 5.13 (s,5H,Cp).

Photolysis

Photolysis was conducted using 700w high-pressure arc lamp with the intensity of UV radiation at 365nm of about 2.7 mw/cm^2 at a distance of 15cm from the sample tube. Surrounding the lamp is a quartz well through which is pumped cooling water. The entire apparatus was placed in a thermostated water bath which controls the temperature at 30℃ within $\pm$0.2℃.

By irradiating a 2×10^{-4}M solution in CH_2Cl_2 in a sample tube (i.d. 1.75 ± 0.01cm), the photolysis of [cyclopentadien-Fe-arene]PF_6 was monitored by measuring the absorbance decrease in the initiator absorption band at about 240nm. The photolysis conversion and quantum yields of photolysis were calculated according to the reported method [9]. For each photoinitiator salt, 3-5 quantum yield determinations were made and were averaged to give the reported value.

Photopolymerization

0.04g photoinitiator was dissolved in 0.1ml chloroepoxy propane. The above solution was mixed with 2 g epoxide and stirred completely. Then the formulated mixture was cast on a glass plate to a thickness of about 100 μm. The thickness was controlled by the matrix 100 μm thick. Then the mixture was irradiated by 700W high-pressure Hg lamp with a measured intensity of the irradiation of 1.10mw/cm^2 (365nm). The lamp was placed over the plate at a height of 20cm.

After irradiation, the glass plate with the mixture was weighed (W_1) and then was put into anhydrous alcohol/acetone for about 30 minutes to remove the uncured compositions. Taken from ethanol, the glass plate with cured resin was dried in a oven at 80℃ and then weighed(W_2). The Gel yield (%) was calculated according to the following formula:

Gel yield = $(W_2-W_0)/(W_1-W_0)$

W_0: the weight of the glass plate (g)

DSC measurement

DSC thermograms of epoxide/initiaor blend uncured systems before radiation and after radiation were measured using dynamic DSC analysis (Perkin-Elmer Pyris1) with a heating rate of 10℃/min and calibration range of 30-200℃ under a nitrogen flow.

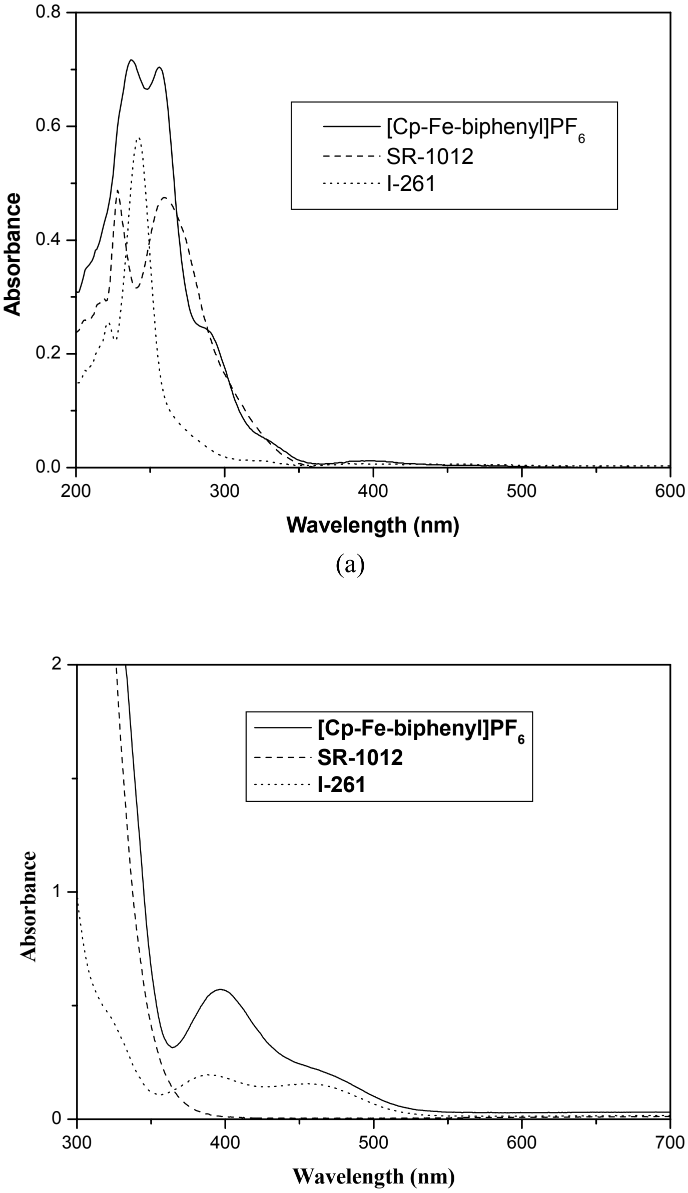
Sample preparation is same with the above description. 2wt% photoinitiator was dissolved in 0.1ml chloroepoxy propane and was added to epoxide and stirred completely. 8-10 mg sample were instantly taken out and airproofed with aluminum foil. Other part of sample was cast on a glass plate to a thickness of about 1mm and than irradiated by high-pressure Hg lamp. After 3 minute, the sample was taken out and the amount of sample was also limited to 8-10 mg.

Results and discussion

UV absorption and photoinitiating activity

Whether a photointiator can initiate an epoxy system under high pressure Hg lamp, its UV spectrum is very important, especially in the region above 300nm. In Figure1, the UV spectra of [Cp-Fe-biphenyl] PF_6, I-261 and SR-1012 are shown. These three spectra were recorded at the same molar concentration so that a direct comparison of their molar extinction coefficients can be made. Their strongest absorptions lie in 200nm-300nm, which belongs to π - π upfield. Compared with SR-1012, [Cp-Fe-biphenyl] PF_6 and I-261 possess stronger absorptions at wavelength greater than 350 nm, which belongs to d-d upfield of iron arene complexes. The absorption peaks of [Cp-Fe-biphenyl] PF_6 above 350nm are at 396nm and 442nm respectively. The molar extinction coefficients(ε) of [Cp-Fe-biphenyl]PF_6 are 277 $M^{-1}.cm^{-1}$ and 138 $M^{-1}.cm^{-1}$, which are higher than that of I-261(389nm, 75$M^{-1}.cm^{-1}$; 465nm,59 $M^{-1}.cm^{-1}$).

It has been recognized that [cyclopentadien-Fe-arene] PF_6 salts generate an iron-based Lewis acid with photoinitiated activity by photolysis(Scheme1) [6]. So the photodecomposition rate is important to the photoreactivity of initiator. According to the method established in the previous papers[9], the photolysis rate of [Cp-Fe-biphenyl]PF_6 and I-261 was studied by irradiating a 2×10^{-4}M solution in dichloromethane, using high-pressure arc lamp with the UV radiation at 365nm. Quantum yields of photolysis and the conversion were determined by UV



(a)

(b)

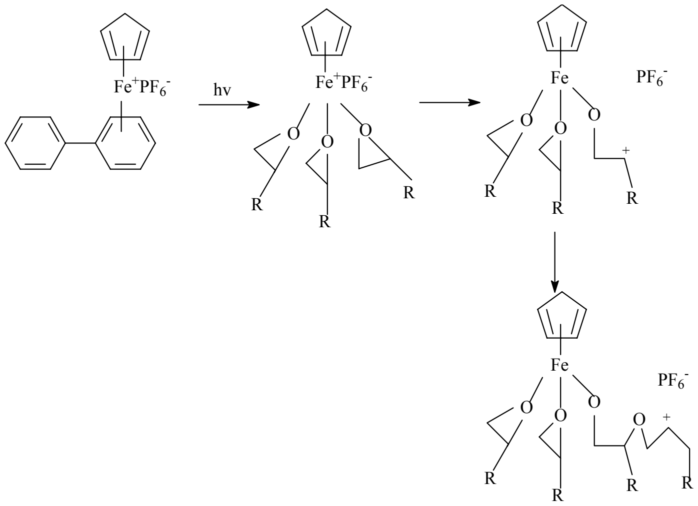
Figure 1. UV-Vis spectra of [Cp-Fe-biphenyl]PF$_6$ and I-261 in dichloromethane; Concentration: (a) is 5×10^{-5}mol/L; (b) is 2×10^{-3}mol/L

spectroscopy following the decrease in the initiator absorption band (about at 240nm) with the irradiation time. Table1 lists the time of entire photolysis and the quantum yields of initiators disappearance. As can be seen in Table1, the photolysis rate of [Cp-Fe-biphenyl] PF$_6$ is much quicker than I-261.

Table 1. The time of entire photolysis and the quantum yields of initiators disappearance by measuring the absorbance decrease in the initiator absorption band at about 240nm.

Photoinitiator	Time of entire photolysis (s)	Quantum yields
[Cp-Fe-biphenyl] PF_6	60	0.26
I-261	180	0.09

I=2.7 mw/cm^2 (365nm)



Scheme 1. Typical ring opening reaction of epoxide by an iron-arene complex

Photoactivity of the epoxy mixture ERL4221+GCC (2:1) initiated by different cationic photoinitiators under a 700W high-pressure mercury lamp is compared in Figure2. The photoinitiating activity of [Cp-Fe-biphenyl] PF_6 is much higher than that of mono-arene iron complex I-261. It is approximately the equal level of the photosensitivity of the system photoinitiated by Sutomer SR1012 (diaryliodonium salt).

From Figure2, it also can be seen that organic peroxide, benzoly peroxide BPO could promote the photopolymerization of epoxy system initiated by [Cp-Fe-biphenyl] PF_6 significantly. The photoinitiating activity of [Cp-Fe-biphenyl] PF_6 +BPO (1:1) is higher than SR-1012 under 700w high pressure mercury lamp.

From Scheme 1, ferrocinium salts undergo photolysis to generate an iron-based Lewis with the loss of the biphenyl ligand. Coordination of this latter species with an epoxy monomer is followed by ring-opening polymerization. The ring-open and the polymerization reaction could start in the ligand sphere of the iron cation, for the reason of the absence of electrons in the iron cation with two charges. It was commonly recognized that the photosensitizing role of peroxide BPO carried out through oxidizing iron cation from two valence to a higher three valence and then enhance the rate of complex with epoxides.

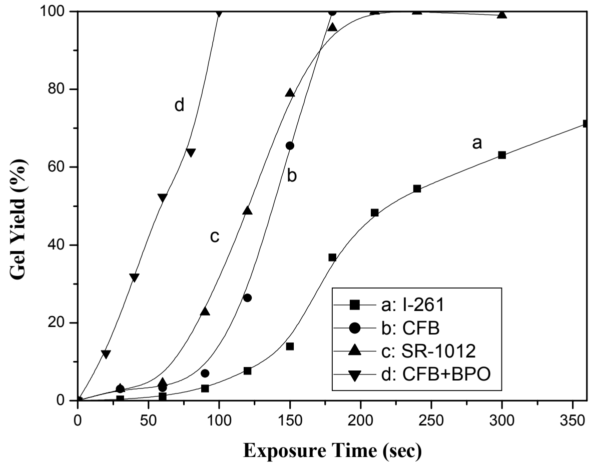


Figure 2. Photopolymerization of ERL4221+GCC(2:1) initiated by different cationic photoinitiators, I=1.1 mw/cm^2 (365nm)

Thermal stabilities

An important property of photo-resists is the inherent thermal stability of the photoinitiator since pre- and post-exposure bakes can influence the physical state of the material. It is 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, D.S.C was employed to measure the onset of thermally initiated polymerization [10].

The samples of three epoxy monomers GCC, ERL4221, TDE85 and oligomer E44 with 2% [Cp-Fe-biphenyl]PF$_6$ were evaluated over a temperature range between 50℃ and 160℃ at a heating rate of 10℃ min-1 respectively. See Figure 3 for D.S.C scan. As implied from the onset of the exotherm record for the GCC/[Cp-Fe-biphenyl]PF$_6$ and ERL4221/[Cp-Fe-biphenyl]PF$_6$ blends, these two systems are stable under 200℃.

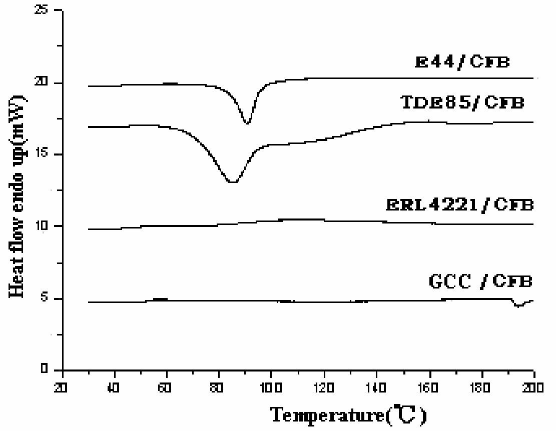


Figure 3. D.S.C. scans from mixtures of 2% [Cp-Fe- biphenyl] PF$_6$ (CFB) and epoxy oligomer

However, the onset temperatures of the exotherm recorded for the TDE85/[Cp-Fe-biphenyl]PF_6 and for the E44/[Cp-Fe-biphenyl]PF_6 are 71.6℃ and 84.0℃. That indicates the heat polymerization can occur without UV radiation in these systems, and temperature in excess of the onset temperatures should be avoided when processing these materials.

In table 2, the exotherm value was listed. For the exotherm value of the system E44/ [Cp-Fe-biphenyl] PF_6 is little, this polymerization may be caused by impurities in expoxy resin.

The dark-cure after UV radiation

An important difference between cationic and radical polymerizations is the active center lifetime [11]. For cationic polymerizations, the rate of consumption of active centers is very slow, the dark-cure can occur. From scheme1, the polymerization initiated by iron arene complexes can be considered as a two-step process: (1) Liberation of the active initiator by photolysis; (2) Heat treatment to complete the polymerization to a fully crosslinked resin. Because of forming the complex of Cp-Fe^+ with oxygen and opening the ring are endothermic reactions, the heat treatment is very important in the dark-cure.

After irradiating the system of epoxides/[Cp-Fe-biphenyl] PF_6 for a pre-determined period of 3minute, the dark-cure was monitored in the dark as a function of heating temperature by DSC. In Fig.4, compared with the exotherm record for none radiation in Fig.3, the record for these four systems after radiation rise remarkably (Table2). So the occurrence of dark-cure was confirmed. Less exotherm value indicated that the system of ERL4221/[Cp-Fe- biphenyl] PF_6 had cured nearly completely by UV radiation. The system of E44/[Cp-Fe- biphenyl]PF_6 can cure completely when it was heated to 90℃, by both the effect of dark-cure and that of heat polymerization, However the dark-cure of the systems GCC /[Cp-Fe-biphenyl]PF_6 and TDE85/[Cp-Fe-biphenyl]PF_6 occurred from 50℃ to above 150℃.

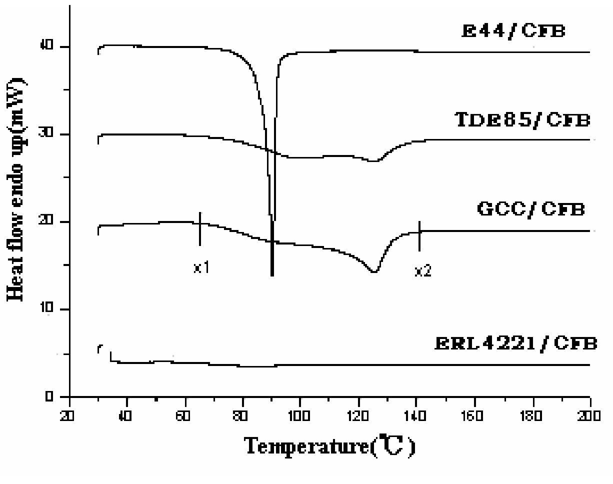


Figure 4. D.S.C. scans from mixtures of 2% [Cp-Fe- biphenyl] PF_6(CFB) and epoxides after pre-radiation for 3 minute by 700W high pressure Hg lamp

Table 2. Thermal analysis on various epoxy system initiated by [Cp-Fe- biphenyl]PF_6 from 30℃ to 150℃

	No radiation		After pre-radiation for 3min.	
	Onset ℃	DeltaH J/g	X1- X2 ℃	DeltaH J/g
GCC	none	none	63.2-143.6	300.0
ERL4221	none	none	55.2-98.5	9.4
TDE85	71.6	102.9	56.2-146.5	232.4
E44	84.0	27.9	60.7-100.3	201.3

Conclusions

In this paper, [cyclopentadien-Fe-biphenyl] PF_6 was prepared to photoinitiate epoxy monomers and oligomer with high-pressure Hg lamp as light source. The photoinitiating activity of [Cp-Fe-biphenyl] PF_6 is much higher than that of I-261. That of [Cp-Fe-biphenyl] PF_6 +BPO (1:1) is higher than that of SR-1012. Without UV radiation, GCC/[Cp-Fe-biphenyl]PF_6 and ERL4221/[Cp-Fe-biphenyl]PF_6 blends are stable under 200℃. However, the heat polymerization of TDE85/[Cp-Fe-biphenyl]PF_6 can occur at 71.6℃. The dark cure of four epoxy systems were evaluated by DSC. After radiating the system of epoxides/[Cp-Fe-biphenyl] PF_6 for a pre-determined period, the exotherm record rise remarkably.

References

1 Decker C, Thi Viet, Thi HP (2001) Polym. Int. 50:986
2 Robert V, Attila I, Andras V, Istvan C, Istvan R (1996) Radiat. Phys. Chem. 47: 457
3 Crivello JV (1999) J. Polym. Sci.: Part A: Polymer Chemistry. 37: 4241
4 Crivello JV, Lee JL (1990) J. Polym. Sci., Chem. Ed.. 28:479
5 Crivello JV, Lam JHW (1980) J Polym Sci Chem Ed. 18:1021
6 Meier K, Zweifel H (1986) J. Image. Sci. 30:174
7 Lohse F, Zweifel H (1986) Adv. in Polym. Sci. 78:69
8 Nesmeyanor AN, Vol,kenau NA, Boleaova IN (1963) Tetrahedron Letters 25:1725
9 Chen XD, Yong YL, Liang ZhX(1993) Chem J Chin. Univ. 14:1605
10 Everett JP, Schmidt DL, Rose GD (1997)Polymer. 38:1719.
11 Sipani V, Scranton AB(2003) J. Photochem. Photobio.A:Chem. 159:189