

NOTE

Studies on Active Center Concentration in Photopolymerization of Cyclohexene Oxide Initiated with Iron–Arene Complex

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INTRODUCTION

Organometallic compounds as photoinitiators for the epoxy polymerization have been described in the past. Strohmeier reported that manganese decacarbonyl is a photoinitiator for epichlorohydrin.¹ Other organometallic carbonyl compounds are listed in the literature.^{2–4} Kaeriyama mentioned the use of zirconocene dichloride as a photoinitiator for phenyl glycidyl ether.⁵ Organohalogen compounds and organometallic aluminium complexes^{6,7} have also been reported as cationic photoinitiators. Iron–arene complexes have been described as a class of highly efficient photoinitiators for the epoxy polymerization.^{8–10} The major advantages of iron–arene complexes include their relatively high thermal stability and high sensitivity to ultraviolet (UV) radiation.¹¹ The photolysis of iron–arene complexes in the presence of epoxides does not always lead to rapid polymerization at room temperature. Without prior irradiation, iron–arene complexes are not active thermal initiators of epoxide polymerization, even when heated up to a higher temperature. Therefore, the iron–arene complexes seem to be the most promising compounds among all organometallic initiators listed above.

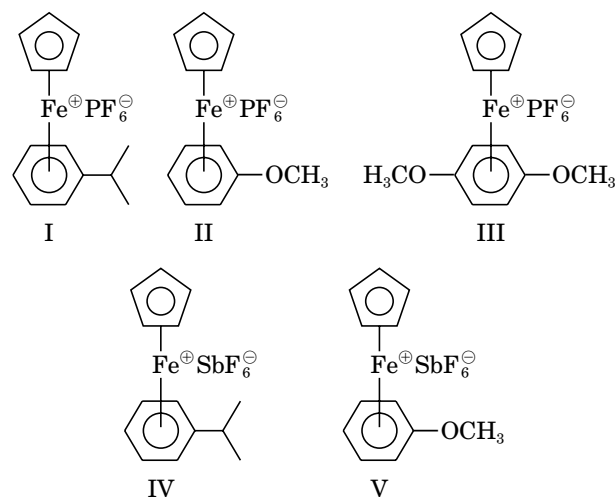
In a previous work, we have studied the photolysis process and photolysis kinetics of cyclopentadienyl–cumene iron hexafluorophosphate (Irgacure 261) via fluorescence spectra.¹² The initiation mechanism for epoxide polymerization initiated by iron–arene complex was proposed by Lohse and Zweifel¹³ yet little work has been done in this respect. The aim of this research is to investigate the activity of iron–arene complex and

the temperature effect on photopolymerization of cyclohexene oxide which, we believe, might shed some light on the initiation mechanism.

EXPERIMENTAL

Synthesis of Iron–Arene Complexes

Cyclopentadienyl–iron–arene complexes were prepared by a technique described in the literature.¹⁰



Photopolymerization of Cyclohexene (CHO)

CHO (Fluka) was purified by distillation after stored overnight in 5 Å molecular sieves. Photopolymerization was carried out in a quartz test, which was thermo-

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Table I Results of the Elemental Analysis of Synthesized Iron-Arene Complexes

	C (%)		H (%)		C : H	
	Measured	Calcd	Measured	Calcd	Measured	Calcd
II	38.20	38.42	3.53	3.74	1 : 1.11	1 : 1.17
III	38.36	38.54	3.87	3.94	1 : 1.21	1 : 1.23
IV	35.03	35.18	3.68	3.77	1 : 1.26	1 : 1.28
V	31.01	30.93	3.06	3.01	1 : 1.18	1 : 1.17

stated. A 250 W high-pressure mercury lamp was used as the light source.

Determination of the Concentration of Cationic Active Centers [P^*]

The determination was carried out by treating the polymerization system with sodium phenoxide solution in 1,2-dichloroethane for 1 h. The mixture was extracted three times with 1 mol/L aqueous NaOH; the organic layer was separated and dried over Na_2SO_4 ; and, finally, 1,2-dichloroethane was added up to a fixed volume. The absorbance of the solution at 272 nm was measured on a Shimadzu UV-3400 spectrophotometer, and an extinction coefficient of $1.93 \times 10^{3.14}$ was adopted to calculate [P^*].

RESULTS AND DISCUSSION

The results of elemental analysis of synthesized iron-arene complexes are listed in Table I. Table I shows that the purity of the synthesized complexes is satisfactory. Complex (I) (Irgacure 261) was supplied by Ciba-Geigy.

The data of absorption spectrum of (I) in the UV and visible region are shown in Table II. The absorption spectrum of complex (I) is similar to those all five iron-arene complexes studied.

Table II The Data of Absorption Spectrum of Complex (I) in UV and Visible Region

Solvent	λ_{max} (nm)	$\nu \times 10^{-4}$ (cm^{-1})	ϵ_{max} ($\text{L mol}^{-1} \text{cm}^{-1}$)
Methanol	241	4.15	1.14×10^4
Methanol	388	2.57	72.3
Methanol	453	2.21	57.8

Figure 1 shows the changes of the active center concentration [P^*] during polymerization at 35°C. It is found that the [P^*] values in CHO photopolymerization have a linear relationship with polymerization time at a given initiator concentration. For these initiators, the active center concentrations [P^*] at the same polymerization time increases in the following order: III > II > I; i.e., the order of initiation activity is (III) > (II) > (I). It is noted that this order is in accordance with the order of the electron-donating ability of the arene group of these photoinitiators.

The initiation activity of iron-arene complex also depends upon the nucleophilicity of the anion employed, as shown in Figure 2. The active center concentration increases in the order of $\text{SbF}_6^- > \text{PF}_6^-$, i.e., the nucleophilicity of the anion employed has markedly influenced the initiation activity of the iron-arene complex and polymerization rate.

Figure 3 shows the [P^*] values in CHO photopolymerization in 1,2-dichloroethane at different temperatures. The photoinitiator concentration was 4.05×10^{-2}

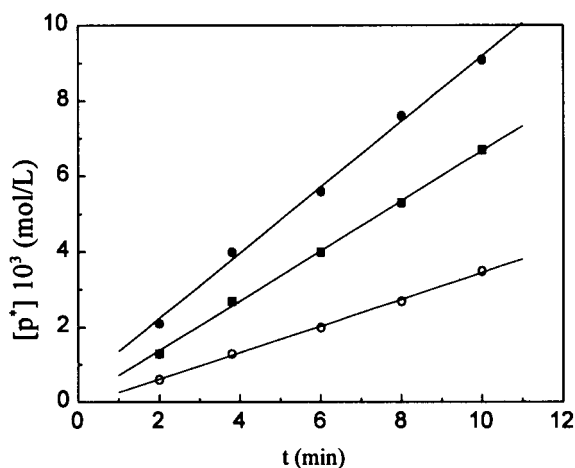
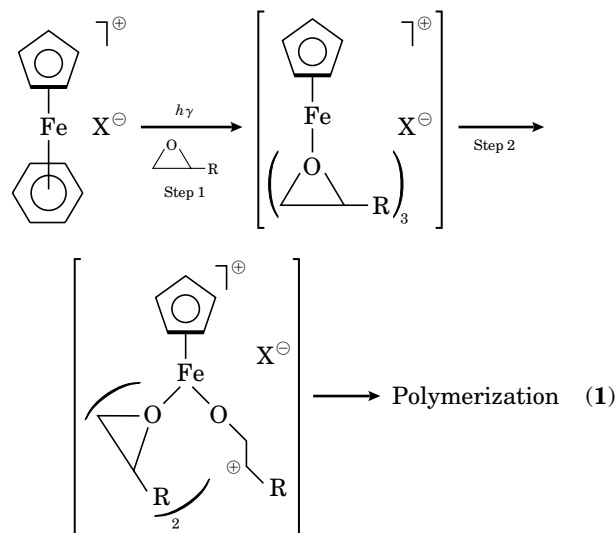


Figure 1 The changes of the active center concentration [P^*] during CHO polymerization. The concentration of the photoinitiator is 4.05×10^{-2} mol/L; the polymerization temperature is 35°C. Initiator: ○, I; ■, II; ●, III.

mol L. The $[P^*]$ value shows a pronounced maximum value at a certain temperature and decreased rather sharply at an elevated temperature. The temperature at which the $[P^*]$ value is maximum decreases with the increase of initiation activity of the photoinitiator. It is clear that the polymerization rate first increases with the increase of temperature and then decreases.

Lohse and Zweifel¹³ and Roloff et al.¹⁵ proposed a mechanism for the initiation in epoxide photopolymerization with the iron–arene complex as a photoinitiator, as shown in Scheme 1.



Photolysis of the iron–arene complex removes one of the uncharged aromatic ligand and yields an unsaturated iron cation¹²; then a new iron complex, in which the tridentate arene ligand can be replaced by three

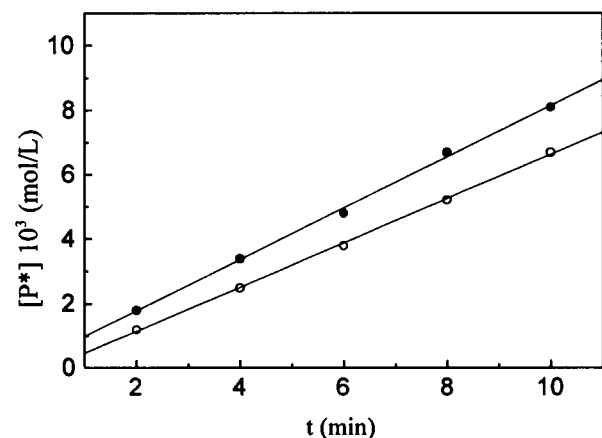


Figure 2 Comparison of the active center concentration $[P^*]$ during CHO polymerization initiated by iron–arene complexes with various anions. Initiator: ●, II; ○, V. The concentration of the photoinitiator is 4.05×10^{-2} mol/L; the polymerization temperature is 35°C .

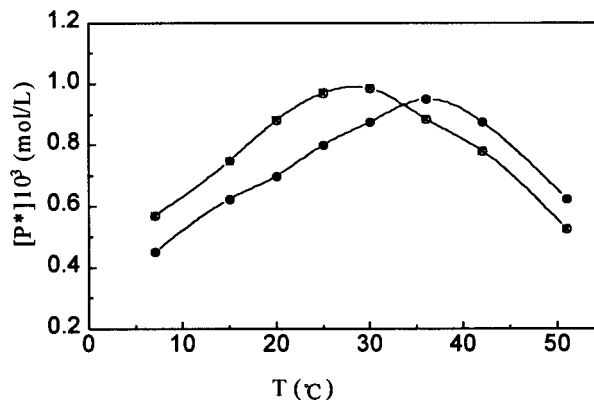


Figure 3 Effect of polymerization temperature on the active center concentration in CHO polymerization. The concentration of the photoinitiator is 4.05×10^{-2} mol/L; the polymerization time is 20 min. Initiator: ●, I; ⊕, II.

epoxides during the photolytic step, is formed. Ring opening and polymerization reaction could thus start in the ligand sphere of the iron cation leading to cyclopolyethers.

To account for our results, we assume that low temperature facilitates the complexation of epoxides, and the ligand-exchanged iron complex having three coordinated epoxide functions is stable (step 1); while high temperature favors the ring-opening reaction (step 2) and is unfavorable to the stability of ligand sphere of the iron cation. The effect of temperature on step 1 turns out to be contrary to that on the step 2. In fact, Gill¹⁶ reported that a $[\text{CpFe}(\text{CH}_3\text{CN})_3]^+$ (Cp denotes cyclopentadienyl) complex forms in low temperature (-40°C) photolysis of $[\text{CpFe}(\text{arene})]^+$ in acetonitrile, and it decomposes at 20°C . Furthermore, Lohse and Zweifel¹³ found in the course of his investigations that the polymerization including iron–arene complex and epoxides was irradiated at -88°C , and polymerization took place after heating up the preirradiated samples to a certain higher temperature.

Financial support of this work by the National Natural Science Foundation the People's Republic of China is gratefully acknowledged.

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