

Synthesis and Curing Behavior of a Novel Ferrocene-Based Epoxy Compound

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ABSTRACT: A novel ferrocene-based epoxy compound of glycidyl ester of 1,1'-ferrocene dicarboxylate was synthesized by the reaction of 1,1'-ferrocene dicarboxylate and epichlorohydrin. The resultant epoxy compound showed an irreversible redox process in cyclic voltammetry (CV) measurement. The curing behavior of glycidyl ester of 1,1'-ferrocene dicarboxylate and dicyandiamide system was investigated by nonisothermal measurement using the Ozawa's approach

with the heating rate of 5, 10, 15, and 20°C/min, respectively. It was found that both the diffusion of the compound and the curing temperature have effect on the curing process, and the effect of temperature was greater. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1594–1599, 2008

Key words: electrochemistry; ferrocene; epoxy compound; thermosets; crosslinking

INTRODUCTION

Ferrocene derivatives have caught considerable attention for their electronic, electrochemical, magnetic, and catalytic properties.^{1–4} They have been applied in the fields such as modified electrodes,^{5,6} molecule devices,^{7,8} electrochemical sensors,^{9–11} and catalysts,^{12,13} among which the application as burn-rate catalysts for composite solid propellants is of particular interest.¹⁴ The ferrocene-based burn-rate catalysts have more advantages, such as better microscopic distribution, better fluidity, and better ignitability of the propellant, compared with other conventional burn-rate catalysts.¹⁵ However, the migration of ferrocene derivatives in the propellants which occurred upon curing and during storage may lead to malfunctioning of the propellant in rocket flights.^{16,17} The immobilization of ferrocene moiety to the propellant binder by covalently linking is an effective way to avoid this problem. Subramanian grafted vinyl ferrocene to hydroxyl-terminated poly(butadiene) and used it as a propellant-binder-

cum-burn-rate catalyst.¹⁵ They found that the chemically linked ferrocene in the binder could augment the burning rate. Some ferrocene derivatives with reactive groups were also synthesized.^{18,19} However, the detailed curing behaviors of such derivatives have not been reported.

We synthesized a novel ferrocene-based epoxy compound of glycidyl ester of 1,1'-ferrocene dicarboxylate by the reaction of 1,1'-ferrocene dicarboxylate and epichlorohydrin. Since the oxirane group can react with the curing reagent, it can be immobilized in the crosslinked propellants networks and effectively prevent the ferrocene moiety from migration. The understanding of redox properties and curing behavior of glycidyl ester of 1,1'-ferrocene dicarboxylate are of great importance for its application in burn-rate catalyst. In this article, we investigate redox properties of glycidyl ester of 1,1'-ferrocene dicarboxylate by cyclic voltammetry (CV) measurement and study its curing behavior by nonisothermal measurement using Ozawa's approach.

EXPERIMENTAL

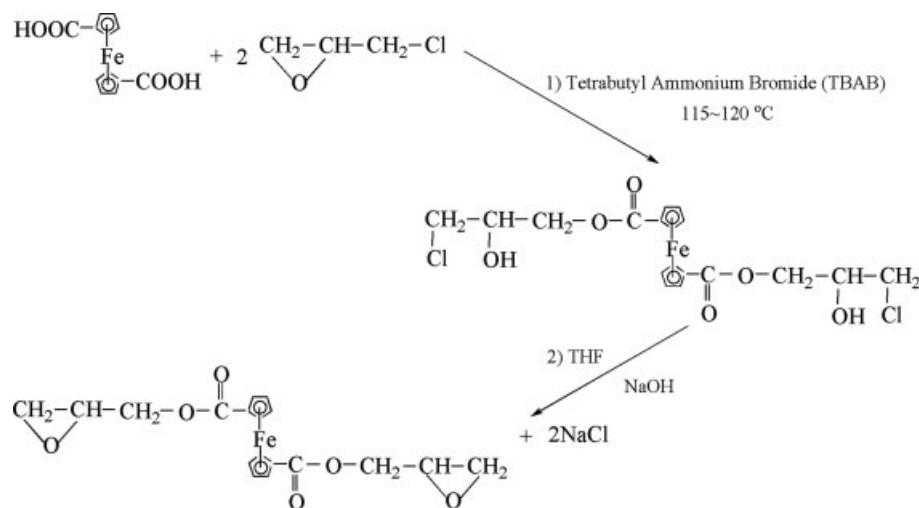
Materials

Ferrocene, tetrabutyl ammonium bromide, and NaHSO₄ were purchased from Sinopharm Chemical Reagent Ltd. Co. Epichlorohydrin was obtained from Shanghai WuLian Chemical Plant. AlCl₃, LiClO₄, CH₂Cl₂, CHCl₃, THF, NaOH, and Na₂CO₃ were purchased from East of China Chem. Ltd. Co.

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Scheme 1 Preparation process of glycidyl ester of 1,1'-ferrocene dicarboxylate.

Dicyandiamide was supplied by Ningbo Yinzhou East Sea Powder Coating Ltd. Co. CH_2Cl_2 , CHCl_3 , and THF were dehydrated by 4A molecular sieve before use and the others were used as received. 1,1'-ferrocene dicarboxylate was synthesized as described in Ref. 20.

Synthesis of glycidyl ester of 1,1'-ferrocene dicarboxylate

Glycidyl ester of 1,1'-ferrocene dicarboxylate was synthesized as following: 0.8121 g (0.003 mol) of 1,1'-ferrocene dicarboxylate, 5 mL (0.064 mol) of epichlorohydrin, and 0.0201 g (6.2×10^{-5} mol) of tetrabutyl ammonium bromide were mixed in a 25-mL three-necked flask with a magnetic stirrer and a reflux condenser. The system was heated at 115°C for 2.5 h and then excessive epichlorohydrin was removed under vacuum. The product was dissolved in 10 mL of THF at room temperature and after that 0.7 mL of 40 wt % NaOH solution was added dropwise in 15 min. The reaction was continued for another 5 h and glycidyl ester of 1,1'-ferrocene dicarboxylate solution was obtained after removing inorganic salts by centrifugal separation. The product was purified by repeating the process of removing the solvent by vacuum at room temperature, dissolving it in 10 mL of THF, and separating the inorganic salts by centrifugal machine for three times.

Preparation of samples

The samples for differential scanning calorimetry (DSC) measurement were prepared as following: 0.0285 g (3.39×10^{-4} mol) of dicyandiamide was dissolved in 2.5 mL of acetone/EtOH (4/1 v/v) mixed solution, then 0.3180 g (8.27×10^{-4} mol) of glycidyl ester of 1,1'-ferrocene dicarboxylate was added. After thoroughly mixed by magnetic stirring,

the solvent was removed under vacuum. The resultant sample was kept at 185°C for 90 min before thermogravimetric analysis (TGA) measurement. The samples for CV measurement were prepared by covering the glassy carbon disk electrode with a solution of glycidyl ester of 1,1'-ferrocene dicarboxylate in THF and then allowing the solvent to evaporate at room temperature.

Characterization

^1H NMR spectra of glycidyl ester of 1,1'-ferrocene dicarboxylate in CDCl_3 were recorded with an AVANCE model DMX-500 NMR spectrometer, using TMS as a standard. CV measurements were performed on a CHI-630A electrochemical analyzer (CH Instruments, Inc., Austin, TX) in an undivided three-electrode cell.² The working electrode was a glassy carbon disk electrode with diameter of 3 mm, which was polished to a mirror finish with 0.05- μm Al_2O_3 paste on felt, cleaned by ultrasonication successively in 0.1M NaOH, 1 : 1 HNO_3 , anhydrous ethyl alcohol, and double distilled water, respectively, before use. A platinum wire electrode was used as the counter electrode and an Ag wire electrode was used as the reference electrode. All electrodes were purchased from CH Instruments. DSC test was carried out on a DS822 under nitrogen atmosphere, relative to indium standard. TGA measurement was performed on a Netzsch STA 409 PG/PC instrument (Germany) at a 20°C/min heating rate from 25 to 720°C in a flow of nitrogen.

RESULTS AND DISCUSSION

Chemical composition

The synthesis procedure of glycidyl ester of 1,1'-ferrocene dicarboxylate is shown in Scheme 1.

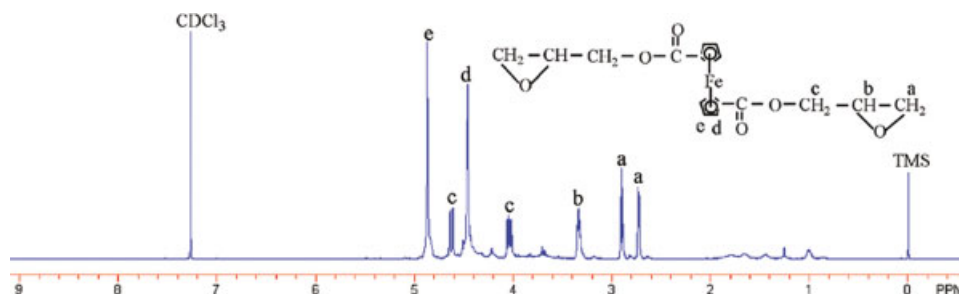


Figure 1 ^1H NMR spectrum of glycidyl ester of 1,1'-ferrocene dicarboxylate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Epichlorohydrin was reacted with the carboxyl of 1,1'-ferrocene dicarboxylate under the catalysis of TBAB. Glycidyl ester of 1,1'-ferrocene dicarboxylate was obtained after the ring-closing reaction under the catalysis of NaOH.

Figure 1 shows the ^1H NMR spectrum of glycidyl ester of 1,1'-ferrocene dicarboxylate. The Ha in oxirane ring was observed at 2.72–2.74 ppm (2H, q) and 2.89–2.91 ppm (2H, t) whereas Hb in oxirane ring was observed at 3.32–3.35 ppm (2H, m). The Hc was assigned at 4.01–4.06 ppm (2H, m) and 4.61–4.65 ppm (2H, q). The Cp ring protons appeared at 4.45–4.47 ppm (4H, q) and 4.86–4.87 ppm (4H, t).

Redox property of glycidyl ester of 1,1'-ferrocene dicarboxylate films

The process of propellants burning is a redox process and the mechanism of the burn-rate augmentation catalyzed by ferrocene derivatives may be as follows: Fe^{2+} in ferrocene moiety is oxidized into Fe^{3+} and gives a charge to fuel such as ammonium perchlorate, the charge-balance of the fuel is destroyed and promotes their split process, which results in the burn-rate augmentation. So redox property is important to burn-rate catalyst for composite solid propellants. The compounds with lower E_p may have better burn-rate catalysis ability.²¹ Figure 2 shows the cyclic voltammograms of different coverage content of glycidyl ester of 1,1'-ferrocene dicarboxylate on a glassy carbon electrode in aqueous LiClO_4 . The peak-to-peak separation, ΔE_p , of the glycidyl ester of 1,1'-ferrocene dicarboxylate is 106 mV which is larger than 60 mV indicating that the redox process is an irreversible electrochemical process.³ The values of E_p almost unchanged at different coverage content show that the coverage content has little effect on the redox property. The reduction of i_p was mainly caused by the increase of the film thickness which cumbered the transfer of charges during redox process. Compared with the 2,2-bis(alkylferrocenyl)propane with $E_{pa} > 405$ mV and $E_{pc} > 197$ mV prepared by Bian and Zhao,²¹ the E_{pa} was 800 mV and

the E_{pc} was 694 mV for the glycidyl ester of 1,1'-ferrocene dicarboxylate indicating that it was harder to be oxidized than 2,2-bis(alkylferrocenyl)propane.

Curing behavior of glycidyl ester of 1,1'-ferrocene dicarboxylate

Curing process affects the mechanical property of composite solid propellants directly. As a novel synthesized epoxy compound, the understanding of curing reaction of glycidyl ester of 1,1'-ferrocene dicarboxylate is favorable for its application. The curing process of glycidyl ester of 1,1'-ferrocene dicarboxylate/dicyandiamide system shown in Scheme 2 and its curing behavior was analyzed by nonisothermal measurement using Ozawa's approach.²²

The curing processes of glycidyl ester of 1,1'-ferrocene dicarboxylate and dicyandiamide were carried out on a DS822 under nitrogen atmosphere. Figure 3

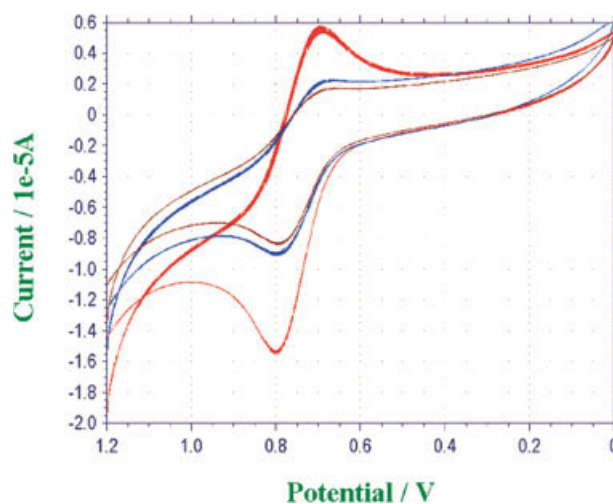


Figure 2 Cyclic voltammograms of glycidyl ester of 1,1'-ferrocene dicarboxylate films on a glassy carbon electrode. In aqueous 0.4M LiClO_4 , at a scan rate of 0.1 V/s, at 25°C, the coverage contents were 1.42×10^{-7} g/cm², 1.02×10^{-7} g/cm², and 6.09×10^{-8} g/cm² from outer to inner. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

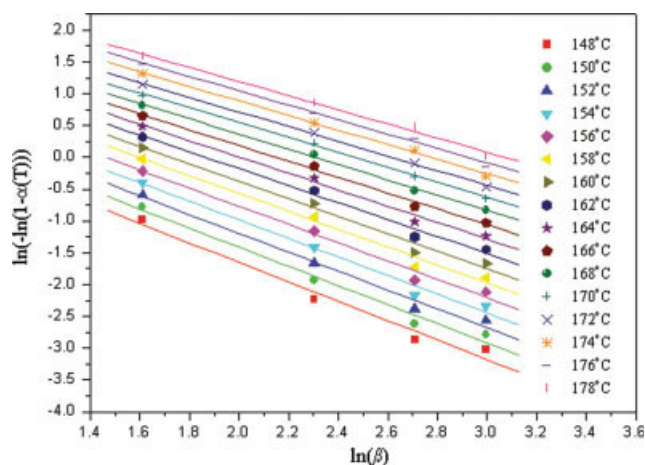


Figure 5 Plot of $\ln\{-\ln[1-\alpha(T)]\}$ versus $\ln(\beta)$ for temperatures ranging from 148 to 178°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The eq. (2) can be transformed into eq. (3) by getting logarithm:

$$\ln(\beta) = \ln A - \frac{E}{RT_p} \quad (3)$$

The T_p have gotten in DSC measurement, and the points can be obtained by plotting $\ln(\beta)$ versus $(1/(1/T_p))$. After linear simulation, A and E can be determined:²³

$$\ln(\beta) = 2.43 - 63.91/T_p \quad (\text{correlation coefficient } r = 0.9998) \quad (4)$$

where the value of action energy E is 531 J/mol, and pre-exponential factor A is 11.4°C/min.

According to Ozawa's theory, the relationship of the curing degree and the constant heating rate can be defined as eq. (5):²³

$$\alpha(T) = 1 - \exp\left(\frac{-k_0}{\beta^{n_0}}\right) \quad (5)$$

where $\alpha(T)$ is the curing degree at a certain temperature T , k_0 is the Ozawa reaction rate constant; n_0 is the Ozawa exponent; and β is the constant heating rate.

The eq. (5) can be transformed into eq. (6) by getting double-logarithm:

$$\ln\{-\ln[1 - \alpha(T)]\} = \ln k_0 - n_0 \ln \beta \quad (6)$$

k_0 and n_0 can be determined by plotting $\ln\{-\ln[1 - \alpha(T)]\}$ versus $\ln\beta$ at constant temperatures. $\alpha(T)$ obtained by different heating rate and temperature were shown in Figure 4 and the linear simulation of plot $\ln\{-\ln[1 - \alpha(T)]\}$ versus $\ln\beta$ is shown in Figure 5.

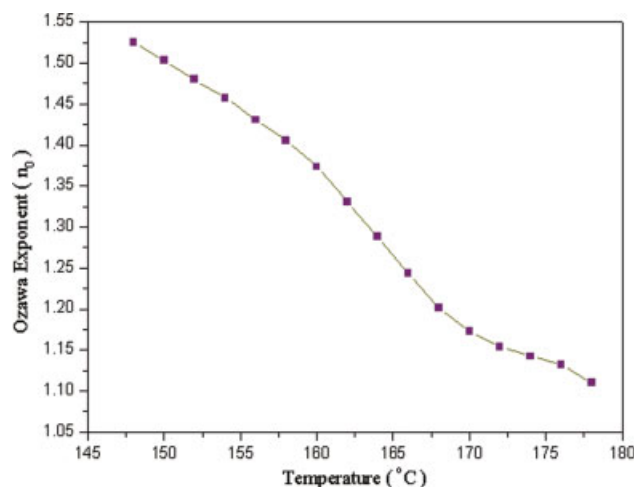


Figure 6 Variation of Ozawa exponent as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The change of Ozawa exponent (n_0) versus temperature is shown in Figure 6, n_0 decreased from 1.53 to 1.11 with the increase of temperature. It was supposed that with the advance of curing reaction, more gel formed and the monomer diffusion affected on curing reaction greater which result in the decrease of n_0 .²³ The decrease of n_0 was small compared with that of a novolac-type phenolic resin which decreased from 3.5 to 1 when the temperature increased from 146 to 170°C.²³ As for glycidyl ester of 1,1'-ferrocene dicarboxylate and dicyandiamide curing system, the molecules are much smaller than novolac-type phenolic resin and the space among the crosslinked points was large enough for the monomers to diffuse, so the form of gel has little effect on the move of molecule, and the n_0 changed little.

Figure 7 shows the change of Ozawa rate constant (k_0) along with temperature. k_0 increased with the

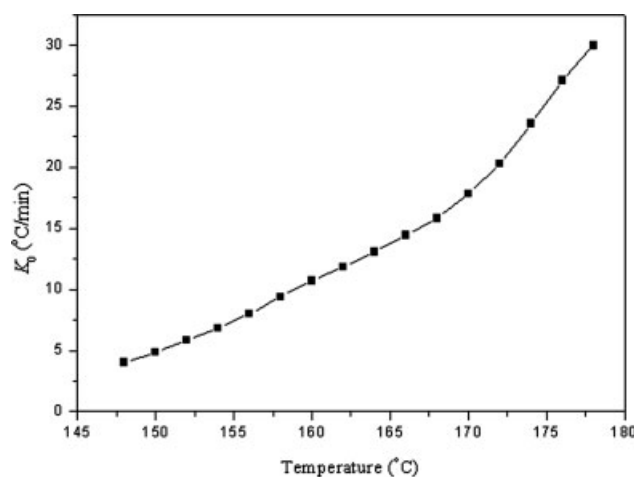


Figure 7 Ozawa reaction rate constant (k_0) for different temperature.

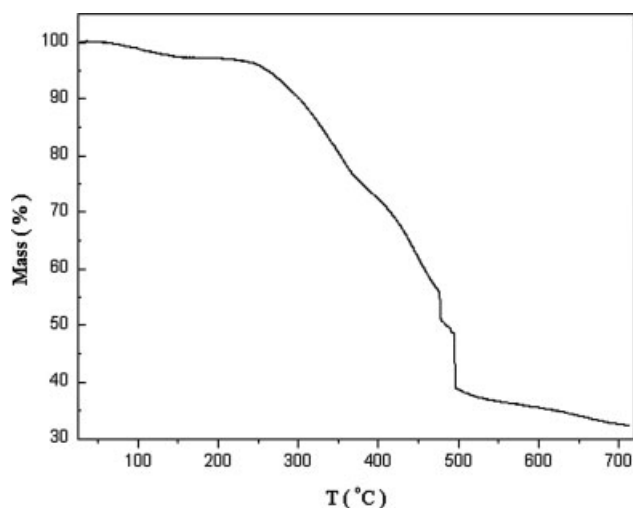


Figure 8 TGA curve of the cured ferrocene-based epoxy compound.

rise of temperature. The reaction rate is affected by two factors. One is the monomer diffusion. The crosslinking degree of the system increased with the increase of temperature which led to the increase of viscosity and result in the decrease of reaction rate. The other is the temperature which can promote the reaction rate. The k_0 increased with the increase in temperature showed that the effect of the temperature on the reaction rate was greater than the effect of monomer diffusion.

Thermal stability of the cured ferrocene-based epoxy compound

The thermal stability of the cured ferrocene-based epoxy compound was characterized by TGA measurement, and the result is shown in Figure 8. The weight reduced gradually and remained about 90% before 300°C. When the temperature above 300°C, ferrocene, and the crosslinked structure began to degrade and the weight lost quickly and remained at about 38% at 500°C.

CONCLUSIONS

A novel ferrocene-based epoxy compound was synthesized by the reaction of 1,1'-ferrocene dicarboxylate and epichlorohydrin. The CV measurement showed that the resultant epoxy compound showed an irreversible redox process. The curing behavior was investigated by nonisothermal measurement using Ozawa's approach. It was found that the dif-

fusion of the compounds had effect on the curing process of glycidyl ester of 1,1'-ferrocene dicarboxylate and dicyandiamide system; however, the effect of temperature was greater. The parameter of Ozawa's approach of this system was determined. The novel ferrocene-based epoxy compound has potential application in burn-rate catalyst for composite solid propellants.

References

- Chen, T.; Wang, L.; Jiang, G. H.; Wang, J. J.; Dong, X. C.; Wang, X. J.; Zhou, J. F.; Wang, C. L.; Wang, W. *J Phys Chem B* 2005, 109, 4624.
- Wang, X. J.; Wang, L.; Wang, J. J.; Chen, T. *J Phys Chem B* 2004, 108, 5627.
- Wang, X. J.; Wang, L.; Wang, J. J. *J Polym Sci Part B: Polym Phys* 2004, 42, 2245.
- Valincius, G.; Ignatjev, I.; Niaura, G.; Kažemžkaitė, M.; Talai-kytė, Z.; Razumas, V.; Svendsen, A. *Anal Chem* 2005, 77, 2632.
- Alonso, B.; Armada, P. G.; Losada, J.; Cuadrado, I.; González, B.; Casado, C. M. *Biosens Bioelectron* 2004, 19, 1617.
- Casado, C. M.; González, B.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *Angew Chem Int Ed Engl* 2000, 39, 2135.
- Nlate, S.; Ruiz, J.; Sartor, V.; Navarro, R.; Blais, J. C.; Astruc, D. *Chem Eur J* 2000, 6, 2544.
- Oh, S. K.; Baker, L. A.; Crooks, R. M. *Langmuir* 2002, 18, 6981.
- Yoon, H. C.; Hong, M. Y.; Kim, H. S. *Anal Biochem* 2000, 282, 121.
- Stone, D. L.; Smith, D. K. *Polyhedron* 2003, 22, 763.
- Kim, C.; Park, E.; Song, C. K.; Koo, B. W. *Synth Met* 2001, 123, 493.
- Köllner, C.; Pugin, B.; Togni, A. *J Am Chem Soc* 1998, 120, 10274.
- van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem Rev* 2002, 102, 3717.
- Grevels, F. W.; Kuran, A.; Özkar, S.; Zora, M. *J Organomet Chem* 1999, 587, 122.
- Subramanian, K. *J Polym Sci Part A: Polym Chem* 1999, 37, 4090.
- Menke, K.; Gerber, P.; Geißler, E.; Bunte, G. *Propel Explos Pyrotech* 1999, 24, 126.
- Ünver, A.; Dilsiz, N.; Volkan, M.; Akovali, G. *J Appl Polym Sci* 2005, 96, 1654.
- Jong, S. J.; Fang, J. M. *J Org Chem* 2001, 66, 3533.
- Kishore, K.; Verneker, V. R. P.; Dharumraj, G. V. *J Polym Sci Polym Lett Ed* 1984, 22, 607.
- Zhi, Y. G.; Dong, C. E.; Han, J.; Zheng, W. Z.; Zhang, L. F. *Chem Res Appl* 2000, 12, 413.
- Bian, Z. X.; Zhao, Q. H. *Chin J Appl Chem* 2004, 21, 923.
- Wang, D. Z. *Production and Application of Epoxy Resin*, 2nd ed.; Chem Industry Press: Beijing, 2001; Chapter 7, p 285.
- de Medeiros, E. S.; Agnelli, J. A. M.; Joseph, K.; de Carvalho, L. H.; Mattoso, L. H. C. *J Appl Polym Sci* 2003, 90, 1678.
- Park, B. D.; Riedl, B.; Hsu, E. W.; Shields, J. *Polymer* 1999, 40, 1689.
- Kenny, J. M.; Opalicki, M. *Compos A* 1996, 27, 229.
- Ozawa, T. *J Therm Anal* 1970, 2, 301.