

# Curing Kinetics and Structural Changes of a Di[(*N-m*-acetylenylphenyl) phthalimide] Ether/[(Methyl) diphenylacetylene] Silane Copolymer

Zeliang Dai, Qi Chen, Lizhong Ni, Ning Song, Wenkai Zhang

Key Laboratory for Ultrafine Materials, Ministry of Education, East China University of Science and Technology, Shanghai 200237, China

Received 4 January 2005; accepted 29 July 2005

DOI 10.1002/app.23596

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Differential scanning calorimetry, Fourier transform infrared (FTIR) spectroscopy, and  $^{13}\text{C}$ -NMR were used to characterize the curing kinetics and structural changes of a copolymer of di[(*N-m*-acetylenylphenyl) phthalimide] ether (DAIE) and [(methyl) diphenylacetylene] silane (MDPES). The results show that the apparent activation energy ( $E$ ) and reaction order ( $n$ ) calculated according to the Kissinger method were nearly the same as those calculated according to the Ozawa method.  $E$  was 160.4 kJ/mol and  $n$  was 0.96 with the Kissinger method, and  $E$  was 158.1 kJ/mol and  $n$  was 0.95 with the Ozawa method. The FTIR and solid-state  $^{13}\text{C}$ -NMR results also indicate that with increas-

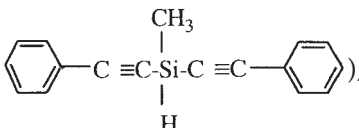
ing curing temperature, the peaks assigned to Si—H and C $\equiv$ C bonded to phenylene carbons decreased, broadened, and finally vanished, whereas the peaks assigned to the C=C carbons and phenyl carbons increased and broadened. Crosslinking reactions in the curing of the DAIE/MDPES copolymer were possible due to the hydrosilylation reaction and the Diels–Alder reaction. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2126–2130, 2006

**Key words:** activation energy; crosslinking; kinetics (polym.); NMR; structure

## INTRODUCTION

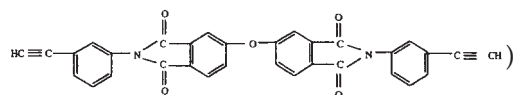
About 10 years ago, there were many scientists who had researched chemical compounds containing the Si(H)—C $\equiv$ C group. The polymers of these chemical compounds possessed a high temperature resistance after crosslinking reactions. In particular, Itoh et al.<sup>1,2</sup> studied the synthesis of poly{[bis(ethynylphenyl) silylene]phenylenes} (MSPs), its high temperature-resistance properties and mechanical properties, and its thermosetting mechanism.

In this article, a new chemical compound named [(methyl) diphenylacetylene] silane

(MDPES; ) which was

different from MSP in its structure,<sup>3</sup> was used. The testing results show that the polymer of MDPES exhibited an extremely high temperature resistance, and thermogravimetric analysis in an air atmosphere showed a temperature at 5% weight loss ( $T_{d5}$ ) of 568°C (whereas the  $T_{d5}$  of MSP was 567°C). Its dielectric dissipation factor ( $\tan \delta$ ) was 2.47

$\times 10^{-3}$  at a frequency of 1 MHz.<sup>4</sup> However, it was difficult to make the polymer of MDPES into composites because of its poor bonding with fiberglass-reinforced material. To increase its mechanical properties, in this study, MDPES was modified with di[(*N-m*-acetylenylphenyl) phthalimide] ether (DAIE;



Kuroki et al.<sup>5</sup> studied the thermosetting mechanism of MSP with  $^{13}\text{C}$ -NMR, solid-state  $^{29}\text{Si}$ -NMR, and computational chemistry. They concluded that the intermolecular crosslinking reactions were due to (1) the Diels–Alder reaction between —Ph—C $\equiv$ C and C $\equiv$ C and (2) the hydrosilylation reaction between Si—H and C $\equiv$ C, which proceeded up to 150°C and (3) the hydrosilylation reaction between Si—H and C $\equiv$ C, which proceeded above 150°C; a highly thermally stable structure was formed. Only the hydrosilylation reaction occurred above 300°C.

Recently, many scientists have also been studied the thermosetting mechanism of acetylene-terminated chemical compounds and acetylene-terminated polymers. For example, Stefeik et al.<sup>6</sup> studied the curing reaction of poly[(acetylenyl) imide] with  $^{13}\text{C}$ -NMR methods. They concluded that the Diels–Alder reaction was not the main reaction in the intermolecular crosslinking reaction because there was only less than

Correspondence to: L. Ni.

30% acetynyl that reacted in the crosslinking reaction. Ratto et al.<sup>7</sup> studied the thermal polymerization reaction of bis(acetynyl) phenylate with IR methods and found that the curing reaction mainly formed the conjugated polyene structures, so the Diels–Alder reaction was not the main reaction. Ding et al.<sup>8</sup> studied the curing kinetics and structural characterization of an arylacetylene polymer with differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopic methods. The results indicate that cis-conjugated polyene structures were predominantly formed during the curing of the arylacetylene polymer.

In this study, DSC, FTIR, and NMR methods were used to characterize the thermosetting kinetics and the structural changes of a DAIE/MDPES copolymer. Moreover, we discuss the possible occurrence of crosslinking reactions.

## EXPERIMENTAL

### Preparation of MDPES

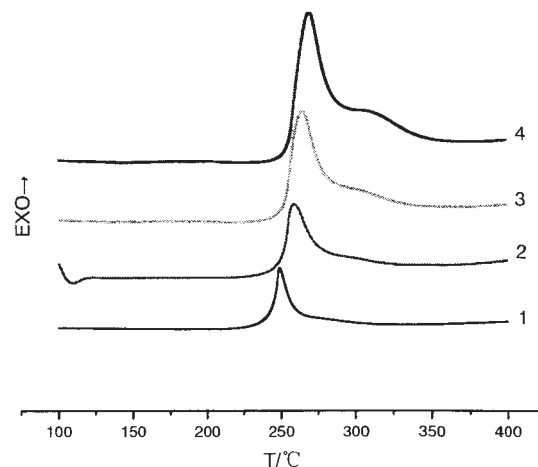
MDPES was prepared according to a previously applied method from a Chinese patent.<sup>3</sup>

### Preparation of DAIE<sup>9</sup>

A 2-L, four-necked, round-bottom flask equipped with an overhead stirrer, water-cooled condenser, additional funnel, and inlet was charged with 4,4'-oxydi(phthalic) anhydride (54.6 g, 0.176 mol) and acetone (1200 mL). The vessel was sealed and purged with nitrogen. Mamino-phenylacetylene (37.8 g, 0.32 mol) was added via the addition funnel over 30 min, and the originally white solution turned pale yellow. We allowed the reaction to continue for 30 min; then, the reaction flask was heated to 59°C with a heating mantle after the addition of nickel acetate, acetic anhydride, and triethylamine into the vessel. The reaction was complete in 4 h. The reaction mixture was washed with sodium bicarbonate and was then filtered under some pressure. The products were recrystallized from the hot-mixed solvents acetone and *N,N'*-dimethylformamide; this yielded white crystals (60 g, 80%). With high performance liquid chromatography (HPLC) analysis of the purified products, the results show that the purity of DAIE was 97.3%.

### Preparation the DAIE/MDPES copolymer

A 300-mL, three-necked, round-bottom flask equipped with an overhead stirrer and an inlet used to equip the heat indicator was charged with DAIE and MDPES. The mass of DAIE was as 0.8 times the mass of MDPES. The vessel was sealed and purged with nitrogen. The thermal polymerized reaction was com-



**Figure 1** DSC curves of the DAIE/MDPES copolymer at different  $\beta$ 's: (1) 5, (2) 10, (3) 15, and (4) 20°C/min.  $T$  = heating temperature.

pleted at 200°C over 2 h. After the reaction was complete, we obtained the tawny preformed polymers.

### Characterization methods

DSC testing was carried out with a differential scanning calorimeter (QBG-3, DuPont 1090, Dupont, Newark, DE). The measurement was conducted with nitrogen protection at different heating rates ( $\beta$ 's), including 5, 10, 15, and 20°C/min.

To characterize the structural changes of the DAIE/MDPES copolymer, the cured polymers, which were ground into a powder to be extracted in acetone for 8 h, were tested with an IR spectrometry analyzer (Nicolet Magna-IR550) by the KBr pressed-disc method.

## RESULTS AND DISCUSSION

### Thermosetting kinetics of the DAIE/MDPES copolymer

Figure 1 shows the DSC curing of the DAIE/MDPES copolymer at different  $\beta$ 's. An exothermic peak occurred in the range from 210 to 360°C because of the crosslinking reactions between DAIE and MDPES during the hyperthermic treatment. Table I shows the dynamic DSC results of the DAIE/MDPES copolymer. With increasing  $\beta$ , the temperature of the polyreaction moved to a higher temperature, and the reaction heat increased.

According to the Kissinger method, the peak reaction rate is assumed to reach a maximum at the apical temperature ( $T_p$ ). The apparent activation energy ( $E$ ) of the curing reaction of the polymer was calculated by the following equation:

**TABLE I**  
Dynamic DSC Testing Results of the DAIE/MDPES Copolymer

$\beta$ (°C/min-)	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)	$\Delta H$ (J/g)
5	224.2	249	258.5	414
10	250.6	258.8	273.9	362.7
15	251.7	263.8	278.5	420.1
20	253.9	268.6	281.7	476.9

$T_i$  = initial reaction temperature;  $T_f$  = final reaction temperature.  $\Delta H$  = thermal in reaction.

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{E}{R} \quad (1)$$

According to the Ozawa method,  $E$  of the curing reaction of the polymer was calculated by the following equation:

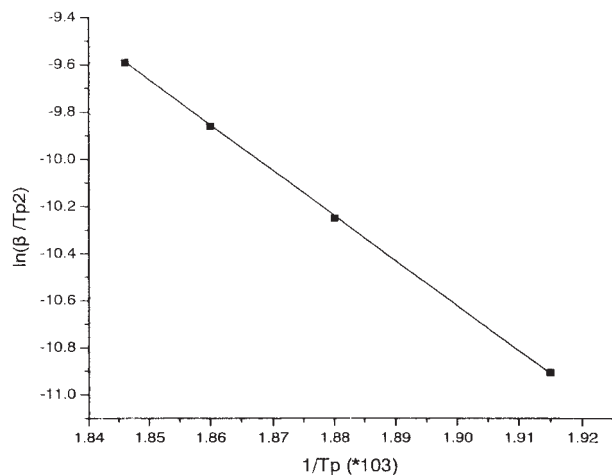
$$\frac{d\ln\beta}{d(1/T_p)} = -1.052\frac{E}{R} \quad (2)$$

According to the Crane experience equation, the reaction order ( $n$ ) of the curing reaction of DAIE and MDPES could be calculated as follows:

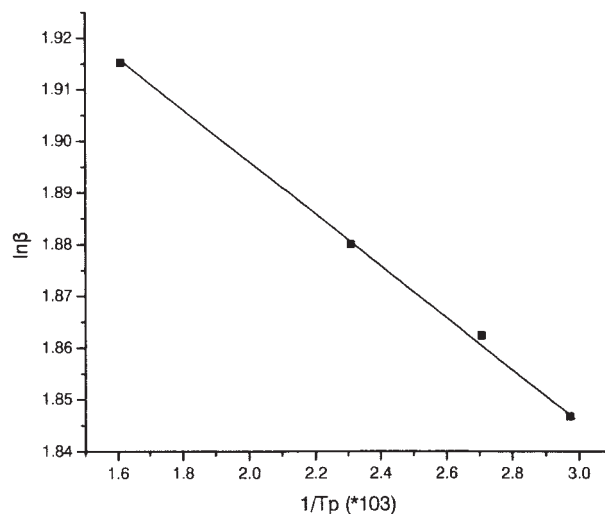
$$\frac{d(\ln\beta)}{d(1/T_p)} = -(E/nR + 2T_p) \quad (3)$$

where  $\beta$  is the heating rate (K/min),  $T_p$  is the apical temperature (K),  $E$  is the activation energy (J/mol), and  $R$  is the molar gas constant ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

According to the Kissinger method, Figure 2 shows the relationship between  $\ln(\beta/T_p^2)$  and  $1/T_p$ . The graphic was a line whose equation was  $y = -19,291.8x + 26.0412$ . The gradient constant of this line was



**Figure 2**  $\ln(\beta/T_p^2)$  versus  $T_p$ .



**Figure 3**  $\ln\beta$  versus  $1/T_p$ .

$-19,291.8$ , so  $E$  was calculated as  $160.4 \text{ kJ/mol}$  according to the equation  $-E/R = -19,291.8$ .

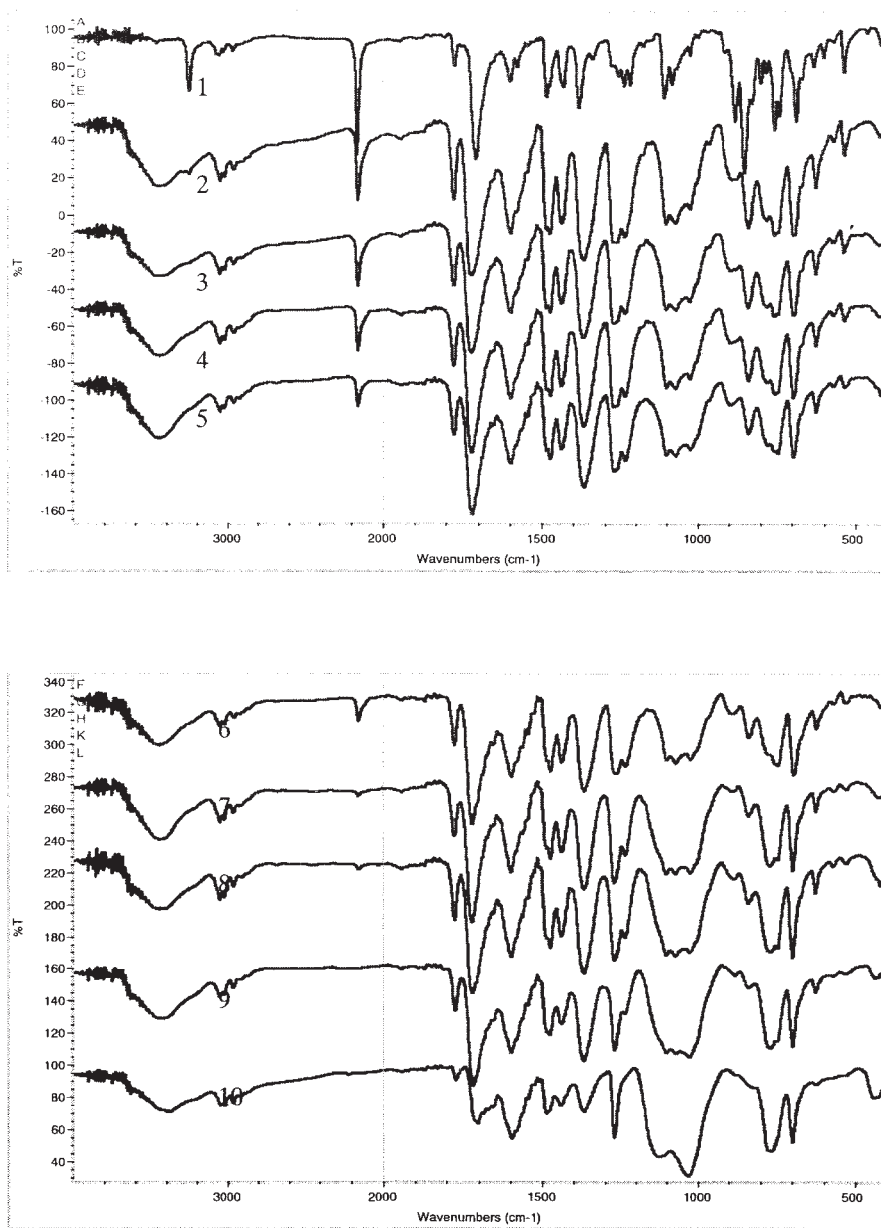
According to the method, Figure 3 shows the relationship between  $\ln\beta$  and  $1/T_p$ . The graphic was a line whose equation was  $y = -20,004x + 39.92110$ . The gradient constant of this line was  $-20,004$ , so  $E$  was calculated as  $158.1 \text{ kJ/mol}$  according to the equation  $-1.052E/R = -20,004$ .

If the numerical value of  $E/nR$  was much greater than the numerical value of  $2T_p$ , the numerical value of  $2T_p$  could be neglected, and the gradient constant of the line drafted according to Crane experience equation was  $-E/nR$ . The results shown in Figure 3 indicate that the numerical value of  $-E/nR$  was  $-20,004$ . According to the Kissinger method,  $E$  was calculated as  $160.4 \text{ kJ/mol}$ , and  $n$  was calculated as  $0.96$ , which indicated that the curing reaction approached a first-order reaction.  $E$  was calculated as  $158.1 \text{ kJ/mol}$  according to the Ozawa method, and  $n$  was calculated as  $0.95$ , which also indicated that the curing reaction approached a first-order reaction.

The calculation results indicated that the calculated  $E$  and  $n$  by the Kissinger method were nearly the same as those calculated by the Ozawa method.

### Structural changes of the DAIE/MDPES copolymer during curing

Figure 4 shows the FTIR spectra of the DAIE/MDPES copolymer as cured at various temperatures. The peaks at  $3290$  and  $634 \text{ cm}^{-1}$  of the mixture of DAIE and MDPES before curing were assigned to the  $\equiv\text{C}-\text{H}$  group. These peaks decreased and broadened when the copolymer was cured at  $200^\circ\text{C}$  for 2 h, and they vanished when the copolymer was cured at  $220^\circ\text{C}$  for 4 h. The peak at  $2190 \text{ cm}^{-1}$  assigned to the  $\text{Si}-\text{H}$  and  $\text{C}\equiv\text{C}$  bonded to the phenylene carbons



**Figure 4** FTIR spectra of the DAIE/MDPES copolymer at different solidified temperatures: (1) the mixture of DAIE and MDPES, (2) the prepolymer, and the copolymer cured for 4 h at (3) 220, (4) 240, (5) 260, (6) 280, (7) 300, (8) 320, (9) 340, and (10) 360°C. % T = transmittance.

decreased and broadened with increasing curing temperature and vanished when the copolymer was curing at 340°C for 4 h in the same way. This decrease in the peaks was caused by the conformational distribution of the products by a crosslinking reaction. The cured DAIE/MDPES samples had many new peaks at 1280 and 1590  $\text{cm}^{-1}$ , which increased and broadened with increasing curing temperature. These peaks were assigned to the C=C and phenyl carbons, respectively.

From the FTIR spectra results, it was suggested that the benzene ring was formed and the C≡C bonds changed into C=C bonds with curing. The benzene

ring was caused by the coupling reaction between two C≡C bonds, and the C=C bonds were caused by the hydrosilylation reaction between Si—H and C≡CH over a wide temperature range from 200 to 360°C.

Figure 5 shows the  $^{13}\text{C}$ -NMR spectra of the DAIE/MDPES copolymer samples cured at various temperatures. The peak at 87.3 ppm of the DAIE/MDPES copolymer sample at 200°C was assigned to the C≡C carbons. These peaks decreased and broadened when the sample was cured at 300°C. The peak at 130.1 ppm assigned to the phenylene carbons bonded to C≡C decreased and broadened with increasing curing temperature. The samples of the DAIE/MDPES copoly-

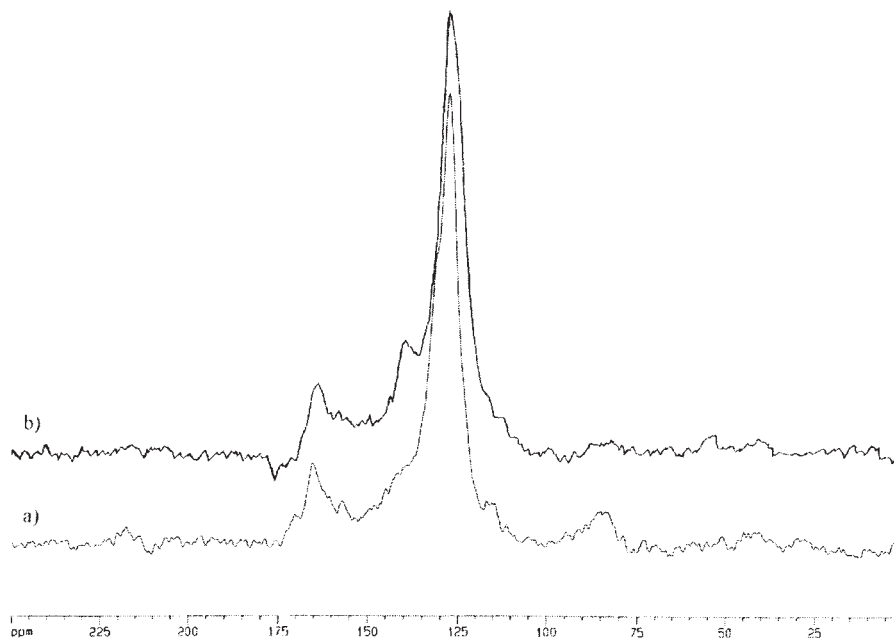
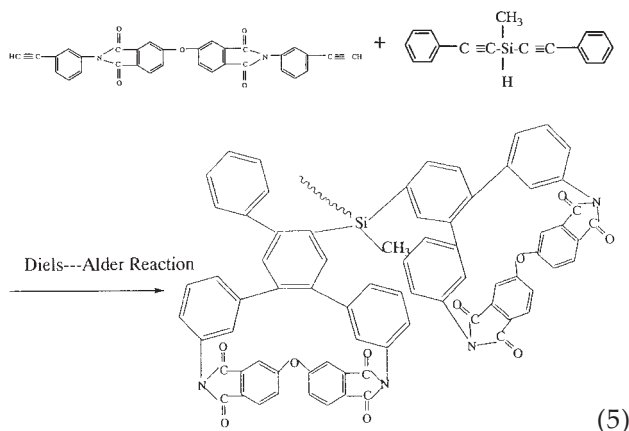
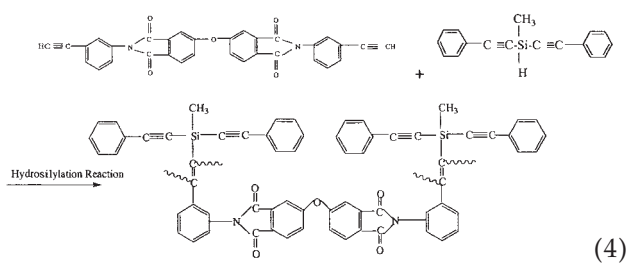


Figure 5  $^{13}\text{C}$ -NMR spectra of the DAIE/MDPES copolymer at various curing temperatures: (a) 200 and (b) 300°C.

mer cured at 300°C had a new peak at 142.5 ppm, which was assigned to the  $\text{C}=\text{C}$  and phenyl carbons bonded to the  $\text{C}=\text{C}$  bond.

According to the structural changes in the DAIE/MDPES copolymer during curing, the crosslinking reactions were possibly due to the hydrosilylation reaction and the Diels–Alder reaction. Equation (4) shows the hydrosilylation reaction formula from the curing of the DAIE/MDPES copolymer. Equation (5) shows the Diels–Alder reaction formula from the curing of the DAIE/MDPES copolymer:



## CONCLUSIONS

DSC was used to characterize the curing kinetics of the copolymerization of DAIE and MDPES. The results showed that  $E$  and  $n$  calculated according to the Kissinger method were nearly the same as those calculated according to the Ozawa method.  $E$  was 160.4 kJ/mol and  $n$  was 0.96 with the Kissinger method, and  $E$  was 158.1 kJ/mol and  $n$  was 0.95 with the Ozawa method.

FTIR and  $^{13}\text{C}$ -NMR spectra were used to characterize the structural changes of the DAIE/MDPES copolymer cured at various temperatures. The results show that with increasing curing temperature, the peaks assigned to the  $\equiv\text{C}-\text{H}$  group and those assigned to the  $\text{Si}-\text{H}$  and  $\text{C}\equiv\text{C}$  groups decreased, broadened, and finally vanished, whereas the peaks assigned to the  $\text{C}=\text{C}$  carbons and the phenyl carbons increased and broadened with increasing curing temperature. The results indicated that the crosslinking reactions were possibly due to the hydrosilylation reaction and the Diels–Alder reaction.

## References

1. Itoh, M.; Lnoue, K.; Iwata, K. *Macromolecules* 1997, 30, 694.
2. Hong, L.; West, R. *Macromolecules* 1998, 31, 2866.
3. Chen, Q.; Ni, L.-Z.; Li, Y. *Chin. Pat.* CN1421446A (2003).
4. Chen, Q.; Ni, L.-Z.; Hu, C.-P. in *Preprints of Third East Asia Polymer Conference*; Chengdu, China, 2004; p 42.
5. Kuroki, S.; Okita, K.; Itoh, M. *Macromolecules* 1998, 31, 2804.
6. Sefeik, M. D.; Stefskal, E. O.; McKay, R. A. *Macromolecules* 1979, 12, 423.
7. Ratto, J. J.; Dynes, P. J.; Hamermesh, C. L. *J Polym Sci Polym Chem Ed* 1980, 22, 1035.
8. Ding, X.-W.; Qi, H.-M.; Zhuang, Y. Q.; Wang, J. *J East China Univ Sci Technol* 2001, 27, 161.
9. Chen, Q.; Ni, L.-Z.; Dai, Z.-L.; Hu, C.-P. *Chin. Pat. Appl.* 2004100184092 (2004).