Curing Reactions of Bismaleimidodiphenylmethane with Mono- or Di-functional Allylphenols. High Resolution Solid-State ^{13}C NMR Study

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ABSTRACT: Analysis of the curing reactions of bismaleimidodiphenylmethane (BMI) with diallylbisphenol-A (DABA) or *o*-allylphenol (AP) with the high resolution solid-state ^{13}C NMR technique revealed that while cured products of BMI and AP are formed through *ene*-reaction and the sequential Diels–Alder reaction, no Diels–Alder reaction occurs in the case of DABA and only *ene*-reaction and polymerization proceed. This shows that the crosslinking of such widely used curing system proceeds via a different manner suggested previously.

KEY WORDS Curing Reaction / Diels–Alder Reaction / *ene*-Reaction / Bismaleimide / Diallylbisphenol-A / Solid-State ^{13}C Nuclear Magnetic Resonance /

The curing system of bismaleimide has been widely used as thermosetting polyimides, which provides excellent thermal stability but brittleness simultaneously because of the high crosslinking density of the network. In order to add toughness to bismaleimide resins, modification has been made by the addition of diallyl compounds such as diallylbisphenol-A (DABA).^{1,2} The course of this reaction has been investigated and *ene*- and Diels–Alder reactions were suggested to be involved in this curing system based on the model reaction of *N*-phenylmaleimide (PMI) and *o*-allylphenol (AP).^{3–5} The preceding paper showed that the thermal reaction of PMI and AP gave *ene*- and Diels–Alder adducts but PMI and DABA did not give the Diels–Alder adduct.⁶ However, the practical curing reaction remains uncertain because the curing products are generally insoluble toward almost of organic solvents, which prevents to characterize the reaction products.

High resolution solid-state NMR with CPMAS (cross polarization magic angle spinning), developed by Schaefer,⁷ has been applied to the analysis of insoluble polymer such as cured thermoset resins.⁸ Our previous studies showed that the solid-state ^{13}C NMR is useful to investigate the curing reactions of bismaleimide resins.^{9–12} Although the solid-state ^{13}C NMR spectrum of the cured product of bismaleimidodiphenylmethane (BMI) with DABA has been illustrated by Carduner *et al.*^{13,14} detailed descriptions are not available. On the basis of fundamental data of the model reactions, we report in this paper the direct measurements of the curing reactions of BMI and DABA with a high resolution solid-state ^{13}C NMR.

EXPERIMENTAL

Materials

BMI, purchased from Wako Pure Chemical Industries, was recrystallized from chloroform–methanol. DABA

was obtained from Mitsui Toatsu Chemicals Inc. PMI and *o*-AP were purchased from Wako Pure Chemical Industries.

Sample Preparation

Mono- or di-functional maleimides and mono- or di-functional allylphenols were mixed in a round bottom flask and heated by an oil bath at 150°C for 15 min. Continuous stirring led to a homogenous melt. This mixture was put in a closed aluminous vessel and heated at 175°C for 2 h, at 200°C for 1 h, and at 250°C for 1 h in an air oven. Each stage samples were analyzed by liquid-state and solid-state ^{13}C NMR.

Liquid-State ^{13}C NMR Measurements

NMR spectra were obtained for samples dissolved in dimethyl- d_6 sulfoxide (DMSO- d_6) or CDCl_3 at room temperature and were recorded on a JEOL JNM-GSX400 spectrometer.

Solid-State ^{13}C NMR Measurements

High resolution solid-state ^{13}C NMR spectra, CPMAS spectra, were acquired with a JEOL JNM-EX270W spectrometer equipped with a Doty Scientific CPMAS probe at room temperature. For these measurements, cryoground products were packed into MAS rotors. Sideband interference was eliminated by total suppression of spinning sidebands (TOSS).¹⁵ Contact time was 2 ms, repetition time 5 s and spinning rate about 4 kHz.

RESULTS AND DISCUSSION

In the preceding paper, we assigned the products formed from the thermal reaction of PMI and AP with liquid ^{13}C NMR spectral data.⁶ At first, comparison between the liquid and solid state ^{13}C NMR spectra was made. Figure 1 shows their spectra for a reaction mixture of PMI and AP (molar ratio 2/1) treated at 175°C

Figure 1. ^{13}C NMR spectra of the reaction products of PMI/AP system treated at 175°C for 2 h: (a) liquid-state NMR spectrum in $\text{DMSO}-d_6$; (b) CPMAS spectrum (* spinning sidebands); (c) CPMAS spectrum using TOSS.

for 2 h. Solid-state ^{13}C NMR spectra were obtained by CPMAS and spinning sideband interference was eliminated by TOSS. TOSS is clearly of great advantage to distinguish important signals around 75 ppm. A signal at 75 ppm ascribed to the 3:1 adduct (the Diels–Alder adduct) was observed. Thus, the CPMAS ^{13}C NMR spectra made it possible to analyze the components of the products, taking notice of the signal around 75 ppm.

The curing reaction of BMI with DABA (molar ratio 2/1) was carried out under several heating conditions and analyzed by liquid-state ^{13}C NMR and CPMAS ^{13}C NMR as shown in Figure 2. On the basis of fundamental data of the model reactions,⁶ assignments of these spectra were made. The liquid-state ^{13}C NMR spectra of a melt mixture and initial stage of curing (at 175°C for 30 min) could be measured in $\text{DMSO}-d_6$, while additional curing products could be monitored only by CPMAS ^{13}C NMR

spectra because of insolubility. As observed in the model reaction of PMI and DABA, the *ene*-adduct was formed after treatment at 175°C for 30 min and assigned from the signals at 176 and 179 ppm (carbonyl carbons), but formation of 3:1 adduct was not observed. CPMAS ^{13}C NMR spectra of all stages in the curing reaction showed no distinct signal at 75 ppm in contrast to the model reaction. (A small peak around 70 ppm is the remains of spinning sideband that was not completely removed by TOSS.) The signal at 170 ppm (carbonyl carbon of unreacted BMI), 134 ppm (olefinic carbon of unreacted BMI), and 115 ppm (terminal sp^2 carbon of allyl group) decreased with curing, but the signals at 176, 45, and 30–40 ppm corresponding to carbonyl carbon of reacted BMI, methyne carbon of polymerized BMI, and sp^3 carbons of polymerized DABA and the *ene*-product, respectively, increased. Consequently, this curing reac-

Figure 2. ^{13}C NMR spectra in $\text{DMSO}-d_6$ (a', b') and CPMAS ^{13}C NMR spectra (a–e) of the cured products of BMI/DABA system treated at different temperatures: (a) and (a') melt mixture at 150°C for 15 min; (b) and (b') at 175°C for 30 min; (c) at 175°C for 2 h; (d) at 175°C for 2 h and at 200°C for 1 h; (e) at 175°C for 2 h, at 200°C for 1 h, and at 250°C for 1 h.

tion produces only the *ene*-adduct and polymer of BMI and DABA but the Diels–Alder reaction observed in the model reaction does not proceed.

In the CPMAS ^{13}C NMR spectra, signals in the 30–50 ppm region also provided useful information on the products because ^{13}C NMR spectra data of the model reaction showed signals at about 34, 35, 40 ppm for methylene and methyne carbons ascribed to the *ene*-adduct and a signal around 45 ppm for methyne carbon of the polymer of maleimides. The broadened

signals in this region in Figure 2 indicate that the polymerization of BMI proceeds even at low temperature (175°C).

To examine differences between the model reaction and the above described curing reaction, thermal reactions of BMI/AP (1/1) and PMI/DABA (4/1) systems were investigated.

Figure 3 shows CPMAS ^{13}C NMR spectra of BMI/AP and PMI/DABA systems treated at several temperatures. In the thermal reaction of BMI and AP, a signal at

Figure 3. CPMAS ^{13}C NMR spectra of the reaction products of BMI/AP system (a–c) and PMI/DABA system (d–f) treated at different temperatures: (a) and (d) at 175°C for 2 h; (b) and (e) at 175°C for 2 h and at 200°C for 1 h; (c) and (f) at 175°C for 2 h, at 200°C for 1 h, and at 250°C for 1 h.

75 ppm was observed after heating at 175°C similarly to the PMI/AP system (Figures 3a–c). This signal decreased by heating at 250°C, possibly due to a *retro* Diels–Alder reaction at this temperature. In the thermal reaction of PMI and DABA, a signal at 75 ppm was not observed similarly to the curing reaction of BMI with DABA (Figures 3d–f).

In the presence of AP, Diels–Alder adducts were formed with both of BMI and PMI, but Diels–Alder reactions hardly proceeded when DABA was used. This leads to conclusion that whether the Diels–Alder reaction proceed or not is dependent on the structures of allylphenols.

CONCLUSION

This study using high resolution solid-state ^{13}C NMR revealed that the curing reaction of BMI with DABA involved only the *ene*-reaction and polymerization but the Diels–Alder reaction did not accompany in contrast to the model reaction of PMI and AP. The cured products of BMI with AP formed through *ene*-reaction and sequential Diels–Alder reaction. This difference between BMI/DABA and BMI/AP was demonstrated only by CPMAS ^{13}C NMR.

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