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Thermal Reactions of *N*-Phenylmaleimide and Mono- or Di-functional Allylphenols

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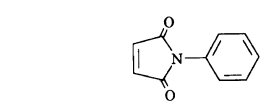
ABSTRACT: Thermal reactions of *N*-phenylmaleimide (PMI) and *o*-allylphenol (AP) or diallylbisphenol-A (DABA) were investigated using ^{13}C NMR and GPC in order to obtain information on the curing of bismaleimidodiphenylmethane (BMI) with DABA, widely used as thermosetting bismaleimide resins. In the thermal reactions of PMI and AP, 1 : 1 and 3 : 1 adducts were generated through *ene*-reaction and sequential Diels–Alder reactions accompanying the polymer of PMI and AP. The products from PMI and DABA were the *ene*-adduct and polymer but the Diels–Alder adduct could not be detected, in contrast to PMI/AP system. This difference in reactivity for PMI–AP and PMI–DABA may be due to steric repulsion of DABA and is discussed briefly by AM1 molecular orbital calculations.

KEY WORDS Curing Reaction / Diels–Alder Reaction / *ene*-Reaction / *o*-Allylphenol / Diallylbisphenol-A / *N*-Phenylmaleimide / ^{13}C Nuclear Magnetic Resonance

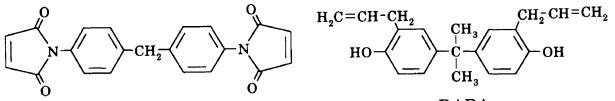
Thermosetting bismaleimide resins are used as matrix resins for multilayer print circuit boards and advanced composites in aerospace. Although they possess excellent thermal stability, the cured resins are brittle owing to their aromatic nature and high crosslinking density of the network. To reduce brittleness, typical modifications include chain extension by aromatic diamines such as diaminodiphenylmethane, or diallyl compounds such as diallylbisphenol-A.[1,2]

The curing of bismaleimide with diallylbisphenol-A may proceed through chain extension by an *ene*-reaction and crosslinking by the Diels–Alder reactions.[1–5] In the first step, the bismaleimide with diallylbisphenol-A oligomerizes by *ene*-reaction as revealed by ^{13}C NMR investigations.[3,4] The second step is based on Wagner–Jauregg reaction (the Diels–Alder reaction of a diene containing an aromatic ring with maleimides),[6] that is, the Diels–Alder reaction of the initial *ene*-adduct with another maleimide followed by rearrangement of the double bond to give the product as proposed by Zahir *et al.*[1] Diels–Alder reaction followed by *ene*-reaction is also proposed.[5] Our research group[7,8] and Reyx *et al.*[9] reported that the thermal reaction of *N*-phenylmaleimide (PMI) and *o*-allylphenol (AP), monofunctional model compounds, gave the *ene*-adduct, which underwent the Diels–Alder reaction twice with two molars of PMI to form the 3 : 1 adduct.

In spite of some proposals as described above, the practical crosslinking mechanism is still not well understood. In this paper, the detail of thermal reactions of PMI and mono- or di-functional allylphenols are described to obtain information on the curing of bismaleimidodiphenylmethane (BMI) with diallylbisphenol-A (DABA) and new aspects of curing are shown.



PMI AP



BMI DABA

EXPERIMENTAL

Materials

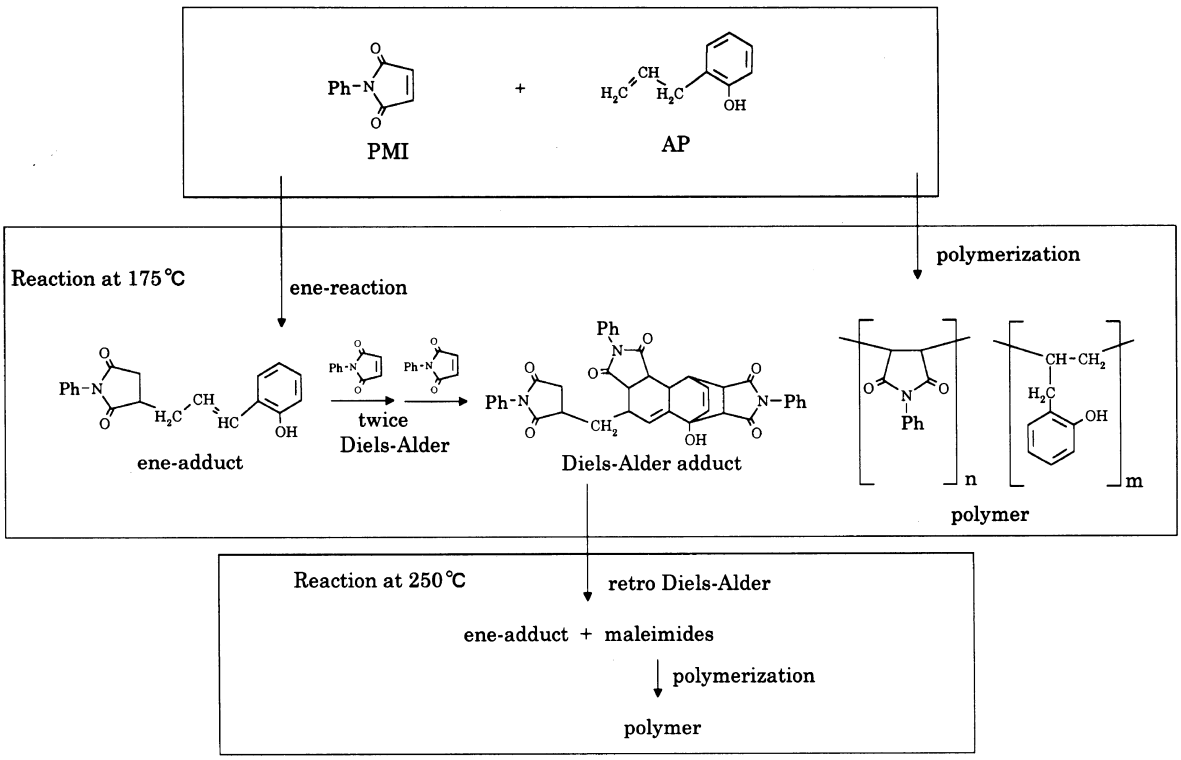
DABA was obtained from Mitsui Toatsu Chemicals Inc. PMI and AP were purchased from Wako Pure Chemical Industries.

Sample Preparation

N-Phenylmaleimide 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 ^{13}C NMR, GPC, and FD-MS (Field Desorption Mass Spectrometry).

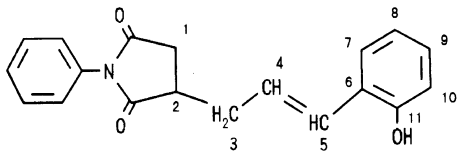
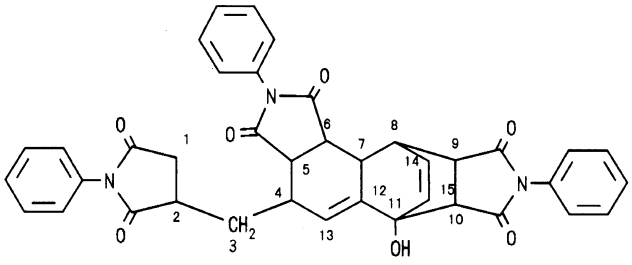
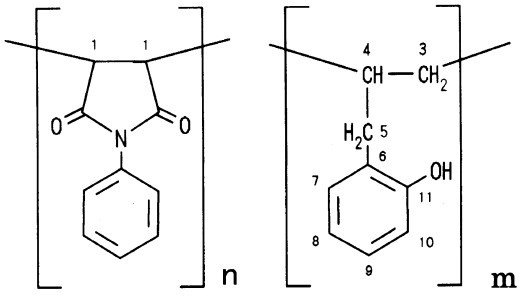
Isolation and Identification

The reaction products were fractionated by HPLC and each fraction was identified by ^{13}C NMR and FD-MS. Assignments of ^{13}C NMR spectra were made on the basis of chemical shifts in the literature.[7–9] HPLC conditions were as follow: Model, Japan Analytical Inc. LC-908; column, JAIGEL-3H + JAIGEL-2H; eluent, chloroform (3.8 ml min^{-1}); detector, refractive index.



Scheme 1. Thermal reaction of PMI and AP.

Table I. Chemical shift assignments for reaction products of PMI and AP

Structures	Chemical shift/ppm
 1 : 1 Adduct (PMI–AP)	(C=O) 178.4 and 175.5, (C1), 35.1, (C2) 39.9, (C3) 33.8, (C4) 126.1, (C5) 128.7, (C6) 123.9, (C7) 129.2, (C8) 120.9, (C9) 128.7 (C10) 115.9, (C11) 152.8
 3 : 1 Adduct ([PMI]$_3$–AP)	(C=O) 179.0, 178.8, 177.3, 177.2, 176.3, 176.1, 176.0, 175.9, 175.8, 175.2, and 175.0, (C1) 35.6, (C3) 37.4 and 38.0, (C3) 34.8, (C4) 41.1, (C5) 43.3 and 43.5, (C6) 42.2, (C7) 33.7 and 34.1, (C8) 35.5, (C9) 45.7 and 45.8, (C10) 48.0, (C11) 75.1 and 75.2, (C12) 141.0 and 141.5, (C13) 120.2 and 120.6, (C14) 130.9 and 131.0, (C15) 134.2 and 134.5
 Polymer ([PMI]$_n$[AP]$_m$)	(C=O) 176 (b), (C1) 45 (b), (C3–C5) 30—40, (C6) 126, (C7) 129, (C8) 121, (C9) 127, (C10) 116, (C11) 154

GPC Measurements

GPC was performed using a chromatograph made of a Waters, Model GPC-209G, and four columns of G4000HXL, G3000HXL, G2000HXL, and G1000HXL. Analysis was performed in tetrahydrofuran (THF) at room temperature (detector: refractive index).

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.

FD-MS Measurements

Mass spectra were taken on a Hitachi M-80B by field desorption mass spectrometry.

RESULTS AND DISCUSSION

Model Reactions of PMI and AP

The thermal reactions of PMI and AP (molar ratio 2/1) were carried out at first for obtaining fundamental ^{13}C NMR spectral data. When a mixture of PMI and AP was heated at 175°C for 2 h, three products were fractionated by HPLC as the major components. Analysis of these components by ^{13}C NMR showed the formations of the expected 1 : 1 and 3 : 1 adducts of PMI and AP by the *ene*-reaction and sequential Diels–Alder reaction accompanying the polymer containing AP as well as PMI. A summary of the reactions is illustrated in Scheme 1.

The assignments by ^{13}C NMR are as follows: the spectrum of the 1 : 1 adduct shows two carbonyl signals at 175.5 and 178.4 ppm, methyne signal at 39.7 ppm, and methylene signals at 35.1 and 33.8 ppm, which are suitable for the *ene*-adduct structure. The signals of the 3 : 1 adduct appeared at 175—179 ppm for carbonyl carbons, at 75.1 and 75.2 ppm for quarternary carbons with hydroxyl groups, and at 33—48 ppm for aliphatic carbons. All data are listed in Table I. These assignments agree well with previously reported data.[7–9] The polymer showed broad signals at 176 ppm for the carbonyl carbon and at 45 ppm for the methyne carbon, respectively, ascribed to the polymerized PMI. The additional broad signals at 154, 120, and 115 ppm for the phenolic aromatic carbons and at 30—40 ppm region for the methylene and methyne are ascribed to the polymer of AP.

The curing of bismaleimide resins is usually carried out with gradual rise in temperature. Change in the composition of a 2 : 1 mixture of PMI and AP during gradual raising of reaction temperature was monitored by GPC chromatograms and ^{13}C NMR spectra (Figure 1). Peaks in the chromatograms were separated by fractionation into individual components. Referring to

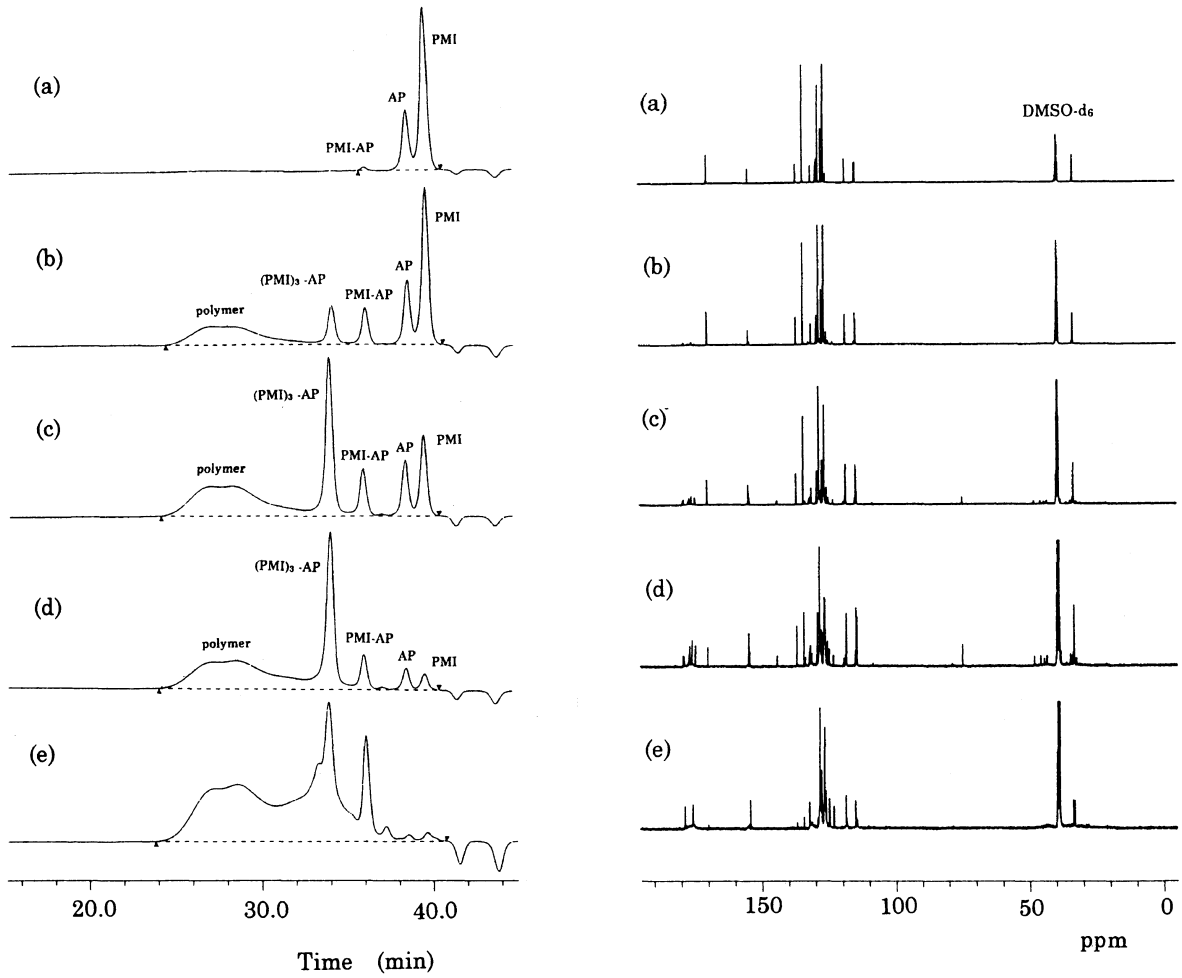


Figure 1. GPC chromatograms and ^{13}C NMR spectra of the reaction products treated at different temperatures in the PMI/AP system: (a) melt mixture (at 150°C for 15 min); (b) at 175°C for 30 min; (c) at 175°C for 2 h; (d) at 175°C for 2 h and at 200°C for 1 h; (e) at 175°C for 2 h, at 200°C for 1 h, and at 250°C for 1 h.

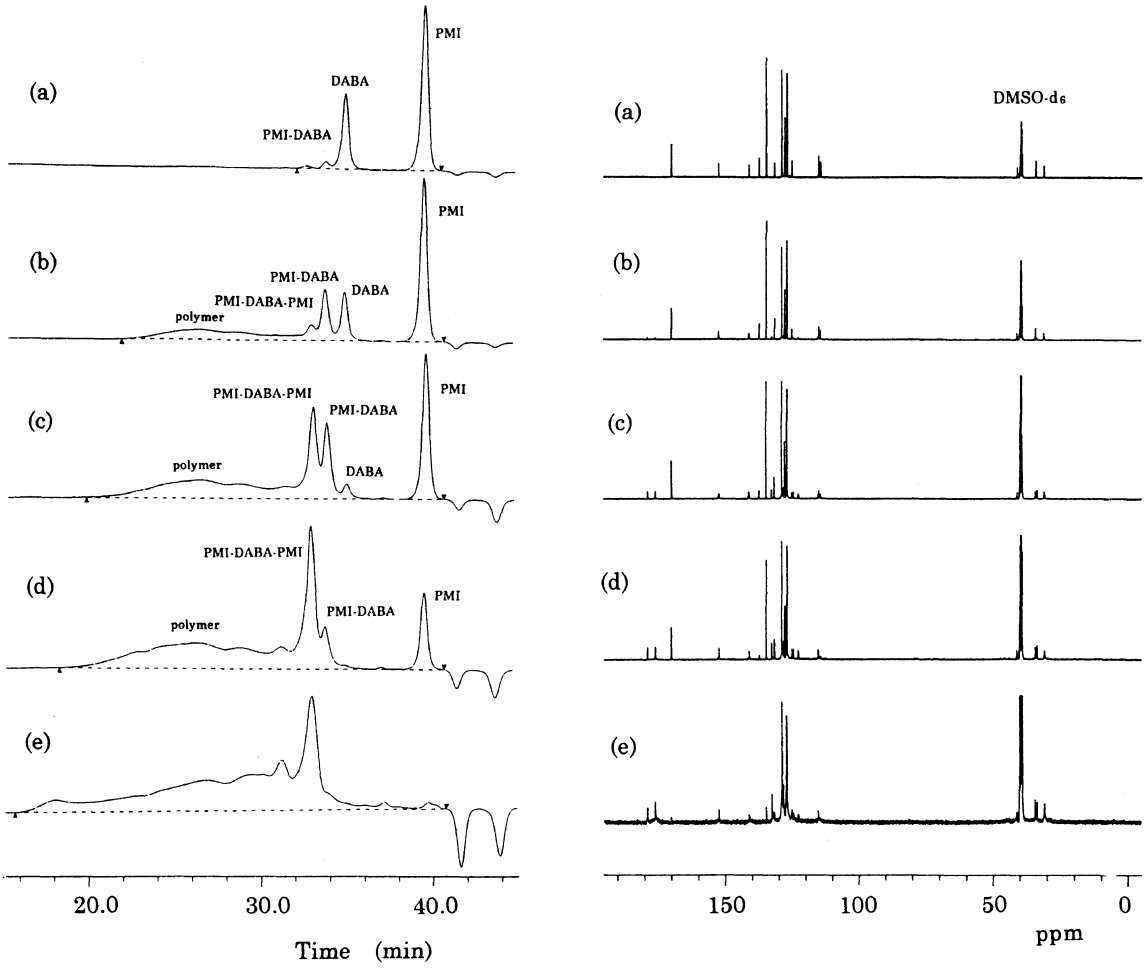


Figure 2. GPC chromatograms and ^{13}C NMR spectra of the reaction products treated at different temperatures in the PMI/DABA system: (a) melt mixture (at 150°C for 15 min); (b) at 175°C for 30 min; (c) at 175°C for 2 h; (d) at 175°C for 2 h and at 200°C for 1 h; (e) at 175°C for 2 h, at 200°C for 1 h, and at 250°C for 1 h.

the analyzed data as stated above, the course of the reaction could be surveyed. The polymer and 3 : 1 adduct were formed even at the initial step of the reaction (at 175°C for 30 min). Increase in these products was observed with progress of the reaction until the stage at 200°C for 1 h, but the relative proportion of 3 : 1 adduct decreased and that of the polymer, the 1 : 1 adduct, and unidentified oligomers with lower molecular weights increased after heating at 250°C. In the corresponding ^{13}C NMR spectra, increase of signal intensity at 75 ppm ascribed to 3 : 1 adduct was seen with heating until the stage at 200°C for 1 h, but this signal disappeared after heating at 250°C. Although thermally rearranged products of the 3 : 1 adduct have been reported by Reyx,[9] signals of this product could not be confirmed in these ^{13}C NMR spectra.

Based on these results, proposed thermal reaction mechanisms of the PMI/AP system are summarized in Scheme 1. The *ene*-reaction of PMI and AP formed the 1 : 1 adduct at first, which reacted with 2 molars of PMI further by twice Diels–Alder reaction to give the 3 : 1 adduct. These reactions and polymerization of AP and PMI proceeded at 175°C, but the 3 : 1 adduct decomposed at 250°C by *retro* Diels–Alder reaction to reproduce the 1 : 1 adduct and PMI, which grew the polymer.

Thermal Reactions of PMI and DABA

Figure 2 shows GPC chromatograms and ^{13}C NMR spectra of the thermal reactions of the PMI/DABA system (molar ratio 4/1). These GPC chromatograms seemed to show the reaction to proceed to form the main product at *ca.* 33 min and polymers and thus the former product was separated from the mixture treated at 200°C for 1 h. Identification of this component by ^{13}C NMR spectrum revealed that the main product was a 2 : 1 adduct of PMI and DABA formed by the *ene*-reaction (Table II). The chromatogram (Figure 2c) represented the reaction course because all products were involved. The FD-MS spectrum of this reaction mixture was measured. As shown in Figure 3, the intense peaks correspond to PMI–DABA and PMI–DABA–PMI *ene*-adducts (*m/z* 481 and 654), but the peak corresponding to the 3 : 1 adduct of PMI and DABA (*m/z* 827) is very weak. The ^{13}C NMR spectra of this mixture showed signals ascribed to the starting materials and two *ene*-adducts of PMI and DABA and broad signals ascribed to polymers, but no signal around 75 ppm for the Diels–Alder adduct (3 : 1 adduct) could be detected. This is a contrast to the PMI and AP system. Thus, in the case of PMI and AP, the Diels–Alder adducts were formed, but the Diels–Alder reaction hardly proceeded when DABA was used. This leads us to conclude that facility of Diels–Alder reaction is dependent upon the

structural difference between AP and DABA and this difference is significant in curing reactions used generally.

To examine such differences in reactivity, molecular calculations were performed using the MOPAC package with the PM3 Hamiltonian. The Diels–Alder reactions of the *ene*-adducts and PMI were adopted as models.

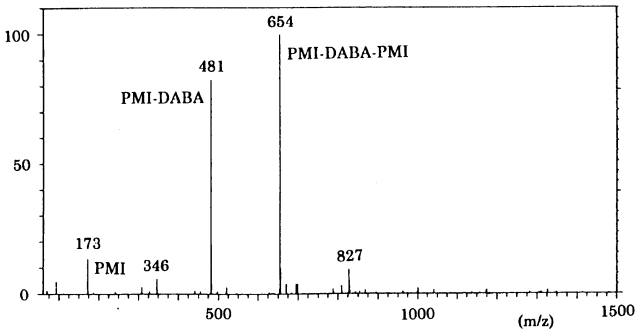
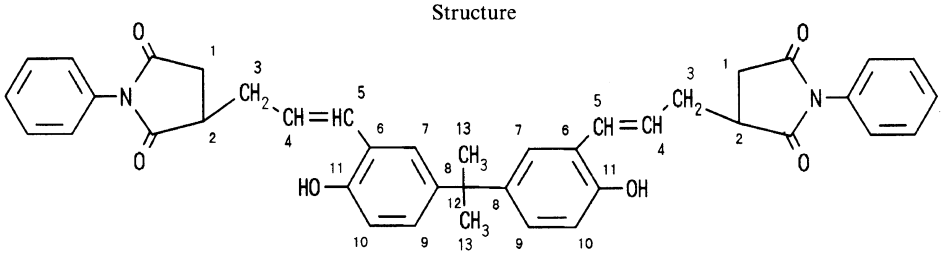


Figure 3. FD-MS spectrum of the product of the PMI/DABA system treated at 175°C for 2 h.

The results are shown in Table III. The activation energies calculated from the *endo*-transition states were 40.2—43.0 kcal mol^{-1}, much higher compared to general Diels–Alder reactions. No remarkable differences in activation energies for *ene*-adducts of PMI–AP and PMI–DABA were observed. However, the activation energy for *retro* Diels–Alder reaction of PMI/DABA system was smaller by 6—9 kcal mol^{-1} than that of PMI/AP system. That is, the Diels–Alder adduct of DABA may be less stable than that of AP, which would accelerate the retro Diels–Alder reaction at a high temperature. This situation would be caused by steric hindrance of allyl or methyl groups in DABA. An apparent difference in the molecular structures between AP and DABA is that these attached substituents and electronic nature of the diene moieties are almost equivalent in AP and DABA and thus steric effect should be a chief factor controlling reactivity.

Table II. Chemical shift assignments for PMI–DABA–PMI

Structure

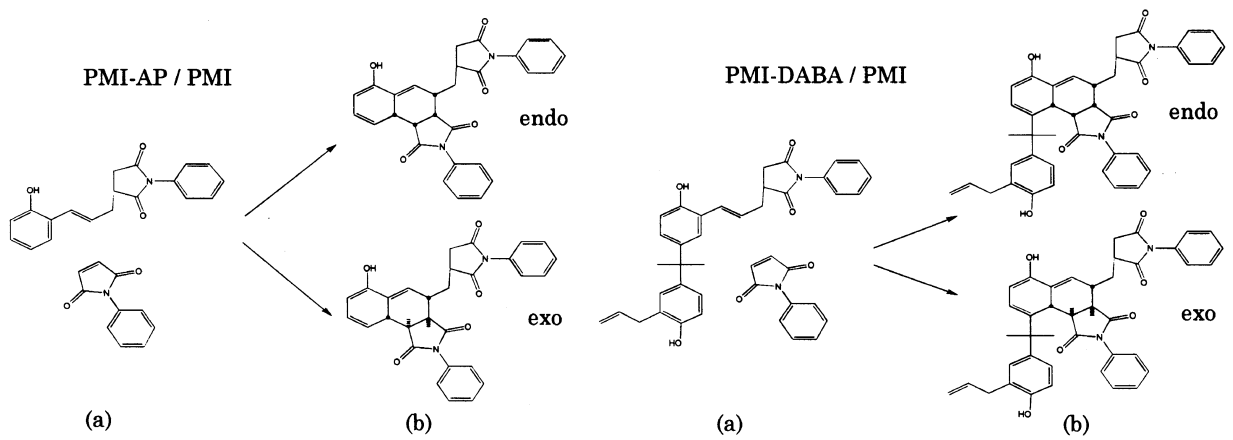


Chemical shift/ppm

(C=O) 178.7 and 175.9, (C1) 35.1, (C2) 39.6, (C3) 33.7, (C4) 125.7, (C5) 128.8, (C6) 123.0, (C7) 125.5, (C8) 143.0, (C9) 129.5, (C10) 115.6, (C11) 151.0, (C12) 41.7, (C13) 31.0

Table III. Calculated heats of formation, activation energies, and heats of reaction

Systems	Heat of formation/kcal mol^{-1}				Activation energies	Heat of reaction	Activation energies of *retro* Diels–Alder
	(a)		Transition state	(b)	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
PMI–AP/PMI	−81.2	*endo*	−40.7	−96.4	40.5	−15.2	55.7
		exo	−41.0	−100.4	40.2	−19.2	59.4
PMI–DABA/PMI	−97.8	*endo*	−59.4	−106.6	40.6	−8.8	49.4
		exo	−54.8	−105.5	43.0	−7.7	50.7



CONCLUSION

The crosslinking structure of BMI and DABA suggests that the *ene*-reaction and sequential Diels–Alder reactions give the 3 : 1 adduct based on only the model reactions of PMI/AP system. However, our investigation of the thermal reaction of PMI/DABA system showed that DABA prevented the following Diels–Alder reaction with the initial *ene*-adduct and PMI probably due to steric hindrance of DABA. Crosslinking may thus proceed through the *ene*-reaction and polymerization but not by the Diels–Alder reaction in the curing of BMI with DABA.

REFERENCES

1. S. Zahir, M. A. Chaudhari, and J. King, *Makromol. Chem., Macromol. Symp.*, **25**, 141 (1989).
2. K. A. Barett, M. A. Chaudhari, and B. H. Lee, *SAMPE J.*, **25**, 17 (1989).
3. K. R. Carduner and M. S. Chattha, *Polym. Mater. Sci. Eng.*, **56**, 660 (1987).
4. K. R. Carduner and M. S. Chattha, *Am. Chem. Soc., Symp. Ser.*, **367**, 379 (1988).
5. T. Abraham, *J. Polym. Sci., Part C, Polym. Lett.*, **26**, 521 (1988).
6. T. Wagner-Jauregg, *Tetrahedron Lett.*, **13**, 1175 (1967).
7. T. Enoki, K. Ishii, H. Okubo, and S. Shibahara, *Netsukoukasei Jushi*, **12**, 9 (1991).
8. T. Enoki, T. Takeda, and K. Ishii, *High Perform. Polym.*, **7**, 399 (1995).
9. D. Reyx, I. Campistron, and C. Caillaud, *Macromol. Chem. Phys.*, **196**, 775 (1995).