Mid- and Near-Infrared Spectroscopic Investigations of *N*-Phenylmaleimide (NPM)/Amine Reactions

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ABSTRACT: The reactions between *N*-phenylmaleimide (NPM) and several amines have been examined by both mid-infrared (mid-IR) and near-infrared (near-IR) spectroscopy. Significant overlap exists among several functional groups of NPM/amine systems in the mid-IR spectral region. Interference between these absorptions significantly reduces the utility of mid-IR spectroscopy for quantitative studies of NPM/amine reaction kinetics. In contrast, the absorption bands of these functional groups are well separated in near-IR spectra. The ability of near-IR spectroscopy for studying the kinetics of the reactions between the maleimide-containing compound with amines is clearly established. Near-IR absorptions suitable for quantitative studies of these reactions are identified. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 267–276, 1998

Key words: *N*-phenylmaleimide (NPM); bismaleimide; mid-infrared (mid-IR); near-infrared (near-IR or NIR); Fourier transform infrared (FTIR) spectroscopy

INTRODUCTION

Maleimide-containing compounds, such as bismaleimides, are prime candidates for forming advanced structural materials, such as those needed for aerospace, electronics, and other applications.[1–10] The maleimide double bonds can undergo addition polymerization without generating volatile byproducts. The cured resins exhibit low moisture absorption, excellent thermal stability, high flame retardancy, desirable dielectric properties, and thermal and mechanical properties superior to most epoxy resins. In a system containing a bismaleimide monomer and a diamine, polymerization proceeds via addition reactions between the amine groups and the maleimide double bonds, and via homopolymerization reactions between the maleimide double bonds.[2–4,9] A fundamental understanding of these reactions is essential if consistent products having reproducible thermal and mechanical properties are to be obtained.

Polymerization reactions involving bismaleimides and other maleimide-containing compounds proceed via nucleophilic or Michael addition reactions at the double bonds inasmuch as these double bonds have adjacent carbonyl groups.[11] Although bismaleimides such as 1,1′-(methylenedi-4,1-phenylene) bismaleimide (BMI) can be crosslinked directly through homopolymerization reactions, they usually are reacted with aromatic amine hardeners, such as 4,4′-methylenedianiline (MDA), to overcome the brittleness characteristic of bismaleimides. For bismaleimide/aromatic amine systems, polymerization proceeds through two mechanisms. At relatively low temperatures, chain extension proceeds via nucleophilic attack of the maleimide double bonds by the amine groups (Fig. 1). In addition, both crosslinking and further chain extension reactions occur as a consequence of homopolymerization reactions, particularly at higher temperatures.
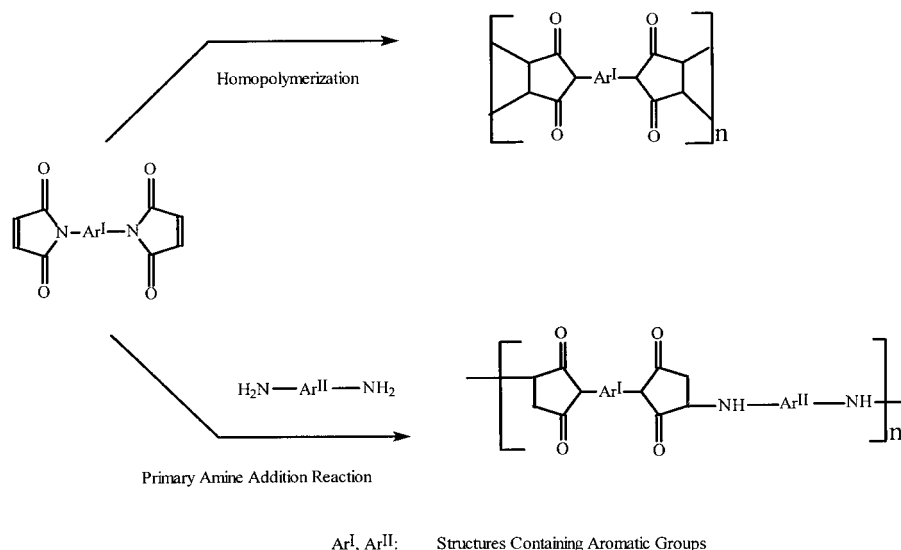
Figure 1 Mechanisms proposed in the literature for bismaleimide/aromatic amine reactions.

Bismaleimide polymerization has been studied by diverse analytical techniques, including Fourier transform infrared (FTIR) spectroscopy,[2-4,9] gel permeation chromatography (GPC) or size exclusion chromatography (SEC),[3,4,9,10] nuclear magnetic resonance (NMR),[4,10,12] differential scanning calorimetry (DSC),[3,5-7,13,14] and fluorescence spectroscopy.[15] DSC and FTIR spectroscopy have been the techniques employed most often. Unlike DSC methods, which quantify the chemical kinetics based upon overall heats of reaction and the enthalpies of the individual reactions, IR spectroscopy directly monitors changes in the functional groups of interest as the reactions proceed.

Prior mechanistic studies of bismaleimide reactions have employed either bismaleimide model compounds[2-4] or monofunctional maleimide compounds.[3,8,10] Crivello studied the addition reaction of N-phenylmaleimide (NPM) with aniline.[10] In the melt, this reaction proceeds slowly at 150°C, yielding N,N'-diphenylaspartimide (DAP, or N-anilinophenylsuccinimide)[2] as the sole product. The reaction rate can be enhanced by changing the polarity of the solvent, as demonstrated by studies at 130°C utilizing o-dichlorobenzene or benzonitrile. Itoya et al. studied this reaction over a temperature range from 20°C to 150°C, for time periods of as long as 70 h, and at pressures between 0.1 and 500 MPa.[8] Crosslinking reactions between NPM and DAP were mentioned without elaboration for temperatures above 180°C.

FTIR spectroscopy has yielded valuable insight into the chemical reactions between bismaleimides and various curing agents. Mid-infrared (mid-IR) spectra typically have been utilized in such studies. Di Giulio and coworkers studied curing BMI with the MDA system and identified 12 component peaks in the region between 3000 and 4000 cm^{-1}, including the maleimide $=C-H$ stretching band at 3099 cm^{-1} and the primary amine $N-H$ stretch at 3469 cm^{-1}.[2] Changes in the spectral features were determined from difference spectra and correlated with the cure conditions. The extent of cure and the reaction mechanisms for the BMI/MDA system have been studied by both Tungare[3] and Donnellan et al.[4] While the IR peaks due to the amine groups may be used for quantitative analysis, the overlap between the carbonyl overtone band and the $N-H$ stretching band in the region near 3460 cm^{-1} complicates interpretation of the results, thus limiting the quantitative information that can be obtained from mid-IR spectroscopy.

The near-infrared (near-IR) region (4000–12000 cm^{-1}) has been useful for monitoring the amine functional groups in thermosetting resins such as epoxies[16-20] and polyamic acid resins;[21] however, near-IR studies on bismaleimide and maleimide-containing compounds have been very limited to date.[22] Near-IR spectra often have well-isolated overtone and combination bands for the amine and maleimide $=C-H$ functional groups. In addition, near-IR spectroscopy presents several

potential advantages over mid-IR techniques, such as enhanced resolution, higher energy sources, and lower oscillator strengths.[19,23,24]

In the work reported herein, the reactions between NPM and several amines have been studied. Changes in the absorptions associated with the maleimide double bonds and primary amine functional groups characteristic of these polymerization reactions are reported.

EXPERIMENTAL

Starting Materials

NPM (Aldrich Chemical Company, Inc., Milwaukee, WI, 97% purity) was used as the source of the maleimide functional group. MDA (Aldrich Chemical Company, Inc., 97% purity) and aniline (Aldrich Chemical Company, Inc., 99.5+% purity) were the primary aromatic amines studied. Jeffamine® D-230, an aliphatic amine having a molecular weight of ~230, was obtained from Texaco Chemical Company (Houston, TX). All chemical reagents were used as received. DAP was synthesized within the high-temperature transmission cell by reacting NPM with aniline at an initial molar ratio of 1 : 1 at 180°C.[8,10] The structures for these reagents are given in Figure 2.

FTIR Spectroscopy

All mid-IR spectra were obtained from a Mattson Instruments NOVA CYGNI 120 spectrometer employing a rare-earth oxide source, a Ge-coated KBr beamsplitter, and a TGS detector. Sixteen scans were coadded at a resolution of 4 cm^{-1} for each spectrum. The near-IR spectra were obtained using a Mattson Instruments NOVA CYGNI 120 spectrometer equipped with a tungsten halogen source, a quartz beamsplitter, and an indium antimonide (InSb) detector. Sixteen scans were coaveraged at a resolution of 8 cm^{-1} for each spectrum. NaCl windows were employed for both mid- and near-IR spectra.

The *in situ* mid-IR and near-IR spectra were obtained with a SpectraTech high-temperature transmission cell. The NPM or NPM/amine mixture was placed in the sample cell according to the methods described below. After obtaining the background spectrum, the sample cell was heated to the desired temperature. Isothermal *in situ* data were collected as a function of time.

Sample Preparation

Pure Component Spectra

For the mid-IR experiments involving liquid samples, such as aniline and Jeffamine® D-230, a drop of the liquid was pressed between two NaCl windows. For near-IR experiments, the liquid was injected into the transmission cell between a pair of NaCl windows separated by a 0.5-mm Teflon spacer. When the pure component, such as NPM or MDA, was solid at room temperature, the reagent was heated above its melting point and then transferred via a plastic syringe into the temperature-controlled mid-IR transmission cell equipped with a 0.025-mm lead spacer. In the corresponding near-IR experiments, each reagent was first heated above its melting point and then transferred via a plastic syringe into the temperature-controlled transmission cell equipped with a 0.5-mm Teflon spacer.
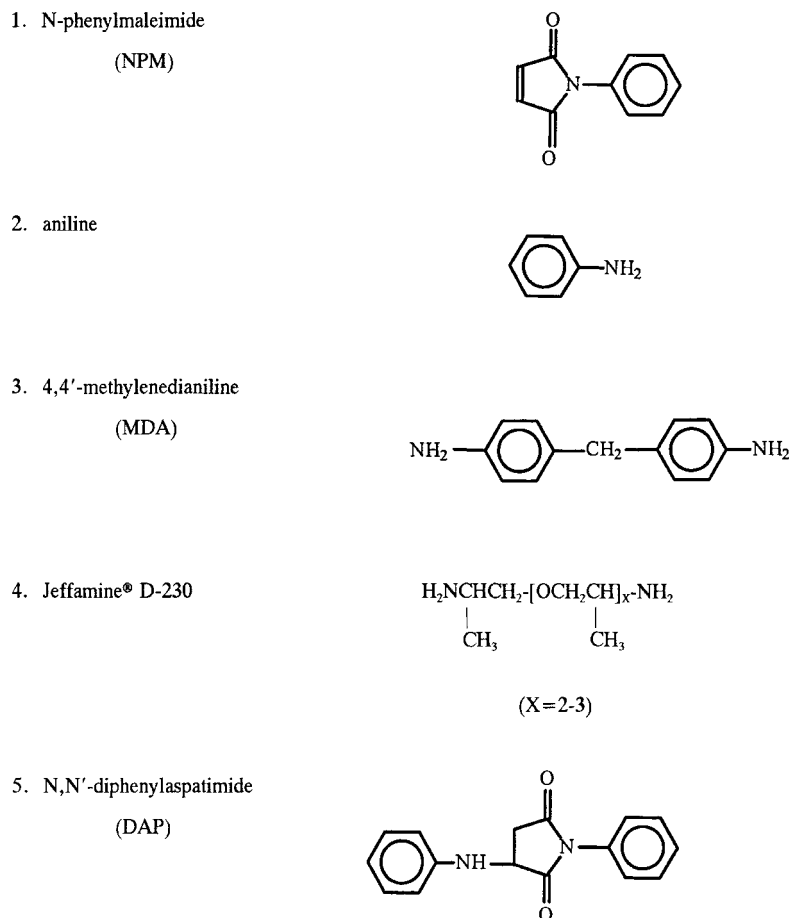
In Situ *Mid-IR and Near-IR Spectra*

To study homopolymerization of NPM *in situ*, NPM was melted at 95°C and subsequently transferred with a plastic syringe into a SpectraTech high-temperature transmission cell. For studies of amine addition reactions, each NPM/amine mixture having the desired molar ratio between the reactants was melted at 90°C. Each solution was immediately transferred into a high-temperature transmission cell equipped with a 0.025-mm lead spacer for mid-IR experiments or a 0.5-mm Teflon spacer for near-IR experiments. During sample preparation, the temperature of the cell was controlled at 95°C for studies of homopolymerization and from 80 to 90°C for studies of the amine addition reactions. Once filled, the sample cell was sealed by stoppers. No evidence of reaction during sample preparation at 90°C was observed for the NPM/aromatic amine mixtures based upon a comparison with the pure component spectra. In addition, changes in spectra of the NPM/aromatic amine systems were not observed following reaction at 90°C for 10 min.

RESULTS

NPM and Amine Spectra

Selected peak assignments for the mid-IR and near-IR spectra of NPM and the amines studied

1. N-phenylmaleimide
   (NPM)

2. aniline

3. 4,4'-methylenedianiline
   (MDA)

4. Jeffamine® D-230

   $H_2NCHCH_2\text{-}[OCH_2CH]_x\text{-}NH_2$
        | |
       CH_3 CH_3

   (X=2-3)

5. N,N'-diphenylaspatimide
   (DAP)

Figure 2   Structures of the chemical reagents employed.

are given in Tables I and II, respectively. The mid-IR and near-IR spectra of NPM and the amines are shown in Figures 3 and 4, respectively. Figure 3(a–e) shows the mid-IR spectra of NPM, aniline, MDA, Jeffamine® D-230, and DAP, respectively. Figure 4(a–e) shows the corresponding near-IR spectra. The mid- and near-IR spectra of aniline and Jeffamine® D-230 were collected at room temperature, while the mid- and near-IR spectra NPM and MDA in the melt were collected at 110°C. The spectra of DAP were obtained from the *in situ* data for the NPM/aniline system (at an initial molar ratio of 1 : 1) reacted at 180°C for 140 min.

Figure 5(a,b) shows the comparison between the mid-IR spectra of NPM at 110°C and aniline

Table I   Selected Mid-IR Peak Assignments for NPM and Several Amines

Absorption Band	Peak Position (cm^{-1})				
	NPM	Aniline	MDA	Jeffamine® D-230	DAP
N—H asymmetric stretch (for primary amine)		3433	3444	3360	
					3383
N—H stretch (secondary amine)					3337
Maleimide =C—H stretch	3104				
Maleimide C—N—C stretch	1148				

Table II   Selected Near-IR Peak Assignments for NPM and Several Amines

	Peak Position (cm^{-1})				
Absorption Band	NPM	Aniline	MDA	Jeffamine® D-230	DAP
Secondary amine N—H overtone					6633
Primary amine N—H combination		5035	5035	4925	
Maleimide =C—H stretch overtone	6100				

at room temperature. The maleimide functional groups of NPM have several characteristic absorption bands in the mid-IR region. The maleimide =C—H stretching band located at 3104 cm^{-1} partially overlaps with several adjacent peaks, such as the aromatic C—H stretch at 3070 cm^{-1}. The primary amine functional group of aniline also has several characteristic absorption bands in the mid-IR region. The N—H deformation band at 1620 cm^{-1} closely overlaps with the aromatic C=C stretching band at 1602 cm^{-1}. If these two spectra are compared, then significant

interference exists between the first overtone of the carbonyl C=O stretch of NPM at 3476 cm^{-1} and the primary amine stretching band of aniline at 3433 cm^{-1}, and between the C=C aromatic ring stretching band of NPM and the N—H in-plane bending mode of aniline in the region adjacent to 1600 cm^{-1}.

Figure 5(c,d) shows the corresponding near-IR spectra of NPM and aniline. The strong absorption band at 6100 cm^{-1} is the overtone of the maleimide =C—H stretch; this absorption is well separated from adjacent absorption peaks such as
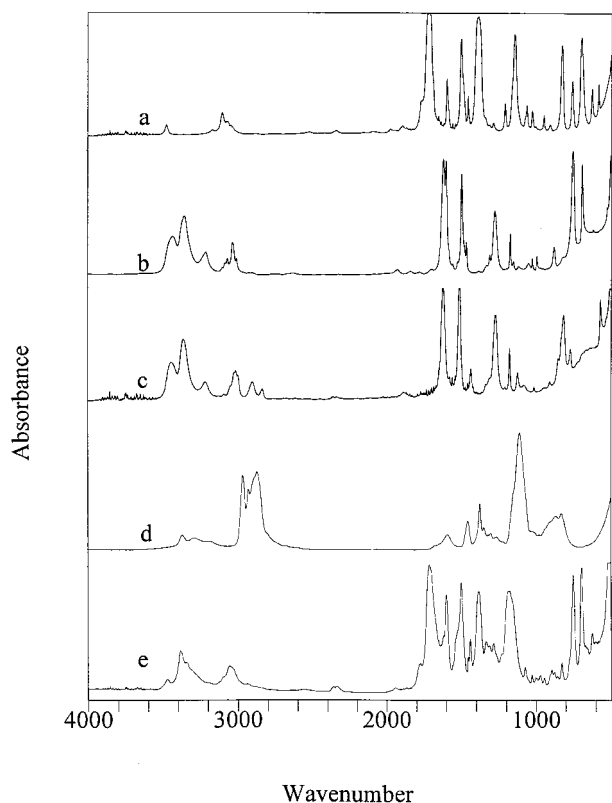
Figure 3 Mid-IR spectra of (a) NPM at 110°C, (b) aniline, (c) MDA at 110°C, (d) Jeffamine® D-230, and (e) DAP at 180°C.
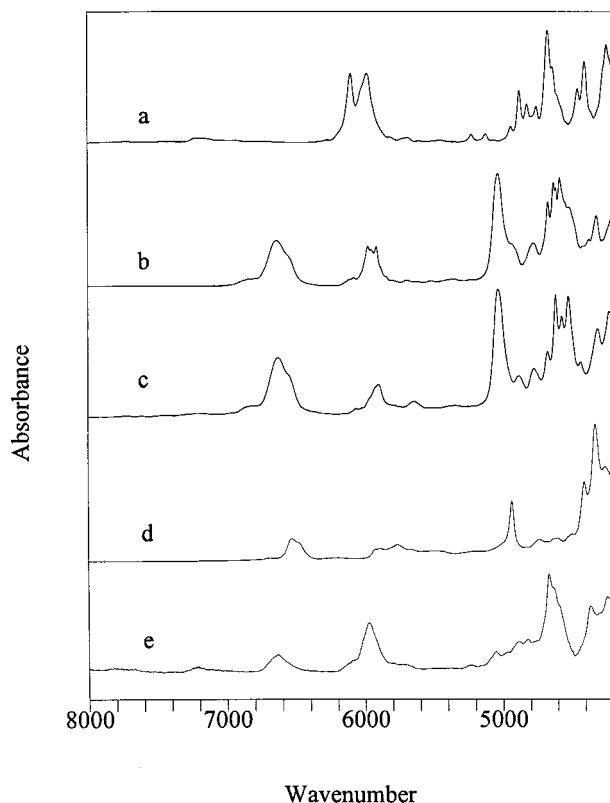
Figure 4 Near-IR spectra of (a) NPM at 110°C, (b) aniline, (c) MDA at 110°C, (d) Jeffamine® D-230, and (e) DAP at 180°C.
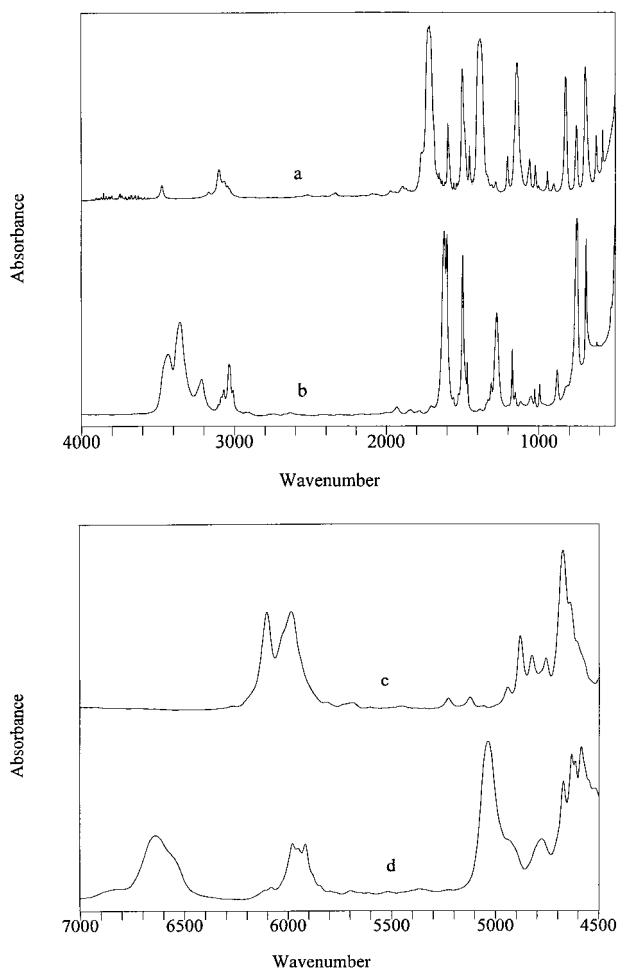
Figure 5 Mid-IR spectra of (a) NPM at 110°C and (b) aniline; near-IR spectra of (c) NPM at 110°C and (d) aniline.

the aromatic C—H bands at 5984 cm^{-1}. Other peaks associated with maleimide double bonds, such as those at 4874 and 4664 cm^{-1}, show more interference with absorption bands either from NPM or from aniline than that of the absorption peak at 6100 cm^{-1}. Since the primary amine combination peak at 5035 cm^{-1} in the aniline spectrum does not overlap with the absorption peaks from NPM, primary amine concentrations can be monitored easily during the NPM/aniline reaction. The same is true for the near-IR spectra of the NPM/MDA system. For the NPM/Jeffamine® system, the primary aliphatic amine combination at 4925 cm^{-1} overlaps with the C=O band at 4930 cm^{-1} from NPM, but the overtone bands in the region from 6400 to 6650 cm^{-1} representing primary amine and secondary amine functional

groups do not interfere with any absorption peak from NPM.

Homopolymerization of NPM

Homopolymerization of NPM was studied by isothermal *in situ* mid-IR spectroscopy at 180°C and isothermal *in situ* near-IR spectroscopy at 160°C. For *in situ* mid-IR spectroscopy, the change in intensity of the maleimide =C—H absorption peak at 3104 cm^{-1} was monitored as a function of reaction time. Since the carbonyl functional groups do not participate in the homopolymerization reactions, the absorption peak of the carbonyl first overtone at 3447 cm^{-1} was chosen as an internal standard. For *in situ* near-IR spectroscopy, the intensity change of the maleimide =C—H absorption band at 6100 cm^{-1} was monitored as a function of reaction time. Since the aromatic C—H groups do not participate in the homopolymerization reactions, the absorption peak of aromatic C—H overtone at 5984 cm^{-1} was chosen as an internal standard for the near-IR data.

The extent of the homopolymerization reaction (α) was calculated according to the following formula.

$$\alpha = 1 - \{(A_{\mathrm{func,t}}/A_{\mathrm{int,t}})/(A_{\mathrm{func,0}}/A_{\mathrm{int,0}})\} \quad (1)$$

where $A_{\mathrm{func,0}}$ and $A_{\mathrm{func,t}}$ represent the absorbance of maleimide =C—H functional groups at the start of the reaction and following reaction for time, t (min), respectively. These absorbances were obtained by a slice integral method;[19,25] the details are provided in Table III. $A_{\mathrm{int,0}}$ and $A_{\mathrm{int,t}}$ represent the absorbances of the carbonyl absorption band at 3476 cm^{-1} and the aromatic C—H

Table III   Peak Assignments for NPM Homopolymerization

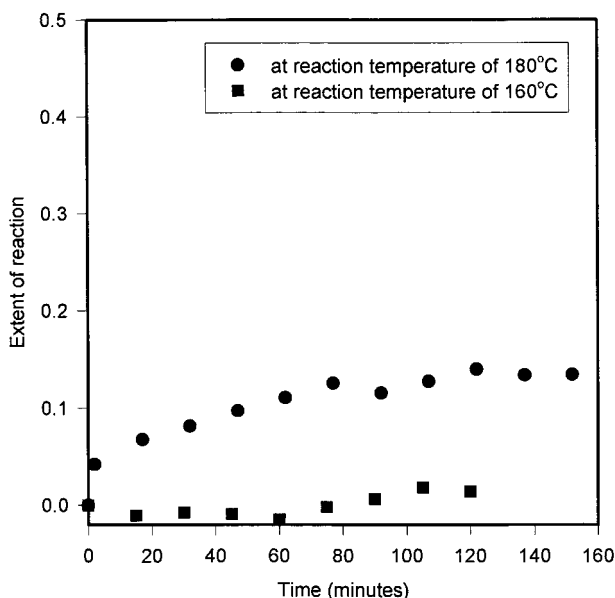| Absorption Band	Peak Position (cm^{-1})	Integration Range (cm^{-1})
Mid-IR spectra		
C=O first overtone	3476	3456–3495
Maleimide =C—H stretch	3104	3090–3112
Near-IR spectra		
Maleimide =C—H overtone	6100	6084–6118
Aromatic C—H stretch overtone	5984	5931–6014

overtone at 5984 cm^{-1}, which were used as internal standards for *in situ* mid-IR or *in situ* near-IR data, respectively. The extent of reaction (α) for the maleimide $=$C$-$H stretching band at 3104 cm^{-1} as calculated above is shown in Figure 6. Significant homopolymerization occurs at 180°C over the reaction times studied.

Figure 6 also presents the *in situ* near-IR data obtained by monitoring the maleimide $=$C$-$H stretch overtone at 6100 cm^{-1} at 160°C over 2 h. In this case, homopolymerization of NPM is limited. Homopolymerization of NPM in the absence of catalysts, therefore, can be neglected if the reaction temperature is <160°C.
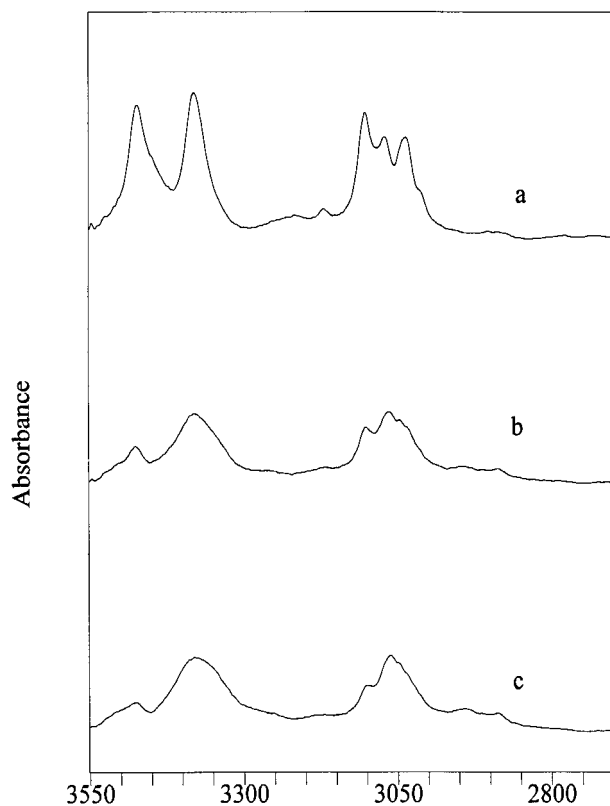
NPM/Amine Reactions

In situ mid-IR data in the region between 2700 and 3550 cm^{-1} are presented in Figure 7 for the reaction of NPM with aniline at an initial molar ratio of 2 : 1 and at 180°C. The decrease in intensity of the absorptions at 3466 and 3096 cm^{-1} was due to the conversion of primary amine groups and maleimide double bonds, respectively. DAP formed during the reaction, resulting in an increased line width for the N$-$H stretching absorbance near 3400 cm^{-1} [Fig. 7(c)], due to the formation of the secondary amine.[3,9]

In situ mid-IR data in the region from 600 to 2000 cm^{-1} for a mixture of NPM and aniline at

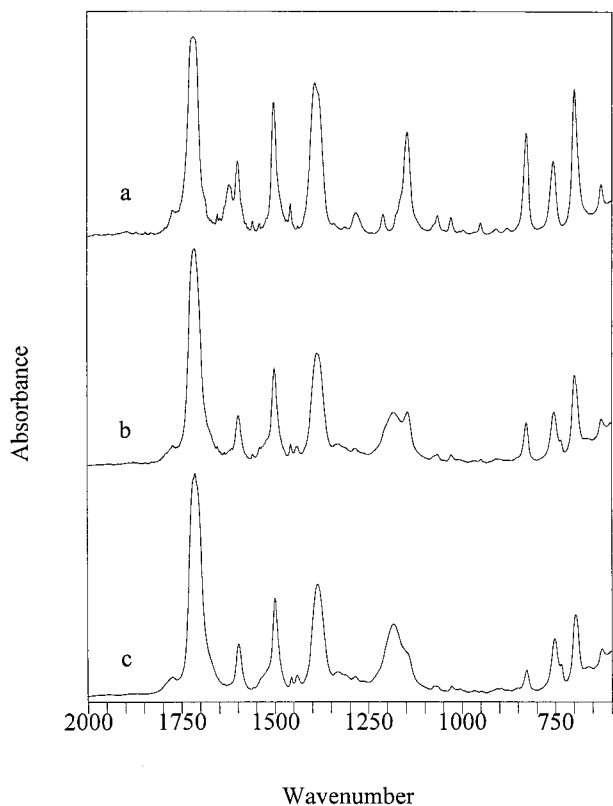**Figure 7** *In situ* mid-IR spectra (upper wavenumber region) for the NPM/aniline system at an initial molar ratio of 2 : 1 and at 180°C: (a) the initial spectrum, (b) the spectrum following reaction for 130 min, and (c) the spectrum following reaction for 350 min.

Figure 6 The conversion of maleimide functional groups versus time at 160°C and 180°C, respectively.

an initial molar ratio of 2 : 1 and at 180°C are shown in Figure 8. The N$-$H in plane bending mode near 1616 cm^{-1} decreased due to the depletion of primary amine functional groups, but quantifying this change in intensity is difficult due to the overlap with nearby aromatic C$-$H bands. The changes observed in the spectra near 1145 cm^{-1} cannot be used to quantify the conversion of the maleimide double bond since there is significant overlap with the C$-$N$-$C succinimide stretching band at 1178 cm^{-1} which forms during polymerization.[2,3,9] The absorption bands at 818 and 614 cm^{-1} have been assigned to the aromatic C$=$C deformation and NH$_2$ wagging modes, so that those absorption peaks are not suitable for the quantitative analysis reactions involving primary amine functional groups.[3,26]

The *in situ* near-IR spectroscopic data obtained at 170°C for a mixture of NPM/aniline at an initial molar ratio of 1 : 1 are shown in Figure 9. The absorbances for both the primary amine combina-
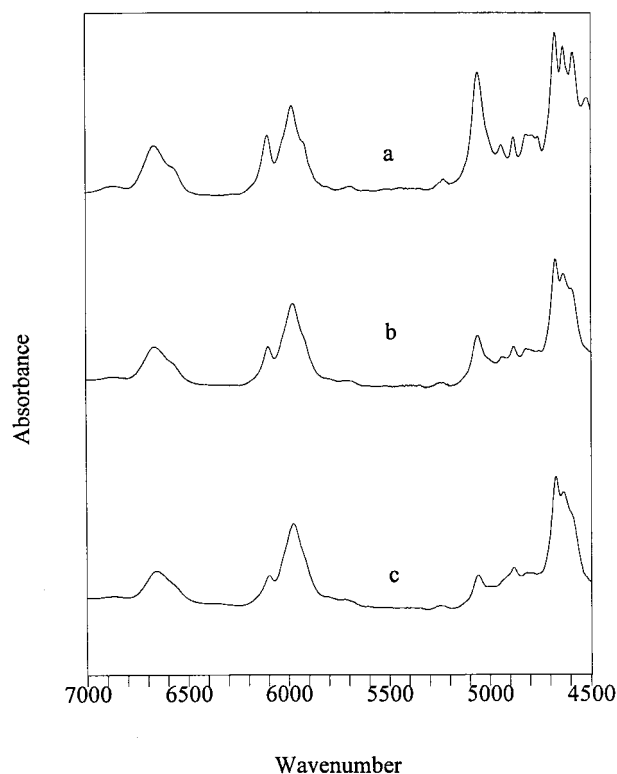
Figure 8 *In situ* mid-IR spectra (lower wavenumber region) for the NPM/aniline system at an initial molar ratio of 2 : 1 and at 180°C: (a) the initial spectrum, (b) spectrum following reaction for 130 min, and (c) spectrum following reaction for 350 min.

tion band at 5045 cm^{-1} and the maleimide $=$C—H stretching overtone band at 6100 cm^{-1} decreased as the reaction proceeded. Intensity changes are also observed in the absorption band at 4877 cm^{-1} and other absorption bands associated with the maleimide double bond in the near-IR region of less than 4800 cm^{-1}.

Figure 10 plots conversion versus reaction time for both primary amine and maleimide functional groups for a mixture of NPM/aniline at an initial molar ratio of 1 : 1 and at 180°C. The conversion of both the primary amine and maleimide $=$C—H functional groups was calculated based upon the absorbance ratios defined in eq. (1). The absorbances were determined by a slice integral method; the details are provided in Table IV. A substantial amine addition reaction between primary amine and maleimide functional groups can be observed. The conversion of maleimide functional groups exceeds 90% following reaction for 140 min. The conversion rate for primary amines

slows significantly after 1 h and appears to approach an ultimate conversion <90%.

The initial spectrum of a solution of NPM and Jeffamine® D-230 at an initial molar ratio of 4 : 1 and the spectrum of this solution following reaction at 160°C for 2 h are shown in Figure 11(a,b). The reaction between NPM and primary amine groups was confirmed in Figure 11(b) by the substantial decrease in intensity of the maleimide absorption bands at 6100, 4871, and 4349 cm^{-1}, respectively, and of the primary amine absorption band at 4925 cm^{-1}. Over the same time period, the N—H combination band at 4512 cm^{-1} showed a slight increase. *In situ* near-IR experiments also indicated that the absorbance of the secondary amine N—H group at 6486 cm^{-1} had not changed significantly, suggesting that crosslinking reactions between the maleimide functional groups and secondary amine groups are not significant at 160°C over this time period. Figure 11(c) is the spectrum of same solution following reaction at 160°C for 16 h. After complete disappearance of

Figure 9 *In situ* near-IR spectra of the NPM/aniline system at an initial molar ratio of 1 : 1 and at 170°C: (a) the initial spectrum, (b) the spectrum following reaction for 61 min, and (c) the spectrum following reaction for 121 min.
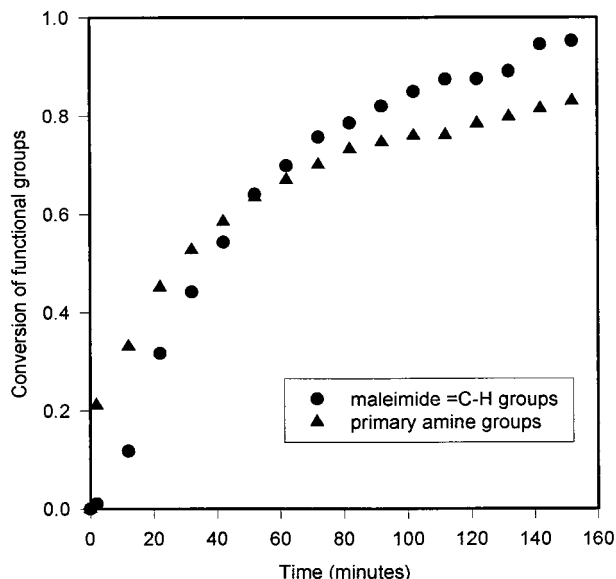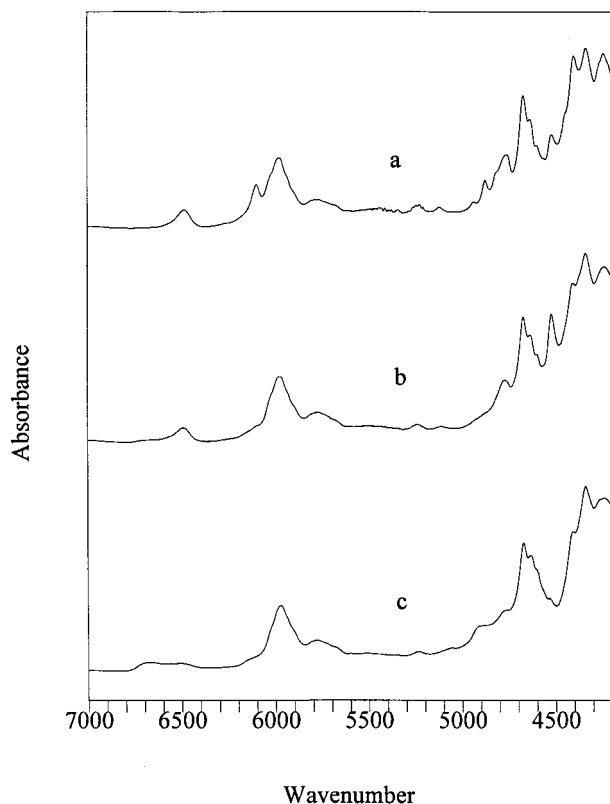
Figure 10 The plot of conversion versus reaction time for both primary amine and maleimide functional groups for a mixture of NPM/aniline at an initial molar ratio of 1 : 1 and at 180°C.
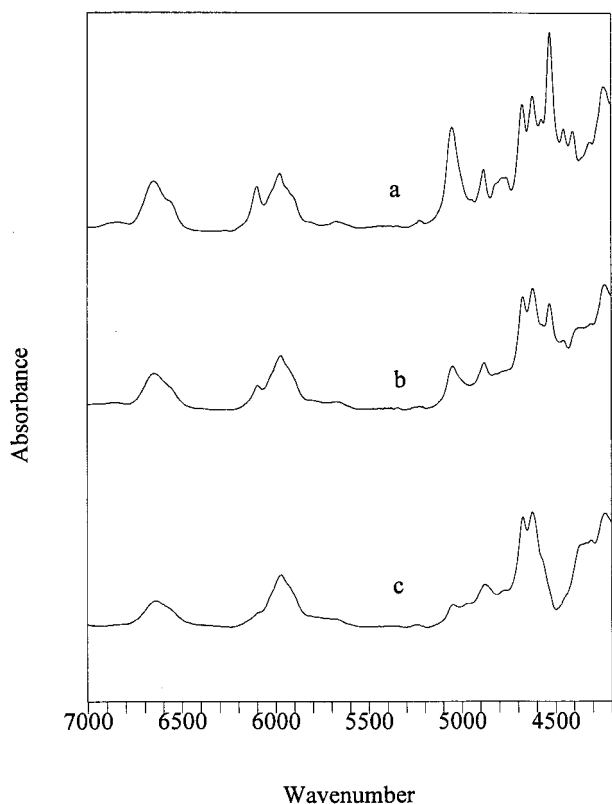

Wavenumber

Figure 11 *In situ* near-IR data for the NPM/Jeffamine® D-230 system at an initial molar ratio of 4 : 1 and at 160°C: (a) the initial spectrum, (b) the spectrum following reaction for two h, and (c) the spectrum following reaction for 16 h.

the primary amine band at 4925 cm^{-1}, the secondary amine absorption at 6486 cm^{-1} and the absorption band related to N—H groups at 4512 cm^{-1} shows a marked decrease in intensity. Therefore, the secondary amine plays an important part in crosslinking reactions of the residual maleimide double bonds in NPM once primary amine functional groups become unavailable for reaction.

Figure 12 shows *in situ* near-IR spectra of the NPM/MDA system at an initial molar ratio of 2 : 1 and at 165°C. As in the case of the NPM/aniline system, the well-separated band of maleimide C—H overtone absorption at 6100 cm^{-1} and the

isolated primary amine combination band near 5040 cm^{-1} demonstrate that near-IR spectra are suitable for quantitative studies of NPM/aromatic amine reactions. The absorption bands associated with maleimide =C—H stretch in the region from 4880 to 4740 cm^{-1} and the absorption band at 4510 cm^{-1} associated with the primary N—H groups clearly decreased in intensity as the reaction proceeded as well.

CONCLUSIONS

In the mid-IR spectra of NPM/aromatic amine mixtures, the primary amine N—H stretching bands near 3440 cm^{-1} show significant overlap with the carbonyl overtone band. In addition, the primary amine N—H in-plane bending mode overlaps significantly with aromatic ring stretch-

Table IV Peak Assignments for the Near-IR Spectra for NPM/Aniline

Absorption Band	Peak Position (cm^{-1})	Integration Range (cm^{-1})
Maleimide =C—H stretch	6096	6084–6118
Primary amine N—H combination	5048	5034–5080
Aromatic C—H stretch overtone	5963	5931–6014

Figure 12 *In situ* near-IR data for the NPM/MDA system at an initial molar ratio of 2 : 1 and at 165°C: (a) the initial spectrum, (b) the spectrum following reaction for 30 min, and (c) the spectrum following reaction for 120 min.

ing bands near 1600 cm^{-1}. In the near-IR region, the primary amine N—H combination bands are free of such spectral interferences. The maleimide =C—H overtone absorption at 6100 cm^{-1} is well separated with adjacent aromatic C—H overtone bands. Therefore, near-IR spectroscopy is very beneficial for accurately quantifying and monitoring the reactions characteristic of maleimide functional groups. For the NPM/Jeffamine® mixture, near-IR spectroscopic data demonstrated that reactions between maleimide double bonds and both primary and secondary aliphatic amines play an important role in the formation of the final product.

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