Cure Reaction Pathways of Bismaleimide Polymers: A Solid-State ^{15}N NMR Investigation

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ABSTRACT: The cure reaction pathways of a bismaleimide resin with a diamine are investigated using solid-state ^{15}N NMR spectroscopic techniques with specifically labeled monomers. These techniques provide clear identification of at least three different reaction pathways in the curing resin, one of which has previously been only postulated. In the homopolymerized bismaleimide resin system, maleimide ring addition has previously been shown to be the only observable reaction. When co-reacted with an amine, Michael addition of the amine to the maleimide ring has also been observed. Furthermore, a ring-opening aminolysis reaction, which has been observed in solution with specific reagents and conditions, has been suggested to occur under cure conditions. We show conclusively that this aminolysis reaction occurs to a significant extent during the cure of the neat resin and that this product can remain in the network structure even after a high-temperature postcure treatment. The existence of the amide product is demonstrated using bismaleimide resin formulations selectively labeled with ^{13}C and ^{15}N at specific sites. The ^{15}N chemical shifts and the $^{13}C-^{15}N$ scalar couplings are consistent with and confirm the amide product formation. Furthermore, under certain cure and postcure conditions, the aminolysis reaction is reversible which may significantly affect the final network structure.

1. Introduction

Bismaleimide (BMI) polymers are an important class of polymers for high-performance structural materials applications. They exhibit a good balance of high-temperature use capability, damage tolerance, and processibility that makes them attractive for aerospace applications. Typically, bismaleimide resins are thermally cured with a coreactant, such as a diamine, to increase the toughness of the cured system. In such systems, there are several competing cure reaction pathways and the final network structure, polymer properties, and environmental stability depend not only on the constituents of the resin system, but also on the thermal history used in processing.[1,2] Since these polymers are used in critically demanding applications, it is imperative that we understand the chemical state of the cured polymer and, in addition, possible environmental degradation processes at a molecular level. Further information on the details of the chemical and network structure at a molecular level is fundamental to understanding degradation pathways and to the development of meaningful structure−property relationships and lifetime-prediction methodologies.

Various spectroscopic techniques and model monomer systems have been used to study the cure of bismaleimide/diamine systems. Much of this research is aimed at investigating the mechanical properties of the cured polymer system and determining a single overall rate constant for the cure process.[1−5] This objective is driven by the observation that many of the physical and mechanical properties of these polymer systems depend on the cure cycle used.[1,2] Recently, there have been several noteworthy efforts to elucidate the reaction mechanisms which occur during the cure of bismaleimide/diamine systems. These investigations have utilized IR, DSC, and NMR in an attempt to investigate the mechanisms and kinetics of the curing reaction.[2,6−11] Their common interest has been to establish the reaction pathways during the cure of these systems and to determine the relative rates of these competing reactions. However, there has been a considerable amount of conflicting information regarding these pathways. It is generally assumed that the only reactions, which occur during the cure, were the homopolymerization of the maleimide rings and the Michael addition reaction of the amine across the double bond of the maleimide ring. Several other reactions are possible, such as, the ring-opening aminolysis reaction, which has been observed between specific imides and amines in solution,[7,10,12] and has been proposed under certain conditions in the cure of neat imide/amine systems.[6] Furthermore, the secondary amine product from the Michael addition reaction has been shown to react further under specific conditions,[13] but not react under other conditions.[7,10,14]

In this study, we use solid-state ^{15}N NMR spectroscopy to examine the details of the cure reaction pathways in bismaleimide/diamine polymer systems. We have focused on reaction mixtures of 1,1′-(methylene-4,1-phenylene)bismaleimide (MPBM) and 4,4′-methylenedianiline (MDA) (monomers A and B in Figure 1). These monomers were chosen to model bismaleimide systems because of their importance in commercial resin formulations. We will show that ^{15}N NMR spectroscopy with isotopically enriched resins enables us to clearly identify reactants and products in these systems and to quantitatively follow the cure.

2. Experimental Section

Materials. The starting materials for the synthesis of both 4,4′-methylenedianiline (MDA) and 1,1′-(methylene-4,1-phenylene)bismaleimide (MPBM) were obtained from Aldrich Chemical Co. and used as received unless specified. Isotopi-

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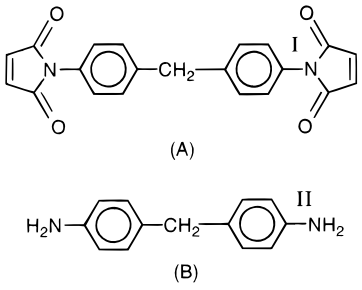

Figure 1. Monomers (A) 1,1′-(methylene-4,1-phenylene)-bismaleimide (MPBM) and (B) 4,4′-methylenedianiline (MDA). Labels I and II correspond to the NMR spectra.

cally labeled aniline (^{15}N, 98%+) and maleic anhydride (1,4-$^{13}C_2$, 99% and 2,3-$^{13}C_2$, 99%) were obtained from Cambridge Isotope Laboratory and used as received. The aniline was diluted to 20% ^{15}N isotopic enrichment prior to use with freshly distilled aniline from Aldrich Chemical Co. to extend the amount of labeled material available and as a compromise between sample cost and the time required to obtain the necessary signal-to-noise ratio.

The 4,4′-methylenedianiline (MDA) was synthesized and purified using the method suggested by Biller.[15] Approximately 9 mL of distilled water was placed in a 50-mL round-bottom flask in a thermostated water bath at 40 °C. Trifluoroacetic acid (54 mmol) was added to the water with stirring. Aniline (54 mmol) was added slowly followed by the dropwise addition of formaldehyde (13 mmol) as a 37 wt % solution diluted with 1 mL of distilled water. The solution was then raised to 50 °C for 30 min, then to 70 °C for 30 min, and finally to 90 °C for 1 h. The solution was then cooled slowly to room temperature during which crystals of the TFA·MDA salt precipitated. The crystals were collected, washed with cold distilled water, dissolved in methanol, and neutralized with sodium hydroxide. The MDA precipitates as fine light brown flakes with the addition of water to the solution. The flakes are filtered, washed again with cold water, and vacuum-dried. The crystalline flakes gave a melting point at 90 °C in good agreement with literature values. The yield based on total aniline was 25%. ^{1}H NMR ($CDCl_3$, ppm): 6.88 (d, 7.86 Hz, 4H, aromatic), 6.52 (dd, 7.86 Hz, 2.1 Hz, 4H, aromatic), 3.65 (s, 2H, CH_2), 3.42 (br, 4H, NH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): 144.2 (d, 10.6 Hz, ^{15}N−^{13}C), 131.9, 129.5, 115.2, 40.1. ^{15}N-{^{1}H} NMR ($CDCl_3$, ppm): 10.4.

The 1,1′-(methylene-4,1-phenylene)bismaleimide (MPBM) was synthesized from a portion of the ^{15}N-labeled MDA using the method of White et al.[10] 4,4′-Methylenedianiline (3.1 mmol) was dissolved in approximately 2.5 mL of chloroform and added dropwise to a solution of maleic anhydride (6.2 mmol) in 3 mL of chloroform at 0 °C. The mixture was then stirred for 2 h at room temperature. The bright yellow bisamic acid precipitate was collected and vacuum-dried. Yield of the bisamic acid was greater than 97%. The bisamic acid (3.0 mmol) was then dissolved in approximately 3.0 mL of acetone along with acetic anhydride (6.0 mmol), nickel acetate tetrahydrate (1.1 mmol), and triethylamine (2.0 mmol). The solution was stirred for 2 days at room temperature. At the end of the reaction, the precipitate was filtered, washed with water, and dried under vacuum. The overall yield of MPBM, based on MDA, was 45.5%. The MPBM initially contained a trace amount of the bisamic acid reaction intermediate, which was readily removed on a silica chromatographic column using chloroform as the solvent. Highly pure bright yellow crystals of MPBM were then obtained from the chloroform solution, which gave a melting point at 160 °C in agreement with literature values. ^{15}N{^{1}H} NMR ($CDCl_3$, ppm): 122.7.

Polymerization. Two different formulations of the MPBM/MDA resins were studied. The 1:0 system, which represents the homopolymerization of MPBM, was studied at cure temperatures of 175, 200, and 225 °C. The 1:1 ratio, which represents a stoichiometric equivalence of the primary amine and the maleimide, was studied at cure temperatures of 130, 150, and 175 °C. All formulations were prepared by drying the monomers carefully in a vacuum oven, weighing out the required amount of each monomer, and grinding the components together with a mortar and pestle. The total monomer weight was approximately 0.25 g. The monomer was then placed in a septum-sealed test tube and repeatedly evacuated and purged with nitrogen gas to remove oxygen from the system. The tube was immersed in a thermostated silicon oil bath at the desired cure temperature. At the end of the desired cure time, the tube was removed and quenched in ice water. The tube was cleaned and opened, and the partially cured polymer was removed and ground to a fine powder.

Instrumentation. Solid-state NMR experiments were performed on a General Electric Omega 400 PSG system using a Doty Scientific 5-mm High-Speed MAS probe. A General Electric 5-mm broadband probe was used for high-resolution liquid spectra. All of the ^{15}N NMR spectra are referenced to external ^{15}N-labeled glycine at 0.0 ppm.[16,17] Solid-state cross-polarization experiments were generally used for qualitative characterization. Typical experimental parameters included a ^{1}H 90° pulse length of 5 ms, a CP contact time of 2−6 ms, a pulse delay of 5−10 s, and a spinning speed of approximately 5000 Hz. Quantitative data was obtained using a single pulse experiment with gated proton decoupling and waiting at least 5 times the longest ^{15}N T_1 between pulses. The ^{15}N T_1 relaxation times were measured by the method of Torchia[18] for all components of both 1:0 and 1:1 MPBM/MDA ratios as well as at the initial and final stages of the cure. Interestingly, the ^{15}N T_1's do not change significantly with the degree of cure. The primary amine of the MDA has the shortest ^{15}N T_1 value at 4.6 s, while the imide nitrogen of the MPBM has the longest T_1 at 145 s. Thus, we use at least a 750-s pulse delay for all single-pulse experiments. The long pulse delay and the short acquisition time (50 ms) with gated decoupling serve to minimize the negative nuclear Overhauser effect. A 40 Hz Gaussian apodization was applied to the FID prior to Fourier transformation.[19] Relative peak areas were determined by fitting the experimental data with a Gaussian line shape using a nonlinear least-squares routine which was part of the Omega software.[20]

3. Results and Discussion

The ^{15}N NMR solution and CPMAS spectra of pure MPBM and MDA monomers are shown in Figure 2a−d. For all of the spectra in this paper, the resonance labels correspond with the particular structures in Figures 1 and 3. The ^{15}N resonances of the MDA at 10.4 ppm and MPBM at 122.7 ppm in the solution spectra are well-separated, and we find no evidence of impurities. Note that the chemical shift of these resonances in solution is slightly different than in the solid state. In the solid-state ^{15}N spectrum of MPBM, we find a single broadened peak at 127.3 ppm, which is typical of an amorphous organic solid. Interestingly, multiple peaks were previously observed in the solid-state ^{13}C NMR spectra of crystalline MPBM as well as MDA.[6] In the solid-state ^{15}N NMR spectra for crystalline MDA, we find two inequivalent peaks at 24.1 and 21.2 ppm. However, only a single resonance is observed at 22.1 ppm when the MDA is amorphous, such as when the reaction mixture is initially melted and quenched. Since the solution spectra show no isomeric impurities, this splitting may be attributed to solid-state packing effects in the crystalline MDA.[6] A single-crystal structure has been reported for MDA;[21] however, this structure indicates a single, independent molecule within the unit cell. The different intensities in the solid-state NMR spectrum suggests there may be a mixture of crystalline and/or amorphous forms or there may be different environments within a single crystalline form which is different from this structure.

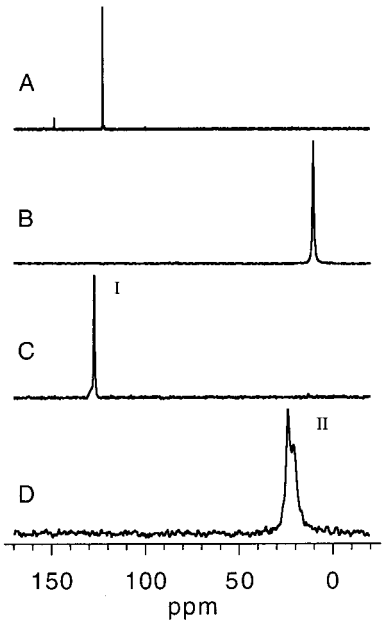

Figure 2. ^{15}N NMR spectra of (A) MPBM in $CDCl_3$, (B) MDA in $CDCl_3$, (C) crystalline MPBM via CPMAS, and (D) crystalline MDA via CPMAS.

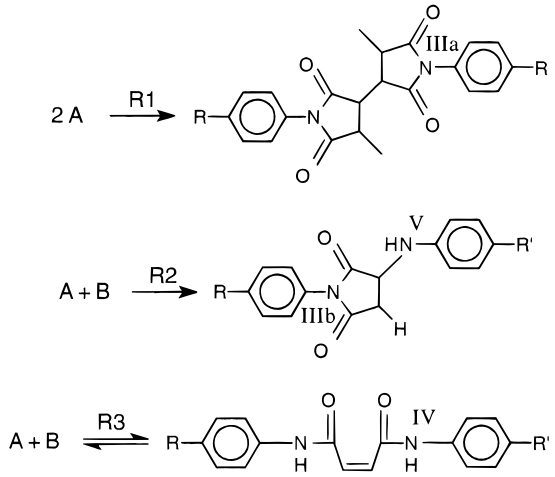

Figure 3. Predominant reaction pathways for maleimide−amine systems: R1, maleimide homopolymerization reaction; R2, Michael addition reaction; R3, ring-opening aminolysis reaction. A and B refer to the monomers in Figure 1. The labels correspond with the NMR spectra.

In MPBM/MDA systems, several reactions are possible. The primary cure reactions believed to occur are shown in Figure 3. Two of these reactions, the maleimide−maleimide cross-linking reaction, R1, and the Michael addition or amine−maleimide chain extension reaction, R2, are widely believed to be the predominant reactions that occur in a thermal cure of these monomers and have been reported by many other authors.[1−11,13] The commonly held view is that R2 predominates at low temperatures (<180 °C) and, at higher temperatures (180−220 °C), R1 occurs at a comparable rate.[6,13] The ring-opening aminolysis reaction, R3, has been observed in certain solvents[7,10,12] and has been tentatively observed under normal cure conditions,[6] but has not been conclusively demonstrated under these conditions. Of course, several other reactions are possible, such as the reaction between a secondary amine, from the Michael addition, and another imide group to form a tertiary amine group. However, Crivello[14] and Tungare and Martin[13] have

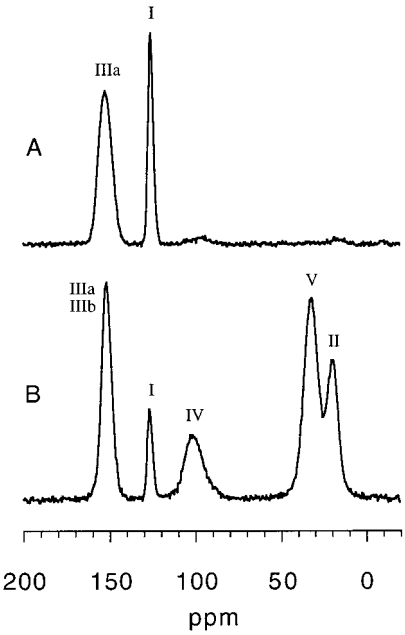

Figure 4. ^{15}N CPMAS NMR spectra for (A) homopolymerized ^{15}N MPBM after 316 min at 200 °C and (B) a 1:1 reacted system of ^{15}N MPBM:^{15}N MDA after 21.5 min at 150 °C.

shown that in model systems these reactions either do not occur at all or are extremely slow and require excess imide for the reaction to occur.

The homopolymerization of bismaleimides, including MPBM, has been studied extensively.[6,8,9,22] This reaction has been examined by IR, DSC, SEC, and ^{1}H and ^{13}C NMR and the effects of time and temperature have been thoroughly investigated. It is generally assumed that a linear polymeric product is formed via the R1 reaction whether this reaction is initiated thermally or anionically. However, it is clear that the extent of reaction depends on the temperature at which vitrification occurs and that the reaction does not go to completion.[6,19,22]

In our investigation of the homopolymerization of MPBM, again only the R1 reaction is observed. Figure 4a shows a typical ^{15}N NMR solid-state CPMAS spectrum of homopolymerized MPBM that has only partially reacted after 316 min at 200 °C. The MPBM monomer peak still exists at 127.3 ppm and a new resonance, attributed to the succinimide ring product, occurs at 152.8 ppm. The areas from the curve fit can be directly used as a quantitative measure of the relative concentration of the species attributed to each resonance. The extent of reaction for the homopolymerization is then given by $A_{III}/(A_I + A_{III})$. Above 200 °C, the reaction proceeds relatively quickly, and the extent of reaction for Figure 4a is approximately 0.56. At both 200 and 225 °C, the cure reaction slows and seems to reach a limit at approximately 0.60−0.70 even after 272 h at these temperatures. This conversion is slightly lower than that observed by Fry and Lind[6] at similar temperatures. Preliminary investigations using DSC have indicated that the degree of conversion can be pushed higher but this requires extreme temperatures of 300−400 °C.[19] This indicates that at lower temperatures the low degree of conversion is due to vitrification of the reacting system, which is consistent with other reports in the literature.[22]

The reaction of MPBM with MDA has also been thoroughly investigated in the literature. White et al.[10]

investigated the reactions of secondary diaminoalkanes with MPBM using IR and solution-state ^{1}H NMR. They reported that in a proton-donating solvent (*m*-cresol) high molecular weight linear polyimides were formed and that no soluble amides were observed or expected. Later, White[7] studied high molecular weight step growth linear polymers from the reactions of bismaleimides with diamines (including MPBM and MDA). He found that MPBM and MDA in a 1:1 molar ratio in solution (20−30% solids) catalyzed by carboxylic acids yielded a high molecular weight soluble polyimide through the R2 reaction mechanism. He also found that the acid-catalyzed reaction of ethylene or propylenediamine with certain aromatic BMIs yielded a soluble polyamide through an R3 reaction that left the maleimide double bonds completely intact.

Tung[2] studied the cure of the MPBM/MDA system at several different ratios of MPBM/MDA (1:0, 2:1, 1:1, 1:2) which, in principle, would vary the network architecture from a densely cross-linked system to a linear thermoplastic. Each ratio was investigated at several different cure temperatures (140, 180, and 210 °C) as well. He used succinimide ring analogues of proposed MPBM/MDA reaction products to identify IR absorption regions of interest and subsequently followed changes in these IR regions using spectral differencing methods to monitor the cure reactions. However, only the R1 and R2 mechanisms were considered in his analysis. Tung concluded that at low temperatures (140 °C) in 1:1 and 1:2 systems, the R2 chain extension reaction was predominant and at higher temperatures (180−210 °C), the R1 homopolymerization reaction was predominant.

Fry and Lind[6] used ^{13}C CPMAS NMR spectroscopy to study the MPBM/MDA system at the same stoichiometric ratios and cure conditions as Tung.[2] They were able to detect differences in the polymer network structure resulting from different cure schedules, even after identical post cure treatments, and were able to provide quantitative information about the extent of cure throughout the cure cycle. They employed model compounds and isotropic chemical shift correlative methods to identify their ^{13}C spectral resonances and based their mechanistic and kinetic analysis on the different carbonyl carbon resonances. A peak at 169 ppm was assigned to the carbonyl resonance in the unsaturated maleimide ring, and a peak at 175 ppm is assigned to those carbonyl carbons in reacted rings. The carbonyl carbon peaks of the R1 and R2 reactions could not be resolved. A small carbonyl resonance at 162 ppm was "tentatively" assigned to the R3 reaction product. This product was most pronounced for higher MDA ratios and lower temperature cures; however, they were unable to quantify its extent of reaction. Furthermore, this resonance "decreased substantially with post curing". In their final analysis, Fry and Lind assumed that R1 and R2 were the primary reaction pathways, but did not rule out the possibility of the R3 reaction or some other reaction taking place. Ultimately, they reached the same conclusions as Tung.[2]

In this study, when MPBM is polymerized with MDA, the ^{15}N Bloch decay and CPMAS spectra reveal multiple reaction products, as shown in Figure 4b for a 1:1 stoichiometric ratio reacted for 21.5 min at 150 °C. The unreacted monomer peaks for MPBM and MDA are still observed at 127.3 and 22.1 ppm, respectively. The peak at 32.7 ppm is assigned to the secondary amine product of the R2-type Michael addition reactions, based on literature values for the chemical shift of substituted aniline compounds.[23] The resonance at 100.7 ppm is in the general region for an amide product[23] and is tentatively assigned as the amide linkage product of the R3 reaction. The succinimide ring nitrogens of the R1 and R2 reactions appear to be indistinguishable in the solid-state spectra; thus, the resonance at 152.8 is assigned to the succinimide ring products of both reactions.

Table 1. Mass Balance Ratio from Equation 1 for 1:1 MPBM/MDA Systems

	T_{cure}	
time (min)	130 °C	175 °C
2.15		1.05
3.16	1.12	
4.64		1.03
10.0	1.08	1.05
31.6	0.98	1.00
100.0	0.96	1.04

Table 2. Relative Concentrations for 1:1 MPBM/MDA Systems after 10 min at 150 and 175 °C

T_{cure} (°C)	I	II	III	IV	V
150	0.41	0.49	0.49	0.10	0.41
175	0.21	0.38	0.66	0.13	0.49

To verify that the data is quantitative, we can examine the ratio of maleimide to amine at each point in the cure cycle. The ratio of total amine to total maleimide, reactants and products, is given by eq 1, where A_n corresponds to the area of a Gaussian curve fit for a given resonance. Equation 1 is based on the

$$\frac{\text{amine}}{\text{maleimide}} = \frac{(A_{II} + A_V + (0.5A_{IV}))}{(A_I + A_{III} + (0.5A_{IV}))} \qquad (1)$$

assumption that R1−R3 are the only reactions taking place and should always be equal to the initial stoichiometric ratio. Some relative ratios are given in Table 1 for the lowest and highest cure temperatures. We see that normally this ratio is within about 5% of what it should be for this stoichiometry, indicating that the data is indeed quantitative, within the measurement error, throughout the cure cycle. There is a slightly larger error in the ratio for the shortest time at the lowest temperature. This is due to the fact that so little reaction has taken place that the signal is small, which increases the error involved in determining the curve fit area.

We can examine the extent of reaction in the MPBM/MDA system. The relative concentration of each product can be calculated on the basis of either the total amine or the total maleimide concentration where the total area is defined by either the numerator or denominator of eq 1. Thus, the amount of succinimide product at 152.8 ppm relative to total maleimide is given by $A_{III}/(A_I + A_{III} + (0.5\ A_{IV}))$. The relative concentrations of reactants and products following a 10 min cure at 150 and 175 °C are given in Table 2. After 10 min at 150 °C, 59% of the MPBM has reacted, 49% to form succinimide and 10% to form amide. However, after 10 min at 175 °C, 79% of the MPBM has reacted, 66% to form succinimide and 13% to form amide. It is interesting to note that the same relative concentration of amide is obtained from using either the total maleimide or the total amine concentration. Furthermore, we have observed that this amount of amide forms within the first

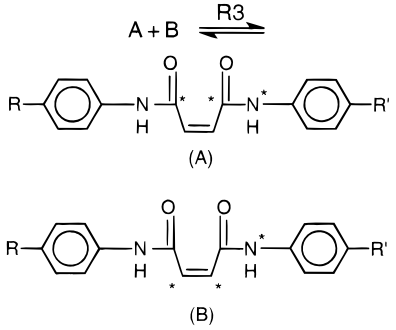

Figure 5. R3 reaction scheme for ^{15}N MDA with (A) 1,4-^{13}C MPBM and (B) 2,3-^{13}C MPBM. A and B refer to the monomers in Figure 1.

few minutes at each temperature and appears to remain relatively constant throughout the cure. This is consistent with the results obtained by Fry and Lind.[6]

Clearly, products from both the R1 and R2 reactions contribute to the succinimide resonance at 152.8 ppm; however, the reaction with the amine is much faster than the homopolymerization alone. The fraction of this resonance generated from either the R1 or the R2 reaction can be determined from a quantitative single pulse spectrum by a mass balance on the reactants and products. Since the amount of secondary amine is directly proportional to the amount of succinimide derived from the R2 reaction, the difference between the amount of succinimide and the amount of secondary amine should be the amount of succinimide formed from the R1 reaction. These calculations show that approximately 18% of the succinimide product is from the R1 reaction at 175 °C, while only 9% is from R1 at 150 °C. This result is consistent with other observations in the literature that the homopolymerization of the maleimide is favored at higher temperatures and that the amine addition is favored at lower temperatures,[2,6] even though the amine addition is also considerably slower at lower temperatures.

The following discussion focuses on whether the resonance at 100.7 ppm is, indeed, the amide product of the R3 reaction. At low extents of cure, the resulting oligomers are soluble in various solvents. One can then use high-resolution NMR techniques to examine these products. In the following experiment, the reaction products were not isolated and the entire reaction mixture was dissolved in a suitable solvent. ^{1}H NMR spectroscopy was used to examine a MPBM/MDA mixture, which had reacted for 5 min at 150 °C and was then dissolved in DMSO. These spectra reveal a complex set of resonances in the region expected for an amide group at approximately 12.2 ppm. These peaks were not observed when the partially reacted mixtures were dissolved in $CDCl_3$. Varma[9] had reported that the proton resonances for amide groups incorporated into the backbone structure appear at 10.3 and 10.7 ppm in DMSO; however, this is not conclusive evidence for the R3 reaction.

To investigate further whether this resonance is the amide product, we performed a series of high-resolution experiments to examine the ^{13}C−^{15}N scalar coupling. We prepared MPBM with ^{13}C-labeled maleic anhydride in the 1,4 positions and in the 2,3 positions and then reacted these monomers with ^{15}N-labeled MDA for 5 min at 150 °C. The R3 reaction schemes for these cases are shown in Figure 5. The resulting oligomers are soluble in $CHCl_3$, and we can obtain the high resolution

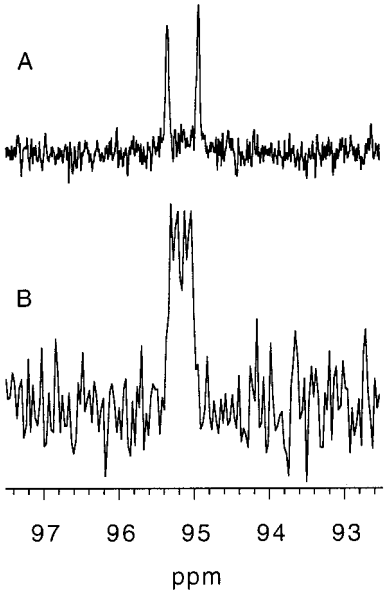

Figure 6. ^{15}N NMR spectra of the amide region of (A) 1,4-^{13}C MPBM:^{15}N MDA and (B) 2,3-^{13}C MPBM:^{15}N MDA reaction mixtures in $CDCl_3$ after curing for 5 min at 150 °C.

^{15}N{^{1}H} liquid NMR spectra necessary to resolve the ^{13}C−^{15}N coupling. The amide nitrogen region of the ^{15}N-{^{1}H} liquid NMR spectra for the 1,4-^{13}C MPBM:^{15}N MDA and the 2,3-^{13}C MPBM:^{15}N MDA reaction products are shown in Figure 6. The splitting patterns observed are clearly consistent with the proposed R3 reaction. The measured single-bond ^{13}C−^{15}N scalar coupling in the case of the 1,4-^{13}C MPBM:^{15}N MDA system is 16.8 Hz. The two- and three-bond scalar couplings measured from the spectrum of the 2,3-^{13}C MPBM:^{15}N MDA system are 7.3 and 3.7 Hz, respectively. These ^{13}C−^{15}N coupling constants are consistent with literature values for one-, two-, and three-bond couplings.[23,24] This is strong evidence that the resonance at 100.7 ppm is due to the amide product from the R3 reaction.

The ^{13}C−^{15}N labeling scheme is also useful for examining the secondary amine reaction products from the R2 Michael addition reaction. The ^{15}N spectra of the secondary amine region for these same two cases are seen in Figure 7, parts a and b. In the 1,4-^{13}C MPBM:^{15}N MDA reaction mixture, one might expect to see this ^{15}N resonance split by a two-bond coupling and again by a three-bond coupling, as in the amide region of 2,3-^{13}C MPBM:^{15}N MDA discussed above. However, we observe only a single doublet with a coupling constant of 1.2 Hz. Recall that in the secondary amine product there is no carbon−carbon double bond between the 2 and 3 carbons of the imide ring. Apparently, the larger coupling constants in the amide arise from a contribution of the π-bonding electrons in this structure.[24,25] Indeed, according to Axenrod,[24] π-bonding electronic structures are necessary in order to observe ^{13}C-^{15}N J couplings of two bonds or greater. In the 2,3-^{13}C MPBM:^{15}N MDA reaction mixture, the observed pattern is a doublet of doublets arising from a single-bond coupling which is further split by a two-bond coupling. The measured coupling constants are 10.4 and 2.4 Hz, respectively, which are consistent with a directly bonded ^{13}C and a two-bond distant ^{13}C.[24]

An interesting and useful aspect of the proposed R3 reaction is that the product amide nitrogens from both the maleimide ring and the primary amine become

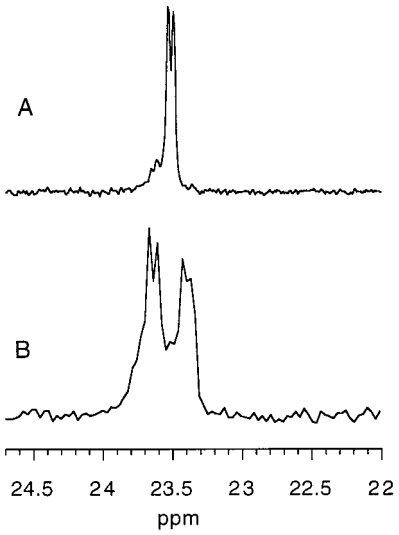

Figure 7. ^{15}N NMR spectra of the secondary amine region of (A) 1,4-^{13}C MPBM:^{15}N MDA and (B) 2,3-^{13}C MPBM:^{15}N MDA reaction mixtures in $CDCl_3$ after curing for 5 min at 150 °C.

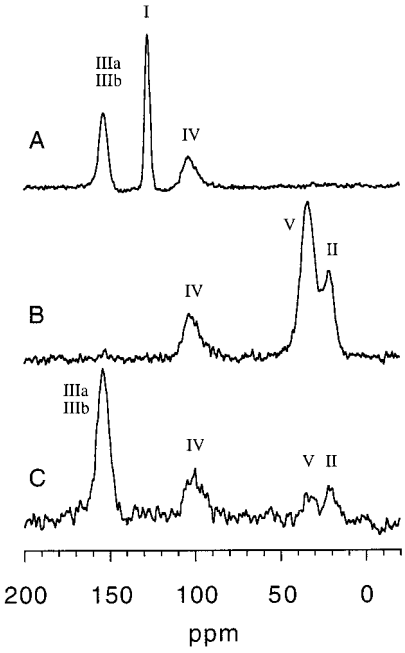

Figure 8. ^{15}N CPMAS NMR spectra of (A) ^{14}N MPBM:^{15}N MDA cured for 30 min at 150 °C, (B) ^{15}N MPBM:^{14}N MDA cured for 10 min at 150 °C, and (C) ^{15}N single pulse MAS NMR spectrum of (B) cured for 4 h at 150 °C and post cured for 8 h at 225 °C.

chemically and magnetically equivalent. Therefore, we expect the ^{15}N resonance of the amide product would occur at an identical chemical shift if we react ^{15}N MPBM with ^{14}N MDA, or if we react ^{14}N MPBM with ^{15}N MDA. The resulting spectra for these experiments are shown in Figure 8, parts a and b. Notice that the amide nitrogen resonance occurs in both spectra at 100.7 ppm. Furthermore, only the specific ^{15}N resonances for the particular reactants and associated products are observed, which implies that (i) only those sites specifically labeled with ^{15}N are observable, (ii) that the reverse R3 reaction does not occur to a significant extent on this time scale, and (iii) that the relative concentrations calculated above provide an accurate picture of the state of the system during the cure. If the reverse R3 reaction were extremely facile, one would expect to see additional resonances in these spectra, since there is an equal probability that either of the amide nitrogens could return to the imide or the amine. Clearly, these spectra are consistent with the R1−R3 reactions.

On the other hand, additional resonances are observed when the ^{15}N MPBM:^{14}N MDA system is fully cured and postcured, as shown in Figure 8c. Under these conditions, ^{15}N resonances occur not only in the succinimide and amide regions, but also in the secondary and primary amine regions. Note that some of the amide appears to be stable under these conditions. In addition, some of the amine and imide, generated in this reverse R3, react further via the Michael addition to succinimide and secondary amine. The existence of what appears to be primary amine suggests that some of this imide must also react via R1 to form succinimide and is thus not available to the amine. This demonstrates that the R3 reaction is not only reversible under certain conditions, but more importantly that the thermal history has a substantial affect on the final chemical structure of the network.

4. Summary

Solid-state ^{15}N NMR spectroscopy enables us to unequivocally determine the reaction mechanisms in the MPBM/MDA resin system. Our results demonstrate that there are three primary competing cure reactions. The R1 addition reaction of the maleimide rings occurs in the homopolymerization of MPBM and at high temperatures in the coreacted systems of MPBM/MDA. The R2 Michael addition or chain extension reaction between the primary amine and the double bond of the maleimide ring occurs readily at low cure temperatures. The R3 ring-opening or aminolysis reaction occurs readily over a wide range of curing temperatures. In fact, we observe the amide product under all stoichiometric ratios of MPBM/MDA, except the 1:0 ratio, and at all of the cure temperatures investigated to date. The existence of this reversible reaction pathway must be included in any measurement of kinetic data or consideration of the network structure. The fact that the amide can react further to form other reactive species, such as primary amine, is extremely important in understanding the molecular state of the cured polymer and may be a factor in the environmental degradation of such polymer systems.

Our results show that solid-state ^{15}N NMR spectroscopy is a powerful technique for investigating chemical processes at the molecular level in nitrogen-containing polymer systems. The technique offers highly resolved spectra and a means to readily identify and quantify reaction mechanisms and kinetics. Additionally, chemical interactions of the polymer with its service environment can be readily identified and quantified with solid-state ^{15}N NMR spectroscopy. We have observed that, in fully enriched polymer specimens, degradation reactions can be detected and identified at conversions of less than 1%. This work is still in progress. Armed with such specific information about the molecular level chemical environment will enable us to make meaningful improvements in processing and lifetime prediction methodologies for these high performance materials.

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