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Carbonization Reactions in Novolac Resins, Hexamethylenetetramine, and Furfuryl Alcohol Mixtures

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The carbonization process of novolac resins cured by hexamethylenetetramine (HMTA) in the presence of furfuryl alcohol (FA) was studied by a high-resolution solid-state NMR technique. Most reactions occur below 600 °C, and aliphatic species disappear above 800 °C. Nitrogen (2−3%) is present in the carbon materials obtained. The process can be influenced by the starting novolac structures, ca. the ratio of *ortho*/*para* reactive sites, and the FA content in the systems. When a novolac resin contains a high ratio of *para*-reactive sites, the carbonization reaction occurs at relatively lower temperatures, and the rate is relatively fast. High FA content slows down the carbonization process, and reactions occur at relatively high temperatures. Starting novolac structures and FA content in the systems also vary the nitrogen structures during the process and the structure distribution in the carbon materials at 800 °C.

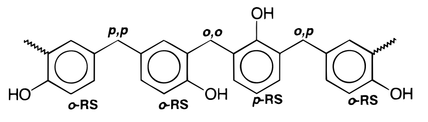
Introduction

Phenol-formaldehyde and furfuryl alcohol (FA) resins have been used commercially as starting materials to produce glassy carbons with high carbon yields. The carbonization reactions of phenolic and FA resins and the properties of the carbon materials derived from the resins have been investigated a great deal for several decades.[1−14] The resins have also been applied as binding materials in carbon composites,[15,16] reduction composites, and refractories in the aluminum and steel industries. The combination of the two resins in carbonization could provide improved mechanical and processing properties, especially when the resins are used as binding materials in which FA also acts as a solvent for the novolac resins. The understanding of the relationship between the structures of the starting polymer resins, the carbonization chemistry, and the properties of the carbon materials obtained after pyrolysis is fundamental to the application and modification of the carbon materials. However, few studies have addressed the chemical processes that occur when a mixture of phenolic and furfuryl alcohol resins is cured,[17] with for example hexamethylenetetramine (HMTA); there are no reports on the carbonization of the phenolic/furfuryl alcohol systems.

Recently we reported on the chemistry of reacting novolac/FA resins with HMTA.[18] A highly cross-linked homogeneous network that incorporates both novolac and furan entities is formed after curing the mixture to 205 °C. Minor amounts of nitrogen-containing structures are generated in the process. The pyrolysis of novolac and FA resins proceed by different reaction pathways; therefore, it was of interest to study the carbonization process of the homogeneous mixture of novolac/FA resins. The chemical structure, especially the nitrogen structure in the carbon products obtained, is another interesting issue to be examined. This article reports our study on the carbonization reactions of HMTA-cured novolac/FA resins. High-resolution, solid-state NMR techniques were used to follow the changes of chemical structure during the pyrolysis up to 800 °C.

Experimental Section

Samples. Two different novolac resins in two novolac/HMTA/FA formulations were used to examine the effect of the structures of starting materials on the carbonization process



o- or p-RS: *ortho*- or *para*-reactive site

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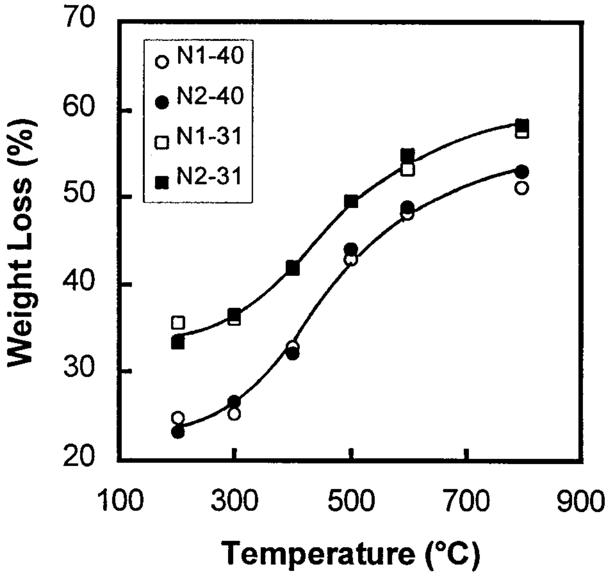

Figure 1. Weight loss of N1-40, −31 and N2-40, −31 after pyrolysis to 800 °C.

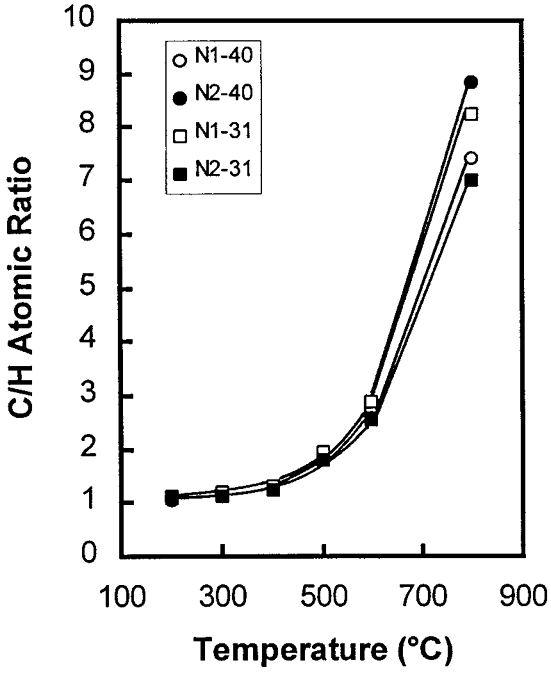

Figure 2. The C/H atomic ratios of N1-40, −31 and N2-40, −31 after pyrolysis to 800 °C.

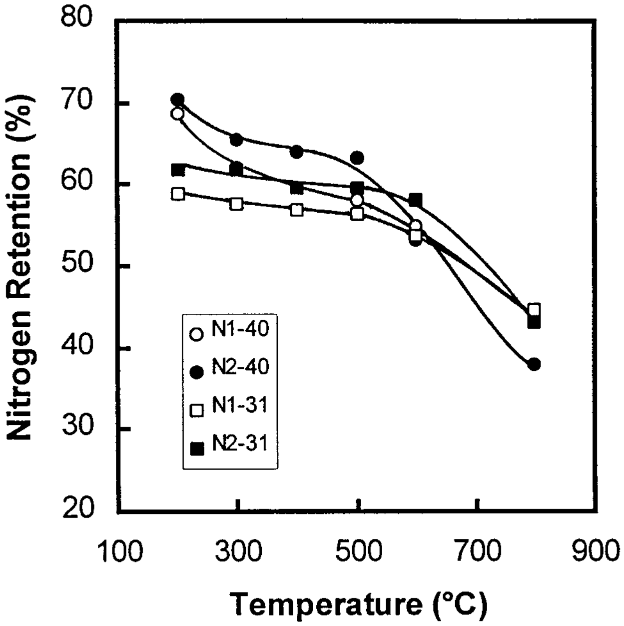

Figure 3. The nitrogen retention of N1-40, −31 and N2-40, −31 after pyrolysis to 800 °C.

Table 1. The C/H/N/O Weight Ratio of the Resins after Pyrolysis to 800 °C

samples	C/H/N/O
N1/HMTA/FA = 40/8/52	90.8/1.0/2.9/5.3
N2/HMTA/FA = 40/8/52	90.2/0.9/2.6/6.3
N1/HMTA/FA = 31/4.3/64.7	92.2/0.9/1.8/5.1
N2/HMTA/FA = 31/4.3/64.7	91.5/1.1/1.8/5.6

and chemical structures of the derived carbons. Novolac-1 (N1) was a high-*ortho*-linked resin (N1) and novolac-2 (N2) was a conventional resin.

The number-averaged chain length of both resins was about 8 phenols linked with methylenes as determined by their solution ^{1}H NMR spectra. The ratio of *ortho-ortho*, *ortho-para*, and *para-para* methylenes in the two resins was 48:49:3 (N1) and 25:53:22 (N2) as detected by their solution ^{13}C NMR spectra; thus, the ratios of *ortho-* and *para*-unsubstituted phenolic positions (reactive sites) of the two resins were calculated as 58:42 (N1) and 88:12 (N2). To enhance the structures derived from HMTA in carbon materials, 99% ^{13}C- and ^{15}N-enriched HMTA was synthesized with use of 99% ^{13}C-enriched formaldehyde and 99% ^{15}N-enriched ammonia. FA was obtained from Hopkin & Williams Ltd. and was distilled before use. The preparation and curing of novolac/HMTA/FA = 40/8/52 and 31/4.3/64.7 resins has been described.[18] After curing to 205 °C/4 h by a 35-h cycle, about 1 g of each cured resin (block) was baked in a Tetlow furnace at a rate of 50 °C/h in an argon atmosphere to 300, 400, 500, 600, and 800 °C, respectively. After pyrolysis, the samples were ground into fine powders for analysis. Two N/HMTA/FA ratios of 40/8/52 and 31/4.3/64.7 were used, and the samples are referred to as N1-40, N2-40, N1-31, and N2-31, respectively, in the text.

NMR Experiments. High-resolution solid-state NMR experiments were carried out using a Varian Unity Inova-300 spectrometer at resonance frequencies of 75 MHz for carbon-13 and 30 MHz for nitrogen-15 under conditions of cross-polarization (CP), magic angle sample spinning (MAS), and high-power dipolar decoupling (DD). The 90° pulse width was of 3.7 μs, whereas the rate of MAS was approximately 10 kHz, so no spinning sideband appeared in a range of 0−200 ppm for ^{13}C spectra. No spinning sideband was observed for ^{15}N spectra when using a 10-kHz MAS spinning rate. The chemical shift of ^{13}C spectra was determined by taking the carbonyl carbon of solid glycine (176.03 ppm) as an external reference standard. For ^{15}N spectra, the ^{15}N resonance of 99% enriched HMTA (44 ppm) was taken as an external reference.[18,20]

The quantitative observation of structures in the resins during carbonization processes requires a single pulse sequence with a very long relaxation delay (usually 5 times of ^{13}C or ^{15}N T_1). The T_1 of carbon materials can be extremely long, which makes it extremely difficult to conduct such measurements. In this article, a qualitative comparison among CP/MAS spectra of a resonance of similar systems after baking to the same temperatures has been made assuming a similar cross-polarization capability of the resonance.

Results and Discussion

The weight loss data of the novolac/HMTA/FA resins after curing and pyrolysis are shown in Figure 1. Resins using N1 and N2 behaved similarly with respect to weight loss on baking, and the difference between the

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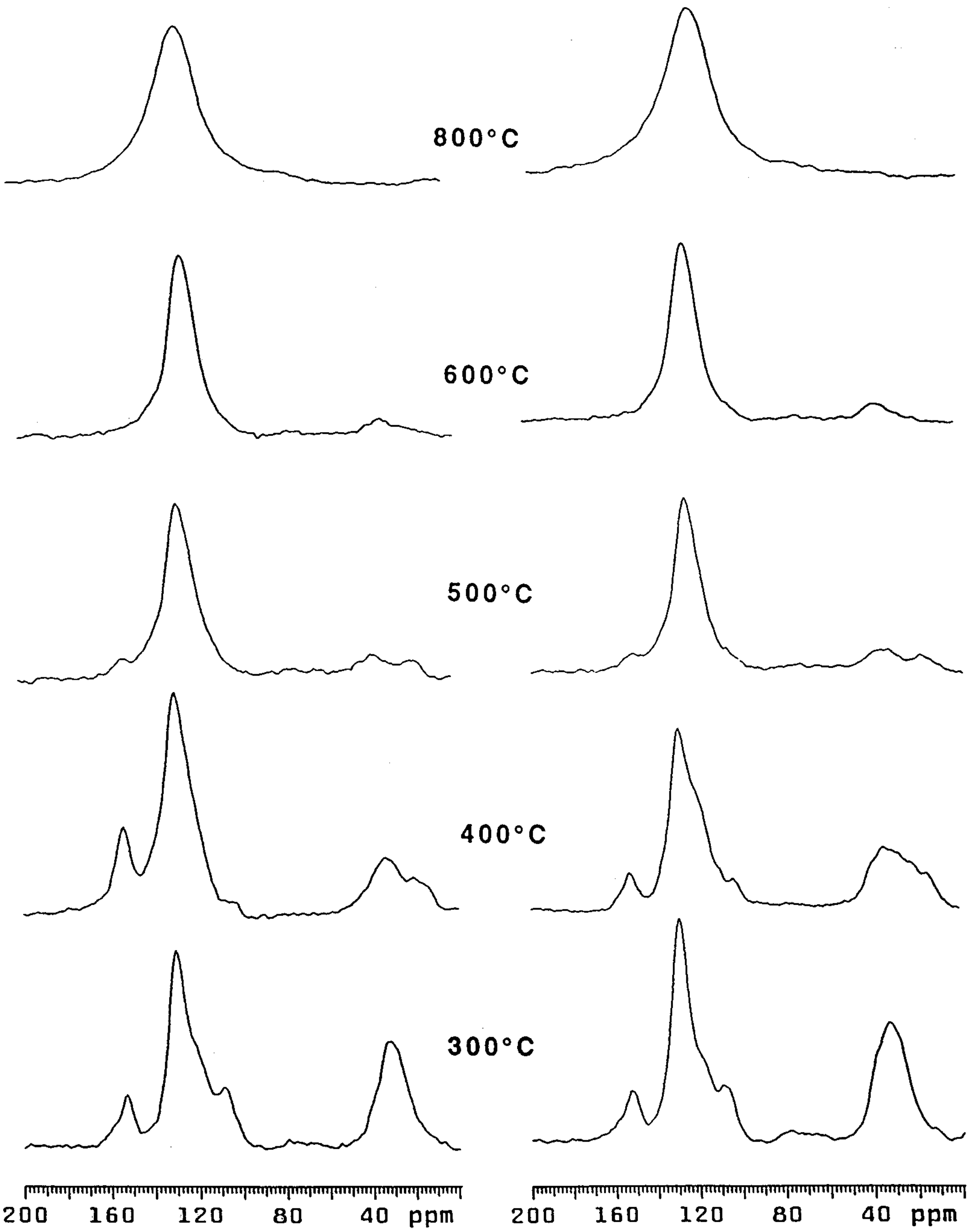

Figure 4. ^{13}C CP/MAS NMR spectra of N1-40 (left) and N2-40 (right) after pyrolysis. Unlabeled HMTA was used in the resins.

two formulations (40/8/52 and 31/4.3/64.7) seems to be mainy caused by the weight loss after curing to 205 °C. The novolac/furan ring ratios of the 40/8/52 and 31/4.3/64.7 systems after curing to 205 °C were estimated to be 54/46 and 47/53 according to their weight loss and elemental analysis. In the baking process, significant weight loss occurred from 300 to 600 °C, and the carbon yield of the resins after baking up to 800 °C was about 48% and 42% for 40/8/52 and 31/4.3/64.7 systems, respectively. The difference between N1 and N2 systems was 2−3%. The C/H atomic ratio is an important parameter in characterizing the carbonization process (aromaticity of carbons) for polymer resins. For novolac/HMTA/FA systems, as shown in Figure 2, a rapid increase of the C/H atomic ratio occurred above 400 °C, especially above 600 °C. The error bar of the C/H atomic ratio in carbons containing very low hydrogens after baking to 800 °C increased, and thus, the C/H ratios of these carbons appeared as a random order. X-ray diffraction results showed a broad peak for all these four samples after baking to 800 °C, indicating amorphous carbons were obtained.

The carbon, hydrogen, and nitrogen contents of the carbons are listed in Table 1, together with the oxygen content calculated by difference. Note that about 2−3% of nitrogen also remained in the baked resins up to 800 °C, and these nitrogen species derived from HMTA that acted as a cross-linker in the systems. The nitrogen content of these systems was examined during the pyrolysis process as shown in Figure 3. A quick loss of nitrogen occurred above 500−600 °C for most samples, except N1-40, which experienced a relatively quick decay across the whole temperature range. In all cases, the nitrogen retention values in N1 systems were lower than those in N2 systems below 500 °C. This result is related to the stability of nitrogen-containing structures

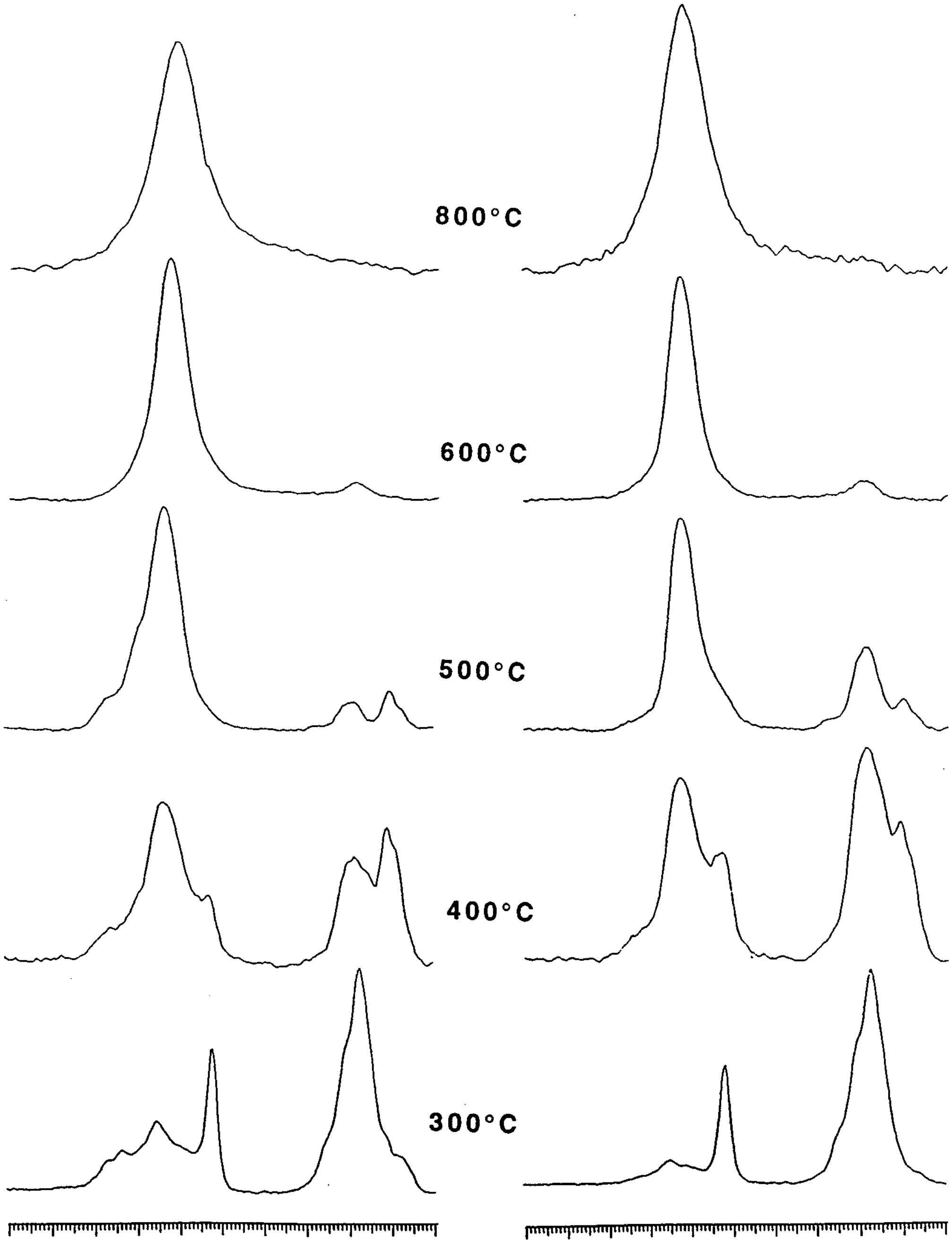

Figure 5. ^{13}C CP/MAS NMR spectra of N1-40 after pyrolysis. Labeled HMTA was used in the resins. Left spectra were observed with a contact time of 2 ms, and right spectra with a contact time of 20 μs.

formed during the curing process (below 205 °C),[18−24] the major ones being amides/imides, imines, nitriles, and amines. The structures linked at *ortho*-phenolic positions are more stable than those linked at *para*-positions, and therefore, N2 contains more stable nitrogen structures. The stability of *ortho*-linked nitrogen-containing structures was also evident in the initial pyrolysis stage and resulted in a slow decrease of the nitrogen content for N2 systems.

High-resolution solid-state NMR is a powerful technique to study the structure change in the resins during the pyrolysis. ^{13}C CP/MAS spectra (contact time, 2 ms) for N1-40 and N2-40 systems using unlabeled HMTA after baking to various temperatures are shown in Figure 4. After heating the resins to 300 °C, the resonances at 30−40 ppm are due to various methylene linkages between phenol rings and furan rings in conjunction with those between phenol or furan rings. The peak at 152 ppm is due to the OH-substituted carbons of phenols and the 2- and 5-carbons of furan rings, whereas the strong resonance at 128 ppm is assigned to aromatic carbons. The 3,4-carbons of furan rings appear at 108 ppm. Some minor resonances were also observed in the range of 60−85 ppm because of the

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formation of a series of ether structures. As the temperature increased, the relative intensity of aliphatic carbons and oxygen-substituted resonances at 152 ppm decreased, whereas the peak at 128 ppm increased and generally shifted to 122 ppm above 500 °C. The intensity of the peak at 108 ppm also decreased with increased temperature and disappeared above 600 °C. At 500 °C, the aliphatic carbons observed are mainly methyl groups at 15−20 ppm and methylenes, methines, or even quaternary carbons at 28−36 ppm. At 600 °C, the peak at 33 ppm still appeared, but only a broad peak at 120 ppm was obtained after baking to 800 °C for both resins, indicating the formation of large carbon sheets.

No significant difference between N1-40 and N2-40 was noticed where unlabeled HMTA was used (Figure 4). To enhance the structures derived from HMTA in carbon materials, HMTA enriched with both ^{13}C and ^{15}N was used, and the ^{13}C CP/MAS spectra of N1-40 are shown in Figure 5. By use of a long contact time such as 2 ms, all ^{13}C resonances can be observed because the magnetization of non-hydrogen-bonded carbons can be polarized by other hydrogen atoms in the system via effective spin diffusion in rigid systems. This cannot occur when a very short contact time, ca. 20 μs, is used; thus, only directly hydrogen-bonded resonances (except mobile CH_3 groups) can be detected. Note that the resonances at 10−50 ppm observed at 300 °C were strongly enhanced when using labeled HMTA, compared with those in Figure 4, indicating some of these methylene linkages and methyl groups were derived from HMTA. The shoulder at 41 ppm is attributed to the *para-para* methylene linkages between phenol rings, because the N1 resin contains 42% of *para*-reactive sites that are more reactive to form stable methylene linkages. Most of these resonances can also be observed in spectra using 20 μs contact time, except those mobile CH_3 groups. Compared with the spectra using unlabeled HMTA, a strongly enhanced peak at 103 ppm also was detected, and this peak could also be seen in spectra using a contact time of 20 μs. This suggests the peak due to a CH═CH species possibly formed when furan rings were broken during the pyrolysis.[12] The result also provided evidence that the methylene linkages derived from HMTA could be involved in the reaction, because the resonance was enhanced using labeled HMTA. The CH═CH structure could be formed by losing water molecules (oxygen from furan rings and hydrogen from methylenes) after fission of furan rings. Its intensity decreased with increased temperature and disappeared above 500 °C. The ether structures at 60−85 ppm (at 300 °C, Figure 4) are barely visible in Figure 5, indicating those ether methylenes were derived from FA, and HMTA did not contribute to these structures. The methyl group intensity (15−20 ppm) increased with increasing temperature and became rigid as the signal also appeared in spectra with the short contact time. Their intensity decreased more rapidly than other aliphatic resonances above 500 °C. After baking to 600 °C, the peak at 33 ppm was observed (aliphatic species) when either 2 ms or 20 μs contact time was used, indicating that hydrogen-bonded aliphatic carbons (CH_2 and/or CH) still remained. At 120 ppm, only a broad peak was observed after baking to 800 °C no matter whether labeled or unlabeled HMTA was used (Figures 4 and 5), indicating aliphatic resonances were too minor to be observed.

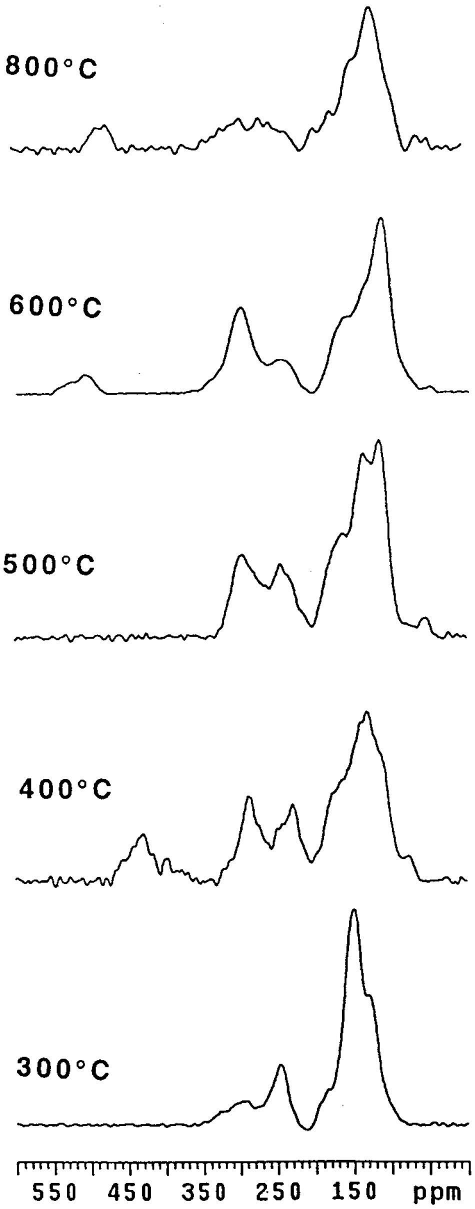

Figure 6. ^{15}N CP/MAS NMR spectra of N1-40 using labeled HMTA after pyrolysis up to 800 °C. The contact time was 2 ms.

The variation of nitrogen structures in the resins during pyrolysis can be studied by the ^{15}N high-resolution solid-state spectrum that gives a wide chemical shift range indicative of nitrogen structures.[25] ^{15}N CP/MAS spectra of N1-40 (Figure 6) indicate that the major nitrogen structure of the resin after heating to 300 °C included imides (150 ppm) and amides (120 ppm). Small amounts of nitriles (250 ppm) and imines (280−320 ppm) were also present.[18,19−22,25] Increased temperature caused the loss of nitrogen (Figure 3), and the chemical structures were also changed. The imides/amides peak became broader and the relative intensity of imines at 280 ppm increased after heating to 400 °C. Some oxidized species were also formed around 450 ppm

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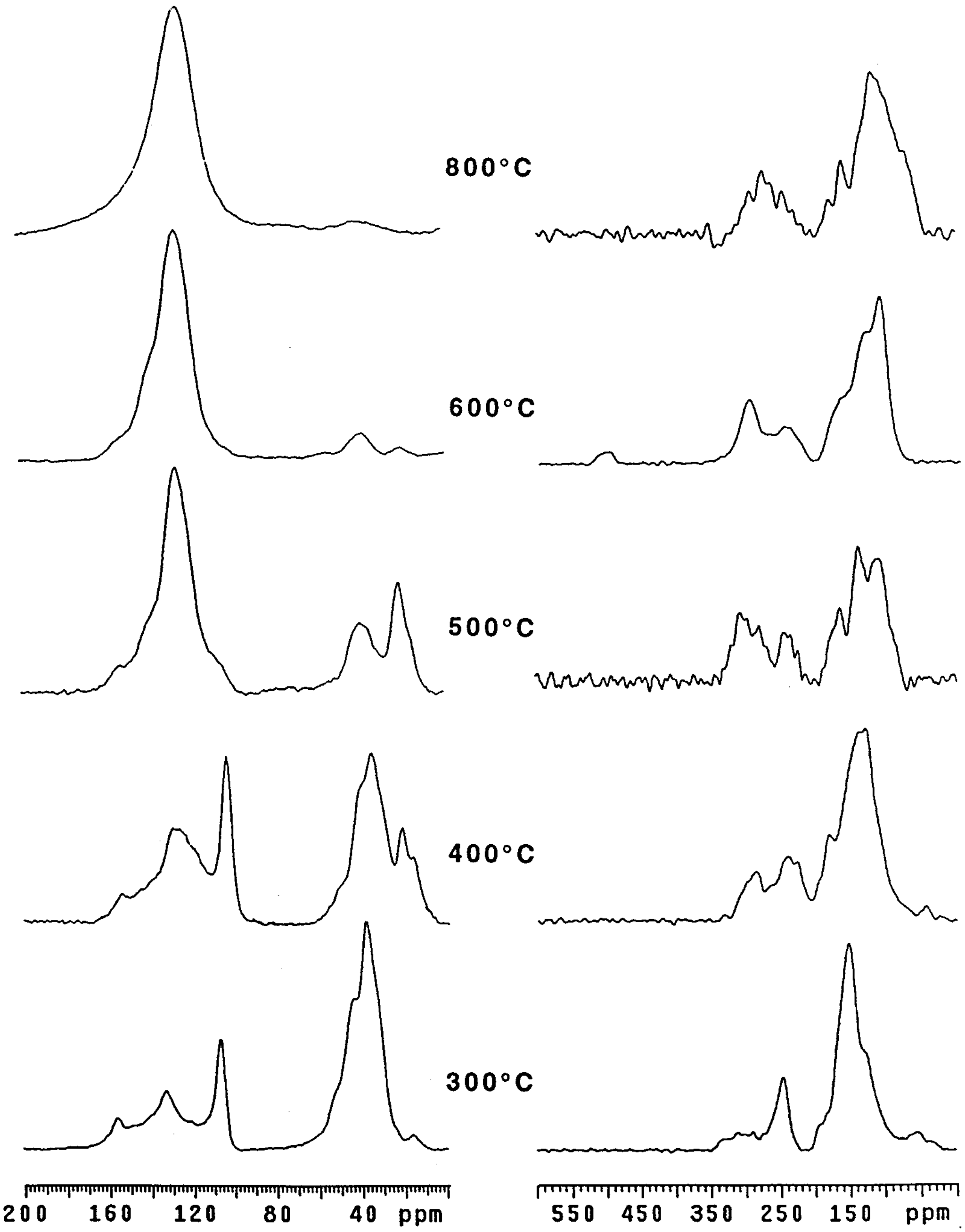

Figure 7. ^{13}C (left) and ^{15}N (right) CP/MAS spectra (contact time, 2 ms) of N1-31 after pyrolysis up to 800 °C.

and disappeared after baking to 500 °C. Other oxidized species (at 500 ppm) were also formed when the resin was baked above 600 °C. Because the pyrolysis was conducted under an argon atmosphere, the oxygen for oxidation could only come from the decomposition of the resin. The minor peaks at 30−60 ppm are caused by amine species formed by decomposition of the nitrogen-containing linkages in the network during the pyrolysis. After baking to 800 °C, three broad peaks were detected at 80, 250, and 450 ppm because of residual amides, nitriles, quinoline/acridine structures, and $-NO_2$ species.[18,20,21,25] The nitrogen content in the resin was 2.9% at 800 °C.

^{13}C and ^{15}N CP/MAS spectra of N1-31 resin (using labeled HMTA and 2-ms contact time) after baking to various temperatures are shown in Figure 7. The reaction process was similar to that for N1-40, but the reactivity difference was apparent. At 300−400 °C heating range, N1-31 experienced a relatively slow carbonization process compared with N1-40; the resonances at 102, 35, and 15 ppm showed relatively strong intensities at 400 °C compared with N1-40. Taking into account that 4.3% labeled HMTA was used in N1-31 whereas 8% labeled HMTA was present initially in N1-40, the difference between N1-31 and N1-40 was quite remarkable. At the same time, the relative intensity of methyl groups also increased, and then decreased slowly with increase of temperature. At 600 °C, methyl resonances at 15 ppm can still be noticed in N1-31, but they have disappeared in N1-40. A broad peak at 33 ppm can also be observed even after baking the resin to 800 °C. Most of nitrogen structures in N1-31 were similar to those in N1-40; however, no oxidized species were detected at 400 and 800 °C for N1-31. Note that the rate of nitrogen loss of N1-40 was also faster than N1-31, as shown in Figure 3. The nitrogen content in the N1-31

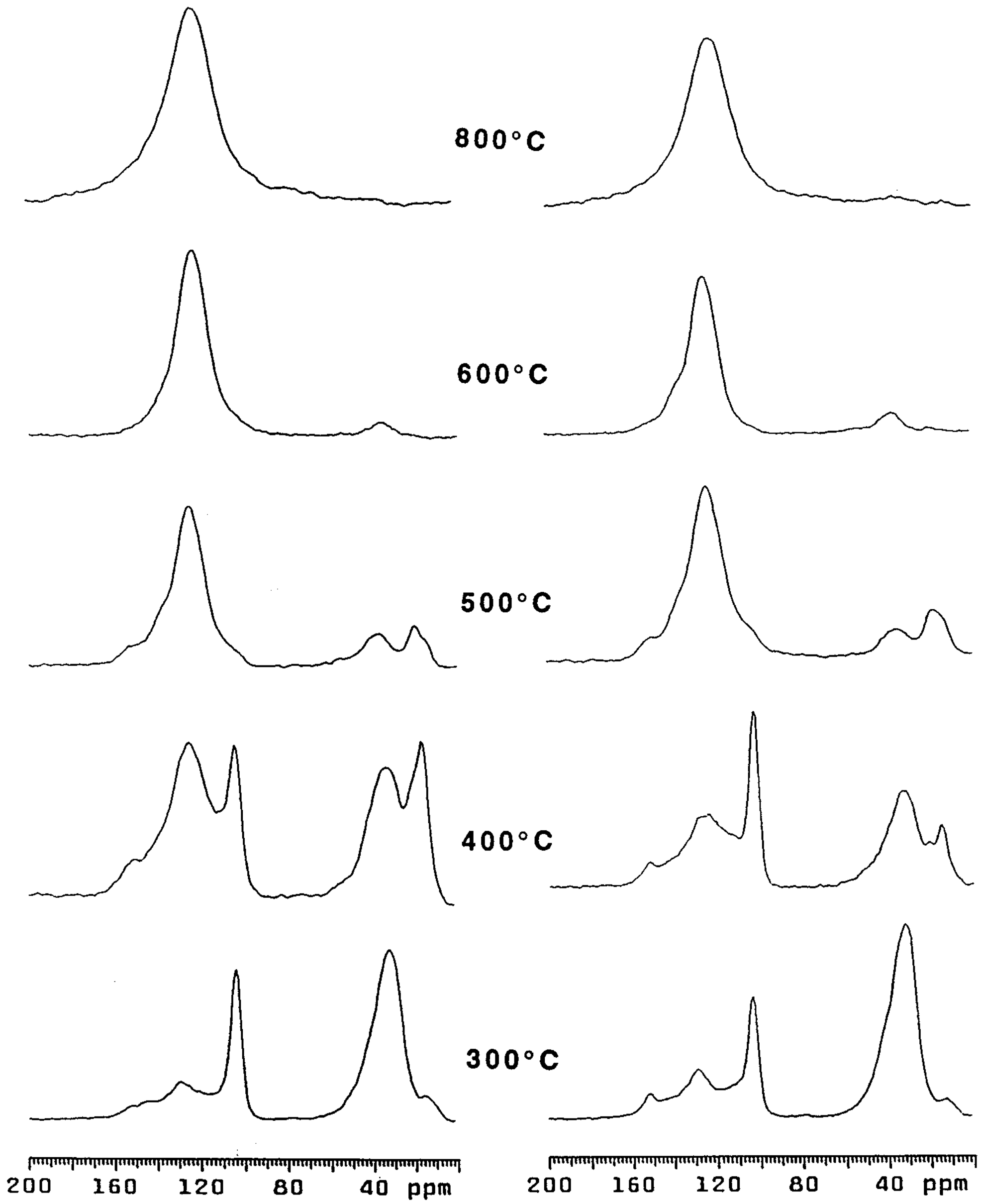

Figure 8. ^{13}C CP/MAS spectra (contact time, 2 ms) of N2-40 (left) and N2-31 (right) after pyrolysis up to 800 °C. Labeled HMTA was used.

after baking to 800 °C was 1.8%. The result indicates that FA caused the carbonization process to occur slowly, and the reaction occurred at relatively higher temperatures. Usually the break and disappearance of furan rings during pyrolysis occurred at 300−500 °C at which benzene rings were produced simultaneously.[6,12] Thus, N1-31, which contains more FA, requires a longer time and higher temperatures to convert the large number of furan rings, relative to N1-40, to benzene rings. Therefore, the high FA content delays the carbonization process of novolac/FA resins.

The ^{13}C and ^{15}N CP/MAS spectra of N2-40 and N2-31 are shown in Figures 8 and 9. Their reaction courses were similar to N1-40 and N1-31. N2-40 also carbonized more quickly than N2-31 systems in the 300−400 °C range. The intensities at 103 and 35 ppm of N2-31 at 400 °C were higher than those in N2-40 (taking aromatic peak at 122−128 ppm as initial reference), and the methyl intensity also increased and then decreased slowly in N2-31. The aliphatic resonances at 35 ppm also decreased more slowly in N2-31, because the peak could be noticed even at 800 °C in N2-31, but not in N2-40. The nitrogen structure distribution in N2-40 is also different from that in N2-31. N2-40 contained more imides/amides and oxidized species, but N2-31 presented more nitriles and quinoline/acridine structures in the resin after baking to high temperatures.

N1-40 was more reactive than N2-40 in carbonization process in the 300−400 °C range; at 400 °C, N1-40 displayed relatively low intensities at 103 ppm and 10−50 ppm (aliphatic carbons) compared with N2-40. As reported previously, *para*-reactive sites in novolac reins are more reactive in the initial formation of curing intermediates and then converting to methylene linkages between phenol rings. N1 contains a higher ratio of *para*-reactive sites than N2, and their reactivity also appeared in the initial stage of pyrolysis process. An increase of FA content significantly delayed the *carbonization* process in the low-temperature range. This contrasts with the FA effect on *curing* of novolac/HMTA systems in which FA acted as a good solvent for the initial reactions and let the curing start at relatively

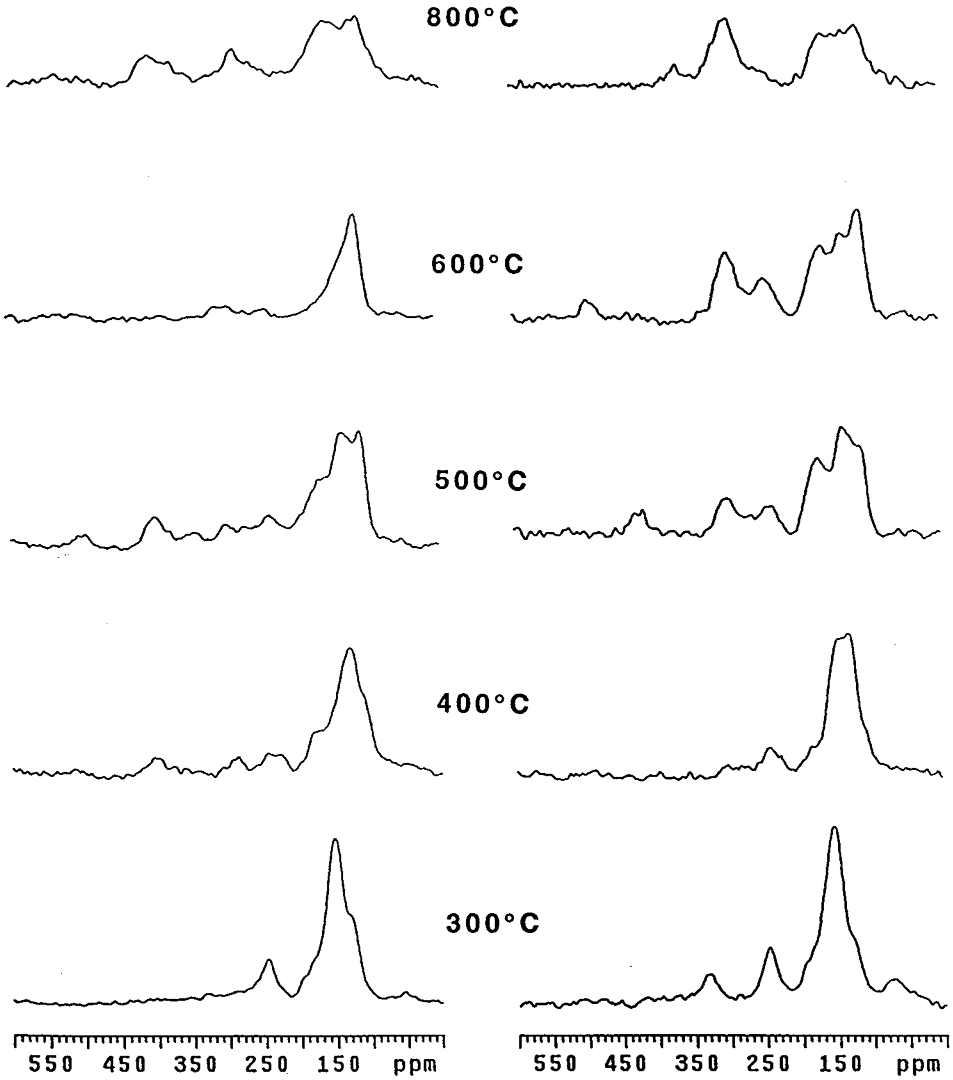

Figure 9. ^{15}N CP/MAS NMR spectra of N2-40 (left) and N2-31 (right) using labeled HMTA after pyrolysis up to 800 °C.

low temperatures.[18] However, the two resins in N1-31 to N2-31 did not show significantly different reactivity in the carbonization process, possibly because the effect of the FA content was dominant and caused a lower reactivity in these systems; the effect of novolac structure became less important. However, we did observe the effect of novolac structure on the distribution of nitrogen structures in the baked resins (compare Figure 7 with Figure 9). The carbons obtained from the resins still showed a different distribution of nitrogen-containing structures. Currently, an investigation of novolac, resole, FA resins, in conjunction with novolac/HMTA and novolac/HMTA/FA systems is being conducted by our group. The carbonization processes of these resins are being compared, and the relationship between the starting materials and their carbon structures/properties after pyrolysis is being examined.

Conclusion

Carbonization reactions of novolac/HMTA/FA resins mainly occur at a temperature range of 300−600 °C, and aliphatic species disappear above 800 °C. Nitrogen (2−3%) still remains in the carbon materials obtained after baking to 800 °C. The pyrolysis process can be influenced by the chemical structure of the starting novolac resins (ca. the ratio of *ortho/para* reactive sites) and the FA content in the mixed systems. Where a novolac resin contains a high ratio of *para*-unsubstituted phenolic positions as reactive sites, the system undergoes a relatively fast reaction and the carbonization occurs at relatively lower temperatures, because the *para* sites are more reactive in both the curing and initial pyrolysis processes. A high FA content slows down the carbonization process, causing the intensities of aliphatic carbons to decrease more slowly and reactions occur at relatively high temperatures. Original novolac structures and FA content in the systems also vary the nitrogen structures during the carbonization process and the structure distribution in the carbon materials obtained at 800 °C.

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