Analysis of Volatiles Evolved During High-Temperature Treatment of Thermally Stable Polymers. I. Nitrogen-Containing Acetylene-Terminated Resin

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SYNOPSIS

Cured samples of a nitrogen-containing acetylene-terminated resin, N,N'-(1,3-phenylene-dimethylidene)bis(3-ethynylaniline), have been heated at 10°C/min up to 900°C in a pyroprobe attached to a gas chromatograph/mass spectrometer (GC/MS). Analysis of the volatiles evolved during heating identified both gases and higher boiling compounds. The major higher boiling compounds are benzene, toluene, xylene, aniline, benzonitrile, m-methylaniline, and m-methylbenzonitrile; the gases include ammonia, methane, and traces of carbon dioxide. Correlations between sample temperature and the evolution of each of these compounds have been made. The onset of all volatile formation occurs between 450 and 500°C. The higher boiling volatiles peak, then end by approximately 700°C, while the gases peak then fall off but are still being evolved at 900°C. Average weight loss measurements of 13.6% at 700°C and 15.7% at 900°C agree with previously published thermogravimetric analysis (TGA) data. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

There is a need for polymeric-type materials that can function at high temperatures, retain good mechanical and physical properties, and possess the advantage of being lightweight as compared to metals or ceramics. Many polymers used in high-temperature applications or as precursors to carbon have deficiencies that negatively impact the final material properties. One of the biggest problems lies in the large amounts of volatile compounds given off as the polymer or precursor is heated or carbonized. This can lead to large weight losses, low carbon yields, void formation, excessive shrinkage, and loss of mechanical strength.[1,2]

Typical polymers used as precursors to glassy (nongraphitizing) carbon are phenol-formaldehyde resins (PFR),[3,4] polyfurfuryl alcohol resins (PFAR),[3-5] and rayon fiber (cellulose).[6,7] Due to the large amounts of oxygen in the original polymer structures, these materials lose H_2O, CO_2, CO, and other small molecules containing carbon. The net results are large weight losses (at 1000°C, 37 and 39 wt % losses for PFR and PFAR, respectively), depressed carbon yields (at 1000°C, 85% for PFR and PFAR; at 1300°C, 30% for rayon), and the expected shrinkage and void formation.

Polyimides have been investigated as both precursors for graphitic carbon[8-11] and as pyrolyzed thin films for heat-resistant applications.[12] As in the previous examples, the presence of oxygen and, in this case, nitrogen in the polymers leads to the formation of gaseous volatiles upon heating, with CO_2 and CO being the dominant species and HCN, CH_4, and N_2 being evolved to a much lesser extent. The weight losses are also substantial, being 30–50% at 1000°C, depending on the initial polymer structure.

Acetylene-terminated resins show promise as precursors for high-temperature materials due to their lack of evolution of volatile by-products upon polymerization and their ability to flow easily at lower temperatures before substantial polymerization takes place. The problem is that most resins of this type that have been synthesized contain many heteroatoms such as oxygen, nitrogen, sulfur, and

fluorine in the monomer structure between the reactive acetylene end groups.[2] Upon treatment at higher temperatures the presence of these heteroatoms will cause volatiles to be given off, thus leading to the aforementioned undesirable effects.

There are many other polymers or polymer precursors used in very high temperature applications or as precursors to either glassy or graphitizable carbon, many of which contain few if any atoms other than carbon or hydrogen. These materials include polyacrylonitrile (PAN),[7] polycarbonate,[13] anthracene polymers,[14] phenylene oxide polymers,[1] and p-polyphenylene.[15] In general, the results for these materials are better (i.e., less volatiles and higher weight retention), but there is still room for improvement.

Our goal is to develop better materials for very high temperature applications through developing new polymeric precursor systems. From the examples cited above one can conclude that decreasing volatile formation upon heating can lead to a better

ultimate material with superior properties. One approach we are taking is the examination of volatiles given off as a function of the structure of the initial starting material and the temperature to which the sample is heated. To accomplish this we have designed an analysis system that consists of a pyroprobe interfaced directly to a gas chromatograph/mass spectrometer (GC/MS). We can heat a sample at any rate to any temperature up to 1400°C and easily separate and analyze the volatiles given off. In this manner we can systematically examine many potential polymers and precursors to determine which types of polymers, functional groups, moieties within the molecules, etc. are desirable and which are detrimental to the formation of a superior high-temperature material.

We have chosen to start this study with the examination of an in-house developed material; namely, a nitrogen-containing acetylene-terminated resin, N,N'-(1,3-phenylenedimethylidene)bis(3-ethynylaniline):
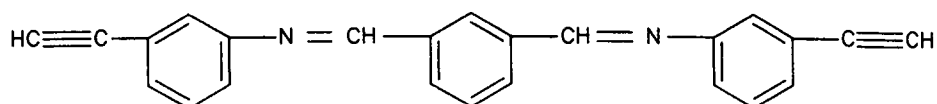
The synthesis, characterization, and high-temperature properties of both this meta–meta–meta (mmm) isomer and the meta–para–meta (mpm) isomer [N,N'-(1,4-phenylenedimethylidene)bis(3-ethynylaniline)] have previously been reported.[16-18] These materials exhibit excellent thermal stability to very high temperatures, losing less than 20 wt % up to 1000°C, despite the presence of nitrogen in the resin. For this study only the material derived from the all-meta (mmm) isomer was examined.

EXPERIMENTAL

Sample Preparation

The synthesis, characterization, and curing of the all-meta (mmm) acetylene-terminated resin have previously been reported.[17,18] The samples used in this study were thermally cured in air by heating the precursor for 2 h at 120°C, 1 h at 145°C, 2 h at 150°C, 1 h at 200°C, 1 h at 250°C, and 50 h at 300°C. Small chips of the appropriate size were cut from the bulk samples and used for analysis.

Instrumentation

Sample weights, which ranged from 300 to 1750 μg, were measured on a Perkin-Elmer AD2Z Autobalance. The pyrolysis unit used was a CDS Pyroprobe 2000 equipped with a temperature-controlled interface to the GC. A resistively heated platinum coil filament probe was used; the samples were placed in quartz tubes (held in place by quartz glass wool plugs) inserted into the coil. For each run the probe was programmed for the desired starting temperature, heating rate, and final temperature; the interface was held at 225°C.

The GC/MS system used was a Hewlett-Packard Model 5890 Series II gas chromatograph attached to a Hewlett-Packard Model 5971A mass selective detector. The system was controlled by a Hewlett-Packard HP 59970 MS ChemStation. The capillary column used was HP-1 crosslinked methyl silicone gum, 12 m × 0.22 mm × 0.33 μm film. The GC injection port, onto which the pyroprobe interface was directly attached, was held at 225°C. The GC oven was programmed for the desired starting temperatures, dwell times, heating ramps, final temperatures, and final dwell times. Subambient GC oven

temperatures were achieved by the use of liquid carbon dioxide. The MS was kept under high vacuum (1–4×10^{-5} torr) at 280°C. Helium was used as the carrier gas throughout the entire system.

RESULTS AND DISCUSSION

There were a number of reasons for using the material that had undergone the above mentioned cure cycle. First, these conditions are part of a standardized heating procedure developed to ensure uniformly cured samples for comparative material properties evaluations;[16] thus, the results obtained in this study can be correlated with other data. Second, samples cured in this manner exhibit no weight loss,[17] which means that, to this point in the cure, no volatiles have been given off. Third, the thermogravimetric analysis (TGA) of the solid chip form of this material cured in this manner (TGA run under nitrogen) has been reported.[17] By using the same heating rate, the same solid chip form of the material, and an inert atmosphere, we can directly compare the weight losses at various final temperatures to ensure correlation of the data. Fourth, a preliminary examination of the volatiles given off at high temperature (to 900°C) of this material has been performed via FT-IR.[17] The only products observed were methane and ammonia, with trace amounts of carbon monoxide and carbon dioxide. It

was felt that examination of this material under the more sensitive GC/MS conditions might detect other compounds being evolved upon heating.

The first series of experiments was designed to detect and identify any higher boiling volatiles given off upon heating the material to 700°C, and to see the effect, if any, of changing the initial sample heating in the pyroprobe upon the formation of these volatiles. To do this the GC oven was held at either −20 or −25°C while the sample was being heated in the pyroprobe, with the MS turned off. Any gaseous products (methane, ammonia, etc.) were swept out of the way while any less volatile material was condensed and collected at the head of the GC column. Once the pyrolysis run was complete, the MS was turned on and the GC oven ramped at 20°C/min to 230°C, in order to separate and detect any compounds collected. The sample data and pyroprobe conditions for all runs are given in Table I; this first series of experiments includes runs 1–4. For run 2 the GC oven lost low-temperature control so the pyroprobe run was stopped at that point, which was 650°C, and the experiment completed from there. Note that, in most cases, the samples were ramped at 10°C/min starting from either 400 or 450°C. This was done because, according to TGA data, at this heating rate the onset of sample weight loss does not occur until after 450°C. Prior to that an observed 2–3% weight loss is attributed to absorbed water.[16,17]

A typical total ion chromatogram (TIC) for one

Table I   Sample Information and Pyroprobe Heating Conditions for Pyroprobe–GC/MS Runs

Run	Initial Sample Weight (μg)	Initial Heating Conditions[a]	Heating Ramp (°C/min)	Final Temp. (°C)	Final Sample Weight (μg)	Weight Percent Lost
1	361	To 450°C	10	700	315	13
2	396	To 100°C then 50°C/min to 450°C	10	650	358	10
3	299	To 400°C	10	700	255	15
4	319	To 700°C then hold for 60 s	—	—	N/A	N/A
5	1234	To 400°C	10	700	1075	13
6	1742	To 400°C	10	900	1455	16
7	736	To 400°C	10	700	641	13
8	747	To 400°C	10	700	653	13
9	670	To 400°C	10	700	578	14
10	574	To 400°C	10	700	496	14
11	635	To 400°C	10	700	551	13
12	492	To 400°C	10	700	423	14
13	599	To 450°C	10	900	504	16
14	764	To 450°C	10	900	649	15

[a] These were accomplished by letting the probe heat as fast as it could to the desired temperature; the manufacturer does not give a heating rate for this operation, but the observation is that the desired temperature is achieved in 1 s or less.

of these runs is shown in Figure 1, along with identification of the compounds contained within the major peaks. The mass spectra of these compounds were compared with mass spectra of known samples of the compounds to confirm peak identification. It can be seen that the main compounds evolved from the samples are toluene, xylene, aniline, benzonitrile, m-methylaniline, and m-methylbenzonitrile. In the case of xylene the MS evidence was not conclusive enough to positively identify the meta isomer; however, from the structure of the starting material and the nature of the other volatiles, one would assume this is the isomer present. The other minor peaks in the TIC are due to either septum bleed or to very small amounts of other volatiles given off by the material. Some of these minor peaks have been identified as being 1,3-benzenedicarbonitrile, 3-aminobenzonitrile, aniline substituted with either two methyl groups or one ethyl/ethylene group, and benzene substituted with a total of four carbon/hydrogen moieties. Changing the conditions for the initial sample heating in the pyroprobe had no effect on the type of volatiles evolved, but did lead to some minor changes in the relative amounts of each compound. As noted in Table I, a final sample weight was not obtained for run 4. Upon removal from the pyroprobe, the sample fell apart, which is not sur-

prising due to the severe nature of heating. It is interesting to note that the same volatiles were detected in this run as in the slowly heated runs, despite the huge differences in sample heating rates.

The second series of experiments was designed to detect and identify lower boiling and gaseous volatiles given off upon heating the sample, to both 700 and 900°C. As in the previous case the GC oven was held at −20°C while the sample was heated in the pyroprobe; however, here the MS was left on during the probe heating (and for 5 min before and after probe run to obtain baseline measurements). The gaseous volatiles were detected as they came off the sample; the higher boiling volatiles were retained at the head of the GC column and were not analyzed. The sample data and pyroprobe conditions for these experiments (runs 5 and 6) are given in Table I. The larger sample sizes were necessary to ensure adequate amounts of volatiles for detection.

The TIC for run 6 is shown in Figure 2. In order to identify which products are coming off, selected ion chromatograms (ICs) are extracted from the TIC. Compounds detected include benzene (IC 78), ammonia (IC 17), methane (IC 15, chosen because in the mass spectrum of ammonia there can be a fairly intense peak at 16), and carbon dioxide (IC 44). For illustration the selected ICs for ammonia
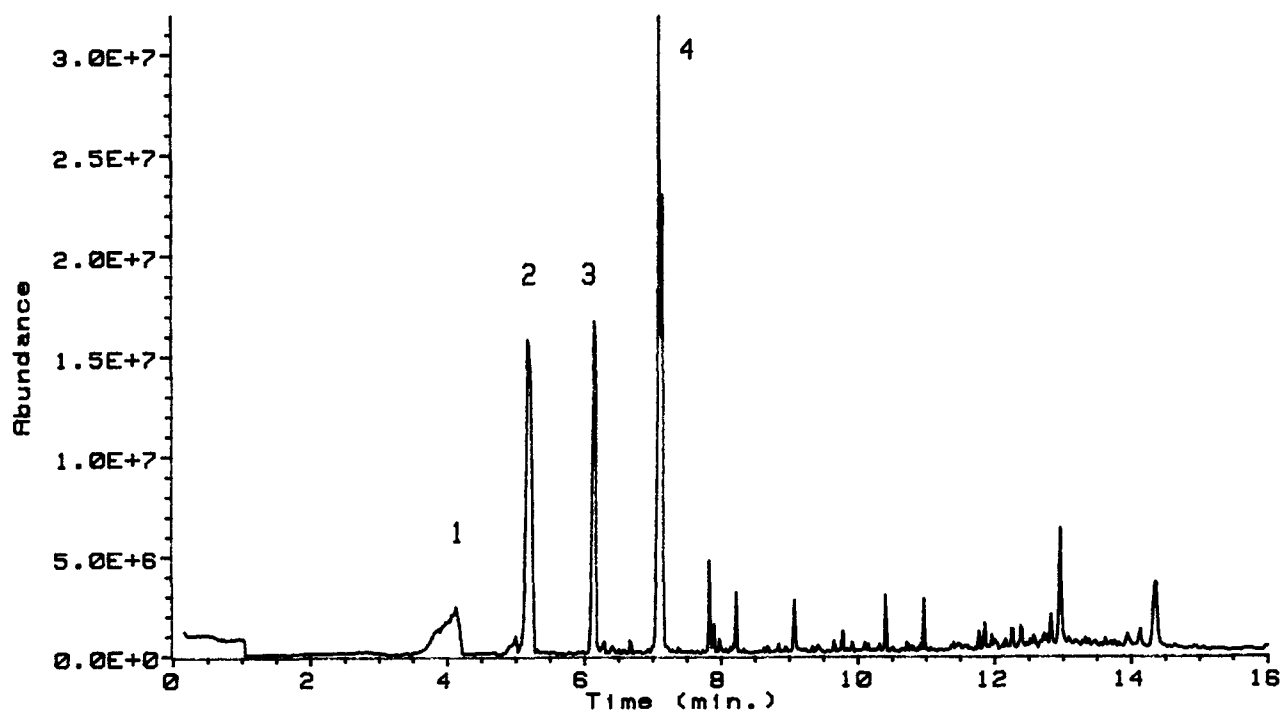

Figure 1 Total ion chromatogram (TIC) for run 2. Peak assignments: (1) toluene, (2) xylene, (3) aniline and benzonitrile, (4) m-methylaniline and m-methylbenzonitrile.
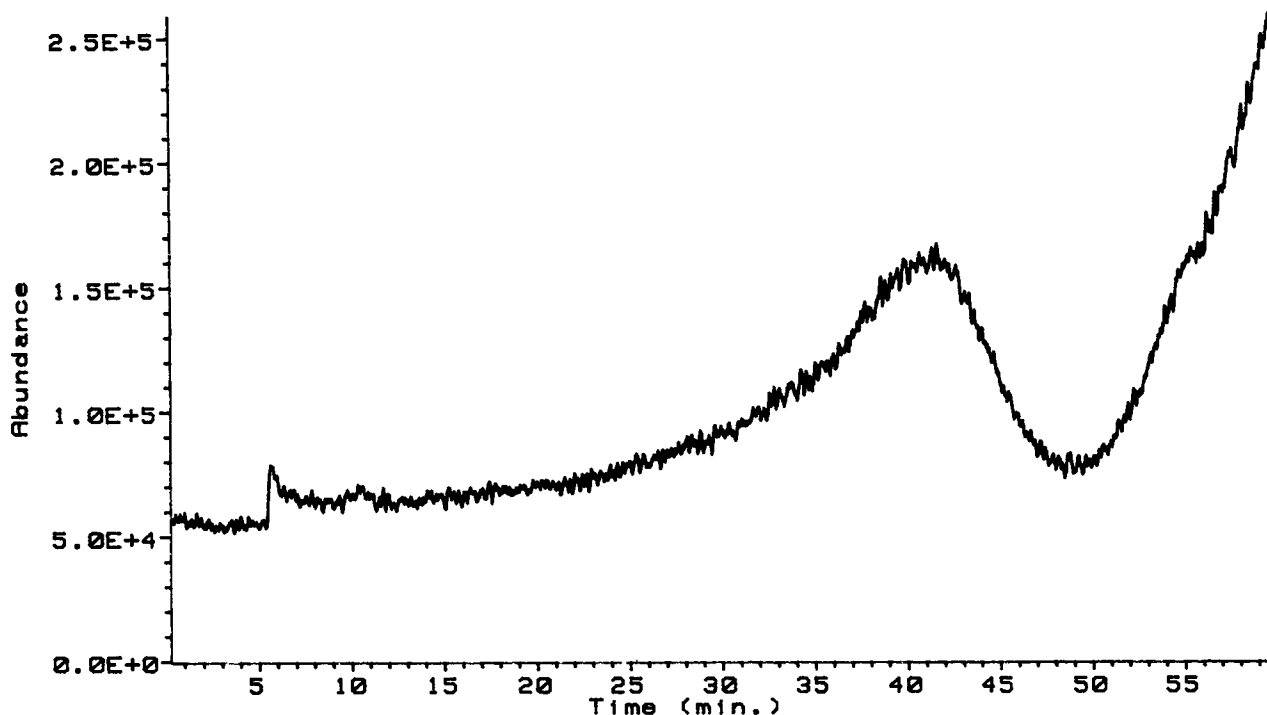
Figure 2 Total ion chromatogram (TIC) for run 6. First and last 5 min are baseline measurements with the pyroprobe turned off.

and methane are shown in Figures 3 and 4. There may also be a very small amount of ethylene (IC 28) present; the data was not conclusive enough to make a positive determination. Compounds for which there was no evidence include acetylene (IC 26), ethane (IC 30), and hydrogen cyanide (IC 27). The upswing at the end of the TIC in Figure 2 (above 48 min) is due to bleed of toluene (IC 92) through the system.

For the gaseous volatiles (NH_3, CH_4, and CO_2), one can directly correlate the time with the temperature of the sample, knowing the probe heating conditions and the retention times of these gases in the capillary column, which is equal to the retention time of air, 0.5 min. The data for onset, maximum, and end temperatures of evolution for these gases is given in Table II, along with the results by FT-IR from TGA. It can be seen from Figures 3 and 4 that at 900°C ammonia evolution, while dropping, is still occurring at a substantial rate as compared to methane evolution, which is nearly complete. The FT-IR data was obtained by periodically sampling the effluent TGA gases and assigning a relative intensity to the signal from the gases of interest. Overall, there is very good agreement between the two sets of data. Although the TGA/FT-IR method did not detect any of the higher boiling volatiles, it

worked very well on analyzing the relative amounts of gases. Since there is no oxygen in the polymer structure, it is assumed that the CO_2 detected arose from surface oxygen and/or CO_2 picked up by the sample during air cure. Supporting evidence can be seen in Table II—the CO_2 is quickly given off (peak onset and maximum temperatures are the same) and rapidly falls off after the initial heating surge.

The third series of experiments was designed to detect the higher boiling volatiles as they came off the samples and to correlate their formation with sample temperature (as with the gases in the previous experiments). In this case the GC oven was kept hot, being held at either 150 or 180°C, while the sample was heated in the pyroprobe; the MS was left on during the probe run (and for 5 min before and after for baseline measurements). The sample data and pyroprobe conditions for this set of experiments (runs 7–14) are given in Table I. Runs 8 and 13 were done with the GC oven at 180°C, the remainder at 150°C.

A typical TIC for one of the runs (run 8) is shown in Figure 5. In order to follow the evolution of each of the seven compounds (benzene, toluene, xylene, aniline, benzonitrile, m-methylaniline, and m-methylbenzonitrile) selected ICs must be extracted from the TIC, as was done in the previous gas anal-
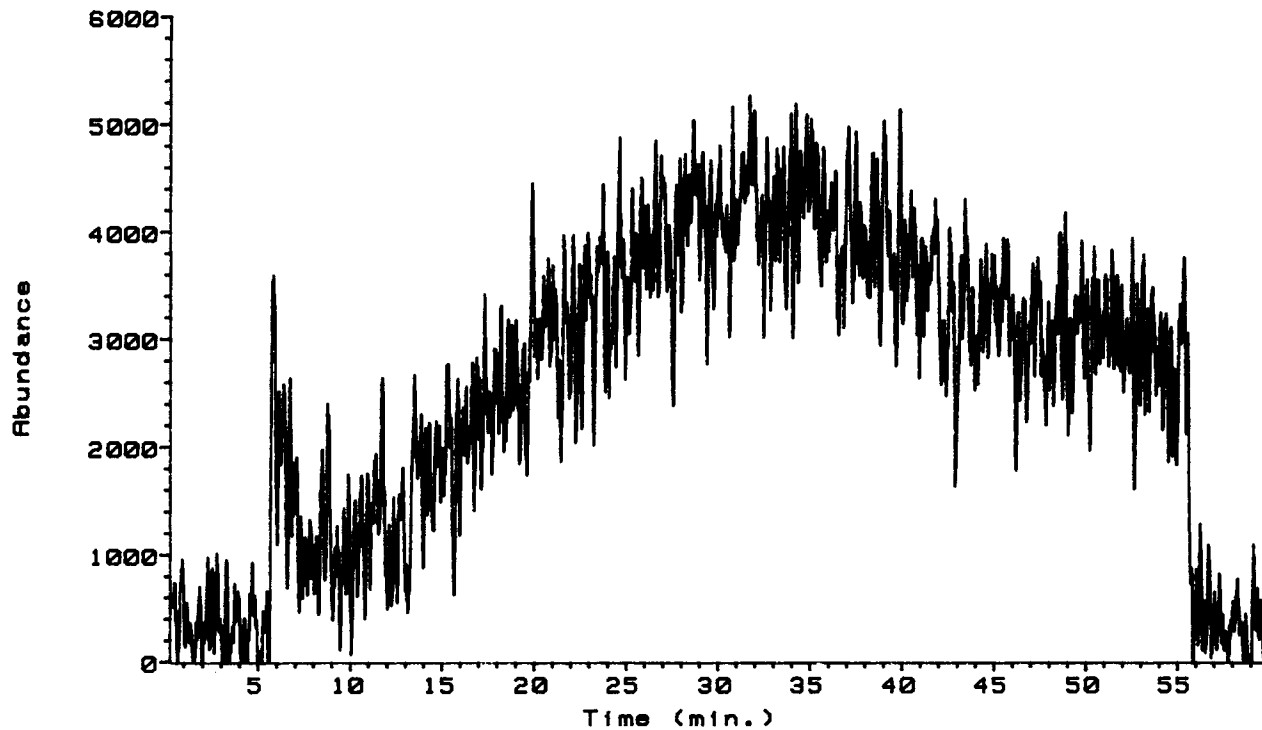
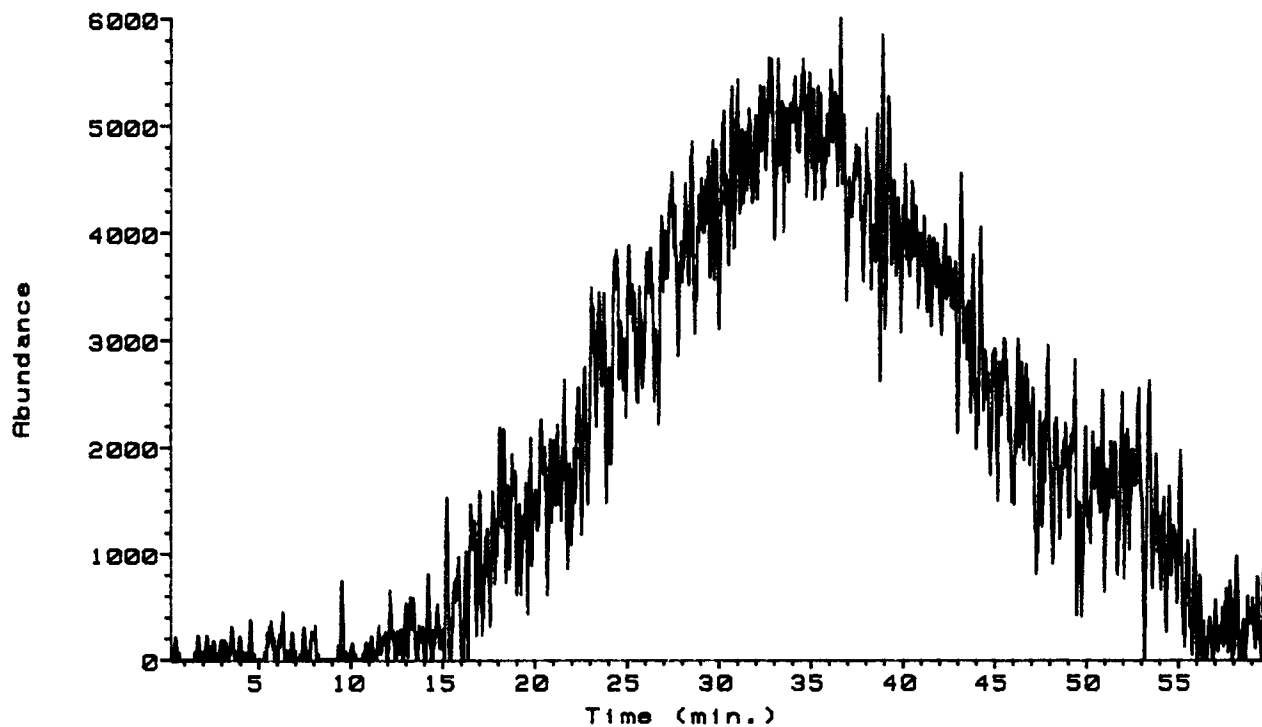**Figure 3**   Selected ion chromatogram (IC 17) from TIC in Figure 2 showing ammonia evolution.

Figure 4   Selected ion chromatogram (IC 15) from TIC in Figure 2 showing methane evolution.

Table II Results of Gas Evolution Studies

A. From Pyroprobe-GC/MS

Gas	Run	Peak Onset Temperature (°C)	Peak Maximum Temperature (°C)	Peak End Temperature (°C)
CH₄	5	510	680	> 700
(IC 15)	6	490	680	> 900
NH₃	5	450	670	> 700
(IC 17)	6	440	650	> 900
CO₂	5	400	400	450
(IC 44)	6	400	400	460

B. From TGA/FT-IR

Temperature (°C)	Relative Amounts		
	CH₄	NH₃	CO₂
450		Weak	Trace
500	Weak	Strong	
600	Strong	Strong, decreasing	
750	Strong, decreasing	Strong, decreasing	Trace

ysis. One must be careful in picking the proper ICs to monitor so that overlapping is not a problem. The IC chosen for each compound should be unique or present in another compound only to a few percent. By examining and comparing the mass spectra of all the pure compounds, it was determined that
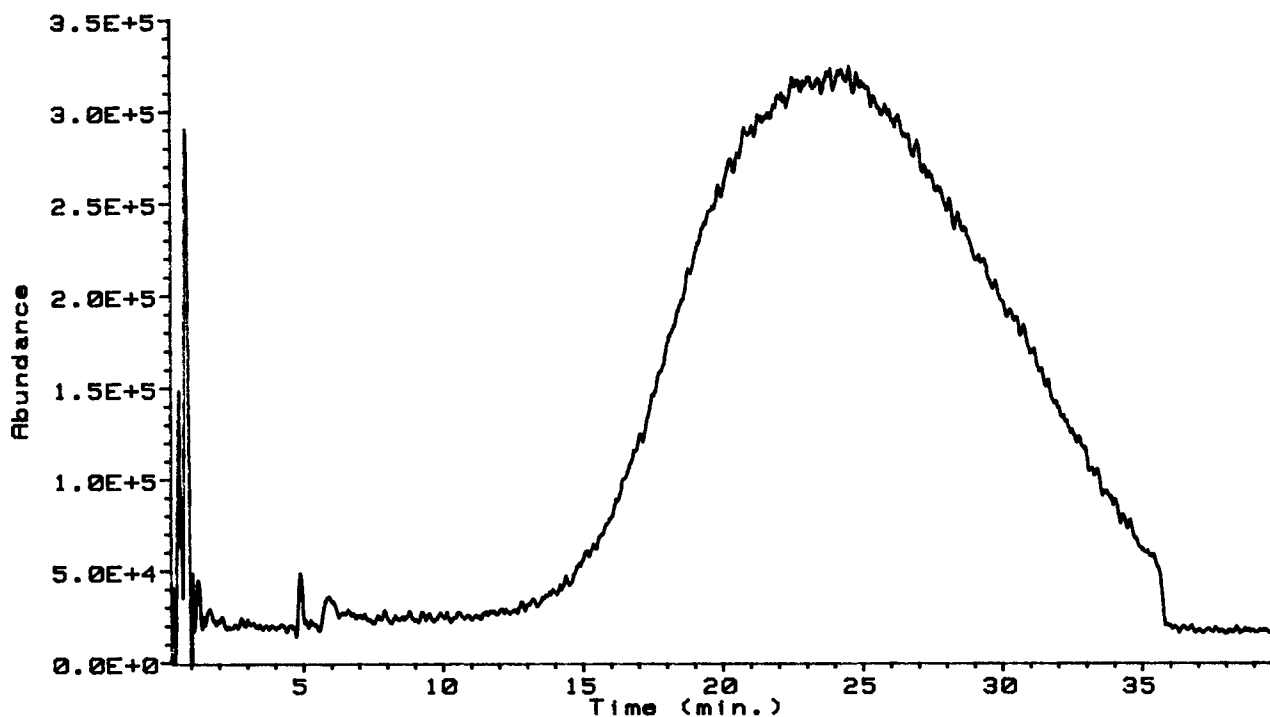

Figure 5 Total ion chromatogram (TIC) for run 8. First and last 5 min are baseline measurements with the pyroprobe turned off. Sharp peaks appearing from 0–5 min are septum bleed.

Table III   Results of Temperature Correlations for Evolution of Higher Boiling Volatiles

Compound (Selected IC Chosen)	Run	Peak Onset Temperature (°C)	Peak Maximum Temperature (°C)	Peak End Temperature (°C)
Benzene	Ave. 7–12	480	630	> 700
(IC 78)	Ave. 13–14	460	630	710
Toluene	Ave. 7–12	470	600	~ 700
(IC 92)	Ave. 13–14	450	590	680
Xylene	Ave. 7–12	480	550	640
(IC 105)	Ave. 13–14	460	550	640
Aniline	Ave. 7–12	460	600	~ 700
(IC 93)	Ave. 13–14	450	590	690
Benzonitrile	Ave. 7–12	480	590	~ 700
(IC 103)	Ave. 13–14	460	570	690
m-Methylaniline	Ave. 7–12	470	550	650
(IC 107)	Ave. 13–14	460	540	640
m-Methylbenzonitrile	Ave. 7–12	460	530	650
(IC 117)	Ave. 13–14	460	530	660

indeed there was a unique (or nearly so) IC for each, and these are given in Table III. For illustration the selected ICs for m-methylaniline (IC 107) and toluene (IC 92) from run 8 are shown in Figures 6 and 7.

In order to correlate time with sample temperature one needs to know the retention time of the higher boiling volatiles at the GC oven temperatures. Injection of small samples of the pure compounds into the GC/MS with the GC oven at 150 and 180°C led to the determination that the retention times are all between 0.5 and 1 min. To simplify calculations it was assumed all compounds had a retention time of 0.5 min—this will introduce a maximum er-
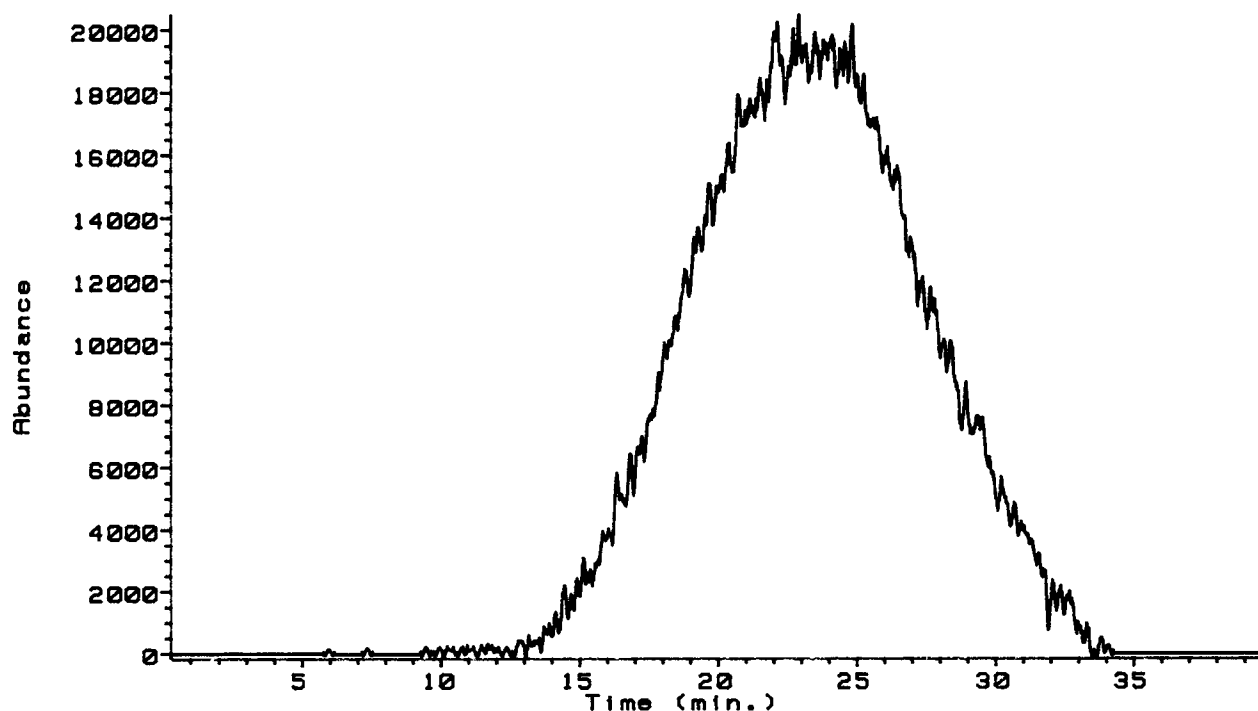

Figure 6   Selected ion chromatogram (IC 107) from TIC in Figure 5 showing m-methylaniline evolution.
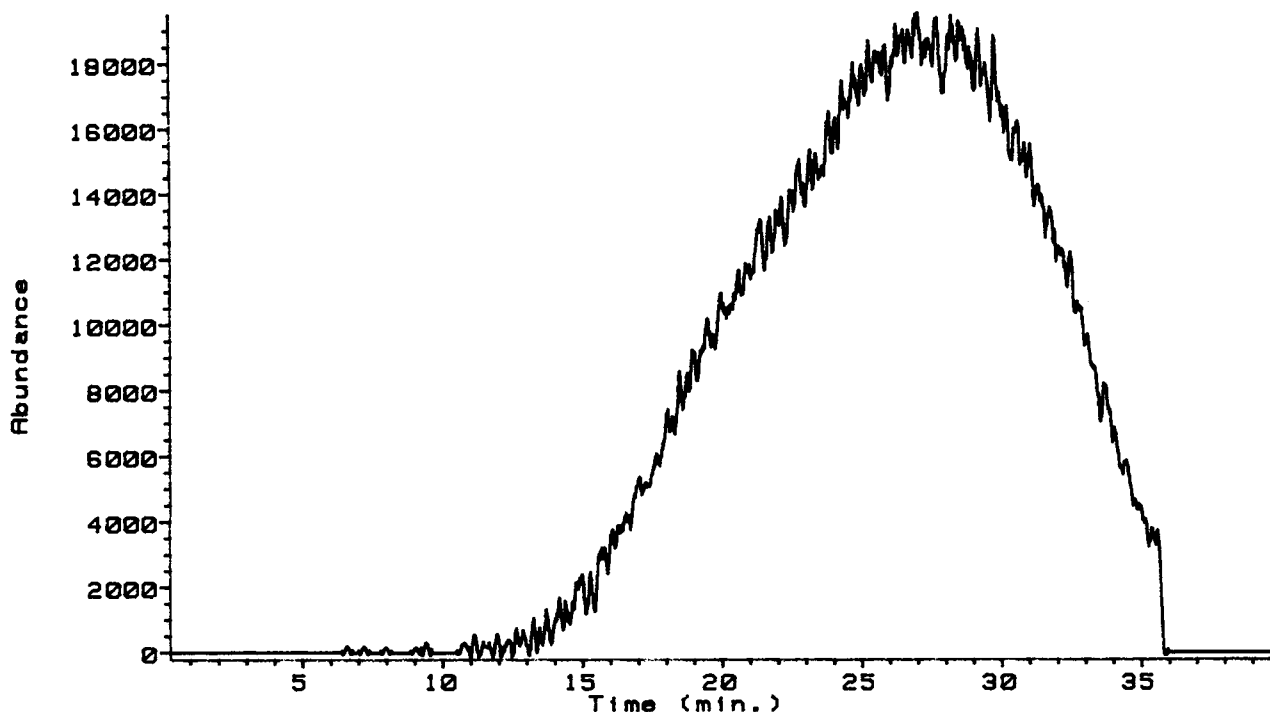
Figure 7   Selected ion chromatogram (IC 92) from TIC in Figure 5 showing toluene evolution.

ror of 5°C into the temperature correlations, which is well within experimental error. The data derived from the selected ICs for the onset, maximum, and end temperatures of evolution for these seven higher boiling volatiles is given in Table III, listed in the order of most to least volatile (based on compound boiling points). Runs 13 and 14 are listed separately from the others because of the different initial probe heating conditions and the higher final probe temperature (see Table I). Note that for some peak end temperatures ~ 700°C appears. In these cases at least one but not all of the runs showed the compound of interest still being evolved at 700°C. It was not possible to calculate an exact peak end temperature, thus the approximation.

The evolution of all these compounds starts in the 450–480°C range, which corresponds to the beginning of sample weight loss as measured by TGA.[17] The peak maximum and end temperatures do show trends, but not as they are listed, with compound volatility. The disubstituted benzene compounds (xylene, *m*-methylaniline, and *m*-methylbenzonitrile) peak in the 530–550°C range and end in the 640–660°C range, being the initial compounds to do so. The monosubstituted benzene compounds (toluene, aniline, and benzonitrile) peak later, in the 570–600°C range, and end later, in the 680– ~ 700°C

range. Benzene (no substitution) peaks the latest, 630°C, and ends latest, > 700°C.

TGA shows a decrease in the rate of weight loss with temperature at approximately 725°C.[17] This corresponds very well with the data obtained here that shows by slightly above 700°C the only higher boiling volatile still evolving is benzene, and that amount is rapidly diminishing. Much above 700°C only gases are being given off, which would lead to a slower weight loss rate. The percent weight losses measured by TGA at 700 and 900°C are 13 and 16%.[17] In this study nine runs went to 700°C (see Table I) with an average weight loss of 13.6%, and three runs went to 900°C with an average weight loss of 15.7%. Again, there is excellent agreement between the TGA data and the data obtained in this study.

CONCLUSIONS

The nitrogen-containing acetylene-terminated resin studied here shows promise as a high-temperature material for applications in composites or as a potential precursor for carbon. Thermally cured samples exhibit very good weight retention at high temperature, losing only 16 wt % at 900°C. The volatiles

that comprise this weight loss can be divided in two categories—gases and higher boiling volatiles. The major higher boiling volatiles have been identified as benzene, toluene, xylene, aniline, benzonitrile, *m*-methylaniline, and *m*-methylbenzonitrile; the gases evolved include ammonia, methane, and carbon dioxide (formed from oxygen and/or carbon dioxide adsorbed on the surface). Correlations have been made between sample temperature and the evolution of each of these compounds. It was found that the onset of evolution of all volatiles from the sample occurs between 450 and 500°C. The maximum and end of evolution temperatures increase in the order of disubstituted benzene compounds, monosubstituted benzene compounds, benzene, and gases. At 900°C only the gases (ammonia and methane) are still being evolved, but the relative amounts are decreasing. Currently we are attempting to extract quantitative data from these measurements in order to determine relative and absolute amounts of each compound evolved. This information will help determine the mechanism of high-temperature degradation of the polymer and lend insight into which moieties within the material are the most and least thermally stable.

This pyroprobe–GC/MS technique is currently being applied to other potential thermally stable polymeric systems in order to increase our database and understanding of how these materials break down upon exposure to high temperatures. Work is also in progress to determine the behavior of the material examined in this work as well as other materials at even higher temperatures (> 900°C) for the potential uses cited above.

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