

Analysis of Volatiles Evolved During High-Temperature Treatment of Thermally Stable Polymers. II. Polybutadiyne

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SYNOPSIS

Polybutadiyne samples were heated at 20°C/min up to 1200°C in a pyroprobe attached to a gas chromatograph/mass spectrometer (GC/MS). Analysis of the volatiles evolved during heating identified carbon dioxide (adsorbed on polymer surface), methane, ethylene, benzene, toluene, and traces of higher aromatics. Correlations have been made between sample temperature and evolution (onset, maximum, and end temperatures) of each of the five listed volatiles. Average polybutadiyne weight loss at 1200°C was $14 \pm 2\%$. Two cure studies were performed in the pyroprobe, and it was shown that both weight loss and volatile evolution were affected. The results were consistent with a higher degree of polymer cross-linking as cure time and temperature increased. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The area of high-temperature stable polymers is one of great interest, due to the many potential applications of such materials as lightweight replacements for metals and ceramics, new resins for composites, and new and improved precursors to both glassy and graphitic carbon. Many systems currently used possess the drawback of giving off substantial amounts of volatile compounds when subjected to high temperatures, leading to large weight losses, low carbon yields, void formation, excessive shrinkage, and loss of mechanical strength.¹

Our goal was to develop better materials for very high temperature applications through developing new polymers and polymeric precursor systems which are high in carbon content and give off a minimal amount of volatiles when heated. To assist our studies, we developed an analysis system consisting of a pyroprobe interfaced directly to a gas chromatograph/mass spectrometer (GC/MS) which can identify volatiles evolved from a material as it is heated, at any rate, up to 1400°C. This tool enables us to systematically examine many potential polymers and polymeric precursors to determine which

structures, types of polymers, functional groups, etc., are desirable when attempting to develop a superior high-temperature material.

In the first article of this series, we detailed the analysis of the volatiles evolved during high-temperature treatment of a nitrogen-containing acetylene-terminated resin using our pyroprobe/GC/MS system.² This study examines the volatiles evolved upon heating samples of polybutadiyne, a highly conjugated all carbon-hydrogen material. The polymer was synthesized via a thermal vapor-deposition polymerization of butadiyne.^{3,4} The material exhibits excellent thermal stability, losing less than 20% up to 1000°C. It shows promise as a coating for carbon fibers to promote adhesion to matrix resins in composites^{5,6} and has potential for high-temperature carbon-carbon composite applications.

EXPERIMENTAL

Sample Preparation

The vapor-phase thermal polymerization of butadiyne has previously been reported.^{3,4} The polybutadiyne used in this study was deposited onto Pyrex glass as a thin film, then lifted from the glass by treatment with concentrated hydrofluoric acid. For analyses, the black film (less than 1 mil thick) was crushed into very small flakes.

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Instrumentation

The polybutadiyne IR spectrum was obtained on a Perkin-Elmer 1800 Fourier transform infrared spectrophotometer using a horizontal attenuated total reflectance (ATR) cell (single beam, single ratio, 1000 scans). The differential scanning calorimetry (DSC) experiment was performed on a DuPont 910 differential scanning calorimeter controlled by a DuPont thermal analyst 2100 system. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermogravimetric analyzer (TGA 7) controlled by a Perkin-Elmer thermal analysis data station (TADS). Both DSC and TGA experiments were performed under nitrogen at a heating rate of 10°C/min.

Samples for pyroprobe-GC/MS analysis were weighed to the nearest ± 10 μg on a Mettler AE 163 balance. The pyrolysis unit used was a CDS Pyroprobe 2000 equipped with a temperature-controlled interface to the GC. The GC/MS system consisted of a Hewlett-Packard Model 5890 Series II gas chromatograph attached to a Hewlett-Packard Model 5971A mass selective detector; it was controlled by a Hewlett-Packard HP 59970 MS ChemStation. Further details on instrumentation can be found in the first article of the series.²

RESULTS AND DISCUSSION

Polymer Characterization

Prior to pyroprobe-GC/MS analysis, we needed to determine if our polybutadiyne sample, which was not freshly made and had been treated with hydrofluoric acid to remove it from the glass polymerization substrate, was the same in structure and behavior as previously analyzed, freshly made polybutadiyne. A previously obtained IR transmission spectrum (using complimentary polyethylene and Teflon-supported films) exhibited bands characteristic of terminal acetylenic and aromatic or olefinic groups.³ The IR reflectance spectrum obtained on our sample was extremely similar to the transmission IR spectrum, with the notable exception of two additional peaks in the 2300–2400 cm^{-1} range; we attributed them to CO_2 (Ref. 7) which had adsorbed onto the surface of the polymer film with time. We have seen this same effect of CO_2 adsorption on other samples²; pyroprobe-GC/MS analysis will be able to confirm the presence of adsorbed CO_2 . Also, an experiment was performed where a bulk polybutadiyne sample exposed to air was heated rapidly in an evacuated IR cell: Methane and carbon dioxide were de-

tected, again indicating the presence of surface-adsorbed CO_2 , since there is no oxygen in the polymer itself.³ Previous TGA results (on a DuPont 951 thermogravimetric analyzer, under N_2 , 10°C/min heating rate) showed onset of an appreciable weight loss around 470°C, with 10 and 20% weight losses at 800 and 1100°C, respectively.³ Our results, under the same conditions but on a different apparatus, showed onset of an appreciable weight loss around 400°C and a 14% weight loss at 800°C, which is within experimental error.

The exact structure of this vapor-deposited polybutadiyne is not known, but IR results indicate that terminal acetylenic groups are present. Efforts had previously been made to thermally polymerize these groups in an attempt to form a crosslinked, more stable material.³ DSC results of polybutadiyne vapor deposited onto thin films of polyethylene, poly(vinylidene fluoride), polytetrafluoroethylene, and poly(tetrafluoroethylene-co-hexafluoropropylene) showed that a thermally induced exotherm did occur, but the specific details of the exotherm (onset and maximum temperatures, shape of peak) were not clear due to the interfering melting points of the polymer support films.⁴ If the exact exotherm reaction profile is known, one can design curing experiments for the polybutadiyne which will ensure that an optimal level of crosslinking is being achieved.

DSC results for bulk vapor-deposited polybutadiyne have not been previously reported. We analyzed our unsupported polybutadiyne film by DSC, and the results are shown in Figure 1. No melting endotherms are observed up to 450°C; this is in agreement with X-ray diffraction results which showed no crystalline reflections.³ The onset of the acetylene reaction exothermic peak occurs around 120°C. The peak rises rapidly up to 200°C, then continues to rise at a lower rate until it peaks around 400°C, followed by a rapid decrease up to 450°C. Therefore, a curing experiment would best be carried out at a temperature between 200 and 400°C, where there is appreciable acetylene reaction occurring without substantial weight loss (as measured by TGA).

Pyroprobe-GC/MS Results

The first series of pyroprobe-GC/MS experiments was designed to detect and identify all volatiles given off upon heating the polybutadiyne to 1200°C. To accomplish this, the GC oven was held at either 30 or 35°C, while the sample was heated in the pyroprobe at 20°C/min from 300 to 1200°C. The MS

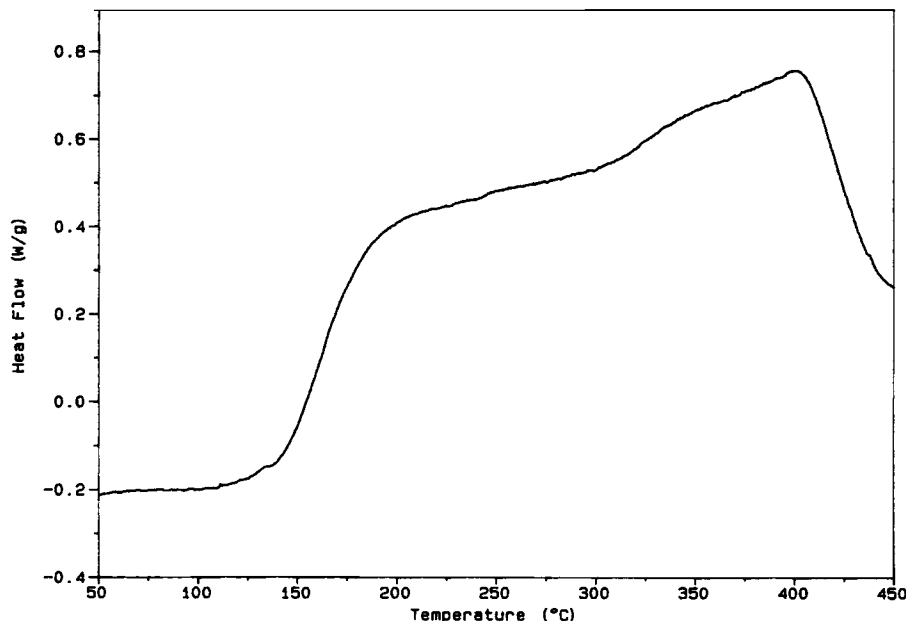


Figure 1 DSC results for unsupported polybutadiyne film.

was turned on 1 min prior to the pyroprobe to obtain a base-line measurement. Any low boiling volatiles or gases were detected as they came off the sample; higher boiling volatiles were retained at the head of the GC column. Once the pyroprobe run was completed, the GC oven was ramped at 20°C/min to 240°C to separate and detect any higher boiling compounds collected.

Three runs were performed, with sample weights of 1040, 1410, and 3220 μg . The average weight loss at 1200°C was $14 \pm 2\%$, which is smaller than the weight losses measured by TGA. This is most probably a physical sample loss effect. The polybutadiyne film is extremely thin and lightweight; for analyses, the material is crushed, leading to fine, almost dust-like particles. In the pyroprobe, the sample is held in a quartz glass tube between two plugs of quartz glass wool—there is no way to physically lose any of the sample. In both TGA apparatuses, the sample is loaded onto an open pan which is enclosed in a chamber with a slow steady flow of gas (in this case, nitrogen). One can envision some of the sample being “lost” by the nitrogen flow physically blowing the fine particles out of the pan. If one looks closely at the TGA tracings, it appears as if there is a very slight downward slope to the lines, which could indicate a very slow steady weight loss as described above. Therefore, the weight losses measured on the pyroprobe-GC/MS samples are probably more accurate for assessing the thermally induced volatile weight loss.

The total ion chromatogram (TIC) for a typical run is shown in Figures 2 and 3. Figure 2 depicts the portion of the TIC where low boiling volatiles and gases were detected as they came off the sample. Figure 3 shows the portion of the TIC where higher boiling compounds were eluted and detected upon heating the GC oven. The four peaks due to compounds evolved from the polybutadiyne are marked; the remainder are extraneous peaks, mostly due to septum bleed. These higher boiling compound peaks are very small—they are about an order of magnitude smaller than one would expect based on pyrolysis results of other systems.^{2,3} Note that the peaks eluting between 56 and 58 min are due to septum bleed; the compound peaks are generally of the same size, illustrating the small amounts of these compounds present. Therefore, the amounts of these compounds being evolved from polybutadiyne are very low, and they most probably account for only a small portion of the total amount of volatiles.

The compounds composing the four numbered peaks in Figure 3 were identified. The mass spectra (MS) were compared with the MS of known samples to facilitate peak identification. Peak 1 is naphthalene and peak 2 is methylnaphthalene (MS evidence not conclusive enough to positively identify the 1- or 2-isomer). The MS of peak 3 is similar, but not identical, to that of acenaphthalene, indicating that the eluting compound is probably an “acenaphthalenelike” fragment which has split off the sample. Peak 4 is either anthracene or phenanthrene; the

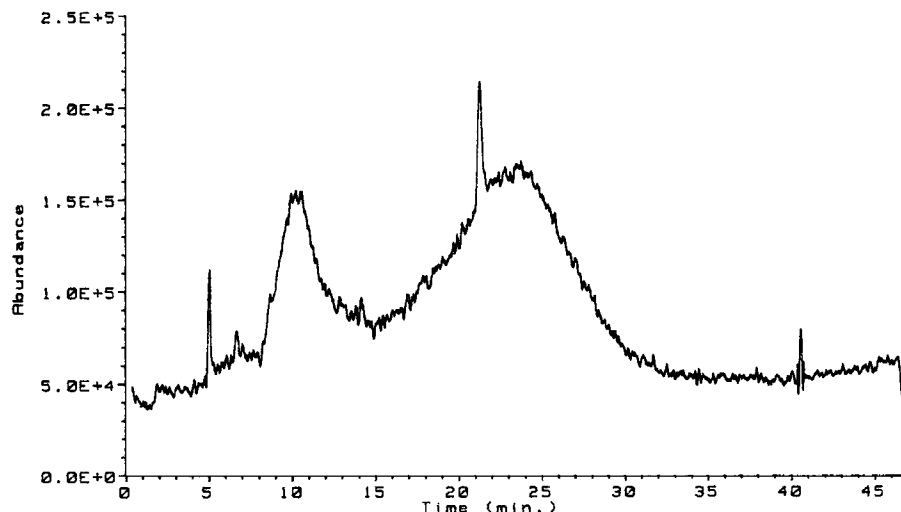


Figure 2 Total ion chromatogram (TIC) for a typical run showing evolution of lower boiling volatiles and gases as they come off the sample. First and last 1 min are base-line measurements with the pyroprobe turned off.

MS data are not conclusive, but there is a slightly better match to anthracene.

To identify which gases and low boiling compounds are coming off the sample (portion of the TIC shown in Fig. 2), selected ion chromatograms (ICs) are extracted from the TIC. Compounds detected include toluene (IC 92), benzene (IC 78), ethylene (IC 27), methane (IC 15), and carbon dioxide (IC 44). For illustration, the selected ICs for benzene and methane are shown in Figures 4 and 5. For these volatiles, one can directly correlate the retention time with the temperature of the sample, knowing the probe heating conditions (given above) and the retention times of each compound in the capillary column at the preset oven temperature. For the gases (ethylene, methane, and carbon dioxide), the retention times at both 30 and 35°C are equal to the retention time of air, 0.5 min. The retention time for benzene at both 30 and 35°C is 1.5 min, while the retention times for toluene at 30 and 35°C are 3.5 and 3.0 min, respectively. The data derived from the selected ICs for the onset, maximum, and end temperatures of evolution for these volatiles are given in Table I. Each data point is the average temperature of three runs, rounded to the nearest 10°C.

The onset of appreciable weight loss as measured by TGA is in the 400–470°C range; this falls between the lower-temperature onset of evolution of the light gases, ethylene and methane, and the higher-temperature onset of evolution of the heavier volatiles, toluene and benzene. The light gases also reach a peak maximum at a lower temperature than do the heavier volatiles, but the difference between the two

is much smaller. The peak end temperatures do not follow this same pattern; the end of evolution is in the order of toluene, ethylene, benzene, then methane. There does appear to be a correlation between compound volatility and the entire range of gas evolution (peak end temperature minus peak onset temperature). The ranges for toluene, benzene, ethylene, and methane (listed in increasing order of volatility) are 220, 430, 560, and 730°C. The carbon dioxide data is consistent with previous results for samples with adsorbed CO₂ (Ref. 2)—an initial rapid surge of CO₂ upon heating the sample, peaking around 400°C, followed by a very sharp 50–60°C decrease of CO₂ evolution to zero.

Two postpolymerization cure studies were performed in the pyroprobe, to see how any thermally induced acetylenic crosslinking would affect the volatiles evolved. For these cure studies, only the lighter compounds (toluene, benzene, ethylene, methane, and carbon dioxide) were monitored. In the first study, a polybutadiyne sample (3530 μg) was cured in the pyroprobe at 325°C for 1 h. This temperature was chosen since it is the highest temperature at which the polymer can be thermally crosslinked without appreciable volatile evolution (not including desorption of CO₂). The GC/MS was turned on during the cure, to monitor any volatiles which might evolve and be detectable.

During the cure, the polybutadiyne sample lost 4% by weight. The only compound detected by the MS was CO₂; it all desorbed during the course of the cure (in the first 16 min). Within detection limits, no other volatiles were observed. The same sample

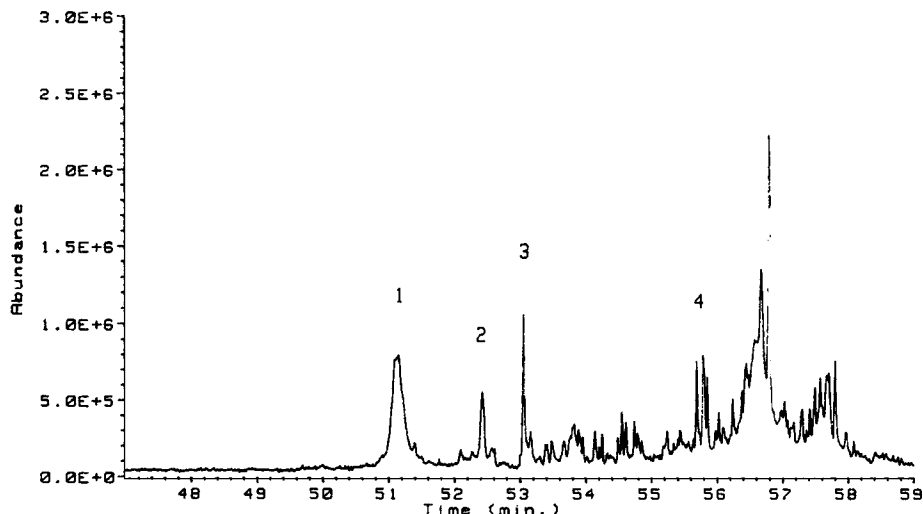


Figure 3 Total ion chromatogram (TIC) for a typical run showing the evolved high boiling volatiles after GC separation. Peak assignments: (1) naphthalene; (2) methylnaphthalene; (3) "acenaphthalenelike" fragment; (4) anthracene or phenanthrene.

was then heated in the pyroprobe as were the others, 300–1200°C at 20°C/min, and the volatiles monitored by GC/MS. As expected, during this run, no CO₂ evolution was detected. The weight loss during this step was 9%, for an overall weight loss of 13% (same as for the other runs with no curing step). The same four volatiles were detected—toluene, benzene, ethylene, and methane. Their evolution was correlated with sample temperature, as before. These results are given in Table II(A). The evolution of toluene is unaffected; the onset of evolution of benzene is delayed 80°C, but the peak maximum and peak end temperatures are unchanged. For both

ethylene and methane, the range of evolution is compressed; both have a higher peak onset temperature and a lower peak end temperature. Thus, during just the 300–1200°C heating cycle after 325°C/1 h cure, less weight was lost than with no cure and evolution of the lightest volatiles was affected most.

To determine if curing could cause a larger effect on the volatiles evolved, a second multistep cure was performed on a polybutadiyne sample. The sample (4180 μg) was cured in the pyroprobe as follows: heated to 100°C, ramped 10°C/min to 200°C, held for 1 h, ramped 10°C/min to 300°C, held for 1 h, ramped 10°C/min to 400°C, and held

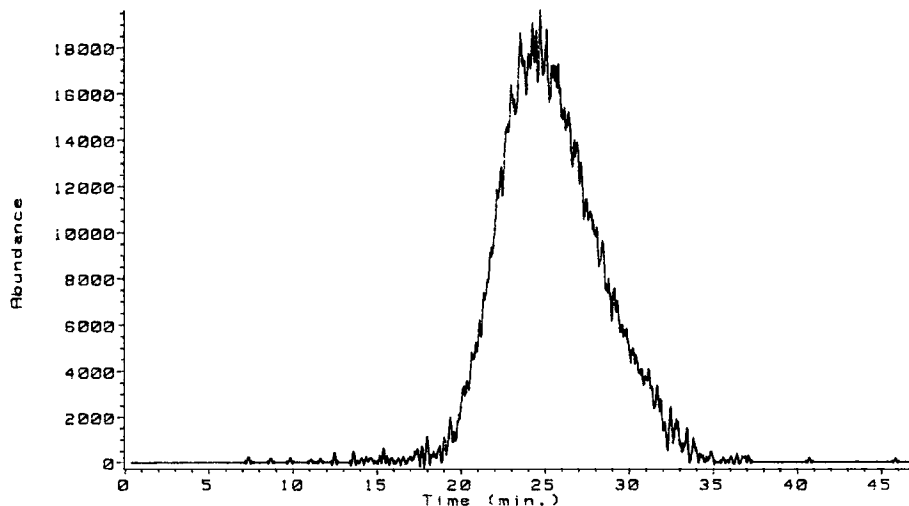


Figure 4 Selected ion chromatogram (IC 78) from TIC in Figure 2 showing benzene evolution.

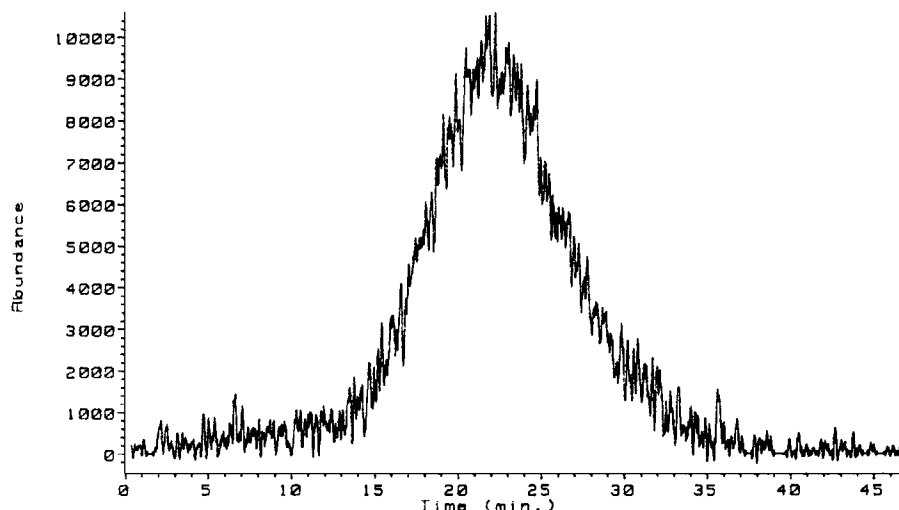


Figure 5 Selected ion chromatogram (IC 15) from TIC in Figure 2 showing methane evolution.

for 1 h. These cure conditions, which involve a longer cure time (3.5 h vs. 1 h) and a higher ultimate cure temperature (400 vs. 325°C), will allow the acetylene groups to react to a greater extent and should lead to a more thermally stable, more highly crosslinked material. The GC/MS was turned on only during the final cure steps (10°C/min from 300 to 400°C, then held for 1 h). Based on the results of the previous cure study, it was assumed that the only volatile evolved from the sample prior to these steps was adsorbed CO₂.

During the multistep cure, the sample lost 9% by weight. The GC/MS results for the final cure steps show that only a trace of toluene and benzene are evolved while heating to and holding at 400°C. Some ethylene is present; most of it is evolved during the first 20 min at 400°C. Methane evolution begins in the 300–330°C range and is continuous during the entire 400°C cure; it begins to taper off in the last 5–10 min at 400°C. Thus, the bulk of the sample weight loss comprises adsorbed CO₂, ethylene, and

methane, with methane evolution being the most prominent.

Next, this sample was heated in the pyroprobe as were the others—300–1200°C at 20°C/min—with the GC/MS monitoring volatile evolution. The weight loss during this step was 6%, with an overall weight loss of 15%. Again, curing causes the weight loss during the final heating to 1200°C to decrease, but it has no effect on overall sample weight loss. The same four volatiles as before were detected and their evolutions correlated with sample temperature. The results appear in Table II(B). For benzene and toluene, the peak maximum and end temperatures are lower, leading to a smaller temperature range of evolution (as compared to the uncured material). For ethylene and methane, the peak onset temperatures are higher while the peak maximum and end temperatures are lower, leading to an even more compressed range of evolution. This behavior is consistent with crosslinking of the polybutadiyne to a more thermally stable structure, leading to less

Table I Results of Gas Evolution Studies (Average of Three Runs)

Gas	Peak Onset Temperature (°C)	Peak Maximum Temperature (°C)	Peak End Temperature (°C)
Toluene (IC 92)	610	720	830
Benzene (IC 78)	530	730	960
Ethylene (IC 27)	370	680	930
Methane (IC 15)	330	690	1060
Carbon dioxide (IC 44)	300	410	460

volatile evolution over a narrower temperature range. These effects are much more pronounced for the second longer multistep cure at a higher ultimate temperature than for the first 325°C/1 h cure, which is consistent with a higher degree of crosslinking during the multistep cure.

There is a consistency of the volatile species identified in this study with what is known of the polybutadiyne structure. Based on spectroscopic and thermal characterization, the polybutadiyne structure has been analyzed as comprising sequences of polyene (I) and polyacene (II) with significant quantities of pendant terminal acetylenic groups,³ as shown in Figure 6. Thermal treatment causes the disappearance of the terminal acetylenic groups, and analysis indicates formation of more polyacene and/or an intermolecular trimerization to a trisubstituted benzene structure.^{3,4} The aromatic volatile species (fused and single-ring structures) observed in this study are consistent with a thermal cracking of this polybutadiyne structure. The evolution of methane (detected both in this study and in a previous pyrolysis/IR study³) from such a hydrogen-deficient polymer is remarkable. There is precedent for the thermal evolution of methane from acetylenic polymers,⁹ although the mechanism is not understood.

CONCLUSIONS

Polybutadiyne is an interesting high-temperature stable material, potentially useful in composite and encapsulation applications. Upon heating, the polymer weight loss, as measured on pyroprobe samples, averages 14% at 1200°C. Pyroprobe-GC/MS studies

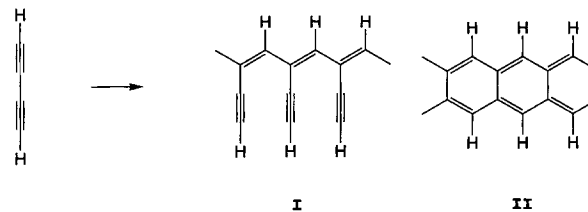


Figure 6 Proposed polyene (I) and polyacene (II) structural units of polybutadiyne.

shows that this weight loss comprises mostly adsorbed CO₂, methane, ethylene, benzene, and toluene; very small amounts of higher aromatics are also detected. Correlations have been made between sample temperature and the evolution of these gases and low boiling compounds, with the onset, maximum, and end of evolution temperatures for each volatile tabulated.

DSC shows that, upon heating, even in the solid state, there are thermally induced acetylene reactions occurring, as evidenced by the presence of an exotherm. Postpolymerization cure studies in the pyroprobe, with GC/MS analysis of the volatiles evolved both during and after cure, confirm that the material crosslinks. The weight loss during sample heating to 1200°C (after cure) decreases as the time and temperature of cure increases. The evolution of the gases and low boiling volatiles is affected greatly by the cure. In general, curing causes a smaller range of evolution of a given compound (higher onset and/or lower end of evolution temperatures), with the effect being greater for a longer-time, higher-temperature cure.

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Table II Results of Gas Evolution Studies on Samples After Cure

Gas	Peak Onset Temperature (°C)	Peak Maximum Temperature (°C)	Peak End Temperature (°C)
(A) After 325°C/1 h cure			
Toluene	620	710	840
Benzene	610	730	970
Ethylene	490	690	870
Methane	470	730	1010
(B) After multistep cure			
Toluene	590	640	770
Benzene	520	680	930
Ethylene	460	640	870
Methane	450	660	980

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