SECURITY CLASSIFICATION OF THIS PAGE

AD-A280 447

REP

1a. REPORT SECURITY CLASSIFICATION

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AEOSR-TR- 94 0364

6a. NAME OF PERFORMING ORGANIZATION
Pennsylvania State Univ

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NL

6c. ADDRESS (City, State and ZIP Code)
110 Technology Center
University Park, PA 16802

7b. ADDRESS (City, State and ZIP Code)
110 Duncan Ave Suite B115
Bolling AFB DC 20332-0001

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
AFOSR/

8b. OFFICE SYMBOL (If applicable)
NL

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F49620-93-1-0311

8c. ADDRESS (City, State and ZIP Code)
110 Duncan Avenue Suite 8115
Bolling AFB, DC 20332-0001

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61103D	3484	CS	

11. TITLE (Include Security Classification) (MURI) Basic Solutions to Carbon/Carbon Oxidation: Science & Technology

12. PERSONAL AUTHOR(S)
Ian R. Harrison, T-C Chung, Ljubisa Radovic, Carlo Pantano, Peter A. Thrower

13a. TYPE OF REPORT
Annual Technical

13b. TIME COVERED
FROM 4/15/93 TO 4/14/94

14. DATE OF REPORT (Yr., Mo., Day)
1994,5,13

15. PAGE COUNT
47

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

SEE ATTACHED

DTIC
ELECTE
JUN 21 1994
S G D

498

94-18976

DTIC QUALITY INSPECTED 2

94 6 20 093

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Ian R. Harrison / Maj Erstfeld

22b. TELEPHONE NUMBER (Include Area Code)
(814) 865-3130
202 767-5021

22c. OFFICE SYMBOL
NL

DD FORM 1473, 83 APR

EDITION OF 1 JAN 73 IS OBSOLETE.

SECURITY CLASSIFICATION OF THIS PAGE

AEOSR-TR- 94 0364

AF #F49620-93-1-0311

Basic Solutions to Carbon/Carbon Oxidation: Science and Technology

1993-94 Annual Report
Abstract

The attached report addresses the first year of a program aimed at developing basic solutions to carbon/carbon composite oxidation. In particular, one primary thrust is the development of boron containing carbons through pyrolysis of boron containing polymers. Additionally, a basic understanding of the oxidation mechanisms in carbons and boron containing carbons is being sought.

Several new boron containing precursors have been synthesized, which can be converted to B/C materials after pyrolysis. In particular, polyacrylonitrile (PAN) has been copolymerized with a boron-containing monomer (vinylcatecholborane.) Approximately 68% of the original boron is retained after pyrolysis yielding a product with 3.4% boron. 1,4-polybutadiene (PBD) has been hydroborated to contain large amounts of boron. Model compounds have been used to prepare polydiyne with considerable amounts of boron. In the latter two cases, direct analysis for % boron is not yet available. Preliminary TGA data suggests that PBD containing boron results in a more stable structure.

An apparatus has been designed, built and tested for the production of fibers from small quantities of material (5 gm.) In particular, a dry-jet wet spinning apparatus was used to produce fibers from Courtelle's special acrylic fiber (SAF) precursor. Penn State fibers in an undrawn state are comparable to commercial SAF fibers. DSC/TGA have been used to examine the stability of fibers produced from various solvents. Similarly, a small scale apparatus for production of pitch-based fibers has been developed and is operational.

We have developed the capability to fabricate boron-doped carbons using boron implantation in carbons and chemical vapor deposition of $B_x C_{(1-x)}$.) Surfaces of implanted materials (HOPG and vitreous carbon) were examined by SEM and exhibited microcracking. Annealing in Argon at 2300°C caused the depth profile of boron (SIMS) to change dramatically. These boron-doped or CVD materials will be used as standards for films, fibers and bulk materials, which result from earlier synthesis and processing routes described earlier.

In anticipation of analysis of B/C carbons prepared by PSU investigators, boron containing chars were obtained from Aerospace Corporation. Preliminary non-isothermal TGA suggests that boron does not inhibit the early stages of oxidation. However, in these samples, little is known of the chemical form of the boron used.

Attempts have been made to model the oxidation process using an existing HMO-based computer program. Early results suggest that in the presence of boron C-C bonds, at edge carbon atoms are weakened; while C-O bonds are strengthened. Experimental tests of theoretical prediction are planned.

☒
☐
☐
Justification ....
By ....
Distribution /

Availability Codes	
Dist	Avail and / or Special
A-1	

AF # F49620-93-1-0311

Basic Solutions to Carbon/Carbon Oxidation: Science and Technology

1993-94 Annual Report
April 15, 1993 - April 14, 1994

Dr. Ian R. Harrison
Dr. M-C. Chung
Dr. Carlo Pantano
Dr. Ljubisa Radovic
Dr. Peter Thrower

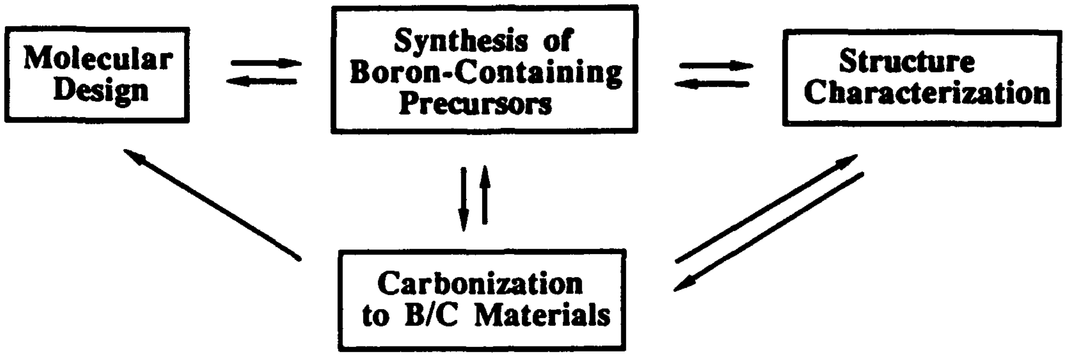
The Pennsylvania State University
325 Steidle Building
University Park, PA 16802

TABLE OF CONTENTS

Dr. T. C. Chung

Task 1. Synthesis of Boron Containing Polymers as B/C Precursors

The first year of our research has been a challenging and productive one. Progress has been made in several significant areas of synthesis for B/C high oxidative stable materials. Overall, exploratory activities have focused on synthesis of boron-containing precursors which may be converted to B/C materials after the carbonation process. The working scheme is illustrated below:



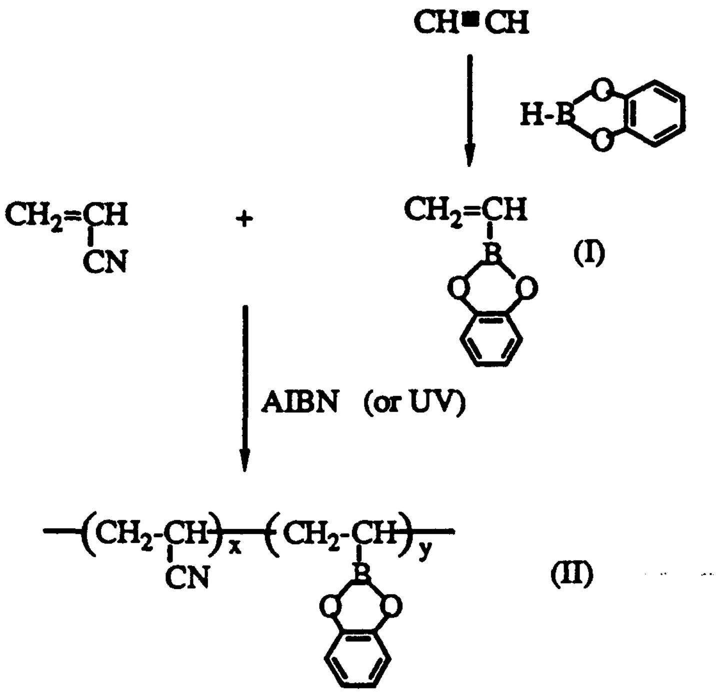
Relationships among molecular design, synthesis, characterization and evaluation of carbonation have been constantly evaluated and synthetic routes modified in our search for ideal boron containing precursors and carbonation conditions. The ideal B/C precursors should have three important characteristics: - (1) processable by convention methods, solution and/or melting, (2) integration of boron into the graphitic matrix during carbonation and (3) high yield of both carbon and boron with the minimum of gaseous byproduct during pyrolysis.

Our synthesis work has focused on three potential B/C precursors based on polyacrylonitrile (PAN), 1,4-polybutadiene and polydyne backbones. The chemistry necessary to introduce boron into those polymers has been developed. We currently have a great deal of understanding regarding the reaction mechanism and subsequent control of the reaction process. Selected products were characterized and evaluated by pyrolysis.

(A) PAN Containing Boron

Polyacrylonitrile (PAN) is a traditional precursor for carbon fibre. The role of PAN containing boron in the carbonation process is a challenging and complex one, especially with regard to yield and chemical structure of boron in B/C product. This study provides valuable information on the role of boron and the boron moiety, which is effectively incorporated into the carbon structure.

PAN containing boron is a new material and the logical synthesis route is by copolymerization of acrylonitrile and boron containing monomers. Unfortunately, most alkylborane moieties readily react with the free radicals used during PAN synthesis. To avoid potential side reactions, we used a protecting group, the catechol ligand, in boron containing monomers. Equation 1 illustrates the reaction scheme in the preparation of a boron containing monomer, namely vinylcatecholborane, which can be copolymerized with acrylonitrile monomers in free radical copolymerization reactions.



Equation 1

(a) Synthesis of Boron Containing Monomer - Vinylcatecholborane

Several routes were tried to prepare vinylcatecholborane (I). The Grigard reaction between vinylmagnesium chloride and chlorodialkylborane has an unsatisfactory yield due to complex formation. However, the reaction involving acetylene and catecholborane offers high yield (>70%) and convenient process conditions. In fact, this route can be easily scaled-up to large scale production. The reaction was carried in a pressure reactor by mixing acetylene gas (with an acetone stabilizer) and catecholborane in toluene at 70°C for 1 hour; vinylcatecholborane was obtained by distillation. Apparently, the addition reaction selectively stops at the mono-hydroboration step.

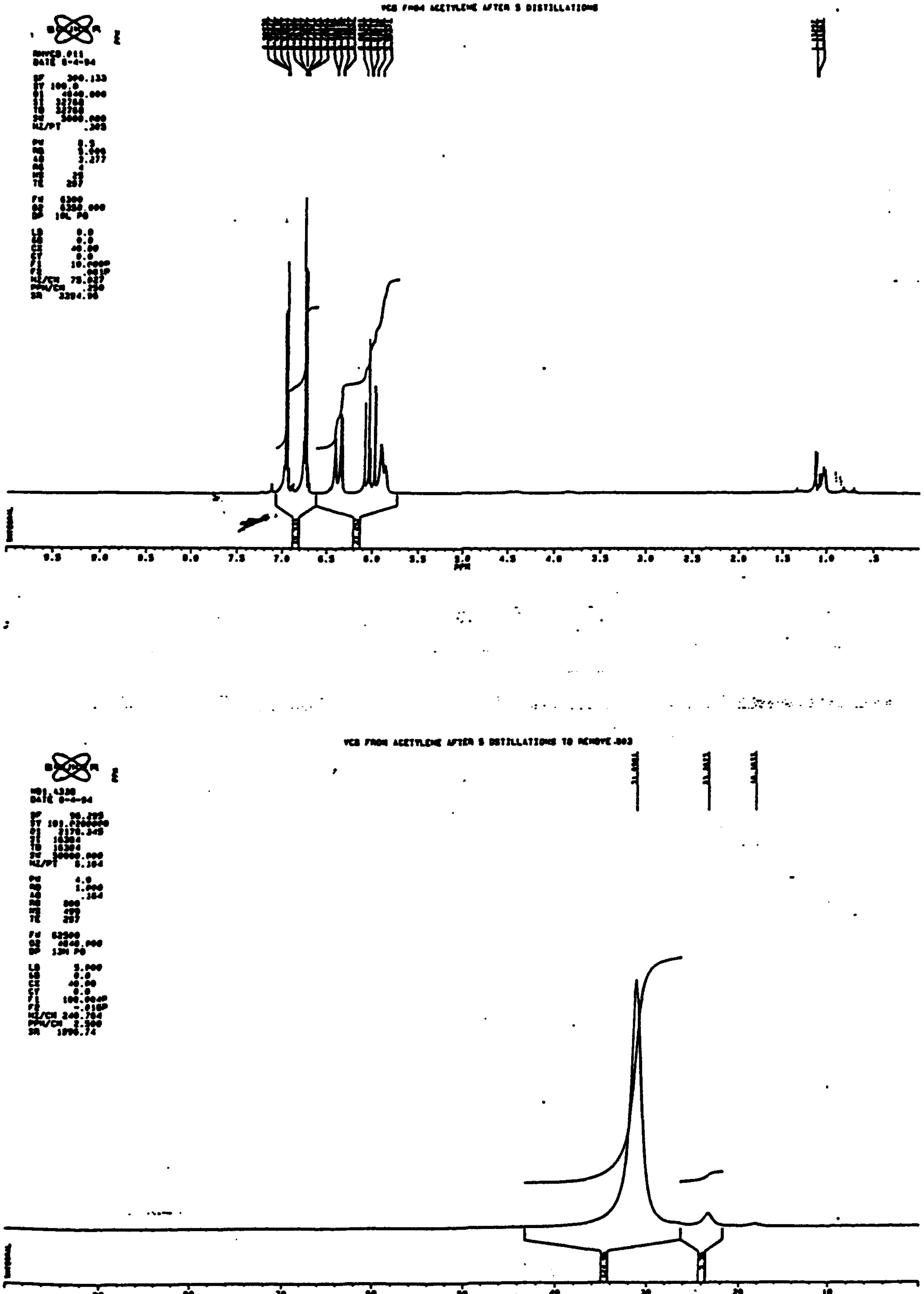

VCB FROM ACETYLENE AFTER 5 DISTILLATIONS
PPM
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
VCB FROM ACETYLENE AFTER 5 DISTILLATIONS TO REMOVE.003
90
80
70
60
50
40
30
20
10
PPM

Fig. 1

Spectra in Fig. 1 provide direct evidence of vinylcatecholborane. The chemical shift at 31 ppm in the ^{11}B NMR spectrum corresponds to boron with dialkoxy and vinyl ligands. In the ^{1}H NMR spectrum, the intensity ratio of vinyl (5.8-6.5 ppm) versus aromatic group (6.7-7.1 ppm) clearly indicates the molecular structure of vinylcatecholborane.

(b) Homo- and Co-polymerization between Acrylonitrile and Vinylcatecholborane

Vinylcatecholborane has been homopolymerized or copolymerized with acrylonitrile, where reactions were initiated by thermal and photo processes. In the free radical process, AIBN initiator was used at 65°C. In contrast, the photo process was carried out at ambient temperatures by using an UV source; Table 1 summarizes experimental conditions and results.

Table 1 The Summary of Copolymerization* Between Acrylonitrile and Vinylcatecholborane

Sample	Monomer Feed Ratio (AN/VCB)	Reaction Time (hrs)	Yield (wt %)	Copolymer Ratio (AN/VCB)	Color
I-A	0/1	24	60	0/1	white
I-B	1/1	24	60	1/1	yellow
I-C	3/1	1	16	1.8/1	yellow
I-D	5/1	1	20	**	yellow

* at 65°C using AIBN initiator. ** under investigation.

In all reactions, high molecular weight polymers with appreciable solution viscosities were observed. Determination of polymer molecular weight is currently under investigation. Apparently, the catechol ligand is an effective protecting group which avoids side reactions between boron compounds and free radicals. Poly(vinylcatecholborane) homopolymer is a white powder. However, copolymers of poly(acrylonitrile-co-vinylcatecholborane) are yellow, which indicates that some complexes may be formed between acrylonitrile(base) and catecholborane (acid).

Fig. 2 shows the ^{1}H NMR and ^{11}B NMR spectra of poly(vinylcatecholborane) (Sample I-A) which was obtained by thermal initiation process.

After polymerization, the boron chemical shift moves down field to 36 ppm, corresponding to alkydialkoxylborane. Similar results were observed in the photo-polymerization cases. It is interesting to note that catecholborane group in polymer form is more acidic than the monomer form. The difference (~ 5 ppm) in chemical shift, between monomer and polymer, clearly indicates a contribution of electron density from vinyl group to boron in vinylcatecholborane monomer. Proton peaks of aromatic (6.4-7.2 ppm) and aliphatic protons (0.8 and 1.2 ppm) match well in the

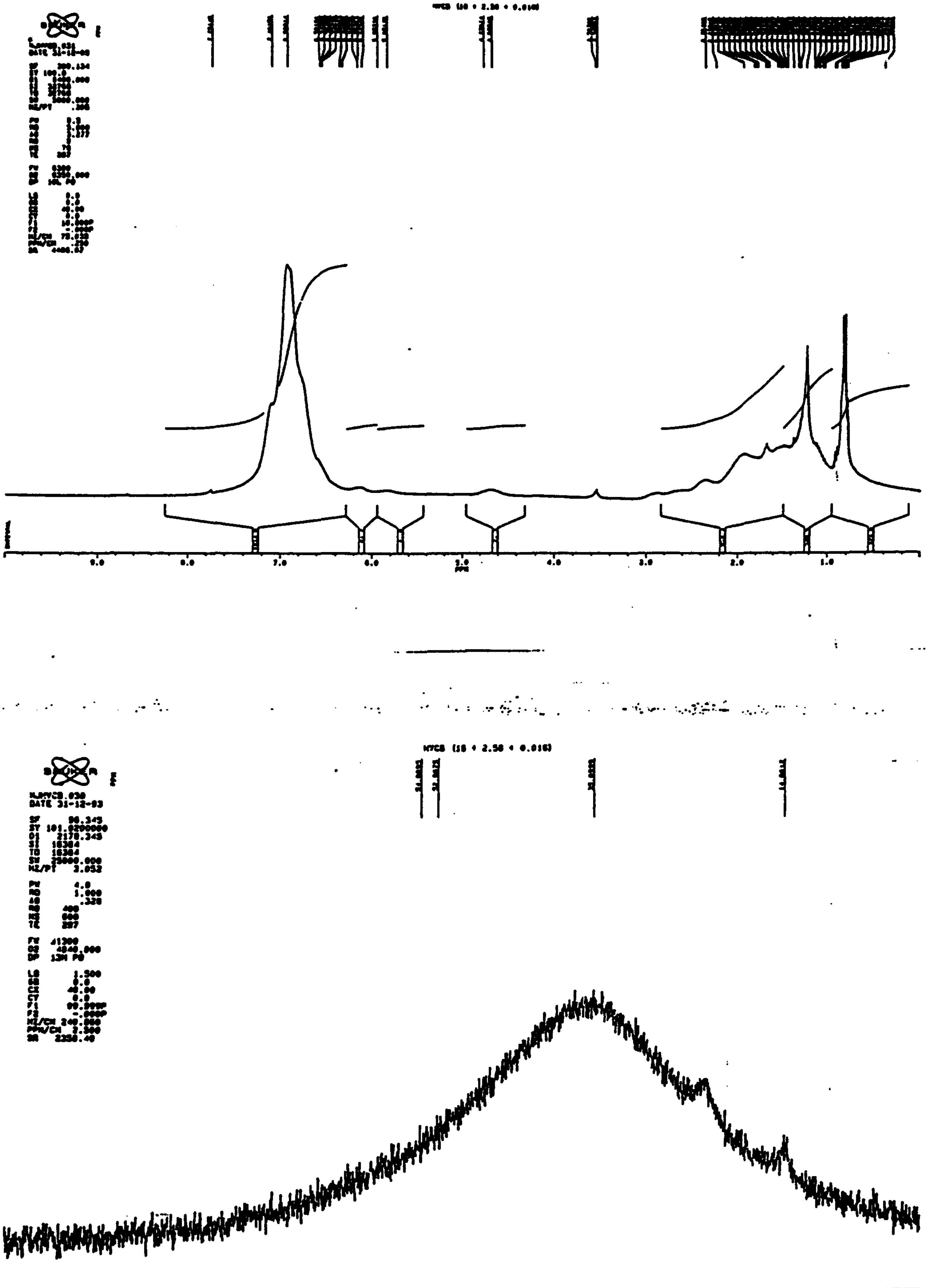


Fig. 2

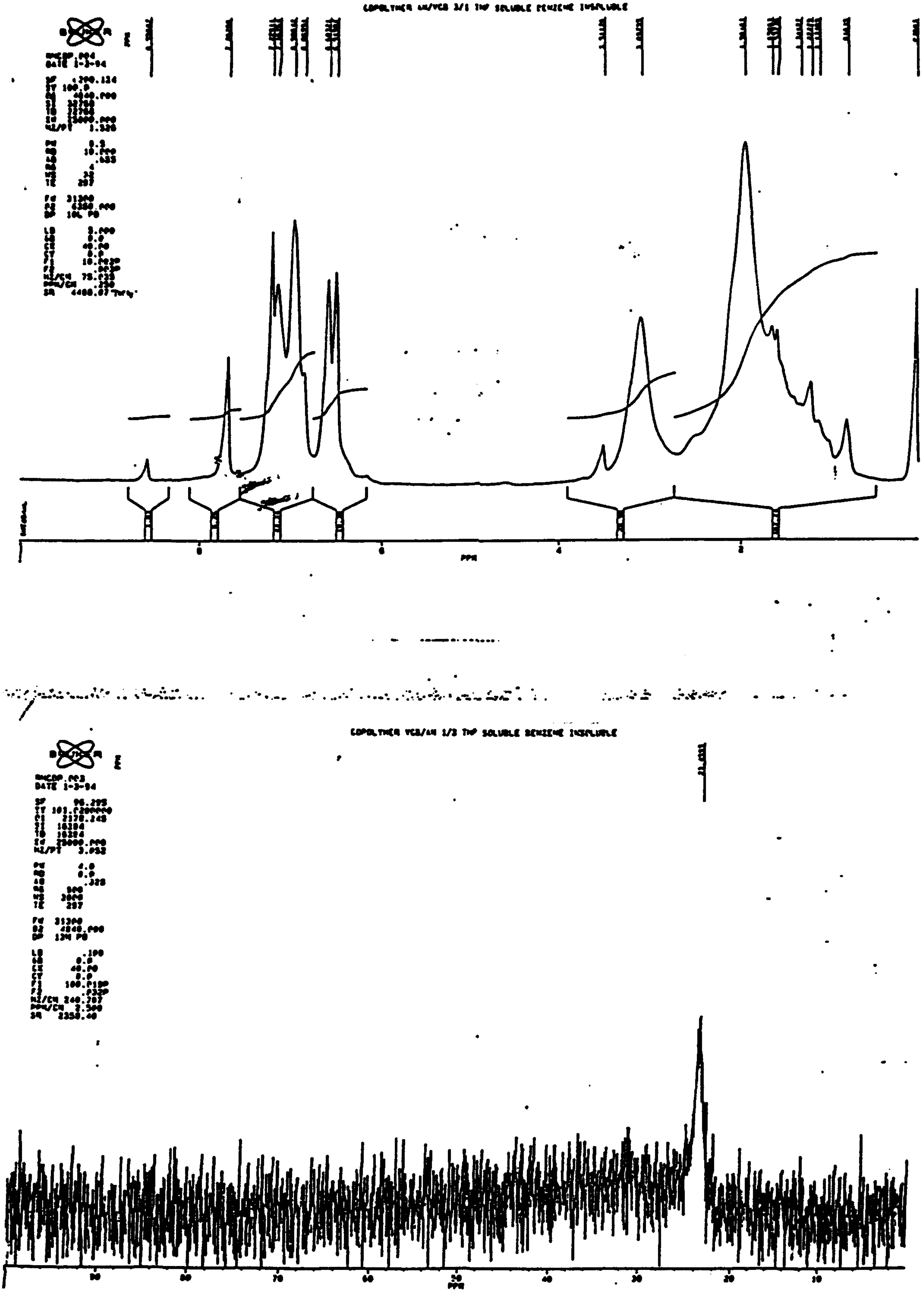

COPOLYMER AN/VCB 3/1 THF SOLUBLE BENZENE INSOLUBLE
DATE 1-3-94
8
6
4
2
PPM
COPOLYMER VCB/AN 1/3 THF SOLUBLE BENZENE INSOLUBLE
DATE 1-3-94
90
80
70
60
50
40
30
20
10
PPM

Fig. 3

predicted intensity ratio for poly(vinylcatecholborane). The molecular structure of poly(vinylcatecholborane) was also supported by elemental analysis results as shown in Table 2.

Table 2 The Elemental Analysis Results of Poly(vinylcatecholborane)

Elements	Carbon	Hydrogen	Boron	Oxygen
Theoretical Value (Wt.%)	65.75	4.79	7.53	21.93
Experimental Value (Wt.%)	62.46	5.06	7.33	*

* no determination

Both theoretical and experimental values are very close; slight differences may result from handling the air sensitive sample.

In copolymerization reactions, yellow copolymers were obtained with about 60% yield in 24 hours. There were no apparent changes in reactivity with various monomer feed ratios. Copolymer composition is dependent on monomer feed ratio and reaction time. Based on results obtained at low conversions, vinylcatecholborane (VCB) monomer is slightly more reactive than acrylonitrile (AN). Fig. 3 shows the ^{1}H NMR and ^{11}B NMR spectra of poly(acrylonitrile-co-vinylcatecholborane) (sample I-C) with a feed ratio of AN/VCB = 3/1.

Final copolymer composition (AN/VCB = 1.8/1) was determined by proton intensities from aromatic protons (6.4-7.2 ppm) and aliphatic protons (0.8-3.7 ppm), in both AN and VCB units. ^{11}B NMR spectrum of the copolymer shows the boron chemical shift at about 23.5 ppm which is a 12 ppm up-field shift from poly(vinylcatecholborane) homopolymer. Such an up-field shift clearly indicates complexes formed between acrylonitrile(base) and catecholborane (acid) groups in the copolymers. In fact, the copolymers are yellow in all compositions. The degree of complexation will be quantified by UV-Visible studies.

(c) Carbonization Studies

Carbonization studies of poly(acrylnitrile-co-vinylcatecholborane) copolymers were carried out under the same conditions as polyacrylonitrile. Fig. 4 shows DSC comparison between copolymer (Sample I-C) and PAN. The thermal process was carried out by heating the sample under a nitrogen atmosphere at a heating rate of 1°C/min.

As expected, PAN starts losing its weight around 250°C and its yield is about 40% at 740°C. The I-C sample, containing 5 weight % of boron, constantly loses its weight until 450°C. It is apparent that there is some solvent in the copolymer, which usually form complexes with boron moieties, the solvent is very difficult to remove by simple drying processes. However, there

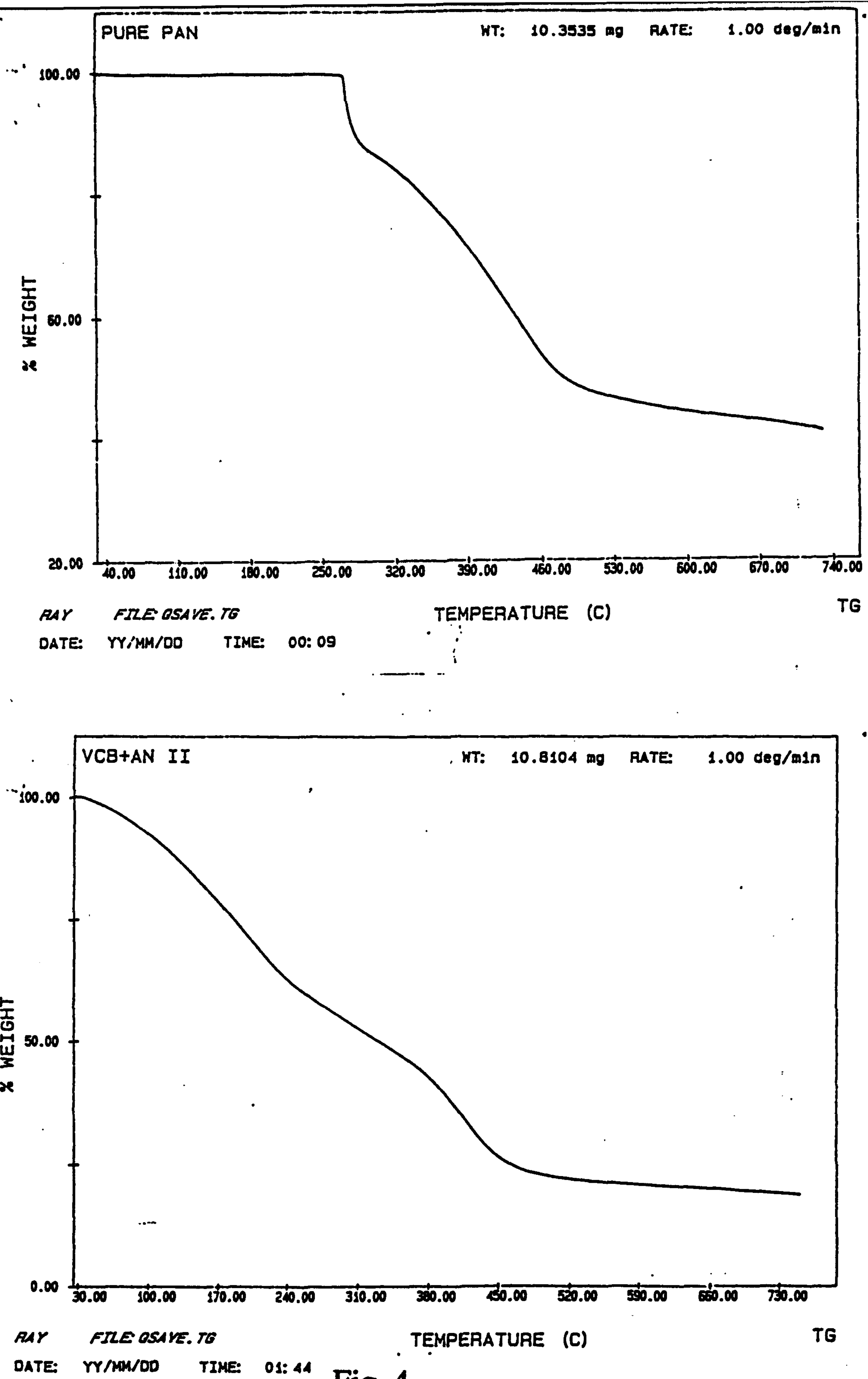
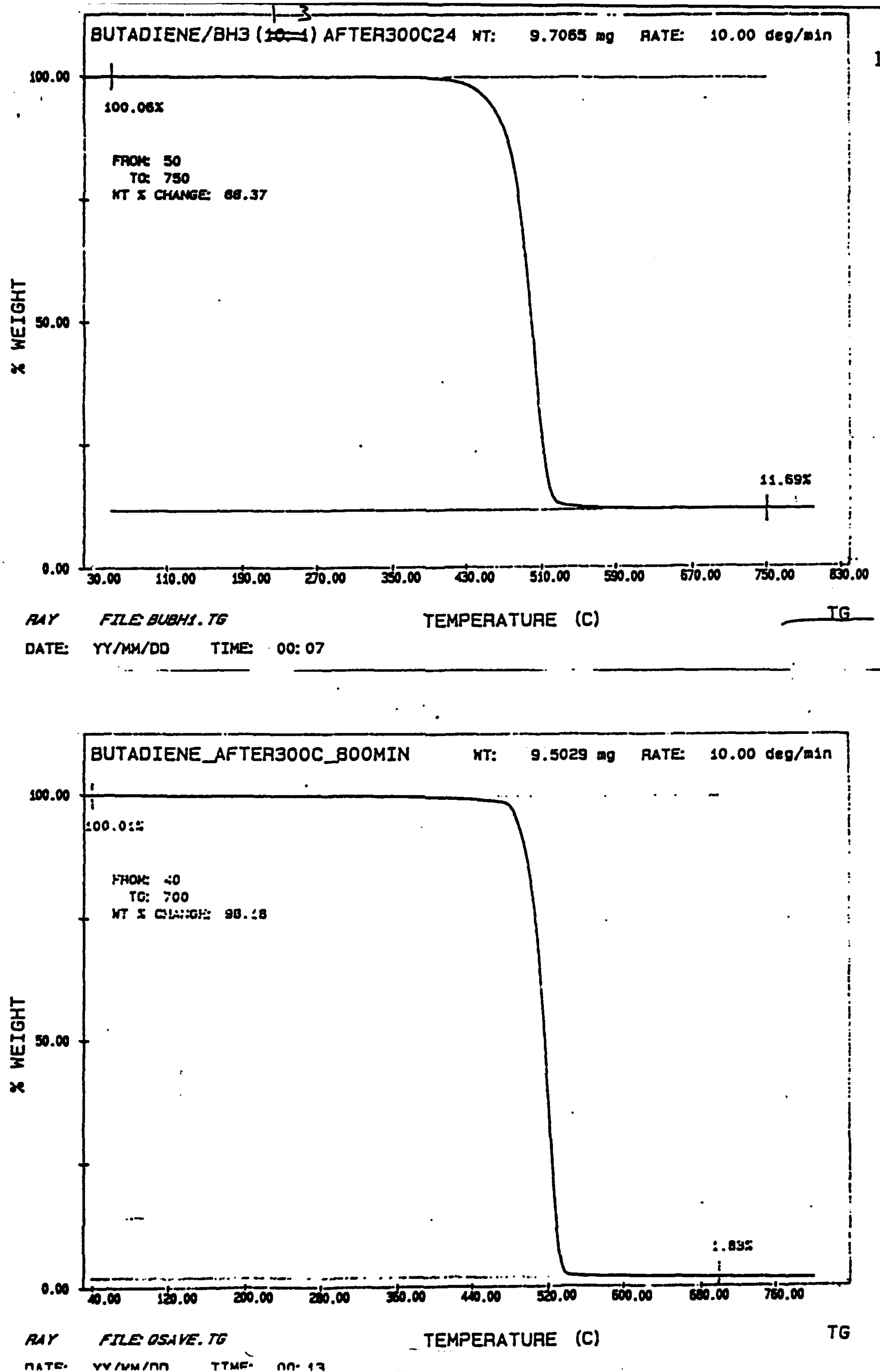

PURE PAN
WT: 10.3535 mg RATE: 1.00 deg/min
100.00
60.00
20.00
% WEIGHT
40.00
110.00
180.00
250.00
320.00
390.00
460.00
530.00
600.00
670.00
740.00
TEMPERATURE (C)
TG
RAY FILE: OSAVE.TG
DATE: YY/MM/DD TIME: 00:09
VCB+AN II
WT: 10.8104 mg RATE: 1.00 deg/min
100.00
50.00
0.00
% WEIGHT
30.00
100.00
170.00
240.00
310.00
380.00
450.00
520.00
590.00
660.00
730.00
TEMPERATURE (C)
TG
RAY FILE: OSAVE.TG
DATE: YY/MM/DD TIME: 01:44

Fig. 4



BUTADIENE/BH3 (~~10:1~~ 1:3) AFTER300C24 WT: 9.7065 mg RATE: 10.00 deg/min

100.06%

FROM: 50
TO: 750
WT % CHANGE: 88.37

11.69%

RAY FILE: BUBH1.TG

DATE: YY/MM/DD TIME: 00:07

BUTADIENE_AFTER300C_800MIN WT: 9.5029 mg RATE: 10.00 deg/min

100.01%

FROM: 40
TO: 700
WT % CHANGE: 98.18

1.83%

RAY FILE: OSAVE.TG

DATE: YY/MM/DD TIME: 00:13

Fig. 5

is about 25 weight % remaining at 740°C. Elemental analysis results before and after pyrolysis are summarized in Table 3.

Table 3 A Comparison of Elemental Analysis Results before and after Carbonization of Poly(acrylnitrile-co-vinylcatecholborane)*

Elements	Carbon	Hydrogen	Boron	Oxygen
Before (Wt.%)	66	5	5	16
After (Wt.%)	75	0.86	3.4	**

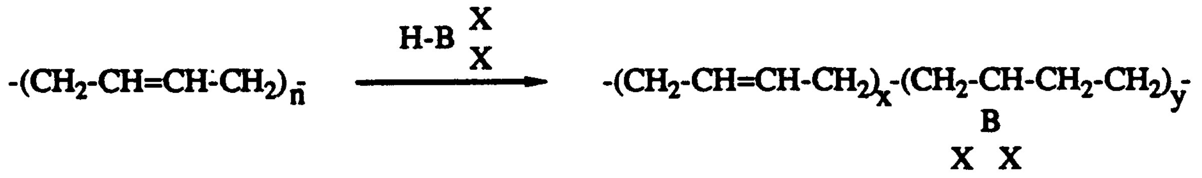
* Sample I-C ** no determination

About 68% of the original boron present was retained after pyrolysis. The high % of boron incorporated in the final product is very encouraging. The nature of the boron species is currently under investigation using solid state ^{11}B and ^{13}C NMR spectrometers. More experiments are needed to find optimum conditions for high yield products.

(B) 1,4-Polybutadiene Containing Boron

The easy way to introduce boron into a polymer is by hydroboration of an unsaturated polymer, such as 1,4-polybutadiene (PBD). It is known that PBD is stable up to relatively high temperatures, about 440°C. However, PBD catastrophically decomposes above 450°C. It is of interest to see if there are any changes due to incorporation of boron elements which may enhance carbonization reactions below the decomposition temperature.

PBD containing boron was prepared by hydroboration as shown in Equation 2.



$$-(\mathrm{CH_2\text{-}CH{=}CH\text{-}CH_2})_n- \xrightarrow{\mathrm{H\text{-}B}\genfrac{}{}{0pt}{}{\mathrm{X}}{\mathrm{X}}} -(\mathrm{CH_2\text{-}CH{=}CH\text{-}CH_2})_x\text{-}(\mathrm{CH_2\text{-}}\underset{\underset{\mathrm{X\;X}}{\mathrm{B}}}{\mathrm{CH}}\mathrm{\text{-}CH_2\text{-}CH_2})_y-$$

Equation 2

This reaction is very efficient even under mild reaction conditions. Overall results are very similar to those of the corresponding small organic molecules. Despite the high molecular weight of PBD and the substituent group X (hydrogen, alkyl and halide groups) in the borane reagent, the concentration of boron in polymer is controlled essentially quantitatively by the amount of reagent used during the reaction. Detailed information of the distribution of boron in the polymer and any changes in molecular weight of the polymer during the reaction is currently being developed.

In a pyrolysis study, a borane-containing PBD, obtained using diene/ BH_3 ratio of 1/3 ratio, was tested side-by-side with a pure PBD sample. The boron containing PBD turned to deep black at 300°C while pure PBD was still completely white. The observation implies some degree of carbonization enhancement by the boron species. Fig. 5 compares the TGA curves of the two samples.

A major difference between the two samples is the % residue, about 12% for borane-containing PBD and almost nothing for pure PBD, after thermal treatments up to 750°C. It is interesting to note that there is only carbon, hydrogen and boron (no oxygen) present in the final product. Structural information is being developed using solid state NMR and elemental analysis. More experiments are needed, such as changing the ratio of double bonds and boron, or changing the substitute group (X), which may offer early crosslinking reactions at lower temperatures.

(C) Polydiyne Containing Boron

Both boron and carbon pyrolysis yields are important for ideal polymer precursors. Polydiyne (PDY) has a one-dimensional carbon skeleton with single and triple bonds alternating between carbon atoms; this the closest one-dimension composition to carbon. In the past, the insolubility of PDY always hindered attempts to prepare high molecular weight polymer. Incorporation of boron atoms between diacetylene units in PDY significantly alters its backbone rigidity and increases interaction with solvent. A model polymer chain may be schematically represented below:

$$\left(C \;\; \underset{X}{B} \;\; C \;\; C \;\; R \;\; C \right)_n$$

X = halogen, alkyl, etc.

The chemistry is based on the coupling reaction between lithium derivatives of acetylenic structure with boron halides to form alkynylborane. To find appropriate reaction conditions, a control reaction was studied as illustrated in Equation 3.

$$\text{R-C}\blacksquare\text{C-H} \xrightarrow{\text{n-BuLi / ether}} \text{R-C}\blacksquare\overset{-}{\text{C}}\,\overset{+}{\text{Li}} \xrightarrow{BCl_3} (\text{R-C}\blacksquare\text{C})_3\text{B}$$

R : Alkyl or phenyl groups

Equation 3

Both alkylacetylene and phenylacetylene were evaluated using n-BuLi/ether as the metallation agent and for subsequent coupling reaction with BCl_3 (acetylene/BCl_3 = 3/1). The product was obtained by solvent extraction. Fig. 6 shows the ^{11}B and ^{13}C spectra of trihexynylborane.

It has been earlier documented that alkenyl and alkynyl species attached to boron atoms exhibit π-interaction between the alkenyl/alkynyl π-electron system and the vacant p orbital of the

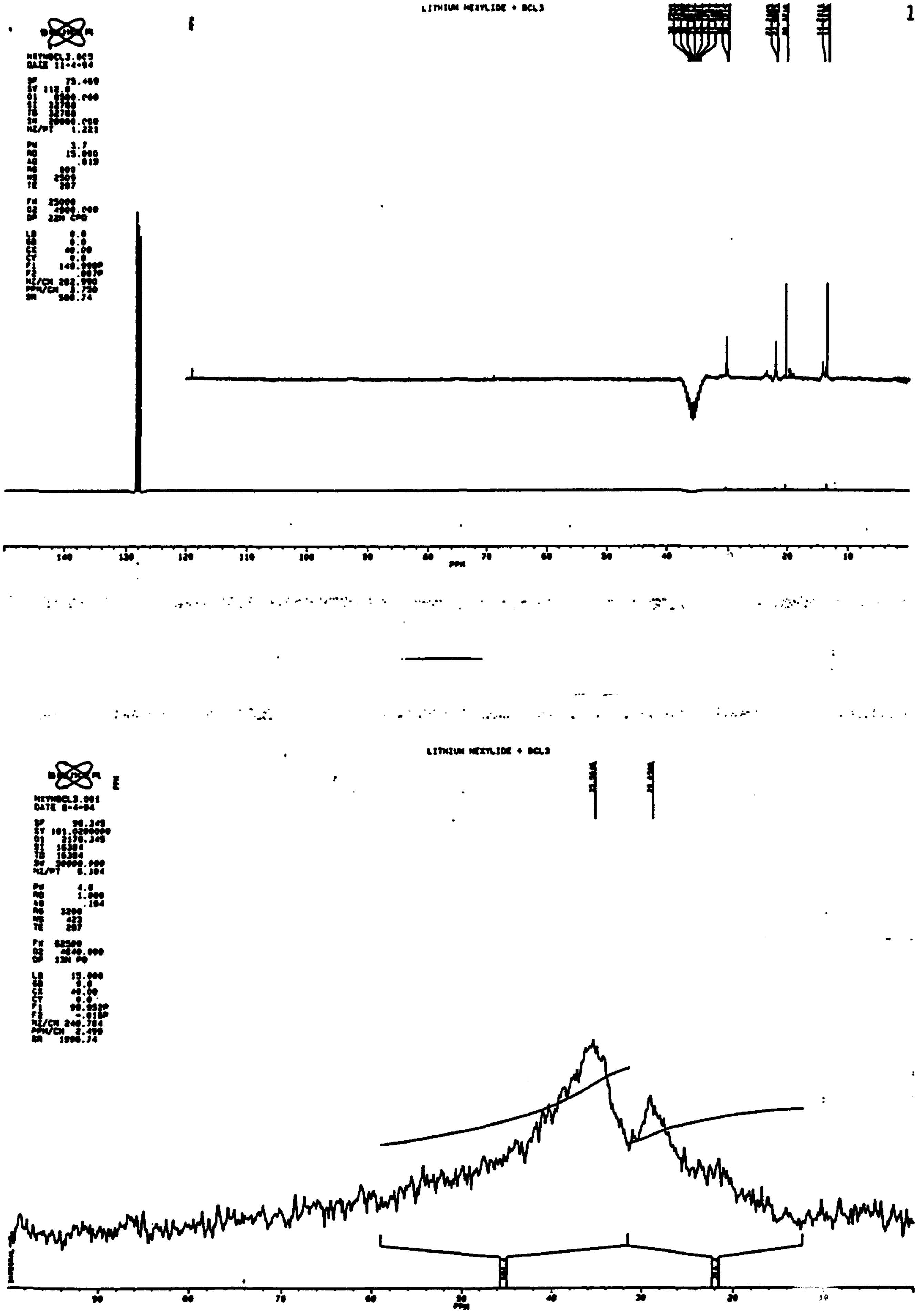

LITHIUM HEXYLIDE + BCL3
HEXHBCL3.0C3
DATE 11-4-94
SF 75.469
SY 112.0
O1 6500.000
SI 32768
TD 32768
SW 40000.000
HZ/PT 1.221
PW 3.7
RD 15.000
AQ .819
RG 800
NS 2509
TE 297
FW 25000
O2 4900.000
DP 22H CPD
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 149.999P
F2 .007P
HZ/CM 282.990
PPM/CM 3.750
SR 300.74
140
130
120
110
100
90
80
PPM
70
60
50
40
30
20
10
LITHIUM HEXYLIDE + BCL3
PPM
HEXHBCL3.001
DATE 6-4-94
SF 96.345
SY 101.0200000
O1 2170.345
SI 16384
TD 16384
SW 30000.000
HZ/PT 6.104
PW 4.0
RD 1.000
AQ .164
RG 3200
NS 423
TE 297
FW 62500
O2 4840.000
DP 13H PO
LB 15.000
GB 0.0
CX 40.00
CY 0.0
F1 98.952P
F2 -.016P
HZ/CM 240.784
PPM/CM 2.499
SR 1996.74
INTEGRAL
90
80
70
60
50
PPM
40
30
20
10

Fig. 6

boron atom. This manifests itself in broadening and weakening of the peak due to the ^{13}C nuclei directly attached to the boron atom. It can be observed in the ^{13}C spectra of trihexynylborane that the alkynyl carbon atoms (normally seen at 69 and 84 ppm), are not visible at all, indicating a direct attachment to a boron atom. Two chemical shifts (35 and 29 ppm) in ^{11}B NMR spectrum indicate some dihexynylchloroborane associated with trihexynylborane. The reaction is incomplete, which to some degree, may be due to insufficient lithium hexylide in the coupling reaction.

Synthesis of comparable polymer molecules is currently under investigation and preliminary results indicate the presence of trialkynylborane species in the polymer. So ate NMR and elemental analysis studies are being employed to determine the exact molecular st ure. Additionally, we intend to further refine coupling methods such that polymer molecules obtained with boron atom in the backbone remain soluble at room temperature, and form intermolecular crosslinks only at elevated temperatures. Polymer backbones containing aromatic moieties are also under investigation, with the intent to increase electron delocalization, and hence improve the stability of the carbon fibers eventually obtained.

Dr. Ian R. Harrison

Task 2.2 Fiber Formation of B/C Polymers and Transformation to Carbons

The objective of this task is to arrive at a basic understanding of structure/property relationships in B/C polymer fibers and carbon fibers, and the dependence of such relationships on spinning process parameters. Polymers processed into fibers possess properties very different compared to those in bulk or film form; this being primarily due to the high degree of orientation of the polymer molecules in a fiber along the fiber axis. This task aims at constructing a small-scale carbon fiber manufacturing line, spinning the precursor fiber and taking the precursor fiber through the subsequent stages of drawing, stabilization and carbonization to the final carbon form, whilst studying the evolution of structure at each stage and correlating it with observed properties, thereby aiding in the optimization of processing.

2.2.1 Design of appropriate apparatus for spinning precursor fiber and converting precursor fiber to carbon fiber

- *Design and development of a small-scale fiber spinning line for dry-jet wet spinning of Polyacrylonitrile (PAN) fibers as precursors to Carbon fibers*

A small-scale dry-jet wet spinning line for the production of PAN-based precursor fibers is operational. The spinning apparatus is ideally suited for production of trial quantities of fibers. It allows spinning of fibers from sample sizes as small as 5 gms, a small (~10 mm) air gap has been incorporated between the spinneret and coagulation bath to produce better orientation of the precursor fiber (this translates to better mechanical properties of the resulting carbon fiber), an ultrasonic wash bath aids in efficient removal of solvent from the coagulated fiber and provisions have been made to control parameters to produce precursor fibers with varying process histories. Preliminary spinning trials indicate good mechanical properties of the fibers (ref. Table 4). The values listed are for the as-spun fiber. This fiber was spun after dissolving the as-received Courtelle Special Acrylic Fiber (SAF) precursor in 60% aqueous $ZnCl_2$. It is possible that after drawing, there could be a significant improvement in the mechanical properties. A schematic of the spinning apparatus is shown in Fig. 7.

Table 4. Mechanical properties for PAN precursors

	PennState Precursor (as-spun, not drawn)	**Courtelle SAF** (commercial precursor)
Diameter (µm)	60.0	11.3
Tenacity (gpd)	5.9 ± 0.4	6.6 ± 0.9
Modulus (gpd)	104.4 ± 6.8	86.7 ± 12.0
Elongation (%)	9.2 ± 1.2	15.3 ± 0.6

Typical Spinning Conditions:

Spinning Solution : 7-9 % PAN in 60% aq. $ZnCl_2$, 20°C
Coagulation Bath : 30 % aq. $ZnCl_2$, 5°C
Ultrasonic Wash Bath : water, 50°C
Stretch Bath : water, 85°C

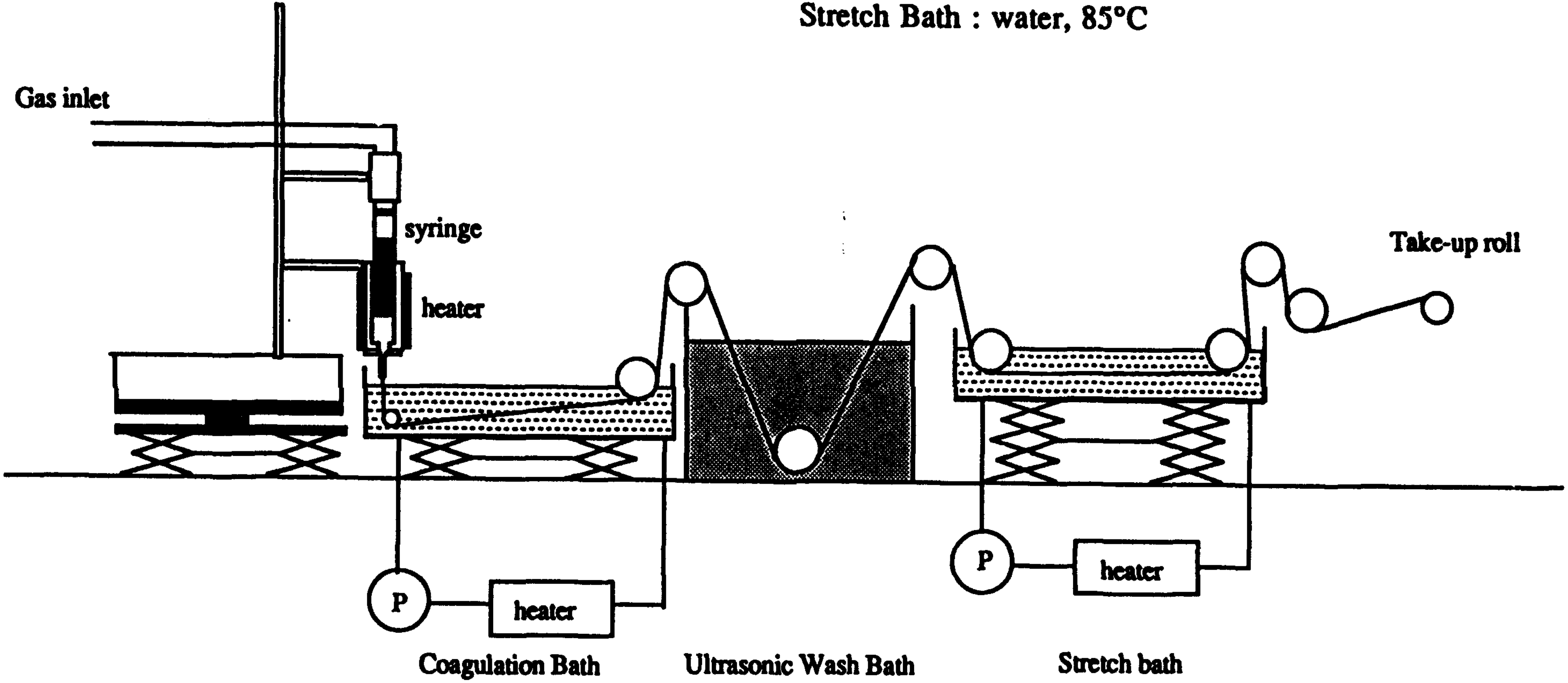


Fig. 7 **Dry-jet Wet spinning set-up for PAN fibers**

- *Design and development of a small-scale fiber spinning line for melt-spinning of Pitch fibers as precursors to carbon fibers*

A small-scale melt spinning line for production of pitch-based precursor fibers is operational. The apparatus is extremely flexible in its capabilities. It allows fiber spinning from small sample sizes (≈ 50 gms) and incorporates parameters to produce precursor fibers with varying process histories. Provision has also been made to spin monofilaments as well as hollow fibers. The apparatus is depicted in Fig. 8.

- *Set-up of a drawing, stabilization and carbonization line*

A furnace for the drawing of as-spun fiber is in its final stages of construction. The same furnace will be used to stabilize the PAN precursors at 270°C and then carbonize the fiber at 1000°C to its final carbon form.

2.2.2 Study of processing parameters in relation to carbon fiber manufacture

- *Influence of solvents used during spinning on the stabilization behavior of PAN*

This study was undertaken to study the influence of spinning solvents used on the stabilization behavior of PAN. The stabilization exotherm of PAN has often been used to decide on the appropriate oxidative treatment to be given to a particular fiber, since it is very indicative of the start of the process, the total heat evolved and the final oxidation temperature. In general, a broad exothermic peak due to nitrile group oligomerization during heating starting at low temperatures and a high carbon yield are desired. This translates directly to better fiber properties and higher productivity.

Typical solvents for PAN display a highly polar molecular structure. This is required to break up the nitrile dipoles from adjacent chains paired in an anti parallel, low energy arrangement. Organic solvents like N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO) and inorganic solvents like aqueous Zinc Chloride ($Zncl_2$) and aqueous Sodium Thiocyanate (NaSCN) in the right concentrations are used in preparing the spinning dope. It was of interest to study the effect of different spinning solvents during stabilization. Thermal techniques used were Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Solvents of interest were N,N-Dimethylformamide (organic), Zinc Chloride (inorganic), Sodium Thiocyanate (inorganic). It has earlier been shown that appropriate quantities of zinc ions incorporated in PAN fibers containing acidic groups facilitate the process of stabilization by leading to an increase in the rate of oxidation [1]. Better

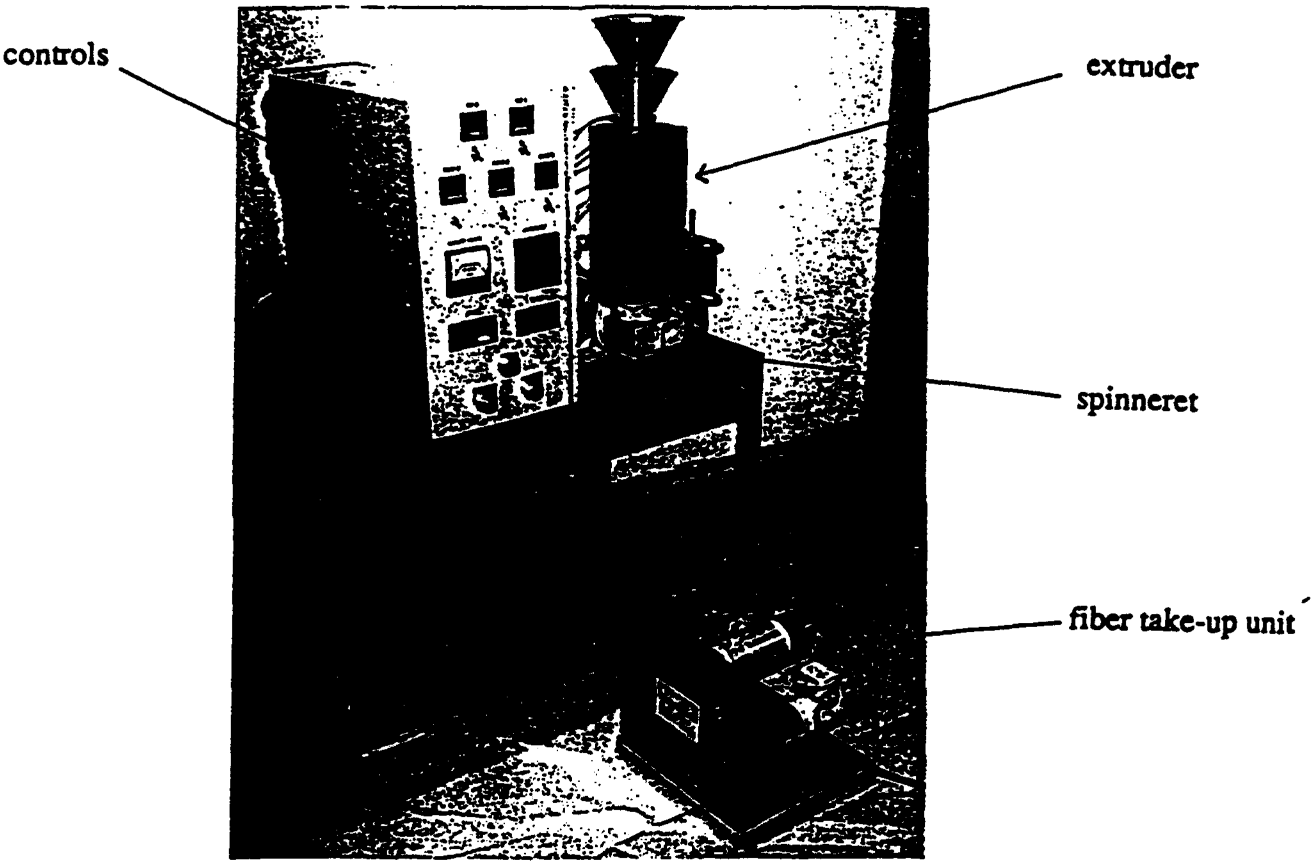


Fig. 8 Melt-spinning set-up for Pitch fibers

Table 5. Sample Preparation for stabilization studies of Pure PAN

Sample #	Solids %	Solvent	Coagulant
101	?	?	?
103	18%	100% DMF	75% aq. DMF
105	6%	60% aq. $ZnCl_2$	30% aq. $ZnCl_2$
107	5%	50% aq. NaSCN	15% aq. NaSCN

101 - As received PAN

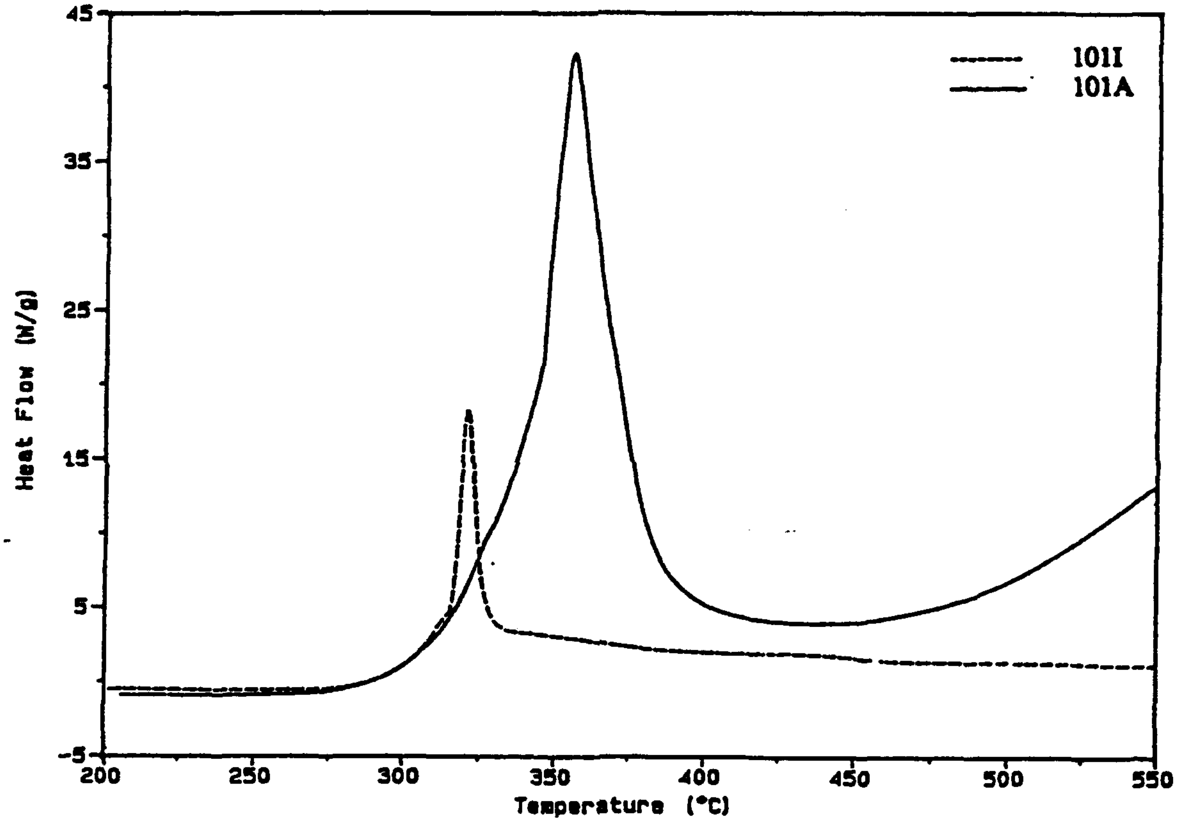


Fig. 9 DSC curves for Pure PAN in air and in argon

mechanical properties of carbon fibers so derived has also been claimed. However, the mechanisms involved have not been elucidated upon.

Samples for thermal studies were made by dissolving the pure PAN powder (from Aldrich) in the appropriate solvents, under conditions listed in Table 5. Coagulation was effected by immersing a glass slide coated with the viscous polymer solution into the coagulating medium at room temperature. The polymer gel was then stripped off and immersed in the coagulant for a total time of 1 minute. Excess solvent was removed by immersing the coagulated polymer in boiling water for a minute, after which it was dried at room temperature under vacuum. It is assumed that some solvent remains in the polymer due to strong interactions between the PAN molecule and the solvent molecules, even after the most thorough washing treatments. A DuPont DSC 2910 was used to study the stabilization exotherm of various PAN samples. All experiments were done in open cells at heating rates of 20°C/min., under both inert (argon) and oxidative (air) conditions. Weight-loss studies were carried out in a Perkin-Elmer TGS-2 Thermal Gravimetric Analyzer (TGA) to maximum temperatures of 900°C under atmospheric pressure at 10°C/min. in argon and in air. Suffixes of 'I' and 'O' to the sample numbers indicate treatments under inert and oxidizing conditions respectively.

The DSC exotherms for pure PAN powder in argon and air are shown in Fig. 9. Two differences are obvious; heating in air shifts the main peak to higher temperatures and gives rise to a much more intense exotherm than heating in argon. DSC plots of variously treated samples are shown in Figs. 10 and 11. It can be seen that for samples exposed to $ZnCl_2$ and NaSCN, the exotherm is much broader and less intense, the difference being most obvious for samples treated with $ZnCl_2$ (# 105). The same trend is seen for heating in air and in argon. Similar behavior is reflected in the Weight-loss curves (Figs. 12-14).

Future Work

Similar experiments on commercially used polymeric precursors are planned. It is postulated that use of appropriate solvents could lead to carbon fibers with shorter processing times and a good balance of properties. However, usage of low boiling point organic solvents like DMF (boiling point : 153°C) could have definite advantages in the dry-jet wet spinning process. It is postulated that evaporation of a small amount of the solvent is the air gap could lead to the formation of a sheath around the extruded fiber, while at the same time allowing for some degree of orientation due to stretch. Formation of a thin sheath could regulate pore formation in the extruded filament. It has been shown that the fibrillar morphology of the PAN precursor is a direct consequence of the collapse of pores formed during the coagulating step [2].

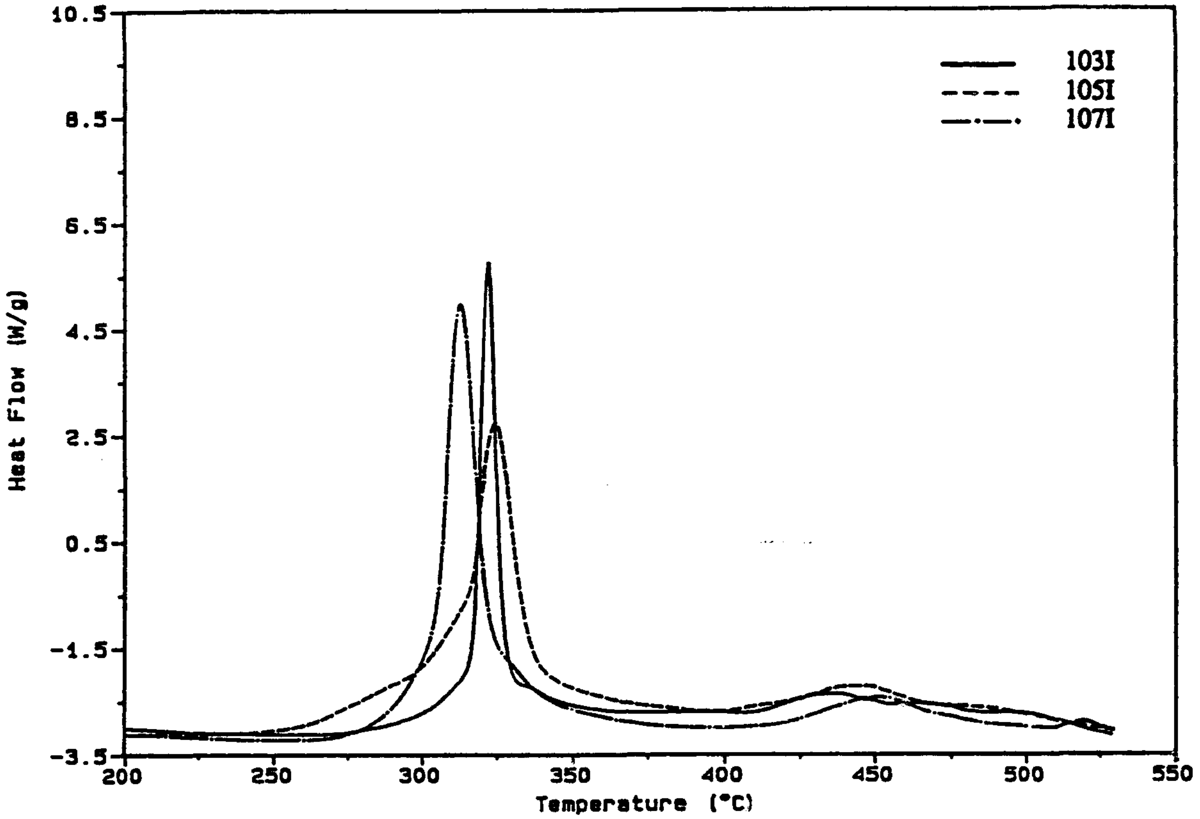


FIG. 10 DSC curves for samples 103, 105 and 107 in Argon

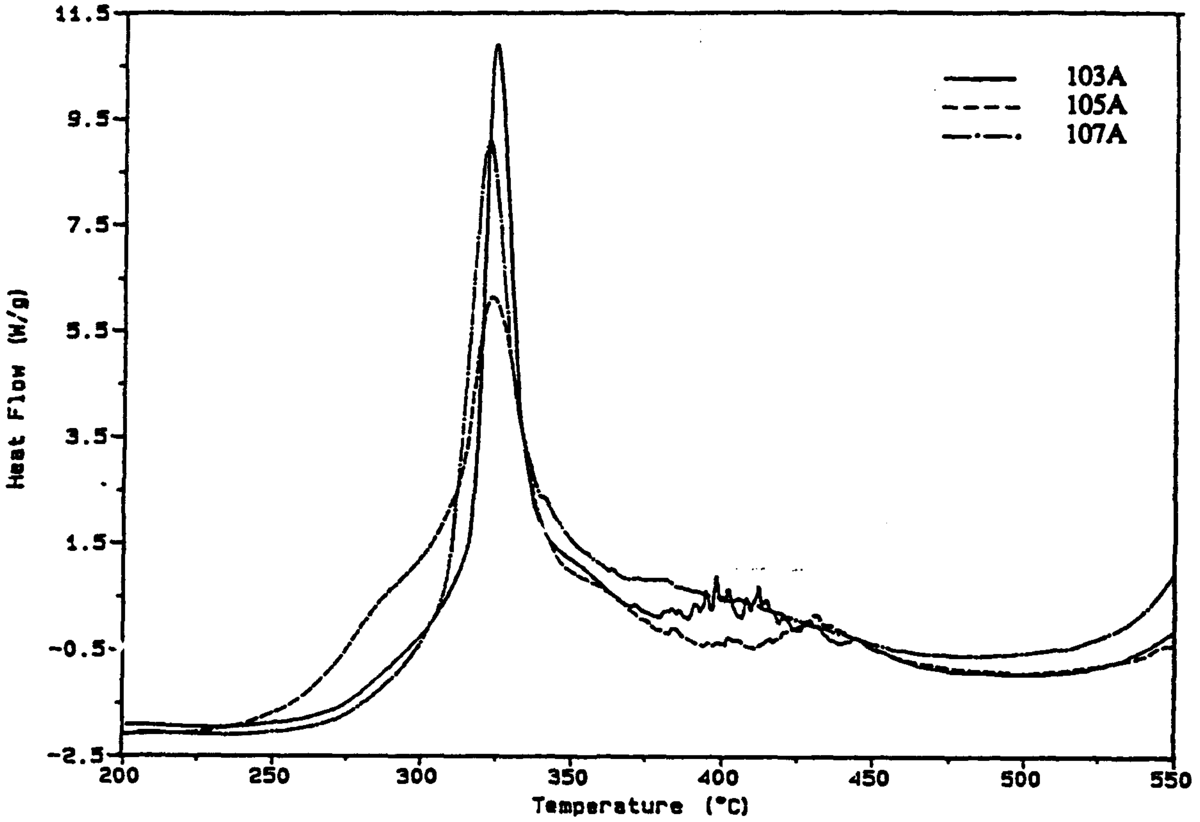


FIG. 11 DSC curves for samples 103, 105 and 107 in Air

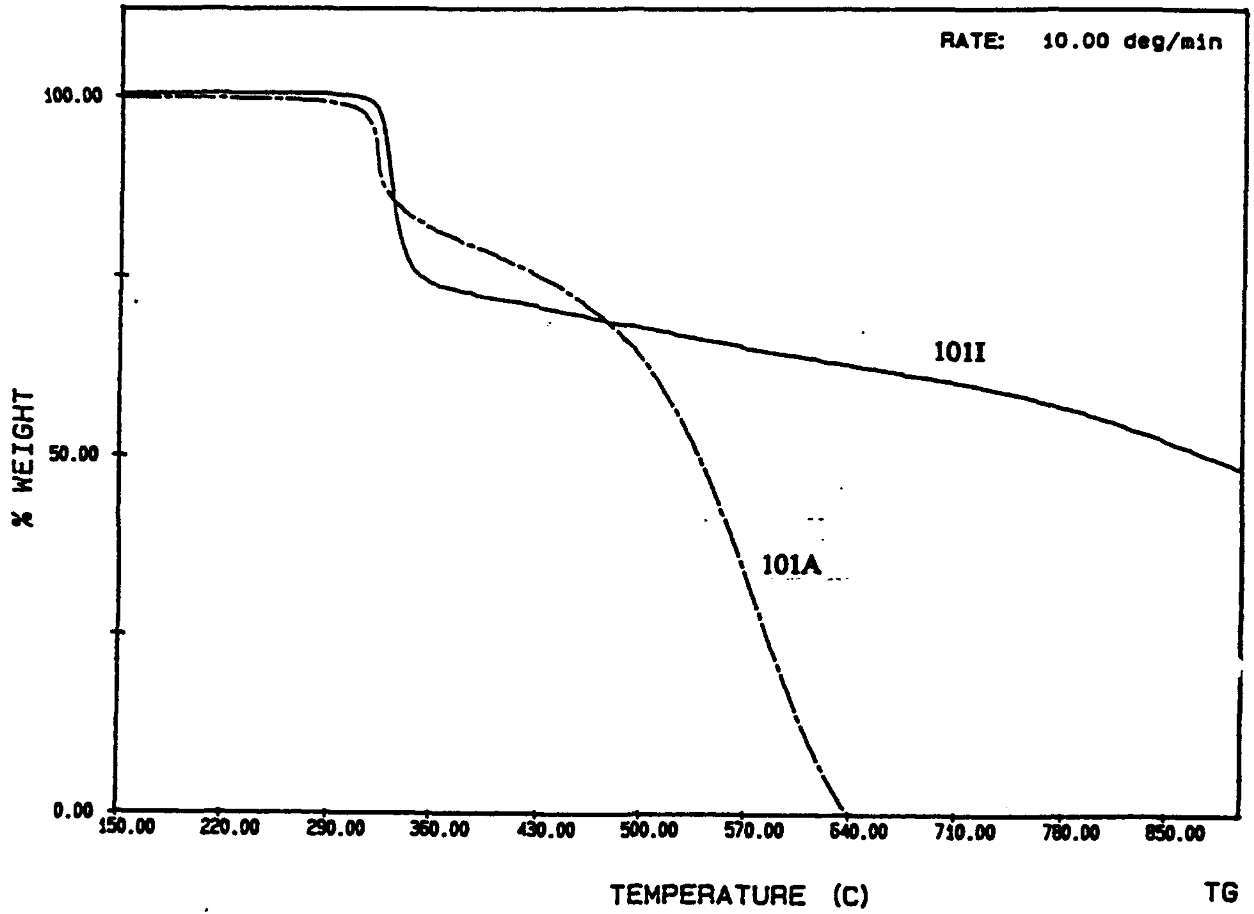


Fig. 12 TGA weight-loss curves for Pure PAN in air and in argon

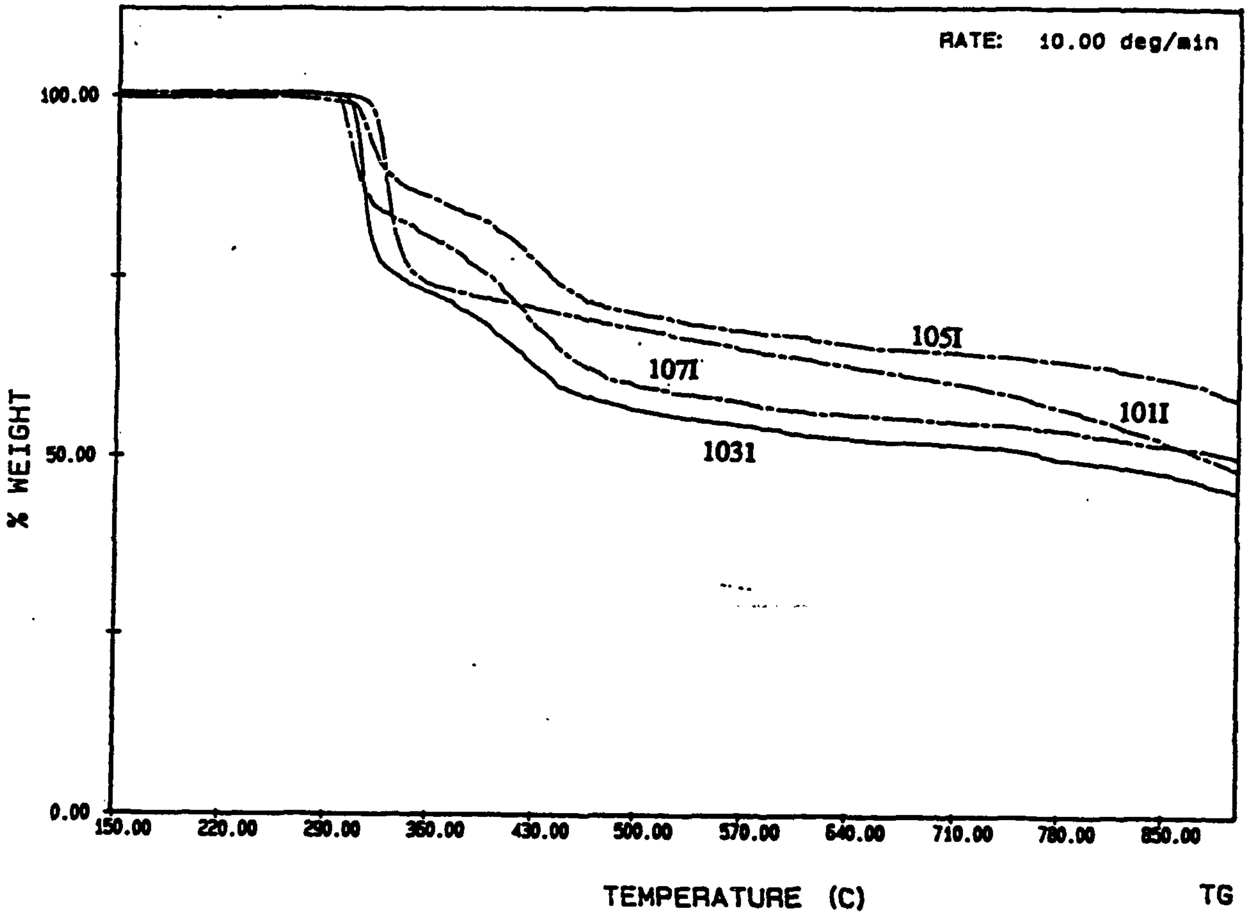


Fig. 13 TGA weight-loss curves for samples 101, 103, 105 and 107 in argon

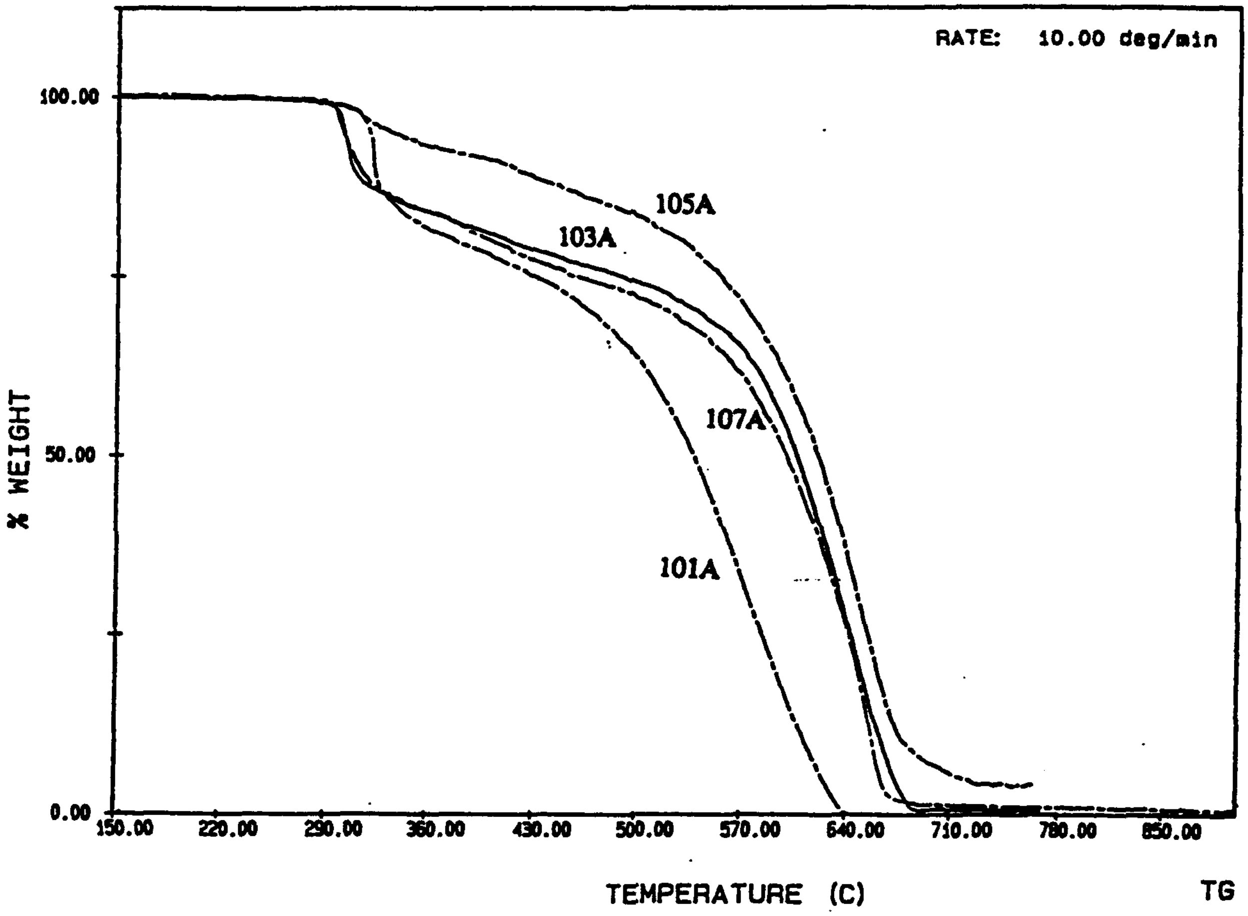


Fig. 14 TGA weight-loss curves for samples 101, 103, 105 and 107 in air

However, it is unclear whether the fibrillar morphology is beneficial or detrimental to the precursor fiber and the resulting carbon fiber.

Spinning of polymers obtained from Task 1 will also be performed.

References

1. US Patent 4397831 (1983)
2. US Patent 3080210 (1963)

Dr. Carlo Pantano

Task 2.3 Polymer Processing of B-Enriched Carbon Thin Films

The chemical, structural and transport properties of boron in polymers and carbons are fundamental to every facet of this program. In order to evaluate the new polymers being developed under Task 1, it will be necessary to establish baseline properties using well characterized reference materials. These reference materials can also be used to evaluate the mechanism of boron inhibition of carbon oxidation under Task 3.

We have developed the capability to fabricate boron-doped carbons using two methods:

(i) boron ion implantation in carbon, and

(ii) chemical vapor deposition of B_xC_{1-x}.

Moreover, we have developed methods for the quantitative compositional and in-depth analysis of the boron-doped materials. To date, we have evaluated the behavior of boron after ion-implantation into highly-oriented pyrolytic graphite (HOPG) and vitreous carbon. The effect of annealing in an inert atmosphere upon the carbon structure and redistribution of boron has also been studied. The chemical vapor deposition (CVD) system has been constructed, but film depositions are only now beginning.

Boron Ion Implantation in Carbon. Boron ion implantations were performed at 75 KeV using a Varian Ion Implanter (Model 350 D). Two sets of specimens have been prepared and characterized. In each set, both vitreous carbon (EMC Industries) and HOPG (Union Carbide) were simultaneously implanted. One set was implanted with 8.7×10^{15} B^+/cm^2 and the other set with 8.7×10^{16} B^+/cm^2. Some additional implantations were performed at two different angles (normal to, and slightly off-normal on the basal face) to determine whether the HOPG structure would channel or otherwise influence boron implantation.

The initial concentration and depth distribution of boron in the various materials were obtained using quantitative SIMS depth-profiling (CAMECA IMS - 3F, Cs^+ @ 12 KeV). Figs. 15 and 16 show depth profiles for the HOPG and vitreous carbon substrates, respectively. In the HOPG, the boron concentrations at the peak of the implant profiles are .5-5 atom percent. In the vitreous carbon substrates, the peak concentrations are 1-10 atom percent. The implantation extends to about .5μm.

The surfaces of these implanted materials were examined in the SEM. The HOPG exhibited a microcracked surface layer due to implantation. It is not known whether this layer formed due to boron in the surface or due to the heat generated during the implantation. The vitreous carbon substrates did not show any detectable surface layer structure, although the high dose implantation created a small, but detectable number of reaction products at the surface.

Highly Oriented Pyrolitic Graphite

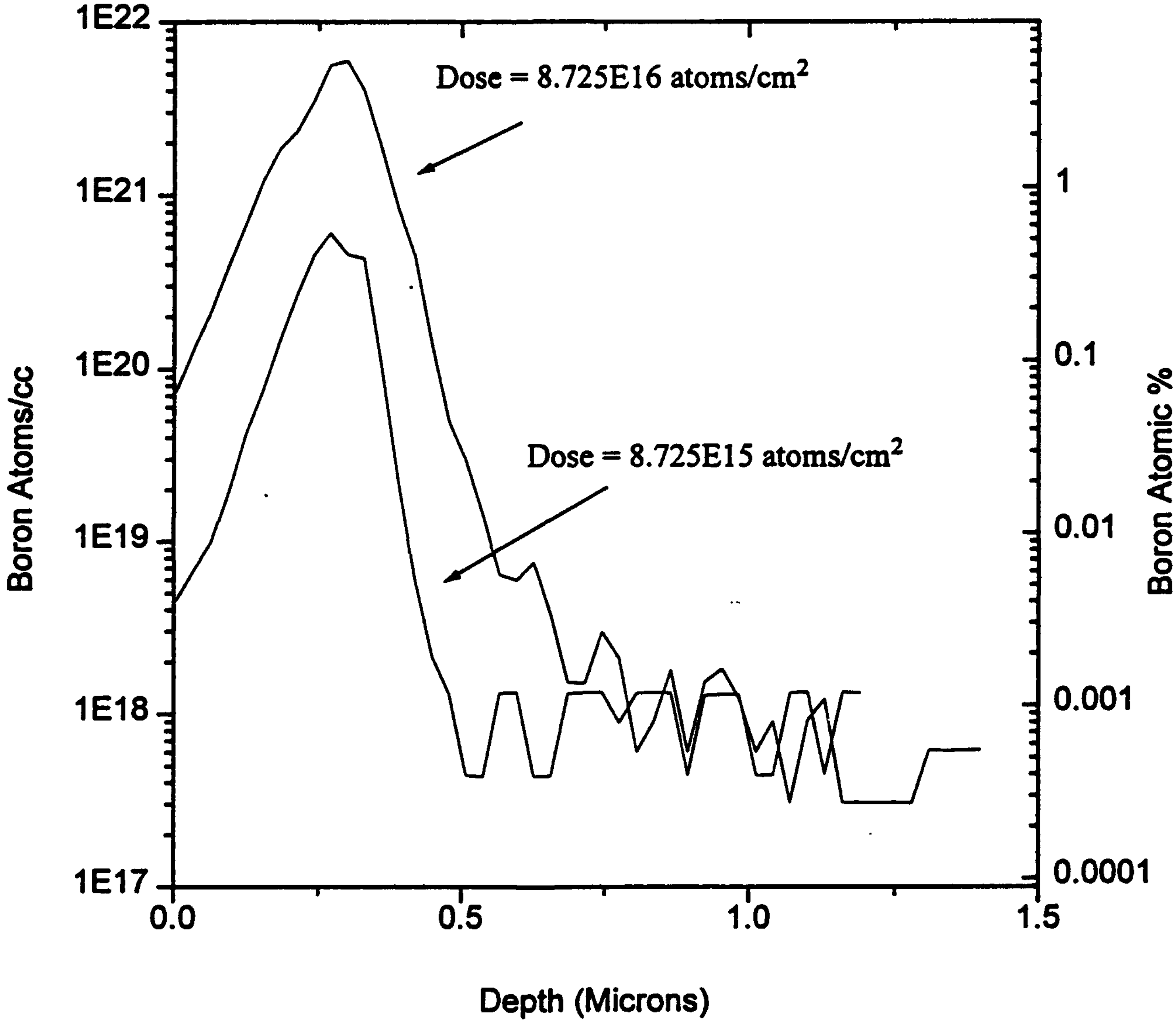


Fig. 15

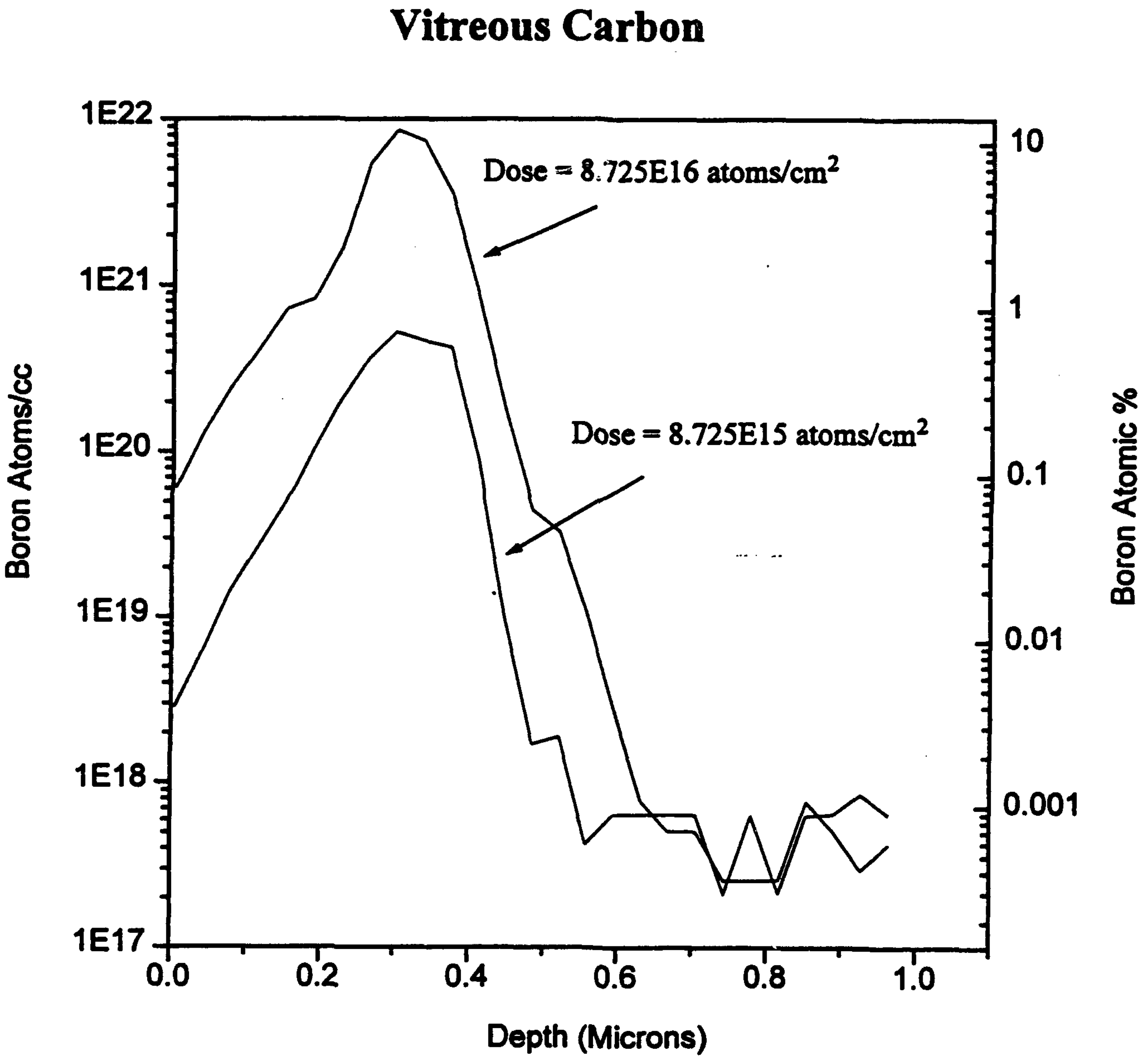

Vitreous Carbon
1E22
1E21
1E20
1E19
1E18
1E17
Boron Atoms/cc
10
1
0.1
0.01
0.001
Boron Atomic %
0.0
0.2
0.4
0.6
0.8
1.0
Depth (Microns)
Dose = 8.725E16 atoms/cm^2
Dose = 8.725E15 atoms/cm^2

Fig. 16

2.2

The various implanted carbons were subjected to a 15 minute anneal in Argon at 2300°C. The depth distributions of the boron before and after the anneal are compared in the SIMS depth profiles of Figs. 17-20. The diffusion of boron has significantly lowered the boron content in the surface layer. In the HOPG case, some lateral diffusion of boron (along the basal planes) seems to have occurred because the boron concentration falls to the original background concentration at a depth of 1.5 - 2.0 µm. In the vitreous carbon, the diffusion extends 40-50 µm in depth. The complete diffusion profiles for the vitreous carbon samples are compared in Fig. 21. These experiments will be repeated over a range of temperatures and times to establish diffusion data for boron in carbon. The preparation of carbons with higher levels of implanted boron will also be attempted to determine solubility limits for boron and to create surfaces (after annealing) with higher uniform levels of boron. These specimens will then be used for selected oxidation experiments.

The boron-implanted carbons were also examined using x-ray diffraction. One objective was to determine whether any lattice-substitution of B-for-C had occurred due to implantation and/or annealing in the HOPG. The other objective was to follow the effect of boron implantation upon graphitization of the vitreous carbon. The lattice parameters—presented in Table 6—reveal little effect of the boron. More interesting is the case of the vitreous carbon, where it is evident that the presence of boron (at > 1 atom percent) has enhanced graphitization; the XRD data are presented in Fig. 22. It is to be emphasized, though, that these data were obtained on a standard 2θ diffractometer. Thus, most of the probed region of the sample contained no boron. Ideally, a thin-film diffractometer would be used to enhance sensitivity to the thin boron implanted layer (equipment not available). On the one hand, this means that the apparent absence of lattice parameter changes or graphitization at <1 atom percent boron may be due to the limited surface sensitivity of the standard diffractometer. On the other hand, the vitreous carbon sample, wherein graphitization was detected, must contain significant quantities of graphitized carbon. These experiments are continuing.

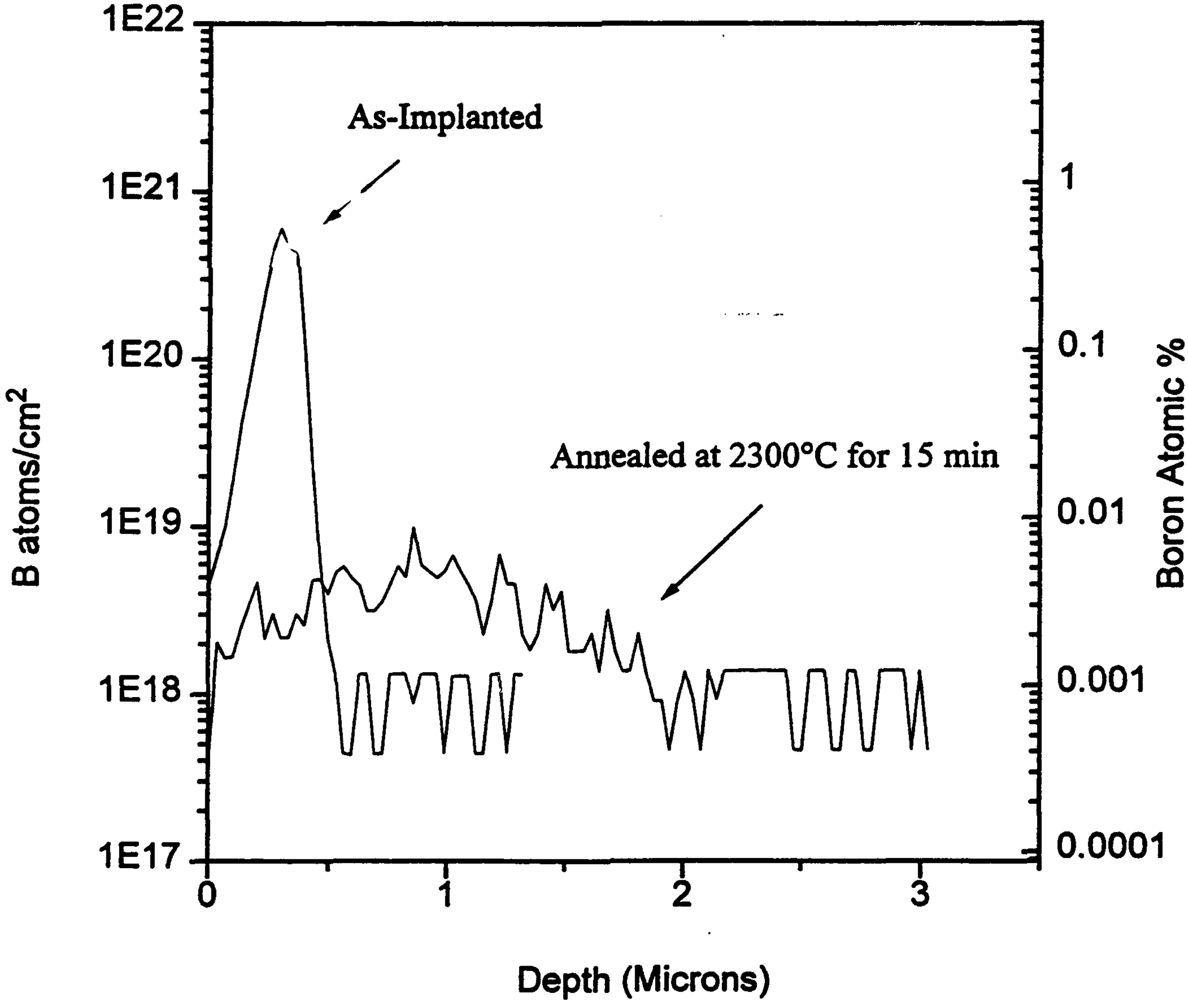
CVD of B_xC_{1-x}. Fig. 23 shows the reaction chamber that has been constructed to deposit boron doped carbon films. The deposition is based upon the reaction of benzene with boron trichloride. It is already established that BC_3 can be deposited (albeit slowly) using this chemistry. The objective in this program is to prepare carbon films with various amounts of boron (up to and including BC_3). These films will be used to characterize the concentration-dependence of boron incorporation into graphite. They will also be used to provide reference standards for the films, fibers and bulk materials processed using the polymers developed under Task 1. And finally, these films will be used to study the boron concentration dependence of oxidation under Task 3.

Table 6 X-Ray Diffraction Analyses of Ion-Implanted Carbon

SUBSTRATE	Maximum Atomic Percentage Boron (As-Implanted)	ANNEALED	LATTICE PARAMETERS (Â)
HOPG	0	No	3.358
	0.54	No	3.357
		Yes	3.358
	5.3	No	3.358
		Yes	3.357
Vitreous	0	No	Amorphous
		Yes	Amorphous
	0.74	No	Amorphous
		Yes	Amorphous
	12	No	Amorphous
		Yes	Amorphous & 3.393

Anneal →2300°C for 15 minutes

Pure graphite →3.354 Â



Boron Concentration Profile in HOPG with 8.7E15 B atoms/cm^2

Fig. 17

Boron Concentration Profile in HOPG
with 8.7E16 B atoms/cm^2

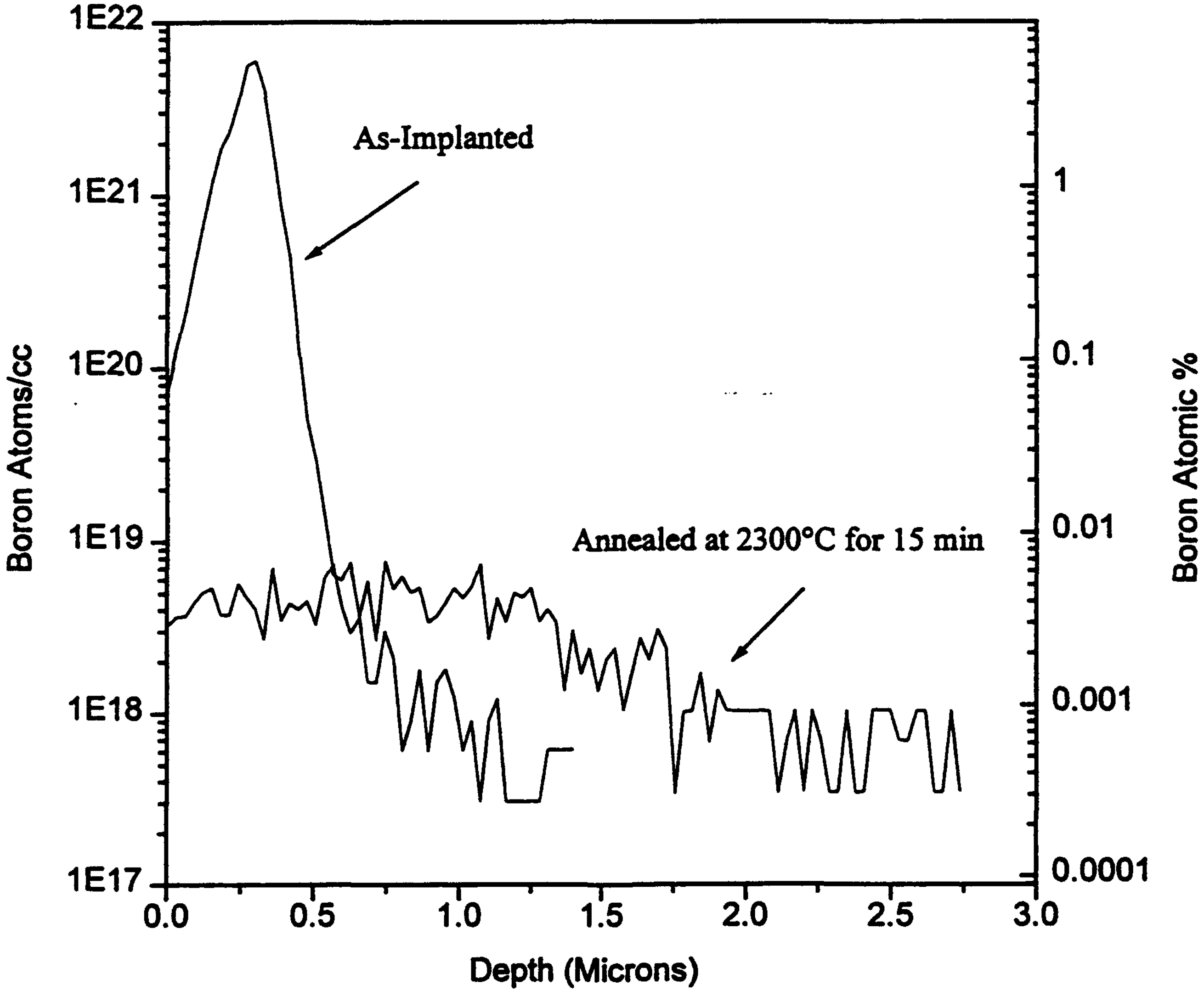


Fig. 18

Boron Concentration Profile in Vitreous Carbon with 8.7E15 B atoms/cm^2

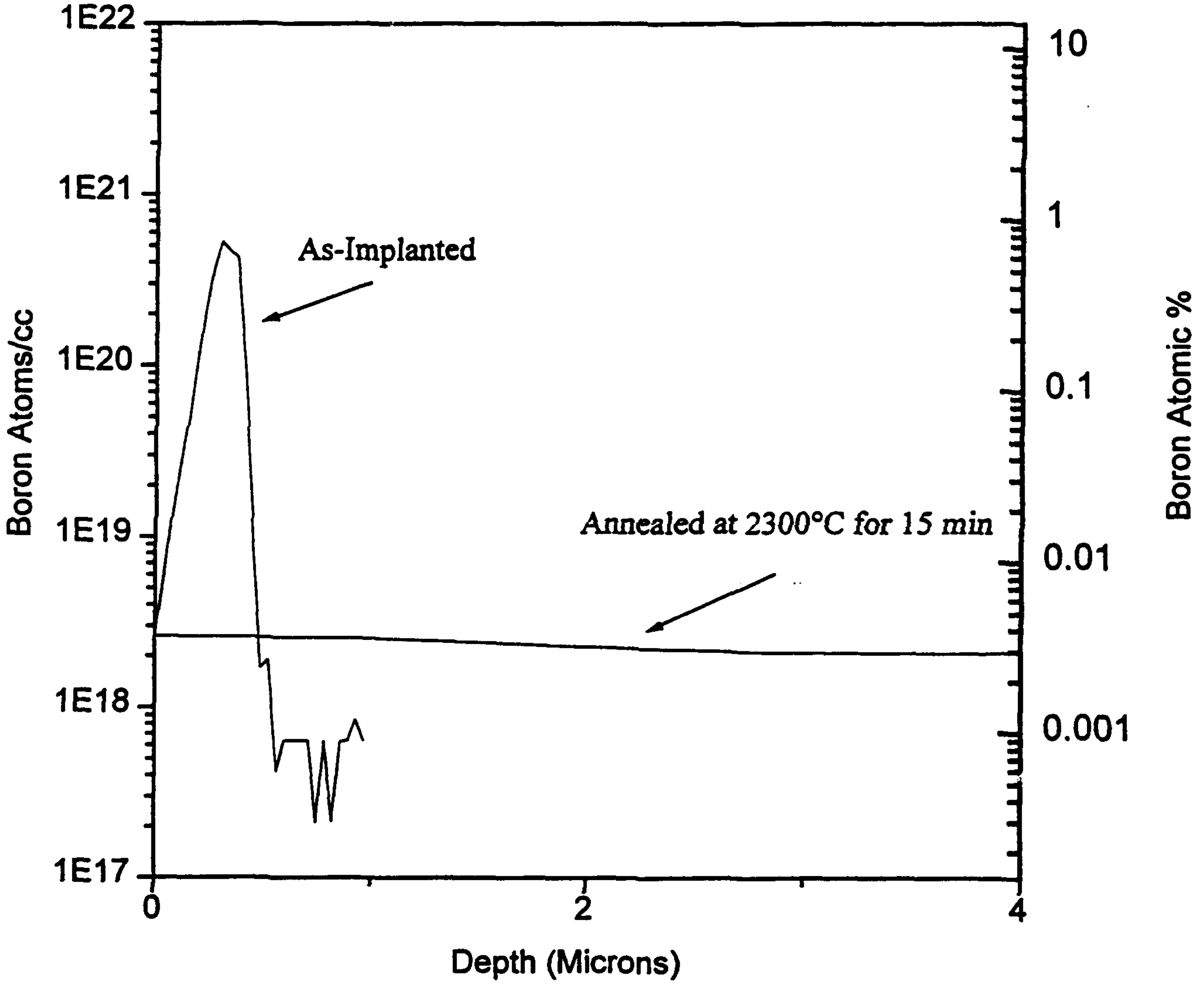


Fig. 19

Boron Concentration Profile in Vitreous Carbon with 8.7E16 B atoms/cm^2

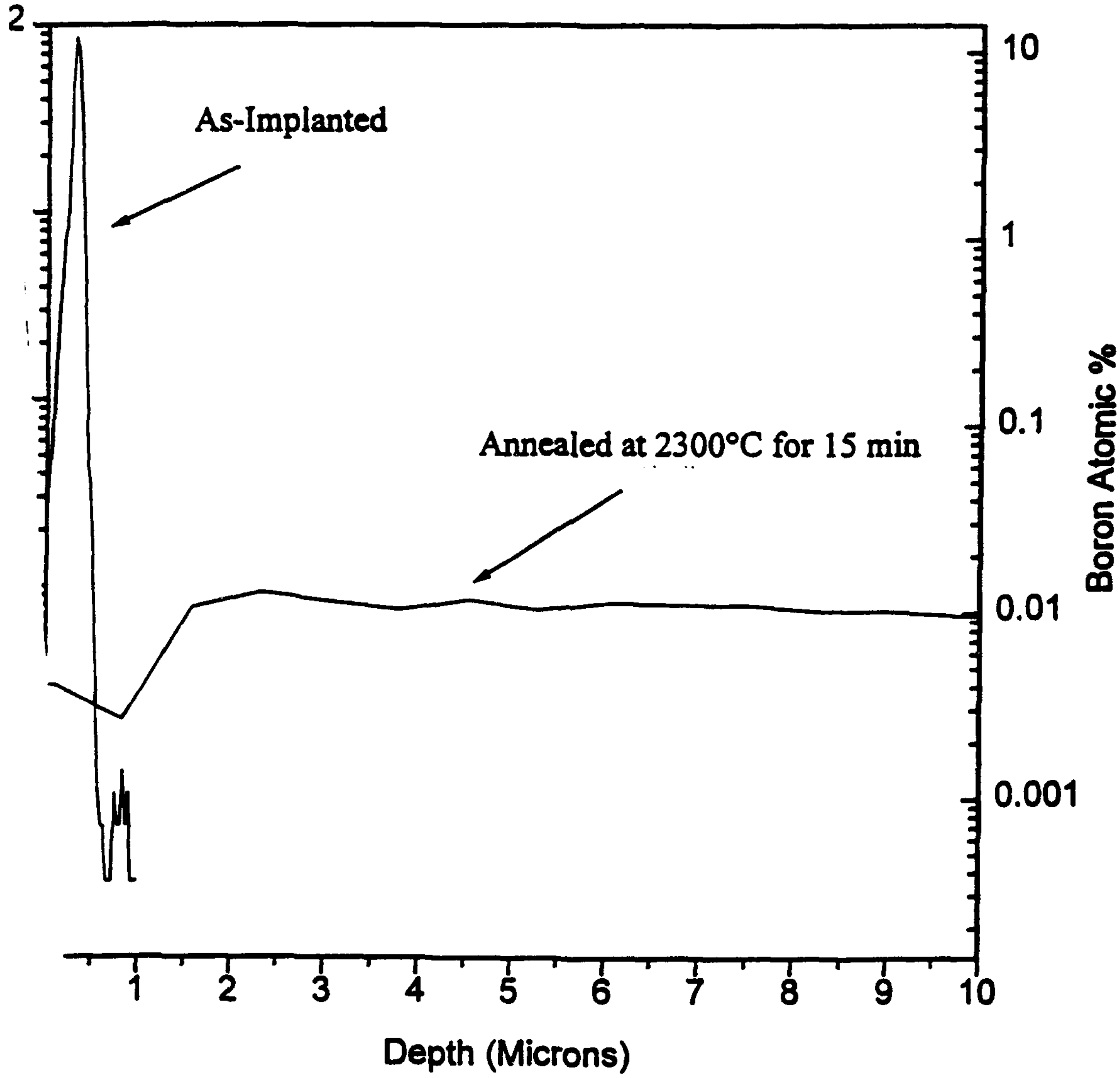


Fig. 20

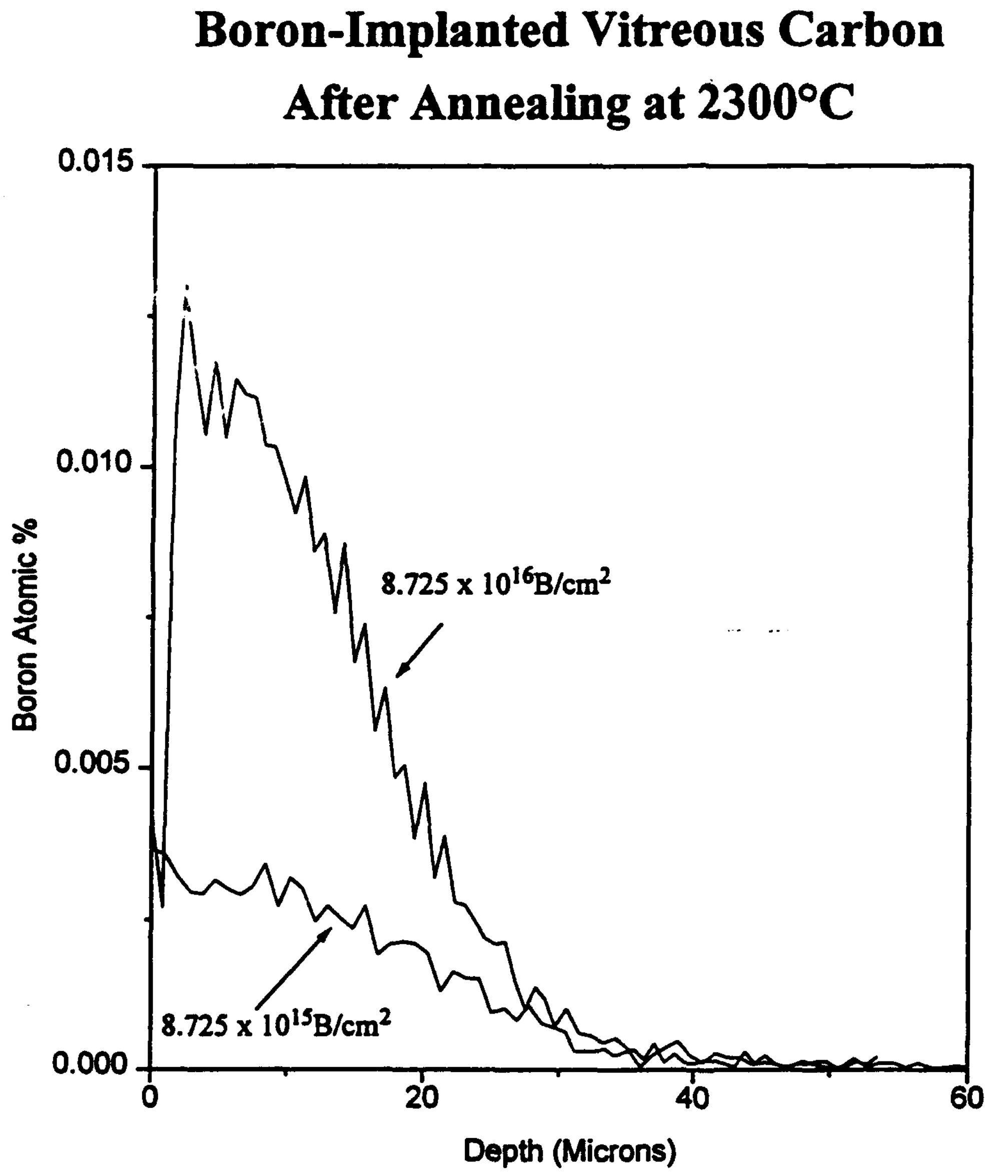

Boron-Implanted Vitreous Carbon
After Annealing at 2300°C

Fig. 21

Vitreous Carbon

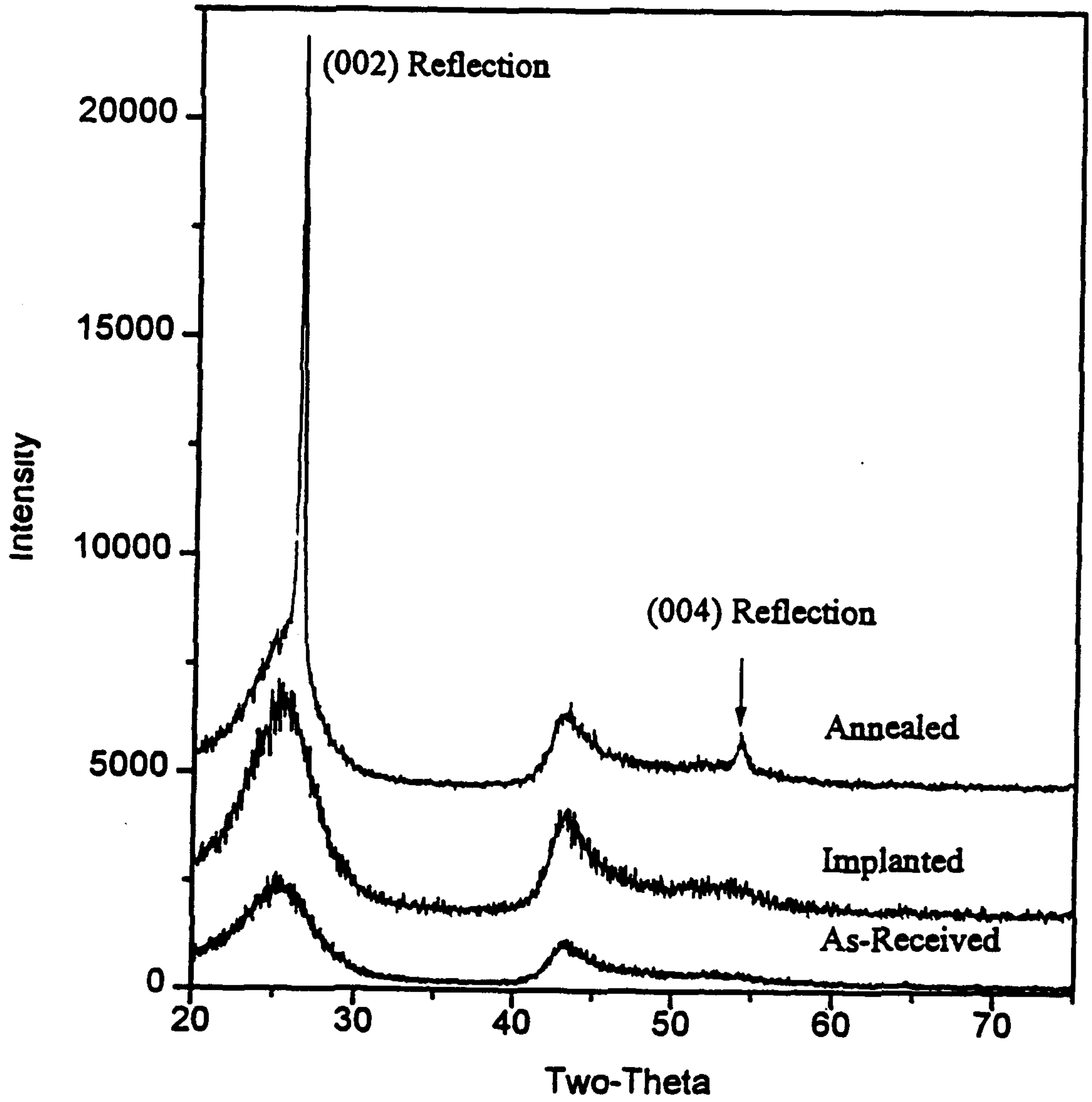


Fig. 22

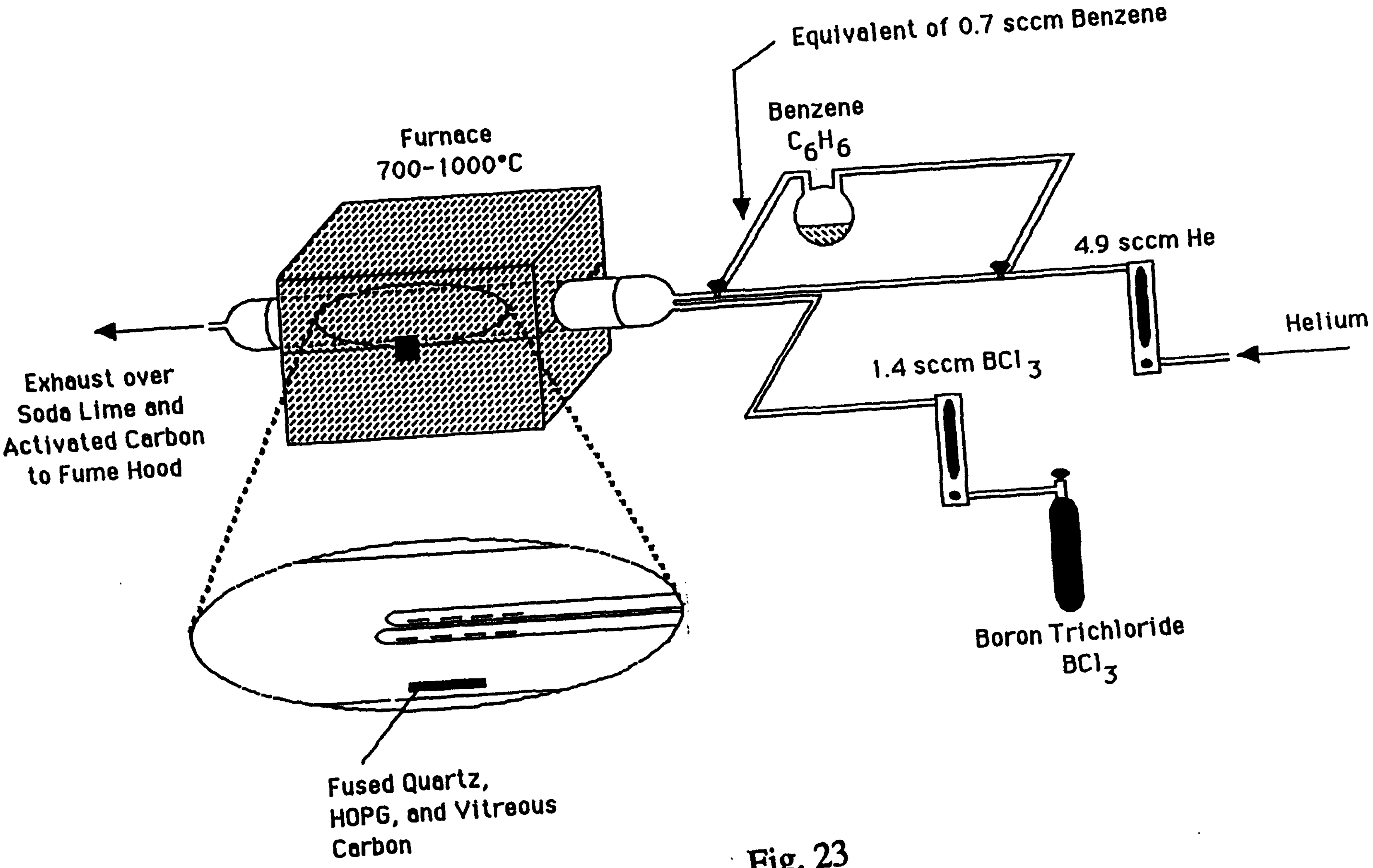

Equivalent of 0.7 sccm Benzene
Benzene
C_6H_6
Furnace
700-1000°C
4.9 sccm He
Helium
1.4 sccm BCl_3
Exhaust over
Soda Lime and
Activated Carbon
to Fume Hood
Boron Trichloride
BCl_3
Fused Quartz,
HOPG, and Vitreous
Carbon

Fig. 23

2.9

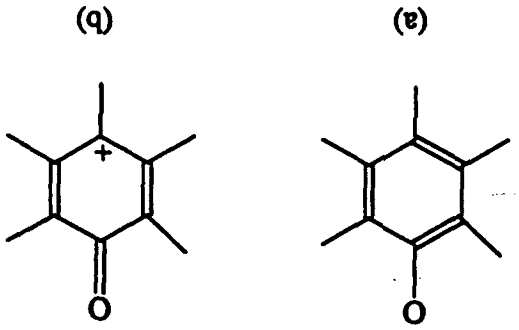
Dr. Ljubisa Radovic
Dr. Peter Thrower

Task 3.1 Oxidation Resistance of Inhibited C/C Composites

There are four proposed mechanisms by which boron can inhibit carbon oxidation:

(1) enhancement of graphitization;
(2) diffusion barrier to oxygen;
(3) specific site blockage;
(4) electron transfer theory.

Mechanisms (1)-(3) are well documented and well understood. Mechanism (4) is the most interesting, the least understood and the focus of our work. It is based on the electron transfer theory of catalysis, i.e., on the well known experimental fact that transition metals (with unfilled d bands) catalyze carbon reactions. Two possible structures of carbon/oxygen surface intermediates are shown below:



The catalyst is thought to act as an electron acceptor that induces type (b) distribution of the π electrons, weakens the C-C bond and decreases CO desorption activation energy. There is little experimental evidence, however, to support this mechanism, and the alternative oxygen transfer mechanism is favored by most investigators.

By analogy with this electronic effect of a catalyst, an inhibitor should induce type (a) distribution of the π electrons. (This issue is explored theoretically in Task 3.3; see below.)

In preparation for the analysis of boron-containing carbons generated in Task 1, samples of boron-containing chars were obtained from Aerospace Corporation (courtesy of G. Rellick). Boron was incorporated into the polyarylacetylene (PAA) resin in the form of a carborane, $C_2B_{10}H_{12}$ (Zaldivar et al., 1991). Both the sample with 5% boron and the control sample (containing no boron) were cured at 250°C in a mold under ~400 psi and subsequently carbonized at 1100°C. The x-ray diffraction profiles of the chars were found to be essentially the same

(Zaldivar et al., 1991). It was of interest, therefore, to study their oxidation resistance. Fig. 24 summarizes our preliminary results. Both samples were subjected to nonisothermal thermogravimetric analysis in oxygen. Despite the uncertainty related to the kinetics of conversion of boron into boron oxide upon boron exposure to oxygen (which will affect the shape of these TGA profiles), it is obvious from the figure that boron does not *inhibit* oxidation during the initial stage of reaction. The observed crossover may be due to the formation of a protective layer of boron oxide. This hypothesis needs to be substantiated by further studies. The samples were also subjected to heat treatment at 2900°C in our laboratory. The analysis of their oxidation resistance is under way.

Task 3.3 Modeling the Oxidation Behavior of Coatings and Composites

Molecular orbital theory, at its widely varying levels, is a popular and increasingly powerful tool for elucidating the mechanism of heterogeneous reactions in general, and carbon reactions in particular (Chen et al., 1993). We have begun a relatively straightforward analysis of the effect of substitutional boron on carbon oxidation using the simple Hückel molecular orbital (HMO) theory. The program was obtained from the Quantum Chemistry Program Exchange, Indiana University (Van Catledge, 1979). This approach is based on the finding of Stein and coworkers (Stein et al., 1987; Stein and Brown, 1987) that HMO theory was a reliable method for examining the π-electron properties of very large benzenoid polynuclear aromatic hydrocarbons.

As mentioned in Task 3.1, the fact that substitutional boron does not contribute a π electron to carbon's π electron cloud suggests that it may alter the mechanism of carbon oxidation. Specifically, the questions to be addressed are the following:

(1) Which bonds are strengthened and which bonds are weakened by boron incorporation in different amounts and locations in the carbon structure?

(2) Which step in the reaction mechanism (e.g., adsorption, desorption, or surface reaction) is most likely to be affected by boron?

Fig. 25 and Table 7 summarize our initial attempt to address these questions. The free valence index and the bond order were chosen as the relevant reactivity parameters. A bond order of 1.000 corresponds to the strength of the π bond in ethylene; the lower the number, the lower the bond strength. A carbon structure consisting of 150 atoms was used. Boron atoms were systematically inserted in place of carbon, and the effect of this substitution on C-C and C-O bond strengths was investigated. It is seen in Table 7 that in the presence of boron (B/C = 1/150, i.e., 0.67% B), C-C bonds at edge carbon atoms are weakened, while C-O bonds are strengthened. This is an interesting result, but not very surprising, as Allardice and Walker (1970) and Jones and Thrower (1987) have shown that the apparent activation energy decreases when B is added to carbon in concentrations < 5%. The immediate practical implication is that CO should be desorbed at lower temperatures during carbon gasification. This hypothesis can be tested easily using temperature-programmed desorption.

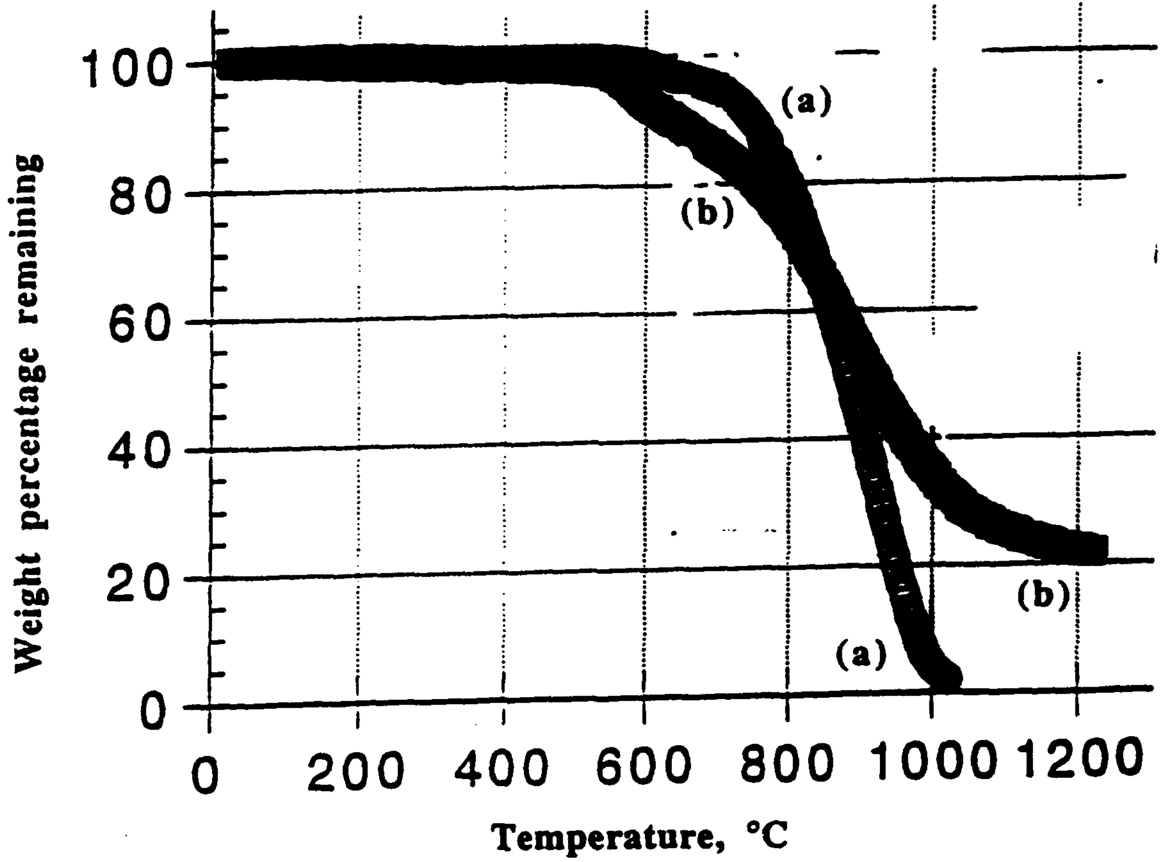


Fig. 24 Nonisothermal TGA results for (a) PAA char and (b) boron-doped PAA char. Conditions: 1 atm air, 5 °C/min, 60 cc/min, ~5 mg sample (<125 μm).

Table 7

Results of HMO calculations for a carbon crystallite having 150 carbon atoms

Position of B atom [a]	Bond Order [a]		
	C1-C2	C1-C6	C-O
None	0.44972	0.44972	0.64302
4	0.41404	0.41404	0.70458
5	0.41405	0.44951	0.68166
6	0.43402	0.34611	0.71919

[a] See Fig. 25

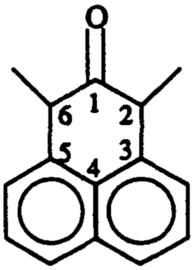


Fig. 25 Portion of a carbon crystallite (containing 150 atoms) to which boron is added substitutionally, and which contains chemisorbed oxygen at the edge (see Table 7).

References

Allardice, D. J. and P. L. Walker, Jr., *Carbon* **8**, 375 (1970).

Chen, S. G., R. T. Yang, F. Kapteijn and J. A. Moulijn, *Ind. Eng. Chem.* **32**, 2835 (1993).

Jones, L. E. and P. A. Thrower, *J. Chim. Phys.* **84**, 1431 (1987).

Stein, E. S., R. L. Brown and S. A. Kafafi, in *Proc. 1987 Intern. Conf. Coal Sci.*, Elsevier, Amsterdam, 495 (1987).

Stein, E. S. and R. L. Brown, *J. Amer. Chem. Soc.* **109**, 3721 (1987).

√an Catledge, F., QCPE 385, 1979.

Zaldivar, R. J., R. W. Kobayashi and G. S. Rellick, *Carbon* **29**, 1145 (1991).