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Synopsis

Carborane substituted polyphosphazenes were prepared by the thermal polymerization of phenyl-carboranyl penta chlorocyclotriphosphazene. Successive isothermal vacuum pyrolyses were conducted on the polymer and examined for structural changes by infrared spectroscopy. The degradation products were ascertained by gas chromatography-mass spectrometric analysis. It was found that the presence of the carborane group improves the thermal stability of the polymer by retarding the ring-chain equilibrium processes of decomposition.

INTRODUCTION

Progress in the field of phosphazene chemistry has been rapid and a variety of polyorganophosphazene polymers have resulted. Polyorganophosphazenes with interesting chemical and physical properties such as resistance to alkali and acids (except concentrated sulfuric acid), water and oil repellant, high degree of fire resistivity, and flexibility at low temperatures (-60° to -80°C) have been synthesized.[1-3] The alternating phosphorus and nitrogen atoms in the backbone of phosphazene polymers is responsible for the high degree of torsional mobility and accounts for the low glass transition temperature (Tg) values and the transparency of the polymer to ultraviolet radiation.[1]

The susceptibility of the phosphorus-chlorine bond to hydrolysis has been surmounted by nucleophilic substitution reactions (Fig. 1) involving the replacement of halogen atoms of polydichlorophosphazenes by alkyl, aryl, amino, alkoxy, and aryloxy groups.[1-4] Hydrolysis of the hexachlorocyclotriphosphazene trimer to the oxophosphazane (Fig. 2, ref. 5), which is thermally unstable due to its P-N-P type bonding.

The addition of the phenylcarborane group on the hexachlorocyclotriphosphazene ring followed by thermal polymerization and the replacement of remaining chlorine atoms with trifluoroethoxy groups (Fig. 3) result in an enhancement of the thermal stability of phosphazene polymers.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (I) trimer, obtained from Ethyl Corp., was sublimed (at 0.05 mm, 80°C) and recrystallized from redistilled hexane. The purified hexachlorocyclotriphosphazene trimer had a melting point range of 110° to 112°C. Phenylacetylene and n-butyl lithium (1.6 molar in hexane) were obtained from Aldrich Chemicals and used as received. Trifluoroethanol and tetrahydrofuran were obtained from Fisher Chemical; the tetrahydrofuran was dried over sodium and redistilled. Decarborane was obtained from Alfa Chemicals and diethyl ether from Mallinckrodt.

Analytical Equipment

Infrared spectra were recorded on a Nicolet MX-1, Fourier Transform Infrared spectrometer. Gas chromatography-mass spectrometric analysis of the polymer's decomposition products was accomplished using a Hewlett-Packard model #5710A gas chromatograph with a 6-ft column packed with 3% OV 101 on 80/100 mesh Supelcoport AWDC and interfaced with an all-glass jet separator to a Hewlett-Packard model #5980A mass-spectrometer computer system. Successive pyrolyses of the polymer were conducted using a Chemical Data Systems model #120 Pyroprobe by heating the identical sample (2 mg) for 40 sec at the desired pyrolysis temperature. After analysis of the pyrolysis products the probe was allowed to cool before subjecting the polymeric residue to the next pyrolysis temperature for the same time period.

Thermogravimetric analyses were obtained with a DuPont 990 thermoanalyzer.

Polymer Synthesis

The synthesis of the poly(phenylcarboranyl-trifluoroethoxy) phosphazene[6] involves the thermal polymerization of carboranyl-substituted halocyclotriphosphazene trimer. The chlorine atoms of this linear polymer are substituted with alkoxy groups by reacting the polymer with sodium trifluoroethoxide. The method of synthesis followed in this study is as follows:

Synthesis of Phenylcarborane (II)

A solution of decarborane (20 gm, 164 mmole) in 150 ml acetonitrile was refluxed for 2 hr. The solution becomes light yellow and is then allowed to cool to a white precipitate (bisacetonitrile-decarborane), filtered, and washed with 20 ml of acetonitrile to remove the slightly yellow colored supernatant. Bisacetonitrile decarborane (13.6 gm, 67.3 mmoles) and phenylacetylene (8.3 gm, 81.3 mmole) in 140 ml of benzene were refluxed for 4 hr. The mixture was allowed to cool and the sediment removed by filtration. The filtrate was treated with 100 ml of trimethylamine. The resulting mixture contained a small amount of sediment and was removed by filtering. The filtrate was rotoevaporated and the resulting solid material was placed in a sublimator (62°C at 0.05 mm). The sublimate removed (m.p. was 69°C) and confirmed by infrared spectroscopy (Fig. 4).

Synthesis of Sodium Trifluoroethoxide

Sodium (2.18 gm, 95 mmoles) and 20.5 ml of trifluoroethanol were allowed to react at ambient conditions and the unreacted sodium was separated by filtration. The sodium trifluoroethoxide solution was dried in a vacuum oven at 80°C overnight.

Synthesis of Phenyl-lithiocarboranes

A solution of phenylcarborane (1.38 gm, 6.23 mmoles) in 10 ml of anhydrous diethyl ether was cooled in an ice bath. N-butyl-lithium (3.95 ml, 6.32 mmoles) was added by drops and the solution was vigorously stirred for 15 min until it appeared cloudy and yellowish. The mixture was further stirred for 1 hr; upon standing an oily layer separated from the ether solution. This solution was used in situ for the organometallic substitution reaction on the trimer.

Reaction of the Phenyl-lithiocarborane with the Hexachlorocyclotriphosphazene (I) trimer

To the freshly prepared phenyl-lithiocarborane solution, the trimer (I) (2.2 gm, 6.3 mmoles) which was dissolved in 15 ml anhydrous ether was added by drops with vigorous stirring at 0°C within approximately 15 min. The mixture was allowed to warm slowly to ambient temperature and stirred for an additional 12 hr. The solvents were removed and the solid material placed in a vacuum sublimator (60°C, evacuated to 0.05 mm) after which the sublimable solid compounds were removed. The temperature of the oil bath was then increased to

130°C to yield a crystalline sublimate which was further purified by recrystallization from hexane (m.p. was 133°C) and confirmed by infrared spectroscopy (Fig. 5).

Polymerization of Phenylcarboranyl-pentachlorocyclotriphosphazene (II)

A 2.0 gm sample of phenylcarboranyl-pentachlorocyclotriphosphazene was placed in a 10 by 1.0 cm Pyrex ampule. The sample tube was evacuated to 10^{-5} torr for 1 hr. The sample was degassed by three freeze-thaw evacuation cycles to thoroughly degas the sample. The tube was sealed and encased in a wire-mesh screen jacket. The screen encased ampule was then placed in an oven at 250°C and its viscosity periodically checked visually for several days until the melt was very viscous and resistant to flow. The sample was sublimed at 90°C, 0.05 mm to remove any unreacted trimer. The polymer was stored under vacuum until used in the halogen substitution reaction with sodium trifluoroethoxide.

Reaction of Linear Poly (phenylcarboranyl) dichlorophosphazene with Sodium Trifluoroethoxide

The phenylcarboranyl poly (dichlorophosphazene) polymer was dissolved in 15 ml of dry tetrahydrofuran and treated with a solution of sodium trifluoroethoxide (14 mmoles) in dry tetrahydrofuran for 120 hr at 66°C. The solution was concentrated and neutralized with dilute hydrochloric acid. The precipitate that developed was filtered, washed with distilled water, and dried. The poly (phenylcarboranyl-trifluoroethoxy)-phosphazene polymer (IV) was obtained by a fractional precipitation of the tetrahydrofuran solution of the polymer (IV) into benzene.

Film Preparation

Samples were prepared by dissolving 2.5 mg of polymer (IV) in 2 ml dry tetrahydrofuran and were dropped on a 1.8 by 4.0 cm aluminized mirror and allowed to evaporate in air at ambient conditions.

Pyrolysis Technique

The aluminized mirror coated with the polymer film was placed in a pyrolysis tube and evacuated for 2 hr at a pressure of 10^{-5} torr. The sample was removed from the pyrolysis tube and placed in a reflectance cell and an infrared spectrum of the film taken.

Successive isothermal vacuum (10^{-5} torr) pyrolyses were performed on the same polymer and its polymeric residues were examined for structural changes by infrared spectroscopy.

RESULTS AND DISCUSSION

The thermal stability of the polymer was ascertained by thermogravimetric analysis (TGA) in dry nitrogen and in air which showed high char yields of 57 and 61%, respectively, at 800°C (Fig. 6). The weight loss versus temperature of the polymer is less in air than in nitrogen which may be due to the buildup of an oxide film on the surface of the polymer.

Some of the low molecular weight compounds were removed by drying the polymer at 75°C for 16 hr after which a thermogravimetric analysis was conducted in air and in nitrogen at a heating rate of 10°C/min. The result of the TGA (Fig. 7) indicated higher char yields in air (65%) than in nitrogen (59%). The effect of thermal aging on the polymer's char yield was determined by TGA of their polymeric residues after heat treatment at 300°C in a nitrogen environment. The polymer was heated at 5°C/min to 300°C, cooled to ambient temperature and heated (5°C/min) to 800°C in the thermal analyzer. A portion of the polymer sample was held at 300°C for 1 hr and heated (10°C/min) to 860°C. A comparison of char yield due to thermal aging is presented in Figure 8. The improvement in the thermal stability of this class of phosphazene polymer is realized when one considers that this carborane-substituted polymer is analogous to the poly(bis-trifluoroethoxy) phosphazane. A comparison of the thermal properties of poly(bis-trifluoroethoxy) phosphazane and its carborane-substituted analog are summarized in Table I. The high char yield in air of the carborane-substituted polymer is a unique property and is indicative of its stability and resistance to thermal-oxidative degradation.[7]

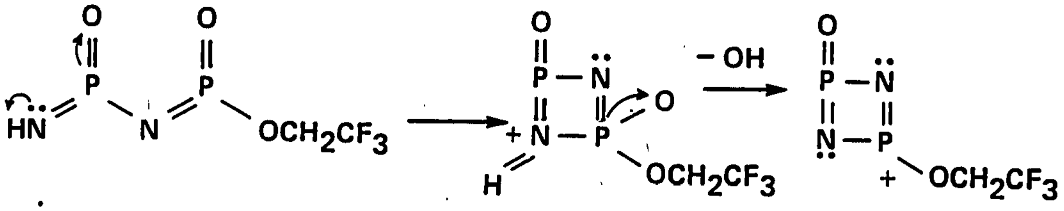
Infrared spectra of the virgin polymer film (Fig. 8) showed a weak absorption at 3600 to 3100 cm^{-1} representative of O-H and/or N-H group absorptions in this region; however, absorption at this range is most likely attributable to O-H group absorptions due to a small amount of hydrolysis resulting from atmospheric moisture pickup. The P-Cl group is quite sensitive and liable to undergo hydrolysis (Fig. 2, ref. 5). Absorption at 1720 cm^{-1} is due to the $P = 0$ group which confirms that a small amount of hydrolysis has occurred. A weak absorption at 3018 cm^{-1} is a C-H stretching frequency and a strong P-O-C absorption at 1080 cm^{-1} and 963 cm^{-1} is due to the trifluoroethoxy substituent. Strong absorption at 1176 cm^{-1} is due to CF group of trifluoroethoxy group. Absorption at 2600 cm^{-1} is due to B-H bond oscillations of the carborane cage group and the strong absorption at 1280 cm^{-1} and 775 cm^{-1} is by the P-N backbone.

Pyrolyses of the polymer film at 100°C and 150°C at 10^{-5} torr for 1 hr resulted in no observable structural changes except for a decrease in the intensity of absorption at 3600-3100 cm^{-1} (O-H group). Pyrolysis of the film for 1 hr (10^{-5} torr) at 200°C indicated a decrease in the intensity of absorption as well as the disappearance of absorptions at 3600-3200 cm^{-1} (O-H stretching) and at 1740 cm^{-1} (P = O). The absence of absorption at these frequencies seems to indicate the removal of the thermally unstable products resulting from a small amount of atmospheric moisture pickup (Table II). The polymer residue was vacuum pyrolyzed (10^{-5} torr) for 1 hr at 300°C and infrared spectral analysis indicated a decrease in absorption at 2600 cm^{-1} suggesting a reduction in the borane content of the polymer. The trifluoroethoxy group is removed at this temperature as indicated by the absence of absorptions at 1080 cm^{-1} (P-O-C) and 3018 cm^{-1} (C-H stretch). The loss of the trifluoroethoxy groups results in increased crosslinking between phosphazene chains in the polymeric residue.[7]

The infrared spectra of the polymer residue after vacuum pyrolysis at 400°C indicate that very little of the borane is left in the polymer based on the very weak absorption at 2600 cm^{-1} (B-H). Pyrolysis above

400°C resulted in no significant weight loss or discernible structural changes based on infrared spectroscopy (Fig. 6).

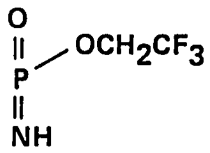
Pyrolysis probe temperatures were selected based on TGA and infrared data. The probe temperatures selected were 200°C, 300°C, and 400°C. Total ion current traces of gas chromatographic effluents after their respective probe pyrolyses are shown in Fig. 9. After probe pyrolysis at 200°C for 40 sec, four minor peaks and two major peaks are indicated. The minor peaks at retention times (RT) 4.9, 5.2, 5.9, and 6.1 min are impurities and low molecular weight polymer chains containing trifluoroethoxy and phenylcarboranyl groups. The minor peak with a retention time of 5.2 min had a mass spectrum which showed a parent peak at 729 atomic mass units (amu) and peaks at m/e 99, 83, 69, 64, and 63 which are characteristic fragmentations associated with trifluoroethoxy group ($CF_3CH_2O^+$, $CF_3CH_2^+$, C^+F_3, $CF = C^+H_2$, and CF_2C^+H fragments). Fragmentation patterns characteristic of the carborane group undergoing electron impact were also observed[8] and indicate that this low molecular weight P-N compound contains trifluoroethoxy and phenylcarboranyl groups. Mass spectra of the compound having retention times of 5.9 and 6.1 min could not be assigned a structure based on their fragmentation pattern that could be related to the polymer. It was concluded that these compounds are possibly contaminants or impurities of unknown origin. The two major peaks at RT 6.7 and 8.0 min are the pyrolysis products that are indicative of structural changes observed by infrared spectroscopy of the polymeric film. The first major peak is due to the small amount of hydrolysis. The mass spectra of the compound had a parent peak $M^+ - 222$ and a base peak at m/e 205 (Table II). The compound has a molecular weight of 222 and undergoes rearrangement to form a base peak as described below:



(M)$^+$M/E–222

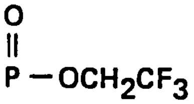
M/E–205

Other peaks confirming this structure are as follows:



$HN=P(=O)OCH_2CF_3$

M/E–161

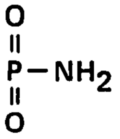


$O=P-OCH_2CF_3$

M/E–146

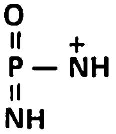
$HN=P-OCH_2CF3$

M/E–145



$O=P(=O)-NH_2$

M/E–79



$HN=P(=O)-\overset{+}{N}H$

M/E–77

$CH_2=CF_2$

M/E–64

$\overset{+}{C}H=CF_2$

M/E–63

FT-IR spectra of the polymer residue (Fig. 8) confirms the loss of the hydrolysis product as evidenced by the absence of absorptions characteristic of the O-H and P = 0 groups (Fig. 2). The other major pyrolysis product at this probe temperature has an RT of 8.0 min (Fig. 9a) and a parent peak M^+ - 283 amu. Mass spectra of this compound (Fig. 10) in addition to the parent peak (M^+ - 283) had an ion cluster (212-222 m/e) which is characteristic of the carborane cage during electron impact due to the loss of protons from the borane cage.

Probe pyrolysis of the polymeric residue at 300°C for 40 sec produced three minor peaks and one major peak (Fig. 9b). The fragmentation of the minor peak (RT = 0.7) indicates that it has a trifluoroethoxy group with mass peaks at 99, 83, 69, 63, 31, and 30 m/e whose source is the trifluoroethoxy substituent. At this temperature all of the trifluoroethoxy group have been thermally cleaved from the polymer. The minor peak at RT = 6.6 min is a residue of the hydrolysis product and indicates that the short duration of the probe pyrolysis time (40 sec) was not sufficient time to remove all of this product as compared with the 1 hr pyrolysis time of the film. A low molecular weight fraction (630 amu) with RT = 5.2 min is a trifluoroethoxy containing PN chain. Probe pyrolysis of the polymer residue at 400°C for 40 sec produced four minor peaks and one major peak. The peak at RT = 0.4 min is similar to the compound produced at 300°C based on its fragmentation. The peak at RT = 5.2 min (Fig. 9c) is a low molecular-weight polymer fragment. The major peak at RT = 8.0 min is phenylcarborane.

FT-IR spectra of the polymer film after successive pyrolyses are in agreement with the results obtained by probe pyrolysis, gas chromatography (GC), and mass spectrometry (MS) analyses. Structural changes in the polymer residue due to pyrolysis as ascertained by infrared spectral analysis of the pyrolyzed film with the GC-MS data are summarized in Table I.

The thermal degradation of the polymer occurs by the following processes. The initial weight-loss is not due to thermal degradation but rather a purging process which consists of the removal of low molecular weight compounds and products related to hydrolysis of the P-Cl bond due to atmospheric moisture pickup. The primary thermal reaction involves the loss of trifluoroethoxy groups from the polymer during pyrolysis at 300°C which results in crosslinking between phosphazene chains producing a thermally stable polymer residue (Fig. 8). The second thermal reaction occurs during pyrolysis at 400°C and involves the loss of phenylcarborane from the polymer resulting in more crosslinking and a highly thermal/thermal-oxidatively resistant char structure.

The carborane group has a considerable propensity for electron withdrawal or acceptability which is responsible for the inductive characteristics[9] its interactions with the phenyl ring and its greater electron mobility that allows the phenylcarborane to function as an energy sink. The phenylcarborane in the PN backbone may sterically hinder and thereby inhibit helical coil formations which are low-energy pathways to the formation of cyclic compounds of depolymerization.[10,11]

The phenylcarborane group in the polymer backbone has resulted in a substantial improvement of the thermal stability of the polymer by retarding ring-chain mechanisms of depolymerization.

ACKNOWLEDGMENTS

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10. J. R. MacCallum and J. Tanner, Macromol. Sci. Part A, 4, 481 (1970).

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TABLE I

POLYMER DECOMPOSITION TEMPERATURE AND CHAR YIELD

POLYMER	NITROGEN ATMOSPHERE			AIR ATMOSPHERE		
	PDT, °C	TEMPERATURE, °C MAX. RATE OF WEIGHT LOSS	% CHAR YIELD AT 800°C	PDT, °C	TEMPERATURE, °C MAX. RATE OF WEIGHT LOSS	% CHAR YIELD AT 800°C
POLY (PHENYLCARBORANYL-TRIFLUOROETHOXY) PHOSPHAZENE (IV)	110	395	61	110	380	57
POLYMER (IV) (DRIED AT 75°C FOR 16 hr)	120	465	59	120	455	65
POLY (2,2,2, TRIFLUOROETHOXY) PHOSPHAZENE	370	410	0	180	412	0

PDT – POLYMER DECOMPOSITION TEMPERATURE

TABLE II

MAJOR PYROLYSIS PRODUCTS OF POLYMER (IV) BASED ON FT–IR AND GC–MS DATA

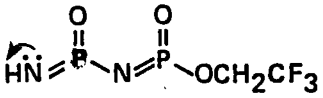
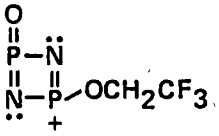
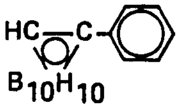
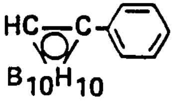
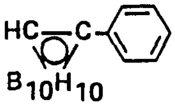
PYROLYSIS TEMP., °C	CHANGE IN INFRARED ABSORPTION, cm^{-1}	TOTAL ION CURRENT		MASS M/e, amu	PROBABLE STRUCTURE
		RT (min.)	REL. PEAK HT.		
200	3500-3200 (O-H) 1720 (P=O) (WEAK)	6.7	93	222	
				205	
	3018 (C-H) 2600 (B-H)	8.1	36	223	
300	3018 (C-H) (VERY WEAK) 2600 (B-H) (DECREASE) BROAD BANDS 1500-1300 1250-750 (P=N)	8.0	94	223	
400	2600 (B-H) (VERY WEAK) BROAD BANDS 1500-1300 1250-750 (P=N)	8.0	97	223	

Figure Legend

Fig. 1. Nucleophilic substitutive reactions for circumventing hydrolysis.

Fig. 2. Hydrolysis reactions of hexachlorocyclotriphosphazene trimer (I).

Fig. 3. Synthesis scheme for poly (phenylcarboranyl-di-trifluoroethoxy-phosphazene (IV).

Fig. 4. FT-IR spectra of phenylcarborane (II).

Fig. 5. FT-IR spectra of phenylcarboranyl-pentachlorocyclotriphosphazene (III).

Fig. 6. Thermogravimetric analysis of polymer (IV) in dry nitrogen and air.

Fig. 7 Thermogravimetric analysis of polymer (IV) after drying for 16 hrs. at 75°C in nitrogen.

Fig. 8. The effect of thermal aging on char yield.

Fig. 9. FT-IR spectra of polymer (IV) film and after successive isothermal vacuum pyrolyses.

Fig. 10. Total ion current traces of gas chromatographic effluents.

Fig. 11a. Mass spectra of hydrolysis product after pyrolysis at 200°C.

Fig. 11b. Mass spectra of phenylcarborane fragment after pyrolysis at 200°C.

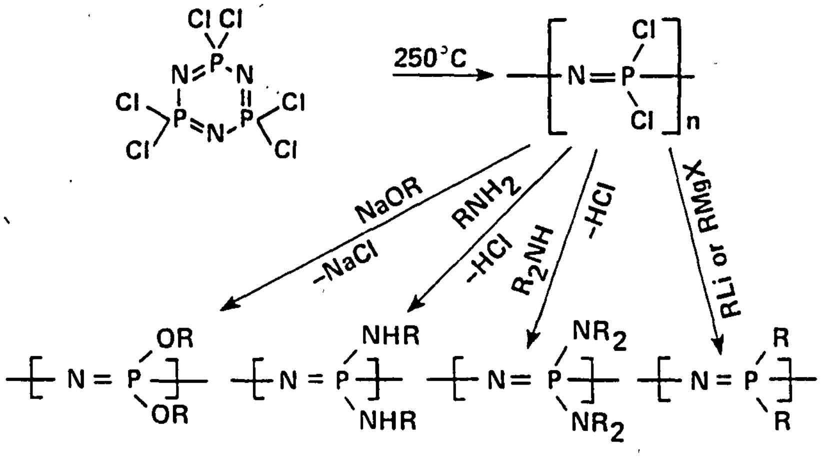


Fig. 1

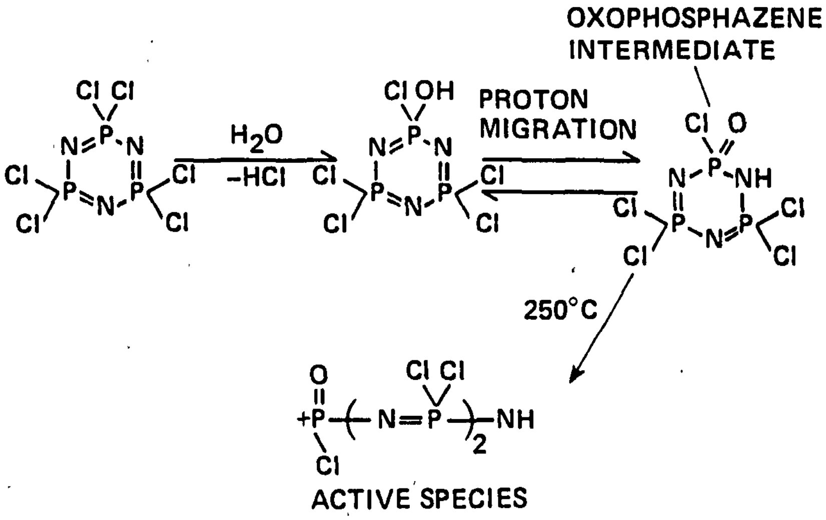

OXOPHOSPHAZENE INTERMEDIATE
H_2O
−HCl
PROTON MIGRATION
250°C
ACTIVE SPECIES

Fig. 2

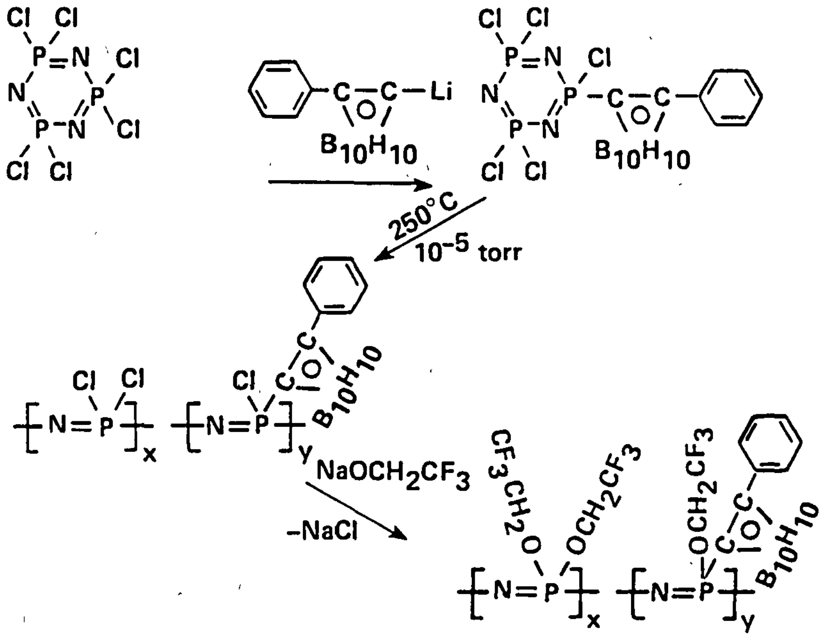


Fig. 3

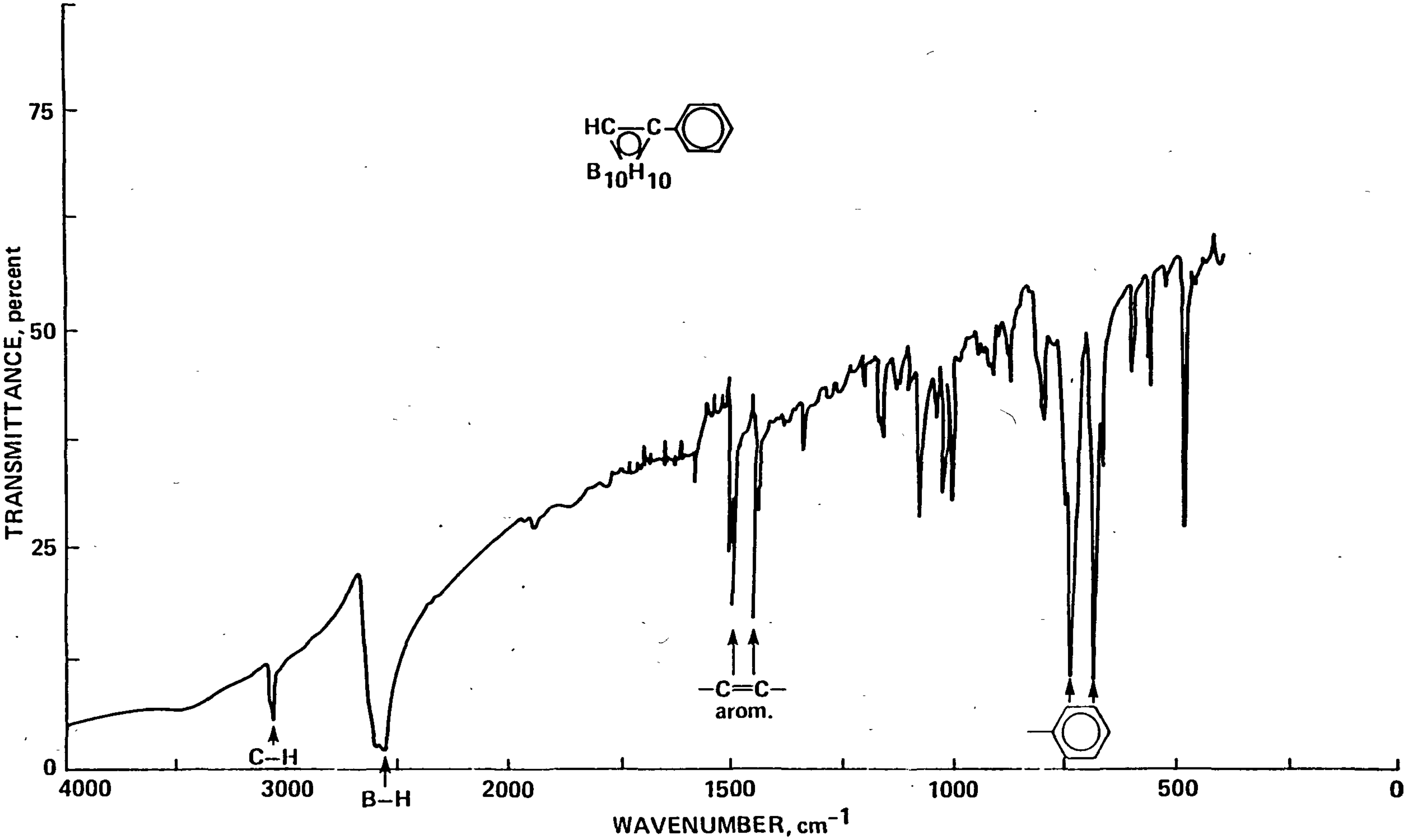

HC—C—
$B_{10}H_{10}$
TRANSMITTANCE, percent
75
50
25
0
C—H
B—H
—C=C—
arom.
4000
3000
2000
1500
1000
500
0
WAVENUMBER, cm^{-1}

Fig. 4

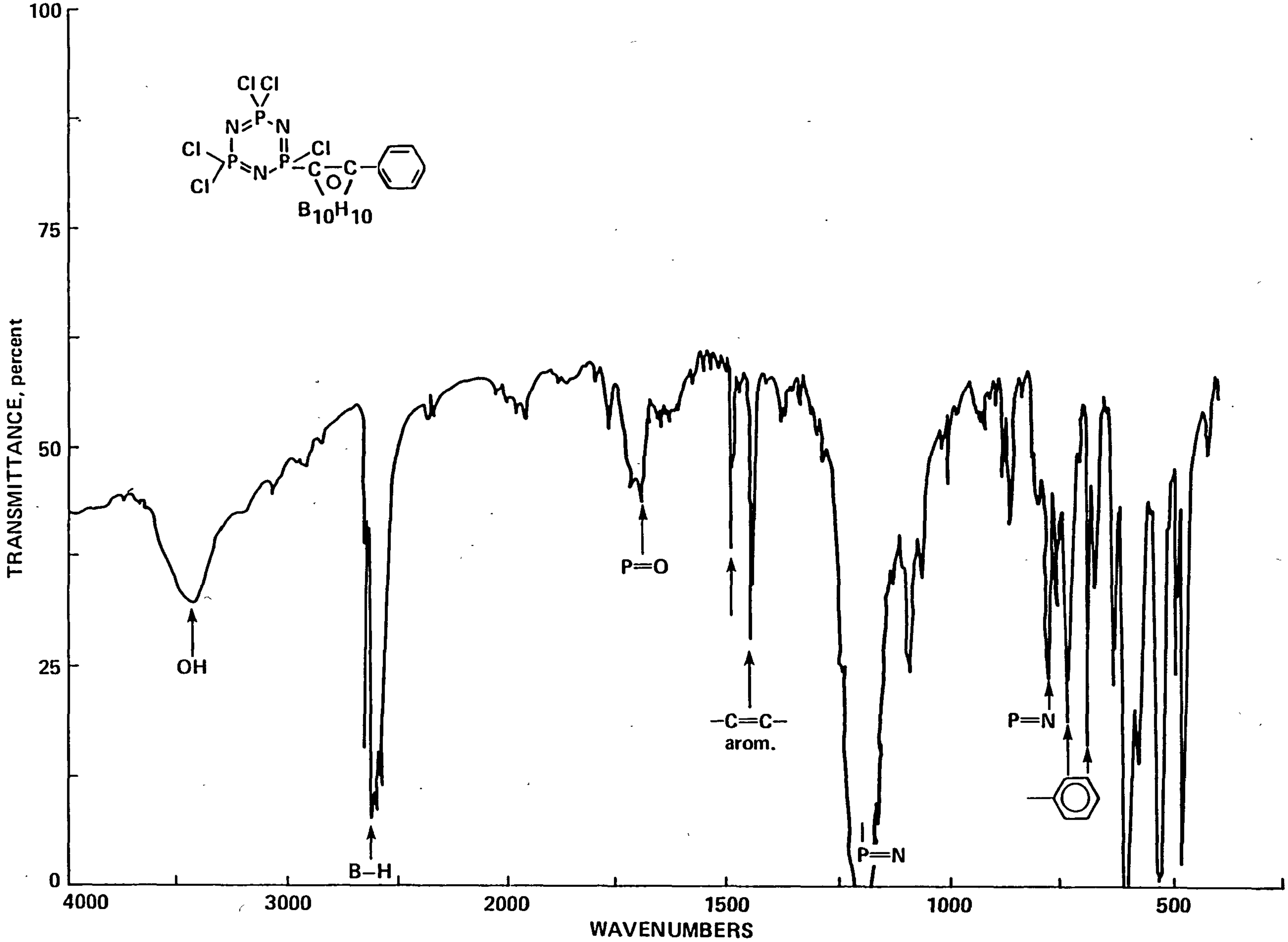

100
75
50
25
0
TRANSMITTANCE, percent
4000
3000
2000
1500
1000
500
WAVENUMBERS
OH
B–H
P=O
–C=C–
arom.
P=N
P=N
Cl Cl
P
N
N
Cl
Cl
P
N
P
Cl
C
C
O
$B_{10}H_{10}$

Fig. 5

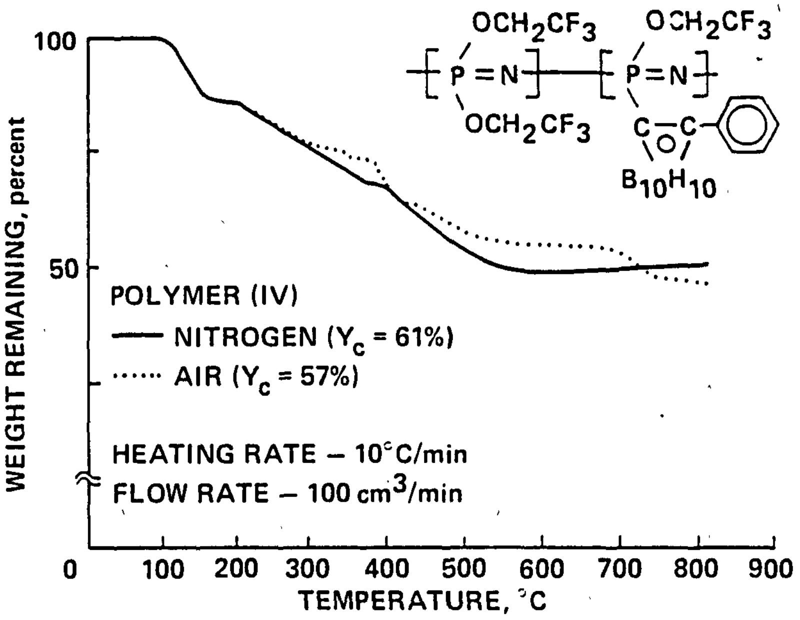

100
50
0
100
200
300
400
500
600
700
800
900
TEMPERATURE, °C
WEIGHT REMAINING, percent
OCH2CF3
OCH2CF3
P=N
OCH2CF3
P=N
C—C
O
B10H10
POLYMER (IV)
NITROGEN (Yc = 61%)
AIR (Yc = 57%)
HEATING RATE – 10°C/min
FLOW RATE – 100 cm3/min

Fig. 6

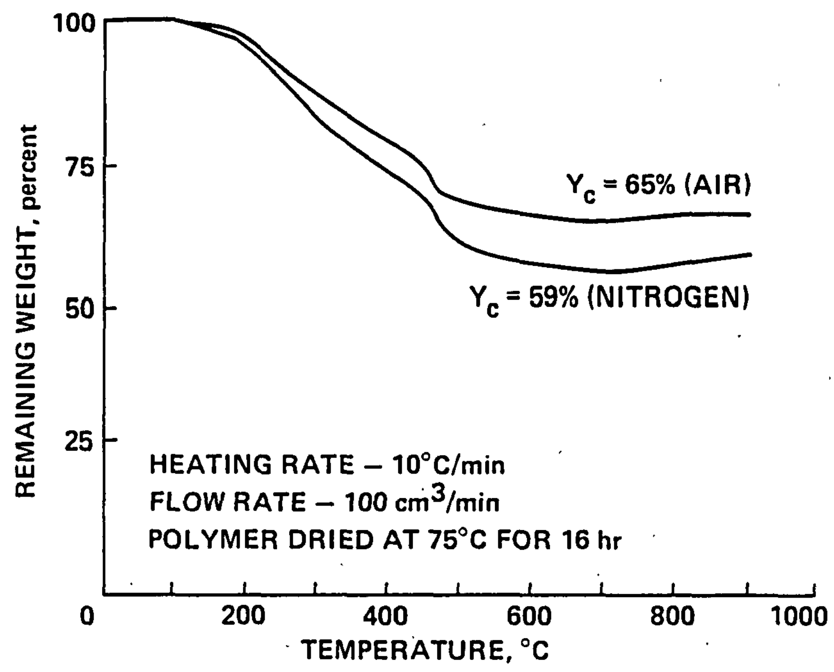

100
75
50
25
0
200
400
600
800
1000
REMAINING WEIGHT, percent
TEMPERATURE, °C
Y_c = 65% (AIR)
Y_c = 59% (NITROGEN)
HEATING RATE – 10°C/min
FLOW RATE – 100 cm³/min
POLYMER DRIED AT 75°C FOR 16 hr

Fig. 7

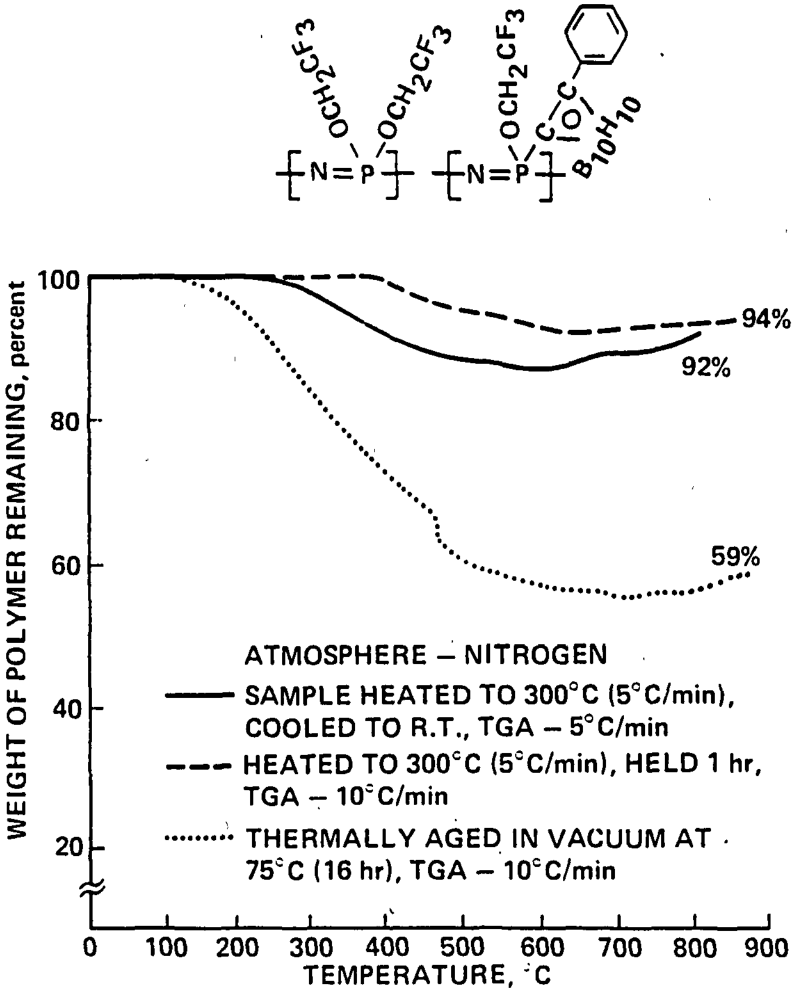

OCH2CF3
OCH2CF3
N=P
OCH2CF3
N=P
C—C
O
B10H10
WEIGHT OF POLYMER REMAINING, percent
100
80
60
40
20
0
100
200
300
400
500
600
700
800
900
TEMPERATURE, °C
94%
92%
59%
ATMOSPHERE – NITROGEN
SAMPLE HEATED TO 300°C (5°C/min), COOLED TO R.T., TGA – 5°C/min
HEATED TO 300°C (5°C/min), HELD 1 hr, TGA – 10°C/min
THERMALLY AGED IN VACUUM AT 75°C (16 hr), TGA – 10°C/min

Fig. 8

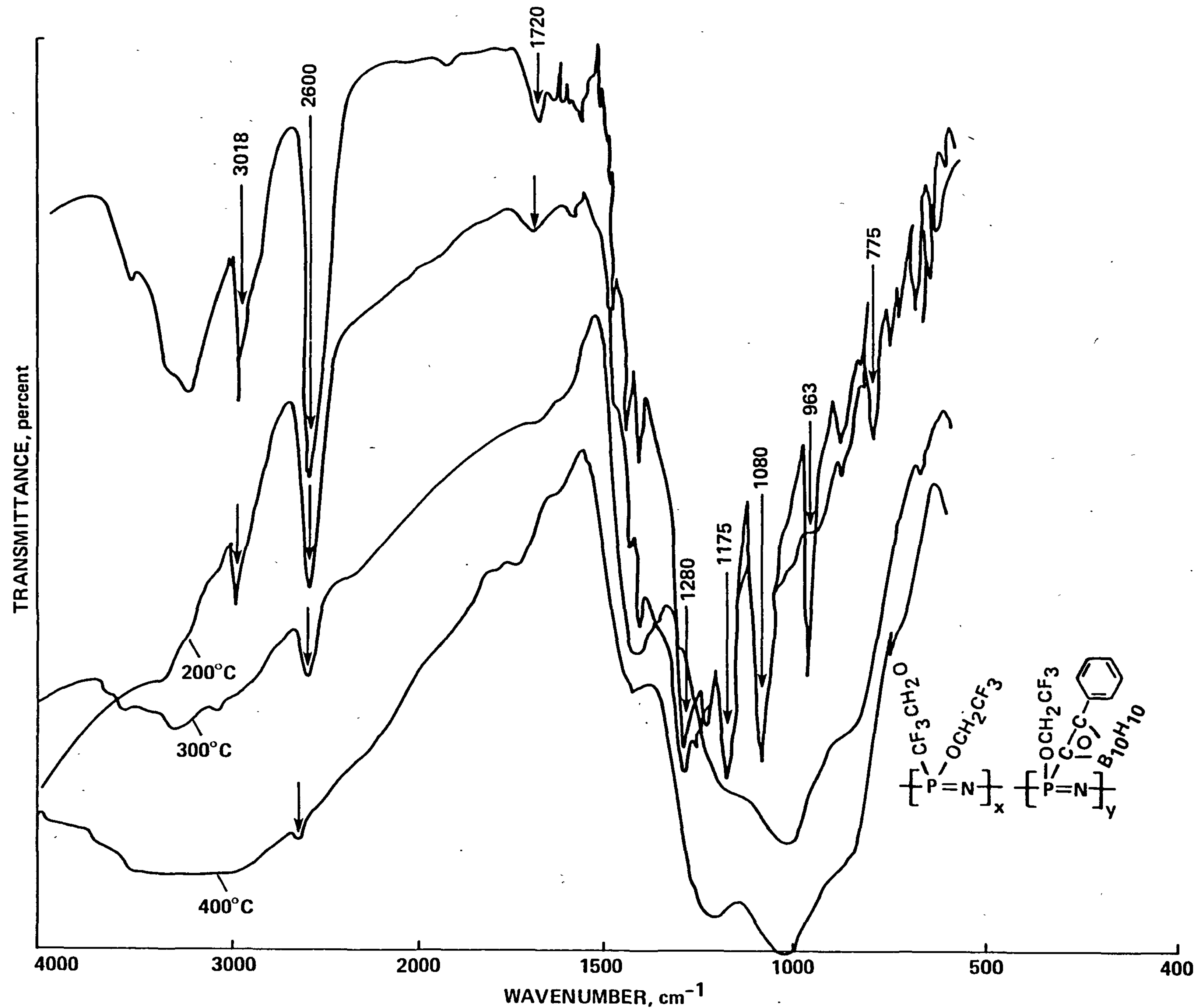
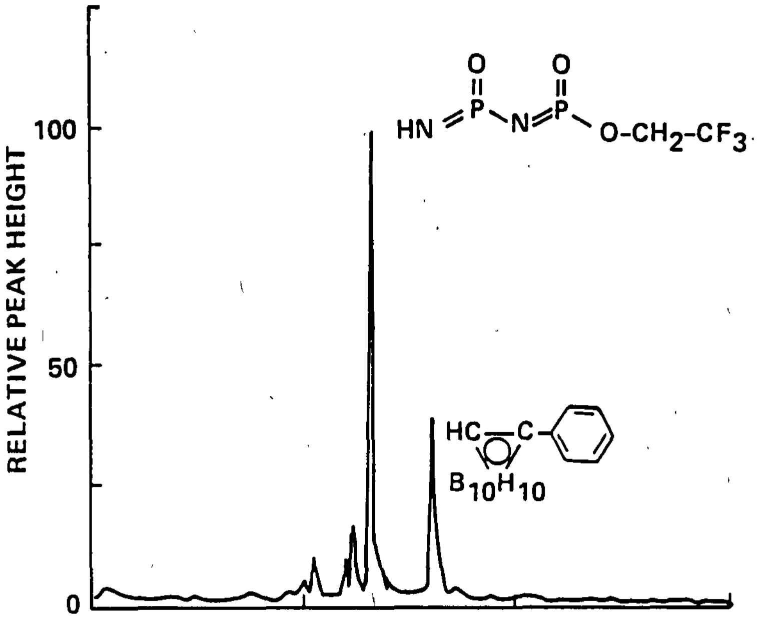
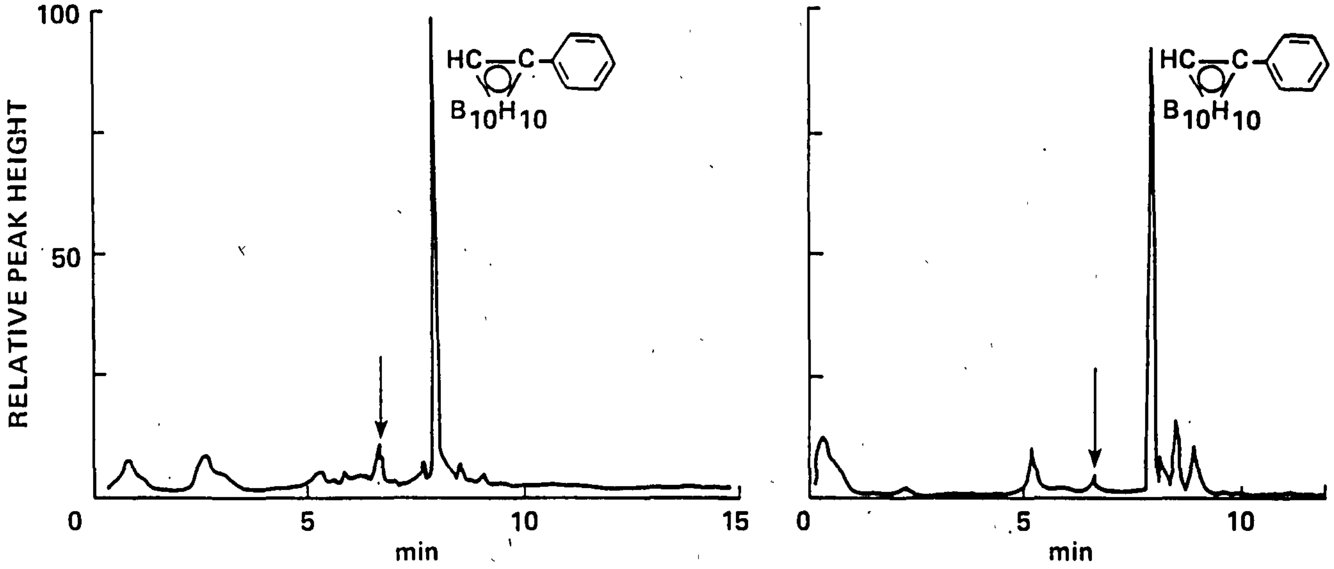

1720
2600
3018
775
963
1080
1175
1280
200°C
300°C
400°C
TRANSMITTANCE, percent
4000
3000
2000
1500
1000
500
400
WAVENUMBER, cm^{-1}
CF$_3$CH$_2$O
OCH$_2$CF$_3$
P=N
x
OCH$_2$CF$_3$
C—C
O
B$_{10}$H$_{10}$
P=N
y

Fig. 9



(a) PYROLYSIS PRODUCT – 200°C



(b) PYROLYSIS PRODUCT – 300°C

(c) PYROLYSIS PRODUCT – 400°C

Fig. 10

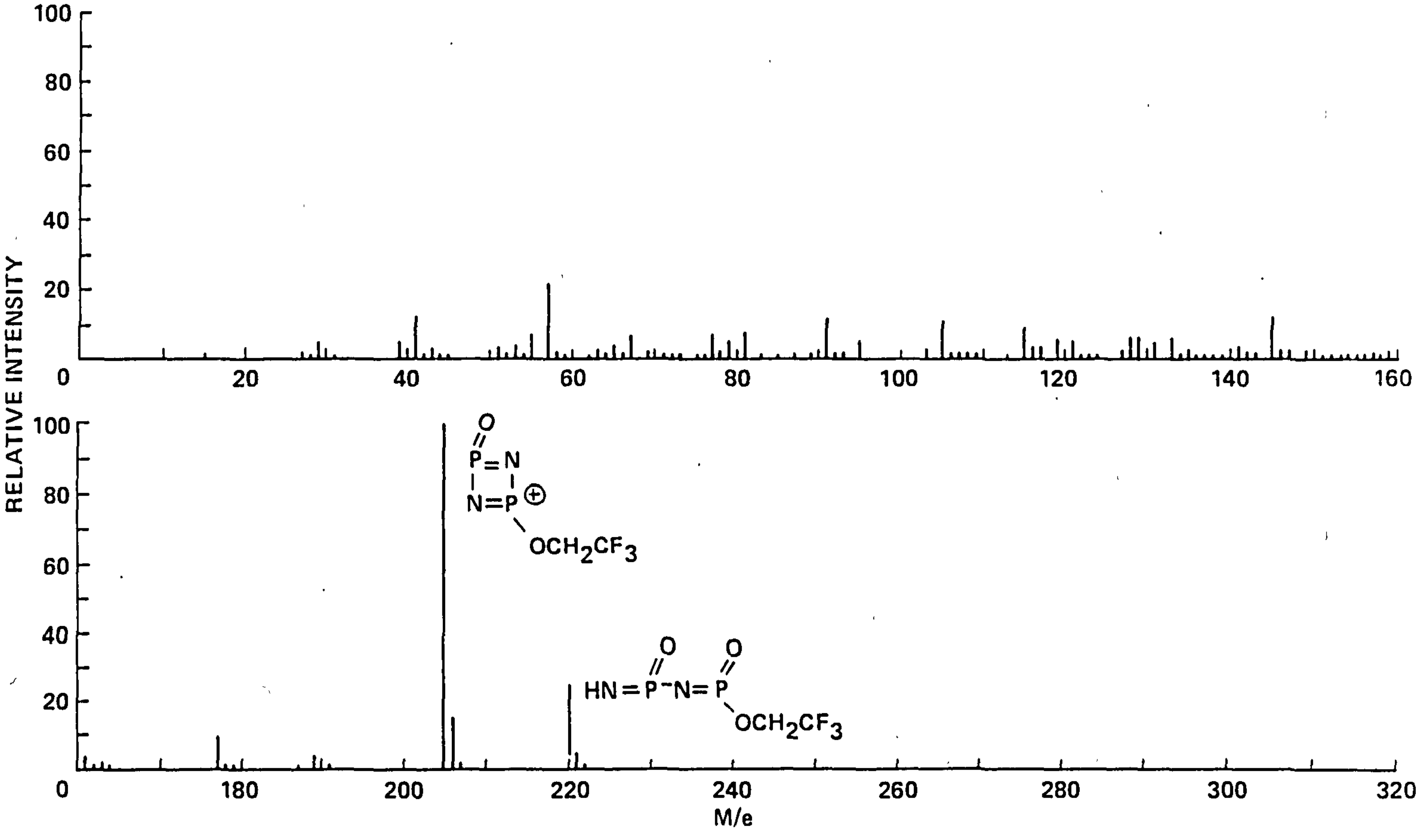

RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
M/e
O
P=N
N=P
⊕
OCH2CF3
HN=P-N=P
O
O
OCH2CF3

Fig. 11a

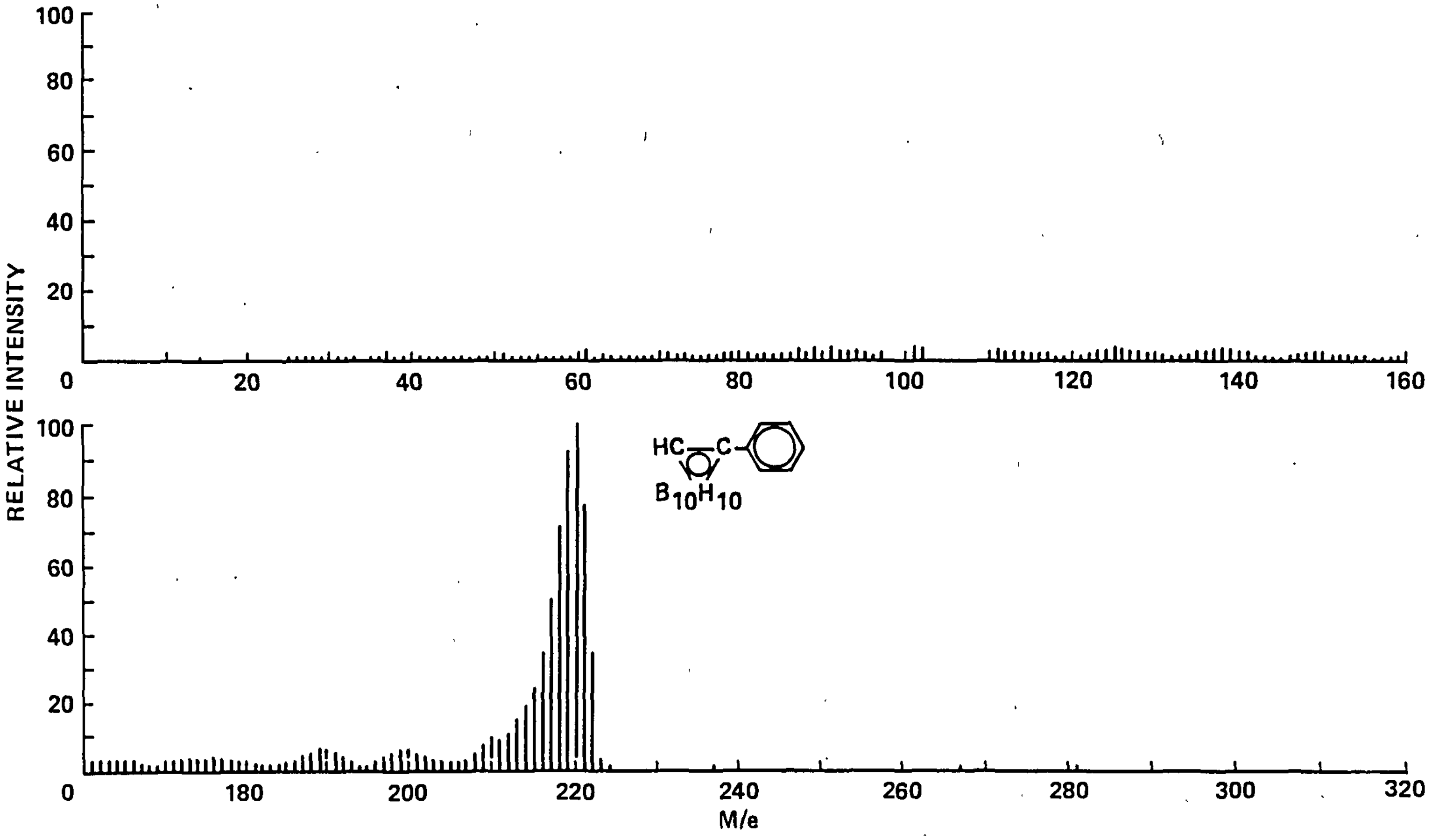

RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
100
80
60
40
20
0
180
200
220
240
260
280
300
320
M/e
HC
C
$B_{10}H_{10}$

Fig. 11b

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16. Abstract

Carborane substituted polyphosphazenes were prepared by the thermal polymerization of phenyl-carboranyl penta chlorocyclotriphosphazene. Successive isothermal vacuum pyrolyses were conducted on the polymer and examined for structural changes by infrared spectroscopy. The degradation products were ascertained by gas chromatography-mass spectrometric analysis. It was found that the presence of the carborane group improves the thermal stability of the polymer by retarding the ring-chain equilibrium processes of decomposition.

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