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THERMOANALYTICAL CHARACTERIZATION OF POLYPHENYLACETYLENE

I. High polyphenylacetylene synthesized through metathesis polymerization

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Abstract

Differential scanning calorimetry, thermogravimetry, thermogravimetry/mass spectrometry and infrared spectroscopy were used to study the thermal behaviour of high polyphenylacetylene obtained through the $Mo(CO)_6$ catalyzed metathesis polymerization of phenylacetylene. The exothermic peaks observed in nitrogen are explained by crystallization or a solid state transition, initiation and decomposition to aromatic compounds, and the endothermic peaks by volatilization. In oxygen the exothermic peaks are explained by crystallization or a solid state transition, initiation, oxidation, cross-linking and decomposition. The TG and MS results indicate that the polymer is stable to ca. 250°C with solvent molecules trapped in the polymer matrix evolving below this temperature.

Keywords: metathesis polymerization, molybdenum hexacarbonyl, polyphenylacetylene, thermal analysis

Introduction

In spite of a relatively large number of studies on the thermal stability of low molecular mass ($\bar{M}w < 10^4$) polyphenylacetylene obtained from Ziegler–Natta catalytic systems [1–5] to our knowledge much less is known about the thermal behaviour of high (i.e. high molecular mass) polyphenylacetylene obtained from metathesis catalytic systems [6].

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In the case of the low molecular mass polyphenylacetylene only exothermic peaks in the temperature range 100–235°C were observed on DTA for *cis*-polyphenylacetylene [3]. The exothermic peaks at 180 and 200°C were attributed to an irreversible, structural *cis-trans* isomerization. On TG no mass loss was observed in the temperature range of the exothermic peaks while an increase in mass was observed above 350°C. A mass loss above 300°C was reported in a later thermal analysis study [7]. A DSC study on the same *cis*-polymer revealed exothermic peaks at 145, 155 and 182°C [4]. These peaks were attributed to thermal cyclization, *cis–trans* isomerization and aromatization respectively. With the aid of spectroscopic methods it was confirmed that the exothermic peaks observed on DTA and DSC represent *cis–trans* isomerization and rearrangements in a new conformation followed by cyclization and aromatization [5].

No peaks were observed on DTA for *trans*-polyphenylacetylene [1] and no glass transitions were reported for amorphous polyphenylacetylene. Only TG results were reported for high polyphenylacetylene obtained with metathesis catalysts showing a mass loss above 200°C in nitrogen and in oxygen [6].

In this study the thermal behaviour of polyphenylacetylene obtained from the alkyne metathesis catalytic system $Mo(CO)_6/C_6H_5OH$ was investigated by DSC, TG, TG/MS and IR after an earlier, preliminary study showed different thermal analysis results than what was expected from the previous studies on polyphenylacetylenes [8]. An exothermic peak at 243°C on DSC and a mass loss above 260°C on TG were observed for polyphenylacetylene with a *trans*-rich structure [9].

Experimental

Synthesis of polyphenylacetylene

Polyphenylacetylene was synthesized as described previously [8] with the aid of the $Mo(CO)_6/C_6H_5OH(C_6H_5OH/Mo$ molar ratio = 100) metathesis catalytic system at 120°C. Light yellow polyphenylacetylene with $\bar{M}_w = 3.465 \times 10^4$ (weight average molecular mass was determined by gel permeation chromatography using polystyrene standards [8]) and a measure of *cis* structure content of 0.940 (i.e. a 'more *trans*' structure [9]) was obtained from the IR spectrum of the polymer. To determine the *cis* structure content the absorption ratio of the vibration bands at 870 cm^{-1} and 910 cm^{-1} were used [10]. The vibration bands at 870 cm^{-1} and 910 cm^{-1} are characteristic of the *cis* structure and *trans* structure in polyphenylacetylene respectively.

Infrared spectroscopic analysis (IR)

IR spectra were obtained on a Perkin-Elmer FTIR-1615 instrument at a resolution of 2 cm^{-1} using KBr pellets containing ca. 2% polymer.

Differential scanning calorimetry (DSC) and thermogravimetry (TG)

Samples in powder form (5–15 mg) were analyzed in aluminium pans using TA Instruments' DSC 910S and TGA 2950 systems connected to a Thermal Analysis 2000 Data Station. The heating rate was 20 deg·min^{-1} and the gas flow rate 150 cm^3·min^{-1}. Nitrogen 5.0 and medical oxygen supplied by Fedgas were used. The data station gave enthalpy values in J·g^{-1} and the DSC instrument was calibrated using indium and zinc as standards for temperature and enthalpy respectively.

Thermogravimetry/mass spectrometric analysis (TG/MS)

TG/MS analyses were done on a Perkin Elmer TGS2 instrument connected via a capillary tube to a Hewlett Packard MSD scanning a 10–400 amu mass range. The same heating rate and gas flow rate as before were used. Helium 5.0 supplied by Fedgas was used.

Results and discussion

In nitrogen

The DSC, TG and DTG thermal analysis curves in nitrogen are illustrated in Fig. 1 and the thermal analysis results are summarized in Table 1. TG/MS results in helium are summarized in Table 2, physical properties of the polymer upon heating in Table 3 and IR spectra are illustrated in Fig. 2.

Both exothermic peaks (peaks at 239, 257 and 495°C) and endothermic peaks (peaks at 141 and 339°C) were observed on DSC. The exothermic peaks at 239 and 257°C, both which are irreversible, seem to be of major significance. A two step mass loss was observed on TG although a more complex mass loss pattern, indicating at least seven processes, is evident from the DTG curve.

The slow (ca. 0.03% °C^{-1}) initial mass loss of ca. 5% observed from 60–215°C was originally ascribed to volatilization of solvent molecules trapped in the polymer matrix [8]. This interpretation is strengthened by the occurrence of the endothermic peak at 141°C DSC and the shape of the DTG curve in this region which are consistent with a volatilization process [11]. This was confirmed by TG/MS. The solvent used in the synthesis of the polymer, chlorobenzene, was identified by MS to be the gaseous compound evolved in this temperature range (Table 2).

The peak shoulder at 239°C on DSC is not accompanied by a mass loss (Table 1) while the exothermic peak at 257°C corresponds to the onset temperature of the major mass loss step on TG. The only change observed below 250°C is a change in the physical properties of the polymer. The colour of the polyphenylacetylene changes from light yellow to yellow brown and the polymer takes on

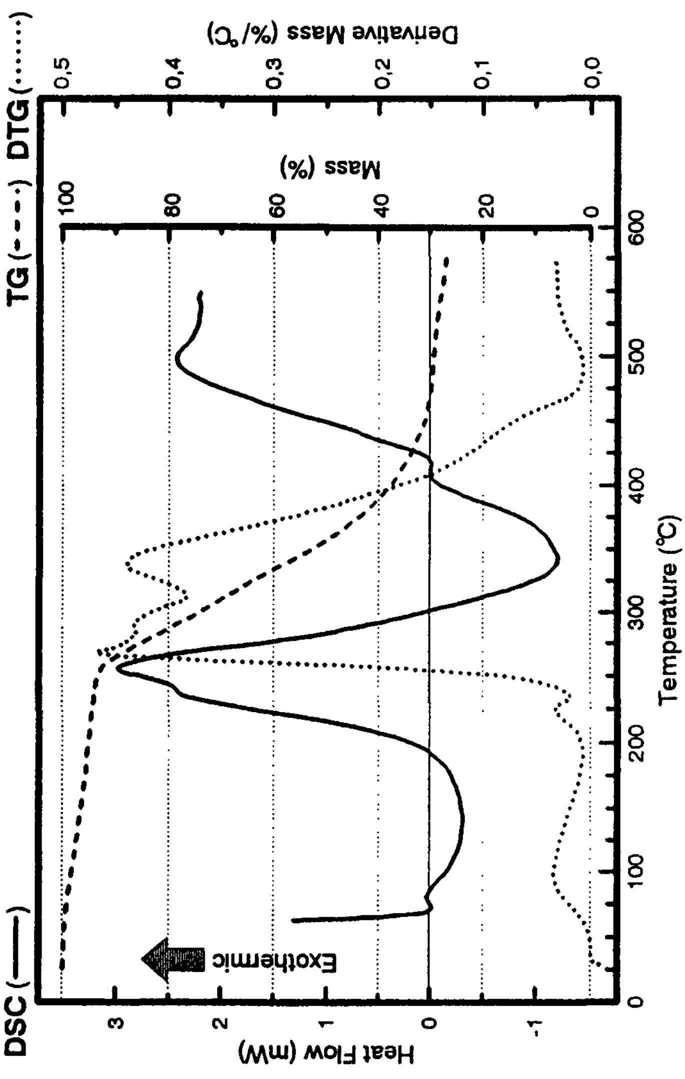


Fig. 1 Thermal analysis curves of polyphenylacetylene in nitrogen

a glasslike appearance (Table 3). This means that the exothermic peaks at 239 and 257°C may be due to crystallization or a solid state transition and the initiation of a decomposition process respectively [11]. The confirmation of this is currently under further investigation.

Table 1 Summary of thermal analysis results of polyphenylacetylene

Temp./ °C	DSC Onset temp./ °C	DSC Enthalpy/ $J \cdot g^{-1}$	TG/DTG Mass loss/ %	TG/DTG Rate/ %/°C
(a) In nitrogen				
98	–	–	2	0.03
141	71	15.2	3	0.02
225	–	–	6	0.03
239	213	–97.3	7	–
257			7	–
269	–	–	11	0.46
292	–	–	22	0.43
339	310	48.1	42	0.44
437	–	–	67	0.09
495	Exotherm		70	0.04
(b) In oxygen				
101	–	–	2	0.01
214	–	–	5	0.02
223	211	–257.9	6	–
290	–	–	19	0.44
373	Exotherm		42	0.20
498	–	–	70	4.28
>512	Exotherm		100	–

The major mass loss (ca. 60%) that occurred between 250 and 500°C can be attributed to polymer chain scission (decomposition) followed by aromatization of low molecular mass scission products, which are volatile in this temperature range. The volatilization of the aromatic products is observed on DSC as an endothermic peak [11] at ca. 339°C partially superimposed on the exothermic peak at 257°C. Mainly 5′-phenyl-*m*-terphenyl was formed together with small amounts of quaterphenyl and isomers thereof (Table 2). The boiling points of these compounds fall within this temperature range. The exothermic peak at 495°C on DSC can be attributed to the slow decomposition of the remaining polymer at a rate of ca. 0.04% $°C^{-1}$

Table 2 TG/MS analysis of polyphenylacetylene in helium

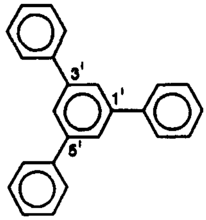
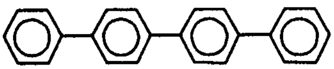
Heating range/ °C	Gaseous compounds
60–215	C_6H_5Cl
250–350	 5'-phenyl-m-terphenyl (main product)  quaterphenyl

Table 3 Physical properties of polyphenylacetylene heated to different temperatures

Heating temp./ °C	Polymer colour	Appearance	$\frac{A_{870}}{A_{910}}$ (1)	Solubility in CH_2Cl_2
Before heating	light yellow	powder	0.940	soluble
(a) In nitrogen				
250	yellow-brown	glasslike	1.014	soluble
500	dark yellow-brown	glasslike	1.000	soluble
(b) In oxygen				
250	yellow-brown	glasslike	0.990	soluble
335	black-brown	glasslike	–	soluble
490	black	glasslike	–	less soluble

(1) $\frac{A_{870}}{A_{910}}$: measure of cis content from IR spectra

The polyphenylacetylene was heated in nitrogen to different temperatures corresponding to the thermal events on TG. The residue after heating in each case was analyzed by IR (Fig. 3). The IR spectrum of the polyphenylacetylene before heating (Fig. 3a) is identical to that reported in literature [8, 9]. The main features are absorptions at 1494–1440 cm^{-1} and 1605 cm^{-1} due to stretching vibrations of aromatic and polyconjugated trisubstituted carbon–carbon double bonds respectively; at 3049 cm^{-1} C–H stretching vibration of an olefinic hydrogen; and at 3020 cm^{-1}, 2000–1800 cm^{-1} and 747–688 cm^{-1} C–H stretching, overtone and out-of-plane bending vibrations of a monosubstituted phenyl ring respectively.

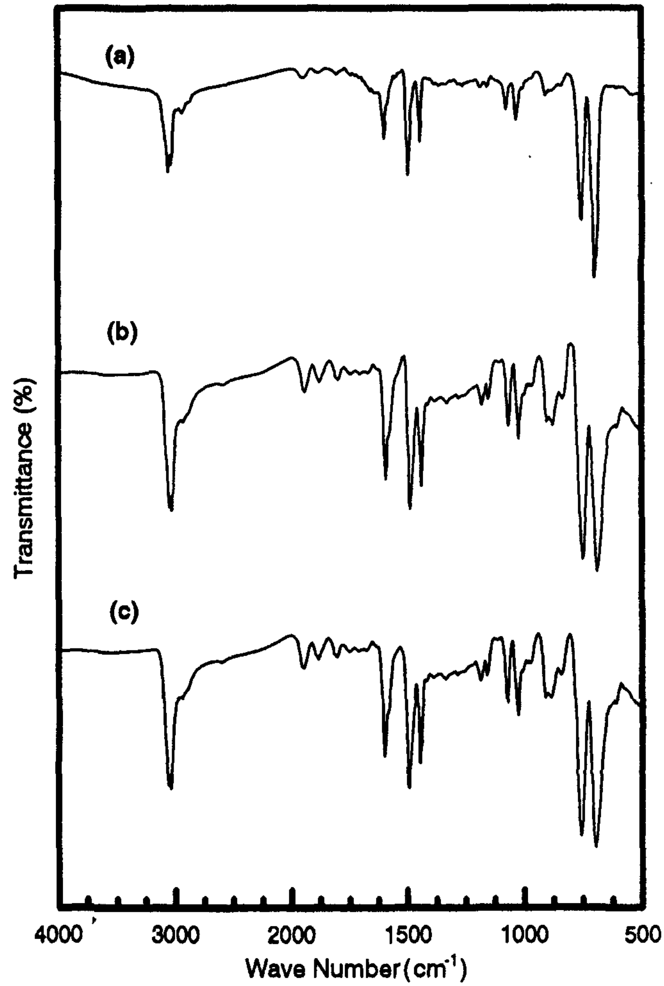


Fig. 2 IR spectra of polyphenylacetylene (a) before heating, and after heating to (b) 250°C and (c) 500°C in nitrogen

The IR spectra of the residues after heating to 250°C (Fig. 3b) and 500°C (Fig. 3c) show that the polyphenylacetylene did not undergo any major structural changes upon heating to 500°C. The only structural change observed upon heating is a change in the geometrical structure (Table 2) i.e. the measure of *cis* structure content has changed from 'more *trans*' to 'more *cis*' [9]. This may be

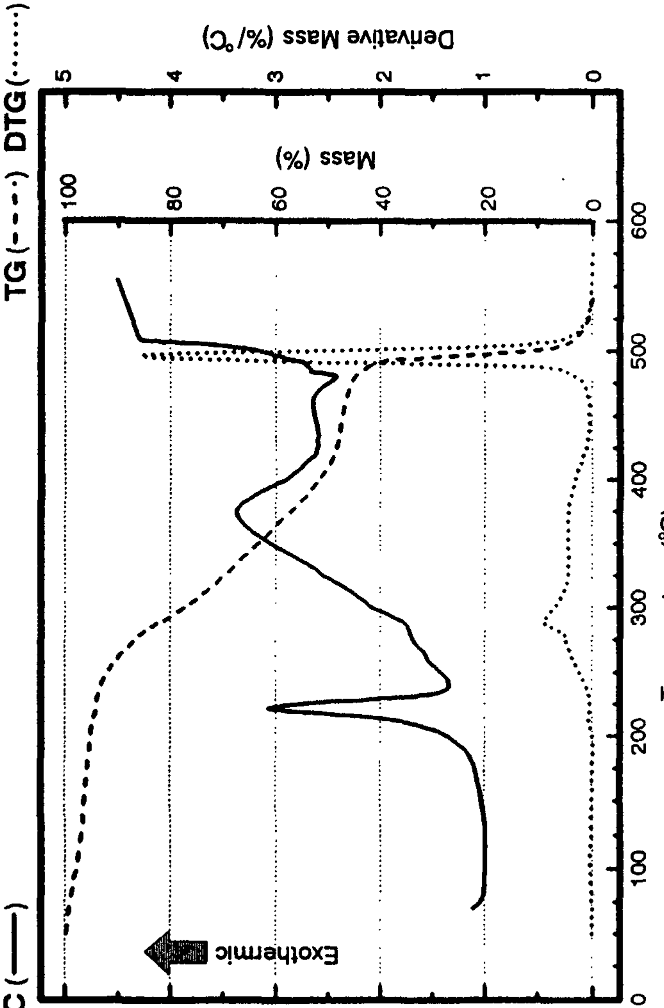


Fig. 3 Thermal analysis curves of polyphenylacetylene in oxygen

due to a structural *trans–cis* isomerization taking place with the crystallization or solid state transition, or it may be due to chain scission of the polymer taking place mainly at *trans* configurations in the polymer chain, changing the *cis*:*trans* ratio. No mention is made of *trans–cis* isomerization in literature and no peaks were observed on DTA for *trans*-polyphenylacetylene [1].

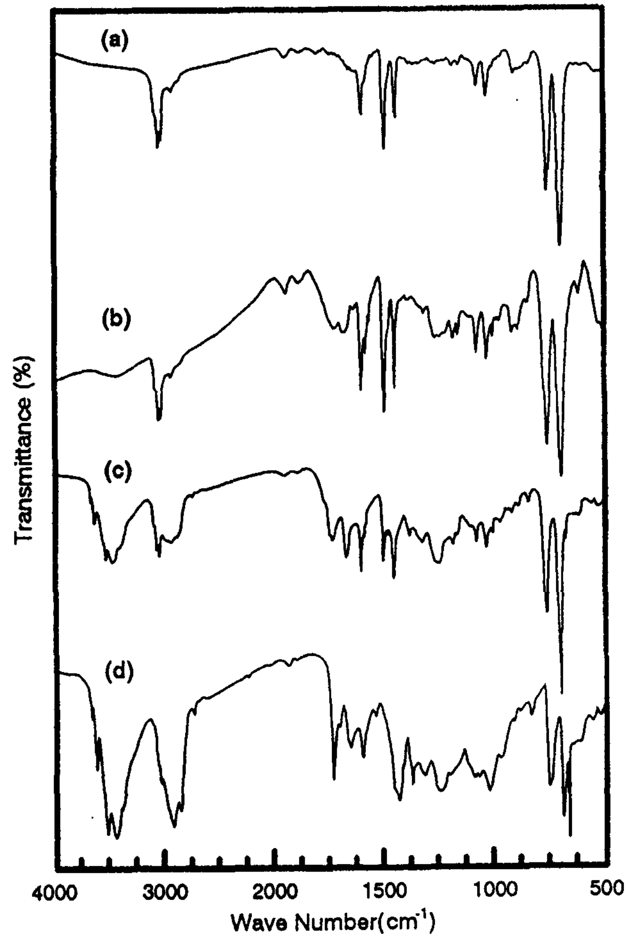


Fig. 4 IR spectra of polyphenylacetylene (a) before heating, and after heating to (b) 250°C, (c) 335°C and (d) 490°C in oxygen

In oxygen

The DSC, TG and DTG thermal analysis curves in oxygen are illustrated in Fig. 3 and the thermal analysis results summarized in Table 1. Physical properties upon heating of the polymer are summarized in Table 3 and IR spectra are illustrated in Fig. 4.

The DSC and DTG curves in Fig. 3 are on significantly different scales from those in Fig. 1. The DSC curve, therefore, shows apparently only exothermic peaks at 223, 373°C and above 512°C. Similarly, the lower rates of mass loss are almost lost in the baseline of the DTG curve. The exothermic peak at 223°C (no mass loss observed) appears in the same region as the exothermic peaks attri-buted to crystallization or solid state transition and initiation of a decomposition process in Fig. 1. If the colour changes and physical appearances in oxygen and nitrogen are compared (Table 3) it seems as if similar processes may occur in oxygen but are concealed by a different process represented by the strong exothermic peak at 223°C. This process is most probably the initiation step of pro-cesses taking place at higher temperatures i.e. oxidation, cross-linking and decomposition. The reason for this high enthalpy is not clear although it is possible that it represents the activation energy of this initiation step.

There distinct mass loss steps are observed on TG. The first of ca. 6% from 60–215°C is again associated with solvent molecules trapped in the polymer matrix (compare the DTA curves in this region). The second step from 242–427°C (ca. 60% mass loss) is similar to the second step in nitrogen but not so complex. From DTG a broad mass loss of 0.20% $°C^{-1}$ over the entire heating range is observed with a sharper mass loss of 0.44% $°C^{-1}$ at 290°C. This step corresponds with the exothermic peak at 373°C on DSC and can be attributed to oxidation, cross-linking and decomposition or most probably a combination of all three [5, 11]. The third step observed around 498°C (ca. 70% mass loss) shows a sharp mass loss rate of 4.28% $°C^{-1}$ on DTG and corresponds to the onset temperature of the exothermic peak above 512°C. All of the remaining polymer is converted to gaseous compounds at this point, which may be the evidence of simultaneous oxidation and decomposition processes.

The same procedure was followed in oxygen than in nitrogen i.e. heating of polyphenylacetylene to temperatures corresponding to the thermal events on TG and analyzing the residue, if any, by IR (Fig. 4). Upon heating to 250°C new vibrations were observed at 3699–3183 cm^{-1}, 1731 cm^{-1}, 1667 cm^{-1} and 1250 cm^{-1} (Fig. 4b). These vibrations can be assigned to O–H stretching vibration, C=O stretching vibration of ketones, C=O sterching vibration of carboxylic acids and C–O stretching or O–H bending vibrations of carboxylic acids respectively. A change in the geometrical structure similar to the one observed in nitrogen is also observed i.e. an increase in the *cis* content (Table 3). Heating to 335°C not only shows a dramatic increase in the intensity of these vibrations but also the formation of new vibrations at 3000–2710 cm^{-1} and 1380 cm^{-1} which can be assigned to C–H stretching vibrations of alkanes and C–H bending vibrations of secondary alkanes (Fig. 4c). A further dramatic increase in the intensities of the above-mentioned vibrations together with vibrations at 1451 cm^{-1} (C–H bending vibrations of alkanes), 1436 cm^{-1} (C–H bending vibrations of ketones), 1030 cm^{-1} (C–C bending vibrations of tertiary alkanes or substituted alkanes) and 661 cm^{-1} ($(CH_2)_n$ rocking vibrations) are observed upon heating to 490°C (Fig. 4d).

Although most of the vibrations indicating the monosubstituted phenyl ring and geometrical structure of polyphenylacetylene becomes undiscernible upon heating to 490°C, it is possible to use the C–H out-of-plane bending vibrations of 747–688 cm^{-1} to conclude that the polymer chain with its phenyl rings is still present in the residues. The polymer chain is most probably shorter as is evidenced by the mass loss on TG. The IR spectra suggests the formation of polymers with hydroxyl (or hydroperoxy at lower temperatures), carbonyl and carboxylic groups, and cross-linked polymer chains. The extent of cross-linking seems to be limited if the solubility of the residues in CH_2Cl_2 is examined (Table 3). Even after heating to 490°C the residue is quite soluble in CH_2Cl_2.

Conclusions

High polyphenylacetylene obtained through the metathesis polymerization of phenylacetylene with the $Mo(CO)_6/C_6H_5OH$ catalytic system is stable up to ca. 250°C when heated in nitrogen and in oxygen. This is in agreement with literature results which also found that the nitrogen and oxygen atmosphere do not seem to influence the thermal stability of polyphenylacetylene [6]. The mass loss observed in this region is due to the volatilization of chlorobenzene trapped in the polymer matrix.

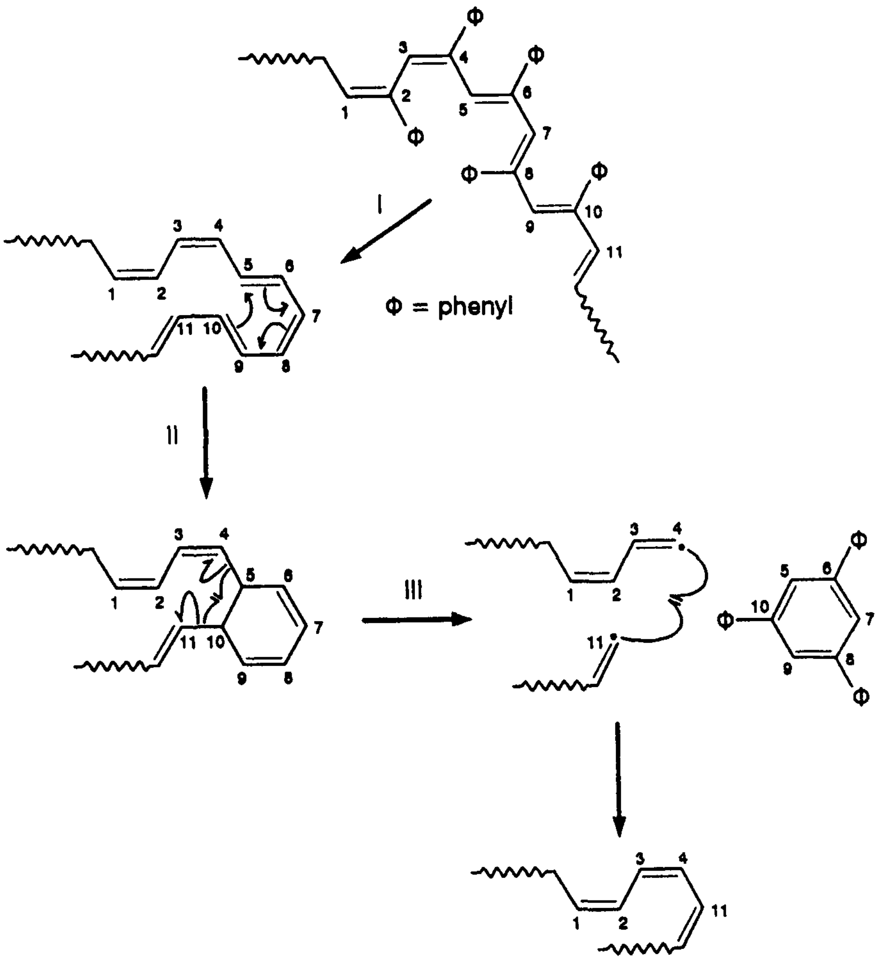
The exothermic peaks observed between 150–260°C in nitrogen and in oxygen are related to similar processes i.e. crystallization or a solid state transition and initiation of processes taking place at higher temperatures. The crystallization or solid state transition is most probably synonymous to structural *trans-cis* isomerization because an increase in *cis* content and a change in colour (Table 3) are attributed to crystallization [12]. This observation also links the processes mechanistically.

Various mechanisms have been proposed to explain the decomposition of polyacetylenes to aromatic compounds i.e. (1) free radical chain scission followed by aromatization [13] and (2) thermal cyclization followed by aromatization via free radical chain scission [4]. Mechanism 2 is in agreement with the results obtained in this study because an increase in *cis* content (i.e. *trans-cis* isomerization) precedes mass loss on TG and because of the low enthalpy associated with the exotherms [4]. Mechanism 1 requires chain scission prior to isomerization. Mechanism 2 (Scheme 1) consists of the following three steps:

Step I *trans-cis* isomerization,

Step II thermal cyclization and

Step III aromatization of cyclohexadiene rings via scission of the polymer chain.



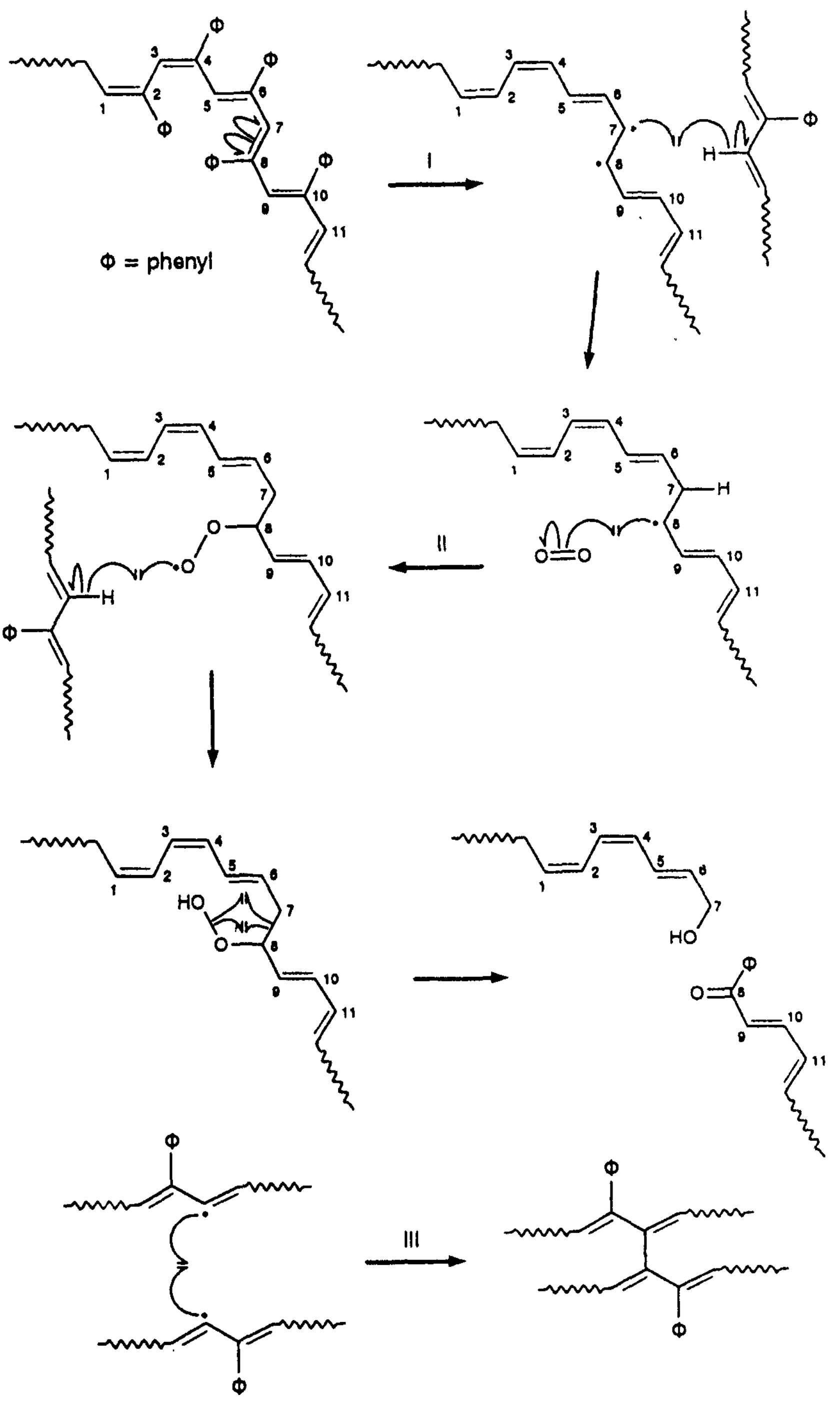
Sheme 1 Mechanism of the thermal decomposition of polyphenylacetylene in nitrogen (phenyl groups are omitted for clarity)

The formation of quaterphenyl is uncertain from this mechanistic point of view.

The results obtained in oxygen, supported by the results in nitrogen, are in agreement with the biradical mechanism proposed for the oxidation of polyphenylacetylene [6] illustrated in Scheme 2. This mechanism consists of the following steps:

Step I biradical formation followed by monoradical formation via H• abstraction,

Step II oxidation followed by hydroperoxide formation and scission of the polymer chain to yield hydroxyl, carbonyl and carboxyl compounds, and



Sheme 2 Mechanism of the thermal oxidation of polyphenylacetylene (phenyl groups are omitted for clarity)

Step III cross-linking of macro radicals formed on H• abstraction.

Not shown in Scheme 2 is the formation of carboxyl compounds. These compounds form as a result of the further oxidation of the hydroxyl compound to an aldehyde and eventually to a carboxylic acid.

The biradical mechanism is preferred over the basic autoxidation mechanism mainly because (a) *trans-cis* isomerization requires biradical formation followed by rotation, (b) autoxidation of conjugated or nonconjugated systems of double bonds require a methylene group α to the double bond [14], and (c) support from electron spin resonance and other studies [6].

The solubility of the polymer residues can be attributed to a limited extent of cross-linking. Cross-linking is most probably limited due to the oxidation of the macro radicals yielding α-hydroxy ketones. Conjugation may also play a role in the observed solubility.

From these results and the results available in literature it is obvious that the molecular mass, geometric structure and synthesis method each plays a major role in determining the thermal behaviour of polyphenylacetylene.

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9 The terms *trans*-rich and 'more *trans*' are used because according to Simionescu *et al.* [3] the absence of a vibration band at 740 cm^{-1} in the IR spectrum of polyphenylacetylene indicates a *cis* structure content less than 40%.
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Zusammenfassung — Mittels DSC, TG, TG/MS und IR wurde das thermische Verhalten von hochpolymerem Polyphenylacetylen untersucht, welches über die $Mo(CO)_6$-katalysierte Metathesepolymerisation von Phenylacetylen hergestellt wurde. Die in Stickstoff beobachteten exothermen Peaks wurden mit Kristallisation oder einer Feststoffumwandlung, Initiierung und Zersetzung zu aromatischen Verbindungen erklärt, die endothermen Peaks hingegen mit dem Verdampfen. In Sauerstoff werden die exothermen Peaks mit Kristallisation oder einer Feststoffumwandlung, Initiierung, Oxidation, Vernetzung und Zersetzung erklärt. TG- und MS-Ergebnisse zeigen die Beständigkeit des Polymers bis ca. 250°C, wobei unterhalb dieser Temperatur in der Polymermatrix eingeschlossene Lösungsmittelmoleküle abgegeben werden.