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THERMOANALYTICAL CHARACTERIZATION OF POLYPHENYLACETYLENE

II. Comparison of polymers synthesized through metathesis polymerization with different $C_6H_5OH/Mo(CO)_6$ molar ratios

A. S. Luyt and H. C. M. Vosloo[1]*

Department of Chemistry, University of the North (Qwaqwa Campus), Private Bag X13,
Phutaditjhaba, 9866, South Africa
[1]Department of Chemistry, Potchefstroom University for Christian Higher Education,
Potchefstroom, 2520, South Africa

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Abstract

DSC and TG were used to compare the thermal behaviour of different samples of polyphenylacetylene obtained through the metathesis polymerization of phenylacetylene using different $C_6H_5OH/Mo(CO)_6$ molar ratios as catalytic systems. In nitrogen the lower molecular mass group of samples give only one exothermic peak below 300°C that is attributed to decomposition to aromatic compounds. The higher molecular mass group of samples give also an exothermic peak shoulder at 239°C, which is explained by crystallization or solid state transition. In oxygen a strong exothermic peak is observed at 223°C, which is not accompanied by mass loss and is attributed to an initiation step of processes taking place at higher temperatures. The higher molecular mass group, however, show much larger transition enthalpies and increased rates of mass loss at the higher temperatures. The difference between the two groups are explained by longer chain lengths and changes in geometrical structure as a result of higher $C_6H_5OH/Mo(CO)_6$ molar ratios.

Keywords: DSC, TG, metathesis polymerization, polyphenylacetylene

Introduction

In a previous study [1] it was found that the C_6H_5OH/Mo molar ratio plays a major role in the metathesis polymerization of phenylacetylene in the presence of the $Mo(CO)_6/C_6H_5OH$ catalytic system at 120°C. It drastically influenced the reaction rate of the polymerization reaction as well as the molecular

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* Author to whom correspondence should be addressed.

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mass of the resulting polyphenylacetylene. In both cases a C_6H_5OH/Mo molar ratio ≥100 was needed for optimum results.

In this study different polyphenylacetylenes at various C_6H_5OH/Mo molar ratios were synthesized and the thermal behaviour of each studied by DSC and TG.

Experimental

Synthesis of polyphenylacetylene

Polyphenylacetylene was synthesized as described previously [1] with the aid of $Mo(CO)_6/C_6H_5OH$ metathesis catalytic systems at 120°C. Different C_6H_5OH/Mo molar ratios were used to synthesize the polymers (Table 1). Light yellow polyphenylacetylene with different $\overline{M}_w$ values and *cis* structure contents were obtained (Table 1). Weight average molecular masses were determined by gel permeation chromatography using polystyrene standards [1, 2]. To determine the *cis* structure content of each polymer the absorption ratio of the infrared vibration bands at 870 cm^{-1} and 910 cm^{-1} was used as described before [3].

Table 1 Cocatalyst/catalyst ratios during synthesis, molecular mass values and *cis* structure contents of polyphenylacetylene samples

Polymer samples	2	3	4	5	6	7
$C_6H_5OH/Mo(CO)_6$	6.25	25	50	100	150	200
$\overline{M}_w \cdot 10^{-4}$	1.801	1.720	1.710	3.465	3.918	3.313
A_{870}/A_{910}	0.907	0.921	0.934	0.940	0.948	0.974

DSC and TG

These techniques were carried out as reported in Part I of this series [3].

Results and discussion

In nitrogen

The DSC and TG thermal analysis curves in nitrogen are illustrated in Figs 1 and 2, and the major thermal analysis results are summarized in Table 2.

In a previous paper [3] a detailed discussion was given of the different events observed in the DSC and TG curves of sample 5 (Figs 1d and 2d). An exothermic peak at 239°C was observed which overlaps with a stronger exothermic peak at 257°C. Because no mass loss is associated with the first exothermic peak, it was interpreted as being either crystallization (*trans–cis* isomerization) or a solid state transition.

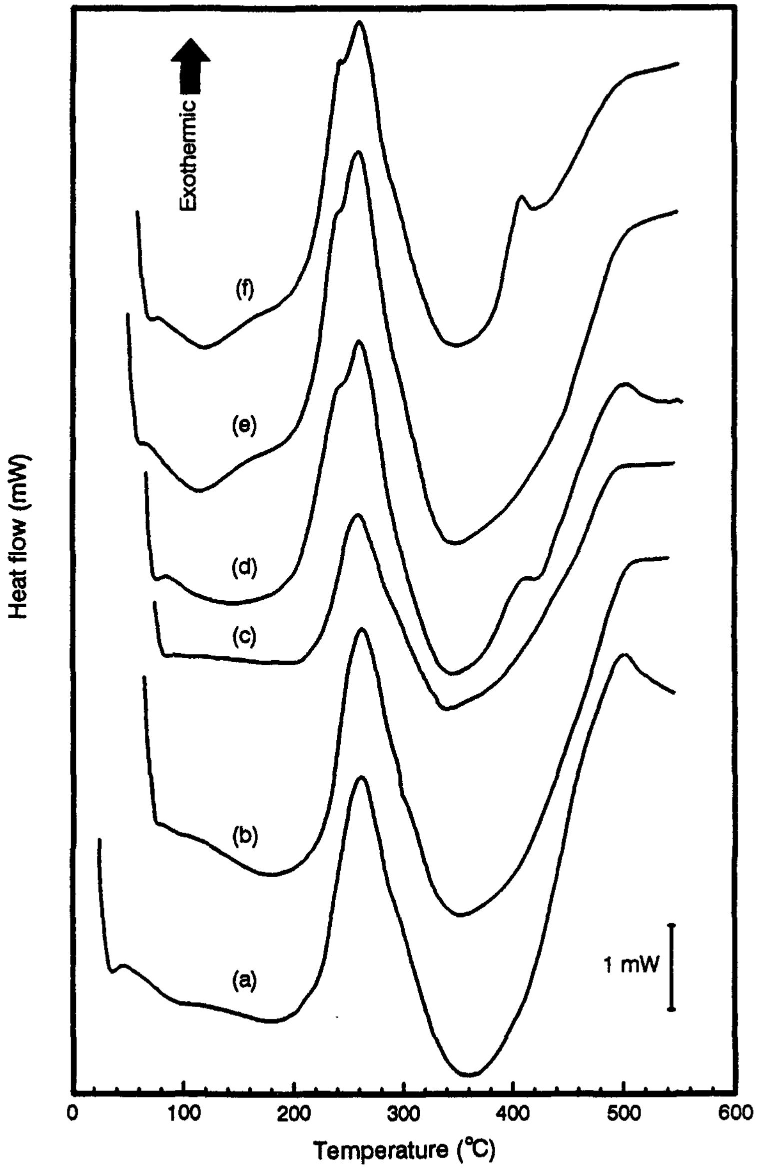

Fig. 1 DSC curves in nitrogen of (a) Sample 2, (b) Sample 3, (c) Sample 4, (d) Sample 5, (e) Sample 6 and (f) Sample 7

When comparing the DSC curves in Fig. 1, it is clear that the above-mentioned exothermic peak shoulder does not appear in curves (a)–(c), that are the DSC curves for the lower molecular mass samples. It also becomes more prominent with increasing phenol content in the reaction mixture. From Table 1 it is clear that the first three samples have molecular mass values of very much the same order, but that it is only about half the value of those for the last three samples. It may, therefore, be explained that the last three samples are less amorphous because of their longer chains and higher *cis* structure content thus crystallizing more readily.

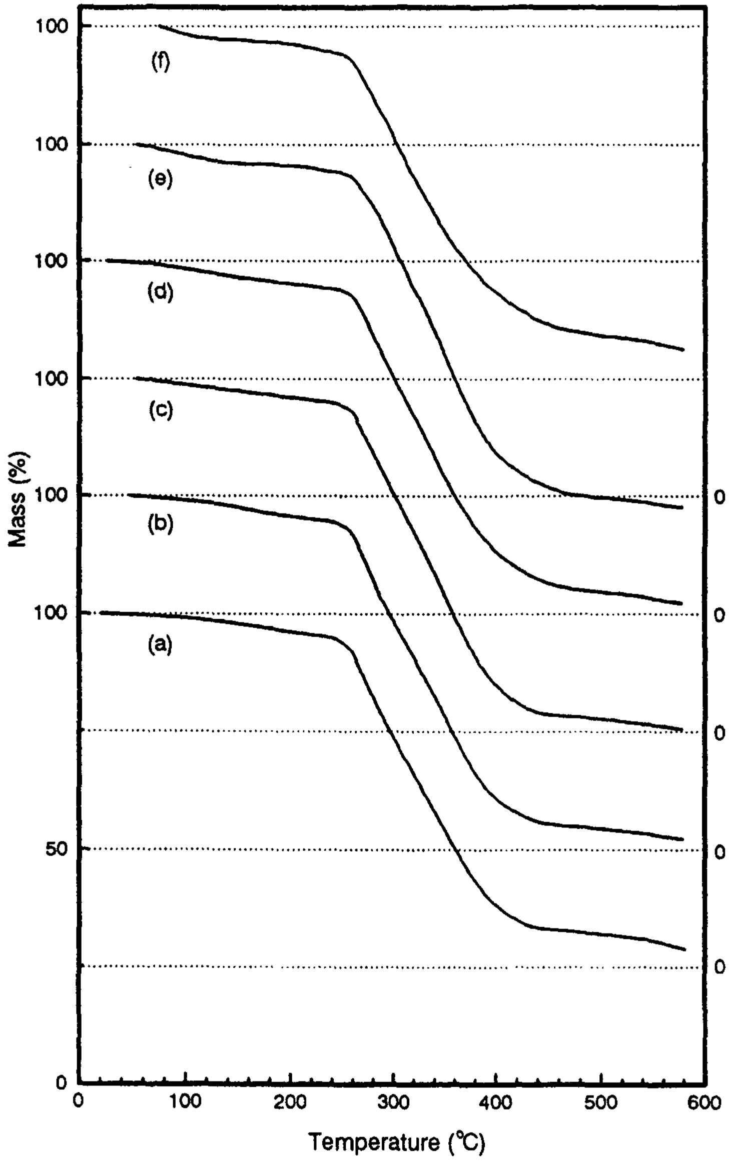

Fig 2 TG curves in nitrogen of (a) Sample 2, (b) Sample 3, (c) Sample 4, (d) Sample 5, (e) Sample 6 and (f) Sample 7

Table 2 DSC and TG data of the polymer samples in nitrogen

Sample	DSC		TG	
number	Onset / °C	ΔH / J·g^{-1}	Onset / °C	Mass loss / %
2	220	90	259	69
3	225	84	260	77
4	225	83	259	73
5	202	142	259	75
6	208	164	259	73
7	213	170	258	71

In the previous paper [3] the exotherm at 257°C that corresponds with the onset temperature of the major mass loss step on TG, together with thermal events at higher temperatures, were attributed to thermal cyclization followed by aromatization of cyclohexadiene rings via scission of the polymer chain. The primary aromatization product was established to be 5′-phenyl-*m*-terphenyl. If the first three samples are taken as a group, the onset temperature and reaction enthalpy of the main, well defined exotherm are constant within experimental error (Table 2). The last three samples, however, show an increase in onset temperature and reaction enthalpy with increasing phenol content in the reaction mixture. A possible explanation is that the increasing phenol (or cocatalyst) content, above a certain maximum, does not only increase the molecular mass of the polymer, but also changes the geometrical structure in such a way that more energy is needed to initiate the decomposition and aromatization processes, with the actual processes being more exothermic with increasing phenol content. The onset temperatures of these samples are also lower than those of the first three samples. It is because of the development of the peak shoulder as discussed above.

The endothermic peaks at ca. 140 and ca. 340°C evident in the DSC curves of all the samples were attributed to the volatilization of solvent molecules trapped in the polymer matrix and the volatilization of the aromatic decomposition products respectively.

Within experimental error no real difference could be observed between the TG curves of the different samples in nitrogen.

It therefore seems as if the phenol content in the polymerization of phenylacetylene with $Mo(CO)_6$ influences not only the molecular mass of the polymer, but that the influence on the geometrical structure is more notable as is evident from the infrared absorption ratio. It is, however, clear that it has no observable influence on the onset temperature and the overall percentage mass loss in nitrogen.

In oxygen

The DSC and TG analysis curves in oxygen are illustrated in Figs 3 and 4, and the major thermal analysis results are summarized in Table 3.

As with the analyses in nitrogen, a detailed discussion was given of the different events observed in the DSC and TG curves of sample 5 (Figs 3d and 4d) [3]. Mention was made of exothermic peaks at 223, 373 and above 512°C as well as three distinct mass loss steps on TG. No mass loss accompanied the exothermic peak at 223°C, which appears in the same region as the major exothermic peaks in nitrogen. This exothermic peak was assigned to the initiation step of oxidation, cross-linking and decomposition processes taking place at higher temperatures. The other exotherms are accompanied by mass loss and were assigned to the oxidation, cross-linking and decomposition processes taking place simultaneously.

Table 3 DSC and TG data of the polymer samples in oxygen. (Values in brackets indicate second major mass loss step)

Sample	DSC		TG	
number	Onset / °C	ΔH / $J \cdot g^{-1}$	Onset / °C	Mass loss / %
2	185	93	242(487)	52(42)
3	185	98	240(481)	45(41)
4	198	140	255(487)	47(46)
5	211	258	251(456)	46(48)
6	219	236	261(450)	44(50)
7	222	232	253(446)	44(50)

As can be seen from Fig. 3 and Table 3, there is a general increase in onset temperature and enthalpy for the first exothermic peak with increasing phenol content in the reaction mixture, but that the actual values closely relate to the molecular mass data of the different polymer samples (Table 1). These exotherms are also much stronger than those observed in nitrogen. As discussed in our previous article, the reason for this is not clear although it is possible that it represents the activation energy of the initiation step.

The higher phenol content could have changed the geometrical structure in such a way that the initiation step requires a higher activation energy.

When the TG curves in Fig. 4 are investigated, an interesting observation is made. Up to about 450°C no real difference between the mass loss of the different samples can be observed. For the last mass loss step, however, there is a distinct difference between the first three polymer samples and the last three polymer samples. The mass loss rate for samples 5–7 is clearly higher than that for samples 2–4. This can only be linked to the possible change in geometrical structure as a result of the higher phenol content in the reaction mixture, which may lead to the aromatization, oxidation, cross-linking or decomposition mechanisms being slightly different for the two groups of samples.

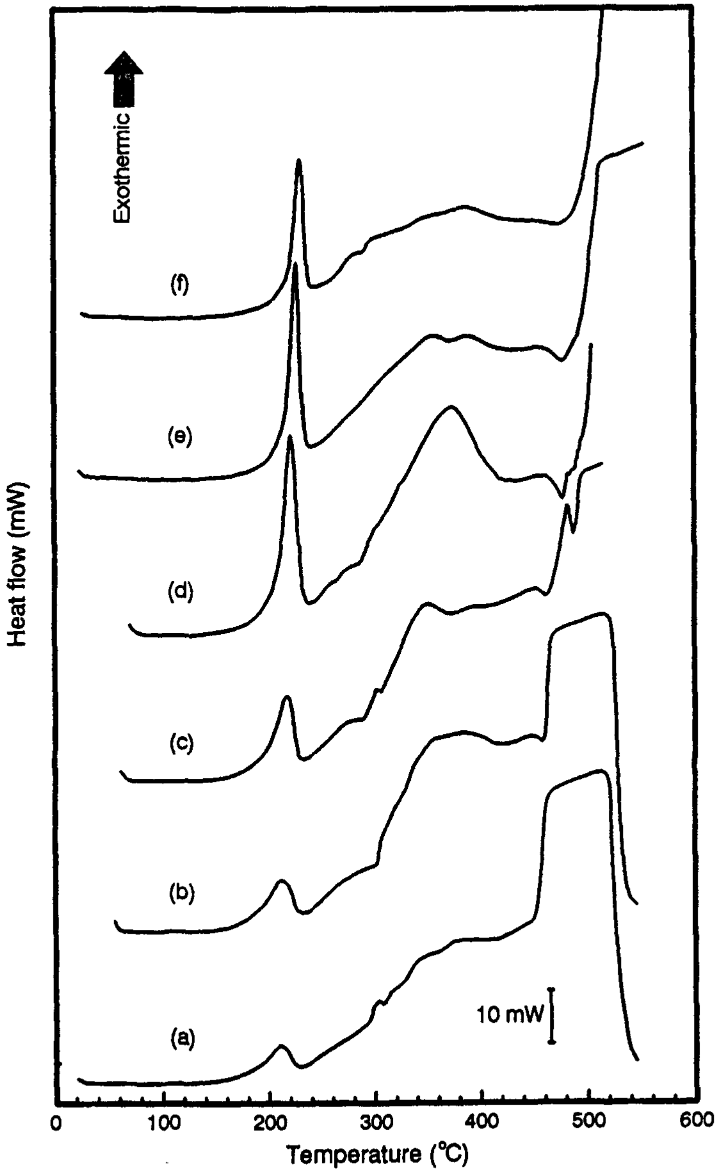

Fig. 3 DSC curves in oxygen of (a) Sample 2, (b) Sample 3, (c) Sample 4, (d) Sample 5, (e) Sample 6 and (f) Sample 7

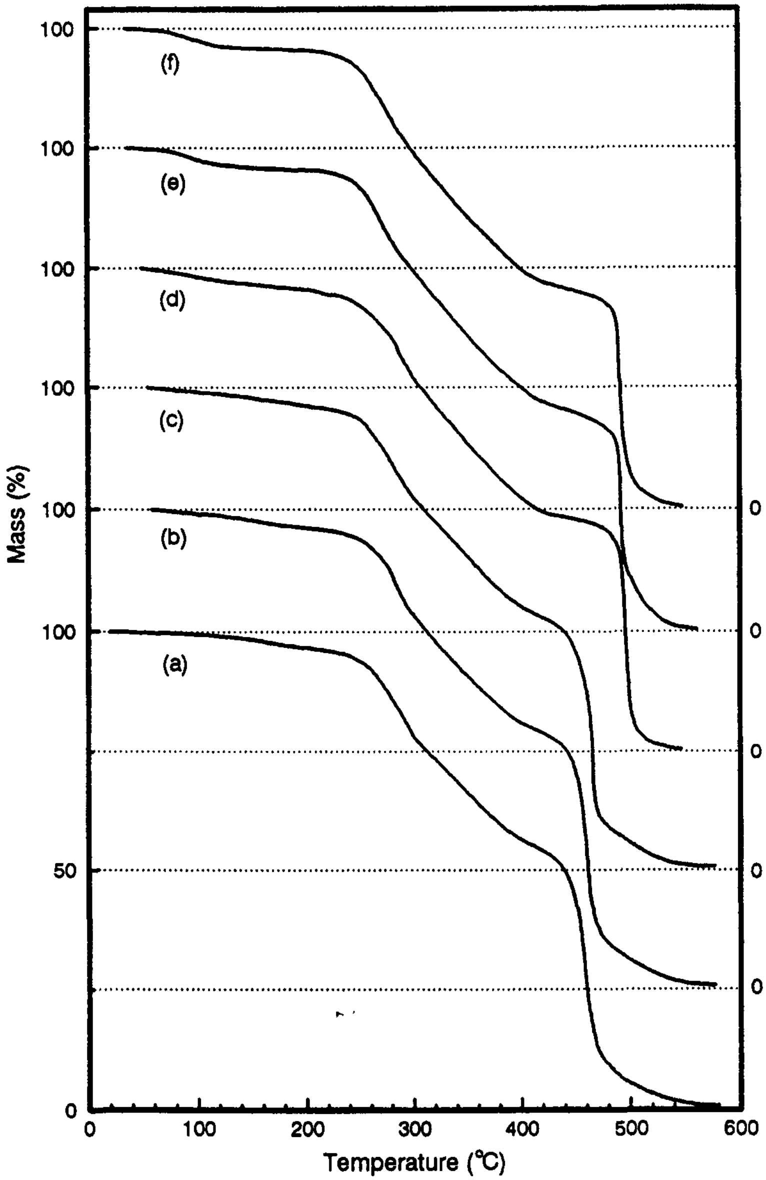

Fig. 4 TG curves in oxygen of (a) Sample 2, (b) Sample 3, (c) Sample 4, (d) Sample 5, (e) Sample 6 and (f) Sample 7

Conclusions

It seems as if the samples under investigation may be divided into two groups with regard to their thermal behaviour. The samples in the lower molecular mass group do not show any peak shoulder at 239°C in nitrogen, they have exothermic peaks in nitrogen at 257°C and in oxygen at 223°C with lower enthalpy values than those of the other samples and they show slower rates of mass loss at about 480°C in oxygen. The samples in the higher molecular mass group do show a peak shoulder at about 239°C in nitrogen, their exothermic peaks at 258°C in nitrogen and 223°C in oxygen have higher enthalpy values and higher rates of mass loss are observed at about 480°C in oxygen. These differences may be attributed to longer chain lengths and changes in geometrical structure that may have given rise to slightly different aromatization/oxidation/cross-linking/decomposition mechanisms.

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Zusammenfassung — DSC und TG wurden für einen Vergleich des thermischen Verhaltens verschiedener Proben von Polyphenylacetylen eingesetzt, welches über die Metathesepolymerisation von Phenylacetylen unter Anwendung verschiedener Molverhältnisse $C_6H_5OH/Mo(CO)_6$ als Katalysatorsystem hergestellt wurde. In Stickstoff ergeben die Gruppen der Proben mit niedrigerer Molmasse nur einen exothermen Peak bei 300°C, welcher der Zersetzung der aromatischen Verbindungen zugeschrieben werden kann. Die Gruppen der Proben mit höherer Molmasse ergeben auch eine exotherme Peak-Schulter bei 239°C, welches mit der Kristallisation oder der Feststoffumwandlung erklärt wird. In Sauerstoff wird bei 223°C ein starker exothermer Peak beobachtet, der von keinem Massenverlust begleitet wird und dem einleitenden Schritt eines bei einer höheren Temperatur stattfindenden Vorganges zugeschrieben wird. Die Gruppen mit höherer Molmasse zeigen jedoch stets größere Umwandlungsenthalpien und erhöhte Geschwindigkeiten für den Massenverlust bei den höheren Temperaturen. Der Unterschied zwischen diesen beiden Gruppen wird durch größere Kettenlängen und eine Veränderung der geometrischen Struktur als Ergebnis eines größeren $C_6H_5OH/Mo(CO)_6$ Molverhältnisses erklärt.