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Thermoanalytical characterization of polyphenylacetylene

III. Use of modulated differential scanning calorimetry (MDSC)

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Abstract

Four polyphenylacetylene samples, synthesized using different C_6H_5OH/Mo molar ratios, were investigated thermoanalytically by modulated temperature differential scanning calorimetry (MTDSC) in order to clarify a non-reversible exothermic event observed between 473 and 523 K on normal DSC. A stepwise, non-reversible change in heat capacity suggests the presence of internal reactions within the sample, that are followed by decomposition with loss of volatile products. © 1998 Elsevier Science B.V.

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1. Introduction

Conventional differential scanning calorimetry (DSC) and thermogravimetric (TG) investigations of polyphenylacetylene (PPA) samples, synthesized through metathesis polymerization of phenylacetylene in the presence of the $Mo(CO)_6/C_6H_5OH$ catalytic system at 393 K, have been reported and discussed [1,2]. Several processes were observed during the heating of the samples in a differential scanning calorimeter. The first could be described with some certainty as the evolution of solvent trapped in the polymer matrix. Above 530 K, a series of exotherms were observed that can, with confidence, be ascribed to decomposition based on TG-MS results. Between these two events other exotherms were observed. The origin of these was uncertain, but was provisionally described as crystallization or a solid-state transition. It was further established that the C_6H_5OH/Mo molar ratio determines to a large extent the thermal behaviour of the polymer. In the proposed mechanism [1] *trans/cis* isomerization and cyclization formed part of the degradation process.

There was some uncertainty as to whether a glass transition occurred during the heating of the polymer, because none was observed in previous analyses [1,2]. Masuda et al. [3] have reported softening temperatures for polyalkynes ca. 483 K, but Cukor and Rubner [4] have questioned these values, stating that the softening temperature depends very much on the heating conditions.

Modulated temperature differential scanning calorimetry (MTDSC) is a relatively new technique which

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provides information about reversing and non-reversing processes during thermal events, in addition to the conventional DSC heat flow and temperature information [5–7]. A heat flux DSC cell arrangement was used with a sinusoidal ripple overlaid on the conventional linear temperature ramp to yield a heating profile in which the sample temperature was increasing continuously with time.

In this study, the MDTSC technique was used to establish the possible presence of a glass transition and to clarify the second thermal event described as crystallization or solid-state transition [1].

2. Experimental

The synthesis and characterization of the polyphenylacetylene samples were as previously described [1,2]. Information on the samples used in this study is summarized in Table 1.

2.1. Modulated temperature differential scanning calorimetry (MTDSC)

TA-Instruments DSC 2920 fitted with a special MDSC^{TM} heat exchanger and mechanical cooling connected to a computer was used with samples of between 3 and 5 mg encapsulated in aluminium pans. The samples were equilibrated at 323 K without modulation, after which they were heated to 543 K at 3 K min^{-1} for a duration of 60 s and an amplitude of ± 1 K. Analyses were carried out in an N_2 atmosphere at a gas flow rate of 65 cm^3 min^{-1}.

3. Results and discussion

The heat flow and reversing heat capacity curves for sample 1 is shown in Fig. 1, where four thermal events are observed. Following an initial broad, weak endotherm (which is attributed to evaporation of solvent trapped in the polymer matrix [1,2]), two well-defined exotherms are observed in the 425–525 K range. Neither of these exotherms are reversible (Fig. 5). The second exotherm is accompanied by a strong increase in heat capacity, which is not reversed on cooling (Fig. 5). This means that the increase in C_p is not due to a glass transition. Previous thermogravimetric analyses show a major mass loss above 520 K [1,2]. This helps explaining the fourth event, which is accompanied by a decrease in heat capacity, as the evolution of decomposition products. In our previous discussion of this system [1], the second event or first exotherm was attributed to crystallization/solid-state transition, immediately followed by cross-linking and/or decomposition. This is, however, unlikely, since the third event is accompanied by an increase in heat capacity, while both cross-linking and decomposition would usually have shown a decrease in heat capacity. We have proposed that *trans*/*cis* isomerization and cyclization preceded the eventual decomposition process.

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

Polymer samples	1	2	3	4
C_6H_5OH/Mo	25	50	100	150
A_{870}/A_{910}	1.14	1.30	1.08	1.05

Fig. 2 shows the heat flow and reversing heat capacity curves for sample 2. The observations are similar to those for sample 1, except that the second exotherm is seen as a shoulder on the high-temperature side of the main exotherm with another shoulder following it. An increase in heat capacity, which is stronger than that observed for sample 1, occurs above the first exothermic peak. In this case, the first and second exotherms overlap much more than is the case with sample 1. When compared to Fig. 1, it seems as if the evolution of decomposition products starts at a somewhat higher temperature. The explanation of these observations is similar to that for sample 1, except that, apparently, the internal reactions occurring in this temperature range are not so well-separated as is the case with sample 1.

The heat flow curve for sample 3 in Fig. 3 shows the initial endotherm followed by an exotherm starting at a higher temperature than in the case of the previous two samples. There is also only a hint of a peak shoulder towards the end of the high-temperature side of the exotherm. The heat capacity again shows a strong increase in the temperature range of the second half of the main exotherm. This increase in heat capacity is even stronger when compared to the same event in the previous two samples. At the maximum

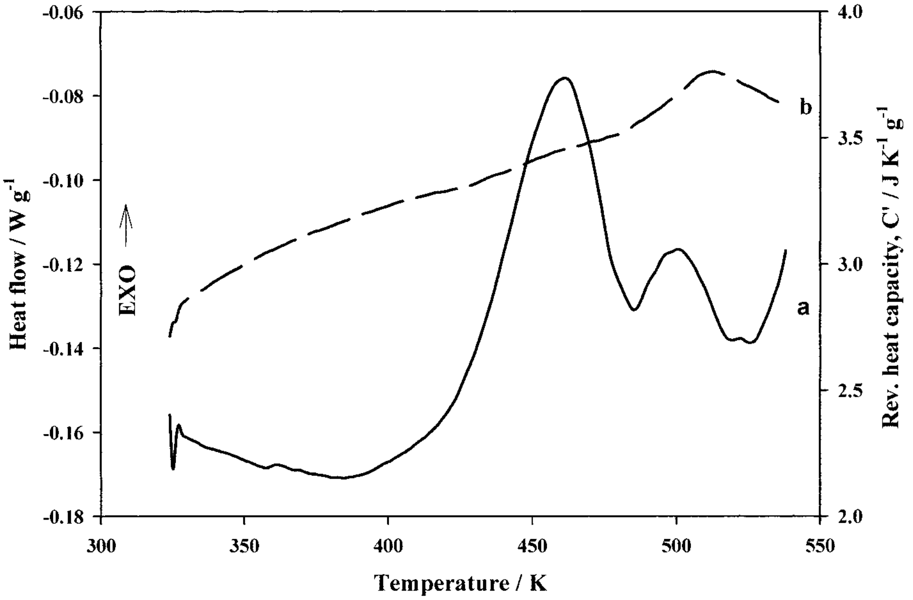

Fig. 1. (a) Heat flow and (b) reversing heat capacity curves for polyphenylacetylene sample 1.

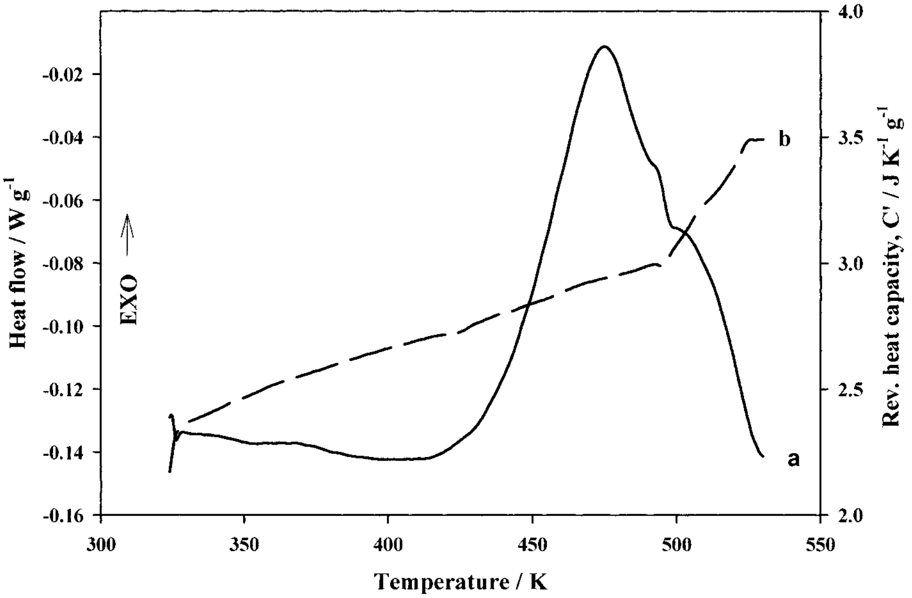

Fig. 2. (a) Heat flow and (b) reversing heat capacity curves for polyphenylacetylene sample 2.

temperature of the analysis, there is only a slight indication of the heat capacity curve levelling off, which shows that the evolution of volatile decomposition products started at an even higher temperature for this sample. Given the previous results it would seem reasonable to assume that the two (at least) exothermic processes observed in samples 1 and 2 have become so close that they formed a single peak.

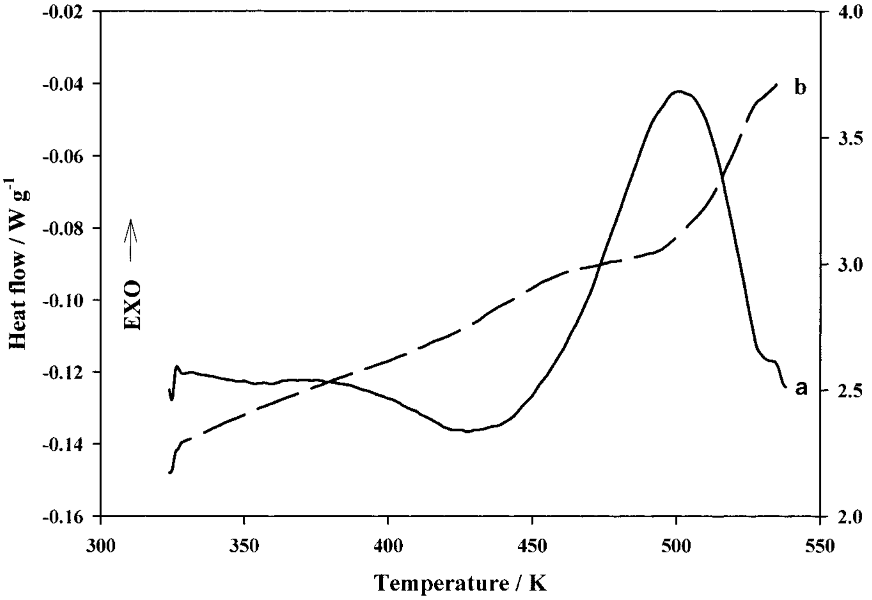

Fig. 3. (a) Heat flow and (b) reversing heat capacity curves for polyphenylacetylene sample 3.

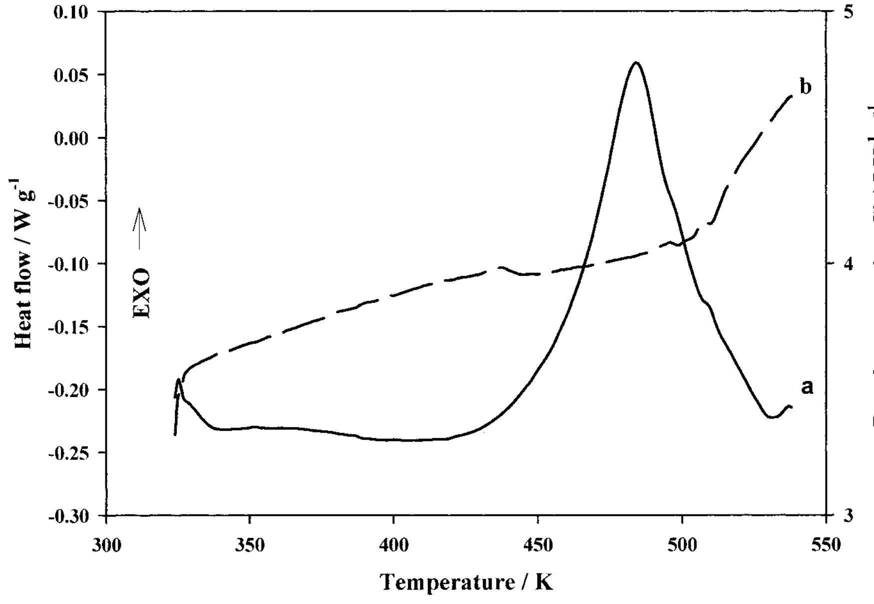

Fig. 4. (a) Heat flow and (b) reversing heat capacity curves for polyphenylacetylene sample 4.

The exotherm in the heat flow curve for sample 4 in Fig. 4 is much sharper than those observed for the previous three samples. In this curve, there is also a slight indication of a peak shoulder on the high-temperature side of the heat flow curve. The heat capacity curve again shows an even stronger increase in heat capacity than was the case for any of the other samples. The increase in heat capacity coincides with

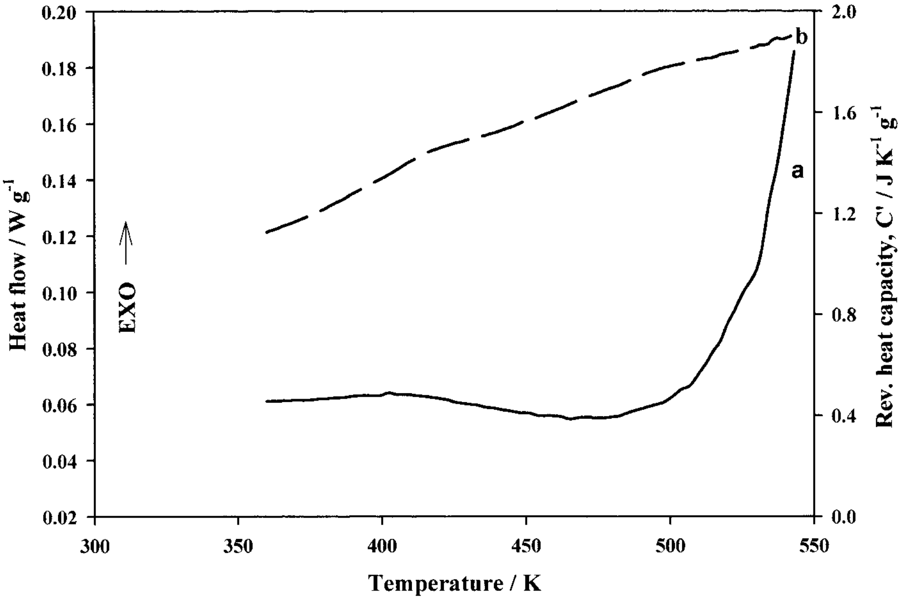

Fig. 5. (a) Heat flow and (b) reversing heat capacity curves for the cooling of polyphenylacetylene sample 1 after being heated to 548 K at 3 K min^{-1}.

the peak shoulder at ca. 505 K. For this sample, at the highest temperature of analysis, there is no levelling off of the heat capacity, indicating that the release of volatile decomposition products starts at an even higher temperature. Again, the explanation of these observations is similar to those for the previous samples.Fig. 5

For all four the samples under investigation, no glass transition was observed within the 323–543 K range. The samples were also analysed over the 233–323 K range. No thermal events were observed over this temperature range, indicating the absence of a glass transition over the 233–543 K range.

4. Conclusion

1. For all the samples under investigation, the heat flow curves show a weak endotherm between 623 and 673 K, previously described as evaporation of solvent trapped in the polymer matrix.
2. With increasing $C_6H_5OH/Mo(CO)_6$ molar ratio the observed heat flow events, in the 423–523 K range, change from two well-defined exotherms through a broad exotherm with a well-defined shoulder to an exotherm with no shoulder or a slight indication of a shoulder.
3. The heat capacity changes become stronger and more well-defined with increasing $C_6H_5OH/Mo(CO)_6$ molar ratio.
4. The evolution of volatile decomposition products occurs at slightly higher temperatures with increasing $C_6H_5OH/Mo(CO)_6$ molar ratio.
5. Above 530 K, the sample decomposes.

After the loss of residual volatiles there would appear to be an exotherm which is not accompanied by a step change in C_p, followed by a second exothermic process, that possibly consists of more than one step, that includes a step increase in C_p. The two events became closer in temperature as the $C_2H_5OH/Mo(CO)_6$ ratio increased. We considered whether the step increase in heat capacity might be due to the *trans*/*cis* isomerization and cyclization steps in the previously proposed mechanism [1]. It does, however, seem as if neither of the two reactions would give rise to such a marked increase in heat capacity. It may, therefore, be concluded that the proposed mechanism [1] may need some revision in view of these newly acquired results.

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References

[1] H.C.M. Vosloo, A.S. Luyt, J. Therm. Anal. 44 (1995) 1261.
[2] A.S. Luyt, H.C.M. Vosloo, J. Therm. Anal. 44 (1995) 1277.
[3] T. Masuda, N. Sasaki, T. Higashimura, Macromolecules 8 (1975) 717.
[4] P. Cukor, M. Rubner, J. Polym. Sci.: Polym. Chem. 18 (1980) 909.
[5] B. Wunderlich, Y. Jin, A. Boller, Thermochim. Acta 238 (1994) 277.
[6] A. Boller, Y. Jin, B. Wunderlich, J. Therm. Anal. 42 (1994) 307.
[7] M. Reading, D. Elliott, V.L. Hill, J. Therm. Anal. 40 (1993) 949.