Thermochimica Acta, 24 (1978) 81–88

ON THE PROCEDURE OF DIFFERENTIAL THERMAL ANALYSIS OF POLYACRYLONITRILE IN AIR

YU. N. SAZANOV, N. A. SHIROKOV AND B. E. GOLTSIN
Institute of Macromolecular Compounds, Academy of Science of the USSR, Leningrad (U.S.S.R.)
(Received 28 June 1977)

ABSTRACT

The effect of the design of the instrument and the experimental procedure of DTA on thermal effects in the polyacrylonitrile (PAN) powder in air at the temperature range 200 to 400°C has been investigated. The occurrence of two main exothermic effects accompanying the thermal transformation of PAN was established. It was found that the differences in the values and ratios of these effects depending on the peculiarities of design of thermoanalysers, the sample weight and its dispersity, the position of the thermocouple ball in the sample and the heating rate are mainly caused by different accessibility of PAN for air oxygen. The data obtained make it possible to attribute the low temperature exo-effect to the thermal transformation of PAN and the high temperature exo-effect to its thermooxidative transformation.

INTRODUCTION

Many papers deal with thermal transformations of polyacrylonitrile (PAN) over the temperature range 150–400°C. The interest in this problem is quite understandable but so far the abundance of chemical, chemico-physical and physico-mechanical data has not led to a generally accepted description of processes taking place during the thermal treatment of PAN. The overwhelming majority of workers emphasize the complex character of these processes and their dependence on the conditions of thermal treatment. Extensive spectral investigations of PAN samples in various stages of thermal treatment in an inert and oxidative atmosphere and in vacuum have been used to develop schemes of PAN transformation which take into account reactions of cyclization, dehydrogenation, oxidation, depolymerization, etc.[1–5]. There are some interesting papers in which transformations of PAN in the course of thermal treatment have been investigated by methods of thermal analysis, mainly by DTA and DSC, and often in combination with spectral and gravimetric methods[6–11]. In some papers, data are reported on the qualitative and quantitative composition of gaseous products of the pyrolysis of PAN over the temperature range investigated[10, 12].

The analysis of these papers suggests that the process of transformation of

PAN into an insoluble cyclic structure depends on so many factors that any attempts to establish the general mechanism of this transformation and the exact sequence of its stages are bound to fail.

In this connection, recommendations concerning the regulation of the pyrolysis of PAN should take into account quite definite conditions of the synthesis of the polymer, methods of its isolation and the preparation of samples used for thermal treatment and, last but not least, the conditions of the thermal treatment itself. These conditions are: the time of the thermal treatment, the mass of PAN undergoing this treatment and the characteristics of the gas medium surrounding the PAN sample during the treatment. Each of these main conditions depends on several factors. Some of them may govern the process of thermal transformation of PAN and, hence, the properties of the final product. Thus, factors characterizing the time of the thermal treatment are the rate of the temperature rise, the time of the isothermic treatment, the number of these treatments, etc.

When the effect of mass is considered, one should take into account its concentration in a certain volume, the degree of sample dispersity and the packing density. The effect of the gas medium should be considered not only in relationship to its activity with respect to PAN in each stage of the thermal treatment but also from the standpoint of its exchange dynamics and the accessibility of the entire mass of the sample for this medium.

The above conditions of the PAN thermal treatment are, in fact, the conditions of thermal analysis. However, up to the present, no systematic published data have appeared in the literature on the effects of the procedure of thermal analysis on the qualitative and quantitative characteristics obtained by DTA–DSC or TG methods.

The purpose of this work was to study in detail the effect of the procedure of thermal analysis of PAN on its transformations over the temperature range 200 to 400°C.

EXPERIMENTAL

Powdered PAN was obtained by polymerization of acrylonitrile in water with the redox system: potassium persulphate + sodium bisulphite at 25°C. The polymer was filtered, washed with water and dried under vacuum; intrinsic viscosity in dimethylformamide (25°C) was 4.1.

The polymer powder was screened on sieves with a vibrator. Fractions with particle diameters (in mm) of 1–0.5; 0.5–0.3; 0.3–0.1 and less than 0.1 were used to investigate the effects of the particle size on the results of thermal analysis. In other experiments, the finest fraction was used (less than 0.1 mm). The crucibles were filled with the powder avoiding its dense packing except in those experiments in which the effect of the packing density on the results of thermal analysis was investigated.

DTA was carried out with a PRT-1000 M thermoanalyser (Central Design Bureau, Academy of Science of the USSR) and a MOM derivatograph (Hungary). The latter was also used for TG. Figure 1 shows the shape and size of standard

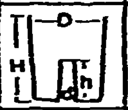
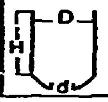
index	crucible cross	material of crucible	H	h	D	d
A1 A2		Platinum glass	12 24 12 12	8 1 1 1	9,5 5 5 10	3 .. .. ..
B		Platinum	4,5	8	9,5	3
C		Ceramic glass	20 12	-	6 6	-
D		Glass	12	-	5	1,5

Fig. 1. Crucibles used in thermal analysis of PAN samples. Sizes in mm.

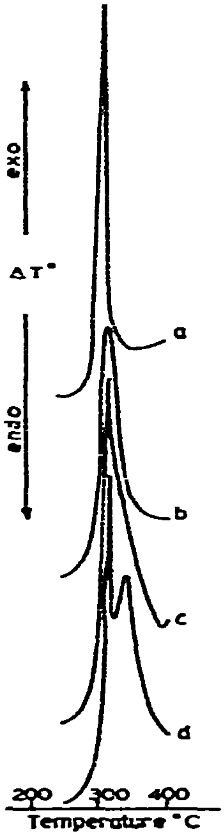
crucibles used with the derivatograph (A1, B) and the PRT(C). Crucibles A1 and B were fixed on the ceramic tubes of the thermocouple in such a manner that the thermal junction was in a special pocket inside the sample and was separated from it by the crucible walls and an air gap. Crucible C was placed in the cell of the metallic block and the thermocouple was introduced into it from above directly into the sample. Figure 1 also shows glass crucibles prepared by us for the PRT (C) and the derivatograph (A2 and D). A thin membrane formed the central part of the bottom of crucible A2 and the thermocouple was in contact with it and thus supported the crucible; this permitted the recording of thermal effects in lower layers of the polymer. Crucible D was a tube with the opening in the bottom for the thermocouple ball which could be introduced into any layer of the polymer. A Pt–Pt (Rd) thermocouple was used. As a rule, the DTA signals were recorded with an EZ 10 potentiometer recorder (Czechoslovakia) and the marks of the temperature of the reference sample measured with another recorder were also recorded on the same chart. The conditions of analyses are given in the legends to the Figures, the sample weight was 5–40 mg and the heating rate was 2.5–20°C min^{-1}.

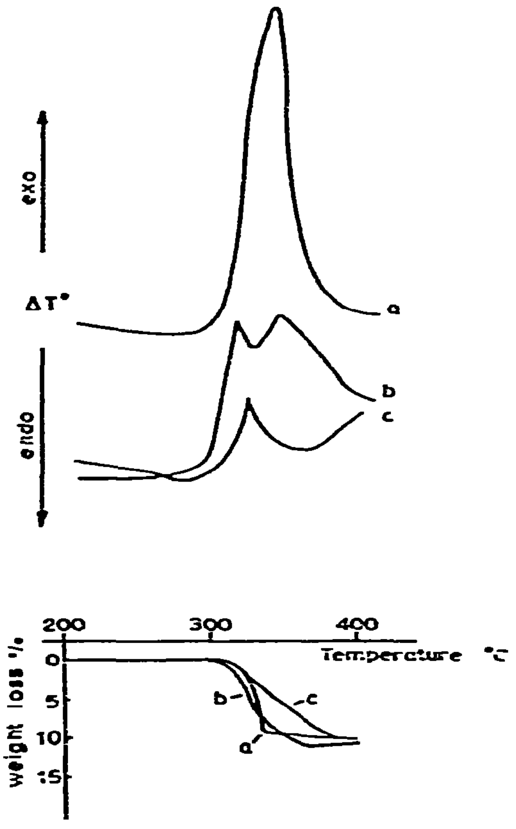
RESULTS AND DISCUSSION

Numerous DTA and TG experiments carried out with powdered PAN samples showed a complex dependence of thermal effects on a number of factors concerning the design of thermoanalysers and the procedure used. Although the effects of these factors are interrelated, shall consider them separately.

Construction of the sample holder

Sample holders in the PRT thermoanalyser and in the derivatograph either





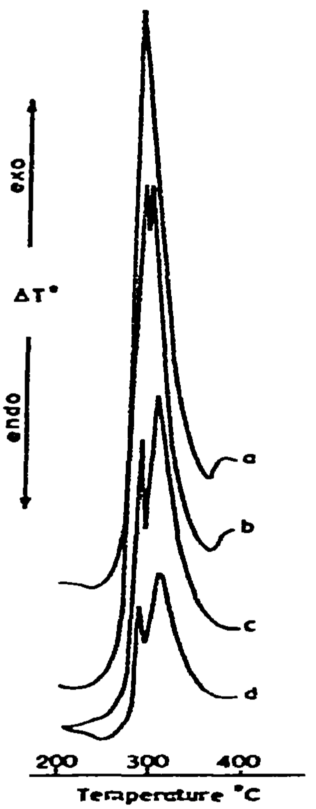


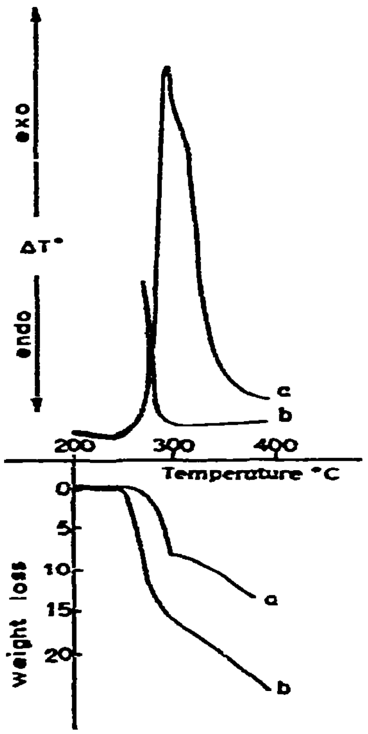
Fig. 2. DTA curves of PAN obtained with a derivatograph: (a) = crucible B and (b) = crucible A1, and with a PRT-1000M; (c) = crucible C, thermocouple ball in the center of the sample; (*d*) = crucible C, the thermocouple ball at the crucible bottom. Sample weight, 20 mg; heating rate, 10°C min^{-1}.

Fig. 3. DTA-TG curves of PAN obtained with a derivatograph in crucibles A2 with different values of H/D: (a) = 1.2; (b) = 2.4; (c) = 4.8. Sample weight, 20 mg; heating rate, 10°C min^{-1}.

Fig. 4. DTA curves of PAN, obtained with a derivatograph at different height (*h*) of the thermocouple ball in the crucible. (a) *h* = H; (b) *h* = 0.5 H; (c) *h* = 0.25 H; (d) *h* = 0. Crucible D is full (sample weight, 20 mg), heating rate, 10°C min^{-1}.

permit a direct contact between the measuring thermocouple and the sample (PRT) or make it possible to record thermal effects through the crucible walls (derivatograph). Moreover, there is a considerable difference between the crucible geometry of these instruments (Fig. 1). Doubtless, these factors are responsible for the differences in the DTA curves in Fig. 2. In order to investigate the effect of geometrical parameters, glass crucibles of a special design were prepared (the thermojunction was placed in the center of the crucible bottom) which differed in height and in diameter. Fig. 3 shows that the DTA curves recorded for the same sample weights of PAN in these crucibles are different. These data indicate that, when PAN is heated in an oxidative atmosphere, two exothermic processes occur; they take place either simultaneously or successively depending on the geometric parameters of the crucible. In wide crucibles, i.e., in thin polymer layers, the processes virtually cannot be separated (Fig. 3, curve a). When the ratio of height-to-diameter increases, both processes can be observed separately in the lower layers of the PAN sample as two DTA peaks (Fig. 3, curve b). In a very deep crucible (Fig. 3, curve c), the second (high temperature) peak of DTA almost disappears whereas the first (low temperature) peak becomes only a little weaker. Similar dependences were observed in the PRT crucibles when the thermocouple was introduced into deep layers of the sample.

The effect of the depth of immersion of the thermojunction into the sample was also investigated for the PRT crucibles and for a special crucible of the derivatograph with an opening in the bottom for the introduction of the thermocouple directly into the sample. Figure 4 shows that, in powdered PAN samples, thermal effects greatly change with depth and the effect of the sample thickness is more or less similar to that of the crucible depth. Thus, it is clear that the immediate contact of the thermojunction with the sample provides better possibilities for a detailed study of the pattern of thermochemical transformations of PAN as compared to the standard



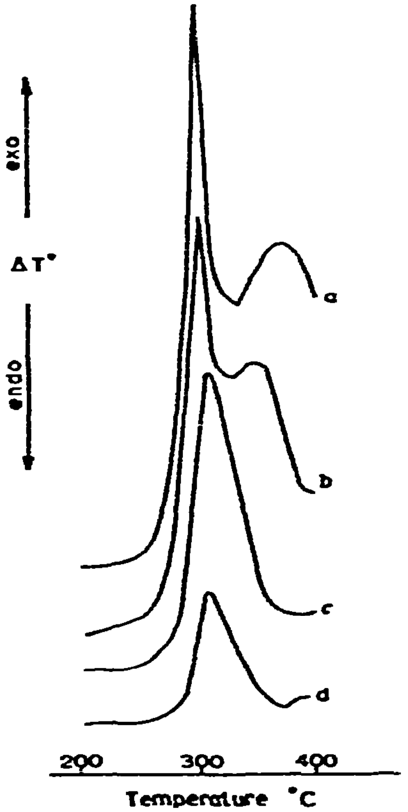
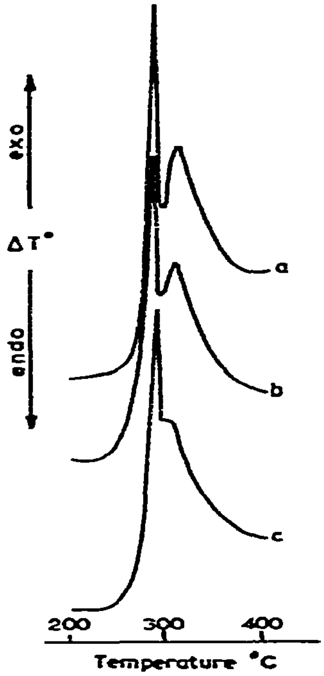


Fig. 5. DTA–TG curves of PAN obtained with a derivatograph in air (a) and in helium (b), crucible A1. Sample weight, 40 mg; heating rate, 10°C min^{-1}.

Fig. 6. DTA curves of PAN obtained with a PRT-1000M in crucible C. Sample weights: (a) = 30 mg; (b) = 20 mg; (c) = 10 mg; (d) = 5 mg; *h* = 0; heating rate, 10°C min^{-1}.



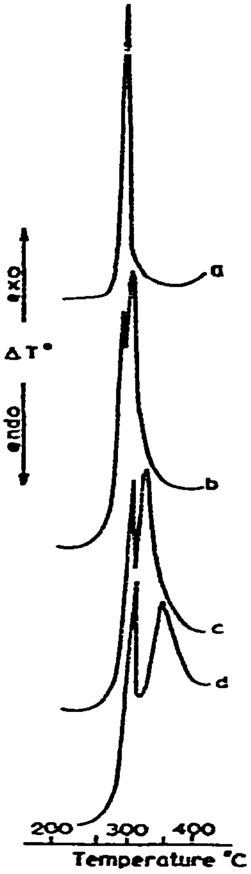


Fig. 7. DTA curves of PAN samples with different particle diameter: (a) 0.1–0.3 mm; (b) 0.3–0.5 mm; (c) 0.5–1.0 mm. Crucible D is full (sample weight 30–40 mg); h = 0.25 H; heating rate, 10°C min^{-1}.

Fig. 8. DTA curves of PAN obtained with a derivatograph at different heating rates: (a) 2.5°C min^{-1}; (b) 5°C min^{-1}; (c) 10°C min^{-1}; (d) 20°C min^{-1}. Crucible D is full (sample weight, 20 mg); h = 0.25 H.

method of measurements with a derivatograph. In the latter procedure, thermal effects are smoothed down and averaged over time and space owing to the transfer through crucible walls.

A marked effect of the above geometrical factors on the course of exothermic processes in PAN is certainly related to changes in the atmosphere surrounding the sample during pyrolysis. It is known that, when PAN is heated in an inert atmosphere, a single very pronounced exothermic effect is observed accompanied by intense gas evolution (Fig. 5). Comparison of DTA and TG curves in air and in helium (Figs. 3 and 5) suggests that the first exo-effect in air and the exo-effect in helium are substantially of the same nature. The influence of oxygen is evident: the exo-effect shifts to high temperatures (by 10–20°C) and its area increases while the weight loss becomes slower. When the depth of the crucible and the thickness of the sample increase, the admission of oxygen and the removal of the gases formed become more difficult and this suppresses the oxidation process. Figure 3 shows that these factors determine the position and the intensity of the second exo-effect and that this effect is not related to the sample weight losses. These data suggest that the second exo-effect is due to the oxidation of the product formed as a result of thermal transformation of PAN which is characterized by the first exo-effect. If the entire mass of PAN is accessible for oxygen, both processes occur virtually simultaneously.

Sample weight

The change in the sample weight in the same crucible leads not only to quantitative but also to qualitative changes in the pattern of thermooxidative transformation of PAN (Fig. 6). This is not surprising because the sample weight is related to its geometry, to the ratio of height-to-diameter and to the volume of gases evolved in pyrolysis. Thus, a certain minimum "critical" mass of the sample exists for each crucible; starting from this mass, it is possible to observe the separation of both exo-effects.

Sample dispersity

DTA curves for fractions of a PAN sample with different particle diameters are shown in Fig. 7. The DTA curve for the finest fraction is shown in Fig. 8 (curve c). A decrease in the size of the particles is accompanied by an increase in the second exo-effect. This may be associated with the increasing surface of the powder and, hence, with its stronger interaction with oxygen. Consequently, by regulating the dispersity of the PAN sample, it is possible to control the course of oxidative reactions for obtaining the end product with required properties. The packing density of the PAN powder in the crucible also affects thermooxidative reactions taking place in it. The effect of the packing density differs for crucibles of different construction and for sample layers of different depth. Presumably, the packing density affects both the accessibility of single layers for oxygen and the efficiency of transfer of the heat evolved inside the sample to crucible walls and to the thermocouple.

Heating rate

Heating rate is of primary importance for the thermal analysis of PAN. When the heating is slow (2.5°C min^{-1}), none of the above factors lead to the separation of both processes. Figure 8 shows that the shape of the DTA curves changes regularly with increasing heating rate. Both exo-effects shift to high temperatures, but the shift of the second effect is much greater. It should be noted, however, that the difference in positions of the maxima of the first and the second exo-effects on the time scale remains constant. It amounts to 1.8 min and, presumably, is determined by the geometry of the crucible and the sample. Moreover, the depth of the minimum between the peaks increased with the heating rate and, at the rate of 2.5°C min^{-1}, it is close to zero. Probably, this change in the patterns of thermal effects is related both to the kinetics of thermal processes and to the dynamics of the gaseous exchange in the atmosphere surrounding the sample.

CONCLUSIONS

Thermal analysis of powdered PAN samples has been carried out with a derivatograph and a PRT-1000M thermoanalyser with different modes of temperature measurements. On the basis of these data, the following conclusions can be made.

When the sample is heated in an oxidative atmosphere at temperatures ranging from 200 to 400°C, at least two processes occur characterized by a considerable exothermic effect. These effects are strongly influenced by the design of the thermoanalyser and the experimental procedure. Factors determining the accessibility of the polymer for air oxygen are of the greatest importance as far as both the quality and the quantity are concerned. By varying the crucible geometry, the sample volume and dispersity as well as the heating rate, it is possible to control the course of thermal and oxidative reactions in PAN. The immersion of the thermocouple into different layers of the polymer powder also leads to different patterns of thermooxidative processes.

The data obtained show the complexity of thermooxidative transformations of PAN under actually observed technological conditions of its thermal treatment and may aid in the choice of the procedure of thermal analysis approaching these conditions.

REFERENCES

1 N. A. Kubasova, M. V. Shishkina, N. F. Zaliznaya and M. A. Geiderikh, *Vysokomol. Soedin., Ser. A*, 10 (1968) 1324.
2 N. A. Kubasova, M. M. Kusakov and M. V. Shishkina, *Vysokomol. Soedin., Ser. B*, 11 (1969) 193.
3 V. F. Gachkovsky, *Vysokomol. Soedin., Ser. A*, 13 (1971) 2207.
4 G. D. Litovchenko, V. M. Bondarenko, N. F. Konnova and M. T. Azarova, *Zh. Prikl. Spektrosk.*, 23 (1975) 251.
5 I. A. Drabkin, L. D. Rozenshtein, M. A. Geiderikh and B. E. Davydov, *Dokl. Akad. Nauk SSSR*, 154 (1964) 197.
6 P. Dunn and B. C. Ennis, *J. Appl. Polym. Sci.*, 14 (1970) 1795.
7 E. V. Thompson, *J. Polym. Sci., B*, 4 (1966) 361.
8 J. N. Hay, *J. Polym. Sci., A-1*, 6 (1968) 2127.
9 V. I. Kasatochkin, T. D. Yaresko, Z. S. Smutkina, M. E. Kazakov and O. I. Egorova, *Vysokomol. Soedin., Ser. A*, 17 (1975) 187.
10 E. Fitzer and D. J. Müller, *Carbon*, 13 (1975) 63.
11 A. R. Monahan, *J. Polym. Sci., A-1*, 4 (1966) 2391.