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THERMAL ANALYSIS OF ACRYLONITRILE POLYMERIZATION AND CYCLIZATION IN THE PRESENCE OF N,N-DIMETHYLFORMAMIDE

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Abstract

This paper examines the polymerization of acrylonitrile to poly(acrylonitrile)(PAN), and its cyclization, in bulk form and using N,N-dimethylformamide (DMF) as solvent in which both monomer and polymer are soluble. Thermal analysis of the resultant products after polymerization has been performed by DSC and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). Scanning electron microscopy has been used to study the morphology of the resultant products and after thermal treatments. The DSC thermal curve of PAN-DMF sample is quite different from the PAN bulk sample, showing a single sharp exothermic peak associated with nitrile group polymerization (cyclization) of PAN at lower temperature (240°C) than that of bulk PAN sample (314°C). Cyclization of PAN was confirmed by IR spectroscopy. It was found that the amide molecules are difficult to eliminate completely in the product obtained after the polymerization reaction, even after prolonged heating at 110°C, and remain occluded. The formation of a complex by dipolar bonding is also possible and it is discussed. It is concluded that the amount of heat evolved as well as the temperature interval over which it is released are influenced by the chemical processing of PAN when using DMF as solvent of both monomer and polymer. Pyrolysis of these PAN samples revealed the release of occluded molecules of DMF, and several compounds containing nitrogen produced from the thermal degradation processes. All these results are interesting to know the chemical processing of carbon fibres and activated carbon fibres from PAN modified precursors.

Keywords: acrylonitrile, cyclization, DMF, DSC, hexanedinitrile, morphology, poly(acrylonitrile), pyridine derivatives, pyrolysis, SEM

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Introduction

Carbon fibres and activated carbon fibres are produced by carbonising a raw material, such as poly(acrylonitrile) (PAN) fibre [1–22]. Carbon fibres, as excellent reinforces for composites, are now important industrially and have gained a wide range of applications in the industrial and engineering fields, from sport articles to the aerospace industry [1–8]. Activated carbon fibres have received increasing attention in recent years as an adsorbent, filter, etc., for filtering automobile gasoline, deodorizing tobacco smoke, recovering solvents and purifying water [20–25]. The advantage of fibrous active carbon, compared to finely powdered active carbon, is the higher bulk volume of the former which can lead to higher adsorption rates because of the more open base structure [22, 23]. PAN fibres have been found to be the most suitable precursors for making high-performance carbon fibre [1–19]. Further developments have shown that carbon fibres can be useful as functional electrical materials [26, 27]. For instance, the preparation of semiconducting carbon fibre by pyrolysis of PAN precursor has been described [26]. PAN fibres, with a novel coiled morphology, as precursors for semiconducting carbon infrared detection elements have been also prepared [27]. However, a careful control of pyrolysis conditions is required for the preparation of semiconducting carbon fibres.

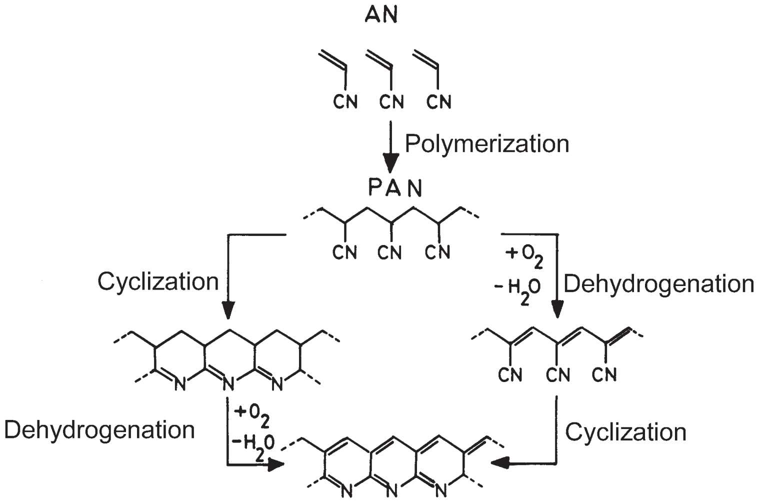

Fig. 1 Mechanistic pathways for the thermal degradation of PAN and reactions involved in the cyclization of PAN fibres, after Fitzer *et al.* [5] and Fitzer [8]

An important step in preparing carbon fibre from the PAN fibre is to heat the precursor at 200 to 300°C in air or in an oxygen-containing atmosphere, i.e., the stabilization process. This process leads to the formation of a ladder polymer in stabilized fibre. Subsequently, carbonization and graphitization is carried out at higher temperatures in an inert atmosphere to obtain a particular type of carbon fibres. The reaction steps involved in the formation of stabilized PAN (fibres) have been studied and confirmed by several authors [5, 8, 13, 17, 28–33]. However, in spite of several studies using various analytical tools, the chemistry of the stabilization of PAN remains complicated and not well understood. Mechanistic pathways were suggested for the thermal degradation of PAN, with the formation of extended two-dimensional structures via condensation of the cyclization products (Fig. 1). It has been also reported [5] that the stabilized polymer contains about 8 mass% of oxygen. The cyclization process for PAN fibres (homopolymer) occurs because of a free radical initiation stage, followed by oxidative reactions. The cyclization of nitrile pendant groups of PAN which give polyimine type structure (Fig. 1), seems to be well accepted as the main reaction during stabilization [13]. These imine sequences are postulated to be three to six units long. The presence of polar groups C=O, OH and COOH in the chains facilitates the initiation of the cyclization process through a nucleophilic attack and accelerates the subsequent oxidative ring closure reactions (Fig. 1). Thus, the overall reaction time for the stabilization process is reduced, enabling considerable savings in manufacturing costs [17]. This could be the case when DMF is used for the processing of PAN as discussed in the present work.

Taking into account the mechanistic pathways, it is assumed that three main reaction steps take place during the stabilization process of PAN [5, 8, 13, 17, 33–36]:

1. Cyclization of pendant nitrile groups, leading to ladder-type structures, as described above.
2. Formation of conjugated electron systems via dehydrogenation reactions along the polymer backbone and in the condensed ring structures.
3. Oxidation reactions, resulting in the formation of carbonyl and hydroxyl functionalities.

Since the stabilization process in atactic polymers leads only to a partial cyclization and dehydrogenation, a variety of olefinic and aliphatic structure units in aromatic and non-aromatic rings with heteroatoms is expected in the reaction products. The stereochemistry of the precursor material is important and have been reported to vary over a broad range [35]. The detection of exothermic DSC peaks in the range 200–350°C can be associated to nitrile group polymerization of PAN, i.e., cyclization, although it is evident that many side reactions, such as the formation of ammonia or even depolymerization, occur in the same temperature region, as reported by Grassie and McGuchan [36]. During subsequent carbonization in a non-oxidizing atmosphere, oxygen atoms and the heterocyclic nitrogen are split off and planar polyaromatics are formed. All these stabilization and carbonization reactions result in volatile byproducts according to the previous results of Fitzer *et al.* [5]. Some mass loss from chain scission and elimination of HCN and NH_3 accompanies the cyclization reactions [13]. Oxygen, which is added and is present during stabilization, is mostly present as –OH and C=O groups. However, some authors [36–38] have suggested that oxygen becomes attached to the imine nitrogen atoms to give a nitrone (N–O) moiety based on infrared spectroscopy and model compound studies. The presence of oxygen promotes cross-linking and helps in the aromatization of the cyclized sequences with the elimination of water, both being essential for the basal plane formation in carbon fibres. Peebles [39] has reviewed the various mechanisms of thermo-oxidative degradation of PAN polymer. The major evolved volatile byproducts formed during the stabilization treatment of PAN in air are H_2O, CO_2 (from dehydrogenation and cross-linking), HCN, and even nitrogen. The evolution of HCN and N_2 is mainly due to the intermolecular condensation of ladder-type structures containing ring nitrogen in large sections. Other pyrolysis products identified during carbonization are H_2, NH_3, CO, CH_4 and C_4 hydrocarbons [13, 37, 38]. Elemental nitrogen is formed at the highest carbonization temperatures. The final high-temperature carbon fibres still contain a small percentage of nitrogen. An important mass loss in PAN is achieved after elimination of all the volatile byproducts.

The modification of PAN fibres is also an interesting way to produce high-performance carbon fibres [18, 19]. Acrylonitrile is a particular case among vinyl monomers regarding the solvent dependence of the propagation rate constant in homogeneous free radical polymerization [11]. With this objective in mind, polymerization of acrylonitrile has been studied in bulk form and using N,N-dimethylformamide (DMF) as solvent in the reaction medium. It should be noted that both monomer and polymer are soluble in this solvent. Then, it was interesting to investigate the chemical processing of these PAN samples using thermal methods.

Experimental

Samples and procedure

The sample materials of PAN and modified PAN were prepared in the laboratory. As a general procedure of polymer preparation, 2 mL of acrylonitrile (AN, 99%, Carlo Erba) and 0.7 mass% of benzoyl peroxide (Merck) as polymerization initiator [17, 28, 29], were intensively mixed. The product was then heated in a closed flask (to avoid liquid evaporation) at 60°C for 24 h to polymerize the AN, followed by a drying treatment at 110°C. This step was also carried out using a 25 mass% solution of AN in DMF. The final products were lightly ground using a centrifugal mill (ZSM-1) with knives of stainless steel.

Methods

DSC curves were obtained using a Mettler equipment (model Mettler FP85), by heating from 30 to 400°C in air at a heating rate of 10°C min^{-1}. Finely powdered samples (10 mg each) were weighed and encapsulated in flat-bottomed aluminium pans of 45 μL volume with crimped-on lids. Evolved heats were determined following calibration with indium (28.4 J g^{-1}) using the integration of the areas under the endothermal peaks and corrected base lines.

Analytical pyrolysis was carried out at 700°C in a CDS Pyroprobe 190 unit consisting of a Pt coil heated at a rate of 20°C ms^{-1}. The samples (2 mg) were placed in a quartz tube using quartz wool for end plugs. The pyrolysis unit was mounted in the injection block of a HP 5988 A GC-MS system. The volatile pyrolysis products were separated on a DB-5 (J&W Scientific) fused silica capillary column (30 m×0.25 mm i.d.). The products were first concentrated in a loop of the column in a liquid nitrogen cold trap, and then GC oven was heated from 40 to 300°C at a rate of 6°C min^{-1}, with a 10 min final hold. The pyrolysis products were identified by comparing their electron impact mass spectra with mass spectra in libraries, and with the mass spectra and GC retention time of standard compounds.

The morphology of original and thermal treated PAN samples (coated with Au) was studied under scanning electron microscopy (SEM) using a JEOL equipment (Model JSM-5400) at 20 kV. An energy dispersive X-ray (EDX) system (Oxford Link ISIS) was fitted to the SEM equipment to perform chemical analysis of the samples using a Si–Li detector with Be window.

Results and discussion

Some interesting results concerning the polymerization of acrylonitrile (AN) in the presence of DMF were found. If the polymerization reaction is carried out without any solvent (bulk form), a hard compact is obtained with a yellowish-white colour. The shape of the flask where this experiment was carried out appeared to be filled by the compacted product. Thus, it was necessary to break the flask in order to recover the sample after the elimination of the glass fragments. In contrast, if DMF is used, an increase in viscosity of the liquid and the formation of a dark brown colour as a consequence of polymer formation can be observed. Then, the polymer is separated by centrifugation. It was necessary to dry the solution at 110°C to remove the liquid. This procedure facilitates the handling by the control of the monomer concentration in the solvent (DMF), i.e., the viscosity control. It can be used when the polymer must be maintained in solution, or in a further processing step such as to prepare PAN as fibres or coils by using spinning techniques [6, 7, 13, 14, 27, 29]. These fibres would be precursors of carbon fibres after stabilization, precarbonization and carbonization at a temperature up to 800–3000°C in an inert atmosphere [5, 13, 14]. However, it is difficult to eliminate DMF completely in the final product even after prolonged heating at 110°C, possibly because of the formation of bound DMF molecules and molecular interactions with the same PAN, as it will be discussed in this paper.

Figure 2 shows the DSC curves of both PAN samples. A broad DSC exotherm is observed for the bulk sample at 314°C. The PAN sample obtained using DMF showed a single sharp peak at 240 and a broad exotherm of low intensity centered at ca 302°C. It has been reported [31] that an exothermic reaction ranging between 200 and 350°C, in an inert atmosphere, is typical of PAN. However, the present DSC runs were performed in air and the effect of this atmosphere on the PAN samples cannot be neglected. The maximum exotherm peak temperature and the evolved heat are lower for the PAN sample obtained using DMF, as compared with the bulk PAN sample according to the results of Fig. 2. The ‘melting temperature’ reported for PAN is extremely high (320°C) [11]. In the present case, the presence of DMF decreases the melting temperature. DMF can be considered to exert a plasticized effect on PAN, as previously pointed out [11] or even is capable of forming ‘complexes’ with PAN as suggested by Keller *et al.* [33]. Low molec-

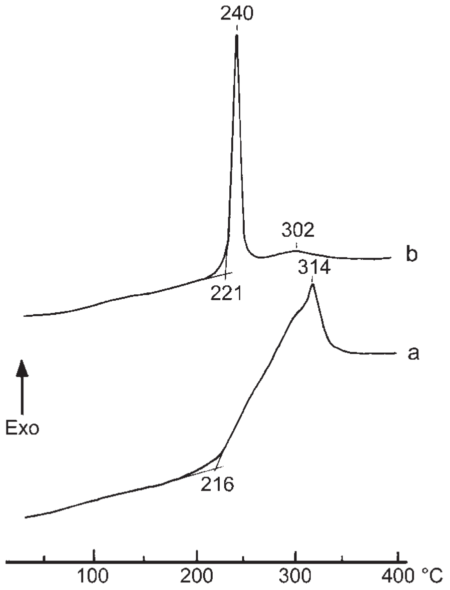

Fig. 2 DSC curves of PAN samples obtained in a – bulk form and b – using DMF

ular mass substances offering a high dipole moment, such as amides, have a strong plasticization effect on PAN fibres. Moreover, the dominant characteristic of the PAN molecule is the presence of the strongly polar nitrile (CN) groups at an intramolecular distance of only a few tenths of a nanometer. The CN groups have a variety of ways in which to interact with their surroundings. The lone pair orbital situated at the nitrogen and oriented 180^0 away from the CN bond is perfectly suited to participate in hydrogen bonding with water or other Brönsted acids, as well as in electron-donor-acceptor complex formation with Lewis acids [11]. Thus, molecular interactions DMF-PAN are expected. Intermolecular dipole-dipole interactions between polymer molecules are replaced by interactions of polymer CN groups with dipoles of the additive. The presence of the 'plasticizing' compound provides increased mobility of individual segments of the polymer molecules. If all polymer CN dipoles interact with the dipoles of a liquid, a strongly polar 'additive', dissolution of the polymer is likely [11]. This is the case when DMF is used.

Melting studies of PAN fibres using DMF [14] suggested characteristic enthalpy changes associated with first order transitions, which is in accordance with the sharp DSC peak observed in Fig. 2 when DMF is used for PAN polymerization, establishing the presence of true crystals in the precursor fibres. It should be noted that PAN fibres have been considered to have a disordered, amorphous, phase as well as an ordered phase [11, 13, 14, 17]. The atactic nature of PAN means that the ordered phase cannot be regarded as truly crystalline, but it is thought that the molecular chains have a regular helical configuration owing to strong intermolecular dipole–dipole interactions between nitrile pairs. Bound nitrile group pairs are formed as a result of intermolecular attractions. It is thought that the amorphous phase is a composed of irregular helical configurations having less intermolecular nitrile group pairings. Changes in molecular structure of PAN molecules is initiated in the amorphous phase and then forms the boundaries of the ordered phase as reported in literature [7, 17].

As mentioned above, DMF is difficult to completely eliminate in the product obtained after the polymerization reaction and even after prolonged heating at 110°C. DMF molecules remain occluded, possibly by the formation of bonded DMF molecules with the same PAN. As a result of this kind of interaction, the DSC diagram is quite different from the bulk sample (without any solvent). The maximum DSC peak temperature is lower (240°C) as compared with PAN sample in bulk form (Fig. 2). The onset temperatures are practically the same for both PAN samples. It can be deduced that the amount of heat evolved as well as the temperature interval over which it is released (exothermic DSC effect), are influenced by the chemical processing of PAN when using DMF as solvent of both monomer and polymer. When PAN is heated in an inert or oxidizing atmosphere, C–N bonds are converted into C=N bonds and a cyclization reaction takes place. Thus, the stability in the structure of PAN during oxidation is achieved through the conversion of an open chain structure into a closed chain aromatic structure. These reactions result in the formation of ladder polymers in stabilized fibres. Thus, the thermoplastic chain molecule is transformed into a non-meltable ladder polymer by cyclization, dehydrogenation and oxidation, as discussed in introduction. The cyclization of PAN during stabilization is always associated with a large exotherm in DSC curves [5, 13], as was observed in Fig. 2 for both PAN samples. The broadening of the exothermic peaks is a result of the cyclization process, which is modified by the action of DMF as the solvent used in the present case for PAN polymerization. It should be noted that the cyclization of the nitrile groups of PAN, which occurs between 250–300°C (10°C min^{-1}), is extremely exothermic, and causes some fragmentation of the chain due to the rapid heat build-up in the sample because the heat does not dissipate at a sufficiently rapid rate [34]. A very sharp exothermic peak at ca 290°C was reported [26] for commercially obtained PAN precursors, and associated to a so-called ‘violent’ exothermic, which shows an onset temperature of 260°C. Lakeman *et al.* [27], using DMF for processing PAN fibres, found this peak at a somewhat lower temperature (275°C), but no heating rate conditions were reported. Fitzer *et al.* [5], studying homopolymer PAN, observed a sharp DSC peak with a maximum peak temperature of ca 284°C, in nitrogen, at a heating rate of 5°C min^{-1} and a broader DSC peak centered at ca 305°C, in air, at the same heating rate. It is interesting to note that broad DSC peaks were observed by Fitzer *et al.* [5] studying copolymer PAN under the same conditions as described above. The detection of exothermic DSC peaks in the temperature range between 200 and 350°C can be associated with nitrile group polymerization of PAN, i.e., cyclization, although it is evident that many side reactions, such as the formation of ammonia or even depolymerization occurs in the same temperature region, as reported by Grassie and McGuchan [35]. The cycization of PAN was confirmed by IR spectroscopy after thermal treatment (data not shown), with the reduced intensity of the absorption band at ca 2220 cm^{-1} assigned to C–N stretching and the appearance of a broad IR band centered around 1690 cm^{-1} associated to C=C and C=N stretching, in accordance with molecular models depicted in Fig. 1.

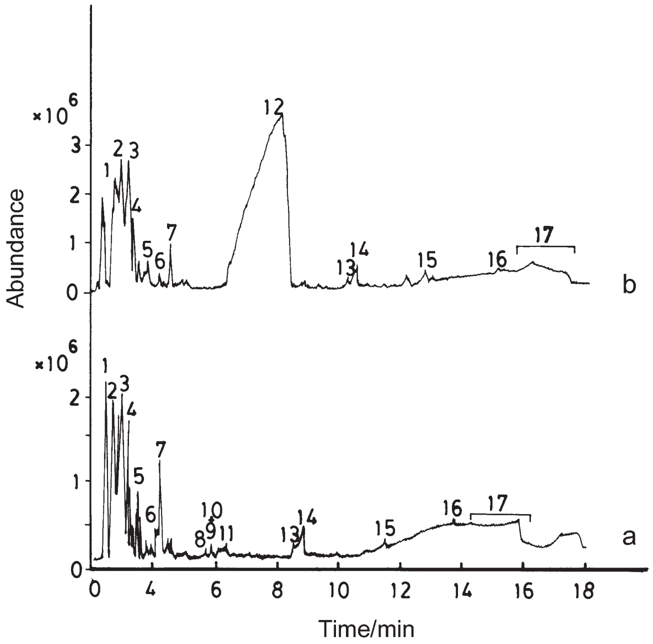

Fig. 3 Total ion chromatograms of the products released in the pyrolysis of PAN samples obtained in a – bulk form, and b – using DMF. Numbers refer to the compounds: 2-propenenitrile (acrylonitrile), peak labelled **1**, and 2-methyl-propenenitrile **2** and their respective isomers (**2**, **4**), and 2-methylene-butanenitrile (**5**); 2,4-pentadienenitrile (**6**); different types of cyclized compounds, such as methylpyridine (**10**), vinylbenzene (**11**); dimethylpyridine (**13**) and benzonitrile (**14**), and methyl derivatives (methyl- and dimethylbenzonitrile) (**15**, **16**); alkyldinitriles, such as the compound hexanedinitrile (**17**). Peak labelled (**12**) corresponds to DMF

To further investigate differences between both PAN samples, pyrolysis of these samples was performed at 700°C and studied by GC-MS. Figure 3 shows the total ion chromatograms of the thermal degradative products obtained after the pyrolysis experiments. The programs of these PAN samples are very similar, although there are some differences: the sample obtained in bulk form has a predominance of nitrile compounds, such as 2-propenenitrile (acrylonitrile), peak labelled (**1**), and 2-methylpropenenitrile (**2**) and their respective isomers (**2**, **4**), and 2-methylene-butanenitrile (**5**). The presence of 2,4-pentadienenitrile (**6**) can also be detected in a low relative proportion. Different types of cyclized compounds, such as methylpyridine (**10**), dimethylpyridine (**13**) and vinylbenzene (styrene) (**11**) appear in the pyrogram. Aromatic nitriles, such as benzonitrile (**14**) are detected in a relatively high proportion as compared with pyridine derivatives, and its methyl derivatives (methyl- and dimethylbenzonitrile) (**15**, **16**) which can be also observed. All these compounds could be derived from cyclized PAN structures which are not completely degraded by the thermal treatment of pyrolysis. Finally, alkyldinitriles, such as the compound hexanedinitrile (**17**), have also been identified. These kinds of compounds could be formed after the final molecular breakdown of cyclized structures with six-member rings by intensive thermal treatment of pyrolysis.

When DMF is used for the preparation of PAN, the pyrogram of this sample (Fig. 3) shows the compounds corresponding to PAN thermal degradation, with slight variations in their relative abundance. The peaks corresponding to DMF can be also detected, where a large peak associated to this compound is released upon Py-GC/MS (peak labelled **12**). This result strongly suggests that this solvent is occluded in the PAN samples and was not eliminated after drying under the present experimental conditions. A possible PAN-DMF complex, as discussed previously, could be formed in the first step of the processing of PAN using DMF as the solvent medium (both monomer and polymer are soluble in DMF). However, this solvent can be eliminated at relative high temperatures, such as the ones used in the pyrolysis conditions, which were used to obtain the programs. It is an indication of the strong bond between DMF and PAN, based on polar interactions.

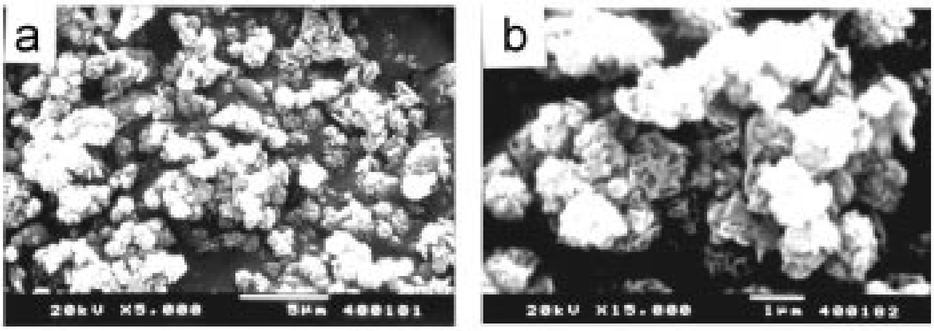

Fig. 4 SEM micrographs of PAN samples obtained in a – bulk form at low and b – high magnifications

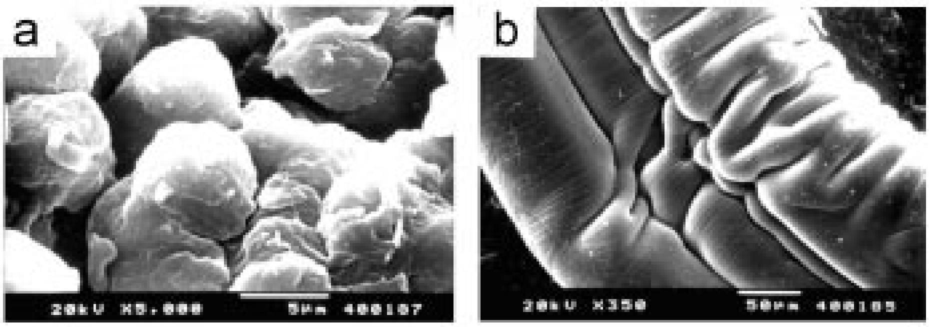

Fig. 5 SEM micrographs of PAN samples obtained a – using DMF at low and b – very low magnifications showing details of morphologies observed (see the text)

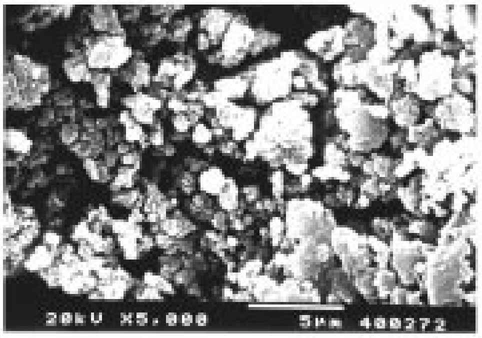

Fig. 6 SEM micrograph of a PAN sample obtained in bulk form after cyclization by thermal treatment at 220°C during 24 h in air

Finally, the SEM study provided differences in morphology of the samples. Figures 4 and 5 show selected SEM pictures of PAN samples obtained in bulk form and those obtained using DMF. There are differences in morphology between both PAN samples, with formation of larger round aggregates in the case of PAN samples obtained in the presence of DMF (Fig. 5), which appeared non porous in contrast with PAN bulk samples (Fig. 4) as observed at high magnification. Figure 5 also shows that this sample has a fairly smooth surface. Moreover, sometimes long aggregates with appearance of kidney structures or intestines were found in PAN samples obtained with DMF observed

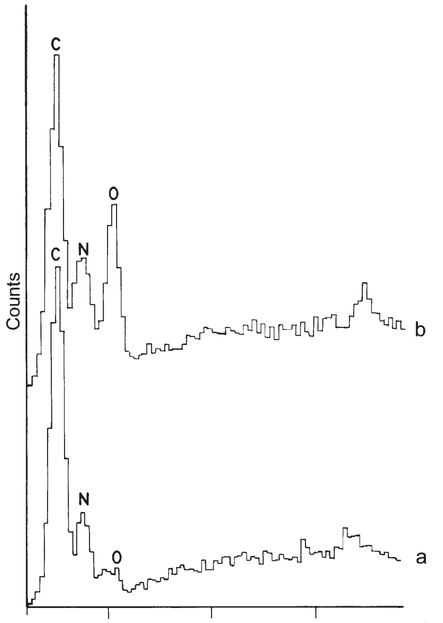

Fig. 7 EDX analysis of PAN samples obtained a – in bulk form and b – after cyclization as observed in the SEM pictures of Figs 4 and 6, respectively

at low magnification (Fig. 5b). This is an indication of the more gelled products formed when DMF was used in the preparation of PAN and the characteristic effect of DMF as plasticizing compound already mentioned in the DSC study.

After cyclization, the morphology in both cases is preserved. For example, Fig. 6 shows a SEM picture of a PAN sample obtained in bulk form after cyclization by thermal treatment at 220°C during 24 h in air. Only slight variations can be appreciated as compared with Fig. 4. However, the EDX analysis of this original PAN sample and after cyclization (Fig. 7) demonstrated the incorporation of oxygen in higher proportion in the PAN sample produced after this thermal treatment. This result is in accordance with the molecular model depicted in Fig. 1 and will influence the subsequent process of stabilization of the resultant carbon fibre.

Summary and conclusions

In this paper, the polymerization of acrylonitrile to poly(acrylonitrile) (PAN) in bulk form and using N,N-dimethylformamide (DMF) has been studied using thermal analysis. DMF is a solvent in which both monomer and polymer are soluble. Thermal analysis of the resultant products after polymerization has been performed by DSC and Py-GC/MS. The morphology of the original products and after thermal treatment was studied by SEM. It was found that the DSC thermal curve of PAN-DMF sample is quite different form the PAN bulk sample, showing a single sharp exothermic peak associated with nitrile group polymerization (cyclization) of PAN at lower temperature (240°C) than PAN sample in bulk form (311°C). The amide molecules were difficult to completely eliminate in the product obtained after the polymerization reaction, even after prolonged heating at 110°C, and remain occluded. The formation of a complex PAN-DMF by dipolar bonding was discussed. It was concluded that the amount of heat evolved as well as the temperature interval over which it is released are influenced by the chemical processing of PAN when using DMF as solvent of both monomer and polymer. The cyclization of PAN by thermal treatment was confirmed using IR spectroscopy. Pyrolysis of these PAN samples at 700°C revealed the release of occluded molecules of DMF, and compounds produced from the thermal degradation processes. Different types of cyclized compounds, such as pyridine derivatives and aromatic nitriles were identified. All these compounds could be derived from cyclized PAN structures which are not completely degraded by the thermal treatment of pyrolysis. Alkyldinitriles, such as hexanedinitrile, have also been identified associated to the final molecular breakdown of cyclized structures with six-member rings by the thermal treatment of pyrolysis. SEM has shown morphology differences of the resultant products in the presence or not of DMF after polymerization, but it is not the case after thermal treatment for cyclization. All these results were interesting to know the chemical processing of carbon fibres and activated carbon fibres from PAN modified precursors.

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