Pergamon

Carbon 37 (1999) 1–6

CARBON

IR and X-ray characterization of the ferromagnetic phase of pyrolysed polyacrylonitrile

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Received 16 April 1998; accepted 30 April 1998

Abstract

The polymer was prepared by γ-ray induced polymerization in air and pyrolysis under argon at various temperatures in the range 600–900°C. The content in the carbon and oxygen increases at the expense of decreasing content in nitrogen and hydrogen. The ferromagnetic phase separated from the residue resulted by the pyrolysis of polyacrylonitrile has been analysed using Fourier transform infrared, X-ray diffraction and elemental analysis. The experimental data suggest a layered structure of this polymer with an interlayer spacing of ca 3.5 Å and various chemical functions grafted on graphite domains. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: A. Char; B. Pyrolysis; B. Infrared spectroscopy; B. X-ray diffraction; D. Magnetic properties

1. Introduction

It is known that pyrolysis of polyacrylonitrile (PAN) at 500–800°C leads to hydrogen cyanide, low molecular weight nitriles (such as monomer and dimer), methacrylonitrile [1], a residue with a condensed polycyclic structure consisting of a graphite-like network [Fig. 1(A)] and high-spin structures [Fig. 1(B)] [2–8]. Such structures are interesting for the study of ferromagnetic phenomena in organic compounds [9,10].

The aim of the present work was to characterize the structures of such magnetic compounds obtained by pyrolysis of a PAN polymer at 600–900°C in argon. The polymer was prepared by radiation induced polymerization of acrylonitrile. Pyrolysis was followed by separation of the ferromagnetic fraction.

2. Experimental

High purity acrylonitrile monomer (product of UCB, Belgium) was used for the synthesis of polymer. Before polymerization, the monomer was distilled to remove any polymerization inhibitor.

Radiation induced polymerization was carried out in air by ^{137}Cs γ-rays, using a Gammator M 38 (Radiation Machinery Inc., Parsippany, NJ, U.S.A.) facility; the dose rate was 542 Gy h^{-1}. The polymer was ground in a china mortar before submission to the thermal treatment.

The pyrolysis was carried out in argon atmosphere, at several temperatures from 600 to 900°C. The conditions of this treatment were as follows: heating rate 20°C min^{-1} approximately, keeping at the required pyrolysis temperature for 2 h, quenching with cold water after pyrolysis (5 min).

The black powder obtained after grinding of the pyrolysis product in an agate mortar shows a density of ca 2 g cm^{-3}. Using a magnetic separator with high magnetic field gradient induced by high energy Nd–Fe–B magnets (30 kOe), a ferromagnetic fraction of 1% wt from total mass of pyrolysis product has been obtained.

Infrared (IR) spectra were recorded with a JASCO Fourier transform infrared (FTIR) Model MCT 5E (Jasco Corporation, Tokyo, Japan) spectrophotometer

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PII: S0008-6223(98)00168-7

or by an IR-75 (Karl Zeiss, Jena) spectrophotometer, using the KBr disk method. In order to mix well the initial or pyrolysed polymer with KBr we used an agate grinder. One should notice that the KBr disk method is more suitable in this case than the attenuated total reflectance one, in spite of the fact that a portion of the spectrum (between 4000 and 3000 cm^{-1}) could be obscured because of a particle radiation scattering effect and residual moisture in KBr [11].

Wide angle X-ray diffraction (XRD) spectra were recorded on a Rigaku 4012 A1 diffractometer (Rigaku Corp., Tokyo, Japan) providing Cu Kα radiation (1.542 Å). The conditions were as follows: applied voltage, 40 kV; current, 30 mA; and a glass tube 0.5 mm in diameter as the sample holder. Detection and recording of X-ray spectra were made by means of a 7.0 cm diameter cylindrical camera. A Narumi NLM-201 micro photometer (Narumi Co. Ltd., Saitama, Japan) was used for the analysis of the diffraction spectra.

3. Results and Discussion

3.1. Magnetic properties

Part of the powdered samples prepared by the pyrolysis of PAN at temperatures 600–900°C was attracted by a magnet. The content of this magnetically active part was 1% (w/w) from the product.

The static magnetic susceptibility data were obtained by an extracting sample magnetometer. The present results of magnetic susceptibility of the pyro-PAN ferromagnetic fraction as a function of the pyrolysis temperature are listed in Table 1.

The magnetic separator used in our experiments could attract part of paramagnetic compounds, resulting in a dilution of ferromagnetic component. This could be an explanation for the small values of the magnetic susceptibility.

Table 1
Change in magnetic susceptibility of PAN as a function of pyrolysis temperature

Pyrolysis temperature (°C)	$\chi \times 10^7$ (emu g^{-1})
600	6.10
700	7.19
800	9.93
900	12.76

The increase in magnitude of the susceptibility with increasing pyrolysis temperature seems to be related to the changes in chemical composition and IR spectra of samples described below.

The susceptibility at 8 kOe was almost independent of measurement temperature over the range 80–300 K. This aspect proves the ferromagnetic characteristic of the studied material. The lack of extrinsic sources of magnetism due to the analytical grade purity of the raw material allows us to remark the intrinsic ferromagnetism in pyro-PAN.

3.2. Characterization of the chemical structure by XRD

PAN is a low-crystallinity polymer from the point of view of XRD analysis. The strong line observed in the spectrum of the initial polymer is due to its crystallinity. Two other weak lines were also observed in the spectrum of the initial polymer.

The crystallinity line and other initial ones vanished by pyrolysis. Diffraction spectra of the pyrolysed samples (see Fig. 2) exhibit three lines corresponding to spacing of 3.55, 2.07 and 1.20 Å, respectively.

The first line is usually assigned to the space between

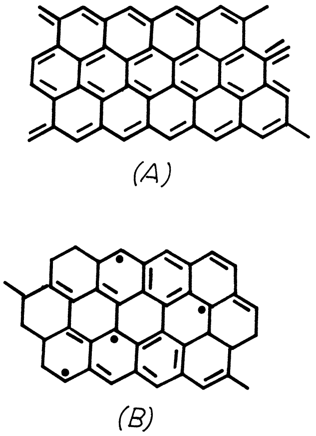

Fig. 1. Chemical structures resulted from the pyrolysis of PAN at 500–900°C in absence of oxygen [8].

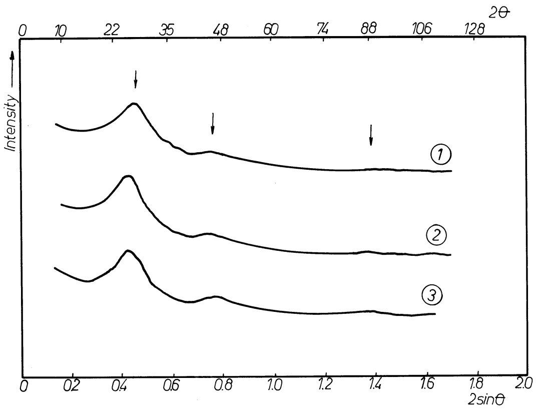

Fig. 2. XRD spectra from PAN pyrolysed at various temperatures: 1, 600°C; 2, 700°C; 3, 900°C. The arrows indicate the position of the main lines.

Table 2
Changes in interplanar distances in PAN pyrolysed at various temperatures

Pyrolysis temperature (°C)	Diffraction angle	Spacing (Å)
600	25.58	3.48
700	25.42	3.50
900	25.09	3.55

two superposed planes of a graphite-like structure. The corresponding distance is 3.35 Å in pure graphite. The larger spacing found in case of our samples (see Table 2) could be explained by the disordering of the structure obtained on pyrolysis. The nitrogen heteroatoms and the grafted functional groups on aromatic rings could play the role of local defects and result in structure disordering. The incomplete pyrolysis conversion of the initial polymer could also have similar effects. The probable structure of the analysed samples seems to be that of a ladder polymer. Similar values for interplanar distance were also reported by X-ray analysis of the residues obtained by pyrolysis of compounds, such as natural coal [1] and PAN [12].

The interplanar spacing rises slowly with increasing pyrolysis temperature, suggesting a higher disordering of the structure. On the other hand, the nitrogen and hydrogen content decrease as the pyrolysis temperature increases (see Table 3). Thus supplementary disordering of the structure could be produced by the elimination of small molecules, such as H_2O, HCN, NH_3, N_2, CO or CO_2, which most likely generate pores.

The second and third lines (10) and (11) are assigned to an imperfect hexagonal net structure within the layers. The intensities of these lines are low with the sample pyrolysed at 600°C, but they increase as increasing the temperature of pyrolysis (see Fig. 2), suggesting a growing-up of this network.

3.3. Characterization by IR spectroscopy

The FTIR spectrum of initial PAN synthesized by radiation induced polymerization of pure acrylonitrile is shown in Fig. 3. The positions of the absorption bands indicate a good agreement between the IR spectra of PAN used in this work and literature data [11,13–15,20].

Table 3
Chemical composition of some pyrolysed PAN samples found by elemental analysis

Pyrolysis temperature (°C)	Element content		
	Carbon (%)	Nitrogen (%)	Hydrogen (%)
Initial	66.33	26.00	5.47
600	68.51	11.93	3.69
900	75.46	6.28	1.46

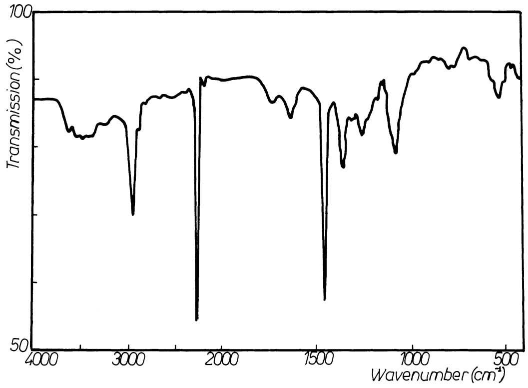

Fig. 3. FTIR spectrum from initial PAN. Conditions: apparatus: JASCO FTIR; resolution: 2; scans: 64; gain: 2; apodization: CS; atmosphere: nitrogen.

The absorption band at 1730 cm^{-1} is due to carbonyl compounds resulted from the radiation-induced oxidation of the polymer in the presence of air. This band was also observed in PAN synthesized by peroxide initiation polymerization [13], but usually it is considerably low.

The absorption bands at 2940 and 2240 cm^{-1}, assigned to CH_2 groups (rocking) and CN, respectively, disappeared almost completely on pyrolysis owing to elimination, cyclization and aromatization reactions [18,20]. Simultaneously, new peaks appeared at 1560 and 800 cm^{-1} due to C=C, C=N and =C–H, respectively, as Figs. 4 and 5 show.

A comparison of IR spectra from magnetic and non-magnetic fractions led to the conclusion that there are certain differences between their compositions. Thus, the absorption bands assigned to several types of polar compounds such as phenols (namely: ca 3620, 3580,

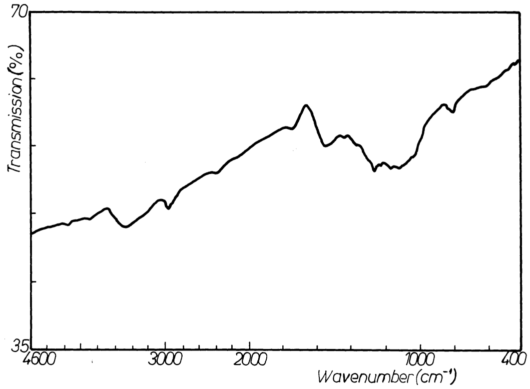

Fig. 4. FTIR spectrum of PAN pyrolysed at 600°C (magnetic fraction). Conditions: apparatus: JASCO FTIR; resolution: 2; scans: 64; gain: 2; apodization: CS; atmosphere: nitrogen.

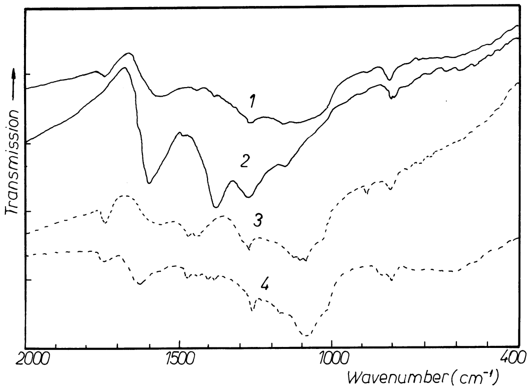

Fig. 5. IR spectra in region 2000–400 cm^{-1} of magnetic fractions of PAN pyrolysed at: 1, 600°C; 2, 700°C; 3, 800°C; and 4, 900°C. Conditions: apparatus: JASCO FTIR; resolution: 2; scans: 64; gain: 2; apodization: CS; atmosphere: nitrogen.

3450, 1340, 1225, 1175, 750, 700 and 600 cm^{-1} [11,14]) pyridones or quinolones (ca 3450, 2800, 2400, 1690, 1670 and 1650 cm^{-1} [14,19]) or pyridine-*N*-oxide type compounds (ca 1300–1200 and 960 cm^{-1} [14,19]) were observed mainly in the spectrum of the magnetic fraction.

The bands corresponding to non-polar compounds, such as pyridine or quinoline-type (ca 3020, 1655, 1625, 1590, 1220, 1180, 1140, 1050, 900, 785 and 660 cm^{-1} [14–17]) or substituted benzene rings (exhibiting absorption bands at 3100–3000 cm^{-1}, 1620–1580, 1520–1480, 1130–1100, 1070–1000, 900–870, 830–815, 805–765 and 725–675 cm^{-1} [15,16,19], depending on substitution degree) were observed in both fractions. This suggests that polynuclear aromatic condensed structures exist in both fractions. Most of these structures consist in condensed nitrogen containing heterocycles. The intensities of these bands seem to be higher in non-magnetic fraction as compared to those of magnetic part. The polynuclear aromatic compounds could exist in magnetic fraction as stable radicals. The electronic paramagnetic resonance (EPR) analysis of pyrolysed PAN revealed the radical character of compounds belonging to magnetic fraction [21].

In the IR spectrum of the magnetic fraction of sample treated at 600°C (see Figs. 4 and 5) one can notice several absorption regions, as follows:

- 3500 cm^{-1}, due to NCH, OH and CO...NCH (assigned to hydrogen bonds) [14];
- 1740 cm^{-1}, due to carbonyl compounds resulting from the reactions of the oxygen initially contained in the polymer and produced by radiation-induced oxidation;
- 1690–950 cm^{-1} region contains several other bands. The absorption band between 1690 and 1490 cm^{-1} region is due to C=C, C=N and C=O vibrations [17]. It could be assigned to certain functional groups such as: phenols; pyridones; quinolines; pyridine or quinoline grafted on a polynuclear aromatic structure. The width of the maximum at 1560 cm^{-1} is perhaps due both to the existence of CO...NH bonds and to the variety of functional groups.

The presence of aromatic rings including N-containing heterocycles in the analysed sample is proved by absorption band at 1560 cm^{-1}; the C=C absorption occurs also in the same region [14–17,19].

The absorption bands observed at ca 1280 cm^{-1} ($\nu_{\text{N–O}}$ in aromatic compounds [14]), 1263 cm^{-1} (C–N vibrations [17]), could be assigned to compounds similar to pyridine-*N*-oxide, or to other containing N–O groups such as a nitroxide radical that involves a nitrogen atom belonging to an aromatic condensed heterocycle structure.

- Several weak absorption bands were observed in 950–650 cm^{-1} region. They are characteristic for vibrations in the aromatic systems. Cyclic compounds containing conjugated C=C and C=N double bonds also exhibit absorption in this region, which is ascribed to aromatic ring vibrations [11].

The experimental results suggest a structural formula for the sample decomposed at 600°C consisting in a graphite type of islands ranged in overlapped layers. In the same plane, more islands could be bound by methylene bridges or by C–C bonds. Most of the nitrogen atoms belong to aromatic polycondensed heterocycles. Local inhomogenities of the structure could consist in functional groups (such as C=O, –OH, –NH, –N=, etc.) on the edges of the polynuclear islands. Both these inhomogeneities and the bonds between islands could cause a disordering of the lattice. Because it is possible to graft several different functional groups on one and the same polynuclear aromatic island, hydrogen bonds could colligate functional groups in the same plane or in different neighbouring ones. The interactions between CO and NH groups grafted in favourable positions, in overlapped planes, result in the ordering (to a certain extent) of the structure. This could explain the smaller value of the interplanar spacing observed on this sample by XRD.

The N–O groups could appear as nitroxide radicals stabilized by conjugation with polynuclear aromatic islands on which they are grafted. It is also possible for stable radicals to exist on polynuclear carbocyclic systems (type B in Fig. 1), but their concentration is expected to be rather small at low pyrolysis temperatures.

The opacity of the pyrolysed samples increases as the pyrolysis temperature increases and the graphite domains grow up (see Fig. 5).

The absorption at 3450 cm^{-1} due to N–H stretching did not decrease in the samples decomposed at higher temperatures. This suggests that N–H groups are produced by the decomposition of aromatic heterocycles which disappear during the carbonization process, when the carbon content of the substance increases. IR data of the pyrolysed samples suggest a destruction of the nitrogen containing heterocyclic structures that could result in the formation of pores and nitrogen containing functions. The increasing of absorption at ca 3450 cm^{-1}, shown in Table 4, supports this assumption. It seems probable that the nitrogen-containing groups represent an intermediate state in the removal of nitrogen and other non-carbon elements from the polymer.

The absorption bands observed in spectrum of the sample pyrolysed at 900°C are similar to those observed in the spectra of samples pyrolysed at lower temperatures, but their intensities seem to be lower (see Fig. 5), perhaps because of elimination of non-carbonic elements.

A relatively weak absorption band is observed between 1760 and 1700 cm^{-1}. The most important peaks are those at 1744 and 1712 cm^{-1}, which could be assigned to carbonyl groups grafted on polynuclear aromatic systems [9] and to several other structures such as quinolone type. The absorption at 1743 cm^{-1} is low at 600°C, increases at 700–800°C and decreases again after 800°C. This behaviour suggests a relative stability of oxygen containing functions at lower temperatures. At higher temperatures they are decomposed, and a part of oxygen is involved in other combinations (ketones, phenols) while another (small one) leaves the solid residue as CO_2 and H_2O.

In the 1700–1520 cm^{-1} region a relatively intense band is observed at ca 1630 cm^{-1} due to $\nu(C{=}C)$ and $\nu(C{=}N)$ in aromatic polynuclear systems [14,17]. Other bands observed in the spectrum of sample pyrolysed at 900°C, namely those at around 1260 cm^{-1} ($\beta_{=CH}$ or CN vibrations [14]), 1166 cm^{-1} (ν_{CN} [11]), 1100–1000 cm^{-1}, 850–700 cm^{-1} ($\nu_{=CH}$) could be assigned to condensed aromatic heterocyclic compounds [15,17,19] or condensed aromatic hydrocarbon rings [14,19]. The intensity of these bands seems to be weaker than those observed in the samples pyrolysed at lower temperatures, perhaps because of increasing of the number of totally substituted benzene rings and of decreasing of number of functional groups as a result of enhanced carbonization. However, the band at 1100 cm^{-1} and the absorption in the 950–650 cm^{-1} region seems to increase with increasing temperature of pyrolysis suggesting the growing-up of the aromatic polynuclear network.

Table 4
IR absorbance and position of absorption maximum of the band at ca 3450 cm^{-1} in PAN pyrolysed at various temperatures

T (°C)	A_{3450}	ν (cm^{-1})
600	0.08	3444
800	0.07	3449
900	0.39	3446

The peak at 1380 cm^{-1} is usually ascribed to $\delta_s(CH_3)$. In this case it could be assigned to an absorption related to a structural irregularity of carbon [14].

The shifting of the peak ca 1600 cm^{-1} to higher frequencies (see Fig. 5) as the pyrolysis temperature increases could be associated with the decreasing of nitrogen content of pyrolysed polymer (see Table 3). The content of aromatic rings appears to reach a maximum at 700°C (probably due to a maximum in heterocyclic content), followed by a sharp decrease at higher temperatures because of nitrogen removal. The concentration of aromatic rings increases slowly after 800°C, but they are different in kind (containing carbon only, like graphite).

The peak at 1264 cm^{-1} is well resolved and it suggests that an important part of the remaining nitrogen could be found as compounds of type of pyridine-*N*-oxide at the edges of the domains (islands) with graphite-like structure.

On the basis of the obtained experimental data, one could suppose a structure of the magnetic phase of PAN pyrolysed at 900°C consisting in relatively large graphite-like network domains (islands). Nitrogen-containing heterocycles and their decomposition products are included in, or grafted on the edges of these islands. Some functions containing oxygen and short unsaturated hydrocarbon chains, obtained in the decomposition process, are also grafted on the edges of the graphite-like domains. Part of these groups goes out of the plane causing the disordering of the structure. Interactions by hydrogen bonds seem to be less probable because of the large dimensions of graphite domains that determine the existence of large distances between the groups able to interact.

An important part of the nitrogen atoms in heterocycles is included in N–O groups, part of them being nitroxide radicals. Other radicals could be located on the carbon atoms inside the graphite-like domains. Both the nitroxide and carbon located radicals are stabilized by conjugation and could be involved in ferromagnetic properties observed for pyrolysed PAN.

4. Conclusions

We performed a structural characterization of the magnetic part of PAN samples obtained by γ-ray irradiation in air and pyrolysed at several temperatures in the 600–900°C range in argon atmosphere. In the IR spectra we noticed certain lines which could be ascribed to aromatic polynuclear compounds or to organic functional groups. Magnetic properties seem to be related to the existence of chemical species such as nitroxide radicals, and radicals grafted on the carbon atoms belonging to graphite-like structures. Further investigations are necessary to improve the structural characterization, to find out the best pyrolysis conditions, and to clear up the role of impurities.

Acknowledgements

The authors would like to thank Professor A.T. Balaban for valuable advice in elaboration of this paper. The Romanian authors are greatly indebted to the Gunma University, Faculty of Engineering for the opportunity offered in elaboration of this work.

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