

STUDY ON THE GASEOUS PRODUCTS OF HIGH TEMPERATURE PYROLYSIS OF ACRYLONITRILE POLYMERS BY ON-LINE FTIR METHOD

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ABSTRACT

The gaseous products of high temperature pyrolysis (300°C to 960°C) of acrylonitrile polymers were measured continuously under nitrogen atmosphere by on-line Fourier Transform Infrared Spectroscopic method (FTIR). From the variations of characteristic peaks it was found that the nitrogen of macromolecules evolved were mainly in the form of hydrogen cyanide and ammonia. During the pyrolysis amorphous carbonaceous element was formed, and crosslinked to form network structure. Three kinds of samples were used for comparison. The experimental results show that the gaseous products of volatile small molecules were HCN, NH₃, CH₄, C₂H₆ and cyanide. CO and CO₂ were also formed when copolymers of PAN were thermally pyrolyzed.

INTRODUCTION

It is well known that the polyacrylonitrile (PAN)-based carbon fibres were formed when the PAN fibres were heated and the ring-closing reaction of which occurred easily. In order to obtain the high-performance carbon fibres from PAN, the pyrolysis of acrylonitrile polymers have been investigated by using many different methods^[1-9]. Up to date, no study on the characterizations of gaseous products of high temperature pyrolysis of acrylonitrile polymers has been reported.

In a previous paper the authors have reported the results of in-situ FTIR study on the changes of chemical constitution of acrylonitrile (AN)/diacetone acrylamide(DAA)/methyl acrylate(MA) copolymers during low temperature pyrolysis under different atmospheres^[10]. In this study, the variations of chemical composition of the gaseous products from high temperature pyrolysis of three kinds of PAN samples are studied under nitrogen atmosphere by on-line FTIR method, the change in molecular structures is also discussed.

EXPERIMENTAL

Three types of samples were used in this study, i.e., homopolymer of acrylonitrile and AN/DAA/MA copolymer of weight ratio 91:6:3 synthesized by ourselves, AN/IA(itaconic acid) copolymer of weight ratio 98:5:1.5 supplied by Jilin Research Institute of Chemical Technology.

Figure 1 is a flow diagram of the experimental apparatus. At first, the sample was placed in a quartz boat, then put it into a specialized pyrolytic furnace. All experiments were performed in purified N₂ and heated according to a linear program. The heating rates were: 6°C/min from room

temperature to 300°C and 10°C/min till 960°C. The gaseous products were passed through light pipe(about 150°C), the spectra of gaseous products were continuously collected.

FTIR spectra were recorded on a Digilab 15C model FTS systems. All spectra shown were obtained under the conditions of 10 scans, at 8 cm⁻¹ resolution, at 4000—650 cm⁻¹ wave numbers and single-beam operation.

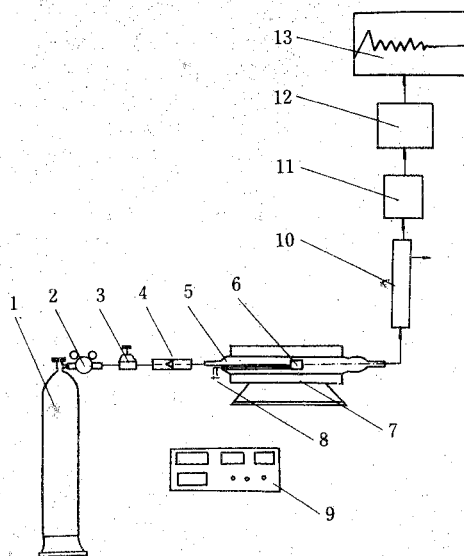


Fig.1 Flow diagram of the experimental apparatus

1. high pressure gas cylinder; 2. reducer; 3. accurate regulating valve; 4. flow meter; 5. quartz tube; 6. sample boat; 7. pyrolysis furnace; 8. thermocouple; 9. temperature controller; 10. light pipe; 11. detector; 12. data processing; 13. plotter

RESULTS AND DISCUSSION

1. The variations of the gaseous products for high temperature pyrolysis of acrylonitrile polymers

The frequencies of the absorption bands in the infrared spectra for high temperature pyrolysis of acrylonitrile polymers are listed in Table 1.

Table 1 Infrared spectra and assignments for the gaseous products of high temperature pyrolysis of acrylonitrile polymers

Frequency(cm ⁻¹)	Assignment
3337, 3279, 713	HCN
946, 929	NH ₃
3012, 1303	CH ₄
2978	saturated hydrocarbon
2249	alkyl cyanide
2357	CO ₂
2179, 2114	CO

As can be seen from Fig.2, the absorption bands of hydrogen cyanide (HCN) of pure polyacrylonitrile(3) pyrolyzed decreases with increasing pyrolysis temperature and reach minimum values at 530°C. Above that temperature the absorption increases slowly. At temperature higher than 880°C, the absorption turns to decrease again.

The changes in spectra below 530°C show that HCN are produced from breakup of unladdered portions of the molecule, while the HCN absorption at 880°C was due to intermolecule elimination. When the AN/IA(1) and AN/DAA/MA(2) copolymers were pyrolyzed under the same experimental condition (figure omitted), the changes of the characteristic bands of HCN formed by sample(1) and (2) were similar to those of sample(3), only the peak temperature of HCN released were different.

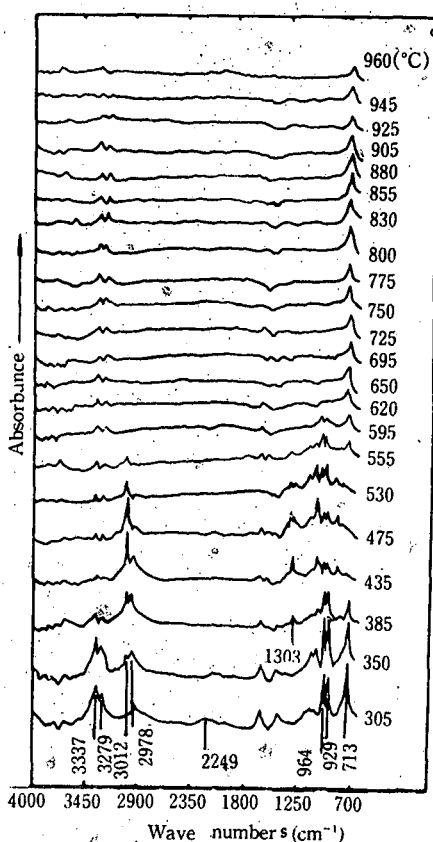


Fig.2 IR spectra of pure polyacrylonitrile with changing pyrolysis temperature at 300°C—960°C

The characteristic bands of the ammonia (NH_3) for sample(3) increases with rising temperature. When the pyrolysis temperature rising to 350°C, the absorption reaches a maximum, the bands are weakened rapidly with increasing temperature. Above 700°C, the absorption band of NH_3 is nearly disappeared. Whereas the absorption band of NH_3 of sample(1) decreases with rising pyrolysis temperature, and at 695°C the absorption band still could be seen. The change of NH_3 absorption band of sample(2) at 435°C is more pronounced than at 385°C, then reducing with rising pyrolysis temperature, at 695°C the change of absorption band becomes the smallest. Afterward, the absorption band increases with temperature till 855°C. These phenomena show that

different types acrylonitrile polymers produce NH_3 not in the same way, and some differences may exist in the break-up of the bond in the molecular chain of unladdered structure and aromatization of the end ring of ladder structure.

The characteristic absorption bands of the methane(CH_4) of sample(3) also increase with rising pyrolysis temperature. The absorption of CH_4 has a peak at 435°C , then drops quickly, and undetectable above 595°C . Whereas the characteristic absorption band of CH_4 for sample(1) is the highest at 475°C , rising the temperature further the absorption falling gradually and undetectable above 625°C . For sample(2), the band shape is similar to that of HCN but the absorption band falls to a minimum at 680°C .

The absorption band of the saturated hydrocarbon(e.g. ethyl-) reduces with increasing pyrolysis temperature, and disappears above 555°C . Whereas the characteristic absorption of copolymers weakens above 475°C . This may be due to the alkyl contribution in alkyl cyanide, and the cyano group absorption decreases as temperature increasing. The spectrogram of sample(1) shows that the characteristic absorption band of carbon dioxide(CO_2) decreases with rising pyrolysis temperature. When the pyrolysis temperature rises to 530°C , the band of CO_2 attains to a minimum, then increases again till 855°C . Whereas the characteristic absorption of CO_2 of sample(2) increases with rising pyrolysis temperature. Above 750°C , the band became weaker, afterward it increases gradually till 905°C , above that temperature decreases again.

When the copolymer(1) is under heating the absorption band of carbon monoxide(CO) appears (as shown in Fig.3.) and increases with increasing pyrolysis temperature. The absorption band begins to decrease when the temperature passed over 435°C and increases again over 700°C . Whereas below 600°C , the pattern of CO produced by sample(2) is similar to that of (1), but increases above 600°C and decreases again above 900°C .

It is difficult to obtain the results given by Fig.3. from the IR spectrum measured discontinuously. These results and the regular IR spectrum are measured continuously. These phenomena show that the acrylonitrile copolymer releases CO_2 and CO through the intermolecular condensation and the break up of chains and oxygen-containing groups.

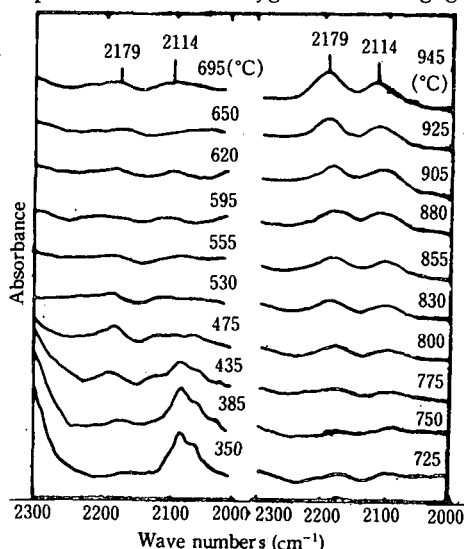


Fig.3 The change of characteristic absorption band with temperature varied over the $2300\text{--}2000\text{ cm}^{-1}$ range during the thermal degradation of AN/IA copolymer, in N_2

2. The influence of pyrolysis temperature on the intensity of the absorption peak of different gaseous products

As can be seen from Fig.4, the intensity of HCN peak from pure polyacrylonitrile(3) drops rapidly as the pyrolysis temperature raising from 300 to 960°C, the amount of HCN produced falls to a minimum at about 530°C, then increases slowly. The intensity of the peak reaches to a maximum value when the temperature raising to 880°C. For AN/IA copolymer(1), the absorption intensity of HCN increases with temperature till 435°C, then drops rapidly, and falls to a minimum at about 620°C, above that it increases slowly again, and a high peak at 880°C. For AN/DAA/MA copolymer(2), the absorption intensity of HCN falls to a minimum at 620°C too, then increases rapidly and reaches the highest value at 880°C. These similarities show that the peak of HCN below 500°C may be resulted from the break-up of the unclosed ring step-ladder structure under heating, but the second peak of HCN may be due to the intermolecular elimination of the ladder polymer.^[5] Therefore we assume that the network structure of the conjugated carbon might be formed as follows,

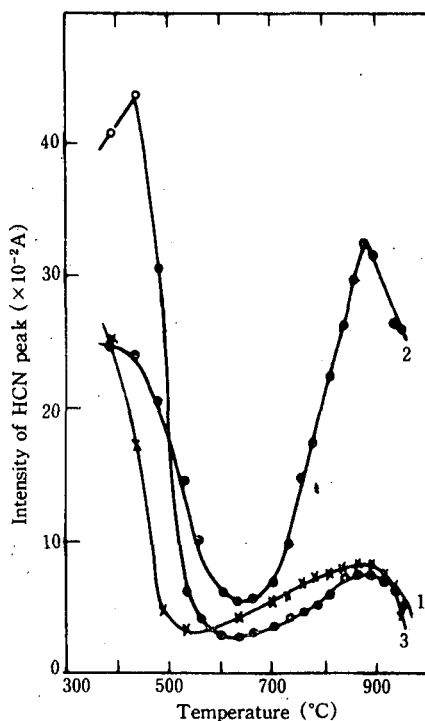
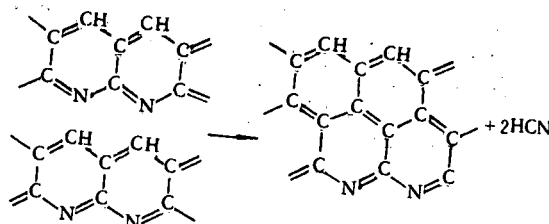


Fig. 4 Influence of pyrolysis temperature on the intensity of the absorption peak of HCN produced from polymers 1, AN/IA copolymer; 2, AN/DAA/MA copolymer; 3, pure polyacrylonitrile

As can be seen from Fig.5, a part of the nitrogen in PAN macromolecule is released in the form of NH_3 during acrylonitrile polymer pyrolyzed. The amount of NH_3 released by sample(3) increases with temperature, but decreases rapidly when the temperature is over 350°C , above 600°C it drops slowly. That of sample(1) decreases rapidly with raising temperature but above 600°C the dropping of NH_3 for sample(1) is as much as that of sample(3). The first peak of NH_3 of sample(2) appears at 435°C , the amount of NH_3 released is a minimum at 695°C and again a peak appears at 855°C , but its is much lower than that at 435°C . These variations of NH_3 might be caused by the difference in the breakup of the bond of un-ladder structure and the aromatization of the end-ring of ladder polymer in different samples. Hence the evolution of NH_3 for pyrolytic acrylonitrile polymer could be assumed as:

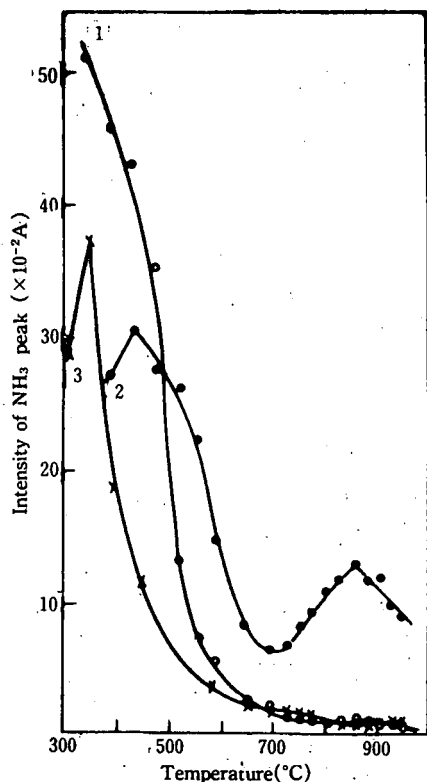
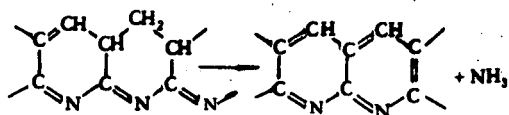


Fig.5 Influence of pyrolysis temperature on the intensity of the absorption peak of NH_3 produced from polymers

1, AN/IA copolymer; 2, AN/DAA/MA copolymer;
3, pure polyacrylonitrile

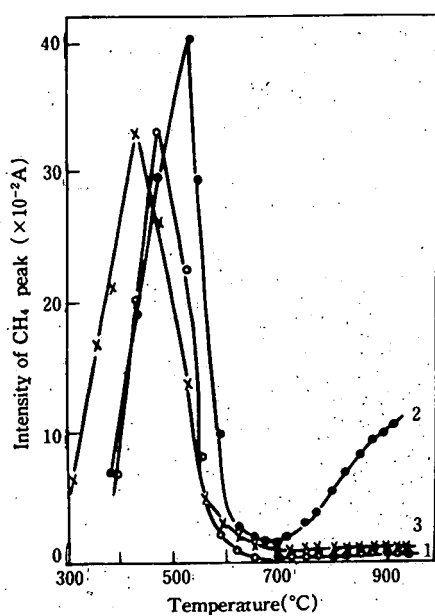


Fig.6 Influence of pyrolysis temperature on the intensity of the absorption peak of CH_4 produced from polymers

1, AN/IA copolymer; 2, AN/DAA/MA copolymer;
3, pure polyacrylonitrile

As mentioned above, the small molecules, HCN and NH_3 might be derived from the nitrogen of the acrylonitrile polymer which decomposed at 300°C – 960°C . Of course, it can not exclude that a part of nitrogen of the macromolecule released as N_2 (because N_2 is a homogeneous molecule which has no IR spectrum)^[7]. These explanations are in coincidence with the experimental results by Bromley^[3] and Казаков, et.al^[4].

Fig.6. shows that the absorption intensity of CH_4 increases linearly with raising of the temperature. The absorption intensities of sample(3), (1) and (2) reach their peak values at 435°C , 475°C and 535°C respectively. Further raising the temperature the released quantity drops rapidly. When temperature is over 695°C , the quantities of CH_4 from samples(3) and (1) attain some steady values, but that from sample(2) still increases.

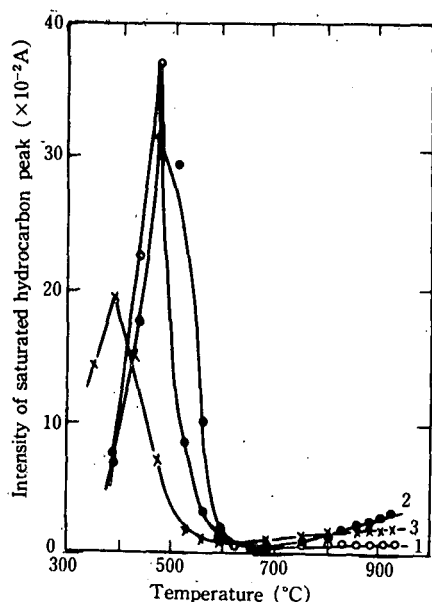


Fig.7 Influence of pyrolysis temperature on the intensity of the absorption peak of saturated hydrocarbon.

1, AN/IA copolymer; 2, AN/DAA/MA copolymer;
3, pure polyacrylonitrile

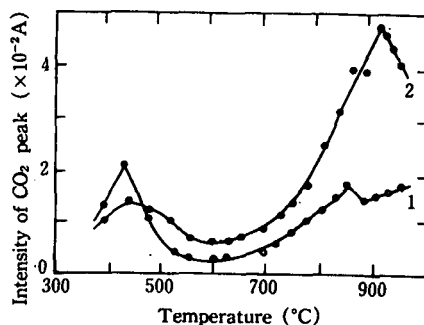


Fig.8 Influence of pyrolysis temperature on the intensity of the absorption peak of CO_2 produced from copolymers.

1, AN/IA copolymer; 2, AN/DAA/MA copolymer

Fig.7. shows that the absorption of the released saturated hydrocarbon increases with pyrolysis temperature. Heating to 385°C and 475°C , the absorption intensities for pure polymer(3), copolymer(1) and (2) reach maximum values respectively, then drop to the lowest values at 620°C , afterward the absorption intensity increase slightly.

From Fig.8 and 9 we can see that when the copolymers AN/IA(1) and AN/DAA/MA(2) pyrolyzed in nitrogen atmosphere, there are two peaks of CO_2 , which appear at 620°C and 855°C for sample(1) (as shown in Fig.8), and for sample (2) at 695°C and 905°C , and the production of sample(1) is smaller than that of (2). The pattern of CO released is almost the same as of CO_2 (as shown in Fig.9). The production of sample(1) at 435°C is higher than sample(2), but at higher temperature the production of sample(2) becomes much higher. This might be the result of the

break-up of the high thermal stable oxy-condensed ring aromatic hydrocarbon chain, and forming CO_2 and CO by oxygen radicals and carbon during the pyrolysis of polyacrylonitrile.

To sum up, in spite of the polymer samples have different carbon formations there appear some similarities during pyrolysis, they may not converse into element directly, instead through some chemical reactions to enable the nitrile group in polymer crosslinking, forming the conjugated groups. The six-membered ring of carbon and nitrogen after dehydrogenation produces aromatic ring, again pyrolyzed at high temperature, the small molecules were formed and evolved. The decomposing residues further were condensed, again through the condensed ring aromatization, and the carbon-rich hydrogen-poor macromolecule of the great area numerical ring aromatic hydrocarbon formed. In the higher reaction stage this material in part came into condensed reaction and a certain amount of the carbonized products was obtained. The pyrolytic behavior during carbonization of acrylonitrile polymers are different. Especially, the pyrolytic gaseous products of the polymer containing DAA are remarkably different from others. These informations have been referred valuable.

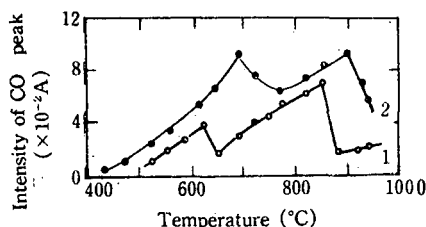


Fig.9 Influence of pyrolysis temperature on the intensity of the absorption peak of CO produced from copolymers 1, AN/IA copolymer; 2, AN/DAA/MA copolymer

Keywords:

Pyrolysis; Acrylonitrile; Polymer; FTIR

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