Pyrolysis Gas Chromatographic Analysis of Polyacrylonitrile

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ABSTRACT: Pyrolysis gas chromatographic analysis of polyacrylonitrile under an inert atmosphere was made in a temperature region of 500–900°C. It was confirmed that the main degradation products are various kinds of lower nitriles that include CH_2CHCN, CH_3CN, and HCN. In addition, lower hydrocarbons such as CH_4 and C_2H_4, which are related to secondary decomposition, were detected. Various thermo-analytical data were obtained, including those concerning the relation between retention time and the polarity of nitriles, and the dependence of the products' limiting yield on pyrolysis temperature. Based on the above results, specific applications of the pyrolysis gas chromatographic analysis and the utility of this procedure in the study of thermal degradation of polyacrylonitrile are described. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 473–478, 2001

Key words: polyacrylonitrile; pyrolysis gas chromatographic analysis; degradation mechanism; nitriles; hydrocarbons; methane

INTRODUCTION

There have already been many studies about the thermal degradation of polyacrylonitrile (PAN) by means of instrumental analysis.[1–5] However, very few pyrolysis gas chromatographic (PyGC) analyses have been made. In the systematic study by Bell et al.[6] of the thermal degradation of PAN, degradation kinetics, the limiting yield of lower nitrile compounds, and the unique degradation mechanism (including an elimination of HCN from such structural irregularity as head-to-head linkage using a single column packing agent), were reported. The utility of this procedure for PAN was made clear in this study. However, herein we discuss the degradation of PAN in relation to the potential utility of this procedure from a different point of view.

Generally, thermal degradation is performed in one of the following: 1. isothermal conditions; 2. under programmed uniform heating rates; or 3. under rapid pyrolysis conditions. The PyGC procedure described herein relates to the third type of degradation. Because the polymer sample is smoothly transferred into a high temperature furnace that is maintained above 500°C, degradation occurs rapidly and almost complete fragmentation results. In contrast to this, in the first and second cases, the sample is generally heated slowly under specified conditions. Degradation is initiated from a chemically weak bond and the overall reaction proceeds gradually. Thus, quite different experimental results can be expected using the third method.

One can use this procedure as a powerful analytical tool for the investigation of the thermal degradation process of PAN. For example, if PAN is preheated under suitable conditions, various chemical reactions will occur in the bulk sample. When this sample is pyrolyzed rapidly in a PyGC instrument, the resulting PyGC data will contain significant information on the chemical reactions occurring during the heat treatment. The direct

Table I   Four Different Column Separation Conditions

Notation	Packing Agents	Column[a]	Temperature (°C)
I	PEG-6000	3 mm$^{\phi}$ × 3 m	80
I′	PEG-6000	3 mm$^{\phi}$ × 2	100
II	TCP	3 mm$^{\phi}$ × 2	80
III	Silica-gel	3 mm$^{\phi}$ × 2	150

[a] Stainless steel column (inner diameter × length).

comparison of the PyGC pattern of the original sample and the heat-treated sample will reveal one of the following: 1. what kinds of chemical reactions occurred, or 2. how the specified functional groups were formed during the heat treatment. In this article, the general degradation pattern of PAN, the establishment of standard PyGC conditions, and some specific applications of the PyGC procedure for PAN, are described.

EXPERIMENTAL

Sample

One kind of homogeneously solution polymerized PAN (S-6), in dimethyl sulfoxide by use of 2,2′-azobisisobutyronitrile as a catalyst, was used. The sample preparation conditions have been described previously.[7] The intrinsic viscosity was 2.14 (in *N,N*-dimethylformamide, at 25°C). The sample was essentially an atactic configuration and the isotactic percentage, determined by ^{13}C-NMR spectra, was 26% (triad tacticity).[8]

PyGC Analysis

The instrument used was the Shimadzu GC 4B-PTF, which is equipped with a small pyrolysis furnace (horizontal-insertion type) and two kinds of detectors: a flame ionization (H_2) and a thermal conductivity detector. The sample was mounted in a platinum boat and inserted in the furnace. To make an effective separation of the decomposition products, three different types of column packing agents were used: poly(ethylene glycol) (PEG-6000), tricresyl phosphate (TCP), and silica gel (see Table I). The PyGC conditions were as follows: sample weight, 1–2 mg; pyrolysis temperature, 500–900°C; pyrolysis time, 10–15 s; atmosphere, in He stream (30–40 mL/min).
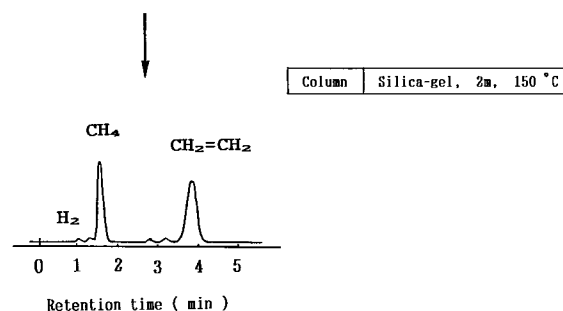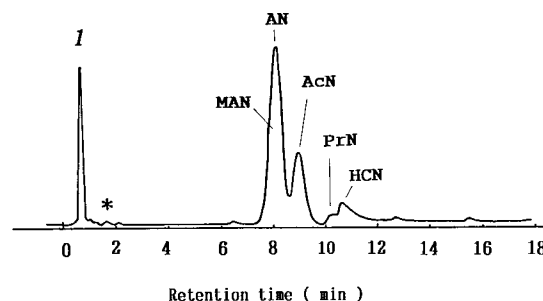

Figure 1 Typical PyGC pattern of PAN. Bottom, lower hydrocarbons were effectively separated by use of silica-gel column.

RESULTS AND DISCUSSION

Typical PyGC Pattern of PAN under Inert Atmosphere

Typical PyGC results of PAN are shown in Figure 1 (top). Six kinds of lower nitriles: acrylonitrile (AN), acetonitrile (AcN), propionitrile (PrN), isobutyronitrile (iso-BtN), methacrylonitrile (MAN), and hydrogen cyanide (HCN), were identified. These results were in agreement with the results obtained by Bell et al.,[6] except that PrN and iso-BtN were not reported there. From Figure 1, it is apparent that random fragmentation of the polymer chain is prevalent at this pyrolysis temperature (700°C). The fragmentation mechanism can be qualitatively described as shown in Figure 2.

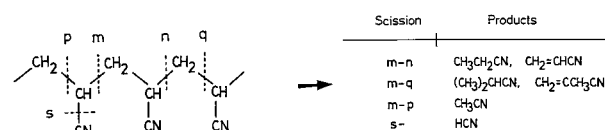In Figure 1, a sharp intense peak (1) appeared in quite a short retention time. (A similar sharp

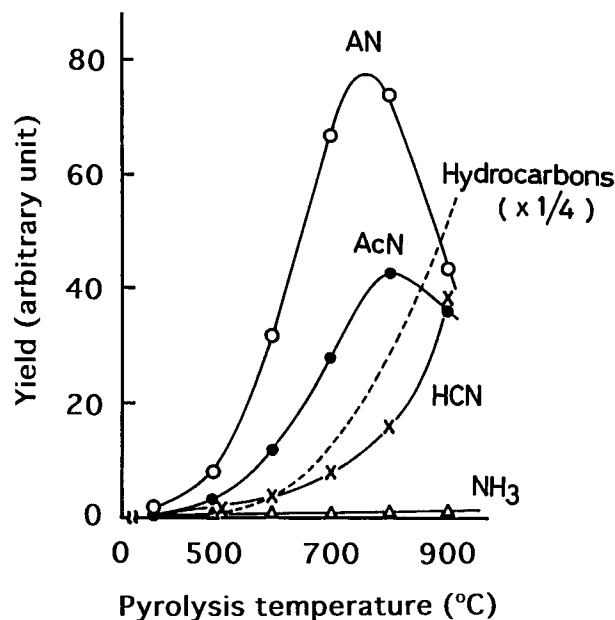**Figure 2** Random fragmentation mechanism.

$$H_2 \quad + \quad CH_2\text{=}CHCN$$

$$CH_3CH_2CN \longrightarrow \quad CH_2\text{=}CH_2 \quad + \quad HCN$$

$$CH_4 \quad + \quad CH_3CN$$

$$H_2 \quad + \quad CH_2\text{=}CCH_3CN$$

$$(CH_3)_2CHCN \longrightarrow \quad CH_2\text{=}CH_2 \quad + \quad CH_3CN$$

$$CH_4 \quad + \quad CH_2\text{=}CHCN$$

Figure 3 Secondary decomposition mechanism.

first peak (1) appeared in the PyGC pattern in the work of Bell et al.[6]: TCP was used as a column packing agent, but the identification of the peak was not yet apparent.) Though an adsorbed small amount of air showed a similar sharp peak in this region, it was estimated that the fragmented products are of quite a low molecular weight (C_1-C_2 compounds) from the value of the retention time. To detect the kinds of compounds, a silica gel column, which is effective in the separation of lower hydrocarbons, was used. It is apparent that methane (CH_4) and ethylene (C_2H_4) are the main degradation products formed (Fig. 1, bottom). By what mechanism or by what reaction pathways are these lower hydrocarbons formed?

Possibility of Secondary Decomposition

One possible explanation is the secondary decomposition of fragmented nitriles (the reaction of Fig. 3). To confirm whether this is so, lower saturated nitriles such as PrN and iso-BtN, were injected by a syringe and pyrolyzed. The resulting PyGC pattern is shown in Figure 4. It is clear that the pattern is very similar to the one obtained for PAN. The relative yields of each product were also similar to those of PAN. In this way, the secondary decomposition mechanism was confirmed. It is possible to say, therefore, that CH_4 and C_2H_4 are typically formed by the secondary decomposition of fragmented lower saturated nitriles.

Dependence of Yield on Pyrolysis Temperature

When the pyrolysis temperature was increased, the limiting yield of the degradation products generally increased, although above 750°C, nitrile yields tended to decrease (Fig. 5). Nitriles, therefore, showed a distinct maximum in the yield curve. However, the limiting yield of HCN and lower hydrocarbons increased rather rapidly when the pyrolysis temperature was increased. The results indicate that there is a more complete fragmentation with the increase of the pyrolysis temperature, although no new products were detected within this experimental range.

A rather odd behavior was observed with HCN. That is, when the pyrolysis temperature was high and a large amount of HCN was produced, HCN was the only nitrile in which retention time progressively decreased (Figs. 6 and 7). This is probably because of the strong hydrogen bonding in HCN.[9,10] Nitriles generally associate through strong dipole–dipole interaction rather than through hydrogen bonding.[11] This exceptional hydrogen bonding capability in HCN strongly affects the interaction with the PEG that was used as a column packing agent, particularly in a lone pair of oxygen electrons on a PEG polymer backbone. A similarly odd behavior has been reported in the interaction between nitric monoxide and

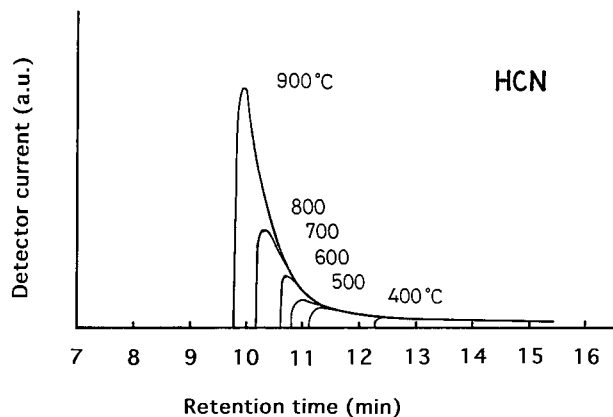**Figure 4** Pyrolysis behavior of propionitrile.

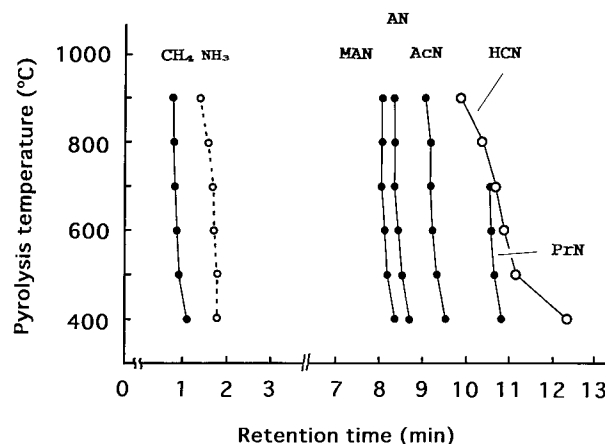**Figure 5** Dependence of yield on pyrolysis temperature.

Figure 7 Variation of retention time as a function of pyrolysis temperature. The broken line indicates the peak of NH_3, which was not clearly detected from pure PAN.

molecular sieve.[12] The above results indicate that: 1. intermolecular interaction is quite complex but interesting, and 2. precautions are necessary for the understanding of the PyGC results based on its apparent pattern.

Retention Time and Interaction Parameter of Nitriles

Generally, retention time or retention volume is closely related to the number of carbon atoms in the compounds.[13] In the case of aliphatic hydrocarbons, for example, the retention time is linearly dependent on the number of carbon atoms

in the semi-logarithmic plot of both quantities. The results are shown in Figure 8. Retention time rather decreased when the number of carbon atoms was increased. The results disagreed with our expectation.

Because nitriles are highly polar compounds, the retention time will be defined not only by the number of carbon atoms but also by the intensity of their polarity. The dipole moment is a typical parameter of polarity, and represents the bulk dielectric property of nitriles. Therefore, the value of the dipole moment divided by the number of carbon atoms (or molecular weight) will be a measure of an empirical interaction parameter.
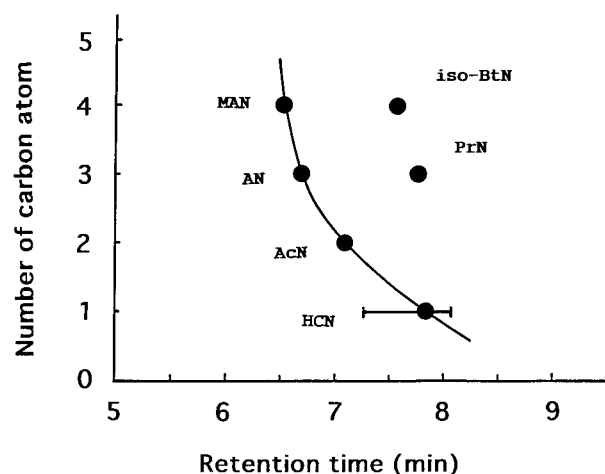
This plot is shown in Figure 9. A fairly good

Figure 6 A progressive shifting of HCN.

Figure 8 Relationship between retention time and an empirical parameter.
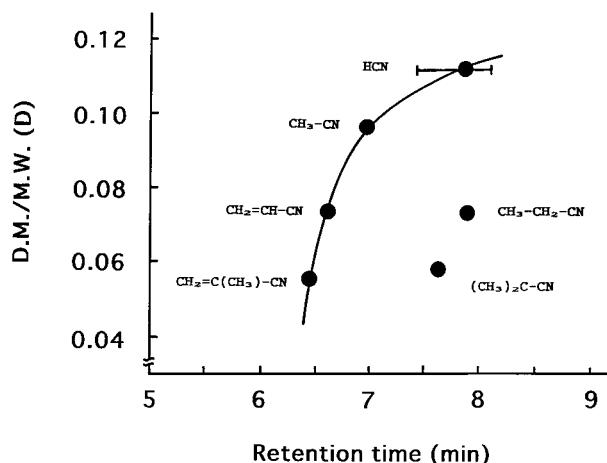
Figure 9 Replotting of the relationship between retention time and an empirical parameter.

Table II   Variation of Limiting Yield from PAN by Heat Treatment

Products	Yield
CH_4	$+$
NH_3	$+$
MAN	$-$
AN	$-$
AcN	$-$
PrN	$-$
HCN	$-$

The symbol plus ($+$) indicates an increase, whereas minus ($-$) indicates a decrease in its yield from PAN after prolonged heat treatment.

The heating conditions were as follows: temperature, 230°C; heating time, 1–3 h; and atmosphere, in N_2.

relation was obtained between these empirical parameters. In the case of saturated nitriles, however, a remarkable deviation from the above relationship was observed. This is probably because of the aliphatic nature in these nitriles: electronegative property due to the nitrile group is weakened by the aliphatic nature of saturated chain sequence, although chain end (or branching) characterized as topological factor,[14,15] may play an important role in such structure-properties relationships.

The PyGC Procedure in the Study of Degradation of PAN

Thus, standard P-GC conditions were established. Herein, this procedure is applied to the solution of several unanswered problems about PAN.

In example (A), when PAN was heated to a high temperature, a deep yellowish discoloration invariably occurred. This reaction is believed to be an intramolecular ring formation (conjugated double bond in nitrile side groups). When such heat-treated samples were pyrolyzed, the yield of nitrile compounds decreased drastically with a remarkable increase of methane (CH_4) and ammonia (NH_3) (Table II).

It must be noted that CH_4 does not come from PAN without chain fragmentation. We consider that excess methane (CH_4) is derived from the methyl groups ($—CH_3$), which are formed by disproportionation in the bulk sample by heat-treatment (Fig. 10), and chain fragmentation is closely related to the existence of some structural disor-

der, such as head-to-head (or tail-to-tail) in PAN.[16] Although the existence of structural disorder along the main chain is well known typically in poly(vinyl alcohol),[17,18] the lack of longitudinal order in PAN (laterally ordered polymer)[19] seems to be closely related to the results herein.

Figure 11 shows the relationship between peak height and peak area of methane (CH_4). There was a linear relationship between these two. Because this is *a kind of calibration curve*, we can estimate the concentration of fragmented chain end ($—CH_3$) in the heat-treated PAN samples based on the assumption of the above-mentioned reaction mechanisms.[20]

It is also interesting to note that ammonia (NH_3) is detected abundantly from heat-treated samples. This means that NH_3 is formed via amino or imino groups ($NH_2—$ or $NH—$), and it takes considerable time for the formation of these functional groups. The significance of kinetic factor in the thermal reaction of PAN was extracted in this way. At least, rapid pyrolysis of pure PAN did not ensure the formation of ammonia within this experimental range, although there was a considerable disparity in the production of NH_3 in the literature.[1–6]
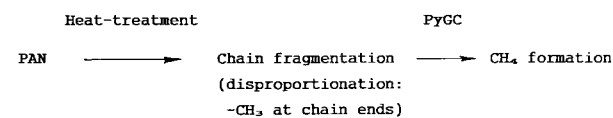

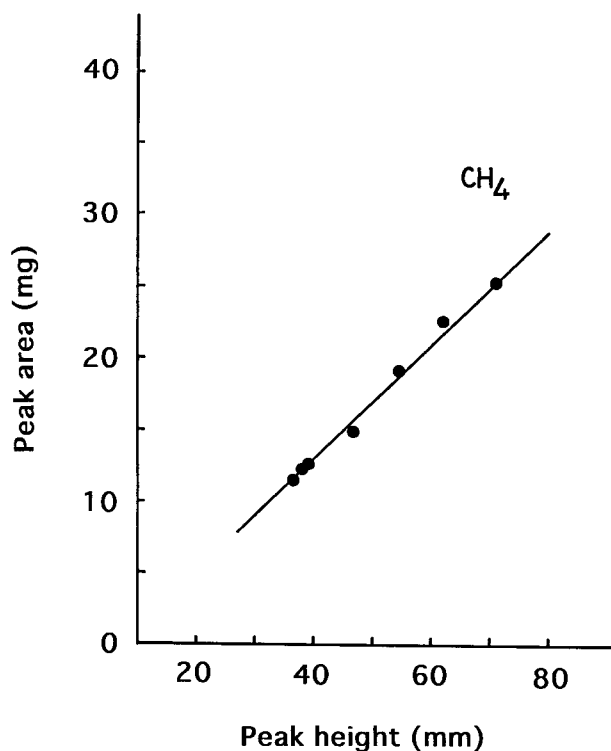**Figure 10** Possible reaction mechanisms for CH_4 formation.

Figure 11 Relationship between peak height and peak area of methane (CH_4). When different amounts of CH_4 gas are injected successively by a syringe and corresponding detector responses are plotted on this figure, a simple calibration curve permitting the estimation of the concentration of fragmented chain ends (CH_4) is obtained.

CONCLUSIONS

- PyGC analysis of one kind of homogeneously solution polymerized PAN was performed in detail. The standard PyGC conditions for PAN were established.
- Six kinds of lower saturated and unsaturated nitriles were confirmed. In addition, CH_4 and C_2H_4 were identified.
- Fragmentation mechanism was qualitatively discussed. The significance of secondary decomposition was emphasized.
- Fragmentation was connected to the structural disorder along the main chain (head-to-head, etc.) in PAN.
- Potential utility of PyGC procedure in the study of degradation of PAN for some cases was demonstrated.

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