Forensic Chemical Study on Nylon Fibers by Acid-Catalyzed Pyrolysis Gas Chromatography

YUZI TAKEKOSHI,^a SUSUMU KANNO,^a SHOZI KAWASE,^a

TADASHI KIH^o and SHIGEO UKAI^b

Scientific Investigation Research Laboratory, Gifu Pref. Police H.Q.,^a 2-1-1 Yabuta-minami, Gifu 500, Japan and Gifu Pharmaceutical University,^b 5-6-1 Mitahora-higashi, Gifu 502, Japan

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We developed a method for forensic identification of minute fibers of 6-nylon and 6,6-nylon by acid-catalyzed pyrolysis gas chromatography (PyGC).

The fibers were pyrolyzed in the presence of phosphoric acid with a Curie point pyrolyzer directly connected to a gas chromatograph and a gas chromatograph/mass spectrometer. Phosphoric acid promoted production of specific volatile substances such as 3 isomers of hexenenitrile and ϵ -caprolactam from 6-nylon and adiponitrile from 6,6-nylon.

The phosphoric acid-catalyzed PyGC was able to identify a smaller amount of nylon fibers than the conventional non-catalyzed PyGC.

Key words — acid-catalyzed pyrolysis GC; 6-nylon fiber; 6,6-nylon fiber; phosphoric acid; forensic identification

Introduction

Fibers are one of the most common and important trace evidences at a crime scene.^{1,2)} They provide important data demonstrating the contact of the victim(s) with suspect(s) or the relationship between the scene and the victim(s)/or suspect(s).

Pyrolysis gas chromatography (PyGC) is one of the most common forensic means of identifying fibers as are microscopic morphological observation and Fourier transform infrared microspectroscopy.³⁾

Among the fibers widely used in Japan, 6-nylon and 6,6-nylon are not easy to differentiate by infrared spectroscopy, because there is little difference in their infrared spectra. PyGC analysis of 6-nylon⁴⁾ and 6,6-nylon,⁵⁾ however, shows their respective characteristic peaks, although those left at crime scenes are often too minute to detect these peaks. We previously reported on acid-catalyzed PyGC to identify cotton fibers⁶⁾ and cotton/

polyester mixed fibers.⁷⁾ In the present study, this method was applied to the identification of minute fibers of 6- and 6,6-nylon.

Materials and Methods

Materials — 6-Nylon fiber of standard fabrics for color fastness test was purchased from Japan Standards Association. 6,6-Nylon fiber was supplied from Asahi-Kasei Co.

Apparatuses and Conditions for PyGC and PyGC/Mass Spectrometry — Curie point JHP-2 and JHP-3 type pyrolyzers (Japan Analytical Industry Co., Ltd.) directly connected to a gas chromatograph with an FID detector (Shimadzu GC-7AG) and a gas chromatograph/mass spectrometer (Shimadzu QP-1000) were used for the experiment.

A fused-silica capillary column DB-5 (30 m $\times$ 0.25 mm i.d.; film thickness, 0.25 μ m; J & W) was used for the GC column. The column oven temperature was initially held at 80°C for 2 min and raised at 10°C/min to 250°C. The temperature of the injector and detector was maintained at

280°C. As carrier gas, nitrogen was used at a flow rate of 1.2 ml/min. The split ratio was 10:1. The temperatures of the pipe and oven of the pyrolyzer were 250°C and 120°C, respectively. Pyrolysis was performed at 590°C using pyrofoils for 590°C applications.

The identification of peak substances was carried out by PyGC/mass spectrometry (MS) under the following conditions: ionization energy, 70 eV (EI method) and 20 eV (CI method); ionization electric current, 60 μ A (EI method) and 200 μ A (CI method). In the CI method, isobutane was used as a reaction gas.

Procedures for Acid-Catalyzed PyGC—A single 6-nylon fiber (about 10 mm in length and 4.0 μ g weight) or 6,6-nylon fiber (about 10 mm in length and 2.5 μ g weight) was placed in the pyrofoil. After adding 2 μ l of 10% phosphoric acid aqueous solution, the fiber was wrapped with the pyrofoil and was subjected to PyGC.

Results and Discussion

Evaluation of Acid-Catalysts for Fiber Pyrolysis

According to the above procedures for acid-catalyzed PyGC, aqueous solutions (2 μ l) of hydrochloric acid, sulfuric acid, nitric acid, or phosphoric acid at concentrations of 2.5–20% were examined as acid-catalysts for acid-catalyzed PyGC of 6-nylon and 6,6-nylon.

In Fig. 1 are shown 2 pyrograms of 6-nylon by the 10% phosphoric acid-catalyzed PyGC method and the conventional non-

catalyzed method. Phosphoric acid caused a remarkable increase in the production of 3 peaks 1-a, 1-b and 1-c with the retention time (t_R) of about 4.5 min, and peak 2 with the t_R of about 10.5 min. Nitric acid, in contrast, produced no marked peak from 6-nylon. Sulfuric acid promoted productions of peak 2 but not peaks 1-a, 1-b or 1-c, while hydrochloric acid promoted production of peaks 1-a, 1-b and 1-c but not peak 2.

In Fig. 2 are shown 2 pyrograms of 6,6-nylon by the 10% phosphoric acid-catalyzed PyGC method and the conventional non-catalyzed method. Phosphoric acid caused a remarkable increase in the production of peak 3 with the t_R of 9.5 min. The three other acids produced no marked peak from 6,6-nylon. Phosphoric acid was thus evaluated to be the optimal catalyst for both 6-nylon and 6,6-nylon in acid-catalyzed PyGC.

In the case of pyrolysis at 445°C and 670°C, phosphoric acid caused a remarkable increase in the production of 4 peaks 1-a, 1-b, 1-c and 2 from 6-nylon, and peak 3 from 6,6-nylon as well as the case of pyrolysis at 590°C.

Identification of Peak Compounds from 6-Nylon and 6,6-Nylon in PyGC

Identification of the 4 peaks in the pyrogram of 6-nylon, were carried out by PyGC/MS. Their EI and CI mass spectra are shown in Fig. 3. Based on mass spectral data, the corresponding compounds to peaks 1-a, 1-b

Fig. 1. Pyrograms of a Single 6-Nylon Fiber Obtained by Conventional Pyrolysis and 10% H_3PO_4 -Catalyzed Pyrolysis

Fig. 2. Pyrograms of a Single 6,6-Nylon Fiber Obtained by Conventional Pyrolysis and 10% H_3PO_4 -Catalyzed Pyrolysis

Fig. 3. Mass Spectra of Major Products in Acid-Catalyzed Pyrolysis of 6-Nylon Fiber Using EI and CI Ionization

Fig. 4. Mass Spectra of Major Product in Acid-Catalyzed Pyrolysis of 6,6-Nylon Fiber Using EI and CI Ionization

and 1-c in Fig.1 had the same molecular weight of 95 and were estimated to be 3 isomers of hexenenitrile [$\text{CH}_2=\text{CH}-(\text{CH}_2)_3-\text{CN}$, $\text{CH}_3-\text{CH}=\text{CH}-(\text{CH}_2)_2-\text{CN}$ and $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CN}$], respectively.

The corresponding compound to peak 2 was identified as ϵ -caprolactam because its mass spectrum was identical to the standard spectrum of ϵ -caprolactam. ϵ -Caprolactam is a monomer and a material for the synthesis of 6-nylon. Ohtani *et al.*⁴⁾ also reported this compound was observed as the main peak by

conventional PyGC.

Identification of peak 3 in the pyrogram of 6,6-nylon was carried out by PyGC/MS. The EI and CI mass spectra are shown in Fig. 4. The corresponding compound to peak 3 was identified as adiponitrile because its mass spectrum was identical to the standard spectrum of adiponitrile. A small amount of cyclopentanone, which was reported as the main pyrolysis product of 6,6-nylon by conventional PyGC,⁵⁾ was also observed with the t_R of about 4.0 min.

Evaluation of Concentrations of Phosphoric Acid in Acid-Catalyzed PyGC

The optimal concentration of phosphoric acid in acid-catalyzed PyGC of 6-nylon fiber was evaluated, focusing on ϵ -caprolactam, the most specific pyrolysis product. As shown in Fig. 5, in comparison with the conventional non-catalyzed PyGC, ϵ -caprolactam was not increased at the phosphoric acid concentration of 2.5%. However, the amount increased 2.5 fold at the concentration of 5%, 2.8 fold at the concentration of 10%, and 1.7 fold at the concentration of 20%. Hexenenitriles in-

Fig. 5. Effect of Concentration of H₃PO₄ on Yields of ε-Caprolactam in 6-Nylon Fiber Pyrolysis

creased to similar degrees at phosphoric acid concentrations of 2.5%, 5% and 10% but did not markedly increase at a concentration of 20%.

The optimal concentration of phosphoric acid in acid-catalyzed PyGC of 6,6-nylon fiber was evaluated focusing on adiponitrile. As shown in Fig. 6, in comparison with the non-catalyzed PyGC method, adiponitrile increased 4.2 fold at a phosphoric acid concentration of 2.5% and 4.5 fold at concentrations of 5% and 10% but did not increase at a concentration of 20%.

The optimal concentration of phosphoric acid was decided to be 10% for 6-nylon and 6,6-nylon in acid-catalyzed PyGC.

Conclusion

We developed a phosphoric acid-

Fig. 6. Effect of Concentration of H₃PO₄ on Yields of Adiponitrile in 6,6-Nylon Fiber Pyrolysis

catalyzed PyGC method for identifying minute single fibers of 6- and 6,6-nylon.

Phosphoric acid promoted production of specific volatile compounds such as 3 isomers of hexenenitrile and ε-caprolactam from 6-nylon and adiponitrile from 6,6-nylon, resulting in higher efficiency in the identification of 6-nylon and 6,6-nylon than by the conventional non-catalyzed PyGC method. In this phosphoric acid-catalyzed PyGC method, the identification limit of both fibers is a 5 mm length of single fiber, which is 1/3 the amount for 6-nylon and 1/4 the amount for 6,6-nylon, compared with the non-catalyzed PyGC method.

This phosphoric acid-catalyzed PyGC method is similar to the conventional PyGC method except that phosphoric acid is added, and is a simple, rapid and useful method for analyzing minute single nylon fibers.

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