

# Pyrolysis GC/MS Studies on Plasma-Polymerized Pyrrole

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## SYNOPSIS

Pyrolysis gas chromatography/mass spectrometry and infrared spectrometry have been carried out for plasma-polymerized pyrrole (PPPy). The major thermal decomposition products have been identified as nitriles with less than four carbons and alkyl pyrroles. Evolution of only monosubstituted alkyl pyrroles, such as 2-methylpyrrole and 2-ethylpyrrole, suggests that PPPy consists of monosubstituted pyrrole rings. This is also supported by the result that the IR spectrum of PPPy differs from that of the electrochemically polymerized pyrrole, which consists of disubstituted pyrrole rings. Evolution of linear nitriles shows evidence that a PPPy molecule has the main chain containing nitrogen atoms. The mechanism of polymerization of pyrrole in the discharge is considered to be similar to that of aromatic hydrocarbons, which mechanism involves a process of production of acetylene.

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## INTRODUCTION

Good polymeric films are prepared in a radiofrequency discharge from pyrrole, which has neither difunctional double bonds nor difunctional end groups.<sup>1-3</sup> This leads us to characterize plasma-polymerized pyrrole (PPPy) in terms of chemical structure. However, there are few reports<sup>2,3</sup> on the polymer structure of PPPy, because of solubility difficulties. Good information can be obtained on the polymer structure of insoluble polymers from their thermal decomposition products.

In the present article, we present the thermal decomposition products of PPPy, identified by pyrolysis gas chromatography/mass spectrometry (GC/MS), and attempt to obtain information on the polymer structure from its thermal decomposition products, considering together the structural information from the infrared (IR) spectrometry and the elemental analysis. For comparison with PPPy, electrochemically polymerized pyrrole (EPPy) was used.

## EXPERIMENTAL

### Materials

The plasma-polymerization of pyrrole was carried out by a SAMCO plasma-polymerizer (SAMCO International Laboratory Co., Japan), which consisted of a monomer-supply system, an evacuable bell jar (the bottom side was 22.0 cm in diameter, the top side was 9.6 cm in diameter, and the height was 30 cm), housing a parallel pair disc electrodes that were 7 cm in diameter (the interelectrodes spacing was 3.5 cm), an argon flow system, and an alternating power supply of 13.56 MHz frequency. The PPPy sample studied was polymerized under 10 Pa of pressure in the jar at 5 W of power. The sample of EPPy was prepared by the electrochemical oxidation of pyrrole in a three-electrode cell. A platinum plate, a platinum wire, and a potassium chloride calomel were used as the working, the counter, and the reference electrodes, respectively. The solution containing  $10^{-2}$  M of pyrrole, with 0.1 M of tetraethylammonium tetrafluoroborate in acetonitrile, was bubbled with nitrogen during the polymerization, and was conducted under 7 mA of current with a Hokuto-Denkoh 550 DC galvanostat. The product film, detached from the platinum plate, was im-

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mersed in ammonia water for two days, in order to obtain a neutral EPPy molecule.

For obtaining the reference mass spectra, 2-methylpyrrole and 2-ethylpyrrole were synthesized by reduction of 2-formylpyrrole and 2-acetylpyrrole with hydrazine monohydrate.<sup>4</sup> The reagents used were purchased from Aldrich Chemical Co. Other compounds for obtaining reference mass spectra were also purchased from Aldrich Chemical Co.

### Pyrolysis GC/MS and IR Techniques

Details of the pyrolysis GC/MS technique are presented elsewhere.<sup>5,6</sup> The measurement was carried out under the following conditions: Pyrolyzer temperature, 773 K; GC column size, 4 m × 4 mm; GC column temperature, from 303 to 503 K (4 K min<sup>-1</sup>); MS total emission current, 213 μA; MS electron energy, 70 V; MS ion energy, 12 V; potential of secondary electron multiplier, 2.00 kV. The flow rate of helium (carrier gas) was 51.3 cm<sup>3</sup> min<sup>-1</sup> and the sample size was about 5 mg.

The IR spectra were obtained for the sample in a potassium bromide disc by using a JASCO A-3 IR spectrophotometer.

## RESULTS

Figure 1 shows a pyrogram of PPPy, thermally decomposed at 773 K. The mass spectrum of Peak 1 seemed to be a mix of the mass spectra of a large amount of hydrogen cyanide, a small amount of air, and a small amount of carbon dioxide (perhaps pro-

duced by oxidation by oxygen in air). The retention time of this peak is given as zero min. Products of Peaks 2 through 4 are considered to be hydrocarbons with less than four carbons, from their mass spectra, though the strict assignment was not carried out here. Table I shows the results on assignment of Peaks 5 through 14 by pyrolysis GC/MS techniques. Retention times and mass spectra for reference compound were obtained by pyrolysis GC/MS run under the same conditions. Agreement between mass spectra of a sample peak and a reference compound was judged by the coincidence of their parent peaks, and by mean distance,  $\Delta$ , between the respective relative intensities for the largest seven peaks:

$$\Delta = [\sum (H_i^p - H_i^r)^2]^{1/2}/7$$

where  $H$  denotes the relative intensity (the maximum intensity is given as 100) and the superscripts  $p$  and  $r$  denote peak and reference. Table I suggests that Peaks 5, 6, 7, 8, 10, 12, 13, and 14 are assigned to acetonitrile, acrylonitrile, propionitrile, isobutyronitrile, *n*-butyronitrile, pyrrole, 2-methylpyrrole, and 2-ethylpyrrole, respectively. There is a similarity between the mass spectra of Peak 9, Peak 11, cis-crotononitrile, trans-crotononitrile, and allyl cyanide. Nevertheless, Peak 9 is assigned to cis-crotononitrile, because of coincidence between the retention times of Peak 9 and cis-crotononitrile. Peak 11 should be assigned to either allyl cyanide or trans-crotononitrile, but its assignment is not clear in the present work. The results on pyrolysis GC/MS for EPPy are entirely different from those for PPPy, though its details are not described here.

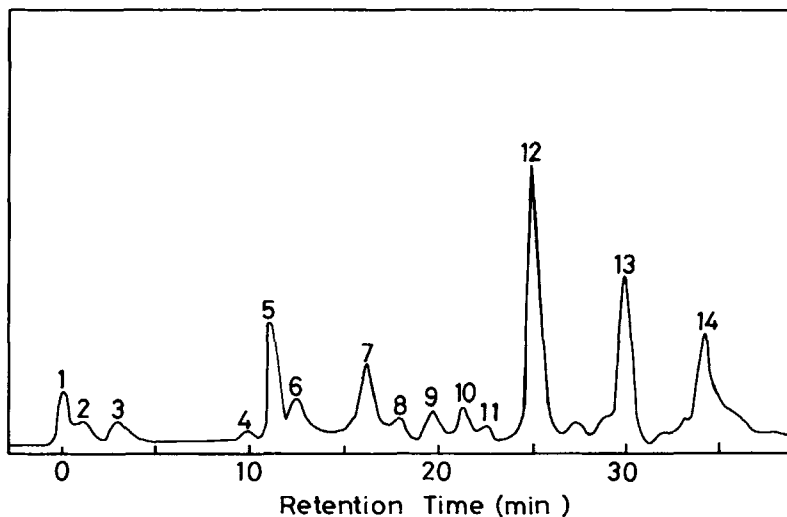


Figure 1 A program of PPPy, thermally decomposed at 773 K.

Table I Assignment of Peaks 5–14

Peak No.	$t_R$ /min	Referenced Compound	$t_R$ /min	$\Delta^a$
5	11.4	Acetonitrile	11.7	$2.9 \pm 0.1$
6	12.5	Acrylonitrile	12.5	$3.5 \pm 0.2$
7	16.2	Propionitrile	15.8	$3.7 \pm 0.1$
8	18.0	Isobutyronitrile	17.8	$3.6 \pm 0.3$
9	19.8	Cis-crotononitrile	19.3	$3.1 \pm 0.2$
9	19.8	Trans-crotononitrile	22.0	$3.1 \pm 0.2$
9	19.8	Allyl cyanide	22.2	$3.2 \pm 0.3$
10	21.8	<i>n</i> -butyronitrile	21.6	$3.6 \pm 0.3$
11	22.6	Trans-crotononitrile	22.0	$3.4 \pm 0.3$
11	22.6	Allyl cyanide	22.2	$3.4 \pm 0.3$
12	25.0	Pyrrole	24.8	$2.8 \pm 0.1$
13	30.0	<i>N</i> -methylpyrrole	23.8	$8.7 \pm 0.2$
13	30.0	2-methylpyrrole	29.5	$3.4 \pm 0.2$
14	34.2	2,5-dimethylpyrrole	32.8	$12.2 \pm 0.2$
14	34.2	2-ethylpyrrole	33.4	$3.5 \pm 0.2$

<sup>a</sup> The mean values and the standard deviation values in the duplicate run are shown for  $\Delta$ .

The IR spectrum of PPPy is also different from that of EPPy, as shown in Figure 2. In the IR spectrum of EPPy, there are broad bands associated with a pyrrole ring vibration in the 1000–1200  $\text{cm}^{-1}$  region,<sup>8</sup> and most of the bands associated with hydrogen atoms are absent, because of the liberation of hydrogen in the polymerization, as estimated from the data on elemental analysis in Table II. In the similar wave number region in the IR spectrum of PPPy, there are bands that are thought to be as-

sociated with pyrrole ring vibration. By reference to common texts of organic chemistry,<sup>9</sup> the bands at the 2250  $\text{cm}^{-1}$  range are thought to be due to either C $\equiv$ N stretching and/or to C=C stretching, and the bands at the 1630  $\text{cm}^{-1}$  are due to either C=N stretching and/or to C=C stretching. The band at the 2950  $\text{cm}^{-1}$  range may also be assigned to aliphatic C—H stretching modes. For liquid pyrrole, the N—H stretching, C—H stretching, C—H out-of-plane bending, and N—H out-of-plane bending

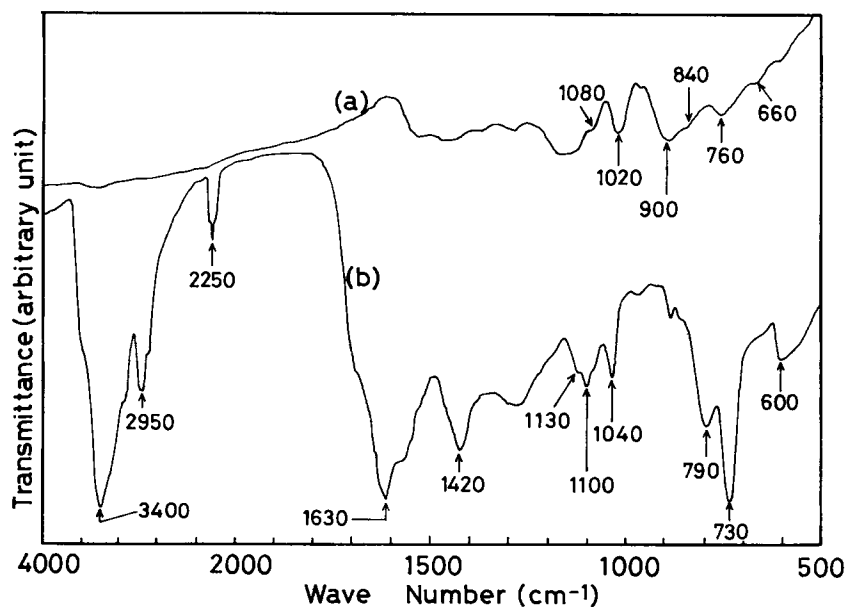


Figure 2 IR spectra of (a) EPPy and (b) PPPy.

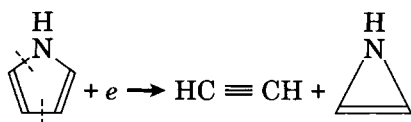
**Table II Results of Elemental Analysis for PPPy and EPPy**

	Ratio		
	C/N	H/N	H/C
PPPy	4.51	5.32	1.18
EPPy	4.01	4.12	1.03

modes occur at 3400, 3100, 768, and 565  $\text{cm}^{-1}$ .<sup>7</sup> Since these frequencies are scarcely influenced by the surrounding atoms, the bands at 3400, 3100, 730 (and/or 790), 600  $\text{cm}^{-1}$ , in the IR spectrum of PPPy, may be assigned to the modes mentioned above, respectively. The bands at 730 and 790  $\text{cm}^{-1}$  are similar to the absorptions associated with monosubstituted benzene ring vibration, which appear in the IR spectra of plasma-polymerized benzene, styrene, and toluene.<sup>10-12</sup>

## DISCUSSION

Neiswender<sup>11</sup> has suggested a process of formation of a poly(styrene)-like polymer from benzene in a discharge, involving an equilibrium between benzene and acetylene, accompanied by formation of styrene from benzene and acetylene. In analogy with this process, pyrrole in the discharge is in equilibrium with acetylene and acetylenimine ( $\text{C}_2\text{H}_2\text{NH}$ ):



Production of a cation of acetylenimine by electron bombarding is well known in studies of mass spectrometry on pyrrole.<sup>13</sup> A polymer, from a vinyl pyrrole, which is produced from uncleaved pyrrole and acetylene consists of monosubstituted pyrrole rings. This is made evident by the discrepancy in IR spectra between PPPy and poly(pyrrole-2,5-diyl)-like EPPy,<sup>8</sup> and by the thermal decomposition products: a relatively large amount of 2-methylpyrrole and 2-ethylpyrrole, and, on the contrary, small amount of 2,5-dimethylpyrrole. The bands at the 2250  $\text{cm}^{-1}$  range in the IR spectrum of PPPy are considered to be due to the cyanomethyl substituents

formed by the addition of acetylenimine to double bonds in the main chain with isomerization.

It is also considered that imino-1,3-butadiene-4-yl, produced only by the first cleavage of a C—N bond of pyrrole in the discharge, is polymerized by radical coupling. If PPPy consists of imino-1,3-butadiene-4-yl units, the evolution of a large amount of pyrrole in the thermal decomposition of PPPy is interpreted by a ring-closing depolymerization of the same sort as poly( $\epsilon$ -caprolactam) is subject.<sup>14</sup>

Evolution of large amount of nitriles in the thermal decomposition of PPPy is interesting because no nitriles evolve from pyrrole in the general thermal decomposition. Nitriles are thought to evolve from the main chain, including cyano( $-\text{C}\equiv\text{N}$ ), nitrilo( $-\text{N}=\text{C}$ ), and/or cyanomethyl, the existence of which may be confirmed in the IR spectrum of PPPy.

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