

## Thermal Decomposition Products of Polyacrylonitrile

YOSHIO TSUCHIYA and KIKUO SUMI, *National Research Council at Canada, Division of Building Research, Fire Research Section, Ottawa, Ontario, Canada K1A 0R 6*

### Synopsis

The decomposition products of a polyacrylonitrile yarn thermally decomposed at temperatures of 400°, 600°, and 800°C, under a flow of either air or nitrogen, have been analyzed by GC and GCMS. Hydrogen cyanide and 16 other nitriles were identified and quantified. Decomposition products contained a series of aliphatic nitriles of various chain lengths, and HCN was the predominant toxic product.

### INTRODUCTION

Polyacrylonitrile is a polymer used in the manufacture of a synthetic fiber widely used for clothing. The monomer acrylonitrile is a major component of copolymers such as modacrylics and ABS. If burned, these materials yield decomposition products that are significant from a toxicity point of view.

Hydrogen cyanide is known to be one of the main decomposition products of polyacrylonitrile,<sup>1-7</sup> the quantity produced being temperature dependent, with greater quantities produced at higher temperatures. Ammonia is produced<sup>5,8,9</sup> at temperatures much lower than that at which HCN is generated<sup>9</sup> and in smaller quantities.<sup>5,9</sup>

Organic nitriles have been found as well in the decomposition products. Straus and Madorsky<sup>2</sup> and Monahan<sup>4</sup> reported that acrylonitrile and vinyl acetonitrile are two of the major products; and Takayama<sup>3</sup> and Bell et al.<sup>10</sup> found that acrylonitrile and methacrylonitrile are major products. Other reported nitriles include cyanogen,<sup>4</sup> acetonitrile,<sup>2,4,10</sup> and propio- and butyronitrile.<sup>2</sup> Quantitative data regarding these nitriles are of interest from the toxicity point of view.

In the present study, polyacrylonitrile has been decomposed at different temperatures and in different atmospheres, and the products have been analyzed quantitatively. Detailed analysis of the nitriles has been extended beyond that of previous investigations.

### EXPERIMENTAL

#### Materials

The polyacrylonitrile sample used in the study was a commercially available, 100% polyacrylonitrile yarn. For confirmation of the sample, a reagent-grade

TABLE I  
 Gas-Chromatographic Conditions

Type of column	Stationary phase	Carrier gas	Detector	Temperature	Purpose
Packed, 2 m, 1/8 in. O.D., stainless steel	80/100 Porapak Q	He	hydrogen flame ionization	programmed, 6°C/min from 25° to 225°C	qualitative and quantitative analysis of aliphatic nitriles and HCN
Support coated, open tubular, 100 ft, 0.02 in. I.D., stainless steel	Carbowax 20M	He	hydrogen flame ionization	several fixed temperatures between 50° and 200°C	qualitative and quantitative analysis of aliphatic and aromatic nitriles
Support coated, open tubular, 100 ft, 0.02 in. I.D., stainless steel	OS-138 Poly-phenyl ether	He	hydrogen flame ionization	several fixed temperatures between 50° and 200°C	qualitative analysis of aliphatic and aromatic nitriles

polyacrylonitrile resin and the yarn were compared by NMR in deuterated dimethyl sulfoxide solutions. Both samples showed very similar NMR spectra having secondary and tertiary protons only. In preliminary pyrolysis experiments and GC analyses, both samples showed similar decomposition patterns.

### Thermal Decomposition and Analysis

Samples of about 1 g were decomposed in a quartz tube electrically heated at 400°, 600°, or 800°C under a flow of either nitrogen or air. Details of thermal decomposition apparatus have been described.<sup>11</sup>

HCN in the decomposition products was trapped in a 0.4% NaOH solution and quantity determined by a cyanide ion electrode, Orion Model 94-06, and by a modified Liebig's silver nitrate titration in which *p*-dimethylaminobenzylidene rhodanin indicator was used.<sup>12</sup>

For the analysis of organic products, condensable products were collected in a cold trap at -78°C. Noncondensable gases were collected in a plastic bag.

A Perkin-Elmer Model 881 gas chromatograph and Finnigan Model 3100D GC-MS were the main tools for the analysis of the organic products. The gas-chromatographic conditions are given in Table I.

## RESULTS AND DISCUSSION

Preliminary experiments indicated that most species of organic products were nitriles and low molecular weight hydrocarbons. Identification of the nitriles was, therefore, the first major study undertaken. As neither the GC retention data nor mass spectrometry data on nitriles were complete except for a few simple compounds, these data were obtained at DBR/NRC using pure chemicals. The data are summarized in Tables II and III.

TABLE II  
Retention Indices of Nitriles

Compound	Molecular weight	Source of comps. *	HB2000 **	Porapak Q **	Carbowax 20M C	OS138 C
Hydrogen cyanide	27	6		317		620 50
Cyanogen	52	1		295		
Acetonitrile	41	1	785	458	935 50	745 50
Acrylonitrile	53	1	793	500	919 50	730 50
Propionitrile	55	2	828	550	958 50	800 50
Vinyl acetonitrile	67	2	949	631	1085 50	893 50
Crotonitrile	67	3	896	615	1014 50	860 50
Crotonitrile } cis & trans	67	3	896	651	1067 50	920 50
Methacrylonitrile	67	4		578	900 50	783 50
Butyronitrile	69	2	907	650	1023 50	883 50
Isobutyronitrile	69	1		614	920 50	815 50
Valeronitrile	83	2	1005	756		
Hexanenitrile	97	4		864		
Malononitrile	66	3			1940 150	1300 175
Fumaronitrile	78	5			1665 125	1164 100
Succinonitrile	80	3			2072 150	1508 175
Glutaronitrile	94	3			2026 150	1569 175
2-Methylene glutaronitrile	106	3			1940 150	1524 175
2-Methyl glutaronitrile	108	7			1928 150	1543 175
2-Methyl-4-Methylene glutaronitrile	120	7			1845 150	1502 150
2,4-Dimethyl glutaronitrile	122	7			1808 150	
Benzonitrile	103	1			1553 125	1313 150
Phenyl acetonitrile	117	1			1865 150	1535 175
1,4-Dicyanobenzene	128	5			2199 175	1762 200
1,3-Dicyanobenzene	128	5			2218 175	1788 200
1,2-Dicyanobenzene	128	5			2333 175	1878 200

- \* 1 Matheson Coleman & Bell  
 2 Eastman  
 3 ICN, K&K Laboratories  
 4 City Chemical  
 5 Aldrich Chemical  
 6 Fumico  
 7 Decomposition products of polyacrylonitrile, tentative identification

\*\* Determined by linear programming temperature

Sixteen nitriles were identified in the present study by GC retention and GC-MS analysis. Cyanogen and vinyl acetonitrile were not found, although the latter was reported by some earlier workers<sup>2,4</sup> as one of the main components of degradation products. It was most probably methacrylonitrile, which was not identified by the early workers but was found to be one of the main products in the present study. The study that first reported vinyl acetonitrile was made using MS without GC in the analysis. The MS of vinyl acetonitrile and methacrylonitrile are very similar, as may be seen in Table III.

The results of quantitative analysis are shown in Table IV. Hydrogen cyanide was the major product in all the decomposition conditions studied, the quantity increasing with temperature. Ammonia was not determined because the toxicity of this decomposition product is insignificant compared to that of HCN when polyacrylonitrile is involved in fire. Other major products included acetonitrile, acrylonitrile, methacrylonitrile, glutaronitrile, 2-methylglutaronitrile, 2-methyleneglutaronitrile, and benzonitrile. At higher temperatures, quantities of lower molecular weight nitriles increased. Also at higher temperatures, the relative quantity of all the aliphatic dicyanides decreased while that of all the aromatic cyanides increased. The former are considered to be the primary products from the scission of the polymer chain followed by intramolecular radical transfer. The aromatic nitriles are considered to be products of secondary cyclization.

TABLE III  
MS Analysis of Nitrites<sup>a</sup>

	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E	M/E
Hydrogen cyanide	28	2	27	100	26	17	14	2	13	2	12	2	12	4					
Cyanogen	53	3	52	100	38	3	26	16	24	5	18	53	17	9	14	1	12	4	
Acetonitrile	41	100	40	54	39	23	38	16	28	11	26	7	25	5	14	23	13	8	12
Acrylonitrile	53	66	52	44	51	24	50	6	38	7	37	4	27	20	26	100	25	11	14
Propionitrile	55	6	54	37	53	4	52	8	51	7	40	5	28	100	27	20	26	22	15
Vinyl acetonitrile	67	27	66	8	52	8	41	100	40	27	39	53	38	23	37	17	27	53	26
Crotononitrile } cis & trans	67	36	66	9	52	9	41	100	40	28	39	56	38	30	37	23	27	38	26
Crotononitrile	67	32	66	11	52	11	41	100	40	25	39	55	38	29	37	22	27	35	26
Methacrylonitrile	67	42	66	15	52	20	51	14	41	100	40	25	39	63	38	25	37	23	27
Butyronitrile	52	4	41	100	40	8	39	15	38	6	29	79	28	16	27	50	26	13	15
Isobutyronitrile	68	36	54	21	52	13	42	100	41	29	39	22	28	58	27	31	26	20	15
Valeronitrile	55	16	54	40	43	86	41	100	39	26	29	24	28	26	27	66	26	14	15
Hexanenitrile	68	20	57	20	55	52	54	60	43	21	41	100	39	30	29	47	28	26	27
Malononitrile	66	100	65	11	51	4	50	4	40	19	39	80	38	80	28	60	27	13	26
Fumaronitrile	78	60	77	25	52	27	51	100	50	11	39	11	38	25	27	11	26	35	25
Succinonitrile	79	25	55	100	52	37	51	24	40	92	39	17	38	17	28	35	27	25	26
Glutaronitrile	54	67	52	13	51	7	41	100	40	23	39	17	38	11	28	46	27	43	26
2-Methylene glutaronitrile	106	10	66	100	52	26	51	19	40	21	39	65	38	12	28	26	27	24	26
2-Methyl glutaronitrile	68	45	55	25	54	60	52	17	41	100	40	16	39	27	28	47	27	49	26
2-Methyl-4-methylene glutaronitrile	120	6	119	6	68	13	67	73	66	100	54	41	52	23	41	22	40	43	39
2,4-Dimethyl glutaronitrile	80	6	69	5	68	72	55	100	54	45	53	7	52	13	42	13	41	68	39
Benzonitrile	103	100	76	80	75	26	52	22	51	46	50	80	39	28	38	24	37	26	24
Phenyl acetonitrile	117	86	116	34	90	100	89	60	63	60	51	86	50	57	39	86	38	34	27
1,4-Dicyanobenzene	128	61	101	32	76	29	75	44	51	51	50	100	39	22	38	36	37	67	26
1,3-Dicyanobenzene	128	100	101	50	76	44	75	62	51	53	50	88	39	26	38	32	37	41	26
1,2-Dicyanobenzene	128	100	101	42	76	35	75	55	51	50	50	92	39	28	38	33	37	45	26

<sup>a</sup> Source of compounds: refer to Table II.

TABLE IV  
Thermal Decomposition Products of Polyacrylonitrile

Decomposition products	Weight per cent of products of original polymer					
	In nitrogen			In air		
	400°C	600°C	800°C	400°C	600°C	800°C
Hydrogen cyanide	1.9	7.6	16.2	2.0	8.4	13.2
Acetonitrile	0.10	1.87	8.1	0.32	1.29	3.09
Acrylonitrile	0.15	5.97	18.3	0.99	4.46	6.26
Propionitrile	0.16	1.87	1.01	0.59	0.40	0.27
Crotonitrile			T <sup>a</sup>			
Methacrylonitrile	0.90	6.16	4.14	3.10	0.93	1.03
Isobutyronitrile	0.20	0.92	1.12	0.67	0.38	0.49
Succinonitrile	0.08	0.65	0.56	0.21	0.09	T
Glutaronitrile	0.34	4.71	0.11	1.94	0.16	
2-Methyleneglutaronitrile	0.20	4.29	0.05	1.01	0.06	
2-Methylglutaronitrile	0.72	3.14	T	2.26	0.02	
2-Methyl-4-methyleneglutaronitrile	0.19	0.62	T	0.71		
2,4-Dimethylglutaronitrile		T		T		
Benzonitrile		0.19	4.09		0.82	2.32
1,4-Dicyanobenzene		0.06	0.57		0.11	0.39
1,3-Dicyanobenzene		0.11	0.96		0.16	0.61
1,2-Dicyanobenzene		T	0.52		T	T
Total	4.94	38.2	55.7	13.8	17.3	27.7

<sup>a</sup>T: Trace amount.

The polymer sample was completely volatilized at all the pyrolysis conditions. The somewhat low, total weight percentage of analyzed products was largely due to loss of viscous condensates in the trap and connecting lines. In addition, H<sub>2</sub>O and oxides of carbon were not included in the total.

Mass spectra of the viscous condensates showed a regular cyclic pattern consisting of prominent peaks at mass numbers  $(28 + 53n)$ ,  $(42 + 53n)$ ,  $(55 + 53n)$ , and  $(67 + 53n)$ , where  $n$  is an integer of 0, 1, 2, 3, 4, 5, . . . . The number 53 is the molecular weight of a monomer unit. The major fragments of a number of aliphatic nitriles have mass numbers 28, 42, 55 and 67; those of aromatic do not. It is suggested that the decomposition products contain several homologous series of aliphatic nitriles.

Toxicity data for nitriles are scarce in the literature. Threshold limit values are HCN, 10 ppm; acetonitrile, 40 ppm; and acrylonitrile, 20 ppm. A level of 110 to 135 ppm of HCN is dangerous to life, but 160 ppm of acetonitrile or 135 ppm of acrylonitrile is not lethal.<sup>13</sup> The authors were unable to find data for other nitriles in the literature. In all the experimental conditions studied, the volume of HCN produced was more than that of any other nitrile. Volume ratios of total volatile nitriles to HCN ranged from 0.5 to 2. The contribution of nitriles to toxicity cannot be evaluated owing to the lack of toxicity data.

## CONCLUSIONS

Thermal decomposition of polyacrylonitrile produces mainly hydrogen cyanide and other nitriles. HCN and 16 other nitriles were identified in the products. Cyanogen and vinyl acetonitrile, reported by earlier workers, were not found in

this study. The quantities of HCN, acetonitrile, acrylonitrile, and aromatic nitriles increased at higher temperatures owing to greater fragmentation and cyclization, and relative quantities of aliphatic dicyanides decreased. Mass spectra of the viscous condensates suggested the presence of a series of aliphatic nitriles of varied chain length in the products.

Concerning the toxicity of the thermal decomposition products of polyacrylonitrile in fires, HCN appears to be the primary toxicant. It is not possible to evaluate the contribution of individual nitriles to the toxicity of the products owing to lack of data on the acute inhalation toxicity of these compounds.

The authors wish to thank J. Boulanger and D. W. Morwick for assistance in conducting experiments. This paper is a contribution from the Division of Building Research, National Research Council of Canada and is published with the approval of the Director of the Division.

### References

1. H. Nagao, M. Uchida, and A. Yamaguchi, *Kogyo Kagaku Zasshi*, **59**, 698 (1956).
2. S. Straus and S. L. Madorsky, *J. Res. Nat. Bur. Stand.*, **61**, 77 (1958).
3. Y. Takayama, *Kogyo Kagaku Zasshi*, **61**, 1021 (1958).
4. A. R. Monahan, *J. Polym. Sci. A-1*, **4**, 2391 (1966).
5. K. Hiramatsu, *Shitsuryo Bunseki*, **15**, 17 (1967).
6. W. Makschin, *Faserforsch. Textiltech.*, **20**, 321 (1969).
7. K. Sumi and Y. Tsuchiya, *J. Fire Flamm.*, **4**, 15 (1973).
8. H. Nagao, M. Uchida, and A. Yamaguchi, *Kogyo Kagaku Zasshi*, **59**, 940 (1956).
9. W. N. Turner and F. C. Johnson, *J. Appl. Polym. Sci.*, **13**, 2073 (1969).
10. F. A. Bell, R. S. Lehrle, and J. C. Robb, *Polymer*, **12**, 579 (1971).
11. K. Sumi and Y. Tsuchiya, National Research Council of Canada, Division of Building Research, *BRN 99*, May 1975.
12. ASTM D2036-75. Standard Methods of Test for Cyanides in Water, 1976 Annual Book of ASTM Standards, Part 31, p. 500, ASTM, Philadelphia, 1976.
13. *Documentation of the Threshold Limit Values*, 3rd ed., Amer. Conf. Govern. Ind. Hygienists, Cincinnati, 1971.

Received January 19, 1976