

Articles

Direct Fluorination of Nitrogen-Containing Ladder Polymers, Two New "Graphitic" Fluorocarbon Polymers

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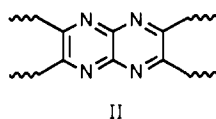
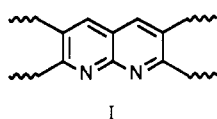
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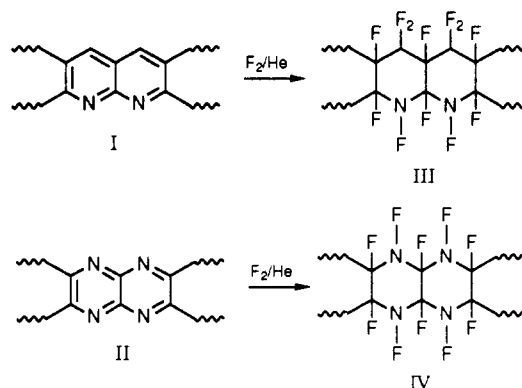
Paracyanogen and pyrolyzed poly(acrylonitrile) have been perfluorinated using elemental fluorine and have retained their polymeric fused ring structures. The two new materials produced by this method were characterized by infrared spectroscopy, electron impact mass spectrometry, elemental analysis, iodometric titration, and thermogravimetric analysis. Some chemical and physical properties are discussed as well as several possible applications in light of the discussed properties of these materials.

Introduction

Ongoing research in the area of high-performance lubricants has sparked the following investigation into the production of two new materials. Previous results on the direct fluorination of graphite have shown that a superior material can be produced.¹⁻³ Additionally, numerous fused aromatic compounds (polynuclear hydrocarbons) have been successfully fluorinated to produce saturated compounds which retain their original polycyclic structures.⁴ For these reasons, two nitrogen-containing polymeric materials with extended aromatic "ladder" structures have been chosen for this study. Pyrolyzed polyacrylonitrile (I) and paracyanogen (II) have been



subjected to direct fluorination to produce perfluorinated analogs. Both these nonfluorinated materials are extremely stable thermally and are useful as carbon fiber/filler materials in composite solids. The structures of I and II are not known with certainty; however, they are believed to exist in a linear polycyclic structures as shown.⁵ I is commonly known as "black orlon" and consists of chains of fused pyridine rings. II is a solid polymeric form of cyanogen commonly known as paracyanogen; however, it is more correctly referred to as poly(pyrazinopyrazine). Fluorination of I and II appears to have produced the saturated analogs III and IV, respectively. Character-



ization of the perfluorinated products provides evidence that the fused polycyclic structures were retained.

Experimental Section

Electron impact mass spectra were obtained on a Bell and Howell 21-491 mass spectrometer operating at 70 eV. Infrared analysis was performed on a Biorad FTS-40 Fourier transform infrared spectrometer. Samples were prepared for infrared analysis by grinding with KBr and pressing into transparent pellets. Thermogravimetric analysis was performed on a Perkin-Elmer 7 Series thermal analysis system from ambient temperature to 500 °C at a rate of 20 °C/min. Samples were submitted to Schwarzkopf Microanalytical Laboratory for elemental analysis. Fluorine was obtained from Air Products and diluted with reagent-grade helium. The ladder polymers for this study were prepared in the following manner.

Pyrolyzed polyacrylonitrile (I) was prepared from poly(acrylonitrile), $[\text{CH}_2\text{CH}(\text{CN})]_n$ (Aldrich Chemical Co). The organic polymer was pyrolyzed at 280 °C in a stream of dry air ($\sim 20 \text{ cm}^3/\text{min}$).^{6,7} After pyrolysis the temperature was reduced to 150 °C and the tube evacuated to $3 \times 10^{-3} \text{ mmHg}$ for 24 h to ensure that no volatiles remained on the polymer prior to fluorination.

Paracyanogen (II) was prepared from the pyrolysis of oxamide, $\text{H}_2\text{NC}(\text{O})\text{C}(\text{O})\text{NH}_2$ (Aldrich Chemical Co). The oxamide was pyrolyzed in an evacuated, sealed, stainless steel bomb at 300 °C for $\sim 100 \text{ h}$. The bomb was cooled to 200 °C and reevacuated

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Table I. Fluorination Conditions

F ₂ (cm ³ /min)	He (cm ³ /min)	time (h)
0	50	2
2.5	50	24
2.5	25	24
3.0	12	24
3.0	3	24
3.0	0	24
0	50	12

for several hours, again to insure the removal of all volatile materials prior to fluorination. Infrared analysis of the paracyanogen obtained in this manner is identical to that previously reported.⁸

Once the polymers had been properly prepared they were each placed in a nickel boat which was placed inside a nickel tube. The polymers were fluorinated at ambient temperature under the conditions reported in Table I.

Results and Discussion

The products of perfluorination are both white, moisture-sensitive powders. Both materials are slowly degraded by atmospheric moisture, IV more quickly than III. The materials oxidize iodide ion to iodine due to the presence of the N-F moiety. A series of iodometric titrations⁹ showed that IV required twice the number of equivalents of titrant as did III. This result supports the proposed structures, IV having twice as many N-F moieties as does III.

Previous unpublished results using paracyanogen prepared from Ag(CN) or Hg(CN)₂ produced inferior perfluorinated material. Metal contamination was believed to be the cause of several problems including spurious elemental compositions and pronounced atmospheric degradation. Samples of II prepared from metal salts invariably contain large amounts of the metal which is extremely difficult to remove without effecting the polymer. For this reason an alternate source of II was used for this study. Initially, cyanogen was subjected to both UV¹⁰ and thermal polymerization conditions.^{11,12} These methods, however, proved to be far too inefficient, producing only small amounts of II over long periods of time. The method ultimately used was that outlined above for the pyrolysis of oxamide.

The infrared spectra of III and IV from 500 to 1500 cm⁻¹ are shown in Figures 1 and 2, respectively, and appear quite similar. Wavelengths from 400 to 4000 cm⁻¹ were scanned; however, no additional information was gained outside the window shown. Both spectra are dominated by the strong, broad absorbance between 1100 and 1300 cm⁻¹ due to C-F stretching. A less prominent absorbance just below 1000 cm⁻¹, assigned to the N-F stretch, is more intense in IV than in III. Other smaller feature below 800 cm⁻¹ are attributed to structural deformations and bending modes.¹³ The absence of absorbances in the 1500–2000-cm⁻¹ region confirm that no unsaturation, either C=C or C=N, remain in the final perfluorinated products.

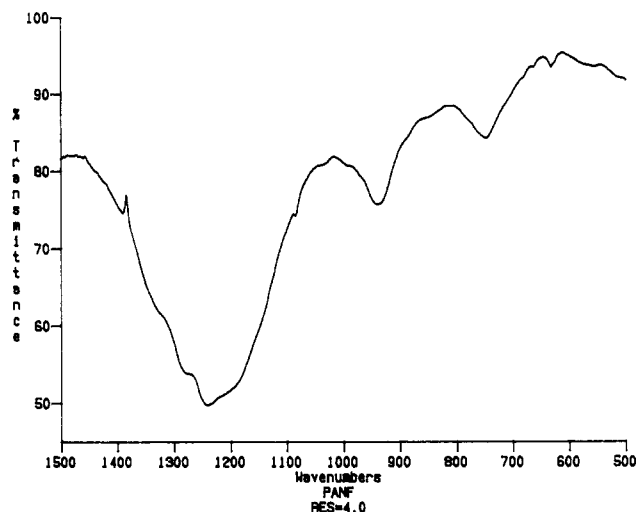


Figure 1. Infrared spectrum of perfluorinated pyrolyzed poly-(acrylonitrile) (III).

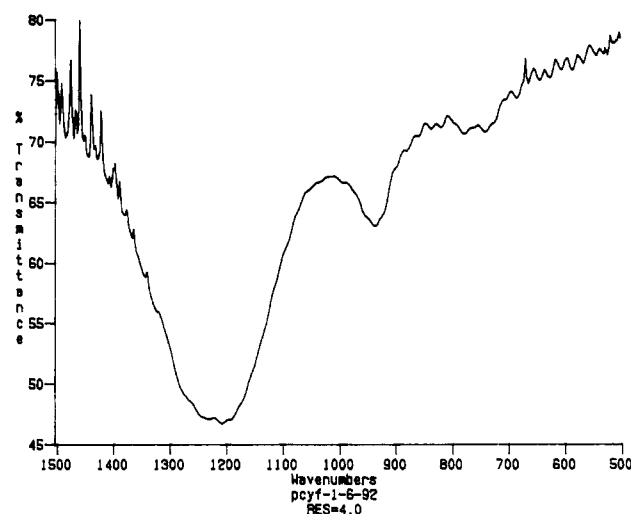


Figure 2. Infrared spectrum of perfluorinated paracyanogen (IV).

Table II. Electron Impact Mass Spectra Results

III		IV	
fragment	mass	fragment	mass
CF ₃	69	CF ₃	69
C ₂ F ₃	81	C ₂ NF ₂	76
C ₂ NF ₃	95	CNF ₃	83
C ₂ F ₄	100	C ₂ NF ₃	95
C ₂ NF ₄	114	C ₂ NF ₄	114
C ₂ F ₅	119	C ₃ N ₂ F ₃	121
C ₃ F ₅	131	C ₃ N ₃ F ₃	135
C ₂ NF ₆	152	C ₃ N ₂ F ₅	159

Mass spectral analysis of III and IV showed fragments consistent with the proposed saturated fused ring structure. Table II lists the observed mass numbers along with their assigned fragment. The consistently low fluorine to carbon/nitrogen ratios in the observed fragments are indicative of a ring structure. The absence of the characteristic C_nF_{2n+1} fragments of a perfluorinated straight chain compound precludes this type of product.

The results of the elemental analysis of III and IV are listed in Table III along with the theoretical values for the proposed structures. The results for III are in excellent agreement with the calculated values, while those for IV show some deviation. This may reflect the increased

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Table III. Elemental Analyses Results

	III		IV	
	calcd	found	calcd	found
C	24.83	24.87	18.75	22.02
N	9.65	9.34	21.87	20.30
F	65.52	65.33	59.37	53.66

TGA File Name: payf
 Sample Weight: 5.972 mg
 Fri Feb 27 13:47:28 1992
 PCYF

PERKIN-ELMER
 7 Series Thermal Analysis System

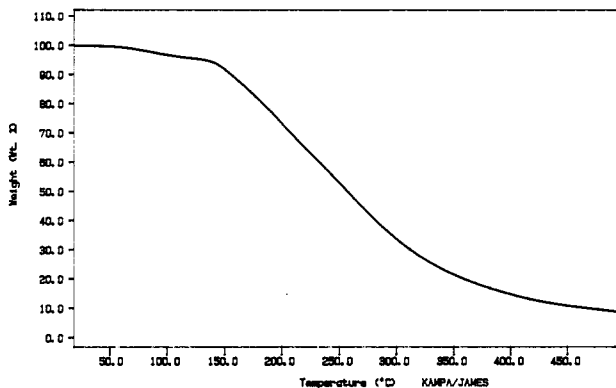


Figure 3. TGA curve of perfluorinated pyrolyzed poly(acrylonitrile) (III).

difficulty in maintaining the difunctional structure during fluorination or may simply be a result of the greater sensitivity of IV to decomposition after fluorination.

Evaluation of these new materials by NMR techniques was not possible due to the lack of a suitable solvent. A wide variety of organic as well as inorganic solvents failed to dissolve the fluorocarbons. Solid state NMR techniques were also not applicable due to the inherent problems associated with NMR spectra of polymeric materials having a high degree of fluorination.

The thermal stability of these new materials was of special interest in regard to their possible use as high-performance lubricants. Melting point data for both III and IV was obtained using capillaries which were open to the atmosphere. III melted sharply at 310 °C producing a liquid which began to yellow at 340 °C. IV proved to be less thermally robust than III, exhibiting a melting point of 175 °C with the liquid yellowing above 200 °C. Thermal gravimetric analysis (TGA) confirmed that both these materials exhibit inferior thermal properties to graphite fluoride.^{1,2} Figures 3 and 4 show TGA curves for III and IV respectively. It is clear that IV deteriorates more quickly than III. Approximately 50% of IV's original weight is lost by 250 °C compared to III having lost only 20% at that temperature. Material III has a region of maximum weight loss in the range 275–350 °C. IV shows an area of comparable degradation at 160–300 °C.

TGA File Name: panf
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 Wed Aug 14 15:01:31 1992
 PANF

PERKIN-ELMER
 7 Series Thermal Analysis System

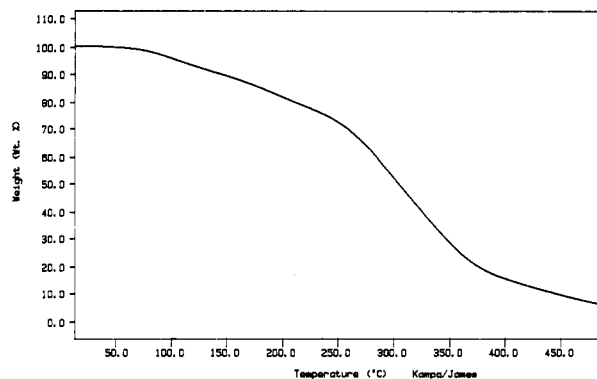


Figure 4. TGA curve of perfluorinated paracyanogen (IV).

These two new materials may find use as more reactive forms of solid graphitic fluorine compounds for use as fluorine-containing cathodes in high-energy lithium batteries. New synthetic methods to prepare higher molecular weight paracyanogen and pyrolyzed poly(acrylonitrile) may be a route to increase the thermal stability of the subsequent perfluorinated polymers. However, it may be expected that these fluorocarbon polymers should always be less stable than graphite fluoride $[(CF_{1.12})_n]$ which contains no carbon–nitrogen bonds. Another possible application for these new polymeric materials is as a solid source of fluorine. Making use of the reactive fluorine bound to nitrogen, these polymers act as mild fluorinating agents. Recent work has shown molecular N–F compounds to be useful selective fluorinating agents.^{14–17}

The controlled fluorination of two polymeric solids has produced perfluorinated materials with retention of extended polycyclic chains. This result further illustrates the generality of the techniques developed in these laboratories for the preparation of novel highly fluorinated materials.^{18–21}

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