HCN Polymers: Composition And Structure Revisited By High Resolution Mass Spectrometry. Jean-Yves Bonnet\textsuperscript{1*}, Roland Thissen\textsuperscript{1}, Maëliss Frisari\textsuperscript{1}, Véronique Vuitton\textsuperscript{2}, Éric Quirico\textsuperscript{1}, Léna Le Roy\textsuperscript{2}, Nicolas Fray\textsuperscript{2}, Hervé Cottin\textsuperscript{2}, Sarah M. Hörst\textsuperscript{3} and Roger Yelle\textsuperscript{3}. \textsuperscript{1}Laboratoire de Planétologie de Grenoble, France, \textsuperscript{2}LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques), France, \textsuperscript{3}Lunar and Planetary Laboratory Arizona USA

Introduction

A lot of solar system materials, including cometary ices and Titan aerosols, contain dark matter that can be interpreted as complex nitrogen bearing organic matter [1]. In the large panel of analogs synthesized in the laboratory, HCN polymers are of great interest. In fact they may be present in Titan atmosphere and in comet nuclei. In this last context, they can be reprocessed as a CN distributed source [2] when volatiles sublimes and ejects from the nucleus CHON grains [3]. The presence of HCN polymers is suggested because HCN molecule has been directly observed in 1P/Halley comet [4] and others. HCN polymers are also of prebiotic interest [5]. However, the chemistry and structure of such polymers are poorly understood, and a great analytical effort has to be continued. In this way we present a high resolution mass spectrometry (HRMS) analysis of HCN polymers. It was shown [6] that this is a suitable technique to elucidate composition and structure of the soluble part of tholins analogs of Titan’s atmosphere aerosols. The present work is part of an effort of our team to describe and discriminate the two HCN containing materials.

Samples and experimental procedures

Based on the previous study of [6] and on the fact that HCN polymers have never been studied by HRMS, we used a LTQ-Orbitrap XL high resolution mass spectrometer to analyse the HCN polymers. These are produced at LISA by direct polymerisation of pure liquid HCN, catalyzed by ammonia. The polymers present a very low oxygen abundance, and if present, oxygen is only detectable as a trace element. HCN polymers have been completely dissolved in CH\textsubscript{3}OH and then injected in the mass spectrometer by ElectroSpray Ionization (ESI). This atmospheric pressure ionization process produces positively charged ions (protonated), or negatively charged ions (deprotonated), but it does not fragment molecules and, thanks to the high resolution, allows a direct access to the stoichiometry of all the molecules present in the samples. We have acquired spectra in the mass range 50 to 1000 Da. In addition we have performed fragmentation analyses (MS/MS) of selected ions. This kind of analysis provides complementary data on the different chemical functionalities present in our polymers. Complementary data are also provided by transmission infrared micro-spectroscopy. This technique gives access to the terminative chemical functionalities present in the polymers. For infrared spectroscopy, polymer powder was crushed onto a diamond window and then placed in an environmental cell, under high vacuum conditions (< 10\textsuperscript{-7}mbars). We have also acquired spectra with a KBr pellet.

Results

In the entire mass range studied, more than 1600 different molecules have been detected (Figure 1). Thanks to the high resolution of the Orbitrap, we obtained the atomic content of each molecule presents in the sample. By applying data treatments, we are able to classify molecules contained in such samples. First of all, in Figure 2 we can see that all the molecules present in the polymers have $N/C$ and $H/C$ ratios that converge towards a value of 1 as their mass increases. This is a very important observation because, instead of seeing molecules pointing only to the (1:1) ratio couple (i.e. equal elemental composition in H, C and N), in these samples we can also observe a lot of molecules outside the (1:1) ratio couple. Therefore HCN polymers are not homogeneous samples, but are instead composed of a wide variety of molecules. Another interesting observation is the fragmentation pattern in MS/MS experiments.
A systematic loss of NH\textsubscript{3} (-17Da) and of HCN (-27Da) is observed that shows presence of amines in the HCN polymers that is not obvious from their monomer structure. These results are consistent with the IR measurements. During the last decades, different polymerisation processes have been evoked [7] and [5] for example. As noted before the wide variety of molecules observed in our samples, may bring clues on the polymerization process. To explore this statement, standard molecules (with known composition and structure) were analyzed with the Orbitrap in MS/MS and results were compared with those of HCN polymers ones. Our analytical effort was particularly concentrated on the (HCN)\textsubscript{4}, because it is a critical intermediate in the different polymerisation processes proposed in the literature [8]. Diaminomaleonitrile (standard molecule), is not a good candidate for the structure of (HCN)\textsubscript{4} because HCN loss is observed and not NH\textsubscript{3} while the (HCN)\textsubscript{4} in our sample readily losses HCN and HN\textsubscript{3}. This result tends to prove that the polymerization pathway proposed by [9], who suggested that diaminomaleonitrile is the tetramer precursor of the HCN polymers, is not the right one. Infrared spectra give an access to terminating chemical groups present in HCN polymers. This spectroscopy shows that HCN polymers contain also methyl goups (CH\textsubscript{2}, CH\textsubscript{3}), and likely C=\text{N}, in addition to nitrile and amine. These results are another evidence of a complex structure and composition of HCN polymers, and are complementary with HRMS results.

In conclusion this study demonstrates that HCN polymers are not composed of a wide variety of compounds. In addition, large elemental composition differences have been observed when changing the polymer synthesis protocol. This demonstrates that there is not one HCN polymer but that it is a broad family of material. A polymerization process has also been potentially discarded by MS/MS studies of standard molecules. Our analytical effort is on-going.

References


Figure 2: H/C vs N/C for all the molecules present in the polymers. We can easily observe that all the molecules converge toward a value of 1 for both ratios. The large distribution of molecules arround this (1:1) ratio couple demonstrate a complex polymerization pathway. The big pink dot is the average of all the molecules in the samples. The color scale indicates the mass.