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Synthesis of HCN Polymer from Thermal Decomposition of Formamide

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Prolonged heating of formamide ($HCONH_2$) at 185°C or 220°C produces a black insoluble product. The FT-IR spectroscopy and the X-ray photoelectron spectroscopy (XPS) suggest that the product has the chemical structure of a polymer of hydrocyanic acid: $(HCN)_x$. The pyrolysis of $(HCN)_x$ prepared from formamide produces a large amount of gaseous HCN in a wide range of temperatures together with ammonia (NH_3) and isocyanic acid (H—N—C=O).

During the thermal decomposition of formamide to produce $(HCN)_x$, the volatile products evolved were monitored with gas phase infrared spectroscopy. At 185°C, the gaseous product released were CO_2, CO and NH_3 while at 220°C, also HCN was detected. In both cases, a white sublimate was collected in the upper part of the reaction vessel. It consists of ammonium carbamate and its hydrolysis products ammonium carbonate and hydrogen carbonate. It is therefore possible to synthesize the polymer of hydrocyanic acid $(HCN)_x$ starting from formamide avoiding to handle the dangerous hydrocyanic acid.

Keywords: Formamide, polymerization, hydrocyanic acid, $(HCN)_x$, FT-IR, XPS, Raman spectroscopy, pyrolysis.

1 Introduction

Hydrogen cyanide is known for quite a while to polymerize spontaneously and sometime explosively into a brown-black solid also known in the past as azulmic acid (1). The polymerization of HCN may occur in bulk or even in aqueous and non-aqueous solvents (2, 3). The polymerization is catalyzed by trace amounts of amines or other impurities and appears anionic in the polymerization mechanism (2, 3). HCN polymerizes also under high pressure. At room temperature, 1.3 GPa is sufficient, while at 90 K, the polymerization threshold is shifted at 4 GPa (4). The resulting polymer is described as similar to that obtained by bulk polymerization (4). High energy radiation α particles and γ are able to produce complete and massive polymerization of HCN (5) and similar results are obtained by UV photons, for instance, at 185 nm (6). Naturally, HCN and its polymers can be obtained by sparking CH_4, NH_3, H_2O and H_2 (7). A complete survey of the optical and infrared spectral properties of HCN polymers is available (6) and the structure of the polymer has been investigated with solid state NMR spectroscopy (8).

The HCN polymers have incredible implications in the abiotic synthesis of amino acids and nucleobases by hydrolytic treatment (9, 10) and dark matter derived by HCN and/or cyanogen $(CN)_2$ polymerization (11, 12) is thought to be abundant on the surfaces of comets and meteorites (9–11) and may be present in a certain environment in the interstellar medium (9, 12). The HCN polymers should have played a key role in the molecular evolution to life (10).

Additionally, the HCN polymer can be used as a starting material for the synthesis of carbon nitride materials, and is expected to have unique mechanical properties as wear resistance coating and hardness (13–21). In the present work, it is shown that the HCN polymer can be synthesized starting more safely from the thermal decomposition of formamide avoiding to use the dangerous and poisonous HCN. The resulting product has been characterized by several spectral techniques and annealed by thermal treatments.

2 Experimental

2.1 Materials and Equipment

Formamide was obtained from Aldrich or Fluka and was >98% pure by GC.

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FT-IR spectra were recorded on a Nicolet IR-300 from ThermoFischer in transmission mode with samples embedded in KBr pellet. Gas phase spectra were made on samples collected with a 10 cm path cell equipped with BaF_2 windows. Thermal analysis was made on a Linseis thermobalance model L81+DTA under nitrogen flow. TGA-FTIR spectra were obtained by connecting the thermobalance to an IR cell with a path length of 10 cm and BaF_2 windows. The gas phase spectra were recorded by using N_2 as vector gas.

Raman spectra have been excited by the 514.5 nm radiation of an Ar ion laser and analyzed by a Jobin-Yvon monochromator equipped with a CCD detector cooled at 77K. Stray light rejection has been obtained by a noch filter for the specific laser frequency. XPS analyses have been performed by an AXIS-ULTRA spectrometer with a basic pressure in the range of 10^{-9} torr. The X-ray radiation was generated by Al Kα line decay (1486 eV) at operating conditions of 10 KV and 15 mA. The emitted photoelectrons have been analyzed with an hemispherical electron energy analyzer. The acquisition conditions of the high resolution XPS spectra were: pass energy 40 eV, energy step width 0.025 eV and dwell time 300 ms.

2.2 Thermal Decomposition of Formamide at 220°C

Formamide (300 ml) was heated in a conical flask equipped with a condenser and magnetic stirring bar. The temperature was kept at 220°C in an external oil bath. The formamide was thermally treated for a total of 17 h and became black. Periodically, it was necessary to wash the interior of the condenser with a spatula to remove a white sublimate which formed copiously. The white sublimate consists mainly of ammonium hydrogen carbonate and derivatives. Such a product was recognized from its FT-IR spectrum, its thermal behavior, the ammonia odor and the characteristic reaction of the sublimate with diluted hydrochloric acid: release of CO_2. The formation of the sublimate was accompanied by the release of hydrocyanic acid, recognized from its characteristic odor. The reaction

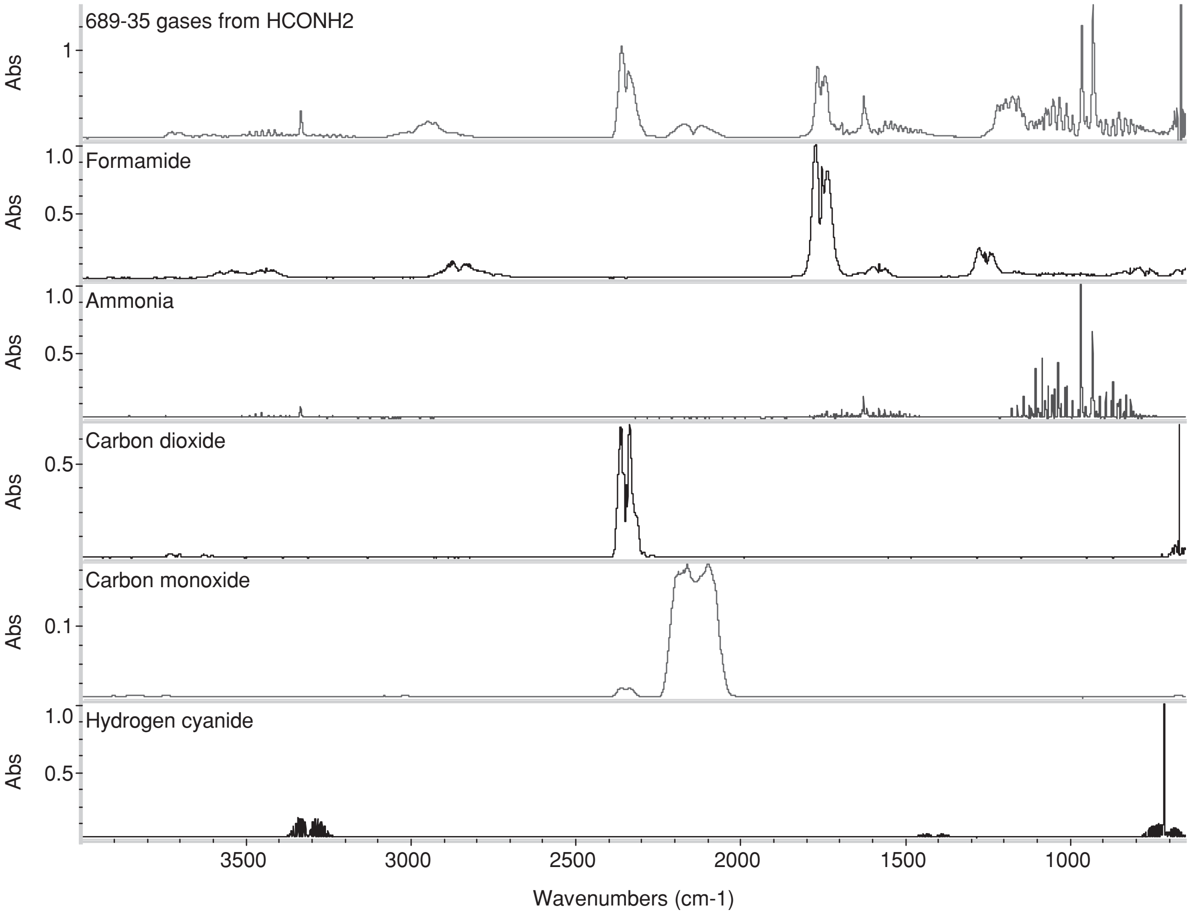


Fig. 1. Gas phase FT-IR spectra of the products released by thermal decomposition of formamide at 185°C. The main products detected are CO_2, CO and NH_3. No HCN production was detected. Of course the decomposition products are accompanied by formamide vapors. The top spectrum was recorded on the vapour phase products derived from formamide decomposition. The other spectra are standard reference spectra taken from the Omnic library of our spectrometer.

mixture was then distilled under reduced pressure to recover the unreacted formamide leaving back a black residue. The black solid residue was refluxed for 2 h with 250 ml of methanol and then was filtered with the aid of an aspirator. The methanol solution passed through the filter with a dark-orange color and on the filter a black solid powder was collected, washed further with acetone, and left to dry in air. Yield 5.8 g.

2.3 Thermal Decomposition of Formamide at 185°C

Formamide (125 ml) was heated in an oil bath as described in section 2.2. The temperature was set at 185°C for 40 h. In these conditions, there was little production of the white sublimate of $NH_4HCO_3/(NH_4)_2CO_3$ and no release of HCN. Instead, ammonia and other products were steadily released (see Results and Discussion section). The mixture became completely black and, as described in 2.2, it was first distilled under reduced pressure to recover the unreacted formamide and the black residue was refluxed with 100 ml of methanol for 1 h and filtered with the aid of an aspirator. Methanol passed yellow in color through the filter leaving a black insoluble residue. The black residue was further washed with an excess of methanol and left to dry in air. Yield 1.46 g.

3 Results and Discussion

3.1 Analysis of the Products Released from the Thermal Decomposition of $HCONH_2$

Formamide is not stable at temperature above 185°C and decomposes into CO, CO_2, and NH_3 (22, 23). Above 200°C, the decomposition also involves HCN formation (22, 23). In a series of two distinct experiments, we have analyzed the decomposition products of formamide: the gaseous products were collected in a gas cell and the solid white sublimate was collected and analyzed directly. Figure 1 shows the FT-IR spectra of the gases released by $HCONH_2$ at 185°C: the presence of CO_2, CO and NH_3, as well as formamide vapor, is clearly evident. No HCN was detected. Instead, at 220°C, the production of ammonia appears enhanced (Fig. 2) in comparison to the experiment at lower temperature and there is evidence of the formation of HCN.

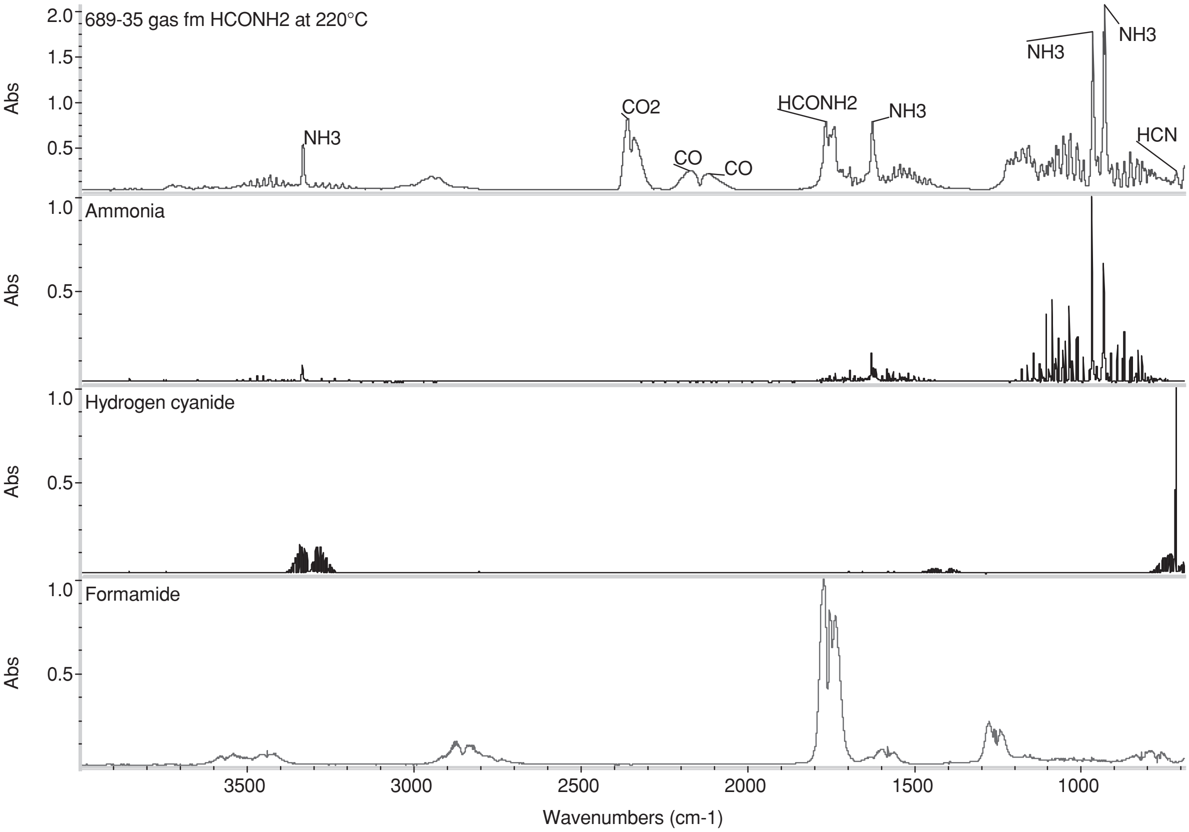


Fig. 2. Gas phase FT-IR spectra of the products released by thermal decomposition of formamide at 220°C (measured in the external oil bath). The main products detected are still CO_2 and NH_3. The presence of HCN was detected at 714 cm^{-1}. Other components shown in Figure 2 are CO and $HCONH_2$ vapors. The top spectrum was recorded on the vapour phase products derived from formamide decomposition. The other spectra are standard reference spectra taken from the Omnic library of our spectrometer.

Fig. 2 shows that CO_2 and CO are formed as well at higher temperature. In both conditions 185°C and 220°C the release of gaseous products is accompanied by the production of a white sublimate. The amount of white sublimate is obviously much higher when the decomposition of $HCONH_2$ is conducted at 220°C. The analysis of the white sublimate by FT-IR spectroscopy and decomposition with diluted HCl revealed that it consists essentially by ammonium carbonates $(NH_4)_2CO_3$ and $(NH_4)HCO_3$ and ammonium carbamate $NH_2\text{-}COO(NH_4)$. The latter is formed quite easily when anhydrous ammonia reacts with carbon dioxide. Since in our reaction conditions ammonia and CO_2 are released anhydrous from formamide, the initial reaction product is just ammonium carbamate:

$$2\,NH_3 + CO_2 \rightarrow NH_2\text{-}COO(NH_4)$$

Once the carbamate enters in contact with humid air, it is converted into a mixture of carbonates:

$$2\,NH_2\text{-}COO(NH_4) + 2\,H_2O \rightarrow (NH_4)2CO_3 + (NH_4)HCO_3 + NH_3$$

3.2 Non-volatile Products Formed by Thermal Decomposition of Formamide

Prolonged heating of formamide produced a black insoluble solid which was recovered by distilling off the unreacted formamide. The black residue shows a FT-IR spectrum (Fig. 3) which resembles that of the $(HCN)_x$ polymer (2, 3, 6) and, in some instances, also that of paracyanogen (11, 12, 24, 25). The infrared absorption spectrum is very simple and characterized by a broad band between 1670 and 1050 cm^{-1} with two peaks at 1673 and 1623 cm^{-1} attributable to imine chains –C=N- and other two sub-bands at 1390 and 1263 cm^{-1} which were observed in $(HCN)_x$ prepared directly from HCN (2, 3, 6). Another feature of the polymer obtained from thermal decomposition of formamide is the broad infrared absorption band between 3150 and 3400 cm^{-1} attributed to amine N—H stretching (25).

As shown in Figure 3, methanol extraction of the insoluble matter did not cause changes in the infrared spectrum. Instead, the thermal treatment under inert atmosphere (nitrogen) causes the shift of the absorption bands originally located at 1670 and 1620 cm^{-1} to a unique band at

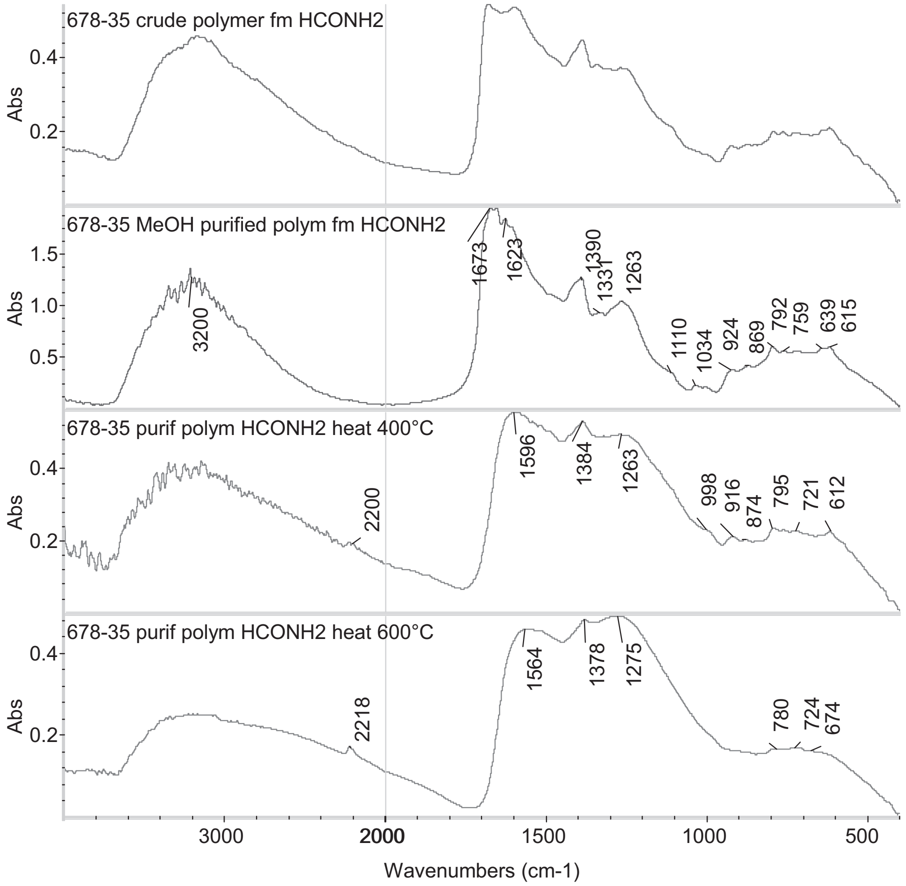
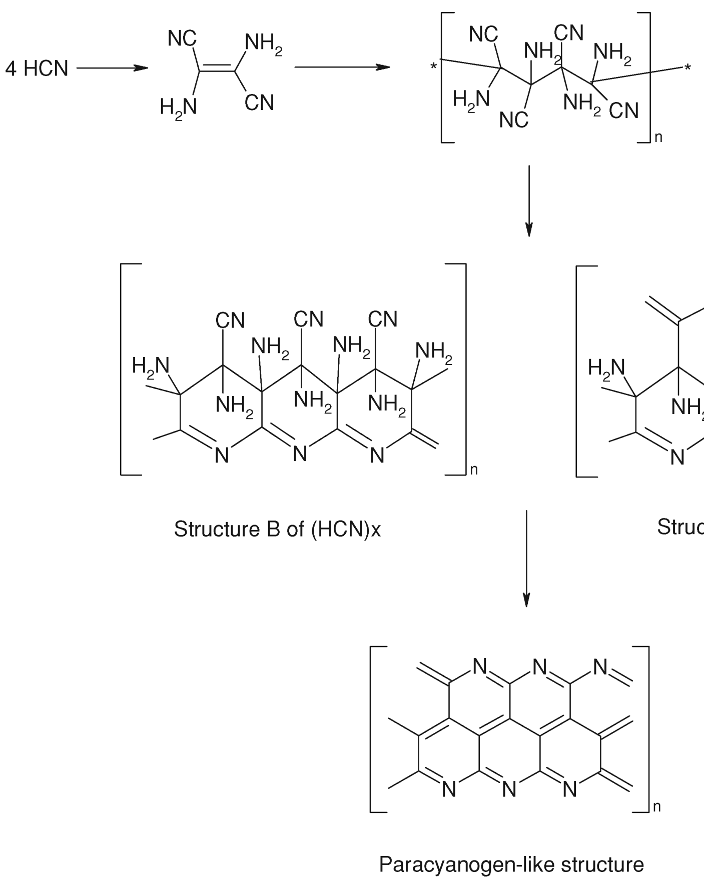


Fig. 3. FT-IR spectra in KBr of the solid black polymer formed by the thermal decomposition of $HCONH_2$. From top to bottom are shown the spectra of the crude polymer, polymer purified with CH_3OH extraction and polymer treated at 400° and 600°C under nitrogen atmosphere.



Sch. 1. Formation and structure of HCN polymers.

1600 cm^{-1}. Such a band shift is accompanied by the growth of the absorption bands at about 1380 and 1270 cm^{-1}, a phenomenon also already observed in the thermal treatment of paracyanogen $(CN)_x$. After the thermal treatment, both at 400°C and at 600°C, it is possible to also observe a new absorption band at about 2200 cm^{-1} attributable to the $-C{\equiv}N$ stretching.

As shown in Scheme 1, the structure of $(HCN)_x$ has been proposed to derive from a HCN tetramer: diaminomaleonitrile (9) which polymerizes into a chain with amine and nitrile pendant groups which cyclizes into a ladder polymer resembling, for certain instances, paracyanogen (2, 3, 9, 26). Further thermal treatment of $(HCN)_x$ may lead to a complete release of amine groups leaving an azotated polycondensed ring structure (Scheme 1). The structure of $(HCN)_x$ has been confirmed by NMR spectroscopy (8, 26), although other possible chemical structures for the polymer have been proposed (26). The molecular weight of the acetylated derivative of $(HCN)_x$ was found in the range of 300–900 Daltons (26).

The infrared spectra of the polymeric product formed from $HCONH_2$ thermal decomposition shown in Figure 3 appear consistent with the infrared spectra of $(HCN)_x$ prepared directly from HCN (2, 3, 6).

3.3 XPS Analysis of the Polymer from $HCONH_2$

The chemical analysis of $(HCN)_x$ polymerized in water shows an elemental composition of C = 41, 4%, H = 4.0%, N = 43.2% and O = 11,4% and no evidence of the $\nu_{C\equiv N}$ stretching band at 2200 cm^{-1} (3,6). Instead, $(HCN)_x$ obtained by bulk and anhydrous polymerization shows an elemental analysis completely in line with the theoretical expectation for $(HCN)_x$ and a strong $\nu_{C\equiv N}$ stretching (2, 3, 6). The infrared spectra of Figure 3 have shown that the polymer from $HCONH_2$ is more similar to the spectrum of $(HCN)_x$ polymerized in water because of the absence of the $\nu_{C\equiv N}$ stretching. Also the X-ray photoelectron spectroscopy (XPS) is consistent with this interpretation.

XPS spectroscopy is able to give quantitative information on the bonding state of the elements present onto the sample surface through the "chemical shift." In our case, the investigation was made looking at both N_{1s} photoelectron signal and the C_{1s} signal. In Figure 4, we report the N_{1s} signals recorded on the pristine $(HCN)_x$ sample prepared from $HCONH_2$ and on the thermally annealed samples at 400°C and 800°C under N_2. The XPS N_{1s} signals of Figure 4 were deconvoluted according to a published approach (27) and reported in Table 1. A drawback of the N_{1s} signal analysis regards to the fact that it is not possible to distinguish

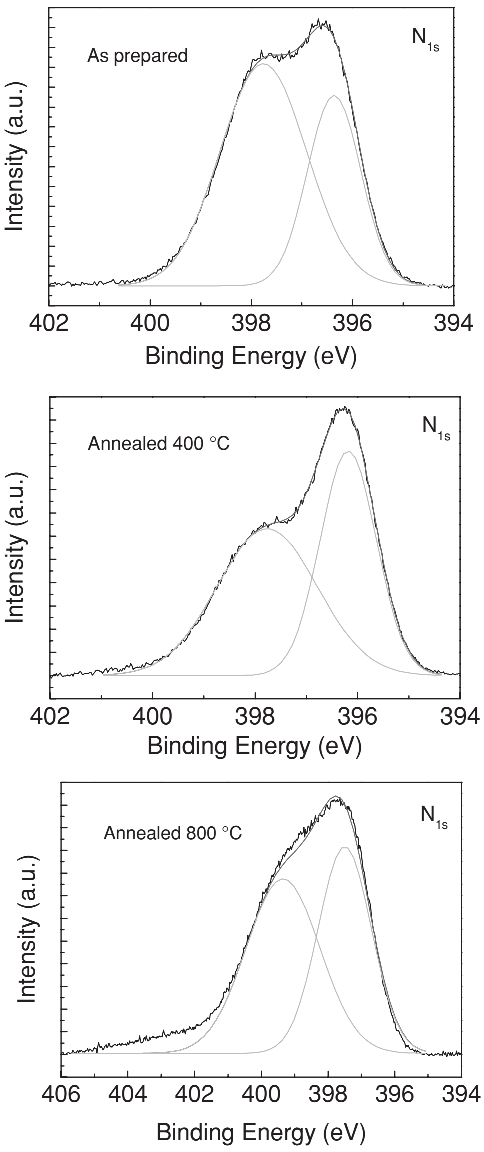


Fig. 4. XPS N_{1s} of the polymer prepared by thermal decomposition of $HCONH_2$ before and after the thermal treatments at 400°C and 800°C under N_2.

between the C—N and the C≡N moieties because they have the same chemical shift.

Indeed the imine —C=N— chain has been detected and the presence of C-NH_2 and/or C≡N moiety confirmed as well (Table 1 and Fig. 4) and this is consistent with the proposed structure of $(HCN)_x$ (Scheme 1) and confirms that this polymer is also the result of the thermal decomposition of $HCONH_2$. Since the detection of the C≡N groups would be in contrast with the infrared spectra which do not show the $\nu_{C\equiv N}$ stratching, XPS signal at 396.2 eV is definitely assigned to a C-N bonding state, at least for the as prepared, pristine, sample. Thus, the structure A of Scheme 1 is fully supported both by XPS and by FT-IR spectroscopy.

Table 1. $(HCN)_x$ from $HCONH_2$ composition from XPS N_{1s} signal

Moiety	*As Prepared Atomic conc. %*	*400°C, N_2 Atomic conc. %*	*800°C, N_2 Atomic conc. %*
C—N or C≡N	34.62	46.13	46.20
C=N	65.37	53.86	53.80

The thermal treatment of the sample (under N_2) shows an increase in the C—N and/or C≡N content. This result is consistent with the fact that the thermally annealed samples show the C≡N stretching band at 2200 cm^{-1} in the infrared spectra of Figure 3 which was not present in the pristine polymer. Since the thermal treatment of the sample implies its depolymerization into HCN and other products, it is reasonable to propose that the polymer passes from structure A (Scheme 1) to structure B (Scheme 1) which contains also C≡N groups. This interpretation is supported by the XPS spectra.

The deconvolution and analysis of the C_{1s} signal recorded on the pristine $(HCN)_x$ sample yields the following composition: C—N 49.25%, C=N 36.32%, C—C 10.86% and C-O 3.56%. Thus, the XPS analysis confirms that the product of the thermal decomposition of $HCONH_2$ consists in a $(HCN)_x$ polymer with the presence of small amounts of oxygen. In section 3.2 we have established, on the basis of the FT-IR spectroscopy, that the $(HCN)_x$ polymer derived from $HCONH_2$ is similar to the polymer prepared from HCN in aqueous solution. A characteristic of such polymer is the oxygen content which was found with the XPS analysis.

3.4 TGA-FTIR of the Polymer Derived from $HCONH_2$

The polymer prepared from $HCONH_2$ was pyrolyzed in a thermobalance and the gases released were collected in an infrared gas cell and analyzed in all ranges of temperatures explored (from room temperature to 850°C under N_2 flow. The spectra in Figure 5 show that the polymer prepared from $HCONH_2$ releases HCN above 360°C. HCN was recognized from the absorption bands at 3331 and 3279 cm^{-1} (28, 29). Unexpectedly, another component released above 360°C was isocyanic acid: H-N=C=O identified from the bands at 2282 and 2256 cm^{-1} (28, 30) Small amounts of CO are also produced as suggested by the bands at 2169 and 2117 cm^{-1} (28, 29). Figure 6 shows another portion of the infrared spectrum of the evolved products. In addition to the mentioned products HCN, HCNO and traces of CO, another component is released from the polymer: ammonia. NH_3 is recognized from the bands at 965 and 931 cm^{-1} (28, 29) and its evolutions starts already at 240°C, reaches a peak at 360°C, and becomes negligible above 575°C. The absorption band at 714 cm^{-1} is due to HCN (28, 29) which is continuously released up to 850°C. A previous work on the pyrolysis

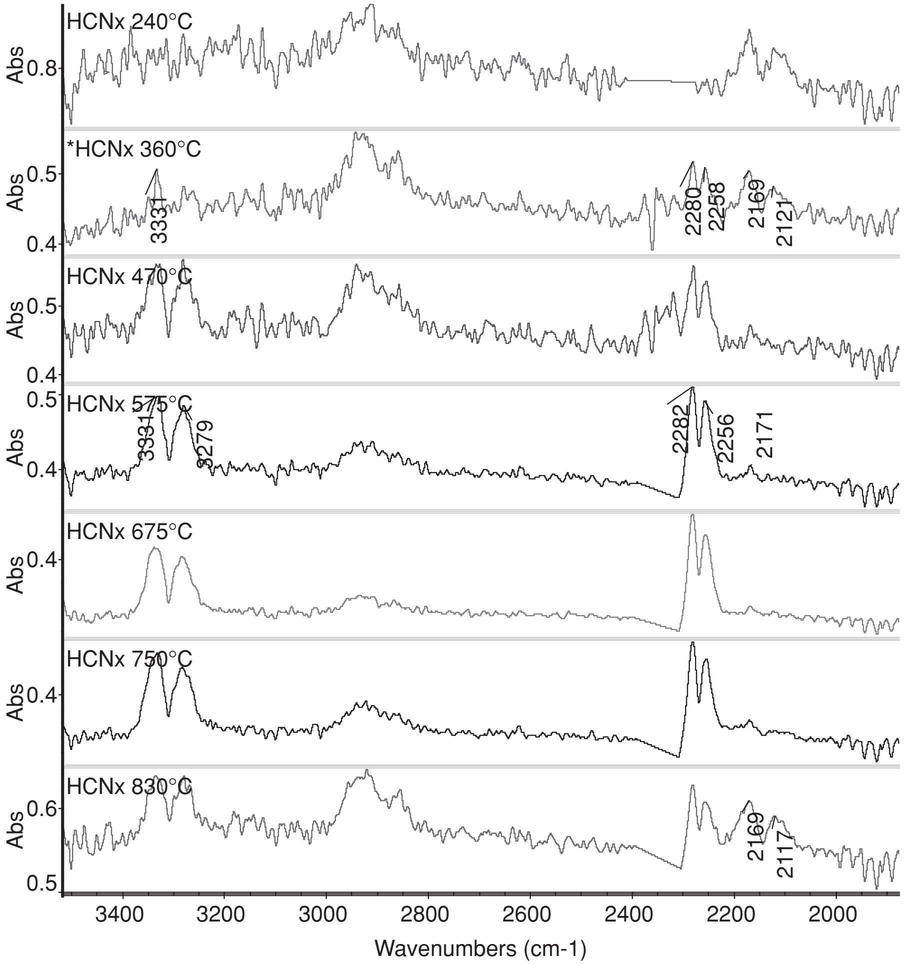


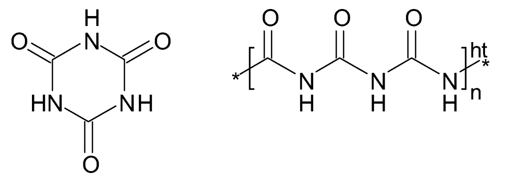
Fig. 5. Gas phase FT-IR spectra of the products evolved from the decomposition of the $HCONH_2$ polymer in a thermobalance under N_2 flow and at a heating rate of 10°C/min. The spectra show that the polymer releases HCN above 360°C. HCN is recognized from the absorption bands at 3331 and 3279 cm^{-1}. Another component released above 360°C is isocyanic acid: H-N=C=O identified from the bands at 2282 and 2256 cm^{-1}. Small amounts of CO are also produced as suggested by the bands at 2169 and 2117 cm^{-1}.

and UV photolysis of pure $(HCN)_x$ have already shown that it decomposes essentially in gaseous HCN and NH_3 (31).

The pyrolysis of the $HCONH_2$ polymer has shown that it consists of an HCN polymer since it releases back HCN in a wide range of temperature. Additionally, there is the release of HCNO which should be present as well in the polymer structure or as a separate structure, for instance as a linear polymer or as a cyclic oligomer. It is possible that the thermal decomposition of formamide produces also cyanuric acid or its linear oligomer (Scheme 2). In fact, it has already been shown that the ion bombardment of frozen $HCONH_2$ produces isocyanic acid at low temperature (32). Thus, its trimer or oligomer known as cyanuric acid is formed from the thermal decomposition of formamide. Once cyanuric acid is heated to a high temperature, it decomposes back quantitatively to isocyanic acid (33).

3.5 Raman Spectroscopy of the Polymer Derived from $HCONH_2$

The Raman spectra of the $(HCN)_x$ samples prepared from thermal decomposition of formamide are shown in Figure 7. The Raman spectrum of the pristine sample is compared with those annealed under N_2. As shown in Figure 8, the Raman spectra show a monotonic increase in the I_D/I_G ratio with the level of thermal treatment



Sch. 2. Chemical structure of cyanuric acid (left) or its linear oligomer (right).

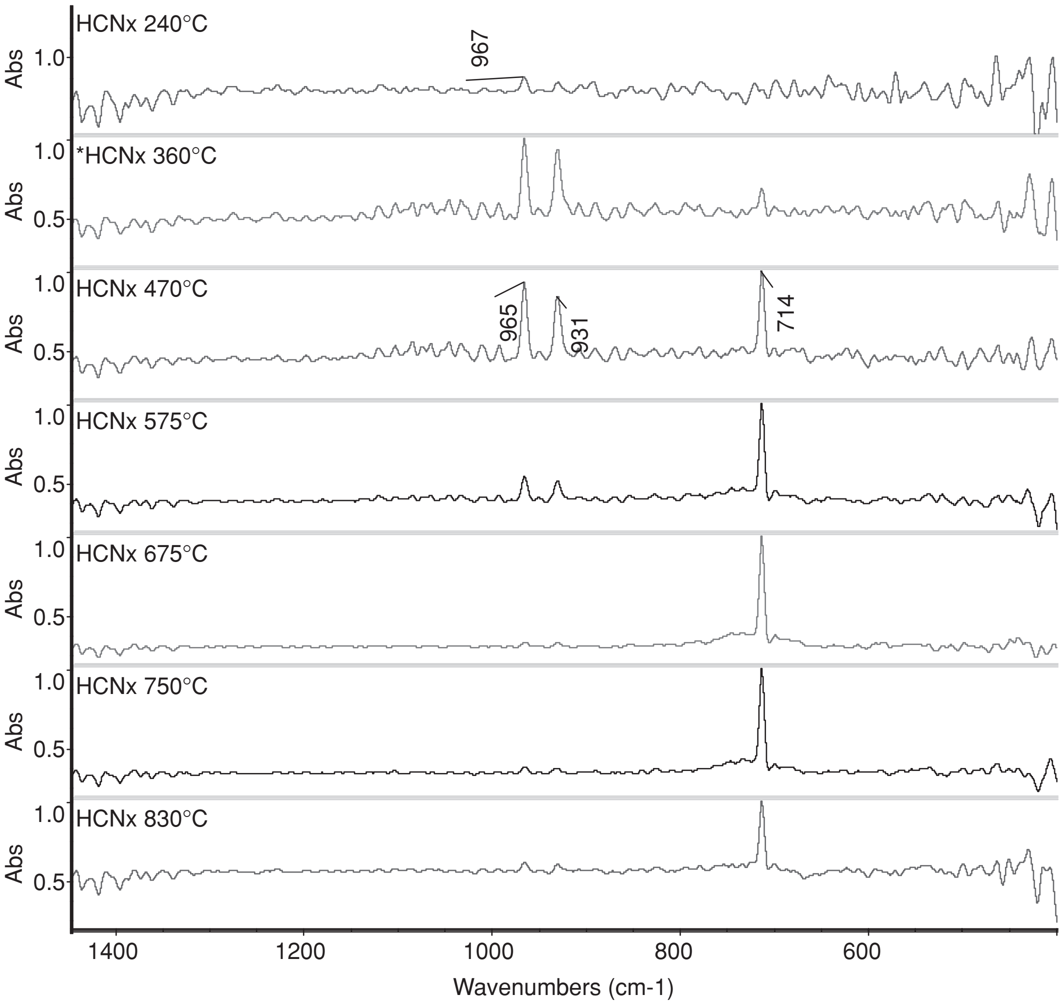


Fig. 6. Gas phase FT-IR spectra of the products evolved from the decomposition of the $HCONH_2$ polymer in a thermobalance under N_2 flow and at a heating rate of 10°C/min. This portion of the FT-IR spectrum shows that another component is released from the polymer: ammonia. NH_3 is recognized from the bands at 965 and 931 cm^{-1} and its evolutions starts already at 240°C, reaches a peak at 360°C and becomes negligible above 575°C. The absorption band at 714 cm^{-1} is due to HCN which is continuously released up to 850°C.

undergone by the $(HCN)_x$ samples, i.e., pristine, 400°C and 800°C.

As widely reported in the literature (34, 35), the I_D/I_G ratio provides qualitative and quantitative information about the order of a carbon-based structure, since its value is directly related to the number of structural defects in the material. In particular, it is widely accepted that the G band is due to the relative vibration of the sp^2 carbon atoms, while the D peak is linked to the breathing modes of the rings and that the electronic vibrational states of sp^2 aromatic clusters can be mapped onto those of graphite. Then, the Raman spectra depend formally on the ordering of the sp^2 sites, due to the resonant enhancement of their vibrations.

In our specific case, an increase of the I_D/I_G ratio can be considered as proof of the increasing disorder of the sample, following the general relationship given by (36):

$$I_D/I_G = CL^2$$

Where L is the aromatic cluster diameter or in-plane correlation length and C is a constant which depends on the excitation wavelength (0.055 for the 514.5 nm radiation). Figure 8 shows the increase in the I_D/I_G ratio together with the blue shift of the G band once the annealing temperature is increased. Again this latter phenomenon is correlated with the above mentioned change in the local symmetry structure, leading to a picture compatible with the structural evolution of the $(HCN)_x$ polymer which has a ladder structure and by thermal treatment is converted in a paracyanogen-like structure as shown in Scheme 1.

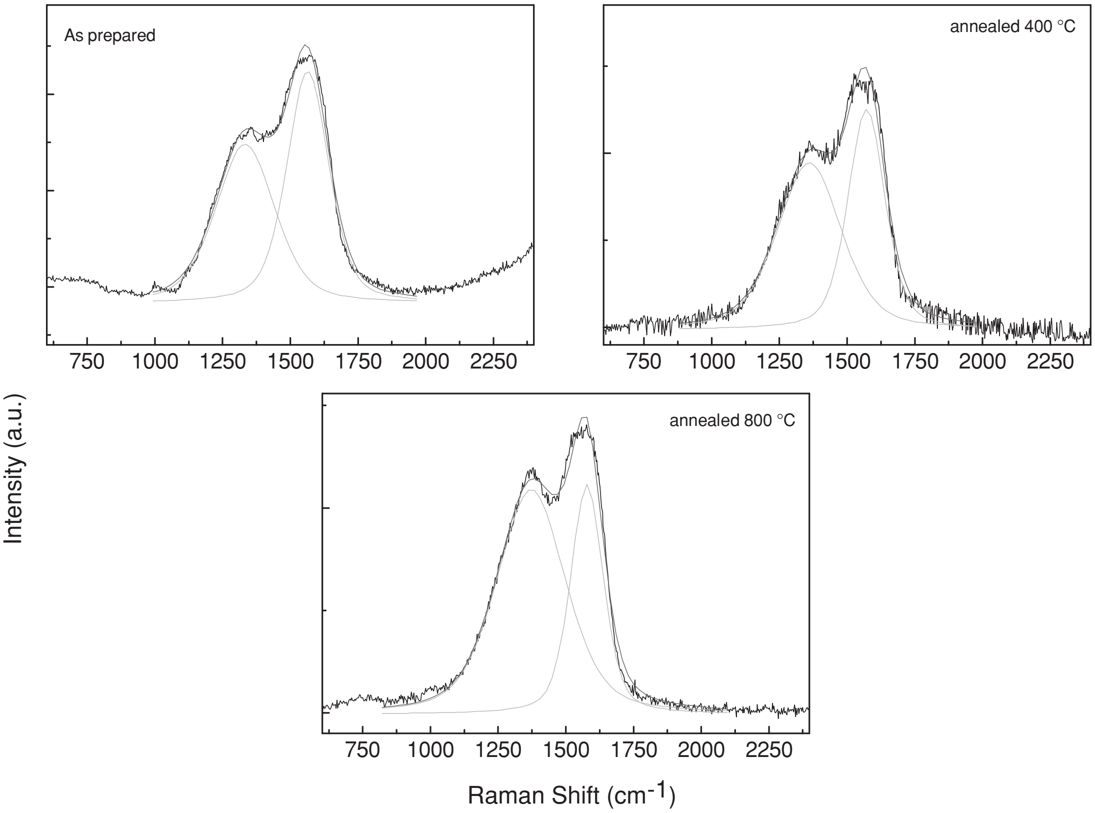


Fig. 7. Raman spectra of polymer derived from thermal decomposition of $HCONH_2$. Thermal treatment (under N_2) of the polymer at 400° and 800°C implies a change in the I_D/I_G ratio with an increase in the I_D mode.

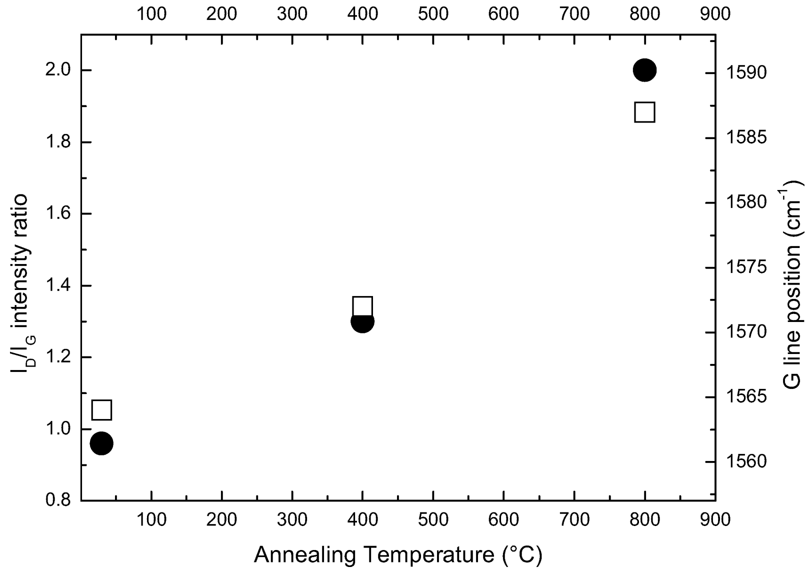


Fig. 8. Raman parameters obtained through an analysis of the D and G bands in the as prepared and annealed polymer samples obtained from $HCONH_2$. Changes in the local structure are evidenced by a shift of the G-line position and the increase in the I_D/I_G ratio.

4 Conclusions

Formamide, when heated in an open vessel at 185°C, releases CO_2, CO and NH_3. At 220°C, the production of NH_3 is enhanced and also HCN is released. In both cases, ammonium carbamate (NH_2-$COONH_4$) is formed and deposited as a white sublimate in the upper part of the reaction apparatus and converted to a mixture of ammonium carbonate and hydrogen carbonate when in contact with humid air.

In addition to the release of the above mentioned gases, prolonged heating of formamide produces a black insoluble precipitate whose FT-IR and XPS spectra corresponds to that of $(HCN)_x$, a polymer formed by the spontaneous polymerization of hydrocyanic acid (anhydrous or in solution). Additionally, the pyrolysis of the polymer formed from formamide releases gaseous HCN, isocyanic acid H-N=C=O and ammonia, confirming once again its nature as an HCN polymer. Raman spectroscopy was used to investigate the structure of $(HCN)_x$ prepared from formamide suggests a trend to disordered graphitic structure after heating at 400°C and 800°C under N_2.

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