

A TG/FTIR study on the thermal degradation of poly(vinyl pyrrolidone)

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Abstract The aim of this study was to gain some fundamental knowledge on the thermal degradation pathways of poly(*N*-vinyl pyrrolidone) using Thermogravimetry coupled with Fourier Transform Infrared Spectroscopy (TG–FTIR) in addition to IR and ^1H NMR spectroscopic studies of the partially degraded samples. It was found that the vinyl pyrrolidone is the main volatile products of the thermal degradation of PVP which implies that the predominant mechanism during thermal degradation of this polymer is the depolymerization to monomer of the polymeric main chain; however, it is evident that simultaneous reactions may be involved yielding oligomers. FTIR and ^1H NMR spectra of partially degraded samples of PVP exhibited very similar characteristics to that observed for undegraded samples although the ^1H NMR spectra suggest the presence of simultaneous reactions as the fragmentation of polymeric main chain.

Keywords Thermal degradation · Thermal decomposition · PVP · TG/FTIR

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Introduction

Poly(*N*-vinyl-2-pyrrolidone), PVP, has been attracted a great deal of attention in these days as it has been widely used for applications in various fields. This polymer is a synthetically derived vinyl polymer with a unique combination of properties, such as good solubility in both water and a range of organic solvents, remarkable capacity to interact with a wide variety of organic and inorganic compounds, good biocompatibility, non-toxicity to living tissues, etc. PVP has been widely used in the biomedical field, the cosmetic and food industrial sectors which are closely related to the human health. PVP has also been widely used as a medical additive or polymeric modifier. In fact, the PVP is one of the most frequently investigated classes of materials for use in medicine and in other applications interfacing with biological systems [1–5].

Despite the applications above mentioned, there are only a few papers related to the thermal decomposition behavior of this polymer and the suggested mechanisms in these works differ radically from each other, i.e., the mechanism involved in the thermal decomposition of PVP is still a matter of controversy. In this regard, Peniche et al. [5] pointed out that the formation of pyrrolidone is the main product of the thermal degradation of PVP. In contrast, Bianco et al. [3] suggested that the main volatile products of the thermal degradation of PVP are compounds with ester groups, ammonia (NH_3) and hydrocarbons (unsaturated structures). They claimed that the ester formation was a consequence of the scission of $\text{N}-\text{C}=\text{O}$ bond and that the ammonia formation depended on the presence of NH_2 groups which were probably formed by the protonation of the nitrogen atom in the PVP. Finally, the presence of evolved products related to $\text{C}-\text{H}$ bonds and unsaturation suggested the scission of the main chain of PVP. On the other hand,

Bogatyrev et al. [4] suggested that thermal decomposition of the PVP is accompanied by breakdown of both main chain and side groups. This process involves elimination of the monomer units from the ends of the main chain and an increasing number of the break in the main chain.

The aim of this study was to gain some fundamental knowledge on the thermal degradation pathways of poly(*N*-vinyl pyrrolidone) using Thermogravimetry coupled with Fourier Transform Infrared Spectroscopy (TG–FTIR) to analyze the evolved gases during decomposition. In addition, the partially degraded samples were also studied by both IR spectroscopy and ^1H Nuclear Magnetic Resonance (NMR).

Experimental

Poly(vinyl pyrrolidone), PVP, used in this study was purchased from Aldrich Chemical Co. (MI USA) and it has a mass average molecular mass M_w of 260,000 g/mol and a T_g of 451 K.

Thermal degradation of PVP was performed using a Perkin Elmer TG/FTIR system which consists of a TGA Pyris 1 coupled to a FTIR 1600. Samples masses ranging from 15 to 20 mg were heated from 323 to 873 K at a rate of 10 K/min in a dry nitrogen atmosphere. The flow rate of nitrogen into the cell for TG/IR experiments was approximately 60 mL/min. The heated line that transfers evolved gases from the TG to the FTIR was maintained at 523 K and the IR cell was held also at 523 K. IR spectra (a total of 38) were recorded in the spectral range of 4,000–650 cm^{-1} with a 4 cm^{-1} resolution and eight scans.

As thermogravimetry coupled with infrared spectroscopy studies only provides information regarding the released gases from the degraded polymer, PVP was also partially degraded and examined by FTIR and ^1H NMR. For these experiments, samples were taken from the TG pan when a significant mass loss was detected. FTIR spectra of the partially degraded samples were obtained from KBr pellets by transmission technique using a Nicolet Magna spectrometer with a resolution of 4 cm^{-1} and 50 scans. Proton nuclear magnetic resonance spectra were obtained with a 400 MHz spectrometer (Bruker, Germany) using deuterated chloroform as solvent and tetramethylsilane as reference.

Results and discussion

TG mass loss curve and the corresponding derivate curve (DTG) obtained for PVP are shown in Fig. 1a. It is evident that this polymer exhibited only one mass loss which started at 668 K and its maximum rate decomposition

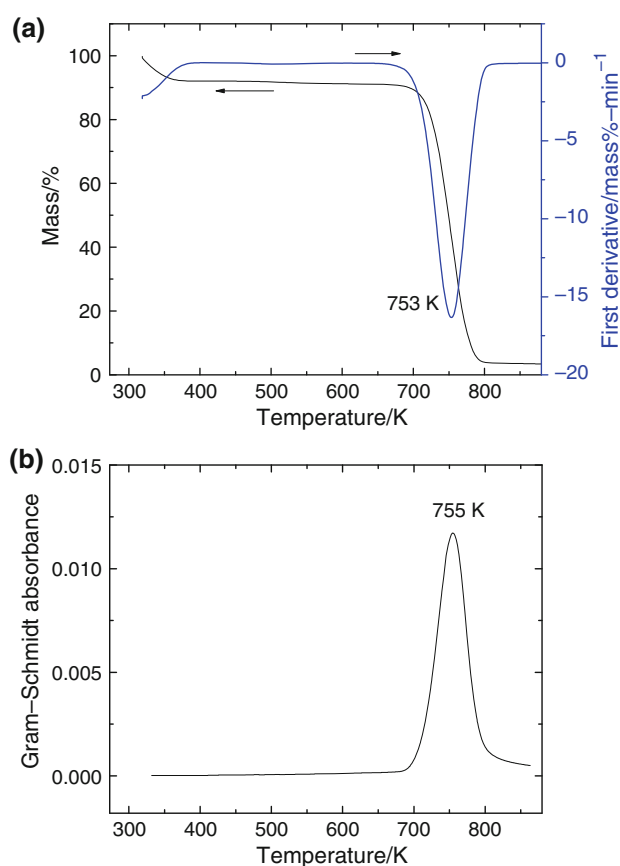


Fig. 1 TG and DTG curves (a) and Gram–Schmidt plot for PVP (b)

temperature was located at 753 K. As expected, Gram–Schmidt plot showed the presence of only one region of evolved gases (see Fig. 1b), clearly related to the peak of the DTG curve.

It has been reported by several authors that the thermal degradation of PVP exhibits only one mass loss [1, 5–8], although some studies have found two degradation stages [3, 9–11]. In the last case, the first mass loss is small (3.5 wt%) and was reported by Bianco et al. [3] and Mendes et al. at 573 K, whereas Rao et al. [9] at and Kim et al. [10] at 523 K; the second weight loss (main transition) was located at 723 K. In additional experiments carried out in our laboratory using PVP films, we also obtained two degradation stages at 523 and 748 K and their TG/FTIR results (not shown) demonstrated that the additional peak was due to moisture which was acquired during film manufacturing. Another interesting point is the fact that the percentage of residual mass is close to 3.5%. This value falls within the range reported by other authors [1, 3, 5, 9].

Figure 2a shows the stack plot of IR spectra of evolved gases from thermal degradation of PVP as a function of temperature while Fig. 2b shows the IR spectrum of the evolved gases, at the maximum evolution rate. As observed, the spectrum showed a very intense band at 1,750 cm^{-1}

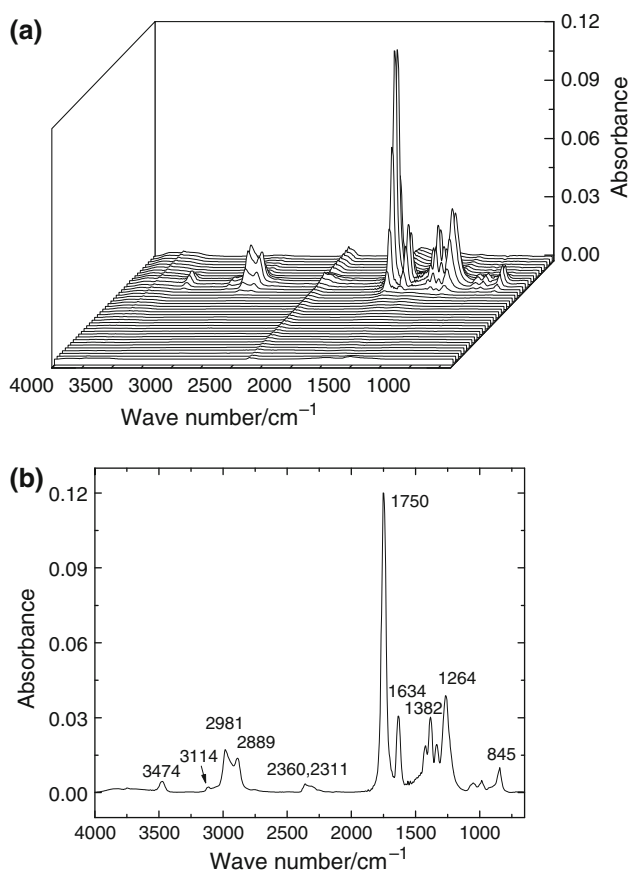


Fig. 2 Stacked plot of FTIR spectra (a), and FTIR spectrum obtained at 753 K (b), of the evolved gases obtained during thermal degradation of PVP

which was associated to carbonyl stretching of the five-membered cyclic lactam structure. Absorption bands at 2,981 and 2,889 cm^{-1} , related to C–H stretching for aliphatic compounds and a band at 1,634 cm^{-1} due to C=C stretching of unsaturated group (alkene) were also observed. The presence of unsaturated compounds in the evolved gases generated during the thermal degradation of PVP was confirmed by the appearance of bands at 3,114 and 845 cm^{-1} , associated to =C–H stretching and =C–H bending vibrations, respectively. In a similar manner, the presence of aliphatic compound was confirmed by the appearance of bands at 1,422 and 1,382 cm^{-1} , attributed to C–H bending vibration from methylene groups. Finally, a band at 3,474 cm^{-1} which is related to N–H stretching vibration and a band at 1,264 cm^{-1} associated to C–N stretching vibration from pyrrolidone structure were also detected.

Taking into account the above mentioned results, it is possible to postulate that the main evolved volatile product obtained from thermal degradation of PVP is its corresponding monomer, i.e., vinyl pyrrolidone. To prove this hypothesis, we analyzed by FTIR a sample of pure vinyl pyrrolidone, VP (this compound was also obtained from

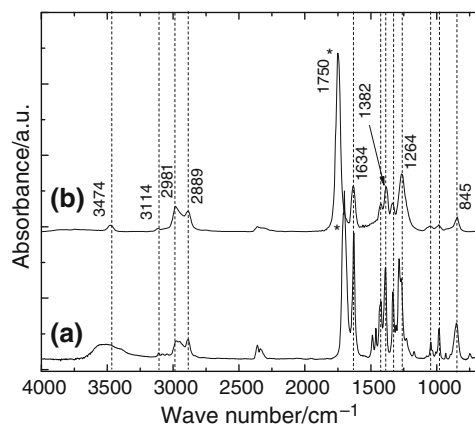
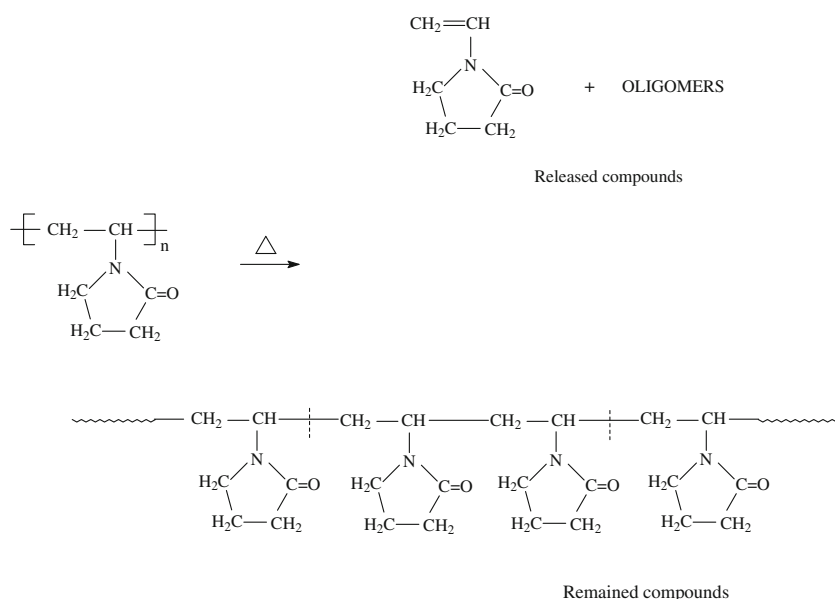


Fig. 3 FTIR spectra of (a) a sample of pure vinyl pyrrolidone, and (b) evolved gases from thermal degradation of PVP

Aldrich Chemical Co.; purity 99%) and the result is displayed in Fig. 3a. As noted, this spectrum shows a good match to that obtained for the evolved gases (see Fig. 3b), except for carbonyl band located in the range 1,700–1,750 cm^{-1} . In this case, the spectrum of pure VP showed a band at 1,701 cm^{-1} whereas that obtained for the evolved gases exhibited a band at 1,750 cm^{-1} . It is well known that the carbonyl stretching frequency is influenced by the sample physic state (solid, liquid, gas); for example, the carbonyl band of the FTIR spectrum in gaseous phase of a carboxylic acid absorbs at higher wave number (ca. 1,780 cm^{-1}) than that corresponding in liquid phase (1,700 cm^{-1}) [12]. Thus, the shift of the carbonyl band is clearly justified considering the physical state of the monomer.

The fact that the spectrum of VP was similar to that obtained for the evolved gases imply the predominant mechanism during thermal degradation of this polymer is the depolymerization to monomer of the polymeric main chain (see Scheme 1). However, it is evident that secondary reactions may be involved as there was a residual mass obtained at 873 K and due to the fact that small bands associated with of carbon dioxide in the released gases were observed. In this regard, it can be said that, in general, polymers suffering depolymerization to monomer as methyl methacrylate do not yield residual mass and the only explanation is if one considers that the depolymerization is not the unique degradation pathway. On the other hand, it was observed that the ratio between the intensity of the bands at 1,750 and 1,634 cm^{-1} (I_{1750}/I_{1634}) in the spectrum of the released gases was higher than that recorded for VP, i.e., the band related to carbonyl groups (1,750 cm^{-1}) in the spectrum of evolved gases are higher than that for VP indicating a major presence of compounds containing carbonyl groups in the evolved gases or less unsaturated compounds such as PVP oligomers.

Scheme 1 Suggested mechanism for thermal degradation of PVP



As in our study, Peniche et al. [5] and Bianco et al. [3] obtained similar spectra during thermal decomposition of their PVP samples but the analysis of the results was very different. For example, Peniche et al. [5] concluded that the obtained spectra strongly suggest the formation of pyrrolidone as the main product of the thermal degradation of PVP. In contrast, Bianco et al. [3] claimed that the very intense absorption band at $1,748 \text{ cm}^{-1}$ was apparently associated with ester formation as consequence of the scission of the $\text{N}-\text{C}=\text{O}$ bond. The suggested chain scission was confirmed by the presence of absorption bands at 930, 970, and $3,336 \text{ cm}^{-1}$.

As thermogravimetry coupled with infrared spectroscopy studies only provides information regarding the released gases from the degraded polymer at various stages, PVP was also partially degraded and examined by FTIR. In general, the changes in chemical structure of polymers can be followed by FTIR after each significant mass loss, in the case of PVP, this procedure was not performed as this polymer exhibited only one mass loss and the residual mass after this transition was very small (ca. 3 wt%). Therefore, the changes in the polymer structure were studied by FTIR in the remaining mass at 753 K, i.e., at the maximum rate of decomposition.

Figure 4 shows the FTIR spectra of the non-degraded PVP and that heated at 753 K. As noted the spectrum of PVP heated at 753 K was very similar to the undegraded polymer although subtle differences were observed, i.e., a slight shift of the carbonyl band to higher wave number (see inset). This fact confirms that the main degradation pathway during thermal decomposition of this polymer is the depolymerization to monomer of the polymeric chain. Peniche et al. [5] observed that the IR spectra of the

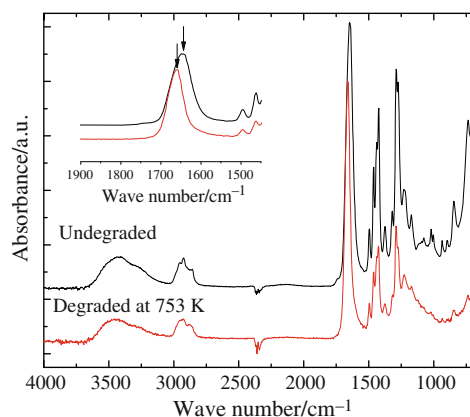


Fig. 4 FTIR spectra of PVP samples: undegraded PVP and degraded at 753 K

residues obtained after 1 h at 623 and 648 K under nitrogen atmosphere exhibited all the characteristic peaks of the starting material (PVP) and do not provide enough information on the degradation but when they used thermogravimetric analysis coupled to the FTIR their results were similar to those obtained by us.

The proton nuclear magnetic resonance (^1H NMR) spectra of the PVP samples (undegraded and degraded at 753 K) are shown in Fig. 5. For undegraded PVP, the main chain methine ($-\text{CH}_2-\text{CH}-$) and methylene protons ($-\text{CH}_2-\text{CH}-$) are assigned around 4.1–3.4 ppm and 1.8–1.3 ppm, respectively. The side chain methylene protons are assigned in the range 3.5–3.0 ppm ($-\text{CH}_2-\text{N}$), 2.5–2.1 ppm ($-\text{CH}_2-\text{C}=\text{O}$), and 2.1–1.8 ppm ($-\text{CH}_2-\text{CH}_2-\text{CH}_2$). It was also noted that the signal are formed by various peaks in the ranges reported previously, which suggest that they are sensitive to configurational sequences.

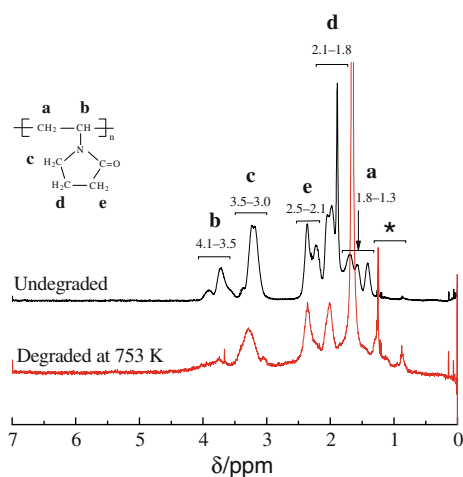


Fig. 5 ^1H NMR spectra of the PVP samples: undegraded and degraded at 753 K

As FTIR results, the ^1H NMR spectrum of PVP heated at 753 K was similar to that of undegraded polymer although some differences were observed. For example, the additional signals exhibited by undegraded PVP samples (related to triad sequences [13]) practically disappeared in the degraded spectrum. This could be due to the reduction of molecular mass in the degraded samples as result of (a) the depolymerization process suggested previously, which seems to be the main degradation pathway of PVP, and (b) the fragmentation of polymeric main chain. The reduction of molecular mass was determined by GPC measurements using an Agilent HPSEC 1100 chromatographer. This analysis was performed using a 10^4 – 10^6 ZORBAX PSM 1000S column, chloroform as solvent and 1 mL/min flow rate. The molecular mass was determined from the retention time using a calibration curve derived from monodisperse standard polystyrene (PS), and the values of molecular mass of polymers were calculated as PS equivalents. The analysis showed that PVP partially degraded has a M_w of 34,500 g/mol which confirms the previous hypothesis.

In addition to the typical PVP broad signals, the ^1H NMR spectra of the polymers presented small signals at 1.24 and 0.87 ppm (*) which were attributed to protons of methyl groups from end-chains; these signals are more evident in degraded PVP due the fragmentation of the polymeric chains. The presence of methyl groups in the chain end in PVP is not unusual [14–16] and it has been attributed to the fact of that the solvent, used during PVP polymerization, may act as a chain transfer agent [14].

Conclusions

The thermal degradation of poly(*N*-vinyl-2 pyrrolidone) was studied using TG coupled FTIR and IR and ^1H NMR

spectroscopic studies of the partially degraded samples. It was found that the vinyl pyrrolidone is the main volatile products of the thermal degradation of PVP which could implies that the predominant mechanism during thermal degradation of this polymer is the depolymerization to monomer of the polymeric main chain; however, it is evident that simultaneous reactions may be involved yielding oligomers. FTIR and ^1H NMR spectra of partially degraded samples of PVP exhibited very similar characteristics to that observed for undegraded samples although the ^1H NMR spectra seems to confirm the presence of simultaneous reactions as the fragmentation of polymeric main chain.

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