Study of the Thermal Degradation of Poly(*N*-vinyl-2-pyrrolidone) by Thermogravimetry–FTIR

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SYNOPSIS

The thermal degradation of poly(*N*-vinyl-2-pyrrolidone) (PVP) was studied by dynamic thermogravimetric analysis (TGA) in the range 200–600°C under nitrogen and oxygen atmospheres at various heating rates. The apparent activation energy of the degradative process was determined by the application of kinetic treatments, giving an average value of 242 kj/mol in N_2, whereas in the presence of oxygen, two trends may be considered: At relatively low temperatures (200–400°C) and degrees of conversion, α, lower than 0.5, we obtained an average value of 199 kj/mol, whereas in the temperature interval 400–600°C with degrees of conversion higher than 0.5, the value of E_a was 306 kj/mol. Isothermal experiments carried out in N_2 in the interval 350–400°C gave an average value of $E_a = 231$ kj/mol, in good agreement with that obtained from dynamic treatments. The FTIR spectra of the volatile compounds evolved in degradation experiments carried out in N_2 as well as in the presence of oxygen suggest that PVP is thermally degraded, predominantly, by the release of the pyrrolidone side group and the subsequent decomposition of polyenic sequences. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the last decades, there has been an increased interest in the use of poly(*N*-vinyl-2-pyrrolidone) (PVP) for various purposes, such as a stabilizer in suspension polymerization,[1] as a polymeric matrix in template[2–4] and step template[5–7] polymerizations and in drug-delivery systems, as a binder and regulator of the disolution rate.[8] Recently, we studied the free-radical copolymerization of PVP with furfuryl methacrylate and we observed that the thermal behavior of these systems was strongly dependent on the copolymer composition.[9] The general pattern of the thermogravimetrical curves of these copolymers exhibited two degradation steps in the intervals 260–320°C and 350–520°C, respectively. The weight loss in the low-temperature interval increased linearly with the weight fraction of furfuryl methacrylate in the copolymer, whereas the weight loss in the higher-temperature interval increased for copolymers rich in vinylpyrrolidone.

To attain an adequate insight into this behavior, we carried out a study of the thermal degradation of the corresponding homopolymers. In a recent work,[10] the thermal behavior of poly(furfuryl methacrylate) (PFM) was analyzed by thermogravimetry, using N_2 as the inert atmosphere, as well as under thermooxidative conditions, in the presence of oxygen. The present article describes the thermal behavior of PVP studied by thermogravimetry under N_2 as well as O_2 atmospheres.

EXPERIMENTAL

Monomer Preparation and Polymerization Procedure

N-Vinyl-2-pyrrolidone (PVP) (supplied by Fluka) was distilled under reduced pressure and used with-

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out further purification. Polymerization of PVP was carried out in a DMF solution at 50 ± 0.1°C in a Pyrex glass ampule sealed off under high vacuum using 2,2′-azobisisobutyronitrile (AIBN) as initiator. Monomer and initiator concentrations were 1.0 mol/L and 1.5×10^{-2} mol/L, respectively. The sealed ampule was shaken vigorously and immersed in a water bath held at the required temperature of polymerization. After 24 h, the ampule was removed from the bath, and, at once, the content was poured into a large excess of diethyl ether. The precipitated sample was washed with the precipitant mixture and dried under vacuum until constant weight was attained.

Polymer Characterization

The polymer was analyzed by ^{1}H-NMR spectroscopy with a Bruker AM-200 spectrometer working at 200 MHz. The spectrum was recorded at 40°C on 5% (w/v) deuterated chloroform. Infrared spectra were recorded in a Perkin-Elmer 457 infrared spectrometer at room temperature using KBr pellets.

Thermal Degradation

Dynamic and isothermal thermogravimetric analyses (TGA) were carried out with a Perkin-Elmer TGS-2 system coupled to a microprocessor programmer System-4 as the temperature control unit. The samples were dried in the thermobalance at 100°C for 30 min under nitrogen atmosphere before starting the experiment. Thermogravimetric analyses were carried out with 8–10 mg of finely powdered samples on a platinum pan under nitrogen or oxygen atmosphere with a nominal gas flow rate of 5 mL per second. In isothermal experiments, the samples were dried in the oven at 100°C for 30 min under nitrogen atmosphere and then heated at 80°C/min until the experimental temperature was reached, taking as zero time the moment at which the temperature of the system was stabilized automatically.

TGA–FTIR Experiments

Combined thermogravimetric analysis–Fourier transform IR spectroscopy were carried out using an FTIR spectrometer (Perkin-Elmer 1720/X) coupled to a thermogravimetric analyzer (Perkin-Elmer TGA 7). To obtain a good resolution of the IR spectra, the flow rate was adjusted to 45 mL/min and the temperature of the transfer line between the thermobalance and the FTIR light pipe was kept at 195°C. The experiments were carried out under N_2 or a mixture of N_2/O_2 (67/33, v/v %) at a heating rate of 40°C/min until 650°C.

RESULTS AND DISCUSSION

Dynamic Experiments

The thermogravimetric curves of PVP obtained at a heating rate of 10°C/min under nitrogen and oxygen atmospheres are shown in Figure 1. The degradation process of PVP in nitrogen atmosphere shows only one main degradative curve. The polymer begins to lose weight at 280°C and continues up to 550°C with 96% weight loss. The residue at 600°C is about 3.4%.

On the other side, the degradation process of PVP in oxygen atmosphere exhibits a complex curve with at least two distinct components: In the first step, the system begins to lose weight at 250°C and continues up to 440°C with a total weight loss about 70 wt %. The second step goes from 440 to 550°C, with a weight loss amounting to 30 wt %. The diagrams drawn in Figure 1 clearly show that the thermooxidative degradation of PVP gives rise to the volatilization of degraded products at lower temperatures and initial higher rate than does the degradative process in an inert atmosphere, N_2. This behavior can be accounted for considering that in the interval of temperatures 200–400°C the presence of oxygen could give rise to the formation of peroxide residues, which easily decompose at relatively low temperatures. This means that the formation of active radicals is favored in oxidative conditions. However, at higher temperatures (400–500°C), the concentration of degradative free radicals is very high and the formation of peroxides does not contribute effec-

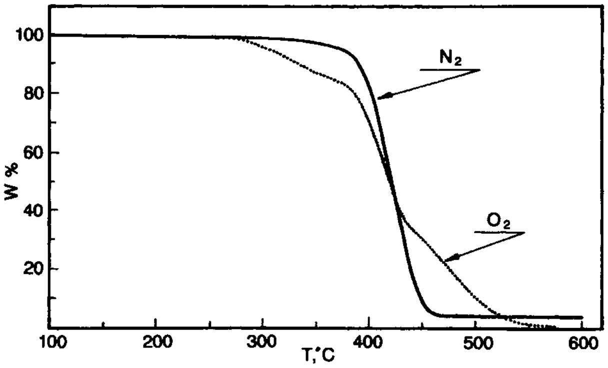


Figure 1 Thermogravimetric curves for the decomposition of PVP heated at 10°C/min under (——) nitrogen and (-----) oxygen.

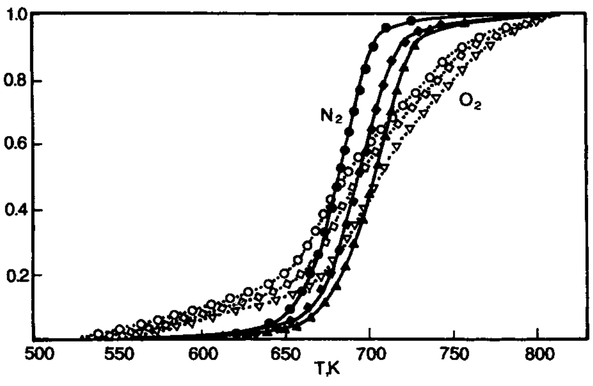


Figure 2 Plot of the degree of conversion (α) vs. temperature at various heating rates: (●) 0–5°C/min; (◆, ◇) 10°C/min; (▲, ▽) 20°C/min; (——) N_2; (----) O_2.

tively to the increase of this parameter, but the oxygen also offers an adequate medium to produce a decrease of the concentration of active degradative species in comparison with the process in N_2, because of its ability to act as an inhibitor or deactivating agent of radicals, as it has been widely demonstrated in a great number of free-radical reactions.

The kinetics of the thermal degradation of PVP under nitrogen as well as under oxygen atmospheres was studied considering as a first approximation that the degradative process follows a first-order degradation reaction. In this sense, if β is the heating rate (kept constant during the experiment), the degradation rate can be expressed as

$$(d\alpha/dt) = (A/\beta)f(\alpha)e^{-E/RT} \qquad (1)$$

where A and E are the Arrhenius preexponential factor and the apparent activation energy, respectively; R, the gas constant; T, the absolute temperature; and α, the degree of conversion, related to the sample weight by the equation

$$\alpha = (W_0 - W_t)/(W_0 - W_f)$$

where W_0 is the initial mass of the sample; W_t, the sample mass at time t; and W_f, the final mass.

The variation of α with T for PVP at heating rates of 5, 10, and 20°C/min under nitrogen and oxygen atmospheres is shown in Figure 2. As usual, the diagrams are shifted to higher temperatures for higher heating rates, independently of the atmosphere used in the experiment.

Using Doyle's integral approximation,[11] Ozawa[12] showed that for a given value of α the temperature and the heating rate (β) are related by the expression

$$\log \beta = -0.457(E/RT) + \text{Constant} \qquad (2)$$

From the curves α vs. T for various heating rates, it is possible to determine the temperatures corresponding to a given degree of conversion. Then, from the slope of the lines obtained plotting the logarithm of the heating rate vs. the reciprocal of the absolute temperature, the apparent activation energy E can be calculated. Figures 3 and 4 show the so-called Ozawa plots obtained for PVP in nitrogen and ox-

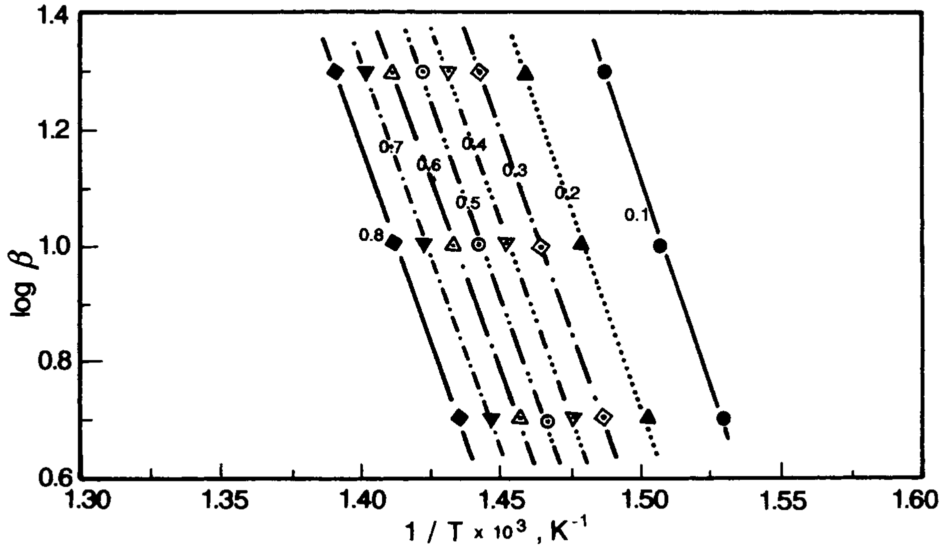


Figure 3 Logarithm of the heating rate (β) vs. the reciprocal of the absolute temperature for PVP under nitrogen atmosphere, for the values of conversion α indicated in the diagrams.

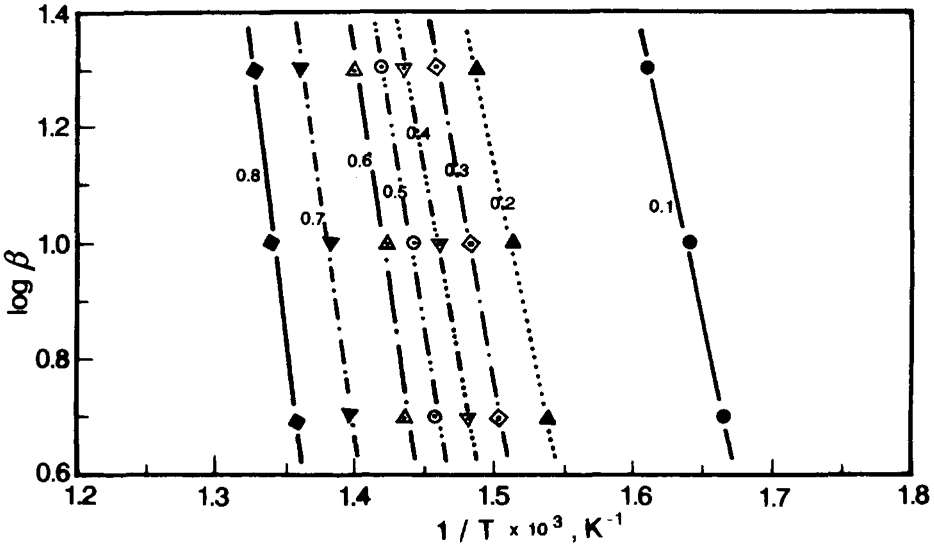


Figure 4 Logarithm of the heating rate (β) vs. the reciprocal of the absolute temperature for PVP under oxygen atmosphere, for the values of conversion α indicated in the diagrams.

ygen, respectively. A least-squares analysis leads to the activation energy values showed in Table I.

It can be seen from Table I that the apparent activation energy of the thermal degradation of PVP under nitrogen atmosphere has an average value of 242 kJ/mol in the whole temperature interval studied. However, when the thermal degradation is carried out under oxygen atmosphere, two distinct apparent activation energy values can be reported: a value of 199 kJ/mol for $\alpha < 0.5$ (corresponding to temperatures lower than 430°C) and 306 kJ/mol for $\alpha > 0.5$ (corresponding to temperatures higher than 430°C). These results are consistent with the two degradation steps reflected in the thermogram drawn in Figure 1 and explain the characteristic effect of the oxygen in both temperatures intervals, since the formation of peroxides at low temperatures gives rise to a decrease of the apparent activation energy of the degradative process, considering that a free-radical mechanism is followed.

Table I Dynamic TGA of PVP in Nitrogen and in Oxygen Atmospheres and Apparent Activation Energy, E_a, of the Main Degradation Step Determined for Several Degrees of Conversion, α

	E_a (kJ/mol)	
α	PVP (N_2)	PVP (O_2)
0.1	250.8	197.7
0.2	244.5	203.6
0.3	245.0	175.6
0.4	244.1	217.4
0.5	247.5	267.9
0.6	240.4	326.0
0.7	243.3	296.4
0.8	245.0	339.8
0.9	222.0	301.4

Isothermal Experiments

To gain additional insight into the mechanism of degradation of PVP, the thermogravimetric behavior under isothermal conditions in the temperature interval corresponding to the first degradation step of PVP in nitrogen atmosphere was studied. The kinetic study was carried out by recording thermograms in isothermal conditions at 350, 375, and 400°C. In all cases, a limiting weight loss amounting to 87% of the total sample weight was reached after treatments of 60 min. The resulting α vs. time curves for the three temperatures studied are shown in Figure 5. From these diagrams, the activation energy values were determined according to the following procedure:

If the kinetic expression for the decomposition process is considered to be

$$-d\alpha/dt = k \cdot F(1-\alpha) \tag{3}$$

and its integrated form is

$$F(1-\alpha) = k \cdot t \tag{4}$$

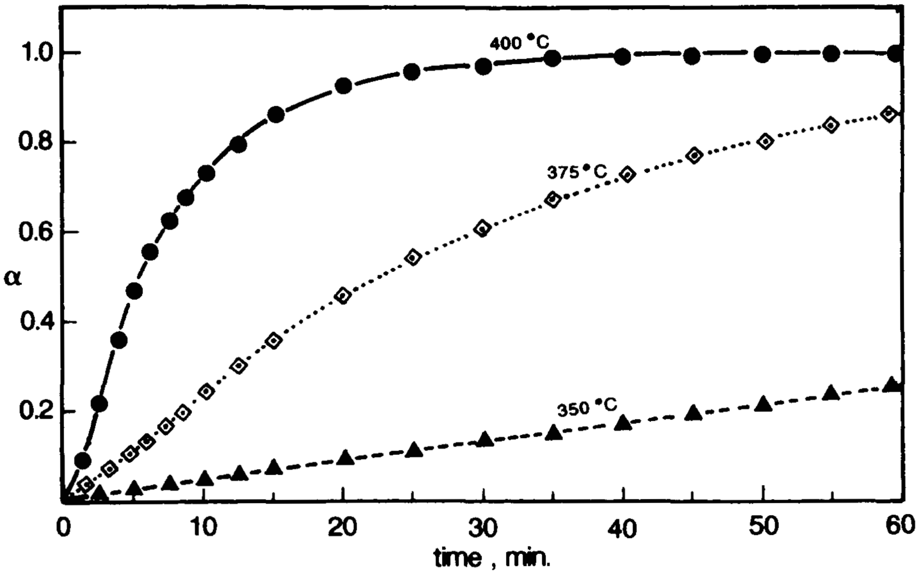


Figure 5 Isothermal TGA of PVP. Plots of the degree of conversion (α) vs. time at 250, 275, and 300°C under nitrogen.

provided that the values of $F(1-\alpha)$ for a given value of α does not depend on the temperature, eq. (4) can be written considering the expression of Arrhenius $k = A \cdot e^{-E/RT}$ as

$$F(1-\alpha) = A \cdot e^{-E/RT} \cdot t$$

$$\text{or} \quad e^{E/RT} \cdot F(1-\alpha)/A = t$$

and, therefore,

$$E/RT + \ln[F(1-\alpha)] - \ln A = \ln t \qquad (5)$$

Using eq. (5), plots of the time necessary to reach a certain degree of conversion vs. the inverse of temperature were drawn. They are shown in Figure 6, and the apparent activation energies obtained

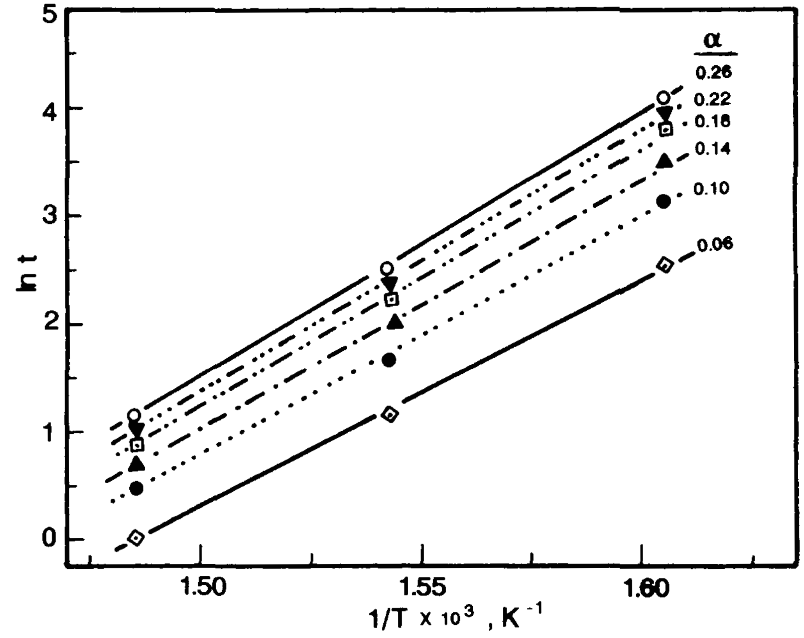


Figure 6 Plot of the logarithm of the time necessary to reach a given degree of conversion (α) vs. the inverse of the absolute temperature for the isothermal degradation of PVP under nitrogen atmosphere.

Table II Isothermal TGA of PVP in Nitrogen Atmosphere and Apparent Activation Energy in the Temperature Interval 350–400°C of the Main Degradation Step Obtained at Various Degrees of Conversion

α	0.06	0.10	0.14	0.18	0.22	0.26
E_a (kJ/mol)	208.0	208.6	209.5	210.0	209.8	210.5

from the slopes of the lines are listed in Table II for the conversion interval studied. The apparent activation energy values obtained are in the range of those reported in Table I for the dynamic experiments.

TGA-FTIR Analysis

The IR spectra of the residues of isothermal degradation of PVP in nitrogen and in oxygen are shown in Figure 7. It can be observed that the IR spectra of the residues obtained after 1 h at 350 and 375°C under nitrogen and oxygen exhibit all the characteristic peaks of the starting material and do not provide enough information on the degradation process. To clarify the degradative mechanism of the thermal treatment of PVP, we decided to apply the combined technique of thermogravimetric analysis coupled to the FTIR of the volatile released products.

The study of the thermal behavior of polymeric systems combining the traditional thermogravimetric analyzer (TGA) with FTIR can be very useful, since it provides an adequate way to simultaneously characterize the thermal behavior and, subsequently, to analyze decomposition products.[13] In this sense, we applied this treatment to the thermal degradation of PVP in N_2 or a combined N_2/O_2 atmosphere, in the experimental conditions indicated above.

In experiments carried out under N_2 atmosphere, the reconstruction of a Gram–Schmidt chromatogram[14] gives only one intense peak in the interval 8–12 min, with a width at half-height of 1.3 min. Figure 8(a) shows the FTIR spectrum of volatile

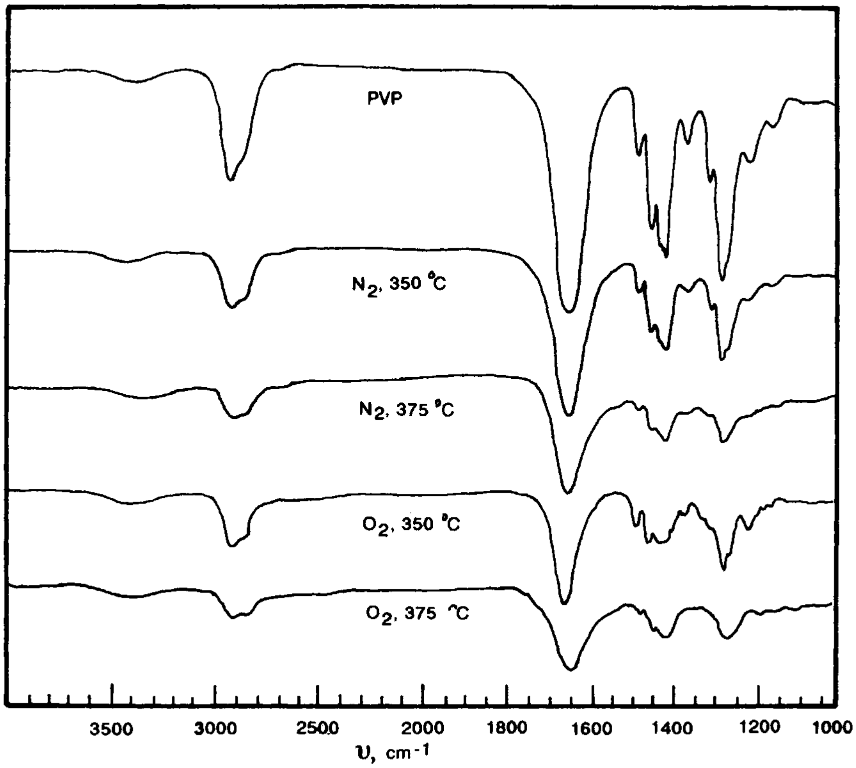


Figure 7 Infrared spectra of PVP and the residues obtained after 1 h of treatment in the experimental conditions indicated in the spectra.

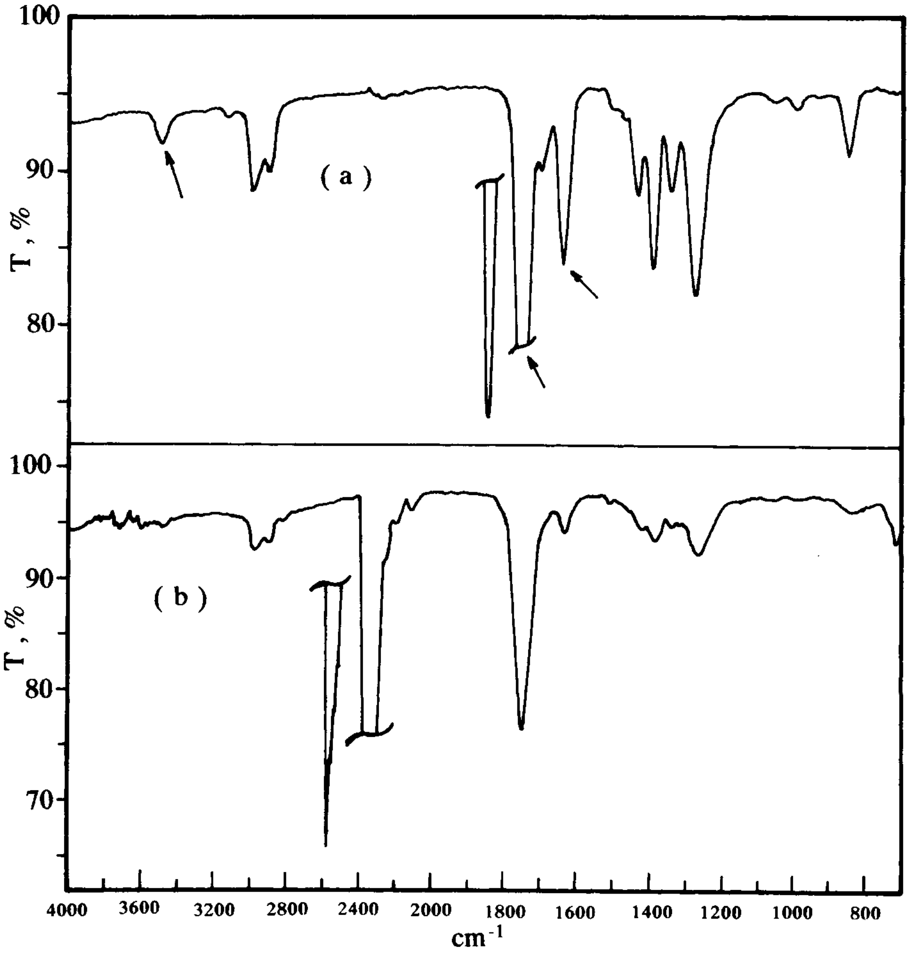
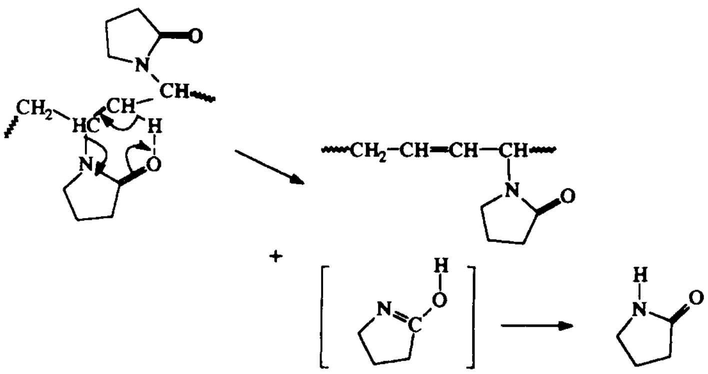


Figure 8 FTIR of volatile products of the thermal degradation of PVP in (a) N_2 atmosphere and (b) N_2/O_2, 67/33 v/v %, atmosphere.

compounds evolved during the treatment. It is interesting to stress that there is a clear difference in the spectrum of PVP or those of residues after thermal treatments programmed, shown in Figure 7. The carbonyl carbon absorption of PVP at 1661 cm^{-1} is shifted to 1750 cm^{-1} in the spectrum of the collected degradation products, which could be assigned to monosubstituted lactams. This assignment is supported by the appearance of signals at 1633 and 3480 cm^{-1} [marked by arrows in Fig. 8(a)], typical of groups N — H.[14] This spectrum strongly suggests the formation of pyrrolidone as the main product of the thermal degradation of PVP in the interval of temperatures studied in the present work.

Figure 8(b) shows the FTIR spectrum of the degradation products evolved in the thermal process under oxidant conditions, i.e., N_2/O_2, 67/33, v/v %. The Gram–Schmidt chromatogram in this case has two main components that appear in the interval 8–10 min, with a very sharp distribution (a half-height of 0.70 min) associated with the main components identified in the FTIR spectrum: the sharp absorption described for pyrrolidone at 1750 cm^{-1} and the typical absorption of CO_2 at 2363 cm^{-1}.[14] This spectrum justifies the formation of pyrrolidone and the oxidation of polyenic sequences that at the temperature of degradation (above 400°C) are not stable even in an inert atmosphere.

It is well known that a number of polymers are thermally degraded by releasing the side substituents giving rise to the formation of volatile products of known chemical composition and structure and the formation of polyenic chains that subsequently give rise to the formation of oxidation products in the presence of oxygen (mainly CO_2) or, alternatively, aliphatic and aromatic hydrocarbons of low molecular weight in an inert atmosphere. Perhaps the most classical example is the mechanism of degradation of poly(vinyl acetate) or copolymers ethylene–vinyl acetate, which release acetic acid when



Scheme 1

they are treated at temperatures higher than 250°C.[15] In the same way, poly(vinyl chloride) above 200°C is affected by degradation, releasing hydrochloric acid, and above 300°C, the polyenic sequences in polymeric chains give rise to the formation of low molecular weight aliphatic and aromatic hydrocarbons with benzene and toluene in high yield.[15]

On the other hand, it has been suggested[16,17] that the mechanism of the thermal degradation of poly(vinyl alcohol) might be similar to that of poly(vinyl acetate). Once one molecule of water is eliminated to produce the first double bond in the chain, the hydrogen of the methylene group in the α-position in respect to the double bond and the C — OH group are activated enough to release another molecule of water. Repetition of such a reaction would lead to a highly conjugated structure for the residue that is broken down at temperatures above 300–350°C.

According to the bond energy, the N — C linkage (292 kJ/mol) is weaker than the C — C (348 kJ/mol), C — O (351 kJ/mol), or C — H (391 kJ/mol).[18] Therefore, it can be reasonably expected that the thermal degradation proceeds through the breaking of the C — N bond better than the random scission of the C — C main chain. This behavior could justify the release of pyrrolidone as the main product of the initial step of the degradative pathway. Also, in the monomeric sequences along the polymeric backbone, the carbonyl oxygen of the pyrrolidone side ring may be rather close to the hydrogen atoms connected to the β-carbons of the main chain, since PVP presents a glass transition temperature, T_g, equal to 85°C,[9] higher than that of PVC (T_g = 81°C) or poly(vinyl acetate) (T_g = 32°C).[19] These facts support a degradative mechanism through the release of the pyrrolidone side group as it is represented in Scheme I, but as the release of this volatile fragment takes place at temperatures of 350–400°C, the polyenic sequences are not stable at the temperature of the process and therefore decompose to give a hydrocarbon compound of low molecular weight. This also explains the similar spectra of the residue of the polymer partially degraded at low temperature with the original PVP.

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REFERENCES

1. M. S. El-Aasser, Y. Y. Lu, C. M. Tseng, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **24,** 2995 (1986).
2. J. Ferguson and S. A. O. Strah, *Eur. Polym. J.*, **4,** 611 (1968).
3. J. Ferguson, S. Al Alawi, and R. Granmayer, *Eur. Polym. J.*, **19,** 475 (1983).
4. N. Shavit and J. Cohen, in *Polymerization in Organized Systems,* H. Elias, Ed., Gordon and Breach, London, 1977, p. 213.
5. F. Higashi and Y. Toguchi, *J. Polym. Sci. Poly. Chem. Ed.*, **18,** 2875 (1980).
6. F. Higashi, K. Sano, and H. Kakinohi, *Polym. Prepr. Jpn.*, **25,** 52 (1979).
7. F. Higashi, K. Sano, and H. Kakinohi, *J. Polym. Sci. Polym. Chem. Ed.*, **18,** 1841 (1980).
8. B. D. Ratner, in *Comprehensive Polymer Science,* G. Allen and J. C. Bevington, Eds., Pergamon Press, Oxford, 1989, Vol. 7, p. 215.
9. D. Zaldívar, C. Peniche, A. Bulay, and J. San Román, *Polymer,* **33,** 4625 (1992).
10. C. Peniche, D. Zaldívar, A. Bulay, and J. San Román. *Polym. Degrad. Stab.*, **39,** 21 (1993).

11. C. D. Doyle, *J. Appl. Polym. Sci.,* **6,** 639 (1962).
12. T. Ozawa, *Bull. Chem. Soc. Jpn.,* **38,** 1881 (1965).
13. J. Khorami, A. Lemieux, H. Menard, and D. Nadeau, in *Compositional Analysis by Thermogravimetry,* C. M. Earnest, Ed., ASTM, Baltimore, MD, 1988, p. 147.
14. D. O. Hummel and F. Scholl, *Atlas of Polymer and Plastics Analysis,* 2nd ed., VCH and Carl Hanser Verlag, Munich, 1988, Vol. 1.
15. N. Grassie, in *Polymer Handbook,* 3rd ed., J. Brandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1989, p. II/365.
16. J. B. Gilbert and J. J. Kipling, *Fuel,* **12,** 249 (1962).
17. R. T. Conley and R. Malloy, in *Thermal Stability of Polymers,* R. T. Conley Ed., Marcel Dekker, New York, 1970, p. 263.
18. B. Wunderlich, *Thermal Analysis,* Academic Press, San Diego, CA, 1990, p. 70.
19. P. Peyser, in *Polymer Handbook,* 3rd ed., J. Brandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1989, p. VI/209.

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