Influence of Chain Microstructure on Thermodegradative Behavior of Furfuryl Methacrylate-N-Vinylpyrrolidone Random Copolymers by Thermogravimetry

CARLOS PENICHE,[1] DIONISIO ZALDÍVAR,[1] ANNA BULAY,[2] and JULIO SAN ROMÁN*,[3]

[1]Centro de Biomateriales, Universidad de la Habana, 10400 Havana, Cuba, [2]Plastmassi, Petrovsky Proezd 35, 111 112 Moscow, Russia, and [3]Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006-Madrid, Spain

SYNOPSIS

The thermal behaviour of random copolymers of furfuryl methacrylate (F) and N-vinylpyrrolidone (P) was studied by means of dynamic thermogravimetric analysis (TGA) in the range 100–600°C. The dynamic experiments show that these copolymers exhibit two degradation steps in the intervals 260–320°C and 350–520°C, respectively. The normalized weight loss in the low temperature interval increases as the mole fraction of F in the copolymer m_F increases, whereas an inverted trend in the high temperature interval is observed. The apparent activation energy E_a of the first degradation step for copolymers prepared with different composition, was obtained according to the treatment suggested by Broido. A plot of the values of E_a versus the F diad molar fraction in the copolymer chains m_{FF} gave a straight line that indicates that there is a direct relationship between the thermogravimetric behaviour of these systems and their corresponding microstructure, that is, the distribution of comonomeric units along the copolymers chains. The first decomposition step was also studied by isothermal TGA and a good linearity for the variation of the weight loss percentage ΔW versus m_F at least during the first 30 min of treatment was obtained. These results also indicate that from a kinetic point of view the isothermal degradation in these conditions follows a first order behaviour and the corresponding reaction rate constants increase linearly with m_{FF}. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

After the last energy crisis the advanced countries have demonstrated an increasing interest toward the use of renewable raw materials for many different applications in the field of materials science and technology. In this sense we have been interested in the rational use of acrylic derivatives of furfural because of its accessibility from vegetable residues rather abundant in Cuba, such as corn husks and sugar cane.[1] In order to synthesize polymeric systems that could be used as biomaterials for biomedical applications, we have studied recently the behaviour in free radical copolymerization and the properties of copolymers of the couple furfuryl methacrylate-

N-vinylpyrrolidone.[2] The polymers and copolymers obtained at low and high conversion in solution of dimethylformamide are readily soluble in several polar solvents, but they become cross-linked if the polymerization is carried out in the presence of oxygen or simply if poly(furfuryl methacrylate) or F-P copolymers are dried in air at relatively low temperatures (50–60°C). This may be a consequence of the low stability of the C — H bond in the position 5 of the furfuryl ring, which is very sensitive to oxidative reactions promoted by O_2 and even catalyzed by the UV component of sunlight.[1] In order to attain a deeper insight into this behaviour the thermal degradation of poly(furfuryl methacrylate)[3] and poly(N-vinylpyrrolidone)[4] has been analyzed previously by thermogravimetry, using N_2 as an inert atmosphere as well as under thermooxidative conditions in the presence of O_2. In the present article the influence of the chain microstructure of F-P co-

---

* To whom correspondence should be addressed.

polymers on their thermodegradative behaviour is described.

EXPERIMENTAL

Monomer Preparation

Furfuryl methacrylate (F) was prepared by transesterification of methyl methacrylate with furfuryl alcohol in the presence of sodium carbonate as catalyst and ionol as inhibitor following the procedure described elsewhere.[2]

N-vinylpyrrolidone (P), supplied by Fluka, was distilled under reduced pressure and used without further purification.

2,2'-Azobisisobutyronitrile was purified by fractional crystallization from methanol, mp = 104°C.

N,N-Dimethylformamide (DMF) was dried over anhydrous magnesium sulphate for 2 days and later with phosphoric anhydride overnight. After drying DMF was distilled under reduced pressure of nitrogen. Other reagents were of extra-pure grade and used as purchased.

Polymerization Procedure

Free radical polymerization of P and copolymerization with F were performed in DMF solution at 50°C, in Pyrex glass ampules sealed under high vacuum. Monomer and initiator concentrations were 1.0 mol/L and 1.5×10^{-2} mol/L, respectively. The sealed ampules were shaken vigorously and immersed in a water bath held at the required temperature of polymerization. After the proper reaction time, the ampules were removed from the bath and at once the content was poured into a large excess of diethyl ether. The precipitated samples were washed with the precipitant and dried under vacuum until constant weight was attained.

The polymerization of F was carried out under the same conditions described above, but using benzene as solvent and methyl alcohol as precipitant.

Polymer Characterization

The copolymers obtained from mixtures of F and P as well as the corresponding homopolymers were analyzed by ^{1}H-NMR spectroscopy with a Bruker AM-200 spectrometer working at 200 MHz. The spectra were recorded at 40°C on 5% (w/v) solutions. Deuterated chloroform was used as solvent for the copolymers as well as for poly(furfuryl methacrylate), whereas for poly(N-vinylpyrrolidone) the solvent used was deuterated water.

Thermal Degradation

Dynamic and isothermal thermogravimetric analysis were carried out with a Thermobalance Perkin–Elmer TGS-2 system, coupled to a microprocessor programmer System-4 as the temperature control unit. All the thermogravimetric analysis were performed with 6–8 mg of finely powdered samples in a platinum pan under nitrogen atmosphere with a constant flow of 50 mL/min. Dynamic experiments were run at a constant heating rate of 10°C/min. In isothermal experiments, the samples were dried in the oven at 150°C for 20 min and then heated at 100°C/min until the experimental temperature was reached (a few seconds), taking as the zero time the point in which the temperature of the system was stabilized automatically.

RESULTS AND DISCUSSION

F and P copolymerize readily by a free radical mechanism in the experimental conditions outlined above, giving rise to the formation of linear (not cross-linked), random copolymers in the whole interval of compositions. The average molar composition of the monomer feed and that of the corresponding copolymers samples prepared at low conversion are quoted in the first and second columns of Table I. The composition of copolymer samples was determined by ^{1}H-NMR spectroscopy according to the method reported previously.[2] The reactivity ratios of these monomers were determined by the application of linearization methods of the general copolymer composition equation, according to the terminal copolymerization model suggested by Lewis and Mayo[5] as well as by the application of the nonlinear least squares analysis reported by Tidwell and Mortimer,[6] being the most approximate values $r_F = 3.92$ and $r_P = 0.004$.[2] These values make clear the strong tendency to cross propagation for macroradicals ending in active units of P in comparison with the relatively high tendency of F toward the addition to F ending active macroradicals. This means that for a wide composition interval the P units will be isolated in sequences of F units.

From the values of the reactivity ratios r_F and r_P, the first order Markovian transition probabilities P_{FP}, P_{PF}, P_{FF}, and P_{PP} can be determined according to the following equations[7]:

$$P_{FP} = 1 - P_{FF} = 1/(1 + r_F \cdot X) \qquad (1)$$

$$P_{PF} = 1 - P_{PP} = 1/(1 + r_P/X) \qquad (2)$$

Table I   Composition, Conditional Probabilities FF, Diad Molar Fraction, and Run Number Data of F-P Copolymers Obtained by Free Radical Copolymerization of Furfuryl Methacrylate (F) and N-Vinylpyrrolidone (P) in DMF Solution at 50°C

Feed (M_F)	Copolymer (m_F)	Conversion (Wt %)	p_{FP}	P_{PP}	m_{FF}	R
0.050	0.53_4	3.0	0.829	0.929	0.084	88.3
0.100	0.56_0	3.5	0.697	0.965	0.161	82.1
0.150	0.60_1	2.9	0.591	0.978	0.248	75.3
0.200	0.64_2	3.8	0.505	0.984	0.297	68.6
0.400	0.80_1	3.7	0.277	0.994	0.566	45.4
0.500	0.87_3	3.8	0.203	0.996	0.664	35.7

M_F and m_F are the molar fraction of P in the monomer feed and in the copolymer samples, respectively.

where $X = [F]/[P]$ is the ratio of the concentration of F and P in the monomer feed and P_{ij} are the conditional probabilities, that is, the probability that a monomer j (j = F or P) adds to an i (i = F or P) ending radical.

The parameters P_{ij} enable the determination of other important statistical parameters that characterize the microstructure of the copolymer, the distribution of comonomeric units along the copolymer chain. In this way the molar fraction of ij diad sequences m_{ij} can be determined from the relation $m_{ij} = m_i \cdot P_{ij}$, where m_i is the molar fraction of monomer i in the copolymer. Also, the run number "R" defined by Harwood and Ritchey[8] as the average number of monomers alternations in a copolymer for sequences of 100 monomeric units is quite useful for characterizing the sequence distribution and can be used to estimate the variation of the physical properties of copolymers with the composition. This parameter can be determined by the expression:

$$R = 200/(2 + r_F \cdot X + r_P/X). \qquad (3)$$

The values of the conditional probabilities P_{ij}, molar fraction of diads m_{FF} and R has been collected in Table I for the experimental compositions used in the present work.

TGA Dynamic Experiments

The thermograms of F-P copolymers obtained at a constant heating rate of 10°C/min under nitrogen atmosphere has been drawn in Figure 1, together with those of the corresponding homopolymers poly-F and poly-P. The degradation process of poly-F in nitrogen atmosphere exhibits two distinct steps. In the first the weight loss starts at temperatures of 230–240°C up to a temperature of 340–350°C cor-

responding to the 70% weight loss. The second step, which corresponds to the 20% weight loss, is complete at 530–550°C, with a residue not volatilized at 600°C of about 9 wt %. In a previous work[3] we suggested that the thermal degradation of poly-F proceeds through the formation of cyclic structures of 2,4-dimethylglutaric anhydride in the macromolecular chains, together with the partial depolymerization of polymer segments as well as intermolecular cross-linking through the reaction of the relatively reactive C — H bond in the position 5 of some furfuryl side aromatic rings.

However, the thermal degradation of poly(vinyl pyrrolidone) in the experiment causes the cleavage of the pyrrolidone side ring about 280–300°C; but the polyenic sequences formed as a consequence of the volatilization of the pyrrolidone residue are not stable enough at these temperatures suffering the
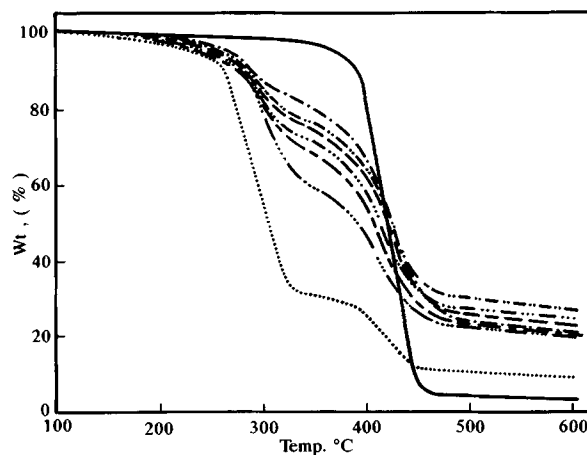

Figure 1   Thermogravimetric curves for the decomposition of poly-P (—), poly-F (· · ·) and F-P copolymers heated at 10°C/min under nitrogen. (– · – ·) $m_F = 0.53$; (– · · –) $m_F = 0.56$; (– –) $m_F = 0.60$; (– · · · –) $m_F = 0.64$; (— –) $m_F = 0.80$; (– · · · · –) $m_F = 0.87$.
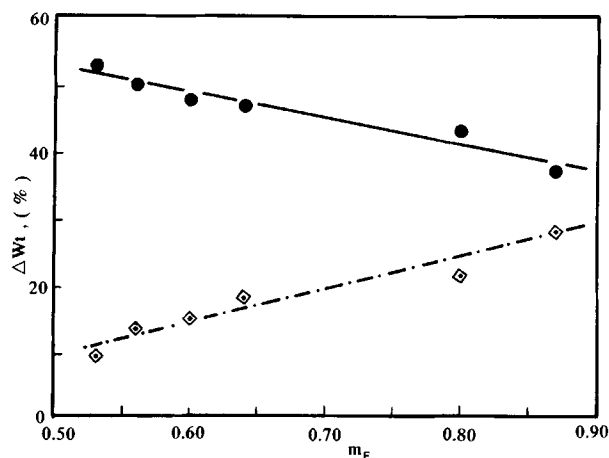
Figure 2   Percent weight loss versus mole fraction of furfuryl methacrylate (m_F) for the two degradation stages of F-P copolymers. ($\Diamond$) 260–320°C; ($\bullet$) 350–530°C.

random scission, giving a thermogram that reflects the practically total loss of weight when a temperature of 550°C is reached.[4] The permanent residue at 600°C amounts to only 3.4%.

In view of the differences of the thermal behaviour of both polymers poly-F and poly-P, we considered that it could be interesting to study the influence of the composition of F-P copolymers in the thermal degradation processes of random homogeneous copolymers prepared at very low conversion. As it can be observed in the thermogravimetric curves drawn in Figure 1, the diagrams of F-P copolymers lie between those of the corresponding homopolymers, as it happens in general with random copolymer systems.[9] Similar to poly-F, the diagrams of all the copolymer samples studied show two well-distinguished decomposition stages; but there is a clear dependence of the intensity of the weight loss as-

sociated with the average composition of the corresponding copolymers.

The first degradation step for copolymers F-P starts approximately at a temperature of 260°C and continues up to 320°C, with a weight loss that increases as the mole fraction of F in the copolymer m_F increases, whereas the second one occurs in the temperature interval 350–530°C, with a weight loss that decreases as m_F increases. As shown in Figure 2, the variation of the percent weight loss shows a well-defined linear dependence. However, the temperature of the maximum decomposition rate T_{MDV} for the first degradation step (Table II) does not seem to present a clear dependence with the copolymer composition. Another interesting fact is that the residue at 600°C represents only 9 wt % for poly-F and only 3.4 wt % for poly-P. However, in the fourth column of Table II, the copolymer sample show a residue higher than 20% for all the copolymer samples studied. Probably the presence of isolated P units between relatively long sequences of F provides structures in which the isolated double bonds formed by the thermal cleavage of the pyrrolidone side residue, gives rise to more stable segments than the conjugated polyenic sequences arising from the thermal degradation of pure poly-P homopolymer.[4] The relative stabilization of thermal degradation by copolymerization with respect to pure homopolymers, has been reported for several systems. For example, the stabilization of structures of methyl methacrylate units in polymeric systems derived from this monomer in copolymers with other acrylic monomers such as methyl[10] or butyl[11] acrylates, or even with styrene,[12] has been explained considering a change in the mechanism of unzipping depolymerization of methyl methacrylate sequences by the introduction of other comonomeric units that follow

Table II   Apparent Activation Energy for the First Decomposition Stage of poly-F and F-P Copolymers (Broido's method)

m_F	E_a (kJ/mol)	T_{MDV} (°C)	Residue at 600°C (Wt %)
0.53	260.4	286	25.0
0.56	249.4	300	22.9
0.60	245.7	300	26.5
0.64	231.1	297	23.5
0.80	207.5	310	21.6
0.87	172.5	296	21.0
1.00	146.0	300	9.0

The temperature of maximum decomposition rate (T_{MDV}) for this stage and the residue at 600°C are also shown.
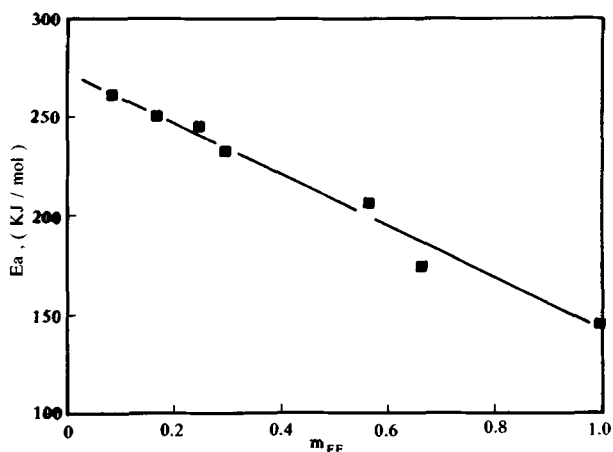
Figure 3 Apparent activation energy values for the first degradation step of poly-F and F-P copolymers (Broido's method) as a function of F molar diad fraction (m_{FF}).

other thermodegradative mechanisms. In these cases, it has been considered that the depolymerization process, once initiated, proceeds up to the first different unit and might then stop because of some alternative reaction of the new type of radical chain end.[9]

The apparent activation energy for the first step of the thermal degradation of poly-F and copolymers F-P were determined from the thermogravimetric curves following the method suggested by Broido.[13] The kinetic treatment considers the following equation for dynamic experiments carried out at constant heating rate:

$$\ln[\ln(1/Y)] = -E_a/RT$$
$$+ \ln[(R/E_a)(Z/RH)T_m^2] \quad (4)$$

where Y is the fraction of initial molecules that remains in the original state, not decomposed; T_m is

the temperature of the maximum reaction rate of weight loss; and RH is the heating rate. From the slope of the plots of $\ln[\ln(1/Y)]$ versus $1/T$ can be determined E_a considering that the degradation process follows a single mechanism. Values of E_a for copolymer samples with different composition are collected in the second column of Table II. In all instances, the values were determined using the least squares method with a 95% confidence interval. The value of E_a obtained for the homopolymer poly-F agrees reasonably well with the results obtained by the application of the method suggested by Ozawa,[14] which gave a value of $E_a = 163$ kJ/mol for the first step of the thermal degradation process of poly-F in the same experimental conditions used in this work.[3] The data quoted in the second column of Table II, makes clear that E_a decreases with increasing m_F. Moreover, Figure 3 shows the diagram of the variation of E_a with the molar fraction of diad sequences of F m_{FF}, giving a straight line that demonstrates that there is a direct influence not only of the average composition of copolymer samples, but also of the distribution of monomeric units along the copolymer chains, reflecting the importance of the microstructure in determining the response of a copolymer system when subjected to a thermodegradative process. In fact, we have reported that the analysis of products of poly-F partially degraded indicate the formation of cyclic structures of 2,4-dimethylglutaric anhydride along the polymeric chains as indicated in Scheme I.[3] This means that if this mechanism holds in the case of copolymers, the presence of two consecutive units (a diad FF) is necessary for the formation of one cycle of 2,4-dimethyl glutaric anhydride in the main chain. The probability that sequences of F participate in the formation of such anhydride structures increases with increased av-
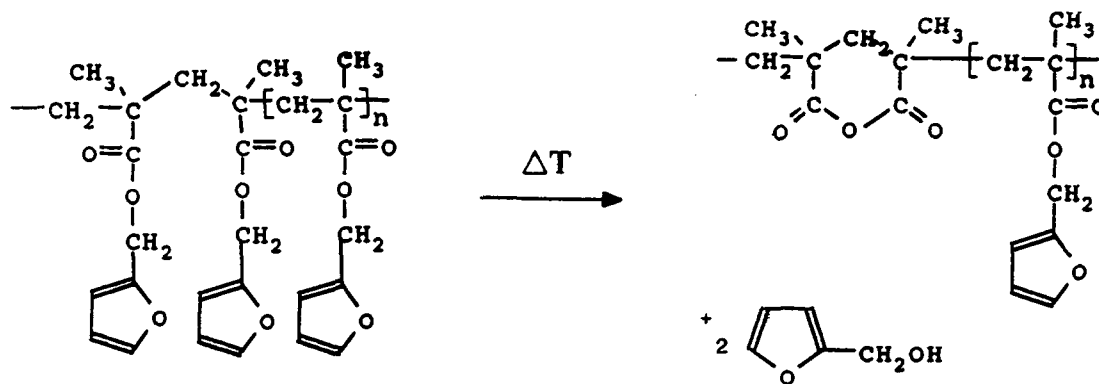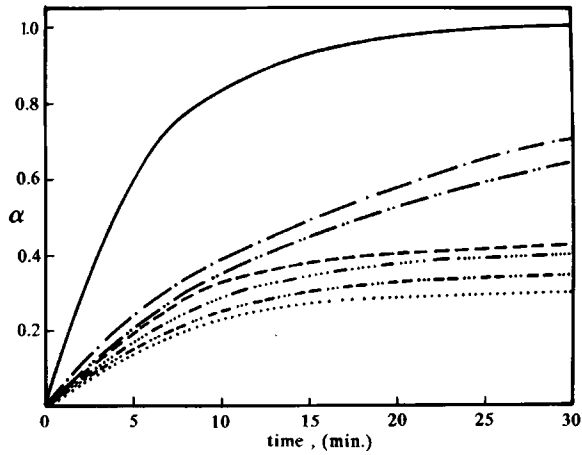

Scheme 1

Figure 4   Isothermal TGA of poly-F and F-P copolymers. Plot of the degree of conversion, α, versus time at 275°C under nitrogen. (—), poly-F; ($\cdots$) $m_F = 0.53$; (— $\cdots$) $m_F = 0.56$; (— $\cdots$ —) $m_F = 0.60$; (— —) $m_F = 0.64$; (— $\cdot$ —) $m_F = 0.80$; (— $\cdot$) $m_F = 0.87$.

erage molar fraction of F in the copolymer chains, which in turn is favoured according to the values of the reactivity ratios mentioned for this copolymerization system.

Isothermal Experiments

The kinetic behaviour of the copolymerization system F-P was also studied in isothermal conditions in order to obtain accurately the kinetic parameters and the possible influence of the microstructural characteristics as outlined. Figure 4 shows the dia-
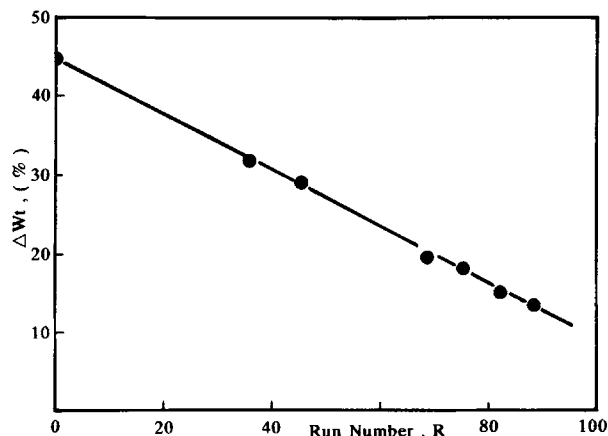

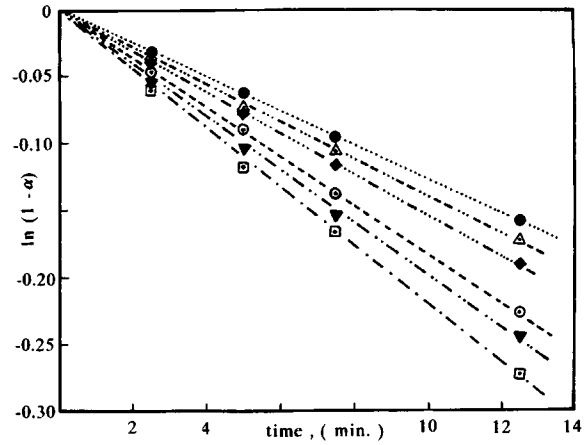**Figure 6**   Isothermal TGA of F-P copolymers. First-order logarithmic plots for the initial 15 min heating at 275°C under nitrogen. (●) $m_F = 0.53$; (△) $m_F = 0.56$; (◆) $m_F = 0.60$; (○) $m_F = 0.64$; (▼) $m_F = 0.80$; (□) $m_F = 0.87$.

grams of the conversion degree α with the time of treatment at a constant temperature of 275°C. It is clear from this figure that in all cases the F-P system seems to reach a limit conversion in a treatment time of about 20 min, with increasing values of α as the molar fraction of F in the copolymer chains increases. As we have indicated before, the run number is a statistical parameter characterizing the microstructure of copolymer chains, and gives a clear idea of the average number of alternates of both co-monomeric units along the copolymer segments for high molecular weight copolymers. In this way, Figure 5 shows the diagram of the limit percentage weight loss after 30 min of treatment as a function
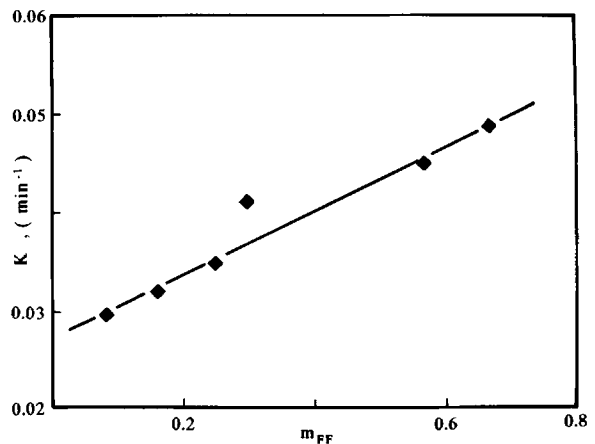

Figure 5   Percent weight loss (ΔW) of poly-F and F-P copolymers after 30 min of isothermal experiments at 275°C under nitrogen versus the run number, R.

Figure 7   First-order reaction rate constant (k_1) for the initial 15 min of isothermal degradation of F-P copolymers at 275°C under nitrogen versus m_{FF}.

Table III   First Order Reaction Rate Constants for the Isothermal Decomposition of poly-F and F-P Copolymers at 275°C in Nitrogen Atmosphere

m_F	0.53	0.56	0.60	0.64	0.80	0.87	1.00
k_1 (min^{-1})	0.029	0.032	0.035	0.041	0.045	0.049	0.182

of the run number of the corresponding copolymer samples analyzed. The straight line obtained indicates the direct relationship between the cleavage of the furfuryl residues and the subsequent formation of cyclic structures in the copolymer backbone, with the presence of sequences of F units that makes this mechanism possible. According to this diagram, when the number of sequences of F units is small (high run number), the percentage weight loss is also very low; that is, in the diagram a run number of about 85 corresponds to a weight loss of about 12%, whereas if the run number decreases to 40, the limit weight loss amounts to 30%.

In all cases, the kinetics of the thermal process during the first 15–20 min of isothermal treatment at 275°C fits a first-order scheme satisfactorily (Fig. 6). The reaction rate constants obtained from the slope of these diagrams are collected in the Table III. Finally Figure 7 shows the linearity of the variation of the average kinetic rate constant with the molar fraction of F diads along the copolymer chains. This result makes clear that in the experimental conditions of the isothermal treatment, the degradation mechanism is the same for all the copolymer samples analyzed and correlates mainly with the elimination of furfuryl residues and the formation of cyclic anhydride structures. The presence of vinyl pyrrolidone units has little effect in this step of the degradative process, because it represents only the disruption of F pure sequences, which is also noted by the variation of the limiting conversion of the degradative process under the mild isothermal conditions used.

REFERENCES

1. A. Gandini, in *Comprehensive Polymer Science,* 1st Suppl., S. L. Aggarwal and S. Russo, Eds. Pergamon Press, Oxford, 1992, p. 527.
2. D. Zaldívar, C. Peniche, A. Bulay, and J. San Román, *Polymer,* **33,** 4625 (1992).
3. C. Peniche, D. Zaldívar, A. Bulay, and J. San Román, *Polym. Degrad. Stab.,* **40,** 287 (1993).
4. C. Peniche, D. Zaldívar, A. Bulay, and San Román, *J. Appl. Polym. Sci.,* **48,** (1993).
5. G. Odian, *Principles of Polymerization,* 3rd ed., Wiley, New York, 1991.
6. P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci. A,* **3,** 369 (1965).
7. J. L. Koenig, *Chemical Microstructure of Polymer Chains,* Wiley, New York, 1980.
8. H. J. Harwood and W. M. Ritchey, *J. Polym. Sci.,* **B2,** 601 (1964).
9. I. C. McNeill, in *Comprehensive Polymer Science,* Vol. 1, 1989 p. 483.
10. N. Grassie and B. J. D. Torrance, *J. Polym. Sci. A-1,* **6,** 3303, 3315 (1968).
11. N. Grassie and J. D. Fortune, *Makromol. Chem.,* **162,** 93 (1972); **168,** 1, 13 (1973); **169,** 117 (1973).
12. N. Grassie and E. Farish, *Eur. Polym. J.,* **3,** 305 (1967).
13. A. Broido, *J. Polym. Sci. A-2,* **7,** 1761 (1969).
14. T. Ozawa, *Bull. Chem. Soc. Jpn.,* **38,** 1881 (1965).