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DEGRADATION OF PHOSPHORYLATED POLY(*N*-VINYLCARBAZOLE) BY THERMOGRAVIMETRY†

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ABSTRACT

The thermal degradation of phosphorylated poly(*N*-vinylcarbazole) was studied by thermogravimetry. The onset degradation temperature decreases with respect to that of unmodified poly(*N*-vinylcarbazole), indicating a lower thermal stability for the phosphorylated sample. The activation energy values for the degradation process were calculated from the thermograms by treating it as a kinetic analysis; these values are smaller than those for unmodified samples and depend on molecular weight, phosphorous contents, and heating rate.

INTRODUCTION

Thermogravimetry is one of the most useful techniques in the study of thermal degradation of solids [1], and it can also be extended to the study of thermal stability and properties of polymers [2], copolymers [3], and composites [4].

†In memory of Prof. G. Martín Guzmán.

We use this technique to study how the thermal properties of polymers such as *N*-vinylcarbazole and acenaphthylene are modified by the introduction of several groups in their structure. Chemical modification of poly(*N*-vinylcarbazole) was the subject of several research papers [5–11], and it was made obvious that its thermal properties are modified when different groups are introduced in the carbazole group.

Pielichovski et al. [7] studied the phosphorylation reaction of poly(*N*-vinylcarbazole) as well as the kinetics of the thermal degradation of some phosphorylated derivatives. Our purpose with this work is to determine the influence of molecular weight and heating rate on the thermal degradation of phosphorylated poly(*N*-vinylcarbazole).

EXPERIMENTAL

Poly(*N*-vinylcarbazole) samples were obtained by cationic polymerization at 273 K using Ph_3CSbCl_6 as initiator and dichloromethane as solvent [12]. The samples were fractionated and characterized by gel permeation chromatography and viscometry as previously described [13]. Molecular weights are listed in Table 1. The polydispersity in all cases is ≤ 1.3.

A portion of each sample was phosphorylated by the method proposed by Pielichovski et al. [5]. $AlCl_3$ was used as catalyst, PCl_3 as phosphorylating reagent, and 1,2-ethylene chloride was employed as solvent at 343 K.

The C, H, and N contents of the phosphorylated samples were obtained using a Perkin-Elmer Elemental Analyzer 2400 CHN, and the phosphorous contents were determined by difference (Table 1). It was not possible to determine the molecular weight of phosphorylated samples as they were insoluble, so the values listed correspond to the unmodified samples.

Thermogravimetric degradations were carried out using a Perkin-Elmer Thermobalance TGS 2 in a dry nitrogen atmosphere. A standard procedure starting

TABLE 1. Characteristics and Thermal Properties (at β = 10°C/min) of the Samples

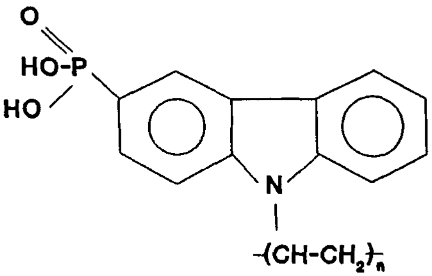
Sample	$M_w \times 10^{-6}$ [a]	% P	T_i, °C	E, $kJ \cdot mol^{-1}$
FR1-P	3.90	7.19	359	32.4
FR2-P	1.09	9.50	381	30.4
FR3-P	0.552	8.88	352	33.5
FR4-P	0.350	11.20	331	27.6
FR5-P	0.230	9.58	376	30.5
FR7	0.226	–	513	50.9
FR7-P	0.226	7.44	441	34.8
FR8	0.117	–	458	60.7
FR8-P	0.117	7.66	429	45.5

[a] Unmodified samples.

from room temperature and going to 900°C was followed for dynamic studies. Heating rates between 1 and 50°C·min^{-1} were employed.

RESULTS AND DISCUSSION

The IR spectra of phosphorylated samples showed a band at 900–1100 cm^{-1} ascribed to P—O—H groups and a remarkable wide band in the 1100–1230 cm^{-1} range due to superposition of P—O band vibrations and asymmetric vibration of PO_2^- groups. The remaining bands are specific for poly(*N*-vinylcarbazole). According to these results and the phosphorylation reaction carried out, the monomeric unit was concluded to be



Analysis of the phosphorus contents (Table 1) reveals that in some phosphorylated samples there is more than one H_2PO_3 group incorporated for each monomeric unit (11.4% would be the phosphorus content with one H_2PO_3 group per monomeric unit).

Figure 1 shows the percent weight loss as a function of temperature for the same sample at two heating rates, and Fig. 2 shows the same plot for both phosphorylated and unmodified samples. A similar behavior was observed for all the samples.

Analysis of the thermograms indicates that there is a slight weight loss (< 1%) from 100°C; this weight loss could be related to residual solvent, although all the samples were carefully dried. The unmodified samples reached 100% weight loss at 900°C (final temperature) while the phosphorylated samples showed a weight loss higher than 80% at this temperature. In these cases, however, the lack of organic residues indicated that degradations were complete.

The intersection of initial and final baselines with the experimental curve was used to define the onset (T_i) and final (T_f) temperatures of decomposition. Table 1 shows T_i values at 10°C·min^{-1}.

Comparison of the unmodified samples FR7 and FR8 and the phosphorylated samples FR7-P and FR8-P indicates that the T_i value decreases when the H_2PO_3 group is introduced. Taking the initial temperature as a measure of thermal stability, it can be concluded that the thermal stability of phosphorylated poly(*N*-vinylcarbazole) decreases with respect to the unmodified sample.

The same effect was reported by Trebacz [10] who studied several substituted poly(*N*-vinylcarbazoles); thus, the initial decomposition temperature goes from 250°C for the 3-iodo derivative to 378°C for the 3,6-diacetyl derivative. The de-

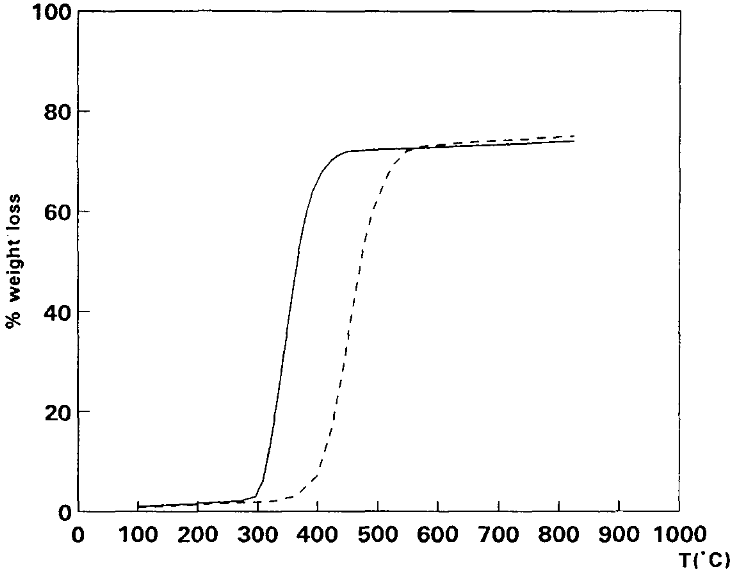


FIG. 1. Percent weight loss as a function of temperature: (——) 1°C/min, (- - -) 50°C/min.

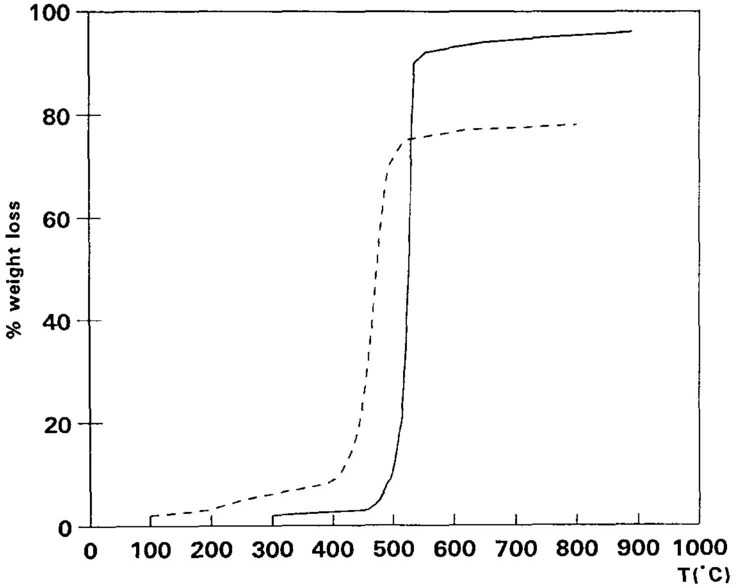


FIG. 2. Percent weight loss as a function of temperature: (——) unmodified, (- - -) phosphorylated.

crease in T_i results from the interaction among the substituents, the carbazole ring, and the main vinyl chain, and depends mainly on the size and electronegativity of the substituent group. These values, as in our case, are lower than those for the unmodified poly(*N*-vinylcarbazole), but the comparison of thermal stability of different derivatives is difficult because there is no information about molecular weight and substituted group contents.

There is no significant dependence of T_i on molecular weight (determined for the unmodified sample) as deduced from FR2-P and FR5-P samples. The phosphorus content is similar in both cases, but the molecular weights of the unmodified samples are very different. The same conclusion is reached from FR7-P and FR8-P samples.

Table 2 shows that there is a small increase of the initial temperature of decomposition with the heating rate, indicating higher thermal stability. This is probably due to problems related to heat diffusion in the sample matrix.

The kinetic parameters for the degradation process have been obtained by the McCallum and Tanner method [14]:

$$\log [F(C)] = \log \frac{AE}{\beta R} - 0.48E^{0.44} - \frac{0.45 + 0.22E}{T \times 10^{-3}}$$

where E is the activation energy, β is the heating rate, and A is the preexponential factor. $F(C)$ is tabulated for different reaction orders; if $n = 1$:

$$F(C) = -\ln (1 - C)$$

where C is the fractional weight loss.

A plot of log $F(C)$ vs $1/T$ (Fig. 3) shows that the linear portion is coincident with the characteristic step for the degradation process of phosphorylated poly(*N*-vinylcarbazole). The activation energy can be obtained from the slope (Tables 1 and 2). A comparison between unmodified samples (FR7, FR8) and the corresponding phosphorylated ones (FR7-P, FR8-P) indicates that a sizable decrease in the activation energy is caused by the introduction of the H_2PO_3 group in poly(*N*-vinylcarbazole). This can be explained by assuming that the species formed in the degradation process of phosphorylated samples are more unstable than those from

TABLE 2. Activation Energy and Onset of Decomposition Temperatures as a Function of β (heating rate) for Some Samples

	FR1-P		FR2-P	
β, °C·min^{-1}	T_i, °C	E, kJ·mol^{-1}	T_i, °C	E, kJ·mol^{-1}
1	311	35.6	—	—
2	319	32.5	354	31.1
10	359	32.4	381	30.4
20	—	—	391	28.8
30	—	—	399	28.7
40	399	28.8	402	27.2
50	407	28.3	—	—

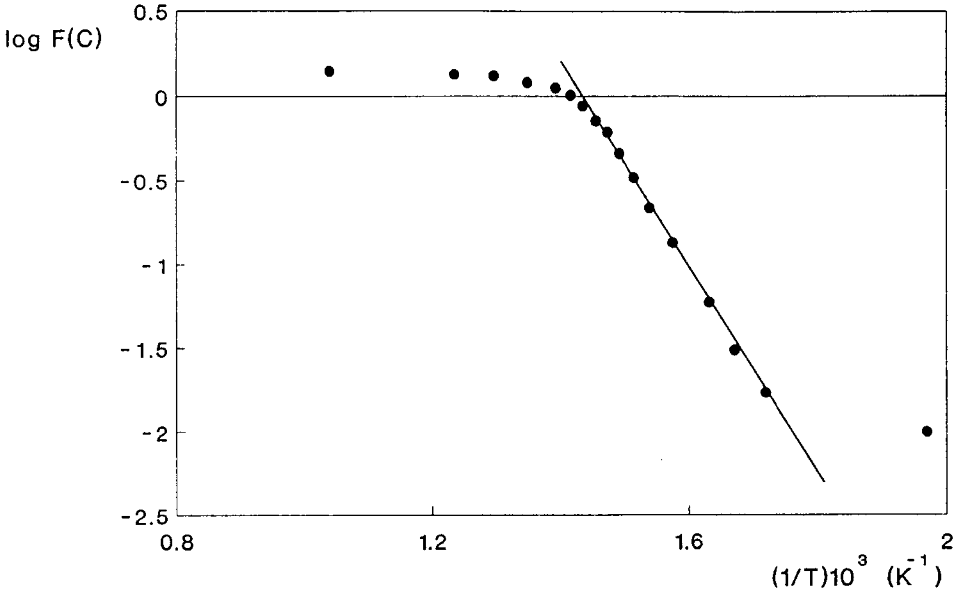


FIG. 3. Kinetic analysis by the McCallum and Tanner method.

unmodified samples. Therefore, the decrease in E is more pronounced the higher the phosphorus content of a sample. We can see this in samples FR5-P and FR7-P with similar molecular weights.

On the other hand, the activation energy does not depend on molecular weight when it is very high. This can be observed in samples FR2-P and FR3-P whose phosphorus contents are similar. The same behavior was suggested by González et al. [15] for unmodified poly(*N*-vinylcarbazole). This result can be explained by supposing that chain scission is unaffected by the rest of the chain segments. However, for low molecular weight materials the molecular weight has a relatively important effect on E for modified samples (samples FR7-P and FR8-P with similar phosphorus contents) as well as for unmodified ones (samples FR7 and FR8). This leads to the assumption that the degradation process could involve inter- and intramolecular interactions (flexibility effects).

Table 2 shows E and T_i values for two samples (FR1-P and FR2-P) at several heating rates. There is a small decrease in E and a remarkable increase in T_i when the heating rate is increased. This indicates that at higher heating rates the thermal stability increases, but when degradation begins, it occurs faster. This dependence shows the importance of heating rates in these studies.

CONCLUSIONS

The results of this work clearly show the decrease of thermal stability of poly(*N*-vinylcarbazole), as indicated by low E and T_i, when the H_2PO_3 group is introduced. This effect can be attributed to interactions of this group with the carbazole ring. Measurement conditions must also be controlled because they are important factors influencing the degradation temperature and kinetic parameter.

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