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Thermogravimetric study of the degradation of phosphorylated poly(acenaphtylene)

A. Flores, M. Rodríguez, L.M. León *

Departamento de Química Física, Facultad de Ciencias, Universidad del País Vasco (UPV/EHU), Apdo. 644-48080 Bilbao, Spain

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Abstract

The thermal stability of phosphorylated poly(acenaphtylene) has been studied and compared with that of the unmodified poly(acenaphtylene). The results indicate that the introduction of phosphorus into the polymeric chain gives rise to a decrease in the thermal stability this effect being related with the phosphorous content in the sample. Some differences have been found in the behaviour of low molecular weight poly(acenaphtylene) with respect to that of high molecular weight.

Keywords: Degradation; Poly(acenaphtylene); Thermal stability

1. Introduction

In a previous study [1] we have reported that the thermal stability of poly(acenaphtylene) does not depend on molecular weight but it is affected in some proportion by the heating rate. These results lead us to study how the thermal properties of this polymer are affected by the incorporation of phosphorus into the macromolecular chain. As in the previous work, the McCallum and Tanner method [2] has been employed to carry out the kinetic analysis from thermogravimetric data.

2. Experimental

Phosphorylated poly(acenaphtylene) (PACE) samples were obtained by phosphorylation of several PACE fractions using the same method proposed by

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* Corresponding author.

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Table 1
Characteristics of the phosphorylated poly(acenaphtylene) samples

Sample	[a]$M_n \cdot 10^{-5}$	[a]$M_w \cdot 10^{-5}$	%C	%H	%P
PACE-2P	4.85	6.51	66.2	4.75	11.4
PACE-3P	3.11	3.93	65.4	4.82	11.7
PACE-4P	2.04	2.53	62.5	4.87	12.8
PACE-0-5P	0.048	0.059	91.8	5.23	1.18
PACE-0-4P	0.048	0.059	84.7	4.99	4.06
PACE-0-3P	0.048	0.059	72.4	4.88	8.92
PACE-0-2P	0.048	0.059	70.4	4.95	9.68

[a] Unmodified samples.

Pielichowski et al. [3] for the phosphorylation of poly(N-vinylcarbazole). $AlCl_3$ was used as catalyst, PCl_3 as phosphorylating reagent and 1,2-ethylene dichloride as solvent, at 343 K.

All the PACE samples used for the phosphorylation reaction (except that named PACE-0) are the same as in the previous work [1], so that the synthesis and characterization have been already described.

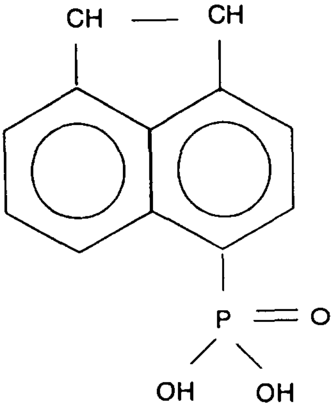
The sample PACE-0 has been synthesized by cationic polymerization of acenaphtylene using sulphuric acid as initiator and methylene dichloride as solvent, at 298 K [4]. It was characterized by Gel Permeation Chromatography (GPC) in a Waters chromatograph, using tetrahydrofuran as solvent, at 298 K. The Universal Calibration method [5] was employed to determine the molecular weight.

It was not possible to obtain the molecular weight of the phosphorylated fractions as they were insoluble; so the molecular weight which appears in Table 1 corresponds to the unmodified fractions.

The C and H contents for the phosphorylated samples were obtained by elemental analysis using a Perkin–Elmer Analyzer CHN 2400. IR spectra were performed in a Matson spectrometer mod. Polaris. Thermogravimetric degradations were carried out in a Perkin–Elmer Thermobalance TGS-2 using a stream of dry nitrogen. A standard procedure starting from room temperature and going to 900°C was followed for dynamic studies.

3. 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(acenaphtylene). According to these results, and from the phosphorylation reaction performed, we can conclude that the monomer unit is:



Since the characteristics of the incoming group have been established and from the known C and H contents of the samples, the phosphorous contents can be obtained as well. Table 1 shows these results as well as the molecular weight of the unmodified samples. As it can be seen from the table, two kinds of samples have been utilized: the samples PACE-2P, 3P and 4P, with high molecular weight and with a similar phosphorous content (near to 13.4% which would correspond to an H_2PO_3 group incoming for each monomeric unit); and the last four samples which have been obtained from a low molecular weight PACE sample (PACE-0) and which have different phosphorous contents.

In Table 2 the percent of phosphorylated monomeric units for all the samples as well as the final conversion (in % mass loss) are shown. Figure 1 shows the percent of mass loss as a function of temperature for both unmodified samples, PACE-2 and the phosphorylated PACE-2P; a slight mass loss from 100°C can be observed for the modified sample which could be related to residual solvent although all the samples

Table 2
Degradation parameters (heating rate = 10 °C min^{-1})

Sample	% of phosph. monom. units	T_i (°C)	Conv. (%)	E (kJ mol^{-1})
PACE-2	0	403.1	96.3	129
PACE-2P	85.1	386.0	44.1	6.50
PACE-3	0	405.2	96.2	134
PACE-3P	87.3	391.1	43.0	6.64
PACE-4	0	401.8	97.0	133
PACE-4P	95.5	385.0	46.2	6.66
PACE-0	0	377.0	97.0	70.5
PACE-0-5P	8.81	369.0	85.0	57.9
PACE-0-4P	30.3	364.9	75.0	37.4
PACE-0-3P	66.6	352.1	68.7	19.2
PACE-0-2P	72.2	347.0	57.7	18.6

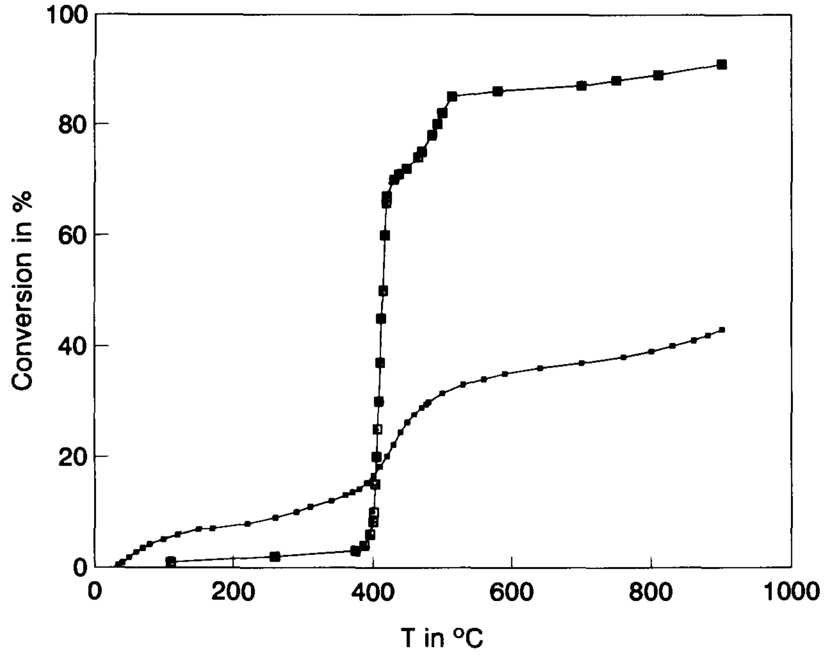


Fig. 1. Mass loss (in %) as a function of temperature (heating rate = 10°C min^{-1}): ■: PACE-2; ●: PACE-2P.

were carefully dried. As it can be seen in this figure, the mass loss at 900°C (end of the experiment) for the unmodified sample is near 100% whereas for the phosphorylated one the mass loss is 43.0% only.

Figure 2 shows the influence of the phosphorous contents on the degradation of PACE; as it can be seen the higher is the phosphorous content in the sample the lower is the final mass loss.

As it can be seen from the figures, the thermal degradation can be characterized by a step to which corresponds the higher mass loss for the lower change in temperature. After that step the degradation continues in a progressive manner until the final temperature. The onset temperature for that characteristic step has been calculated by the intersection of the initial base line with the experimental curve in each case, and it may be utilized to characterize the thermal stability of the samples. These values are shown in Table 2. As it can be noted, the onset temperature (T_i) for the phosphorylated samples is lower than that for the unmodified one so we can conclude that the thermal stability of poly(acenaphtylene) decreases as the H_2PO_3 group comes into the polymeric chain. Besides, the loss of thermal stability depends on percent of modified monomeric units as it can be deduced from the phosphorylated samples arising from the unmodified PACE-0. This behaviour is similar to that previously reported [6] for phosphorylated poly(N-vinylcarbazole); so we can conclude that the interaction between the phosphorylated acenaphthylene groups and the polymeric chain leads to

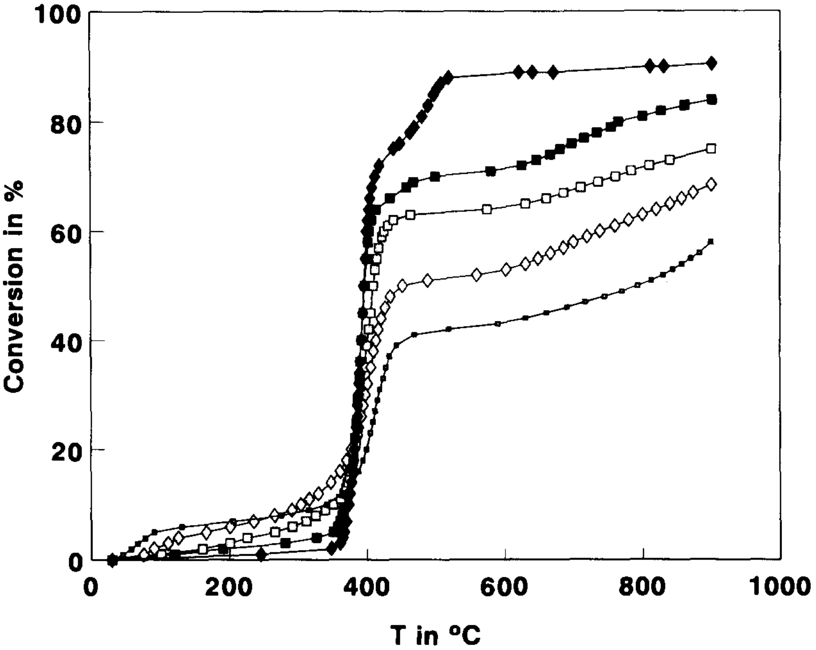


Fig. 2. Influence of the phosphorous contents on the degradation of PACE (heating rate = 10°C min^{-1}): ◆ : PACE-0; ■: PACE-0-5P; □: PACE-0-4P; ◇: PACE-0-3P; ●: PACE-0-2P.

scission of the chain at the characteristic step of the degradation at a lower temperature than for unmodified PACE.

As it has been noted before, the phosphorylated samples did not reach the 100% mass loss when the final temperature of 900°C was attained; however if the sample was maintained at 900°C after the end of the experiment there was a continuous mass loss until 100%; this fact allows us to conclude that the degradation in all cases is total. The analysis of the residual products was difficult as they were insoluble but it was possible to verify the presence of residual organic functions with similar bands to those in the original polymeric sample. In conclusion, they consist in residues from the degradation process the elimination of which is a slow process.

As it has been already reported [1] the onset temperature of degradation does not depend on molecular weight; however, as it can be seen in Table 2, T_i is only 377°C for the sample PACE-0 whose number average molecular weight is 4800, whereas it is approx. 400°C for the unmodified samples of high molecular weight; that is to say the low molecular weight poly(acenaphtylene), is less stable. This fact could be related with different synthesis way of PACE-0 (cationic) with respect to the other samples (radical). As reported before [4] the cationic polymerization of acenaphtylene yields polymeric chains of low molecular weight and then more flexible than those of high molecular weight.

The behaviour of phosphorylated samples is similar to that of the unmodified ones; at high molecular weight there is no dependence of T_i on molecular weight as it can be seen for the samples PACE-2P and PACE-3P which have a similar phosphorous content and different molecular weight. However for the sample PACE-0-2P which has a similar phosphorous content than previously but a very low molecular weight, the onset temperature is only 347°C; this difference cannot be ascribed to the small difference in the phosphorous contents but, as for the unmodified polymer, to a higher chain flexibility and therefore to an enhanced interaction between the phosphorylated acenaphtylene group and the main polymeric chain.

The kinetic parameters for the degradation have been obtained by the McCallum and Tanner method [2]:

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

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

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

where C is the fractional mass loss.

A plot of log $F(C)$ versus T^{-1} shows that in all cases the linear portion is coincident with the characteristic step for the degradation. Tables 2–4 show the values of activation energy at several heating rates. As it can be seen, for the sample PACE-0 (unmodified and of low molecular weight) the activation energy is lower than values for samples of high molecular weight whatever may be the heating rate.

The no dependence of activation energy on molecular weight for high molecular weight samples (PACE-2, PACE-3 and PACE-4) can be explained by considering that the chain scission is unaffected by the rest of the chain segments. Probably this is not the situation at low molecular weight (PACE-0) as there exists flexibility effects and so the activation energy is lower.

The activation energy for the phosphorylated samples is lower than that for the unmodified one this effect increasing the higher the phosphorous content is. This fact can be explained by assuming, as for phosphorylated poly(N-vinylcarbazole) [6], a lower stability of the species derived from phosphorylated samples with respect to those from unmodified samples.

Table 3
Activation energy (kJ mol^{-1}) at several heating rates for high molecular weight samples

Sample	Heating rate (°C min^{-1})				
	10	20	30	120	150
PACE-2[a]	129	128	112	62	64
PACE-2P	6.50	6.38	6.17	3.08	2.93
PACE-3[a]	134	120	104	69	–
PACE-3P	6.64	6.36	6.19	2.90	3.26

[a] From reference [1].

Table 4
Influence of the phosphorous contents on the activation energy

Sample	% of phosph. monom. units	Heating rate (°C min^{-1})	
		10	120
PACE-0	0	70.5	49.6
PACE-0-5P	8.85	57.9	44.1
PACE-0-4P	30.3	37.4	30.4
PACE-0-3P	66.6	19.2	16.6
PACE-0-2P	72.2	18.6	16.1

In Tables 3 and 4 the effect of heating rate on the activation energy is shown; as it can be seen in Table 3, for high molecular weight samples the behaviour is similar for unmodified and phosphorylated samples, this is a drastic decrease of E when β increases from 10 to 120°C cm^{-1}. For low molecular weight samples (Table 4) the change is smaller and it shows relation with the percent of phosphorylated monomeric units. At higher phosphorous contents the effect of heating rate on E is smaller.

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