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Thermogravimetric study of the degradation of poly(acenaphthylene)

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Abstract

The influence of molecular weight and heating rate on the thermal degradation of poly(acenaphthylene) has been studied by thermogravimetry. The results indicate that the activation energy does not depend on molecular weight but decreases with increasing heating rate.

INTRODUCTION

Poly(acenaphthylene) (PACE) is a polymer with interesting thermal, electrical and photochemical properties. Its thermal stability has been studied by pyrolysis gas–liquid chromatography and pyrolysis mass spectrometry [1]. In this work, thermogravimetry was used to analyse the degradation of several fractions of PACE at different heating rates. The McCallum and Tanner method [2] was used to carry out the kinetic analysis.

EXPERIMENTAL

Acenaphthylene was thermally polymerized in bulk by heating for several hours slightly above its melting point. The polymer was fractionated by precipitation with methanol at 25°C from a 10% (w/v) benzene solution. The molecular weights of the fractions were determined by gel-permeation

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TABLE 1

Characteristics of poly(acenapthylene) samples

Fraction	$\bar{M}n \times 10^{-5}$	$\bar{M}w \times 10^{-5}$	$\bar{M}w/\bar{M}n$
PAC G1	6.7	10.4	1.5
PAC E1	6.8	10.0	1.5
PAC E2	4.8	6.5	1.3
PAC E3	3.1	3.9	1.3
PAC C1	2.9	3.8	1.3
PAC E4	2.0	2.5	1.2
PAC E6	1.2	1.3	1.1
PAC F9	0.7	0.9	1.3

chromatography (GPC) in tetrahydrofuran at 25°C on a Waters chromatograph, using the Universal calibration method [3]. The characteristics of the samples are listed in Table 1.

Thermogravimetric degradations (TG) were measured with a Perkin-Elmer TGS-2 thermobalance using samples of 6–7 mg. A standard dynamic heating procedure was followed, from room temperature to 900°C. Heating rates between 10 and 150°C min^{-1} were employed in a stream of dry nitrogen.

RESULTS AND DISCUSSION

The % mass loss, plotted as a function of temperature at two heating rates, is shown in Fig. 1. Similar thermograms were obtained for all the samples at each heating rate.

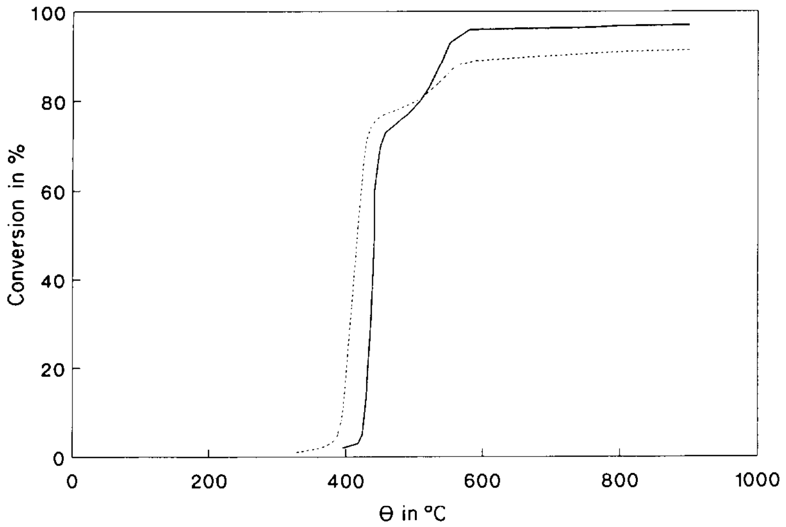

Fig. 1. Conversion (%) as a function of temperature: - - -, 10°C min^{-1}; —— 120°C min^{-1}.

TABLE 2

Onset decomposition temperatures as a function of heating rate for some samples

Fraction	Heating rate/(°C min^{-1})						
	10	20	30	40	80	120	150
PAC G1	402.0	421.1	424.7	–	400.0	394.2	395.6
PAC E1	404.0	425.5	–	428.2	436.0	390.6	391.7
PAC E4	401.8	428.5	418.7	415.0	429.0	392.7	–

In all cases, an initial mass loss (<1%) was observed due, in our opinion, to residual solvent despite the exhaustive purification and vacuum drying procedures performed with all samples.

This was followed immediately by a step between 400 and 500°C corresponding to the highest mass loss (70–75%); this step is considered to be characteristic of the thermal degradation of PACE. Degradation proceeds further, and at about 555°C for all samples, the mass loss was >92% and the thermal degradation of PACE can be considered complete.

The intersection of the initial and final baselines with the experimental curve was used to define the onset and final temperatures of decomposition. These are listed in Table 2 at different heating rate values β. It can be seen that when β increased from 10 to 40°C min^{-1}, T_i increased. However, for higher heating rate values, 120 and 150°C min^{-1}, T_i decreased. This behaviour could be due to different thermal lags within the sample under different conditions. Similar effects were also observed in the case of the final temperature T_f. With higher heating rates, greater differences between T_f and T_i were obtained. The differences were independent of molecular weight. Taking the initial degradation temperature as a measure of the thermal stability, the results indicate that molecular weight has no effect on the thermal stability; however, there is a slight dependence on heating rate. The final mass loss depended on neither molecular weight nor heating rates.

The lack of dependence of these degradation characteristics on molecular weight is a consequence of the degradation mechanism, which is perhaps influenced by the high rigidity of the chain of this polymer [4].

The kinetic parameters for the degradation process have been obtained from the McCallum and Tanner equation [2]

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

where E is the activation energy, A is the frequency factor and β is the heating rate. $F(C)$ depends on the reaction order. If $n = 1$

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

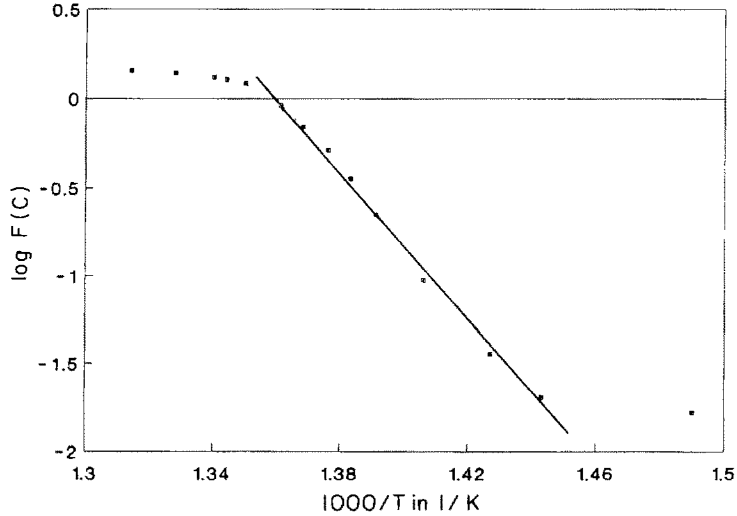

Fig. 2. Kinetic analysis by the McCallum and Tanner method (sample PAC E1).

in which C is the fractional conversion. A plot of $\log F(C)$ versus $1/T \times 10^{-3}$ gives a straight line, from whose slope and intercept the activation energy and the frequency factor, respectively, can be obtained. As can be seen in Fig. 2, the linear portion of this plot is coincident with the characteristic step for the degradation process of PACE. Table 3 gives the values of the activation energy for several samples, obtained by the least-squares method.

As has been seen for the onset temperature T_i, the activation energy showed no dependence on molecular weight, but there was a dependence on heating rate. Figure 3 shows this dependence using the mean value of the activation energy at each heating rate (standard deviations are about 5–8 kJ mol^{-1}). The activation energy decreases with increasing heating rate,

TABLE 3

Activation energy values (kJ mol^{-1}) at different heating rates

Fraction	Heating rate/(°C min^{-1})						
	10	20	30	40	80	120	150
PAC G1	127	123	95	–	77	61	61
PAC E1	131	128	112	99	82	74	74
PAC E2	–	128	112	101	80	62	64
PAC E3	–	120	104	89	76	69	–
PAC C1	127	125	106	94	–	–	–
PAC E4	133	118	101	91	76	63	–
PAC E6	147	128	107	88	–	–	–
PAC F9	–	–	95	89	–	–	–

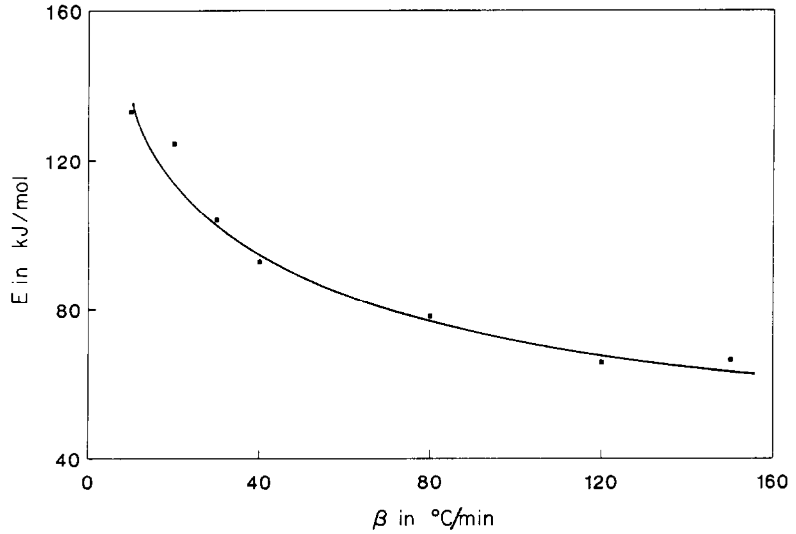

Fig. 3. Dependence of activation energy on heating rate.

and reaches a constant value at higher heating rates. It can be concluded that the degradation process is faster under these conditions. The lack of dependence of the activation energy on molecular weight confirms a mechanism involving random scission of the polymeric chain.

As can be seen in Fig. 1, the degradation process involves a second step, with more than 72% mass loss; this could correspond to the degradation of acenaphthylene dimers and acenaphthene, the formation of which has been indicated by Hammond and Lehrle [1] from pyrolysis GLC studies.

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