

# TIHERMAL STABILITY AND DEGRADATION MECHANISM FOR TWO MAIN-CHAIN LIQUID CRYSTAL POLYESTERS A TG-MS study\*

G. Ellis\*\*, C. Marco, J. del Pino and M. A. Gómez

Departamento de Física e Ingeniería de Polímeros, Instituto de Ciencia y Tecnología de Polímeros, CSIC, c/Juan de la Cierva, 3, 28006-Madrid, Spain

## Abstract

The thermal stabilities of two thermotropic liquid crystal polyesters were analysed by means of thermogravimetric analysis (TG), as a function of the chemical structure of the aliphatic spacer between the aromatic-triad mesogenic units. TG was combined with mass spectrometry to confirm that the degradation mechanism previously observed in a Fourier transform infrared study of the degrading polymers follows a  $\beta$ -*cis*-elimination process.

**Keywords:** degradation mechanism, FTIR, liquid crystal polyesters, mass spectroscopy, TG-MS, thermal stability

## Introduction

Liquid crystal polymers present a diverse set of properties which depend on the nature of the structural unit. Variations in the chemical structure or polarity of this unit can produce very considerable changes in the mesophasic properties of the polymer and the corresponding thermal transitions, and can lead to alterations in the thermal stability of the system.

Thermotropic polyesters based on a mesogenic triad unit with three aromatic rings and polymethylene flexible spacers of the type described by Lenz *et al.* [1-4] and Bilibin *et al.* [5-8], have been prepared and extensively characterized in our research group [9-18]. We have systematically studied the effects of variations of the chemical structure of the monomer on the thermotropic behaviour of these materials, introducing modifications in both the mesogenic units and the flexible spacer. In the latter, the length and nature of the aliphatic chain were varied, and in some cases long and short branches were introduced.

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\*\*Author for correspondence. e-mail: gary@fresno.csic.es

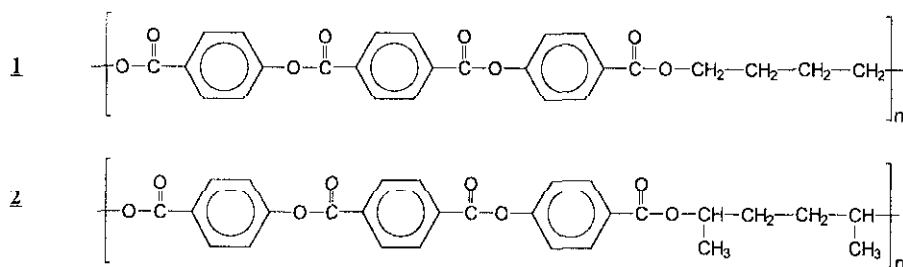
In the majority of these systems, the liquid crystal – isotropic transition normally occurs at a temperature in excess of 300°C, where the polymers are usually thermally unstable. The processing limits of these materials are of fundamental importance, since any thermal degradation can lead to a structural modification of the polymer which, although slight, can induce important alterations in the thermotropic behaviour.

The thermal decompositions of a range of these polyesters were previously studied in our research group by means of TG, FTIR spectroscopy and molecular modelling [15, 16]. The degradation mechanism was proposed to occur by a *cis*-elimination reaction via a cyclic intermediate which involves a hydrogen atom on the  $\beta$ -carbon of the aliphatic spacer, a process analogous in its early stages to the degradation mechanisms encountered for other aromatic polyesters, such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) [19–21].

In this paper, a coupled TG-MS system was used to analyse the gases evolved during the dynamic degradation of two specific polyesters, poly(oxytetramethyleneoxycarbonyl-1,4-phenyleneoxyterephthaloyloxy-1,4-phenylcarbonyl) (P4TOB), with four methylene units in the linear spacer, **1** and its branched analogue with 1,4-methyl substitution in the flexible spacer (P4DMTOB), **2**. The data obtained are compared with previously recorded FTIR data in order to confirm the reactions which occur in the first stages of the degradation of these polymers.

## Experimental

P4TOB, **1**, and its substituted analogue, P4DMTOB, **2**, shown in Scheme 1,



were prepared via the three-stage method reported by Bilibin *et al.* [8], which is described in more detail elsewhere [10–14]. The thermal properties and characterization of **1** and **2** were reported previously [16, 22].

The inherent viscosities of the polymers were measured with an Ubbelohde viscometer at a concentration of 0.5 g cm<sup>-3</sup> of polymer in *p*-chlorophenol at 45°C.

Thermal stability measurements were carried out with a coupled TG-MS system, consisting of a Mettler TG-50 thermobalance, controlled by a TA-4000 ther-

mal analysis system, coupled to a Balzers MSC-200 Thermocube mass spectrometer, with a detection limit of 200 a.m.u., controlled by Quadstar 421 software allowing the measurement of ion currents and gas concentrations.

Dynamic measurements were carried out in an inert nitrogen atmosphere, with a dry flow rate of  $150 \text{ ml min}^{-1}$ , between 50 and  $650^\circ\text{C}$ , at a heating rate of  $10^\circ\text{C min}^{-1}$ . Sample sizes of around 10 mg were selected in order to compromise between efficient operation of the thermobalance and overloading of the mass spectrometer. The following characteristic degradation temperatures were used in the analysis:  $T_i$ =initial degradation temperature,  $T_{10}$  and  $T_{50}$ =temperatures corresponding to 10% and 50% mass losses, respectively, and  $T'$ =temperature of maximum rate of mass loss.

The evolved volatiles were immediately carried off in the  $\text{N}_2$  gas flow via a heated  $200^\circ\text{C}$  fused silica transfer line to the mass spectrometer for on-line analysis. The first scan was synchronized with the start of the temperature ramp in the TG, and a mass scan for each  $^\circ\text{C}$  increment in programme temperature was collected. The main components evolved over the temperature cycle were monitored in the more accurate selected multiple ion mode, and the data were obtained as ion current intensity *vs.* time.

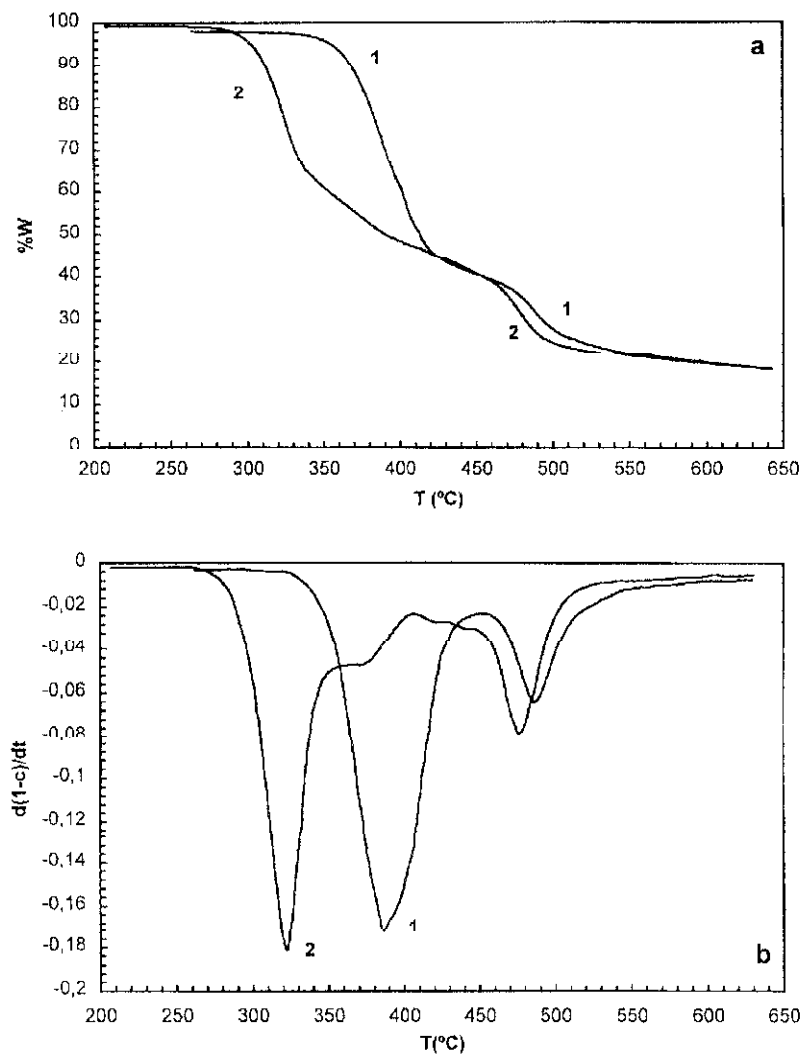
Isothermal analysis was carried out at different temperatures, such that the process occurs over a reasonable time scale up to a conversion around 20% mass loss. Temperature, mass loss and differential mass loss data from the TG were acquired, evaluated with Mettler TA-72 software, and correlated with the data from the mass spectrometer.

## Results and discussion

Figure 1a compares the thermogravimetric curves for the two polyesters, and clearly shows that for the polymer with 1,4-dimethyl substitution, **2**, the onset of degradation occurs at a significantly lower temperature than for the polymer with the unsubstituted linear spacer, **1**. Figure 1b presents the variation in the rate of degradation as a function of temperature for both polymers; in each case, at least

**Table I** Inherent viscosities, transition temperatures and characteristic degradation temperatures

| Polyester                                  | P4TOB, 1 | PDM4TOB, 2 |
|--|----------|------------|
| $\eta_{\text{inh}}$ ( $\text{dL g}^{-1}$ ) | 0.33     | 0.28       |
| $T_g$ ( $^\circ\text{C}$ )                 | 75       | 75         |
| $T_1$ ( $^\circ\text{C}$ )                 | 285      | 185        |
| $T_i$ ( $^\circ\text{C}$ )                 | 350      | 295        |
| $T_{10}$ ( $^\circ\text{C}$ )              | 390      | 330        |
| $T_{50}$ ( $^\circ\text{C}$ )              | 430      | 388        |
| $T'$ ( $^\circ\text{C}$ )                  | 410      | 342        |



**Fig. 1** TG curves (a) and DTG curves (b) for the P4 polyesters with linear, **1**, and branched, **2**, spacers

two fundamental stages are observed in the degradation process. The values of the characteristic degradation temperatures, together with the inherent viscosities of the polyesters, are given in Table 1. It is clear that differences in thermal stability cannot be associated with molecular weight, given that the inherent viscosities of the two materials are very similar.

The TG and MS data are presented in Figs 2–5. The elimination of the aliphatic spacer as a volatile diene in principle accounts for the first mass loss ob-

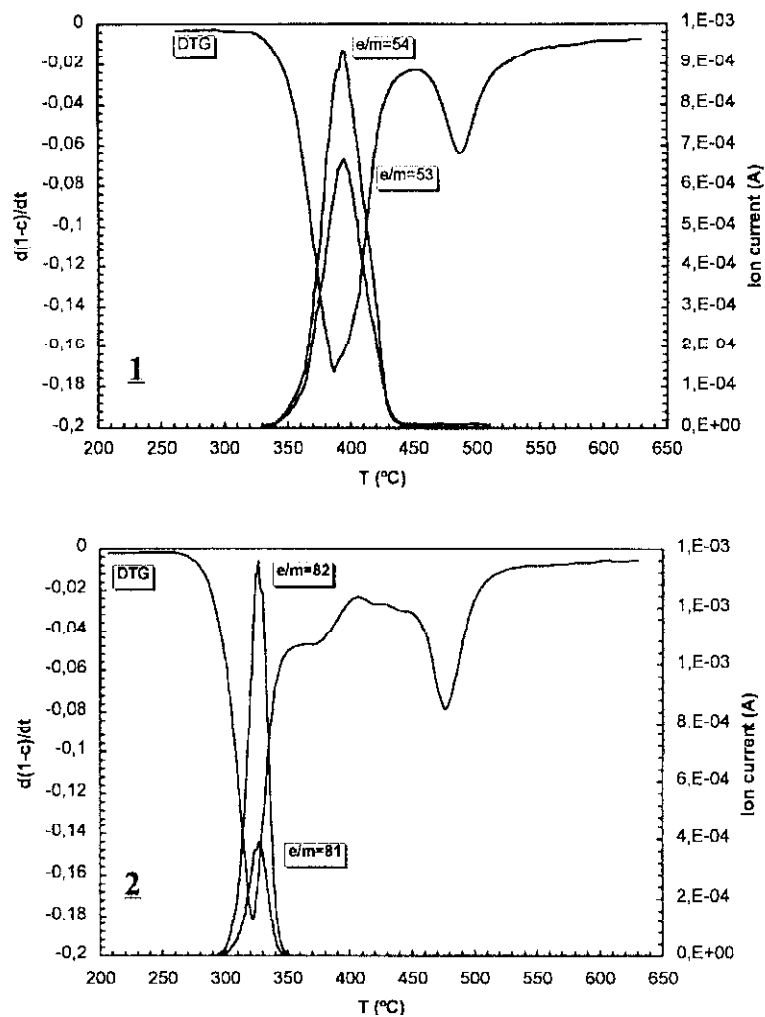


Fig. 2 Ion current detected in the mass spectrometer vs. temperature (lower curves) and differential TG curve (upper) for polyesters (a) **1** and (b) **2**

served in the degradation, which starts at around 350°C in the case of **1** and at around 290°C for **2** (Table 1). The identification of volatile fragments with  $e/m=54$  and 53 a.m.u. in the corresponding mass spectrum of **1** (Fig. 2, upper curve) and fragments with  $e/m=82$  and 81 a.m.u. in the mass spectrum of **2** (Fig. 2, lower curve) corresponds perfectly with the onset of mass loss and the first maximum in the decomposition rate represented by the differential TG curves (upper curve in each graph). Immediately before the second maximum in the degradation rate in both cases, these volatile fragments are no longer detected.

Figure 3 shows that the elimination of a volatile fragment with  $e/m=44$ , which corresponds to  $\text{CO}_2$ , starts slightly after the elimination of the diene in both cases, and at an initially very low rate. In **1**, the first maximum in the elimination of  $\text{CO}_2$  occurs at around  $460^\circ\text{C}$ , with further maxima at  $500$  and  $550^\circ\text{C}$ , the first of which coincides with the second maximum in the degradation rate shown in the DTG (upper) curve. In **2**, a similar profile is observed, but the rate of elimination of  $\text{CO}_2$  is much lower at these lower temperatures. A significant increase in

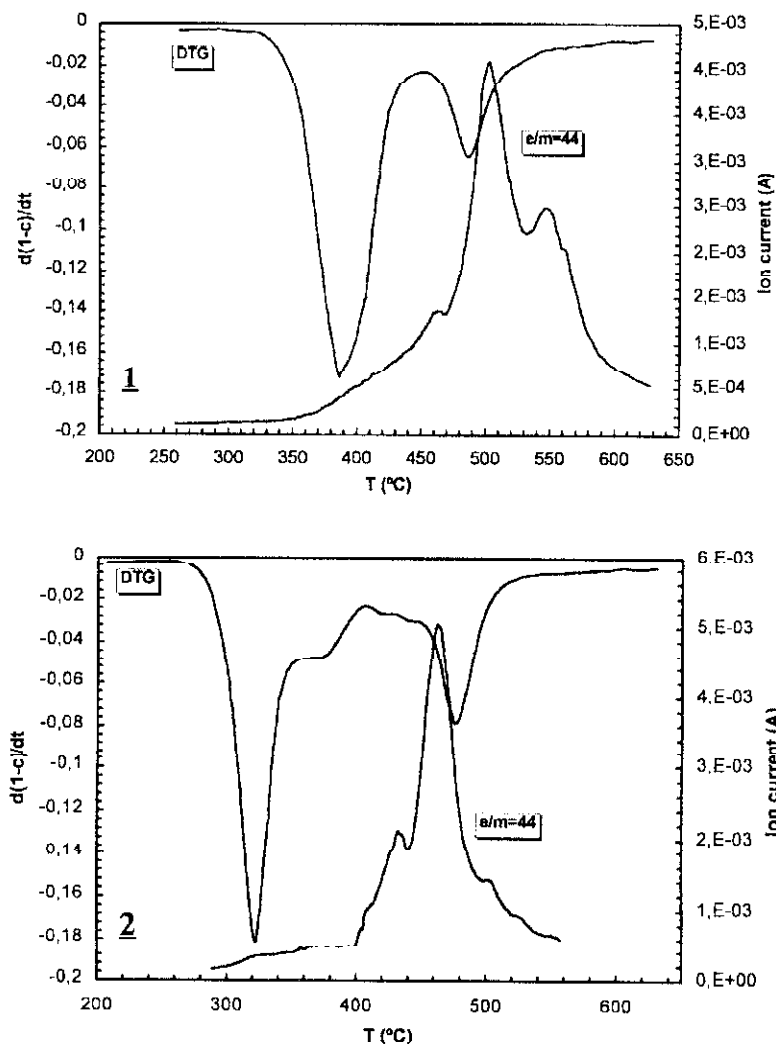


Fig. 3 Ion current detected by the mass spectrometer for mass fragment  $m=44$  corresponding to the  $\text{CO}_2$  vs. temperature (lower curves) and differential TG curves (upper curves) for polyesters (a) **1** and (b) **2**

the rate of elimination of CO<sub>2</sub> is not observed until the material reaches 400°C. The maximum rate of elimination of CO<sub>2</sub> at 460°C correlates very well with the observation of a higher concentration of acidic carbonyls trapped in the solid residues seen in the FTIR spectra [16].

It is important that the residual mesogenic fragments produced after the decarboxylation process can experience scission of the terephthalate ester group, i.e. the internal ester group, producing a carboxonium ion [19, 20] which generates the fragments corresponding to benzene and phenol, amongst others [21].

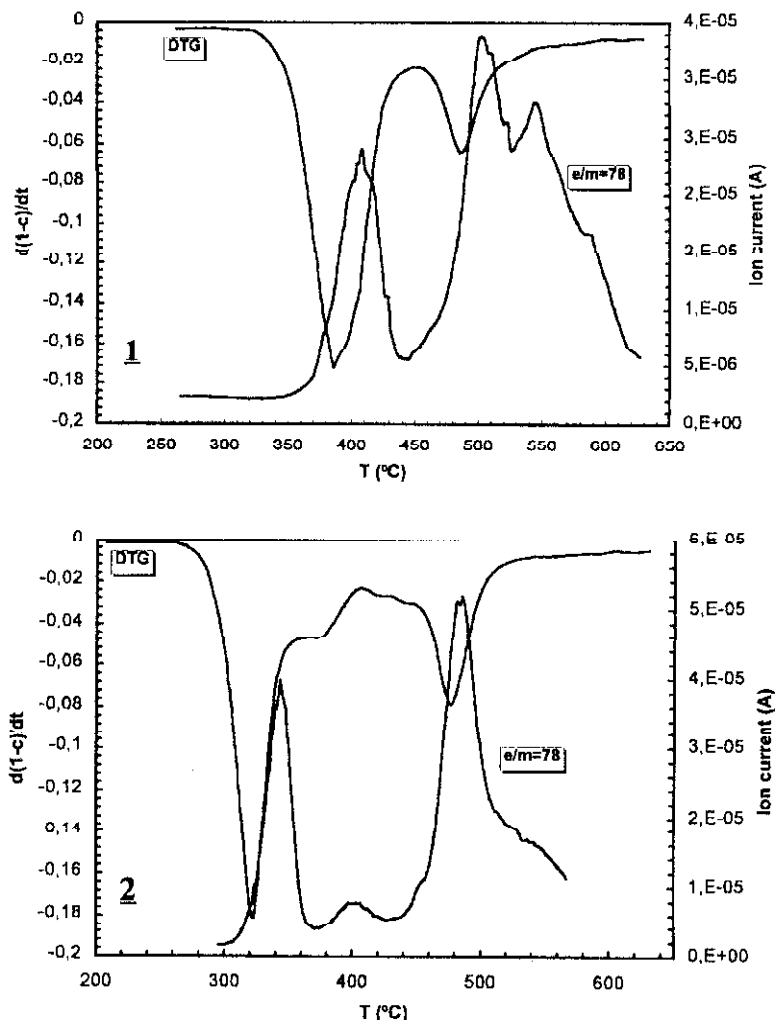


Fig. 4 Ion current detected by the mass spectrometer for mass fragment  $m=78$  corresponding to the benzene vs. temperature (lower curves) and differential TG curves (upper curves) for polyesters (a) **1** and (b) **2**

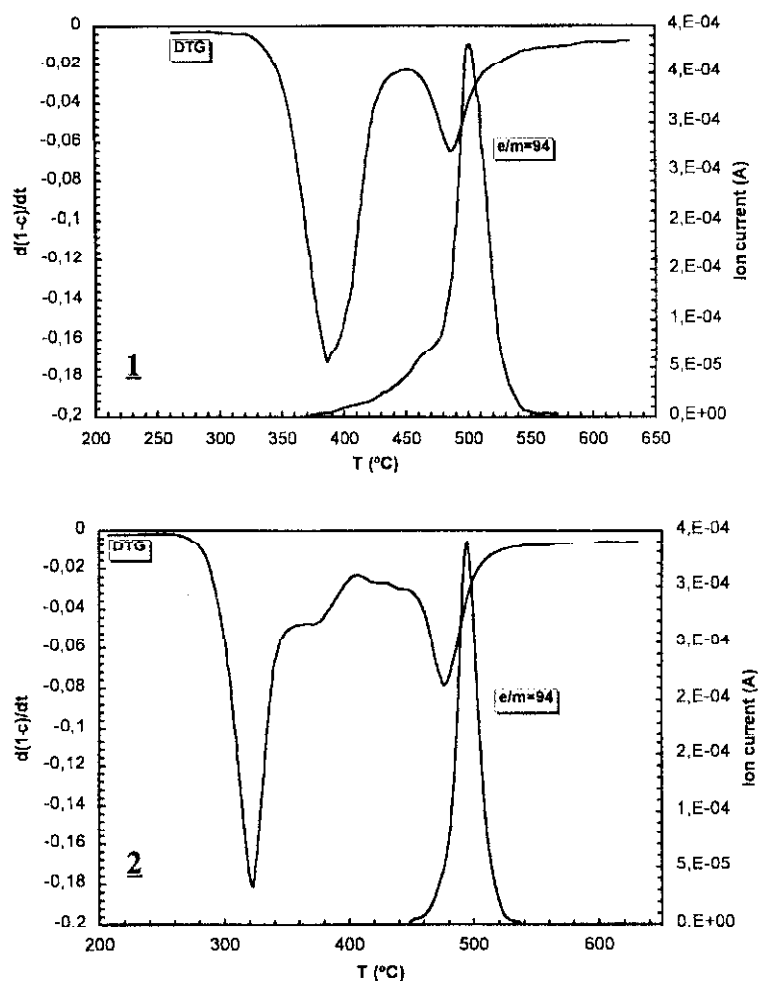


Fig. 5 Ion current detected by the mass spectrometer for mass fragment  $m=94$  corresponding to the phenol vs. temperature (lower curves), and differential TG curves (upper curves) for polyesters (a) **1** and (b) **2**

Figures 4 and 5 show the MS data for the fragments with  $e/m=78$  and  $94$ , corresponding to benzene and phenol, respectively. It can be observed that in the case of **1**, both fragments start to be detected at around  $390^{\circ}\text{C}$ , corresponding to a mass loss of around 10% in **1**, and reach a maximum rate of elimination at around  $500^{\circ}\text{C}$ , coinciding with the second maximum in the rate of degradation (upper curve). In **2**, similar behaviour is observed for the benzene fragment, although a third, weak maximum in the detection of this fragment occurs at around  $400^{\circ}\text{C}$ . However, the phenolic volatiles are not detected in **2** until after the second maximum in the DTG curve.

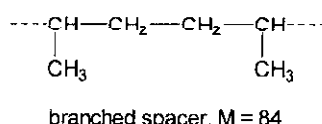
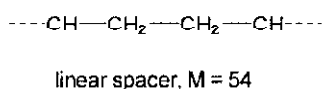
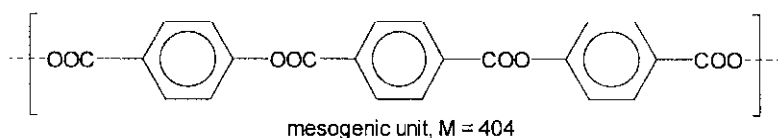


The fragmentation of the mesogen, is observed by the appearance of benzene and phenol volatiles once the diene is eliminated at the maximum rate, and clearly indicates that the process of rupture of the mesogen is differentiated from the process of  $\beta$ -elimination in the flexible spacer, although on the time scale of the experiments reported here there is a partial overlapping of the two processes.

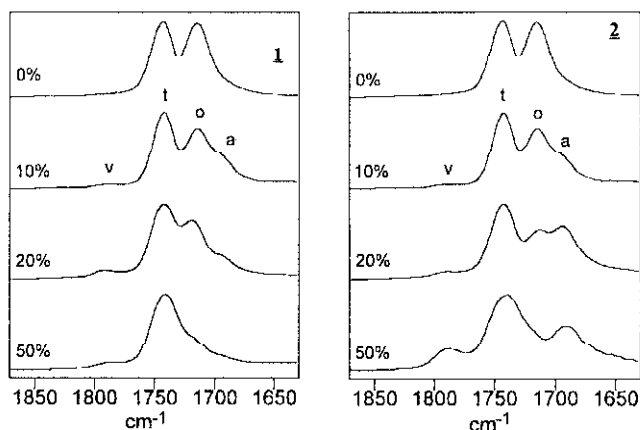
Correlation of the fragmentation observed by MS with the mass loss in the TG curves clearly supports the evidence that the  $\beta$ -elimination, decarboxylation and mesogen rupture overlap. In the case of **1**, the initial step in the TG curve corresponds to a mass loss of around 40–50%. Table 2 shows the calculated molecular weight% for different parts of the polymer repeat unit. Elimination of the flexible spacer in this case accounts for only 11% of the mass loss. Decarboxylation of the outer carboxylic acid groups raises the eliminated mass to 31%, the rest being due to the onset of the elimination of benzene and phenol fragments, as clearly observed by MS. In the case of **2**, the elimination of the spacer accounts for 17% of the observed mass loss, which, with the oxybenzoate carboxylic groups, rises to around 36%. At the lower temperatures involved, the loss of benzene is only just starting, which explains the inflexion in the TG curve.

**Table 2** Correlation of weight loss by TG with possible chain fragmentation

| Calculated                   | P4TOB, 1 |         | PDM4TOB, 2 |         |
|------------------------------|----------|---------|------------|---------|
|                              | mass     | % total | mass       | % total |
| Total mass                   | 458      | 100     | 488        | 100     |
| Mesogen                      | 404      | 88.2    | 404        | 82.8    |
| Spacer                       | 54       | 11.1    | 84         | 17.2    |
| Outer CO <sub>2</sub>        | 88       | 19.2    | 88         | 18.0    |
| Total CO <sub>2</sub>        | 176      | 38.4    | 176        | 36.1    |
| Spacer+outer CO <sub>2</sub> | 142      | 31.0    | 176        | 36.1    |

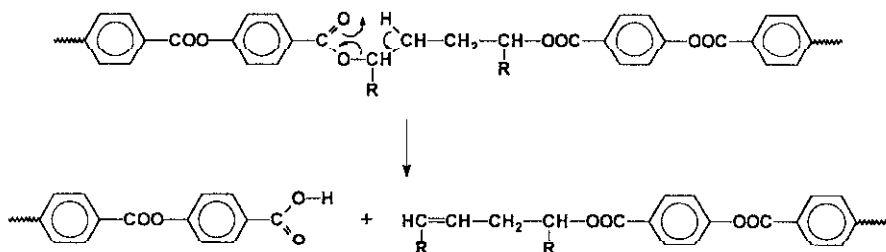


In a previous study [16], FTIR spectroscopy was used to study a series of solid residues of both polyesters, prepared under the same conditions of dynamic degradation, halted abruptly during the temperature programme at the temperatures



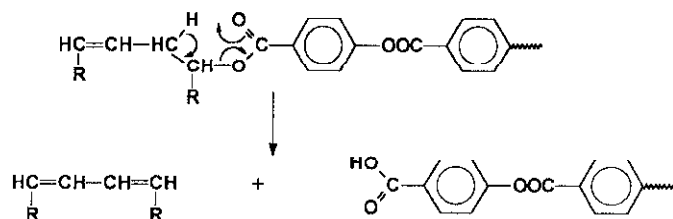
**Fig. 6** FTIR spectra between  $1870$  and  $1630\text{ cm}^{-1}$  of the two polyesters for different % mass losses. Annotations in samples with 10% mass loss:  $v$ =first overtone band of a vinyl  $\text{CH}_2$  deformation;  $t$ = $\nu_{\text{C=O}}$  of the terephthalate ester group;  $o$ = $\nu_{\text{C=O}}$  of the oxybenzoate ester group; and  $a$ = $\nu_{\text{C=O}}$  of a carboxylic acid residue

corresponding to 10, 20 and 50% mass loss. In order to illustrate these results clearly, Fig. 6 presents the FTIR spectra obtained between  $2000$  and  $1550\text{ cm}^{-1}$  for both polyesters. The gradual disappearance of the carbonyl stretching vibration at around  $1716\text{ cm}^{-1}$  with the progress of the thermal decomposition, the appearance and increase in concentration of acidic carbonyl groups, and the possible observation of the formation of vinylic groups [16], together with other important variations in the spectra, have provided spectroscopic evidence for the first stage of the degradation mechanism, which proceeds via a cyclic intermediate involving a hydrogen atom of the carbon in the  $\beta$ -position of the aliphatic spacer:



The rupture of the ester link connecting the mesogenic unit with the flexible spacer, via a  $\beta$ -*cis*-elimination, generates an acidic terminal group on the aromatic triad, and a vinylic termination on the other chain fragment, as observed for other polyesters in the same series [15]. The corresponding  $\beta$ -*cis*-elimination

at the other extreme of the aliphatic chain generates another acid termination on the subsequent mesogen, and a volatile diene:

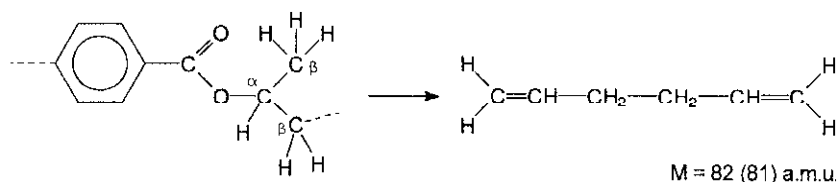


Later, a further possibility involves the loss of the carboxylic acid residue by a decarboxylation process, resulting in the generation of a phenyl termination on the mesogenic unit, and the elimination of carbon dioxide, as described below:

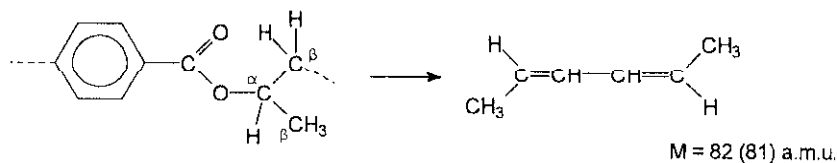


It is only after the scission of the internal ester that a similar decarboxylation reaction can occur, leading to the elimination of benzene.

#### $\beta$ -H (methyl)



#### $\beta$ -H (methylene)



**Fig. 7** Possible cyclic intermediates and resultant mass fragments for the elimination of the flexible spacer in polyester 2

The lower thermal stability of **2** was previously explained by the use of molecular mechanics modelling [16] to be due to the *cis*-elimination process occurring via a cyclic intermediate involving one of the hydrogen atoms on the methyl carbon, rather than on the methylene carbon, the only possibility for the linear spacer. As can be observed in Fig. 7, the elimination of a methyl hydrogen atom produces a terminal vinyl group on the subsequent diene. The  $1790\text{ cm}^{-1}$  band was attributed to this group [15, 16], and is clearly observed in the FTIR spectra. The elimination via a methylene hydrogen atom produces a diene with the same

mass, both with intermediate C=C double bonds and methyl end groups. For a non-vinyl double bond, the overtone band at around  $1790\text{ cm}^{-1}$  would not be observed in the FTIR spectrum [22]; thus, the evidence seems to support the elimination of the methyl hydrogen atom. However, measurement of the evolved gases by FTIR spectroscopy is required in order to confirm the absence of methyl groups in the diene volatiles, and degradation via both types of cyclic intermediate is not ruled out at this stage.

## Conclusions

MS coupled with TG has been used to study the thermal degradation of some liquid crystal polyesters. From the results obtained, the MS data confirm the degradation mechanism proposed from FTIR and TG studies reported earlier. The combination of spectroscopic and thermal methods is essential to the understanding of the degradation processes which occur in this type of material.

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