Thermal degradation of new copolymers from pyromellitic anhydride

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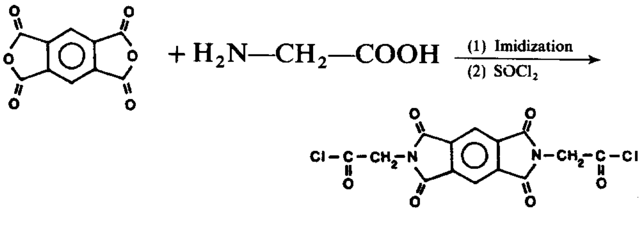
A series of new copolyimides has been synthesized from pyromellitic anhydride. Copoly(imide esters) and copoly(imide amides) were synthesized from bis(*N*-methylcarboxychloride)pyromellitimide with diols and amines, respectively. One copoly(imide amine) was obtained from bis(*N*-allyl)pyromellitimide and piperazine via the Michael reaction. The thermal degradation of the copolymides obtained was studied by direct pyrolysis mass spectrometry. Our results show that a selective β-CH hydrogen transfer reaction occurs in copoly(imide esters) containing 1,3-propyl and 1,6-hexane diols, while an intramolecular ester exchange process takes place in copoly(imide ester) with a neopentylglycol moiety. Copoly(imide amide) containing 1,6-hexane diamine decomposes by an N–H hydrogen transfer process, although extensive crosslinking is observed, while that containing piperazine decomposes by an α-CH hydrogen transfer. In contrast, copoly(imide amine) undergoes a very selective depolymerization process, yielding bis(*N*-allyl)pyromellitimide and piperazine.

(Keywords: thermal degradation mechanisms; mass spectrometry; direct pyrolysis m.s.; polyimide copolymers)

INTRODUCTION

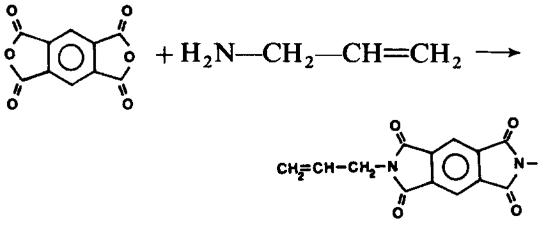
Polyimides are well known and their thermal decomposition behaviour has been extensively investigated[1–10]. These polymers present processing problems and considerable effort is still being devoted to improving these properties. Copolymerization of imides with flexible monomer units has been reported more recently[11–15].

We have synthesized a series of copolymers from pyromellitic anhydride: poly(imide esters), polymers I–III in *Table 1*; poly(imide amides), polymers IV and V in *Table 1*; and one poly(imide amine), polymer VI in *Table 1*. These copolymers were synthesized starting from monomers **1** and **2**, according to equations (1) and (2), respectively:



Monomer 1

1 + X—R—X Copolymers I–V X = OH, NH_2, NH



Monomer 2

In the present study, our main interest has been directed towards the investigation of the thermal degradation pathways of these copolyimides by thermogravimetry (t.g.) and by direct pyrolysis mass spectrometry (d.p.m.s.). In the d.p.m.s. technique[16], polymers were introduced via the direct insertion probe of the m.s. and the temperature increased gradually until thermal degradation reactions occur; the volatile compounds formed were then ionized and detected as soon as they are formed. A general advantage of this technique is that pyrolysis is accomplished under high vacuum, and therefore the thermal products are volatilized and readily removed from the hot zone. This, together with the low probability of molecular collision and fast detection, reduces the occurrence of secondary reactions, so that the probability of detecting primary thermal degradation products is enhanced. A series of temperature–time

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‡ On leave from Warsaw, June–Oct 1988

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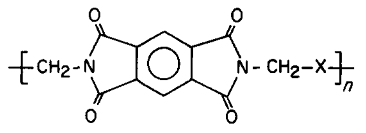
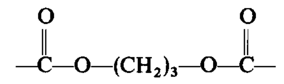
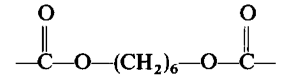
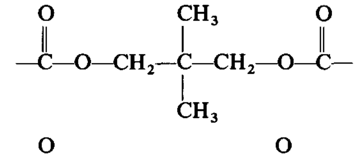
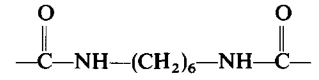
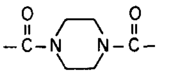
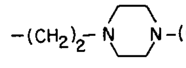
Table 1 Structure and thermogravimetric data of the copolyimides studied



	x	PDT^a (°C)	R^b (%)
I	 $-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-$	400	28
II	 $-\overset{O}{\overset{\|}{C}}-O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-$	400	21
III	 $-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-O-\overset{O}{\overset{\|}{C}}-$	435	27
IV	 $-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-$	405	50
V		470	36
VI		280	0

^{a} Temperature of maximum rate of polymer degradation from t.g. experiments

^{b} Wt% residue at 600°C from t.g. experiments

resolved mass spectra are then collected, in which every mass spectrum obtained is that of the mixture of compounds formed by pyrolysis.

When mass spectral analysis of polymers is performed by using a linear heating rate, the total ion current (*TIC*) curves essentially reproduce the differential thermogravimetric (d.t.g.) curves, so that their maxima correspond to the maximum rate of thermal decomposition of the polymer in the mass spectrometer. The use of t.g. and m.s. allows us to evaluate simultaneously the temperature, the amount and the chemical nature of volatile compounds evolving in each thermal decomposition step.

In previous studies we have investigated the thermal degradation mechanisms of several classes of polymers, including polyesters and polyamides[16,17]. Our results show that the thermal degradation processes occurring in the copolyimides in *Table 1* are characterized by extensive hydrogen transfer reactions. A selective β-CH hydrogen transfer reaction occurs in copolyimides I and II while an intramolecular ester exchange takes place in copoly(imide ester) III. Copolymer IV decomposes by an N–H hydrogen transfer process, although extensive crosslinking is observed. Copolymer V decomposes by an α-CH hydrogen transfer. In contrast, copolymer VI decomposes by a very selective depolymerization process, yielding bis(*N*-allyl)pyromellitimide and piperazine.

EXPERIMENTAL

Materials

All chemicals used were analytical-grade commercial products and were used without any further purification.

Synthesis of monomer I

Glycine (2-aminoacetic acid) (2.30 g, 44 mmol) was dissolved in 200 cm^3 mixture of pyridine and acetic acid (2:3). Pyromellitic dianhydride (4.36 g, 20 mmol) was added, with stirring. The mixture was refluxed for 2 h and after cooling to room temperature white crystals of bis(*N*-carboxymethyl)pyromellitimide (BPC) precipitated. These were filtered and dried *in vacuo* at 50°C overnight. Yield 6.3 g (94.8%); m.p. 345°C. The structure of the imide unit has been confirmed by i.r. and its molecular weight was determined by mass spectrometry.

Chlorination of BCP. BCP (3.0 g, 9.0 mmol) was dissolved in a mixture of 20 cm^3 of thionyl chloride and 4 cm^3 of dimethylformamide (DMF) and refluxed under a nitrogen atmosphere for 72 h as described in the literature for an analogous compound[15]. After cooling, the reaction mixture was filtered and the crystals were washed with dry benzene and dried under vacuum at 50°C overnight. Molecular weight 368 (by m.s.); yield 3.1 g (92.0%); m.p. 234°C.

Synthesis of monomer II

Pyromellitic dianhydride (4.36 g, 20.0 mmol) was dissolved in 40 cm^3 of methanol. Then 2.6 g (44.0 mmol) of allylamine was added to the solution and stirred for 30 min. The precipitated white crystals were filtered and washed with ethanol and transferred into a flask in 40 cm^3 of DMF and heated up to boiling point for 2 h. Yield 5.6 g (94.5%); m.p. 213–215°C; molecular weight 296 (by m.s.).

Copolymer syntheses

Poly(imide esters) were synthesized by solution condensation in DMF under a nitrogen flow. Monomer I was treated with the corresponding diols in stoichiometric amounts and under anhydrous conditions. Typically 0.44 g (2 mmol) of monomer I was dissolved in 5 cm^3 of DMF and 2 mmol of the corresponding diol in nearly 2 cm^3 of DMF, which was added to the former solution. After stirring for 2 h, the precipitated polymer formed was filtered, washed with acetone, alcohol and ether, and dried *in vacuo* at 50°C for 24 h.

Poly(imide amides) were prepared by condensation of monomer I with diamines in DMF and triethylamine to neutralize the HCl evolved during reactions. In a typical procedure, 0.44 g (2 mmol) of monomer I was dissolved in 5 cm^3 of DMF, and the corresponding amount of diamine was dissolved in 4 cm^3 of a mixture of DMF and trimethylamine (1:1). This solution was added to the first one with stirring. After 1 h the precipitate was filtered, washed with water, ethanol and ether, and dried overnight at 50°C. The yield was almost quantitative.

Preparation of poly(imide amine). Monomer II (2.96 g, 10.0 mmol) and piperazine (0.86 g, 10.0 mmol) were dissolved in 10 cm^3 DMF and stirred for 48 h at room temperature. The precipitate was filtered and washed with water, ethanol and ether, and dried *in vacuo* at 50°C overnight. Yield 3.2 g (83%).

Thermogravimetry. A Perkin–Elmer Thermal Analyzer TGS-2 was used to determine the thermal stability of the polymers. Experiments were carried out on ~2 mg samples under nitrogen at a flow rate of 60 cm^3 min^{-1}, at a heating rate of 10°C min^{-1} up to 800°C. The temperature of the maximum rate of polymer degradation (*PDT*) corresponds to the temperature (°C) at which d.t.g. curves reach their maxima and are collected in *Table 1*.

Mass spectrometry

Mass spectra were obtained using a Kratos MS 50 double-focusing mass spectrometer equipped with an Eclipse/120 data system from Data General using DS 90 Kratos software. Pyrolysis was carried out using the standard direct insertion probe for solid materials, heated from 50°C to 460°C at a heating rate of $10°C\,min^{-1}$, by continuously scanning the mass spectrometer and storing the mass spectra obtained. Electron impact (EI) mass spectra were obtained at 18 eV. Chemical ionization (CI) was performed using isobutane (99.96%) as reagent gas purchased from Matheson Gas Products. Source temperature was 300°C and acceleration voltage 8 kV.

RESULTS AND DISCUSSION

Copolymers I and II

The electron impact (EI) and isobutane chemical ionization (CI) mass spectra of pyrolysis products generated at 400°C from copoly(imide esters) I and II are reported in *Figures 1* and *2*, respectively.

The EI mass spectra (*Figures 1a* and *2a*) appear to be dominated by peaks at $m/z = 229, 243, 287$ and 327, which are assigned in *Table 2* to EI fragment ions formed by EI fragmentation of pyrolysis products.

To reduce fragmentation of the molecular ions, the pyrolysis was performed in chemical ionization mode by using isobutane as reagent gas. In *Figures 1b* and *2b* appear the peaks at $m/z = 333$, which can be assigned to the protonated molecular ion (MH^+) of bis(*N*-carboxymethyl)pyromellitimide (*Table 2*). Peaks at $m/z = 373$, 413, 701 and 745 (*Figure 1b*) and peaks at $m/z = 83$ and

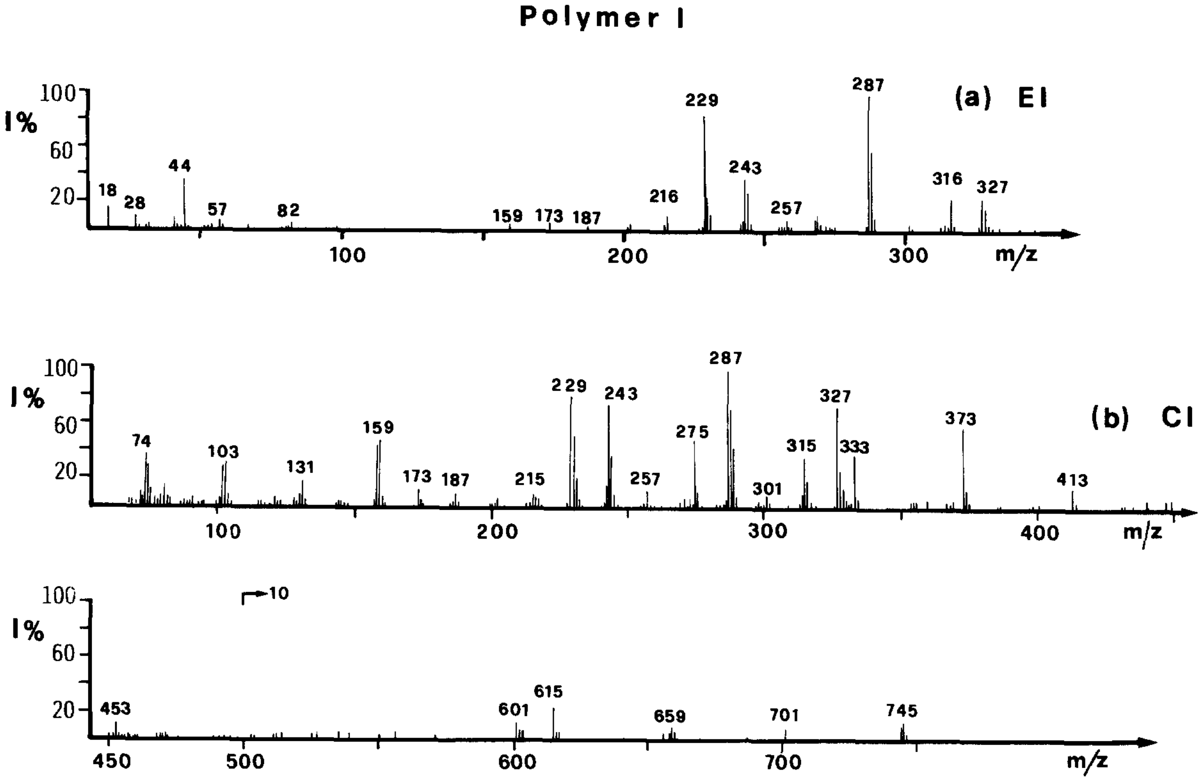


Figure 1 (a) EI, 18 eV and (b) CI, isobutane mass spectra of the pyrolysis products generated at 400°C from polymer I

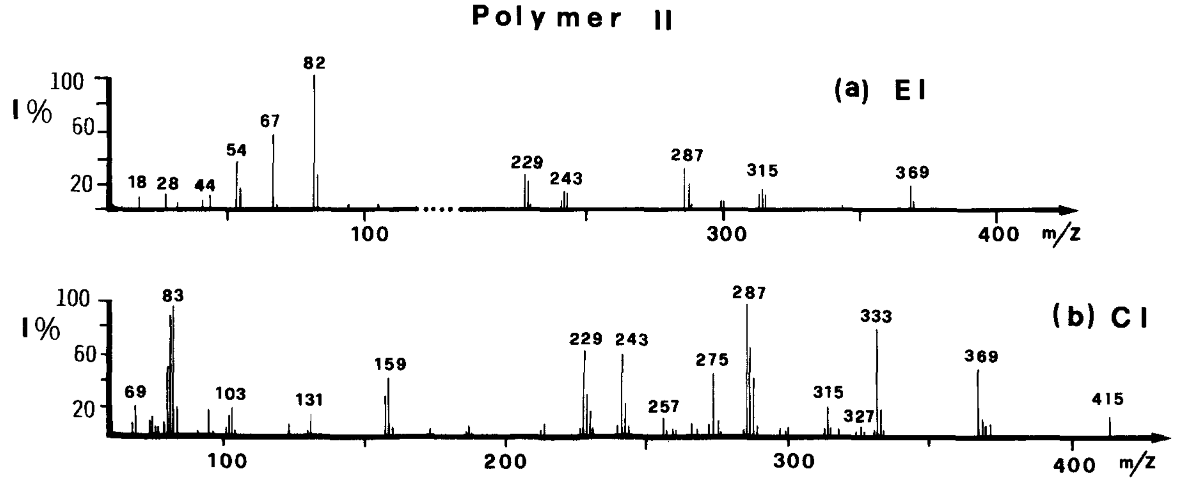
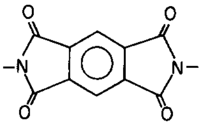


Figure 2 (a) EI, 18 eV and (b) CI, isobutane mass spectra of the pyrolysis products generated at 400°C from polymer II

Table 2 Molecular ions of thermal degradation compounds and EI/CI fragment ions observed in the d.p.m.s. of polymers I and II

Structure[a]	$x=1$		$x=4$		EI/CI fragments
	M^+	MH^+	M^+	MH^+	
$CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH_2$	–	–	82	83	–
$HOOC{-}CH_2{-}PYM{-}CH_2{-}COOH$	–	333	–	333	–
$HOOC{-}CH_2{-}PYM{-}CH_2{-}COO{-}(CH_2)_x{-}CH{=}CH_2$	–	373	–	415	–
$PYM{-}CH_2{-}COO{-}(CH_2)_x{-}CH{=}CH_2$ | $CH_2{-}COO{-}(CH_2)_x{-}CH{=}CH_2$	–	413	–	–	–
$CH_2{-}PYM{-}CH_2{-}COO{-}(CH_2)_x{-}CH{=}CH_2$ | $COO{-}(CH_2)_x{-}OOC{-}CH_2{-}PYM{-}CH_3$	–	701	–	–	–
$CH_2{-}PYM{-}CH_2{-}COO{-}(CH_2)_x{-}CH{=}CH_2$ | $COO{-}(CH_2)_x{-}OOC{-}CH_2{-}PYM{-}CH_2{-}COOH$	–	745	–	–	–
$H{-}PYM^+$					215
$H{-}PYM{-}CH_2^+$					229
$CH_3{-}PYM{-}CH_2^+$					243
$H{-}PYM{-}CH_2{-}CO^+$					257
$HOOC{-}CH_2{-}PYM^+$					275
$HOOC{-}CH_2{-}PYM{-}CH_2^+$					287
$HOOC{-}CH_2{-}PYM{-}CH_2{-}CO^+$					315
$CH_3{-}PYM{-}CH_2{-}COO{-}CH_2{-}CH{=}CH_2$					327
$CH_2{=}CH{-}(CH_2)_4{-}OOC{-}CH_2{-}PYM{-}CH_2^+$					369
$CH_3{-}PYM{-}CH_2{-}COO{-}(CH_2)_3{-}OOC{-}CH_2{-}PYM^+$					601
$CH_3{-}PYM{-}CH_2{-}COO{-}(CH_2)_3{-}OOC{-}CH_2{-}PYM{-}CH_2^+$					615
$HOOC{-}CH_2{-}PYM{-}CH_2{-}COO{-}(CH_2)_3{-}OOC{-}CH_2{-}PYM{-}CH_2^+$					659

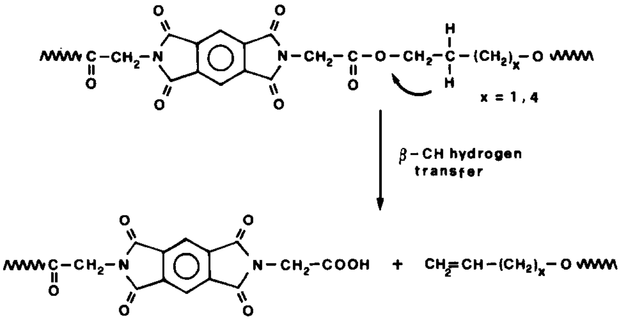
[a] PYM =



415 (*Figure 2b*) are due to MH^+ ions of pyrolysis products with carboxylic and/or olefinic end-groups (*Table 2*).

These results appear to establish that a selective β hydrogen transfer process is responsible for the thermal degradation of copoly(imide esters) I and II (*Scheme 1*). The latter is characteristic of the thermal degradation of aliphatic polyesters[17].

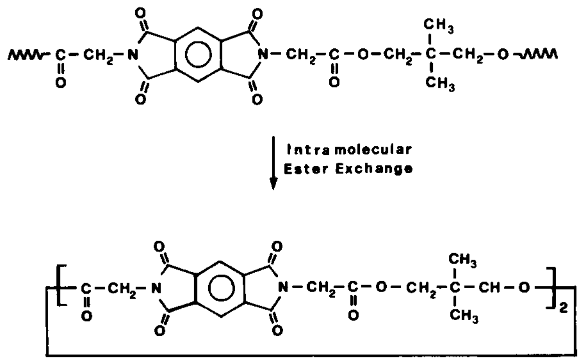
Scheme 1



Copolymer III

The EI and CI mass spectra of copoly(imide ester) III are reported in *Figures 3a* and *3b*, respectively. Analysis of these spectra reveals the absence of peaks corresponding to pyrolysis products with carboxylic and olefinic end-groups, which were present in the case of copolymers I and II. However, there is a peak at $m/z=800$ in the EI spectrum (*Figure 3a*), which appears at $m/z=801$ in the CI spectrum (*Figure 3b*), which has been assigned (*Table 3*) to a cyclic imide ester formed from copolyimide III by an intramolecular ester exchange process (*Scheme 2*).

Scheme 2



In fact, the neopentyl alcohol moiety in copolymer III is lacking β hydrogens, so that a β hydrogen transfer process cannot occur here[17]. Copolymer III decomposes at higher temperatures with respect to copolymers I and II (as shown by t.g. data in *Table 1*), by an intramolecular ester exchange process (*Scheme 2*). The cyclic monomer cannot be formed because of ring strain and therefore the cyclic dimer (peak at $m/z=800$) is the lowest molecular ion corresponding to cyclic oligomers observable in *Figure 3*. The remaining peaks correspond to fragment ions and are assigned in *Table 3*. Thermal decomposition pathways involving an intramolecular exchange process have been observed previously for several homopolyesters[17].

Copolymer IV

In *Figures 4a* and *4b* are shown the EI and CI mass spectra of the pyrolysis products generated at 400°C from copolyimide IV. The comparison of the two spectra

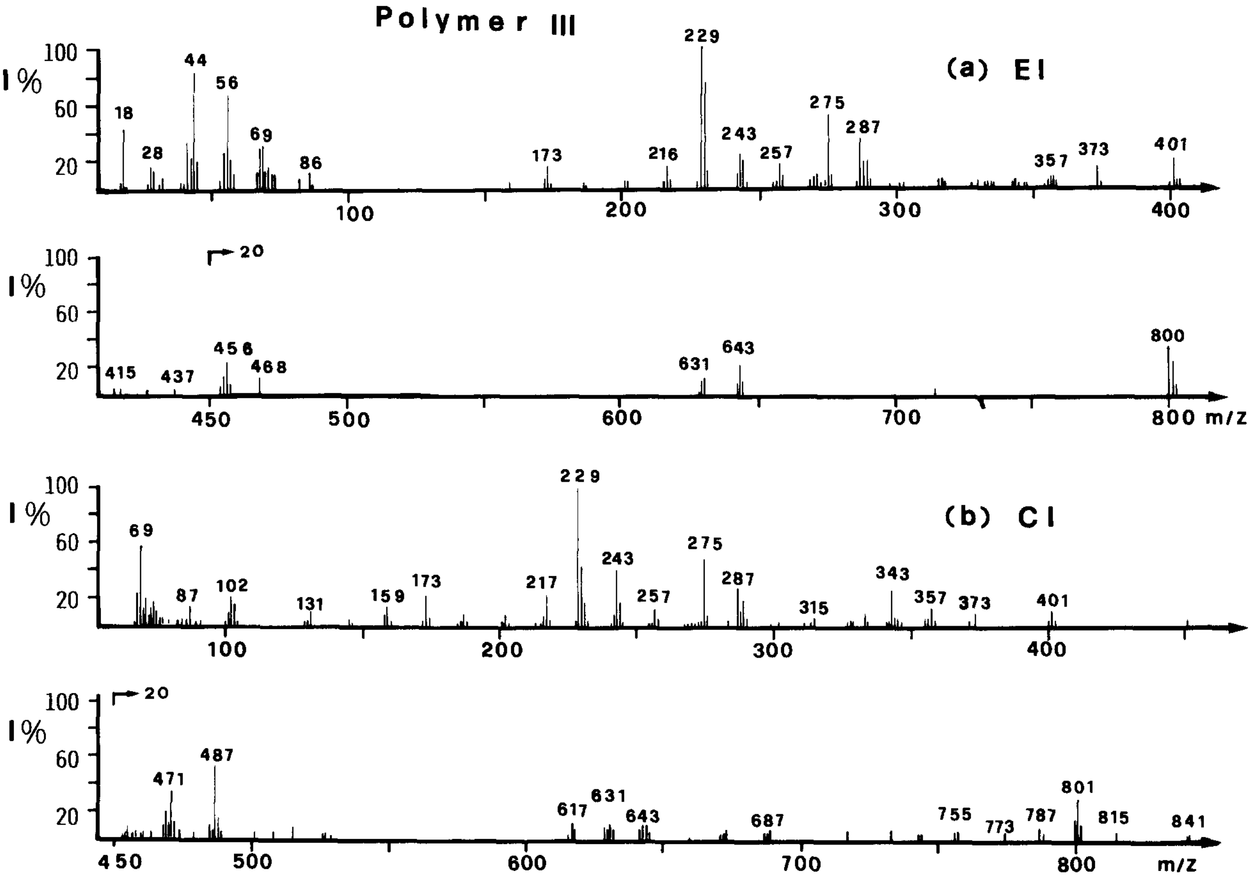


Figure 3 (a) EI, 18 eV and (b) CI, isobutane mass spectra of the pyrolysis products generated at 435°C from polymer III

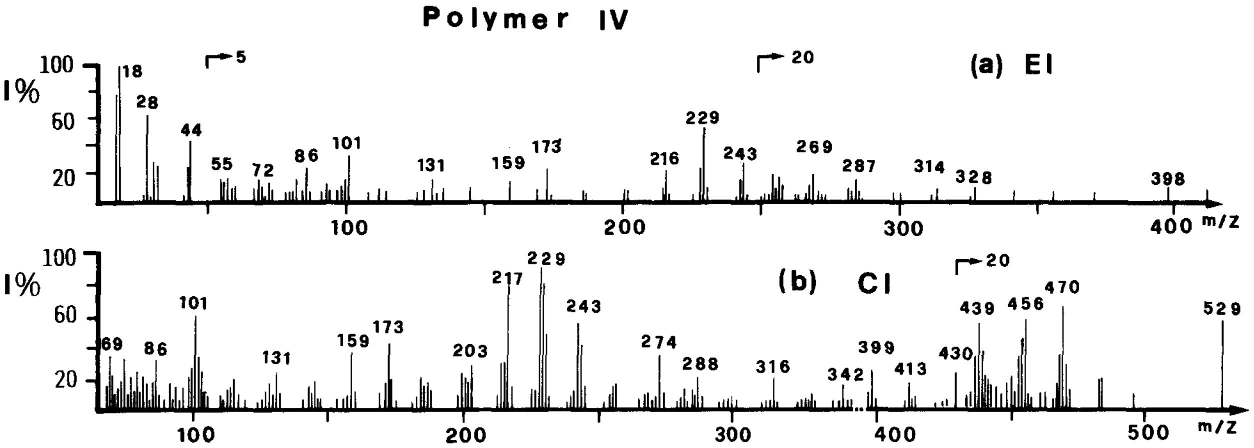


Figure 4 (a) EI, 18 eV and (b) CI, isobutane mass spectra of the pyrolysis products generated at 435°C from polymer IV

allows one to distinguish between the molecular ions of pyrolysis compounds from fragment ions. The structural assignments of the peaks appearing in both spectra are reported in *Table 4*.

In the CI spectrum (*Figure 4b*) the peaks at $m/z = 399$, 413, 456 and 470 can be assigned to MH^+ ions of pyrolysis products with isocyanate and imide or *N*-methyl end-groups (*Table 4*). These compounds could have originated by an N–H hydrogen transfer from the amide group to the methylene of the *N*-methylpyromellitimide moiety of copolymer IV (*Scheme 3*). This process has been observed in some polyamides[17].

Peaks at $m/z = 274$, 288 and 430 (*Figure 4b*) can be assigned as MH^+ ions of compounds with amide

Scheme 3

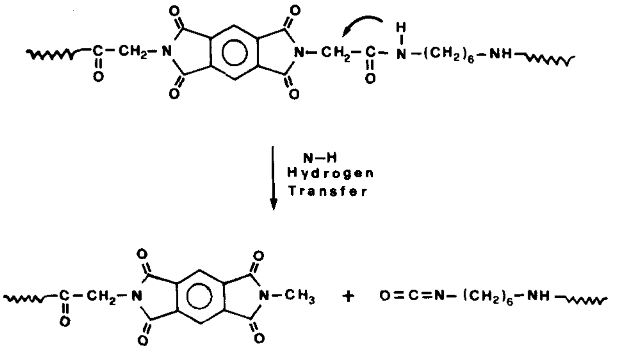
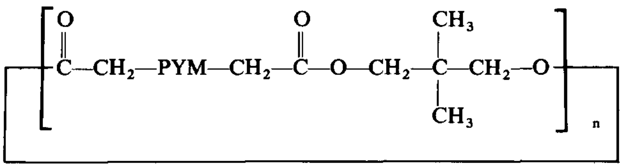
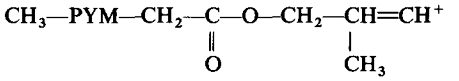
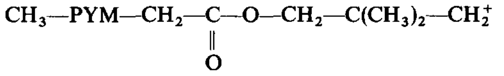
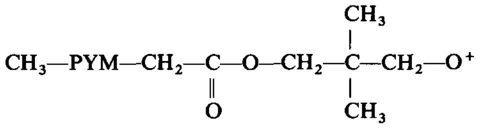
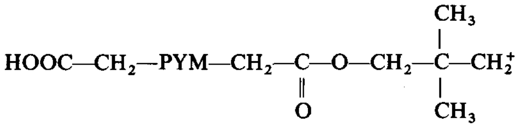
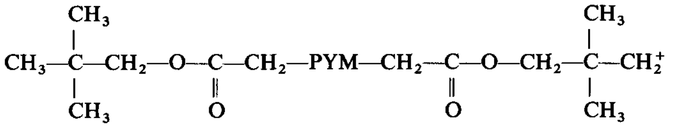
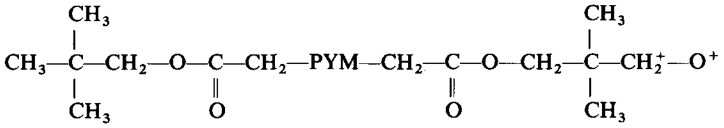
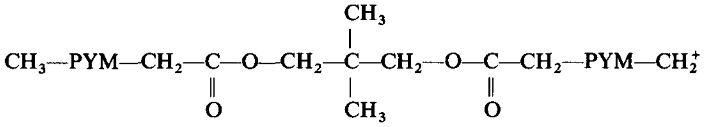
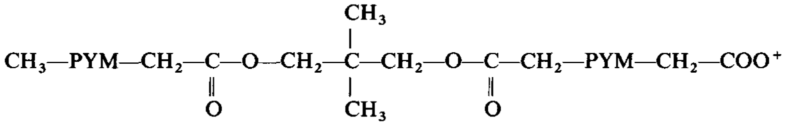
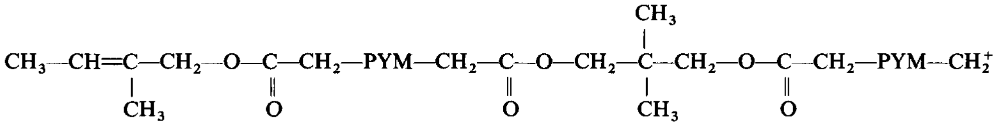
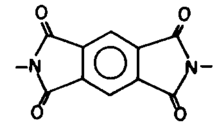


Table 3 Molecular ions of thermal degradation compounds and EI/CI fragment ions observed in the d.p.m.s. of polymer III

Structure[a]	M^+	MH^+	EI/CI fragments
 $\left[\overset{O}{\overset{\|}{C}}{-}CH_2{-}PYM{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O\right]_n$	800	801	-
$H{-}PYM{-}CH_2^+$			229
$CH_3{-}PYM{-}CH_2^+$			243
$H{-}PYM{-}CH_2{-}CO^+$			257
$HOOC{-}CH_2{-}PYM^+$			275
$HOOC{-}CH_2{-}PYM{-}CH_2^+$			287
 $CH_3{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\underset{\mid}{CH}}{=}CH^+$			343
 $CH_3{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}C(CH_3)_2{-}CH_2^+$			357
 $CH_3{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O^+$			373
 $HOOC{-}CH_2{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2^+$			401
 $CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2^+$			471
 $CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2^+{-}O^+$			487
 $CH_3{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}PYM{-}CH_2^+$			643
 $CH_3{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}PYM{-}CH_2{-}COO^+$			687
 $CH_3{-}CH{=}\underset{CH_3}{C}{-}CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}PYM{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}PYM{-}CH_2^+$			755

[a] PYM =



end-groups (*Table 4*), while the peak at $m/z = 217$ is due to pyromellitimide (*Table 4*). Also present is a peak at $m/z = 529$ which might be assigned to the MH^+ ion of compounds with amine groups at both ends (*Table 4*). These compounds can arise by secondary thermal degradation processes implying less defined multiple hydrogen transfer, hydrolysis and crosslinking. As a matter of fact, a high residue (50%) (*Table 1*) obtained by t.g. experiments and the presence of the peak at $m/z = 18$ corresponding to water is observed in *Figure 4a*.

Copolymer V

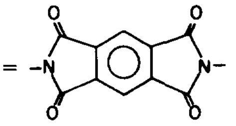
The *PDT* of this copolyimide appears at higher temperature (470°C) with respect to the previous copolymer (405°C) because the N–H hydrogen transfer observed in copolymer IV cannot occur. Some other decomposition pathway must therefore occur, which requires a higher activation energy.

In *Figures 5a* and *5b* are shown the EI and CI mass spectra of pyrolysis products formed at 460°C from copolyimide V. Also in this case a comparison of the two

Table 4 Molecular ions of thermal degradation compounds and EI/CI fragment ions observed in the d.p.m.s. of polymer IV

Structure[a]	M^+	MH^+	EI/CI fragments
H—PYM—H	216	217	
H—PYM—CH_2—CO—NH_2	–	274	
CH_3—PYM—CH_2—CO—NH_2	287	288	
H—PYM—CH_2—CO—NH—$(CH_2)_6$—N=C=O	398	399	
CH_3—PYM—CH_2—CO—NH—$(CH_2)_6$—N=C=O	412	413	
H_2N—$(CH_2)_6$—NH—OC—CH_2—PYM—CH_2—CO—NH_2	–	430	
H_2N—OC—CH_2—PYM—CH_2—CO—NH—$(CH_2)_6$—N=C=O	455	456	
CH_3—NH—CO—CH_2—PYM—CH_2—CO—NH—$(CH_2)_6$—N=C=O	–	470	
H_2N—$(CH_2)_6$—NH—OC—CH_2—PYM—CH_2—CO—NH—$(CH_2)_6$—NH_2	–	529	
CH_3—PYM^+			229
CH_3—PYM—CH_2^+			243
H—PYM—CH_2—CO^+			257
H_2N—OC—CH_2—PYM—CH_2—CO^+			314
CH_3—NH—OC—CH_2—PYM—CH_2—CO^+			328
CH_3—$(CH_2)_3$—NH—OC—CH_2—PYM—CH_2^+			342
CH_3—$(CH_2)_5$—NH—OC—CH_2—PYM^+			356

[a] PYM =



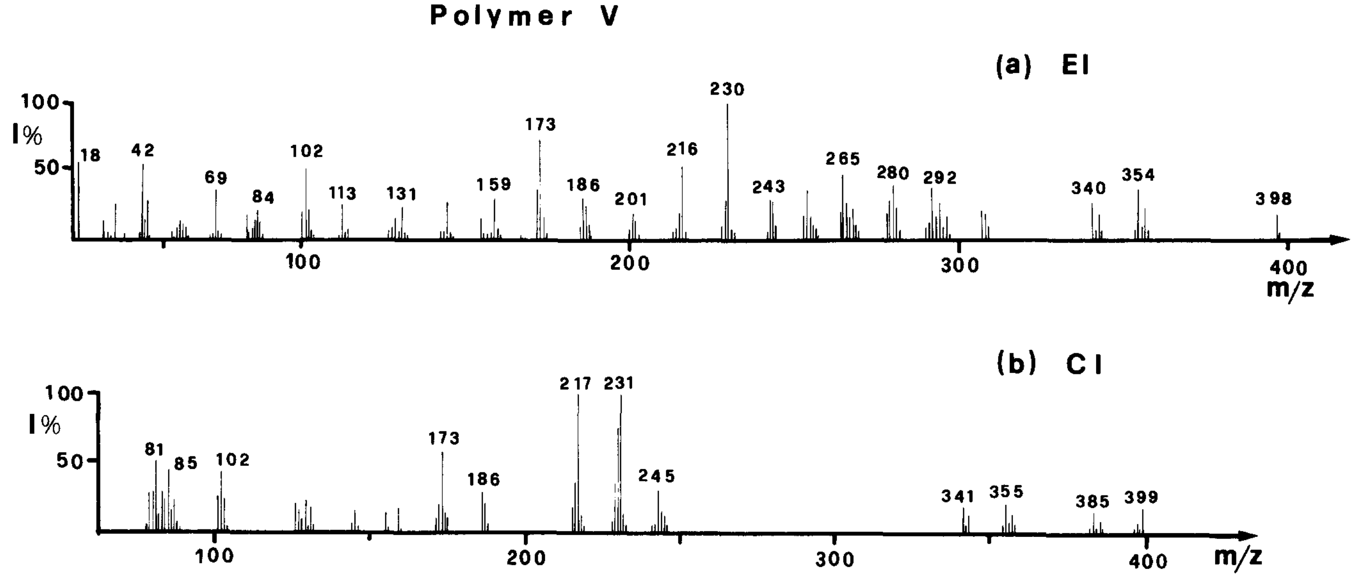


Figure 5 (a) EI, 18 eV and (b) CI, isobutane mass spectra of the pyrolysis products generated at 460°C from polymer V

spectra is helpful in distinguishing molecular ions from m.s. fragment ions.

Peaks at $m/z=217$ and 231 (*Figure 5b*) can be assigned in *Table 5* to MH^+ ions of pyromellitimide and to its *N*-methyl homologue respectively. Peaks at $m/z=341$, 343, 355 and 357 are due to MH^+ ions of pyrolysis compounds with piperazine and N–H or *N*-methyl end-groups (*Table 5*).

These pyrolysis compounds can be formed by an α-CH hydrogen transfer process towards the *N*-methylene and/or the nitrogen of the pyromellitimide moiety in copolymer V, producing unsaturated piperazine and *N*-methyl or N–H end-groups, together with CO and ketene (*Scheme 4*). In fact, a peak at $m/z=42$ assignable to ketene is observed in *Figure 5a*.

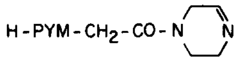
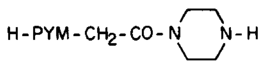
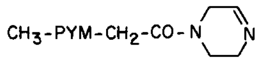
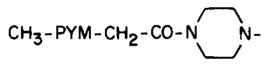
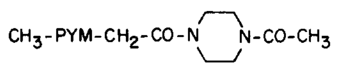
Copolymer VI

The thermal degradation of copolymer VI occurs at lower temperatures with respect to the previous copolymers, with the *PDT* appearing at 280°C (*Table 1*). In *Figure 6b*, the isobutane CI mass spectrum of pyrolysis compounds evolved at 280°C by copolymer VI is shown. In this spectrum two peaks appear at $m/z=297$ and 87 which can be assigned to MH^+ ions of bis(*N*-allyl)-pyromellitimide and piperazine, respectively. The presence of these compounds implies a depolymerization process leading to the formation of starting materials (*Scheme 5*). Indeed, this copolymer has been prepared by a Michael addition reaction between bis(*N*-allyl)pyromellitimide and piperazine.

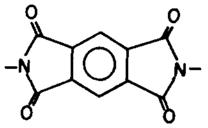
CONCLUSIONS

Thermal decomposition of the copolyimides investigated occurs around 400–470°C, as indicated by the *PDT* values listed in *Table 1*. One notable exception is given by copoly(imide amine) VI, which depolymerizes at lower

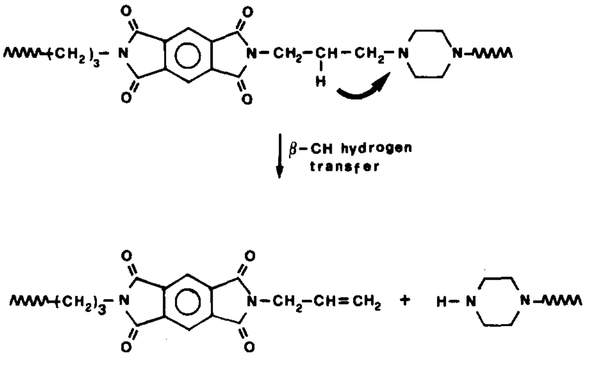
Table 5 Molecular ions of thermal degradation compounds observed in the d.p.m.s. of polymer V

Structure[a]	M$^+$	MH$^+$
$CH_2{=}CO$	42	–
H—PYM—H	216	217
H—PYM—CH_3	230	231
CH_3—PYM—CH_3	244	245
	340	–
	342	343
	354	355
	356	357
	398	399

[a] PYM =



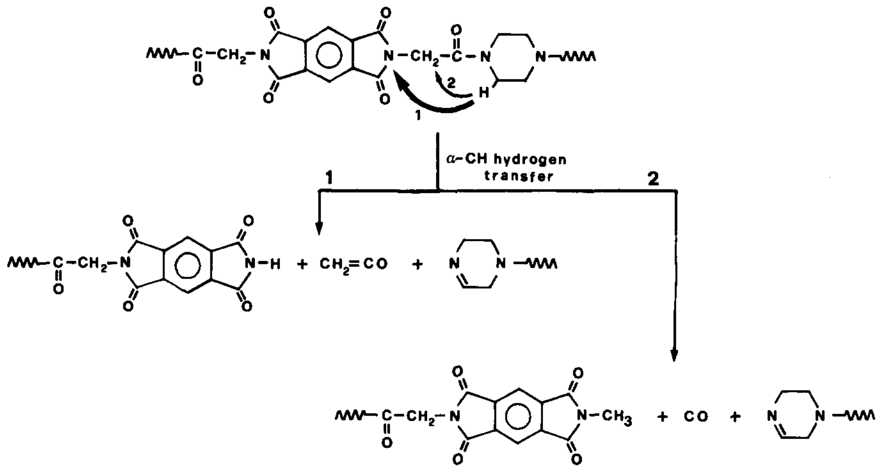
Scheme 5



temperature (280°C, *Table 1*) without leaving a charred residue.

The presence of highly thermally stable pyromellitimide units apparently does not substantially improve the thermal decomposition temperature of these materials, which decompose in the usual range of the other comonomer component. That is to say, the thermal stability of these copolymers corresponds to that of the weakest unit present along the polymer chain. As a matter of fact, the thermal decomposition pathways of

Scheme 4



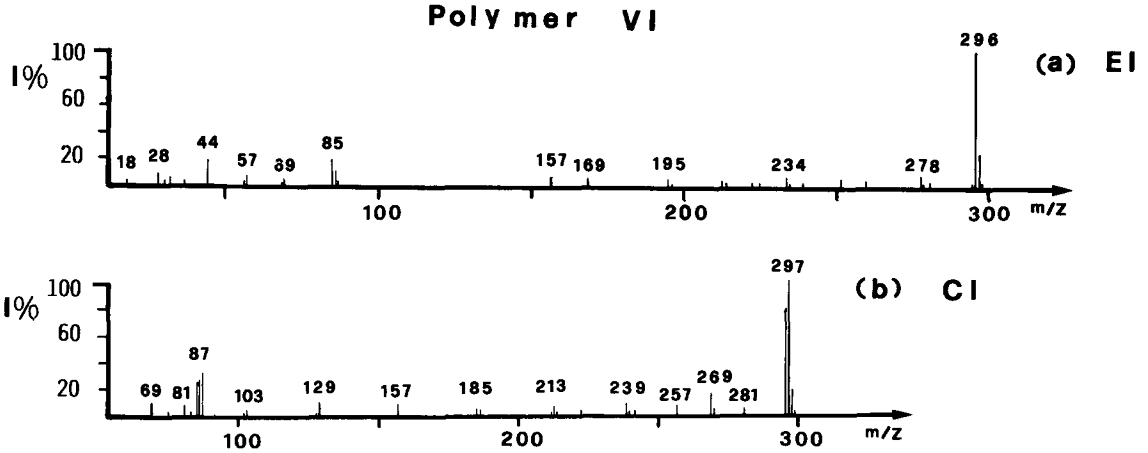


Figure 6 (a) EI, 18 eV and (b) CI, isobutane mass spectra of the pyrolysis products generated at 280°C from polymer VI

copolymers I–V reflect those occurring in polyesters and polyamides[17].

Furthermore, the depolymerization reaction responsible for the very low temperature of decomposition of copoly(imide amine) VI is, to the best of our knowledge, novel and previously unreported.

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