Selective Formation of Cyclic Monomer, Dimer, or Trimer in the Pyrolysis of Isomeric Dihydroxybenzene Phthalate Polyesters

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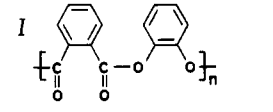
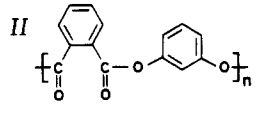
ABSTRACT: The thermal degradation processes occurring in the pyrolysis of the isomeric aromatic polyesters I–III synthesized by condensation reaction between phthaloyl chloride and catechol, resorcinol, or hydroquinone, respectively, were investigated. Data obtained by direct pyrolysis mass spectrometry (DP-MS) indicate that the thermal decomposition processes of these polymers yield only and selectively cyclic 1,2-dihydroxybenzene phthalate, bis(1,3-dihydroxybenzene phthalate), and tris(1,4-dihydroxybenzene phthalate) as a function of the polymeric structure. These results were also confirmed by GPC and MS analyses of the pyrolytic materials collected during the thermal degradation experiments under vacuum of polymers I–III. As a consequence, it is possible to identify each of the three isomeric polymers just on the basis of their DP-MS spectra.

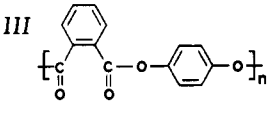
Introduction

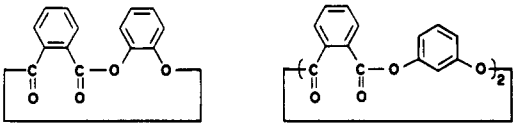
The thermal degradation mechanisms of polyesters have been extensively studied.[1–4] As in other cases of carbonyl-containing polymers,[5–8] intramolecular exchange reactions predominate in the primary thermal fragmentation processes of polyesters.[2] Usually, cyclic oligomers of different sizes and abundances are produced in the above-mentioned processes, and the cyclic distribution law often indicates the mechanism of pyrolytic compound formation.[2,9–12]

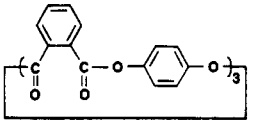
In the case of totally aromatic polyesters, the formation of cyclic products is strongly influenced by conformational preferences or restrictions along the polymer chain.[4] In this article we report the cases of three isomeric aromatic polyesters I–III obtained by condensation reactions between phthaloyl chloride and catechol, resorcinol, or hydroquinone that, contrary to the instances of totally aromatic polyesters reported elsewhere,[4] decompose, generating only and selectively cyclic 1,2-dihydroxybenzene phthalate (IV), bis(1,3-dihydroxybenzene phthalate) (V), and tris(1,4-dihydroxybenzene phthalate) (VI), respectively.











The thermal degradation products were examined by both direct pyrolysis of the polymers in the ion source of a mass spectrometer (DP-MS)[2,13,14] and GPC and MS analyses of the pyrolytic materials collected during the decomposition of polymers I–III in a glass reactor maintained under vacuum at the temperature of the maximum rate of polymer degradation.

The data reported in the present study indicate that the intramolecular ester-exchange reactions, responsible for the thermal fragmentation of polyesters I–III, cause the selective formation of only one cyclic product of different size as a consequence of the ortho/ortho, ortho/meta, or ortho/para structure of each isomeric polymer. As a consequence, it is also possible to positively identify each of the three isomeric polymers just on the basis of the pyrolytic product composition, easily obtained by means of their DP-MS spectra.

Experimental Section

Materials. All solvents and basic materials were commercial products appropriately purified before use.

Cyclic 1,2-Dihydroxybenzene Phthalate Synthesis. Two solutions were introduced simultaneously, dropwise, and at the same rate into 700 mL of freshly distilled THF placed in a four-neck flask (1 L) maintained at 0 °C (ice bath) under stirring and an N_2 flow. These solutions consisted of the following: Solution A, 15 g of catechol (0.136 mol), 30 g of triethylamine (TEA), and tetrahydrofuran (THF) up to 100 mL; solution B, 28 g of phthaloyl chloride (0.136 mol) and THF up to 100 mL.

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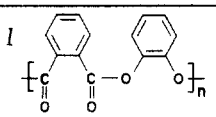
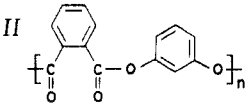
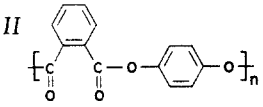
Table 1. Structure, Average Molecular Weight (M_{GPC}), Inherent Viscosity, Thermal Stability (PDT), TIC, and Percent Thermal Stable Residue of Polyesters I–III

polymer structure	M_{GPC} (n)[a]	η_{inh}[b] (dL/g)	PDT[c] (°C)	% residue at 600 °C[d]	TIC[e]
I 	6100 (25)	0.09	320	0	250
II 	5500 (23)[f]	0.11	450	26	320
III 	insoluble	0.15	450	28	400

[a] M_{GPC} values measured with respect to polystyrene standards in correspondence to the maxima of the GPC curves. Also reported in parenthesis the number-average degree of polymerization. [b] $\eta_{inh} = (\ln \eta_r)/c$; $c = 0.5$ g/dL using dimethylformamide as solvent. [c] TG experiments under N_2, flow rate 60 mL/min, heating rate 10 °C/min. [d] From TG experiments. [e] Temperature of maximum intensity of the total ion current from DP-MS experiments. [f] Polymer partially soluble in THF.

About 3 h after the addition, the suspension was refluxed for 1 h and then cooled in a freezer, and the white triethylamine hydrochloride was filtered. The clear solution was evaporated to leave a green, thick oil from which the fraction of cyclic oligomers at a lower molecular weight was extracted with ethyl ether and then evaporated until dry.

The mixture of oligomers was chromatographed on a silica gel (particle size 70–230 mesh, Merck) column (h = 90 cm, i.d. 3 cm), using a solution of ethyl ether from 25 to 40% in petroleum ether (bp 35–60 °C). The cyclic catechol phthalate was the first product eluted from the column; it was collected, evaporated to dryness, and crystallized from THF/*n*-hexane to give white crystals (yields of ~11%) having a melting point of 136–138 °C. The compound was characterized by ^{1}H-NMR (multiplets between 7.97 and 7.65 ppm and between 7.07 and 7.00 ppm), ^{13}C-NMR [signals at 164.364, 145.202, 140.316, 127.917, and 125.954 (quaternary carbons) and 135.255, 132.270, 125.331, 123.662, 122.935, and 109.537 ppm (tertiary carbons)], and positive FAB mass spectrometry (molecular ion detected as MH^+ at m/z 241).

Polyester Syntheses. Polyesters I–III were synthesized by the solution method starting from phthaloyl chloride and catechol, resorcinol, and hydroquinone, respectively, in THF using TEA as the HCl acceptor. In a typical procedure, 1.1 g (0.01 mol) of hydroquinone was dissolved in 30 mL of THF together with 2.02 g (0.02 mol) of TEA. A solution of phthaloyl chloride (2.03 g, 0.01 mol) in 20 mL of THF was then added at 0 °C under stirring in an N_2 atmosphere. After 15 min the mixture was heated to 25 °C and maintained under vigorous stirring for 10 h. The solid material formed was recovered by filtration, repetitively washed with H_2O to avoid any traces of triethylamine hydrochloride, and dried under vacuum. The residue, polymer III, was then dissolved in hot dimethylformamide (DMF), and a white material was recovered after reprecipitation in ethanol (yield 65%). Since polymers I and II are soluble in THF, they were collected by direct precipitation of their THF solutions in ethanol and purified according to the procedure described above.

GPC Analysis. A Waters 6000 A apparatus, equipped with four μ-Styragel columns (in the order 1000-, 500-, 10000-, and 100-Å pore size) attached in series, was used. The analyses were performed at 25 °C using THF as eluant at a flow rate of 1 mL/min. A Model R401 differential refractometer (Waters) was used as the detector. The instrument was calibrated with a mixture of five polystyrene standards (Polysciences; molecular weights between 2000 and 1 200 000) for the M_{GPC} determination of the polymer samples.

Viscometric Analysis. Inherent viscosities of the polymers examined ($\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL) were measured in a Desreux-Bishoff suspended-level viscometer. The measurements were performed in *N*-methylpyrrolidone (NMP) at 30 ± 0.01 °C.

^{1}H-NMR and ^{13}C-NMR Analyses. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker 200 A-CF spectrometer using $CDCl_3$ as solvent.

Thermal Properties. Thermogravimetric analyses were performed with a Perkin-Elmer TGS-2 apparatus in an N_2 atmosphere (flow rate 60 mL/min) with a heating rate of 10 °C/min.

Mass Spectrometric Analyses. DP-MS experiments were carried out on a Kratos MS 50 S double-focusing mass spectrometer equipped with an Eclipse/120 data system (Data General) using the standard direct insertion probe for solid materials, heating from 50 to 600 °C at a heating rate of 10 °C/min. The source temperature was 300 °C. Electron impact (EI) mass spectra were obtained at 18 eV. Mass spectral scans (from m/z 2000 to m/z 20) were made continuously and the corresponding spectra stored.

FAB analyses were performed using the standard FAB source. Mass spectra were recorded with a UV recorder. Xenon was used as bombarding gas with an energy of 8 kV. Spectra were obtained by using 3-nitrobenzyl alcohol as a matrix and a scan rate of 30 s/decade.

Pyrolysis of Polyesters I-III. The pyrolyses of polyesters I–III were performed on pellets of ~200 mg placed at the bottom of a sublimation apparatus in which the upper part was cooled and maintained at 0 °C. In each pyrolytic experiment, this system, maintained at ~10^{-2} Torr, was immersed in a melted mixture of $NaNO_3/KNO_3$ (48/52%) heated at 420 °C in the cases of polymers II and III and 300 °C in the case of polymer I (temperatures corresponding to the PDT values; see Table 1). The material sublimated on the cooled zone was collected and examined without further treatment by GPC and MS analyses.

Results and Discussion

The inherent viscosities and the GPC-average molecular weight (M_{GPC}) values (estimated considering the elution volumes corresponding to the maxima on the GPC traces with respect to polystyrene standards) of polyesters I–III are reported in Table 1.

The structural characterization of these materials was attempted by NMR and FAB mass spectrometric analyses.

Because the production of synthetic polymers by condensation reactions is often accompanied by the formation of sizable amounts of oligomers,[9] the FAB-MS technique, allowing the detection of these species, affords the possibility to proceed to the structural identification of the polymers.[17] The positive FAB mass spectra of polyesters I–III appear very similar as expected considering that these polymers differ only by the isomeric structure of the dihydroxybenzene unit present in their repeating unit. In Figure 1, for brevity, only the spectrum of polyester II is reported as an example.

The FAB mass spectrum consists essentially of a series of intense peaks at m/z 241, 481, 721, 961, 1201, 1441, 1681, and 1921, corresponding to molecular ions [as $(MH)^+$] of cyclic oligomers (up to octamer). The other two series of peaks, which appear with low intensity at

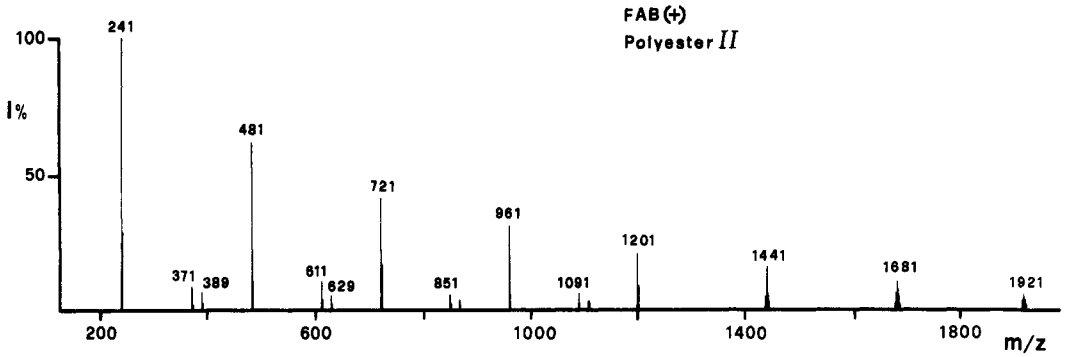


Figure 1. Positive FAB mass spectrum of polyester II.

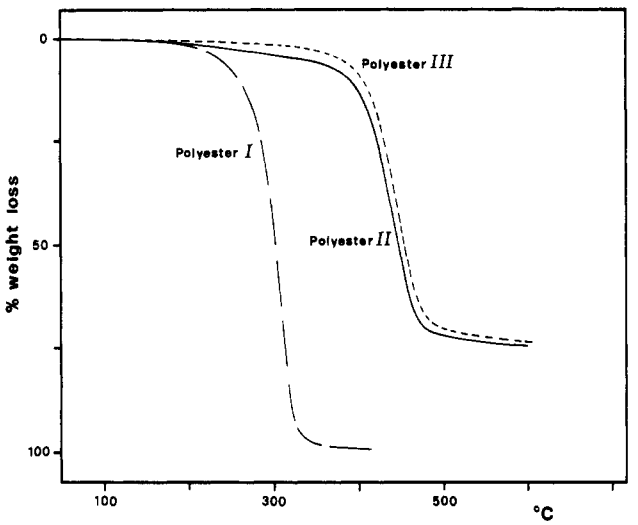


Figure 2. Thermogravimetric curves of (- - -) polyester I, (—) polyester II, and (- · -) polyester III recorded under a N_2 flow and with a heating rate of 10 °C/min.

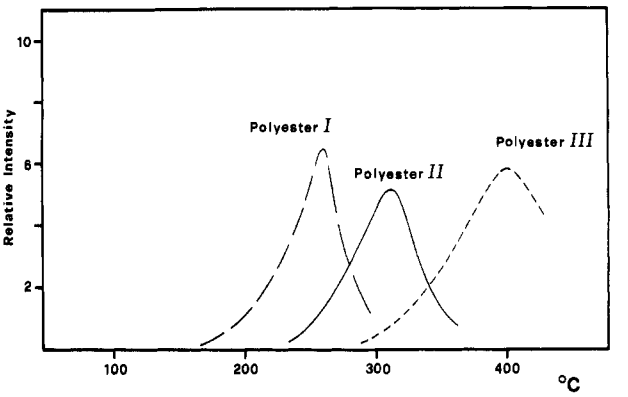


Figure 3. Total ion current curves of (- - -) polyester I, (—) polyester II, and (- · -) polyester III obtained by DP-MS experiments.

m/z 371 + n240 and 389 + n240, are due to secondary fragmentation phenomena.

It appears that polyesters I–III cannot be distinguished only on the basis of FAB data.

Generally, NMR analysis does not give significant results in the case of condensation polymeric materials containing large repeating units.[15] However, in the present case, the three NMR spectra (omitted for brevity) are slightly different, showing that polyesters I–III, though they cannot be individually identified, are different materials.

The thermal behavior of the totally aromatic polyesters I–III was investigated by TG experiments under a nitrogen flow and with a heating rate of 10 °C/min. The weight loss curves vs temperature are shown in Figure 2. The thermal degradation of polyesters takes place in one stage, and the temperatures of the maximum rate of polymer decomposition (PDT) are listed in Table 1. There is a considerable difference between the thermal stability of polyesters II and III (ortho/meta and ortho/para isomers) and that of polyester I (ortho/ortho isomer), which appears to be much less thermally stable (a difference of 130 °C in the PDT values). In the polyester II and III cases the TG curves show also the formation of a moderate amount (~25% at 800 °C) of persistent residue.

To investigate the mechanism of thermal decomposition of polyesters I–III, direct pyrolysis of the polymers in the ion source of a mass spectrometer (DP-MS), in each case heating the polymer at 10 °C/min from 50 to 600 °C, was performed. As widely reported,[2,13,14] an advantage of the DP-MS technique is that pyrolysis is accomplished under high vacuum, and therefore the formed thermal fragments are readily removed from the hot zone and detected. In this way, the occurrence of secondary reactions is strongly reduced, so that almost exclusively primary pyrolytic products are examined. Consequently, the information thus obtained is of particular importance in determining the thermal degradation mechanism of a polymer.[2]

All three investigated polyesters show a single step of thermal degradation, and their total ion current (TIC) vs temperature curves are shown in Figure 3. It can be observed that the TIC maximum temperatures appear at lower values with respect to the corresponding PDT values (see also Table 1). This behavior can be explained by assuming a pressure effect on the thermal degradation processes of polyesters I–III.[16]

Figure 4a shows the EI (18 eV) mass spectrum at 250 °C (temperature corresponding to the maximum of the TIC curve) recorded during the pyrolysis of polymer I (ortho/ortho isomer). The spectrum exhibits peaks only up to m/z 240, which corresponds to the molecular ion (as M^+) of the cyclic monomer (compound IV). The other peaks at m/z 76, 104, 132, 168, 196, and 212, of which structural assignments are given in Table 2, correspond to EI fragments. This spectrum is exactly like that of the synthesized cyclic monomer (see Experimental Section).

The EI mass spectrum recorded at 320 °C for polyester II (ortho/meta isomer), is shown in Figure 4b. The peak at m/z 480 (peak at higher mass in the spectrum) corresponds to the molecular ion of the cyclic dimer (compound V).

The EI mass spectrum of polymer III (ortho/para isomer), detected at 400 °C, is reported in Figure 4c. Comparing this spectrum with those of Figure 4a,b, one can observe that in the spectrum of Figure 4c a peak also appears at m/z 720 (peak at higher mass in the spectrum) corresponding to the cyclic trimer (compound VI).

Formation of cyclic monomer can be accepted as taking place in the pyrolysis of polyester I in which both benzene units are ortho substituted (compound IV), but this is very unlikely in the case of the isomeric polyester III (ortho/para), lacking the steric requirements necessary for its

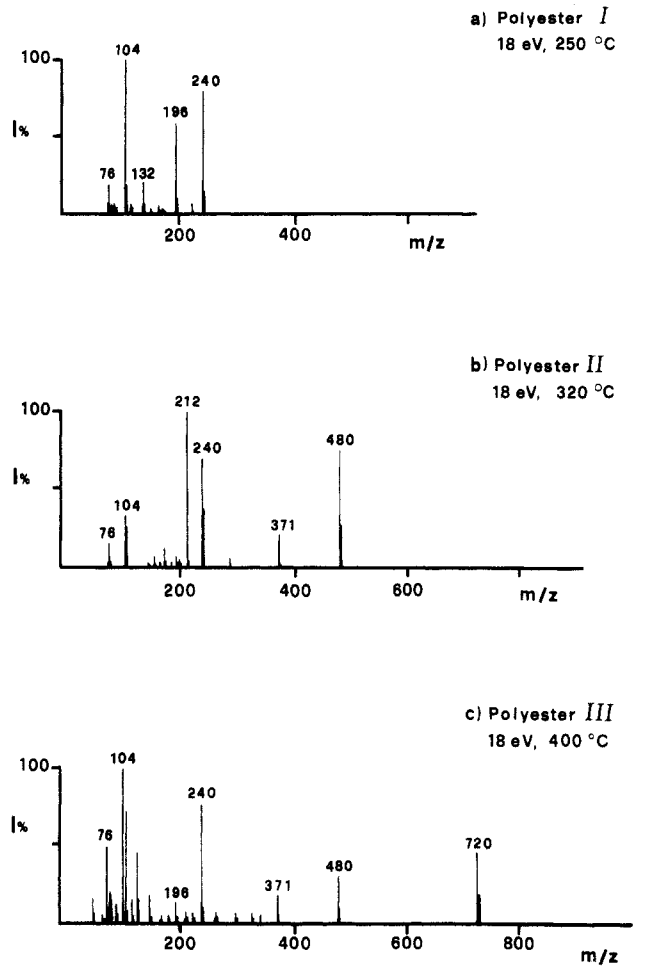
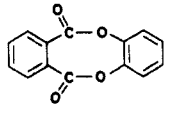
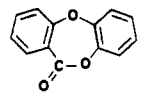
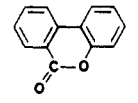
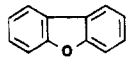
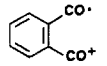
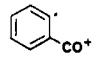


Figure 4. Electron impact mass spectra (18 eV) of (a) polyester I at 250 °C, (b) polyester II at 320 °C, and (c) polyester III at 400 °C.

Table 2. Electron Impact Fragments from the DP-MS Polyester I

structure	*m/z*
	240
	212
	196
	168
	132
	104
	76

formation. Also in the case of polyester II (ortho/meta isomer) the formation of cyclic monomer is in doubt.

A possible explanation of the above-reported MS data is that in the mass spectra of Figure 4b,c the peak at *m/z* 240 is an EI fragment of compounds at higher molecular weight, an event often occurring for cyclic products containing more ester linkages.[14,17,18] However, it might

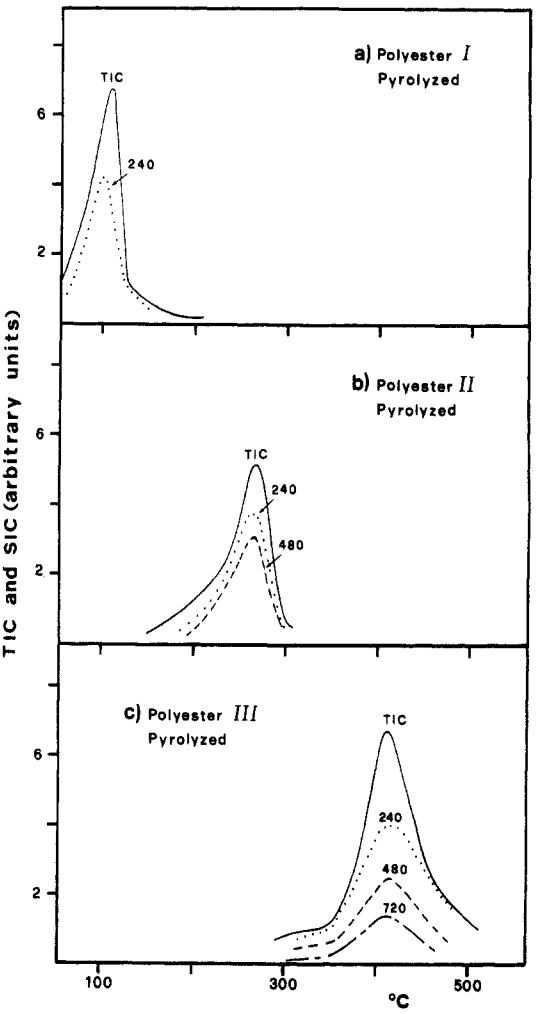


Figure 5. TIC (—) and SIC of peaks at *m/z* 240 (···), 480 (- - -), and 720 (– – –) obtained by DP-MS experiments of materials collected by pyrolysis of (a) polymer I, (b) polymer II, and (c) polymer III.

be observed that only cyclic products are formed in the thermal degradation of polyesters I–III. Furthermore, the composition of the pyrolysis products is characteristic of each polyester and, as a consequence, each polymer can be easily identified on the basis of the DP-MS data.

The observed difference between the PDT values and the TIC maximum temperatures (Table 1) suggests that the thermal degradation of polyesters I–III occurs by a depolymerization mechanism. In fact, under the high-vacuum conditions present in the DP-MS experiments, a more efficient removal of the pyrolytic products causes a strong change in the ring–chain equilibria and, as a consequence, the thermal degradation of these polymers occurs at lower temperatures.[16]

To ascertain the true composition of the pyrolytic materials, polyesters I–III were pyrolyzed in a glass reactor at temperatures of either 300 (polymer I) or 420 °C (polymers II and III) (see Experimental Section). The products that condensed on the cold zone of the apparatus were examined, without further treatment, by GPC, DP-MS, and FAB-MS analyses.

The total ion current (TIC) curves of the three collected materials are reported in Figure 5. Each trace presents only one maximum, which appears at 105 (polyester I), 265 (polyester II), and 400 °C (polyester III), respectively. The mass spectra recorded in the three cases are exactly like those reported in Figure 4a–c, and thus they are omitted here.

The single ion current (SIC) curves (obtained by plotting the intensity of the selected peak vs the temperature) of

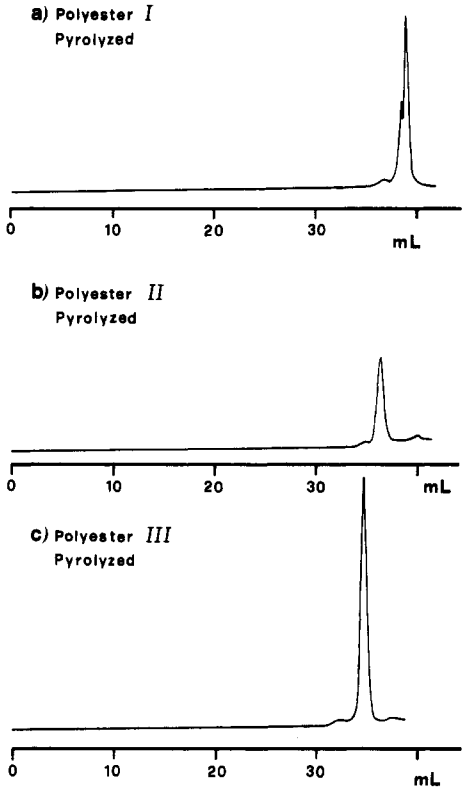


Figure 6. GPC traces of products obtained by pyrolysis of (a) polyester I, (b) polyester II, and (c) polyester III.

the peaks at m/z 240, 480, and 720 are also reported in Figure 5.

In principle, the TIC curve of a mixture of preformed products presents more maxima because each compound sublimates at a different temperature when the sample is heated gradually. When the respective SIC curve is plotted for each product of the mixture, a maximum coincident with one of the maxima of the TIC curve is exhibited.[19]

On the contrary, during the thermal degradation of a polymer which occurs beyond a characteristic temperature, more products may be formed and detected at the same time. So, generally, the TIC and all the SIC curves are coincident. The same behavior is found when the peaks present in the mass spectrum are due to ions generated by EI fragmentation of the same molecular ion. The data of Figure 5 are in agreement with this last hypothesis.

The GPC traces of the three sublimates are reported in Figure 6. It can be observed that only one peak appears in each GPC curve, pointing out that each pyrolytic material consists of essentially only one product. Although the pyrolytic products have different structures (*o*-, *m*-, or *p*-dihydroxybenzene unit in the molecule), their elution volumes (Figure 6) were related with the log M, supposing M = 240 for the compound of Figure 6a, 480 for that of Figure 6b, and 720 for that of Figure 6c. As expected, the linear dependence observed in Figure 7 is consistent with the conclusion that the peaks in the GPC traces are due to oligomeric members of the same series.[18,20]

Further evidence results from examination of the positive FAB mass spectra of the pyrolytic materials reported in Figure 8. Contrary to the DP-MS spectra of Figure 4, as a consequence of the more "soft ionization" of the molecules in the FAB desorption that minimize the fragmentation processes of molecular ions, the FAB mass spectra appear to consist almost exclusively of peaks at m/z 241, 481, or 721 (MH^+). Thus, it can be inferred that the peaks at m/z 240 and 480 appearing in the mass spectrum of polymer III (Figure 4c) are secondary fragments of the molecular ion at m/z 720 (cyclic trimer), and

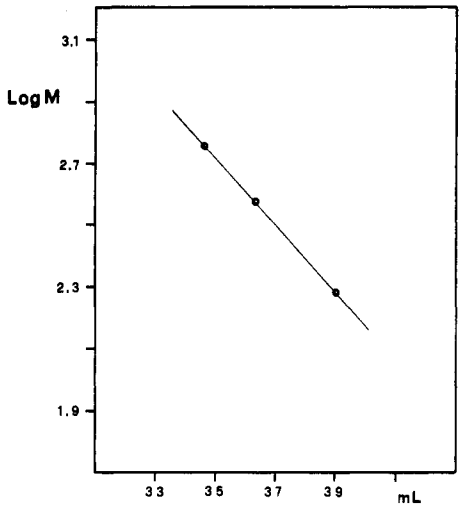


Figure 7. Dependence of the elution volume (GPC) on the logarithm of the molecular weight of the cyclic products (compounds IV–VI).

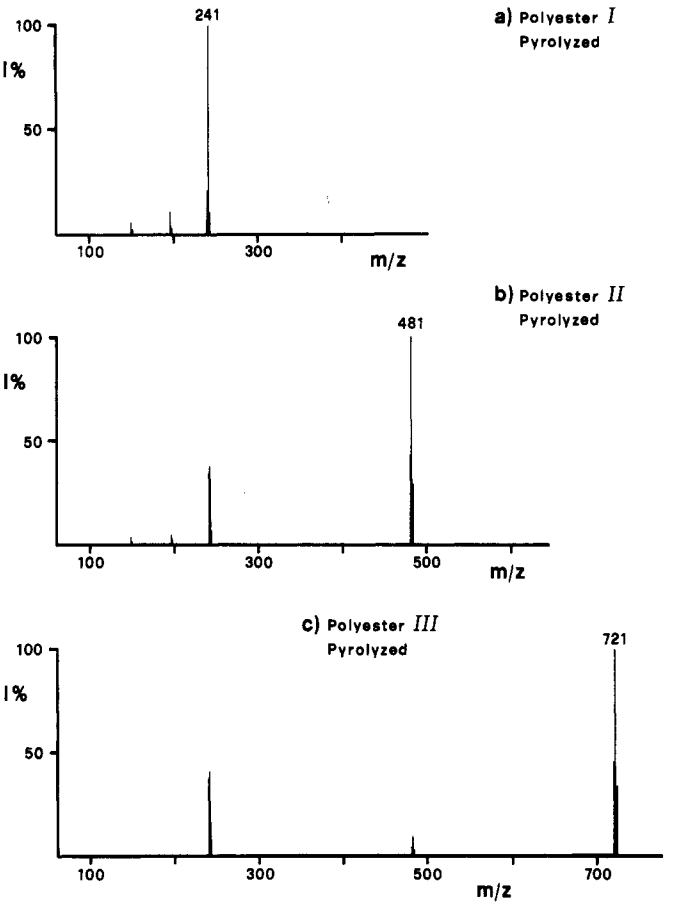


Figure 8. Positive FAB mass spectra of the products obtained by pyrolysis of (a) polyester I, (b) polyester II, and (c) polyester III.

the peak at m/z 240 present in the spectrum of polymer II (Figure 4b) is generated by secondary fragmentation of the molecular ion at m/z 480 (cyclic dimer).

In conclusion, the data presented here show that in the pyrolysis of the isomeric polyesters I–III having the same diacyl unit (phthalic) and a different dihydroxybenzene unit (ortho, meta, or para), only one cyclic product is formed. The size of the cycle generated is a consequence of the structure of the polymer degradated. Thus, a large cycle (30 members), the tris(1,4-dihydroxybenzene phthalate) (compound VI), is generated in the pyrolysis of polymer III containing hydroquinone units, while a small cycle (8 members), 1,2-dihydroxybenzene phthalate (compound IV), is formed in the case of polymer I containing

catechol units. Bis(1,3-dihydroxybenzene phthalate) (compound V) is formed in the pyrolysis of polyester II containing resorcinol units.

On the basis of these data it can be concluded that the thermal degradation of polyesters I–III, occurring through a selective ester-exchange reaction, behaves as a depolymerization process forming almost exclusively one cyclic species. Remarkably, it is possible to identify each of the three isomeric polymers just on the knowledge of the composition of the formed pyrolytic products, easily obtainable by means of their DP-MS spectra.

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