5520 *Macromolecules* **1996,** *29,* 5520−5528

Synthesis and MALDI-TOF MS Characterization of High Molecular Weight Poly(1,2-dihydroxybenzene phthalates) Obtained by Uncatalyzed Bulk Polymerization of *O,O′*-Phthalid-3-ylidenecatechol or 4-Methyl-*O,O′*-phthalid-3-ylidenecatechol

Emilio Scamporrino*

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria, 6, 95125 Catania, Italy

Daniele Vitalini and Placido Mineo

Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, CNR, Viale A. Doria, 6, 95125 Catania, Italy

Received January 16, 1996; Revised Manuscript Received May 6, 1996⊗

ABSTRACT: A new procedure to obtain high molecular weight poly(1,2-dihydroxybenzene phthalates) by bulk polymerization of some spiro-compounds is described. *O,O′*-Phthalid-3-ylidenecatechol (**I**) and 4-methyl-*O,O′*-phthalid-3-ylidenecatechol (**II**) spiro-compounds have been synthesized and used as monomers. Poly(1,2-dihydroxybenzene phthalate) (**III**) and poly(1,2-dihydroxy-4-methylbenzene phthalate) (**IV**) have been prepared by heating at 200 °C of spiro-compounds **I** and **II**, respectively, without addition of catalyst. The resulting polyesters **III** and **IV** have been characterized by GPC, TG, DSC, NMR, FAB-MS, and MALDI-TOF MS analyses. The GPC curves of the obtained materials showed that high molecular weight polyesters, containing only a very little amount of low molecular weight oligomers, have been formed. The structural characterization of these polyesters by FAB and MALDI-TOF mass spectrometric analyses showed that they are constituted exclusively of open-chain macromolecules having both hydroxy end-groups. Data collected suggest that in the bulk polymerization of spiro-compounds **I** and **II** a possible chain growth mechanism of polymerization is active, which is strongly inhibited by acid species.

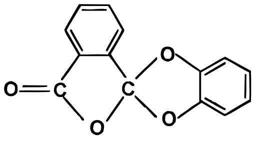
Introduction

Totally aromatic polyesters are a class of inherently flame retardant and UV-resistant materials.[1−3] Unfortunately these polymers are sometimes not melt processable owing to their high melting temperature.[4,5] Consequently the development of new melt processable aromatic polyesters has received a good deal of attention over the past years. Given the number of available diphenols, aromatic dicarboxylic acids, and hydroxy carboxylic acids, many compositions are possible.[1,5−7] Melt processability can also be increased by suitable copolymerization [e.g. copolymers based on *p*-hydroxybenzoic acid (Ekonol fiber,[8] Xydar resin[9,10]) or on Bisphenol-A and a mixture of isophthalic/terephthalic acids (Ardel,[11] U-polymer[12]) have already been commercialized] or blend assemblage.[13]

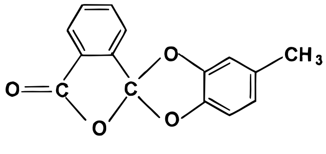
In the case of aromatic homopolyesters, a significant reduction of both glass transition (T_g) and melting (T_m) temperatures can be obtained by the appropriate selecting of monomers; as an example, the dihydroxy and/or diacid structure (ortho, meta, or para) has been found to have a strong effect on the thermal properties of the resulting polyesters.[14,15]

We have recently studied the role of the diphenolic structure on the thermal degradation processes occurring in the pyrolysis of some totally aromatic polyesters obtained by condensation reaction between phthaloyl dichloride and catechol, resorcinol, or hydroquinone.[15] A considerable difference was found between the thermal stability of poly(1,3-dihydroxybenzene phthalate) and poly(1,4-dihydroxybenzene phthalate) [temperature of maximum rate of polymer degradation (PDT) at 450 °C] and that of poly(1,2-dihydroxybenzene phthalate), which appears to be much less thermally stable (PDT = 320 °C).

However, the thermal degradation of these isomeric polyesters occurs in the same way, through a selective mechanism leading to the formation of only one volatile product, different in each case.[15,16] Cyclic trimer, the tris(1,4-dihydroxybenzene phthalate), is generated in the pyrolysis of the otho/para polymer, while cyclic dimer, the bis(1,3-dihydroxybenzene phthalate) is formed in the case of ortho/metha isomeric polymer. Differently, in the thermal degradation of poly(1,2-dihydroxybenzene phthalate), *O,O′*-phthalid-3-ylidenecatechol, which has the same molecular weight as the cyclic diester monomer but the spiro-structure **I** (the same structure of the lower molecular weight product contained in the mixture obtained in the reaction between phthaloyl dichloride and catechol), is produced.[15,16]



I



II

The present work was motivated by the supposition that, by heating, spiro-compound **I** may be directly converted into poly(1,2-dihydroxybenzene phthalate). Data reported here show that, without the addition of catalyst, pure *O,O′*-phthalid-3-ylidenecatechol (**I**) or 4-methyl-*O,O′*-phthalid-3-ylidenecatechol (**II**), heated at 200 °C, reacts to form a high molecular weight polyester containing only a very little amount of low molecular

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.

weight oligomers. On the contrary, when compounds having acid groups are also present together with the spiro-compound **I** or **II**, the formed polymer has a lower molecular weight and contains large amounts of oligomers.

A careful inspection of the composition of the different polyesters formed, made by FAB and MALDI-TOF mass spectrometric analyses,[17-20] reveals that only molecules having hydroxy end-groups are generated in the bulk polymerization of pure spiro-compound **I** or **II**.

The presence of a totally aromatic polyester lacking in low molecular weight oligomers and having only hydroxy reactive end-groups in the macromolecules, makes this new synthetic procedure of interest in the preparation of useful intermediate products, for example, in the segmented copolymer syntheses.[13,21]

Experimental Section

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

Spiro-Compounds I and II Synthesis. *O,O′*-Phthalid-3-ylidenecatechol (**I**) and 4-methyl-*O,O′*-phthalid-3-ylidenecatechol (**II**) were synthesized by the solution reaction, under very dilute conditions, between phthaloyl dichloride and catechol or 4-methylcatechol (in stoichiometric amount) in tetrahydrofuran (THF), using triethylamine (TEA) as the HCl acceptor, under stirring in a N_2 atmosphere.

The extraction and characterization of compounds **I** and **II** contained in the obtained mixtures were performed as described previously.[16]

Bulk Polymerization of Spiro-Compounds. Poly(1,2-dihydroxybenzene phthalate) (**III**) and poly(1,2-dihydroxy-4-methylbenzene phthalate) (**IV**) were prepared by heating of the corresponding spiro-compound **I** or **II** at 200 °C under vacuum, without catalyst. In each experiment, the just purified spiro-compound was placed at the bottom of several glass tubes connected to a rotating pump for 30 min and sealed by flame, maintaining the compound under vacuum (10^{-2} torr). The tubes were then immersed simultaneously in a silicone oil bath maintained at 200 °C and singly extracted at different times; the obtained materials were examined without further treatment.

The procedure described above was also adopted for the bulk polymerization of spiro-compound **I** or **II** in presence of 5% of catechol, 4-methylcatechol, or phthalic acid.

Capping Procedure of Polyesters. In a typical procedure, 1 g of polyester was dissolved in 10 mL of pyridine under stirring and N_2 atmosphere; then 10 mL of acetic anhydride were added, and the solution was maintained at 100 °C for 1 h and at 25 °C for another 2 h. After precipitation in 300 mL of water, the material was filtered, dissolved in 30 mL of THF, precipitated in 300 mL of water, filtered, and dried under vacuum at 60 °C.

HPLC Purification. The spiro-compounds **I** and **II** eluted from the silica gel column were further purified by HPLC on a Varian Vista 5500 HPLC system equipped with a Varian 2050 UV detector, using a μ-Bondapak C_{18} Waters column of 3.9 mm × 30 cm and a CH_3CN/H_2O (70/30) solution as eluant.

GPC Analysis. A PL-GPC 110 Polymer Laboratories thermostated system, equipped with two PL-gel 5 μm Mixed-D columns attached in series, was used. The analyses were performed at 35.0 ± 0.1 °C using THF as eluant at a flow rate of 1 mL/min. A differential refractometer (Polymer Laboratories) was used as the detector. The instrument was calibrated with a mixture of five polystyrene standards (Polysciences; molecular weights between 2000 and 330000 Da) using a PL Caliber GPC Software for the average molecular weight and polydispersity determination of the polymer samples.

FAB-MS Analysis. FAB analysis was performed on a double-focusing Kratos MS 50S mass spectrometer equipped with the standard FAB source. The FAB gun (Ion Tech) was operated with a 7−8 keV xenon beam. The instrument was scanned from *m/z* 10000 to 90, with a scan rate of 30 s/decade. The accelerating voltage was 8 kV. The mass resolution was approximately 6000. Mass spectra were obtained by using an UV-recorder and 3-nitrobenzyl alcohol, or a saturated solution of CH_3COOLi in 3-nitrobenzyl alcohol, as a matrix. The *m/z* values reported in the spectra refer to the more abundant isotope of each element contained in the molecule.

MALDI-TOF Mass Spectrometric Analysis. The MALDI-TOF mass spectra were performed by a Bruker Reflex mass spectrometer equipped with a nitrogen laser (emission at 337 nm, for 3 ns), a flash ADC (time base 8 ns), and a double-plate microchannel detector. Accelerating voltage was 30 kV. The laser irradiance was slightly above threshold (ca. 10^6 W/cm^2). The detection was in the reflection mode (31.4 kV). Ions below *m/z* 500 were removed with pulsed deflection, and 50 transients were summed. The resolution was about 370 (fwhh) at *m/z* 3000.

MALDI spectra, performed in both linear and reflected mode, were obtained by using 2-[(4-hydroxyphenyl)azo]benzoic acid (HABA) as a matrix. In each MALDI experiment the sample was prepared loading on the probe tip about 0.1 nmol of polymer and 40 μmol of matrix, using THF as a solvent. A 0.05 nmol amount of 4-*tert*-butylcalix(4)arenetetraethyl ester (mw = 992, Janssen) and tetrakis(*p*-dodecanoxyphenyl)porphyrin ($C_{92}H_{126}N_4O_4$, mw = 1350, our preparation) as internal standards for *m/z* calibration were also added. The *m/z* values reported in the spectra refer to the more abundant isotope of each element contained in the molecule.

Results and Discussion

Previous data[15] have shown that the poly(1,2-dihydroxybenzene phthalate) pyrolysis occurs through a selective mechanism of thermal degradation leading to formation of only one product of molecular weight 240 Da, having the spiro-structure **I** (*O,O′*-phthalid-3-ylidenecatechol). A similar thermal degradation mechanism has been ascertained for poly(1,2-dihydroxy-4-methylbenzene)phthalate. In fact, DP-MS and NMR data showed that, also in this case, only 4-methyl-*O,O′*-phthalid-3-ylidenecatechol (spiro-compound **II**, molecular weight 254 Da) is formed in the pyrolysis of the polymer.[22]

The selective formation of spiro-compounds **I** and **II** could be explained by assuming active an unzipping mechanism (see below Scheme 1) of thermal decomposition (likewise for the formation of styrene or methyl methacrylate in the pyrolysis of the corresponding polymer).[23] This is usually a reversible reaction and, on this basis, we supposed that spiro-compound **I** or **II** could be directly converted in the corresponding polyester by heating.

In order to verify this hypothesis, in two separate sets of experiments several amounts of purified compound **I** or **II** were placed at the bottom of glass tubes sealed under vacuum (to avoid the presence of H_2O and O_2) and immersed in a silicone oil-bath at 200 °C. The tubes were then extracted at different times and cooled, and the materials inside were examined without further treatment.

The GPC traces of the materials obtained in the case of the spiro-compound **II** after 0.5−24 h of heating are reported in Figure 1 (curves a−d, respectively). All the curves show a peak at an elution volume of about 38 mL corresponding to unreacted spiro-compound **II** and another peak (at lower elution volume) due to the formed polymer. It can be observed that the abundance of the spiro-compound **II** peak decreases as a consequence of the longer heating time (curves a−d) and, at the same time, the amount of polymer increases.

It can be also observed that the maximum of the polymer trace already appears from the lower reaction time (curve **a**, associated at a conversion of about 5%), at an elution volume of about 22 mL, corresponding (by

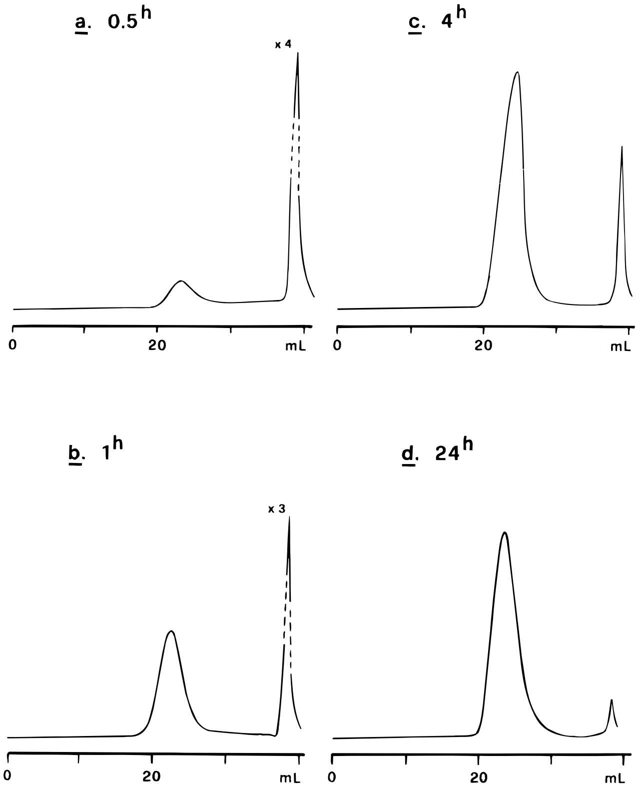


Figure 1. GPC traces of the materials obtained in the bulk-polymerization (200 °C) of 4-methyl-*O*,*O*′-phthalid-3-ylidenecatechol (**II**) after: (a) 0.5 h, (b) 1 h, (c) 4 h, and (d) 24 h of heating.

calibration with polystyrene standards) to a molecular weight of about 80000 Da (polydispersity index about 1.4); furthermore, contrary to all expectations for a polyester or another condensation polymer formation, the GPC traces of Figure 1 do not show peaks corresponding to low molecular weight oligomers in an appreciable amount.

The ^{13}C-NMR spectra of the polymer, separated from the unreacted spiro-compound, exhibit eleven signals at 20.08 ppm (primary carbon), 122.69, 123.31, 127.45, 128.95, 132.11 ppm (tertiary carbons) and 129.85, 136.84, 139.27, 141.17, 164.06 ppm (quaternary carbons). The signals are almost coincident with those present in the ^{13}C-NMR spectrum of poly(1,2-dihydroxy-4-methylbenzene)phthalate obtained by solution condensation between phthaloyl dichloride and 4-methylcatechol. However, comparing the two ^{13}C-NMR spectra (omitted for brevity), it can be observed that in the spectrum of the polyester obtained by solution method appear also several little intense signals because of the presence of many more end-groups due to the lower molecular weight of this sample.

Similar behavior was ascertained in the bulk polymerization of *O*,*O*′-phthalid-3-ylidenecatechol **I**. Obviously, in this last case, because of the absence of the methyl group in the dihydroxybenzene unit, the ^{13}C-NMR spectrum of the polymer shows only seven signals at 124.00, 127.52, 130.00, 132.76 ppm (tertiary carbons) and 131.38, 143.08, 164.91 ppm (quaternary carbons).[22]

The data reported above confirm the direct conversion of the spiro-compounds **I** and **II** in the corresponding polyesters but, contrary to polycondensation reaction in which the formation of moderate amounts of oligomers together with the polymer is a phenomenon often observed,[24−26] in the bulk polymerization of **I** and **II** the obtained polymer is lacking in low molecular weight oligomers (M_{GPC} about 80000 Da) and its polydispersity index (M_w/M_n, from GPC) is less than 1.4. This behavior can be explained by assuming active a different mechanism of polymerization with respect to the condensation reaction. On the basis of the thermal degradation data (above mentioned) and considering that no catalysts were used in the bulk polymerization of spiro-compounds, it can be supposed that, at temperatures around 200 °C, a polarized structure of compound **I** or **II** may initiate the polymerization process according to the chain growth reaction reported in Scheme 1 (route a).

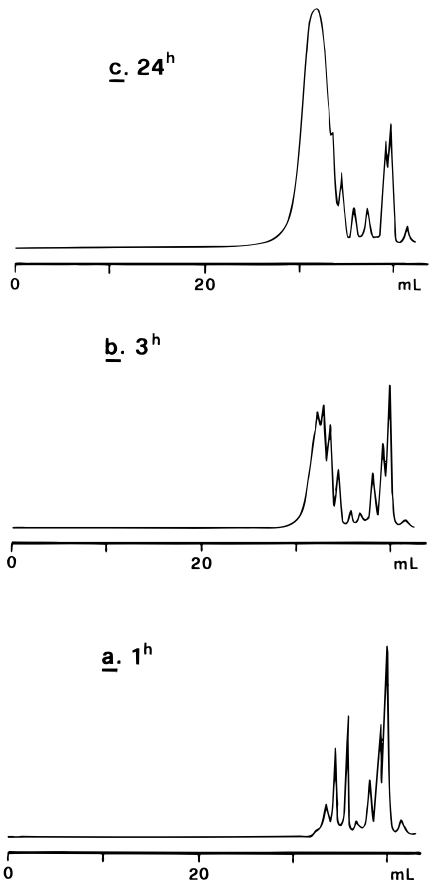


Figure 2. GPC traces of the materials obtained in the bulk-polymerization (200 °C) of a mixture of 4-methyl-*O*,*O*′-phthalid-3-ylidenecatechol (**II**) and phthalic acid (in the molar ratio of 0.95:0.05) after: (a) 1 h, (b) 3 h, and (c) 24 h of heating.

So, the formation of spiro-compounds **I** and **II** occurring in the pyrolysis of the polymers is due to the prevalence (at temperatures > 300 °C) of the inverse unzipping reaction (route b in Scheme 1).

Further polymerization experiments were carried out heating the spiro-compound **I** or **II** after addition of a small amount (about 5%) of phthalic acid, catechol, or methylcatechol. As an example, the GPC traces of the materials obtained after 1−24 h of heating of the spiro-compound **II** containing 5% of phthalic acid are reported in Figure 2. It can be observed that, after 1 h (curve a), only a portion of spiro-compound has reacted, forming a mixture of low molecular weight oligomers. At higher reaction times, the peak of the spiro-compound gradually decreases and the curve shifts toward higher molecular weight values (curves b,c) still showing large amounts of low molecular weight oligomers. The addition of catechol or 4-methylcatechol causes only a reduction in the molecular weight of the polymer. A similar behavior was observed in the case of the spiro-

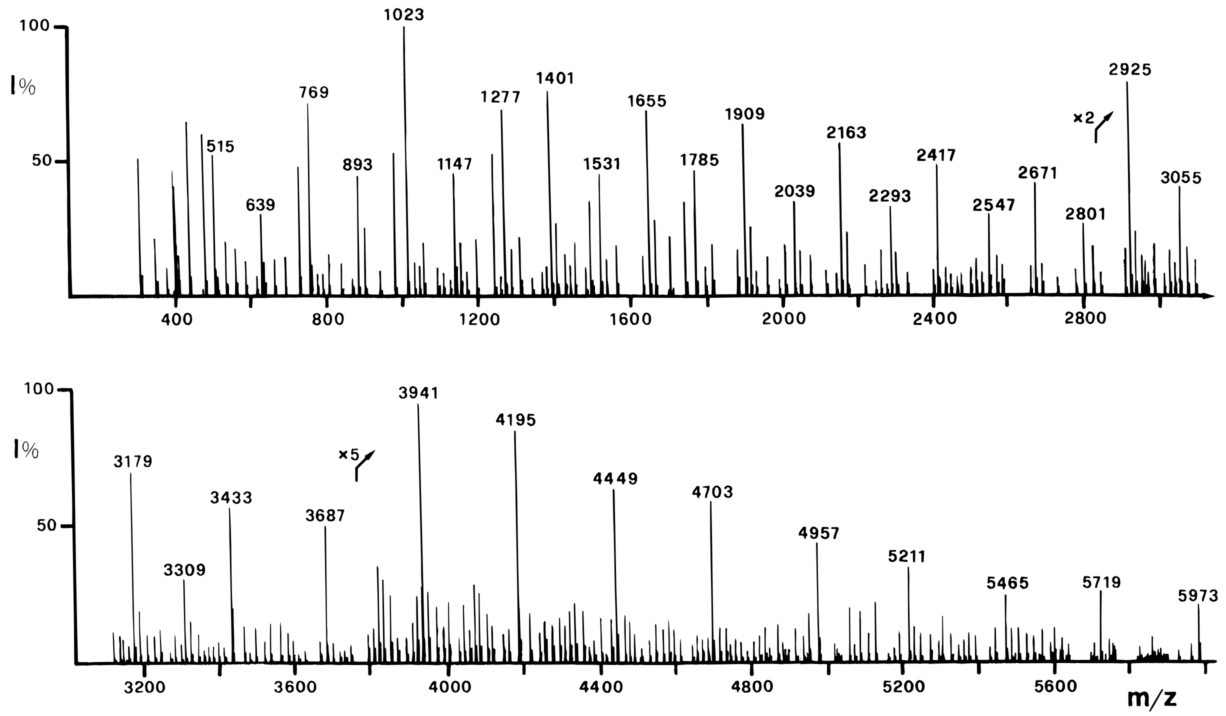
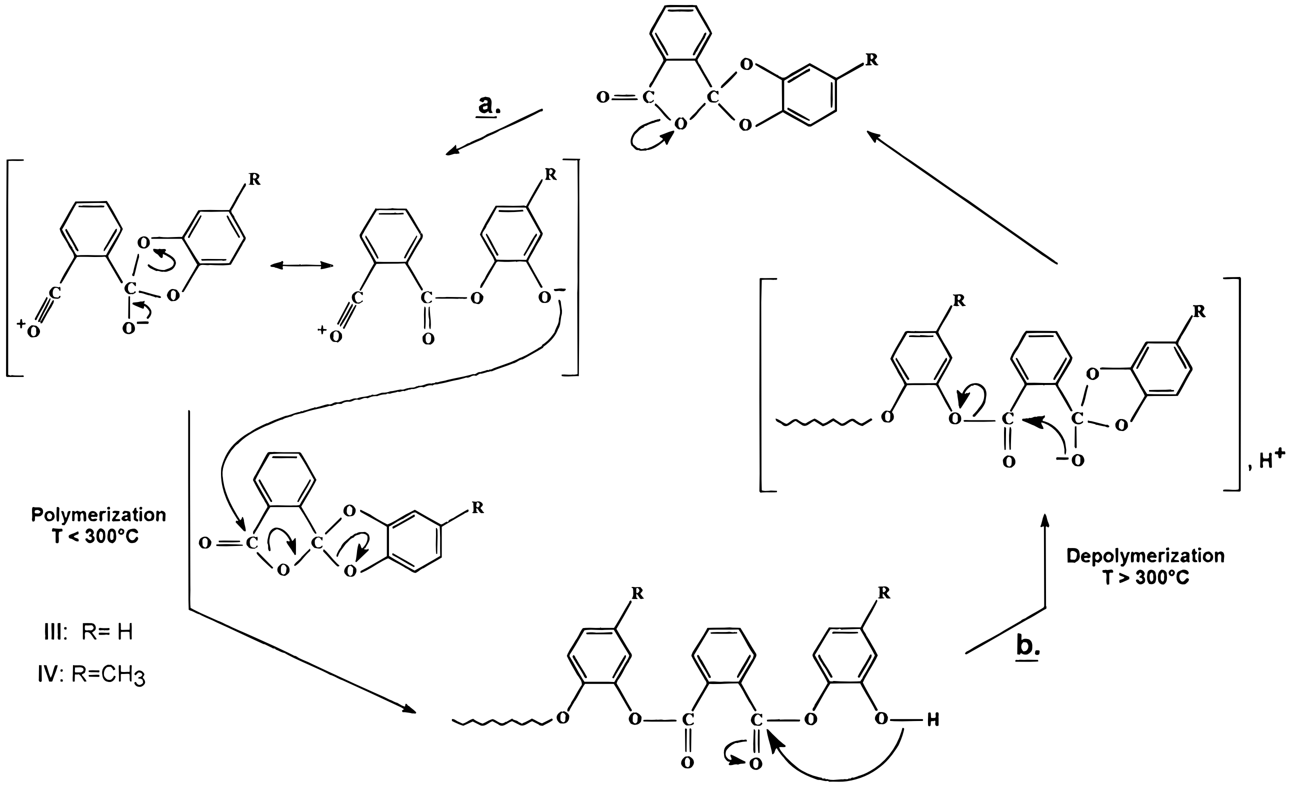


Figure 3. Positive FAB mass spectrum of poly(1,2-dihydroxy-4-methylbenzene phthalate) obtained by heating (200 °C) of spiro-compound **II**.

Scheme 1

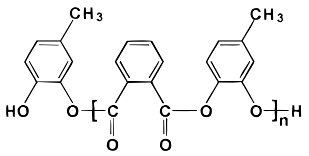
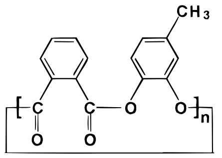


compound **I.** It can be concluded that acid species inhibit the chain polymerization, so that the formation of polyester occurs according to a polycondensation process.

In order to verify if, in the bulk polymerization, besides the molecular weight distribution, the polymer composition also changes with respect to the solution method, the structural characterization of the polymers was attempted by ^{13}C-NMR, FAB-MS, and MALDI-TOF MS analyses. The ^{13}C-NMR data (above reported) do not give significant information besides the structure of the repeating unit of each polymer. On the contrary, FAB and MALDI-TOF spectra allowed an accurate analysis of the polymers with particular attention to the identification of the end-groups of the macromolecules.

In Figure 3 the positive FAB mass spectrum of poly(1,2-dihydroxy-4-methylbenzenephthalate) **IV,** obtained by pure spiro-compound **II** heating, is reported. In order to aid the detection of molecular species, the spectrum was recorded using a saturated solution of CH_3COOLi

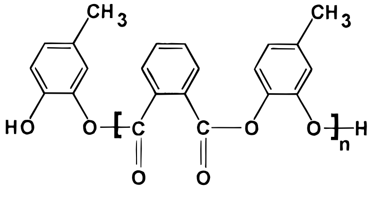
Table 1. Compounds Detected as MLi$^+$ in the Positive FAB Mass Spectrum of Poly(1,2-dihydroxy-4-methylbenzene phthalate) Obtained by Bulk-Polymerization

Structure	m/z (n) ^{a}
	639 (2), 893 (3), 1147 (4), 1401 (5), 1655 (6), 1909 (7), 2163 (8), 2417 (9), 2671 (10), 2925 (11), 3179 (12), 3433 (13), 3687 (14), 3941 (15), 4195 (16), 4449 (17), 4703 (18), 4957 (19), 5211 (20), 5465 (21), 5719 (22), 5973 (23).
	515 (2), 769 (3), 1023 (4), 1277 (5), 1531 (6), 1785 (7), 2039 (8), 2293 (9), 2547 (10), 2801 (11), 3055 (12), 3309 (13)

a) The number in parenthesis corresponds to the number of repeating units contained in each structure.

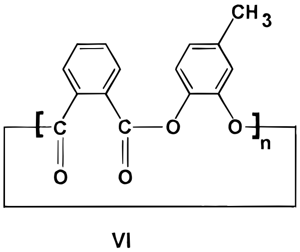
in TNB as a matrix. The structures corresponding to the peaks present in the spectrum are shown in Table 1 (the *m*/*z* values, in the following, refer to the more abundant isotope of each element contained in the molecule).

The spectrum presents peaks up to *m*/*z* values of 6000, and it is constituted essentially by two families of peaks. The most abundant series is constituted from peaks at *m*/*z* 131 + *n*254, with $n = 2-25$, corresponding to open chain products, detected as MLi$^+$ ions (see Table 1), having hydroxy-4-methylbenzene end-groups, as shown in the following formula **V**:



V

The other series of peaks at *m*/*z* 7 + *n*254, with $n = 2-15$, corresponds to the cyclic products detected as MLi$^+$ (see Table 1) having the following structure **VI**:



VI

Considering the kind of polymerization, only cyclic compounds should be formed. So, although FAB-MS is a soft-ionization technique, the peaks corresponding to open-chain compounds **V** could be generated by secondary fragmentation processes.[27]

To clarify this possibility, experiments of MALDI-TOF MS were performed. This is a recently introduced very soft ionization tool that allows the desorption and detection of very large molecules, strongly reducing the occurrence of fragmentation, so that the information obtained by MALDI-TOF is of particular importance in determining the composition of the examined sample. There are, however, several problems associated with MALDI quantitative analysis of mixtures[28−32] and, as a consequence, the polymer average molecular weight evaluation results uncertain; recently, some authors have demonstrated that the MALDI detection response results truthful only in a narrow range of molecular weight values.[33−35]

This is the case of the following reported MALDI mass spectra, which were obtained in the reflected mode in order to have a sufficient mass resolution for a correct *m*/*z* molecular ion assignment of the different species contained in the polymer materials. In fact, although the GPC curves of the examined samples show an average molecular weight of about 80000 Da, with a polydispersity index of about 1.4, mainly peaks with *m*/*z* values of up to about 10000 Da are detected in the MALDI spectra. Also the spectra obtained in the linear mode, of which that of polymer **IV** is reported in Figure 4a, show peaks with a mass distribution centered at lower values (about 30000 Da in the reported case) with respect to those obtained by GPC.

The MALDI failure is rationalized considering the two different separation and detection methods of the molecules in GPC and MALDI experiments.[29,36] In the GPC it is well-known that the columns cause a logarithmic molecular weight separation of the species as a function of the elution time; generally an UV or RI detector is used to value the concentration (in grams) of the eluted species. In the MALDI-TOF, on the contrary, the species are separated as a quadratic function of the time (TOF) and the detector, in this case, counts the ion number (thus moles) of each species. So, to compare the GPC (concentration, in grams, as a function of the elution time) and MALDI-TOF (number of ions, thus moles, as a function of the molecular weight) traces, a normalization is necessary.

As an example, the processed spectrum of the polymer **IV**, obtained by reporting for each mass value (*m*/*z*) the amount in weight of each species, corresponding to the arithmetic product between its ion intensity (ordinate value in the MALDI spectrum of Figure 4a) and its molecular weight, is shown in Figure 4b.

It can be observed that the average molecular weight inferred from the elaborated MALDI spectrum (about 70000 Da, Figure 4b) and from the GPC curve are comparable (an exact coincidence is not expected considering that the GPC is calibrated with polystyrene standards).

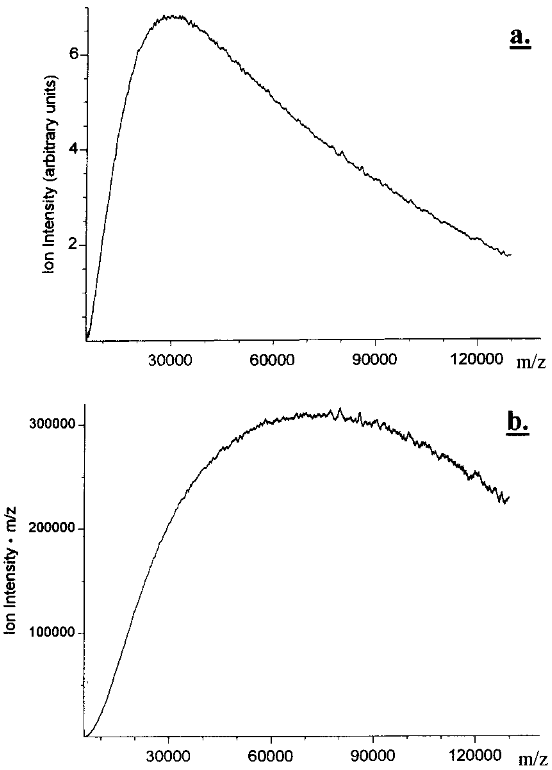


Figure 4. (a) MALDI-TOF mass spectrum of polymer **IV** obtained in linear mode. (b) Mass spectrum of Figure 4a elaborated reporting the arithmetic product between the ion intensities (ordinates in Figure 4a) and the corresponding *m*/*z* values, as a function of the *m*/*z* values.

So, in absence of interference as the different cationization yield of molecular species (better for the oligomers), which should induce an erroneous valuation of the polymer average molecular weight, MALDI-TOF spectra (obtained in linear mode) appropriately elaborated can give a correct mass distribution curve (Figure 4b). Besides, if the abscissa of the elaborated MALDI spectrum is converted in a logarithmic scale, a curve very similar to the corresponding GPC trace of the polymer sample is obtained (data omitted for brevity).

Another problem, connected with the fact that in the time-of-flight method only differences of masses[17−20] are measured, is the detection of absolute mass value associated to each peak present in the MALDI spectrum for a correct valuation of the composition of the species (identification of end-groups) contained in the polymer samples. To this purpose different calibration procedures such as self-calibration,[33] use of an external impulse generator,[28] or the use of external or internal standards of known molecular weight,[20,37] are adopted. To avoid ambiguous results we have chosen the last procedure. For the polyesters here investigated good results were obtained using HABA as a matrix and two pure compounds as standards: a calix(4)arene derivative (mw = 992 Da, see Experimental Section) and the tetrakis(*p*-dodecanoxyphenyl)porphyrin of mw = 1350 Da, prepared in order to have a compound at a very high molecular weight.[22]

The MALDI-TOF spectrum of the bulk polymerized polymer **IV** is reported in Figure 5. The spectrum shows signals up to about *m*/*z* 12000 and is comprised of two series of peaks at *m*/*z* 147 + *n*254 and 163 + *n*254 (see inset), corresponding to a single family of open chain compounds **V**, detected as MNa$^+$ and MK$^+$, respectively, with *n* = 10−47. To avoid confusion, each couple of peaks is identified in Figure 5 by the repeating unit number (*n*) contained in the molecule (for *m*/*z* values, see Table 2).

For further confirmation, a portion of polyester **IV** was also treated with $(CH_3CO)_2O$ in order to cap the open chain molecules with CH_3CO groups. The obtained material showed a higher thermal stability with respect to polymer **IV** (about 40 °C, TG under N_2 data),[15] although the decomposition mechanism resulted unchanged.[22]

In Figure 6 the MALDI-TOF mass spectrum of the capped polymer is reported.

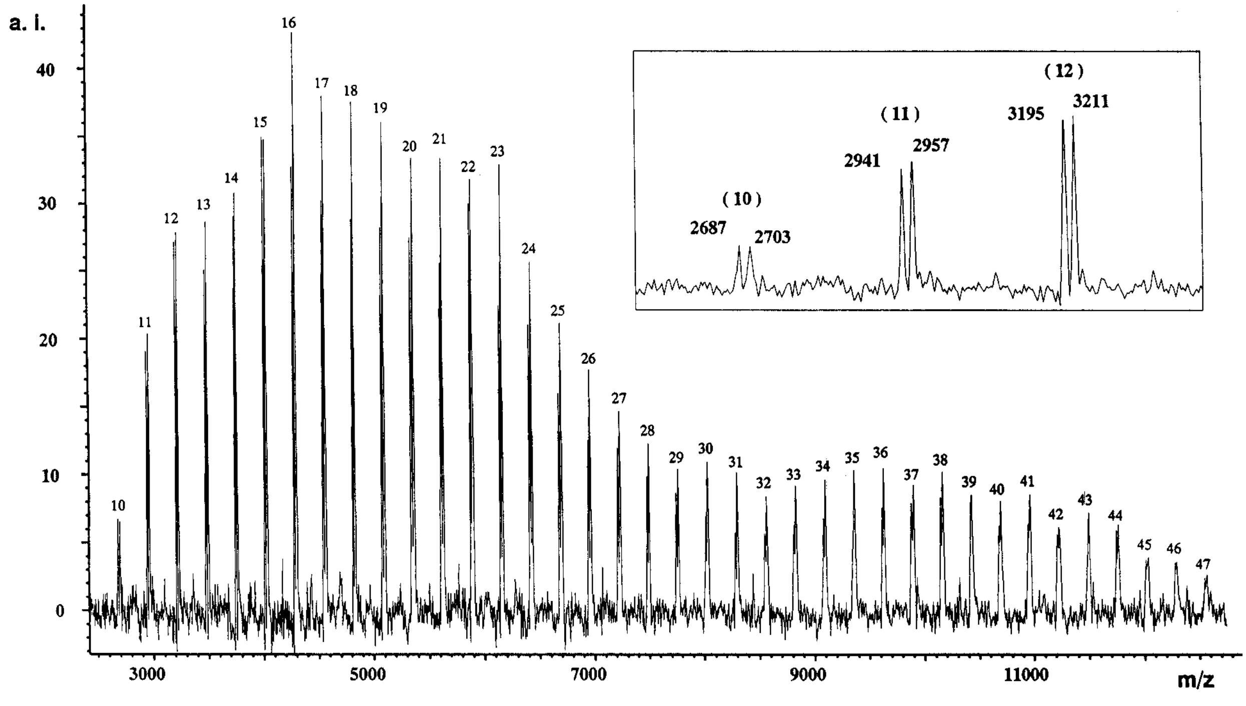
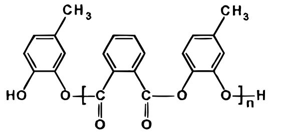
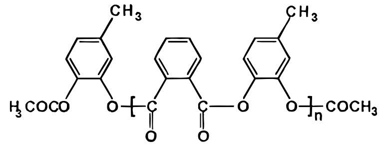
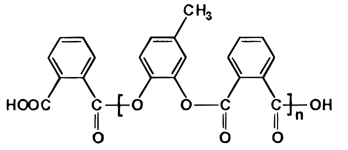
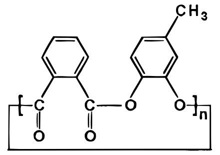


Figure 5. Positive MALDI-TOF mass spectrum of poly(1,2-dihydroxy-4-methyl benzene phthalate) obtained by heating (200 °C) of spiro-compound **II**. The number reported in correspondence of each couple of peaks represents the number of repeating units (*n*) present in the molecule (the associated *m*/*z* values are reported in Table 2).

Table 2. Peaks Detected in the MALDI-TOF Mass Spectra of Poly(1,2-dihydroxy-4-methylbenzene phthalate)

Structure		m/z (n) ^{a}
	as MNa^+	2687 (10), 2941 (11), 3195 (12), 3449 (13), 3703 (14), 3957 (15), 4211 (16), 4465 (17), 4719 (18), 4973 (19), 5227 (20), 5481 (21), 5735 (22), 5989 (23), 6243 (24), 6497 (25), 6751 (26), 7005 (27), 7259 (28), 7513 (29), 7767 (30), 8021 (31), 8275 (32), 8529 (33), 8783 (34), 9037 (35), 9291 (36), 9545 (37), 9799 (38), 10053 (39), 10307 (40), 10561 (41), 10815 (42), 11069 (43), 11323 (44), 11577 (45), 11831 (46), 12085 (47)
	as MNa^+	3787 (14), 4041 (15), 4295 (16), 4549 (17), 4803 (18), 5057 (19), 5311 (20), 5565 (21), 5819 (22), 6073 (23), 6327 (24), 6581 (25), 6835 (26), 7089 (27), 7343 (28), 7597 (29), 7851 (30), 8105 (31), 8359 (32), 8613 (33), 8867 (34), 9121 (35), 9375 (36), 9629 (37), 9883 (38)
	as MK^+	3253 (12), 3507 (13), 3761 (14), 4015 (15), 4269 (16)
	as MNa^+	3325 (13), 3579 (14), 3833 (15), 4087 (16), 4341 (17), 4595 (18), 4849 (19), 5103 (20), 5357 (21), 5611 (22), 5865 (23), 6119 (24), 6373 (25)

a) The number in parenthesis corresponds to the number of repeating units contained in each structure.

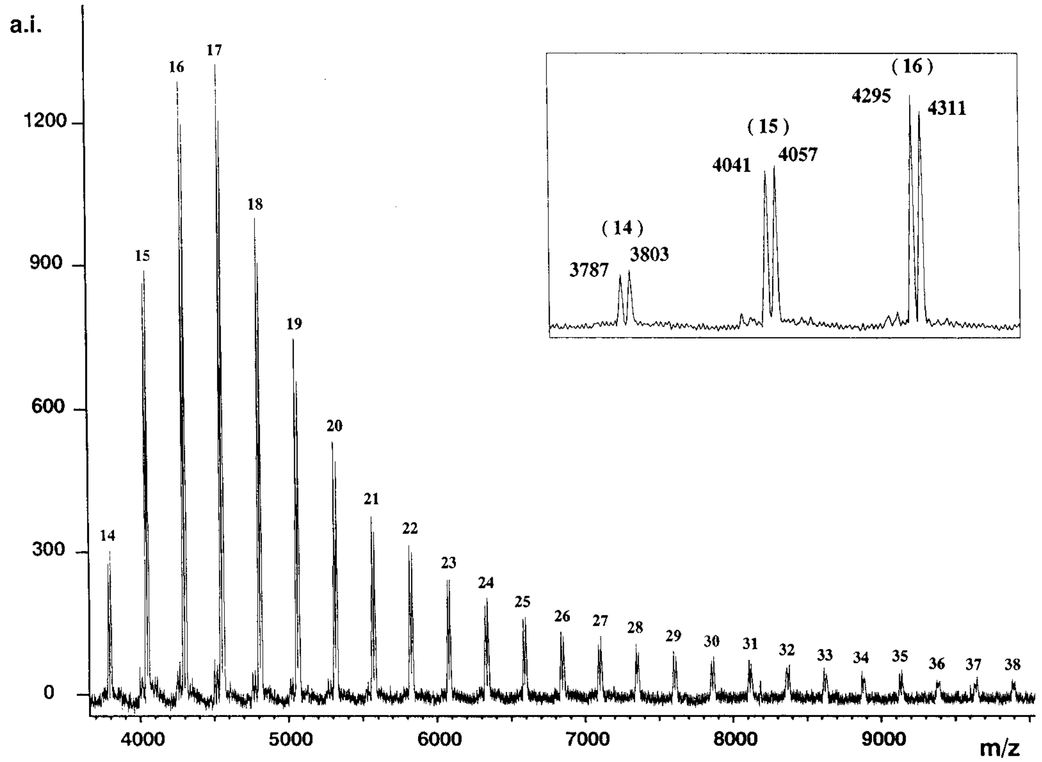


Figure 6. Positive MALDI-TOF mass spectrum of the capped poly(1,2-dihydroxy-4-methylbenzene phthalate) obtained by bulk-polymerization. In correspondence of each couple of peaks is reported the number of repeating units (*n*) contained in the molecule (the associated *m*/*z* values are reported in Table 2).

The peak assignments are reported in Table 2. Also in this case the peaks present in Figure 6 are identified by the repeating unit number (*n*) contained in each molecule. By comparison of the two spectra of Figures 5 and 6, it may be observed that the peaks of Figure 5, corresponding to the open chain compounds **V**, have been replaced in the spectrum of Figure 6 by peaks at *m*/*z* 231 + *n*254 (as MNa^+) and *m*/*z* 247 + *n*254 (as MK^+), corresponding to the same compounds in which the two OH end-groups have been changed in two CH_3-COO groups (Table 2); for instance, the oligomer having $n = 15$ appears in the spectrum of Figure 5 at *m*/*z* 3957 and in that of Figure 6 at *m*/*z* 4041.

In both MALDI spectra, no trace of peaks due to cyclic compounds has been found. Consequently it can be deduced that the polyester obtained by heating of the

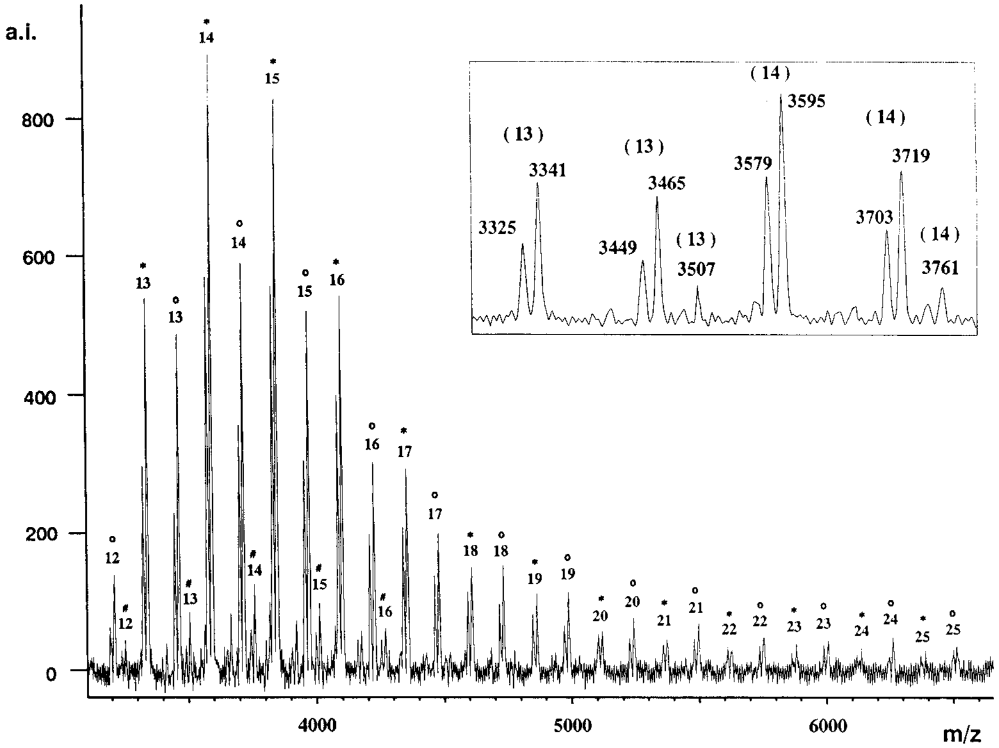


Figure 7. Positive MALDI-TOF mass spectrum of the capped poly(1,2-dihydroxy-4-methylbenzene phthalate) obtained by condensation reaction between 4-methylcatechol and phthaloyl dichloride. In correspondence of each couple of peaks is reported the number of repeating units (*n*) contained in the molecule (the associated *m*/*z* values are reported in Table 2).

spiro-compound **II** is constituted only by open-chain compounds **V**. The peaks corresponding to cyclic structures detected in the FAB-MS spectrum (Figure 3) are thus due to secondary fragmentation phenomena;[27] otherwise, it would be necessary to suppose that the MALDI-TOF technique is not able to detect the cyclic compounds **VI**.

In order to verify this last occurrence, a sample of poly(1,2-dihydroxy-4-methylbenzene phthalate) obtained by condensation reaction between 4-methylcatechol and phthaloyl dichloride (according to the procedure described elsewhere),[15,16] containing both cyclic and open chain compounds, was subjected to FAB and MALDI-TOF analysis. The positive FAB mass spectrum of this polyester resulted so similar to that of Figure 3 as to be omitted for brevity. Its MALDI-TOF spectrum is reported in Figure 6.

Comparing this spectrum with that of Figure 5 one can observe that, beyond the peaks due to open chain compounds **V** (indicated as ◦), a series of low intense peaks at *m*/*z* 205 + *n*254, due to molecular ions (as MK^+) of oligomers with both COOH end-groups (indicated as #), and two series of intense peaks at *m*/*z* 23 + *n*254 and 39 + *n*254 (indicated as *) corresponding to molecular ions of cyclic compounds **VI** detected as MNa^+ and MK^+ (Table 2), are also present in the spectrum.

The presence of these last peaks is diagnostic in confirming that, when present, cyclic compounds are detected in the MALDI spectra.

To verify if cyclic products are formed in the bulk polymerization of pure spiro-compound **I** or **II** but, because of the high temperature, subsequently decomposed and therefore not found in the polymer (MALDI spectrum of Figure 5), a sample of polyester obtained by solution polycondensation and then containing cyclic oligomers (spectrum of Figure 7) was heated for 5 h at 200 °C (under vacuum) and the residual material examined by MALDI-TOF technique. The spectrum of this sample resulted like that of Figure 7, indicating that the cyclic products are stable to protracted heating, and so confirming that they are not formed in the bulk polymerization.

On the basis of these data it can be concluded that, in the heating of pure spiro-compound **I** or **II**, a chain growth mechanism of polymerization, in which only open chain molecules **V** are formed, is active.

Further researches to verify the actuality of the mechanism proposed in Scheme 1, are in progress, examining the polymerization reaction of the spiro-compounds also in solution.

The unexpected results reported here make the bulk polymerization of spiro-compounds **I** and **II** of interest in obtaining totally aromatic polyesters at high molecular weight, containing only very little amount of oligomers and constituted only of macromolecules having reactive hydroxy end-groups useful, for example, to prepare block copolymers. Furthermore the complete reversibility of the reaction reported in Scheme 1 renders poly(1,2-dihydroxybenzene phthalate) and its derivatives interesting also from the point of view of the recycling of material.

Acknowledgment. Partial financial support from the Italian Ministry of University and Scientific and Technological Research 40% and 60%, P.O. CNR-MURST (1994–95), and financial contribution from the Progetto Strategico “Tecnologie Chimiche Innovative” (CNR, Rome) are gratefully acknowledged.

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MA960051+