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Structural Characterization of Oligomers Formed in the Reaction between Phthaloyl Dichloride and Catechol, 4-Methylcatechol, or Dithiocatechol

Emilio Scamporrino* and Francesco Mancino

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

Daniele Vitalini

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

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ABSTRACT: LC and HPLC chromatographic experiments were made to separate the low molecular weight oligomers contained in three totally aromatic polyesters obtained by the condensation reaction between phthaloyl dichloride and catechol, 4-methylcatechol, or dithiocatechol. The characterization of the extracted oligomers was performed by techniques of thermal analysis, i.e. differential scanning calorimetry (DSC) and thermogravimetry (TG), and techniques of structural identification, i.e. nuclear magnetic resonance (NMR), direct pyrolysis mass spectrometry (DP-MS), fast-atom bombardment mass spectrometry (FAB-MS), and X-ray diffraction analysis. Mass spectrometric data show that the lower molecular weight product contained in each of the three polymeric materials has the following composition: $C_{14}H_8O_4$ (mw = 240), $C_{15}H_{10}O_4$ (mw = 254) or $C_{14}H_8O_2S_2$ (mw = 272). All the data collected in this work, and in particular those obtained by NMR and X-ray diffraction analyses, show that these products have a spiro structure, whereas the other extracted products with higher molecular weight are, as expected, cyclic and linear oligomers having ester linkages.

Introduction

The formation of oligomers in the polymer synthesis by condensation reactions is a phenomenon frequently observed[1−4] and it is not only limited to the case of low molecular conversion, which must necessarily yield low molecular weight oligomers, but also includes the case of high conversion where the molecular weight is shifted toward relatively high polymers.

The content, composition, and distribution of oligomers depend very much on the experimental conditions; in each case the knowledge of the amount and composition of the oligomers is often desirable for the evaluation of the polymer properties.[4−7]

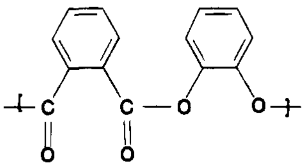
In recent years the separation and characterization of oligomers formed during the polymerization of polyesters, polyethers, polysulfides, polyamides, and several other condensation polymers have been widely described.[8−14]

In this work we report the case of three totally aromatic polyesters: poly(1,2-dihydroxybenzene phthalate) (polymer I),[15] poly(1,2-dihydroxy-4-methylbenzene phthalate) (polymer II), and poly(1,2-bis(thiohydroxy)-benzene phthalate) (polymer III) obtained by condensation reactions between phthaloyl dichloride and catechol, 4-methylcatechol, or dithiocatechol.

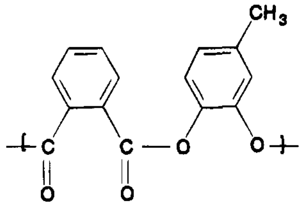
Also in these syntheses, as expected, the polymer production is accompanied by the formation of sizable amounts of oligomers.

Often the oligomers contained in a polymer or copolymer material have been identified directly on the basis of the DP-MS and/or FAB-MS spectra of the crude polymer or of the mixture of the low molecular weight products extracted from the polymer sample.[16−18]

In the present case, the detection and characterization of oligomers has been based on silica-gel and HPLC chromatographic separation combined with techniques of thermal analysis, such as DSC and TG, and structural identification, such as nuclear magnetic resonance (NMR), direct pyrolysis mass spectrometry (DP-MS), fast-atom bombardment mass spectrometry (FAB-MS), and X-ray diffraction analysis. For polymer I, cyclic and linear oligomers up to the tetramer (mw = 960) have been separated and identified.



I



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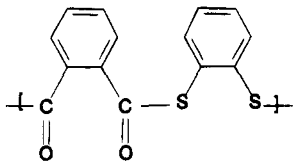

III

Particular care has been addressed to the characterization of the lower molecular weight product formed in the three polymer synthesis. DP- and FAB-MS data show that the composition and molecular weight of these products are as follows: $C_{14}H_8O_4$, mw = 240; $C_{15}H_{10}O_4$, mw = 254; $C_{14}H_8O_2S_2$, mw = 272. On the basis of these data, and also considering the EI-fragmentation behavior and the structure of the polymers obtained (compounds I−III), these products could correspond to the cyclic diester structure IV.

However, ^1H- and ^{13}C-NMR spectra of the pure separated products are quite different from those expected.

The results reported in this paper show that the lower molecular weight oligomer contained in the polymers

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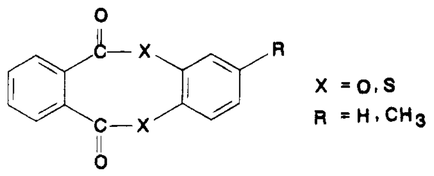


IV

has a spiro structure, whereas those at a higher molecular weight are, as expected, cyclic and linear oligomers, having ester linkages.

Experimental Section

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

Polymer Syntheses. Polymers I–III were synthesized by the solution method starting from phthaloyl dichloride and catechol, 4-methylcatechol, or dithiocatechol (in stoichiometric amounts) in tetrahydrofuran (THF) using triethylamine (TEA) as the HCl acceptor. In each case, after 15 min of reaction at 0 °C under stirring in an N_2 atmosphere, the mixture was refluxed for 3 h and then poured into H_2O. The solid material formed was recovered by filtration, repetitively washed with H_2O to avoid any traces of triethylamine hydrochloride, and dried under vacuum.

Extraction and Separation of Oligomers Contained in the Polymer Materials. Polymers I–III were extracted for 5 h in a Soxhlet apparatus with diethyl ether (Et_2O). The extracted materials, constituted of oligomers, were then chromatographed on a silica gel (particle size 70–230 mesh, Merck) column (h = 90 cm, i.d. = 3 cm), using a solution of Et_2O from 25 to 40% in petroleum ether (PE) (bp = 35–60 °C) as eluant.

All the separated products were collected and purified by two or three running HPLC experiments.

In the case of the mixture extracted from polymer I, the first product (V) eluted from the column was crystallized from ET_2O/PE to give white crystals, has a melting point of 136 °C (DSC determination), an $R_F = 0.47$ (Et_2O/n-hexane, 30/70), and a molecular weight of 240 (positive FAB-MS analysis). The second product (VI) eluted from the column, crystallized from CH_3CN, has a mp = 327 °C, an $R_F = 0.46$ (Et_2O/n-hexane, 70/30), and a mw = 480. The third product (VII), crystallized from Et_2O, has a mp = 174 °C, an $R_F = 0.16$ (Et_2O/n-hexane, 70/30), and a mw = 590. The fourth product (VIII), crystallized from Et_2O, has a mp = 192 °C, an $R_F = 0.07$ (Et_2O/n-hexane, 70/30), and a mw = 960.

In the case of the mixtures extracted from polymers II and III, only the first product eluted from the column was collected. Product IX (extracted from polymer II), crystallized from Et_2O/PE, has a mp = 89 °C, an $R_F = 0.5$ (Et_2O/n-hexane, 30/70), and a mw = 254. Product X (extracted from polymer III), crystallized from CH_3CN, has a mp = 198 °C, an $R_F = 0.44$ (Et_2O/n-hexane, 30/70), and a mw = 272.

GPC Analysis. A Waters 6000 A apparatus, equipped with four μ-Styragel columns (in the order 1000-, 500-, 10 000-, 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. Polymers I–III have a M_{GPC} between 4000 and 6000.

HPLC Purification. The purification of the oligomers eluted from the silica-gel column was performed 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 solution as eluant.

Thermal Properties. Thermogravimetric analyses (TG) were performed with a Perkin-Elmer TGS-2 apparatus in a N_2 atmosphere with a flow rate of 60 mL/min and a heating rate of 10 °C/min. The maximum polymer degradation temperatures (PDT) of polymers I–III are 320, 330, and 280 °C, respectively.

Differential scanning calorimetry (DSC) was performed to determine the melting point of the samples examined by using a Mettler DSC-20 instrument. The heating rate was 10 °C/min, under a N_2 atmosphere.

Mass Spectrometric Analyses. DP-MS analyses were carried out on a VG TRIO 1000 mass spectrometer equipped with LAB-bas software. The experiments were performed by a direct insertion probe for solid materials, heated from 30 to 600 °C at 10 °C/min. Mass spectra were continuously acquired over the whole temperature range with a scan rate of 1 s per decade (mass range 40–1000 Da) and stored.

Exact mass measurements were carried out on a double-focusing Kratos MS-50S mass spectrometer equipped with the standard electron impact (EI) source and the DS 90 data system, using perfluorokerosene for computer calibration.

FAB-MS analyses were performed on a double-focusing Kratos MS 50S mass spectrometer equipped with the standard FAB source. Xenon was used as the bombarding gas, with an energy of 8 keV. The instrument was scanned from 4000 to 90 Da, with a scan rate of 30 s per decade. The accelerating voltage was 8 kV. The mass resolution was approximately 4000. Mass spectra were recorded by using an UV oscillographic recorder. Spectra were obtained by using 3-nitrobenzyl alcohol (TNB) as a matrix. Peak intensity values shown in the mass spectra represent the average of almost three different mass spectra.

^{1}H-NMR and ^{13}C-NMR Analyses. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on an AC 200 F Bruker spectrometer interfaced with an Aspect 3000 computer using the Bruker DISR 90 acquisition software. Samples were solubilized in DMSO-d_6, and the chemical shifts were expressed in ppm by comparison with the signals (2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C) of the nondeuterated 0.1% DMSO.

The DEPT 135° ^{13}C-spectra were acquired with the Bruker microprogram DEPT.AU. DEPT spectra, generally omitted for brevity, in the case of compounds V, VI, and VII are included in Figures 2, 5, and 8, respectively.

The ^{1}H–^{13}C chemical shift correlated experiment (HETCOR) data were acquired with the Bruker microprogram XHCOR.AU. Data points were zero-filled in F_1 and multiplied by an unshifted sinebell function in F_1 and by an exponential function in F_2 before Fourier transformation.

X-ray Analyses. X-ray analyses were performed on single crystals with an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation (λ = 0.7107 Å).

For product X the crystal data are the following: composition $C_{14}H_8O_2S_2$, a = 12.109(2) Å, b = 7.896(1) Å, c = 13.266(2) Å, $\alpha = 90°$, $\beta = 104.61(1)°$, $\gamma = 90°$, V = 1227.4(0.6) Å, dens = 1.474 g/cm^3, μ(Mo Kα) = 4.04 cm^{-1}, in the $\theta/2\theta$ scan mode, $2\theta_{max} = 50°$, 1110 independent reflections for which $I/\sigma_I > 3.00$.

The structure was solved by direct methods and refined to $R = 0.023$, $R_w = 0.072$ (goodness of fit 1.03). Final refinement was achieved with the SHELXTL program. Weights of each reflection in refinement (on F) were calculated from $W = 1/[\sigma^2(F_o) + 0.001182F_o^2]$.

Results and Discussion

The GPC trace reported in Figure 1a shows that the crude sample of polymer I contained a series of low molecular weight compounds. In order to separate these oligomers the material extracted with ethyl ether from the crude polymer was chromatographed on a silica gel column.

The first product eluted from the column was purified by several running HPLC experiments and then crystallized to give white crystals having a melting point of 136 °C (DSC determination) and a molecular weight (mw) of 240.042 (determinated by exact positive EI-MS analysis) corresponding to the composition $C_{14}H_8O_4$.

The ^{1}H- and ^{13}C-NMR spectra of this compound, recorded in DMSO, are reported in Figure 2a,b, respectively. The signals due to the eight aromatic protons contained in the molecule appear as two symmetric

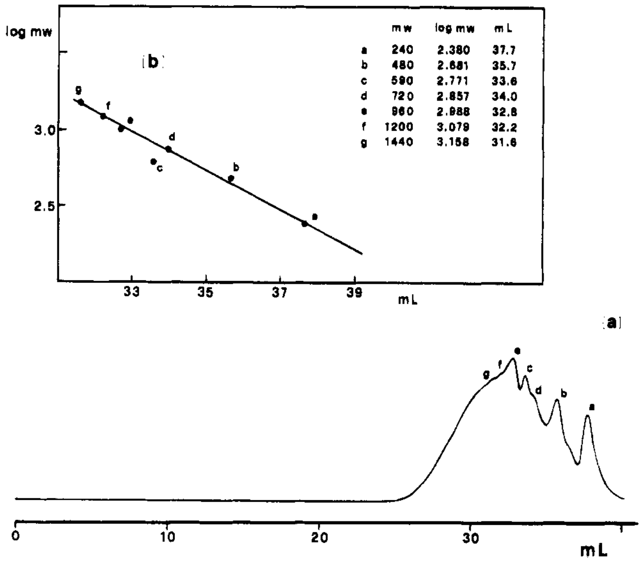


Figure 1. (a) Gel permeation chromatogram (THF as eluant) of polymer I. (b) Dependence of the elution volume on the log of molecular weight of the oligomers (the experimental data are also reported in the figure).

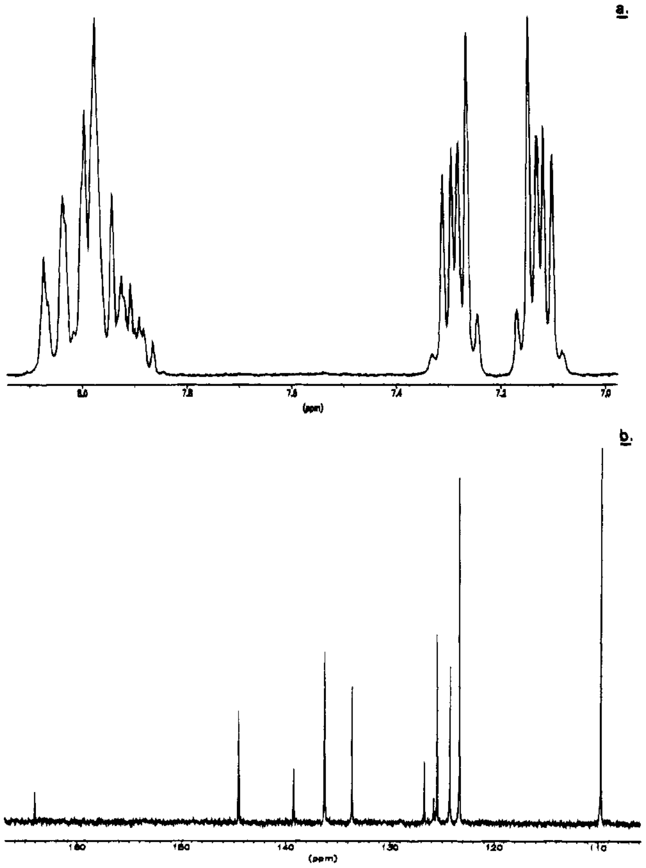


Figure 2. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra in DMSO-d_6 at 25 °C of compound V.

multiplets at 7.12 ppm (2H) and 7.29 ppm (2H) and another complex multiplet at 8.0 ppm (4H). The ^{13}C-NMR spectrum (Figure 2b) shows eleven peaks, many more of the seven being present in the spectrum of polymer I (omitted for brevity) than those expected for the symmetric cyclic diester of structure IV.

By comparison with the DEPT spectrum, the signals at 109.71, 123.29, 124.23, 125.44, 133.63, and 136.26 ppm correspond to tertiary carbon atoms and those at 125.73, 126.67, 139.19, 144.5, and 164.04 ppm are due to quaternary carbon atoms.

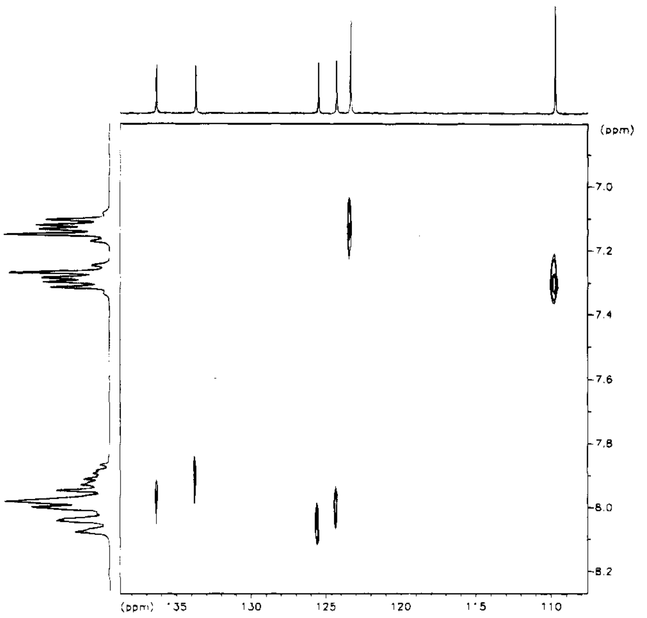


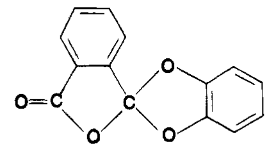
Figure 3. ^{1}H$-^{13}$C correlation spectrum of compound V in DMSO-d_6 at 25 °C. The ^{1}H-NMR and ^{13}C-NMR (DEPT) spectra are shown along the F$_1$ and F$_2$ axes, respectively.

On the basis of the ^{1}H$-^{13}$C chemical shift correlation map (HETCOR) of Figure 3 it can be inferred that the six tertiary ^{13}C peaks reported above correspond to eight CH groups; the peaks at 124.0 and 110.4 ppm, coupled with the four protons of the two multiplets at 7.12 and 7.29 ppm, each correspond to two CH of the catechol unit, whereas the other four carbon signals are connected with the four protons of the multiplet at 8.0 ppm (phthalic unit).

Considering that the molecule contains fourteen carbon atoms, the supposition must be made that the molecule contains two quaternary carbons having the same chemical shift.

The DP-MS spectrum of compound V, recorded in correspondence with the temperature of maximum volatilization rate, is reported in Figure 4a. An intense molecular ion peak appears at *m/z* 240, and the structural assignments of the main fragment ions are given in Table 1.

All these data agree with structure V suggested from Svensson for a so-called "pseudo ester" (mw = 240) formed in the synthesis of cyclic phthaloylcatechol.[19,20]



V

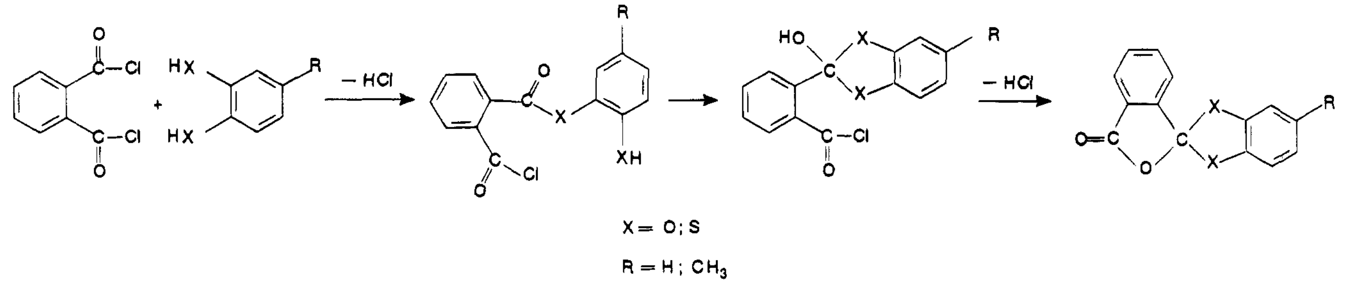
However, it can be observed that there is a difference between the Svensson product which is reported to melt at about 240 °C and our product, extracted from polymer I, which shows a melting point of 136 °C.

A possible mechanism of formation of spiro compound V is reported in Scheme 1.

According to structure V, the four tertiary (two by two equivalent) and two quaternary (equivalent) carbons belong to the symmetric catechol unit.

This assignment also accounts for the shape of the proton signals in the spectrum of Figure 2a. In fact, the couple of symmetric multiplets centered at 7.2 ppm, due to the catechol unit (which collapses to a broad

Scheme 1



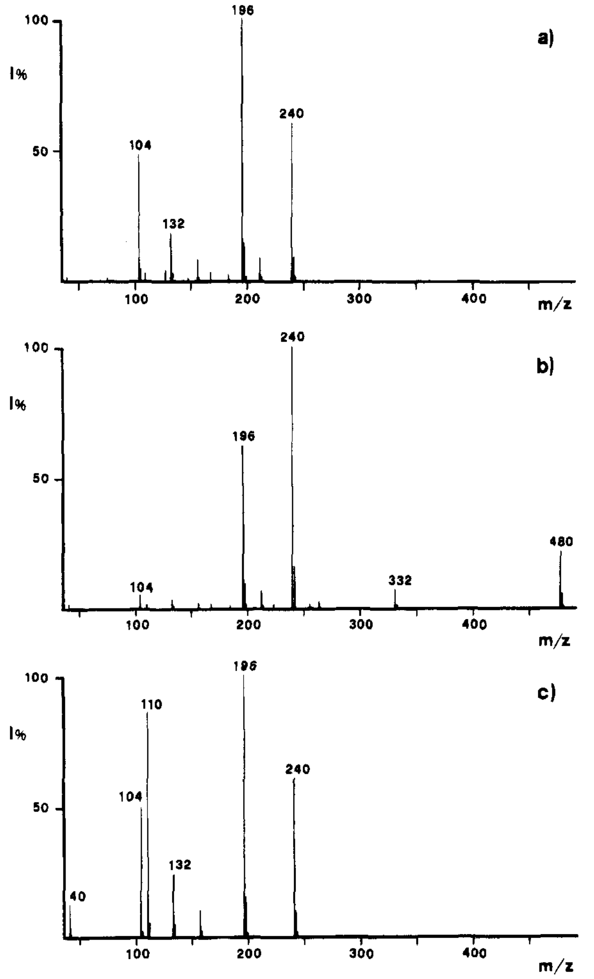


Figure 4. Electron impact mass spectra (EI) at 18 eV of (a) compound V, (b) compound VI, and (c) compound VII.

singlet when the spectrum is recorded in $CDCl_3$) correspond, as expected, to an AA′BB′ system, whereas the complex multiplet at 8 ppm, according to an ABCD system, is due to the asymmetric phthalic unit.

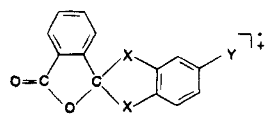
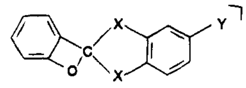
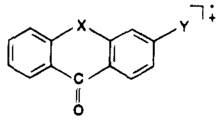
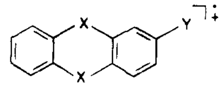
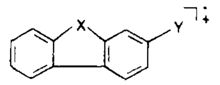
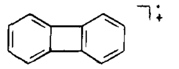
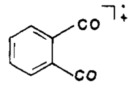
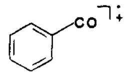
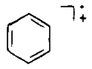
The second product eluted from the column exhibits a mw of 480 (obtained by FAB-MS analysis) corresponding to a $C_{28}H_{16}O_8$ composition, exactly the double of compound V. Its DP-MS spectrum, reported in Figure 4b, is very similar to that of compound V (Figure 4a) apart from the intense peak at *m/z* 480 due to the molecular ion.

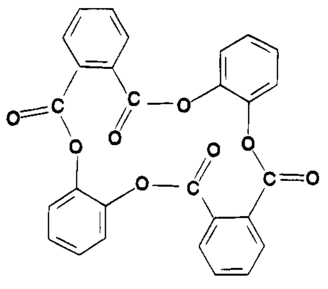
This oligomer is a very thermally stable product that melts at 327 °C without decomposition, a temperature higher than the PDT of polymer I (320 °C; see Experimental Section).

The NMR analysis was very useful in determining the structure of this product. The proton spectrum of Figure 5a (recorded in DMSO at 60 °C) shows two couples of well-resolved and symmetric multiplets at 7.33 (4H) and 7.60 (4H) (catechol unit) and at 7.75 (4H) and 7.99 (4H) ppm (phthalic unit) both connected to an AA′BB′ system. The ^{13}C spectrum of Figure 5b presents only seven peaks of which (by comparison with DEPT spectrum) four (peaks at 122.6, 125.7, 129.4, and 132.1 ppm) were identified as tertiary carbons and three (peaks at 129.6, 140.9, and 163.3 ppm) as quaternary carbons. The HETCOR map of Figure 6 shows that each tertiary carbon signal is coupled with a proton multiplet and then corresponds to four CH, so the three quaternary carbon signals are due to the twelve remaining carbons.

All these data suggest for this oligomer the following symmetric structure:

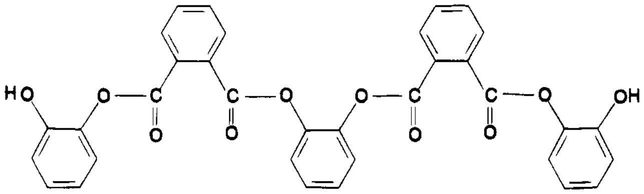
Table 1. Structural Assignments of the Main Fragment Ions (DP-MS)

Structure	X	Y	m/z
	O	H	240
	O	CH_3	254
	S	H	272
	O	H	212
	O	CH_3	226
	O	H	196
	O	CH_3	210
	S	H	228
	O	H	184
	O	CH_3	198
	O	H	168
	O	CH_3	182
	S	H	184
			152
			132
			104
			76



VI

The positive FAB-MS spectrum (omitted for brevity) of the third product eluted from the column, after solubilization in TNB and doping with NaCl, shows a peak at *m/z* 613 corresponding to the molecular ion as $(M + Na)^+$ of a linear oligomer of composition $C_{34}H_{22}O_{10}$ (mw = 590), with two hydroxyl end groups, having the following structure:



VII

Also the peak of the no-doped molecular ion is present in the spectrum at *m/z* 591, as $(M + H)^+$.

Compound VII has a melting point of 174 °C; its DP-MS spectrum, reported in Figure 4c, is very similar to that of compound V (Figure 4a), but an intense peak at *m/z* 110, almost absent in the other DP-MS spectra (Figure 4a,b), is present in the spectrum of Figure 4c. This peak corresponds to the hydroquinone ion probably formed by decomposition of the molecule of compound VII into two molecules of Product V (mw = 240) and a molecule of hydroquinone (mw = 110); its presence in the spectrum is then diagnostic of the open chain structure of compound VII.

In the proton NMR spectrum reported in Figure 7a are present the following signals: 9.84 (s, 2H), 8.06 (m, 2H), 7.79 (m, 6H), 7.43 (s, 4H), 7.05 (m, 6H), and 6.82 (m, 2H) ppm. It has been ascertained that the signal at 9.84 ppm disappears when D_2O is added to the solution, showing that this peak is due to −OH end groups.

Considering that structure VII presents a plane of symmetry in correspondence with the center of the molecule, seventeen peaks (half of the carbon atoms contained in molecule) were expected in the ^{13}C-NMR spectrum; on the contrary, only sixteen signals appear in the spectrum of Figure 7b.

The seven signals indicated with q in Figure 7b, absent in the DEPT spectrum (reported in figure 8), can be assigned to quaternary carbons. The other nine peaks, indicated with t (one less than those expected), are due to tertiary carbons. In order to find the missing peak the $^1H-^{13}C$ HETCOR map of compound VII was performed. In the map reported in Figure 8 it can be observed that the signal of two of the three protons of the multiplet at 7.79 ppm are coupled with the same ^{13}C-signal at 132.43 ppm. Therefore the chemical shifts of the carbon atom of two different couples of CH groups coincide.

The positive FAB-MS spectrum of the fourth product eluted from the column (omitted for brevity) shows essentially an intense peak at *m/z* 961 corresponding to molecular ion $(M + H)^+$ of the cyclic tetramer of formula $C_{56}H_{32}O_{16}$ and structure VIII.

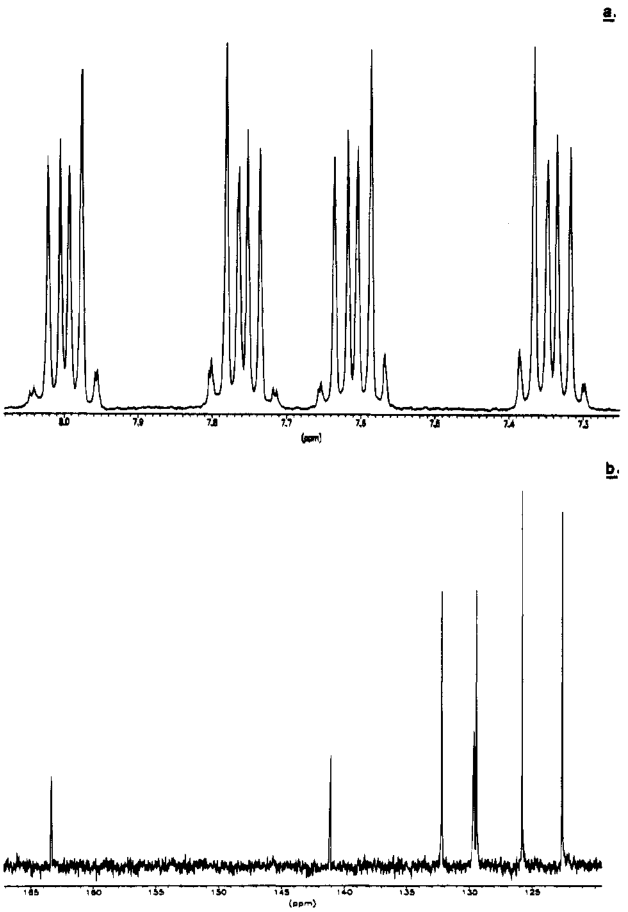


Figure 5. ^1H-NMR (a) and ^{13}C-NMR (b) spectra in DMSO-d_6 at 60 °C of compound VI.

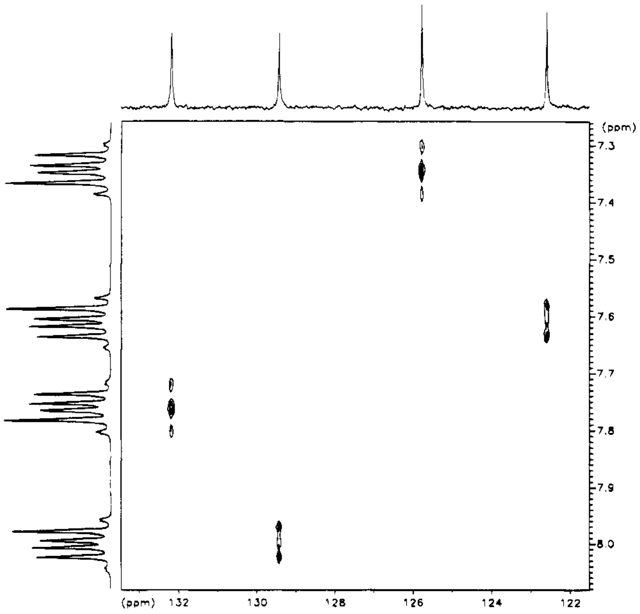


Figure 6. $^1H-^{13}C$ correlation spectrum of compound VI in DMSO-d_6 at 60 °C. The ^1H-NMR and ^{13}C-NMR (DEPT) spectra are shown along the F_1 and F_2 axes, respectively.

In the presence of NaCl or KCl, in the FAB-MS spectrum of the protonated molecule the ion at *m/z* 961 is replaced by the corresponding Na (*m/z* 983) or K (*m/z* 999) derivative peak. This means that compound VIII easily binds ions and there may be a relation between

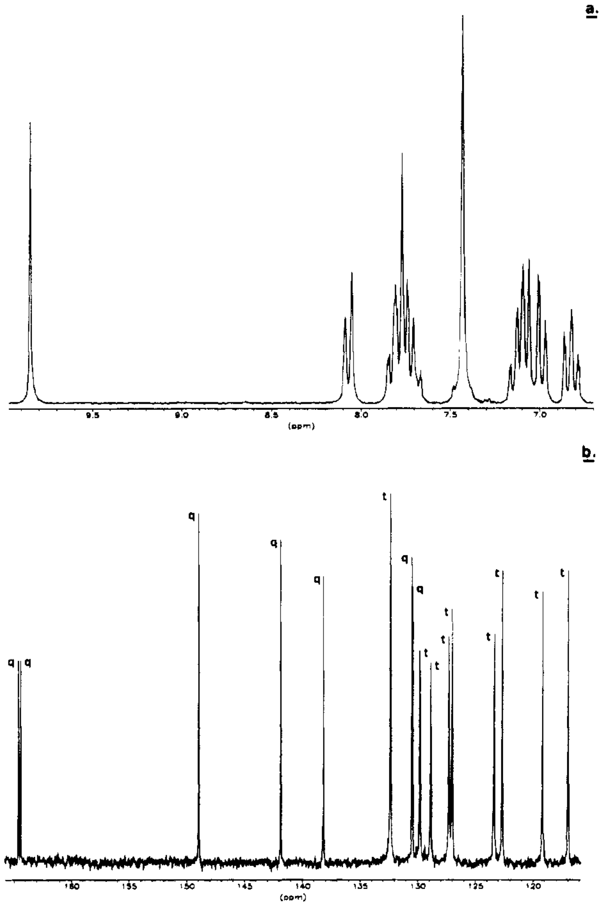
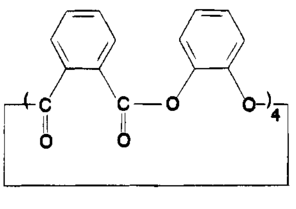


Figure 7. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra in DMSO-d_6 at 25 °C of compound VII.



VIII

the cyclic size and the bound metal ion.

Compound VIII melts at 192 °C with decomposition and its DP-MS spectra appear similar to that of Figure 4a, suggesting that each molecule of cyclic tetramer decomposes, forming four molecules of product V.

The proton NMR spectrum of compound VIII in DMSO (omitted for brevity) shows a couple of symmetric multiplets at 7.44 and 7.77 ppm (AA′BB′ system) due to the phthalic unit. The two multiplets (AA′BB′ system) expected for the catechol unit, in this case are partially overlapped in a multiplet centered at 7.24 ppm.

As expected, the ^{13}C-NMR spectrum of compound VIII shows seven signals, those of cyclic dimer VI (Figure 5b) and of polymer I, at 123.25, 126.84, 129.35, and 132.10 ppm (tertiary carbons) and 129.87, 141.63, and 164.20 ppm (quaternary carbons).

The following fractions eluted from the column resulted in mixtures of more products, and they were not analyzed.

On the basis of the above mentioned assignments, the dependence of the GPC elution volumes with respect to the log of molecular weight of the oligomers contained in polymer I has been determined.

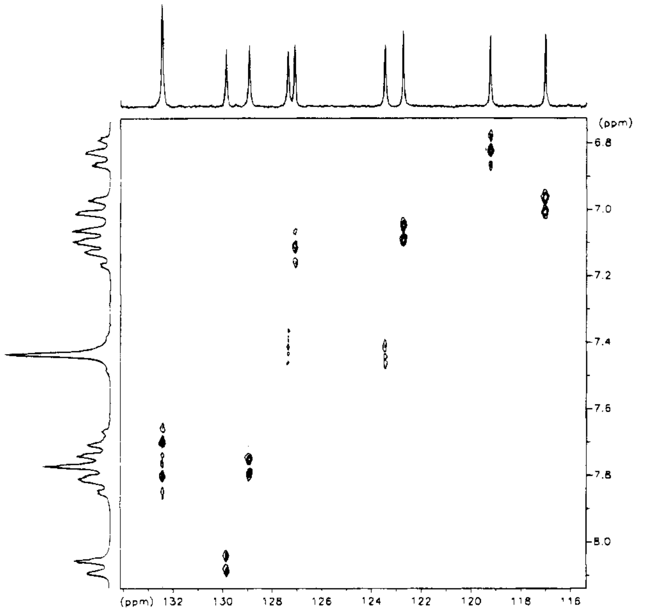


Figure 8. ^{1}H$-^{13}$C correlation spectrum of compound VII in DMSO-d_6 at 25 °C. The ^{1}H-NMR and ^{13}C-NMR (DEPT) spectra are shown along the F_1 and F_2 axes, respectively.

As expected, considering that the GPC peaks in Figure 1a are due to oligomeric members of the same homologous series, a good linear dependence has been obtained,[8] Figure 1b; the GPC peaks have been identified by comparison with pure extracted samples, and in Figure 1b, the points due to cyclic trimer (d), pentamer (f), and hexamer (g) (identified by the FAB-MS spectrum of the crude polymer sample, omitted for brevity) have also been included.

Only point c is not in agreement with the linear GPC law of Figure 1b, but this fact was expected considering that the product corresponding to peak c is a linear dihydroxy-terminated compound, a structure very different from the other cyclic products.[8]

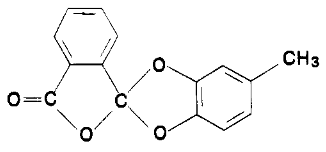
Data reported till now have shown that among the low molecular weight products formed in the synthesis of polymer I, besides the expected cyclic and linear oligomers (compounds VI−VIII), is formed a product having a molecular weight coincident with that of cyclic monomer IV (cyclic diester) but with a different structure (compound V).

All our DP-MS, FAB-MS, and NMR data of compound V are in agreement with the spiro structure proposed by Svensson, although our sample exhibits a different melting point. We have also found that, among the oligomers, only compound V has this unexpected structure.

In order to ascertain if the formation of products similar to compound V occurs also in other cases, the low molecular weight fractions extracted from polymers II and III, obtained by reaction between phthaloyl dichloride and 4-methylcatechol or dithiocatechol, were examined.

As in the polymer I case, both the fractions are constituted of a series of cyclic and linear oligomers. However, we have here restricted the analysis only to the lower molecular weight compound contained in each fraction.

For poly(1,4-dihydroxy-4-methylbenzene phthalate) (polymer II) the lower molecular weight product extracted from the polymer sample has a melting point of 89 °C and its DP-MS spectrum, reported in Figure 9a, appears very similar to that of compound V (Figure 4a), apart from the shifting toward higher mass values (a difference of 14 Da) of some peaks for the presence of the methyl group in the molecule; the molecular ion appears at *m/z* 254 as M^+. For this product, of formula $C_{15}H_{10}O_4$, the following structure can be proposed:

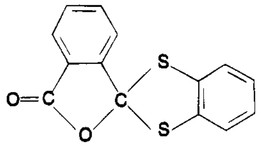


IX

The ¹H-NMR spectrum of compound IX shows a singlet at 2.355 ppm due to the methyl group, a multiplet at 6.87 ppm (3H) due to the catechol unit, and two multiplets at 7.73 ppm (3H) and 7.93 ppm (1H) due to the phthalic unit.

According to the fact that, differently from compound V, in molecule IX all the carbon atoms are not equivalent, its ¹³C-NMR spectrum, reported in Figure 10a, shows fifteen signals. This data constitutes also a confirmation of the structure proposed for compound V. In fact the eleven signals observed in the ¹³C-NMR spectrum of this last product (Figure 2b) were explained by assuming the catechol unit to be symmetric. Consequently, the introduction of a methyl group in the catechol, as in the compound IX case makes magnetically different all carbons, thus increasing the number of ¹³C signals in the spectrum.

The lower molecular weight product extracted from the polymer III sample shows a melting point of 198 °C and a molecular weight of 272, corresponding to a composition of $C_{14}H_8O_2S_2$. As in the preceding cases, this compound has been assigned the following structure:



X

Its DP-MS spectrum is reported in Figure 9b, and the structural assignments of main EI fragment ions are given in Table 1. It can be observed that the same fragmentation pathway of compounds V and IX occurs also in this case.

In the proton spectrum of compound X, as in the case of compounds V and IX, the signals of the phthalic unit appear at a lower field [7.80 ppm (m, H), 7.96 ppm (m, 2H), 8.06 ppm (m, H)] with respect to those of the catechol unit [7.30 ppm (m, 2H), 7.56 ppm (m, 2H)].

The ¹³C-NMR spectrum of compound X (Figure 10b) presents, as expected, eleven signals, as for compound V (Figure 2b).

Due to the presence of the two sulfur atoms in molecule X, some signals of the carbon nuclei appear at very different chemical shift values with respect to the corresponding signals of compound V. In particular, the signal at 104.66 ppm of the carbon atom indicated with 7 in Figure 11 is shifted 21 ppm toward higher fields with respect to the corresponding signals of compounds V (125.73 ppm) and IX (126.13 ppm).

In order to obtain decisive evidence of the structure of compounds V, IX, and X, an X-ray diffraction analysis of single crystals was attempted. Unfortunately, only in the case of compound X was it possible to obtain a suitable single crystal.

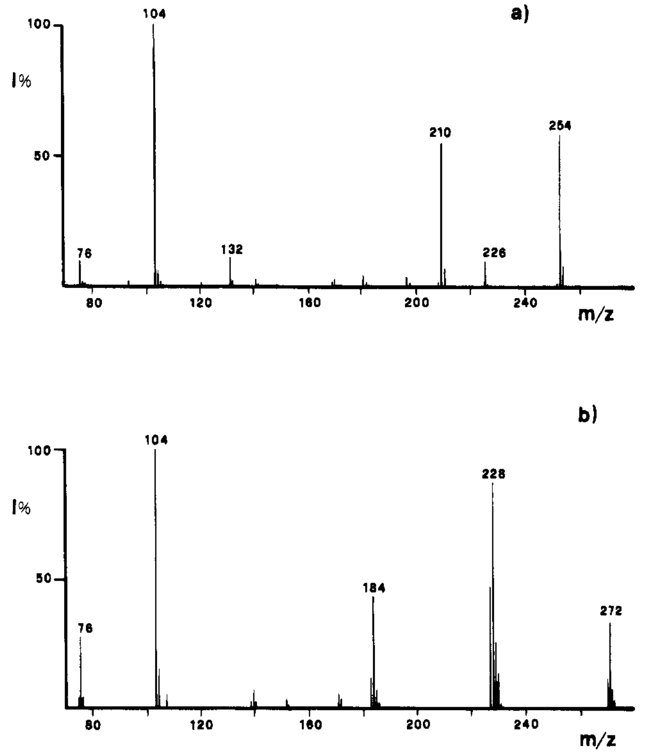


Figure 9. Electron impact mass spectra (EI) at 18 eV of (a) compound IX and (b) compound X.

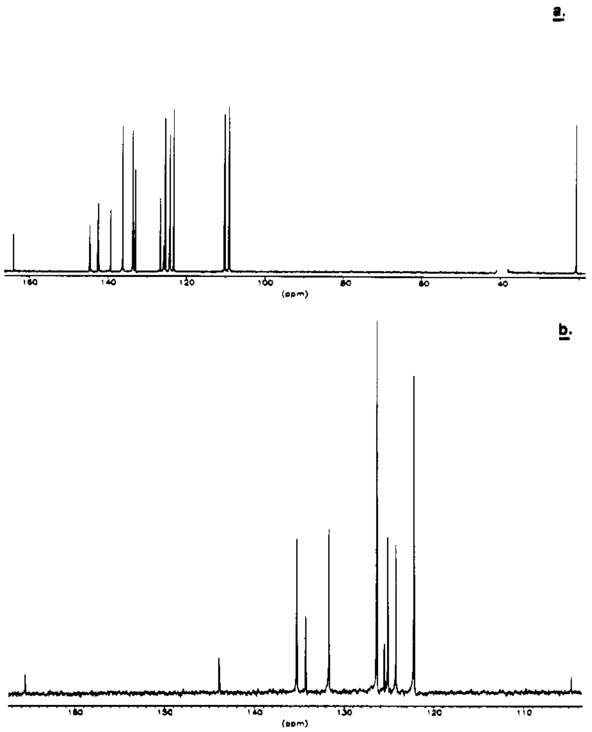


Figure 10. ¹³C-NMR spectra in DMSO-d_6 at 25 °C of (a) compound IX and (b) compound X. The truncated peak is due to DMSO.

On the basis of the atomic coordinates (Table 2), bond lengths (Table 3) and angles (Table 4), and hydrogen coordinates (Table 5), the molecular conformation reported in Figure 11 has been deduced, in which the atomic numbering is also indicated.

In this structure the atoms C_7–C_{14}, O_1, and O_2 are coplanar, likewise the atoms C_1–C_6, S_1, and S_2. Atom

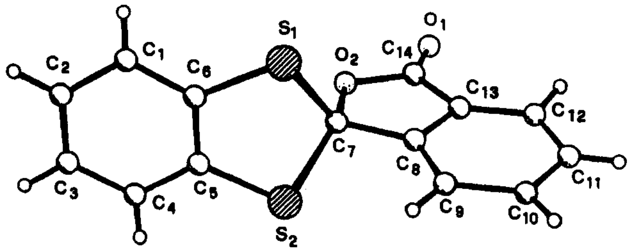


Figure 11. Perspective view of the spiro compound X with the atom numbering scheme.

Table 2. Atomic Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for Compound X

atom	*X*	*Y*	*Z*	*U*[a]
S(1)	6823(1)	480(1)	5193(1)	48(1)
S(2)	7583(1)	1182(1)	3303(1)	51(1)
O(1)	3622(2)	442(3)	2441(2)	67(1)
O(2)	5459(1)	182(2)	3277(1)	48(1)
C(1)	8473(2)	−2036(4)	5680(2)	53(1)
C(2)	9404(3)	−2871(4)	5492(3)	63(1)
C(3)	9779(2)	−2496(4)	4622(3)	63(1)
C(4)	9239(2)	−1281(4)	3923(2)	53(1)
C(5)	8305(2)	−438(3)	4113(2)	42(1)
C(6)	7936(2)	−800(3)	4990(2)	41(1)
C(7)	6374(2)	1256(3)	3866(2)	40(1)
C(8)	5845(2)	2973(3)	3806(2)	38(1)
C(9)	6324(3)	4513(4)	4164(2)	54(1)
C(10)	5615(3)	5917(5)	3963(3)	66(1)
C(11)	4484(3)	5772(5)	3443(2)	62(1)
C(12)	4007(2)	4256(5)	3085(2)	53(1)
C(13)	4715(2)	2853(3)	3276(2)	38(1)
C(14)	4478(2)	1100(4)	2936(2)	46(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthorgonalized **U**(*i*,*j*) tensor.

Table 3. Bond Lengths (Å) for Compound X

S(1)−C(6)	1.759(3)	S(1)−C(7)	1.814(2)
S(2)−C(5)	1.756(3)	S(2)−C(7)	1.805(3)
O(1)−C(14)	1.197(3)	O(2)−C(7)	1.456(3)
O(2)−C(14)	1.367(3)	C(1)−C(2)	1.382(5)
C(1)−C(6)	1.383(4)	C(2)−C(3)	1.375(5)
C(3)−C(4)	1.379(4)	C(4)−C(5)	1.388(4)
C(5)−C(6)	1.378(4)	C(7)−C(8)	1.493(4)
C(8)−C(9)	1.379(4)	C(8)−C(13)	1.376(3)
C(9)−C(10)	1.387(5)	C(10)−C(11)	1.374(5)
C(11)−C(12)	1.361(5)	C(12)−C(13)	1.384(4)
C(13)−C(14)	1.462(4)		

Table 4. Bond Angles (deg) for Compound X

(C6)−S(1)−C(7)	95.7(1)	C(5)−S(2)−C(7)	95.8(1)
C(7)−O(2)−C(14)	110.4(2)	C(2)−C(1)−C(6)	119.1(3)
C(1)−C(2)−C(3)	120.4(3)	C(2)−C(3)−C(4)	120.9(3)
C(3)−C(4)−C(5)	118.8(3)	S(2)−C(5)−C(4)	122.8(2)
S(2)−C(5)−C(6)	116.8(2)	C(4)−C(5)−C(6)	120.4(2)
S(1)−C(6)−C(1)	123.7(2)	S(1)−C(6)−C(5)	115.7(2)
C(1)−C(6)−C(5)	120.5(3)	S(1)−C(7)−S(2)	108.3(1)
S(1)−C(7)−O(2)	109.0(2)	S(2)−C(7)−O(2)	110.3(2)
S(1)−C(7)−C(8)	112.2(2)	S(2)−C(7)−C(8)	112.9(2)
O(2)−C(7)−C(8)	104.0(2)	C(7)−C(8)−C(9)	130.2(2)
C(7)−C(8)−C(13)	108.8(2)	C(9)−C(8)−C(13)	121.0(3)
C(8)−C(9)−C(10)	116.9(3)	C(9)−C(10)−C(11)	121.3(3)
C(10)−C(11)−C(12)	122.0(3)	C(11)−C(12)−C(13)	116.8(3)
C(8)−C(13)−C(12)	121.9(2)	C(8)−C(13)−C(14)	108.4(2)
C(12)−C(13)−C(14)	129.6(2)	O(1)−C(14)−O(2)	120.8(3)
O(1)−C(14)−C(13)	130.9(2)	O(2)−C(14)−C(13)	108.3(2)

C_7 is deviated from the last plane by 0.45 Å and has a bent angle along the line S_1-S_2 of 26.8°. The planes of the two parts of the molecule are almost orthogonal (angle of 85.9°).

Table 5. Hydrogen Coordinates (×10^3) and Temperature Factors (Å^2 × 10^2) for Compound X

atom	*X*	*Y*	*Z*	*U*
H(1)	820(2)	−229(3)	624(2)	5(1)
H(2)	977(3)	−373(4)	592(2)	7(1)
H(3)	1043(2)	−312(4)	444(2)	6(1)
H(4)	946(3)	−102(4)	332(2)	7(1)
H(9)	710(3)	461(4)	450(3)	7(1)
H(10)	587(2)	698(4)	422(2)	5(1)
H(11)	407(3)	669(4)	334(2)	6(1)
H(12)	317(3)	402(4)	274(2)	7(1)

Notwithstanding it has not been possible to obtain X-ray diffraction spectra for compounds V and IX, on the basis of the data collected the structure proposed for these compounds has been proved.

It can then be concluded that in the synthesis of polymer I by the reaction between phthaloyl dichloride and catechol, the formation of the spiro compound V takes place together with that of cyclic and linear ester oligomers like VI, VII, and VIII. Spiro compounds IX and X are likewise formed when 4-methylcatechol or dithiocatecol are used in the synthesis of polymers II and III.

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