CYCLIC AND LINEAR LIQUID CRYSTALLINE FUNCTIONALIZED POLYESTERS WITH MAIN-CHAIN ORTHO-LINKED UNITS. SYNTHESIS AND CHARACTERIZATION OF CYCLIC LC UNIMERS AND DIMERS WITH "U"-SHAPED RIGID MESOGENIC UNITS WITH ALKYL SIDE CHAINS

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Abstract: Although ortho-diphenols had not been extensively used in the synthesis of LC esters, a great variety of molecular structures of low and high molecular weight LC esters containing high proportions of these units can be synthesized. In this paper we describe the synthesis and characterization of new series of low and high molecular weight cyclic and linear LC esters with mesogenic "U"-shaped rigid units with terminal groups which are alkyl chains. Cyclic oligoesters and linear polyesters were formed by the polycondensation of 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) with monosubstituted catechols which are the alkyl esters of 3,4-dihydroxybenzoic acid. Although the great importance that concomitant cyclization reactions have in polyesterifications involving high proportions of ortho-diphenols does not seem to have been considered until now, we have found that these polyesterifications produced linear polyesters along with high proportions of cyclic oligoesters even when reaction conditions disfavored cyclization. Copolymerization with p-hydroxybenzoic acid decreased the amount of cyclic oligomers, however it was necessary to copolymerize with proportions of **PB** higher than 50 mol-% to get copolyesters with low proportions of cyclic oligomers. As far as we know we describe the first examples of cyclic LC oligoesters and cyclic LC unimers and dimers which display enantiotropic LC mesophases stable over broad ranges of temperature. Cyclic dimers display mesophases whose isotropization temperatures (> 300°C) are much higher than that of their linear high molecular mass homologues. Cyclic LC unimers and dimers, linear LC polyesters and model compounds were characterized by FAB-MS, GPC, ^{1}H NMR, DSC and hot-stage polarized microscopy. All these compounds contain reactive C=C double bonds and can be crosslinked thermally and photochemically. Cyclic unimers and dimers can be polymerized termally to produce high molecular mass polymers.

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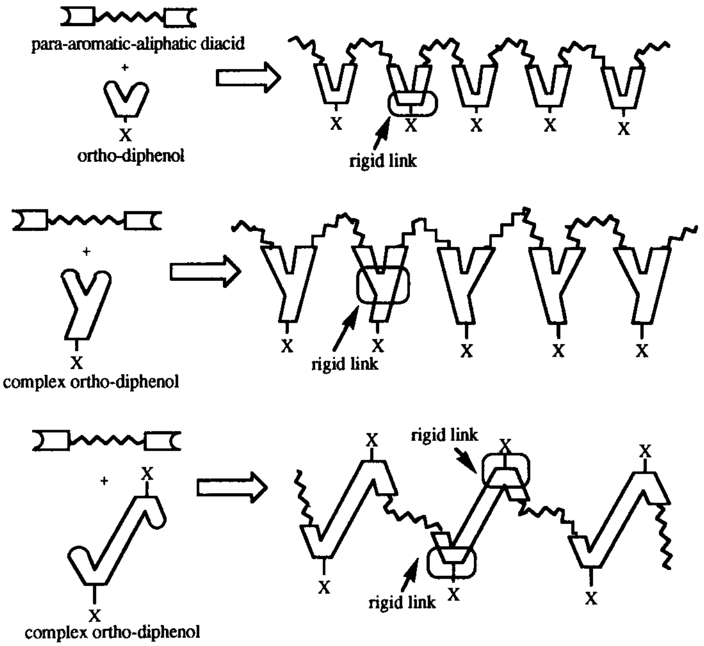
INTRODUCTION

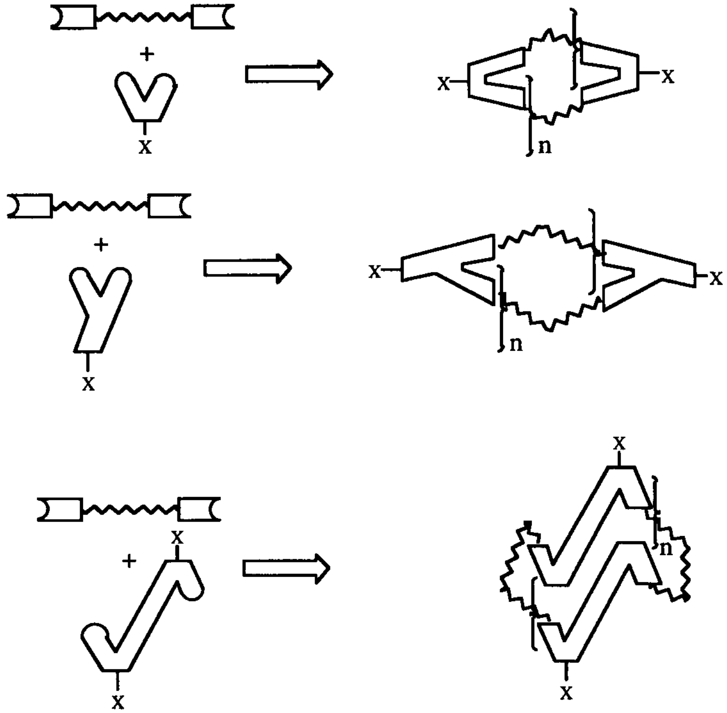
Main-chain liquid crystalline polyesters usually have low solubility and high-temperature transitions. Several ways for lowering their temperature transitions and increasing their solubility have been developed over the last years (Refs. 1-6). Copolymerization with high amounts of bent units may lead to the reduction of the temperature transitions of the copolymers, but a drastic reduction of their T_i may also produce the destruction of their LC properties. However, polymers incorporating high proportions of sharply bent units (ortho-linked units, ortho-diphenols or catechols) in their backbones and showing good solubility in common solvents, low temperature transitions, high thermal stability and in some cases very stable liquid crystalline phases have been reported (Refs. 6-9). Particularly, we have synthesized a great variety of thermotropic main-chain LC polyesters incorporating high proportions ortho-diphenols which had good solubility in common solvents, low temperature transitions and in addition displayed very stable liquid crystalline enantiotropic mesophases. Some examples of these polyesters have been reported previously (Ref. 10) and others will be reported in subsequent papers. These polyesters are characterized by having different shape rigid units in which the ortho-linked units act as rigid links between rod-like mesogenic units (Fig. 2).



Scheme 1. Synthetic scheme of LC polyesters with mesogenic "U", "Y" and "Z"-shaped rigid units with and without terminal groups (X = H or different terminal groups). (Refs. 8 and 10)

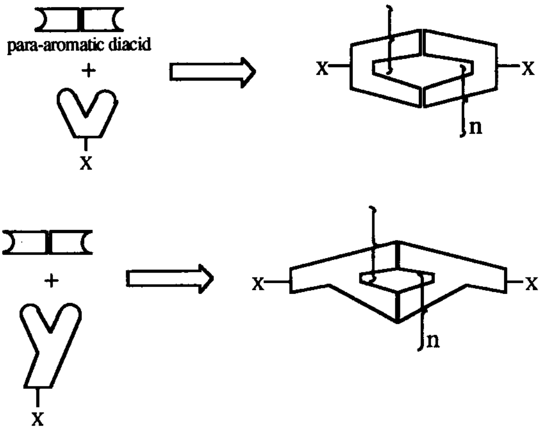
The following illustrations are schematic representations of the formation of aliphatic-aromatic LC polyesters with "U", "Y" and "Z"-shaped rigid units. By polycondensation of simple or complex monomers (Ref. 11), dicarboxylic diacids with ortho-difenols, rod-like mesogenic units are formed which remain linked by the ortho-units.

Our previous experience with polyesterifications involving high proportions of orto-diphenols as comonomers was that they produced two polyesters homologues series, one of low molecular cyclic polyesters and the other of linear polyesters which is due to the influence that the geometry of the orto-diphenols units causes on the relative rates of cyclization and polymerization. The sharply angular geometry of orto-diphenols units favours the proximity of reactive end groups and consequently tends to increase the rate of cyclization at the expense of the rate of polymerization. The following illustrations are schematic representations of the formation of wholly aromatic and aliphatic-aromatic macrocyclic LC polyesters which contain one or more "U", "Y" and "Z"-shaped rigid units.

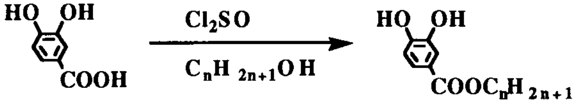


Scheme 2. Synthetic scheme of aliphatic-aromatic macrocyclic LC polyesters containing one or more mesogenic "U", "Y" and "Z"-shaped rigid units with and without terminal groups (X = H or different terminal groups).

These cyclic compounds were formed along with their homologous linear polyesters, by the polycondensations of simple or complex monomers, aliphatic-aromatic or wholly aromatic dicarboxylic diacids with ortho-difenols. It seems that the "U", "Y" and "Z"-shaped conformations of the rigid units of the growing oligomeric chains favour that their reactive end groups came into close proximity and thus cyclization results enhanced against polymerization.



Scheme 3. Synthetic scheme of wholly aromatic macrocyclic LC polyesters formed by two o more mesogenic U and Y-shaped rigid units with and without terminal groups (X = H or different terminal groups).

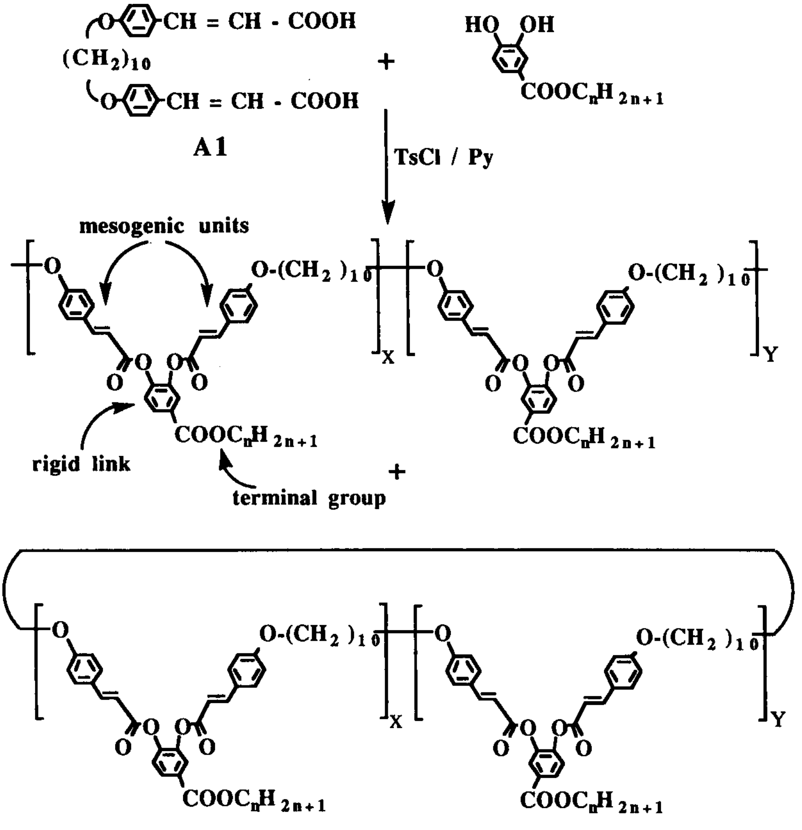


n = 1,2.....and 10, diphenols DF1 to DF10, respectively

Fig. 1. Synthesis of ortho-diphenols **DF1** to **DF10**.

In this paper we describe the synthesis and characterization of cyclic and linear LC polyesters with mesogenic "U"-shaped rigid units with terminal groups (-X) which are alkyl chains. They were formed (Figs 1-2) by the polycondensation of aliphatic-aromatic dicarboxylic diacid 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) (**A1**) with ten ortho-difenols, which are the alkyl esters of 3,4-dihydroxybenzoic acid (**DF1** to **DF10**).

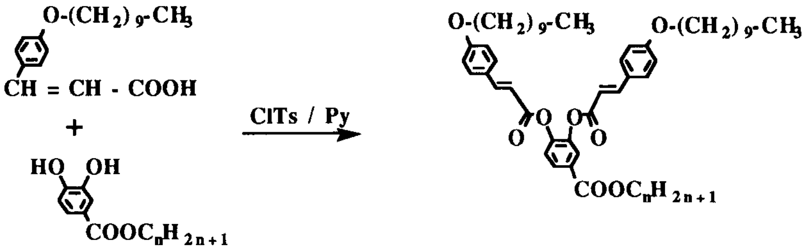
These polyesterifications produced moderately high proportions of cyclic unimers (**U1** to **U10**) and dimers (**D1** to **D10**) (approximately 10 wt-% of each one) along with moderately high molecular weight linear polymers (**P1** to **P10**). The formation of cyclic oligomers has been frequently observed in the synthesis of polycondensation polymers (Ref. 12). However, very few examples of cyclic LC oligomers have been reported (Ref. 13). As far as we know we describe the first examples of cyclic LC oligoesters and cyclic LC unimers and dimers which display enantiotropic mesophases over broad ranges of temperature. Cyclic LC oligoethers have been reported (Ref. 13) but cyclic unimers were not liquid crystalline and cyclic dimers formed mesophases over narrow ranges of temperature.



n = 1,2.....and 10. Ring size = X + Y

Fig. 2. Polymerizations-Cyclizations **PZ1** to **PZ10**, structures of linear polyesters **P1** to **P10** and cyclic unimers (X+Y=1) **U1** to **U10** and cyclic dimers (X+Y=2) **D1** to **D10**.

Also low molecular weight LC model compounds **M1** to **M10** with the same structure as that of the repeating mesogenic units of cyclic and linear polymers were synthesized (Fig. 3). Very few low molecular LC compounds with aromatic ortho-linked units as the rigid link between two mesogenic units have been described until now (Ref. 10a and 14).



n = 1,2.....and 10, model compounds M1 to M10, respectively.

Fig. 3. Synthesis of model compounds M1 to M10.

Recently a great variety of functionalized LC polymers containing reactive C = C bonds introduced in their main-chains by cinnamate groups have been described (Ref. 15). All the compounds described in this paper contained conjugated carbon-carbon double bonds in their main-chains introduced by the cinnamte groups and can be crosslinked by thermal or photochemical reaction of the reactive C = C double bonds.

EXPERIMENTAL PART

Materials.

3,4-dihydroxybenzoic acid (97%), aliphatic alcohols n-$C_nH_{2n+1}OH$ (n=1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11) (99%), p-hydroxybenzoic acid (99%), solvents and all other reagents were analytical grade and used as received. 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) and 4-(deciloxy)cinnamic acid were synthesized as described previously (Ref.10a).

Synthesis. Synthesis of Diphenols DF1 to DF11.

Ten side chain substituted diphenols were synthesized by esterification of 3,4-dihydroxybenzoic acid with linear aliphatic alcohols by one-pot method via acil chloride (Fig. 1) (Ref.16). The synthetic procedure is the following. Thionyl chloride (0.1 mol) was added slowly to the aliphatic alcohol (1 mol) at 0°C. The reaction mixture was stirred for 1 h at 0°C. 3,4-Dihydroxybenzoic acid (0.1 mol) was added to the resulting solution and the mixture was warmed to 120 °C for 3 h until a clear solution was obtained. The excess of the aliphatic alcohol was removed on a rotary evaporator to produce a solid which was recrystallized repeatedly from toluene yielding the alkyl esters of 3,4-dihydroxybenzoic acid as crystalline white solids with a purity (HPLC) 99%.

Polymerizations with tosyl chloride in pyridine as the condensation agent.

Polymerizations **PZ1** to **PZ10** were carried out by direct polyesterification of the dicarboxylic diacid **A1** with the ortho-diphenols **DF1** to **DF11** with tosyl chloride in pyridine as the condensation agent and by a procedure previously described (Ref.17). The polymerizations produced a mixture of cyclic oligomers and high molecular weight polymers. These mixtures were separated into three fractions **F1, F2** and **F3** by successive precipitation in acetone, methanol and water, respectively. **F1** was mostly a mixture of cyclic dimer **D2** and high molecular weight polymer **P2**, fraction **F2** was a complex mixture of cyclic species and low molecular weight polymer and **F3** was cyclic unimer **U2** nearly pure. Cyclic dimer **D2** and high molecular weight polymers **P2** were isolated from fraction **F1** and cyclic unimer **U2** from fraction **F3**. The experimental procedure was as follows.

A representative example of the synthetic procedure used in polimerization **PZ2** is given. A pyridine solution (15 mL) of tosyl chloride (22 mmol, 1.1/1 the proportion mmol tosyl chloride to mmol phenol groups) maintained at room temperature for 30 min was added at once to a hot solution of 4,4′-[1,10-decamethylenebis(oxy)]bis(cinnamic acid) **A1** (10 mmol) and ethyl trans-3,4-dihydroxybenzoate **DF2** (10 mmol) in pyridine (15 mL) and DMF (15 mL) preheated at 120 °C for 10 min; the whole mixture was maintained at 120 °C for 3 h. The cold solution was poured into 500 mL of acetone and the precipitate was filtered off, washed sequentially with diluted HCl, water, $NaHCO_3$ 5% and water, vacuum dried to get fraction **F1** wich was a mixture of cyclic dimer **D2** and high molecular weight polymer **P2**. The solvent of the filtered solution of acetone was evaporated on a rotary evaporator and the residue was poured into 500 mL of methanol. The precipitate was filtered off, washed sequentially with diluted HCl, water, $NaHCO_3$ 5% and water, vacuum dried to get fraction **F2** wich was mostly a mixture of cyclic oligomers and low molecular weight polymer. The solvent of the filtered solution of methanol was evaporated on a rotary evaporator and the residue was poured into 500 mL of ice-HCl (concentrated). The precipitate was collected washed sequentially with diluted HCl, water, $NaHCO_3$ 5% and water, vacuum dried to get fraction **F3** which was the cyclic unimer **U2** nearly pure. Fraction **F3** was dissolved in chloroform and to this solution silica gel was added, the mixture was agitated to room temperature for five minutes and then filtered through a fritted glass funel to remove the silica and the chloroform was evaporated. The product was recrystallized repeatedly from mixtures methanol / acetone to get **U2** as a crystalline white solid with a purity (HPLC) >97%.

The isolation of cyclic dimers and high molecular weight polymers was carried out by the following procedure. Fraction **F1** was dissolved in chloroform. To this solution silica gel was added and the chloroform was evaporated. The product absorbed on silica was separated into fractions by silica gel column chromatography with a mixture of cyclohexanone and methylene chloride (1:100 v/v). The fractions containing the cyclic dimer were collected, the methylene chloride was evaporated to produce a residue mixture of cyclohexanone and the crystallized cyclic dimer, the crystals were filtered off and washed with acetone to get the dimer **D2** as a crystalline white solid with a purity (HPLC) >98%. Once the remaining low molecular weight cyclic oligomers were eluted with a mixture of cyclohexanone and methylene chloride (1:100 v/v), the column was flushed with 500 mL of methylene chloride to separate the higher molecular weight part. The methylene chloride was evaporated to give a liquid residue which was poured into acetone. The precipitated polymer **P2** was filtered off, redisolved in chloroform and reprecipitated in acetone and vacuum dried.

Synthesis copolyesters of p-hydroxybenzoic acid PB21 to PB24.

All the copolyesters of p-hydroxybenzoic (**PB**) were synthesized by the same procedure (see scheme 4). A representative example of the synthetic procedure, for copolymer **PB23**, is given: a pyridine solution (20 mL) of tosyl chloride (33 mmol) maintained at room temperature for 30 min was added at once to a hot solution of diacid **A1** (10 mmol), diphenol **DF2** (10 mmol) and p-hydroxybenzoic acid **PB** (10 mmol) in pyridine (15 mL) and DMF (15 mL) preheated at 120 °C for 10 min; the whole mixture was maintained at 120 °C for 3 h. Isolation of the copolymer was carried out by working up as described above.

Purification of the obtained product **PB23** consisted in its redisolution in chloroform and reprecipitation in acetone three times.

Synthesis of model compounds.

All compounds **M1** to **M10** were synthesized by the same procedure (Fig. 3), by direct esterification with tosyl chloride in pyridine. A representative example of the synthetic procedure, for compound **M2**, is given: A pyridine solution (10 mL) of tosyl chloride (4 mmol) maintained at room temperature for 30 min was added at once to a hot solution of 4-(deciloxy)cinnamic acid (4 mmol) and ethyl trans-3,4-dihydroxybenzoate (2 mmol) in pyridine (10 mL) and DMF (10 mL) preheated at 120 °C for 10 min; the whole mixture was maintained at 120 °C for 3 h. **M2** was separated by pouring the cold solution into ice-HCl (concentrated), washed sequentially with diluted HCl, water, $NaHCO_3$ 5% and water, vacuum dried and recrystallized repeatedly from ethanol to get **M2** as a crystalline white solid with a purity (HPLC) >98%.

Techniques.

GPC analysis were carried out with a Waters 600 pump and controller and Milenium Analytical GPC software. The analysis were performed with a 996 photo diode array detector, THF (1mL/min, 30°C), two PL gel columns of 10^3 and 10^5 Å and a calibration curve constructed with poystyrene standars. HPLC analysis were made with the same instrument with a C8 reverse phase column. Fast atom bombardment mass spectra (FAB-MS) were obtained on a Vacuum Generators (VG) Autoexpec instrument, by using a Cs gun as primary ion source. The matrix for the samples to be bombarded was a 3-nitrobenzyl alcohol/methylene chloride (1/1 v/v) mixture. ^{1}H NMR (300-MHz) spectra were recorded on a Variant XL-300 spectrometer or a Bruker ARX-300. All spectra were adquired at room temperature in $CDCl_3$ and with TMS as internal standard. Textures and thermal behaviour of the melts were examined on a heating stage Linkam THMSE 600 attached to Olympus BX50 polarizing microscope. DSC was performed on a Perkin-Elmer DSC-7 calorimeter calibrated following the standard procedure. The standard heating and cooling rate for thermal analysis was 20 °C/min.

RESULTS AND DISCUSSION.

All the polymerizations were carried out at 120°C in a mixture of pyridine-DMF with tosyl chloride as the condensation agent. Under these conditions significant amounts of ramified polymers, products of transesterification reactions between main chain aromatic ester and side-chain aromatic-aliphatic ester groups, were not observed. Fig. 2 shows the general scheme of the polycondensations of the orto-diphenols **DF1** to **DF10** with diacid **A1** to get two polyesters homologues series, one of cyclic polyesters and the other of linear polyesters. The GPC chromatograms of the reaction mixtures of these polymerizations **PZ1 to PZ10** (Fig. 4) exhibited intense narrow peaks at the low molecular weight region and a very broad peak at higher molecular weight. The low molecular weight peaks corresponding to a mixture of cyclic oligomers and the broad peak to high molecular polymer in about a 30/70 ratio, which shows that although the concentrations of monomers in the reaction mixtures was very high, the proportion of cyclic oligomers was elevated. The formation of high proportions of stable cyclic oligomers under the given conditions may be caused by the existence of a preferred "U"-shaped conformation of the rigid units which enhances cyclization more than polymerization.

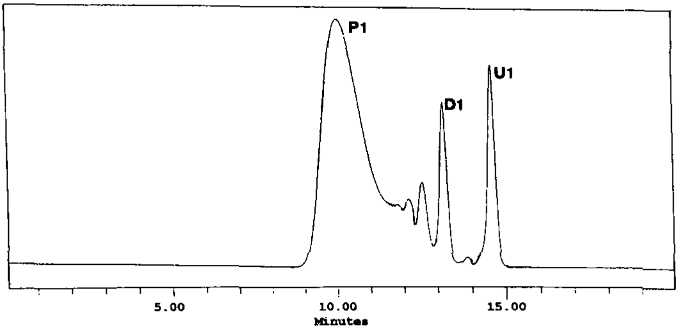


Fig. 4. Representative GPC chromatogram of polymerization mixture **PZ1**.

The rate of these polymerizations was very fast and cyclic oligomers were formed just at the beginning of the reactions, immediately after the condensation agent was added. The amounts and the ratio of cyclic oligomers remained unchanged during the polymerization time showing that they were stable in the medium of reaction and no mechanism was able to reopen them once were formed. A typical distribution of cyclic oligomers was 10% unimers, 8.5% dimers, 5% trimers, and 4% tetramers, 2,5% pentamers. Cyclic unimers and dimers which formation was statistically favoured, were the most abundant species, being the unimers the dominant species. However, the proportion (%) of cyclic unimers and dimers was similar which suggests that ring strain makes formation of unimers somewhat more difficult than dimers.

Cyclic oligomers from dimers on contain several isomers due to the possibility of the variation of the position of the alkyl side chains in orto-linked units of cyclic oligomers. Thus, cyclic unimers contain one isomer and cyclic dimers contain two isomers (Fig. 2).

All the polycondensations proceeded homogeneously and produced three precipitates **F1**, **F2** and **F3** when the mixtures of reaction were successively precipitated with acetone, methanol and water, respectively. The detailed procedure is described in the experimental part. Fig. 5 (at the top) presents representative GPC chromatograms of the fractions **F1**, **F2** and **F3** of polymerization **PZ5**. **F1** contained the most insoluble products of polymerization which are the cyclic dimer and high molecular weight polymers.The cyclic dimers had a moderately high tendency to crystallize from dissolution and the solubility of their crystals in common organic solvents was similar to the solubility of high molecular weight products of polymerizations. The separation of the cyclic dimers from high molecular weight polymers was carried out by silica gel column chromatography with a mixture of cyclohexanone and methylene chloride (1:100 v/v) according with the procedure is described in the experimental part. **F2** was a mixture of cyclic oligomers and low molecular weight polymers which do not precipitated in acetone. Finally, **F3** contained the cyclic unimers nearly pure, which were the most soluble of the cyclic oligomers. The unimers **U1** to **U10** were obtained pure by simple recrystallization of the corresponding fractions **F3**, in mixtures acetone / methanol. Fig. 5 (at the bottom) presents the GPC chromatograms of cyclic unimer **U5**, cyclic dimer **D5** and high molecular weight polymer **P5** isolated from fractions **F3** and **F1** of **PZ5**. Cyclic trimer, tetramer and pentamer were isolated from fraction **F2** but only trimers had purities higher than 90% (HPLC). Further work on the purification and charaterization of these cyclic LC oligomers will be reported in due course.

Molecular weights calculated for cyclic oligomers and model compounds were the same as the molecular weights determined by FAB-MS analysis. Fig. 6 presents the calibration curve used in GPC analysis and the molecular weights calculated for cyclic unimers, dimers, trimers and model compound versus time of elution. The molecular weights determined by GPC were approximately 1,3 times higher than the calculated ones for the lower members (n = 1 to 4) of the series of dimers, trimers and model compounds and 1,5 times higher than the calculated ones for the higher members (n = 4 to 10). These results indicate a larger hydrodynamic volume of the repetitive unit of these compounds in THF compared with polystyrene standars, which is probably due to the presence of the rigid aromatic mesogenic unit with the bulky alkyl side chains.

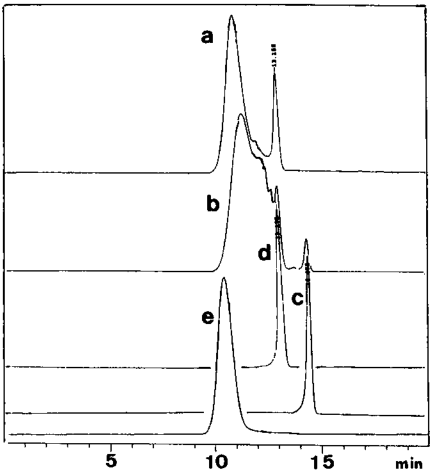


Fig. 5.(at the top) Representative GPC chromatograms of the fractions (a) **F1**, (b) **F2**, (c) unimer **U5**, (d) cyclic dimer **D5** and (e) polymer **P5** (M_n, GPC = 21 721, (M_w/M_n)GPC=1.3) of **PZ5**.

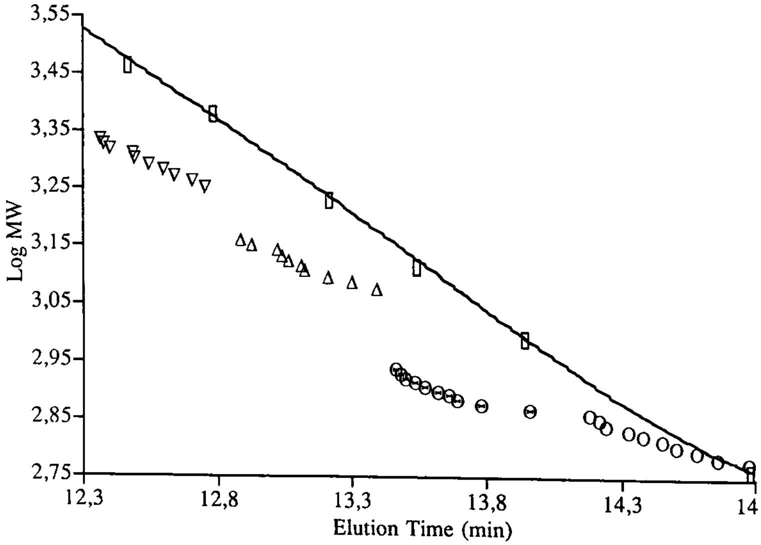


Fig. 6. Calibration curve used in GPC analysis, molecular weights of polystyrene standars versus elution time ( ) . Molecular weights calculated for model compounds (Θ), unimers (O), dimers (Δ) and trimers (∇) versus time of elution.

Figs. 7 and 8 present the 300-MHz ^{1}H NMR spectra (CDCl$_3$, TMS) and the corresponding aromatic protonic assignments of representative compounds, cyclic unimer **U5**, cyclic dimer **D5**, high molecular weight polymer **P5** and model compound **M5**. Cyclic unimer and dimer did not showed resonances characteristic for the chain ends. High molecular weight polymers showed small peaks corresponding to -CH=CH-COO- (6,18-6,30 ppm and 7,58-7,70 ppm) chain ends. The results of the integration of these chain ends groups versus the integration of the main-chain groups allowed us to calculate the molecular weight of the polymers from the ^{1}H NMR spectra (Tab. 1). According with the results obtained in the GPC determination of molecular weights for cyclic oligomers, we assumed that the GPC determined M_n were larger than the calculated ones by a factor of 1,3 for **P1** to **P4** and 1,5 for **P5** to **P10**. Once the GPC determined M_n of the polymers were corrected with the corresponding factor, we found that the RMN calculated M_n were approximately from 10 to 20% higher than the GPC determined and corrected M_n. Thus, we can consider that the high molecular weight polymers contained approximately from 10 to 20% of high molecular weight cyclic polymers.

Tab. 1. GPC and NMR determined molecular weights of polymers **P1** to **P10**.

Polymer	M_n(GPC)	M_w/M_n	M_n(NMR)
P1	14 595	1.72	12 460
P2	15 890	1.36	14 056
P3	10 505	1.35	9 212
P4	9 576	1.21	8 692
P5	21 721	1.32	16 942
P6	9 739	1.40	7 795
P7	9 342	1.44	7 598
P8	9 295	1.51	7 375
P9	15 525	1.34	12 060
P10	11 349	1.37	9 300

^{1}H NMR spectra of model compounds and polymers are nearly the same. However, the NMR spectra of cyclic dimers and unimers are very different. Fig. 9. presents a comparison of chemical shifts of aromatic protonic resonances of representative compounds, cyclic unimer **U5**, cyclic dimer **D5**, polymer **P5** and model compound **M5**. As the ring strain increases from strain-free open chain compounds **M5** and **P5** to cyclic dimer **D5** and finally to unimer **U5**, the aromatic protons of the ortho-unit (i,j,k) shift to lower field while the aromatic protons of cinnamte units shift to higher field. According to experiments of molecular modeling, the "U"-shaped conformation is the lowest free energy conformation of rigid units. In this conformation, as the ring strain increases the two cinnamate units become close to each other and shield the protons of each cinnamate unit. Therefore, these protons are shifted upfield by

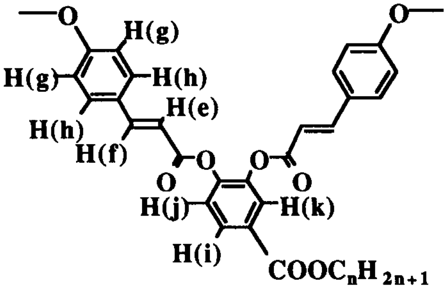


Fig. 7. ^{1}H NMR aromatic peak attribution of rigid unit

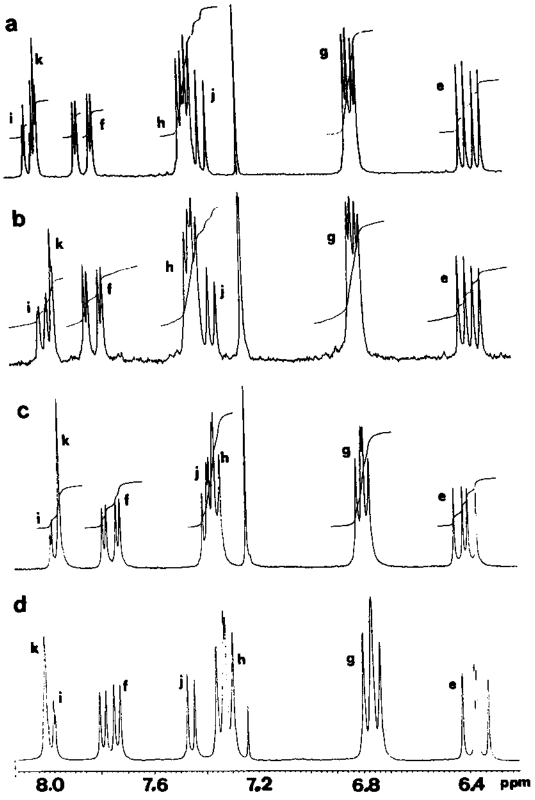


Fig. 8. Aromatic region of the 300-MHz ^{1}H NMR spectra (CDCl$_3$, TMS) and the corresponding aromatic protonic assignments of representative compounds with n = 5. (a, top) model compound **M5**, (b) polymer **P5** (M_n, GPC = 21721, (M_w/M_n)GPC = 1.3), (c) cyclic dimer **D5** and (d, bottom) cyclic unimer **U5**.

this shielding effect. At the same time the carbonyl groups of the cinnamte units became apart from the aromatic protons of the ortho-ring, specially from protons j and k which are no longer shielded by these carbonyl groups and consequently are shifted lowfield. A detailed study of this behaviour concerning molecular modeling studies is currently in progress.

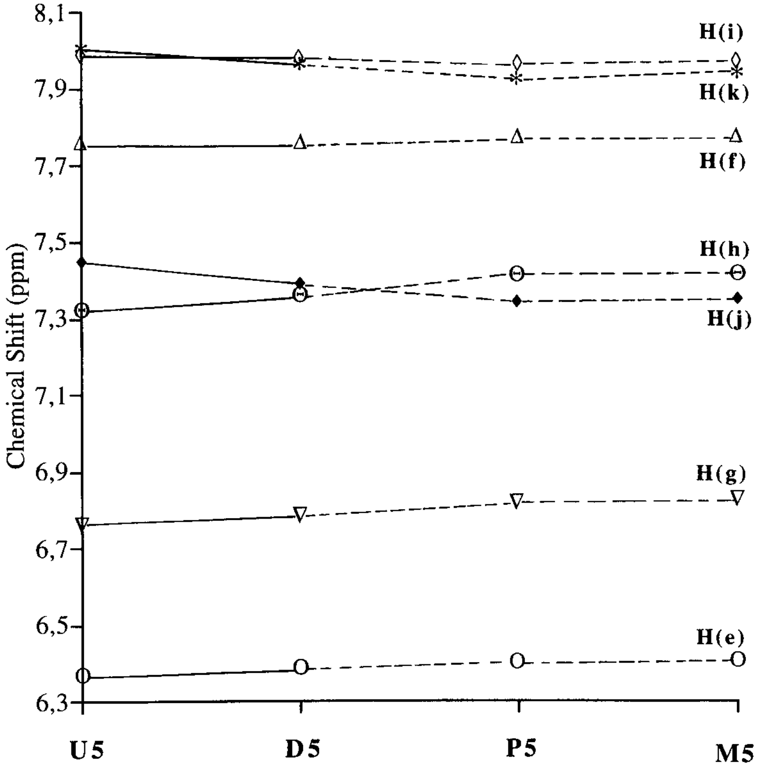
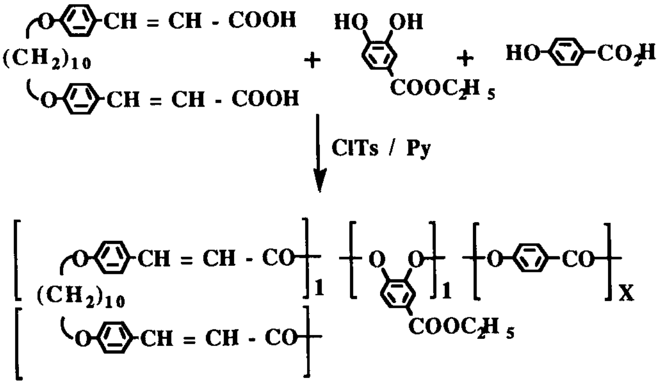


Fig. 9. Comparison of chemical shifts of aromatic protonic resonances of representative compounds with n = 5. Cyclic unimer **U5**, cyclic dimer **D5**, polymer **P5** (M_n, GPC=21721, (M_w/M_n)GPC = 1.3) and model compound **M5**.

Copolymerization with p-hydroxybenzoic acid **PB** has a great interest in the synthesis of liquid crystalline polyesters due to that produces a considerable estabilization of their mesophases along with a notable decrease in their T_m and crystallinity (Ref. 18). We were interested in studing the influence that copolymerization with **PB**, causes in the formation of cyclic oligomers and in the phase diagram of the linear polymers. Therefore, we polycondensed diacid **A1** and diphenol **DF2** with various proportions 11, 20, 33 and 43 mol-% of **PB** to get copolyesters **PB21**, **PB22**, **PB23** and **PB24**, respectively. The 300-MHz ^{1}H NMR spectra

(CDCl3, TMS) of these copolyesters were consistent with the expected compositions and structures. Scheme 4. presents the synthetic scheme of copolyesters **PB**.



Scheme 4. Synthesis of copolyesters **PB21**, **PB22**, **PB23** and **PB24**, X = 0.25, 0.5, 1 and 1.5, respectively.

Fig. 10 presents the proportion (wt-%) of cyclic dimer **D2** in copolyesters **PB21** (M_n, GPC = 12 354, (M_w/M_n)GPC = 1.4), **PB22** (M_n, GPC = 12 542, (M_w/M_n)GPC = 1.36), **PB23** (M_n, GPC = 13 993, (M_w/M_n)GPC = 1.56) and **PB24** (M_n, GPC = 13240, (M_w/M_n)GPC = 1.55) as obtained and after purification (by reprecipitation three times in acetone), versus the amount (mol-%) of p-hydroxybenzoic acid. The proportion of **D2** in the copolyesters decreases with increasing amounts of **PB**. However, it was necessary to copolymerize **A1** and **DF2** with proportions of **PB** higher than 50 mol-% to get copolyesters with non significant amounts of **D2**. This fact is not only due to the tendency of orto-linked units to favour cyclization versus polymerization but also to the tendency of **PB** to react with itself (Ref. 18). Due to the low solubility of **D2** in acetone, significant amounts remained in the copolyesters even after they were redissolved in chloroform and reprecipitated in acetone for three times. Consequently, we found that this method of purification of polymers was not effective in removing the low molecular weight cyclic oligomers.

Low molecular weight model compounds and cyclic unimers and dimers had low tendency to crystallize from the melt which can be ascribed to the low symmetry of the rigid mesogenic units and to the presence of bulky side chains. High molecular weight polymers **P1** to **P10** were readily soluble in common organic solvents such as chloroform, methylene chloride or tetrahydrofurane. **P1** to **P8** were noncrystalline or extremely slow in crystallization according with DSC analysis which is probably caused by the combined effect of the following factors: 1. the formation of bent estructures due to the presence or ortho links, 2. the presence side chains and 3. the random monomeric sequence of these polyesters due to positional isomerism of the side chains. Only polymers with long alkyl side chains **P9** to **P11** showed low temperature melting endotherms-on DSC analysis which were assigned to the melting of the side chains (Fig. 11).

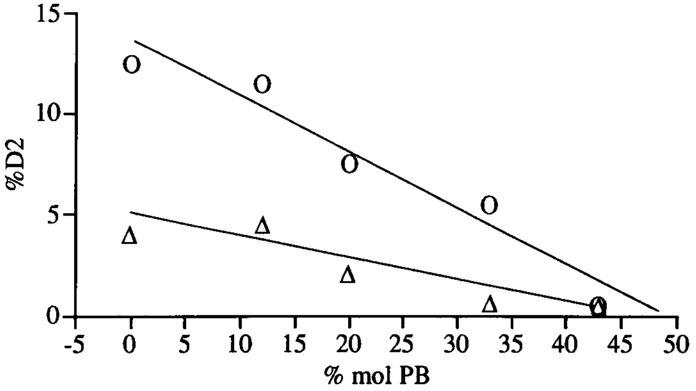


Fig. 10. Proportion (wt-%) of cyclic dimer **D2** in copolyesters **PB21, PB22, PB23** and **PB24** as obtained (O) and after purification (Δ), versus the amount (mol-%) of p-hydroxybenzoic acid.

The attachement of flexible alkyl chains as lateral or pendant substituents of the rigid backbone of a polymer produces an increase of its solubility and a decrease of its melting temperature, due to steric effects which prevent the close packing of their chains in the crystalline phase (Ref. 19). Copolyesters of **PB** also had a very low tendency to crystallize. Probably, structural irregularity caused by the random monomeric sequence together with the random existence of irregular structures, difficults their crystallization.

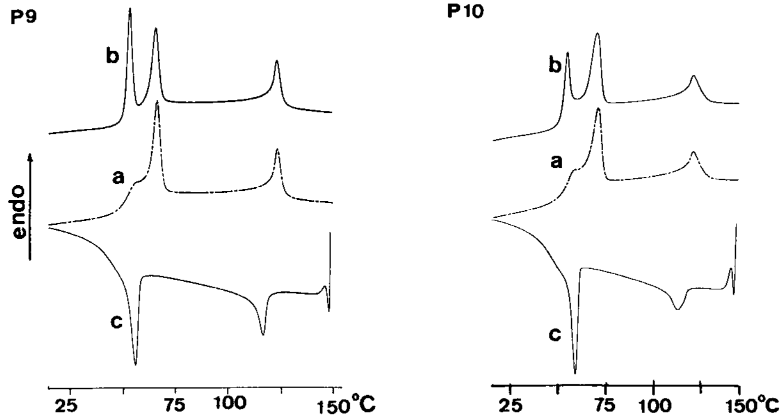


Fig. 11. DSC thermograms for polymer **P9** and **P10**: (a) second heating cycle, (b) annealed at 40°C for 12 h, (c) cooling cycle, heating and cooling rate 20°C/min.

Figs. 12,13,14, 15 and 16 present the phase diagrams of model compounds **M1** to **M10**, cyclic unimers **U1** to **U10**, cyclic dimers **D1** to **D10**, polymers **P1** to **P11** and copolyesters of **PB**, respectively. All these compounds formed enantiotropic mesophases above their T_m's or T_g's stable over very broad ranges of temperatures. Thermal stability of these mesophases was favoured by the presence of substituents of the orto-linked units which extend the mesogenic units along the molecular axis.

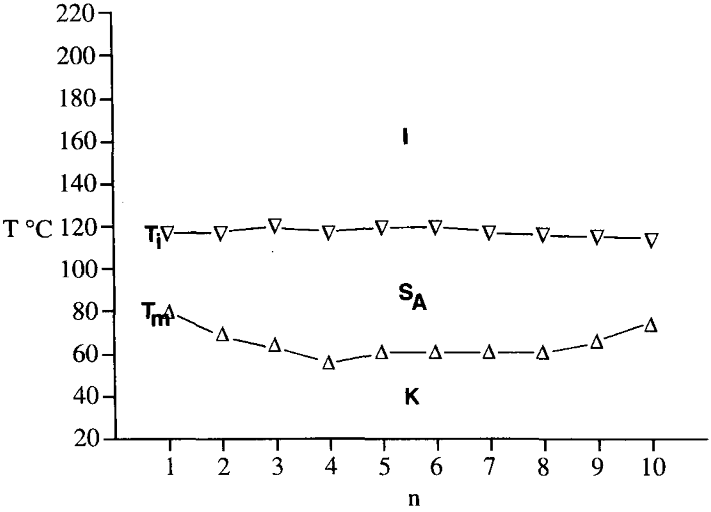


Fig. 12. Phase diagram of model compounds **M1** to **M10**. T_m and T_i crystal mesophase transition and isotropization temperatures, respectively, both determined by DSC at 10°C/min, first heating cycle. K, S_A and I crystalline, smectic A and isotropic phase, respectively.

Model compounds and cyclic unimers formed S_A mesophases above their T_m's. However, the isotropization temperatures of cyclic unimers were considerably higher than T_i's of model compounds which is probably due to the lower proportion of chain ends and higher rigidity of cyclic unimers compared with open chain model compounds. Owing to the restricted length of the decamethylene spacer, conformations of the rigid unit which have lower axial rates than the axial rate of the "U"-shaped conformation, are allowed in open chain compounds while are not in cyclic unimers.

It is known that long alkyl chains produce the stabilization of smectic mesophases (Ref. 20). However, we found that polymers with short side chains displayed smectic mesophases above their Tg's while polymers with long side chains formed nematic phases above their T_m's or T_g's. Furthermore, cyclic dimers showed a similar behaviour. These results do not agree with the generally accepted ones but we have not yet produced a suitable explanation to this behaviour. A detailed study of this behaviour is currently in progress and will be reported in due course. The T_i's of cyclic dimers were the highest (> 300°C) of all synthesized compounds. Their T_i's were considerably much higher than the T_i's of high molecular weight homologues, which is probable due to the higher rigidity of the cyclic dimer structure.

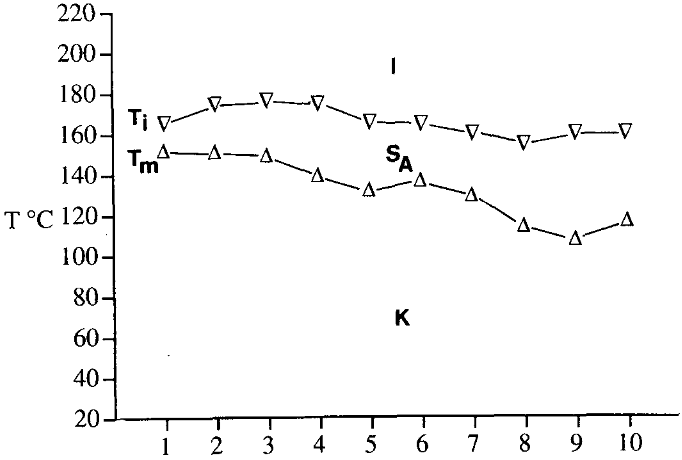


Fig. 13. Phase diagram of cyclic unimers **U1** to **U10**. T_m and T_i crystal mesophase transition and isotropization temperatures, respectively, both determined with the polarizing microscope. K, S_A and I crystalline, smectic A and isotropic phase, respectively.

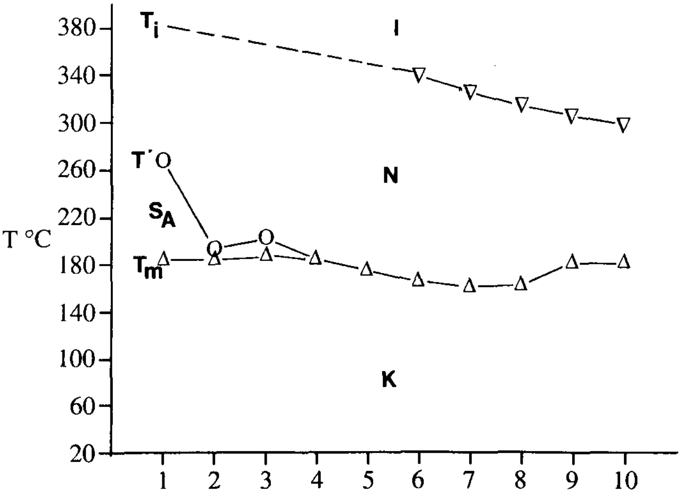


Fig. 14. Phase diagram of cyclic dimers **D1** to **D10**. T_m, T' and T_i crystal mesophase transition, smectic nematic transition and isotropization temperatures, respectively, all

determined with the polarizing microscope. K, N, S and I crystalline, nematic, smectic and isotropic phase, respectively.

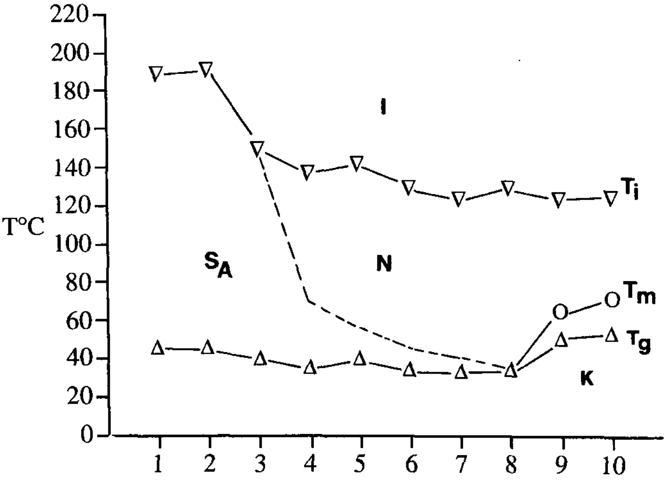


Fig. 15. Phase diagram of polymers **P1** to **P10**. T_g, T_m and T_i mesophase glass, crystal mesophase transition, smectic nematic transition and isotropization temperatures, respectively, all determined by DSC at 20°C/min, second heating cycle. K, N, S and I crystalline, nematic, smectic and isotropic phase, respectively.

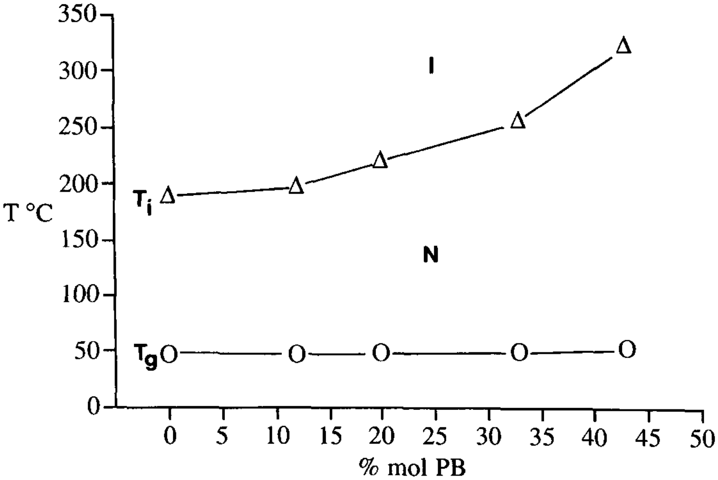


Fig. 16. Phase diagram of copolyesters **P2** and **PB21** to **PB24**. T_g and T_i mesophase glass transition and isotropization temperatures, respectively, determined by DSC at 20°C/min, second heating cycle. N and I nematic and isotropic phase, respectively.

Polymer **P2** formed a smectic mesophase above its T_g whereas copolyesters of **PB**, **PB21** to **PB24** formed nematic mesophases above their above their T_g's. Furthermore, their T_i's were higher than the T_i's of **P2** and increased with the proportion of **PB**. Copolymerization with **PB** increases the rigid rod character of the chains which causes a stabilisation of the mesophase. However, the disorder the sequences produced by copolymerization decreases the degree of order of the mesophases and only nematic phases were formed by these copolyesters.

Samples of the synthesized polymers gelified on the hot stage of the microscope in air and at temperatures above 300°C forming birefringent gels insoluble in all common organic solvents. This high temperature gelation process was probably due to thermal cross-linking reaction between the conjugated double bonds of the cinnamate groups. Furthermore, samples of cyclic unimers and dimers polymerized on the hot stage of the microscope in air and at temperatures above 300°C forming a mixture of cyclic oligomers and high molecular weight polymer which was insoluble in all common organic solvents probably due to its cross-linked structure. Fig. 17 presents typical GPC chromatograms of the THF soluble products of thermal polymerization of cyclic **U2** and **D2**. Additional work of the polymerization of cyclic oligomers and thermal and photochemical crosslinking of polymers will be reported in due course.

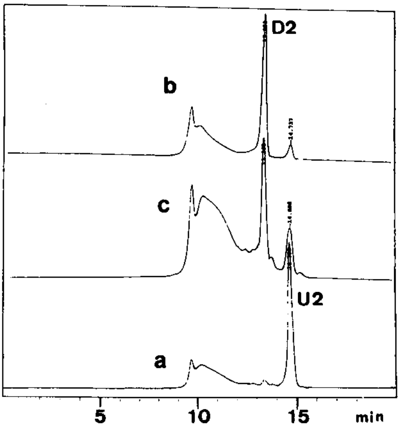


Fig. 17 Typical GPC chromatograms of the THF soluble products of thermal polymerization of (a) **U2** after 5 min at 300°C, (b) and (c) **D2**. at 300°C for 5 and 10 min, respectively.

CONCLUSIONS

Although ortho-difenols had not been extensively used in the synthesis of LC esters, a great variety of low and high molecular weight LC esters containing high proportions of these units can be synthesized. These compounds have definite cyclic or linear structures and shows low temperature transitions, high solubility in common organic solvents and very stable LC mesophases. These characteristics allow the study of the relationship between structure and properties in these compounds which frequently can not be carried out in wholly para-linked polyesters. We report the great importance that concomitant cyclization reactions have in polyesterifications involving high proportions of ortho diphenols, which does not seem to have been considered until now.

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