Synthesis and Characterization of Biocompatible Polyesteramides: PNOBDME ($C_{34}H_{38}N_2O_6$)_n and PNOBEE ($C_{26}H_{22}N_2O_6$)_n as Cholesteric Liquid Crystals

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Abstract

New polyesteramides, poly[oxy(1,2-dodecane)-oxy-carbonyl-1,4-phenylene-amine-carbonyl-1,4-phenylene-carbonyl-amine-1,4-phenylene-carbonyl]: ($C_{34}H_{38}N_2O_6$)_n, named PNOBDME, and poly[oxy(1,2-buthylene)-oxy-carbonyl-1,4-phenylene-amine-carbonyl-1,4-phenylene-carbonyl-amine-1,4-phenylene-carbonyl]: ($C_{26}H_{22}N_2O_6$)_n, named PNOBEE, have been designed and synthesized as cholesteric liquid crystal. Both have been fully characterized by ¹H and ¹³C-NMR, COSY and HSQC and compared to their precursor polyesters PTOBDME and PTOBEE. The thermal behaviour of the new compounds is studied by TG and DSC analysis. Their optical activity is evaluated by optical rotatory dispersion (ORD). Molecular models of the new polymer show helical polymeric chains. Morphology of the samples is also reported by ESEM. The synthetic cholesteric liquid crystal polyesteramides described here have proved to be biocompatible and to act as non-viral vectors in Gene Therapy, transfecting DNA to the nucleus cell.

Keywords: Cholesteric LC; New polyesteramides; Synthetic methods; NMR; Molecular modeling

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Introduction

Liquid crystals are self-organizing systems. With increasing temperature, they do not directly go from the crystalline state into the melt, in the middle they undergo a mesophase state which combine order of perfect crystals and mobility of liquids [1]. The parallel orientation of their longitudinal molecular axes is common to all mesophases (long-range orientational order). Two major classes can be distinguished: nematic (with molecular centers distributed isotropically) and smectic (molecular centers organized in layers). The special array of nematic planes stacked in a helical superstructure with a prevalent screw direction is called the cholesteric mesophase.

Cholesteric liquid crystal polyesters have received much attention in the last few years for their interesting chemical, optical, mechanical and biological properties. Due to their anisotropic formulation and amphiphilic nature, their molecules are able to self-associate and/or aggregate in blocks to form species with supramolecular ordered structure which present desirable material properties.

Chiral, cholesteric liquid crystal poly[terephthaloyl-4-bis-

oxybenzoate-decamethyl-ethylene] [$C_{34}H_{36}O_8$]_n, named PTOBDME, m=9 in **Figure 1**, was obtained by polycondensation reaction between terephthaloyl-bis-(4-oxybenzoyl chloride) (TOBC) and DL-1,2 dodecanediol. Although only racemic materials were used in the synthesis, a cholesteric, chiral morphology, theoretically unexpected, was found. Evidence of this was obtained when a white solid, recrystallized, as the second fraction, from toluene mother liquor after the filtration of the polymer, was identified as -PTOBDME, with $[\alpha]_{589}^{25} = -1.43$ [1.538 gr/100ml, toluene] [2,3]. The synthetic method [4,5], based on the previously reported by Bilibin [6, 7], leads to the obtention of two fractions of different kinetic rates, with different diastereomeric excess [2]. Not always the diastereomer in excess is the same.

A similar result had been previously attained for liquid crystal PTOBEE [$C_{26}H_{20}O_8$]_n, m=1 in **Figure 1**, also with cholesteric mesophase, from polycondensation reaction between the racemic glycol DL-1,2-butanediol and TOBC [4], with a similar mesogen as PTOBDME but with ethyl group along the side chain. Its second fraction was isolated as -PTOBEE, with a value of $[\alpha]_{589}^{25} = -2.33$ [0.0056 mol/l, toluene]. Its structure and diastereomeric excess were characterized by NMR [8].

Both polymers showed interesting technological properties as thermotropic and lyotropic behaviour, self-assembling in nanocavities in solution, with different conformations depending on the solvent and on the concentration [3], getting adsorbed on metal surfaces with reordering of the polymer in the interface [9] and interacting with biomacromolecules [10-13].

Our main interest is the molecular design and chemical modifications of multifunctional cholesteric liquid crystals, PTOBDME and PTOBEE, in order to obtain new chemical formulations involving macromolecular features with new properties, holding their helical structure and macromolecular features. The first feature we considered to be introduced was cationic charge, by entrance of Nitrogen atoms, which will also favour the creation of hydrogen bonds, through intra and intermolecular interactions, giving secondary structures with long range supramolecular order, able to interact with molecules of interest. The functional groups selected to be introduced in precursor PTOBDME and PTOBEE monomers, were amide groups para-substituting both ester groups in the central benzene ring of the terephthalate unit, along the main chain.

The final formulations of the new polyesteramide monomers, named PNOBDME ($C_{34}H_{38}N_2O_6$)_n and PNOBEE ($C_{26}H_{22}N_2O_6$)_n, are shown in **Figure 2a and 2b** respectively. The hydrogen and carbon atoms have been numbered as precursors PTOBDME [2,3] and PTOBEE [4,8], respectively. Their mesogens keep some similarities with Kevlar, wholly aromatic polyamide, difficult to process because it's not soluble in typical solvents [14]. Instead, PNOBDME and PNOBEE contain flexible aliphatic chains that would decrease their stiffness.

The intermediate compound of the monomeric mesogen, NOBA ($C_{22}H_{16}N_2O_6$), was referred in the National Cancer Institute Databases with potential AIDS and cancer activity [15].

Molecular Mechanics conformational analysis, predict helical structure models for PNOBDME and PNOBEE, as designed in **Figure 2**. Instead no helical polymer models were attained in the computational calculations when the amide group enter along the lateral side chain.

We report, the synthesis of polyesteramides PNOBDME [$C_{34}H_{38}N_2O_6$]_n and PNOBEE ($C_{26}H_{22}N_2O_6$)_n. The structure of the polymers so obtained is confirmed by 1H , ^{13}C , COSY and HSQC NMR. The spectra are quite similar to those of precursor PTOBDME and PTOBEE, as it was expected, and the shifts were assigned according to our previous notation [2,8]. Their thermal stability is studied by TG and DSC analysis.

Molecular Mechanics Simulation of PNOBDME

Molecular Mechanics modelling of PNOBDME monomer was attained with the help of Materials Studio Windows v.2018 [16]. UNIVERSAL Force Field was loaded, both atomic mass and charge were considered. The monomer model is shown in **Figure 3a**, with its geometry optimised by minimising the energy to 95 Kcal/

mol. Monomer polymerization was simulated by considering the ^{13}C atom, in **Figure 2a**, as *head atom*, the O atom bonded to ^{13}C as *tail atom* and ^{12}C as *chiral centre*. Homopolymerization was then performed with *Head-to-Tail* orientation, torsion angle between monomers fixed to 180° . Syndiotactic tacticity was finally imposed to the polymer chain. A helical polymer model along the main chain was obtained, **Figure 3b**, whose perpendicular cross section is shown in **Figure 3c**.

Materials

Synthesis of PNOBDME [Poly[oxy(1,2-dodecane)-oxy-carbonyl-1,4-phenylene-amine-carbonyl-1,4-phenylene-carbonyl-amine-1,4-phenylene-carbonyl], ($C_{34}H_{38}N_2O_6$)_n

The new synthetic way is based on our previous experience for

Figure 1 Monomeric unit of cholesteric liquid-crystalline PTOBEE ($m=1$) and PTOBDME ($m=9$). The three different zones of the monomer: mesogen, spacer and flexible side chain are indicated. The asterisk indicates the chiral center. Aromatic-end acid and aliphatic-end alcoholic groups are also specified.

Figure 2 Monomeric unit of polyesteramides: (a) PNOBDME (b) PNOBEE. The asterisk indicates the chiral center ($^{12}C^*$ in PNOBDME and $^{4}C^*$ in PNOBEE). Torsion angle ϕ , along $^{11}C-^{12}C^*$ bond and $^3C-^4C^*$ bond, respectively, are indicated.

the obtention of cholesteric PTOBDME and a method by Sek et al. [17,18] reported for polycondensation reaction to obtain polyesteramide. In this case, we obtained an intermediate acid chloride yield lower than the obtained for the precursor polyesters.

PNOBDME, III in **Figure 4**, was obtained through polycondensation reaction between 4-4'-(terephthaloyl-diaminedibenzoic chloride) NOBC, II in **Figure 4**, and the racemic mixture of DL-1,2-dodecanediol. Notation similar to precursor cholesteric liquid

crystal PTOBDME [2,3] obtained by similar method, has been used.

Starting materials: Terephthaloyl chloride from Sigma-Aldrich Chemie GmbH (Steinheim, Germany); Carbon tetrachloride from Panreac Química (Montcada i Rexach, Barcelona, Spain); NaOH from Panreac Química (Montcada i Rexach, Barcelona, Spain); 4-Aminobenzoic acid from Sigma-Aldrich Chemie GmbH (Steinheim, Germany); Hydrochloric acid from Normapur VWRInternational (Fontenay-sous-Bois, France); Thionyl chloride from Sigma-Aldrich Chemie GmbH (Steinheim, Germany); Chloroform from SDS Votre Partenaire Chimie (Peypin, France); DL-1,2-dodecanediol from Flucka Chemie GmbH (Buchs, Switzerland); Diphenyl oxide from Sigma-Aldrich Chemie GmbH (Steinheim, Germany); Nitrogen from Praxair (Madrid, Spain); Toluene from Merck KGaA (Darmstadt, Germany).

Preparation of NOBA (I in Figure 4): Solutions of 0.1 mol terephthaloyl chloride in 200 ml carbon tetrachloride and 0.2 mol NaOH in water, were added while stirring at room temperature in the course of 15 minutes, to a solution 0.22 mol of 4-Aminobenzoic acid and 0.2 mol NaOH, in 400 ml water mili-Q

Figure 3 Molecular simulation of PNOBDME: (a) Minimum energy monomer (b) Syndiotactic [PNOBDME]₁₀ (c) Polymer cross sectional view.

Figure 4 Scheme of polycondensation reaction of PNOBDME.

grade. Stirring was continued for a further 12 hr. A sediment was separated out, filtered, washed several times with 40 ml of cold water, dried, comminuted and transferred to a vessel where it was mixed for 3 hours with 300 ml of hydrochloric acid. The product was filtered, washed several times with 40 ml of cold water, dried and comminuted. Yield 28 gr (70%).

Preparation of NOBC (II in Figure 4): In the course of 25 minutes 15 gr NOBA were added to 350 ml thionyl chloride, while stirring rapidly at room temperature.

The solution was boiled with the reflux condenser. When the liberation of HCl ended and most of the sediment had dissolved, the hot solution was filtered and cooled down to 0°C for a day. The obtained product that separated out was filtered, vacuum dried and recrystallized in chloroform. Yield: 7.2 gr (48%).

Preparation of PNOBDME: A mixture of 0.017 mol NOBC and 0.017 mol DL-1,2-dodecanediol, was added to 44 ml of diphenyl oxide. Purge with dry nitrogen, was used for 25 min at room temperature and then, while maintaining the gas current, the flask was transferred to a bath containing a high-temperature heat-transfer agent. The polycondensation was carried out for 3 hr. 30 min. at 200°C. The reaction finished when the liberation of HCl ended. The result of the polycondensation reaction was poured into 500 ml of toluene, decanting PNOBDME, which was filtered, washed three times with ethanol and vacuum dried. A *second fraction* of PNOBDME precipitated of the filtrated toluene after 22 weeks which also filtered, washed with ethanol and vacuum dried.

Yield first fraction: 2.6 gr (25.5%);

Yield first and second fraction: 3.1 gr (30.4%).

Synthesis of PNOBEE [Poly[oxy(1,2-buthylene)-oxy-carbonyl-1,4-phenylene-amine-carbonyl-1,4-phenylene-carbonyl-amine-1,4-phenylene-carbonyl]: (C₂₆H₂₂N₂O₆)_n]

PNOBEE, III in Figure 5, was obtained through polycondensation reaction between 4-4'-(terephthaloyldiaminedibenzoic chloride) NOBC, II in Figure 5, and the racemic mixture of DL-1,2-butanediol. Notation of cholesteric liquid crystal precursor PTOBEE has been used.

NOBC [4-4'-(terephthaloyldiaminedibenzoic chloride)], II in Figure 5, was synthesized by reaction of NOBA [4-4'-(terephthaloyldiaminedibenzoic acid)], I in Figure 5, with SOCl₂ and recrystallized in chloroform; previously NOBA was obtained by interface condensation between terephthaloyl chloride and 4-Aminobenzoic acid.

Starting material: DL-1,2-butanediol from Flucka Chemie GmbH (Buchs, Switzerland); Chloronaphthalene from Sigma-Aldrich Chemie GmbH (Steinheim, Germany); Nitrogen from Praxair (Madrid, Spain); Toluene from Merck KGaA (Darmstadt, Germany).

Preparation of PNOBEE: A mixture of 0.015 mol NOBC and 0.015 mol DL-1,2-butanediol, was added to 39 ml of

Figure 5 Scheme of polycondensation reaction of PNOBEE.

chloronaphthalene. Purge with dry nitrogen, was used for 25 min at room temperature and then, while maintaining the gas current, the flask was transferred to a bath containing a high-temperature heat-transfer agent. The polycondensation was carried out for 180 minutes at 200°C. The reaction finished when the liberation of HCl ended. The result of the polycondensation reaction was poured into 500 ml of toluene, decanting PNOBEE, which was filtered, washed with ethanol and vacuum dried. A second fraction of PNOBEE precipitated of the filtrated toluene after 22 weeks which also filtered, washed with ethanol and vacuum dried.

Yield: 2.9 gr (46.5%).

Characterization techniques

The structures of NOBA and NOBC (I and II in **Figures 4 and 5**) are confirmed by conventional NMR techniques: ^1H -RMN, ^{13}C -NMR, COSY (Homonuclear Correlation Spectroscopy), TOCSY (Total Correlation Spectroscopy), NOESY (Nuclear Overhauser Effect Spectroscopy, through-space correlation method) and HSQC (Heteronuclear Single-Quantum Correlation spectroscopy) registered in DMSO-d_6 at 25°C in a Bruker 300MHz NMR spectrometer.

The structures of PNOBDME and PNOBEE have been confirmed by ^1H -RMN, ^{13}C -NMR, COSY, HSQC and HMBC (Heteronuclear Multiple Bond Correlation for correlations between carbons and protons that are separated by two, three, and, sometimes four bonds, in conjugated systems. Direct one-bond correlations being suppressed) obtained in VARIAN 400 MHz and 500 MHz spectrometers, also at room temperature. The solvent used in all cases was DMSO-d_6 from Merck KGaA (Darmstadt, Germany).

^1H chemical shifts were referenced to the residual solvent signal at $\delta=2.50$ ppm (DMSO-d_6) relative to tetramethylsilane (TMS). All the spectra were processed and analyzed with MestReNova v.11.0.3-18688 software [19,20].

Thermal stability measurements were studied on a Mettler

TA4000-TG50 at heating rate of 10°C/min with nitrogen purge between 30-600°C. Thermal behaviour was determined by differential scanning calorimetry (DSC) in a Mettler TA4000/DSC30/TC11 calorimeter, with series of heating/cooling cycles in a temperature range between 0-230°C.

Microcalorimetry was evaluated in a MicroCal Inc., Model: MCS-DSC, within a range of temperature 4-120 °C, at a heating rate of 10-20°C/hora, volume of sample 1.5 ml.

The optical activity of the polymer was mesasured as optical rotatory dispersion (ORD) at 25°C in DMSO from Scharlau Chemie, in a Perkin Elmer 241 MC polarimeter with wavelengths: $\lambda_{\text{Na}}=589$ nm, slit=5 mm, integration time=50 s; $\lambda_{\text{Hg}}=574$ nm, slit=14 mm, integration time=50s; $\lambda_{\text{Hg}}=546$ nm, slit=30 mm, integration time=50 s; $\lambda_{\text{Hg}}=435$ nm, slit=5 mm, integration time=50s; $\lambda_{\text{Hg}}=365$ nm, slit=2.5 mm, integration time=50 s.

The morphology or the samples was observed by Environmental Scanning Electron Microscope (ESEM), PHILIPS XL30.

Results and Discussion

Structural characterization of NOBA and NOBC by NMR

^1H -NMR of NOBA in DMSO-d_6 at 25°C: Figure 6a shows the ^1H -RMN spectrum of NOBA. The chemical shifts were assigned, according to the notation in **Figure 2a** and **Figure 4-I**, as follows.

δ (in ppm from tetramethylsilane): 12.8 (12.74) (s, 2H, C^{13}OOH); 10.7 (10.31) (s, 2H, C^{18}CONH); 8.11(8.18) (s, 4H, C^{20}H); 7.95 (8.30) (m, 4H, C^{16}H); 7.95 (m, 4H, C^{15}H). Predicted values are depicted tilted in parenthesis.

Besides the protons due to ended carboxylic groups, and to amide groups, two strong signals are observed in the aromatic zone of the ^1H -NMR spectrum of NOBA, for to the benzene protons, ^{20}C , ^{15}C and ^{16}C . The last two indistinguishable at 7.95 ppm. The experimental results are in agreement with the chemical shifts calculated by MestReNova v.11.0.3-18688 [19,20].

Figure 6 (a) ^1H -NMR Spectrum of NOBA (b) ^{13}C -NMR Spectrum of NOBA.

^{13}C -RMN of NOBA in DMSO-d_6 at 25°C : The ^{13}C -RMN of NOBA is given in **Figure 6b**. Their experimental chemical shifts are in complete agreement with those predicted (tilted in parenthesis).

δ (in ppm from tetramethylsilane): 167.3 (169.3) ($2\text{C } ^{13}\text{COOH}$); 165.6 (164.7) ($2\text{C } ^{18}\text{C=ONH}$); 143.4 (143.2) ($2\text{C NH-}^{17}\text{C}$); 137.7 (134.2) ($2\text{C } ^{19}\text{C}$); 130.6 (130.5) ($4\text{C } ^{15}\text{CH}$); 128.3 (127.6) ($4\text{C } ^{20}\text{CH}$); 126.1 (125.8) ($2\text{C } ^{14}\text{C-COOH}$); 119.9 (115.8) ($4\text{C } ^{16}\text{CH}$).

COSY OF NOBA in DMSO-d_6 at 25°C : The assignments of peaks in the COSY spectrum of NOBA are given in **Table 1**.

HSQC of NOBA in DMSO-d_6 at 25°C : The HSQC experiment (heteronuclear single quantum correlation) of NOBA appears in **Figure 7**. The corresponding peaks assignment is shown in **Table 2**.

In the HSQC spectrum the correlation between each aromatic C atom with their corresponding H atoms can be seen. Signals due to ^{15}H and ^{16}H , overlapped in the ^1H spectra, appear in the HSQC splitted for the two carbon atoms ^{15}C and ^{16}C respectively. The assymmetric shape of both protons allows their differentiation. While ^{16}H slightly shifts towards lower ppm value, ^{15}H shifts to higher ppm.

The integral ratio of aromatic peaks, ($^{15}\text{H}+^{16}\text{H}$) : ^{20}H , is observed to be 2:1 in the ^1H spectrum, in agreement with the HSQC experiment. The structure of NOBC, **Figure 4-II**, has also been confirmed by NMR experiments. Data are not given as they do not provide further information than NOBA to the present contribution.

Structural characterization of polyesteramide PNOBDME by NMR

The structure of PNOBDME, as described in **Figure 2a**, has been characterized by: ^1H -RMN, ^{13}C -NMR, COSY, TOCSY, NOESY and HSQC, in DMSO-d_6 . In **Figure 8a** the ^1H -NMR spectrum is given,

Table 1: COSY-NMR Assignment for NOBA.

	^1H	^{20}H	$^{15}\text{H}, ^{16}\text{H}$
^1H		8.11	7.95
^{20}H	8.11	1.5	
$^{15}\text{H}, ^{16}\text{H}$	7.95		4.9

Table 2: HSQC signals of NOBA.

	^1H -NMR	^{20}H	$^{15}\text{H}, ^{16}\text{H}$
^{13}C -NMR		8.11	7.95
^{15}C	130.6		2.6
^{20}C	128.3	1.4	
^{16}C	119.9		5.2

Figure 7 HSQC of NOBA.

Figure 8 (a) ^1H -NMR Spectrum of polyesteramide PNOBDME. Peaks between 7-7.8 are due to solvent impurities, diphenyl oxide, used in the synthetic process (b) ^1H -NMR Spectrum of PTOBDME.

compared to that of PTOBDME, in **Figure 8b**. **Figure 9** exhibits the ^{13}C -NMR spectrum.

^1H -RMN: (400MHz, DMSO- d_6 , 25°C): $\delta(\text{ppm})$ 10,7 (s, 2H $\text{C}_{18}\text{ONH-C}$); 10,45 (m, 2H $\text{C}_{18}\text{ONH-C}$); 8,14 (s, 4H, $\text{HNCO-C-C}_{20}\text{H-C-CONH}$); 7,98 (m, 4H, $\text{COO-C-C}_{15}\text{H-CH-C-NHCO}$); 7,98 (m, 4H, $\text{COO-C-CH-C}_{16}\text{H-CNHCO}$); 5,39 (m 1H, $\text{C=OO-CH}'_a\text{H}'_b\text{-C}_{12}\text{H}_\text{c}\text{-R}_1\text{R}_2$); 5,22 (m 1H, $\text{C=OO-CH}_a\text{H}_b\text{-C}_{12}\text{H}_\text{c}\text{-R}_1\text{R}_2$); 4,54 (dd 1H, $J=12\text{ Hz } J=4\text{ Hz } \text{C=OO-C}_{11}\text{H}'_a\text{H}'_b\text{-CH}'_b\text{-R}_1\text{R}_2$); 4,44 (dd 1H, $J=11,5\text{ Hz } J=8\text{ Hz } \text{C=OO-C}_{11}\text{H}'_a\text{H}'_b\text{-CH}'_b\text{-R}_1\text{R}_2$); 3,91 (dd 1H, $J=12\text{ Hz } J=4\text{ Hz } \text{C=OO-C}_{11}\text{H}_a\text{H}_b\text{-CH-R}_1\text{R}_2$); 3,83 (dd 1H, $J=12\text{ Hz } J=5\text{ Hz } \text{C=OO-C}_{11}\text{H}_a\text{H}_b\text{-CH-R}_1\text{R}_2$); 1,85 (m 2H, $\text{CH}_2\text{-C}_{10}\text{H}_2\text{CH-R}_1\text{R}_2$); 1,74 (m 2H, $\text{CH}_2\text{-C}_{10}\text{H}_2\text{-CH}'_b\text{-R}_1\text{R}_2$); 1,50 (m 2H, (m 2H, $\text{C}_9\text{H}_2\text{-CH}_2\text{-CH-R}_1\text{R}_2$); 1,40 (m 2H, $\text{C}_9\text{H}_2\text{-CH}_2\text{CH}'_b\text{-R}_1\text{R}_2$); 1,24 (m 14H, $\text{C}_8\text{H}_2\text{-C}_7\text{H}_2\text{-C}_6\text{H}_2\text{-C}_5\text{H}_2\text{-C}_4\text{H}_2\text{-C}_3\text{H}_2\text{-C}_2\text{H}_2\text{-CH}_3$); 1,21 (m 14H, $\text{C}_8\text{H}_2\text{-C}_7\text{H}_2\text{-C}_6\text{H}_2\text{-C}_5\text{H}_2\text{-C}_4\text{H}_2\text{-C}_3\text{H}_2\text{-C}_2\text{H}_2\text{-CH}_3$); 0,86 (t 3H, $\text{CH}_2\text{-C}_1\text{H}_3$); 0,82 (t 3H, $\text{CH}_2\text{-C}_1\text{H}_3$).

^{13}C -RMN: (400MHz, DMSO- d_6 , 25°C): $\delta(\text{ppm})$ 165,2 (2C $\text{C}_{13}=\text{OO}$ o $2\times\text{C } \text{C}_{18}=\text{ONH}$); 137,4 (2C $\text{HNCO-C-CH-CH-C}_{19}\text{-CONH}$); 130,3 (4C $\text{C=ONH-C-CH-C}_{15}\text{H-C-COO}$); 130,1 (4C $\text{C=ONH-C-CH-C}_{15}\text{H-C-COO}$); 128,7 (4C $\text{C=ONH-C-CH-C}_{20}\text{H-C-C=ONH}$); 128,0 (4C $\text{C=ONH-C-CH-C}_{20}\text{H-C-C=ONH}$); 119,6 (4C $\text{C=ONH-C-C}_{16}\text{H-CH-C-COOH}$); 119,4 (4C $\text{C=ONH-C-C}_{16}\text{H-CH-C-COOH}$); 31,3 (1C $\text{R1R2CH-C}_{10}\text{H2CH2}$); 29,0 28,8, 28,7 and 28,4 (5C $\text{C}_9\text{H}_2\text{-C}_8\text{H}_2\text{-C}_7\text{H}_2\text{-C}_6\text{H}_2\text{-C}_5\text{H}_2\text{-C}_4\text{H}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$); 25,6 22,12 (2C $\text{C}_3\text{H}_2\text{-C}_2\text{H}_2\text{-CH}_3$); 14,0 (1C C_1H_3).

The complete assignment of the ^1H and ^{13}C -NMR chemical shifts for the monomeric unit and the end groups of PNOBDME, are given in **Table 3**, together with their theoretical values calculated

by MestReNova [19,20]. Similar notations as those assigned to precursor cholesteric liquid crystal polyesters PTOBDME [2] have been used.

The proton spectrum can be divided in three zones which structurally would correspond to the *mesogen* including aromatic and amide protons between 11.0-7.00 ppm, the *flexible side chain* formed by aliphatic protons between 2.0-0.5 ppm, detailed in **Figure 8a**, and the *spacer* with the CH_n protons directly attachment to O atoms, between mesogen and side chain, with signals from 5.5-3.5 ppm.

Figure 9 ^{13}C -NMR Spectrum of polyesteramide PNOBDME.

Figure 10 ^1H -NMR of PNOBDME: (a) Aliphatic chain zone (b) Spacer zone.

Table 3: ^1H and ^{13}C -NMR Chemical Shifts (ppm) observed for chiral polyesteramide PNOBDME and Theoretically calculated values.

System (')				System ()				Theoretical Shifts			
Atom	^1H	Atom	^{13}C	Atom	^1H	Atom	^{13}C	Atom	^1H	Atom	^{13}C
^{20}H	8.03	^{20}C	128.7	^{20}H	8.13	^{20}C	127.9	^{20}H	8.18	^{20}C	127.6
		^{19}C	142.4			^{19}C	137.2;139.1			^{19}C	134.2
$\text{N}'\text{H}'$	10.48	^{18}C	165.3	NH	10.71	^{18}C	165.3	NH	10.25	^{18}C	164.7
		^{17}C	144.2			^{17}C	144.2			^{17}C	142.2
^{16}H	7.975	^{16}C	119.7	^{16}H	7.985	^{16}C	119.6	^{16}H	7.95	^{16}C	118.7
^{15}H	7.962	^{15}C	129.8	^{15}H	8.00	^{15}C	130.3	^{15}H	7.98	^{15}C	130.1
		^{14}C	124.7			^{14}C	123.5			^{14}C	125.7
		^{13}C	165.0			^{13}C	165.0			^{13}C	165.9
H'_{c}	5.39	^{12}C	73.2	H_{c}	5.22	^{12}C	73.7	H_{c}	4.55	^{12}C	73.6
$\text{H}'_{\text{a}}, \text{H}'_{\text{b}}$	4.54;4.44	^{11}C	65.8	$\text{H}_{\text{a}}, \text{H}_{\text{b}}$	3.91;3.83	^{11}C	46.7	$\text{H}_{\text{a}}, \text{H}_{\text{b}}$	4.80;4.55	^{11}C	64.3
$\text{H}'_{\text{d}}, \text{H}'_{\text{e}}$	1.79	^{10}C	30.7	$\text{H}_{\text{d}}, \text{H}_{\text{e}}$	1.74	^{10}C	31.8	$\text{H}_{\text{d}}, \text{H}_{\text{e}}$	1.71	^{10}C	30.7
$\text{H}'_{\text{f}}, \text{H}'_{\text{g}}$	1.42	^9C	24.6	$\text{H}_{\text{f}}, \text{H}_{\text{g}}$	1.34	^9C	24.2	$\text{H}_{\text{f}}, \text{H}_{\text{g}}$	1.29	^9C	25.3
^{8-5}H	1.25	^{8-5}C	28.6	^{8-5}H	1.25	^{8-5}C	28.6	^{8-5}H	1.29	^{8-5}C	29.6
^4H	1.25	^4C	28.4	^4H	1.25	^4C	28.4	^4H	1.26	^4C	29.3
^3H	1.25	^3C	31.3	^3H	1.25	^3C	31.3	^3H	1.26	^3C	31.9
^2H	1.25	^2C	22.1	^2H	1.25	^2C	22.1	^2H	1.26	^2C	22.7
^1H	0.85	^1C	13.9	^1H	0.86	^1C	13.9	^1H	0.88	^1C	14.1
Experimental signals aliphatic end group								Theoretical Shifts End group (")			
H''_{c}	4.35	$^{12''}\text{C}$	60.4	H''_{c}	3.81	$^{12''}\text{C}$	70.8	H''_{c}	3.81	$^{12''}\text{C}$	70.8
$\text{H}''_{\text{a}}, \text{H}''_{\text{b}}$	4.54;4.44	$^{11''}\text{C}$	67.5	$\text{H}''_{\text{a}}, \text{H}''_{\text{b}}$	4.53;4.28	$^{11''}\text{C}$	70.8	$\text{H}''_{\text{a}}, \text{H}''_{\text{b}}$	4.53;4.28	$^{11''}\text{C}$	70.8
$\text{H}''_{\text{d}}, \text{H}''_{\text{e}}$	1.89;1.77	$^{10''}\text{C}$	34.6	$\text{H}''_{\text{d}}, \text{H}''_{\text{e}}$	1.44	$^{10''}\text{C}$	34.0	$\text{H}''_{\text{d}}, \text{H}''_{\text{e}}$	1.44	$^{10''}\text{C}$	34.0
$\text{H}''_{\text{f}}, \text{H}''_{\text{g}}$	1.51;1.42	$^9''\text{C}$	26.0	$\text{H}''_{\text{f}}, \text{H}''_{\text{g}}$	1.29	$^9''\text{C}$	25.6	$\text{H}''_{\text{f}}, \text{H}''_{\text{g}}$	1.29	$^9''\text{C}$	25.6
$^{8-5''}\text{H}$	1.21	$^{8-5''}\text{C}$	28.6	$^{8-5''}\text{H}$	1.29	$^{7-5''}\text{C}$	29.6	$^{8-5''}\text{H}$	1.29	$^{7-5''}\text{C}$	29.6
$^4''\text{H}$	1.21	$^4''\text{C}$	28.4	$^4''\text{H}$	1.26	$^4''\text{C}$	29.3	$^4''\text{H}$	1.26	$^4''\text{C}$	29.3
$^3''\text{H}$	1.21	$^3''\text{C}$	31.3	$^3''\text{H}$	1.26	$^3''\text{C}$	31.8	$^3''\text{H}$	1.26	$^3''\text{C}$	31.8
$^2''\text{H}$	1.21	$^2''\text{C}$	22.1	$^2''\text{H}$	1.26	$^2''\text{C}$	2				

evaluated by their integral ratio. The peak observed at 4.35 ppm is, designated as H_c'' in the aliphatic-OH end group. A triplet at 4.25 ppm, is assigned to the OCH_2CH_3 ester in the aromatic end group.

Similarly to H_c protons, three independent pairs of H_aH_b signals, due to the splitting of diastereotopic hydrogen atoms are also observed, two for the monomer marked with (') and without it (") and one for the aliphatic-OH end group marked with (''). The double doublet at 4.54 ppm, and the very complex signal at 4.44 ppm are attributed to H_a' and H_b'' respectively, and the pair of double doublets at 3.91, 3.83 ppm are interpreted as H_a and H_b . Signal at 4.44 would be formed by one double doublet overlapped with a pair of double doublets.

The integral ratio between peaks H_c' (5.39 ppm) and H_a' (4.54 ppm) gives a ratio 1:1. Peaks H_c (5.22 ppm), H_a (3.91 ppm) and H_b (3.83 ppm) present a ratio 1:1:1. The TOCSY experiment, will confirm these assignments and will resolve the overlapped signal at 4.44 ppm. The aliphatic zone, in **Figure 8a**, exhibits multiplets centered at 1.89, 1.77, 1.51, 1.42, 1.25 and 0.86. The last two are directly assigned to (CH_2) and CH_3 , among the first four, only two were predicted. They are resolved also by TOCY. All these signals were also observed for PTOBDME.

The 1H - 1H TOCSY 2D experiment, in **Figure 11**, shows the correlations between the proton signals H_c' , H_c and H_c'' with their respective coupling networks, hence confirming the presence of three independent set of signals.

Besides, the multiplets overlappings due to spin-spin coupling, can be resolved: at 4.44 ppm in signals H_a'' , H_b'' and H_b' ; at 1.77 ppm distinguishing signals H_dH_e , $H_d'H_e'$ and H_e'' ; at 1.44 ppm as due to signals $H_f'H_g'$ and H_g'' . Even a new signal at 1.34 corresponding to H_fH_g could be observed.

The experiment COSY confirmed the assignment with the correlation of double doublets at 4.54 ppm (H_a') and 4.44 ppm (H_b') with multiplet H_c' at 5.39 ppm, and this with 1.79 ppm ($H_d'H_e'$), and this with 1.42 ppm ($H_f'H_g'$). The same correlation is found with double doublet at 3.91 ppm (H_a) and 3.83 ppm (H_b) with 5.22 ppm (H_c), and this with 1.74 ppm (H_dH_e), and finally with 1.34 ppm (H_fH_g). COSY did not let identify the end group overlapping signals.

Correlation between aromatic and amide protons of PNOBDME can be elucidated by 1D -NOESY experiment, in **Figure 12**. When irradiated at 10.71 ppm, the peak NH shows positive NOE with ^{20}H (8.13 ppm) and with ^{16}H (7.985 ppm). Irradiated at 10.48 ppm, $N'H'$ shows positive NOE with ^{20}H (8.03 ppm) and with ^{16}H (7.975 ppm). The 1D -NOESY irradiated at 1.74, H_dH_e showed a broad positive NOE with ^{15}H (8.00 ppm).

These correlations of the aromatic protons with the amide protons and aliphatic would explain the (1:5) proportion observed between signal at 8.13 and overlapped signal centered at 7.97, previously mentioned. More precise differentiation and assignation between of ^{16}H and ^{16}H and also ^{15}H and ^{15}H is hard to be performed with this technique, due to overlapping.

Similarly to the changes in the proportion of integral signals H_c

: H_c' , between the first and second fraction of PNOBDME, different amide protons ratio $NH:N'H'$ can be distinguished in different polymer fractions.

The assignment of carbons directly bonded to protons is carried out by the HSQC experiment, in **Figure 13**. Correlation between protons H_a' (4.54 ppm) and H_b' (4.44 ppm) with the same carbon atom ^{11}C (65.8 ppm) is confirmed. Within proton multiplet around 4.44 ppm, carbon atom ^{11}C (67.5 ppm) is connected with signals H_a'' and H_b'' (4.44 ppm), undiscernable in the proton experiments. The correlation between H_a (3.91 ppm) and H_b (3.83 ppm) with carbon atom ^{11}C at (46.7 ppm) is also observed.

The complex signal of proton centered at 1.77, solved in the TOCSY experiment, is also resolved in HSQC, by three correlation signals between $H_d'H_e'$ (1.79 ppm) with carbon ^{10}C at (30.7 ppm) and H_dH_e (1.74 ppm) with carbon ^{10}C at (31.8 ppm); and H_e'' (1.77 ppm) with carbon ^{10}C (34.6 ppm) which is also correlated with H_d'' (1.89 ppm).

Multiplet around 1.44 can be solved by distinguishing correlation between protons $H_f'H_g'$ (1.42 ppm) with carbon 9C (24.6 ppm) and

Figure 13 HSQC-NMR experiment of PNOBDME: (a) Detail of aliphatic flexible side chain (b) A detail of the spacer zone.

Table 4: ^1H and ^{13}C -NMR Chemical Shifts (ppm) observed and calculated for the repeating unit and aliphatic end group of chiral polyesteramide PNOBEE.

Set of signal of systems (') and ('')				Set of signals system without apostrophe ()				Calculated chemical shifts	
Atom	$^1\text{H}(\text{ppm})$	Ato	$^{13}\text{C}(\text{ppm})$	Atom	$^1\text{H}(\text{ppm})$	Atom	$^{13}\text{C}(\text{ppm})$	Atom	Atom
	DMSO		DMSO		DMSO		DMSO	^1H	^{13}C
^{12}H	8.03	^{12}C	129.2	^{12}H	8.14	^{12}C	128.4	8.18	127.6
		^{11}C	129.4			^{11}C	131.6		137.6
$\text{N}'\text{H}'$	10.48	^{10}C	163.3	NH	10.72	^{10}C	163.3	10.25	164.7
		^9C	143.2			^9C	142.8		140.1
^8H	7.99	^8C	119.9	^8H	7.99	^8C	120.1	7.95	121.5
^7H	7.98	^7C	130.8	^7H	7.98	^7C	130.8	7.88	130.1
		^6C	128.7			^6C	125.8		125.7
		^5C				^5C			165.9
H_c'	5.32	^4C	73.0	H_c	5.15	^4C	74.2	4.55	72.5
H_a', H_b'	4.55, 4.47	^3C		H_a, H_b	3.93, 3.87	^3C	46.5	4.80, 4.55	67.2
H_d'	1.80	^2C	24.0	H_d	1.78	^2C	24.9	1.75	23.5
H_e'	1.01	^1C	10.0	H_e	0.92	^1C	9.9	0.96	7.8
Experimental signals aliphatic end group						Theoretical Shifts End group ('')			
H_c''	4.32	$^4''\text{C}$	62.5					3.81	73.0
$\text{H}_a'', \text{H}_b''$	4.47 *	$^3''\text{C}$	67.7					4.53, 4.28	70.5
$\text{H}_d'', \text{H}_e''$	1.95, 1.76	$^2''\text{C}$	27.9					1.48	26.8
H_f''	1.03*	$^1''\text{C}$	11.1					0.96	7.6

- Overlapped signal
- End group $\text{O}-\text{CH}_2-\text{CH}_3$: 4.28 ppm (^1H -NMR) and 60.2 ppm (^{13}C -NMR); CH_3 : 1.33 ppm (^1H -NMR) and 14.4 ppm (^{13}C -NMR)

relation between signals at 8.14 ppm and 7.98 ppm is 1:3 instead of 1:2, since signal at 8.03 ppm is partially overlapped with signal at 7.98. The complete assignment of this signals was realized with other NMR experiments.

In the proton spacer zone, two multiplets observed at 5.32 ppm and 5.15 ppm, are assigned to protons H_c' and H_c , respectively, within the monomeric unit, according to the terminology previously used for PNOBDEME. A double doublet at 4.55 ppm is assigned to H_a' . A broad and overlapped signal centered at 4.50 ppm should correspond with overlapping of double doublet H_b' and the double doublets $\text{H}_a''\text{H}_b''$ in the aliphatic end-group. A multiplet observed at 4.32 ppm is assigned to H_c'' of the aliphatic end group and quadruplet at 4.28 ppm to CH_2 of ethyl ester end group. Finally double doublet at 3.93 ppm and 3.87 ppm are assigned to H_a and H_b .

The observed aliphatic signals corresponding with the lateral side chain are: A multiplet at 1.89 ppm and a broaden overlapped signal at 1.78 ppm interpreted as H_d , totally assigned with the help of COSY and TOCSY experiments. Triplet at 1.33 ppm is assigned to methyl of ethyl ester end group. While triplets at 1.03, 1.01 and 0.92 corresponding to H_d were also assigned with COSY and TOCSY experiments to H_e'' , H_e' and H_e , respectively.

In the COSY experiment, the expected correlation between ^{12}H (8.14 ppm) and ^8H (7.99 ppm) was overlapped and it was indistinguishable. Signal H_c' (5.32 ppm) shows correlation with H_a' (4.55 ppm), with signal H_b' (4.47 ppm) and with signal H_d' (1.80 ppm). Signal H_c (5.15 ppm) correlates with H_a (3.93 ppm), H_b (3.87

ppm) and with H_d (1.78 ppm). Signal corresponding to H_c'' (4.35 ppm) correlates with H_d'' (1.95 ppm), with H_e'' (1.76 ppm) and with $\text{H}_a''\text{H}_b''$ overlapped at (4.47 ppm). Signal at 4.28 ppm due to CH_2 ethyl in ester end group shows correlation with triplet at 1.33 ppm due to CH_3 in the same end group. Signal H_d'' (1.95 ppm) and H_e'' (1.76 ppm) show correlation with H_f'' (1.03 ppm). In the TOCSY spectrum, of the aromatic zone correlation of amidic proton NH (10.72 ppm) with ^{12}H (8.14 ppm) and ^8H (7.99 ppm) is observed. Also between amidic proton $\text{N}'\text{H}'$ (10.48 ppm) and the overlapped signal of ^{12}H (8.03 ppm) and ^8H (7.99 ppm).

The signal H_c' (5.32 ppm) correlates with H_d' (1.80 ppm) and H_e' (1.01 ppm). The set of signals of aliphatic-OH end group was also resolved by the correlation of H_c'' (4.35 ppm) with $\text{H}_a''\text{H}_b''$ (4.47 ppm), with H_d'' (1.95 ppm), with H_e'' (1.76 ppm) and with H_f'' (1.03 ppm).

In the NOESY-2D experiment the same correlations as in TOCSY-2D were observed, only correlation between H_c' (5.35 ppm) with ^7H (7.98 ppm) and H_b' (4.47 ppm) with ^8H (7.99 ppm). The correlations between H_c (5.15 ppm) and ^8H and H_a and H_b with ^7H were not observed. This could be indicative of a closer structure for system (') than for () system.

After of proton assignment, carbon atoms bonded directly to hydrogens were identified by the HSQC experiment. ^{12}C (129.2 ppm) was related with ^{12}H (8.03 ppm), and ^{12}C (128.4 ppm) with ^{12}H (8.14 ppm); ^8C (119.9 ppm) and ^8C (120.1 ppm) with ^8H and ^8H (7.98 ppm); ^7C (130.8 ppm) is related with ^7H (7.98 ppm); H_c' (5.32 ppm) shows correlation with ^4C (73.0 ppm), while H_c

(5.15 ppm) with ^4C (74.2 ppm); H_a (3.93 ppm) and H_b (3.87 ppm) correlates with carbon ^3C (46.5 ppm). ^2C (24.9 ppm) is related with H_d (1.78 ppm) and ^1C (9.9 ppm) with H_e (0.92 ppm); ^1C (10.0 ppm) with H_e' (1.01 ppm). Signals due to OH-aliphatic end group: H_c'' (4.32 ppm) is related with $^{4'}\text{C}$ (62.5 ppm); $\text{H}_a''\text{H}_b''$ (4.47 ppm) with $^{3'}\text{C}$ (67.7 ppm); H_d'' (1.95 ppm) and H_e'' (1.76 ppm) with $^{2'}\text{C}$ (27.9 ppm) and H_f'' (1.03 ppm) with $^{1'}\text{C}$ (11.1 ppm); signal due to ester ethyl group CH_2 (4.28 ppm) with ^{13}C (60.2 ppm) and CH_3 : ^1H (1.33 ppm) with ^1C (14.4 ppm).

Conformational analysis of PNOBDME and PNOBEE

By using a Karplus type equation [21], the vicinal coupling constants $^3J_{\text{Ha-Hc}}$ and $^3J_{\text{Hb-Hc}}$ can be related with the three possible staggered conformers of torsion ϕ along ^{11}C - $^{12}\text{C}^*$ bond in PNOBDME, and ^3C - $^4\text{C}^*$ in PNOBEE, in the polymer backbone, **Figure 15**, being $m=9$ for PNOBDME and $m=1$ for PNOBEE. In the system designed without apostrophe (), the coupling constants $^3J_{\text{Ha-Hc}}$ (3.7 Hz) and $^3J_{\text{Hb-Hc}}$ (6.0 Hz) indicate the preference for *gt* conformer.

In the system ('), $^3J_{\text{Ha'-Hc'}}$ can not be measured accurately because the peak is not resolved but it is low enough to let us assure the preference of the *gg* conformer; $^3J_{\text{Hb'-Hc'}}$ can not be measured due to the overlapping of H_b' signal with those of H_a'' and H_b'' . The existence of these two independent conformers had also been observed for PTOBDME and PTOBEE and it was also related with the presence of helical structures, the Cotton effect and the sign of the helicity in 1-2 di-*o*-benzoylated *sn*-glycerols [22]. The combination of a helix with two screw senses and the two absolute configurations by the presence of the asymmetric

carbon atom, provide four diastereomeric structures, two pair of enantiomers which would present two independent set of signals by NMR [23-25].

Thermal Behaviour

Thermal stability and differential scanning calorimetry of PNOBDME

The presence of amide groups within the mesogen of PNOBDME causes a 10% weight loss at 310°C in the thermal gravimetric curve, **Figure 16a**, increasing of thermal stability range of precursor polyester PTOBDME, with the same weight loss percentage at 280°C [3].

The DSC experiment of PNOBDME, performed at 10°C/min rate, **Figure 16b**, shows in the first heating run a glass transition at 62.5°C together with a small broad endothermic peak centred at 155.7°C. During the cooling an exothermic peak at 183°C is indicative of crystallization from the mesophase state, higher value than that of PTOBDME (149°C). In the second heating glass transition is observed at 71.6°C, and two broad and small endothermic peaks at 108.7 and 188.3°C.

In a subsequent experiment PNOBDME was heated of up to 230°C at 10°C/min, cooled to 190°C and isothermally heated for 2 hours at this temperature, cooled to 30°C at 10°C/min, and finally heated again to 230°C, at 10°C/min. The isothermal treatment at 190°C after cooling from 230°C, should have produced an induced crystallization process, and an endothermic peak due to the polymer transition to mesophase should have been observed, however only a small endothermic peak at 109°C is observed not caused by the isothermal cooling. This endothermic transition at 109°C was also confirmed by Microcalorimetry (**Figure 16c**).

Thermal stability and differential scanning calorimetry of PNOBEE

PNOBEE thermal stability is given in **Figure 17a**. A 10% weight loss due to thermal decomposition is observed at 330°C, a higher temperature than that observed for PTOBEE at 280°C [4] and PNOBDME at 310°C. The substitution of the ester group in the mesogen by amide caused the increasing of thermal stability with respect to PTOBEE.

In the DSC experiment performed at 10°C/min rate, **Figure 17b**, a glass transition is observed during the first run, around 55°C, and very broad endothermic peak centred at 185.3°C interpreted as the fusion due to transition from crystal to liquid-crystal, another endothermic peak at 233.7°C is observed near the beginning of thermal decomposition; in the cooling run two small exothermic peaks appear at 205.6°C and 183.0°C due to crystallization processes from the mesophase state. In the second heating, no transition is observed. Compared with PTOBEE, with transition to mesophase at 149°C and with exothermic crystal formation at 110°C during isothermal heating, a remarkable difference is observed due to the substitution of ester by amide groups in the mesogen.

Figure 16 (a) Termogravimetric curve of PNOBDME, first fraction (b) DSC analysis of PNOBDME first fraction (c) Microcalorimetry of PNOBDME.

Optical Characterization

Optical characterization of PNOBDME

Although synthesized from starting racemic materials PNOBDME showed unexpected chirality. The first fraction of the polymer did not show a net optical activity but values changing from positive to negative, but the second fraction presented a low but constant value at 598 nm, +1.02°; at 579 nm, +1.65°; and at 435 nm, +2.9° and very high optical activity at 365 nm, +600° or +950° depending of temperature. This behaviour was also observed in PTOBDME and PTOBEE.

In **Figure 18**, Optical Rotatory Dispersion (ORD) values (α) of second fraction of PNOBDME are expressed as Molar Optical Rotation $[\Phi] = [\alpha] M/100$, being M the molecular weight of the

polymer repeating unit, as function of time, at 365 nm, at two different temperatures: 25°C and 20°C.

At 25°C three different slopes are observed, with an intermediate zone from 90 to 210 minutes with an ORD value approximately 600° and after 360 minutes it was stabilized in 950°. At 20°C, after 120 minutes the ORD reached a value of 600° that was maintained.

In both cases, once the ORD value was stabilized to 600° and 950° respectively, if the lamp wavelength was changed to 435 nm and quickly returned to 365 nm, the ORD value initially decreased to +8.6, and recovered its value. This phenomenon could be totally reversible. The variation of ORD with time has been described in helical polyguanidines synthesized starting from chiral monomers or starting achiral monomers with chiral catalysts [26-30].

Figure 17 (a) Thermogravimetric curve of PNOBEE first fraction (b) DSC analysis of PNOBEE first fraction.

Figure 18 Optical Rotatory Dispersion (ORD) of PNOBDME second fraction at 25°C and at 35°C.

Optical characterization of PNOBEE

At the end of this article the optical activity of PNOBEE has not been studied

Morphology

The morphology of powdered PNOBDME without any previous treatment has been studied by SEM. In **Figure 19**, four details are shown of the homogeneous spherical clusters of about 5 μm in diameter homogeneously dispersed.

Conclusions

The synthetic methods of two new multifunctional cholesteric liquid crystal polyesteramides designed as: PNOBDME: $(\text{C}_{34}\text{H}_{38}\text{N}_2\text{O}_6)_n$ and PNOBEE $(\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_6)_n$ are reported and their characterization by ^1H and ^{13}C -NMR, COSY and HSQC, is stated

and compared to their precursor polyesters PTOBDME and PTOBEE.

Molecular models of the new polymers show helical polymeric chains.

The NMR analysis, in agreement with the Molecular Mechanics models, let us to conclude that the enantiomeric polymer chains present stereo regular head-tail, isotactic structure, explained in terms of the higher reactivity of the primary hydroxyl with respect to the secondary one in the glycol through the polycondensation reaction.

According to our previous experience, each enantiomer, with two independent sets of signals observed by ^1H and ^{13}C -NMR, differentiated with apostrophe (') and without it (), could be attributed to two diastereomeric conformers: *gg* and *gt*, related with two possible staggered conformations of the torsion along the chemical bond, containing the asymmetric carbon atom in the spacer, along the copolymer backbone, with two possible helical screw sense of the polymer chain, for all the studied polymers. Chirality in racemic precursor PTOBDME was proposed to be due to the kinetic resolution of a preferable helical diastereomer, such as *Sgt*, with respect to the possible four forms, while the R/S ratio of asymmetric carbon atoms remained 50:50.

The thermal behaviour of the synthesized liquid crystal polyesteramides, studied by TG and DSC analysis, show an endothermic peak assigned to the first order transition from crystalline phase to liquid crystal mesophase.

Optical ORD values are provided for polyesteramide PNOBDME. The unexpected chirality is evaluated. The first fraction of the polymer did not show a net optical activity but values changing from positive to negative, but the second fraction presented a low but constant value at 598 nm, $+1.02^\circ$; at 579 nm, $+1.65^\circ$; and at 435 nm, $+2.9^\circ$ and very high optical activity at 365 nm, $+600^\circ$ or $+950^\circ$ depending of temperature.

Figure 19 SEM images of powdered PNOBDME.

Morphology of powdered PNOBDME is reported by ESEM, showing the homogeneous spherical clusters of about 5 μm in diameter homogeneously dispersed.

The synthetic cholesteric liquid crystal polyestereamides described here are similar to new cationic cholesteric liquid crystal polymers also synthesized in our lab [31].

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