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CONFORMATIONAL ANALYSIS AND MOLECULAR MODELING OF CHOLESTERIC LIQUID CRYSTAL POLYESTERS BASED ON XRD, RAMAN, AND TRANSITION THERMAL ANALYSIS

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ABSTRACT

Molecular modeling of the cholesteric liquid crystal polyester poly-[oxy(1,2-dodecane)oxycarbonyl-1,4-phenyleneoxycarbonyl-1,4-phenylene-carbonyloxy-1,4-phenylenecarbonyl] (PTOBDME), $[C_{34}H_{36}O_8]_n$, synthesized in our laboratory and thermally characterized by differential scanning calorimetry (DSC), was performed to explain both its cholesteric mesophase and 3D crystalline structure. Conformational analysis (CA) was run for the monomer both by systematic search and with molecular dynamics (MD) simulations. Minima energy conformers were “polymerized” with Cerius² and helical, cholesteric molecules were obtained in all cases. Our models agree with the chiral behavior observed by X-ray diffraction (XRD), thermo-optical analysis (TOA) and circular dichroism (CD) experiments. Crystal packing of the polymer molecules were simulated in cells with parameters **a** and **b** obtained from experimental powder X-ray diffraction patterns and **c** calculated from the translational repetitive unit during the theoretical polymerization. Recalculated X-ray powder diffraction patterns of our models matched the ob-

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served ones. Morphology simulation from those crystal models is in good agreement with the crystals observed by optical microscopy. We have also modeled the self-associating nature of those polyesters when dispersed in aqueous media. Simulation of our models surrounded by different solvents, such as water and chloroform, were performed by calculating their interaction energies, coordination numbers, and mixing energies, applying Monte Carlo simulation techniques based on the Flory-Huggins theory. These results were compared with their experimental vibrational Fourier transform (FT)–Raman spectra in the regions in which structural marker bands of the polymer appear.

Key Words: Cholesteric liquid crystals; FT Raman; Solvent effect; Structure simulation; XRD.

INTRODUCTION

A synthesis method previously reported for high molecular weight liquid crystal polyesters based on polycondensation of mesogenic monomers [1] was followed for the synthesis of PTOBEE, $[C_{26}H_{20}O_8]_n$. It was obtained as cholesteric, although synthesized from the racemic mixture of the involved DL-1,2-butanediol. Stereoselective solubilization of the negative enantiomer during its decantation in toluene was claimed to be the reason for this achievement [1,2].

We have obtained the same result for the thermotropic liquid crystal poly[oxy(1,2-dodecane)oxycarbonyl-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyloxy-1,4-phenylenecarbonyl] (PTOBDME) $[C_{34}H_{36}O_8]_n$, which has also been obtained as chiral, cholesteric [3], although synthesized from the racemic mixture of DL-1,2-dodecanediol.

In this article, we present the details for its structural characterization by thermoanalysis, X-ray diffraction (XRD), circular dichroism (CD), and Fourier transform (FT)–Raman spectroscopy. Molecular modeling based on conformational analysis (CA) and XRD analysis were used to try to explain its mesophase and crystalline behavior.

EXPERIMENTAL

Synthesis of Cholesteric PTOBDME

PTOBDME was synthesized in our laboratory according to a method previously reported [1,3] by polycondensation of 4-4'-(terephthaloyldioxydibenzoic chloride) (TOBC) and a racemic mixture of DL-1,2-dodecanediol from Merck-Schuchardt (Hohenbrunn, Germany).

Although synthesized from a racemic mixture of the diol involved, as obtained it is cholesteric and chiral in nature [3]. It was characterized as –PTOBDME, with $[\alpha]_{589}^{25} = -1.43$ (1.538 gr/100 ml, toluene).

Characterization of Cholesteric PTOBDME

The structure of PTOBDME was determined as shown in the structure below by ^1H and ^{13}C nuclear magnetic resonance (NMR). Spectra were registered in $(\text{CD}_3)_2\text{SO}$ at 80°C in a Varian 300-MHz spectrometer.

Thermal stability was studied on a Mettler TA4000-TG50 at a heating rate of $10^\circ\text{C}/\text{min}$ with nitrogen purge (Praxair, Madrid, Spain), and thermal transitions were observed by differential scanning calorimetry (DSC) in a Mettler TA4000/DSC30/TC11 calorimeter by a series of heating/cooling cycles in a temperature range between 10°C and 280°C at $10^\circ\text{C}/\text{min}$.

Circular dichroism was measured in a Jasco J-720 spectropolarimeter between 240 and 400 nm. Thin solid films were prepared at 250°C and smoothly sheared to orient the sample. Spectra were registered after every 90° rotation of the sample.

Simultaneous wide-angle X-ray scattering/small-angle X-ray scattering (WAXS/SAXS) spectra were obtained with the synchrotron radiation source at HASYLAB (DESY, Hamburg). Beam radiation $\lambda_{\text{CuK}\alpha} = 1.54 \text{ \AA}$ was monochromatized by a bent germanium single crystal. Two linear one-dimensional detectors were used. The Interactive Data Manipulation Package OTOKO (C. Boulin, R. Kempf, M. H. J. Koch, and S. M. McLaughlin, 1986) was used to normalize, evaluate, and display raw one-dimensional data.

The modeling work was performed on a Silicon Graphics O2-5000 running IRIX[®], version 6.3. The software used on this platform was Cerius² 4.5 supplied by Molecular Simulation, Incorporated, Instrument (Burlington, MA).

FT-Raman spectra were obtained using an RFS 100/S Bruker spectrophotometer. The 1064-nm line, provided by a Nd:YAG laser, was used. Resolution was set at 4 cm^{-1} , and a 180° geometry was employed. The output laser power

was 150 mW for solid samples and 300 mW for the solutions. Solid samples were recorded in a brass holder, whereas for the liquid samples, 5-mm optical path quartz cells were employed. The FT-Raman spectra were the result of 1000 scans recorded over 20 min.

RESULTS AND DISCUSSION

The thermal stability curve of PTOBDME is shown in Fig. 1. At 280°C, weight loss due to thermal decomposition begins to be observed. The DSC analysis (Fig. 2) shows a broad peak, in the heating range, centered at 67°C assigned to T_g . A slight change of the baseline at about 90° with a negligible enthalpy could be due to some crystalline arrangement over the glass transition. A sharp endothermic peak at 235°C is assigned to the transition from crystal to liquid crystal. Two broad and small peaks centered at 168°C and 197°C, respectively, in the crystal stability yield are also observed. The high exothermic peak appearing at 149°C when cooling is interpreted as due to a crystallization process from the mesophase state. Degradation to shorter molecular chains precedes the isotropic state.

Circular dichroism obtained for oriented thin films of PTOBDME rotated every 90° is shown in Fig. 3. It exhibits the exciton coupling effect, present when more than two chromophores of π -electron systems, independently involved in an optically active molecule, strongly correlate with each other. The observed curves change their sign with the sample rotation, probably due to the orientation of the different coils or antipode stereostructures with the opposite CD sign. These profiles match the calculated CD for a "spiral staircase" geometry well [4].

X-Ray Analysis

Figures 4 and 5 show XRD patterns of PTOBDME registered during heating and cooling ranges, respectively, with a synchrotron radiation source. Two XRD peaks, at $2\theta \approx 16^\circ$ ($d_{100} = 5.5 \text{ \AA}$) and 24° ($3.71 \text{ \AA}$), always present in the entire temperature range, were assigned to the cholesteric mesophase. A third one at $2\theta \approx 19^\circ$ ($d_{010} = 4.7 \text{ \AA}$) and a small one at $2\theta \approx 22.5^\circ$ ($3.95 \text{ \AA}$), disappearing at 240°C during the heating range and appearing again at about 150°C while cooling, were interpreted as due to presence of three-dimensional (3D) order. The crystalline stability temperature field is in agreement with the DSC curves. This means a cholesteric mesophase is always present and coexists with crystalline phase in the crystal stability temperature range.

Molecular Modeling and Conformational Analysis of PTOBDME Monomer Unit

Molecular modeling of PTOBDME monomer was performed by Cerius²—4.5. The Dreiding-II force field was loaded, and partial atomic charges

Figure 1. Thermogravimetric curve of PTOBDME.

Figure 2. DSC of PTOBDME.

Figure 3. CD of PTOBDME.

Figure 4. WAXS for PTOBDME in the heating range.

Figure 5. WAXS for PTOBDME in the cooling range.

were calculated by the charge-equilibration method. Head (C_H) and tail (O_T) atoms were defined within the monomer. The presence of a chiral C^* atom was also considered and defined rectus in our models. Energy was then minimized. The molecular scheme of the monomer with $R = (CH_2)_9CH_3$, is

where the extended length between C_H and $O_T \approx 23 \text{ \AA}$.

Energetic terms for torsions and Coulomb and Van der Waals interactions were included in the CA of PTOBDME. We had observed that the interaction between mobile atoms on both sides of one benzene ring were negligible in the case of PTOBEE, $[C_{26}H_{20}O_8]_n$, with a shorter lateral chain perpendicular to the mesogen [5]. Then, we made separately independent CA for the two torsions on each terephthalate ester group (bridge) of the mesogen and for the torsions within the flexible spacer (head). Consequently, a simplified model for the mesogen could be reduced in PTOBDME to the three articulated planes I, II, and III, limited by parentheses in the molecular scheme above, connected by ester groups, where torsions CO1 and CBO1 (or CO2 and CBO2) were the independent variables for CA.

Four other independent torsions were defined for the CA within the flexible spacer, along the main chain (head): Phi, which defines the head orientation with respect to the mesogen; Tau, which determines the lateral chain orientation to the mesogen; the torsion CO along the $C_{\text{carbonyl}}O_{\text{ester}}$ bond (i.e., C^{13} in Structure 1), close to 180° ; and C^*-C_H .

Systematic CA were performed for the two torsions (CO1, CBO1) on one terephthalate ester bridge. Four equienergetic minima, about 74 kcal/mol, were observed in the maps (CO, CBO) (Fig. 6) at points **A** ($164^\circ, -44^\circ$), **B** ($-164^\circ, 44^\circ$), **C** ($164^\circ, 141^\circ$), **D** ($-164^\circ, -141^\circ$), very close ($\delta < 5^\circ$) to those found for PTOBEE but with a shorter lateral chain. Figure 6 also shows other secondary

Figure 6. Systematic conformational search map for torsions: 1 = CO, 2 = CBO.

minima, **E** (-42° , -36°) and **F** (41° , 144°) with $E = 80$ kcal/mol [30% higher with respect to the maximum high at (0,0)]. The same results were obtained in the CA of the second terephthalate ester group with two torsions (CO2, CBO2).

The lowest energy conformations for the mesogen would all be combinations: AA, AB, . . . , with $E = 74$ kcal/mol and with molecular T-shape. Due to the conformational map symmetry, only four different solutions exist: conformer AA with two successive rotations of about $+60^\circ$ of planes I, II, and III along the main-chain axis, with formation of a triangular helical cross section. Conformer AB, in which rotation through the O2 bridge is about -60° against the about $+60^\circ$ through O1; hence, planes I and III became parallel. The other two conformers are the enantiomers of AA and AB. Figure 7a shows the conformation AB with a T-shape.

(a)

(b)

Figure 7. (a) PTOBDME monomer with conformation AB; (b) U-shaped monomer with conformation EB.

Molecular models of the monomers with the lowest energy torsion values (from Fig. 6) were fully minimized in energy. After minimization, the same torsional values were found for the terephthalate ester group located far from the lateral chain. Instead, the terephthalate ester group closer to the lateral chain also adopted torsion values corresponding to the secondary energy minima observed in Fig. 6, approaching the mesogen parallel to the lateral chain in a U-shape. Figure 7b shows this effect of the lateral chain, which was not observed in PTOBEE CA [5].

A systematic CA including the four torsions of the mesogen together (CO1, CBO1, CO2, CBO2) was performed later. Full energy minimization was allowed during the conformational search. There were 100 sterically allowed conformers found, with an energy threshold of 10 kcal/mol above the minimum. Besides the conformers AA and AB with $E = 74$ kcal/mol and T-shape, two other (EB and FA) were found with lower E (72 and 73 kcal/mol, respectively); both were U-shaped.

The systematic CA for the four torsions defined for the spacer (head) CO (i.e., $C_{\text{carbonyl}}-O_{\text{ester}}$), Phi, Tau, and C^*-C_H gave 57 sterically allowed conformations after removal of duplicates, with an energy threshold of 10 kcal/mol. The three minimized conformers with the lowest energy, $E = 74.2$ kcal/mol, were selected. They resulted in a unique solution at $(CO, \text{Phi}, \text{Tau}, C^*-C_H) = (-177^\circ, 77^\circ, 64^\circ, 179.75^\circ)$. Note the minimum value found by the program at $C^*-C_H = 179.75^\circ$.

Molecular dynamics (MD) offers one method of conformational searching as thermal energy is introduced into the system. As it flows back and forth between various degrees of freedom, the molecule explores the potential energy surface in the neighborhood of the local minimum from which it starts. Increased simulation temperatures, although unrealistic, should be used to move over energetic barriers surrounding regions with narrow minima in the conformational space and to explore larger areas.

After an ordinary molecular dynamics simulation of the monomer molecule, a simulated annealing is advised, in which the system is deliberately heated to a high temperature (1000 K or more) to permit it to sample alternate conformations, followed by slowly cooling, or annealing, which gradually removes kinetic energy from the dynamic simulation, hence removing residual strains in a structure.

As an alternative to simulated annealing, simulated quenching, which entails a rapid drop in temperature to "freeze" the system, is also advised. Slow heating is carried out by injecting kinetic energy. As the dynamics proceeds at an elevated temperature, conformations ("snapshots") are saved at regular intervals, "frozen" abruptly by energy minimization.

Dynamical calculations with all torsions within the monomer were performed at temperatures between 1600 K and 500 K, followed by quenching or annealing within the PTOBDME monomer. The more outstanding minima are shown in Table 1. The conformer with 68.9 kcal/mol encloses the conformational

Table 1. Torsional Angles for the Minima Energy Conformers Found by Molecular Dynamics Simulation

CO1	CBO1	CO2	CBO2	CO	Phi	Tau	C*—C _H	E, Kcal/mol
170	-45	-177	-53	-175	157	-57	174	55
168	-45	-177	-53	-175	-80.5	-57	-174	56.8
171.3	-46.7	179	-52	-173.8	-80.9	-56.5	173.5	57.7
177.3	59.6	-178.5	115.8	-166.5	-115.8	83.4	83.4	66.5
174.3	53.2	179.7	50.6	-170.2	-160.5	67	176.2	68.9
-166.7	41.8	178.3	118.7	-162.6	-118.5	77.1	58.3	71.6
-165.1	39.2	178.0	118.8	-163.3	-118.4	74.0	-180	73.5

minimum found during the head CA. These were considered global minima, different from the local ones found through systematic CA, for which some torsions had been constrained to 180°, and lateral chain torsions were not included.

Polymer Chains

Homopolymers were built with Cerius², with the monomer torsional values with lowest energy from the CA maps, keeping the same chirality for the C* atom and *trans* connections for torsions C*—C_H and C_H—O_T to reproduce the ordered crystalline fraction observed by XRD.

Cholesteric helical molecules were obtained in all cases. Figure 8 shows the homopolymer built with 20 units from T-shaped AB monomer appearing in Fig. 7A. The helicity of our models could result in the chiral behavior observed by XRD, TOA, and CD measurements.

All simulated polymer chains exhibited different helical cross sections depending on the starting monomer from which the molecule was “polymerized.” Figure 9a shows the cross-sectional view along the helical axis of the polymer chain in Fig. 8. The view in Fig. 9b corresponds to a U-shaped monomer with conformation EB.

Crystalline Structure Modelization

Packing of our polymer molecules was adjusted in crystal models with Cerius² with the help of the experimental PTOBDME powder XRD pattern from which **a** and **b** cell parameters were estimated. All our helical polymer molecular chain models could be packed in one triclinic primitive P1 unit cell with **a** = 5.5 Å, **b** = 4.7 Å, **c** (equal to the pitch length of each simulated polymer helix), **α** = 92°, **β** = 112°, and **γ** = 90°. Molecules were oriented with their main chain parallel to the **c** axis. Figure 10 shows the asymmetric unit cell of the PTOBDME crystal structure corresponding to the polymer chain from Fig. 8. Only one cell

Figure 8. Poly(PTOBDME)₂₀ helical molecule.

has been drawn. Its content is repeated in the x and y directions with **a** and **b** translational vectors to build a three-dimensional polymer crystalline model.

X-ray powder diffraction patterns were recalculated for our crystal models by fitting the cell parameters of each polymer model to match the experimental one. They all matched the observed one. The simulated XRD pattern of the polymer crystal, shown in Fig. 10, appears in the square in the same figure.

The crystal morphology of our polymer crystal models was further simulated with Cerius². The simulated morphology of the crystal appears in Fig. 10 with a rhombohedral shape. It is in good agreement with the rhombohedral crystals observed by optical microscopy, dispersed within the mesophase matrix (Fig. 11), in which some of them are indicated with arrows.

Fourier Transform-Raman Analysis of PTOBDME

In Figs. 12-I and 12-II, we show the FT-Raman spectra of PTOBDME polymer in both the solid state (b) and suspended in water (a), as well as the

Figure 9. Two different perpendicular cross-sectional views of polymer chains from different monomers.

corresponding precursors employed in its preparation: (c) TOBC and (d) DL-1-2-dodecanediol.

In the spectra of dry PTOBDME (Fig. 12-Ib), an intense band at 1751 cm^{-1} is observed that can be attributed to the terephthalate carbonyl stretching bond $\nu(\text{C}=\text{O})$. This band appears at relatively high wavenumbers compared to similar compounds reported in the literature [6,7]. A small shoulder at about 1740 cm^{-1}

Figure 10. Crystal packing simulation of PTOBDME. Recalculated WAXS.

is interpreted as due to the oxybenzoate carbonyl group. A new band, most probably attributed to the structure of the polymer, appears at 1634 cm^{-1} .

The strong band appearing at 1605 cm^{-1} was assigned to $\nu(\text{C}=\text{C})$ in aromatic rings. The band at 1472 cm^{-1} due to methylene scissoring deformations is sensitive to conformational changes of the flexible spacer. A considerable decrease of this group is observed in the polymer with respect to the precursor DL-1-2-dodecanediol (curve d).

In the region of $1350\text{--}1000\text{ cm}^{-1}$ region, the asymmetric $\nu(\text{C}-\text{O}-\text{C})$ stretching vibrations of the ester groups are strongly coupled with the $\nu(\text{C}-\text{C}-\text{C})$ vibrations of the aliphatic chain and $\delta(\text{CH})$ of aromatic rings. Splitting of the stronger TOBC peaks in this region is observed in the polymer spectra.

In the high-wavenumber region (Fig. 12-II), an intense band appears at 3080 cm^{-1} , corresponding to $\nu(\text{C}-\text{H})$ motions in the benzene ring. Although there is a long polymethylene moiety present in this polymer, we only observed

Figure 11. Optical micrograph of rhombohedral crystals of PTOBDME (some of them marked with black arrows) dispersed in mesophase matrix.

very weak bands attributed to the aliphatic (C—H) between 2800 and 3000 cm^{-1} , even weaker when the polymer was dispersed in water, probably due to its highly hydrophobic behavior. A detailed analysis of the methylene C—H stretching reveals a remarkable intensity increase of the I_{2930}/I_{2880} ratio and a decrease for the I_{2880}/I_{2850} relationship. These changes point out the existence of a more disordered structure [8].

The above Raman spectra and the changes observed in the structure marker bands are explained by the presence of helical polymer molecules and their self-association to form cavities. They are also observed by fluorescence when dispersed in an aqueous medium [9], in which the structure of the polymer has a more disordered state in comparison to the solid state or the precursor.

We have studied the FT-Raman spectrum of the polymer in the solid as well as in different solvents, such as water, chloroform, and deuterated dimethyl sulfoxide (d_6 -DMSO) (Figs. 13-I and 13-II). The bands corresponding to the ester moiety and the aromatic ring are very intense in Raman spectra, and they can be employed as markers to carry out a structural study of the polymer. In water, there is a doublet at 1751 and 1740 cm^{-1} (Fig. 13-I), which can be attributed to the $\nu(\text{C=O})$ vibration of terephthalate carbonyl and oxybenzoate carbonyl moieties, respectively. In chloroform, the lower component almost disappears or is moved upward, indicating that a conformational change is operating at the

Figure 12. FT-Raman spectra of PTOBDME polymer, solid and in aqueous solution, and TOBC and DL-1-2-dodecanediol at (I) low and (II) higher wavenumber region.

level of the oxibenzoyl ester bond directly linked to the aliphatic side chain. In contrast, there is only one unique band centered at 1745 cm^{-1} in d_6 -DMSO.

The aromatic $\nu(\text{C}=\text{C})$ band is also sensitive to the polymer structure. This vibration appears as a doublet at 1614 and 1607 cm^{-1} , with relative intensity changes that depend on the medium. In addition, we observed a shoulder at about 1634 cm^{-1} in this region, which is more intense in chloroform. In d_6 -DMSO, this shoulder is not seen, while a downshift is observed for the $\nu(\text{C}=\text{C})$ vibration, and a new band is observed at 1703 cm^{-1} .

The effect of the solvent is also manifested in the high-wavenumber region (Fig. 13-II): The band at about 3080 cm^{-1} reveals two components, at 3083 and 3070 cm^{-1} , of variable relative intensity. In water and in the dried sample (previously in contact with water), there is a prominent band at 3083 cm^{-1} and a shoulder at 3069 cm^{-1} . In chloroform, the intensity of this doublet is inverted, with the more intense band appearing at 3070 cm^{-1} . However, in d_6 -DMSO, there again is only a single unique band centered at 3075 cm^{-1} . As concerns the $\nu(\text{C}-\text{H})$ motions, the more remarkable changes take place in chloroform, in which a significant intensity increase is observed for the bands at 2927 and 2882 cm^{-1} of the aliphatic moiety. The last result is connected to a structural change in this solvent.

Figure 13. Effect of solvent on FT-Raman spectra of PTOBDME plus d_6 -DMSO, $CHCl_3$, and water at (I) low and (II) high wavenumber region.

Structural change in $CHCl_3$ is related to a more disordered structure, which is also connected to the solubility of the polymer in this solvent.

In the region of $1000\text{--}1500\text{ cm}^{-1}$ (Fig. 14), an intense band appearing at 1278 cm^{-1} is assigned to the $\nu(C\text{--}O)$ vibration in the ester group of the terephthalate carbonyl group, accompanied by a lower band appearing at 1267 cm^{-1} attributed to oxibenzoyl groups. A band appearing at 1208 cm^{-1} , which downshifts to 1203 cm^{-1} in d_6 -DMSO, can also be assigned to a $\nu(C\text{--}O)$ vibration. Likewise, the band at 1170 cm^{-1} undergoes shifts to 1164 cm^{-1} in this solvent. Below 1000 cm^{-1} , we observed two weak bands at 760 and 839 cm^{-1} , which can be due to the $\gamma(C\text{--}H)$ motions in the aromatic rings. Other bands can be seen at 626 , 547 , 250 , and 120 cm^{-1} attributable to structural vibrations of the polymer.

The fluorescence results indicate that, in chloroform, PTOBDME self-associates to form nanocavities heterogeneous in size. Most of these structures were filtered through the $0.45\text{-}\mu\text{m}$ filter, but a small fraction of PTOBDME also got through the $0.22\text{-}\mu\text{m}$ filter. This fact can be related to the conformational changes deduced from the FT-Raman spectra. In chloroform, both the $(C=O)$ and $(C=C)$ features are shifted upward, appearing at relatively high wavenumbers, 1751 and 1614 cm^{-1} . This result can be attributed to the adoption of a predominant nonplanar conformation of benzene rings in the mesogen, rigid moiety part of the polymer, as corresponds to the formation of coils.

Figure 14. Effect of solvent on FT-Raman spectra of PTOBDME plus d_6 -DMSO, $CHCl_3$, and water in the region between 1000 and 1500 cm^{-1} .

Simulation of PTOBDME Dispersed in a Solvent

We have also simulated the polymer chain models of PTOBDME surrounded by different solvents, such as water and chloroform, with Cerius² by applying Monte Carlo simulation techniques based on the Flory-Huggins theory [10].

A model for the homopolymer $[PTOBDME]_{33}$ molecule was constructed. Models for water and chloroform molecules were also built, all based on the Dreiding-II force field. Energy was minimized for all the models. Partial charges were then calculated for the models, and the energy was minimized again using the Dreiding-II force field.

The polymer molecule was sketched or loaded in the solvent molecule, with the polymer treated as a chain fragment, acting as blocking atoms in the Monte Carlo simulation.

Interaction energies E_{11} , E_{12} , E_{21} , and E_{22} for all possible interactions $[PTOBDME]_{33}$ - $[PTOBDME]_{33}$, $[PTOBDME]_{33}$ -solvent, solvent- $[PTOBDME]_{33}$, and solvent-solvent were then calculated. Energy distributions were plotted for

all possible pairings, noting the equivalence of E_{12} and E_{21} . Further, coordination numbers Z_{11} , Z_{12} , Z_{21} , and Z_{22} were computed from model clusters.

Miscibility is determined by the energy of mixing: $\Delta E_{\text{mix}} = E_{12} - 0.5(E_{11} + E_{22})$. Energy of mixing was determined as a function of T . E_{mix} is dominated by local interactions between polymer segments and solvent molecules and hence is closely related to the Flory-Huggins interaction parameter $\chi_{\text{FH}}^{(15)}$, chi, which is also a function of T .

$$\chi_{\text{FH}} = Z_{ij} V_{\text{seg}} (\Delta E_{\text{mix}} / RT)$$

Figure 15 shows these variables for a poly[PTOBDME]₃₃ fragment surrounded by water molecules. In Fig. 16, the same calculation results are present for PTOBDME dispersed in chloroform. Comparing the behavior of PTOBDME

Figure 15. Interaction parameter, mixing energy, and coordination number of poly[PTOBDME]₃₃ dispersed in water.

Figure 16. Interaction parameter, mixing energy, and coordination number of poly[PTOBDME]₃₃ in chloroform.

when dispersed in water and chloroform, we observe a tendency for the interaction parameter χ_1 of the polymer in chloroform to increase with temperature, while a decrease is obtained for the same variable in water. This would agree with the acceptable solubility of PTOBDME in chloroform and the highly hydrophobic character of PTOBDME.

The mixing of PTOBDME also shows opposite conduct between the two studied solvents. Hence, the model is able to forecast the opposite behavior for PTOBDME in chloroform versus water.

CONCLUSIONS

Helical cholesteric molecules were modeled for the polymer PTOBDME by molecular mechanics, systematic CA, and MD to explain its chiral behavior.

The monomer models adopted torsional values, with minimum energy obtained by CA. After energy minimization of the whole molecule, secondary minimum energy values were also adopted by the torsions, causing the monomer to adopt a U-shape. These models are appropriate to simulate macroscopic properties experimentally observed. Crystal packing was simulated in cells, with the parameters **a** and **b** obtained from the experimental XRD and with **c** calculated from theoretical "polymerization." Molecules were oriented with their main chains parallel to the **c** axis. Calculated XRD patterns from these models were in good agreement with the observed one. The morphology calculated from the simulated crystals was able to reproduce the rhombohedral shape of crystals observed by optical microscopy dispersed in the cholesteric mesophase matrix.

FT-Raman spectra of PTOBDME were analyzed in detail, both in the solid state and when dispersed in different solvents (water, chloroform, and deuterated dimethyl sulfoxide). Evidence for the self-associating nature of the cholesteric liquid crystal PTOBDME in aqueous media, observed by fluorescence, was obtained from Raman spectra; changes in the structural marker bands of both aliphatic and aromatic moieties in chloroform reflect a conformational change in this solvent. Simulation of the interaction parameter and mixing energy of PTOBDME in water and chloroform confirms this behavior and the highly hydrophobic character of PTOBDME. It also explains the acceptable solubility of PTOBDME in chloroform.

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REFERENCES

1. Pérez-Méndez, M.; Marco, C. New Synthesis, Thermal Properties and Texture of Cholesteric Poly[oxy(1,2-butene)oxycarbonyl-1,4-Phenyleneoxycarbonyl-1,4-phenylenecarbonyloxy-1,4-phenylenecarbonyl], PTOBEE. *Acta Polym.* **1977**, *48*, 502–506.
2. Marco, C.; Pérez-Méndez, M. Kinetics of Isothermal Crystallization of Thermotropic Polyester Poly[ethylethylene-4,4-diphenoxyterephthalate]. *J. Thermal Anal.* **1998**, *53*, 35–47.
3. Pérez-Méndez, M.; Marco Rocha, C. Process for Obtaining Cholesteric Liquid Crystals by Stereoselective Recrystallization. US Patent 6165382, December 26, 2000.
4. Purdie, N.; Brittain, H. G. Analytical Applications of Circular Dichroism. In *Tech-*

- niques and Instrumentation in Analytical Chemistry*; Purdie, N.; Brittain, H.G., Eds.; Elsevier: Amsterdam, 1994; Vol. 14, 104–108.
5. Fayos, J.; Pérez-Méndez, M., to be published.
6. Boerio, F.J.; Bahl, S.K.; McGraw, G.E. Vibrational Analysis of Polyethylene Terephthalate and Its Deuterated Derivatives. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1029–1046.
7. Benedetti, E.; Galleschi, F.; Chiellini, E.; Galli, G. Infrared Study of Phase Transitions in Thermotropic Liquid Crystal Polyesters. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 25–37.
8. Wong, P.T.T.; Siminovich, D.J.; Mantsch, H.H. Structure and Properties of Model Membranes: New Knowledge from High-Pressure Vibrational Spectroscopy. *Biochim. Biophys. Acta* **1988**, *947*, 139–171.
9. Pérez-Méndez, M.; Fayos, J.; Mateo, R. Self-Assembly of Cholesteric Liquid Crystal Polyesters and Their Stereoselective Interaction with Liposomes of DMPC. In *Advances in BioChirality*; Pályi, G., Zucchi, C., Caglioti, L., Eds.; Elsevier Science S.A.: Oxford, UK, 1999; chap. 24.
10. Flory, J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

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