6448 *Macromolecules* **2007,** *40,* 6448−6453

Molecular Modeling of the Intermediate Smectic Mesophase in Polyethylene Terephthalate

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Received March 12, 2007
Revised Manuscript Received July 30, 2007

1. Introduction. Early models of the staged ordering in PET described by Bonart[1−3] remained largely unnoticed until comparatively recently when Keller underlined the thermodynamic grounds for mesophases being favored in an intermediate step in the crystallization of polymers.[4] While PET is one of the most studied polymers, most previous structural studies of crystalline polymers have concentrated on rigid rod liquid crystalline systems such as HBA/HNA. These differ from the PET/PEN system in having extended chains and forming lamellar crystallites of large lateral dimensions. Models of the structure of liquid crystalline random copolymers have taken this morphology into account. In the NPL model of Windle et al.,[5] crystallites were formed by segregation and matching of similar random sequences. It was suggested that the small crystallites were conformationally ordered and consisted of laterally matched sequences of the random chains. This structure was referred to as a non-periodic layer crystallite or NPL. This means that an NPL model is formed over sections of adjacent chains containing the same, but random, sequence arranged in a structure without long periodicity in the chain direction but with crystalline order between the chains.[6]

In the models of Biswas and Blackwell[7−9] ester groups on neighboring chains come into register on or with a distribution about a certain plane, giving rise to a crystallite with some 3D order. The crystalline order decays on moving away from the register plane. In both models, regions of register and unregister were the main difference between the amorphous and the crystalline material since the liquid crystalline polymers have straight chains.

In PET, PEN and indeed their 50% random copolymer small crystallites of the order of 100 Å are separated by entangled amorphous material as indicated by the amorphous halo in the diffraction fiber patterns. When modeling such a system, it is only necessary to consider the chains within the crystallites. The amorphous material may be disregarded, as it does not contribute to the crystal scattering in the fiber diffraction patterns.[10] X-ray fiber diffraction from the 50% PET/PEN random copolymer fibers, shown in an earlier study[10] indicates a greater degree of 3D order than is observed in HBA/HNA liquid crystalline random copolymers that was reported by Biswas et al.[8] Also the detailed experimental wide and small angle fiber diffraction patterns of PET[5] and the effect of the mesophase on the mechanical behavior of the fiber[12] is explained elsewhere.

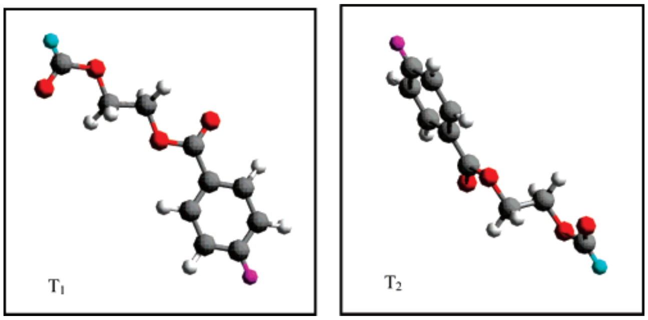

Figure 1. Two molecular models of PET monomer in an energy minimized state as suggested by Nicholson et al.[22] T_1, fully extended and T_2 showing the ethylene bond dihedrals rotated by 80° out of the plane of the benzene ring.

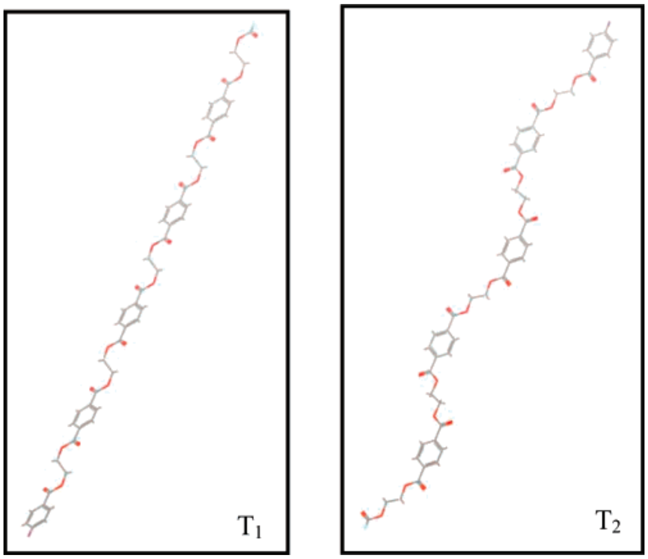

Figure 2. Molecular models of T_1 and T_2 PET chains after energy minimization each composed of 5 monomers.

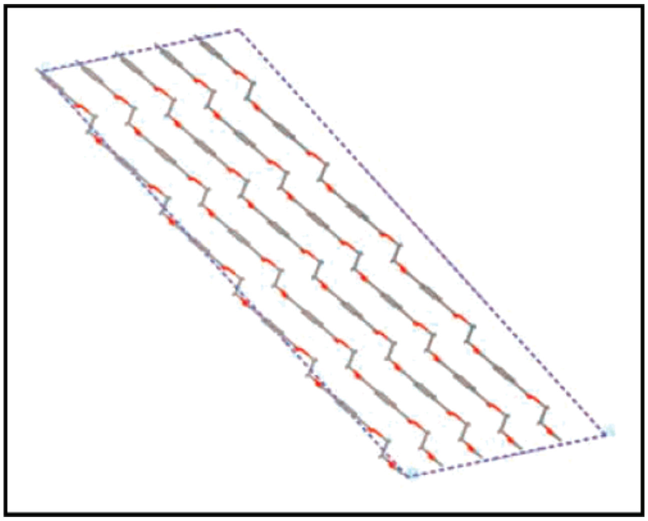

Figure 3. Molecular models PET in a triclinic crystal after energy minimization. It is obvious from the model that there is a kink in the chains even after orientation. The *c*-axis is parallel to the long side of the crystal.

Diffraction pattern simulations for HBA/HNA random copolymers based on perfect plane start or NPL models give sampling on every layer line.[8,13] This is also true for diffraction patterns from models of PET/PEN random copolymer crystallites built using these methods.[14,15] Welsh et al.[16,17] developed a model for PET/PEN random copolymers in which the chains were made up of a set of random sequence of monomers. The chains, initially in random register were allowed to move axially

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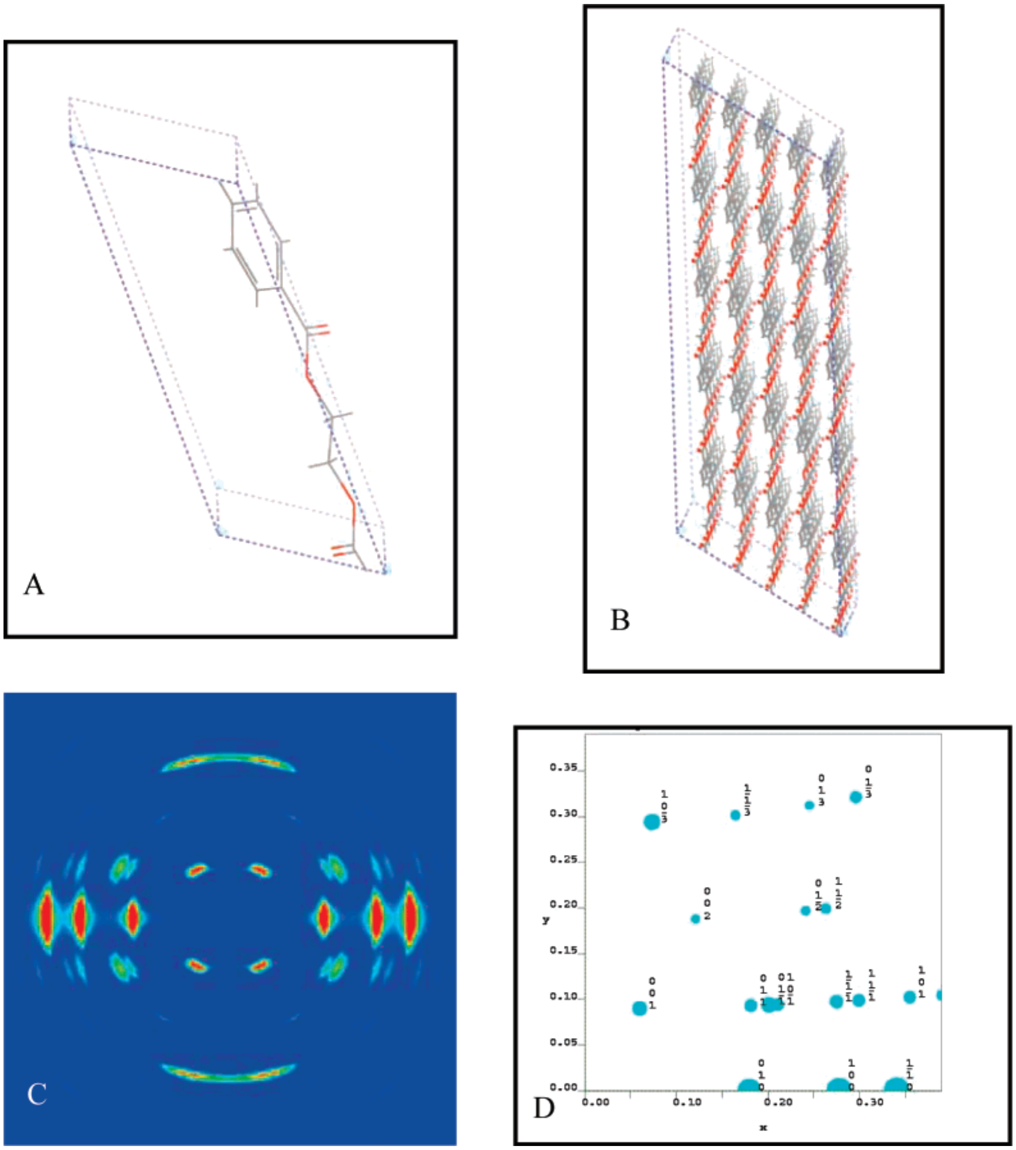

Figure 4. Molecular models of PET in the fully extended conformation, T_1, in a triclinic crystal (A and B) and the simulated diffraction pattern, real (C) and simple indexed (D), showing the absence of the mesophase reflection on the meridian.

into position where they had greater register with neighboring chains. The need for the chains to come into register was seen as being driven by the *"like likes like"* principle, by which it is energetically favorable for aliphatic and aromatic groups to line up with corresponding groups in neighboring chains.

The aim of this paper is to build an atomistic molecular model for the liquid crystalline transient mesophase and the crystalline state, calculate a 2D diffraction pattern in each case and compare them to the experimental results discussed earlier.[11] This will help us to visualize and understand the degree of order present in the mesophase and how might it lead to tilting in PET as reported by Welsh[16] in trying to understand the effect of horizontal register on the crystallinity of such systems.

2. Molecular Simulation Procedure. One of the most efficient molecular simulation software packages is *Cerius^2* supplied by *accelrys*. This software has been used to model liquid crystal polymers on a different length scale by Goldbeck-Wood et al.[18] and by Ishaq et al.[19] to investigate the structure of copolyester prepared from p-hydroxybenzoic acid, biphenol and terephthalic acid.

In this study the monomers, and the crystals were built within *Cerius^2* and the simulated diffraction patterns were produced. The steps involved in this process are summarized as follows:

1. The monomer units were built first using the *Polymer Builder*. PET in the T_1 conformation was directly loaded from the model library, while PET in the T_2 conformation was built using the *Three-Dimensional Sketcher* first and then added to the library afterward.

2. The conformational energy of the monomers was minimized using the Universal Force Field, UFF, under *Smart Minimizer* and found in the *Off Methods* menu. The UFF is recommended for organic molecules. The *Smart Minimizer* is the default energy minimization routine in *Cerius^2* that uses a combination of methods, starting with the steepest descent method, followed by the adopted basis Newton Raphson (ABNR) method, the quasi Newton methods, and ending with the accurate truncated Newton method.

3. The *Polymer Builder* interface was used to build the homopolymer from both conformations. The total energy of the chain was minimized again using the UFF with the same procedure explained in the previous step.

4. The *Crystal Builder interface was then used to build the PET crystals with the unit cell parameters given by Daubery et al.*[20] Afterward the visualization option was used to visualize certain number of crystals, so that the model contains 25 chains, and each chain is five monomers long.

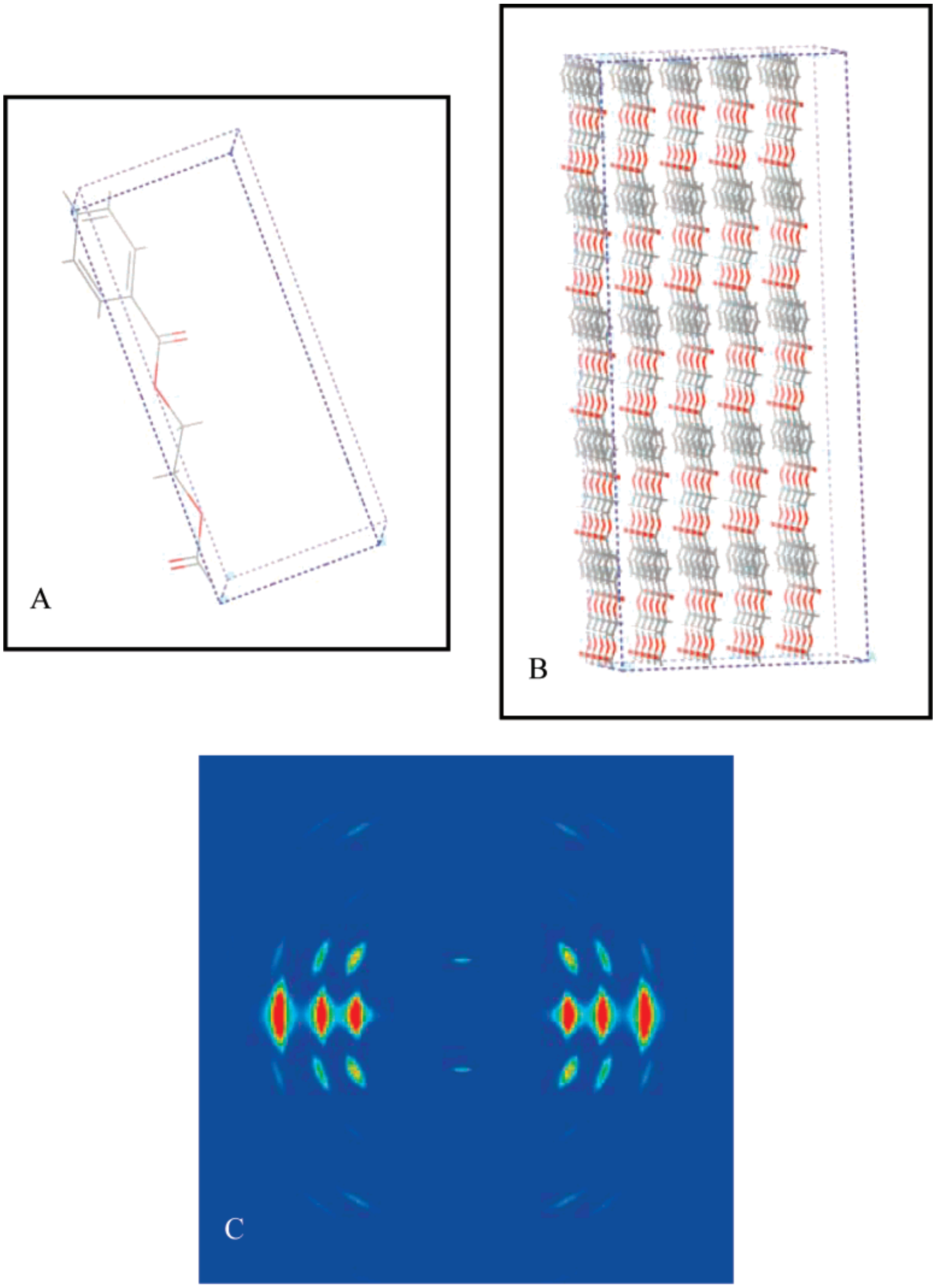

Figure 5. Molecular models of PET in the fully extended conformation, T_1, in an orthorhombic crystal (A and B) and the simulated diffraction pattern (C), showing a very obvious mesophase reflection on the meridian.

5. A crystalline superlattice was then built by removing the borders between the cells formed in the previous step. The program uses the charge equilibrium method described by Rappe and Goddard[21] in order to set the whole charge of the system to zero.

6. The COMPASS, condensed-phase optimized molecular potentials for atomistic simulation studies, version 98.01, force field was used for energy minimization of the whole super crystal lattice using the *Off Instruments* menu. It is a force field enabling accurate and simultaneous predictions of structural, conformational, vibrational, and thermophysical properties of a broad range of molecules and is especially recommended for polymer systems.

7. The resulting super crystal lattice was used to calculate the crystalline diffraction. The two-dimensional X-ray fiber diffraction pattern was calculated with the display range set from a 2θ value of 5 to 40°. The 2θ value is related to the d spacing and the d^* (reciprocal of d) through the Bragg equation:

$$d^* = \frac{1}{d} = \frac{2 \sin \theta}{\lambda} \tag{1}$$

where d is the perpendicular spacing between the lattice planes and λ is the wavelength.

8. The X-ray wavelength was set to be 1.54178 Å as the experiments explained earlier.[10,12] The simulated crystal diffraction was calculated as a flat plate type pattern after specifying the crystallite size in the a, b, and c directions.

Two display modes are used in displaying the diffraction patterns:

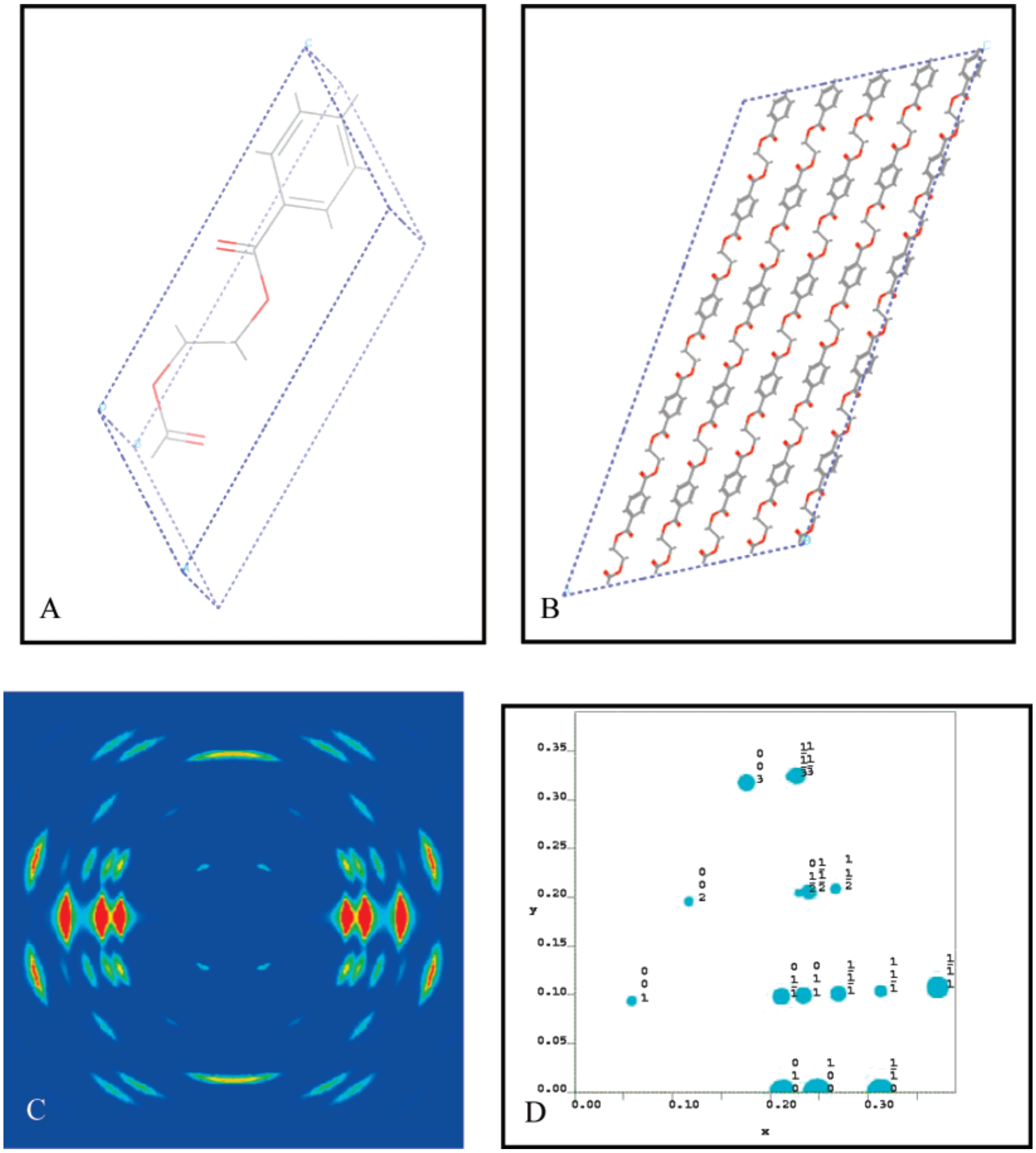

Figure 6. Molecular models of PET in strained conformation, T$_2$, in a triclinic crystal (A and B) and the simulated diffraction pattern, realistic (C) and simple indexed (D), showing the absence of the mesophase reflection of the meridian.

(i) Simple, where reflections are shown as circles with areas proportional to intensities.

(ii) Realistic, where reflections are smeared using crystalline size and orientation distribution value. The orientation distribution of the crystallites can be described by the half-width at half-height of the crystalline orientation distribution function. This distribution was taken to be Gaussian and centered on the fiber axis.

The intensity of the *hkl* reflection is calculated using the following relation:

$$I_{(hkl)} = [\sum f_n \cos 2\pi(hx_n + ky_n + lz_n)]^2 + [\sum f_n \sin 2\pi(hx_n + ky_n + lz_n)]^2 \quad (2)$$

where f_n represents the scattering factor of atom n, and x_n, y_n and z_n are the fractional co-ordinates to the atom n. The summation is done over all atoms in the crystalline super lattice.

3. Modeling of the PET Monomers. Nicholson et al.[22] suggested the presence of two stable molecular models for PET, one in which the monomer, and accordingly the chain, is fully extended (T$_1$) and the other where the ethylene dihedral bond is rotated outside the plane of the benzene ring by an angle of ± 80° (T$_2$). Both models were considered, as shown in Figure 1. It is clear that the fully extended conformation has "all trans" bonds, while the kink introduced in the second "strained" conformation leads to a difficulty in building a straight chain as shown in Figure 2. It has to be mentioned here that PET is not highly planar and the ethylene link is out of the plane of the benzene ring in the energy minimized conformation as shown in Figure 3.

3.1. Modeling of Crystalline and Smectic Order in PET. PET triclinic crystals were built using the crystal lattice parameters determined by Daubery et al.,[20] $a = 4.56$ Å, $b = 5.94$ Å, $c = 10.57$ Å, $\alpha = 98.5°$, $\beta = 118°$, and $\gamma = 112°$. They suggested that one chain passes through each unit cell. Both conformations suggested by Nicholson, T$_1$ and T$_2$[22] were used in the modeling exercise. The smectic order was simulated by building orthorhombic crystals using the same *a*, *b*, and *c* values determined by Daubery et al.[20] but setting the angles: α, β, and γ to 90°. This method of course does not get rid of the crystalline reflections but was adopted to show that the

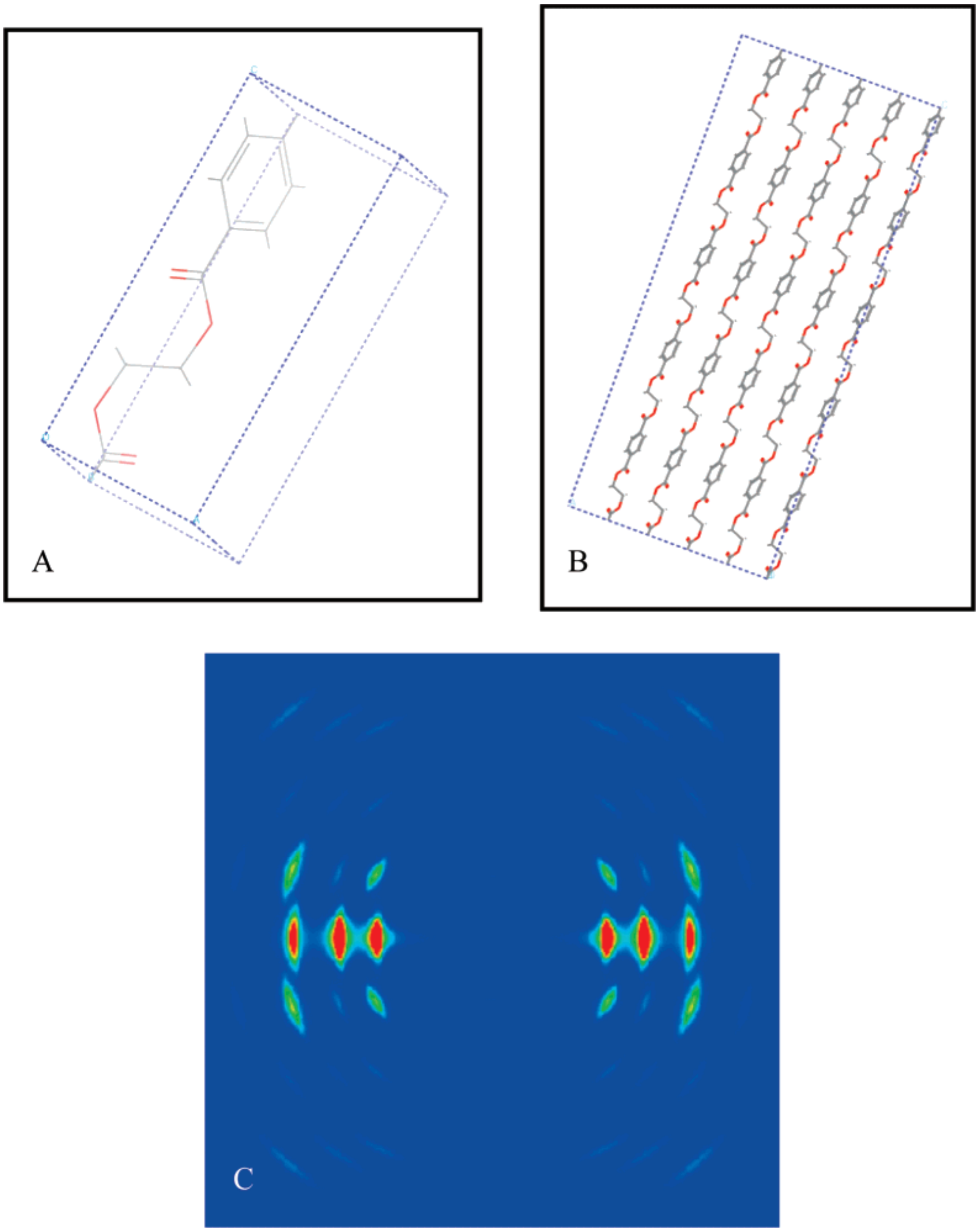

Figure 7. Molecular models of PET in the strained conformation, T_2, in an orthorhombic crystal (A and B) and the simulated diffraction pattern (C), showing the absence of the mesophase reflection on the meridian.

Figure 8. Molecular structure of the T_2 conformation of PET showing (A) the possibility of the formation of two intramolecular hydrogen bonds (represented by the blue dotted lines) in each monomer and (B) the plane passing through all the carbon and oxygen atoms, and the two hydrogen atoms forming the hydrogen bond in the monomer. This results in the formation of two *pseudo* six-membered rings with electron density approximately equal to that of the phenyl group resulting in a sharp decrease of the WAXS contrast of the meridional mesophase reflection.

presence of register perpendicular to the plane of the benzene rings in the chains is a crucial factor in the observation of the smectic reflection on the meridian.

The simulated diffraction of T_1 PET triclinic crystals shown in Figure 4 resembles to a great extent that obtained experimentally and reported earlier.[11] *Cerius*^{2} was used to index all the reflections as shown in the simple diffraction pattern presented in Figure 4D. The indexing shows ideal matching with that reported earlier by Welsh[16] based on the experimental diffraction data.

However, the orthorhombic crystal, illustrated in Figure 5, shows a very sharp and intense reflection on the meridian at a *d* value of 10.57 Å. It is quite clear from the simulated diffraction pattern that the meridional mesophase reflection is a result of the electron density difference along the chains when the horizontal register planes are perpendicular to the chain direction, i.e., the draw direction in the experimental context.

Simulating the diffraction pattern from the T_2 PET triclinic crystals as shown in Figure 6 yields a diffraction pattern that still shows great resemblance to the experimental pattern but, with additional reflections that are not observed experimentally and more intense reflections in the higher layer lines. The main differences in the diffraction patterns observed from the T_1 and T_2 structures can be seen by comparing Figures 4D and 6D. These differences appear to be mainly in the equatorial reflections resulting from the larger lateral distance separating the chains.

On the other hand simulating the diffraction pattern from an orthorhombic crystal with T_2 PET does not show any mesophase meridional reflections as illustrated in Figure 7. This can be explained by carefully examining the T_2 conformation; it is clear that the presence of PET in this conformation might lead to hydrogen bond formation along the chain between the carboxyl and ethylene groups causing the formation of two *pseudo* six-membered rings along each monomer unit and leading to the absence of any electron density difference along the polymer chain that can be picked up through wide-angle X-ray diffraction. This proposed structure is shown in Figure 8. Similar behavior was observed for other polyesters and reported by Donald and Windle.[23]

4. Conclusions. This brief molecular modeling study serves as an exploratory study on the development and existence of the smectic and crystalline phases of oriented PET. The main goal is to compare the simulated diffraction patterns with the experimental ones and as a tool by which indexing of the different reflections is possible. The molecular modeling results obtained in this communication clarify the following points:

1. The meridional mesophase reflections are a result of a smectic-A type arrangement of the polymer chains prior to crystallization. This kind of arrangement, by definition, requires the presence of register planes, perpendicular to the chain direction.

2. Molecular modeling of the diffraction pattern from the triclinic crystals of PET shows the resemblance with the experimental data.[11]

3. The existence of PET chains in the fully extended stiff conformation is responsible for the liquid crystalline transient mesophase reflection, while puckered strained conformations would not lead to the observation of the liquid crystalline smectic arrangement upon orientation.

4. PET chains in a strained conformation do not show the meridional mesophase reflection due to equal electron density along the PET chain as illustrated in Figure 8. This might be the cause of the difficulty in obtaining the mesophase in PET samples by quenching as discussed in our earlier publications.[10−12]

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MA070604O