Communication

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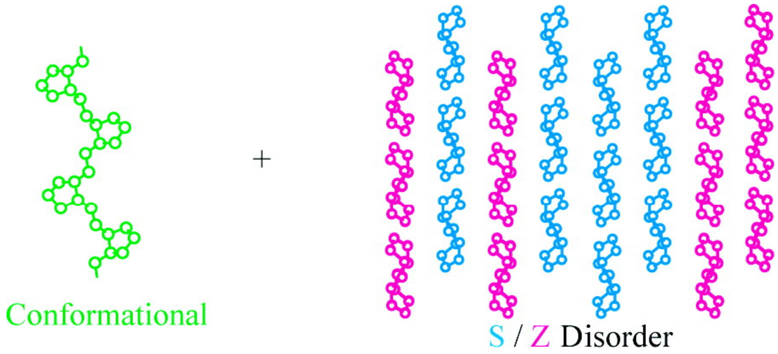

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Alternating Isotactic Ethylene−Cyclopentene Copolymer: A Crystalline Engineering Plastomer Including High Amounts of Structural Disorder

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Cyclo-olefin copolymers (COCs) represent a class of thermoplastic materials of growing interest, with mechanical and physical properties ranging from those of amorphous glasses to those of thermoplastic elastomers.[1] Use of metallocene/ methylalumoxane (MAO) catalysts has allowed obtaining COCs with unprecedented microstructures and properties. The rational choice of the metallocene catalyst precursors allows varying the microstructure of COCs from statistical to alternating and from atactic to fully stereoregular.[1] Using living titanium catalysts, Coates et al. have also obtained multiblock copolymers of ethylene with cyclopentene and other cycloolefins.[2] The properties of these materials depend not only on the nature of cycloolefin but also on composition, sequence distribution of comonomeric units, and stereoregularity. While random ethylene−cycloolefins copolymers are amorphous glasses with a wide range of glass-transition temperatures, good thermal stability, and chemical resistance, alternating ethylene−norbornene copolymers are crystalline materials, independent of the type and degree of stereoregularity, with good transparency and high melting temperatures.[3]

Natta first reported the alternating copolymerization of ethylene (E) and cyclopentene (C) with vanadium-based Ziegler−Natta catalysts.[4] The crystallinity of this copolymer was taken as evidence for the regularity of the chemical and steric structure. It was recognized that the catalytic species acts through a cis opening of the double bond, and a meso-diisotactic microstructure was proposed based on X-ray diffraction analysis.[4]

Coates et al. recently prepared an isotactic alternating ethylene−cyclopentene copolymer (ECC) by an indirect route involving stereoselective ring-opening metathesis (ROMP) followed by hydrogenation.[2] The copolymer obtained by the ROMP mechanism is a highly crystalline product with melting temperature of 185 °C.

The increased control over the microstructure and physical properties of ECCs, achieved by using different catalysts and synthetic routes,[2,5] has refocused the interest for the structural studies of this novel class of engineering plastomers, aiming at building correlations between molecular structure and properties. In this communication, we propose for the first time a model of the crystal structure of alternating isotactic ECC and show how the presence of a high degree of disorder allows maintenance of crystallinity.

A strictly alternating, meso-diisotactic ethylene−cyclopentene copolymer sample has been obtained by ROMP of bicyclo[3.2.0]-hept-6-ene using a chiral molybdenum carbene complex and successive hydrogenation of the unsaturated polymer.[2] The high molecular weight polymer exhibits a high degree of tacticity and high melting temperature (184 °C).

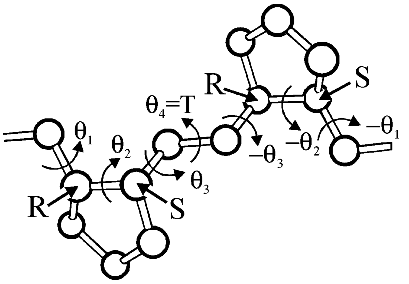

Figure 1. Portion of isolated meso-diisotactic chain of alternating ethylene−cyclopentene copolymer including a pair of cyclopentene rings in twist conformation related by an inversion center placed in the middle of the CH_2-CH_2 bond of the ethylene unit. The absolute configuration of enantiomeric centers RS RS is indicated.

From the X-ray fiber diffraction pattern of compression-molded films a value of the chain axis period of 9.0 Å has been determined, in agreement with the value found from fibers of Natta's ECC samples.[4] The presence of strong meridional reflections on the second and fourth layer lines indicates that two ethylene and two cyclopentene units are included in the chain axis period.

Chains of alternating stereoregular ECC exhibit a ditactic structure due to the regular relative configuration of the two tertiary carbon atoms of a cyclopentene ring (meso or racemo) and the relative configurations of the same atoms in two successive cyclopentene units (isotactic or syndiotactic).[6]

The conformation of the polymer chains in the crystalline state may be defined, using the equivalence principle, in term of its symmetry, which must be compatible with the chemical constitution and configuration.[6] The meso-diisotactic structure of ECC chains is compatible with the presence of an inversion center in the middle of the CH_2-CH_2 bonds of the ethylene units (Figure 1). A possible line repetition group compatible with the experimental chain axis period of 9.0 Å and the identical repetition every two EC constitutional units is $\mathbf{t}i$, corresponding to a succession of torsion angles $(\theta_1\theta_2\theta_3\mathrm{T}-\theta_3-\theta_2-\theta_1\mathrm{T})_n$.

Conformational energy calculations performed on the cis isomer of 1,2-diethylcyclopentane as a model of the cyclopentene ring have indicated that the five-membered ring undergoes small but significant deviations from planarity, spanning a large number of conformations, having a local C_2 (twist) and C_s (envelope) symmetry.[7] The interconversion barrier among the various conformers is ∼12 kJ/mol for *cis*-1,2-diethylcyclopentane, whereas it is close to zero for cyclopentane.

Low internal energy models of the conformation of ECC chains in the crystalline state with $\mathbf{t}i$ symmetry corresponding to $(\mathrm{T}_3\ \theta_2\ \mathrm{T}_3\ -\theta_2)_n$, have been found (Figure 2). The value of θ_2 is included in the range −50 to +50° and depends on the conformation of the cyclopentene rings (twist, envelope, or any intermediate one). The chain axis period is in all cases close to the experimental value of 9.0 Å, regardless of the value of θ_2. This suggests the presence of a high amount of conformational (dynamic) disorder of ECC

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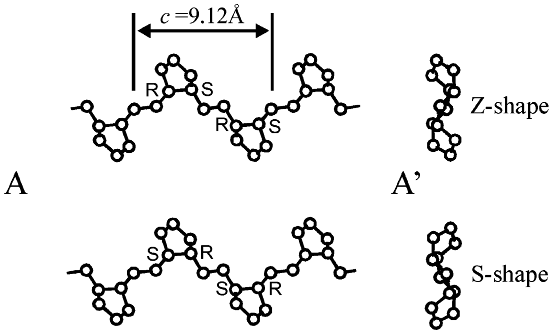

Figure 2. Side view (A) and projection along the chain axis (A′) of the minimum energy conformation with **t***i* symmetry of alternating diisotactic ECC chain in the crystalline state. The chain conformation is $(T_3G^+T_3G^-)_n$ with a chain axis period of 9.12 Å. The sequence of configurations of tertiary carbon atoms in consecutive cyclopentene rings may be $(RS)_n$ or $(SR)_n$, yielding a projection along the chain axis characterized by Z- or S-shape, respectively.

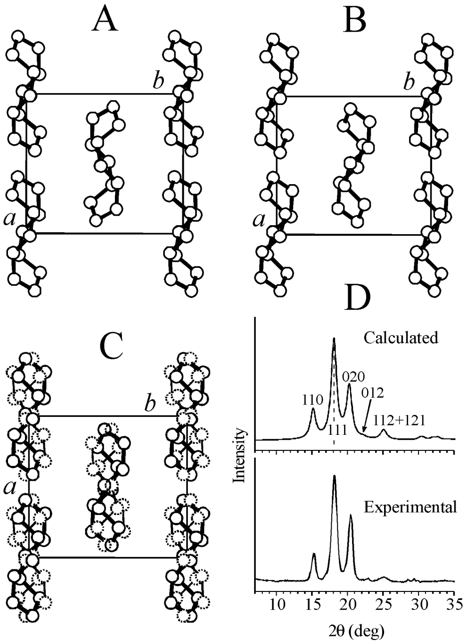

Figure 3. Limit-ordered (A,B) and limit-disordered (C) models of packing of alternating diisotactic ECC chains in the orthorhombic unit cell (a = 7.83 Å, b = 8.76 Å, c = 9.0 Å) according to the space group $P2_1/a$ (b unique axis) (A), $P2_1/n$ (c unique axis) (B), and the statistical space group *Pcan* (C). In each site of the lattice, S and Z chains may be present with the same probability (statistical S−Z disorder). (D) Comparison between the X-ray powder diffraction profile calculated for the limit-disorder model C and the experimental profile (Cu Kα radiation). The Miller indices of the main reflections are indicated.

chains in the crystals, due to the low barrier of interconversion among conformations of cyclopentene rings, analogous to other crystalline polymers containing cyclopentane rings along the main chain[8a] or as side groups.[8b]

Possible models of packing of ECC chains in the orthorhombic unit cell with axes a = 7.83 Å, b = 8.76 Å, and c = 9.0 Å are shown in Figure 3. In the limit-ordered model of Figure 3A, *ac* layers of chains having alternatively Z- and S-shape are stacked along b and shifted by **a**/2 according to the space group $P2_1/a$ (b unique axis). The limit-ordered model of packing shown in Figure 3B is similar to that of Figure 3A, but the chains have the same Z- or S-shape (space group $P2_1/n$, c unique axis). The limit-disordered model of Figure 3C corresponds to the statistical substitution of chains having S- and Z-shape, in each site of the lattice, and may be described by the statistical space group *Pcan*. This statistical substitution is feasible because two chains with S-shape and Z-shape have the barycenters of the cyclopentene rings approximately in the same positions, according to an ideal long-range order.

The best agreement between calculated and experimental diffraction patterns has been obtained for the statistical model of Figure 3C (Figure 3D).

We propose that different kinds of disorder (conformational and statistical S−Z) are simultaneously present in the structure. The real crystalline modifications are intermediate between the limit-ordered and limit-disordered models. While the amount of S−Z structural disorder most likely depends on the microstructure of the chains and on the conditions of crystallization of the sample, the conformational disorder of the rings is always present owing to the low interconversion barrier of cyclopentene rings between twist and envelope conformations. This disorder is dynamic and may be reduced only at low temperatures.

This structure provides an example of a new concept in polymer science that crystallinity may not be destroyed by the presence of high degrees of conformational and packing disorder and the absence of long-range order.

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Supporting Information Available: Experimental and calculation methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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