Crystalline Ethylene−Norbornene Copolymers: Plastic Crystals from Macromolecules

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Plastic crystals are characterized by positional order but orientation disorder of the structural motif.[1] Molecules of plastic crystals are generally close to spherical so that there is no high-energy barrier to their reorientation. The structure of most plastic crystals is cubic, body- or face-centered,[1a] as expected for crystals of motifs having a spherical or globular shape. Typical examples are provided by the structures of ball-like hydrocarbon molecules such as adamantane[2] or norbornane (at temperatures higher than 306 K).[3] The structural origin of the softness and the ease of deformation of plastic crystals is similar to that of the ductility of metals, being related to the large number of slip-planes in close-packed structures and the relatively weak intermolecular interactions between the motifs.

The X-ray diffraction patterns of plastic crystals show, generally, only a small number of reflections and diffuse scattering due to the presence of orientational disorder. Only a long-range order in the position of the barycenters of the molecules, packed in cubic lattices, is present. For instance, adamantane and norborbane are characterized by face-centered-cubic lattices with a = 9.45 Å and 8.73 Å, respectively.[2,3] The X-ray powder diffraction profile of norbornane is shown in Figure 1a.

The issue of the occurrence of plastic crystals of macromolecules has been extensively discussed in the literature.[4] The condition of a spherical shape of the molecules cannot be fulfilled by linear synthetic polymers, which generally crystallize in extended chains or helical conformations.[5] Even though the crystallization of disordered solid mesomorphic forms, characterized by degrees of order intermediate between the ideal order of crystals and the disorder of the amorphous phase, is a common mode of crystallization of synthetic polymers,[4,6,7] orientationally disordered plastic crystals of polymers have not been described so far. In this paper the "crystallinity" in novel polymeric materials, made of copolymers of ethylene and norbornene, has been analyzed, providing, for the first time, evidence of orientational disorder of the structural motif, as in plastic crystals.

The presence of three-dimensional order ("crystallinity") in samples of ethylene−norbornene (E−N) copolymers[8−11] has been related to an alternating sequence of the comonomers along the polymer chains and a regular succession of configurations of stereoisomeric centers in the norbornene units (stereoregularity).[9]

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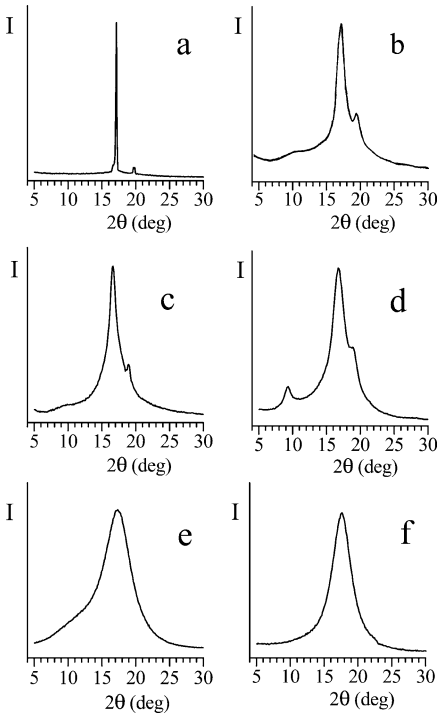

Figure 1. X-ray powder diffraction profiles of norbornane at 40 °C (a), ethylene−norbornene copolymer sample taken from the literature[8] (b), ethylene−norbornene copolymer samples A (c), B (d), and C (e), and liquid norbornadiene (f).

The X-ray diffraction patterns of E−N copolymers, prepared with various metallorganic catalysts, with norbornene contents in the range 40−50 mol %, show a very intense peak with a maximum at 2 sin $\theta/\lambda = 0.186$ Å^{-1} (2θ = 16.7° for Cu Kα radiation). Examples of diffraction profiles of different E−N samples, prepared with different catalysts, are reported in Figure 1 (curves b−e). The profile of Figure 1b corresponds to a sample reported in the literature,[8] whereas the profiles of parts c, d, and e of Figure 1 correspond to three samples A, B, and C, respectively, prepared in our laboratories with different catalysts.[11,12] It is apparent form Figure 1 that the diffraction peak at 2θ = 16.7° may be more or less sharp depending on the sample. The width at half-height of this peak is, indeed, rather large ($\Delta(2\theta) = 4.5°$) in the case of the diffraction profile of sample C (Figure 1e) and similar to that of the halo observed in the X-ray diffraction profile of liquid norbornadiene (Figure 1f), or quite small, $\Delta(2\theta) = 1.6°$, 1.7°, and 2.4° in the case of samples of parts b, c, and d of Figure 1, respectively. The width of 1.6° for the sample of Figure 1b corresponds to microcrystal dimensions of the order of magnitude of 55 Å, as approximately found by the Scherrer formula. In the patterns of Figure 1b−d a second diffraction peak at 2 sin $\theta/\lambda = 0.214$ Å^{-1} (2θ = 19° for Cu Kα radiation) is also clearly observed, whereas in the pattern of Figure 1d of sample B a third peak at 2 sin $\theta/\lambda = 0.105$ Å^{-1} (2θ = 9.3° for Cu Kα radiation) is also present.

The X-ray diffraction profiles of the E−N samples of Figure 1b−d are all reminiscent of the diffraction profiles of plastic crystals, like, for instance, that of norbornane at 40 °C shown in Figure 1a. This suggests that the microcrystals of the alternating E−N copoly-

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mers could be characterized by a similar face-centered-cubic mode of packing, typical of plastic crystals of spherical hydrocarbon molecules. The quite spherical norbornene units could be, indeed, packed in a face-centered paracrystalline lattice having axes $a = b = c \approx 9.30$ Å, $\alpha = \beta = \gamma \approx 90°$,[13] the mean distance between the centers of norbornene units being $(2^{1/2}/2)9.30 \approx 6.57$ Å. In the paracrystalline regions, the polymer chains could be organized locally in fringed micelle bundles.

Evidence of the feasibility of this hypothesis has been obtained by analyzing the X-ray diffraction of oriented fibers of the E−N copolymer samples and studying the conformation of the polymer chains through energy calculations.

Crystalline oriented fiber samples of the E−N copolymer sample A have been obtained by stretching amorphous films at 140 °C and successive annealing of the fibers at 190 °C for 30 min. Amorphous films of the sample A were obtained by quenching the melt in liquid N_2. The corresponding X-ray fiber diffraction pattern indicates that the diffraction peak observed in the powder profiles at $2\theta = 16.7°$ is a first layer line reflection, whereas the second peak at $2\theta = 19°$ is an equatorial reflection. From the fiber pattern the identity period along the fiber axis $c = 8.9 \pm 0.1$ Å has been evaluated, and a quasi-tetragonal unit cell with $a = b \approx 9.4$ Å has been obtained. The calculated crystalline density of 1.04 g/cm^3 is in good agreement with the experimental value of 1.02 g/cm^3. The value of the *c* axis is only slightly different from that of *a* and *b* axes, indicating a quasi-cubic structure.

The presence in the X-ray powder diffraction profile of the sample B of Figure 1d, of the diffraction peak at $d = 9.5$ Å ($2\theta = 9.3°$, Cu Kα radiation), indexed as the 010 reflection, indicates slightly different values of the *a* and *b* axes; from this X-ray pattern we found $a = 9.3$ Å and $b = 9.5$ Å with a similar calculated density of 1.04 g/cm^3.

E−N copolymers with norbornene content in the range 40−50 mol % may contain various types of constitutional and configurational units.[14] In the alternating chain, the configuration of the two chiral backbone atoms in each (E−N−E) unit is always SR or RS (Figure 2), in accordance with a constant *cis*−*exo* insertion of norbornene molecules.[14] The corresponding (N−E−N) diads may be *meso* or *racemic* (Figure 2). If all the diads along the chain were *meso*, the alternating copolymer would be *isotactic*, whereas if all the diads were *racemic*, the alternating copolymer would be *syndiotactic*. The [*meso*]/[*racemic*] ratio may be different depending on the copolymer sample, according to the catalyst and the method of preparation. Sample A is an alternating copolymer with a [*meso*]/[*racemic*] ratio 1.1/1, whereas sample B is an alternating copolymer with prevailingly *meso* configurations, that is, basically isotactic.[11,12]

Conformational energy calculations performed on the portion of the E−N copolymer chain of Figure 2 (N−E−N sequence) have shown that low-energy conformations are possible for either *meso* or *racemic* diads. Wide energy minima have been obtained for values of the torsion angles (defined in Figure 2) $\theta_1 = -\theta_3 = 177°$, $\theta_2 = -174°$, $\theta_4 = 0°$ for the *meso* diad of Figure 2B and $\theta_1 = \theta_3 = 174°$, $\theta_2 = -172°$, $\theta_4 = 0°$ for the *racemic* diad of Figure 2C.

For these energy minimum conformations, the distance between barycenters of the norbornene units is 6.4−6.5 Å, and the space encumbrance is similar for the four different diads; the projections along the C−C bond of the ethylene unit are slightly different, having Z- and S-shapes for the *meso* units and a C-shape for the *racemic* units (Figure 2).

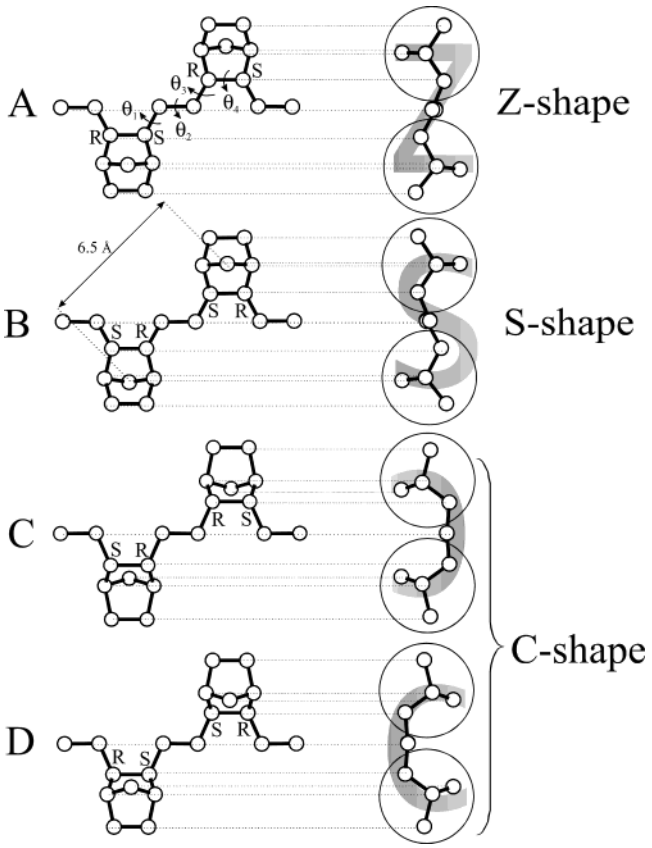

Figure 2. *Meso* (A, B) and *racemic* (C, D) norbornene−ethylene−norbornene (N−E−N) sequences. R and S indicate the configuration of the chiral carbon atoms of the norbornene units. In (A) the definition of the torsion angles θ_1, θ_2, θ_3, and θ_4 is shown. Projections parallel (left) and perpendicular (right) to the C−C bond of the ethylene unit are shown. The atoms of the pseudo-spherical norbornene units are enclosed in circles (right). Depending on the succession of the configurations R and S, the *meso* diads may assume Z- or S-shapes, whereas the *racemic* diads may assume a C-shape with different orientation.

Starting from these models of chain conformation, limit tetragonal (Figure 3A) and orthorhombic (Figure 3B) disordered models of packing of the chains of the alternating copolymers, can be easily built for fully isotactic or syndiotactic configurations of the chains. The few reflections present in the X-ray diffraction patterns allows assuming that in real "crystals" the order rapidly fades away with increasing the distance between the norbornene units, so that the "crystalline" bundles can be better identified as "paracrystalline".[15]

The packing models shown in Figure 3 have been built with regular isotactic macromolecular chains. The comparison between the X-ray diffraction profiles, calculated for the models of Figure 3A,B, and the experimental powder diffraction profiles of samples A and B (Figure 1c,d) is shown in Figure 3C,D, respectively. It is apparent that a good agreement has been obtained for both models; the model of Figure 3A accounts for the diffraction profile of sample A, whereas the model of Figure 3B accounts for the diffraction profile of sample B. The orthorhombic model of Figure 3B having $a \approx 9.3$ Å, $b \approx 9.5$ Å, and $c = 8.9$ Å could be representative of the

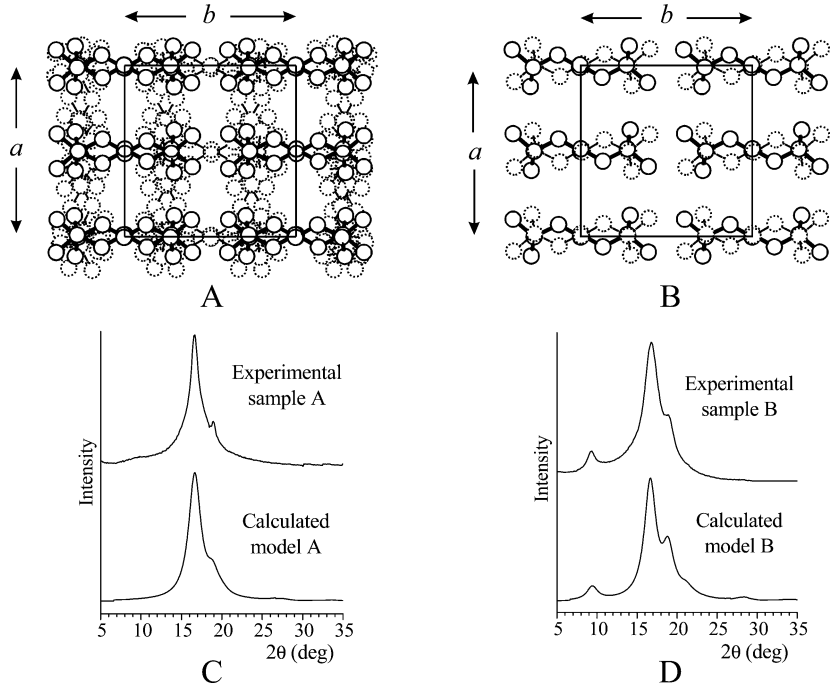

Figure 3. Limit disordered models of packing of alternating isotactic ethylene−norbornene copolymer chains (A, B) and comparison between calculated and experimental X-ray diffraction profiles (C, D). (A) Tetragonal model with $a = b \approx 9.4$ Å and $c = 8.9$ Å. (B) Orthorhombic model with $a \approx 9.3$ Å, $b \approx 9.5$ Å, and $c = 8.9$ Å. In (A), in each site of the lattice isotactic chains with Z- and S-shapes are present with the same probability. Moreover, chains rotated by 90° around the chain axis, leaving the norbornene units basically in the same positions, are shown as dotted lines. In (B), chains with Z-shape (solid lines) and S-shape (dotted lines) occupy lattice sites with the same probability. (C) Comparison between the X-ray diffraction profile calculated for the tetragonal model A and the experimental X-ray powder diffraction profile of sample A (Figure 1c). (D) Comparison between the X-ray diffraction profile calculated for the orthorhombic model B and the experimental X-ray powder diffraction profile of sample B (Figure 1d). The calculated profiles have been obtained with the Cerius program.

paracrystalline bundles in sample B. The tetragonal model of Figure 3A, having $a = b \approx 9.4$ Å and $c = 8.9$ Å, could be representative of the small "crystals" constituting the paracrystalline fringed micelle bundles in sample A, characterized by positional order of the barycenters of the norbornene units and orientational disorder, due to the fact that the chain may connect with equal probability a given norbornene unit with any of its next neighbors.

Whichever the configuration of the diads, all the alternating copolymer macromolecules have a similar shape, which is tolerated in the described regular assembly of norbornene units. The partial three-dimensional order, guided by the ordered positioning of the ball-like norbornene units in a face-centered paracrystalline lattice, is obtained even though the polymers are configurationally disordered, provided that they have a regular alternation of the comonomeric units. The ordered position of the norbornene units is shown in Figure 4. It is apparent that the ball-like norbornene units are organized on a face-centered lattice. In this projection only one of the possible ordered positions of the copolymer chain is shown. As also shown in Figure 3A, the ethylene units, which connect the norbornene units, may assume different positions along *a* and *b* axes, producing orientational disorder of the chains as well as of the quasi-spherical norbornene units, whose barycenters remain organized on the face-centered lattice, producing the strong 111 reflection. The chemical connectivity between the quasi-spherical motifs, through the polymeric chain, produces mechanical properties typical of semicrystalline polymers rather than of plastic crystals, so that the analogy with plastic crystals is mainly related to the structure.

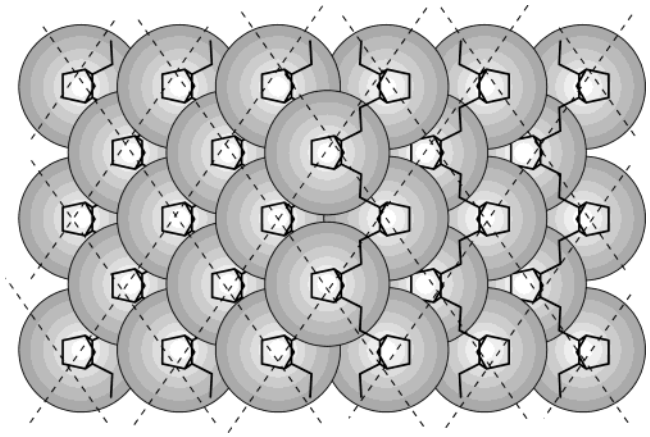

Figure 4. Projection along the *c* axis of the structure of the ethylene−norbornene copolymer, showing the ordered packing of ball-like norbornene units in a face-centered lattice. Only one of the possible ordered positions of the copolymer chain is shown. The dashed lines indicate a family of strongly diffracting (111) planes of the face-centered lattice.

The structural features of the E−N copolymer recall not only the packing of plastic crystals but also that of "ionenes",[16] polymeric ionic salts of general formula $-[-(CH_2)_m-N(R)_2-]_n q.n.X$, where the cationic NR_2^+ and monovalent ($q = 1$) or bivalent ($q = 0.5$) anionic X species are regularly spaced along the main chain. Ionenes may crystallize in pseudocubic tetragonal lattices with ionic sites X and $-NR_2-$ arranged in a regular face-centered lattice.[16] The position of the polymer chain connecting the ammonium groups is disordered, since the chain may connect with equal probability a given N carbon with its eight next neigh-

bors.[16] As in the E−N copolymer, the pseudocubic structure is defined by the packing of spherical motifs, while the arrangement of the polymer chains is interpreted as "random walk". However, a long-range crystalline order is present in ionenes because of the strong electrostatic interactions between cationic NR_2^+ and anionic X groups, whereas only a short-range order is present in E−N copolymers since weak van der Waals interactions among the spherical units are involved.

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References and Notes

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(12) Sample A of the E−N copolymer has been synthesized using a dicarbollide catalyst (η^5-$C_2B_9H_{11}$)Zr[$(N(C_2H_5)_2)_2(NH(C_2H_5)_2]$ activated with Al(^{i}Butyl)$_3$.[11] Sample B has been prepared with the "constrained geometry catalyst" [$(CH_3)_2$Si(3-*tert*-butyl-cyclopentadienyl)(adamantylamido)]Zr(CH_3)$_2$ activated with methylaluminoxane.[11] Sample C has been obtained using [η^5-$C_5(CH_3)_5$]$ZrCl_3$ and methylaluminoxane.[11] Samples A and B have a similar composition of 47 and 49.7 mol % of norbornene units, respectively, and exhibit an alternating structure, as indicated by the ^{13}C NMR analysis,[11] and show similar melting temperatures of 230 °C.[11] Sample C does not present a regular alternating structure.[11]
(13) The value of 9.3 Å for the axis of the cubic lattice has been evaluated assuming that the two diffraction peaks observed in the X-ray diffraction profiles at $1/d = 0.186$ Å^{-1} ($2\theta = 16.7°$) and 0.214 Å^{-1} ($2\theta = 19.0°$) of E−N samples correspond to 111 and 200 reflections, as expected for a face-centered-cubic lattice. Therefore, $a = b = c = d\sqrt{h^2+k^2+l^2} = 5.38\sqrt{3} = 9.3$ Å from the first peak (111 reflection), and $a = b = c = d\sqrt{h^2+k^2+l^2} = 4.67\sqrt{4} = 9.3$ Å from the second peak (200 reflection).
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