Crystal Structure of the Stereoregular Ethylene-*alt*-styrene Copolymer Synthesized with a Zirconocene-Based Catalyst

Leone Oliva, Attilio Immirzi,* Consiglia Tedesco, Vincenzo Venditto, and Antonio Proto

Dipartimento di Chimica, Università di Salerno, via S. Allende, I-84081 Baronissi, Italy

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ABSTRACT: A stereoregular alternating ethylene−styrene copolymer, also stretchable in fiber form, has been obtained with *rac*-isopropylidenebis(1-indenyl)zirconium dimethyldiamide activated by the methyl-alumoxane catalytic system. From X-ray diffraction fiber spectra, an isotactic structure has been assigned to this copolymer as well as the previously described stereoregular ethylene−styrene copolymers. The polymer has zigzag planar chain conformation with phenyl groups oriented perpendicularly to the chain axis. The crystallographic symmetry in *B*2/*m*. Lattice constants (monoclinic, unique axis *c*): *a* = 10.23, *b* = 15.53, *c* = 5.12 Å; *γ* = 98.6°. The disagreement index for measured reflections is R_1 = 0.10.

Introduction

A stereoregular alternating ethylene−styrene copolymer was at first obtained, in a mixture with syndiotactic polystyrene, by Kakugo and co-workers.[1] More recently, in our laboratories it was found that the copolymerization of ethylene and styrene in the presence of *rac*-ethylenebis(1-indenyl)zirconium dichloride and methyl-alumoxane at low temperature affords[2] an alternating stereoregular copolymer whose X-ray diffraction powder spectrum (unoriented samples) and ^{13}C NMR spectrum are similar to those reported by Kakugo et al.[1a] With regard to the tacticity of these copolymers, the latter hypotesized an isotactic structure on the basis of the study carried out by Suzuki et al.[3] on the ^{13}C NMR spectra of hydrogenated poly(phenylbutadienes). Actually the assignment of the resonances to the different stereochemical environments is "not certain and may be interchanged".[3]

A complete analysis of the X-ray diffraction patterns (preferably fiber diffraction patterns) would have been desirable for attributing to this crystalline polymer a certain chain structure. However, the material obtained with the cited catalyst[2] could not be oriented, probably due to the low molecular mass. In order to improve stretchability, we have used a different polymerization catalyst based on an *ansa*-zirconocene compound which has a greater accessibility of the metal atom to the more hindered monomer (styrene). The aim was to obtain the alternating copolymer at higher reaction temperature and, as a consequence, with higher molecular mass. As a matter of fact, we used a catalyst prepared from *rac*-(isopropylidene)bis(1-indenyl)zirconium dimethyl-diamide activated by methylalumoxane since the one-carbon-atom bridge between indenyl moieties, instead of the two-atom bridge of ethylenebis(1-indenyl), should confer the above accessibility. Arai and co-workers were able to synthetize an alternating stereoregular copolymer using a similar compound.[4,5]

Actually, the copolymer obtained with this new catalyst shows a ^{13}C NMR and a powder X-ray diffraction spectrum very similar to those of the previous stereoregular alternating copolymers while the molecular

mass is improved since intrinsic viscosity (see below) is doubled. New samples were actually also stretchable, and oriented samples were obtained. Crystal structure analysis based on the fiber diffraction spectra has been carried out successfully, and the results are reported in this paper.

Experimental Section

Materials. Polymerization grade ethylene was purchased from Società Ossigeno Napoli and used without further purification. Toluene was refluxed for 48 h over metallic sodium and distilled under nitrogen atmosphere. The ethereal solvents (Et$_2$O, DME) were distilled under nitrogen from Na/benzophenone. Styrene was stirred for 1 h over CaH$_2$ at room temperature and distilled under reduced pressure of nitrogen. Methylalumoxane (MAO) was purchased as a 30% toluene solution from Witco and dried in vacuo before the use. Other solvents were used without purification.

Catalyst. *rac*-Isopropylidenebis(1-indenyl)zirconium di-methylamide was prepared as reported in literature[6] by reaction of Zr[N(CH$_3$)$_2$]$_4$[7] with 2,2-bis(1-indenyl)propane. The latter, prepared according to the synthesis reported by Nifant'ev,[8] was obtained as pure yellowish crystals after several crystallizations from methanol (yield 50%).

Copolymerization. The copolymerization was carried out in a 50 mL glass flask charged, under nitrogen atmosphere, with styrene (5 mL) and 500 mg of MAO. The mixture was magnetically stirred and the glass flask thermostated at 20 °C. The inert atmosphere was removed and replaced with ethylene; then 1 mL of a toluene solution containing 3 mg of the zirconocene compound was introduced. The flask was fed with the gaseous monomer at atmospheric pressure for 2 h. Then the reaction mixture was poured in 100 mL of acidified methanol. The copolymerization product recovered by filtration was washed with boiling acetone and dried in vacuo. Yield: 1.2 g.

Viscosity Measurements. The intrinsic viscosity was calculated from viscosity measurements of toluene solutions carried out by using an Ubbelhode type viscometer kept in a thermostatic bath at 50 °C. The result is [η] = 0.49 g dL^{-1}. Previously described samples obtained with *rac*-ethylenebis-(1-indenyl)zirconium dichloride/methylalumoxane[2] gave [η] = 0.27.

^{13}C NMR Analysis. The spectrum of the copolymer dissolved in CDCl$_3$ has been recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode at room temperature. The styrene unit content is 49%

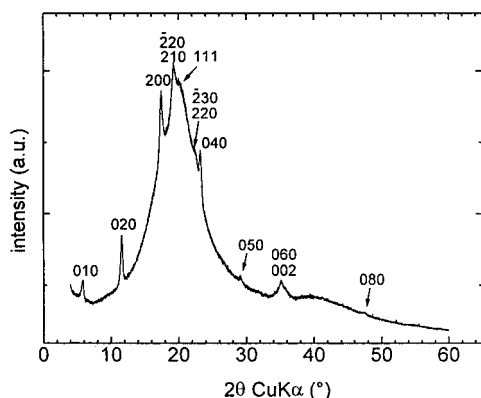* Corresponding author. E-mail: immirzi@chem.unisa.it.

Figure 1. Diffraction spectrum of the unoriented ethylene-*alt*-styrene copolymer recorded by a Philips PW-1700 system using Cu Kα radiation.

and was evaluated on the basis of the relative intensities of the resonances of the secondary carbon atoms.[9]

Density. The crystalline phase density, D_c, was calculated from the densities of semicrystalline samples, D_s, and of amorphous samples, D_a (both measured by flotation in water/glycerine mixtures). According to Tadokoro,[10] $1/D_s = x/D_c + (1 - x)/D_a$, where x is the mass fraction of the crystalline phase. From the values $D_s = 1.02$, $D_a = 1.00$ g cm^{-3}, and $x \approx 0.18$ (from powder diffraction spectra), we obtain $D_c = 1.12$ g cm^{-3}.

X-ray Diffraction Analysis. Wide-angle X-ray powder diffraction spectra were obtained from compression-moulded samples annealed at 110 °C, with Cu Kα Ni-filtered radiation using a PW-1700 Philips powder diffractometer. Oriented fibers were prepared from films obtained either by casting from a THF solution (affording a crystalline material) or by compression moulding (affording an amorphous material). Film strips were stretched at room temperature (draw ratio ∼7:1) and annealed at 110 °C.

Fiber diffraction spectra were recorded using both cylindrical-film techniques (Cu Kα and Cr Kα radiation; photographic recording) and flat-film techniques (Mo Kα radiation; sample-to-film distance 10 cm; Fuji image-plate recording). Measurements of integrated intensities were performed only for reflections visibile in Fuji image-plate spectra, by using the standard software TINA for Fuji film image processing. Structure factors were obtained by applying the appropriate Lorentz−polarization factors.[11]

Data Analysis and Results

X-ray diffraction patterns for unoriented and oriented samples are shown in Figures 1 and 2. Quantitative evaluation of integrated intensities was performed only for reflections visible on the fiber spectrum and recorded with the Fuji image-plate device. Table 1 lists these reflections with assigned indices (see below), observed *d* spacings, and structure factors, in addition to reflections detected in powder or fiber spectra and not measurable. The calculated structure factors (referred to model **B**; see below) and calculated *d* spacings are given for unobserved reflections, also.

The indentity period 5.12 Å, obtained from fiber spectra, suggests a chain structure with all styrene units of the same configuration (isotactic polymer) and with a chain conformation zigzag planar or nearly so.

Although the quality of the fiber spectrum is modest and not all reflections have measurable intensity on the Fuji image plate, it was possible to obtain a monoclinic unit cell having $a = 10.23$ Å, $b = 15.53$ Å, $c = 5.12$ Å, and $\gamma = 98.6°$ with systematic absences of *hk*0 reflections with *h* odd or perhaps of all *hkl* reflections with *h* + *l* odd; the scarcity of nonequatorial reflections makes
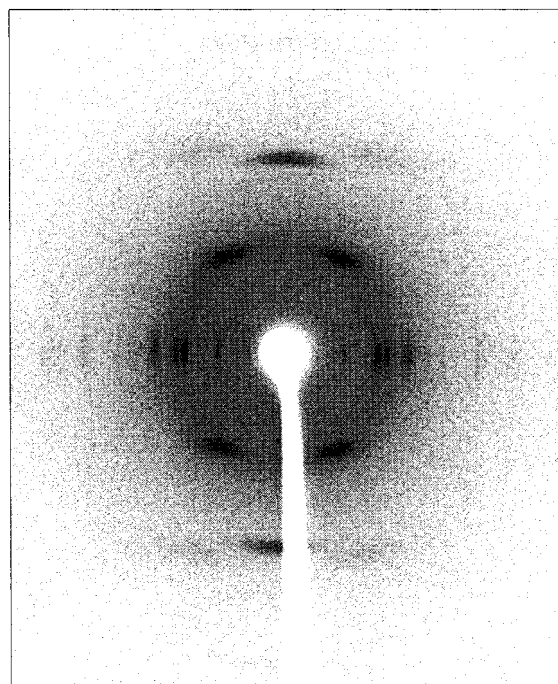

Figure 2. Digital reconstruction of the fiber diffraction spectrum recorded by a Fuji image-plate detector (Mo Kα radiation, flat-film camera, film-to-sample distance 10 cm).

this uncertain. In the former case, the possible space groups are $P2/a$ and $P2_1/a$ (primitives); in the latter case, it is $B2/m$ (base-centered). Since the odd 00*l* reflections are present only in the $P2/a$ case, they could be discriminating. Unfortunately, the tilted-fiber spectra are ambiguous: there is a weak meridional reflection, but indexing is uncertain among 003, 103, 113, and 1̄13.

Since the calculated crystallographic density (1.09 g cm^{-3}) agrees, within the experimental error, with the measured one (1.12 g cm^{-3}) with four $C_8H_8-C_2H_4$ units per cell, the chain must be crossed by a mirror symmetry if the space group is a centered one. In this case, aromatic ring conformation is fixed by symmetry: the rings must lie on a mirror plane.

Structure analysis was approached with the most symmetrical model: a rigid zigzag planar sequence of carbon atoms with bond lengths and angles adjusted so that the identity period is 5.12 Å and the aromatic ring is set perpendicular to the chain axis (see the caption of Figure 3a). The vertical position of the chain is fixed by symmetry and the space group is $B2/m$.

The structure was established by using TRY,[12] an interactive computer program specifically tailored for polymers, which allows structure analysis by systematic application of the trial-and-error method, following the indications of crystal packing, lattice energy, and observed-to-calculated structure factor fitting. TRY makes use of internal coordinates as structural variables. In this case, the variables are three: the overall chain rotation Φ and the chain translations x_0, y_0 along x, y directions. Only if symmetry is lower, are there two other parameters: z_0 translation and the torsion angle of the phenyl groups Ψ.

The evaluation of the lattice energy is performed by TRY as the sum of the van der Waals contributions for all C···C pairs separated by less than 5.30 Å, all H···H pairs separated by less than 3.40 Å and all C···H pairs separated by 4.35 Å. The energy was calculated using the algorithm devised by Halgren.[13]

Table 1. Indexed Reflections, *d* Spacings, and Structure Factors^a

hkl	d_o	d_c	F_o^2	F_c^2	ΣF_c^2
010	15.16	15.34	8	12	
020	7.63	7.67	29	20	
200	5.08	5.06	105	103	103
030		5.11		0	
$\bar{2}$10		5.03		0	
210	4.59	4.60	77	32	77
$\bar{2}$20		4.55		45	
220	3.95	3.96	85	24	115
040	3.83	3.84		41	
$\bar{2}$30		3.90		50	
230	3.39	3.35	b	0	
050	3.07	3.06	12	8	
060		2.56	54	22	30
$\bar{4}$10	2.55	2.56		3	
$\bar{4}$20	2.52	2.52		1	
400		2.53		4	
250		2.46		0	
080	1.91	1.92	18	9	13
$\bar{2}$80		1.89		4	
270		1.91		0	
070		2.19	b	0	
240		2.86	b	0	
260		2.16	b	3	
$\bar{2}$40		3.30	b	32	
$\bar{2}$50		2.82	b	0	
$\bar{2}$60		2.43	b	0	
$\bar{2}$70		2.13	b	3	
410		2.44	b	6	
420		2.30	b	3	
430		2.14	b	4	
450		1.82	b	0	
$\bar{4}$30		2.42	b	22	
$\bar{4}$40		2.27	b	2	
$\bar{4}$50		2.11	b	9	
$\bar{4}$60		1.95	b	0	
$\bar{1}$11		4.46	163	87	144
101		4.57		1	
111		4.30		55	
002		2.56	c	53	
202		2.28	b	11	
032		2.29	b	0	
113		1.67	b	2	
$\bar{1}$13		1.68	b	3	

^{a} F_c^2 values are referred to model **B**. In the case of overlap, reflections are grouped. ΣF_c^2 indicates the sum of calculated values for overlapped reflections. ^{b} Unobserved reflections. ^{c} This reflection was observed on the photographic spectrum but was not measurable on the Fuji image-plate spectrum. It was used only in spectrum indexing.

Step-by-step structural variables were corrected by following either the lowering of lattice energy or the lowering of the R_2 index ($R_2 = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$; the sum is over observed reflections only; in case of overlap, F_c^2 is evaluated as the sum over overlapped reflections). Two alternative models were obtained, roughly similar to each other in the aromatic part but different in chain backbone disposition (see Figure 3); both models give excellent R indices and plausible packing. They differ, however, as unobserved reflections are considered, as shown in Table 2.
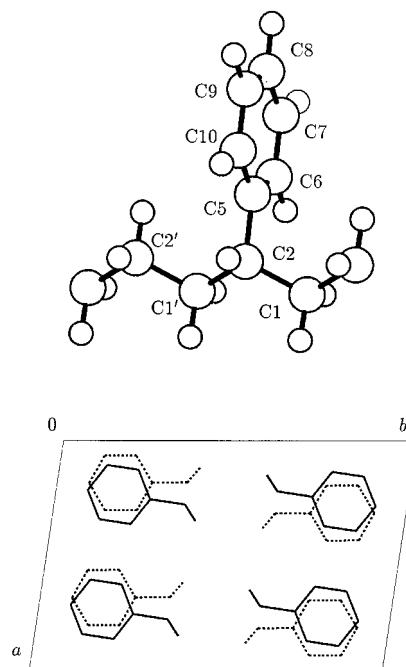

Figure 3. (a) Molecular model composed of a pair of C_8H_8 and C_2H_4 units. Symmetry-equivalent atoms are primed. C–C aliphatic bond lengths are 1.54 Å, and C–C aromatic lengths are 1.40 Å. Chain bond angles are set to 112.5° (this gives the 5.12 Å repeat), and side bond angles CH_2–CH–C_{Ph} are set to 111.4°. The phenyl torsion angle C3–C4–C5–C6 of 63.27° brings the phenyl ring into the crystallographic mirror plane. Hydrogen atom positions, necessary for the evaluation of the packing energy, were obtained using standard sp^3 and sp^2 idealized hybridizations. (b) The two alternative structures. Solid lines (model **B**) indicate the true structure; dotted lines (model **A**), the other one.

Table 2. Results Obtained with the Two Models Illustrated in Figure 3^a

	model **A** (dotted line)	model **B** (solid line)	model **B′**
Φ (deg)	99	90	89
x_0 (Å)	6.36	7.10	7.18
y_0 (Å)	4.15	4.17	4.09
R_1	0.08	0.10	0.13
R_2	0.15	0.17	0.24
lattice energy (kcal)	−1.5	−7.6	−9.2
B_{iso} (Å^2)	11.1	13.0	13.0
F^2(230)	53	0	0
F^2($\bar{2}$40)	0	32	21
F^2($\bar{4}$30)	4	22	17
C···C packing dist (Å)	>3.72	>3.71	>3.71

^{a} Parameters x_0, y_0 indicate the Cartesian coordinates of atom C5 (model origin); Φ is the angle of the C5–C8 direction with the crystallographic x axis. Disagreement indices: $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$; $R_2 = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$.

The dotted-line structure (**A**) has lower R indices, but the unobserved (230) reflection has high F_c^2 and is quite insensitive to small variations of the parameters. The solid-line structure (**B**), with slightly worse R indices, lower lattice energy, and more equilibrated packing distances, also exhibits some unobserved and overcalculated reflections, viz. $\bar{2}$40 and $\bar{4}$30, but the corresponding F_c^2 values are lower. Moreover, these values can be lowered further (see Table 2, last column), with a modest structure rearrangement, by following the indication of lattice energy only.

Any attempt to improve the model by considering statistically mixed packing failed. Model **B** thus appears
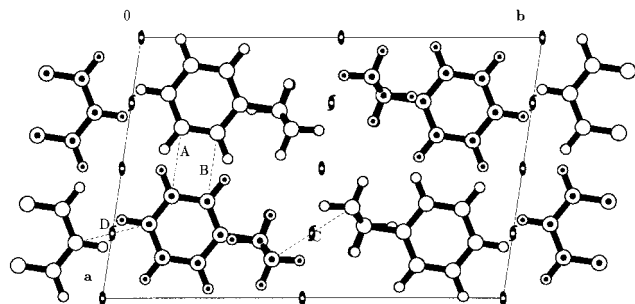
Figure 4. Crystal structure of the ethylene—styrene alternating copolymer. White-atom chains have the phenyl groups at $z = 0.5$, and dotted-atom chains have the phenyl groups at $z = 0.0$. C···C shortest van der Waals distances are $A = 3.71$ Å, $B = 3.71$ Å, $C = 3.74$ Å, $D = 3.91$ Å.

Table 3. Fractional Atomic Coordinates of Model B

atom	x/a	y/b	z/c
C1	0.850	0.409	−0.2500
C2	0.779	0.372	0.0000
C5	0.756	0.272	0.0000
C6	0.864	0.226	0.0000
C7	0.843	0.135	0.0000
C8	0.714	0.089	0.0000
C9	0.606	0.135	0.0000
C10	0.627	0.226	0.0000

convincingly unique. The corresponding atomic fractional coordinates are given in Table 3.

The crystal packing for the resulting structure (see Figure 4) shows that each aromatic ring is surrounded, at exactly the same distance, by four rings, two displaced up by $c/2$ and two displaced down by $c/2$. It is worth noting that all contacts are either aromatic—aromatic or aliphatic—aliphatic carbon atoms. A similar feature is observed in both the α form and the β form of syndiotactic polystyrene.[14]

Finally, we have examined the lower-symmetrical models by waiving the chain crystallographic mirror symmetry. This can be fulfilled either by removing the 2-fold axis crossing the origin and the inversion center on the screw axis at $x = {}^1/_4$ ($P2_1/a$ hypothesis) or by removing the screw axis at $x = {}^1/_4$ and the inversion

center on the 2-fold axis at $x = 0$ ($P2/a$ hypothesis). In both cases, the conditions of z_0, Ψ fixed must be waived. It results, in any case, that the packing energy vs Ψ and vs z_0 has a minimum value just when the ring lies on a plane perpendicular to the chain, and the same applies to R indices, though minima are flat. Thus, the $B2/m$ space group is confirmed.

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