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The blocky structure of Ziegler-Natta "random" copolymers: myths and experimental evidences.

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Experimental.

Two samples of BE-ZN copolymers (BE1 and BE2 with 9.1 and 14.3 mol% of ethylene, respectively) were synthesized with a MgCl₂-supported Ziegler-Natta catalyst with di(isobutyl) phthalate as internal donor combined with (2,3-dimethyl-butan-2-yl)trimethoxysilane as external donor. This catalyst gives high stereospecificity in the homopolymerization of butene with value of fully isotactic *mmm* pentad of 94%. Tri-isobutylaluminum (TIBA) was used as cocatalyst (1.4 g) and the molar ratio between aluminum and the external donor was fixed to 40 mol/mol. The polymerizations were conducted at 75°C for 2h in an autoclave of 4 L volume using hydrogen as molecular weight regulator (H₂=1000 mL).

The samples of copolymers BE-MET were synthesized with a highly isospecific metallocene catalyst as described in the ref. S1. The samples BE-MET1, BE-MET2 and BE-MET3 of Table 1 correspond to the samples iPBEt-8.3, iPBEt-13.8 and iPBEt-16.7, respectively, of Table 1 in the Ref. S1.

The intrinsic viscosities were measured in tetrahydronaphthalene at 135 °C using standard Ubbelohde viscometer. The average molecular masses were evaluated from the intrinsic

viscosities according to the relationship $[\eta] = KM_v^{\alpha}$, with $\alpha = 0.725$ (independent on the copolymer composition),^[S2] and K calculated using a linear combination of the K values of the pure polyethylene ($K_{PE} = 4.06 \times 10^{-4} \text{ dL/g}$) and of isotactic polybutene (iPB) ($K_{iPB} = 1.78 \times 10^{-4} \text{ dL/g}$),^[S2] assuming a constant sample composition in the whole range of molecular weight, $K = X_B K_{iPB} + X_E K_{PE}$, where X_B and X_E are the butene and ethylene weight fractions, respectively, of the copolymer obtained from ¹³C NMR.

The samples of iPBEt-ZN copolymers were fractionated by exhaustive Kumagawa extraction using sequentially boiling diethyl ether (EE), hexane (HE) and heptane (HP). For both samples two fractions, soluble in diethyl ether (sEE) and insoluble in diethylether/soluble in hexane (iEE), were separated.

All fractions were characterized by gel permeation chromatography (GPC) and ¹³C NMR spectroscopy. The concentration of the constitutional sequences, triads BBB, BBE, BEB, EBE, BEE and EEE (with B = 1-butene unit and E = ethylene unit), evaluated from the ¹³C-NMR spectra, are reported in Table S1. The values of average lengths of butene and ethylene sequences were calculated according to Randall et al.^[S3] with equations:

n(E) = (EEE + EEB + BEB)/(BEB + 0.5EEB)

n(B) = (BBB + BBE + EBE)/(EBE + 0.5BBE)

The values of product of reactivity ratio r_1r_2 were calculated from the concentration of constitutional triads according to Carman^[S4] as:

$$r_1 r_2 = 1 + \left(\frac{B}{E}\right) \left(\frac{EEE + BEE}{BEB} + 1\right) - \left(\frac{B}{E} + 1\right) \left(\frac{EEE + BEE}{BEB} + 1\right)^{0.5}$$

Table S1. Concentration of ethylene (Et), concentrations of the comonomeric sequences BBB, BBE, EBE, BEB, BEE and EEE, and average lengths of the ethylene and 1-butene sequences n(E) and n(B) of the BE-ZN copolymer samples and of the corresponding fractions (B = 1-butene, E = ethylene) determined by ¹³C NMR.

Sample	Et	BBB	BBE	EBE	BEB	BEE	EEE	n(E)	n(D)
	(mol%)	(%)	(%)	(%)	(%)	(%)	(%)	<i>(IC)</i>	п(в)
BE1 whole	9.1	76.03	13.30	1.56	7.23	1.51	0.37	1.14	11.07
BE1, sEE	16.3	59.16	20.75	3.79	12.08	3.22	0.99	1.19	5.91
BE1, iEE	7.6	79.33	11.86	1.26	6.29	0.95	0.31	1.12	12.85
BE2 whole	14.3	63.53	19.59	2.59	10.97	2.56	0.75	1.17	6.92
BE2, sEE	16.7	56.60	22.89	3.90	12.83	3.09	0.79	1.16	5.43
BE2, iEE	12.8	67.52	17.21	2.47	9.85	2.15	0.80	1.17	7.87

X-ray powder diffraction profiles (WAXS) were obtained with Ni filtered CuK α radiation with a Empyrean diffractometer by Panalytical. The indices of crystallinity (x_c) were evaluated from the X-ray powder diffraction profiles by the ratio between the crystalline diffraction area and the total area of the diffraction profile. The crystalline diffraction area was obtained from the total area of the diffraction profile by subtracting the diffraction halo of the amorphous phase after suitable scaling. The diffraction halo of the amorphous phase were determined from the diffraction profile of a sample of atactic poly(1-butene).

The calorimetric thermograms and the melting temperatures were obtained with a differential scanning calorimeter (DSC) Mettler DSC-822 performing scans in flowing N2 atmosphere and heating and cooling rates of 10°C/min. The degree of crystallinity has been evaluated from the DSC heating curves as $x_c = \Delta H_m / \Delta H_1^0$ or $x_c = \Delta H_m / \Delta H_{11}^0$, where ΔH_m is the melting enthalpy of crystals of form I or form II and $\Delta H_1^0 = 141$ J/g and $\Delta H_{11}^0 = 62$ J/g are the thermodynamic melting enthalpies of iPB in form II or form I, respectively.^[S5] The values of melting temperature and enthalpy and of the degree of crystallinity of melt-crystallized samples and of samples aged at room temperature are reported in Table S2.

Table S2. Melting temperatures (T_m) and enthalpies (ΔH_m) of crystals of form II and form I and degrees of crystallinity evaluated from X-ray diffraction profiles ($x_{c(WAXS)}$) and from DSC ($x_{c(DSC)}$) of samples crystallized from the melt and samples aged at room temperature of copolymers BE-ZN and their fractions and of copolymers BE-MET.

Sample	Et	7 _m ^a (°C)	$\Delta H_{\rm m}^{\rm a}$ (J/g)	<i>T</i> _m ^b (°C)	<i>Т</i> _m ^b (°С)	ΔH _m ^b (J/g)	$x_{c(WAXS)}^{c}(\%)$	$x_{c(WAXS)}^{c}$ (%)	x _{c(DSC)} ^d (%)	x _{c(DSC)} ^e (%)
	(mol%)	(Form II)	(Form II)	(Form I)	(Form I')	(Form I+I')	melt-crystallized	aged	melt-crystallized	aged
BE1 whole	9.1	85	13.0	95.5	41.2	45.6	26	48	21	32
BE1, sEE ^f	16.3	75	0.5	-	34.0	22.0	5	30	1	15
BE1, iEE	7.6	84	13.4	94.6	40.0	39.0	32	52	22	30
BE2 whole	14.3	77	1.5	89.0	31.9	21.5	12	32	3	15
BE2, sEE ^f	16.7	-	-	88.0	38.0	13.4	0	30	0	9.5
BE2, iEE	12.8	76	3.9	87.6	34.0	30.0	20	38	6	21
BE-MET1 ^g	8.3	-	-	-	52	29.0	0	26	0	21
BE-MET2 ^g	13.8	-	-	-	43	11.0	0	14	0	8
BE-MET3 ^g	16.7	-	-	-	42	12.0	0	16	0	8

^a) From the DSC heating scans at 10 °C/min of melt-crystallized samples cooled from the melt at 10 °C/min. ^b) From the DSC heating scan of meltcrystallized and aged samples. ^c) From the X-ray diffraction profiles of Figure 1. ^d) From $x_c = \Delta H_m / \Delta H_{II}^0$ where ΔH_m is the melting enthalpy of crystals of form II and $\Delta H_{II}^0 = 62$ J/g is the thermodynamic melting enthalpy of iPB in form II. ^e) From $x_c = \Delta H_m / \Delta H_{II}^0$ where ΔH_m is the melting enthalpy of crystals of form I + I' and $\Delta H_{II}^0 = 141$ J/g is the thermodynamic melting enthalpy of iPB in form I. ^f) The DSC curves for the fractions sEE of the samples BE1 and BE2 are not reported in the text. ^g) From ref. 19. The average size of crystals of form II and form I have been evaluated from the widths of the $(200)_{II}$ reflection of form II at $2\theta = 11.9^{\circ}$ and of the $(110)_{I}$ reflection of form I at $2\theta = 9.9^{\circ}$ in the diffraction profiles of Figure 1 applying the Scherrer equation $L(hkI) = K\lambda/\beta\cos\theta$, where β is the width of the reflection peaks $(110)_{I}$ or $(200)_{II}$, θ is the diffraction angle of the two peaks $(2\theta = 9.9^{\circ}$ for the $(110)_{I}$ reflection of form II and $2\theta = 11.9^{\circ}$ for the $(200)_{II}$ reflection of form II) and K = 0.89. The values of size $L(200)_{II}$ and $L(110)_{I}$ are reported in the Table S3.

Table S3. Size of crystals form II ($L(200)_{II}$) of iPB that crystallize from the melt and of crystals of form I ($L(110)_{I}$) in melt-crystallized and aged samples of BE-ZN and BE-MET copolymers, evaluated from the width of the (200)_{II} reflection of form II at $2\theta = 11.9^{\circ}$ and of the (110)_I reflection of form I at $2\theta = 9.9^{\circ}$.

Sample	Et (mol%)	Melt-crystall	ized samples	Melt-crystallized and aged samples		
		<i>L</i> (200) _{II} (nm)	<i>L</i> (110) _I (nm)	<i>L</i> (200) _{II} (nm)	<i>L</i> (110) _I (nm)	
		form II	form I	form II	form I	
BE1 whole	9.1	12	not evaluated	-	9	
BE1, sEE	16.3	not evaluated	not evaluated	9	10	
BE1, iEE	7.6	9	-	-	11	
BE2 whole	14.3	9	8	9	8	
BE2, sEE	16.7	-	-	10	10	
BE2, iEE	12.8	9	-	-	10	
BE-MET1	8.3	-	-	-	11	
BE-MET2	13.8	-	-	-	25	
BE-MET2	16.7	-	-	-	24	

Relation with the structure of the Ziegler-Natta catalytic sites.

The obtained results of the observed crystallization of form II of iPB in samples containing very high concentrations of ethylene of 14-16 mol% (Figure 1A), and the constant melting temperatures of crystals of form II and form I (Figure 2B) that are nearly independent of the ethylene concentration, indicate the presence of long crystallisable butene sequences in a multiblock molecular structure whose length is almost the same in the different fractions of the samples even for large differences in ethylene concentrations. This may be explained and correlated with the structure of the Ziegler-Natta (ZN) catalysts, implying the idea of the multisite nature of these catalysts. A model of the structure of the ZN catalytic site is shown in Figure S1, where L1 and L2 ligands may be chlorine atoms as well as chemisorbed Al species and/or external donors.^[56,57] It is largely accepted that the chiral octahedral steric hindered structure of the Ti active site allows discriminating the prochiral faces of α -olefins, following the chiral configuration of the growing polymer chain.^[56] The model of Figure S1 explains the formation of isotactic polypropylene from the most crowded site A of Figure S1, poorly isotactic and syndiotactic polypropylenes from the less crowded sites B and C of Figure S1, respectively, and eventually formation of stereoblocks if interconversion among the three different sites occurs. This model may be applied to copolymerization of α -olefins, in particular in the presence of ethylene comonomer.^[58]

Our results of crystallization of butene-ethylene copolymers (Figure 3) agree with a model of Figure S1, where the more stereoselective site A of Figure S1 produces chains with isotactic butene sequences of similar high length, regardless of the ethylene concentration, that crystallize in form II of constant melting temperature, whereas sites B and C of Figure S1 produce short and more stereoirregular butene sequences that crystallize in form I of iPB, because they incorporate more easily ethylene. The fact that even at high ethylene concentrations long butene sequences still able to crystallize even in form II of iPB (Figure 1) are produced, suggests that the three sites may interconvert each other (at least in part) (Figure S1). This means that the site A of Figure S1 still works producing long isotactic crystallizable butene sequences (of similar length), even at high ethylene concentrations when the productivity of sites B and C increases and the equilibrium of Figure S1 is shifted towards sites B and C with formation of short (probably less isotactic) butene sequences.



Figure S1. (A-C) Model for the α -olefin insertion at the octahedral Ti-active site of ZN catalyst proposed for the isotactic (A), poorly isotactic (B) and syndiotactic (C) propylene propagation,^[S4,S5] revised according to butene-ethylene copolymerization. L1 and L2 indicate chlorine atoms as well as Al species and/or donor molecules. (A'-C') Revised quadrant schemes where gray quadrants correspond to relatively crowded zones occupied by the groups L1 and L2. The relative amounts of the three sites as well as their interconversion frequencies depend on the ethylene content.

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