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Influence of Regio- and Stereoregularity of Propene Insertion on Crystallization Behavior and Elasticity of Ethene−Propene Copolymers

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It is well-established that propene units can, at least in part, enter into the lattice of orthorhombic polyethylene,[1−3] gradually increasing the disorder in the crystalline phase but leaving substantially unaltered the *trans*-planar conformation of the chains. In fact, as the propene content increases, the a unit cell parameter increases, whereas the b and the c parameters practically retain the dimensions found in polyethylene.[1] For ethene content lower than nearly 85%, a becomes nearly equal to $b\sqrt{3}$, and hence the unit cell becomes pseudohexagonal.[1,3] These copolymer samples present only broad endothermic peaks, whose maximum is positioned in the temperature range between −20 and +50 °C.[2]

This residual crystallinity has a strong influence on the mechanical properties of EP copolymer samples.[2,4]

The crystallinity of ethene−propene copolymers is, of course, dependent mainly on comonomer content (composition) and distribution (constitution), which, in turn, essentially depend on polymerization conditions (first, feed composition) and on the catalytic system. In this contribution we will show that the crystallinity of ethene−propene copolymers is also substantially dependent on regio- and stereoregularity of propene insertion and that this dependence can be easily rationalized in terms of van der Waals interactions into the crystalline lattice.

Ethene−propene copolymers can be prepared with several different types of single center catalysts, the homogeneous nature of catalytic centers accomplishes narrow intermolecular distributions of comonomers. Moreover, different types of catalytic systems give rise to largely different relative reactivities of the two comonomers.[4,5]

It is, however, worth noting that the single-center catalysts used to produce ethene−propene copolymers can differ, not only for comonomer reactivity ratios, but also for possible regiospecificity and stereospecificity with respect to propene insertion. In particular: (*i*) traditional homogeneous vanadium-based catalytic systems[6] are substantially non regiospecific as well as non stereospecific, as for propene copolymerization with ethene.[7] (*ii*) "constrained geometry" catalysts are similar to vanadium-based catalysts being essentially nonregiospecific and completely nonstereospecific, even though the amount of regiomistakes is largely lower.[8] (*iii*) metallocene catalysts are generally regiospecific and can be also stereospecific for the case of *ansa*-metallocenes with a C_2 symmetry.[9]

Microstructural information coming from nuclear magnetic resonance characterizations, relative to several ethene−propene samples, obtained by different single-center catalytic systems and having widely different constitutions and compositions in the range of industrial interest, has been collected in Table 1.[2] Melting enthalpies (as an indirect measure of the pseudohexagonal crystallinity) of these samples, as obtained by differential scanning calorimetry, have been reported versus the ethene molar composition, in Figure 1A. To achieve a more significant comparison between samples with different placements of propene co-units, different constitutions (varying from nearly alternate to nearly block-like) of copolymers obtained by different catalysts have to be accounted for. This has been done by reporting the melting enthalpies versus the amount of polyethylene sequences longer than a fixed value (e.g., longer than 10 ethene units, in Figure 1B). In this plot all the available experimental data are approximately fitted by three lines corresponding to the different placements of propene co-units: a lower one for regio- and stereoirregular (squares), an intermediate one for regioregular and stereoirregular (triangles), and an upper one for regio- and stereoregular (circles). To our knowledge, this is the first evidence of the influence of the regio- and stereoregularity of propene insertion (and more in general of a comonomer insertion) on crystallization behavior of ethene/1-alkene copolymers.

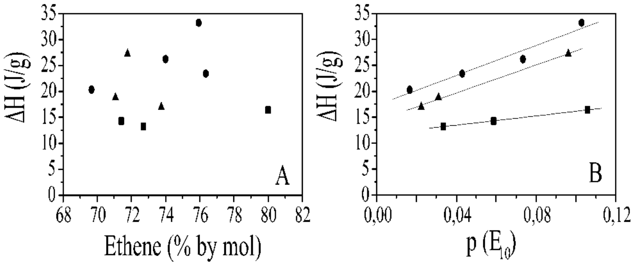

Figure 1. Melting enthalpy (Δ*H*) of the ethene−propene copolymers of Table 1 versus: (A) ethene molar composition; (B) fraction of copolymer sequences of 10 units being constituted only by ethene. Considered copolymers present: (●) regio- and stereoregular or (▲) regioregular and stereoirregular or (■) regio- and stereoirregular placements of propene co-units.

These results are in qualitative agreement with simple energy calculations relative to models of packing of ethene−propene copolymers. Side- and along-the-chain views of *trans*-planar ethene−propene (75/25 by mol) copolymer chains, presenting regio- and stereoregular (A), regioregular and stereoirregular (B), regio- and stereoirregular (C) placements of the propene co-units are compared in Figure 2.

The assumed models of packing include polyethylene *trans*-planar chains in a pseudohexagonal lattice and whose relative orientation is similar to that observed in the monoclinic phase of polyethylene (as for the limiting model structure proposed for the pseudohexagonal form of EP copolymers and reported in Figure 4B of ref 3), and for the sake of simplicity, only the central chain contains propene comonomer units. Three different models corresponding to three different placements of the propene co-units, equal to those of Figure 2A−C, have been considered (Figure 3A−C).

Packing energy maps, as a function of the movements along x and y of the central chain, are reported for the three models in Figures 3A′−C′. It is apparent that for the model of Figure 3C, in which the placements of propene co-units in the central chain are

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Table 1. Catalyst, Ethene/Propene (E/P) Molar Ratio in the Feed, Cocatalyst, Temperature (T_p), and Pressure (P_p) of Polymerization, Intrinsic Viscosity (IV), Ethene Molar Content (E), Lower Limit of the Amount of Regioirregularities (% inv), Stereoregularity of Propene Placement (% *m*), Triads Fractions (E = ethene, P = propene), Product of Reactivity Ratios ($r_1 \times r_2$), Probability of Sequences of at Least 10 Ethene Units ($P(E_{10})$), Melting Enthalpy (ΔH_m) for All Considered Copolymer Samples

	catalyst[a]	E/P	cocatalyst[b]	T_p °C	P_p bar	IV dL/g	E mol %	inv %	%*m*	PPP %	PPE %	EPE %	PEP %	EEP %	EEE %	$r_1 \times r_2$	$P(E_{10})$	ΔH_m (J/g)
1	rac-$(C_2H_4)(H_4\text{-Ind})_2ZrCl_2$	0.13	TIOA/H_2O	50	9.0	3.67	69.7	nd[c]	>99	2.5	8.5	19.2	8.8	30.4	30.5	0.48	0.017	20.3
2	$(4,7\text{-Me}_2\text{-Ind})_2ZrCl_2$	0.06	MAO	50	8.0	1.55	71.1	<1	~20	6.8	6.3	15.8	7.0	28.9	35.2	0.82	0.031	18.8
3	$Me_2Si(Me_4\text{-Cp})(N\text{-Bu})TiCl_2$	1.11	TIOA/H_2O	80	22.0	3.59	71.4	2.7	11	4.4	13.1	11.1	4.2	26.1	41.1	1.81	0.059	14.3
4	$(4,7\text{-Me}_2\text{-Ind})_2ZrCl_2$	0.09	TIOA/H_2O	30	13.8	3.46	71.8	<1	18	7.8	9.6	10.9	2.5	22.8	46.5	1.90	0.096	27.2
5	$V(Acac)_3$	0.12	DEAC	40	15.0	3.38	72.7	14	23	2.4	7.4	17.5	5.8	30.0	36.8	0.57	0.033	13.2
6	meso-$(C_2H_4)(4,7\text{-Me}_2\text{-Ind})_2ZrCl_2$	0.06	TIOA/H_2O	50	9.0	3.74	73.7	<1	nd[e]	0	4.4	21.9	7.2	32.5	34.0	0.20	0.022	17.0
7	rac-$Me_2C(3\text{-tBu-Ind})_2ZrCl_2$	0.20	TIOA/H_2O	50	10.6	3.64	74.0	<1	>99	4.2	9.5	12.3	3.7	25.8	44.6	1.42	0.073	26.2
8	rac-$(C_2H_4)(4,7\text{-Me}_2\text{-Ind})_2ZrCl_2$	0.19	TIOA/H_2O	40	18.0	2.37	76.0	nd[d]	>99	4.3	10.6	9.1	3.0	24.5	48.5	2.60	0.103	33.2
9	rac-$Me_2Si(Ind)_2ZrCl_2$	0.58	MAO	50	0.1	n.d.	76.4	<1	nd[f]	0	4.0	19.7	5.4	30.4	40.5	0.24	0.043	23.4
10	$V(Acac)_3$	0.26	DEAC	40	19.0	3.22	80.0	8	36	1.3	4.4	14.3	3.9	24.9	51.2	0.68	0.106	10.0

[a] Me = methyl, Ind = indenyl, Bu = butyl, Cp = cyclopentadienyl, Acac = acethylacetonate. [b] The molar ratio aluminum/transition metal was generally 1000 while for $V(Acac)_3$ was 300. MAO = mehylalumoxane, TIOA = tri-iso-octyl aluminum, DEAC = diethyl aluminum chloride. [c] nd = not determined; however, the catalytic system is highly regiospecific for propene homopolymerization. [d] nd = not determined; however, the catalytic system is regiospecific for propene homopolymerization. [e] nd = not determined; however the catalytic system is aspecific for propene homopolymerization. [f] nd = not determined; however the catalytic system is isopecific for propene homopolymerization.

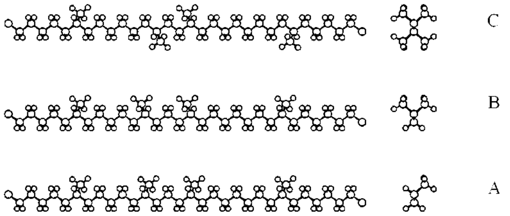

Figure 2. Side- and along-the-chain views of *trans*-planar ethene−propene (75/25 by mol) copolymer chains presenting regio- and stereoregular (A), regioregular and stereoirregular (B), regio- and stereoirregular (C) placements of propene co-units.

regio- and stereoirregular, movements of the central chain from the baricenter of the unit cell do not cause any significant reduction of packing energy (Figure 3C′). Instead, in the case of the model of Figure 3B the copolymer central chain, presenting regioregular propene co-units, can substantially reduce nonbonded interactions of the methyl groups, which are all on the same side of the chain, by small parallel movements of the chain axis (~0.5 Å along both *a* and *b* crystal axes) (Figure 3B′). This energy optimization is, of course, also more efficient in the case of chains with regio- and stereoregular placements of the propene co-units (Figure 3A, A′).

In summary, higher disturbance of the polyethylene crystallinity is achieved, for equal amounts and distributions of propene comonomer units, for regio- and stereoirregular placements of propene co-units. Moreover, both experimental data and calculations on simplified models indicate that regioirregularity of propene insertion is more effective than stereoirregularity in crystallinity disturbance.

This information is relevant for the selection of suitable copolymer microstructures for rubber applications. In particular, for cross-linked rubber, the absence of crystallinity in the unstretched state is required. This, of course, should be associated with a minimum fraction of propene comonomers to obtain glass transition temperatures as low as possible as well as fewer tertiary carbon atoms, potential sources of degradation of the elastomers.

On the other hand, to get thermoplastic elastomeric behavior, some residual crystallinity is needed, and this can be controlled not only by varying the copolymer composition and distribution but also by controlling the regio- and stereochemistry of insertion of the propene units.

It is worth noting that the described influences of the placements of the 1-alkene co-unit on crystallization is not expected to occur for ethene copolymer with comonomers much bulkier than propene, as for instance styrene or 1-octene. In fact, in these cases the comonomer units should be always excluded from the crystalline phase.

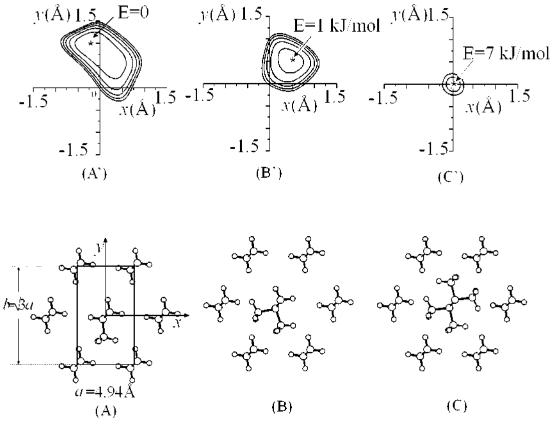

Figure 3. (A−C) Along-the-chain projections of pseudohexagonal models where the central chains contain propene comonomer units, presenting regio- and stereoregular (A) or regioregular and stereoirregular (B) or regio- and stereoirregular (C) placements. (A′−C′) Energy maps, for the models A−C, as a function of movements of the central chain along *x* and *y* axes. Contour lines are reported at intervals of 2 kJ/mol.

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Supporting Information Available: Details about methods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

References

(1) Bassi, I. W.; Corradini, P.; Fagherazzi, G.; Valvassori, A. *Eur. Polym. J.* **1970**, *6*, 709.

(2) Guerra, G.; Ruiz de Ballesteros, O.; Venditto, V.; Galimberti, M.; Sartori, F.; Pucciariello, R. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1095.

(3) Ruiz de Ballesteros, O.; Auriemma, F.; Guerra, G.; Corradini, P. *Macromolecules* **1996**, *29*, 7141.

(4) (a) Galimberti, M.; Martini, E.; Piemontesi, F.; Sartori, F.; Resconi, L.; Albizzati, E. *Macromol. Symp.* **1995**, *89*, 259. (b) Galimberti, M.; Resconi, L.; Martini, E.; Guglielmi, F.; Albizzati, E. (Spherilene srl (Italy)). Eur. Pat. EP-B 586,658, 1993.

(5) Galimberti, M.; Piemontesi, F.; Fusco, O.; Camurati, I., Destro, M. *Macromolecules* **1998**, *31*, 3409 and references therein.

(6) Natta, G.; Pasquon, I.; Zambelli, A. *J. Am. Chem. Soc.* **1962**, *84*, 1488.

(7) (a) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 687. (b) Zambelli, A.; Sessa, I.; Grisi, F.; Fusco, R.; Accommazzi, P. *Macromol. Chem. Rapid Commun.* **2001**, *22*, 297.

(8) Galimberti, M.; Mascellari, N.; Piemontesi, F.; Camurati, I. *Macromol. Rapid Commun.* **1999**, *20*, 214.

(9) Ewen, J. A. *J. Am. Chem. Soc.* **1984,** *106*, 6355.

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