

# Tailoring the Physical Properties of Isotactic Polypropylene through Incorporation of Comonomers and the Precise Control of Stereo- and Regioregularity by Metallocene Catalysts

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Random copolymers of propylene with ethylene, butene, and hexene comonomers have been prepared with different metallocene catalysts. The used catalysts have allowed a precise control of concentration of stereodefects and high degree of comonomer incorporation while maintaining high molecular mass and random distribution of comonomers. Incorporation of ethylene, butene, and hexene produces great enhancement of ductility, flexibility, and toughness, as compared to highly isotactic polypropylene, but with important differences in the values of elastic modulus and strength depending on the comonomer. In propylene–ethylene copolymers, the values of elastic modulus, ductility, toughness, and strength can be tuned by changing the concentrations of *rr* stereodefects and ethylene units, so that stiff and fragile plastics, highly flexible materials, and elastomers can be obtained. Propylene–butene copolymers behave as highly flexible materials with remarkable ductility and toughness and contemporary high strength and stiffness. Propylene–hexene copolymers are highly flexible materials with plastic resistance and strength that decrease with increasing hexene content. These outstanding properties are not easily accessible with propylene-based copolymers produced with traditional Ziegler–Natta catalysts because of nonrandom distribution of comonomers and non-homogeneous composition.

## Introduction

The huge commercial success of isotactic polypropylene (iPP) and the wide range of its applications are basically due to the combination of outstanding physical properties, as the low density, the high tensile strength, stiffness, hardness, and thermal resistance, good environmental resistance, and ease of processability and recycling.<sup>1</sup> The vast majority of products are fabricated with the highly isotactic polymer that melts at about 165 °C, but a variety of possible modifications of the basic material is possible already in the polymerization reactor.

One of the inconveniences of iPP is its limited impact resistance at low temperatures near the glass-transition temperature (nearly 0 °C). Enhancement of the impact properties is generally obtained by blending iPP with various types of elastomers. However, the formation of incompatible phases and interphases generally requires the use of compatibilizing agents. In this context, heterophasic copolymers,<sup>1a,2–6</sup>

where an elastomeric phase, usually ethylene–propylene copolymer rubber, is dispersed uniformly within the polypropylene matrix, give a good stiffness/impact balance.<sup>7</sup> Another alternative for modifying the iPP structure and, therefore, its properties without the necessity of blending it with other polymers is the copolymerization of propene with olefins of different chain lengths. Random copolymers of propylene with ethylene and butene have been commercially produced worldwide and used mainly in the packaging market as materials for film applications, taking advantage of their good transparency, higher impact strength, and lower heat-seal temperature as compared to iPP homopolymer. In particular, propylene-based copolymers are used as low sealing grades in multilayered co-extruded films. These advantages of random copolymers would be due to the incorporation of defects in the chain structure that reduces crystallization tendency of iPP. The less perfect crystals have lower melting temperature and density, resulting in higher clarity. The impact of introduction of constitutional defects on material properties depends on the type and concentration of comonomeric unit. Therefore, understanding the influence of a single type of defect on the crystallization behavior and

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physical properties of iPP is the key for tailoring different polypropylenes having the desired physical properties.

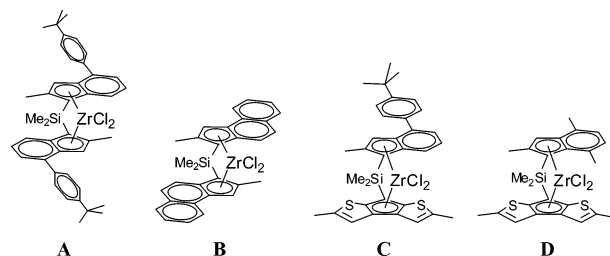
Unfortunately, the random comonomer behavior is somewhat less ideal than the term “random” suggests. It is well-known that in propylene-based copolymers prepared with conventional Ziegler–Natta catalysts, comonomer incorporation is not uniform. Therefore, the lower-molecular weight fractions contain a higher percentage of comonomer and exhibit considerable solubility in hydrocarbons. The non-random distribution of comonomers along the chains and the presence of other types of microstructural defects have prevented so far the study of the effect of a single comonomeric unit on the crystallization behavior and physical properties of iPP.

The discovery of single-center metallocene catalysts has determined great improvements and advantages in polymerization and copolymerization of olefins.<sup>8,9</sup> These organo-metallic catalysts afford exceptional control over chain architecture, including control of concentration of stereo- and regiodefects and efficient uniform placement of constitutional defects, as comonomeric units, along iPP chains. Moreover, many new polymeric materials having microstructures that cannot be obtained with conventional Ziegler–Natta catalysts can be produced with metallocene catalysts.<sup>8,9</sup>

The advantage of using metallocene catalysts is that they afford incorporation of large contents of comonomer, copolymerization of cyclic and other comonomer types that are not easily incorporated with classical Ziegler–Natta catalysts, and excellent control of stereoregularity. In addition, metallocene catalysts may yield copolymers with a truly random comonomer distribution, uniform intermolecular distribution of the comonomer content, low levels of solubles even at high comonomer incorporation, and narrow molecular weight distribution. These characteristics afford another opportunity for modifying the iPP microstructure through the controlled incorporation of constitutional defects, and tailoring different polypropylenes having the desired physical properties.

To date, metallocene-based propylene copolymers have been synthesized with a variety of comonomers giving a wide range of interesting materials.<sup>10–16</sup> All of these studies have highlighted the different effects of different comonomers on the crystallization behavior of iPP,<sup>10–16</sup> but could not

**Chart 1. Structures of Metallocene Catalysts Used in This Study**



discriminate between the influences of stereodefects and constitutional defects on material properties.

In this Article, we report a study of the crystallization properties and mechanical properties of isotactic copolymers of propylene with ethylene, butene, and hexene comonomers prepared with different metallocene catalysts. The used catalysts allow for the synthesis of copolymers with a well-defined microstructure, for instance, samples with a very small concentration of stereodefects or regiodefects and variable amounts of comonomeric units or copolymers with similar concentration of comonomeric units but different concentration of stereo- and regiodefects. This precise control of microstructure affords a unique opportunity for the study of the effects of comonomers of different size and of *rr* stereodefects on the physical properties of iPP. The full understanding of the relationships between microstructure and properties allows tailoring different polypropylenes having desired physical properties that range among those of stiff materials, highly flexible materials with high impact strength, and elastomers.

## Experimental Section

Samples of iPP homopolymer and propylene–ethylene (iPPeT), propylene–butene (iPPBu), and propylene–hexene (iPPHe) copolymers have been prepared at temperatures between 60 and 70 °C with the four metallocene catalysts shown in Chart 1, activated with methylalumoxane (MAO). The two  $C_2$ -symmetric metallocenes **A** and **B** are not completely regioselective, with **A** being almost fully isoselective<sup>17,18</sup> and **B**<sup>19</sup> less isoselective than **A**. On the other hand, the two  $C_1$ -symmetric metallocenes **C** and **D** are fully regioselective but not perfectly isoselective, with **D** being less isoselective than **C**.<sup>20</sup> The MAO-activated metallocenes were either used as toluene solutions (for propylene–hexene copolymers) or supported on spherical  $SiO_2$  particles, or on porous polyethylene or polypropylene

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**Table 1.** Weight Average Molecular Masses ( $\bar{M}_w$ ), Polydispersities ( $\bar{M}_w/\bar{M}_n$ ), Melting Temperatures of Melt-Crystallized Samples ( $T_m$ ), Concentration of Comonomeric Units (mol %), Products of Reactivity Ratios ( $r_P \times r_C$ , with C = Ethylene (E), Butene (B), or Hexene (H)), Contents of Stereoerrors ( $rr$ ), and Concentrations of Secondary 2,1-Erythro Units (2,1e) of iPP Homopolymers (iPPA-D), and Isotactic Propylene–Ethylene, Propylene–Butene, and Propylene–Hexene Copolymers Prepared with the MAO-Activated Metallocenes A–D of Chart 1

sample	catalyst/cocatalyst/ carrier <sup>a</sup>	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$T_m^b$ (°C)	comonomer	mol % comonomer	$r_P \times r_C^c$	$[rr]^d$ %	$[2,1e]^e$ %
iPPA	A/MAO/PE	237 500	2.2	150		0		0.2	0.8
iPPB	B/MAO/PE	254 600	2.0	145		0		1.0	0.7
iPPC	C/MAO/PE	142 400	2.2	140		0		2.5	<0.1
iPPD	D/MAO/PP	247 000	2.3	134		0		3.5	<0.1
AE0.6	A/MAO/PE	n.d.	n.d.	147	ethylene	0.6	n.d.	0.2 <sup>f</sup>	0.7
AE4.0	A/MAO/PE	292 800	2.1	130	ethylene	4.0	1.3	0.2 <sup>f</sup>	0.6
AE7.4	A/MAO/PE	288 600	2.1	115	ethylene	7.4	2.0	0.2 <sup>f</sup>	0.4
DE3.6	D/MAO	n.d.	n.d.	117	ethylene	3.6	1.6	3.6	0
DE13.1	D/MAO	193 400	2.0	55	ethylene	13.1	1.2	3.2	0
AB1.9	A/MAO/SiO <sub>2</sub>	316 500	2.2	143	butene	1.9	n.d.	<0.1	0.5
AB4.3	A/MAO/PE	228 700	2.1	137	butene	4.3	1.0	<0.1	0.4
AB4.4	A/MAO/SiO <sub>2</sub>	207 000	2.0	138	butene	4.4	0.8	<0.1	0.5
AB8.2	A/MAO/PE	178 500	2.0	125	butene	8.2	0.9	<0.1	0.2
AB8.3	A/MAO/SiO <sub>2</sub>	200 000	2.1	123	butene	8.3	0.9	<0.1	0.3
AB13.6	A/MAO/SiO <sub>2</sub>	161 500	2.4	113	butene	13.6	0.8	<0.1	0.1
BB1.6	B/MAO/PE	225 000	2.0	139	butene	1.6	n.d.	1.0	0.6
BB2.8	B/MAO/PE	251 600	2.0	134	butene	2.8	n.d.	1.0	0.5
BB3.7	B/MAO/PE	225 700	2.0	133	butene	3.7	1.6	0.8	0.6
BB6.0	B/MAO/PE	229 000	2.0	123	butene	6.0	1.4	0.7	0.3
CB1.3	C/MAO/PE	172 900	2.1	135	butene	1.3	n.d.	2.4	n.v.
CB4.6	C/MAO/PE	175 700	2.0	125	butene	4.6	n.d.	2.4	n.v.
CB8.2	C/MAO/PE	176 700	2.0	115	butene	8.2	1.2	1.9	n.v.
DB1.4	D/MAO/PE	214 000	2.1	128	butene	1.4	n.d.	3.4	<0.1
DB2.2	D/MAO/PE	214 500	2.0	124	butene	2.2	n.d.	3.4	n.v.
DB6.4	D/MAO/PE	214 400	2.0	114	butene	6.4	1.0	2.5	n.v.
AH1.2	A/MAO	699 600	2.3	139	hexene	1.2	n.d.	0.2 <sup>f</sup>	0.1
AH2.5	A/MAO	430 800	2.0	125	hexene	2.5	n.d.	0.2 <sup>f</sup>	0.2
AH4.2	A/MAO	291 700	2.0	109	hexene	4.2	n.d.	0.2 <sup>f</sup>	0.2
AH6.8	A/MAO	239 500	2.2	96	hexene	6.8	n.d.	0.2 <sup>f</sup>	
AH9	A/MAO	209 800	2.0	87	hexene	9.0	n.d.	0.2 <sup>f</sup>	0.1
AH11.2	A/MAO	266 300	1.9	70	hexene	11.2	0.9	0.2 <sup>f</sup>	
DH18	D/MAO	217 400	1.9	49	hexene	18.0	1.4	3.5 <sup>f</sup>	0

<sup>a</sup> PE = polyethylene, PP = polypropylene. <sup>b</sup> Melting temperatures of samples crystallized from the melt by cooling to room temperature at 10 °C/min, from DSC scans at a heating rate of 10 °C/min. <sup>c</sup> Calculated from <sup>13</sup>CNMR data (see Supporting Information). <sup>d</sup>  $[rr]$  is the percentage of primary stereoerrors over all monomer units,  $[rr] = [mrrm] + [mrrr]$ . The content of stereoerrors in the iPPEt copolymer samples prepared with A/MAO/PE (samples AEX) is not determinable and is assumed to be the same as that found in the corresponding homopolymer iPPA. <sup>e</sup> Secondary insertions 2,1 are only of the erythro type, and their amount is normalized over all monomer units. For iPPEt copolymers,  $[2,1e]$  is the sum of the concentrations of isolated secondary 2,1-erythro units (PSP, P = propylene, S = secondary 2,1 propylene unit) and secondary 2,1e units after ethylene insertion (PESP, E = ethylene). [PSP] and [PESP] are 0.6% and 0.08%, respectively, for the sample AE0.6, 0.27% and 0.31%, respectively, for the sample AE4.0, and 0.09% and 0.29%, respectively, for the sample AE7.4. <sup>f</sup> Postulated values. n.d. = not determinable. n.v. = not visible.

particles following a Basell proprietary technology.<sup>21</sup> All samples are listed in Table 1.

The copolymers have been designed as YEX, YBX, and YHX, where Y is the symbol of the catalyst (A, B, C, or D) and X is the concentration of ethylene (E), butene (B), or hexene (H) comonomeric units.

The microstructural data of all samples have been obtained from <sup>13</sup>C NMR analysis (see Supporting Information). Samples of iPP homopolymer prepared with catalysts A and B (iPPA and iPPB) are highly stereoregular and contain only very small amounts of stereoerrors (0.2 mol % and 1 mol % of  $rr$  triad defects in iPPA and iPPB, respectively) and regiodefects, due to secondary 2,1 erythro units (2,1e) (0.8 and 0.7 mol % of 2,1e units in iPPA and iPPB, respectively). iPP samples prepared with catalysts C and D (iPPC and iPPD) are highly regioregular (no 2,1 regiodefects are detectable) but less stereoregular, and contain only  $rr$  triad stereoerrors<sup>20</sup> in concentrations much higher than those in the samples iPPA and iPPB (2.5 and 3.5 mol % in iPPC and iPPD, respectively).

All catalysts produce iPPEt, iPPBu, and iPPHe copolymer samples with microstructures similar to those of the homopolymer samples prepared with the same catalyst. However, neither the

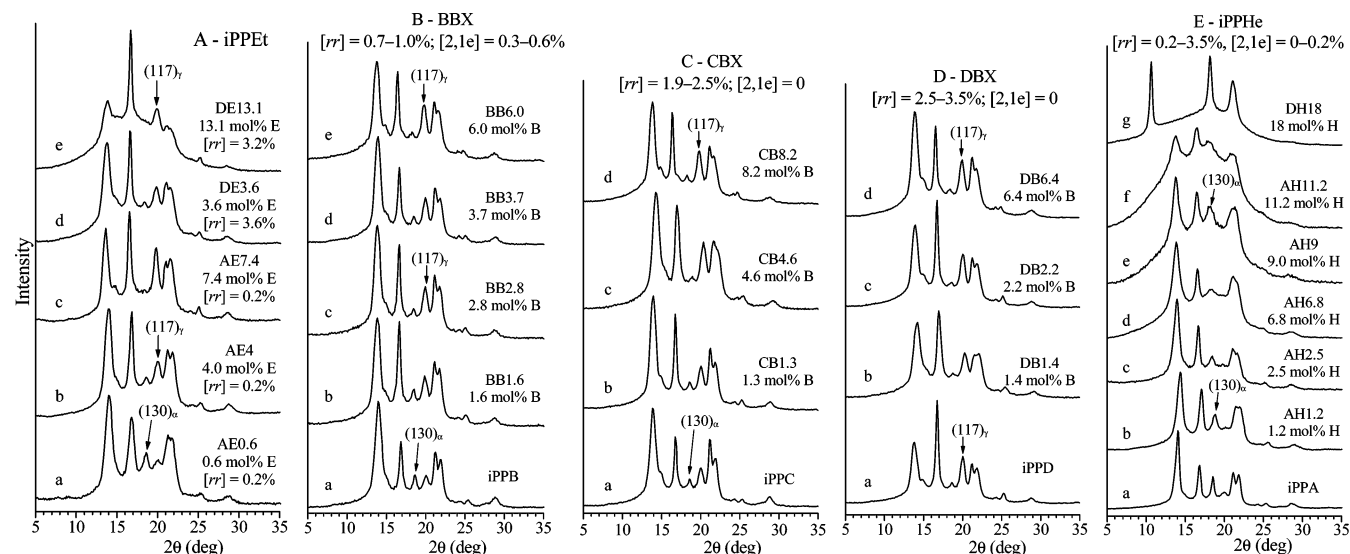
concentration of  $rr$  stereoerrors nor that of 2,1e regiodefects is constant with the comonomer concentration (Table 1). In particular, for iPPBu copolymers the concentrations of  $rr$  defects and 2,1e regiodefects decrease with increasing butene content (Table 1). For iPPEt and iPPHe copolymers prepared with catalyst A, the content of stereoerrors is not determinable and is assumed to be the same as that found in the corresponding homopolymer iPPA (Table 1). The copolymers have a random distribution of comonomers ( $r_1 \times r_2 \approx 1$ ) and narrow molecular weight distributions. The details of NMR analysis are described in the Supporting Information.

Mechanical tests and X-ray diffraction analysis have been performed at room temperature on samples crystallized from the melt by compression-molding, as described in the Supporting Information.

## Results and Discussion

**Structural Analysis.** The chosen metallocene catalysts have afforded a fine-tuning of the microstructure of iPP chains (Table 1) with a controlled incorporation of  $rr$  stereoerrors, 2,1e regiodefects, and constitutional defects (ethylene, butene, or hexene comonomeric units). A parallel analysis of the structure, polymorphic behavior, and mechanical properties of the produced copolymers may allow





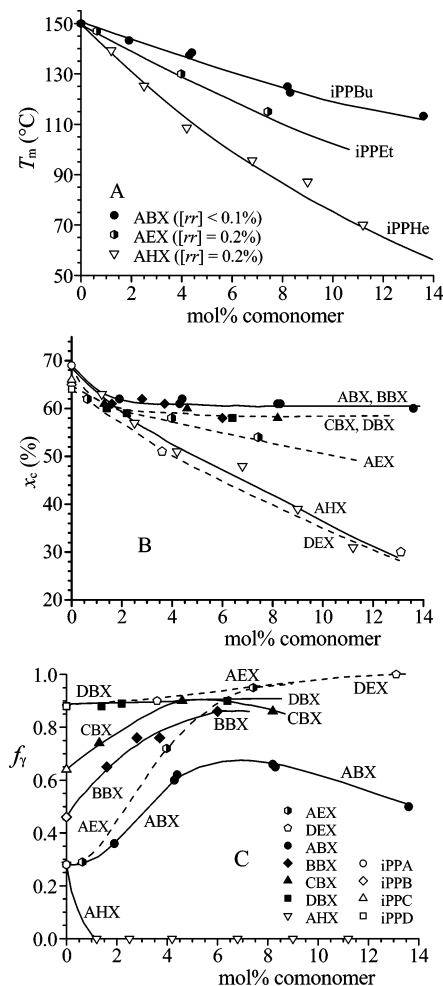
**Figure 1.** X-ray powder diffraction profiles of compression-molded samples of iPPet copolymers prepared with catalysts **A** and **D** (A), of iPPBu copolymers prepared with catalysts **B** (B), **C** (C), and **D** (D), and of iPPHe copolymers prepared with catalysts **A** and **D** (E). The diffraction profiles of iPP homopolymer samples prepared with the same catalysts (profiles a in B–E) are also reported. The  $(130)_\alpha$  reflections at  $2\theta \approx 18.6^\circ$  of  $\alpha$  form and the  $(117)_\gamma$  reflection at  $2\theta \approx 20^\circ$  of  $\gamma$  form of iPP are indicated. The concentrations (mol %) of ethylene (E), butene (B), and hexene (H) units are also indicated.

building correlations between crystal structure and mechanical properties.

The X-ray powder diffraction profiles of compression-molded samples of iPPet, iPPBu, and iPPHe copolymers are reported in Figure 1. All samples of iPPet and iPPBu copolymers crystallize from the melt as a mixture of  $\alpha$  and  $\gamma$  forms, as indicated by the presence of both  $(130)_\alpha$  and  $(117)_\gamma$  reflections at  $2\theta = 18.6^\circ$  and  $20.1^\circ$  of  $\alpha$  and  $\gamma$  forms, respectively, in the diffraction profiles of Figure 1A–D. The amount of  $\gamma$  form, evaluated from the relative intensities of  $(130)_\alpha$  and  $(117)_\gamma$  reflections (see Supporting Information), generally increases with increasing concentration of comonomeric units. Conversely, all samples of iPPHe copolymers crystallize from the melt only in the  $\alpha$  form (Figure 1E), and at high hexene concentration (18 mol %) they crystallize in the trigonal form of iPP (profile g of Figure 1E).<sup>15</sup>

The melting temperatures, the X-ray index of crystallinity, and the amount of  $\gamma$  form in the melt-crystallized samples of copolymers are reported in Figure 2 as a function of comonomer concentration. It is apparent that the melting temperature and the crystallinity decrease with increasing concentrations of comonomer and  $rr$  defects. In both iPPet and iPPBu copolymers, for similar content of comonomeric units (ethylene or butene), the melting temperature decreases with decreasing stereoregularity (Table 1). The comparison of melting temperatures of samples of iPPet, iPPBu, and iPPHe copolymers prepared with the same catalyst **A** (Figure 2A), therefore, containing very small and similar concentrations of  $rr$  and  $2,1e$  defects, allows highlighting the effects of the different comonomers and clearly indicates that iPPBu copolymers always present melting temperatures higher than those of iPPet and iPPHe copolymers with similar concentration of comonomers.

Moreover, the data of crystallinity of Figure 2B indicate that all samples of iPPBu copolymers present high degree of crystallinity, around 60% (regardless of concentration of  $rr$  defects), that do not greatly change with the concentration



**Figure 2.** Melting temperature  $T_m$  (A), X-ray degree of crystallinity  $x_c$  (B), and relative amount of  $\gamma$  form with respect to the  $\alpha$  form  $f_\gamma$  (C) as a function of comonomer concentration of melt-crystallized compression-molded samples of iPP homopolymer samples iPPA ( $\circ$ ), iPPB ( $\diamond$ ), iPPC ( $\triangle$ ), and iPPD ( $\square$ ), of iPPet copolymer samples prepared with catalysts **A** ( $\bullet$ ) and **D** ( $\circ$ ), of iPPBu copolymers prepared with **A** ( $\bullet$ ), **B** ( $\blacklozenge$ ), **C** ( $\blacktriangle$ ), and **D** ( $\blacksquare$ ), and of iPPHe copolymers prepared with **A** ( $\nabla$ ).

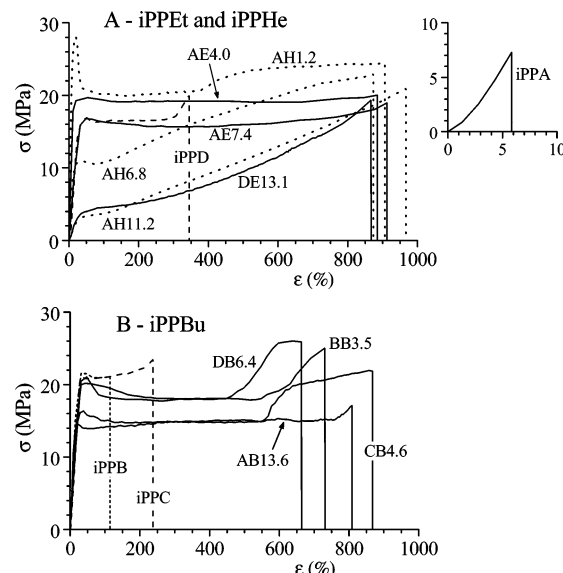
of butene, at least up to nearly 10 mol %. Conversely, a decrease of crystallinity with increasing ethylene or hexene concentration is observed for iPPeT and iPPHe copolymers (Figure 2B). The data of Figure 2A and B suggest that butene units produce disturbance of the crystallization of iPP lower than that produced by ethylene units, notwithstanding the bigger size, and even lower than that of *rr* stereodefects. Hexene units instead exert larger disturbance of crystallinity, at low concentrations (lower than 7–8 mol %), and induce crystallization of the trigonal form at higher concentrations (Figure 1E).<sup>15</sup>

Finally, the data of amount of  $\gamma$  form of Figures 1 and 2C clearly indicate that iPPeT copolymers develop by crystallization from the melt amounts of  $\gamma$  form higher than those observed in iPPBu and iPPHe copolymer samples with similar concentrations of comonomers and stereodefects. It is well-known that the crystallization of  $\gamma$  form is related to the value of the average length of the regular fully isotactic propylene sequences  $\langle L_{iPP} \rangle$ , which in turn depends on the total concentration of defects.<sup>22–25</sup>

The higher is the concentration of defects, the lower is the value of  $\langle L_{iPP} \rangle$ , and the higher is the amount of  $\gamma$  form that crystallize from the melt. Therefore, any defect (stereo- and regiodefects and comonomeric units) should exert a similar effect of interruption of the regular fully isotactic propylene sequences with shortening of the average length of the crystallizable sequences  $\langle L_{iPP} \rangle$ . This effect is common to any defect and may be more or less efficient depending on the effective disturbance of the defect, which, in turn, is related, in the case of copolymers, to the size of the comonomeric units.<sup>11</sup> Surprisingly, the data of Figure 2C indicate that the effect of *rr* defects and ethylene units of inducing crystallization of  $\gamma$  form is stronger than that of bulkier butene and hexene units.

This different behavior is related to the possible inclusion of comonomeric units in the crystals of  $\alpha$  and  $\gamma$  forms of iPP and the different compatibility of the different comonomers within the crystalline lattices of the different polymorphic forms. It has been recently demonstrated that ethylene, butene, and hexene comonomeric units are included in crystals of  $\alpha$  and  $\gamma$  forms of iPP.<sup>10,11,13,15,26</sup> Therefore, the crystallization of  $\gamma$  form of iPP is not only related to the value of the average length of the fully isotactic propylene sequences  $\langle L_{iPP} \rangle$ , which in turn depends on the total concentration of defects, but is also related to the different degrees of inclusion of stereodefects and constitutional defects in the crystals of  $\alpha$  and  $\gamma$  forms and, therefore, differences in partitioning of defects between crystals of  $\alpha$  and  $\gamma$  forms.<sup>11</sup>

The different effects of stereodefects and ethylene, butene, and hexene comonomeric units on melting temperature

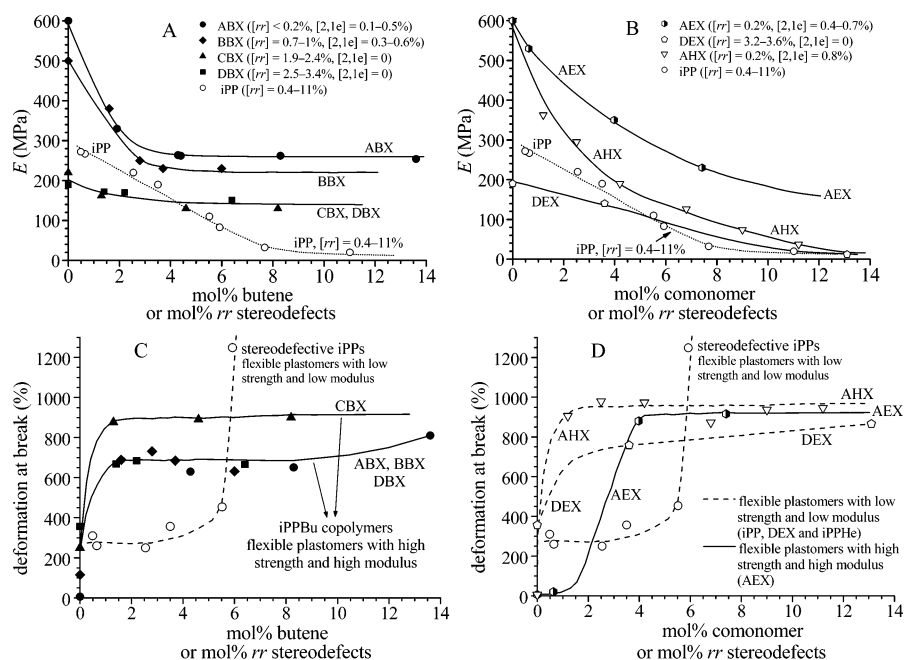


**Figure 3.** Stress–strain curves of some compression-molded films of iPPeT (A), iPPBu (B), and iPPHe (A, dotted lines) copolymers. The stress–strain curves of homopolymer samples iPPB, iPPC, and iPPD, prepared with catalysts B, C, and D, respectively, are shown as dashed lines, whereas that of the sample iPPA prepared with the catalyst A is shown in (A) in enlarged stress and strain scales.

depression, crystallinity, and crystallization of  $\gamma$  form is probably due to the fact that *rr* stereodefects and ethylene units are more easily included in crystals of  $\gamma$  form and, hence, favor crystallization of  $\gamma$  form, whereas butene units are included indifferently in crystals of both  $\alpha$  and  $\gamma$  forms and hexene units are more easily included in crystals of  $\alpha$  form. This hypothesis is consistent with experimental data reported in the literature that have shown that butene units do not prevent crystallization of iPP because propylene and butene cocrystallize in the whole range of comonomer composition,<sup>10</sup> whereas the presence of hexene comonomeric units at concentrations higher than 10 mol % induces crystallization of the trigonal form of iPP that allows incorporation of a high amount of hexene units.<sup>15</sup> Hexene units are, therefore, included in the crystals of  $\alpha$  form for low concentrations and act as a lattice defect, producing a large disturbance of the crystalline lattice and a consequent decrease of melting temperature and crystallinity (Figure 2A,B). For concentrations higher than 10 mol %, a larger amount of hexene units is more easily accommodated in the crystalline lattice of the trigonal form, producing a lower decrease of crystallinity and melting temperature.<sup>15</sup>

**Mechanical Properties.** The stress–strain curves of compression-molded films of some samples of iPPeT, iPPBu, and iPPHe copolymers of Table 1 are reported in Figure 3 and compared to the curves of the corresponding iPP homopolymer samples prepared with the same catalysts. All samples of copolymers show great enhancement of ductility, flexibility, and toughness, as compared to highly stereoregular iPP, but with important differences in the values of elastic modulus and strength. The values of Young's modulus and deformation at break are reported in Figure 4. For iPPeT and iPPHe copolymers, the elastic modulus decreases with increasing ethylene or hexene concentration and decreasing crystallinity (Figure 4B), whereas for iPPBu copolymers the Young's modulus is nearly constant with changing butene

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**Figure 4.** Values of Young's modulus  $E$  (A,B) and deformation at break (C,D) in the stress-strain tests of melt-crystallized compression-molded samples of iPPet copolymers prepared with **A** (●) and **D** (○), of iPPBu copolymers prepared with **A** (●), **B** (◆), **C** (▲), and **D** (■), and of iPPHe copolymers prepared with **A** (▽), as a function of comonomer concentration. The Young's modulus and the deformation at break of samples of stereodefective iPP homopolymer are reported for comparison as a function of the concentration of  $rr$  stereodefects (○).

content and depends basically on the stereoregularity (Figure 4A). For all samples, higher values of modulus are observed for more isotactic samples prepared with the catalyst **A**.

For iPPet copolymers prepared with the catalyst **A**, small amounts of ethylene units (3–4 mol %) produce a great increase of the deformation at break, as compared to those observed for the corresponding homopolymer samples iPPA and iPPB (Figures 3A and 4D), with still high values of the elastic modulus (Figure 4B). The values of tensile strength and of stress at yield point are instead nearly constant with ethylene concentration (at least up to ethylene content of 8–10 mol %) and very similar to those of homopolymer samples. Low values of the elastic modulus of nearly 12 MPa and a strong decrease of the stress at yielding are obtained for less stereoregular samples prepared with the catalyst **D** containing high ethylene concentrations (for instance, the sample DE13.1 with 3.2 mol % of  $rr$  stereodefects and 13.1 mol % of ethylene units, Figure 4B). However, this sample still shows a high value of tensile strength, because it experiences a strong strain hardening at high deformation (Figure 3A), and a value of the tensile strength of nearly 20 MPa, similar to those of the more crystalline samples with lower content of  $rr$  defects and ethylene units, is achieved.

These data indicate that highly isotactic samples of iPPet copolymers prepared with the catalyst **A** with low ethylene content (lower than 1 mol %) show the typical behavior of stiff-plastic materials, with high values of the elastic modulus, as iPP homopolymer prepared with the same catalyst. Samples with ethylene concentrations higher than 1 mol % show similar strength, still high values of modulus (Figure 4B), but much higher ductility and toughness with high deformation at break ( $\epsilon_b \approx 1000\%$ , Figures 3A and 4D). These samples ( $[rr] = 0.2$ –3.6%, ethylene concentrations 1–5 mol %, and melting temperatures in the range 120–140 °C) behave as highly flexible thermoplastic materials

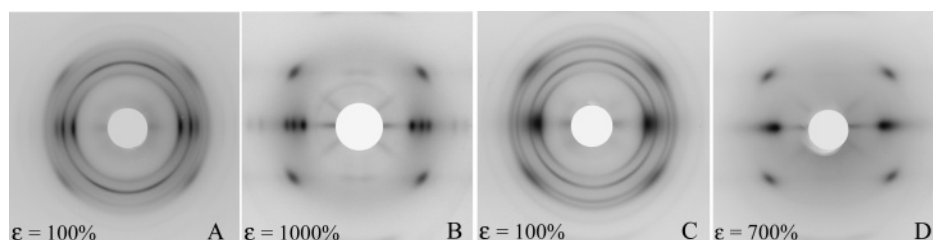
with high modulus. Less isotactic samples with high ethylene contents ( $\sim 13\%$ ) have high ductility, lower modulus, and may show elastic properties despite the high degree of crystallinity. The sample DE13.1 shows, indeed, good elastic recovery after breaking, and its stress-strain curve presents the typical shape of elastomeric materials (Figure 3A), showing a high value of deformation at break and strain hardening at high deformation.

As discussed in the previous section, this sample crystallizes in the  $\gamma$  form of iPP or in  $\alpha/\gamma$  disordered intermediate modifications thanks to the inclusion of most of the  $rr$  stereodefects and of the ethylene comonomeric units in the crystals (Figure 1). The formation of small crystalline domains induces elastomeric properties because crystals act as physical cross-links in the amorphous matrix, producing the elastomeric network. The presence of crystallinity gives high values of the strength, and the strain hardening at high deformation produces values of tensile strength similar to that of more crystalline and stereoregular samples, so that interesting thermoplastic elastomers are obtained.

The outstanding properties of the elastomeric samples DE13.1 are probably related to the increase of crystallinity during stretching and the structural transitions occurring during stretching. The  $\gamma$  form present in the unstretched compression-molded film (profile e of Figure 1A) transforms into the  $\alpha$  form by stretching already at low degrees of deformation (Figure 5A). The  $\alpha$  form obtained at high deformation (Figure 5B) remains stable upon releasing the tension during elastic recovery.

The stress-strain curves of iPPBu copolymer samples (Figure 3B) clearly indicate that the influence of butene units on the mechanical properties of iPP is different from that of ethylene. The presence of butene produces a strong increase of deformation at break with respect to the corresponding iPP homopolymer samples prepared with the same catalyst.





**Figure 5.** X-ray fiber diffraction patterns of fibers of the sample DE13.1 with 13.1 mol % of ethylene stretched at 100% (A) and 1000% (B) deformations and of the sample CB1.3 with 1.3 mol % of butene stretched at 100% (C) and 700% deformations (D).

All iPPBu copolymers show, indeed, high ductility and toughness (Figure 4C), regardless of butene content and concentration of *rr* stereodefects (at least in the analyzed ranges 0.2–3.5 mol % of *rr* defects and 1–14 mol % of butene units). Contrary to iPPet copolymers, whose Young's modulus and stress at yielding decrease with increasing ethylene concentration (Figure 4B), iPPBu copolymers present high values of modulus at any composition (Figure 4A). Both Young's modulus and stress at yielding remain nearly constant with increasing butene content (Figures 3B and 4A). Less stereoregular samples prepared with catalysts **C** and **D** show slightly lower values of the modulus, but very similar to those of the corresponding homopolymer samples prepared with the same catalysts. Only a certain decrease of the modulus as compared to the homopolymers is observed for the more isotactic samples prepared with the catalysts **A** and **B** (Figure 4A). In any case, iPPBu copolymers present high values of modulus in the range 200–350 MPa, high tensile strength, and stress at any strain, regardless of butene concentration. These data indicate that iPPBu copolymers behave as flexible thermoplastic materials with remarkable ductility and toughness and contemporary high strength and stiffness. Contrary to iPPet copolymers, no elastic properties arise even at very high concentration of butene units (compare samples DE13.1 and AB13.6).

These outstanding properties of iPPBu copolymers are related to the crystalline structure and the structural transitions occurring during stretching. As discussed above, butene units are included in crystals of  $\alpha$  and  $\gamma$  forms of iPP and produce a disturbance of the crystallization of iPP lower than that produced by ethylene units, notwithstanding the bigger size. In fact, iPPBu copolymers are crystalline in the whole range of composition from 0 to 100% of butene content,<sup>10</sup> and the degree of crystallinity is nearly constant at very high values, around 50–60%, with increasing butene concentration (Figure 2B), at least up to 10–15 mol %. This is due to complete compatibility of propylene and butene in the crystalline lattice of  $\alpha$  and  $\gamma$  forms. The high and constant values of crystallinity explain the high and constant values of the elastic modulus and the consequent high stiffness and strength of iPPBu copolymers. The enhanced flexibility, ductility, and toughness of iPPBu copolymers, as compared to the highly isotactic homopolymer samples, are instead due to the occurrence of structural transformation during deformation. Crystals of  $\alpha$  or  $\gamma$  forms, or a mixture of both, present in the unstretched compression-molded films depending on the concentration of butene units and *rr* stereodefects (Figure 1B–D) transform by stretching into the disordered mesomorphic form of iPP. The X-ray fiber

diffraction patterns of fibers of the sample CB1.3, with 1.3 mol % of butene stretched at 100% and 700% deformations, and keeping the fiber under tension, are reported in Figure 5C and D, respectively, as an example. It is apparent that the  $\gamma$  form present in the compression-molded film (curve b of Figure 1C) transforms in part in the mesomorphic form already at 100% deformation, as indicated by the presence of the broad halo on the equator in the range  $2\theta = 14$ – $16^\circ$  in the diffraction pattern of Figure 5C. Once the stiff crystals have been broken, the formation of the disordered mesomorphic form after yielding facilitates successive further deformation of the sample up to very high strains, so that the material behaves as a highly flexible material. As shown in Figure 5D, fibers in the pure mesomorphic form are obtained at high values of deformation.

This behavior of iPPBu copolymers is related to the incorporation of butene units within the crystalline phase that allows maintaining a high degree of crystallinity but introduces crystalline defects and structural disorder. These defective crystals of  $\alpha$  and/or  $\gamma$  forms are less resistant to the plastic deformation and, therefore, can be more easily deformed and transformed by mechanical melting and recrystallization into the mesomorphic form. In the case of highly stereoregular iPP homopolymer samples prepared with the same catalysts (in particular the sample iPPA and iPPB, prepared with catalysts A and B), more ordered crystals of  $\alpha$  form, present in the compression-molded films, have much higher plastic resistance and stability, so that most of the crystals cannot be easily deformed without breaking of the sample. This results in highly stiff and fragile materials.<sup>27</sup>

It is worth noting that the transformation of  $\gamma$  or  $\alpha$  form into the mesomorphic form by stretching has also been observed in stereodeficient iPP homopolymer samples containing a high concentration of *rr* triad stereodefects (higher than 5–6 mol %).<sup>24,28,29</sup> It has been argued that this transition occurs through the destruction of the lamellar crystals by pulling chains out from the original crystals, and successive reorganization of chains in crystalline aggregates of the mesomorphic form,<sup>30</sup> which is characterized by bundles of parallel chains in 3/1 helical conformation and small order in the lateral packing.<sup>31</sup> As shown in Figure 5,

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the mesomorphic form is instead not obtained by stretching at high deformation iPPet copolymers. This is probably due to the higher mobility of iPPet chains, as compared to iPP and iPPBu copolymers, that allows fast recrystallization of iPPet into  $\alpha$  form at high deformation immediately after the mechanical melting of the initial crystals.

The stress-strain curves of iPPHe copolymer samples (Figure 3A, dotted lines) indicate that hexene units exert a further different influence on the mechanical properties of iPP. As for ethylene and butene, the presence of hexene produces a strong increase of deformation at break with respect to the corresponding iPP homopolymer samples prepared with the same catalyst (Figures 3A and 4D). All iPPHe copolymers show, indeed, high ductility and toughness, with values of deformation at break of 900–1000%. Contrary to iPPBu copolymers and more similar to iPPet copolymers, the values of Young's modulus of iPPHe copolymers decrease with increasing hexene concentration, from nearly 300–350 MPa of the sample AH1.2 and AH2.5, to nearly 40 MPa of the sample AH11.2 and 13 MPa of the less isotactic sample DH18 (Figure 4B). This is consistent with the decrease of crystallinity of iPPHe samples with increasing hexene content (Figure 2B), as for iPPet samples and contrary to iPPBu copolymers. Another important difference between iPPBu and iPPHe copolymers is that, parallel to the decrease of the elastic modulus, the values of the stress at yielding of iPPHe samples strongly decrease with increasing hexene concentration (Figure 3A). In particular, the more crystalline samples with low hexene content show plastic deformation via necking with a well-defined yielding, whereas less crystalline samples with hexene concentrations higher than 9–10 mol % deform more homogeneously with ill-defined yield point. The values of tensile strength are instead nearly constant with hexene concentration (at least up to a hexene content of 10–15 mol %), and very similar (20–25 MPa) to those of homopolymer samples. The high value of tensile strength and the low values of stress at yielding are related to the strong strain hardening experienced by the samples at high deformation (Figure 3A) and indicate that iPPHe copolymers show easy deformability but high strength. Only at very high hexene contents (higher than 15 mol %), when iPPHe copolymers crystallize in the trigonal form of iPP,<sup>15</sup> is a strong decrease of elastic modulus and tensile strength observed, the latter associated with lacking of strain hardening during deformation.

These data indicate that iPPHe copolymers present the typical mechanical properties of highly flexible materials with plastic resistance and strength that decrease with increasing hexene content (and, therefore, generally, lower than those of iPPBu copolymers) but high values of tensile strength. No elastic properties develop even in the case of the poorly crystalline samples. Also, for these materials, the mechanical properties can be explained on the basis of the structure, inclusion of hexene units in the crystals of  $\alpha$  form of iPP, and structural transformation during deformation. Contrary to butene units, inclusion of hexene units in crystals of  $\alpha$  form produces a large disturbance of the crystalline lattice and a consequent decrease of melting temperature, crystallinity, and plastic resistance of the defective crystals. This,

in turn, induces a decrease of elastic modulus and an increase of ductility and toughness with increasing hexene concentration. Also, in this case, as for iPPBu samples, defective crystals of  $\alpha$  form rapidly transform by stretching into the mesomorphic form<sup>15</sup> that, in turn, facilitates further stretching up to very high values of deformation (1000%), giving high flexibility. The strain hardening during deformation is associated with this polymorphic transformation and a probable increase of crystallinity, resulting in high values of the tensile strength.

The analysis of the crystallization behavior and mechanical properties of copolymers of iPP with ethylene, butene, and hexene prepared with metallocene catalysts has clearly demonstrated that different comonomers produce different effects on the crystallization and mechanical properties of iPP. Stiff-plastic materials, highly flexible materials with tunable strength, and elastomers can be produced through the tailored incorporation of different comonomers and stereodeflects. The key is the use of metallocene chemistry that guarantees a random distribution of comonomers and stereodeflects along the iPP chains, which, in turn, affords for exploiting the effect of defects on material properties.

### Concluding Remarks

Samples of random copolymers of propylene with ethylene, butene, and hexene comonomers have been prepared with different metallocene catalysts. Depending on the structure of the catalysts, samples with different concentrations of *rr* stereodeflects and 2,1e regiodeflects have been obtained. Moreover, high degrees of comonomer incorporation, while maintaining high molecular mass and random distribution of comonomers, have been achieved. This precise control of the microstructure has allowed discriminating the effects of comonomers of different size and of *rr* stereodeflects on the physical properties of iPP and building relationships between structure and mechanical properties.

Ethylene, butene, and hexene co-units are all included in crystals of iPP, producing a decrease of melting temperature and crystallinity. Samples of iPPBu copolymers present melting temperature and crystallinity higher than those of iPPet and iPPHe copolymers, indicating that butene units produce disturbance of the crystallization of iPP lower than that produced by ethylene and hexene units.

All copolymers samples show great enhancement of ductility, flexibility, and toughness, as compared to highly stereoregular iPP, but with important differences in the values of elastic modulus and strength. The different mechanical behavior is related to the different degrees of inclusion of stereodeflects and constitutional defects in the crystals of  $\alpha$  and  $\gamma$  forms of iPP and differences in the partitioning of defects between crystals of  $\alpha$  and  $\gamma$  forms. This results in a different degree of disturbance of crystals with formation of more or less defective crystals, even for similar values of degree of crystallinity.

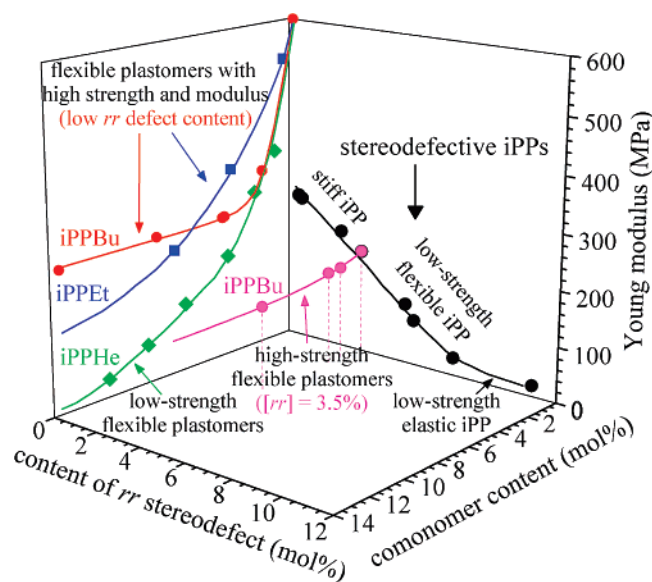
For iPPet copolymers, the values of elastic modulus, ductility, toughness, and strength can be tuned by changing the concentrations of *rr* stereodeflects and ethylene units, so that stiff materials, highly flexible materials with high modulus and strength, and elastomers can be obtained.



Samples of iPPBu copolymers show high values of elastic modulus and strength, similar to iPP homopolymer samples prepared with the same catalyst, regardless of butene content, but much higher ductility. These samples behave as flexible thermoplastic materials with remarkable ductility and toughness and contemporary high strength and stiffness. Samples of iPPHe copolymers present the typical mechanical properties of highly flexible materials with plastic resistance and strength that decrease with increasing hexene content and high values of the tensile strength.

These outstanding properties are related to the structure, the crystal morphology, and the polymorphic transitions occurring during stretching, which are all affected by the presence of comonomers. For iPPBu and iPPHe copolymers, crystals of  $\gamma$  and  $\alpha$  forms, respectively, present in the unstretched compression-molded film transform by stretching into the mesomorphic form, which facilitates successive further deformation of the sample up to very high strains, resulting in highly flexible materials. Stiffness, flexibility, and strength of the materials depend on type and concentration of comonomer through the influence of different comonomers on the crystallization of  $\alpha$  and  $\gamma$  forms and on the crystal morphology. In particular, while the Young's modulus depends basically on the degree of crystallinity, the ductility and flexibility depend on the relationships between crystalline and amorphous phases and crystal morphology. However, both degree of crystallinity and crystal morphology are related to the degree of inclusion of comonomers into crystals that produce more or less defective crystals and different crystal sizes.

In a recent paper, we have shown that similar mechanical properties can be obtained with stereodeficient iPP samples prepared with a series of  $C_1$ -symmetric zirconocene catalysts of the kind of catalysts **C** and **D** of Chart 1.<sup>24,28,29</sup> These catalytic systems are able to produce iPP samples of different stereoregularity, characterized by chains containing basically one type of stereoirregularity ( $rr$  triad defects), whose amount depends on the catalyst structure.<sup>24</sup> Samples with concentrations of  $rr$  defects variable between 0.4% and 11%, melting temperatures in the range 160–80 °C, and mechanical properties of stiff-plastic materials, highly flexible materials, and thermoplastic elastomers have been obtained.<sup>24,28,29</sup> The values of the elastic modulus and deformation at break of these stereodeficient iPP samples are reported in Figures 4 and 6 as a function of the concentration of  $rr$  defects and compared to the values obtained for iPPEt, iPPBu, and iPPHe copolymers. These data show that the properties of iPP can be tailored by incorporating  $rr$  stereodeficiencies and comonomeric units (Figure 6). It is apparent that in the case of stereodeficient iPP homopolymers, highly flexible materials can be obtained by including a significant amount of  $rr$  stereodeficiencies of about 5–6 mol % (deformation at break higher than 1000%; Figure 4C,D), at the expense of the elastic modulus and strength, due to the reduced crystallinity



**Figure 6.** Values of Young's modulus of iPP as a function of concentrations of  $rr$  stereodeficiencies and of comonomeric units. Stereodeficient iPP homopolymers (●) are compared with iPPEt copolymers prepared with the catalyst **A** (blue ■), iPPBu copolymers prepared with **A** (red ●) and **D** (pink ●), and iPPHe copolymers prepared with **A** (green ◆).

(Figures 4A,B and 6). Similar high flexibility and ductility can be obtained with iPPEt, iPPBu, or iPPHe copolymeric materials at lower concentrations of  $rr$  defects, using more stereoselective catalysts, by incorporating small amounts of ethylene, butene, or hexene comonomeric units, with the great advantage of keeping higher values of elastic modulus and strength (Figure 6). In particular, high stiffness and strength may be obtained with iPPBu copolymers for butene concentration variable in a wide range, whereas iPPEt and iPPHe copolymers allow tailoring stiffness and strength of the flexible material by regulating concentration of ethylene or hexene comonomeric units.

These data indicate the novel utility of single-center metallocene catalysts that allow for a precise control of concentration of stereodeficiencies and constitutional defects and producing polypropylenes having controlled desired properties, not accessible with commercial polypropylene produced with traditional Ziegler–Natta catalysts.

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**Supporting Information Available:** Experimental section, details of  $^{13}\text{C}$  NMR analysis, structural characterization, and analysis of mechanical properties (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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